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Par **Boris BIZET**

Design of Waterborne Isocyanate-free Poly(Hydroxy Urethane)s – Poly(Butyl Methacrylate) Hybrids *via* Miniemulsion and Properties of the Cast Films

Conception d'hybrides Poly(Hydroxy Uréthane)s sans Isocyanate – Poly(Méthacrylate de Butyle) en mini-émulsion et propriétés des films résultants

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“Droit devant soi, on ne peut pas aller bien loin.”

Antoine de Saint-Exupéry
<u>Le Petit Prince</u>

GENERAL TABLE OF CONTENT

Chapter 1: State of the Art & Objectives 17

Part A: Hybrid – Non Isocyanate Polyurethanes (H-NIPUs).19

1. Introduction 21
2. NIPUs in a nutshell 22
2.1. NIPUs – what are they? 22
2.1.1. Different pathways to make NIPUs 22
2.1.2. Transurethanization and Aminolysis of cyclic-carbonates compounds 23
2.2. Challenges to overcome 24
2.2.1. Transurethanization process 24
2.2.2. Aminolysis of cyclic-carbonates – Towards PHUs 26
2.3. Valorization of NIPUs 30
3. Hybrid-NIPUs: novel materials for a broad range of properties 30
3.1. NIPU-Epoxy 31
3.1.1. Epoxy-NIPUs through the reaction of partially carbonated epoxy compounds 32
3.1.2. Epoxy-NIPUs through the reaction of homotelechelic prepolymers with curing agents 33
3.1.3. Epoxy-NIPUs through the incorporation of hydroxyurethane modifiers 37
3.1.4. Epoxy-NIPUs from bio-based resources 38
3.2. NIPU-Acrylics 39
3.2.1. Unsaturated cyclic carbonates and their acrylic polymerization 41
3.2.2. (Hydroxy)urethane methacrylates – (H)UMAs 44
3.2.3. Unsaturated NIPU-prepolymers: Poly(hydroxy)urethane methacrylates – P(H)UMAs 49
3.2.4. Radical reactive (H)UMAs – Summary of the synthetic strategies 54
3.3. Other Hybrid-NIPUs 58
3.3.1. Si-containing H-NIPUs 58
3.3.2. Biopolymer-containing NIPUs 66
4. Concluding remarks 70
5. References 71
6. Shortened forms 82

Part B: Water-Based Non-Isocyanate Polyurethanes-Polyureas (NIPUUs) 85

1. Introduction 87
2. Water-soluble NIPUs 88
2.1. NIPU synthesis using water as reaction medium 88
2.2. Modification of NIPUs synthesized in organic solvents 90
3. Hydrogels 93
4. Water-borne Dispersions 94
4.1. Acetone-like process 94
4.1.1. NIPUs dispersion by acetone-like transesterification processes 95
4.1.2. NIPUs dispersion by acetone-like aminolysis processes 99
4.2. NIPU dispersions through interfacial polymerization 101
4.3. NIPU dispersions by mini-emulsion polymerization 101
4.4. PHU dispersions by nano-precipitation 102
5. Water-borne Hybrid-NIPUs (H-NIPUs) 103
5.1. NIPU-Acrylics - HUMAs 103
5.2. NIPU-Epoxy 104
6. Conclusions 106
7. References 107
8. Shortened forms 112

Part C: Objectives & Outline 113

Chapter 2: Bulk Synthesis of Bio-Based Poly(Hydroxy Urethane)s – PHUs 117

1. Introduction 119
2. Experimental 121
2.1. Materials and methods 121
2.2. Standard Procedure for polymerization 123
2.3. Bis-cyclic carbonate synthesis 123
3. Results and Discussion 124
3.1. Activated bio-sourced bis-cyclic carbonates (bisCCs) 124
3.2. Copolymerization of bisCC-C4 and bisCC-C10 with mixtures of diamines 127

3.3. Thermal characterization 132
3.4. Viscoelastic behavior 133
3.5. Theoretical study of the polymerization behaviors of bisCC-C4 and bisCC-C10 134
4. Conclusion 136
5. References 137
6. Shortened forms 141
7. Supporting Information 142
7.1. NMR analyses 142
7.2. IR analyses 152
7.3. DSC analyses (Temperature ramp : 10°C.min-1) 153
7.4. TGA analyses 155
7.5. SEC traces 157
7.6. DFT Study – Structures of the intermediates 157

Chapter 3: Miniemulsion of Non-Isocyanate Polyurethane-Acrylics Hybrids and Properties of the Cast Films Thereof 159

1. Introduction 161
2. Experimental 162
2.1. Materials 162
2.2. Experimental design 162
2.3. Miniemulsification and miniemulsion polymerization 163
2.4. Film casting 164
2.5. Characterization 165
3. Results and Discussion 167
4. Conclusions 177
5. References 178
6. Shortened forms 181
7. Supporting Information 182
7.1. Side Reactions 182
7.2. Solubility 187
7.3. Miniemulsion polymerization using thermal initiators 191
7.3.1. Formulations with thermal initiators 191
7.3.2. Results and discusión 194

7.4. Formulations with redox initiators 196
7.5. SEC-MALLS Traces 199
7.6. DSC Traces 200
7.7. Minimum Film Forming Temperature (MMFT) 201

Chapter 4: Bulk Synthesis of Bio-Based Poly(HydrocyUrethane)s – PHUs 203
1. Introduction 205
2. Experimental 206
2.1. Materials and methods 206
2.2. Synthesis of waterborne grafted PHU-(meth)acrylic hybrids 206
2.3. Characterization 211
2.4. Film casting 213
3. Results and discussion 213
3.1. Synthesis of the functionalized PHUs 213
3.1.1. Methacrylate-terminated PHUs 213
3.1.2. Methacrylate groups distributed along the PHU chains (multifunctionalized) 218
3.2. Synthesis of the hybrid latexes 221
3.3. Film properties 225
4. Conclusions 230
5. References 232
6. Shortened forms 235
7. Supporting Information 236
7.1. monoCC-GMA – Carbonated Glycidyl Methacrylate 236
7.2. Telechelically-functionalized PHUs 236
7.2.1. Formulations 236
7.2.2. NMR Spectra 240
7.3. Multi-functionalized PHUs 244
7.4. Formulations used for the miniemulsions 245

Chapter 5: General Conclusions 247
Conclusions Générales 253
Resumen y Conclusiones 259

CHAPTER 1

STATE OF THE ART

& OBJECTIVES

PART A

HYBRID – NON ISOCYANATE POLYURETHANES (H-NIPUS)

A PATHWAY TOWARDS A BROAD RANGE OF NOVEL MATERIALS

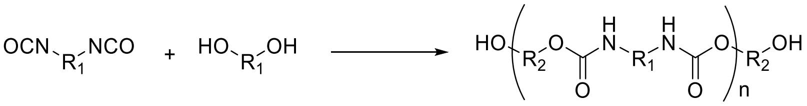
Keywords: Non Isocyanate Polyurethanes - NIPUs
Poly(Hydroxy)urethanes - PHUs
Polymer-Polymer Hybrids
NIPU-Epoxy
NIPU-Acrylics
NIPU-Siloxane

Table of content

1. Introduction 21
2. NIPUs in a nutshell 22
  2.1. NIPUs – what are they? 22
    2.1.1. Different pathways to make NIPUs 22
    2.1.2. Transurethanization and Aminolysis of cyclic-carbonates compounds 23
  2.2. Challenges to overcome 24
    2.2.1. Transurethanization process 24
    2.2.2. Aminolysis of cyclic-carbonates – Towards PHUs 26
  2.3. Valorization of NIPUs 30
3. Hybrid-NIPUs: novel materials for a broad range of properties 30
  3.1. NIPU-Epoxy 31
    3.1.1. Epoxy-NIPUs through the reaction of partially carbonated epoxy compounds . 32
    3.1.2. Epoxy-NIPUs through the reaction of homotelechelic prepolymers with curing agents 33
    3.1.3. Epoxy-NIPUs through the incorporation of hydroxyurethane modifiers 37
    3.1.4. Epoxy-NIPUs from bio-based resources 38
  3.2. NIPU-Acrylics 39
    3.2.1. Unsaturated cyclic carbonates and their acrylic polymerization 41
    3.2.2. (Hydroxy)urethane methacrylates – (H)UMAs 44
    3.2.3. Unsaturated NIPU-prepolymers: Poly(hydroxy)urethane methacrylates – P(H)UMAs 49
    3.2.4. Radical reactive (H)UMAs – Summary of the synthetic strategies 54
  3.3. Other Hybrid-NIPUs 58
    3.3.1. Si-containing H-NIPUs 58
    3.3.2. Biopolymer-containing NIPUs 66
4. Concluding remarks 70
5. References 71
6. Shortened forms 82

1. Introduction

Since their discovery in 1937 by Otto Bayer,[1] polyurethanes (PUs) have become of major interest within the polymer community. These materials are produced through the polyaddition reaction between a diol (or polyol) and a diisocyanate - Scheme 1.



Scheme 1: Reaction of a diol and a diisocyanate to yield polyurethane

By varying the monomer functionality and structure, PUs with an extremely broad variety of thermo-mechanical properties can be produced. These materials find applications in a wide range of fields including foams, coatings, adhesives and elastomers among others. The PU formation process typically consists of a two-step process. First a soft polyol is reacted with an excess of diisocyanate in order to form a homotelechelic NCO-terminated PU prepolymer. In a second step, the addition of a shorter diol (yielding PUs) or diamine (yielding polyurethane-urea – PUU) allows for chain extension. PUs are composed of a succession of hard and soft segments that tend to organize so that hard nano-phases are distributed within the soft phase. This allows for the formation of unique thermoplastic elastomers exhibiting elasticity as well as mechanical strength.

The main drawback of these otherwise high performing materials is that isocyanates are used in their synthesis. Studies have demonstrated the potential link between prolonged exposure time to isocyanates and health issues such as asthma, dermatisis and in some cases poisoning. Some isocyanates are even classified as CMR (carcinogenic, mutagenic, reprotoxic).[2–4]. Those isocyanates not only exhibit a very high toxicity, but also require the use of phosgene in their synthesis. Phosgene is a very toxic gas itself, which can lead to death in case of inhalation. All of this has raised awareness on the need for alternative pathways towards the synthesis of non-isocyanate polyurethanes (NIPUs).

In spite of about two decades of research in the field of NIPUs, the replacement of the isocyanate-based pathways still appears very challenging. This is certainly because of the fact that NIPUs are still cornered by synthesis limits that have yet not been overcome. Therefore, the scope of NIPU materials is still very narrow. Some examples have been published claiming the formation of NIPU (and especially poly(hydroxy urethane)) elastomers,[5] adhesives,[6,7] foam,[8,9] coatings,[10] hydrogels,[11] vitrimers[12] or latexes,[13] but there are still very few and often limited to the lab scale, notably because of the scarcity of the monomers that are usually not commercially available. In this regard, the development of hybrid-materials appears as a potential solution for further valorization of NIPUs.

Hybrid-NIPUs (or H-NIPUs) consist in the synthesis of materials composed of two polymers (or polymers and oligomers), one of them being a NIPU.

Hence, the objective of this review consists in the detailed description of how H-NIPUs can become a solution for the development of novel materials, exhibiting a broad range of properties. To do so, a fast description of the chemistry of NIPUs will be provided to focus later on the synthesis and properties of the different types of H-NIPUs that can be encountered in the scientific literature.

2. NIPUs in a nutshell

2.1.NIPUs – what are they?

2.1.1. Different pathways to make NIPUs

The drive for the implementation of novel pathways for the production of isocyanate- and phosgene-free PUs has led the scientific community to suggest different routes towards the formation of NIPUs. In the last years, numerous studies have been published and have notably been reviewed by Cramail *et al.*[14] and Caillol *et al.*[15] In their review, Cramail and coworkers suggested a classification of the different existing pathways according to their dependence on phosgene and/or isocyanate (Figure 1).

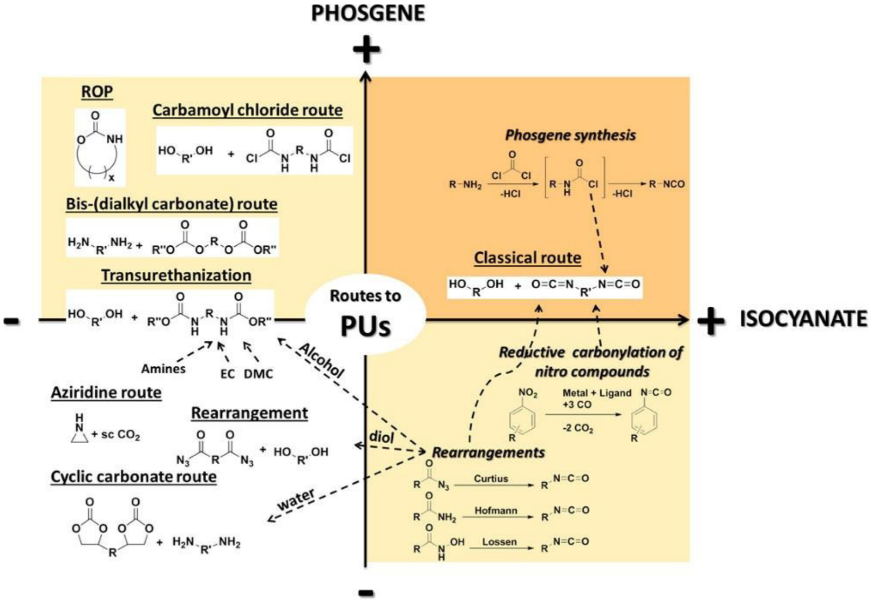


Figure 1: Isocyanate-free and phosgene-free routes towards polyurethanes – from Cramail and coworkers[14]
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Among the less demanding routes in phosgene and/or isocyanate, the copolymerization of CO_2 with aziridines appears as an interesting alternative.[16] This route however still poses challenges in terms of synthesis of aziridines from green pathways as well as the toxicity of the formed compounds. Rearrangement reactions of acyl azide and their subsequent polycondensation reaction with diols – relying on the formation of an *in situ* isocyanate moiety upon polymerization – can be somehow regarded as another potential pathway.[17,18] However, those alternatives have been left aside in particular when comparing with the transurethanization process and the aminolysis of cyclic carbonate compounds. This can certainly be attributed to the toxicity of the components at stake in the synthesis of the corresponding monomers.

2.1.2. Transurethanization and Aminolysis of cyclic-carbonates compounds

The transurethanization process and the aminolysis of cyclic-carbonate compounds have become the most promising pathways towards the implementation of an isocyanate-free route for the production of polyurethane materials. Both of them rely on different monomers, mechanisms and do not yield the exact same products.

The transurethanization (also called transurethane reaction or transcarbamoylation) consists in the reaction of an alcohol onto a carbamate under vacuum, yielding the corresponding polyurethane. As depicted in Figure 2, three types of carbamate compounds can be distinguished: bis-alkylcarbamates, bis-hydroxyalkylcarbamates and AB-type monomers. The advantage of this route is that it is very close to the already well-implemented isocyanate-based process and it yields polymers with chemical structures very close to the ones already known. The removal of the alcohol by-product is of extreme importance since it conditions the degree of polymerization.

On the other hand, PUs can also be formed by aminolysis of cyclic carbonate compounds. The ring opening of the cyclic carbonate yields polyurethanes containing pendent hydroxyl-groups – also called poly(hydroxy urethane)s or PHUs. Depending on the ring opening mechanism at stake, either primary or secondary hydroxyl groups can be formed. This pathway is interesting since it is a polyaddition. Therefore, no by-product has to be removed for the polymerization to proceed. The formed PHUs can be considered as novel materials since the presence of those OH-moieties provides specific properties to the formed materials, as well as the potential for further functionalization.

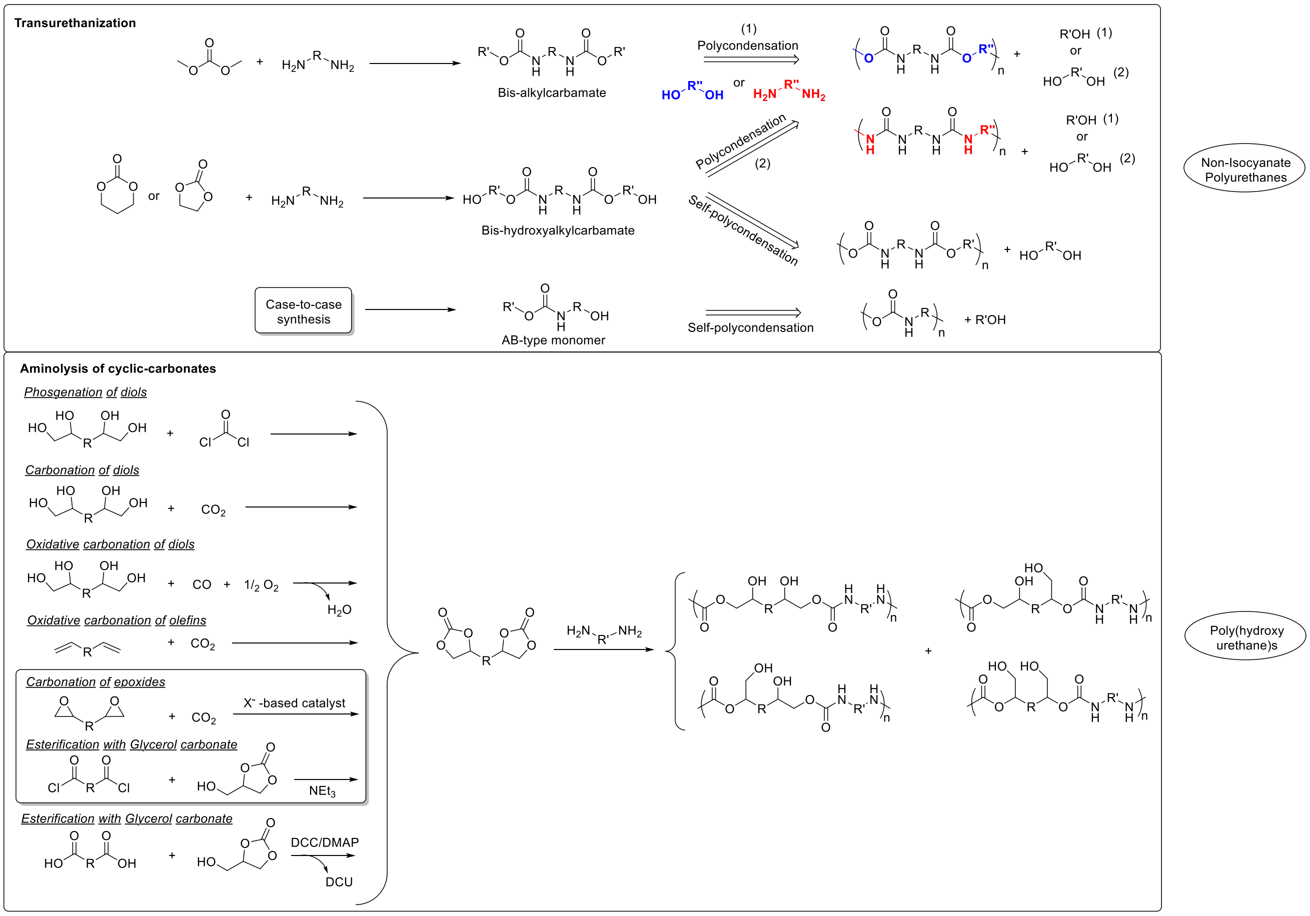


Figure 2: Transurethanization and Aminolysis of cyclic-carbonates towards the formation of non-isocyanate polyurethanes – adapted from Cramail and coworkers[19] and Carré et al[20]

An exhaustive description of the synthesis and underlying challenges in NIPU chemistry has already been extensively described in numerous and recent reviews[14,15,20,21] and is out of the scope of this review. Therefore, only a brief overview of the remaining limitations of NIPU chemistry will be provided in the next section and the reader is strongly encouraged to refer to the previous reviews should more detailed explanations be needed.

2.2. Challenges to overcome

2.2.1. Transurethanization process

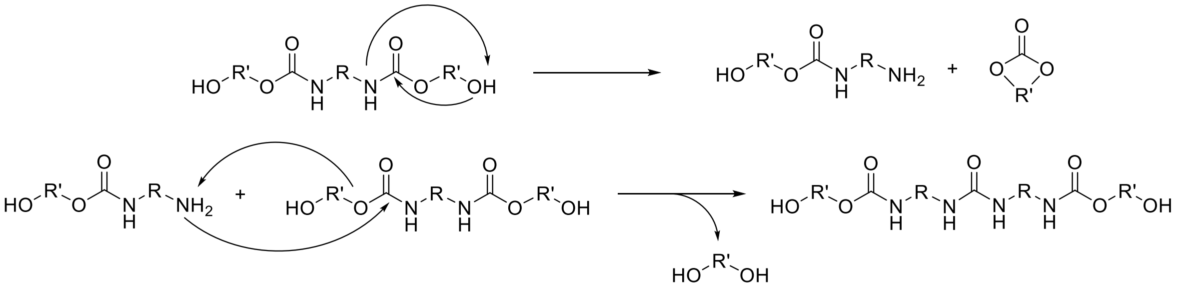
The implementation of the transurethanization process usually requires the synthesis of carbamate-based monomers prior to forming any NIPU. The synthesis and polymerization of the corresponding components has been extensively reviewed by Maisonneuve *et al.*[14] so only the general aspects of this approach will be provided hereafter. The synthesis of bis-alkylcarbamates usually relies on the reaction between a diamine and a dialkyl carbonate (usually dimethylcarbonate as depicted in Figure 2). The reaction is typically conducted in a solvent-free process, and requires catalysis (either organic, metallic or supported catalysts). The polymerization of the bis-alkylcarbamate with a diol also requires the use of a suitable catalyst and is typically performed in bulk, at high temperature with reduced pressure to remove the alcohol and thus allowing achieving high conversion and molar masses. The alkyl substituents (R') usually are methyl or phenyl groups. The first one is removed under vacuum wheareas the second one is known to be a good leaving group (it has a more favorable equilibrium constant). Very recently, Ma *et al.* have performed a detailed study on the nature of the leaving group and have exemplified that ethyl- or tert-butoxyl-moieties could also be suitable leaving groups in the synthesis of polyureas in a transurethanization-like process.[22,23] The quality of the polymerization process is strongly dependent on the quality of removal of the generated alcohol by-product, so that the equilibrium is shifted towards high extents of polymerization. This usually requires a strong optimization, agitation, vacuum quality and high temperatures.

The condensation with diols, yielding NIPUs, usually does not suffer from side-reactions. On the other hand, the condensation with a diamine, yielding NIPUreas, involves N-alkylation side-reactions, hence leading to a deviation from stoichiometry,[22] which affects the degree of polymerization achievable.

The use of bis-hydroxyalkylcarbamates is also appealing. Such monomers are usually originating from the condensation between ethylene or propylene carbonate with a diamine (Figure 2). This provides the advantage of being capable of self-polymerization since the monomer is both a bis-alcohol and a bis-carbamate. Again, careful attention has to be paid on the efficiency of catalysis and quality of alcohol removal. Moreover, backbiting side-reactions can occur yielding urea by-products - Scheme 2. All of this generally leads to the generation of low molar mass polymers and thus hinders any potential industrial implementation.

Finally, the polymerization of AB-type monomer is an interesting pathway since it leaves aside the well-known stoichiometry issue encountered in A-A + B-B-type polycondensation routes. However, there is no commercially available monomer and each monomer design is a case-to-case study that includes a lot of work and optimization.

In summary, in spite of being a very interesting pathway, the transurethanization processes usually require a lot of synthetic work in the monomer design prior to initiate any polymerization step. Moreover, the success of this polymerization route relies on the efficient alcohol removal (shifting the equilibrium towards higher molar mass polymers) and high temperatures and a fine control of the stoichiometric ratio between the involved monomers are often required. This usually yields time and energy consuming processes that is the bottleneck for upscaling.



Scheme 2: Backbiting followed by urea formation in the transurethanization reaction of bis-hydroxyalkylcarbamates – adapted from Maisonneuve et al.[14]

2.2.2. Aminolysis of cyclic-carbonates – Towards PHUs

2.2.2.1. Monomer synthesis

In a similar way to transurethanization, the formation of PHUs relies on the availability of very specific monomers, namely cyclic carbonate compounds. So far, research activities have been mostly focused on the synthesis of bis-cyclic carbonates followed by their subsequent aminolysis with amines. In 2019, Carré *et al.* published a review describing all the different routes towards the synthesis of (generally bio-based) 5-membered bis-cyclic carbonates and those are described in Figure 2.[20] The main goal of this research field consists in getting rid of the use of phosgene, which is historically used in the reaction with a diol moiety to yield the corresponding cyclic carbonate. The description of the different routes towards the formation of bis-cyclic carbonates is out of the scope of this study as it has already been widely documented in the scientific literature.[19,20] The focus will hence be made onto the two more widely utilized pathways, namely the carbonation of bis-epoxide compounds and the esterification reaction of diacids (or derivatives) with glycerol carbonate.

The carbonation of bis-epoxide compounds with CO_2 (regularly used as a sustainable C1 source for the synthesis of bio-based monomers) is carried out under high pressure and temperature. The activation of the epoxy moiety has to be performed with the help of a halide catalyst.[24] Bromine-containing compounds usually are the catalysts of choice. This pathway can be utilized to carbonate various types of epoxides, ranging from mono-epoxide (such as glycidyl methacrylates) to more complex structures such as epoxidized vegetable oils,[25] fatty-acid based[26] or terpene-based monomers.[27]

The esterification reaction of diacids with glycerol carbonate is another interesting route towards the formation of bis-cyclic carbonates. This pathway makes use of a derivative of glycerol, which is a by-product of the biodiesel production industry that has still not got any valorization path.[28] It yields specific ester-activated monomers that have been showed to exhibit superior reactivity as opposed to aliphatic cyclic carbonates. As every esterification reaction, the acid moieties have to be chemically activated and the equilibrium has to be shifted towards the formation of the di-ester. This is usually performed though the chlorination reaction of the acid moieties, yielding di-acyl-chloride moieties,[29,30] or the use of coupling agents. The combination of N,N′-Dicyclohexylcarbodiimide (DCC) with the catalyst 4-Dimethylaminopyridine (DMAP) (also known as the Steglich esterification reaction) is often reported as it allows to reach very high conversions using very mild conditions thanks to the precipitation of the 1,3-Dicyclohexyl urea (DCU) urea by-product formed by DCC upon its reaction with the acid function.[31] However, in both cases, the greenness of the process is reduced due to the formation of very high amounts of by-products.

2.2.2.2. Major challenges yet to overcome

Apart from the difficult access to monomers, the aminolysis reaction of cyclic-carbonate compounds still is a complex reaction, the limits of which are still under investigation. In this review, we will only mention the major challenges that are summarized in Figure 3.

- Enhancing the bis-cyclic carbonate reactivity

Attemps to enhance of the aminolysis reaction by improving the reactivity of the cyclic-carbonate moiety have been reported. This was done by either increasing the ring size or introducing specific moieties in alpha- or beta-position of the cyclic carbonate moiety.[14,15,20]

The increase of the ring size is a synthetic challenge in itself, especially if phosgene-free pathways are desired. The most common moiety is the 5-membered cyclic carbonate, which is thermodynamically very stable. The scientific literature relates the synthesis of 6-, 7- and 8-membered rings, the thermodynamic stability of which is decreased, hence fostering their reactivity in particular towards amines.[14,32–34]

In order to increase the reactivity of 5-membered cyclic carbonates, specific chemical functions have been introduced in alpha- or beta-position of the carbonate ring. In most of the cases, ether or ester moieties are incorporated in beta position of the ring.[29] Acting as an electron withdrawing group, they increase the partial positive charge on the carbonyl carbon and making it prone to react with amines. Numerous other activations have been exemplified as depicted in Figure 3.[20,35–38]

- Playing on the amine structure

The structure of the amine governs its reactivity, the more nucleophilic the higher the reactivity. It is a general agreement that the reactivity of the amines follows the order tertiary amine < secondary amine < primary amine.[39] The tertiary amines exhibit no reactivity in the ring opening of cyclic carbonates. In the case of primary amines, the reactivity is governed by the amine chemical structure and molecular weight.[14,40–42] Aromatic amines are not reactive, and very substituted aliphatic amines exhibit poor reactivity. In addition to this, amines with strong electron-withdrawing groups in alpha or beta position with respect to the amino group were found to be more reactive. Moreover, lower molar masses of the amines increased the chemical reactivity for the aminolysis of cyclic carbonates.[14,43]

- Polymerization conditions

The formation of PHUs yields polymers of very high viscosity, which is the result of a very high density of hydrogen bonds.[44] To overcome this limitation, several solutions can be employed. The most obvious one consists in increasing the reaction temperature, but this increases the probability of side-reactions to occur. The urea formation, due to the reaction of amine with the pre-formed urethane moiety is known to occur at a temperature higher than 100 to 120 °C.[20] In the case of ester-activated bis-cyclic carbonates, the amidification reaction is also observed. Another way of breaking the density of hydrogen bond consists in using a protic solvent that provides a high degree of freedom in the motion of the polymer chain for it to continue reacting. This solvent should preferably be of high polarity to solubilize the monomers and to form a homogeneous reaction medium.

Catalysis is also important. The precise description of each catalytic systems is out of the scope of this review, but it can be noticed that significant improvements of the kinetics of ring opening were achieved, notably when triazabicyclodecene (TBD) was used as catalyst. However, progressive conversion of the formed PHU into polyurea was also noticed, suggesting that careful attention has to be paid when selecting a catalytic system.[45] Detailed information can be found in a recently published review from Sardon and coworkers.[46]

- Molecular weights prospects with regard to PHU synthesis

Despite extensive research activities, and even if PHU can seem promising candidates for the implementation of phosgene- and isocyanate-free pathways towards PUs, it is noteworthy to mention that low molar masses are usually obtained, which limits the mechanical properties. It has also to be pointed out that the solubility limits and the use polystyrene based calibration make unreliable the SEC measurements of the molecular weights complicating the comparison between results reported by different groups.

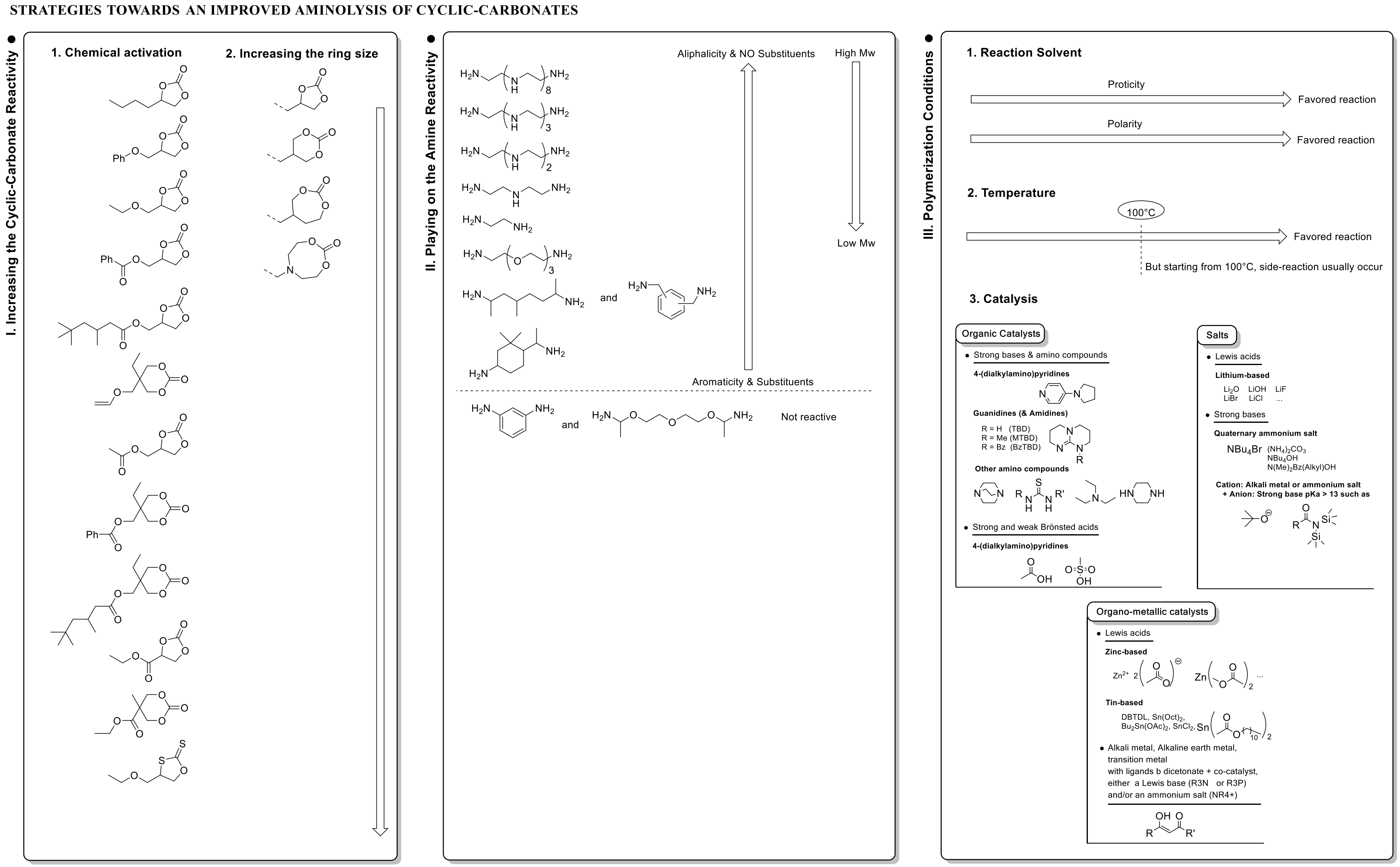


Figure 3: Strategies towards an improved aminolysis of cyclic carbonates – adapted from Maisonneuve et al.[19] Cornille et al.[15] and Carré et al.[20] Reprinted with permission from Chem. Rev. 2015, 115, 22, 12407-12439. Copyright 2020 American Chemical Society.

2.3. Valorization of NIPUs

In short, in spite of being very attractive pathways, both transurethanization and PHU formation are still suffering from limitations cornering them at the academic interest. Very recent research have been focused on the potential use of PHUs as materials, notably by designing very specific – and often bio-based – monomers capable of polymerizing in bulk.[6,10,53–61,30,31,47–52] This allowed for the growing knowledge of the structure-properties relationship of NIPUs that have been summarized in a review from 2016.[62] In this context, there is a growing interest in the valorization of NIPUs *via* the design of polymer-polymer hybrids (also called H-NIPUs) that will be described in the next section of this review – Figure 4.

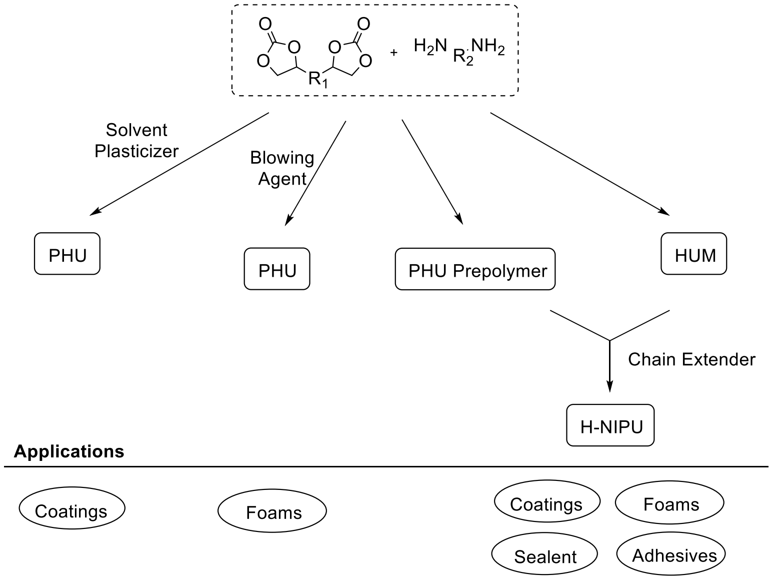


Figure 4: Potential valorization pathways for NIPUs towards their industrial implementation (adapted from Caillol and coworkers[15])

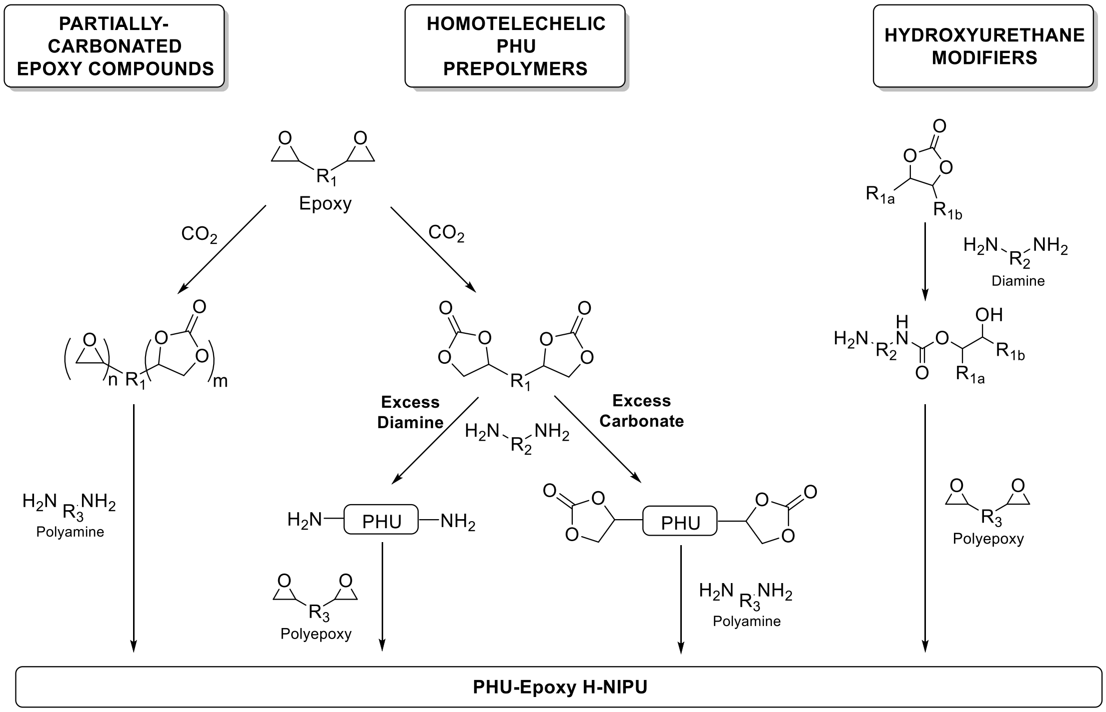
3. Hybrid-NIPUs: novel materials for a broad range of properties

Hybrid-polymers are two or multiphase composites in which each phase is formed by a different material and at least one of them is a polymer. Polymer-polymer hybrids are formed by different polymers. The resulting properties of the final composites usually are a synergistic combination of those of the constituting materials. Polymer-polymer hybrids can be formed by simply mixing two polymers together, but more complex structures can also be achieved by grafting. This usually helps prevent phase separation that can occur especially when the two polymers have a poor compatibility. Quite a few examples of hybrid NIPUs (H-NIPUs) have been published and are summarized in this review as well as the underlying challenges that are rising from such technologies.

3.1.NIPU-Epoxy

The synthesis of NIPU-epoxy hybrids is the eldest process for the formation of H-NIPU.[63] In that work, NIPUs were used as modifiers in order to improve the flexibility of epoxy resins for lacquers and adhesive applications.

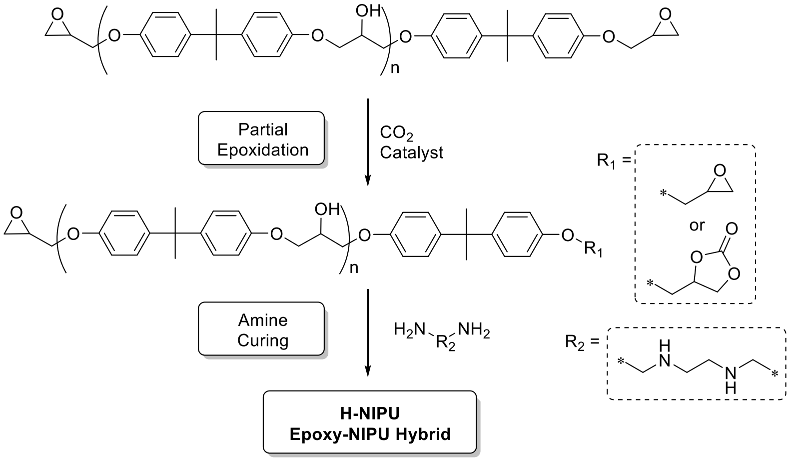
This pioneering work inspired numerous researches, that were well described by Figovsky.[64] In 2017, Cornille *et al.*[15] suggested a classification of three different chemical pathways towards the formation of a NIPU-Epoxy hybrids - Scheme 3. The first route consists in reacting partially carbonated epoxy compounds with a polyamine. Polyamines are able to react with both the epoxy and carbonate moieties to yield H-NIPUs. The second alternative is a 2-step process in which a NIPU-prepolymer is formed prior to reacting in a second step to form the final H-NIPU. Finally, the formation of so-called Hydroxy Urethane Modifiers (HUM) has recently been reported as another possibility. It consists in forming a mono-hydroxy urethane that upon reaction with a polyepoxy yields the final H-NIPU. In all cases, it can be considered that the polymer-polymer hybrids form interpenetrating networks (IPN) in which the NIPU is tangled up with crosslinked epoxy resin.[15,65]



Scheme 3: Different routes towards the formation of polymer-polymer NIPU-Epoxy hybrids – adapted from Cornille *et al.*[15]

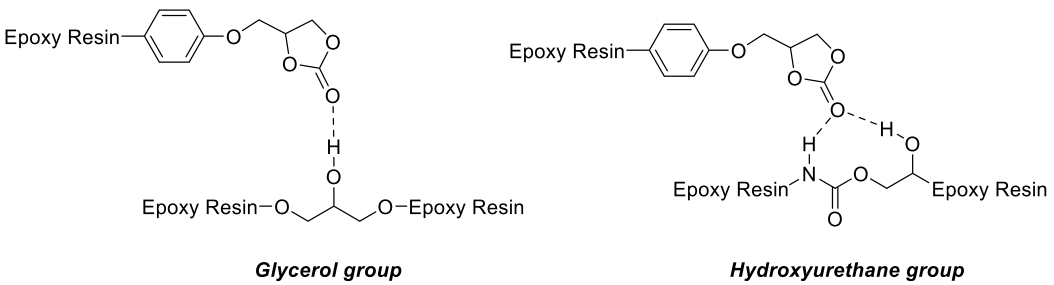
3.1.1. Epoxy-NIPUs through the reaction of partially carbonated epoxy compounds

The partial carbonation of epoxidized compounds was the first approach to synthesize epoxy-NIPU hybrids, likely due to the ease of access to the raw materials at stake in this synthetic process. Rokicki *et al.* pioneered this type on synthetic process by partially carbonating a bisphenol-A diglycidyl ether (BADGE)-based epoxy resin by fixation of CO_2.[63] Different degrees of modifications were achieved before further curing with triethylenetetramine (TETA) to form a 3D network - Scheme 4.



Scheme 4: BADGE-based H-NIPU through the amine curing of a partially carbonated epoxy resin

The authors noticed an increase in viscosity with an increasing degree of carbonation of the modified epoxy resin, that was explained by the presence of a high density of H-bonds within the polymer. Later the effect of carbonation on the viscosity was found to be epoxy-resin dependent.[66] The reactivity of the partially carbonated macro-monomer with TETA was then measured by determining the gelation time. It was found that the gelation time decreased by increasing the carbonate content, hence suggesting that the energetic barrier for the reaction was higher for the epoxy than for the cyclic carbonate moieties. Interestingly, the introduction of carbonate moieties also allowed to decrease both the intensity of the reaction exotherm as well as the time needed to reach it, making such a process very interesting for safety purposes should high amounts of material be produced. Those findings were also confirmed by the work of Bürgel who ran a mechanistic study of this polymerization process.[40] Trying to go beyond the use of partially carbonated BADGE-resin, they performed another study by synthesizing linear telechelic oligomers.[67] It was found that both the degree of carbonation together with the functionality of the curing amine were playing a role in the preference of the amine to react either with the cyclic carbonate or with the epoxy moiety. More precisely, primary amines would rather react with carbonate moieties whereas secondary amines would react with both carbonate and epoxy moieties.[40,65,67] A lower degree of covalent crosslinking in the final IPN was then obtained. The reaction temperature was also found to play a crucial role in the chemical process. Indeed, increasing the reaction temperature led to higher conversions,[67,68] shorter gelation times,[63,66,68] lower viscosity,[63,68] better homogenization of the mixture, and promoted reaction with the epoxy moiety to a higher extent.[63,68] However, side reactions were also noticed starting at 100 °C, suggesting that there is room for optimization of the reaction temperature, which can be very system-dependent.[40] When considering thermo-mechanical properties of the formed H-NIPUs, superior properties were obtained for the modified epoxy resins, especially in terms of impact resistance, hardness, and compressive strength.[66] Good tensile properties could also be obtained , that were attributed to a physical crosslinking that occurs in the obtained IPN which can still be explained by the presence of unreacted cyclic carbonate moieties forming H-bonds with the –NH-functions of the hydroxyurethanes moieties formed upon polymerization - Scheme 5. As an outcome, synergetic effects were also obtained when hydroxyurethane-containing polyamines were synthesized and incorporated into NIPU-Epoxy hybrids.[68–71]

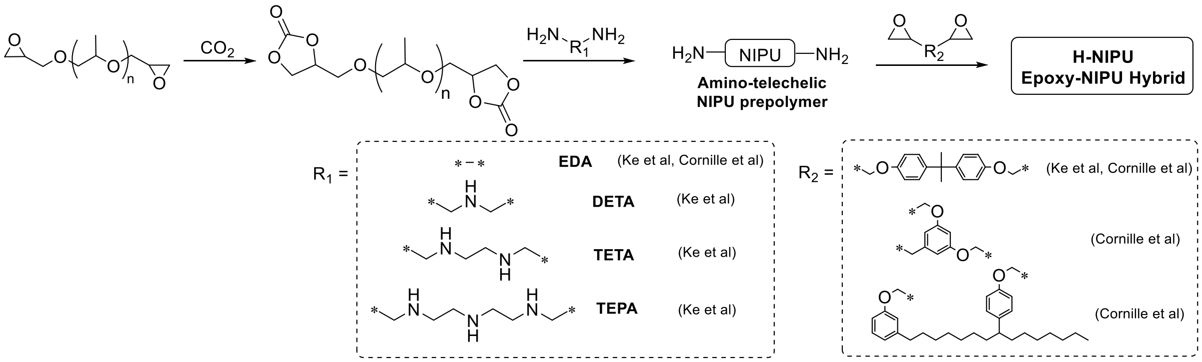


Scheme 5: Physical crosslinking by H-bonding in Epoxy-NIPU hybrids

Figovsky et al. (Polymate Ltd) patented a process in which partially epoxidized compounds were cured with an epoxy resin and oligomeric amines for the preparation of H-NIPUs to be used for preparing constructive glues, sealants, coatings, construction materials among others.[72]

3.1.2. Epoxy-NIPUs through the reaction of homotelechelic prepolymers with curing agents

This chemical pathway relies on a 2-step process in which an amino-telechelic NIPU prepolymer is first formed by reaction between a bis-cyclic carbonate and an excess of diamine monomer. The amino-telechelic NIPU (and more specifically in this case a PHU) prepolymer is subsequently cured with an epoxy compound – Scheme 6.[61,73,74] This technology is particularly appealing for the design of materials with defined sequences of soft and hard segments within the final 3D-hybrid network.



Scheme 6: NIPU-Epoxy H-NIPU formation through the preparation of poly(propylene oxide) bis-cyclic carbonate amino homotelechelic prepolymer prior to further curing with a bis-epoxy compound[61,73,74]

Most published occurrences rely on the preparation of poly(propylene oxide) bis-cyclic carbonate-based amino-telechelic prepolymers. The challenge in this reaction is to form prepolymers of sufficiently high chain length while limiting side-reactions. To do so, several types of diamines[61,74] were utilized in the synthetic process, and process parameters such as the reaction time,[73,74] the reaction temperature[74] and catalysis[74] were investigated. In general, low molar masses were obtained due to the excess of diamine used.

When running model reactions between poly(propylene oxide) bis-cyclic carbonate and ethylene diamine (EDA),[74] it appeared that the selection of the reaction temperatures was a compromise between several parameters. It was found that a temperature of 90°C allowed fast kinetics (around 100 min for the reaction to reach its maximum conversion, generally reaching a value of 90°-95°C), counter-balanced the high viscosity of the reactive mixture and avoided the extent of too many side reactions (such as urea formation by the reaction of the amine moieties onto the forming hydroxyurethanes). The use of triethylenediamine as catalyst improved the kinetics of the reaction but could not diminish the extent of those side-reactions. Moreover, trace of unreacted carbonate could still be observed.

When curing the amino-telechelic prepolymers with bisphenol-A diglycidyl ether (BADGE),[74] the ratio between the amine and epoxy moieties played an important role in the determination of the microstructure of the final hybrid materials. When too low NH_2/Epoxy ratios were used, carbonate moieties could still be observed by infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) analyses revealed non-homogeneous microstructures, that were attributed to an incomplete crosslinking of the material.

Increasing the NH_2/Epoxy ratios led to a better crosslinking of the material as shown by tensile and swelling tests, and SEM analyses (continuous morphologies were observed).

Finally, when too high amounts of diamine were incorporated into the formulation, more linear structure of H-NIPUs were obtained and higher elongations at break could be obtained through tensile tests. Similar trends were obtained with other diamines even if shorter gelation times were obtained.

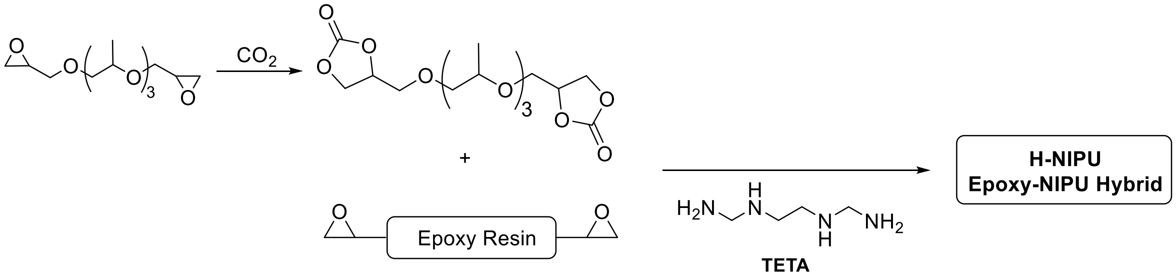
Shortening of the gelation times were observed when secondary amines diamines - namely diethylene triamine (DETA), triethylene tretramine (TETA) and tetraethylene pentamine (TEPA) - were used in the curing process with BADGE. This was attributed to the reaction between the inner secondary amines and BADGE, thus improving the crosslinking degree of the final materials.[61,74] The impact of the NH_2/Epoxy was found to have a similar trend on all kind of properties: mechanical (tensile, hardness), thermo-mechanical (by dynamic mechanical thermal analysis - DMTA) and swelling ability in solvents – namely, there is an intermediate value at which the H-NIPUs are harder, exhibit higher Young's moduli, tensile strength, and lower elongation at break.[74]

In a very recent study, Ke *et al.* studied the influence of the synthetic process of the NIPU onto the properties of the final H-NIPUs.[75] They investigated the influence of methanol as a solvent to circumvent the H-bonding formation as well as the introduction mode of the reagents while forming amino-telechelic NIPUs (in this case also, a poly(propylene oxide)-derived bis-cyclic carbonate was reacted with ethylene diamine – EDA). Dramatic impacts on the molecular weights of the NIPUs oligomers, and their behaviors when curing with BAGDE were observed. In particular, they showed that the higher the molecular weights of NIPU oligomers, the higher the gel content (>90 %) and the higher the Young's modulus and the tensile strength.

The introduction mode of the NIPU monomers was of extreme importance, especially when using methanol as the solvent. The authors compared the NIPUs obtained when adding both the monomers at the same time, having a progressive addition of the diamine onto the bis-cyclic carbonate (bisCC) pre-dissolved in methanol or having a progressive addition of the bisCC onto the diamine pre-dissolved in methanol. In the first case, a rapid reaction rate was observed, but urea formed (due to the reaction between the formed urethane moieties and the unreacted amine). This result was even worse with the regular addition of bisCC into an EDA solution, due to the higher concentration of the diamine in the reactive mixture. The last mode of introduction yielded a NIPU with both the highest molar mass of all as well as a lower kinetics of formation of urea as opposed to batch mode.

Cornille *et al.* exemplified an interesting example of crosslinking with a tri-functional epoxy compound.[73] Quite logically, harder materials exhibited a lower swelling index and a higher degree of crosslinking was obtained when using such a curing agent.

In the case of cyclic carbonate-telechelic oligo-NIPUs (refer to the case "excess carbonate" in Scheme 3), the major challenge consists in the high viscosity arising from the presence of the carbonate moieties. Rokicki *et al.* tried to prepare H-NIPUs from a mixture of a commercial epoxy resin (Epidian 6), cured with an aliphatic cyclocarbonate resin based on triethylene glycol diglicidyl ether (shortened TGDEC below) and TETA – Scheme 7.[66]



Scheme 7: NIPU-Epoxy H-NIPU formation through the preparation of triethylene glycol diglycidyl ether bis-cyclic carbonate (TGDEC) homotelechelic oligomer prior to further curing with a bis-epoxy resin and triethylenetetraamine (TETA)[66]

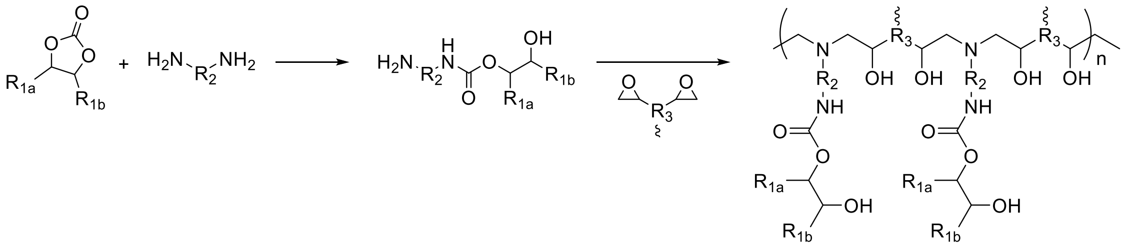
In this example, the viscosity of TGDEC increased compared to the native triethylene glycol diglicidyl ether. However, it was still lower than the viscosity of the Epidian epoxy resin alone. The authors were able to demonstrate that, when mixing Epidian with TGDEC, the higher the content in TGDEC, the lower the viscosity of the mixture. When curing those mixtures with triethylenetetraamine (TETA) to yield the corresponding Epoxy-NIPU hybrids, the polymerization behaviors and the resulting properties were very similar to those described in the case of partially-carbonated epoxy resins.[63] The higher the content in TGDEC, the shorter the gelation times and the lower the exotherms measured by DSC. When comparing the Epidian resin cured with TETA alone with the hybrids, no significant change was observed in hardness. However, the higher the TGDEC, the higher the impact resistance. Moreover, hybrids also exhibited higher tensile strengths, yield strength, and also higher elongations at break when comparing with the Epidian-TETA epoxy resin. These outcomes may look surprising since the degree of covalent crosslinking is lower in the case of hybrids because the functionality of cyclic carbonates is lower than the one of epoxy moieties. The authors attributed the increased mechanical properties to the establishment of a physical crosslinking thanks to H-bonds.

Recent studies reported an increase in toughening of Epoxy-NIPU materials when bis-cyclic carbonate compounds were introduced in the formulation.[76] It was demonstrated in the case of carbonated ethylene glycol diglycidyl ether (bisCC-EDGE) cured with BADGE and DETA that the loading in bisCC – namely the concentration of bisCC moieties in the mixture – was a determining factor in the toughening of the final hybrid. As a general trend, both tensile strength and elongation at break increased up to a point at which the concentration of bisCC was too high to promote crosslinking and unreacted carbonate moieties plasticized the final material, denoting the specific interplay between plasticizing (increasing elongation at break) and crosslinking (increasing tensile strength). The incorporation of a higher amount of H-bonds also conferred better impact resistance to the hybrids. Similar trends were obtained with NIPU-Epoxy non crosslinked blends with poly(propylene carbonate), suggesting the importance of the presence of those H-bonds for the properties of the final materials.[77]

3.1.3. Epoxy-NIPUs through the incorporation of hydroxyurethane modifiers

This chemical pathway relies on a 2-step process in which hydroxyurethane modifers – HUMs – are synthesized prior to be incorporated into epoxy resin diluents for curing purposes. In this route, a mono-cyclic carbonate reacts with an amine to yield the hydroxyurethane moiety - Scheme 3. This approach was patented by the team of Figovsky who synthesized various types of HUMs.[78] It is important to note that this approach was quite different from the other pathways in the sense that the final HUMs were compatibilized to the epoxy resins without being fully incorporated *via* crosslinking – namely, non crosslinked H-NIPUs were obtained. These HUMs were shown to accelerate the curing process of the epoxy-amine. Other types of additives such as diluents, pigments and additives can also be incorporated if needed. It was claimed that the modified epoxy-amine hybrids exhibited improved curing characteristics and provided cured products with better wear resistance, flexibility, well-balanced mechanical properties (hardness, tensile strength), and chemical resistance than conventional comparative compositions.

Other examples exemplifying grafting between the HUMs and the epoxy resins have also been reported.[68,79,80] To do so, mono-cyclic carbonates were put to react with diamines so that the pendant unreacted primary amine moiety can further cure an epoxy resin, hence yield a “comb-like” structure in which an epoxy backbone is modified with pendant hydroxyurethanes - Scheme 8. This methodology is to some extent an equivalent of the Hydroxyurethane Methacrylates (or “HUMAs”) that will be described latter.



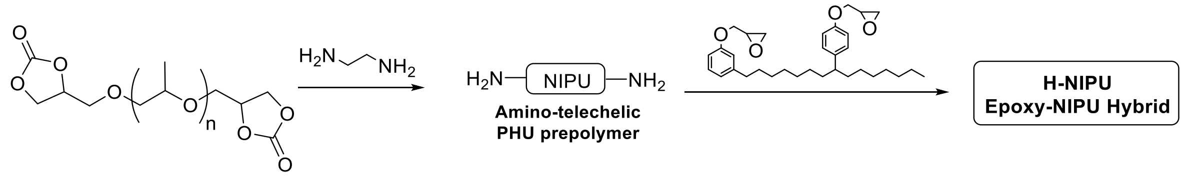
Scheme 8: H-NIPU composed of an epoxy polymer chain modified with pendant hydroxyurethane moieties

Using the versatility of the synthetic process, it is possible to design 3D networks with a controlled number of nodes through a wise selection of the reagents. Thus, diamines containing inner –NH- moieties (for instance Diethylenetriamine - DETA) can be used in the synthesis of HUMs. Superior and tunable mechanical properties could thus be obtained by tensile tests, with Young moduli in the range 0.9 to 12 MPa and elongations at break in the range of 70 to 275 % depending on the diamine used.[79] In 2016, Wazarkar *et al.* demonstrated the potential of such compounds to be used as corrosion protective coatings, with a good balance between the hardness provided by the epoxy resin and flexibility given by the hydroxyurethane moieties.[80] Those properties were enhanced due to the superior adhesion properties of the H-NIPUs onto the substrates due to the presence of pendant hydroxyl moieties.

3.1.4. Epoxy-NIPUs from bio-based resources

In a global context of development of a more sustainable chemistry, some recent studies used bio-based monomers in the synthesis of PHU-Epoxy H-NIPUs.[73,81,82] Parzuchowski *et al.*[82] used partially carbonated soybean oil (CSO) as a modifier for the curing process of a Bisphenol-A Diglycidyl Ether (BADGE)-based resin with different types of amines. A higher reactivity of the amine towards the epoxy moiety than towards the inner cyclic carbonate included in the fatty acid chain of the CSO was observed. This ultimately brings to a phase separation and the formation of spherical domains of CSO-based NIPU trapped in the epoxy-amine resin. In terms of mechanical properties, a similar trend as described before was observed when curing with Triethylenetetramine (TETA) hardener: there is an optimum concentration of carbonate moieties (here about 10 %) that allows for enhanced tensile strength with respect to the native epoxy-amine resin. Higher amounts of carbonate moieties did not fully react and plasticized the obtained hybrids, hence increasing the elongation at break. All in all, a general toughening effect was observed as a positive outcome of the introduction of CSO within epoxy amine formulations.[82] These results agree with those reported by the team of Figovsky who formed Epoxy-NIPU hybrids for adhesive and sealant applications.[81] They found that up to 10% carbonation, similar hardness, superior tensile strength and elongation at break were achieved as opposed to the unmodified epoxy-amine resin. They also claimed that the observed toughening effect was the result of the specific morphologies and the contribution of an aminolysis reaction that occurs upon curing, hence providing new kinds of properties to the final hybrid material. The team of Rokicki also obtained similar results when using hyperbranched polyglycerol instead of CSO.[83]

It is worth mentioning the recent work of Cornille *et al* who synthesized fully bio-based Epoxy-PHU H-NIPUs.[73] They used amino-telechelic PHU prepolymer that reacted with a cardanol-based bis epoxy compounds - Scheme 9. It was necessary to increase the reaction temperature up to a minimum of 50 °C for the curing process in order to form a crosslinked hybrid material. It was noticed that the H-NIPUs exhibited the highest swelling indexes of all synthesized materials, due to the long aliphatic chain contained in the monomer. Gel contents of around 80 % were obtained, which was explained by the low purity of the starting material because of the presence of mono-epoxy compounds. Interestingly, the obtained glass transition temperature was quite low (around 5 °C) due to the flexibility of the utilized reagents.



Scheme 9: Bio-based Epoxy-PHU H-NIPU as designed by Caillol and coworkers[73]

3.2.NIPU-Acrylics

Another approach for the synthesis of H-NIPUs consists in their combination with acrylic polymers. Such a pathway received plenty of attention that resulted in a tremendous development in the synthesis of multifunctional cyclic carbonates. The different synthetic strategies are summarized in Figure 5. A strong focus has been devoted to unsaturated cyclic carbonates since their synthesis could allow for further functionalization and/or crosslinking.[84] More recent approaches involved the synthesis of the so-called Hydroxyurethane Methacrylates (HUMAs), which can be considered as equivalents of the previously described Hydroxyurethane Modifiers (HUMs) in PHU-Epoxy H-NIPUs. The subsequent acrylic polymerization allows for the formation of the final H-NIPUs. Finally, and very recently, the synthesis of unsaturated NIPU pre-polymers, opening the scope of applications towards segmented NIPU-Acrylic networks were published. All of them are reviewed below.

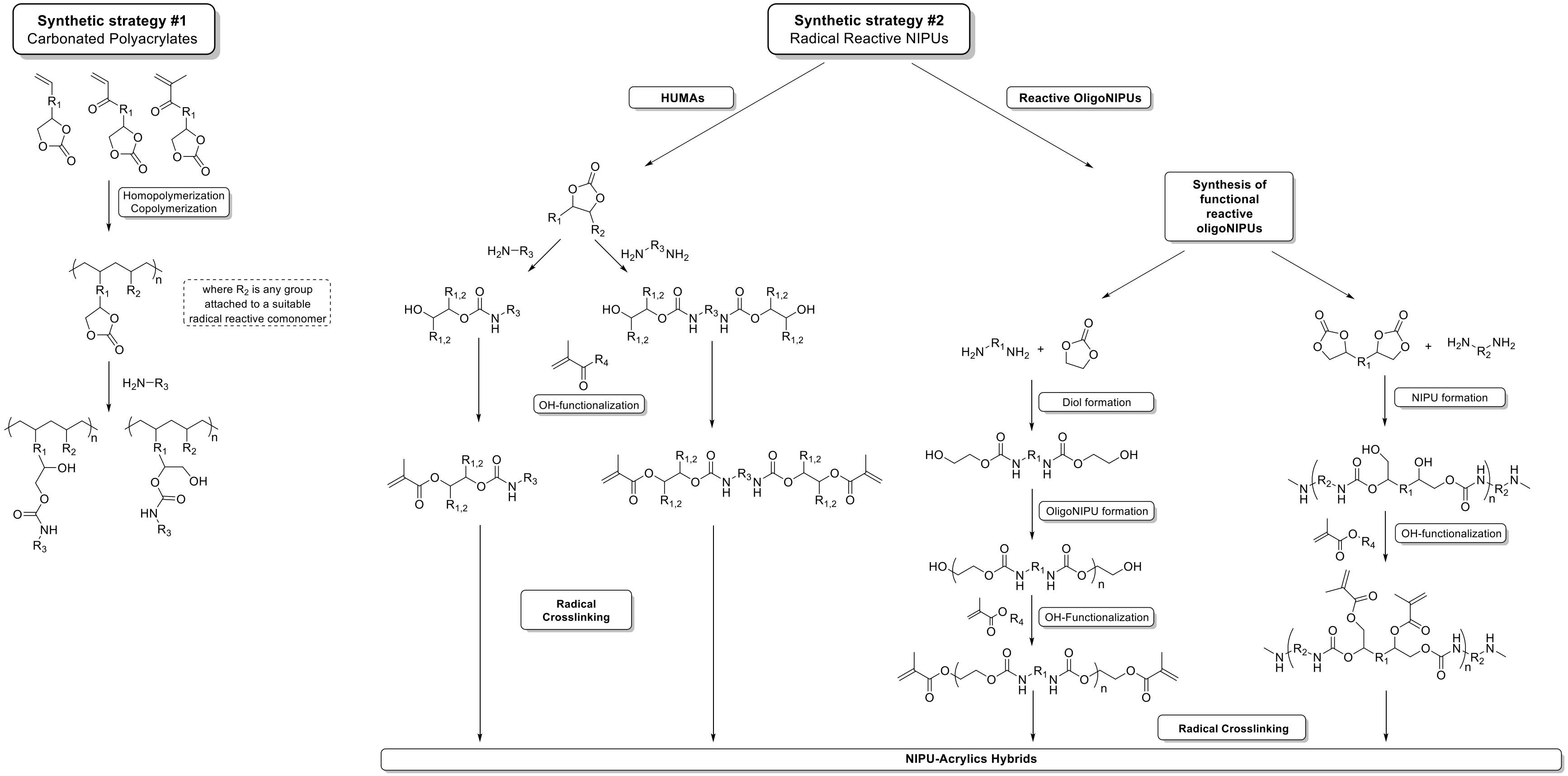


Figure 5: Overview of the different synthetic strategies for the synthesis of NIPU-Acrylics hybrid polymers

3.2.1. Unsaturated cyclic carbonates and their acrylic polymerization

The synthesis of unsaturated cyclic carbonates is a long standing challenge that has been addressed by numerous research teams. The design of such monomers capable of orthogonal chemistry is of great importance and still constitutes the most challenging milestone towards the formation of NIPU-Acrylics H-NIPUs. Boutevin and coworkers[84] have extensively reviewed the synthesis of such compounds up to 2013, as well as their polymerization behaviors through reaction of the carbon-carbon double bond. They include, among others, vinyl ether,[85,86] vinylic,[42] allylic[41,87,88] and allyl ether,[89] styrenic[90,91] and the (meth)acrylic cyclic carbonates[39,92–98] - Figure 6. Most of the synthesized products were aliphatic chains with pendant carbonate moieties, but few articles report the synthesis of NIPU-acrylic hybrids actually made of a crosslinking between polyacrylic and NIPU chains. In these few occurrences, it always consists in a post-functionalization reaction with an amine compound to yield a "comb-like" structure of an aliphatic chain with pendant hydroxyurethane moieties, or with a diamine/triamine for crosslinking purposes. Some of those monomers were indeed directly dimerized with the help of thiol-ene chemistry prior to reacting them with diamines to yield poly(hydroxyurethane)s – PHUs and no NIPU-Acrylic hybrids were synthesized.[41,87,89]

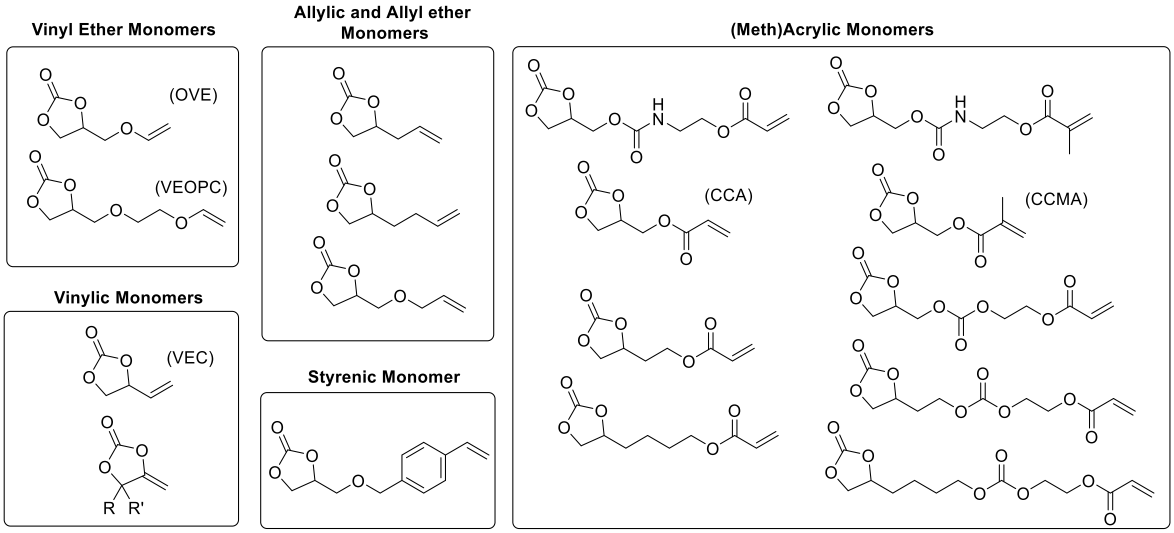
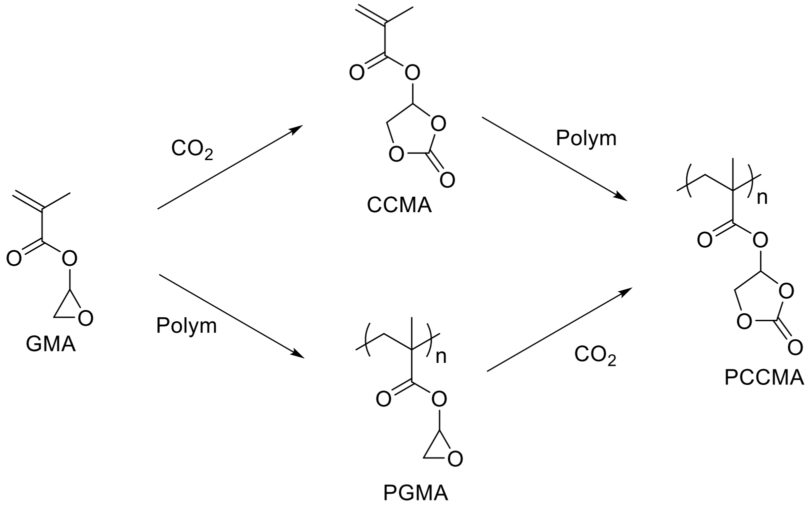


Figure 6: Radical reactive cyclic carbonates

The radical copolymerization of (2-0xo-1,3-dioxolan-4-yl) methyl vinyl ether (OVE) with acrylonitrile, methyl methacrylate, N-phenylmaleimide and maleic anhydride in acetonitrile gave yields up to 87 % depending on the comonomer composition.[85] The authord further reacted the pendant carbonate moieties with butylamine and benzylamine up to 84 % and 96 % conversion respectively. Kalinina *et al.* reported the copolymerization of 3-(2-vinyloxyethoxy)-1,2 propylene carbonate (VEOPC) and N-phenyl maleimide (around equimolar composition) in methylethylketone (MEK) using azobisisobutyronitrile (AIBN) as thermal initiator.[86] The obtained copolymers were post-functionalized with ethylene diamine (EDA) and hexamethylenediamine (HMDA) to form H-NIPUs that were used as coatings. They exhibited good solvent resistance, low moisture absorption but poor adhesion to metal and poor impact strength. Webster and Crain studied the copolymerization of vinyl ethylene carbonate (VEC) with vinyl esters.[42] Further carbonate-amine post-functionalization studies were performed in propylene glycol monomethyl ether. Primary amines born onto primary carbons were preferred. It was shown that the stoichiometric ratio between the cyclic carbonate moieties and the amine was of great importance for the solvent resistance, namely, the less amine was incorporated into the formulation, the lower the solvent resistance. This result was however balanced by the fact that there was a limiting value above which no further improvement was observed. This was correlated with the fact that the crosslinking reaction reaches a maximum conversion, which is a classical result in PHU chemistry. Otherwise, good gloss, pendulum hardness and impact resistance were observed for the formed coatings.

Cyclic carbonate (meth)acrylate (CC(M)A) polymerization has been extensively studied and reported in the scientific literature.[84] Cyclic carbonate methacrylate (CCMA) can be synthesized through many reactions pathways that have been summarized by Webster[95] and Caillol.[84] However, the carbonation reaction by catalytic fixation of CO_2 onto glycidyl methacrylate (GMA) remains the main pathway. It is important to mention that pure CCMA alone is unstable, but stable up to 100 °C when unpurified according to Endo *et al.*[99] This instability can still be an issue after polymerization. Therefore, there is a general agreement on the fact that the radical polymerization of glycidyl methacrylate – GMA – followed by its carbonation reaction with CO_2 presents advantages with respect to the direct polymerization of CCMA - Scheme 10.[100–102]



Scheme 10: Different synthetic pathways towards the formation of poly(CCMA) – adapted from Endo and coworkers[103]

Some research teams tried to make CCMA-containing oligomers react with amine-containing compounds to yield hydroxyurethane. Kihara *et al.* thus functionalized CCMA-containing oligomers with butylamine, benzylamine, cyclohexylamine and dibutylamine.[99] The authors showed that an excess of amine as opposed to the CCMA units was necessary for reaching full conversion. Secondary amines barely reacted due to steric hindrance. Finally, when a diamine such as hexamethylene diamine (HMDA) was introduced with a 1:1 ratio, gelation occurred after 1.5 h in dimethylsulfoxide (DMSO). The infrared (IR) analysis revealed that the reaction was not complete since traces of cyclic carbonate and amine could be observed, trapped in the polymer network. The obtained film was reported as both hard and flexible. The same team published[100] the post-functionalization of a copolymer of CCMA and GMA (30:70, Mn=22000 g/mol, Đ=2.5) *via* an aminolysis reaction with butylamine. In this case, careful attention between the reactivity of the oxirane and the carbonate moieties should be paid. If an acidic treatment was performed prior to aminolysis, then the oxirane moieties would open and the amine would selectively react onto the carbonate moieties. The obtained polymers displayed increased solubility in water and methanol, which was not the case before functionalization with the amine. When the aminolysis was performed before the acidic treatment, crosslinking through an “epoxy-like” mechanism occurred and made the final polymer insoluble. Finally, in 2010, Jana *et al.* used atom transfer radical polymerization (ATRP) in order to synthesize homopolymers, triblock copolymers and terpolymers bearing CCMA moieties in pendant chains.[96] They post-functionalized the CCMA moieties with 2-phenylethylamine in order to modify the solubility and wettability properties of the obtained polymers. The reaction was carried out in dimethylformamide (DMF) and different degrees of functionalization were achieved. Only 40 % of functionalization was enough to make the polymers soluble not only in polar aprotic solvents such as DMF and DMSO but also in more common solvents such as acetonitrile (ACN) and tetrahydrofuran (THF). Higher extents of functionalization (~90 %) allowed solubilizing the polymers in solvents such as chloroform. Finally, the films’ properties were studied, and it was found that functionalizing the CCMA-containing polymers helped transitioning from a quite brittle to uniform, transparent and continuous films when casting them onto glass substrate using DMF as solvent. The water contact angle, while strongly depending on the polymer composition, was shown to continuously increase with the degree of functionalization in spite of the concomitant appearance of hydroxyl groups. This was attributed to the effect of the hydrophobic side group of the 2-phenylethyl amine used. This suggests that tuning of the hydrophilic/hydrophobic balance of the final polymer could probably be achieved by changing the amine.

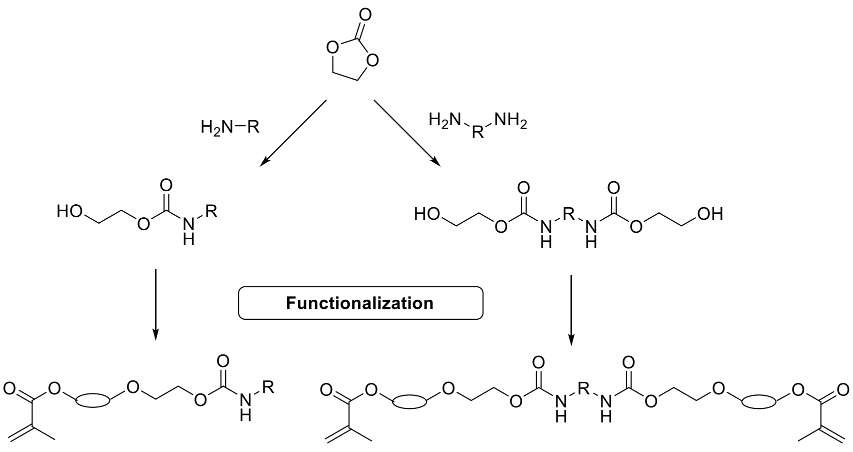
Such technologies were also patented, notably by Figovsky *et al.*[104,105] who claimed the formation of coatings based on the curing reaction between cyclic carbonate methacrylate (CCMA) and amines. They also mixed those technologies with the previously described Epoxy-NIPUs obtaining mechanical properties with an average tensile strength of 40 MPa and an average elongation at break of 55 % depending on the formulation.[104] Iwamura and coworkers also patented aminolysis of cyclocarbonate-based oligomer to produce coating for automotive applications.[106]

Interestingly, CCMA has been incorporated into formulations for emulsion copolymerization. Yang *et al.*[107] patented an interesting process in which different latexes were prepared, some bearing CCMA moieties and others bearing amines. It was shown that those latexes were able to crosslink. The CCMA-functionalized latexes were capable of forming films and further addition of polyamine induced crosslinking. When the CCMA-functionalized and amine-functionalized latexes were blended together, the formed film could be crosslinked by curing at room temperature during 24 h. These films exhibited gel contents around 60 % in acetone, as well as good water resistance. Other patents from BASF disclosed the use of CCMA-functionalized coatings that were able to crosslink according to the same mechanisms described before using primary amine agent for paint applications.[108–110]

Finally, the case of cyclic carbonate acrylate (CCA) has also been studied, although to a lesser extent than for CCMA. The synthetic routes towards the formation of CCA are very similar to those to synthesize CCMA.[111–114] Yields of 85% were obtained through the carbonation of glycidyl acrylate with CO_2 at 60°C in the presence of inhibitors (4-methoxyphenol).[114] The reaction conditions as well as the purification steps are of extreme importance since the monomer can suffer from side-reactions or even start polymerizing at temperatures as low as 40 °C. Homopolymerization of CCA in solution usually led to insoluble polymers, which was explained because of the transfer reaction from the carbonate ring with proton removal and radical recombination.[99,115] The copolymerization with 2-ethylhexyl acrylate was found to be a solution to yield soluble polymers in benzene, chlorinated solvent such as dichloromethane and tetrahydrofuran.[115] Photopolymerization was also implemented.[116,117] To the best of our knowledge, only one example has been reported in which the carbonate moieties were functionalized with butylamine.[115] Kinetic studies on model molecules showed that bulk processes were faster than solution processes.[115]

3.2.2. (Hydroxy)urethane methacrylates – (H)UMAs

(Hydroxy)urethane methacrylates ((H)UMAs) are short oligomers (usually dimers or trimers) synthesized by aminolysis of a cyclic carbonate and an amine, one of them bearing at least one methacrylate moiety. A typical isocyanate-free synthetic approach consists in the formation of a diol, which is subsequently functionalized into a dimethacrylate component (Scheme 11), but more complex structures have also been designed.[21,118,119]



Scheme 11: Formation of UMAs via the aminolysis of ethylene carbonate followed by subsequent functionalization

(H)UMAs were originally designed to be used as reactive diluents. Such compounds can for example be employed in ultraviolet (UV)-curable coatings, which are gaining interest for their fast curing and low energy consumption.[120] Figovsky *et al.* reported UV-curable concrete floor coatings able to cure instantly.[64] A general composition of a UV-curable coating is a mixture of photoinitiator, oligomer and reactive diluent, the latter being used to decrease the viscosity of the global mixture, while polymerizing in the crosslinking reaction to form a 3D-network. According to Wang and Soucek, mono-functional reactive diluents usually lead to a decreased modulus and increased ductility whereas bi- and/or multi-functional reactive diluents have the opposite effect.[118] It was also found that the introduction of acrylic moieties into the (H)UMAs was a suitable method for overcoming the yellowing effect of the PHU caused by sunlight.[105] Due to their versatile composition, and the diversity of components that can be used for copolymerization purposes, UV-curable formulations can find other applications such as biomedical, for instance *via* the development of injectable liquids, paste or gels (dental composite applications being a potential example).[119,121]

Assumption and Mathias published in 2003 a method for synthesizing isocyanate free urethane methacrylates UMAs *via* the ring opening aminolysis of ethylene carbonate with various amines.[119] Hexamethylene Diamine (HMDA), 3-amino-1-Propanol and 2,2-dimethyl-1,3-propanediamine were used, and methacrylic anhydride was utilized in the functionalization step in order to catalytically react with all the hydroxyl groups - Figure 7. The kinetics of the radical photopolymerization of the formed UMAs was measured and extremely fast polymerization rates (plateauing conversion after 100 s reaction time) were obtained. An immediate auto-acceleration was noticed and the fastest polymerization rates were reached after 4 to 5s. The reaction rate was found to strongly depend on the monomer structure of the UMA. In particular, the presence of H-bonding, allowing pre-association effects between the monomers enhanced the polymerization rates, which is in accordance with the work of Jansen *et al.*[92] Wang and Soucek[118] synthesized a series of similar reactive diluents following a similar procedure. They varied the structure of the cyclic carbonate compound to introduce an additional methyl moiety. 2-(methacryloyloxy)ethyl 2-(methacryloyloxy)ethylcarbamate (EOAED), 2-(methacryloyloxy)ethyl 3-(methacryloyloxy)propylcarbamate (POAED), and 1-(methacryloyloxy)propan-2-yl 3-(methacryloyloxy)propylcarbamate (POAPD) were hence synthesized by functionalization with methacrylic anhydride - Figure 7. The formed reactive diluents were tested in a formulation containing an oligo polyester. It was observed a general increase of tensile strength and elongation at break when using the non-isocyanate version of the reactive diluents. In more details, and as already observed in the case of Epoxy-NIPUs, there was an optimum concentration of reactive diluent to be introduced in the formulation. Below this value, tensile strength and elongation at break increased with the reactive diluent content. Above it, they usually decreased. Glass transition temperatures (T_gs), α-transition temperatures T_αs and gel contents also increased with the reactive diluent content, due to the higher crosslinking density. One drawback is the water sensitivity since the water absorption was found to increase with the increase in reactive diluent content. This was attributed to the increase of ester-urethane group concentration, a polar group capable of interacting with water. Finally, the reactive diluents increased the impact resistance.

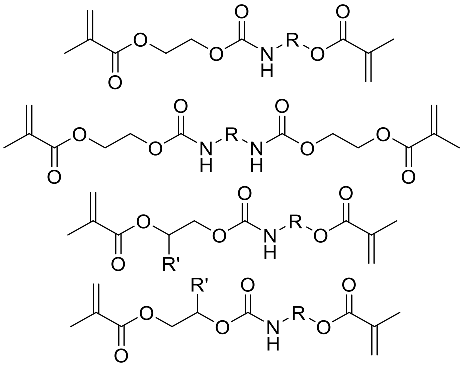
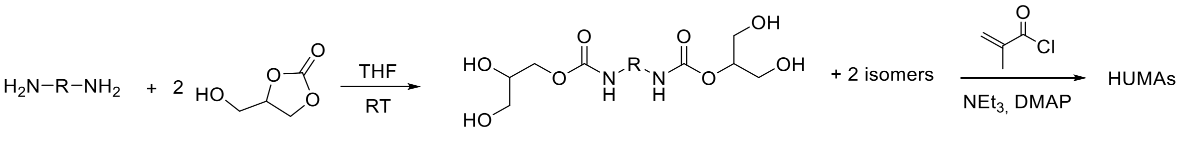


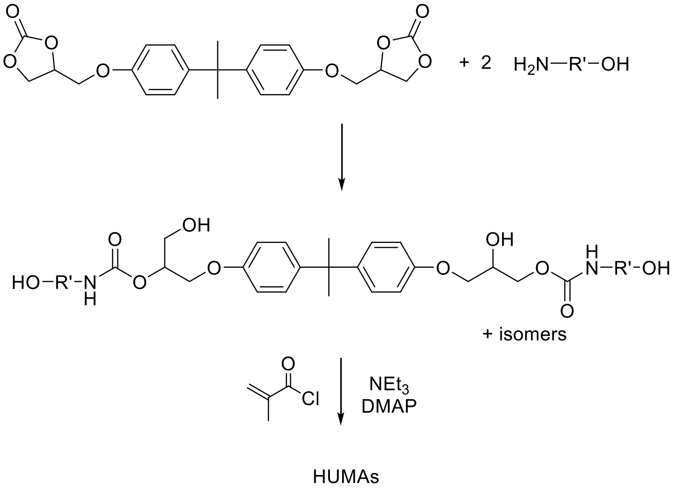
Figure 7: Reactive diluents prepared by Assumption *et al.*[119] and Wang *et al.*[118]

Similar types of multi-functional hydroxyurethane methacrylates (HUMAs) were proposed by Biernat and Rokicki in 2005.[21] The synthetic approach relies on the aminolysis reaction of glycerol carbonate with a diamine. The formed hydroxyurethane quadriols (3 isomers can be obtained) were subsequently modified by reacting with methacryloyl chloride or methacrylic anhydride to form the corresponding quadrimethacrylate - Scheme 12. Various amines could be used for the synthesis, including 1,3-diaminopropane, 1,2-diaminoethane and isophorone diamine (IPDA). Amino-alcohols were also used and yielded trifunctional urethane methacrylates.



Scheme 12: Multifunctional HUMAs via functionalization of glycerol carbonate-based quadriols by methacryloyl chloride according to Biernat and Rokicki.[21] (Note that DMAP stands for 4-Dimethylaminopyridine)

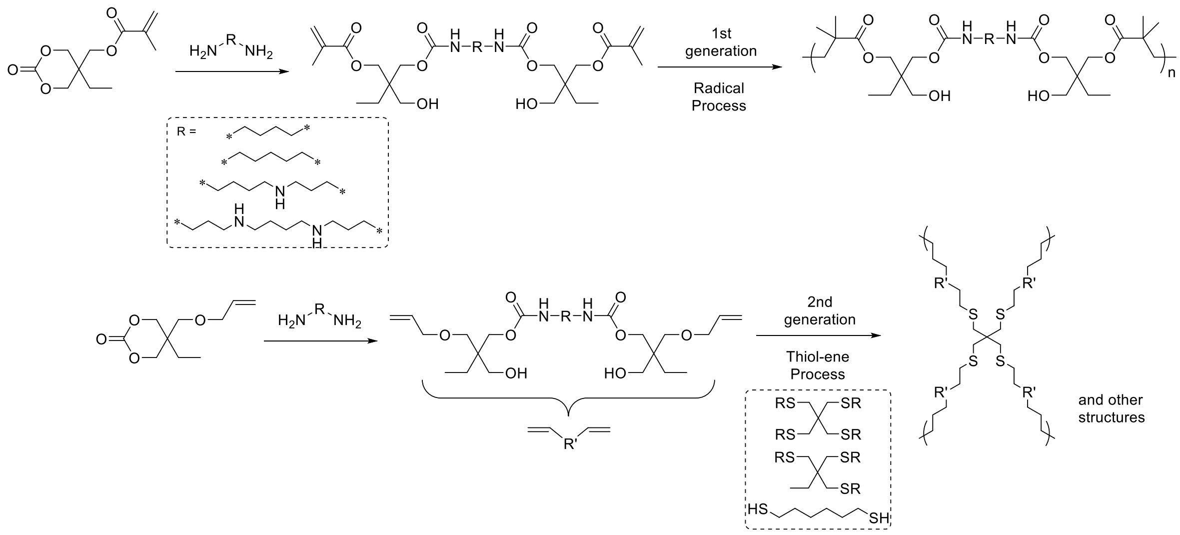
Following a similar approach, the same authors[21] used carbonated- Bisphenol-A Diglycidyl Ether (BADGE) in order to synthesize multifunctional HUMAs. This process was different from the one previously described in the sense that a bis-cyclic carbonate compound was used instead of a mono-cyclic carbonate. The quadri-functionality was brought through the reaction with an amino-alcohol that was further modified with methacryloyl chloride to yield the final products - Scheme 13.



Scheme 13: Multifunctional HUMAs via functionalization of carbonated-BADGE-based quadriols by methacryloyl chloride according to Biernat and Rokicki.[21] (Note that DMAP stands for 4-Dimethylaminopyridine)

The synthesized resins exhibited high flexural strength after curing. The BADGE-based resins had superior toughness than a reference resin for dental compositions. This high flexural strength in combination with a low viscosity make such components extremely interesting reactive diluents. Due to the high crosslinking density, a high hardness is usually obtained.

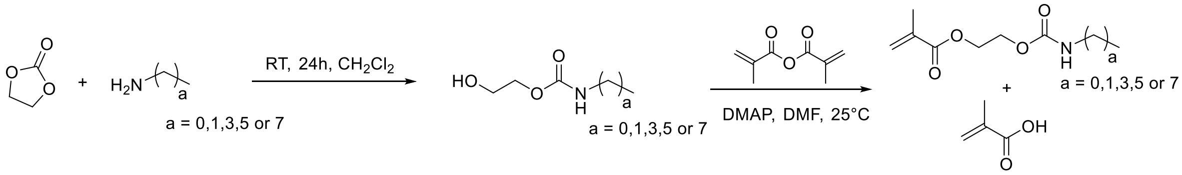
Attention has recently been paid towards the development of new kinds of materials for 3D – printing purposes.[122] The ability of (Hydroxy)urethane Methacrylates – (H)UMAs – to photopolymerize makes them perfect candidates for such applications. To the best of our knowledge, two research teams have recently published isocyanate-free pathways to develop 3D-printable resins. The team of Chen proposed two possible polymerization pathways for the design of 3D-printable resins based on the formation of a diurethane adduct *via* the aminolysis of a vinylic- (or methacrylic-) 6-membered cyclic carbonate monomer with a diamine. The authors suggested two polymerization pathways: a first generation of adducts reacting in a radical photoinduced process whereas a second generation proceeded through a thiol-ene route - Scheme 14.[123,124]



Scheme 14: 3D-printable HUMAs based on a 6-membered cyclic carbonate diurethane adducts, further polymerized either by radical photopolymerization (1st generation)[123] or via thiol-ene chemistry (2nd generation)[124] – adapted from Pyo *et al.*

In the first generation, the diurethane adduct containing methacrylic moieties was formed first and then crosslinked *via* an ultraviolet (UV)-induced process to yield the final material. The obtained products were amorphous and stable up to temperatures higher than 200 °C. They were 3D-printed in a continuous optical printing system using a layer by layer polymerization methodology. Materials of tunable stiffness with smooth contours could thus be designed. In the second generation, a vinylic cyclic carbonate was copolymerized also in a UV-induced process with bi- to quadri-functional thiols. The biocompatibility of these materials for potential biomedical applications was also evaluated. (Hydroxy)urethane Methacrylates – HUMAs – were synthesized through the reaction of a series of diamines with two equivalents of cyclic carbonate methacrylate (CCMA) in a bulk process for 3D-printing purposes.[125] . The HUMAs were further copolymerized with 4-methacryl-oylmorpholine (ACMO) with the help of a photo-initiator. The structure of the diamine was found to have a great influence on the viscosity of the resulting acrylic resin formulation, but all of them remained within industrially acceptable viscosity ranges. Short and flexible etheramines were highlighted as preferable reactive diluents since they offered a compromise between low viscosity and very good mechanical performance (Young modulus of 3600 MPa, and tensile strength of 85 MPa were measured in the case of 1,8-diamino-3,6-dioxaoctane-based HUMAs). Multifunctional HUMAs obtained by functionalization of the pendant OH groups with methacrylate anhydride were also used leading to an increase in thermo-mechanical properties (Young modulus of 4200 MPa instead of 3600 MPa and a T_g of 173 °C instead of 86 °C were obtained).

There are two examples of the use of urethane methacrylates (UMAs) in waterborne systems.[126,127] The UMAs were prepared *via* the aminolysis reaction of ethylene carbonate with a series of aliphatic amines prior to the functionalization with methacrylic anhydride - Scheme 15.[126] This process allowed to target different hydrophobicity level for the reactive diluents, that were subsequently copolymerized with MMA/BA in a seeded semibatch emulsion polymerization in monomer starved conditions, with a solids content of 30 wt%. The same year, the same team investigated more deeply the case of BEM (butyl-based UMA, a=3 in Scheme 15).[127] The emulsion polymerization process (batch vS semibatch mode) as well as the particle morphology (homogeneous vS core-shell) and the location and concentration of BEM within the particle (in the core or in the shell) in terms of film properties were the focus of the study. Those works are reviewed in more details in the Part B of this Chapter dealing with water-based NIPUs.



Scheme 15: Preparation of mono-functional UMAs of different hydrophobicity according to Meng *et al.*[126]

3.2.3. Unsaturated NIPU-prepolymers: Poly(hydroxy)urethane methacrylates – P(H)UMAs

3.2.3.1. H-NIPUs *via* radical polymerization

- Radical reactive telechelic polyurethanes

Longer isocyanate-free urethane methacrylates UMAs (oligoUMA) were designed by Ochiai and Utsuno by functionalizing oligomeric polyurethane diols with glycidyl methacrylate (GMA).[128] The polyurethanes (PUs) originate from a transurethanization process yielding the OH-telechelic oligomers. The ring opening of GMA did not proceed to full conversion so that an excess was employed for maximizing the extent of functionalization. The oligoUMAs were further copolymerized with methyl acrylate (MA) (in a ratio 50:50 in reactive moieties) in dimethylformamide (DMF) at 60 °C using AIBN as thermal initiator for 24 h - Figure 8. The formed polymer almost instantaneously became a gel, which was insoluble in any organic solvent. The formed polymer was composed of a hard PU segment and soft poly(methyl methacrylate) segments. After thermal treatment in the DSC, the PU and the acrylate phase became miscible and a single T_g of 34 °C was obtained. The T_g was found to be higher than both the native PU and poly(MA), a phenomenon that was attributed to the restricted motion of the polymer chains in the 3D network.

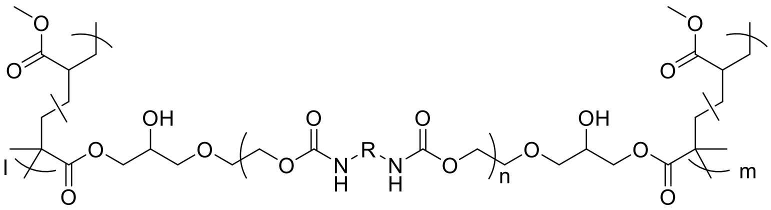
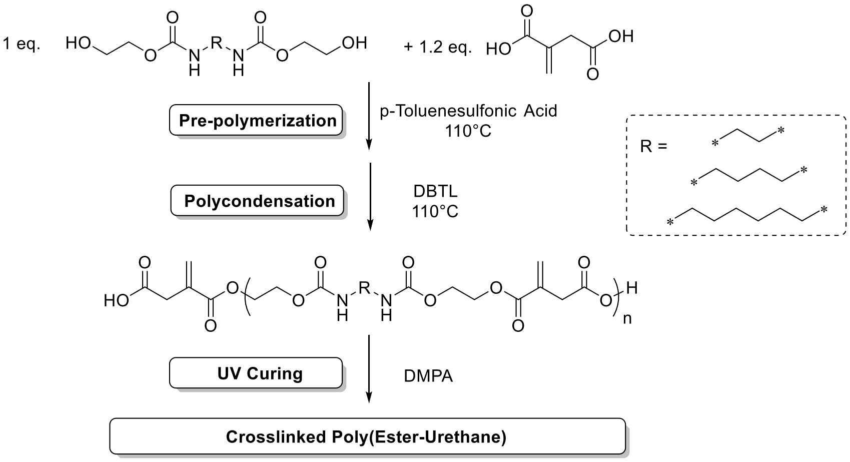


Figure 8: Copolymer from oligoUMA and MA according to Ochiai *et al.*[128]

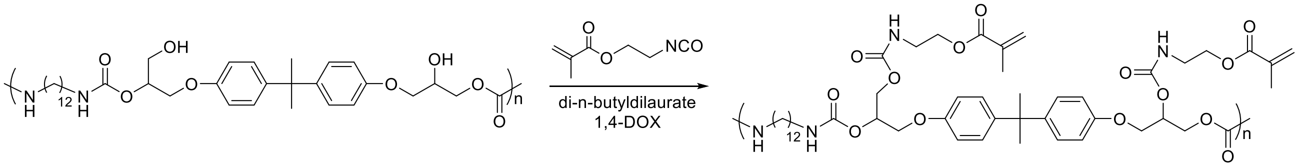
The growing interest in the development of a more sustainable chemistry is pushing the research community to develop more environmental friendly products. In this purpose, Han *et al.* developed a new kind of poly(ester-urethane)s that were functionalized with the bio-based itaconic acid - Scheme 16.[129] NIPU pre-polymers were synthesized by ring opening of ethylene carbonate with various diamines. The formed diols were then reacted with an excess of itaconic acid and subsequent polycondensation led to radical reactive telechelic oligo(Ester-Urethane)s. The latter were further cured by a UV-induced process with dimethylpropionic acid (DMPA). Gel contents in the range 80 to 88 % in acetone were obtained. The tensile strength depended on both the chain length of the diamine and the crosslinking density, with the best mechanical properties obtained in the case of putrescine-based oligo(Ester-Urethane) (Young modulus of 52 MPa, a tensile strength of 2.5 MPa and an elongation at break of 33 %).



Scheme 16: Fully-bio-based HUMAs functionalized by itaconic acid according to Han *et al.*[129]

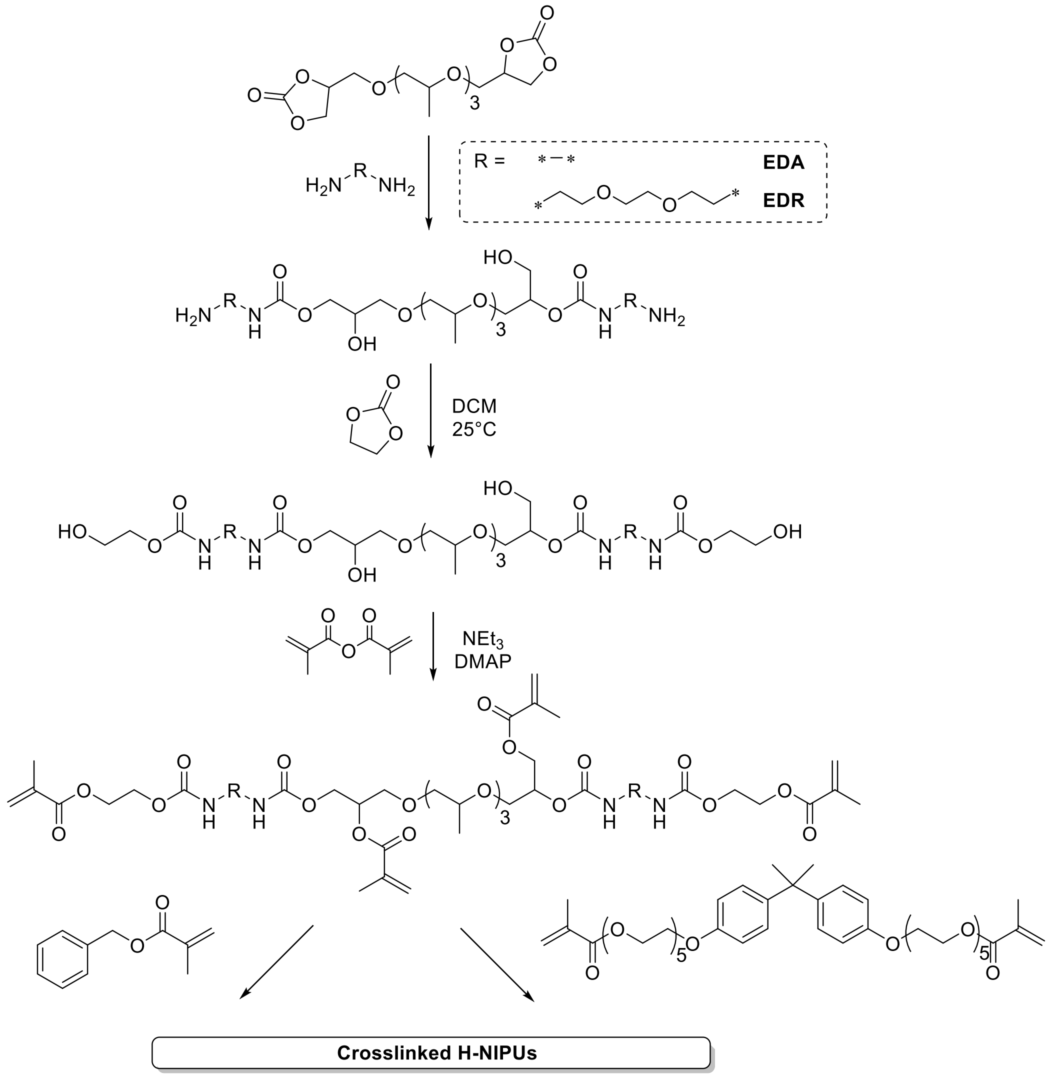
- <u>Hydroxyl-group functionalization</u>

The group of Endo functionalized the pendant OH groups of isocyanate-free oligo(hydroxyurethane)s (oligoPHUs)[130] by reacting 2-methacryloyloxyethyl isocyanate with a carbonated Bisphenol-A Diglycidyl Ether (BADGE)-based oligoPHU - Scheme 17. The temperature of the urethanization should be controlled to avoid polymerization of the methacrylate moieties. Therefore, room temperature was preferred and a full conversion could be obtained. . The advantage of functionalizing pendant OH groups relies on the fact that the degree of functionalization can be controlled. When functionalizing the oligoPHU with 1 eq. of the isocyanate compound with respect to the hydroxyl groups in the oligomer, successful copolymerization with Hydroxyethylmethacrylate (HEMA), methyl methacrylate (MMA) and N-isopropylacrylamide (NIPAM) was achieved in dioxane. In all the cases, the viscosity of the polymerization mixture increased during the reaction until the formation of insoluble gels. T_gs lower than or identical to that the corresponding polymethacylates were measured, suggesting that the distance between crosslinking nodes was sufficiently long to allow mobility of the incorporated PHU chains. It should however be mentioned that this synthetic process, despite being extremely interesting, is unfortunately not fully isocyanate-free, which can seem counterbalancing the isocyanate-free process formation of the native oligoPHU.



Scheme 17: Functionalization of the pendant OH-groups of carbonated BADGE-based oligoPHUs according to Endo and coworkers[130]

A very recent example, from Caillol and coworkers, describes the synthesis of hydroxyurethane Methacrylate (HUMA) capable of crosslinking in a thermal pathway only, without using any initiator.[131] A carbonated poly(propylene oxide) diglycidyl ether (shortened PPOBC) was reacted with ethylene diamine (EDA) or with (ethylenedioxy)diethylamine (EDR) to form a diamino-telechelic compound, which was further functionalized with the help of ethylene carbonate. The formed diol was then modified with methacrylic anhydride into the corresponding HUMA as described in Scheme 18**.** The formed HUMAs were further homopolymerized or crosslinked with either benzyl methacrylate or poly(ethylene oxide) bisphenol A dimethacrylate.



Scheme 18: PPOBC-based HUMAs as prepared by Caillol and coworkers[131]

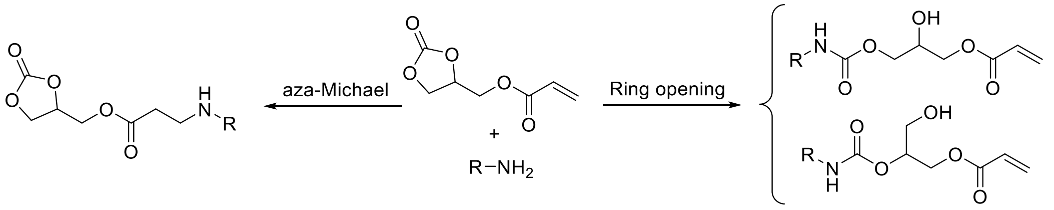
In order to thermally initiate the radical polymerization, a specific temperature program incrementing from 80°C to 150 °C was implemented. The step-by-step increase in temperature was designed so that the formation of bubbles was avoided. High gel contents, above 97% sometimes close to 100 %, were obtained. Swelling in dichloromethane indicated that the solvent uptake was higher in the case of EDA-based methacrylic-NIPUs than in the case of EDR-based ones, a result that was attributed to the higher chain length of EDA-based methacrylic-NIPUs. (The NH2/carbonate ratio was lower in the case of EDA than EDR during the synthesis of the NIPU pre-polymers).

After curing (by homopolymerization, with benzyl methacrylate or with poly(ethylene oxide) bisphenol A dimethacrylate), the thermal stability of the obtained materials was not significantly improved when copolymerizing with aromatic ring-containing acrylic monomers according to TGA ($Td_{5\%}$ of 250°C for EDA and 280°C for EDR were obtained). However, the char yield increased when benzylmethacrylate was used in the formulation. Complex effects on the glass transition temperatures – (T_g) were observed. The T_g of the homopolymer made of EDA-based methaxrylic-NIPUs (43°C) was lower than that of the EDR-based ones (69°C). This was attributed to the longer chain length of the EDA-based NIPUs. When copolymerizing with poly(ethylene oxide) bisphenol A dimethacrylate), lower T_gs were obtained, a result that was attributed to the flexibility brought by the poly(ethylene oxide) moieties. No clear trend was obtained with benzyl methacrylate. With EDA-based methacrylic NIPUs, the T_g increased (52°C) whereas it decreased with EDR-based methacrylic NIPUs (55°C). The authors attributed this effect due to a balance between π-staking interactions, the bulkiness of the aromatic groups (favoring chain mobility) and the NIPU chain lengths.

Dynamic Mechanical Thermal Analysis (DMTA) analyses revealed very broad tan δ peaks, suggesting that the formed materials were highly heterogeneous.

3.2.3.2. H-NIPUs *via aza*-Michael addition

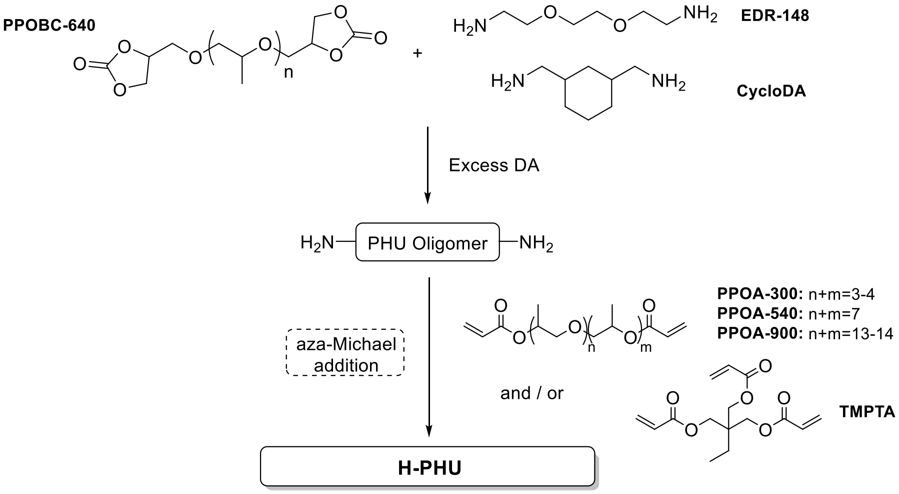
It is striking to notice that very few examples of radical reactive hydroxy-urethanes involve acrylic-modified components. The reason for this is the high reactivity of the acrylic moieties towards amines. Two reactions are in competition. The amine can react either through the ring-opening of the cyclic carbonate moiety resulting in the formation of the classical hydroxy-urethane adducts, or with the acrylic moiety through an *aza*-Michael type mechanism - Scheme 19. For cyclic carbonate acrylate (CCA), Nohra et *al.* proved that the *aza*-Michael type addition was favored compared to the ring opening reaction.[98]



Scheme 19: Competition between ring opening of the cyclic carbonate and *aza*-Michael addition onto the acrylic moiety in the reaction between CCA and an amine

As a matter of comparison, Mülhaupt *et al.* found that only 2 % of methacrylate moieties were converted in an *aza*-Michael addition when the amine was added in excess.[125]

Caillol *et al.* developed new types of hybrid-NIPUs (H-NIPUs), synthesized *via* an *aza*-Michael type process[132] by reacting in a bulk process a polypropylene oxide-based bis cyclic carbonate with an excess of diamine to yield homotelechelic oligoPHUs. The latter further reacted with different poly(propylene oxide) bis-acrylate (PPOA) and trimethylolpropane tris-acrylate (TMPTA) to form the hybrid-NIPUs - Scheme 20.



Scheme 20: H-NIPUs formed via the aza-Michael addition of amino homotelechelic oligoPHUs with polyacrylics – adapted from Caillol and coworkers[132]

The viscosity of the formed PHUs depended on the degree of polymerization and the diamine structure. The H-NIPUs were cured at room temperature and 48 h were needed to ensure an almost complete conversion of the acrylic moieties. The T_g was found in general to be a compromise between the rigidity originating from the amount of the triacrylate and the flexibility provided by the chain length of the bis-cyclic carbonate. However, most of the obtained materials were brittle. When diacrylates were added into the formulation to increase flexibility, the T_gs usually were around -30 °C. Gel contents were higher than 90 % were obtained. Short amino-telechelic oligomers were found to be detrimental to the formulation since they provoked demixing, especially when long acrylic chains were used for curing purposes.

3.2.4. Radical reactive (H)UMAs – Summary of the synthetic strategies

As it can be seen from the previous description, there are numerous synthetic pathways towards the formation of (Hydroxy)urethane Methacrylates - (H)UMAs that are summarized in Figure 9 below.

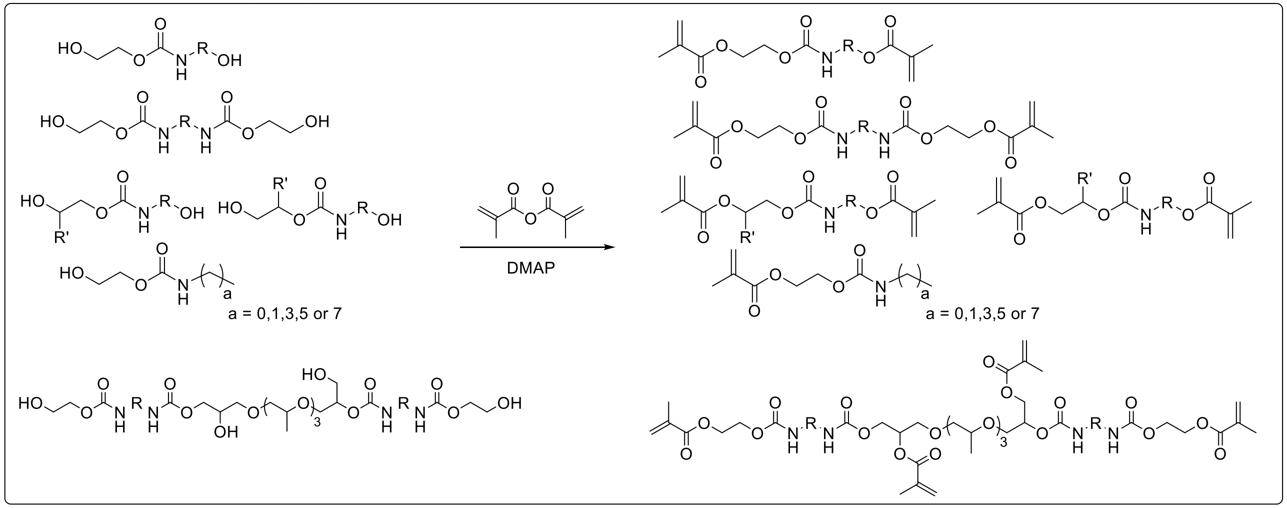
In a majority of cases, esterification reactions are used in order to bring the methacrylate functionality. The use of methacrylic anhydride has been extensively described and proved to be effective in the functionalization of alcohol moieties (coming from both the ring opening of the ethylene carbonate or pendant hydroxyl groups of PHUs) provided that dimethylproprionic acid (DMAP) was used as a catalyst. Interestingly, the functionalization also worked in bulk, meaning that no solvent removal is needed prior to further crosslinking. Methacryloyl chloride was also used for the functionalization of hydroxyl groups. Catalysis is usually needed and triethylamine is often employed in order to avoid the generation of hydrochloric acid (HCl). This brings further issues in terms of processing conditions since solvent and very low temperatures are needed to avoid runaways during functionalization, and therefore further purification of the (H)UMAs are needed before any crosslinking reaction can be envisioned. In all the cases, the raw materials are petroleum-based, although bio-based itaconic acid has been used for the formation of (H)UMAs. Since the itaconic acid is a diacid, an original oligomerization strategy to afford itaconic-homotelechelic poly(ester-urethane)s has been developed.

Epoxidation reaction *via* the ring opening of glycidyl methacrylate has been also used. This reaction was effective but it was found to be long, needed catalysis and was performed in dimethylformamide (DMF), which requires further purification steps.

Another possibility is the formation of carbamate moieties. This can be done using isocyanate-dependent or isocyanate-free pathways. An example of the isocyanate-dependent route was the functionalization of pendant OH-groups of PHUs with 2-methacryloyloxyethyl isocyanate. Despite the success of the functionalization, this methods presents the drawback of using isocyanates. The diurethanization of a radical reactive carbonate appears as a promising pathway towards the formation of methacrylic homotelechelic oligo(H)UMAs. Some examples of fully bio-based oligoUMAs were reported and used in 3D-printing applications.

Functionalization Steps

- Functionalization with methacrylic anhydride

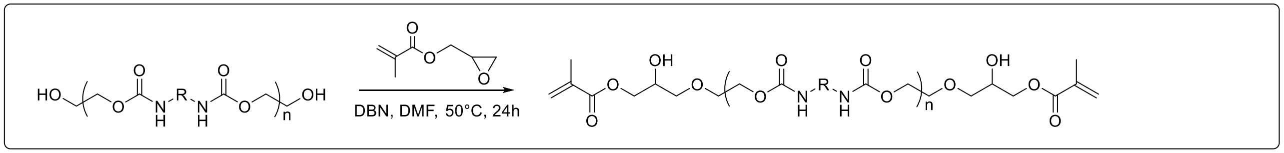


(Assumption *et al*)

(Wang *et al*)

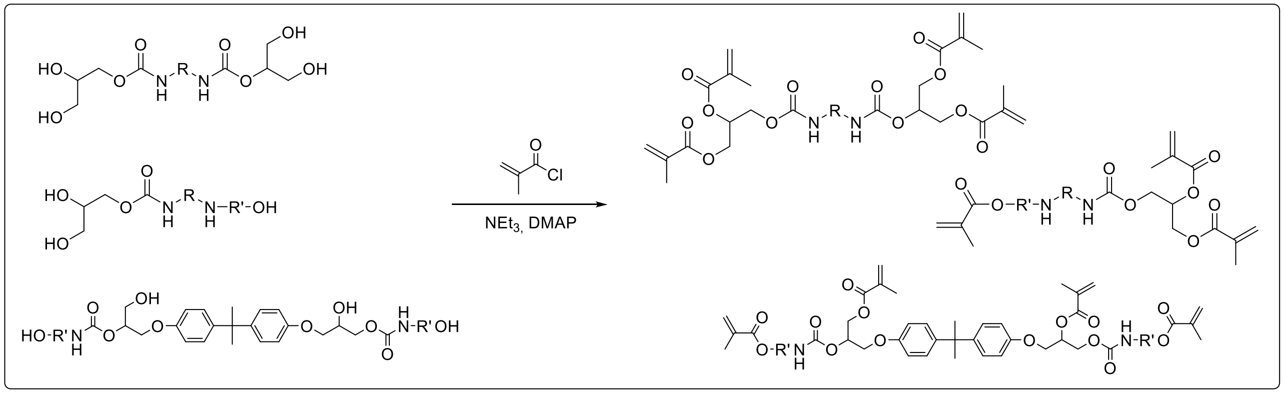
(Caillol *et al*)

- Functionalization with glycidyl methacrylate



(Ochiai *et al*)

- Functionalization with methacryloyl chloride



(Biernat *et al*)

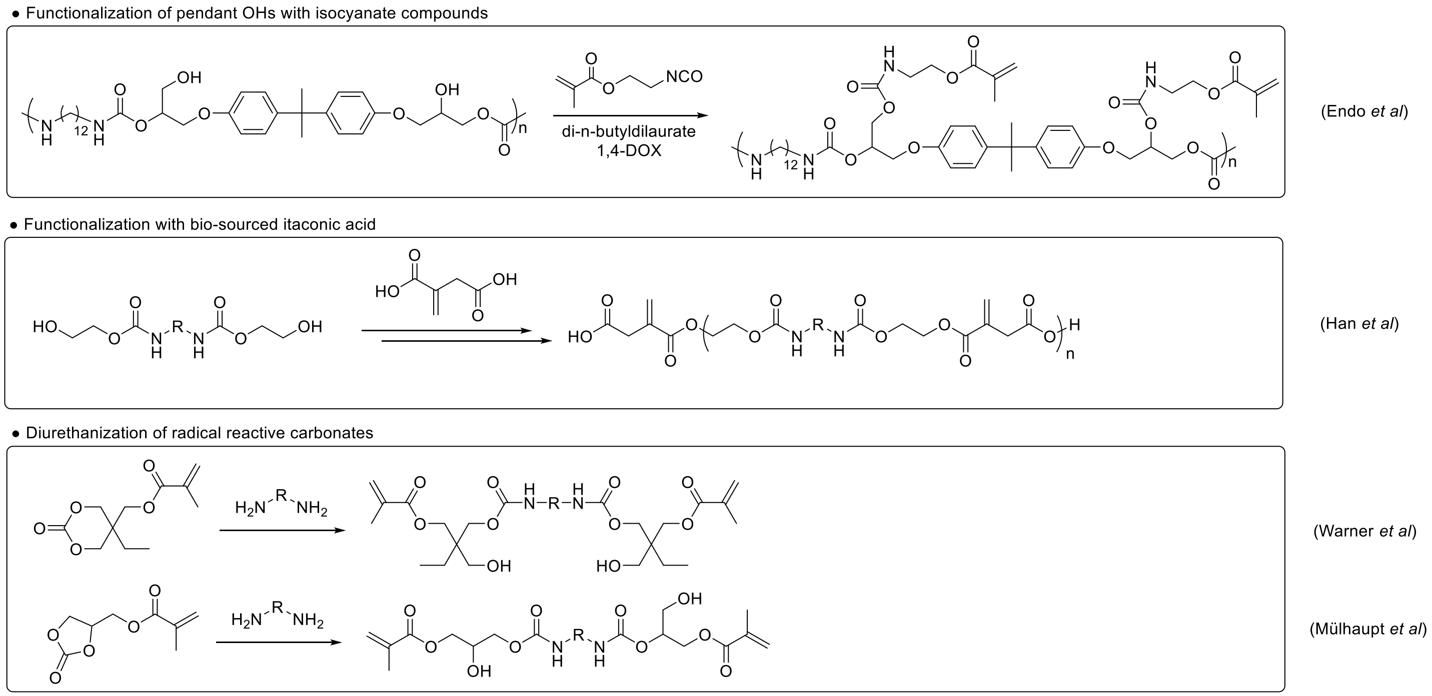


Figure 9: General summary of the different functionalization strategies towards the formation of (H)UMAs

3.3. Other Hybrid-NIPUs

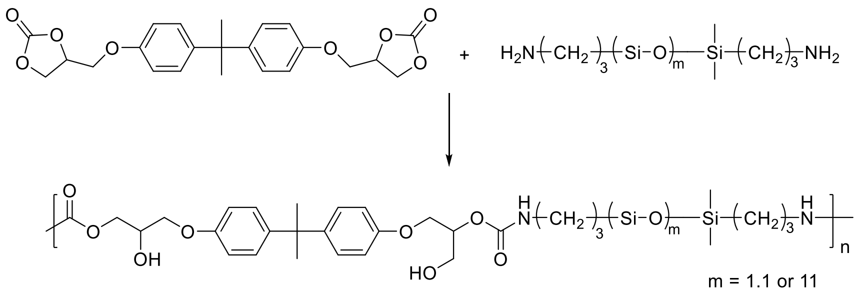
In addition to epoxy and (meth)acrylic NIPUs, new types of hybrids have appeared in the scientific literature. Herein silicon containing H-NIPUs and hybrids combining biopolymers with NIPUs are discussed.

3.3.1. Si-containing H-NIPUs

Silicon and more specifically siloxane-containing H-NIPUs have been prepared in order to confer new kinds of properties to the hybrids. Siloxane moieties can be incorporated through various synthetic means, either in the inner backbone of the final linear NIPU or by acting as crosslinking agents bearing cyclic carbonate or amine moieties, hence yielding a branched or crosslinked architecture. Both routes will be described.

3.3.1.1. Si- containing linear H-NIPUs with inner siloxane backbones

Endo and coworkers and Hanada *et al.* introduced in 2014 a PHU containing siloxane in the inner backbone of the polymer material.[133,134] Their purpose was to achieve improved water resistance and flexibility. They designed a 1 pot-2 steps process in which Bisphenol-A Diglycidyl Ether (BADGE) was carbonated by CO_2 fixation prior to reacting with the siloxane containing diamine - Scheme 21. Propylene glycol methylether acetate (PGMAC) was a suitable solvent to obtain the final PHU in high yields. When comparing the siloxane containing NIPUs with a classical NIPU made of carbonated BADGE and dodecanediamine, it was found that the higher the siloxane content, the higher the solubility of the formed products in solvents of low polarity such as Et_2O. Water contact angle and flexibility increased as the siloxane content increased. The materials had low glass transition temperatures (1 and 26 °C as opposed to 40 °C with dodecanediamine).



Scheme 21: PHU containing siloxane-based inner backbone according to Endo and coworkers[133]

As far as we know, only one example of siloxane-containing bis-cyclic carbonate compounds has been patented. This work was performed by the team of Hanada[135] and preceded the patent on diamino-polysiloxane macromomers.[133] An example of the synthesized bis-cyclic carbonate compounds in provided is Figure 10. The authors targeted applications such as thermal recording medium, artificial leather, thermoplastic polyolefin resin skin material and weather strip material. The obtained bis-cyclic carbonates were further converted by reacting with diamines (hexamethylene diamine (HMDA), bis-aminopropylpiperazine, and xylylenediamine were used). The number average molar masses were in the range 30000-40000 g/mol depending on the siloxane-containing bis-cyclic carbonate and the diamine used. Tensile strengths of around 24 to 35 MPa and elongations at break in the range of 15 to 83 % were obtained, witnessing the possible tuning of the material properties.

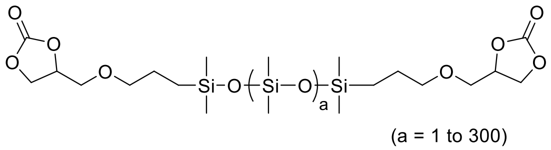


Figure 10: Example of a siloxane-containing bis-cyclic carbonate macromonomer as patented by Hanada *et al.*[135]

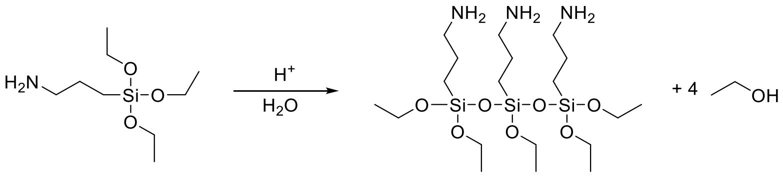
Figovsky *et al.* used a siloxane-containing macromonomer in their Epoxy-Amine H-NIPU systems.[136] They claimed the synthesis of nanostructured H-NIPUs that were constituted by epoxy-function, cyclic carbonate, amine-functional and (meth)acrylate components. Among them, at least one epoxy, amine or (meth)acrylate contained alkoxysilane moieties. The formed polymers crosslink upon curing at ambient conditions by means of atmospheric moisture, yielding nanostructured materials without the need of using water embedding or addition of nanofillers. The materials exhibited improved abrasion resistance and higher impact resistance and flexibility compared with a conventional epoxy resin siloxane based material that was used as a reference.

3.3.1.2. Si- containing branched or crosslinked H-NIPUs with outer siloxane backbones

Another important pathway is the reaction of siloxane or Si-containing reagents bearing cyclic carbonate or amine moieties.

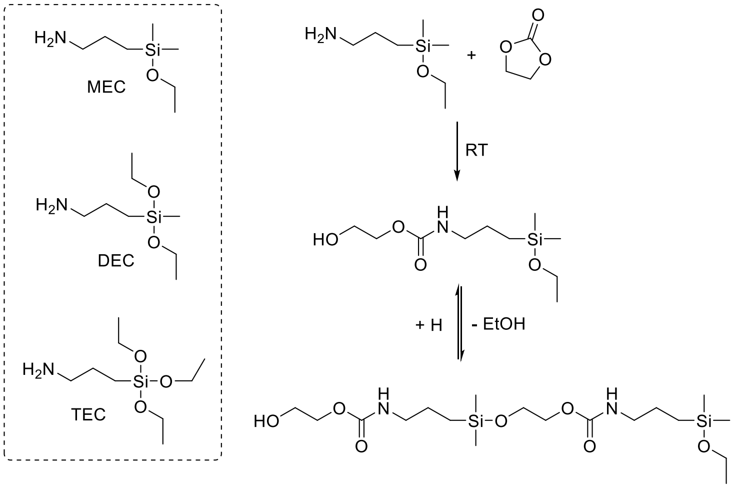
- Si-containing reagents bearing amine moieties

Figovsky and coworkers developed thermostable resins with Si-containing amine components using multiaminosilane agents as hardeners in the curing process of their Epoxy-PHU H-NIPU process.[137] The commercially available γ-aminopropyltriethoxy silane was hydrolyzed to yield the multiaminosilane curing agent. Similar dendro-silanes containing aromatic units were introduced into epoxy and cyclocarbonate resins. Once introduced into the resins, the alkoxy groups were hydrolysed by the humidity of either the air or that of the surface of the substrate. The newly built silanol-hydroxyl groups reacted with the surface hydroxyl groups and forms strong bonds, making them good adhesion promoters.[136]



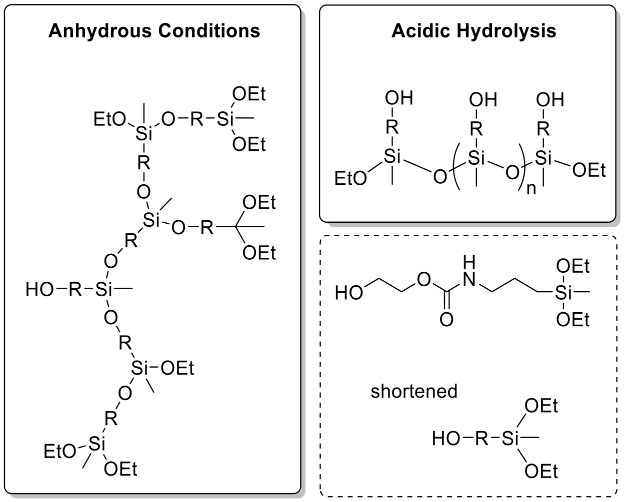
Scheme 22: Multiaminosilane synthesis according to Figovsky and coworkers[137]

Another example is the work Narayan and coworkers[138] who synthesized oligo(siloxane-urethane) through the reaction of 3-amino-propyldimethylethoxysilane (MEC), 3-aminopropyldiethoxymethylsilane (DEC) and (3-amino-propyltriethoxysilane) (TEC) with ethylene carbonate. The formed adducts underwent a spontaneous rearrangement by condensation of the alkoxysilane groups with the hydroxyl functions resulting from the ring opening of the ethylene carbonate as depicted in Scheme 23.



Scheme 23: Oligo(siloxane-urethane) formation from aminopropyl alkoxysilanes according to Narayan *et al.*[138]

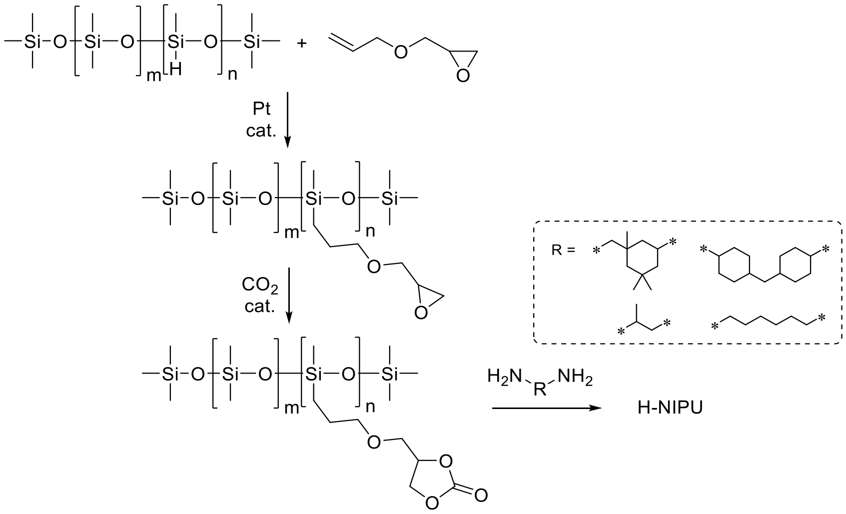
The same team reported the possibility to tune the condensation process for those siloxane-urethane adducts containing two alkoxy groups.[139] In anhydrous conditions, the monomer formed a hyperbranched structure starting from an AB2-type unit. This was not the case under acidic conditions in which a linear structure was formed.



Scheme 24: Condensation process of the DEC-propylene carbonate adduct according to Nerayan *et al.*[139]

- Si-containing reactants bearing cyclic carbonate moieties

Early work in this field was published by Wnek and coworkers in 1994, where they reported the synthesis of polysiloxane polymers bearing cyclic carbonate side chains[140] and studied the influence of the presence of the side carbonate on the dielectric properties and ion conductivity for battery applications. No post-functionalization of the carbonate moieties was carried out. Liu *et al.*[141] published in 2017 the synthesis of cyclic carbonate containing polysiloxane compounds for the production of coatings with improved water resistance. Those adducts were further reacted with a stoichiometric amount of diamines, at 100 °C in a mold for 10 h to yield polysiloxane-PHU. Different degrees of carbonation were tested in order to tune the concentration of hydroxyurethane moieties in the final material - Scheme 25. Differential scanning calorimetry (DSC) analyses revealed only a single glass transition temperature that ranged from 3 to 60°C depending on the amine and the degree of carbonation of the polysiloxane, indicating that no phase separation occurred. The degree of carbonation, namely the extent of crosslinking, influenced the mechanical properties by increasing the tensile strength and Young modulus, but lowering the elongation at break. The same behavior was observed when increasing the amount of cycloaliphatic moieties of the diamine.



Scheme 25: Polysiloxane-PHU H-NIPUs from cyclic carbonate-containing polysiloxanes according to Liu *et al.*[141]

However, and despite the acceptable swelling indexes in water (from 3 to 22 wt%), the water resistance decreased with the degree of crosslinking. This was attributed to the increase in hydroxyl moiety concentration within the formed material. In this regard, introducing more hydrophobic diamines (especially those containing cycloaliphatic rings) was a satisfactory solution to both decrease the swelling in water as well as obtaining materials with higher Young moduli and tensile strengths.

- Si-telechelic PHU prepolymers

To the best of our knowledge, only one example of reactive telechelic-oligoPHUs, involving Si-containing chain ends, has been reported in the scientific literature. This is not surprising as the formation of well-defined reactive telechelic PHUs is still one of the major unsolved issues in this chemistry. This work was undertaken by the team of Caillol who published in 2018 the synthesis of sol-gel hybrid-poly(hydroxyurethane)s.[142] Their synthetic process consists in end-capping difunctional PHU monomer (namely bis cyclic carbonates or diamines) with siloxane-containing amine or mono cyclic carbonate. A subsequent sol-gel process allowed for the latter crosslinking of the siloxane homotelechelic PHU chains - Figure 11. A very high thermal resistance, with $T_{d5\%}$ higher than 300 °C was obtained. The presence of a rubbery plateau with a modulus in the order of magnitude of 10^7 Pa after the alpha transition in the Dynamic Mechanical Thermal Analysis (DMTA) measurements showed that the polymer was crosslinked, which was confirmed by the gel content (90 %) measured by extraction of the soluble polymer with THF.

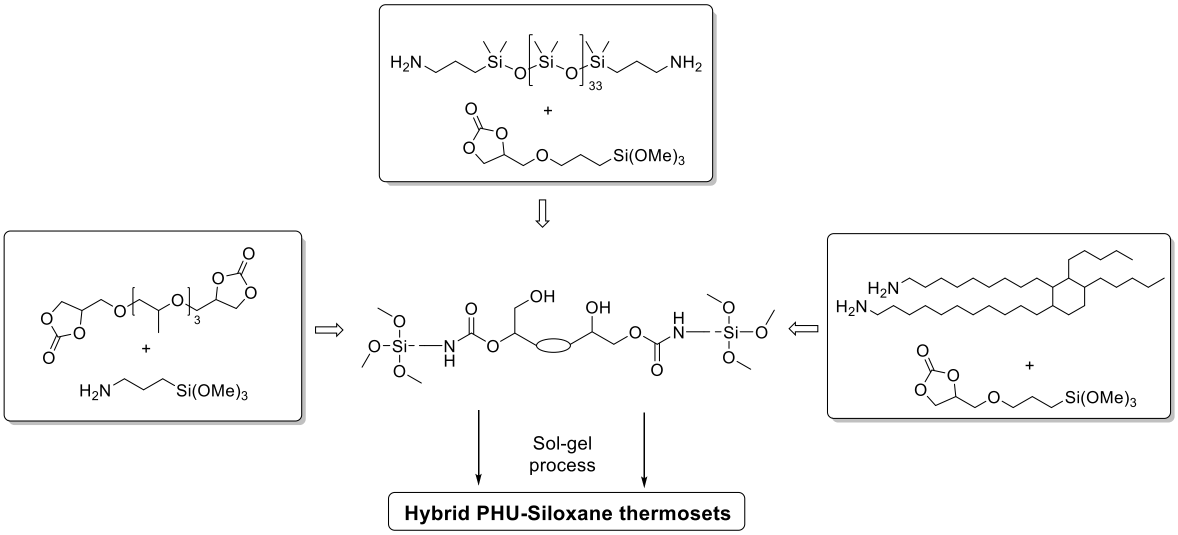
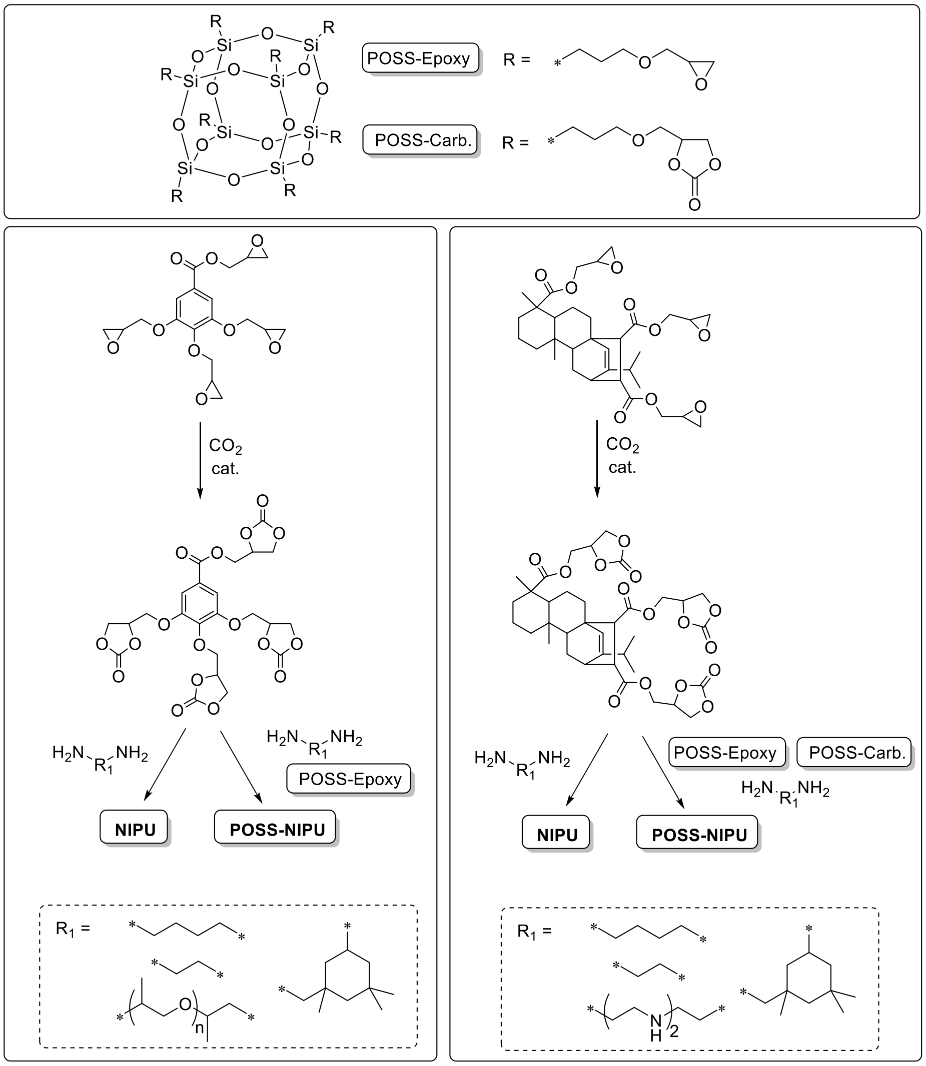


Figure 11: Formation of Hybrid PHU-siloxane thermosets via the synthesis of siloxane homo-telechelic oligoPHUs – adapted from Caillol and coworkers[142]

3.3.1.3. POSS-containing H-NIPUs

Another possibility to introduce Si-containing compounds into NIPUs is through the use of polyhedral oligomeric silsesquioxanes (POSS). This compound has been used to provide novel properties into materials.[143,144] Mechanical properties, thermal stability, water tolerance or dielectric properties were shown to be positively influenced when POSS was incorporated into polymer matrixes. Liu *et al.* incorporated POSS into PHU coatings containing gallic acid[145] or rosin[143] - Scheme 26. In the first example, gallic acid-based epoxy resin was treated by catalytic fixation of CO_2 to form the tetracarbonate. The carbonate was reacted with various diamines and also modified with epoxidized-POSS components in a similar process than the Epoxy-NIPU H-NIPU. The introduction of POSS increased the water resistance of the NIPUs, without being detrimental to other properties such as impact resistance, pencil hardness or flexibility. In general, the increase of the POSS loading induced an increase in the rigidity of the material (some were more brittle) and thermal properties ($T_{d50\%}$ over 300 °C by thermo gravimetruc analyses - TGA), which was attributed to the increase in the crosslinking density. A similar study was performed with rosin-based carbonate compounds, with a slight difference consisting in the fact that both epoxidized-POSS and carbonated-POSS were used in the formulation while reacting with a diamine. Similar enhancements in the properties of the composites were observed upon introduction of POSS into the NIPU formulations. For similar POSS contents, the epoxy-POSS yielded materials with better water resistance than the carbonated-POSS, which was attributed to the formation of urethane linkages. This positive impact of the incorporation of POSS into NIPU formulations on the mechanical properties was confirmed by Blattmann and Mülhaupt.[146] They targeted the development of a solvent-free process for the production of POSS-containing NIPUs and investigated the pot life and gel times of different formulations while incorporating carbonated-POSS. Due to the very high functionality, the curing with diamine led to extremely short pot life and gel time (hundreds of seconds). Because of the improvement in processability, without being too detrimental for mechanical properties, reactive diluents based on carbonated glycidyl ethers were utilized - Figure 12. Superior mechanical properties, with Young moduli of exceptional values (until 4000 MPa) could thus be obtained. Unfortunately, no enhancement in terms of water resistance was observed, which can be explained by the presence of hydrophilic hydroxyurethane moieties.



Scheme 26: POSS-containing NIPUs from gallic acid (left) and rosin (right) according to Liu *et al.*[143,145]

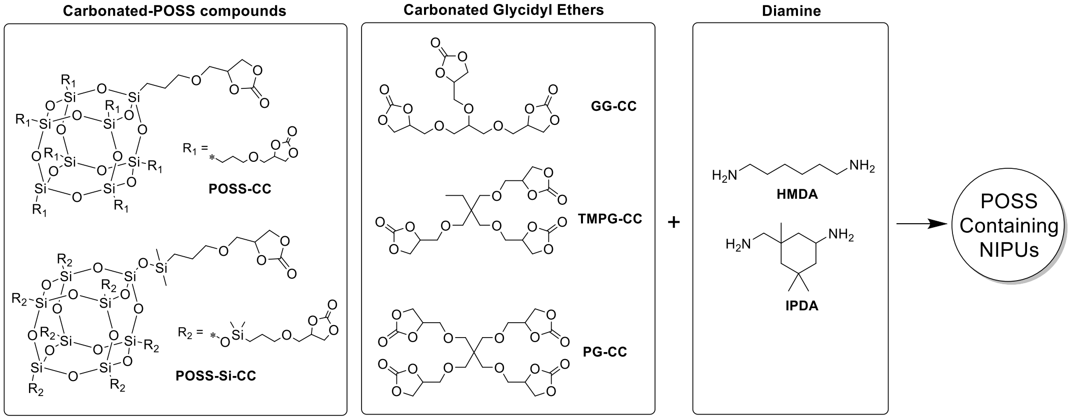


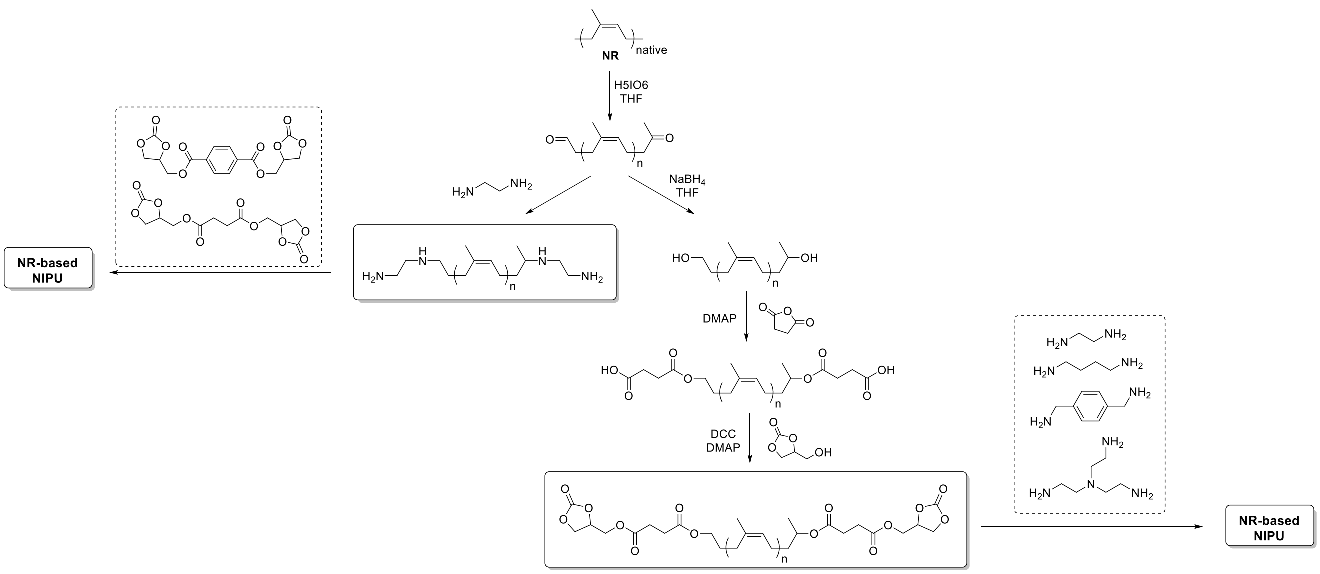
Figure 12: POSS-containing NIPUs according to Blattmann and Mülhaupt[146]

3.3.2. Biopolymer-containing NIPUs

Biopolymers, defined as naturally occurring polymers, are gaining an increasing interest because they are renewable compounds leading towards more sustainable and environmental-friendly materials. These polymers do not need to be synthesized, as opposed to the epoxy and acrylic resins described above. By means of wise chemical modification, the incorporation of such compounds can significantly broaden the final properties of the formed materials. The biopolymers incorporated in NIPUs include natural rubber, and derivatives of wood resources, namely tannin, lignin and cellulose.

3.3.2.1. Natural Rubber H-NIPUs

In 2017, the team of Pilard reported on the use of natural rubber (NR) for the synthesis of NIPUs.[147] Their process consisted in degrading NR in oligo-isoprene, that were further functionalized in diamino- of bis cyclic carbonate compounds - Scheme 27. Different chain lengths of the functional oligo-isoprene were targeted (1000 and 2000 g/mol) and tested in a subsequent polymerization with bis-cyclic carbonates or diamines. The advantage of degrading the NR was not only to get a better control of the chain length, but also to have oligo-isoprene that can be dissolved in solvents such as THF and dioxane, thus allowing reactions in solution to form NIPUs. Dioxane was found to be the most suitable solvent since temperatures as high as 100 °C were necessary for the reaction to proceed. Bulk polymerization was also performed. No formation of by-products such as urea or amides was observed. Interestingly, by playing with the process' conditions and the carbonate to amine ratio, a 100 % conversion could be achieved in the case of carbonate-telechelic NRs. Unfortunately, solubility issues made the characterization by SEC difficult. Low glass transition temperatures were obtained, ranging from -58 to -30 °C. Noteworthy, the longer the chain the lower the T_g, which was attributed to the higher flexibility of the polymer chains by the increasing amount of oligo-isoprene incorporated.



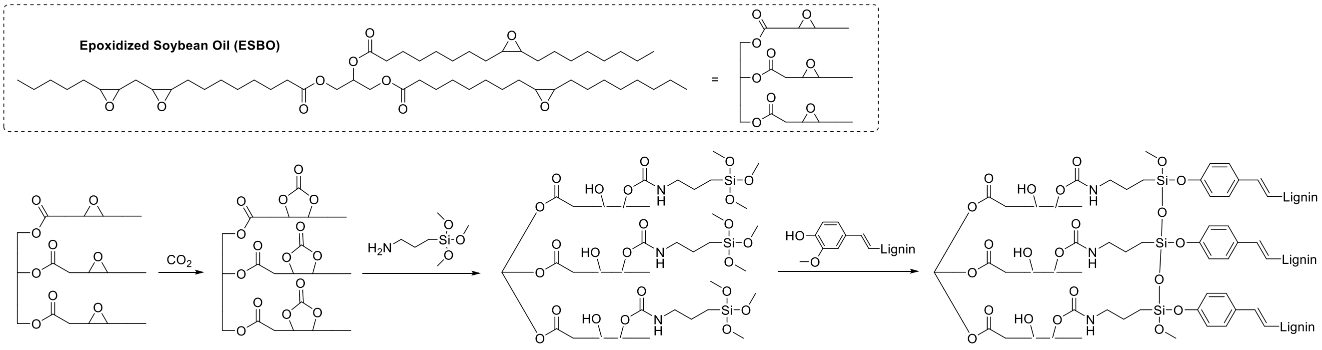
Scheme 27: Natural Rubber-based NIPUs (NR-based NIPUs) – adapted from the work of Pilard and coworkers[147]

3.3.2.2. Lignin and tannin-based H-NIPUs

- Lignin-based H-NIPUs

The use of lignin is gaining momentum in the field of the development of novel polymer materials. Lignin nowadays is considered as the main resource for the synthesis of bio-aromatic monomers. It constitutes 20 to 25 wt% of wood with a world production from the pulp industry reaching 50 million tons/year.[148] Because this resource is low cost and is not in competition with the food industry, substantial efforts are directed towards its valorization. This complex biopolymer however has to be degraded in smaller building blocks prior to using it. Mostly polyols are formed, which made lignin extremely popular in the PU chemistry since it could directly react with isocyanate compounds.[149–152]

However, quite scarce examples of the use of lignin can be encountered in the literature. Among them, Lee and Deng published in 2014 an example in which the phenolic units of lignin were used in combination with a siloxane-modified carbonated soybean oil for the design of lignin-based NIPUs - Scheme 28.[153] During the polymerization process, the condensation of siloxane moieties, yielding –Si-O-Si- groups, occurred. When curing the final materials, at 60 °C, lignin acted as a crosslinking agent and the resulting tensile strength increased with the increase in lignin content. However, when curing at room temperature, the materials were found to be much more flexible, which might be due to an inefficient curing. The increase in lignin content increased the final elongation at break. The authors attributed these findings to the concomitant crosslinking reactions, namely the condensation of siloxane moieties onto themselves, and the condensation of lignin with the siloxane moieties. Knowing this, as well as the fact that lignin acts as a blending agent with the siloxane-modified soybean at low temperature without necessarily crosslinking, lignin was considered to sterically hinder the siloxane auto-condensation, yielding much more flexible materials with increasing lignin loading.



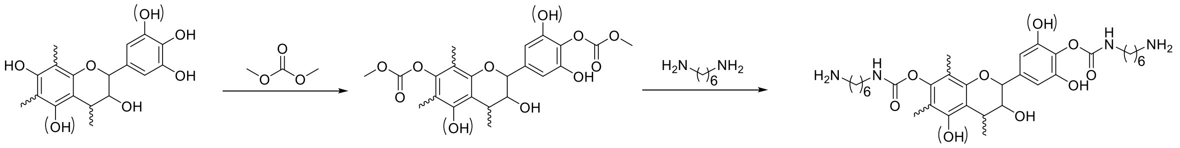
Scheme 28: Preparation of lignin based NIPUs in combination with siloxane-modified carbonated epoxidized oil – adapted from Deng and Lee[153]

Another example of incorporation of soft-wood Kraft lignin was published in 2017 and relates a complete analytical study of the formed products between Kraft lignin, dimethyl carbonate and hexamethylenediamine.[154] The reaction temperature was found to play a significant role in the hardening of the formed materials (180 °C was found to be the best) but degradation was unfortunately noticed. Interestingly, the use of pressure in addition to the increase in temperature allowed the formation of good coatings onto beech wood, presumably due to a better wetting. The hydrophobicity (water contact angle) increased with the incorporation of lignin in the coatings' formulations.

- Tannin-based H-NIPUs

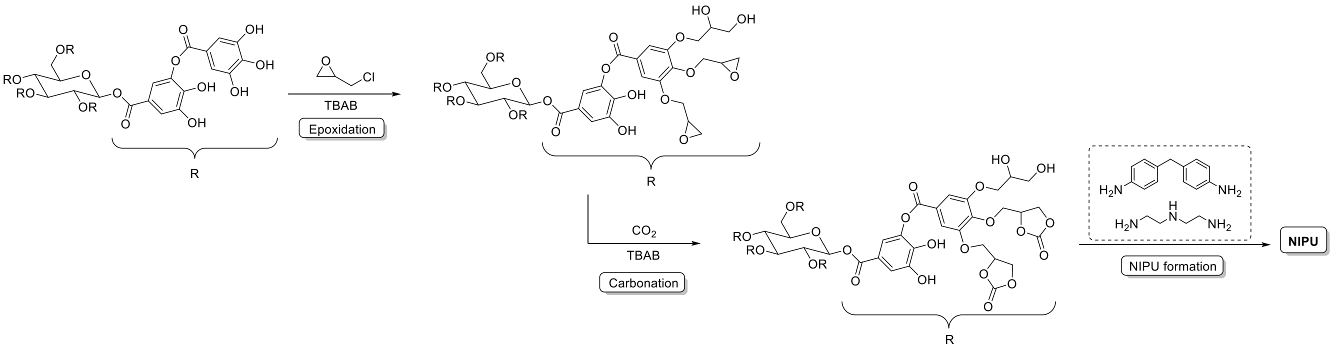
Tannins are extracted in the separation process of wood into its constitutive units, namely cellulose, hemi-celluloses and lignin. The precise definition of tannins has evolved but a common agreement is found in the definition of Swain and Bate-Smith stating that tannins are water-soluble compounds with molecular weights between 500 and 3000 g.mol^{-1}.[155]

Thébault *et al.* published in 2014 and 2015 two studies on the potential formation of tannin-based NIPUs. The first study was performed with hydrolysable chestnut tannins (which have similar phenolic structures as gallic acid) whereas the second involved more complex flavonoid tannins.[156,157] In both cases, the synthetic strategy relied on the functionalization of hydroxyl groups with dimethylcarbonate and then the formed carbonate moieties reacted with a diamine (hexamethylenediamine – HMDA - in this case) – Scheme 29. The formed tannin-based NIPUs were further tested for coating applications onto different medium density fiberboards originating from different kind of trees. Higher water contact angles were measured onto the coated surfaces areas. The authors hence concluded that tannin-based NIPUs could be designed for the development of hydrophobic coatings for wood. In 2017, the same team completed their study with the introduction of fully tannin-based NIPUs by substituting HMDA by an amine functional-tannin compound.[158] PU resins containing more than 70 % of bio-based isocyanate-free components were synthesized. The authors claimed the potential use of such compounds for adhesive and coating applications.



Scheme 29: Tannin-based H-NIPUs, on the basis of flavonoid tannins – adapted from Thébault *et al.*[157]

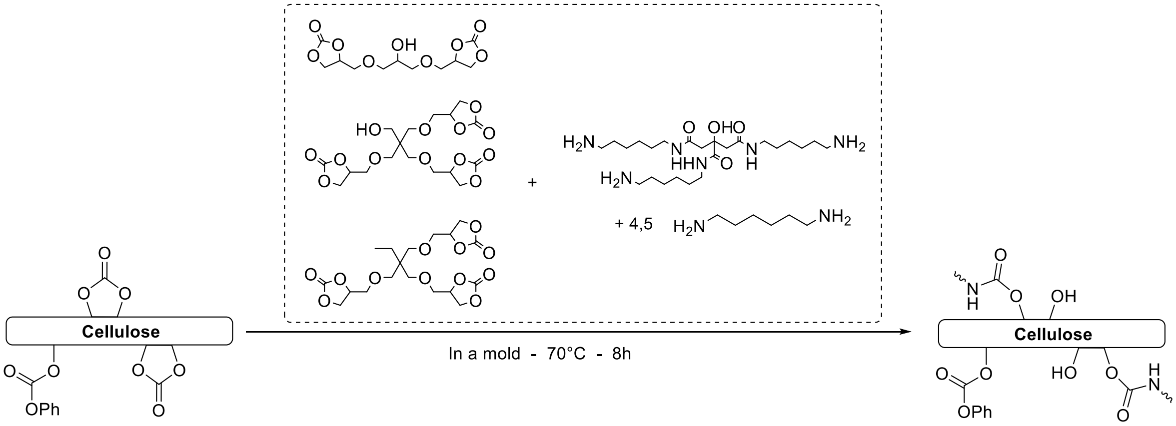
In 2018, Meyer and coworkers published on the use of tannic acid for the formulation of NIPUs - Scheme 30.[55] The synthetic pathway proceeded through the epoxidation of the phenolic moieties of the tannic acid, followed by subsequent carbonation to yield a multi-cyclic carbonate compound. Curing with both aliphatic and aromatic amines was performed to yield the corresponding NIPUs that exhibited good solvent resistance and antioxidant properties.



Scheme 30: Tannic acid-based NIPUs – adapted from the work of Meyer and coworkers[55]

3.3.2.3. Cellulose-based H-NIPUs

To the best of our knowledge, only one example of the use of cellulose has been reported for the synthesis of NIPUs. In the process developed by the team of Mülhaupt in 2013, cellulose carbonate was utilized as a co-reactive bio-based filler to react with other cyclic carbonate and amine comonomers.[159] Cellulose carbonate was prepared by reacting cellulose with diphenyl carbonate with dibutyltin dilaurate (DBTDL) as catalyst and dimethylacetamide (DMAc)-LiCl as the reaction medium. 5 wt% of this modified cellulose was later incorporated into a mixture of tricyclic carbonate and diamines, and then cured. At this low concentration, the cellulose filler mostly acted as a reinforcement additive (the Young modulus increased from 2100 MPa to 2600 MPa with a marginal effect onto the elongation at break). A bottleneck of this process however lies in the dispersion of the carbonated cellulose into the viscous mixture of monomers. At the lab scale, an ultraturrax® apparatus allowed the good dispersion of the filler, but difficulties might arise should higher quantities be needed.



Scheme 31: Preparation of cellulose-based H-NIPUs according to Mülhaupt and coworkers[159]

4. Concluding remarks

Looking back to the described examples, the formation of hybrid-NIPUs can thus be considered as a promising pathway towards the valorization of non-isocyanate polyurethanes. In terms of industrial perspective, epoxy-NIPUs hybrids are the only NIPUs available in the market under the trendmark Green Polyurethanes™,[160] hence highlighting the potential held by H-NIPUs should industrial valorization be envisioned.

It is striking to notice that this type of chemistry is relatively old, especially in the case of epoxy-NIPUs. With the growing interest and challenges of NIPUs, it is expected that more research will be carried out towards the development, understanding and optimization of a broad range of hybrid-polymers, thus expending the existing pool of thermo-mechanical properties.

However, this type of chemistry is also facing its own challenges, the most important one being the compatibilization between the two polymer phases at stake. This is particularly acute in the case of NIPU-acrylics hybrids. This leaves room for considerable studies and improvement of the existing pool of technologies. It is also important to notice the lack of easy access to NIPU monomers, especially industrial cyclic carbonate compounds. In this regard, development of the upscaling of the synthesis of those monomers would favor the development of both NIPUs and H-NIPUs.

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6. Shortened forms

ACMO:	4-methacryl-oylmorpholine
ACN:	Acetonitrile
AIBN:	Azobisisobutyronitrile
ATRP:	Atom Transfer Radical Polymerization
BADGE:	Bisphenol-A Diglycidyl Ether
bisCC:	bis cyclic carbonate
CC(M)A:	Cyclic carbonate (meth)acrylate
CMR:	Carcinogenic, mutagenic, reprotoxic
CO_2:	Carbon Dioxide
CSO:	Carbonated Soybean Oil
DBTDL:	Dibutyltin dilaurate
DCC:	N,N′-Dicyclohexylcarbodiimide
DCU:	1,3-Dicyclohexyl urea
DEC:	3-aminopropyldiethoxymethylsilane
DETA:	Diethylenetriamine
DMAc:	Dimethylacetamide
DMAP:	4-Dimethylaminopyridine
DMF:	Dimethylformamide
DMPA:	Dimethylproprionic acid
DMSO:	Dimethylsulfoxide
DMTA:	Dynamic Mechanical Thermal Analysis
DSC:	Differential Scanning Calorimetry
EDA:	Ethylene Diamine
EDR:	(ethylenedioxy)diethylamine
EDGE:	Ethylene Glycol Diglycidyl Ether
EOAED:	2-(methacryloyloxy)ethyl 2-(methacryloyloxy)ethylcarbamate
FTIR:	Fourier Transformed Infrared
GMA:	Glycidyl Methacrylate
HCl:	Hydrochloric acid
HEMA:	Hydroxyethylmethacrylate
HMDA:	Hexamethylene Diamine
H-NIPU:	Hybrid-Non Isocyanate Polyurethane
HUM:	Hydroxyurethane Modifier
HUMA:	Hydroxyurethane Methacrylates
IPDA:	Isophorone Diamine
IPN:	Interpenetrating Network
IR:	Infrared
MA:	Methyl Acrylate
MEC:	3-amino-propyldimethylethoxysilane
MEK:	Methylethylketone
MMA:	Methyl Methacrylate
NIPAM:	N-isopropylacrylamide

NIPU:	Non Isocyanate Polyurethane
NIPUrea:	Non Isocyanate Polyurea
NMR:	Nuclear Magnetic Resonance
NR:	Natural rubber
oligoPHUs:	oligo(hydroxyurethane)s
oligoUMA:	Oligomers of urethane methacrylate
OVE:	(2-0xo-1,3-dioxolan-4-yl) methyl vinyl ether
PGMAC:	Propylene glycol methylether acetate
PHU:	Poly(hydroxyurethane)
P(H)UMAs:	Poly(hydroxyl)urethane methacrylates
POAED:	2-(methacryloyloxy)ethyl 3-(methacryloyloxy)propylcarbamate
POAPD:	1-(methacryloyloxy)propan-2-yl 3-(methacryloyloxy)propylcarbamate
POSS:	Polyhedral oligomeric silsesquioxanes
PPOA:	poly(propylene oxide) bis-acrylate
PPOBC:	poly(propylene oxide) diglycidyl ether
PU:	Polyurethane
PUU:	Polyurethane-urea
SEC:	Size Exclusion Chromatography
SEM:	Scanning Electron Microscopy
TBD:	Triazabicyclodecene
TEC:	3-amino-propyltriethoxysilane
TEM:	Transmission Electron Microscopy
TEDA:	Triethylene diamine
TEPA:	Tetraethylene pentamine
TETA:	Triethylenetetramine
T_g:	Glass Transition Temperature
TGA:	Thermo gravimetric analysis
TGDEC:	Carbonated resin based on triethylene glycol diglycidyl ether
THF:	Tetrahydrofuran
TMPTA:	trimethylolpropane tris-acrylate
TREN:	Tris(2-aminoethyl)amine
T_α:	α-transition temperatures
VEC:	Vinyl ethylene carbonate
VEOPC:	3-(2-vinyloxyethoxy)-1,2 propylene carbonate
UMAs:	Urethane methacrylates
UV:	Ultraviolet

PART B

WATER-BASED NON-ISOCYANATE POLYURETHANES-POLYUREAS (NIPUUS)

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Table of content

1. Introduction 87
2. Water-soluble NIPUs 88
   2.1. NIPU synthesis using water as reaction medium 88
   2.2. Modification of NIPUs synthesized in organic solvents 90
3. Hydrogels 93
4. Water-borne Dispersions 94
   4.1. Acetone-like process 94
      4.1.1. NIPUs dispersion by acetone-like transesterification processes 95
      4.1.2. NIPUs dispersion by acetone-like aminolysis processes 99
   4.2. NIPU dispersions through interfacial polymerization 101
   4.3. NIPU dispersions by mini-emulsion polymerization 101
   4.4. PHU dispersions by nano-precipitation 102
5. Water-borne Hybrid-NIPUs (H-NIPUs) 103
   5.1. NIPU-Acrylics - HUMAs 103
   5.2. NIPU-Epoxy 104
6. Conclusions 106
7. References 107
8. Shortened forms 112

1. Introduction

Discovered by Otto Bayer in 1937,[1] polyurethanes (PUs) are nowadays ranked as the fifth most utilized type of polymers, finding applications in numerous fields including, among others, foams, packaging, automotive, construction, textile industry, adhesives and coatings.[2–6]

Polyurethanes are also used for biomedical applications[7] including long-term implants and scaffols,[8,9] bone repair,[10] tissue engineering of cardiovascular system[11] and controlled delivery[12,13]

PUs classically originate from a polyaddition reaction between a diol (or polyol), a diisocyanate (or poly-isocyanate) and a chain extender (usually a short diamine or diol). The polyols, acting as soft segments provide flexibility to the final material whereas the isocyanate and the chain extender provide mechanical strength. This leads to the formation of so-called segmented PUs, composed of soft- and hard-segments, which induces a nano-phase segregation, providing the resulting materials with both tensile strength in addition to an interesting elasticity.[14] Variations of the type and proportion of the diisocyanate, polydiol and chain extender allows achieving widely different properties, which is the main reason for the broad range of applications of the PUs. The range of properties can be further extended by hybrids of PUs with other materials such as other polymer,[15] graphene,[16] cellulose nanocrystals,[17] clays[18] and carbon nanotubes.[19]

Circular economy and the need to decrease the dependency from oil are fostering the search for bio-based sources for polyurethanes. Polydiols of vegetal origin have particularly been used in this purpose.[20–28] Actually, these ideas have already reached the market (e.g., Bio TPU™ by Lubrizol and Desmodur® eco N 7300 by Covestro).

In the same line, attempts to substitute the metal catalysts traditionally used for PU synthesis by organocatalysts have been reported.[29,30]

Even with these developments, the production of PUs still depends on the use of isocyanates. There is evidence that prolonged exposure to isocyanates can cause health issues such as asthma, dermatisis and some isocyanates are even classified as CMR (carcinogenic, mutagenic and toxic to reproduction) .[31–33]. An additional drawback of the isocyanates is that phosgene is used in their synthesis. Phosgene is a very toxic gas itself, which can lead to death in case of inhalation. Therefore, there a strong incentive to develop isocyanate-free pathways for the synthesis of PUs and PUreas. Numerous research articles and reviews have focused on the synthesis and process optimization for the formation of non-isocyanate polyurethanes, NIPUs.[34–37] Two major pathways have been proposed, the transurethanization process and the aminolysis of cyclic carbonate compounds. The first route consists in the reaction of a bis-carbamate compound with a diol, yielding regular PUs, whereas the second one consists in a ring-opening reaction of bis-cyclic carbonate compound with a diamine, forming poly(hydroxy urethane)s, or PHUs - Figure 1.

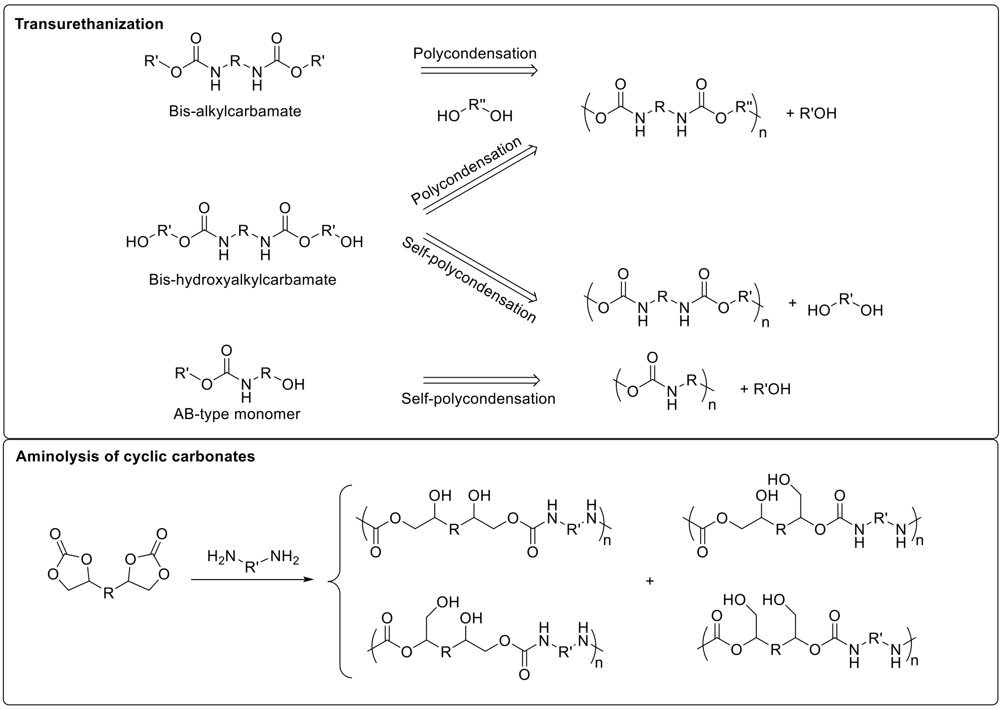


Figure 1: Transurethanization vs Aminolysis of cyclic carbonate compounds

A very specific class of PUs are the water-based systems, which includes both water-soluble and waterborne dispersed PUs. Water-soluble PUs can for example be directed towards bio-medical applications.[38,39] Water-borne PU dispersions are specialty materials that find applications as high performance coatings and adhesives.[40–42] In this regard most of the attempts to develop waterborne self-healing coatings are based on polyurethanes.[43–46]

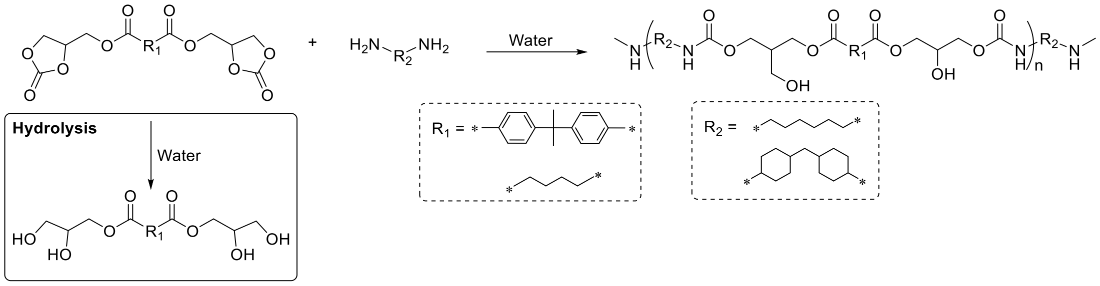
The development of water-based NIPUs and NIPUreas, has gained an increasing interest in the last years because they lead to the design of more eco-friendly processes, in addition to broadening the scope of applications for NIPUs with products that can meet specific performances and market demands. The aim of this mini-review is to summarize this emerging field.

2. Water-soluble NIPUs

2.1. NIPU synthesis using water as reaction medium

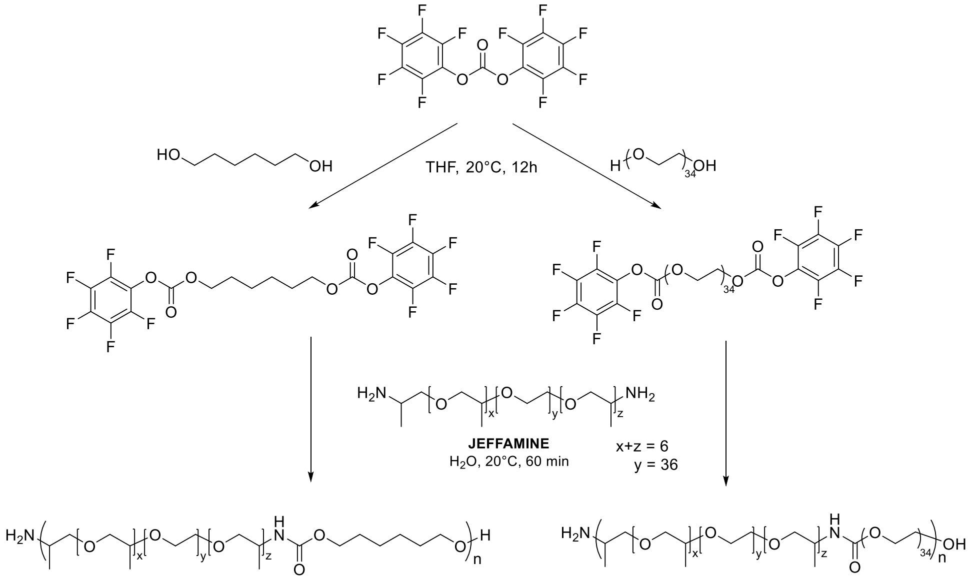
The very first example of NIPU synthesis using water as reaction medium was published by Endo and coworkers[47] who successfully demonstrated that a wise selection of monomers could allow for a chemo-selective reaction of cyclic carbonates with amines, mitigating the hydrolysis that can occur in water. They synthesized both bis phenol A-based and short aliphatic-ether activated bis-cyclic carbonates and reacted them with either aliphatic or cycloaliphatic diamines - Scheme 1. It was found that the aliphatic-ether cyclic carbonates suffered extensive hydrolysis in water and the polyaddition reaction failed. On the other hand, the more hydrophobic bisphenol-A was less affected by hydrolysis and the polyaddition reaction was possible although a water insoluble polymer was obtained. These results may be related to the observation made by Nohra *et al.* who studied the aminolysis of glycerol carbonate with various amines in water at a temperature of 50°C.[48] These authors showed that the longer the length of the reactive aliphatic amine, the lower the extent to hydrolysis as well as the corresponding rates of reaction. It was assumed that longer aliphatic chain lengths hindered the access of water to the cyclic carbonate, hence diminishing its extent for hydrolysis.

At first sight, the effect of the structure of the cyclic carbonates may lead to the conclusion that hydrophobic monomers are preferable since they would minimize the hydrolysis. However, they would be less likely to yield water-soluble polymers and make the chemical more “dispersion-like”. Actually, Endo and coworkers demonstrated that, despite the initial insolubility of the monomers in water, the solubility of the resulting PHU in water depends on the structure of the bis cyclic carbonate. Thus, bis phenol A-based PHUs were insoluble whereas the aliphatic bis cyclic carbonate based PHUs were soluble in water. Moreover, the structure of the diamine, and its water solubility influenced the kinetics of the reactions: the cycloaliphatic diamine yielded a diffusion-limited process whereas for the aliphatic hexamethylene diamine the rate determining step was the nucleophilic addition process.



Scheme 1: Preparation of poly(hydroxyurethane)s in water – adapted from Endo and coworkers[47]

In order to avoid the drawbacks associated with the use of cyclic carbonates in water, Sardon *et al.*[49] explored a transurethanization-like route. The authors designed bis-carbonates based on poly(ethylene glycol)- PEG, or hexanediol that were functionalized with bis(pentafluorophenyl)carbonate that acted both as a chemical activator of the carbonate moiety in the reaction with amine and as a good leaving group. The subsequent dropwise addition of the bio-based commercially available *Jeffamine* (a linear diamine) with trimethylamine was then performed - Scheme 2. Interestingly, the reaction was run at room temperature in water and was complete in one hour.

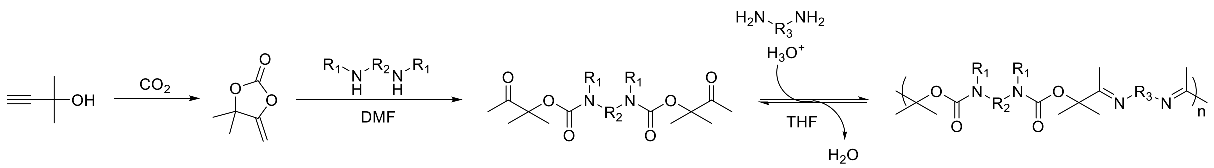


Scheme 2: Homogeneous water-based systems according to Sardon *et al.*[49]

The copolymer structure (balance between hard and soft segments) was tuned by varying the monomer ratio. High conversions (>98%) and polymers with molecular weights ranging from 15 to 16 kDa were obtained. Interestingly, the polymers exhibited melting behaviors in DSC in the range from 27 to 33°C. The extent of crystallinity was found to be dependent on the ratio between the PEG-based carbonate (crystalline) and the hexanediol-based monomer. The glass transition temperatures were found to lie around -55°C.

2.2. Modification of NIPUs synthesized in organic solvents

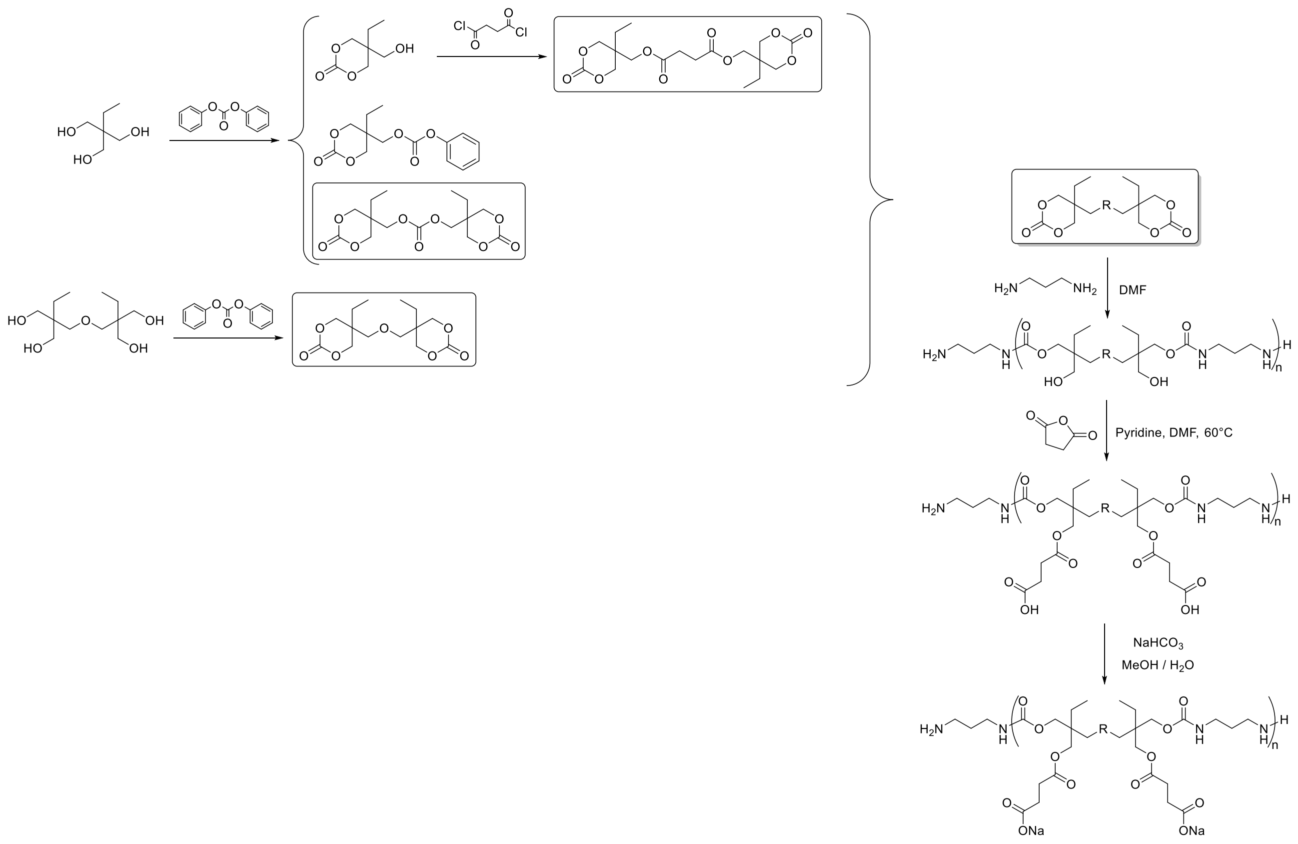
Detrembleur *et al.* also played on the chemical structure of the NIPU to influence its final hydrolytic behavior. They introduced imine linkages within the polymer backbone in order to induce acid-sensitivity.[50] To do so, they reacted propargylic alcohol with carbon dioxide to obtain an unsaturated cyclic carbonate. The subsequent aminolysis of this monomer with a diamine in DMF yielded a diurethane pre-polymer that further reacted with a diamine yielding the corresponding poly(urethane–co–imine), also shortened PUIs – Scheme 3.



Scheme 3: Imine-containing NIPUs – adapted from Detrembleur *et al.*[50]

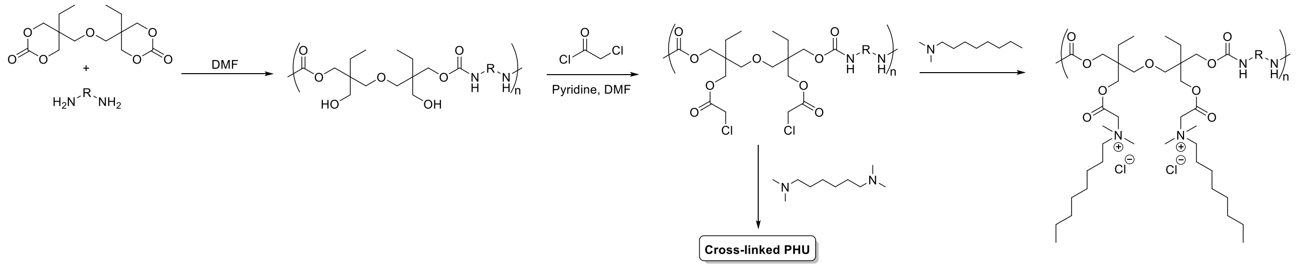
The successful synthesis of the PUIs was found to highly rely on the use of a good Lewis acid that not only catalyzes the polymerization, but also acts as a dehydrating agent, thus shifting the chemical equilibrium towards the formation of the imine by trapping water upon its formation during the imination process. The low cost, low toxic and commercially available titanium-based $Ti(OEt)_4$ was found to be a suitable catalyst for the polymerization. After optimizing the reaction conditions, good conversions (>95%) of the monomers were achieved, forming oligomers with molecular weights ranging from 3000 to 8500 g/mol after quenching and removal of the Lewis acid. The low molecular weights obtained can be explained by the dynamic nature of the imine bond that may have hydrolyzed during the quenching step. The authors interestingly demonstrated the pH-responsiveness of the formed products; the lower the pH, the faster the hydrolysis occurred. Notably at pH 1, some polymers could be fully hydrolyzed within a single day, whereas no polymer degradation was noticed after 24h at pH 7.

PHUs can be made soluble in water through reaction of the pendant OH-groups with succinic anhydride followed by neutralization with sodium bicarbonate - Scheme 4.[51] . The authors introduced carbonate, ester and ether groups in the PHUs and explored their hydrolytic behavior finding that chemical composition of the bis cyclic carbonate affected the hydrolytic behavior under basic conditions pH = 8 – 10,6. Carbonate-containing PHUs hydrolyze faster than ester-containing PHUs, which in turn hydrolyze faster than ether-containing ones. Hydrolysis rate increased as the pH increased. At pH = 8, it was rather slow (less than 15 % for the carbonate containing PHUs), but it accelerated at higher pHs (complete hydrolysis of the carbonate containing PHUs in only 7 days). This denotes the tunability of the system depending on the monomer and thus on the polymer structure. The authors chain-extended the water soluble carbonate-based PHUs with the help of α,α-diisothiocyanate-p-xylene, forming thio-urea bridges[52] and observed that the longer the PHU chain, the better the hydrolytic resistance of the polymer under alkaline conditions. The authors attributed this behavior to the presence of a higher H-bond density that hindered the water influence on the polymer chain. Moreover, the xylene moiety of the chain extender, bringing a higher hydrophobicity, was assumed to play also a role in this reduced water sensitivity.



Scheme 4: Preparation of water-soluble PHUs *via* post-functionalization of pendant OH groups – adapted from Matsukizono and Endo[51]

The same research team demonstrated that functionalizing the pendant OH-groups into quaternary ammonium chloride moieties also gave water-soluble PHU salts.[53] The post-functionalization of the hydroxyl moieties was performed with chloroacetyl chloride prior to reacting with N,N-dimethyl-n-octylamine to yield the corresponding salt - Scheme 5. Some chloroacetyl-derived PHUs exhibited water-solubility depending on the polymer structure. The synthesis however yielded very short oligomers, with molecular weights ranging from 3800 to 6300 g/mol depending on the diamine used. Good yields of functionalization with the amine were obtained (around 80% in every case). Cross-linked polymers were obtained by reacting the functionalized PHUs with tertiary diamines leading to good self-supported films.

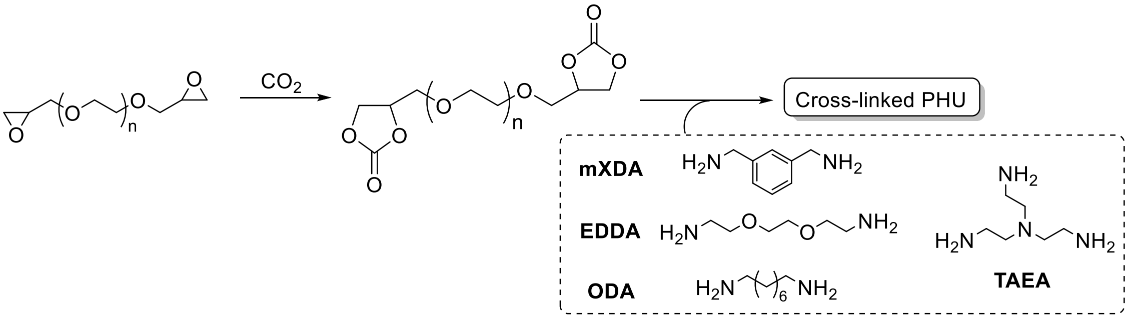


Scheme 5: Quaternary ammonium chloride PHUs – adapted from Matsukizono and Endo[53]

3. Hydrogels

Hydrogels can be defined as 3D cross-linked hydrophilic networks. Their affinity to water provides them with the ability to swell and retain 10 to 1000 times their dry weight in water.[54]

Segmented PUs can be used for hydrogel formation because of their particular mechanical properties and capability of interacting with water through the addition of hydrophilic monomers (e.g. poly ethylene glycol – PEG).[55,56] To the best of our knowledge, only one example of poly(hydroxyurethane)-based hydrogel has been published.[57] The synthesis consisted in having a carbonated polyethylene glycol diglycidylether reacting with various polyamines in bulk. Three diamines were tested: 2,2'-(ethylenedioxy)diethylamine (EDDA), m-xylylenediamine (m-XDA) and 1.8-diaminooctane (ODA) and a triamine, acting as crosslinking agent: tris(2-aminoethyl)amine (TAEA) - Scheme 6. Subsequent swelling in water allowed the absorption of water and the formation of the final hydrogel. The cross-linking degree of the final material (controlled by the amount of triamine introduced) influenced the rheology of the material: a minimum of 0.2 eq. of triamine with respect to the biscyclic carbonate was necessary to avoid free flowing. On the other hand, 0.33 eq. yielded very brittle materials, suggesting a higher crosslinking degree, as confirmed by measurement of the gel content in water (from 67.5 ± 1.2% to 80.7 ± 1.5% when going from 0.2 to 0.33 eq.). Between these two limits, the water uptake of the final material increased as the amount of cross-linking agent decreased (equilibrium water absorption up to 500% were obtained). Moreover, compression tests in the swollen state showed that a higher content in triamine led to higher compression moduli (from 19.1 ± 0.7 to 185.5 ± 36.7 kPa when going from 0.2 to 0.33 eq.), lower strains at break (from 61.0 ± 3.4 to 43.6 ± 5.1% when going from 0.2 to 0.33 eq.) and higher stresses at break (from 43.4 ± 5.4 to 170.0 ±44.7 kPa when going from 0.2 to 0.33 eq.). Those properties were also found to strongly depend on the type of diamine used. For instance, the most hydrophilic EDDA gave the highest equilibrium water absorption (967 ± 9 %) whereas mXDA and ODA gave lower values (505 ± 54% and 214 ± 2% respectively). The difference the last two was attributed to the lower distance between crosslinking points in the case of mXDA, increasing its hydrophilicity. Moreover, the decrease in the equilibrium water absorption (EWA) induced that more stress was needed to compress the hydrogel. This increased the resulting compression moduli (from 37.1 ± 4.3 kPa to 125.3 ± 5.6 kPa for EWA of 967 ± 9% and 214 ± 2%, respectively) and stress at break (from 22.4 ± 8.4 kPA to 830 ± 140 kPa for EWA of 967 ± 9% and 214 ± 2%, respectively). No influence of the introduction of nanoclay (in this case Montmorillonite) on the gel content was observed in the copolymer made of 1eq. of the PEG bis carbonate, 0.2 eq. of the triamine and 0.7 eq. of mXDA, (loading from 1wt% up to 15wt% of clay were studied). It was however demonstrated that it had an effect on the mechanical properties in terms of compression properties. When the nanoclay loading was varied from 2 and 5wt%, the equilibrium water absorption remained around 400%, but the compression moduli varied between 15.7 ± 0.2 kPa and 23.9 ± 1.4kPa, the strain at break between 68.0 ± 0.7 and 79.3 ± 1.6% and the stress at break also varied between 60.0 ± 4.0 and 157.2 ± 4.7 kPa. Higher loadings gave hydrogels with lower equilibrium water absorption (down to 56.9 ± 0.7% at 15wt% loading of nanoclay).



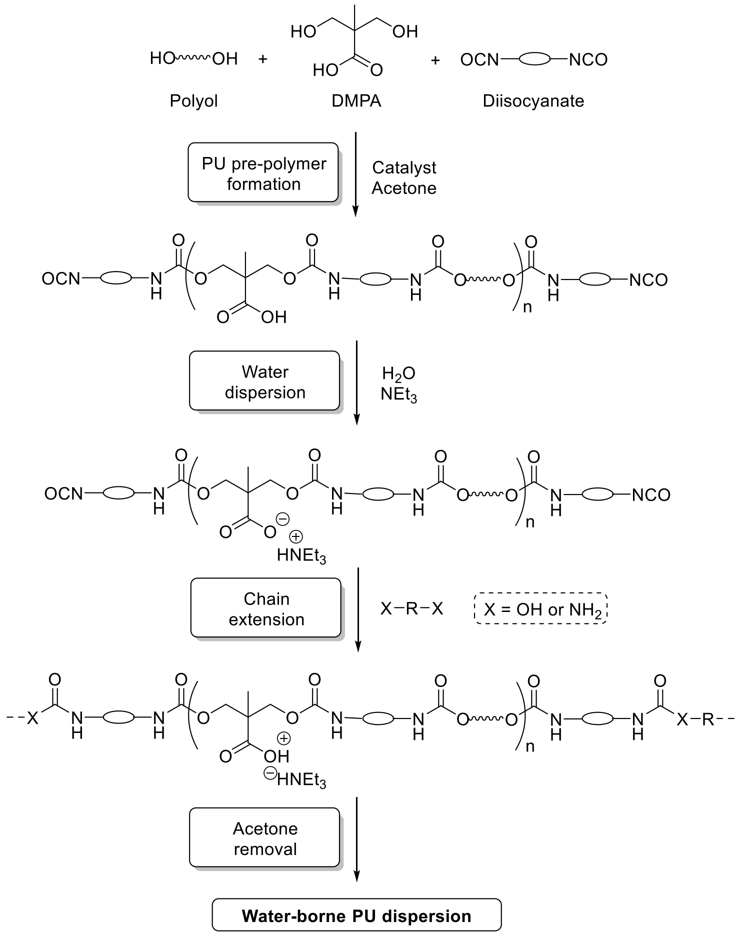
Scheme 6: Preparation of cross-linked PHUs for the formation of hydrogels – adapted from Detrembleur and coworkers[57]

4. Water-borne Dispersions

4.1. Acetone-like process

Dispersions of polyurethanes are very important products in the coating and adhesive markets due to the relatively easy synthesis and good performance. PUs are usually synthesized through the so-called acetone process- Scheme 7.[15,58]. In this process, the PU prepolymers are synthesized in a water miscible low boiling point solvent, commonly acetone. An internal dispersing agent such as dimethylolpropionic acid (DMPA) is usually added into the formulation and allows for dispersion in the water phase upon neutralization (usually performed with the help of trimethylamine). The PU is then chain-extended with a short diol or diamine and after acetone is removed, the PU dispersion is finally obtained.

Most of the published examples of isocyanate-free PUs or PUreas dispersions are inspired in the acetone process, namely the copolymerization of three monomers, including an internal dispersing agent is done in a low boiling point solvent. The subsequent neutralization of the formed polymer chains allows the dispersion upon water addition. The removal of the low boiling point solvent leads to the final waterborne dispersion.

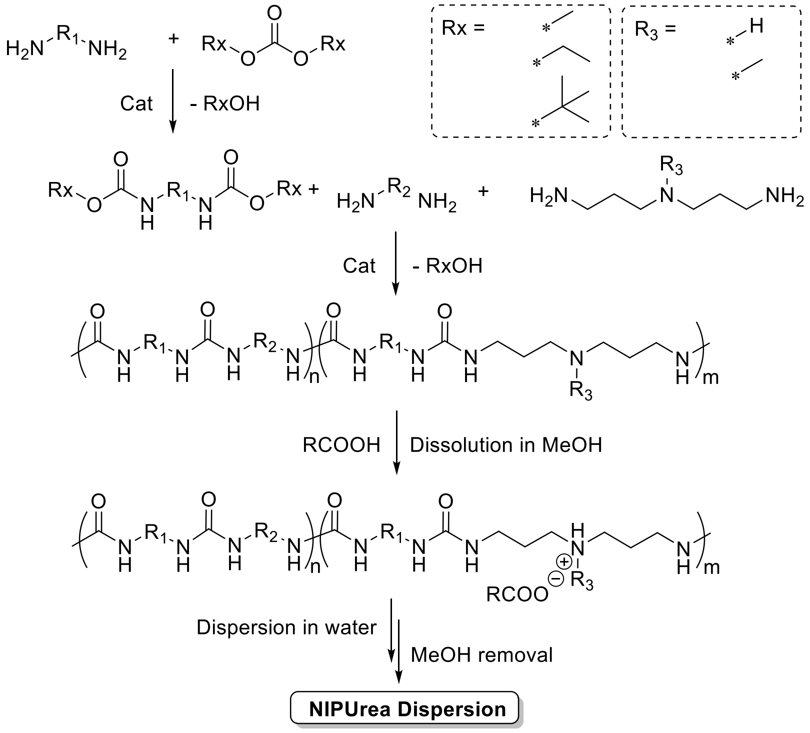


Scheme 7: Water-borne PUs through the acetone process

4.1.1. NIPUs dispersion by acetone-like transesterification processes

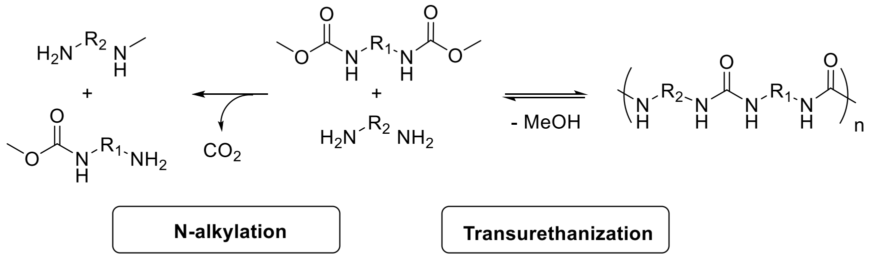
The very first example of NIPU water-based dispersion was published in 1996 by Blank *et al.*,[59] who investigated the properties of cross-linked polyurethane dispersions. They used the transurethanization process for the formation of NIPUs from polyester polyols (with an acid number of 1-2) and bis-hydroxypropylcarbamates and a triol, using a transesterification catalyst (dibutyltin oxide). The reaction was carried out under vacuum with a progressive increase in the temperature up to 175°C. The amount of the formed distillate (1,2-propylene glycol) as well as the increase in viscosity helped monitoring the extent of polymerization. Carboxyl functionality was brought by reacting an anhydride onto the OH chain-ends. 35 and 41wt% dispersion were prepared without any co-solvent (which is a difference with the acetone-process), with a neutralization step by means of diisopropanolamine and/or triethylamine. The cross-linking was performed by addition of water dispersible hexa(methoxymethyl)melamine. The dispersions were used in coating applications and paints.

In 2018, Ma *et al.* published a series of studies exploring non-isocyanate strategies for the production of waterborne polyurea dispersions for coatings.[60,61] Their approach consisted in utilizing a transurethanization-like process in bulk under vacuum. To do so, they copolymerized a bis-alkylcarbamate monomer with two diamines, one of them playing the role of internal dispersing agent (IDA) to form a pre-polymer, that was further dissolved in methnaol. After neutralization, usually with the help of acetic acid, the mixture was slowly added into water. The removal of methanol gave the final dispersion - Scheme 8. The authors demonstrated that during the pre-polymerization step, the nature of the alkyl-leaving group of the bis-carbamate as well as the process conditions (such as high vacuum)were found to be of outmost importance for the reaction to give polyureas with high enough molecular weights.[60,61]



Scheme 8: Preparation of water-borne non-isocyanate polyureas – adapted from Ma *et al*[60,61]

The successful implementation of this process strongly depends on the ability of the transurethanization reaction to proceed without too many side-reactions. The nucleophilic attack of the diamine onto the bis-carbamate to yield the corresponding urea moiety is in competition with the N-alkylation reaction that can proceed through a decarboxylation mechanism – Scheme 9. This reaction is undesirable since it would lead to a deviation from the stoichiometric ratio, and hence to lower molecular weights.

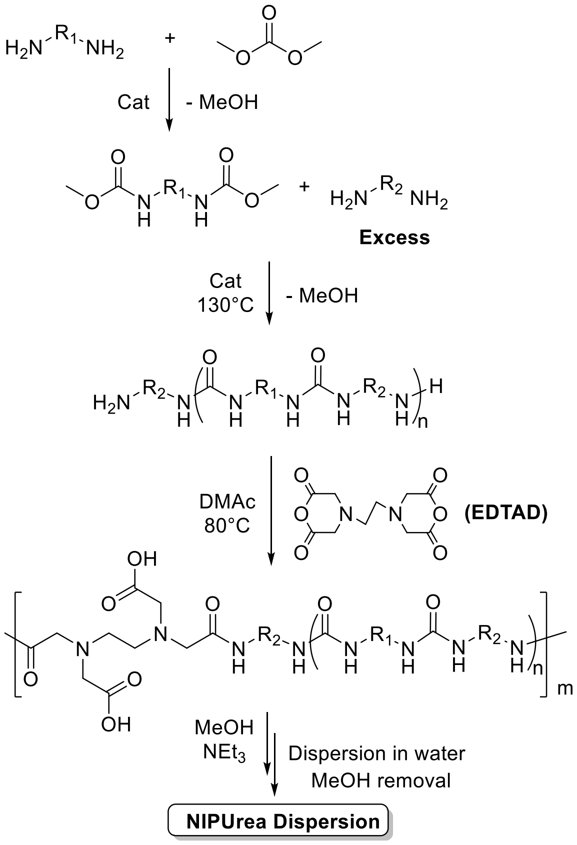


Scheme 9: N-alkylation reaction in competition with the transurethanization in the reaction between a bis-carbamate and a diamine – adapted from Ma *et al.*[60]

The authors demonstrated that the N-alkylation reaction could be mitigated by changing the alkyl moiety located on the bis-carbamate compound[60,61]. Bulkier alkyl-groups reduced the rate of the decarboxylation process, thus favoring the polyurea formation. Indeed, the tert-butoxyl moiety was more selective towards urea formation than the ethyl groups, which itself was more selective than methyl groups. The alkyl moiety on the bis-carbamate also affected kinetics and it was found that the urea formation was faster in the following order: tert-butoxyl > methyl > ethyl. In the case of methyl- and ethyl-group, the bulkier ethyl-group sterically hindered the nucleophilic addition of the diamine onto the bis-carbamate moiety. The case of tert-butoxy group was more intriguing, since faster kinetics was observed despite the bulkiness. The authors explained this fast kinetics by the mechanism of the reaction proceeding *via* the *in situ* formation of an isocyanate moiety. The type of diamine used, and the efficiency of the removal of the generated alcohol also played a very important role in the mitigation of N-alkylation. Regarding the diamines, sterically less hindered primary diamines had faster rates of N-alkylation than the bulkier ones (secondary diamines or primary amines attached to a tertiary carbon). Removal of the alcohol favored the transurethanization reaction and the generation of higher molecular weight polyureas. In general, relatively high molecular weights (16 to 65 kDa) were obtained.[60,61]

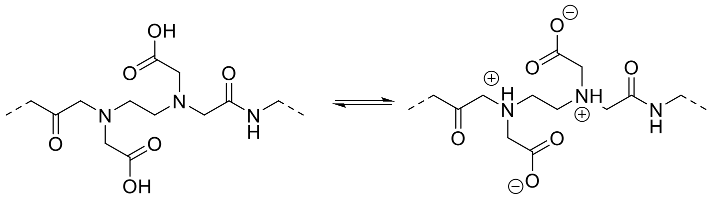
In order to disperse the formed polyurea chains, internal dispersing agents (IDA) were used. Their subsequent neutralization allowed for the polymer chains to form nanoparticles in water. The higher molar percentages (varied from 10 to 30 mol.% in diamine) of IDA were used.[60,61] The higher surface-charge density on the particles led to smaller particles (for example, in the case of a series of copolymers composed of isophorone dimethylcarbamate, 4,7,10-trioxa-1,13-tridecanediamine and 3,3'-diamino-N-methydipropylamine – used as IDA – the particle diameters varied from 280 nm for 10 mol% IDA in diamine to 44 nm for 30mol% IDA in diamine).[60] The coatings cast from these dispersions exhibited pencil hardness ranging between HB and 2B (even B to 6B when changing the diamine) and good resistance to acetone. The molecular weights of the polymer influenced the entanglement densities of the polymer chains and it was observed that polyurea coatings with molecular weights lower tham 30 kDa exhibited poorer impact resistance than coatings with higher molecular weights. Moreover, longer monomers that increase the distance between urea moieties tended to decrease the H-bond density resulting in softer coatings.

In 2018, the same research team demonstrated that ethylenediaminetetraacetic dianhydride (EDTAD) could be successfully incorporated as an IDA into the NIPUrea formulation,[62] Forming two pendent carboxylic acid moieties upon opening of the anhydride opening – Scheme 10.



Scheme 10: Water-borne NIPUreas using EDTAD as internal dispersing agent – adapted from Ma *et al*[62]

The very high density of H-bonds in this system induced gelation, which was also favored by the ionic interactions provided by the zwitterionic form of the amic acid – Scheme 11. The use of an asymmetric isophorone-based bis-carbamate disrupted the establishment of H-bonds between the urea moieties and reduced the extent for gelation.[62]

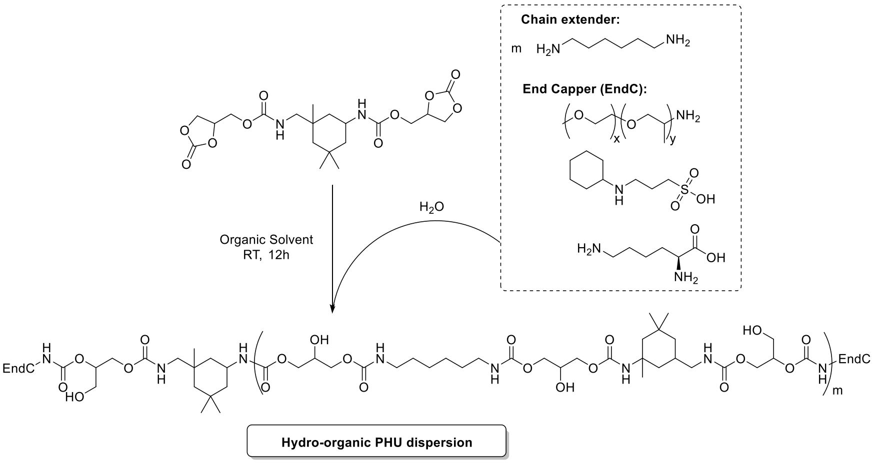


Scheme 11: Zwitterionic form of the amic acid after aminolysis of EDTAD – adapted from Ma *et al*[62]

The advantage of such an internal dispersing agent is the very fine tunability of the neutralization step. The concomitant ionization of the amic acid in its zwitterionic form as well as the neutralization by means of adding triethylamine (NEt_3, TEA) allows for a fine tuning of the particle size of the dispersion (particles diameter ranging from 900 to 8 nm were obtained depending on the conditions). However, the formation of the zwitterionic moiety alone was not enough for stabilizing the dispersion since the polyurea precipitated if no NEt_3 was added prior to dispersion. When increasing the TEA/COOH ratio, the particle size dramatically decreased and the viscosity of the latex increased, which above a certain value can be detrimental for coating applications. As an example, the particle size as measured by dynamic light scattering (DLS) decreased from 900 nm to 14 nm when the ratio was varied from 0.1 to 1.0. In order to circumvent this effect, the authors tried to reduce the concentration of ionic groups in the final polyurea while targeting 100% neutralization of the pendent acidic moieties. This was done by increasing the diamino-prepolymer/EDTAD ratio and neutralizing the carboxyl groups with a stoichiometric amount of trimethylamine. The authors also reduced the ionic content in the final polymer by increasing the molecular weight of the diamino prepolymer. Prepolymer molecular weights ranging from 950 Da to 4750 Da were prepared varying the diamine/carbamate ratio from 2 to 1. Using these prepolymers, the particle size increased from 8 nm ($Mn_{prepolymer}$ = 950 Da) to 61 nm ($Mn_{prepolymer}$ = 4750 Da). Most of the polymers had a relatively high T_g and therefore no film could be cast at room temperature. Coatings could be formed by casting at 50°C for 6 h followed by a thermal treatment at 110-150°C for 24 h. Moreover, these polymers did not form coatings with interesting properties since they were brittle and certainly did not get chain extended enough to reach the minimum entanglement molecular weight, which is needed to obtain polymers with interesting mechanical properties. The coatings were prepared at 50°C on aluminum panels. The curing temperature was found to be very important since higher temperatures led to coating with higher hardness, better adhesion properties as well as better solvent resistance. This was attributed to a non cyclic imidization crosslinking mechanism – namely the reaction between pendent COOH moieties with amides from the polyureas. This result was confirmed by an increase in the gel fraction of the obtained materials.

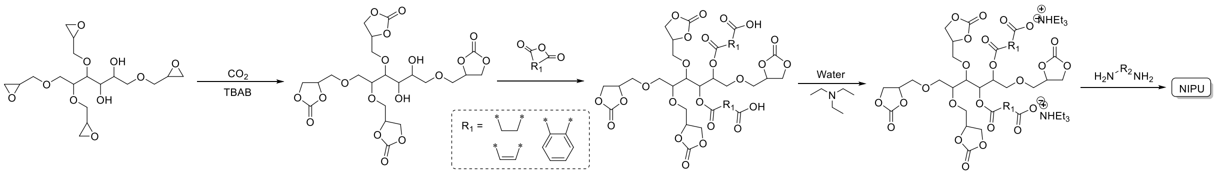
4.1.2. NIPUs dispersion by acetone-like aminolysis processes

Only two examples of poly(hydroxy urethane) dispersions have been reported. The first example dates back to 2008 with a patent from Rhodia.[63] The patent discloses the PHU synthesis and the formation of aqueous dispersions to be used as coatings and adhesives. Most of the examples are in reality hydro-organic solutions and the obtained latexes are not organic solvent-free. In these cases, PHUs were synthesized in an organic solvent such as ethanol or Highlink W (Clariant™). Dihydroxyurethane adducts of isophorone diamine and glycerol carbonate were reacted and functionalized with several ionizable chain ends, such as lysine or N-cyclohexylaminopropane sulfonic acid. The neutralization with trimethylamine or acetic or chlorydric acids led to a water-dispersible PHUs containing an organic solvent in the majority of the cases – Scheme 12. The drawback of this synthetic approach lies in the short oligomers formed upon synthesis. To counter-balance this, in some examples the PHU chains were crosslinked with water-soluble polyisocyanates.



Scheme 12: PHU preparation for further water dispersion by neutralization according to Rhodia[63]

In the second example, Wu *et al.* designed in 2018 a sorbitol-based multi-carbonate capable of being water dispersible.[64] After carbonation of a glycidyl-derivative sorbitol, followed by subsequent derivatization with succinic, maleic or o-phtalic anhydride. After addition of acetone to reduce the viscosity, the formed monomers were neutralized with NEt_3 and dispersed in water to obtain an aqueous cyclic carbonate dispersion with 30 to 40 wt.% solid content after removal of the acetone – Scheme 13.

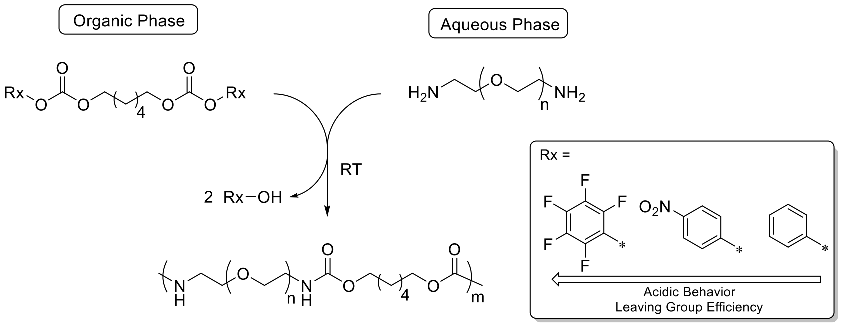


Scheme 13: Sorbitol-based water-dispersible multi-cyclic carbonates according to Wu *et al.*[64]

Subsequent preparation of the water-borne PHUs was performed through the addition of a diamine. Ethyl-, butyl-, hexamethylene-, octamethylene- and isophorone diamines were used. Longer diamine chain lengths led to more flexible films with higher impact resistance. When copolymerization was performed between the succinic sorbitol-based carbonate with mixtures of IPDA and HMDA at different ratios, the pencil and pendulum hardnesses of the coatings decreased with the increase in HMDA content (for IPDA/HMDA ratios going from 1:1 to 1:5, pencil hardnesses went from 2H to F). The T_gs were in the range of 59 to 103°C.

4.2. NIPU dispersions through interfacial polymerization

In 2017, Sardon and coworkers used surfactant-assisted interfacial polymerization for the synthesis of non-isocyanate polyurethane soft nanoparticles.[65] To do so, they extended the work undertaken in 2013 on water-soluble NIPUs[49] based on the design of aromatic leaving groups. In this process, they dissolved the hexanediol-based activated bis-cyclic carbonates in dichloromethane (DCM) and PEG-diamine in water. The reaction was performed at room temperature and the volumetric water to DCM ratio was fixed at 80:20 – Scheme 14.

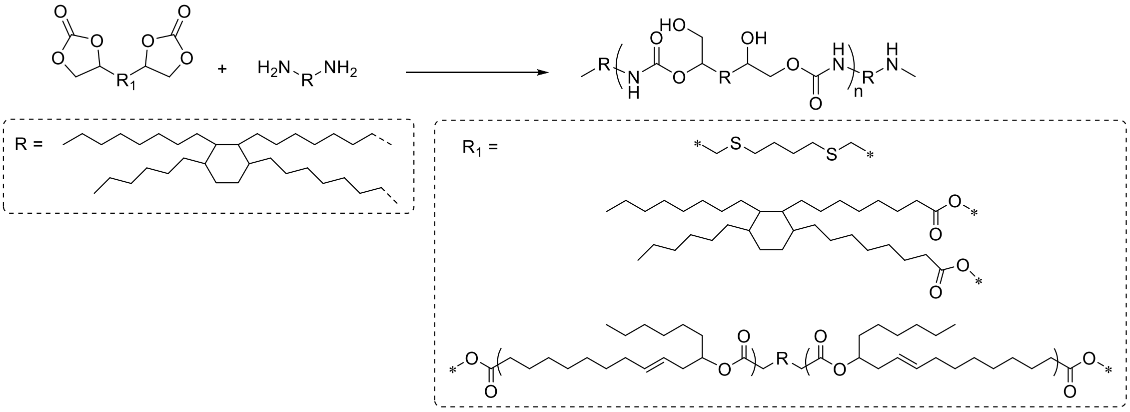


Scheme 14: Interfacial polymerization for the production of NIPU according to Sardon and coworkers[65]

The reaction kinetics was fast, especially in the case of the pentafluorophenolate-activated bis cyclic carbonate and full conversion was achieved with reaction times as short as 10 min. The lower basicity of the pentafluorophenol-based monomer enhanced its ability to act as a leaving group while reacting with a diamine. 2.5 and 5wt.% of sodium dodecyl sulfate (SDS) allowed the formation of stable dispersions with particle sizes of 274 and 162 nm, respectively. Molecular weights of 23000 to 27000 g/mol and dispersities ranging from 1.22 to 1.63 were determined by SEC in DMF. These dispersities are too low for a complete conversion, suggesting problems in the SEC analysis. However, the removal of DCM by evaporation provoked the aggregation of the NIPU particles, which was attributed to the softness of the particles that were not able to maintain their shape. To counterbalance this effect, the polymer was cross-linked with tris(2-aminoethyl)amine (TAEA). With 20mol.% of TAEA, more stable but larger particles were obtained. The doxorubicin loading ability of the NIPU particles was tested as a proof of concept for the applicability of such particles for drug delivery purposes.

4.3. NIPU dispersions by mini-emulsion polymerization

The only example of mini-emulsion of NIPUs has been reported by Cramail and coworkers in 2016. They used fatty-acid based bis-cyclic carbonates in combination with the commercially available Priamine™ 1075 (dimer diamine) in order to form poly(hydroxyurethane)s – PHUs.[66] Tween® 80 was found to be a suitable surfactant - Scheme 15. In the case of the thiol-containing bis cyclic carbonate, the very high hydrophobicity of the fatty-acid-based monomers allowed the polymerization to proceed in mini-emulsion without requiring the use of an additional co-stabilizer to avoid Ostwald ripening.[67] Similar feature was noticed in the case of fatty-acid based water-borne 'classical' PUs.[68] However, in the case of monomers with longer linear aliphatic chain lengths, hexadecane was added to the system for the mini-emulsion to remain stable.



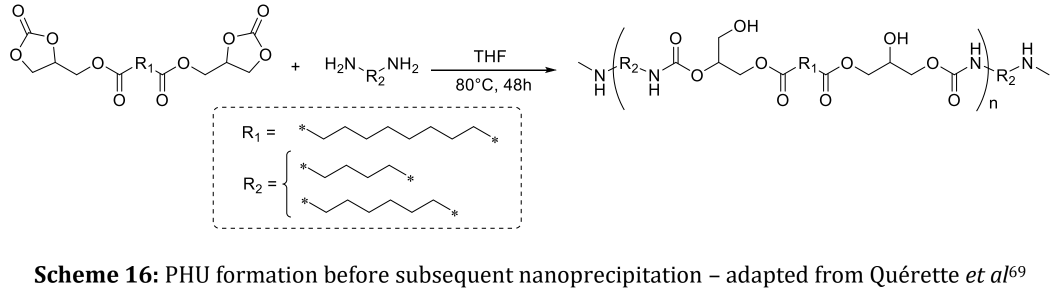
Scheme 15: Mini-emulsion of fatty-acid based poly(hydroxy)urethanes, PHUs – adapted from Cramail and coworkers[66]

The challenge of this process relies in getting latexes of high solids content. Unfortunately, latexes with solids contents higher than 20 wt.%, although stable, presented a secondary population of larger size and a very broad distribution. The molecular weights obtained in miniemulsion were slightly lower than in bulk. Partial hydrolysis of the bis-cyclic carbonate monomers was assumed to be the reason for this phenomenon.

4.4. PHU dispersions by nano-precipitation

Nanoprecipitation basically consists in a solvent-shifting or solvent displacement. A pre-formed polymer – in this case a PHU – is synthesized or solubilized in a semi-polar organic solvent and this solution is added to a non-solvent of the polymer (usually water). The organic solvent and the non-solvent are mutually miscible. Since the polymer is not soluble in the mixture, precipitation occurs forming nanoparticles.

This process was applied to poly(hydroxyurethane)s synthesized by aminolysis of sebacic acid derived biscyclic carbonate with tetramethylene diamine (TMDA) and hexamethylene diamine (HMDA) - Scheme 16.[69]



Scheme 16: PHU formation before subsequent nanoprecipitation – adapted from Quérette *et al*[69]

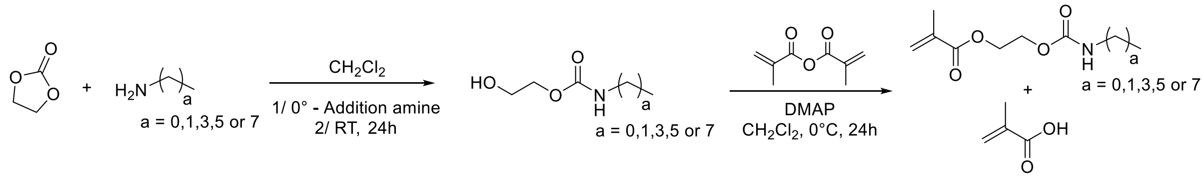
The polymers were synthesized by regular heating or microwave radiation. Only oligomers were formed during the polymerization process, even if the microwave-based process seemed to lead to slightly higher molecular weights. The T_gs were -8 and -16°C for HMDA-based and TMDA-based PHUs, respectively. The choice of nanoprecipitation was made after several unfruitful trials of interfacial polymerization such as the one described by Sardon and coworkers,[65] showing that some water-based NIPU processes are very sensitive to the specific structure of the monomers.

Ethanol and DMSO were suitable solvents, and smaller particles were formed in ethanol. When increasing the polymer concentration in the organic phase, bigger particles were obtained. This was attributed to the increase in viscosity of the solution and the more complex solvent diffusion towards the water phase, although it may also be related to the effect often found in miniemulsification that high viscosity organic phase requires higher energy to be dispersed. The aqueous to organic phase ratio did not exhibit any influence on the nanoparticle size. Ageing by aggregation was found to occur in 28 days, but different kinetics were observed; the ageing was significantly slower when DMSO was used as a solvent. This is linked to the larger particle sizes, decreasing the total number of particles and the resulting rate of coagulation. The main drawback of this technique, in addition to the slow addition of the organic phase into the aqueous phase, is the needed removal of the organic solvent, especially if medical applications are envisioned. As a proof of concept, DMSO was removed by dialysis, and this was found to increase the stability of the dispersion by slowing the ageing.

5. Water-borne Hybrid-NIPUs (H-NIPUs)

5.1. NIPU-Acrylics - HUMAs

Meng *et al*. reported in 2017 two studies describing the use of urethane methacrylate (UMA) reactive diluents in water-borne systems.[70,71] The UMAs were prepared through the aminolysis reaction of ethylene carbonate with aliphatic amines of different chain length followed by functionalization with methacrylic anhydride. Varying the chain lengths allowed tuning the hydrophobicity of the final product – Scheme 17.[70]



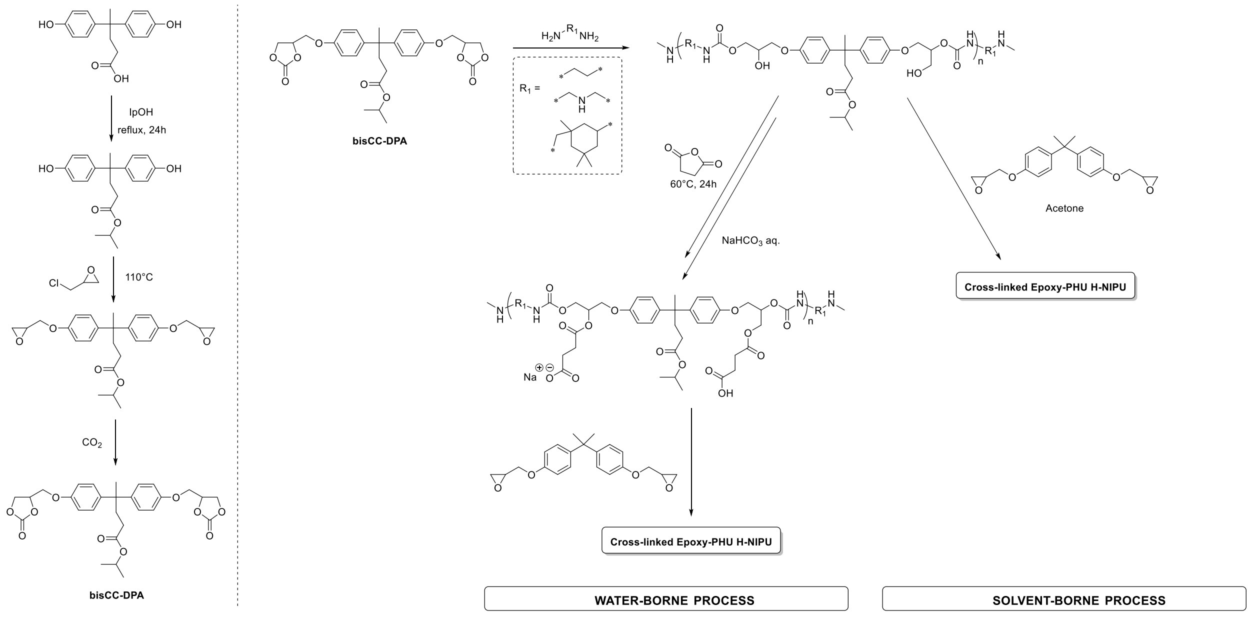
Scheme 17: Mono-functional Urethane Methacrylates (UMAs) of different hydrophobicity for their subsequent incorporation into MMA/BA-based latexes – adapted from Meng *et al.*[70,71]

The copolymerization of these UMAs with MMA/BA was performed in seeded semi-batch emulsion polymerization, targeting a solids content of 30 wt.%. The seed was a MMA/BA (70/30 wt/wt) copolymers prepared in batch. During the semi-continuous operation, the feed was a mixture of MMA/BA (63/37 wt/wt) containing UMA (15 wt% based on total amount of monomers). All the polymerizations were carried out under starved conditions (instantaneous conversion greater than 85%) and within this range it was observed that conversion was slightly lower for the long UMAs. No secondary nucleation was observed during the semi-batch process. TEM images showed a unimodal and uniform spherical morphology. The T_gs and minimum film forming temperatures (MFFTs) of the latexes decreased with the increasing chain length of the UMA. MFFTs close to room temperature were obtained when the aliphatic pendent chain contained sufficiently carbon atoms (6 or 8 in this case). The mechanical properties depended on the amount of UMA incorporated within the copolymer. A specific reinforcement due to the formation of H-bonds was identified especially in the case of the short chain length. The long chains showed a plasticizing effect.

A second article reported the seeded emulsion copolymerization of BEM (butyl-based UMA, a=3 in Scheme 17) with MMA/BA.[71] A seed of MMA/BA (48/52 wt/wt) was first prepared in batch. The seed was used to synthesize BEM/MMA/BA copolymers in batch and semi-batch modes. The process conditions (batch and semi-batch mode), the morphology of the particle (homogeneous and core-shell) and the location and concentration of BEM within the particle (in the core or in the shell) were studied. Because of the difference in reactivity between BEM, MMA and BA (BA reacts much slower than the methacrylates), the copolymer composition was broader in batch and although in both cases a single T_g was observed, the T_g of the batch was broader than that of the semibatch. The composition distribution strongly affected the mechanical properties and the batch latex presented higher Young’s modulus and stress at break than the semicontinuous one, but smaller elongation at break. The mechanical properties were strongly affected by the BEM content. The increase in BEM concentration from 0 to 20 wt.% induced an increase of Young modulus, tensile strength and elongation at break. This is remarkable as commonly the increase in Young modulus and tensile strength is accompanied by a decrease in the elongation at break. Moreover, this effect was much stronger when the BEM was located in the shell of the particles. When located in the core, the participation of BEM in the reinforcement of the mechanical properties was much less significant.

5.2. NIPU-Epoxy

Ma *et al.* carried out the synthesis of a new diphenolic acid (DPA)-based bis cyclic carbonate (bisCC-DPA) compound and its subsequent incorporation into water-borne systems for coating applications.[72] To do so, the native DPA was modified with epichlorohydrin prior to carbonation with CO_2. The protection of the pendant acid group during the esterification reaction was necessary to avoid unwanted side reactions. The formed bisCC-DPA reacted further in N-methyl pyrrolidone (NMP) or propylene glycol methyl acetate (PGMAC) with various diamines to yield the corresponding PHUs. Only short oligomers, with molecular weights in the range 4300-4800 Da and dispersities close to 2 were obtained. The NIPUs were used as coatings both in organic solvent-based and in water-based processes. In the first case, the PHU oligomers were dissolved in acetone prior to functionalizing them with a bisphenol-A diglycidyl ether (BADGE) to yield a 3D-network. Good thermo-mechanical properties were obtained. In the water-borne process, the pendant OH-groups were functionalized with succinic anhydride, followed by ionization with different amounts of $NaHCO_3$. Further dispersion in deionized water and curing with an epoxy resin latex led to the final Epoxy-PHU hybrid NIPUs – Scheme 18. This process is interesting because it makes use of an inner surfactant born onto the NIPU backbone, which plays a similar role than dimethylolpropionic acid in PU. The weight ratio of $NaHCO_3$ to PHU played a crucial role in the formation of the latex, the higher the salt amount the smaller the particles. Surprisingly, the T_g of the cured polymer decreased with the amount of salt, which was attributed to the reduction of the crosslinking density caused by the excess of salt. In addition, the water contact angles decreased with the $NaHCO_3$ content. As a conclusion, a fine optimization of the amount of ionic groups is highly desirable for good quality coating formation.



Scheme 18: Preparation of water-borne diphenolic acid-based Epoxy-PHU hybrid NIPUs – adapted from Ma *et al.*[72]

6. Conclusions

This work reviews the water-based non-isocyanate polyurethane-ureas (NIPUUs), a new class of materials that are a greener alternative to the traditional isocyanate-based polyurethane-ureas.

NIPUUs can be formed by either the transurethanization process, yielding polyurethane/ureas, and the aminolysis of biscyclic carbonates, yielding poly(hydroxyurethane)s (PHUs). Neither of the two approaches is free from problems. N-alkylation side-reaction can occur during the transurethanization process. This side reaction can be mitigated by changing the alkyl moiety located on the bis-carbamate compound. Bulky groups such as tert-butoxyl-, phenyl-, nitrophenyl- and pentafluorophenyl-moieties reduce the side reaction, but the purification of the aromatic moieties remains challenging, and tert-butoxyl-groups work through the formation of an *in situ* isocyanate moiety in their mechanism, which can seem questionable if a full isocyanate-free process is desired. On the other hand, the use of aminolysis in aqueous media is challenging because cyclic carbonates are prone to suffer hydrolysis.

Both water-soluble NIPUUs and waterborne NIPUU dispersions can be prepared by varying the hydrophilicity of the monomers.

In principle, both aminolysis and transurethanization can be used to directly synthesize water-soluble NIPUUs in water. However, the use of aminolysis is precluded by the propensity of the cyclic carbonates to suffer hydrolysis. Transurethanization using functional bis-carbonates allowed obtaining water-soluble NIPUs. A likely easier to apply approach is the modification of NIPUs synthesized in organic solvents. Imines, neutralized carboxyl groups and quaternary ammonium chloride moieties have been used to render the preformed NIPUs soluble in water.

Some widely different methods have been used to synthesize waterborne NIPUU dispersions. A method that looks promising is the acetone-like process. In this process, NIPUUs containing internal dispersing moieties (e.g. carboxyl or zwitterionic) are synthesized in a low boiling point organic solvent such as acetone using either transurethanization or aminolysis. The polymer solution is then dispersed in water and the solvent removed by evaporation. NIPUU dispersions can also be synthesized by interfacial transurethanization with the carbamate in the organic phase and the diamine in the aqueous phase. Miniemulsion polymerization has been used to synthesize NIPU dispersions by the aminolysis process. Poly(hydroxyurethane)s synthesized by aminolysis have been used to prepare NIPU dispersions by nanoprecipitation.

As in the case of classical PUs, it is expected that hybrids composed by NIPUs and other polymers yield materials with synergistic properties. Therefore, NIPU-acrylics and NIPU-epoxy hybrids have been synthesized showing synergistic improvement of the performance.

Substantial advances in the development of water-based NIPUs have been done in the last years. These studies show that the structure of the monomers plays a critical role in both the feasibility of the synthetic process and the type of polymer obtained. Further developments will require easier methods for the synthesis and purification of the monomers, to understand the effect of the polymerization method on the polymer microstructure and that of the microstructure on the performance. It is hoped that these developments will bring water-based NIPUUs closer to industrial implementation.

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8. Shortened forms

BA:	Butyl Acrylate
BADGE:	Bisphenol-A Diglycidyl Ether
CMR:	Carcinogenic, mutagenic, reprotoxic
CO_2:	Carbon Dioxide
DCM:	Dichloromethane
DLS :	Dynamic Light Scattering
DMF:	Dimethylformamide
DMPA:	Simethylolpropionic Acid
DMSO:	Dimethylsulfoxide
DPA:	Diphenolic Acid
DSC :	Differential Scanning Calorimetry
EDDA :	2,2'-(ethylenedioxy)diethyl-amine
EDTAD:	Ethylenediaminetetraacetic Dianhydride
HMDA:	Hexamethylene Diamine
IDA:	Internal Dispersing Agent
IPDA:	Isophorone Diamine
MFFT:	Minimum Film Formation Temperature
MMA:	Methyl Methacrylate
m-XDA:	m-xylylenediamine
$NaHCO_3$:	Sodium Bicarbonate
NIPU:	Non Isocyanate Polyurethane
NMP:	N-Methyl pyrrolidone
ODA:	1.8-diaminooctane
PEG:	Poly(ethylene) glycol
PGMAC:	Propylene Glycol Methyl Acetate
PHU:	Poly(hydroxyurethane)
PU:	Polyurethane
PUI:	Poly(urethane–co–imine)
SDS:	Sodium Dodecyl Sulfate
SEM:	Scanning Electron Microscopy
TAEA:	Tris(2-aminoethyl)amine
TEA:	triethylamine
TEM:	Transmission Electron Microscopy
$Ti(OEt)_4$:	Titanium Ethoxide
T_g:	Glass Transition Temperature
TMDA:	Tetramethylene diamine
UMAs:	Urethane methacrylates

PART C

OBJECTIVES & OUTLINE

From the state-of-the-art, it appears that Hybrid-Non Isocyanate Polyurethanes (H-NIPUs) are interesting new materials with properties arising from a synergistic combination of those of the constitutive units. Moreover, in only a few examples the potential of such hybrid materials in water-borne systems has been explored.[1–3]

Therefore, the purpose of this thesis was to synthesize novel water-borne hybrid-NIPU materials (H-NIPUs) by combining bio-based isocyanate-free poly(hydroxy urethane)s (PHUs) pre-polymers with (meth)acrylates. In order to fulfill this goal, several challenges should be overcome such as the synthesis of specific monomers (in this case bis-cyclic carbonates), the bulk polymerization of these monomers with diamines to form the PHUs, the selection of a suitable acrylic phase to dissolve these PHUs and finally the polymerization of the acrylic phase in a mini-emulsion process. As the characteristics and properties of the hybrids are expected to depend on the interaction between the PHU and the acrylic polymer, both grafted and non-grafted hybrids were synthesized and the properties of the resulting coatings investigated.

The rest of this thesis will be divided in four chapters.

Chapter 2 deals with the bulk synthesis of bio-based poly(hydroxy urethane)s - PHUs. The design of ester-activated bis-cyclic carbonates of different aliphatic chain length is described, as well as their polymerization behavior with various fatty acid-based diamines. The relationship between the structure of the PHU and the thermal and viscoelastic properties is investigated.

Chapter 3 is dedicated to the design of water-borne non-cross-linked PHU-Poly(butyl methacrylic) H-NIPUs using mini-emulsion. In this chapter, a 2-step process was implemented. Fatty acid based-PHUs were firstly synthesized in bulk and then dissolved in a mixture of butyl methacrylate and stearyl acrylate (BMA + SA). The resulting mixture was then emulsified by sonication and the acrylic phase polymerized. Different latexes, having compositions ranging from 0 to 30 wt.% PHU, were obtained, and the polymerization behavior of the acrylic phase was studied, in terms of kinetics and particle size. The performance of the films cast from the hybrid waterborne dispersions was studied.

In Chapter 4, waterborne grafted PHU-poly(meth)acrylate hybrid dispersions were synthesized and the effect of grafting on the particle and film morphologies as well as on the mechanical properties of the films was investigated.

Chapter 5 provides the general conclusions and perspectives to this work.

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CHAPTER 2

BULK SYNTHESIS OF BIO-BASED POLY(HYDROXY URETHANE)S – PHUS

Keywords: Poly(Hydroxy)urethanes - PHUs
Bio-based Polymers
Vegetable Oils
Fatty acids
Polymer Microstructure
Bulk Polymerization

Table of content

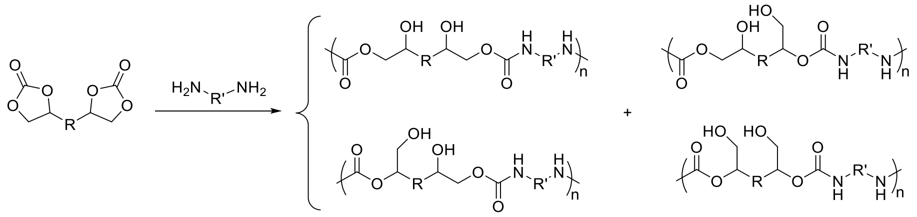
1. Introduction 119
2. Experimental 121
   2.1. Materials and methods 121
   2.2. Standard Procedure for polymerization 123
   2.3. Bis-cyclic carbonate synthesis 123
3. Results and Discussion 124
   3.1. Activated bio-sourced bis-cyclic carbonates (bisCCs) 124
   3.2. Copolymerization of bisCC-C_4 and bisCC-C_{10} with mixtures of diamines 127
   3.3. Thermal characterization 132
   3.4. Viscoelastic behavior 133
   3.5. Theoretical study of the polymerization behaviors of bisCC-C4 and bisCC-C10 134
4. Conclusion 136
5. References 137
6. Shortened forms 141
7. Supporting Information 142
   7.1. NMR analyses 142
   7.2. IR analyses 152
   7.3. DSC analyses (Temperature ramp : 10°C.min^{-1}) 153
   7.4. TGA analyses 155
   7.5. SEC traces 157
   7.6. DFT Study – Structures of the intermediates 157

1. Introduction

Since their discovery by Otto Bayer in 1947,[1] polyurethanes (PUs) have become essential materials in the conception of nowadays' consumer goods. *PlasticEurope* quantifies in 2017 the EU plastic converter demand at 51.2 million tons, including 4 million tons for PUs only (7.7% of the market).[2] Indeed, the versatility of these materials allows them to find various applications in markets including, among others, flexible and rigid foams, footwear, coatings and adhesives.[3,4] These specialty polymers are industrially obtained through the polyaddition of a diol (or polyol) and a diisocyanate (or polyisocyanate). The latter originates from the reaction of the corresponding diamine with phosgene, which has been earmarked as a very toxic compound. Isocyanates are also considered to be very toxic and may be facing regulatory issues in a near future.[5–7]

This is the reason why many research activities have recently been devoted to finding alternatives for the production of isocyanate-free pathways towards the production of so-called non-isocyanate polyurethanes (NIPUs). In 2015, Maisonneuve *et al.* extensively reviewed the different approaches towards the formation of NIPUs, among which the aminolysis of 5-membered bis-cyclic carbonates (bisCCs) by diamines emerges as one of the most promising solutions.[8] This route allows the formation of NIPUs containing pendant hydroxyl groups, also called poly(hydroxy)urethanes (PHUs). Several challenges appear in the chemistry of PHUs and are still hindering their industrial implementation.[9,10] The major one consists in achieving the formation of NIPUs of sufficiently high molecular weight in order to obtain materials with measurable properties. Several explanations and potential solutions have been provided in the scientific literature to explain this phenomenon, including, among others, the low carbonate reactivity,[10] the occurrence of side reactions,[11–16] the formation of hydrogen bonds[17] or the reaction conditions (such as the reaction solvent, the bisCC-diamine ratio, the temperature or the use of a catalyst).[8,9,18–22] There are several ways of increasing the carbonate reactivity. Increasing the size of the carbonate ring from a 5-membered- up to a 8-membered-ring was found to significantly enhance the carbonate reactivity during its aminolysis.[23–31] Chemical activation in β-position of the carbonate ring was also demonstrated to be a powerful technique. By means of different activations, including for instance ester-, ether- or thio-activation, the reactivity of the cyclic carbonate could be tuned. Dramatic impacts on the kinetics of the carbonate conversion – hence on the polymerization process in itself – could be observed.[32–34] Ester-activation was shown to be of particular interest. It was indeed demonstrated to dramatically improve the carbonate reactivity, providing it with a similar reactivity than 6-membered cyclic carbonates, and thus enhancing the kinetics of the reaction.[33,35–43]

It is also known from literature that the ring opening of the cyclic carbonate moiety can yield two types of pendant hydroxyl-moieties. Depending on the mechanism at stake, either primary of secondary pendant OH-groups can be obtained – Scheme 1.



Scheme 1: Different products obtained through the aminolysis of cyclic-carbonate compounds

Another challenge relies in the commonly use of solvents for the synthesis of PHUs. Bis-cyclic carbonates usually are solid compounds with high melting temperatures. In addition to this, they exhibit poor solubility in common organic solvents.[8,44] The use of dimethylformamide (DMF) or dimethylsulfoxide (DMSO) is traditionally reported, as those solvents are able to solubilize both the monomers and the formed PHUs and allow for reactions occurring at relatively high temperatures. However, such solvents are bringing extra issues in terms of purification and then characterization of the formed polymers. In the quest for the formation of NIPU materials, the bulk synthesis of PHUs thus appears as a challenging, but promising pathway. This is the reason why an increasing amount of recent publications focus onto the synthesis of solvent-free NIPUs, and especially PHUs.[19,41,45–59] Bulk synthesis has been employed when bio-resources such as carbonated- vegetable oils, lignin or cellulose derivatives were utilized in the synthetic process. There are however very few studies dealing with the bulk synthesis of linear NIPUs originating from fatty-acid derivatives, and when they do exist, none of them have tried to investigate the influence of the chain length of the bis-cyclic carbonate compound.

In this study, we have considered the investigation of the bulk synthesis of bio-based linear bis-cyclic carbonates of different chain length. Two different bisCCs were synthesized: one from sebacoyl chloride (bisCC-C_{10}) and one from succinic anhydride (bisCC-C_4). The synthesis of bisCC-C_{10} from the acyl chloride derivative of sebacic acid is already well known in the literature and quite established in PHU chemistry.[33,54,60] However, this is not the case for bisCCs of short chain lengths. In this study, we have investigated the ring opening of succinic anhydride with glycerol carbonate. Both bisCCs were subsequently copolymerized with diamines of different chemical structures. The commercially available aliphatic 1,10-diaminodecane (10DA) and the branched Priamine™ 1075 (P1075) were utilized. The impact of the monomer composition onto the microstructure, thermal and visco-elastic properties of the formed PHUs was investigated.

2. Experimental

2.1. Materials and methods

Decane 1,10-diamine (10DA, >98%) was supplied by TCI Europe. Sebacoyl Chloride (97%) was obtained from Alfa Aesar. Glycerol 1,2-carbonate (90%), N,N'-Dicyclohexylcarbodiimide (DCC, 99%) and succinic anhydride (99%) were purchased at ABCR. Trimethylamine (NEt_3, 99%) was provided by Fisher. 4-dimethylaminopyridine (DMAP, 99%) was obtained from Sigma. Dichloromethane (DCM) and acetonitrile (ACN) were obtained from VWR Chemicals. Croda kindly provided Priamine™ 1075 (P1075). All products and solvents (reagent grade) were used as received unless otherwise mentioned.

^{1}H and ^{13}C-NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz and 100.63 MHz for ^{1}H and ^{13}C-NMR respectively) by using DMSO-d6 as a solvent at room temperature, unless otherwise mentioned.

The conversion of the carbonate was calculated using Eq. 1 from the integrals of the CH_2 in alpha-position of the urethane moiety (δ = 2.9 ppm) and of the quaternary carbon of the bis-cyclic carbonate monomers (δ = 5 ppm). The equation Eq. 1 was applied:

$$\text{Conversion (\%)}_{\text{carb}} = \frac{\frac{\int \text{Urethane}_{(\delta_{\text{ppm}}\,=\,2.9)}}{2}}{\frac{\int \text{Urethane}_{(\delta_{\text{ppm}}\,=\,2.9)}}{2} + \int \text{Carbonate}_{(\delta_{\text{ppm}}=5)}} \qquad (1)$$

The urethane : urea : amide ratio was calculated according to the integrals of the labile protons, and the following equations were utilized:

$$\%_{\text{Urethane}} = \frac{\int \text{Urethane}_{\ (\delta_{\text{ppm}}\,=\,7.1)}}{\int \text{Urethane}_{\ (\delta_{\text{ppm}}\,=\,7.1)} + \int \text{Amide}_{\ (\delta_{\text{ppm}}\,=\,7.7)} + \frac{\int \text{Urea}_{(\delta_{\text{ppm}}\,=\,6.8)}}{2}} \qquad (2)$$

$$\%_{\text{Amide}} = \frac{\int \text{Amide}_{\ (\delta_{\text{ppm}}\,=\,7.7)}}{\int \text{Urethane}_{\ (\delta_{\text{ppm}}\,=\,7.1)} + \int \text{Amide}_{\ (\delta_{\text{ppm}}\,=\,7.7)} + \frac{\int \text{Urea}_{(\delta_{\text{ppm}}\,=\,6.8)}}{2}} \qquad (3)$$

$$\%_{\text{Urea}} = 1 - \%_{\text{Urethane}} - \%_{\text{Amide}} \qquad (4)$$

Fourier transform infrared (FTIR) spectra were recorded on a Bruker VERTEX 70 instrument ($4cm^{-1}$ resolution, 32scans, DLaTGS MIR) equipped with a Pike GladiATR plate (diamond crystal) for attenuated total reflectance (ATR) at room temperature.

Polymer molecular weights were determined by Size Exclusion Chromatography (SEC) using dimethylformamide (DMF + lithium bromide LiBr 1g/L) as the eluent. Measurements in DMF were performed on an Ultimate 3000 system from Thermoscientific equipped with diode array detector. The system also includes a differential refractive index detector (dRI) from Wyatt technology. Polymers were separated on two KD803 Shodex gel columns and one KD804 Shodex gel columns (300 x 8 mm) (exclusion limits from 1000 Da to 700 000 Da) at a flowrate of 0.8 mL/min. Column temperature was held at 50°C. Easivial kit of Polystyrene from Agilent was used as the standard (Mn from 162 to 364 000 Da).

Differential Scanning Calorimetry (DSC) thermograms were measured using a DSC Q100-RSC or a DSC Q100-LN2 apparatus from TA Instruments. In the DSC Q100-RSC, the measurements were performed over a temperature range from -80°C to 160°C, with a heating cooling rate of 10°C.min^{-1}. The analyses were carried out in a nitrogen atmosphere in aluminum pans. In the DSC Q-100-LN2, the measurements were performed over temperature ranging from -150°C to 160°C, with a heating cooling rate of 10°C.min^{-1}. The analyses were carried out in a helium atmosphere with aluminum pans. The glass transition temperatures (T_gs) were calculated from the second heating ramp.

Thermogravimetric Analyses (TGA) were performed on a TA-Q500 apparatus from TA Instruments with a heating rate of 10°C.min^{-1} under a nitrogen atmosphere from room temperature until 700°C.

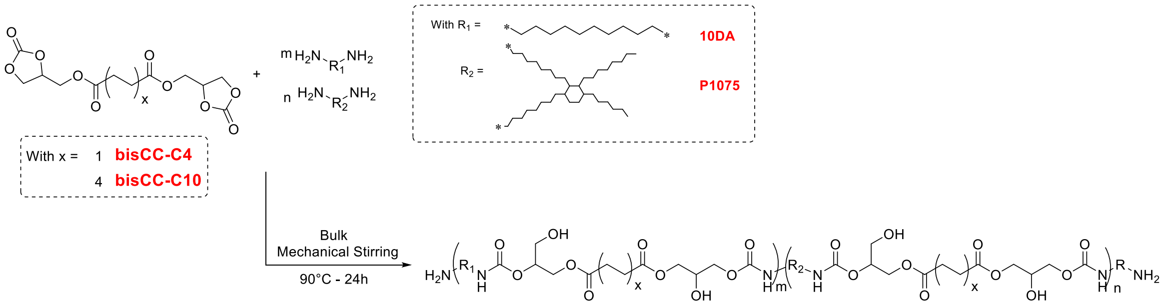
The rheology experiments were carried out in a stress-controlled Anton Paar Physica MCR101 rheometer. Small-amplitude oscillatory experiments were carried out using 25 mm parallel plate geometry. All the experiments were conducted in linear viscoelastic conditions for the studied temperature range (strain = 0.5% and frequency 1 Hz).

Regarding the theoretical mechanistic study, all geometry optimizations were carried out in gas phase within density functional theory (DFT), combined with the 6-31+G(d,p) basis set. Harmonic vibrational frequencies were obtained by analytical differentiation of gradients, in order to determine whether the structures found are minima or transition states.

The frequencies were then used to evaluate the zero-point vibrational energy (ZPVE) and the thermal (T = 298 K) vibrational corrections to the enthalpy (H) in the harmonic oscillator approximation. Single point calculations using the 6-311++G(2df,2p) basis set were performed on the optimized structures in order to refine the electronic energy, and the previously calculated corrections to the enthalpy were used to calculate the H of each species- All DFT calculations were carried out using the Gaussian 16 package.

2.2. Standard Procedure for polymerization

Poly(hydroxy)urethanes (PHUs) were synthesized using bisCC-C_4 and bisCC-C_{10} with 10DA and P1075 as comonomers (Scheme 2). Stoichiometric ratios for the reactive moieties were targeted to maximize the molecular weights according to the Carother's theory. The reactions were performed in bulk at 90°C for 24h in a Schlenk tube using a helical shaped mechanical stirrer specifically designed to fit in the Schlenk vessel. No catalyst was added for the polymerization reactions. No purification of the PHUs was performed after reaction. Conversions were determined by ^{1}H-NMR spectroscopy after 24h reaction time.



Scheme 2: PHU synthesis through copolymerization of bisCC-C_4 and bisCC-C_{10} with 10DA and P1075

2.3.Bis-cyclic carbonate synthesis

bisCC-C_{10} synthesis.

In a three-neck round bottom flask, 2.2 eq. (30 g, 254 mmol) of glycerol carbonate and 2.2 eq. (25.707 g, 254 mmol) of trimethylamine were added to 100 mL of dichloromethane (DCM). This mixture was cooled down with the help of an ice bath and 1 eq. (27.615 g, 115.5 mol) of sebacoyl chloride was added dropwise. The reaction mixture was left under stirring for 24 h at room temperature. After reaction, the product was purified by means of the following liquid-liquid extraction steps: 5 times with 200 mL of an acid solution (5wt.% HCl), followed by 3 times with a basic treatment (stirring with basic alumina during 1h, followed by filtration of the liquid DCM phase), and finally 1 washing step with brine. The isolated organic phase was then dried with $MgSO_4$, filtered over a sintered filter and the dichloromethane was removed under reduced pressure. The obtained white powder was then analyzed by ^{1}H-NMR. The white powder was dried in a vacuum oven at 40°C overnight to remove any traces of remaining solvent. Yield: 50 %

^{1}H-NMR: δ_H (400 MHz, DMSO-d6) 5.10 – 4.97 (2 H, m), 4.57 (2 H, t), 4.43 – 4.17 (6 H, m), 2.33 (4 H, t), 1.51 (4 H, q), 1.25 (8 H, d).

bisCC-C_4 synthesis.

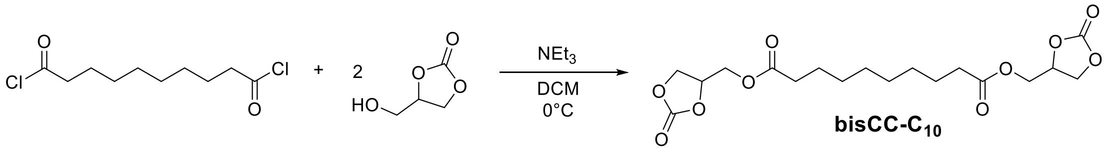
In a three-neck round bottom flask, 1 eq. (2.032 g, 20.33 mmol) of succinic anhydride and 0.3 eq. (0.745 g, 6.10 mmol) of 4-dimethylaminopyridine (DMAP) were added in 30 mL of acetonitrile (ACN). This mixture was heated up to 70°C with the help of an oil bath until solubilization of the reagents and 2.5 eq. (6.000 g, 50.81 mmol) of glycerol carbonate were added dropwise. The mixture was left to react under magnetic stirring during 6h and the conversion of the succinic anhydride into the mono-carbonate derivative was checked by ^{1}H-NMR analysis. The reaction mixture was then cooled down to room temperature and then 1.5 eq. (6.291 g, 30.49 mmol) of N,N'-Dicyclohexylcarbodiimide (DCC) was added. The mixture was left under magnetic stirring overnight (16h) and the formation of a white precipitate of dicyclohexylurea (DCU) was noticed. After checking that full conversion was achieved by ^{1}H-NMR, the reaction mixture was filtered over a sintered filter and the ACN was removed under reduced pressure. The formation of a white powder was noticed. This powder was then washed with cold DCM (50 mL) in a sintered filter to remove the excess of glycerol carbonate, DCC and DMAP that are soluble in it. The purity of the product was checked by ^{1}H-NMR. The final product was then dried in a vacuum oven overnight to remove any trace of remaining solvent. Yield: 40%.

^{1}H-NMR: δ_H (400 MHz, DMSO-d_6) 5.03 (2 H, m), 4.57 (2 H, t), 4.37 – 4.20 (6 H, m), 2.63 (4 H, d, J 1.0).

3. Results and Discussion

3.1. Activated bio-sourced bis-cyclic carbonates (bisCCs)

The synthesis of the bis cyclic carbonate from Sebacoyl Chloride (bisCC-C$_{10}$) was adapted from Carré *et al.* and relies on the esterification reaction between the fatty diacid-based diacyl chloride and glycerol carbonate (Scheme 3).[54]



Scheme 3: Synthesis of the bis cyclic carbonate from sebacoyl chloride (**bisCC-C$_{10}$**).

After purification, the product could be obtained as a white powder with a yield of 50%. The formation of the expected product was attested by ^{1}H-NMR spectroscopy (Figure 1).

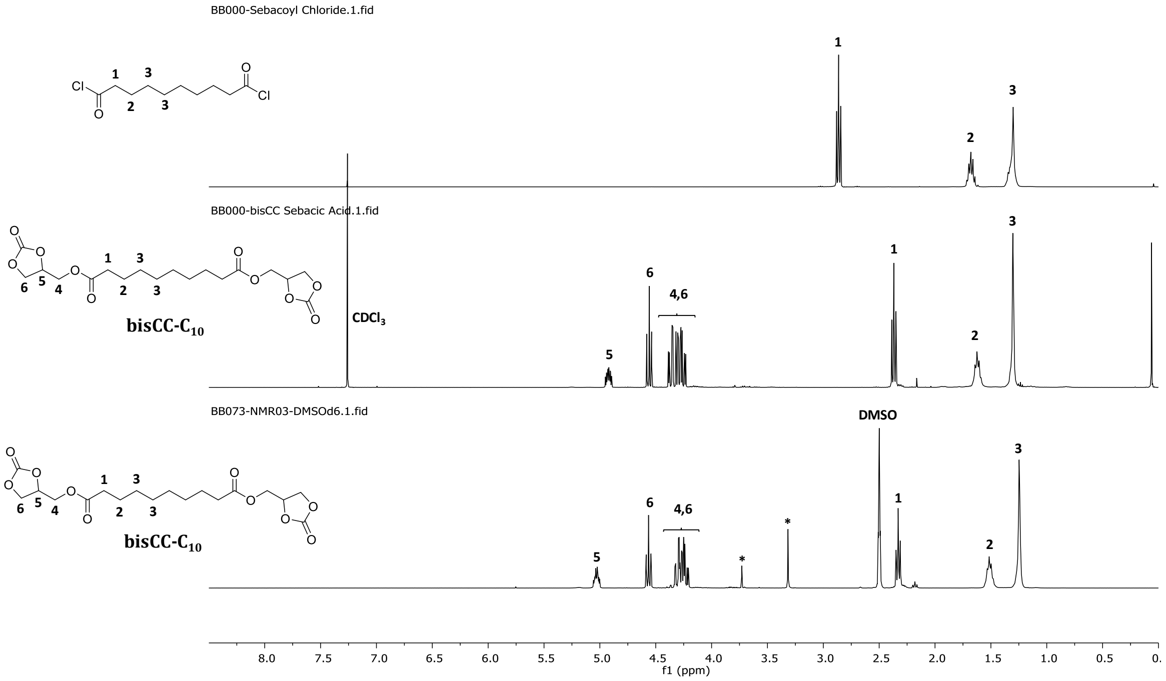
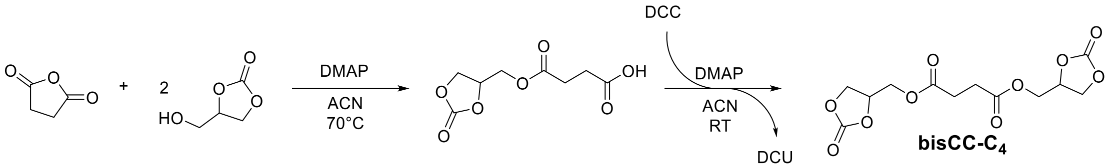


Figure 1: Stacked ^{1}H-NMR Spectra of Sebacoyl Chloride in $CDCl_3$ (top) and **bisCC-C$_{10}$** in $CDCl_3$ (middle) and in DMSO-d6 (bottom)

Another bio-sourced bis-cyclic carbonate monomer of shorter chain length was also synthesized. The synthetic pathway relies on the ring opening of succinic anhydride by an excess of glycerol carbonate (Scheme 4). The reaction proceeded in a 1pot-2step process in acetonitrile. The first step consisted in the formation of the mono-carbonate derivative of succinic acid after 6h reaction as revealed by ^{1}H-NMR spectroscopy (Figure 2). The reaction was catalyzed by 4-dimethylaminopyridine (DMAP). In the second step, the mild Steglich esterification was employed, namely the addition of N,N'-dicyclohexylcarbodiimide (DCC) in combination with the already present DMAP and the unreacted glycerol carbonate allowed the formation of the final bisCC-C$_4$. Acetonitrile (ACN) was found to be a suitable solvent to solubilize both the anhydride and the glycerol carbonate. It also favors the precipitation of the dicyclohexylurea by-product (DCU) that formed upon reaction of the DCC coupling agent, hence shifting the equilibrium of the esterification reaction towards the complete formation of the bis-cyclic carbonate compound. DMAP was also found to be a suitable catalyst as it catalyzes both reaction steps. The purification process consisted in a filtration step to remove the precipitated DCU by-product, then the evaporation of ACN, followed by a washing step with cold dichloromethane to remove the remaining unreacted species without using any chromatographic separation method. The final yield was 40%, yielding 2,57g of product. The ^{1}H-NMR monitoring of the reaction (Figure 2) and the reaction was scaled up to the formation of 16g of bisCC-C$_4$ with a good purity as exemplified by ^{1}H-NMR spectroscopy (Figure 2).



Scheme 4: Synthesis of the bis-cyclic carbonate from succinic anhydride (bisCC-C_4).

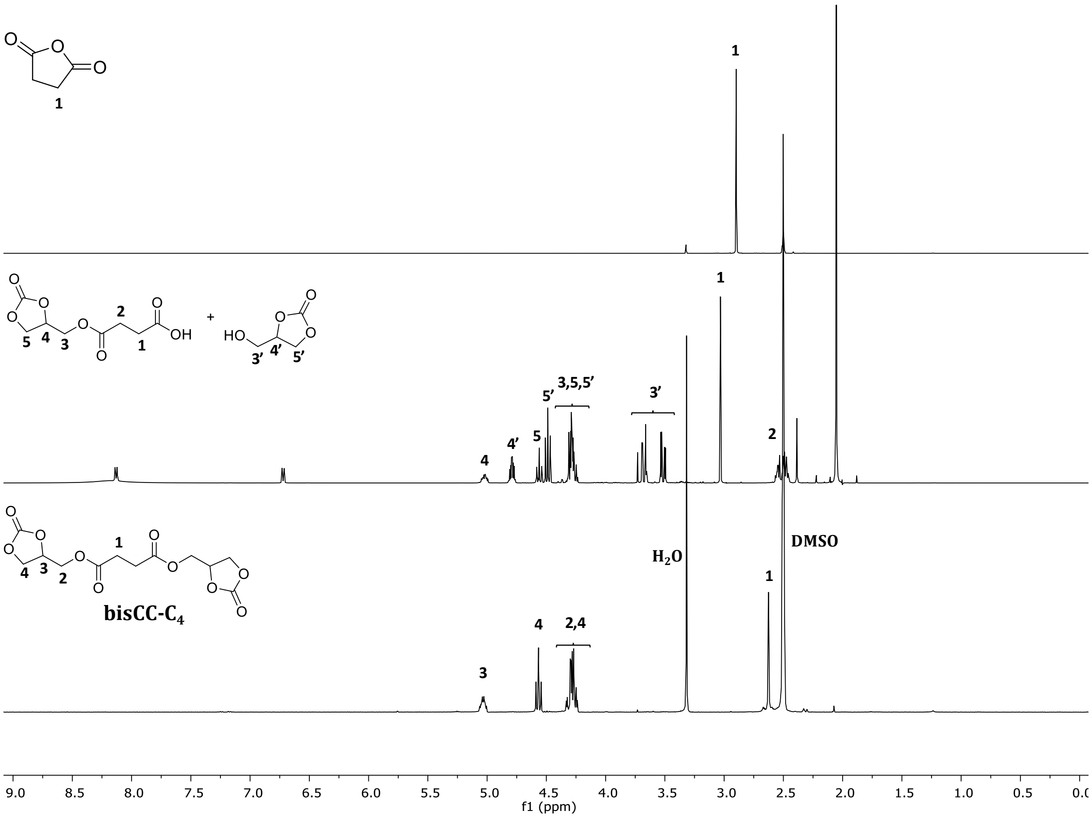


Figure 2: Stacked ^{1}H-NMR Spectra of Succinic Anhydride, the reaction crude before the addition DCC and of bisCC-C_4 (from top to bottom) in DMSO-d6.

Unfortunately, when trying to scale the synthesis up for the formation of about 27g of bisCC-C_4 (and have enough starting material to perform reactions in bulk conditions with mechanical stirring), it was not possible to obtain bisCC-C_4 that was completely pure. As can be seen in Figure 3, traces of glycerol carbonate (around 5 %) were still observed despite several washing steps with cold dichloromethane. Moreover, a low yield of 51% was obtained. Even if such a purity was not satisfactory, it was desired to know the range of properties that could be obtained when decreasing the aliphatic chain length of the bisCC monomer. bisCC-C_4 and bisCC-C_{10} were thus copolymerized with an aliphatic and a branched fatty acid-based diamines (namely 1,10-diaminodecane – 10DA, and the commercially available Priamine™ 1075 – P1075).

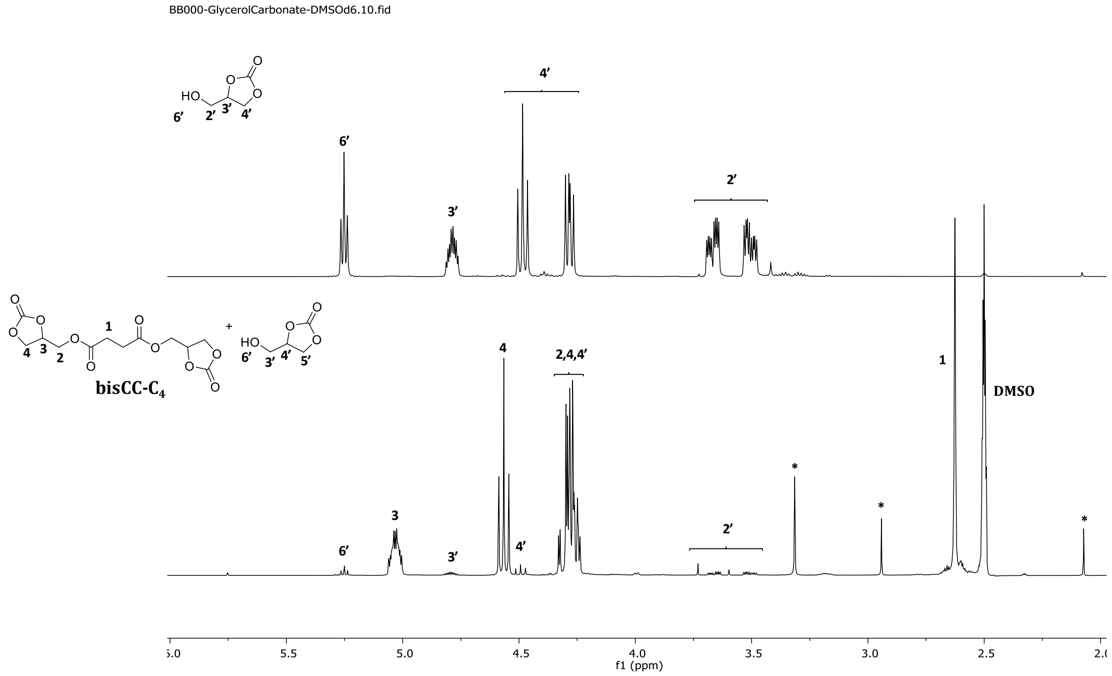


Figure 3: Stacked ^{1}H-NMR Spectra of Glycerol Carbonate and bisCC-C_4 after scale-up (from top to bottom) in DMSO-d6.

3.2. Copolymerization of bisCC-C_4 and bisCC-C_{10} with mixtures of diamines

Achieving the bulk polymerization of PHUs affording sufficiently high molecular weight polymers is of high interest. To do so, it is needed to both overcome the high viscosity of the formed PHUs upon synthesis as well as avoiding side-reactions.[44] On the one hand, high viscosity can be imparted to the formation of hydrogen bonds between the PHU chains.[17] A helical shaped mechanical stirrer specifically designed to fit in the used Schlenk vessel was utilized to provide constant agitation throughout the entire polymerization process. On the other hand, it is known that ester-activated bisCCs suffer from side-reactions.[8,33] The formation of urea and amide by-products has been reported and also explains the low molecular weights generally obtained.

The synthesized ester-activated 5-membered bis-cyclic carbonate compounds were thus polymerized to form poly(hydroxy urethane)s (PHUs). To do so, bisCC-C_4 and bisCC-C_{10} were copolymerized with various ratios of the aliphatic (solid) 1,10-diaminodecane (10DA) and the commercially branched (liquid) Priamine® 1075 (P1075). The monomers reacted during 24h at 90°C in bulk under mechanical stirring - Scheme 2. A temperature of 90°C was chosen since it was high enough to promote both the melting of the diamine and of the formed PHUs. Table 1 summarizes the reactions carried out and the characteristics of the polymers obtained. The purpose of using P1075 in the formulation was to see whether any plasticization of the PHU product would be beneficial for the implementation of the bulk process.

Table 1: Chemical composition and characterization of the PHUs obtained by copolymerization of 10DA, P1075 together with bisCC-C_4 or bisCC-C_{10}, in bulk, at 90°C during 24h

Run	Co-monomers [%]			Conv.^{a} [%]	M_n ^{b} [g.mol^{-1}]	Đ ^{b}	Apparent DP ^{c}
	bisCC-	10DA	P1075				
01	C_4	100%		87	16 700	1.7	34
02	C_4	75%	25%	83	12 500	1.8	21
03	C_4	50%	50%	86	11 900	1.5	18
04	C_4	25%	75%	79	12 000	1.5	16
05	C_4		100%	75	10 400	1.4	12
06	C_{10}	100%		93	33 900	2.2	59
07	C_{10}	75%	25%	88	24 800	2.9	37
08	C_{10}	50%	50%	91	22 700	3.0	30
09	C_{10}	25%	75%	89	19 900	2.9	23
10	C_{10}		100%	70	20 600	2.3	11

[a] Conversions of reactive functions were calculated by ^{1}H NMR.

[b] M_n values were obtained by SEC in DMF with LiBr salts, PS calibration

[c] The apparent Degree of Polymerization (DP) was calculated from the M_n values obtained by SEC

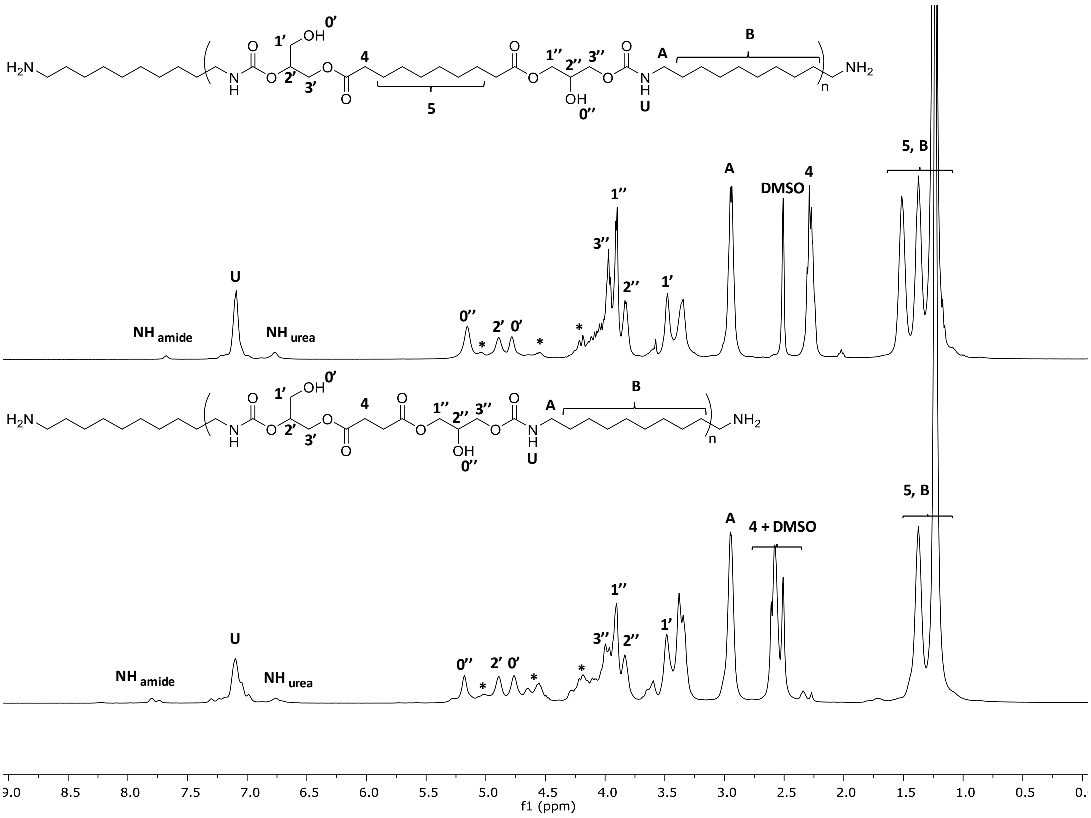


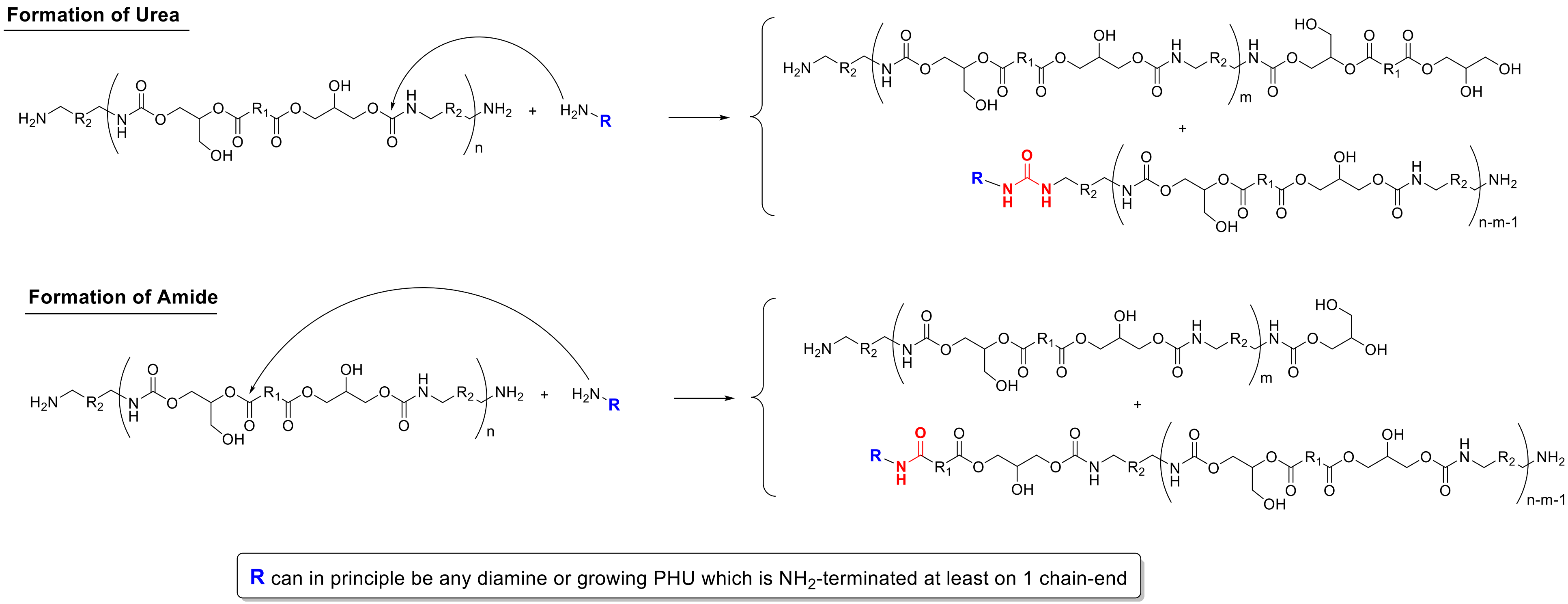
Figure 4: ^{1}H-NMR spectra of PHU 01 (bottom) and PHU 06 (top)

In the reactions (Table 1), the formation of the urethane moiety was checked by ^{1}H-NMR spectroscopy by following the disappearance of the signal corresponding to the quaternary carbon of the cyclic carbonate moiety (in the range of 5.0 ppm). The characteristic signal of the protons located in alpha-position of the urethane moieties ($\underline{CH_2}$-NHC(O)O-) could be identified in the range 2.8-3.2 ppm (Figure 4 – Figure S1 to S10). Infrared spectroscopy (FTIR, in Figure S15 and S16) also revealed the disappearance of the C=O stretching band of the cyclic carbonate moiety at 1800 cm^{-1} and the appearance of the C=O stretching band attributed to the urethane moiety at 1700 cm^{-1} as well as OH moieties (band at 3330 cm^{-1}). The C=O stretching band also exhibited the presence of a shoulder towards lower wavenumbers, that could be explained by stretching of the C=O function of the urea side-product.

The reaction extents gauged by ^{1}H-NMR analysis showed that bisCC-C$_4$ and bisCC-C$_{10}$ did not exhibit the same behavior upon polymerization. The reaction extents usually were higher when bisCC-C$_{10}$ was used as comonomer (approaching 90%), which can be explained by the higher purity of the starting bisCC-C$_{10}$. As a logical outcome according to the Carother's theory, the molecular weights and thus the apparent degrees of polymerization reached higher values in the case of bisCC-C$_{10}$. As a general trend, the molecular weights of the PHUs obtained from bis-CC$_{10}$ were found to be twice as much greater than those from bisCC-C$_4$ (Table 1). This can certainly be explained by the presence of some glycerol carbonate left in the batch of bisCC-C$_4$. Moreover, it could also be noticed that the higher the content in 10DA, the higher the reaction extents, and the higher the resulting apparent degrees of polymerization. Indeed, they were close to 90% in the case of 10DA and between close to 70% in the case of P1075. The lower conversions with P1075 can be explained due to a deviation from the stoichiometric ratio explained by the lower purity of the P1075.

A positive outcome concerns Run 06. Previous works showed that same polymer prepared in DMF exhibited a M$_n$ of 13700 g.mol-1 (Đ = 3.7) for a reaction extent of 93.5% in 7 days at 70°C.[33] In comparison, we managed to reach a significantly higher molecular weight for a similar reaction extent in only 24h. This could suggest that a lower amount of side reactions occurred. A potential explanation of this feature could be the higher temperature, as well as the lower reaction time utilized in our process. The higher temperature would increase the reaction kinetics and the lower reaction time would leave less time for the side reactions to occur.

^{1}H-NMR spectroscopy was used to shed some light on the side reactions by analyzing the chemical microstructure of the formed PHUs (Figure 4). It is known that the amine function can react with the forming urethane and with the ester groups to produce urea and amide moieties, respectively - Scheme 5.[8,33] The quantification of those by-products is important to get an idea on the final polymer microstructure and also to explain the rather low molecular weights obtained. As exemplified by previous works,[33] the urethane : urea : amide ratios can be quantified by analyzing the labile-proton zone (from 6.5 ppm to 8.0 ppm) provided the analyses are performed in DMSO-d6. This was done for both series of PHUs as shown in Figure 5.

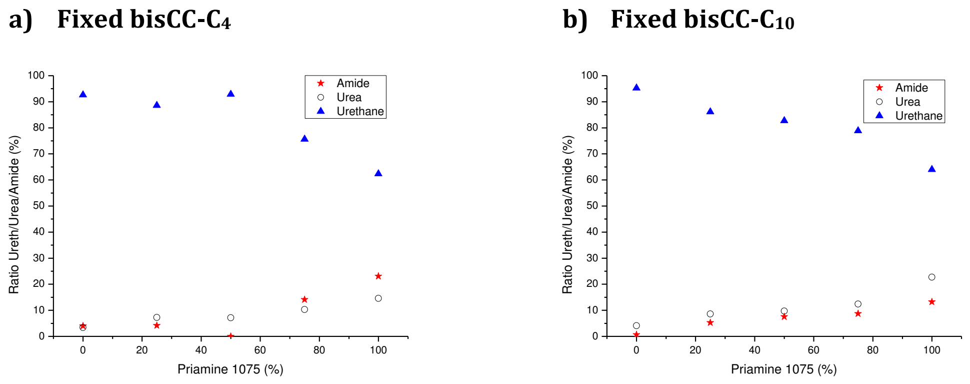


R can in principle be any diamine or growing PHU which is NH$_2$-terminated at least on 1 chain-end

Scheme 5: Suggested mechanism of the reaction between any NH$_2$-terminated compound and the urethane or the ester moieties contained in the backbone of the growing PHUs to yield urea- and amide-containing side-products respectively.

The chemical microstructure of the PHUs showed differences depending on the utilized bisCC comonomer. Higher ratios of urethane moiety were obtained (more than 80%) when high reaction extents (approaching 90%) were achieved, especially when high ratios of 10DA are utilized (Figure 5). This value is in accordance with what is observed in the literature. The formation of up to 10% urea was not a surprise since avoiding this reaction is known to be very improbable.[33] However, the amount of amide formed was in the range of 5 to 20%, which can be considered as a high extent of amidification as opposed to DMF-based processes.[33] This might be due to the use of bulk conditions, in which the reactive chains are in a much intimate contact than in solvents. Moreover, the use of ester-containing bisCCs increases the amount of formed H-bonds in the reactive mixture, yielding highly viscous mixtures. All of these parameters favor the neighboring of the reactive functions and can explain why a high extent of amidification was observed.

When analyzing again the specific case of Run 06, the urea : amide : urethane ratio was of 10.1 : 5.9 : 84 in the DMF process[33] whereas the ratio surprisingly was 4.5 : 0.5 : 95 with the bulk process. This supports the previous statement that the extent of side-reactions was diminished, hence increasing the resulting molecular weights. A potential explanation would be that, because of the higher purity of the monomers (bisCC-C_{10} and the aliphatic 10DA), the amount of added monomers was closer to the stoichiometric ratio). When high amounts of P1075 were used, the lower purity of P1075 would increase the deviation to this stoichiometric ratio. Higher amounts of NH_2-moieties would thus react onto the growing PHU chains and yield side-reactions and the formation of urea and amide by products.


a) Fixed bisCC-C_4

b) Fixed bisCC-C_{10}

Figure 5 : Microstructural Composition (Amide : Urea : Urethane Ratio) of the obtained PHUs by copolymerization of a) bisCC-C_4 and b) bisCC-C_{10} when copolymerized with various ratios of 10DA and P1075 gauged by ^1H-NMR analysis.

3.3. Thermal characterization

The thermal characterizations of the PHUs were carried out by means of TGA and DSC analyses (Table 2). All the glass transition temperatures T_gs were found to be in the range of -18 to -3°C, which can be attributed to the vegetable oil-based flexible monomers. Not surprisingly, the co-monomers having the longer aliphatic chain length yielded the lower values of T_gs. In particular, the introduction of the branched P1075 played a significant role in the decrease of T_g even if low amount of it was incorporated into the formulation. This can easily be understood because of the dangling chains and the induced plasticization effect of this monomer. In the case of the PHUs containing a majority of aliphatic segments (namely, containing low amounts of P1075), an influence of the introduction of the short bisCC-C_4 can be noticed, since it increased the T_g. This can be explained by a higher density of H-bonding due to the higher vicinity of the urethane, ester and pendant hydroxyl moieties. The size of the monomers also played a significant role in the thermal stability of the final PHUs as shown by TGA analyses. Thus, increasing the size of the bisCC dramatically increased the $T_{d,5\%}$. This is likely because when the distance between the ester and pendant hydroxyl moieties increased, chemical reaction between them decreased and thus the higher the stability.

Table 2 : Thermal properties of the synthesized PHUs

PHU	Co-monomers		$T_{d,5\%}$ [a] [°C]	$T_{d,50\%}$ [a] [°C]	T_g [b] [°C]
	Fixed	Varied			
01	bisCC-C_4	0% P1075	199	304	-3
02	bisCC-C_4	25% P1075	206	343	-7
03	bisCC-C_4	50% P1075	207	378	-8
04	bisCC-C_4	75% P1075	200	386	-18
05	bisCC-C_4	100% P1075	202	401	-16
06	bisCC-C_{10}	0% P1075	251	404	-7
07	bisCC-C_{10}	25% P1075	267	418	-12
08	bisCC-C_{10}	50% P1075	267	419	-12
09	bisCC-C_{10}	75% P1075	264	426	-17
10	bisCC-C_{10}	100% P1075	271	429	-17

[a] Measured by TGA analyses, heating ramp: 10°C/min

[b] Obtained thanks to DSC analyses, 2nd heating ramp: 10°C/min

The size of the diamine seemed to play a more significant role in the stabilization at higher temperatures, when higher degrees of degradations were reached. As an example, the $T_{d,50\%}$ increased of more than 100°C in the series using bisCC-C_4 (Run 01 to 05). Finally, it is noticeable that the degradation of the PHUs proceeds in a multiple stage-process as shown by the first derivative curves of the TGA traces (refer to Figure S28 to S37). It could have been expected in the case of the series of the bisCC-C_4-based polymers, since the glycerol carbonate acted as a chain-ender and thus several populations of polymers are degrading in parallel. However, it also seems that the higher the content in P1075, the higher the amount of degradation steps. This outcome is visible in Run 09 and 10 (PHU made of bisCC-C10 with 75% and 100% P1075 respectively – refer to Figure S36 and S37). This may be due to the lower purity of the P1075 starting material even if further investigations would be needed to confirm this outcome.

3.4. Viscoelastic behavior

The rheology experiments presented in Figure 6 revealed a very broad range of viscoelastic properties for the formed PHUs.

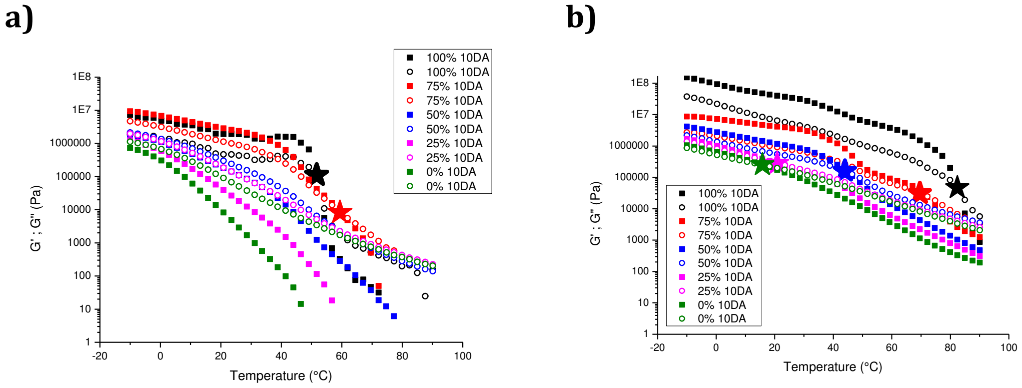


Figure 6 : Temperature dependence of the Storage (G') and Loss (G'') moduli of the obtained PHUs by copolymerization of a) **bisCC-C$_4$** and b) **bisCC-C$_{10}$** various ratios of **10DA** and **P1075**

In this figure, the evolutions of storage and loss moduli (respectively G' and G'') with respect to temperature are presented. In a general trend, the long aliphatic chain monomers, namely 10DA and bisCC-C$_{10}$, increased the storage modulus of the polymer, hence fostering a solid-like behavior. Samples composed of a majority of aliphatic monomers (meaning, containing less P1075 within their formulations) exhibited crystallinity (as also supported by DSC analyses – see the first heating ramps in Figure S17 to S26 in the Supporting Information) and crossovers between G' and G'' could be observed (marked with a star in Figure 6), confirming the transition from a more solid-like material towards a more liquid-like one.

In the rubbery state, the storage modulus G' of those samples was measured in the range of 1.10^7 to 1.10^8 Pa and it then decreased to 1.10^5 Pa after melting in the terminal state. Moreover, even in the case of highly plasticized PHUs, namely containing a high amount of P1075 in their formulation, the materials still exhibited quite high values of storage moduli in the rubbery state (around 1.10^6 Pa for both G' and G'') before transitioning into the terminal state. This highlights the very high viscosity of such materials, which was due to the presence of a high density of H-bonding.

However, the only presence of H-bonds cannot justify why bisCC-C_4-based PHUs reached terminal state at lower temperatures (around 50°C) in comparison to bisCC-C_{10}-based PHUs. An opposite behavior should actually be observed, since the density of the H-bonding network should be higher in the case of bisCC-C_4. The reasons for this can be found in the obtained molecular weights: since the degree of polymerization of bisCC-C_4-based PHUs were lower, the polymer chains are thus less prone to entangle and hence the chains start flowing at lower temperatures.

3.5. Theoretical study of the polymerization behaviors of bisCC-C4 and bisCC-C10

Previous models in the work of Lamarzelle *et al.*[33] have already shown that the ester-activation in β-position of the carbonate ring induced a di-symmetry in the C-O bonds of the carbonate, hence favoring the opening of the 5-membered ring towards the formation of secondary alcohols.[33] However, only the thermodynamics of the carbonate ring opening was considered, without considering the influence of the monomer structure.

Since the aliphatic chain length of the bisCC monomers seemed to have an influence on the resulting properties of the polymers, we have decided to investigate whether it also had an influence on the reaction mechanism. To do so, a kinetic study *via* DFT calculations was performed.

In this purpose, we have considered the addition of ethylamine to the carbonate for both bisCC-C_4 and bisCC-C_{10}. Zabalov *et al.* proposed that the ring opening of the carbonate takes place *via* a six-membered ring intermediate assisted by two amines, the first one performing the nucleophilic attack and the second one behaving as a catalyst.[62] The reaction paths of the formation of the primary and secondary alcohols are represented in Figure 7.

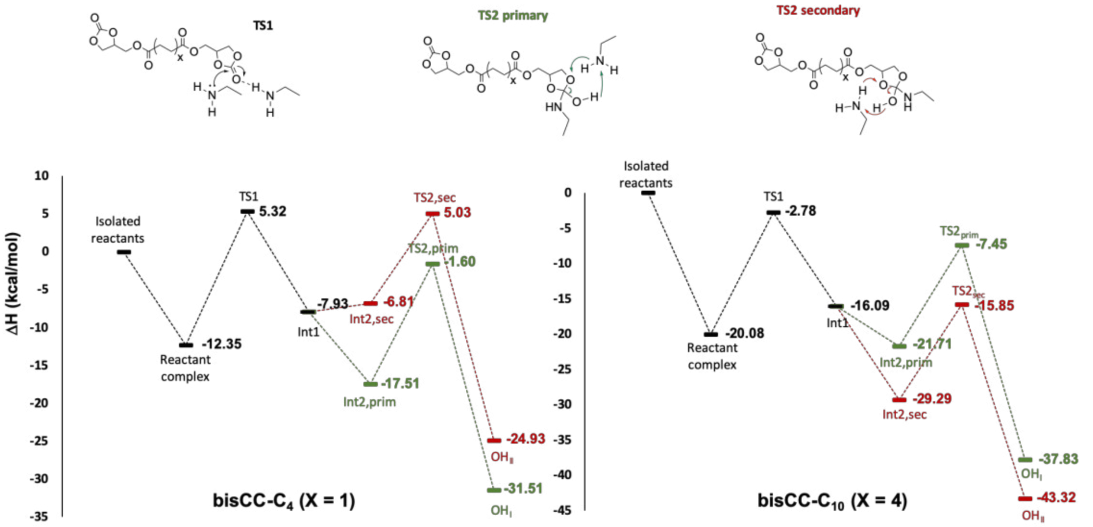


Figure 7 : Reaction mechanism of the ring opening of bisCC-C_4 (left panel) and bisCC-C_{10} (right panel) with ethylamine.

The reaction involves two transition states. Firstly, the nucleophilic attack of the ethylamine to the carbonyl (TS1) and, secondly, the ring opening of the cyclic carbonate to generate a primary ($TS2_{prim}$) or a secondary ($TS2_{sec}$) alcohol. The first step did not present significant energetic differences for both bisCC-C_4 and bisCC-C_{10} and is the rate-limiting step. The barriers from the reactant complex are 17.67 and 17.30 kcal.mol^{-1} for bisCC-C_4 and bisCC-C_{10}, respectively.

The next step is the formation of an intermediate (Int1) consisting of a quaternary carbon, where the carbonyl has been protonated and the C-N bond is completely developed. This intermediate has to rearrange its structure to acquire the proper conformation in order to open the ring to generate a primary or secondary alcohol (Int2).

For bisCC-C_4, the intermediate leading to the primary alcohol is a very stable complex (-17,51 kcal.mol^{-1}), and the reaction proceeds through a second TS at -1.60 kcal.mol^{-1}. The complex is very stable due to the hydrogen bonds established, compared to the intermediate leading to the secondary alcohol (-6.81 kcal.mol^{-1}), *via* a TS at 5.03 kcal.mol^{-1}. Although the barrier for the primary alcohol is slightly larger than for the secondary alcohol (15.91 vs 11.84 kcal.mol^{-1}), the whole reaction path is located below the reactants and is energetically favored for the primary OH.

Regarding bisCC-C_{10}, both intermediates are very stable, since the molecular chain is longer and the coiled conformation due to hydrogen bonding is easier to acquire. Nevertheless, the intermediate leading to the secondary alcohol is more stable (-29.29 kcal/mol) that the same leading to the primary alcohol (-21.71 kcal/mol). Besides, the barrier is also smaller for the secondary OH (13.44 vs 14.26 kcal/mol).

In both cases, the secondary barrier is similar for both primary and secondary alcohols, but the whole path is favored for a different type of OH (primary in the case of bisCC-C_4 and secondary in the case of bisCC-C_{10}).

Those results seem to suggest that, in theory, and contrary to what is commonly described in the literature,[9,33,39,60,63–65] in the case of ester-activated bisCCs, the aliphatic chain length between the two ester moieties matters in the ring opening reaction during the aminolysis of bisCCs. However, if in the case of bisCC-C_{10}, both the energy level of the secondary alcohol product (OH II), and the energetic barrier to reach TS2 are lower and justify the fact that OH II is favored, it seems to be more questionable in the case of bisCC-C_4. Indeed, thermodynamically speaking, the formation of OH I seems favored at -31,51 kcal mol^{-1}, and the intermediate leading to the primary alcohol is a very stable complex (-17,51 kcal.mol^{-1}). However, the energetic barrier to TS2 is smaller for OH II. Thus, there might be a competition between thermodynamic and kinetic control.

Unfortunately, and because of the glycerol carbonate impurity contained in the starting material, it was not possible to experimentally conclude on the results. It would thus be interesting to work again on the synthesis and purification of bisCC-C_4, to get a final answer to this question.

4. Conclusion

In this chapter, a series of PHUs was prepared in bulk starting from two different ester-activated bis-cyclic carbonate compounds (bisCC) of different chain length.

A bis-cyclic carbonate derived from sebacoyl chloride (bisCC-C_{10}) was synthesized by esterification with glycerol carbonate. Another protocol was implemented in order to access a bio-based bisCC of shorter chain length starting from succinic anhydride and glycerol carbonate. The synthesis was proven to work on a small scale, but difficulties arised during the purification process to completely get rid of the glycerol carbonate.

Both bisCCs were then copolymerized in bulk with various ratios of the aliphatic 1,10-decanediamine and the branched and commercially available Priamine™ 1075. It allowed to get access to PHUs with various properties, with tunable thermal and viscoelastic properties. In particular, the use of Priamine™ 1075 was found to decrease the $T_{g,}$, to provide a better thermal resistance and yield very viscous polymers. On the other hand, the aliphatic 1,10-decanediamine yielded solid PHU materials exhibiting melting temperatures around 50°C (in the case of bisCC-C_4) and 90°C (in the case of bisCC-C_{10}).

The bisCCs' aliphatic chain length has thus influences the material's resulting thermal and viscoelastic properties. Moreover, a mechanistic study, *via* DFT, was also performed for both monomers and showed that the aliphatic chain length also played a role into the ring opening mechanism of the bisCC during its aminolysis. It may surprisingly play a role into the favored formation of primary OHs in the case of bisCC-C_4. Unfortunately, the impurity of the bisCC-C_4 starting material did not allow us to reach clear experimental conclusions.

Future prospect would naturally include to re-work on the synthesis of bisCC-C_4, in order to see whether the experimental findings support the theory. Moreover, it could be interesting to vary the aliphatic chain length of the bisCCs to see the impact onto the PHU's microstructure. The investigation of bisCC with an odd-number of carbon atoms in the aliphatic chain would be very interesting since it would cause a dissymmetry in the PHU's architecture.

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6. Shortened forms

ACN:	Acetonitrile
bisCC-C_4:	bis cyclic carbonate from succinic anhydride
bisCC-C_{10}:	bis cyclic carbonate from sebacic acid
Đ:	Polydispersity
DCC:	N,N'-Dicyclohexylcarbodiimide
DCM:	Dichloromethane
DCU:	Dicyclohexylurea
DMAP:	4-dimethylaminopyridine
DMF:	Dimethylformamide
DMSO-d6:	deuterated dimethylsulfoxide
Mn:	Molecular weight (in number)
Mw:	Molecular weight (in weight)
NIPU:	Non Isocyanate Polyurethane
PHU:	Poly(hydroxy)urethanes
P1075:	Priamine™ 1075
T_g:	Glass Transition Temperature
10DA:	Decane 1,10-diamine
DSC:	Differential Scanning Calorimetry
FTIR:	Fourier Transformed Infra-Red-Attenuated Total Reflection
NMR:	Nuclear Magnetic Resonance
SEC:	Size Exclusion Chromatography
TGA:	Thermogravimetric Analyses

7. Supporting Information

7.1. NMR analyses

Run 01

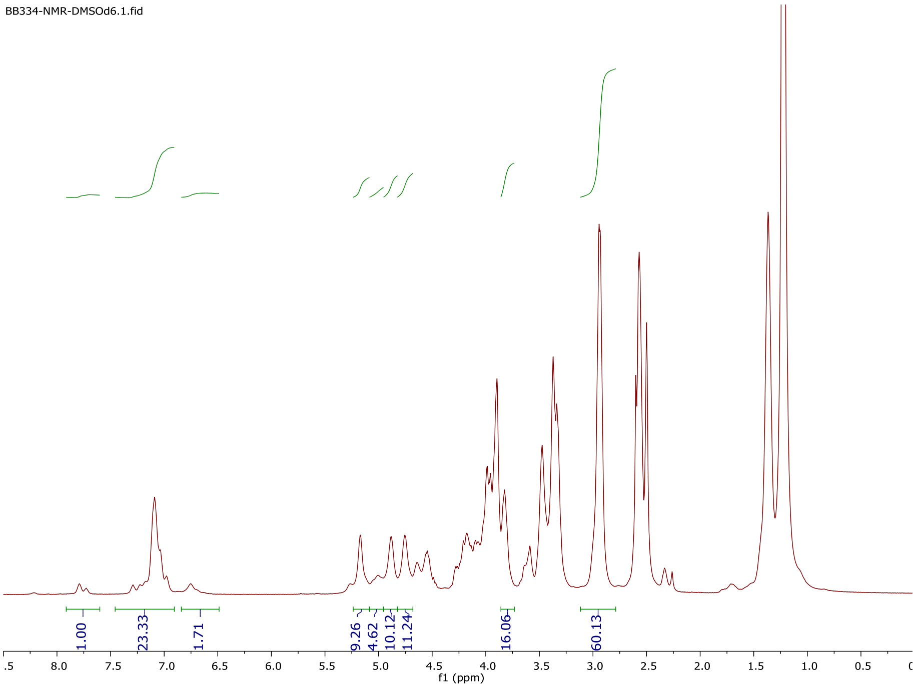


Figure S1: ¹H-NMR spectra of **Run 01** in DMSO-d6

Run 02

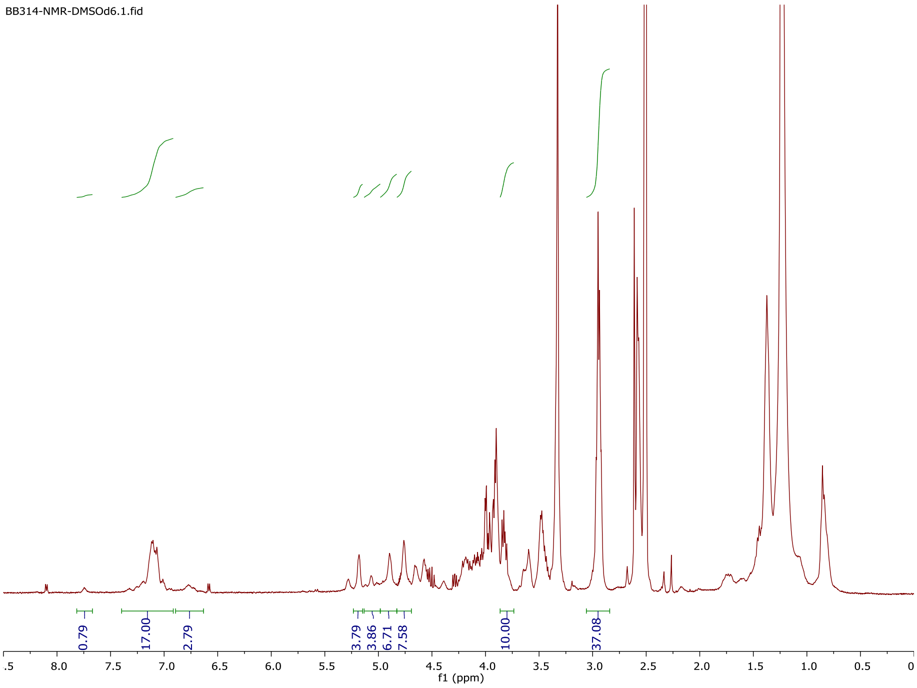


Figure S2: ¹H-NMR spectra of **Run 02** in DMSO-d6

Run 03

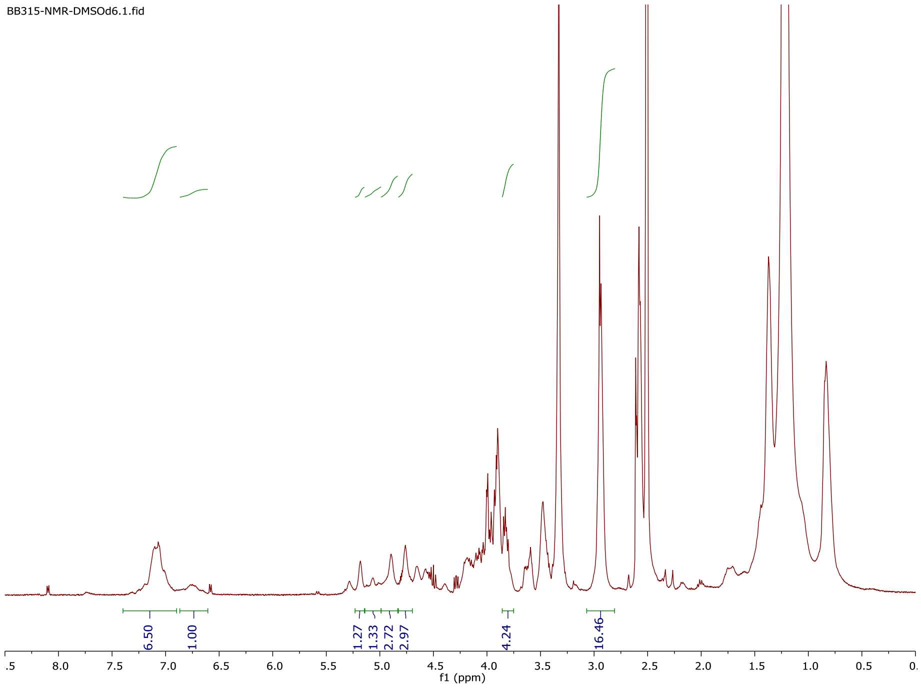


Figure S3: ^{1}H-NMR spectra of **Run 03** in DMSO-d6

Run 04

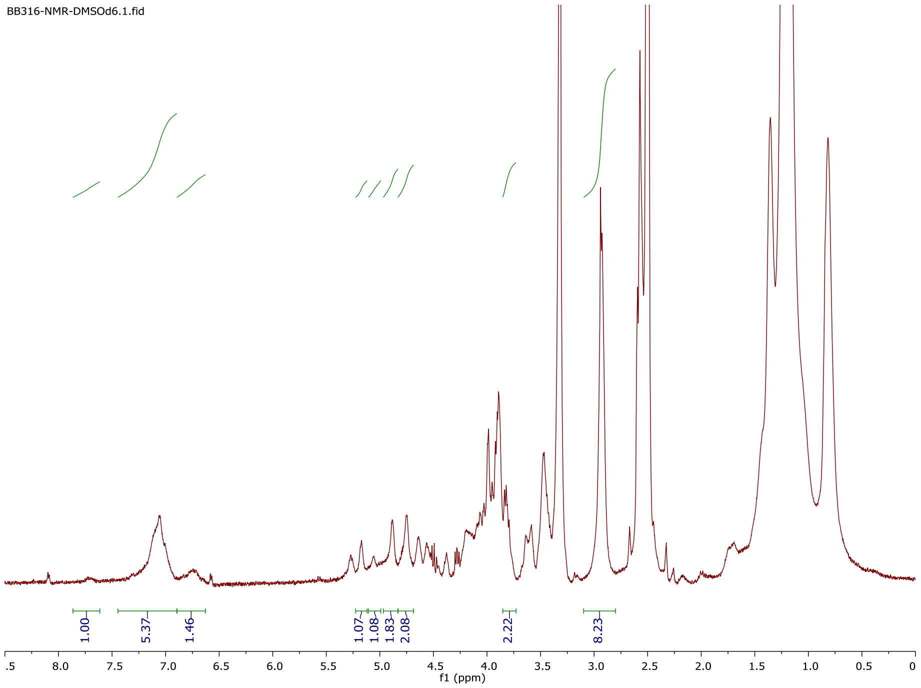


Figure S4: ^{1}H-NMR spectra of **Run 04** in DMSO-d6

Run 05

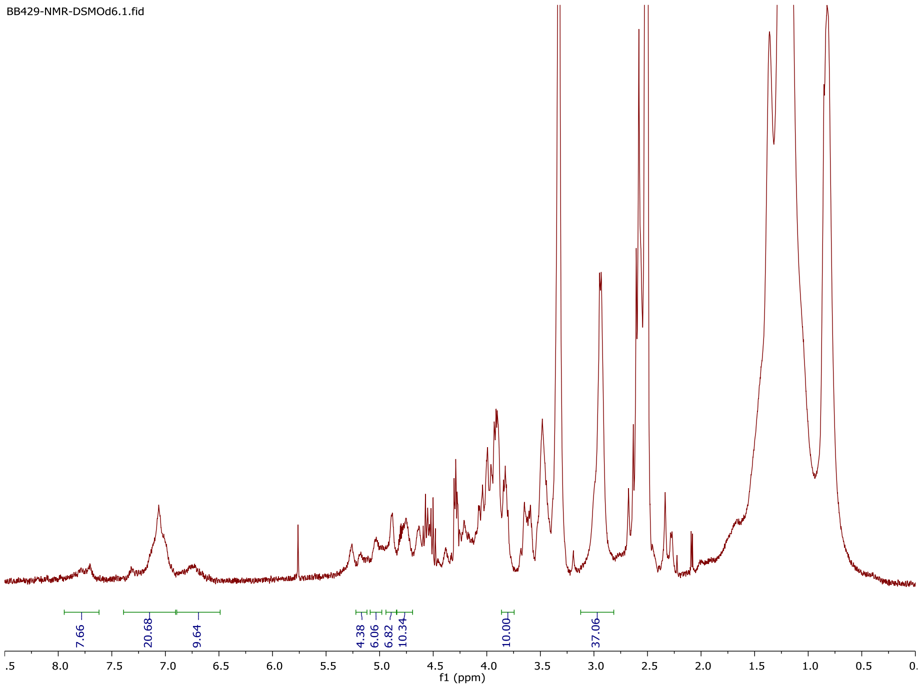


Figure S5: ^{1}H-NMR spectra of **Run 05** in DMSO-d6

Run 06

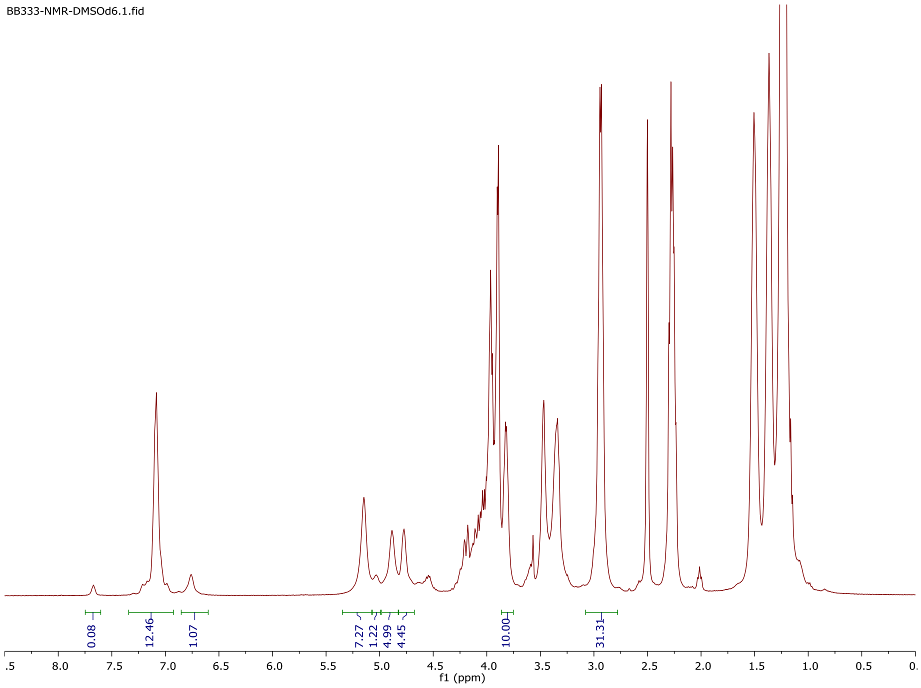


Figure S6: ^{1}H-NMR spectra of **Run 06** in DMSO-d6

Run 07

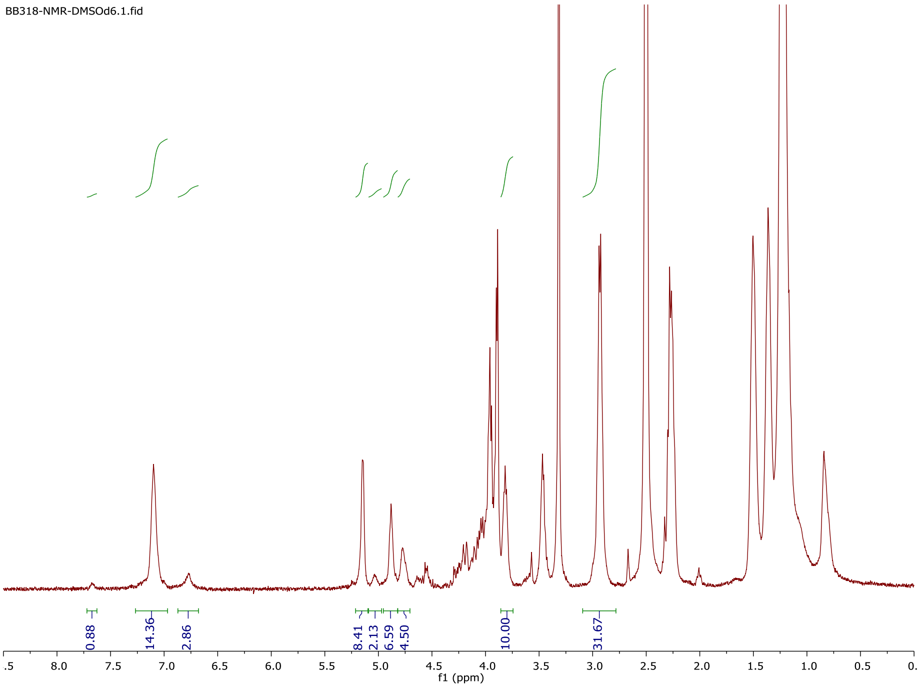


Figure S7: ^{1}H-NMR spectra of **Run 07** in DMSO-d6

Run 08

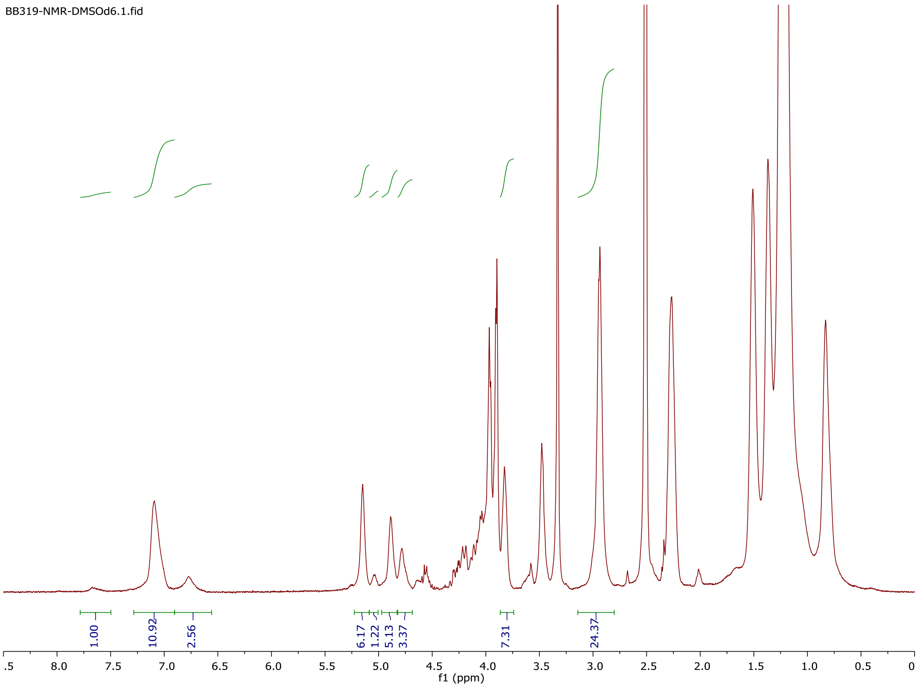


Figure S8: ^{1}H-NMR spectra of **Run 08** in DMSO-d6

Run 09

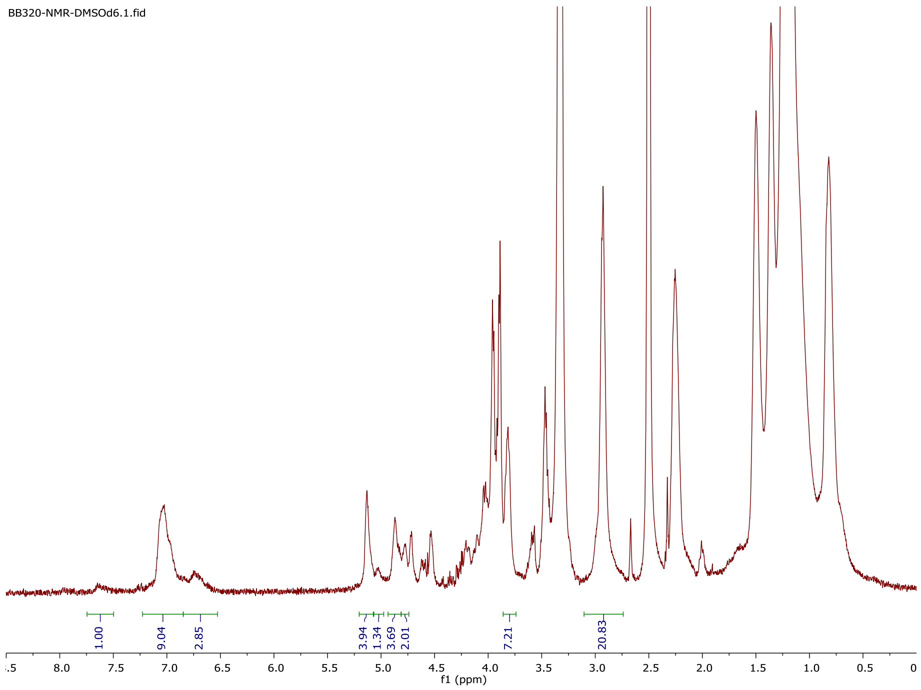


Figure S9: ^{1}H-NMR spectra of **Run 09** in DMSO-d6

Run 10

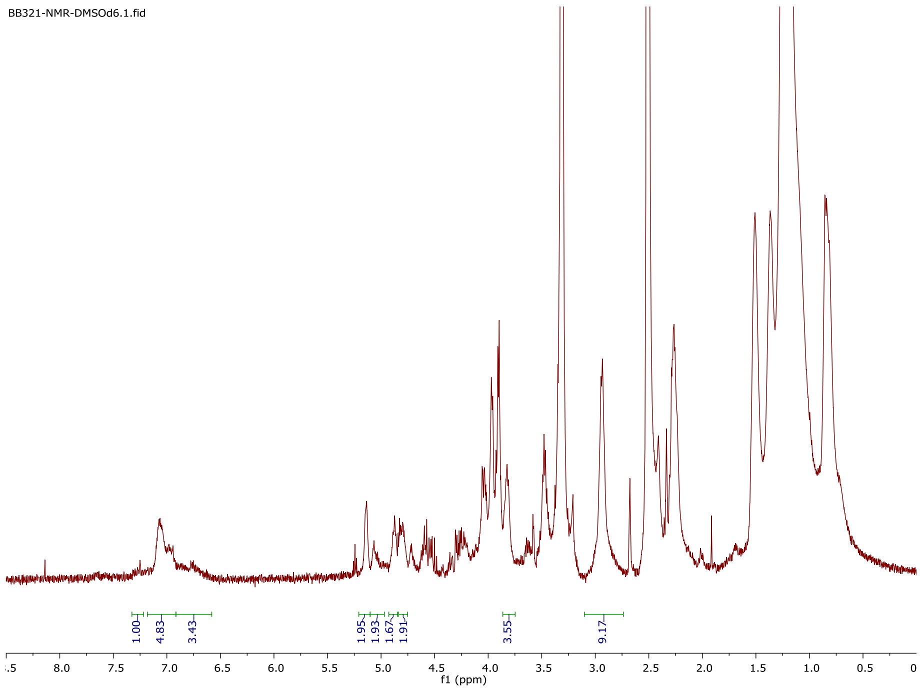


Figure S10: ^{1}H-NMR spectra of **Run 10** in DMSO-d6

Stacked ^{1}H-NMR spectra

Fixed bisCC-C_4

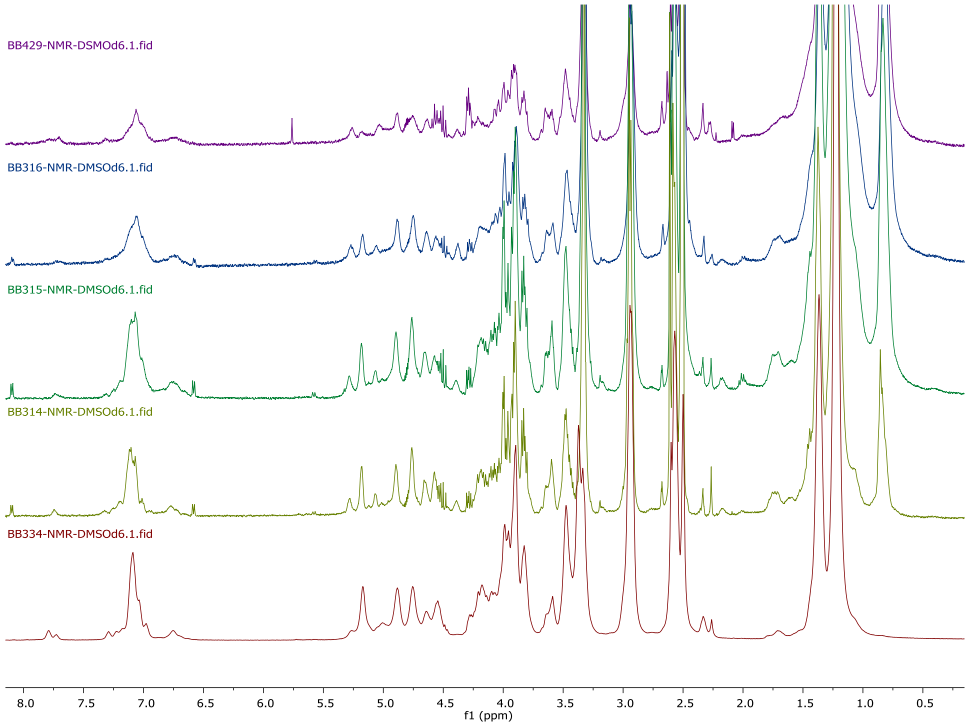


Figure S11: Stacked ^{1}H-NMR spectra of **Run 01**, **Run 02**, **Run 03**, **Run 04** and **Run 05** (from bottom to top) in DMSO-d6

Fixed bisCC-C_{10}

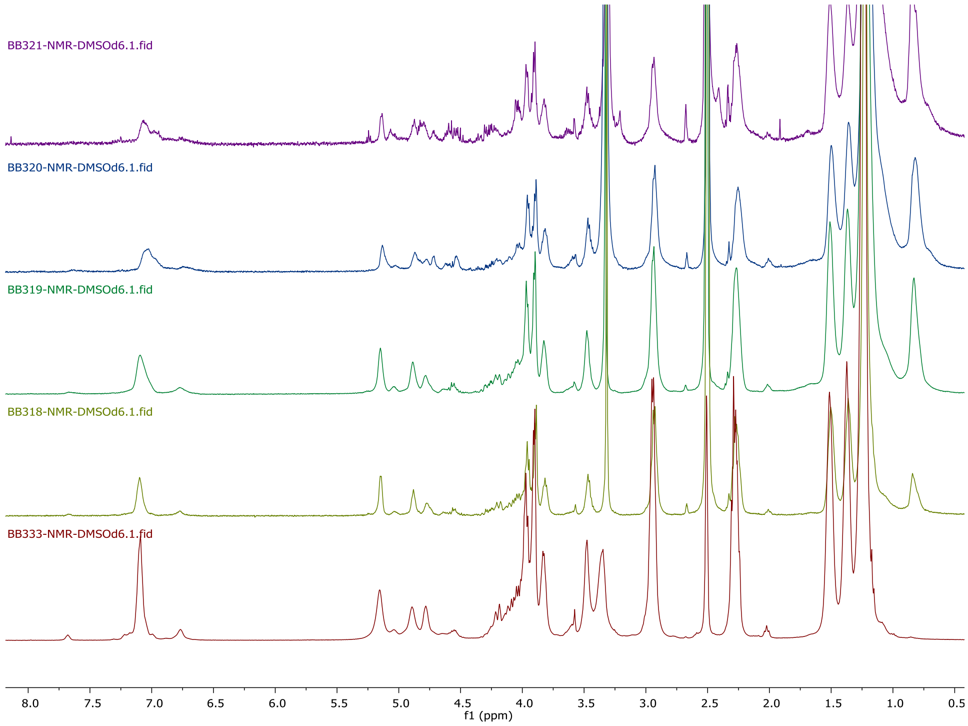
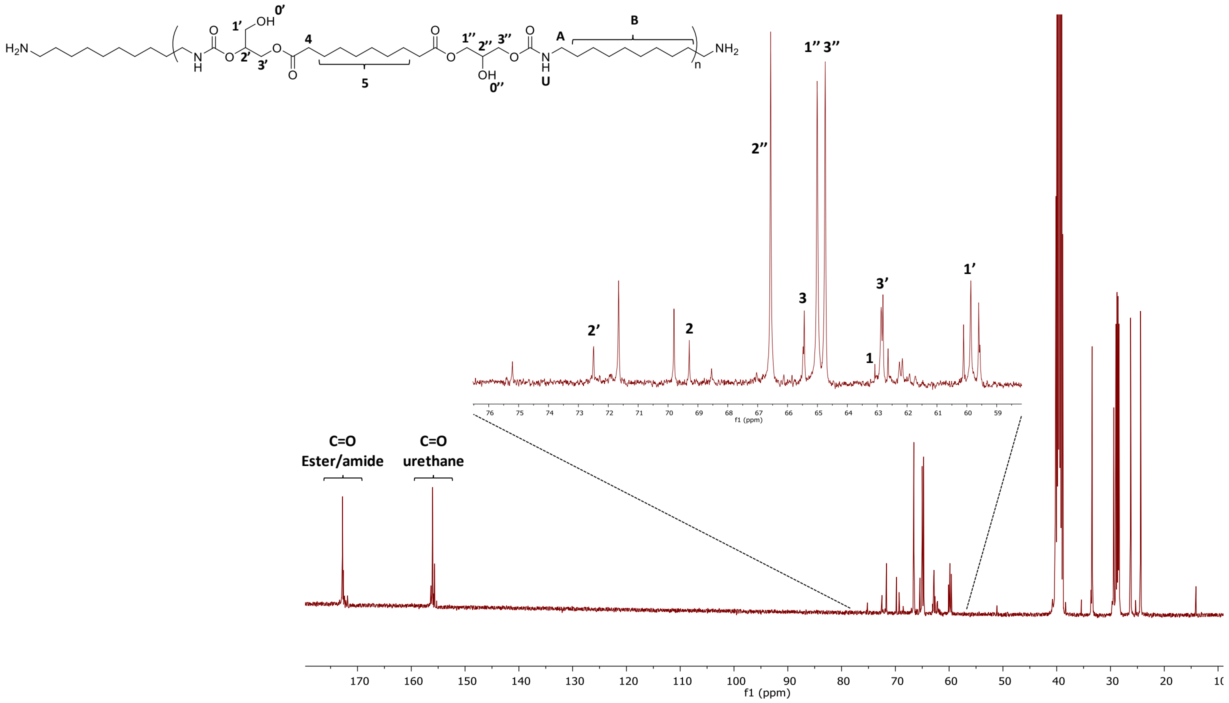


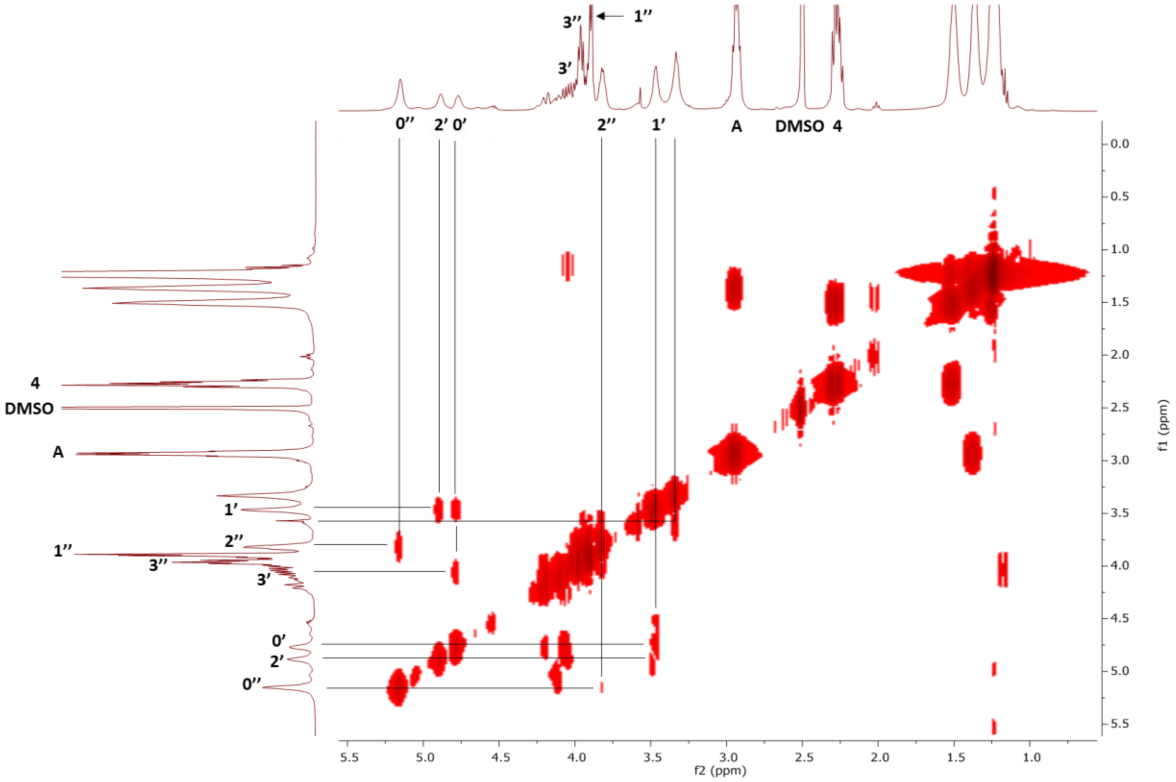
Figure S12: Stacked ^{1}H-NMR spectra of **Run 06**, **Run 07**, **Run 08**, **Run 09** and **Run 10** (from bottom to top) in DMSO-d6

Characterization of **PHU 06**:

a)



b)



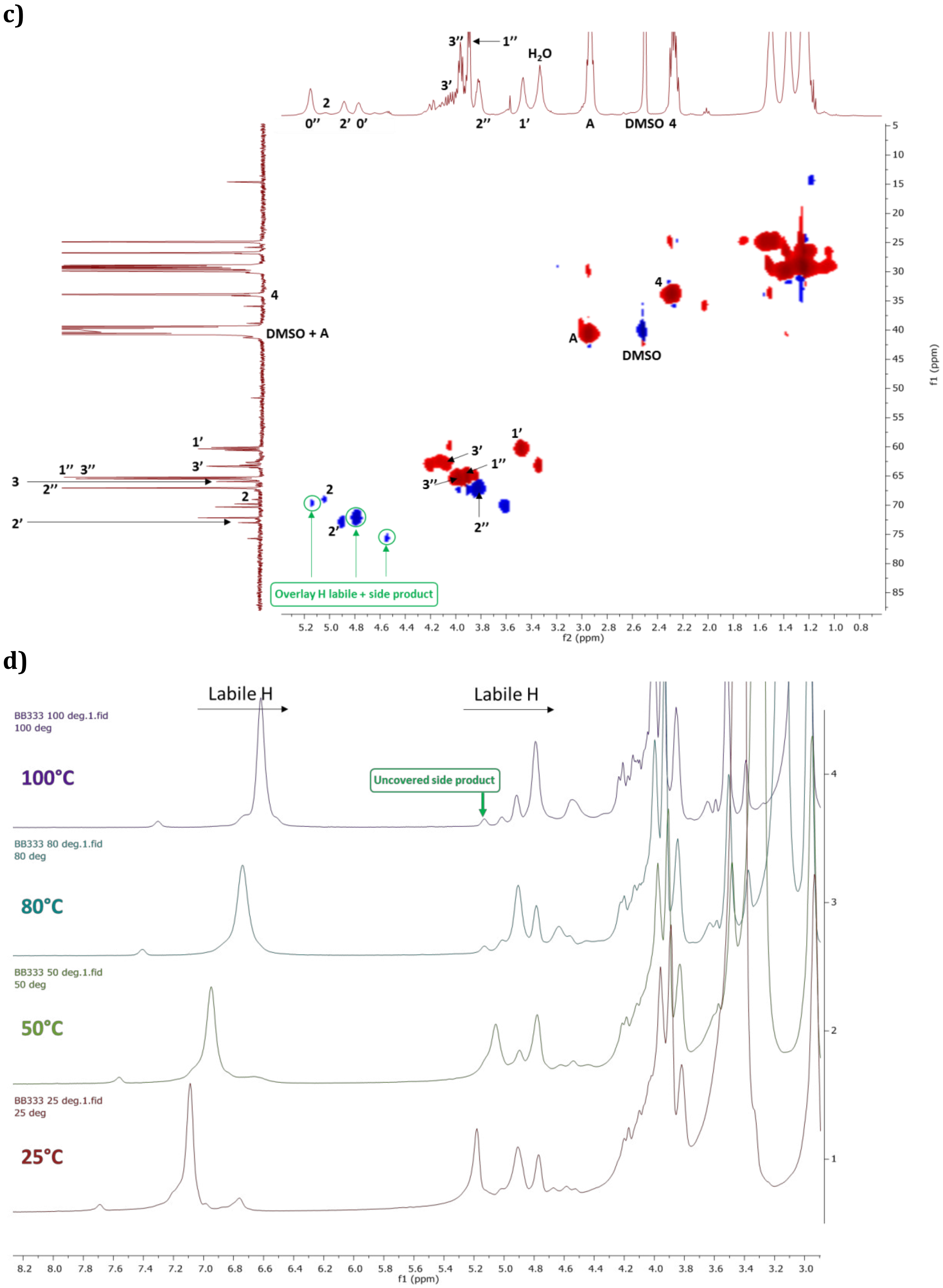
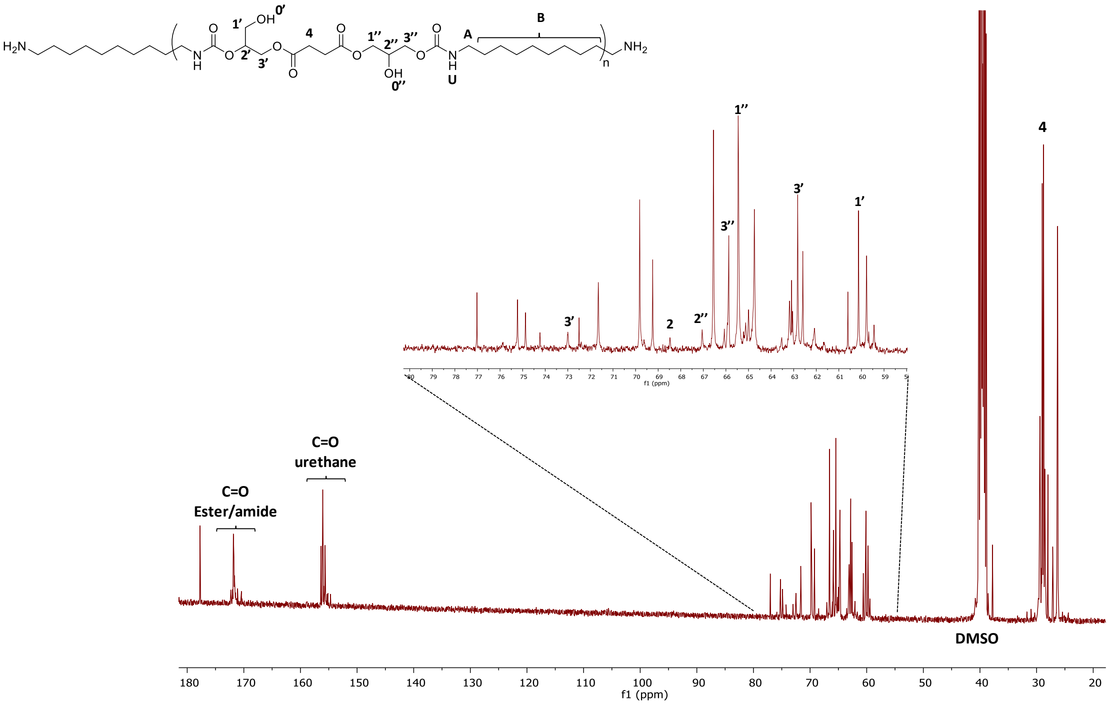


Figure S13: NMR characterization of **Run 06** in DMSO-d6: a) ^{13}C-NMR, b) COSY, c) HSQC, d) ^{1}H-NMR at different temperatures

The characterization of **Run 06** was performed with the help of 2D NMR. Side products were observed, but the complete structure could unfortunately not be fully solved. Proton-carbon correlations could be observed in HSQC at 5.2 and 4.8 ppm (^{1}H-NMR), which seemed counter-intuitive since those peaks are supposed to correspond to labile OH proton according to Lamarzelle *et al.*[33] By raising the temperature, it could be observed that those peaks actually were an overlay between labile protons (attributed to OH moieties) and aliphatic protons, certainly arising from side-products. In the case of Run 05, the extent of formation of side product accounted for about 7% of the peak integration. Regarding the study about the primary and secondary OH group formation, it was supposed that the extent of side-reaction did not affect the resulting trends of OH_I : OH_{II} ratios of the native PHU.

Characterization of **Run 01**:

a)



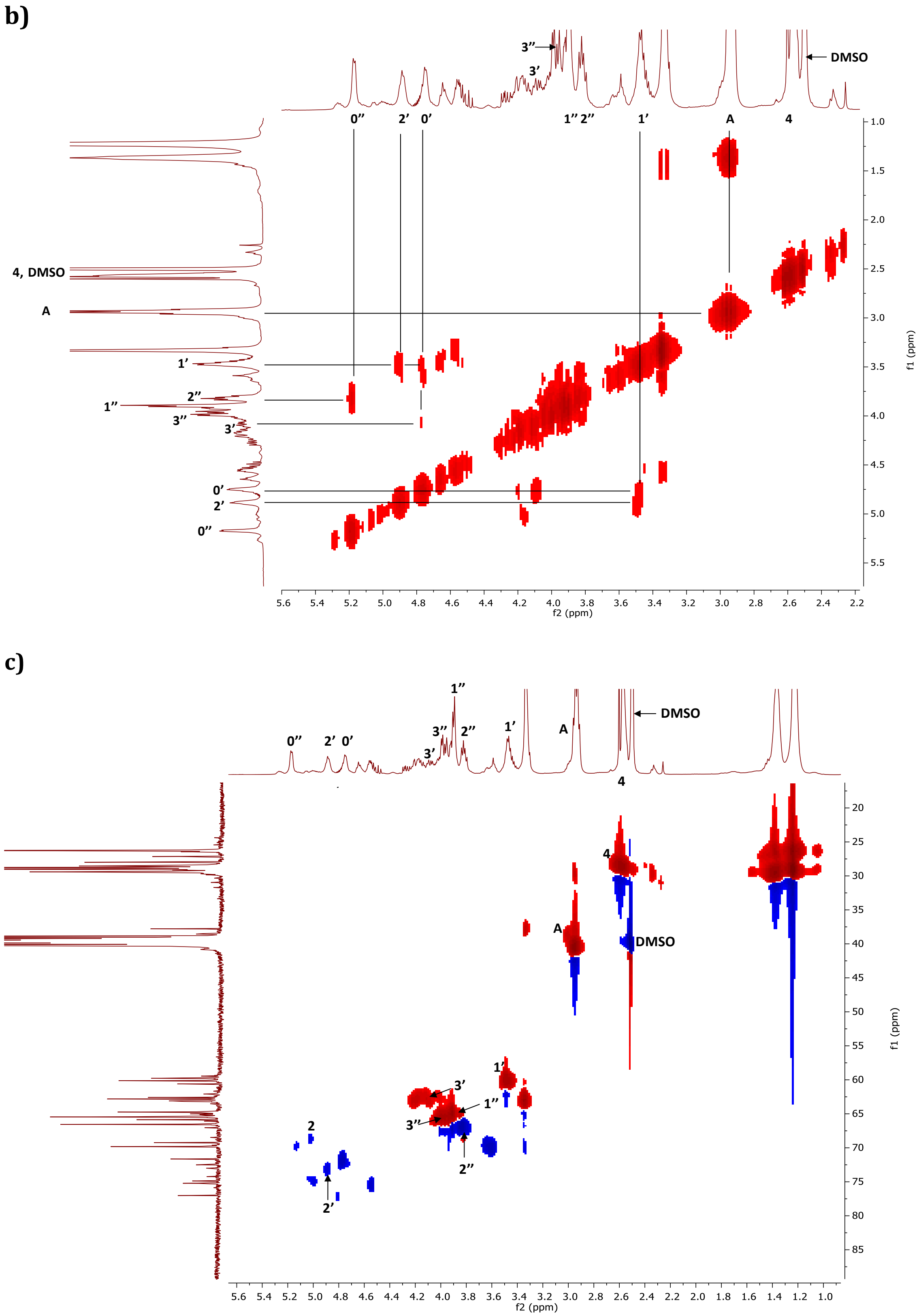


Figure S14: NMR characterization of **Run 01** in DMSO-d6: a) ^{13}C-NMR, b) COSY and c) HSQC

7.2. IR analyses

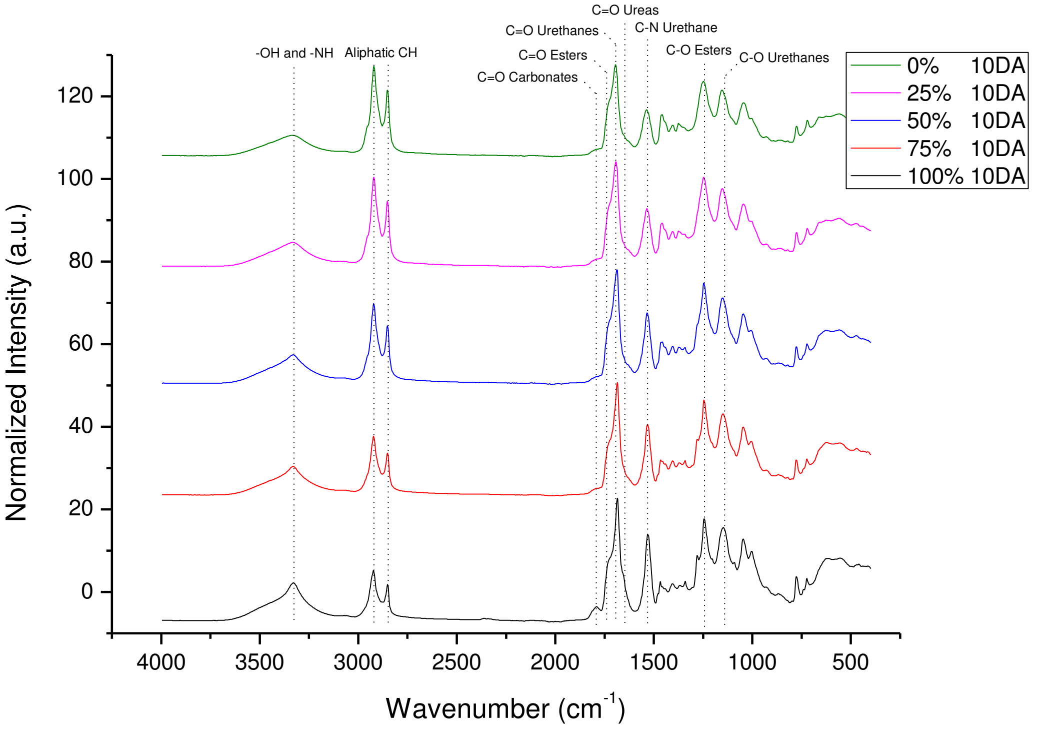


Figure S15: Stacked IR spectra of **Run 01**, **Run 02**, **Run 03**, **Run 04** and **Run 05** (from bottom to top) in DMSO-d6

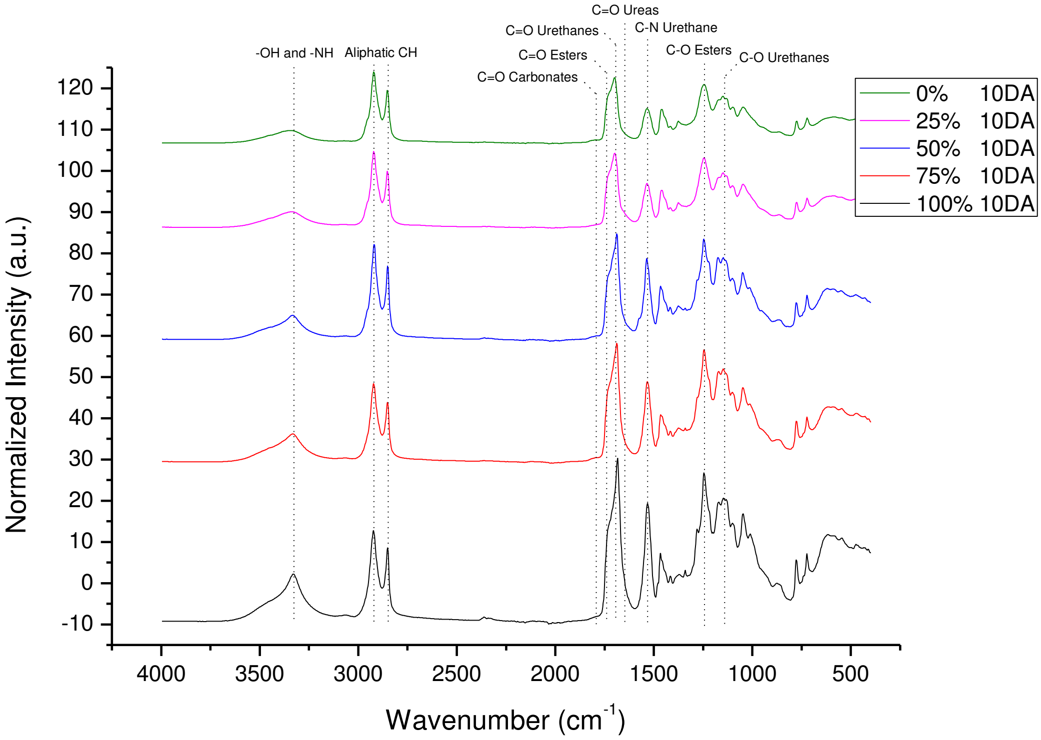


Figure S16: Stacked IR spectra of **Run 06**, **Run 07**, **Run 08**, **Run 09** and **Run 10** (from bottom to top) in DMSO-d6

7.3. DSC analyses (Temperature ramp : 10°C.min^{-1})

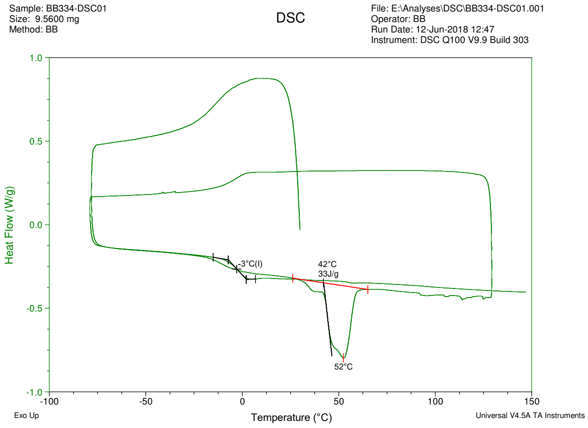


Figure S17: DSC trace of **Run 01** (Exo up)

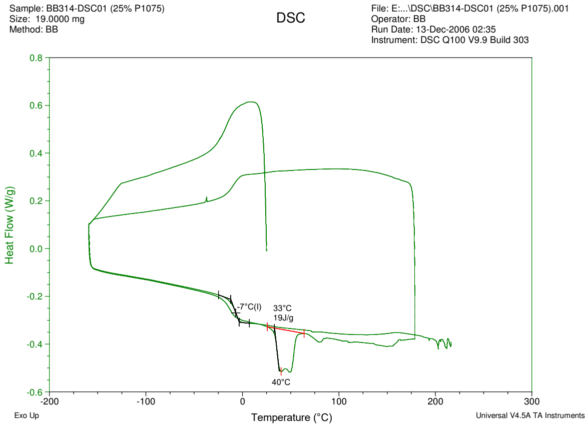


Figure S18: DSC trace of **Run 02** (Exo up)

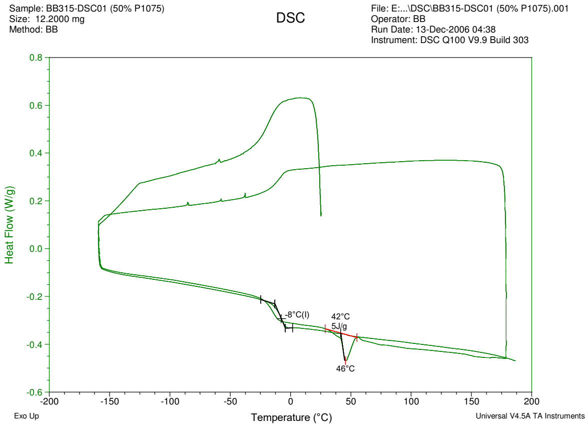


Figure S19: DSC trace of **Run 03** (Exo up)

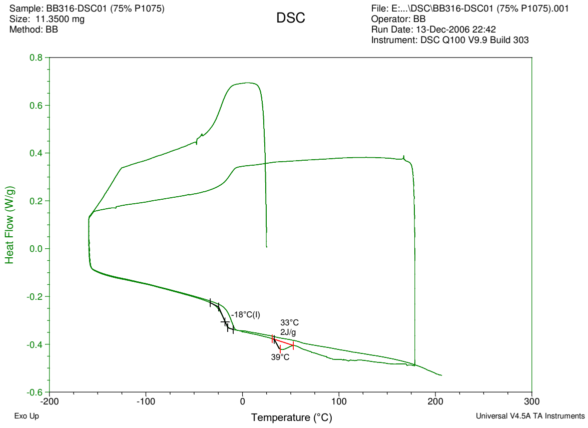


Figure S20: DSC trace of **Run 04** (Exo up)

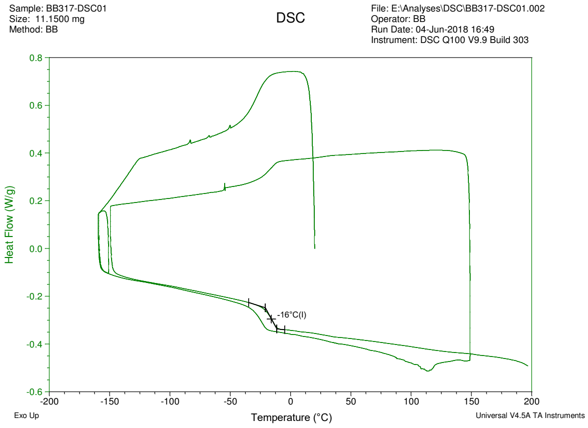


Figure S21: DSC trace of **Run 05** (Exo up)

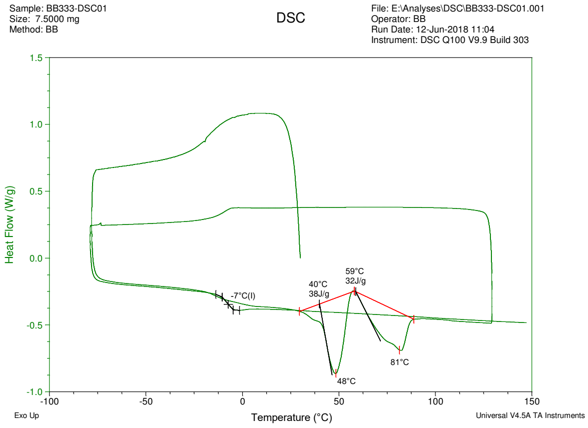


Figure S22: DSC trace of **Run 06** (Exo up)

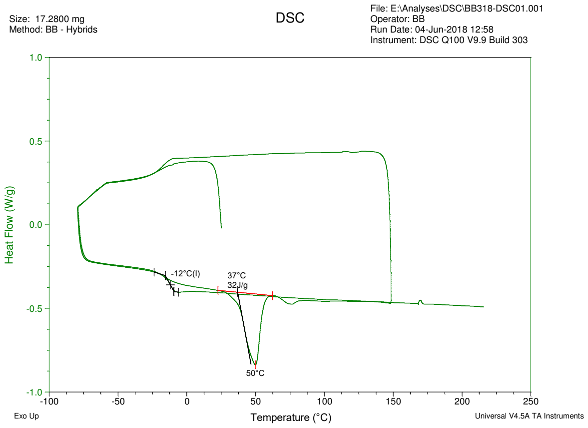


Figure S23: DSC trace of **Run 07** (Exo up)

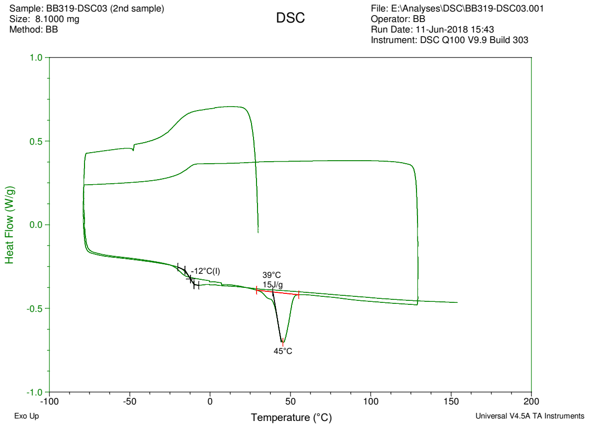


Figure S24: DSC trace of **Run 08** (Exo up)

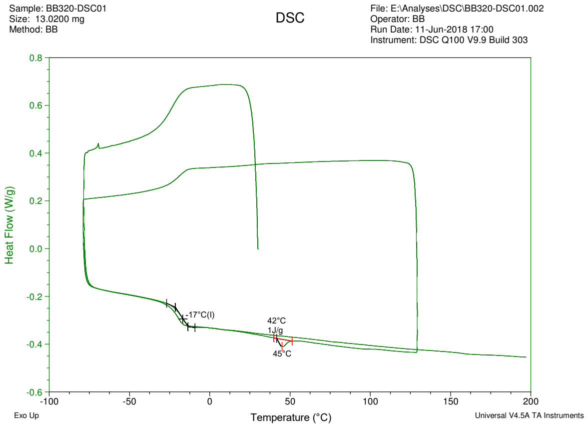


Figure S25: DSC trace of **Run 09** (Exo up)

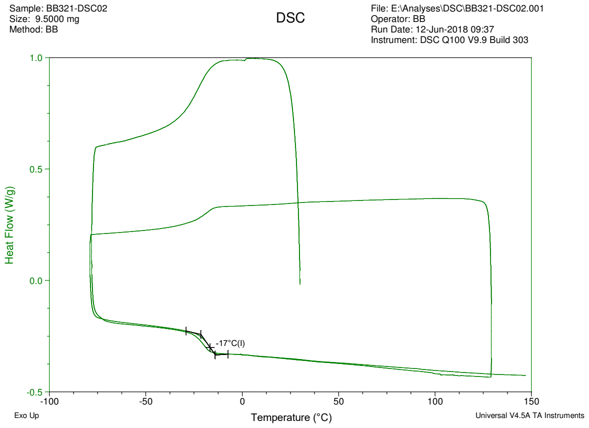


Figure S26: DSC trace of **Run 10** (Exo up)

Overlay: 1st heating ramp

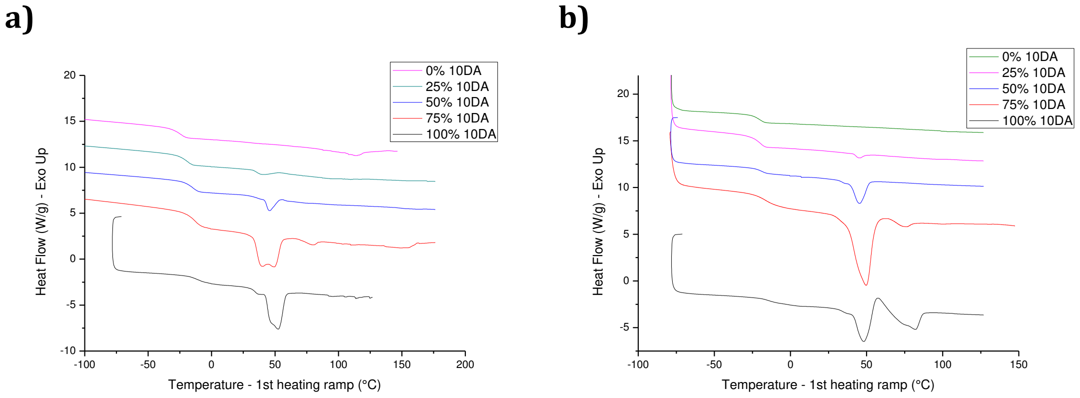


Figure S27: DSC traces of the obtained PHUs by copolymerization of **10DA**, **P1075** together with a) **bisCC-C$_4$** or b) **bisCC-C$_{10}$** (1st heating ramp - 10°C/min)

7.4. TGA analyses

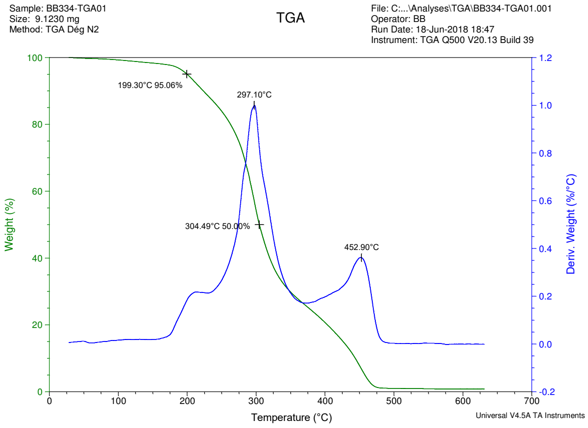


Figure S28: TGA trace of **Run 01**

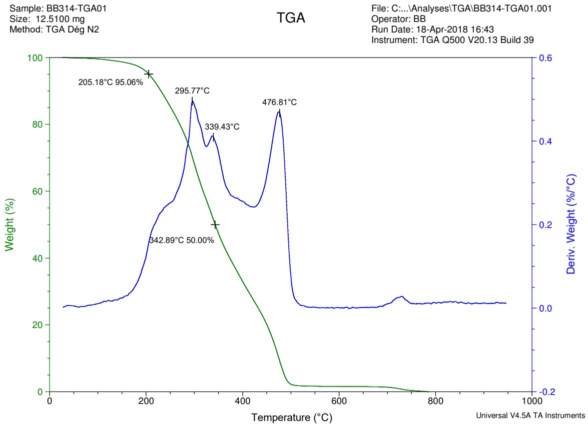


Figure S29: TGA trace of **Run 02**

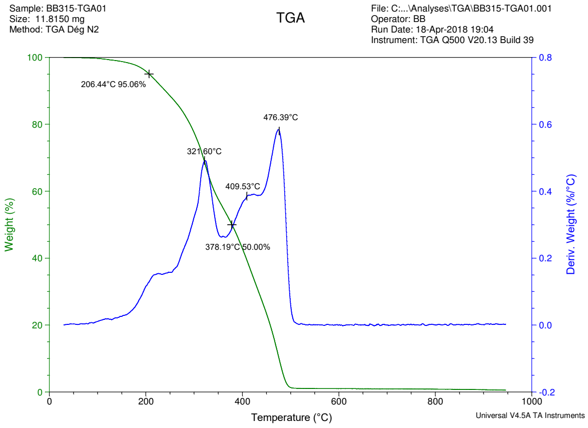


Figure S30: DSC trace of **Run 03**

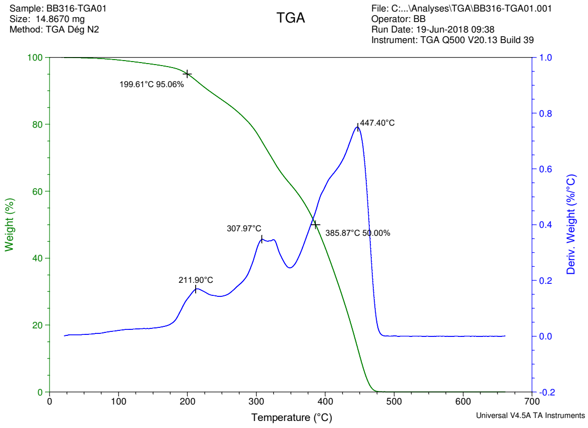


Figure S31: DSC trace of **Run 04**

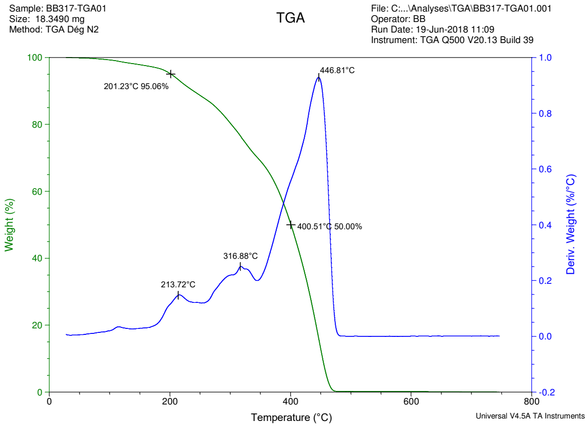


Figure S32: TGA trace of **Run 05**

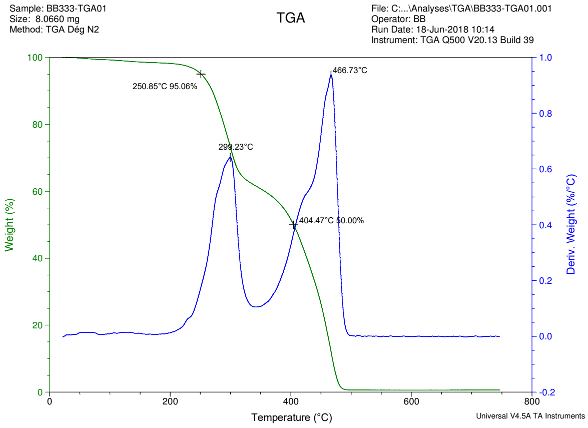


Figure S33: DSC trace of **Run 06**

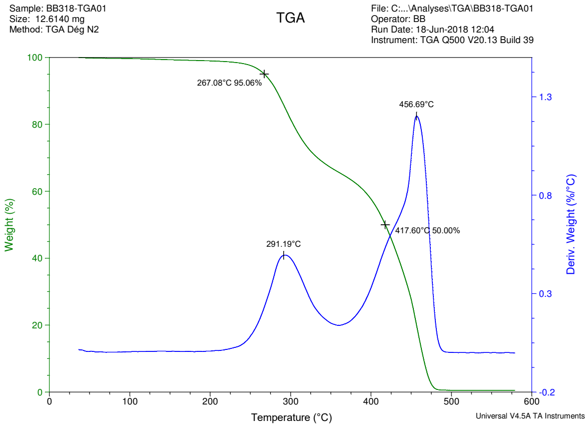


Figure S34: TGA trace of **Run 07**

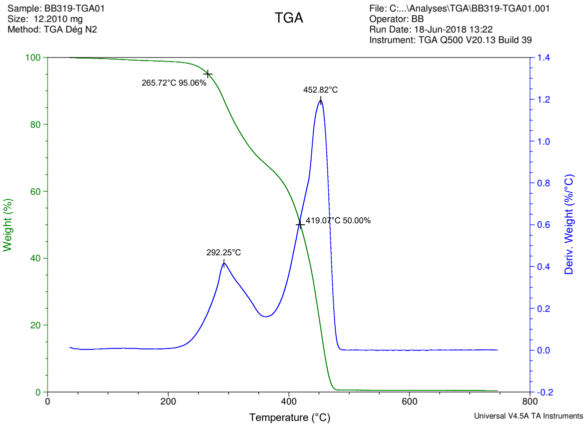


Figure S35: TGA trace of **Run 08**

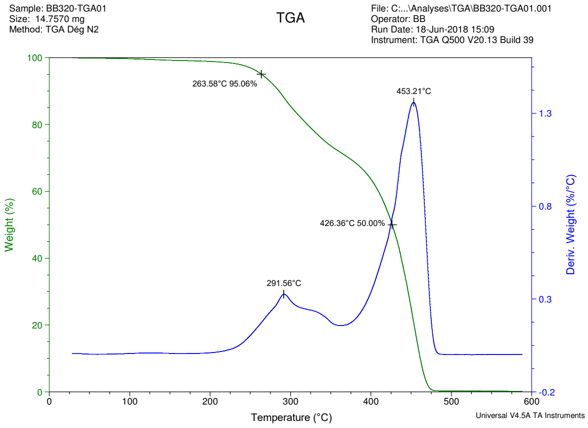


Figure S36: DSC trace of **Run 09**

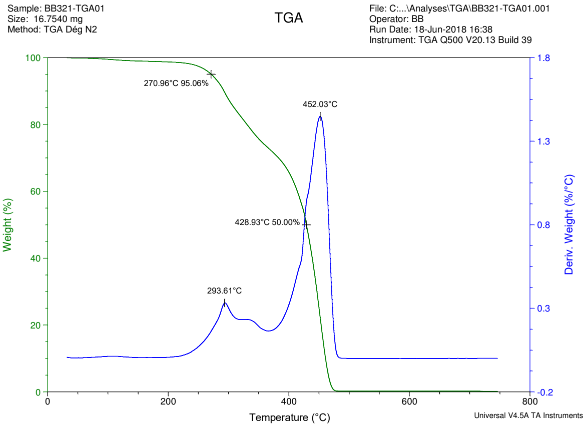


Figure S37: DSC trace of **Run 10**

Overlays

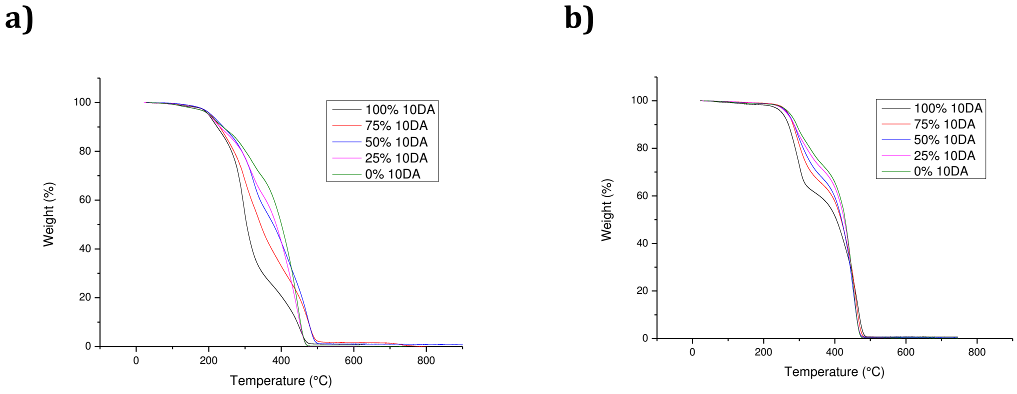


Figure S38: TGA traces of the obtained PHUs by copolymerization of a) **bisCC-C$_4$** and b) **bisCC-C$_{10}$** together with various ratios of 10DA and P1075(10°C/min heating ramp)

7.5. SEC traces

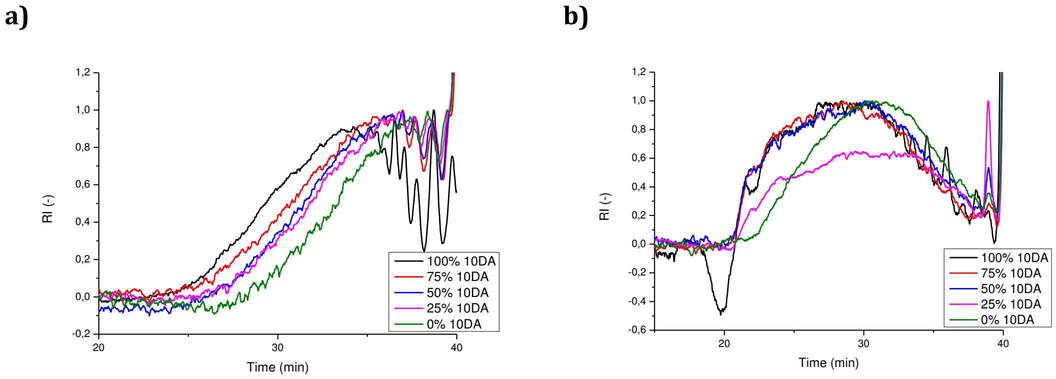
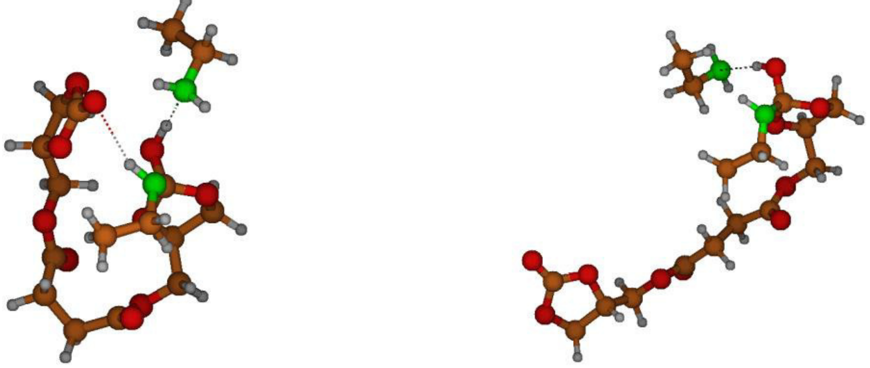


Figure S39 : Size exclusion traces of the obtained PHUs by copolymerization of a) bisCC-C₄ or b) bisCC-C₁₀ with various ratios of 10DA and P1075 together with (DMF, LiBr, PS Standards)

7.6. DFT Study – Structures of the intermediates

Int2, prim – bisCC-C_4

Int2, sec – bisCC-C_4



Int2, prim – bisCC-C_{10}

Int2, sec – bisCC-C_{10}

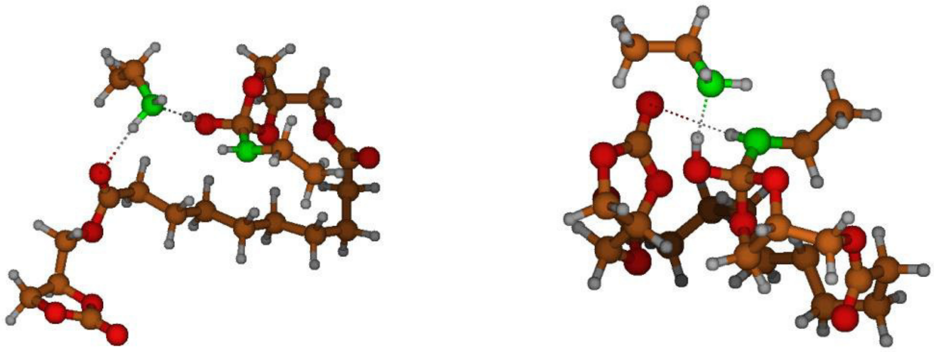


Figure S 40: Structures of the Intermediates Int2, prim and Int2, sec for both bisCC-C4 and bisCC-C10 as obtained by means of DFT calculations

MINIEMULSION OF NON-ISOCYANATE POLYURETHANE-ACRYLICS HYBRIDS AND PROPERTIES OF THE CAST FILMS THEREOF

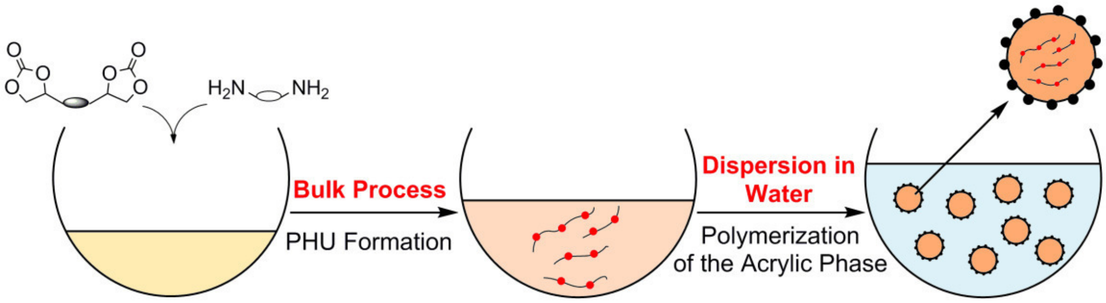


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Table of content

1. Introduction 161
2. Experimental 162
    2.1. Materials 162
    2.2. Experimental design 162
    2.3. Miniemulsification and miniemulsion polymerization 163
    2.4. Film casting 164
    2.5. Characterization 165
3. Results and Discussion 167
4. Conclusions 177
5. References 178
6. Shortened forms 181
7. Supporting Information 182
    7.1. Side Reactions 182
    7.2. Solubility 187
    7.3. Miniemulsion polymerization using thermal initiators 191
        7.3.1. Formulations with thermal initiators 191
        7.3.2. Results and discussion 194
    7.4. Formulations with redox initiators 196
    7.5. SEC-MALLS Traces 199
    7.6. DSC Traces 200
    7.7. Minimum Film Forming Temperature (MMFT) 201

1. Introduction

Accessing high performance polymer materials with satisfactory properties and balanced production cost usually requires the synergistic combination of polymers with different and even antagonist properties. Hybrids of polyurethanes (PU) and (meth)acrylic polymers is one of these synergistic combinations. PUs provide superior mechanical properties such as toughness, flexibility and abrasion resistance,[1–4] whereas poly(meth)acrylics are affording materials with good outdoor and alkali resistance, as well as pigment compatibility.[4–6] PU-(meth)acrylic hybrids are often prepared as waterborne dispersions that find applications as coatings and adhesives. The field has been recently reviewed aiming at establishing the link between synthesis, structure and properties.[7]

The final outlook of that review points out the challenges created by the environmental impacts of both the raw materials used in the synthesis and the need of developing low VOC and preferably VOC-free synthetic routes. Currently, di-isocyanates are used in the PU synthesis, but they may cause health issues such as asthma, dermatitis and even poisoning.[8–10] In addition isocyanates require the use of phosgene in their synthesis and this is a highly toxic gas that can cause death by inhalation. Solvent free PU-(meth)acrylic hybrids have been obtained by synthesizing the PU prepolymer using a mixture of (meth)acrylic monomers as diluents and then dispersing the solution in water.[11–17] However, achieving good colloidal stability is challenging and requires fine tuning of the synthetic approach.[18]

This chapter addresses the challenge of synthesizing isocyanate-free, solvent-free waterborne PU-(meth)acrylic dispersions. The field of water-based non-isocyanate polyurethanes (NIPUs) and polyureas (NIPUUs) has been reviewed in Chapter 1. This review shows that there are only two publications on the synthesis of waterborne NIPU-acrylic dispersions.[19,20] In these works, monofunctional urethane methacrylates (UMA) were prepared by aminolysis of ethylene carbonate and aliphatic amines in methylene chloride and then the resulting product was functionalized with methacrylic anhydride in DMF. The UMAs were copolymerized with MMA/BA in a seeded emulsion polymerization. The method presents some drawbacks as it involves several steps and uses solvents. Furthermore, the hybrids do not contained poly(urethane) chains, but urethane moieties.

In order to overcome these drawbacks in this chapter two complementary strategies were explored. The first one involved the formation of the isocyanate-free polymer by aminolysis of cyclic-carbonate derivatives using (meth)acrylic monomers as reacting media. This process leads to poly(hydroxy urethane)s – often called PHU.[21–23] The idea was to disperse the PHU/(meth)acrylates solution in water through a miniemulsification process, and then polymerize the (meth)acrylic monomers by free radical polymerization.

It will be shown that this at first sight promising idea encounters several serious problems. The second strategy explored was first to form the PHUs by bulk aminolysis of cyclic-carbonate derivatives using bio-sourced vegetable oil-based diamines. Then, the PHU was dissolved in (meth)acrylate monomers and the solution used as the organic phase of a miniemulsion. Subsequent polymerization of the (meth)acylic monomers led to the hybrid PU/(meth)acrylates waterborne dispersion. The performance of the films cast from the hybrid waterborne dispersions was studied.

2. Experimental

2.1. Materials

1,4-butanediamine (4DA, >98%), decane 1,10-diamine (10DA, >98%) and 1,12-diaminododecane (12DA, >98%) were supplied by TCI Europe. 1,6-haxanediamine (6DA, >99%) was obtained from Accros. 1,3-cyclohexanebis(methylamine) (CycloDA, 98%), butyl acetate (BAc, >99%), Butyl acrylate (BA, >99%), butyl methacrylate (BMA, 99%), stearyl acrylate (SA, 97%), 2,2'-azobis(2-methylpropionitrile) (AIBN, 98%) and tert-butyl hydroperoxide (TBHP, 70% in water) were obtained from Sigma. Ascorbic acid (or Vitamin C, AsA, >99.5%) was obtained from Fluka. Croda kindly provided Priamine™ 1075 (P1075). Dow kindly provided alkyl diphenyl oxide disulfonate (Dowfax™ 2A1, D2A1, 45wt% in water). One cyclic carbonates, bisCC-C_{10}, was used. The synthesis of this carbonate is detailed in Chapter 2. All products and solvents (reagent grade) were used as received unless otherwise mentioned. Deionized water was used.

2.2. Experimental design

As explained in the introduction two synthetic strategies were explored. The first one involves the polymerization of the cyclic carbonates and diamines in (meth)acrylic monomers, followed by dispersion in water and subsequent free radical polymerization of the (meth)acrylates.

As amines can potentially react with acrylic monomers, typically in an *aza*-Michael-type mechanism, the occurrence of this reaction was checked. It was found that BA suffered a significant reaction with the amines (Supporting Information – Figures S1 to S4). This is a strong drawback because side reactions consuming diamines will modify the stoichiometry substantially reducing the molecular weight of the polymer formed by this step-growth polymerization. Although BMA was only slightly affected by this reaction (Supporting Information – Figures S5 to S6), the strategy based on the formation of PHU in (meth)acrylates was abandoned and efforts were concentrated in the second strategy that involved the formation of the PHUs by bulk aminolysis of bis-cyclic-carbonate derivatives using bio-sourced vegetable oil-based diamines followed by dissolution of the

PHUs in (meth)acrylic monomers, dispersion in water to form a miniemulsion, and free radical polymerization of the vinyl monomers. Miniemulsion polymerization was used because this process is particularly well suited for the synthesis of hybrid dispersions.[24,25]

Poly(hydroxy)urethanes (PHUs) were synthesized through the aminolysis reaction between bisCC-C_{10} and P1075 (Figure 1). The stoichiometric ratio for the reactive moieties was used to target high molar masses according to the Carother's theory.[26] The reactions were performed in bulk at 90°C for 24h in a Schlenk tube using a helical shaped mechanical stirrer specifically designed to fit in the Schlenk vessel. No catalyst was added for the polymerization reactions. No purification of the PHUs was performed after reaction.

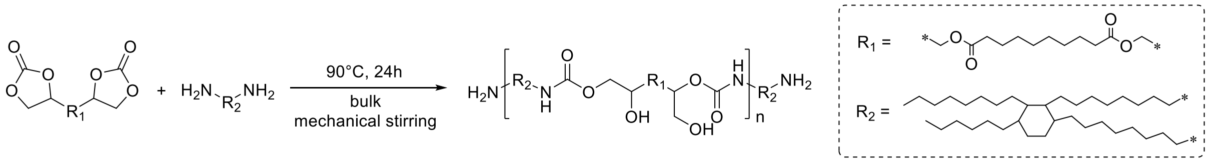


Figure 1: PHU pre-polymer utilized for the synthesis of PHU-Acrylics hybrid materials

A necessary condition for the implementation of the second approach is that the PHU should be soluble in the (meth)acrylates. Therefore, the solubility of the PHUs obtained with a series of cyclic carbonates and diamines in butyl methacrylate (BMA) was determined. As shown in Supporting Information (Section 6.2), the solubility of the cyclic carbonates and diamines in BMA was low (most of the diamines checked were not soluble for formulations targeting 10wt% of PHU in BMA) although the solubility could be improved using P1075.

2.3. Miniemulsification and miniemulsion polymerization

The formulations used are summarized in Supporting Information (Tables S3 to S8 and Table S10 to S13). The organic phase of the miniemulsion was prepared by dissolving P1075-based PHU (0 to 30 wt.% weight based on BMA) in a mixture of BMA and SA (4 wt% of SA) at 80°C. The aqueous phase was a 1 wt% (based on the total organic phase) solution of Dowfax2A1 in deionized water. The organic phase was added drop-wise into the aqueous phase under vigorous magnetic stirring. Then, the miniemulsion was formed by sonicating the coarse emulsion for 30 min with a Hielscher Ultrasonics GmbH (ref UIS250V) using an amplitude of 100% and 0.8s duty cycle. A post-stabilization step is performed by adding 1 wt.% of Dowfax 2A1 based on the total organic phase dissolved in a minimum amount of deionized water.

The miniemulsion was transferred to a 3-neck round-bottom flask and flushed with nitrogen during 30 min at 70°C. Then, the initiator was added in a way that depended on the type of initiator. The performance of thermal initiators was first checked using AIBN and BPO that are oil soluble in a 50 wt% solids content miniemulsion. The initiator was added as a shot. AIBN and BPO were dissolved in a small amount of BMA. The details are summarized in Supporting Information (Section 6.3). A very slow polymerization rate was observed for BPO and only 45% BMA conversion was obtained after 5.5 hours of reaction. Likely, as it was added as a shot, the very hydrophobic BPO could not reach the miniemulsion droplets/particles. This hypothesis is supported by the large particle size obtained with this initiator. AIBN, which has an appreciable water solubility (0.04g/100g H_2O)[27] did not suffer transfer limitations and a complete monomer conversion was achieved in about 1 h. However, this reaction led to an unacceptable fraction of coagulum (27 % after 5.5 hours). Part of this coagulum was due to the long time that the latex was kept at 70°C as coagulum was reduced to about 13% when the reaction was stopped after 1.5 hours). However, this coagulum was still unacceptable. Neither post-stabilization with a higher amount of surfactant nor the use of a carboxylic functional monomer (methacrylic acid) improved the stability.

Coagulation is a second order process of the number of particles, and hence strongly dependent on the solids content (for similar particle sizes). A reaction using about 40wt% solids was carried out using AIBN, and coagulum was reduced to 2.1%, which is an acceptable value for a lab-scale reactor that often gives higher coagulum fractions than the industrial reactors because of the higher internal surface area (agitator reactor wall)/volume and air interfacial area/volume ratios. Although this is a promising result, because of the uncertainties associated to the distribution of the initiator in large reactors, a redox initiator system (tert-butyl hydroperoxide/ascorbic acid, TBHP/AsAc) was chosen.

In the case of the redox system, the TBHP was added to the miniemulsion as soon as it was placed in the 3-neck round-bottom flask, giving time to TBHP to partition between the aqueous and organic phases during the nitrogen purging. When the nitrogen flushing was over, an aqueous solution of AsAc was fed in a semi-batch mode during 2 to 3 h depending on the needs.

The reaction mixture was left under magnetic stirring at 70°C for a reaction time ranging from 1h30 to 5h30. Regular sampling was performed in order to monitor the conversion (by gravimetry) and the particle size (by dynamic light scattering, DLS). At the end of the reaction, the latex was cooled down to room temperature and filtered through an 85 μm nylon mesh in order to collect the fraction of polymer coagulated.

2.4. Film casting

The films were obtained by casting the latexes in silicon molds at 30 °C and 55% relative humidity for 48 hours. Rectangular specimen were cast for tensile tests (10 x 40 x 0.3 mm^3). Square samples were cast for TEM and AFM analyses (10 x 10 x 0.5 mm^3).

Those samples were cut with a cryo-microtome device. In order to study the effect of the casting temperature on film morphology some films were also cast at 45°C and 60°C (55% relative humidity, 24 hours).

2.5.Characterization

^{1}H-NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz) by using DMSO-d6 or $CDCl_3$ as a solvent at room temperature.

The coagulum fraction was measured by filtration of the latex through an 85 µm nylon mesh.

Monomer droplet sizes as well as particle sizes were measured by dynamic light scattering in a Zetasizer Nano Z (Malvern Instruments). The samples were prepared by dilution of the latex in deionized water. The equipment was operated at 25 °C, and the values reported are the z-average values. They are the average of three repeated measurements after 15 sec equilibration time at the programmed temperature.

The molar mass of the soluble fraction of the polymer latexes were determined by SEC/MALLS/RI. The equipment was composed of a LC20 pump (Shimadzu) coupled to a DAWN Heleos II multiangle (18 angles) light scattering laser photometer equipped with an He–Ne laser (λ = 658 nm), and Optilab Rex differential refractometer (λ = 658 nm), all from Wyatt Technology Corp., USA. Separation was carried out using three columns in series (Styragel HR2, HR4, and HR6; with pore sizes from 10^2 to 10^6 Å). The analyses were performed at 35°C and THF was used as mobile phase at a flow rate of 1 mL.min^{-1}.

Particle and film morphologies were analyzed by transmission electron microscopy (TEM) in a TECNAI G^2 20 TWIN microscope operated at 200 kV and equipped with LaB6 filament, and high angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM). When analyzing the particle morphologies, the samples were previously stained by phosphotungstic acid (PTA) adding 2wt% of PTA to the diluted latex. The mixture of diluted latex and PTA was sonicated for 30 min at maximum power in a Bandelin Sonorex sonicator. A drop of this solution was spin-coated onto a carbon-coated cooper grid (300mesh) at 1500rpm for 3 min. In order to analyze the film morphologies, ultra-thin sections of about 80 nm of thickness were obtained at -25°C temperature using a cryo-ultramicrotome device (Leica UC6FC6) equipped with a diamond knife. The ultrathin sections were placed on 300 mesh copper grids. They were analyzed without any staining.

Film morphologies were also analyzed by means of atomic force microscopy (AFM). The films were cut with a cryo-microtome device equipped with a diamond knife (described in the TEM section). The AFM data were directly acquired onto the surface area of the cut film, which was left tight in a specially designed sample holder that was used for cutting the film in the microtome. The peak force quantitative nanomechanical mapping (PF-QNM) method was used for characterization purposes, which allows for the simultaneous recording of topography as well as mechanical properties. The AFM images were acquired at 25°C and 55% relative humidity, using a Multimode 8 microscope and a Nanoscope V controller (Bruker). All the images were processed offline using the commercial software Nanoscope Analysis 1.9 (Bruker). Considering that the images were acquired from the surface area of the films that were still located in the microtome's holder, all the samples were thick enough to avoid any effect of the supporting substrate in the measurement of the nanomechanical properties. The basic idea of the PF-QNM technique, extensively described in the work of Limousin *et al.*[28] and references therein, consists in recording dynamic force curves in a pixel-wise fashion. These curves represent the applied force on the probe while it approaches and retracts from the film surface, as a function of the tip-sample distance and/or interaction time. The user defined feedback parameter, called 'peak force', relates to the maximum load applied to the surface. In the present work, a value of 10 nN was used. We obtained PF-QNM maps with a 256 x 256 resolution, and a frequency modulation (f_m) of 2 kHz. In PF-.QNM, the analysis of the force-distance curves allows the calculation of different nanomechanical maps. In this work, we present the deformation and stiffness maps of the investigated samples. The deformation is a parameter related to the distance penetrated by the AFM tip into the film surface. The stiffness relates to the resistance opposed by the sample to the tip penetration. This latter parameter was calculated as the slope of the approach part of the force-curve distance, by a linear fit. For obtaining PF-QNM quantitative maps it was followed the relative calibration method proposed by Bruker and recently used in the literature.[28–30] All samples were probed using Tap 150AI-G probes, by BudgetSensors (tip radius <10 nm, as estimated from a tip-checker sample provided by Bruker). The deflection sensitivity of the detector was obtained using a sapphire sample, provided by Bruker. Finally, the spring constant was determined to be ~3 N/m according to the Sader method.[31]

Differential Scanning Calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA Instruments using a heating ramp at 10°C.min^{-1} from -80°C to 130°C. The first heating ramp was used to measure the glass transition temperatures (T_gs) in order to get a picture of the properties of the cast films.

The minimum film formation temperature (MFFT) was determined on a steel bar with a temperature gradient that was measured with thermocouples located at regular distances. A thin layer of latex was applied onto the MFFT bar with a film applicator (60 μm thickness) and the water was left to evaporate so that the film can form. The MFFT was defined as the temperature at which both a clear coat was observed and a clear cut could be made with a knife without forming any powder.

Tensile stress-strain measurements were carried out from the cast rectangular films with a texture analyzer (Stable Micro Systems Ltd., Godalming, UK) at a constant velocity of 0.42 $mm.s^{-1}$. The size of the samples was 10 x 40 x 0.3 mm^3. The reported results were the average of at least 3 repeated tensile tests of 3 different specimens. The Young's modulus was determined as the slope of the stress-strain curve at low strain (in the elastic region – before the yield point) and the toughness was calculated as the area under the obtained curve.

3. Results and Discussion

40wt% solids content waterborne PHU-BMA hybrid dispersions were prepared by miniemulsion polymerization using stearyl acrylate (SA) as costabilizer to minimize Ostwald ripening. Tert-butyl hydroperoxide / ascorbic acid (TBHP/AsAc) was used as redox pair. Table 1 summarizes the reactions carried out (details are given in Supporting Information). The PHU was obtained by bulk polymerization of biCC-C_{10} and P1075 as described above. The oil phase of the miniemulsion was a mixture of PHU, BMA, SA and TBHP. It is worth pointing out that TBHP do not suffer any significant decomposition at temperatures below 90°C (half life time = 520h at 130°C),[32] and therefore can be safely mixed with the monomers. Several PHU contents (0 wt%, 10wt%, 20wt% and 30wt%) were used. The organic phase was mixed with an aqueous solution of Dowfax 2A1 under strong magnetic agitation, and then sonicated. After sonication, an additional amount of Dowfax 2A1 was added to post-stabilize the miniemulsion. The polymerizations were carried out at 70°C feeding semi-continuously an aqueous solution of AsAc. Different feeding times were used (2, 2.5 and 3 hours).

Table 1: Summary of the miniemulsion polymerizations

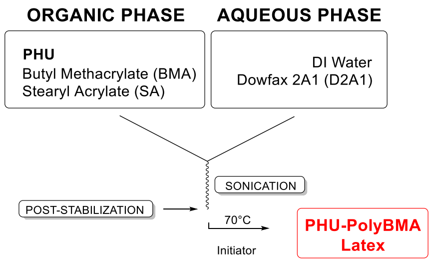
		Composition				
	Basic recipe	PHU	0-30	wt%	96wt%	40 wt% solids
		BMA	100-70	wt%		
		SA	4	wt%		
		Dowfax™ 2A1	1	wt% (wbo)		
		Water				
	Post-Stabilization	Dowfax™ 2A1	1	wt% (wbo)		
		Water	< 1g			
	Initiation	TBHP	0.05	wt% (wbo)		
		AsAc	0.05	wt% (wbo)		
		Water	<1g			

Figure 2 presents the evolution of the gravimetric (BMA+SA) conversion during the miniemulsion polymerizations carried out using different PHU contents and AsAc feeding times. Figure 3 presents the evolutions of the particle diameter and polydispersity index measured by DLS as well as the number of particles determined from the particle diameter and either the polymer content (for 0wt% PHU) or total amount of organic phase for the rest. The reason for this difference is that when PHU was used, it reinforced the effect of the co-stabilizer,[33] and hence the miniemulsion particles likely maintained all the unreacted hydrophobic monomer within the particles during the DLS measurements. When no PHU was used, it is unlikely that stearyl acrylate alone could retain the monomer in the particles under the high dilution used in the DLS measurements.

Figure 2 shows that in all the cases, conversions close to 100% were obtained at the end of the process, although an induction period was usually observed. The reason was that the concentration of AsAc was low at the beginning of the process and the radicals generated were consumed by the inhibitor contained by the monomers (notice that technical monomers were used). In general, the slower the feed rate of AsAc (longer feeding times) the longer the inhibition period. The inhibition period could also be reduced by increasing the flushing time as it is demonstrated in the experiments carried out with 30wt% of NIPU where the inhibition time for a feeding time of AsAc of 2.5 hours was shorter than that of 2 h because a longer flushing time was used (90 min for 2.5 h vs. 60 min for 2h). When the inhibition was overcome, polymerization was fast in most cases.

For the experiments carried out with PHU, Figure 3 shows that particle (droplet) size was roughly constant during the whole process, which is a characteristic of efficiently nucleated well stabilized miniemulsions. The reason is that if the miniemulsion is stable, initially the size of the monomer droplets is determined by DLS and latter the monomer swollen polymer particles are measured. As the difference in volume between monomer droplets and monomer-swollen particles is only due to the density difference that is small, the differences in diameter are negligible. Figure 3 shows that the particle sizes obtained with 10 and 20 wt% of PHU and 2.5 h of feeding time for AsAc were larger than for the other cases. For efficiently nucleated stable miniemulsions, this effect can only be the result of the differences in miniemulsion droplets. It has been demonstrated that miniemulsification by sonication is very sensitive to small details such as the geometry of the system, the position of the sonication tip and the agitation in the flask.[34] Therefore, the observed deviations might be the result of inadverted changes during miniemulsification. In the absence of PHU, the particle size substantially increased during the process, which suggests that SA was not able to form a stable miniemulsion (notice that it has been demonstrated that the presence of polymer reinforces the effect of the costabilizer[33] and therefore the polymerization likely occurred through a mixed emulsion-miniemulsion mechanism). The processes were basically coagulum-free (Table 2).

SEC/MALLS analyses showed bimodal molar mass distributions when PHU was incorporated into the formulation (the low molar mass corresponding to the PHU – Figure

S10). Interestingly, the amount of PHU incorporated into the formulation did not seem to dramatically affect the final molecular weight of the acrylic polymer (all values of M_w were in the range 2.10^6 – $2.5.10^6$ g.mol^{-1}). It may be observed a trend showing that for the same feed rate of AsAc, the higher the PHU fraction, the lower the molecular weight of polyBMA. This is because for similar particle sizes and the same feed rate of AsAc, the frequency of radical entry in the particles was similar, and hence the polymer chains grow a similar time. Under these conditions, the chain length is proportional to the monomer concentration in the particles that decreased as the PHU content increased.

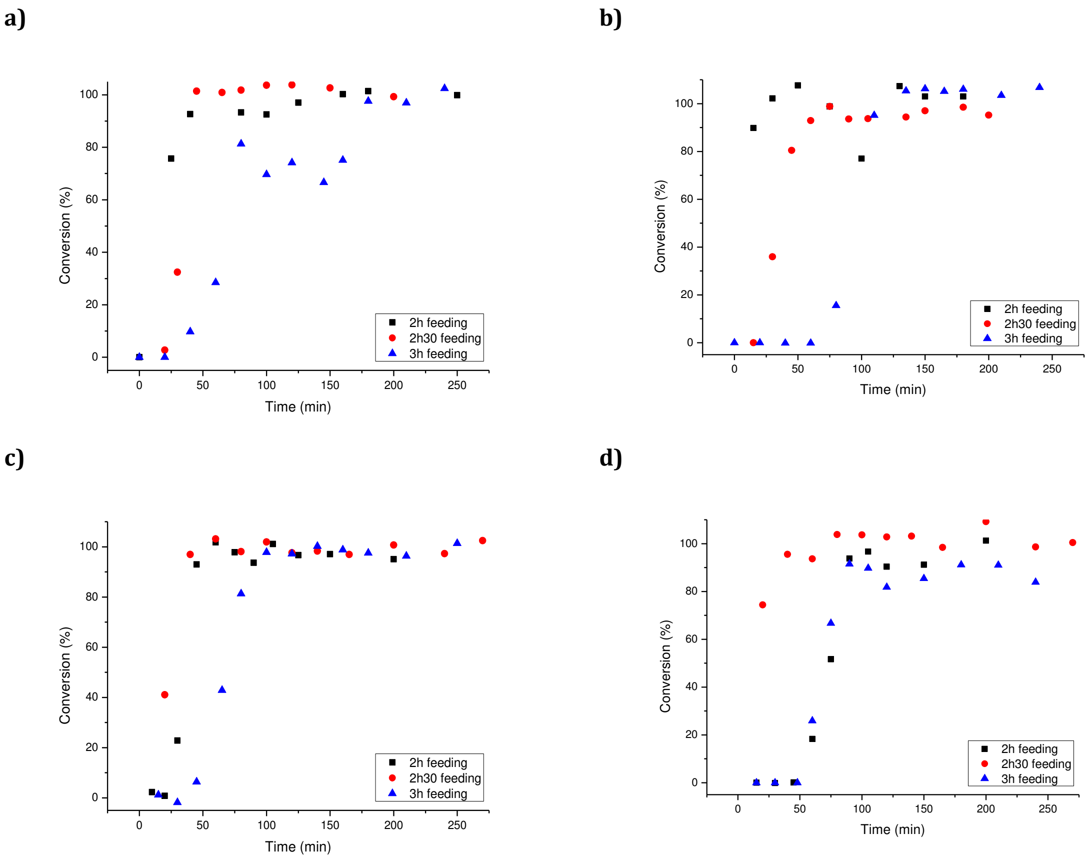


Figure 2 : Effect of the AsAc feeding rate on the evolution of the monomer conversion obtained by gravimetry for different PHU contents. (a) 0 wt.% PHU, b) 10 wt.% PHU, c) 20 wt.% PHU, d) 30 wt.% PHU).

Table 2: Characteristics of the synthesized latexes while investigating the use of redox radical initiators

wt% PHU [wt%]	PHU			Feeding time [h]	Coagulation [wt%]	Particle Size[b] [nm]	M_ns[c] [kg.mol^{-1}]	M_ws[c] [kg.mol^{-1}]	Đ[c]	T_gs[d]	MFFT [°C]
	M_ns[a] [g.mol^{-1}]	M_ws[a] [g.mol^{-1}]	Đ[a]								
0.wt%	-	-	-	2h00	2.3	137	-	-	-	-	-
	-	-	-	2h30	0.9	143	2410	4220	1.7	29	30
	-	-	-	3h00	1.6	137	-	-	-	-	-
10.wt%	-	-	-	2h00	1.8	115	-	-	-	-	-
	21600	43000	2.0	2h30	1.8	142	2480	3780	1.5	-21/28	24
	-	-	-	3h00	1.8	117	-	-	-	-	-
20.wt%*	-	-	-	2h00	1.0	120	-	-	-	-	-
	21700	41100	1.9	2h30	2.1	138	2190	3280	1.5	-20/24	15
	-	-	-	3h00	1.8	116	-	-	-	-	-
30.wt%*	-	-	-	2h00	2.8	138	-	-	-	-	-
	21700	41100	1.9	2h30	4.3	140	2070	3170	1.5	-20/34	< 7
	-	-	-	3h00	1.6	131	-	-	-	-	-

[a] Determined by SEC in DMF, with LiBr salts, PS calibration

[b] Measured by DLS

[c] Determined by SEC/MALLS. Because no LS signal was observed for the low molar mass peak (corresponding to the PHU), only the molar mass corresponding to the poly(BMA-co-SA), which had a LS signal, is reported

[d] Measured by DSC of the dried films, 1st heating ramp (10°C/min)

-: not determined

*: the same PHU was used in the preparation of those latexes

Table 2 also presents the glass transition temperatures obtained by DSC (DSC traces are presented in Supporting Information – Figure S11). It can be seen that the T_gs of both phases were clearly observed and that the values were not affected by the PHU content, which indicates a neat phase separation. In this hybrid, the PHU was the softer phase and polyBMA the harder. Therefore, the PHU content affected the minimum film forming temperature (MFFT). Table 3 shows that MFFT significantly decreased as the content of the soft PHU increased.

The decrease in MFFT with the PHU content suggests that the PHU was located at the outer part of the particles and therefore participating in the formation of the film. Particle morphology was studied by TEM using phosphotungstic acid (PTA) as selective negative staining agent of the PHU. The TEM images are presented in Figure 4. It can be seen that core-shell particles were formed and that in agreement with the hypothesis based on MFFT measurements, the shell was made out of PHU. The shell could only be observed for the highest PHU content (30 wt%).

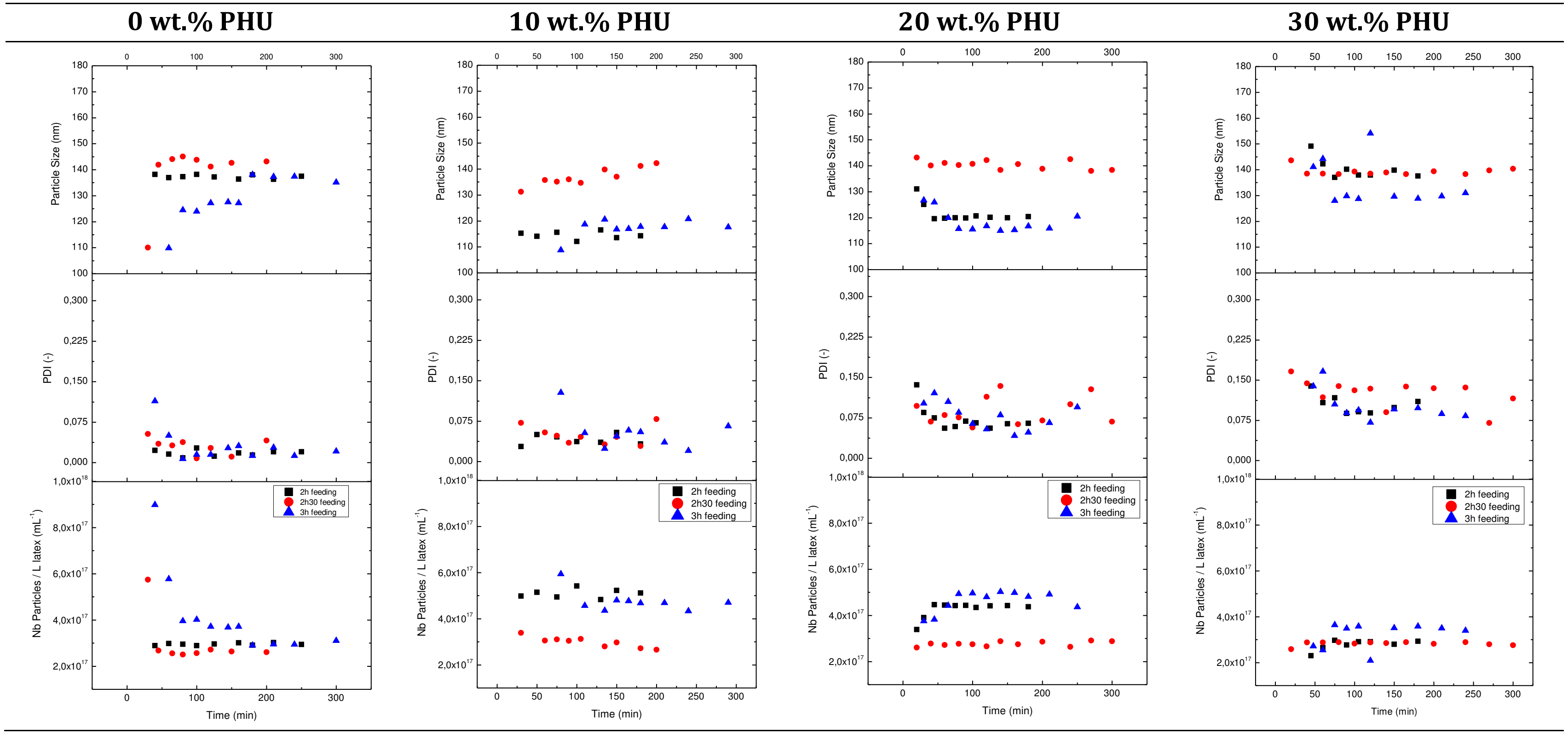
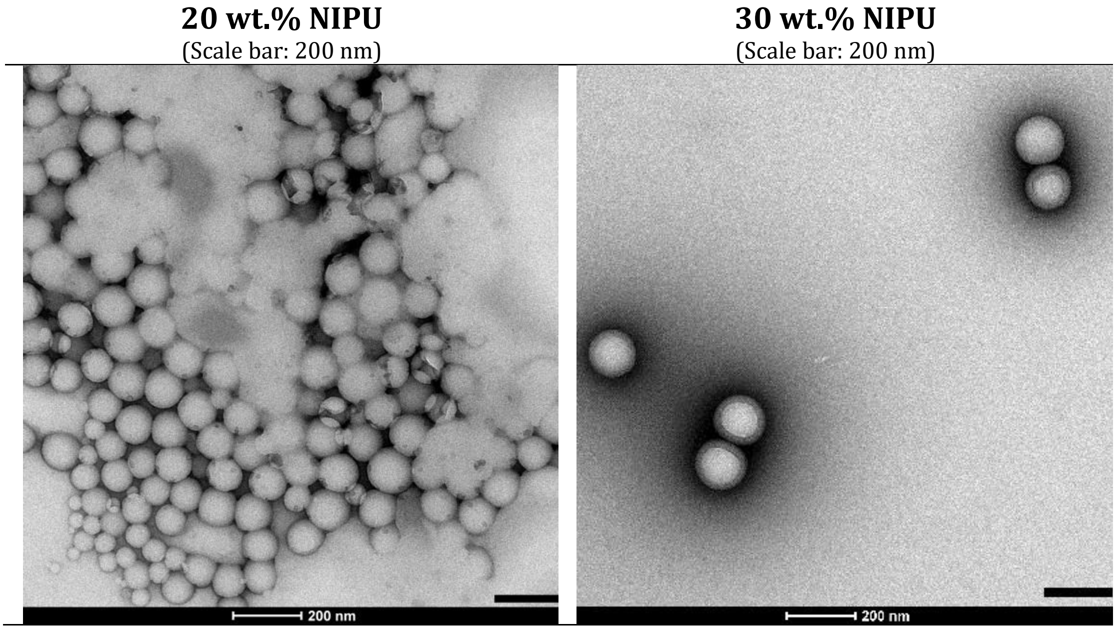


Figure 3: Evolution of the particle size, the polydispersity index (PDI) and of the number of particles


20 wt.% NIPU
(Scale bar: 200 nm)

30 wt.% NIPU
(Scale bar: 200 nm)

Figure 4: TEM images of the polymer particles for the latexes containing 20wt% NIPU (left) and 30wt% NIPU (right) formed with 2h30 feeding of AsAc.

Figure 5 shows that in all cases transparent films were obtained at 30 °C. This indicates that good quality of packing of the particles was achieved during the film formation process, perhaps due to the fact that the casting temperature was equal or higher than the MFFTs. Yellowing of the films could also be noticed in the case of NIPU loadings higher or equal than 20 wt%).

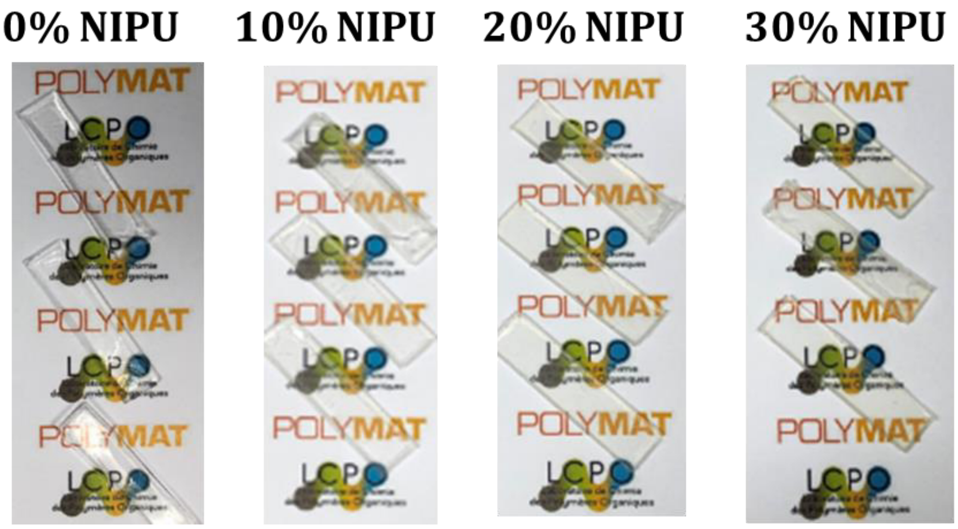


Figure 5: Pictures of the cast films at 30°C with different loadings of NIPU.

Figure 6 presents the effect of the PHU content on the stress-strain curves. This figure also includes the effect of the casting temperature and thermal treatment for the 20 wt%

NIPU hybrid. Table 3 summarizes the effect of these variables on the Young's modulus, strain and stress at break and toughness.

It can be seen that at 30°C, increasing the PHU content led to a softer material with a clear decrease of both Young's modulus and stress at break, and an increase of the strain at break. On the other hand, the effect of the casting temperature is more complex. When the films were cast at 45°C, the Young's modulus and in particular the strain at break increased with respect to the film cast at 30°C, leading to a substantial increase in toughness. However, further increase of the casting temperature led to a decrease in Young's modulus, strain at break and toughness.

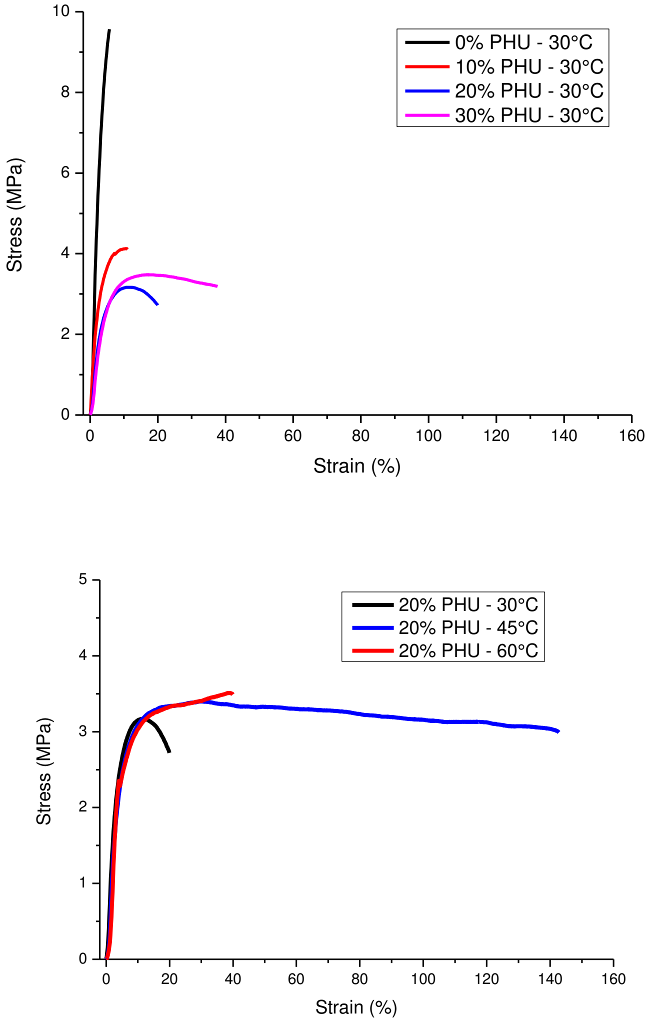


Figure 6: Effect of the of the PHU content and casting temperature on the stress-strain curves.

Table 3: Tensile test results of the cast films depending on the casting temperature as well as the chemical composition

Temperature [°C]	NIPU Content [%]	Young Modulus [MPa]	Strain at break [%]	Stress at break [MPa]	Toughness [MPa]
30	0	336 ± 49	5.7 ± 2.5	9.9 ± 3.7	0.32 ± 0.22
30	10	161 ± 13	6.7 ± 5.1	4.8 ± 1.7	0.22 ± 0.21
30	20	111 ± 11	20 ± 11.9	3.1 ± 0.8	0.54 ± 0.51
30	30	63 ± 21	38.6 ± 10.3	2.7 ± 0.7	0.95 ± 0.13
45	20	126 ± 18	132.1 ± 55.2	3.1 ± 0.5	4.53 ± 2.08
60	20	101 ± 6	38.4 ± 5.3	3.8 ± 0.4	1.3 ± 0.3

Complex effects of the casting temperature and thermal treatments on mechanical properties have been reported for other hybrid systems[28,35–37] and have been explained by the modifications in the film morphology. Therefore, in order to investigate if this was the case in the present system, the morphology of the films was determined by TEM.

Figure 7 presents the TEM images of microtome cuts of the films cast from the 20wt% NIPU at different temperatures. The images showed some dark zones that were attributed to PHU aggregates because their size increased with the casting temperature and in soft-hard polymer-polymer hybrids, it is known that the softer polymer undergoes substantial migration forming large aggregates.[28,38] In order to confirm that aggregates of PHU are formed, AFM measurements were carried out for the films containing 0wt% and 30wt% of PHU. The results presented in Figure 8 clearly show that the PHU migrated to form clusters. The images for 30°C and 45°C were not that different, whereas that of the film cast at 60°C showed a clear phase separation. It can be then speculated that the improvement in mechanical properties observed when the films were cast at 45°C was due to the formation of a better film as a result of the better particle packing and perhaps polymer interdiffusion. Further increase of the casting temperature was detrimental because phase separation occurred.

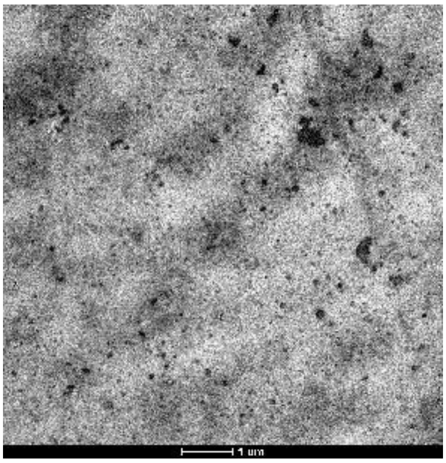
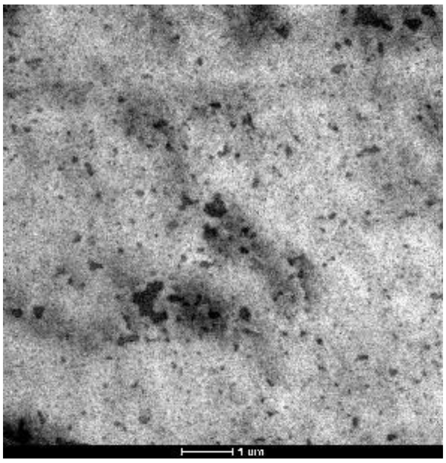
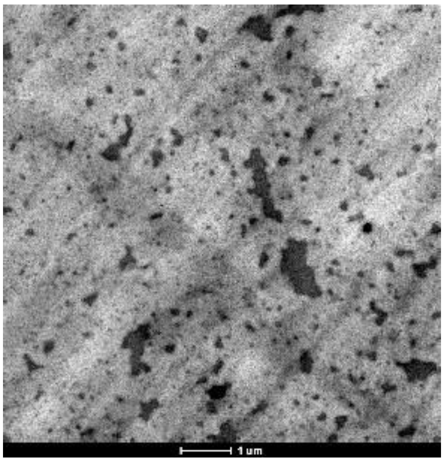
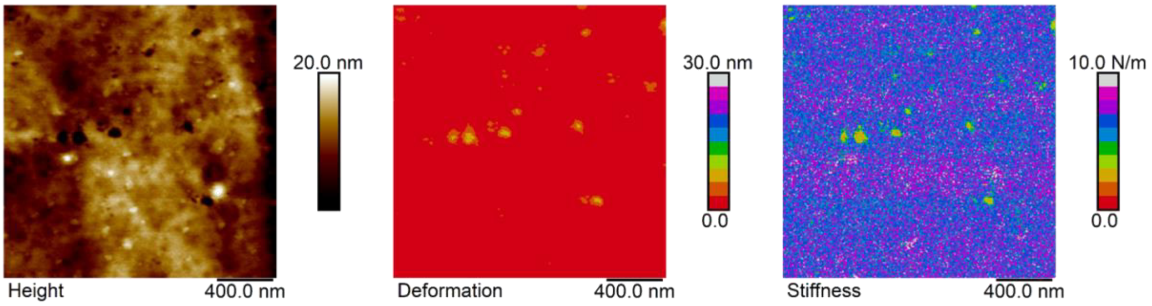
Temperature	**20 wt.% NIPU** (Scale bar: 1 µm)
30°C	
45°C	
60°C	

Figure 7: TEM pictures of cryo-microtome cuts of film prepared with the 20 wt% NIPU hybrid at different temperatures. No staining was performed.

a) 0 wt.% NIPU



b) 30 wt.% NIPU

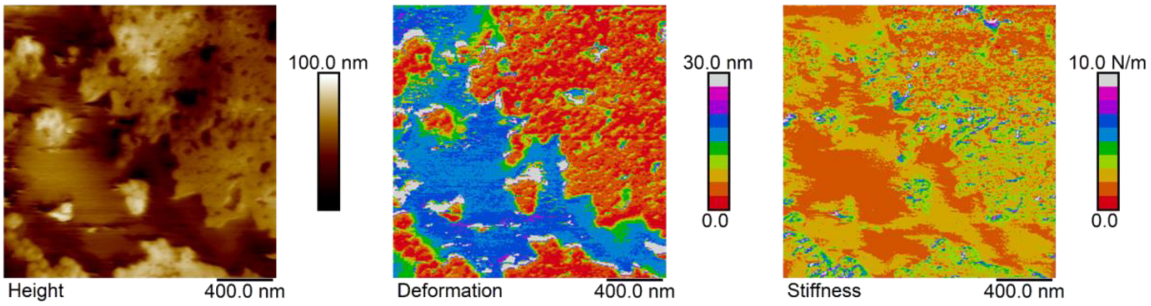


Figure 8: AFM pictures (peak force mode) of the films cast at 30°C from the latexes containing a) 0 wt.% NIPU and b) 30 wt.% NIPU

4. Conclusions

In this chapter, NIPU-(meth)acrylic waterborne dispersions were prepared by miniemulsion polymerization. Two complementary strategies were explored. The first one involved the formation of the isocyanate-free polymer by aminolysis of cyclic-carbonate derivatives using (meth)acrylic monomers as reacting media, dispersion PHU/(meth)acrylates solution in water through a miniemulsification process, and polymerization the (meth)acrylic monomers by free radical polymerization. However, this strategy was not successful because of the combined effect of the reaction of the amines with acrylic monomers by an *aza*-Michael-type mechanism and the poor solubility of the PHU monomers (amines and cyclic carbonates) in butyl methacylate. More success was obtained with the second strategy in which the PHU was first form by bulk aminolysis of cyclic-carbonate derivatives using bio-sourced vegetable oil-based diamines. Then, the PHU was dissolved in (meth)acrylate monomers and the solution used as the organic phase of a miniemulsion. Subsequent free radical polymerization of the (meth)acylic monomers led to the hybrid PU/(meth)acrylates waterborne dispersions. The choice of the initiator system was critical to achieve coagulum free dispersions. AIBN and

TBHP/ascorbic acid could be used, but the redox system offered advantages for scaling up.

Hybrid dispersions containing up to 30wt% of PHU were prepared and it was found that they were formed by core-shell particles with the PHU in the shell. Transparent films were obtained for all compositions, but some yellowing appeared as the PHU content increased. The minimum film formation temperature decreased with the PHU content. Tensile tests showed that increasing the PHU content led to a softer material with a clear decrease of both Young's modulus and stress at break, and an increase of the strain at break. The mechanical properties were also affected by the casting temperature. Increasing the casting temperature form 30 to 45°C, the Young's modulus and in particular the strain at break increased, leading to a substantial increase in toughness, presumably due to a better film formation as a result of the better particle packing and perhaps polymer interdiffusion. However, further increase of the casting temperature to 60°C led to decreases in Young's modulus, strain at break and toughness. TEM images of cross-sections of the films indicate that this was due to a strong phase separation caused by the migration of the soft phase (PHU).

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6. Shortened forms

AIBN:	2,2'-azobis(2-methylpropionitrile) / azobisisobutyronitrile
AFM:	Atomic Force Microscopy
AsAc:	Ascorbic acid (or Vitamin C)
BA:	butyl acrylate
BAc:	butyl acetate
bisCC-C_{10}:	bis-cyclic carbonate derived from sebacic acid
BMA:	butyl methacrylate
BPO:	Bonzoyl peroxide
$CDCl_3$:	deuterated chloroform
CycloDA:	1,3-cyclohexanebis(methylamine)
Đ:	Polydispersity
DLS:	Dynamic Light Scattering
DMF:	Dimethylformamide
DSC:	Differential Scanning Calorimetry
DMSO:	Dimethylsulfoxide
D2A1:	alkyl diphenyl oxide disulfonate (Dowfax™ 2A1)
MMA:	Methyl Methacrylate
Mn:	Molecular weight (in number)
MFFT:	Minimum Film Forming Temperature
Mw:	Molecular weight (in weight)
NIPU:	Non Isocyanate Polyurethane
NMR:	Nuclear Magnetic Resonance
PDI:	Polydispersity index
PHU:	Poly(hydroxy)urethanes
PF QNM:	Peak force – Quantitative Nanomechanical Mapping
PTA:	Phosphotungstic Acid
PU:	Polyurethane
P1075:	Priamine™ 1075
SA:	stearyl acrylate
SEC/MALLS/RI:	Size Exclusion Chromatography / Multi Angle Laser Light Scattering / Refractive Index
TBHP:	tert-butyl hydroperoxide
TEM:	Transmission Electron Microscopy
T_g:	Transition Glass Temperature
UMA:	Urethane Methacrylate
VOC:	Volatile Organic Compound
wt%:	weight percent
^{1}H-NMR:	Proton- Nuclear Magnetic Resonance
4DA:	1,4-butanediamine
6DA:	1,6-hexanediamine
10DA:	Decane 1,10-diamine
12DA:	1,12-diaminododecane

7. Supporting Information

7.1. Side Reactions

Amines and amine-terminated NIPUs can potentially react with acrylic monomers, typically in an *aza*-Michael-type mechanism. During the amynolisis of cyclic carbonates and amines to form PHU, this side reaction will alter the stoichiometry amine/carbonate lowering the molar mass. In order to check the occurrence of this reaction, 10wt% of a stoichiometric mixture of bisCC-C_{10} and P1075 were dissolved in butyl acrylate (BA) and the solution was kept at 70°C for 16h. The reaction temperature was then increased up to 90°C during 9h. The same reaction was performed in butyl acetate (BAc) as a reference reaction to highlight the effect of the vinyl moiety of BA. The reaction was monitored by means of ^{1}H-NMR analyses in $CDCl_3$ and the results are given in Figure S1 to S4.

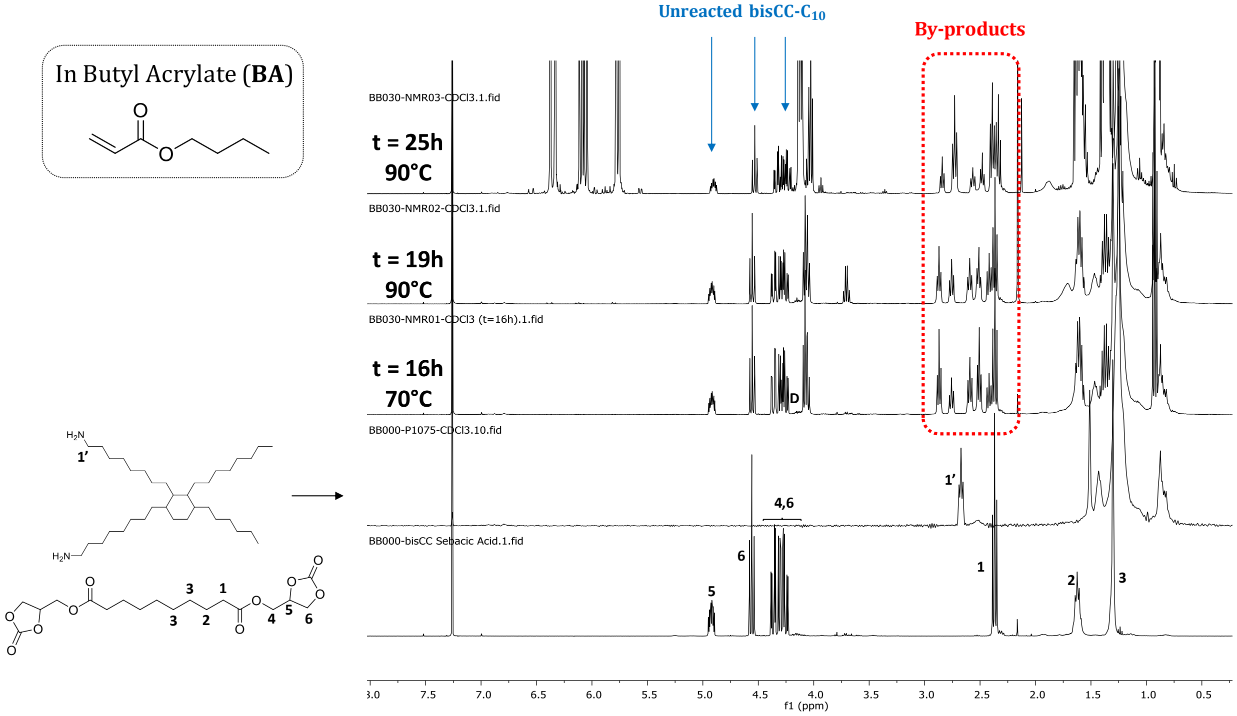


Figure S1: ^{1}H-NMR follow-up of the reaction of a stoichiometric mixture of bisCC-C_{10} and P1075 in BA (10wt% of the PHU monomers in BA)

The formation of the urethane moiety is usually observed thanks to the shift of the peak corresponding to the CH_2 moiety in alpha-position of the amine (1' in Figure S1). When located in alpha-position of a urethane moiety, it should appear in the region 2.9 to 3.4 ppm[1]. This shows that no PHU was formed in the process under the conditions used. This outcome was surprising since the formation of PHUs originating from the reaction between diamine and ester-activated bis cyclic carbonates is known to take place at temperatures as low as 20°C in bulk,[1] or at 70°C in dimethylformamide.[2] It can however be noticed that several peaks appeared in the region 2.3 to 2.7 ppm, suggesting the formation of by-products by side-reactions. In order to clarify if these by-products were the result of a reaction between BA and P1075, a reference reaction was performed by removing bisCC-C_{10} from the reactive mixture and the results are presented in Figure S2, where it can be seen that the peaks of the by-products appeared.

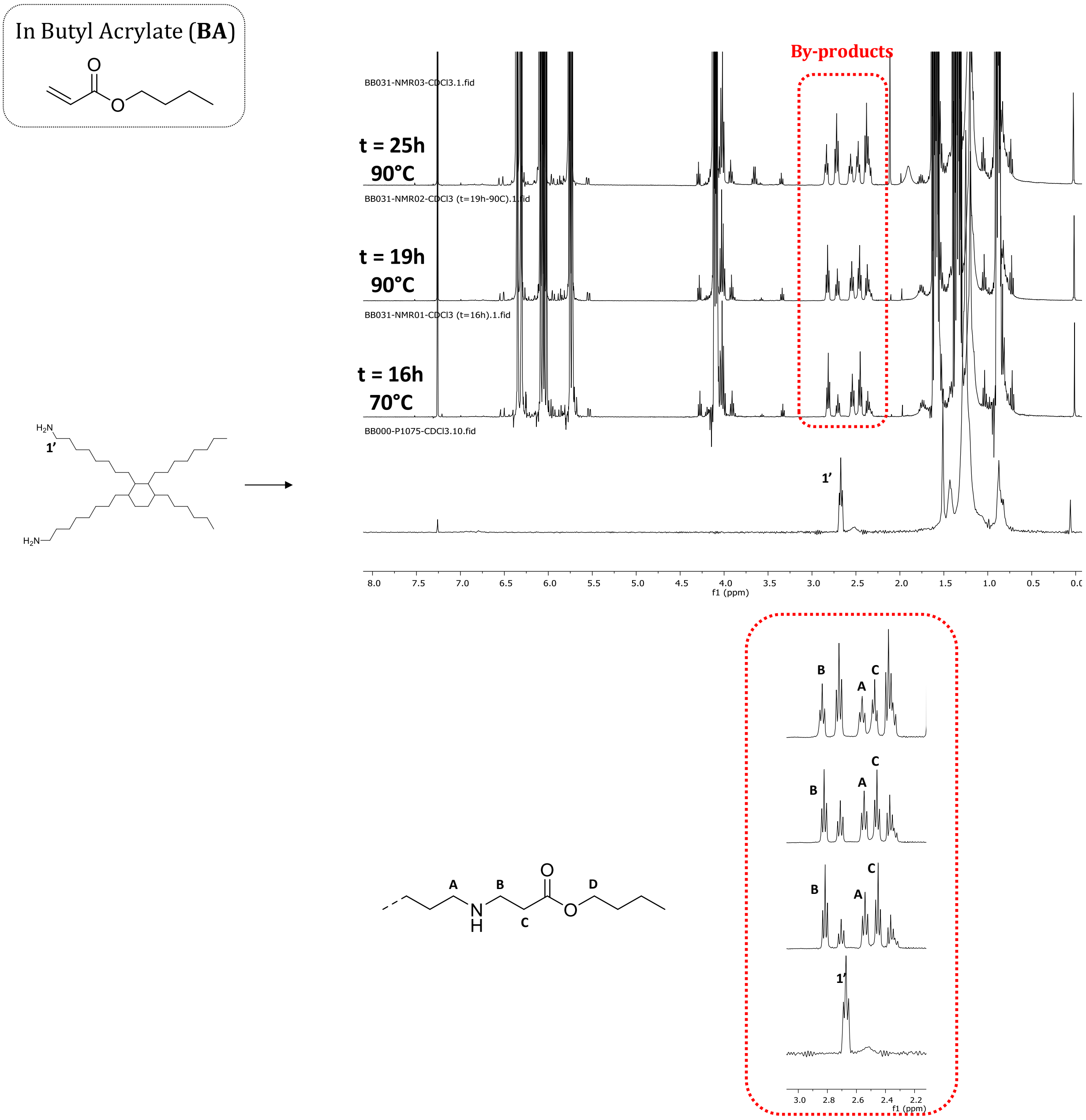
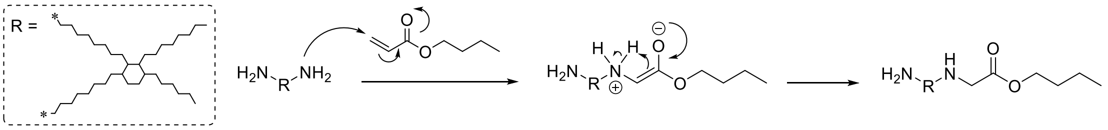


Figure S2: ^{1}H-NMR reaction follow-up (in $CDCl_3$) of P1075 in BA (same conditions as in S1 without adding bisCC-C_{10})

It was therefore clear that by-products were formed by reaction between P1075 and BA. Although all the products were not fully characterized and identified, the formation of adducts originating from an *aza*-Michael-type mechanism (Scheme S1) seems to account for the formation of some of the by-products and supports observations that have already been done in the literature.[3-5] The NMR attribution was done according the work of Endo and coworkers.[6]



Scheme S1: Suggested mechanism for the *aza*-Michael addition of P1075 onto BA. Please note that for clarity purposes, only one amine moiety of the diamine was converted.

In order to check if the vinyl moiety was playing a role in the formation of the by-products, BA was replaced by butyl acetate (BAc). Similar to BA, two reactions were carried out: in the first one, a stoichiometric mixture of bisCC-C_{10} and P1075 were reacted in BAc during 50h at 70°C. The second comparative reaction only used P1075 in BAc that were reacted at 70°C during 19h and then at 90°C during 31h. The resulting ^{1}H-NMR follow-ups in $CDCl_3$ are presented in Figure S3 and Figure S4 respectively.

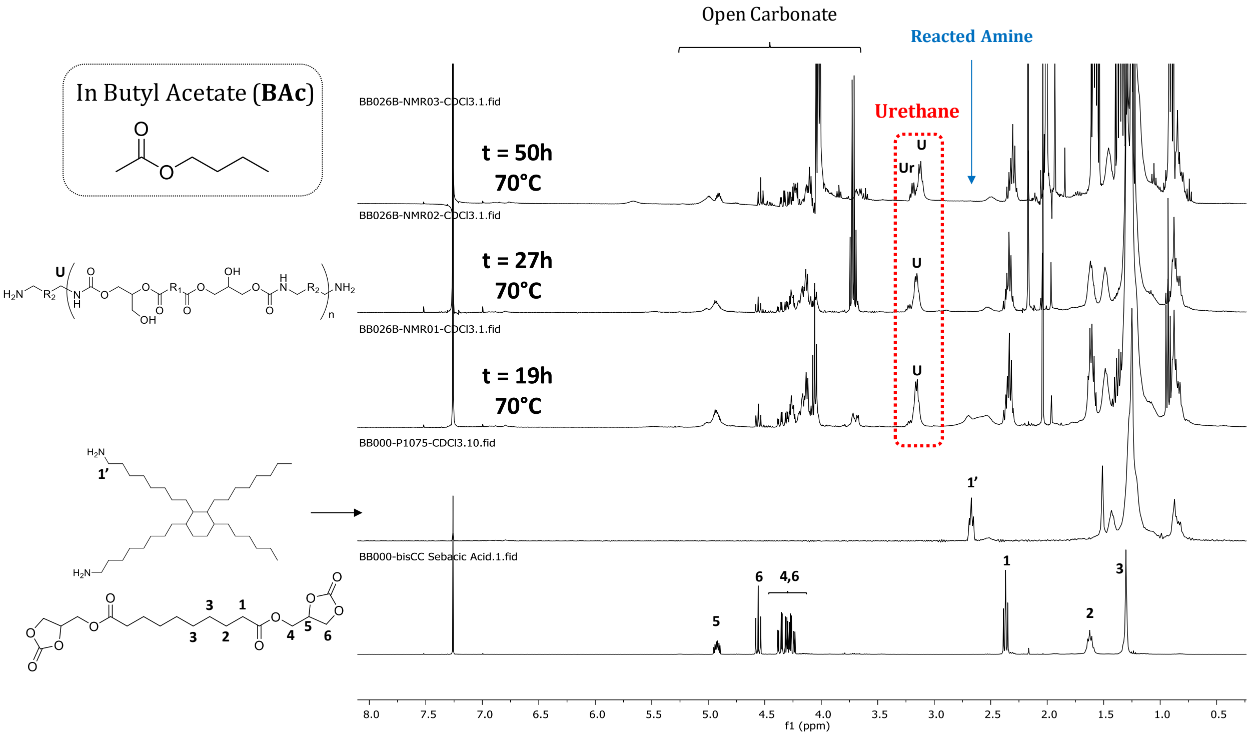
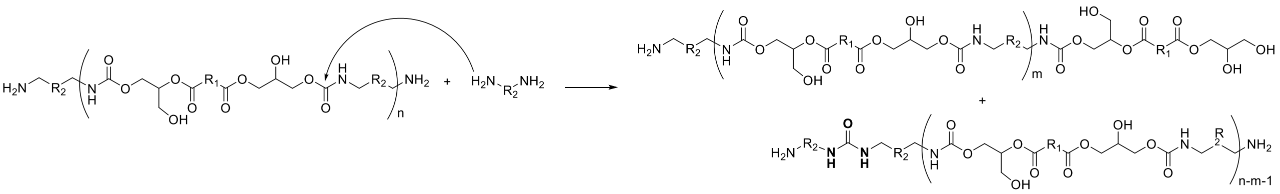


Figure S3: ^{1}H-NMR reaction follow-up (in $CDCl_3$) of the stoichiometric mixture of bisCC-C_{10} and P1075 in BAc

The comparison between Figure S1 and Figure S3 shows that the PHU formation occurred in BAc as opposed to BA. This is attested by the shift of the peak corresponding to the protons attached to the carbon in α-position of the amine and/or urethane moieties from 2.7 to 3.2 ppm in the ^{1}H-NMR spectra. In addition, the formation of urea at long reaction times could be noticed after 27h of reaction and was clearly visible after 50h. This is the result of the reaction of amine moieties onto the already formed carbanate moieties, as described by Cramail and coworkers,[2] a reaction that is known to be hard to avoid.



Scheme S2: Urea formation by reaction of an amine moiety onto the PHU backbone. Please note that for clarity purposes, only one amine moiety of the diamine was converted.

The reaction in BAc did not lead to the formation of the side-products that were observed in the case of BA, despite the longer reaction time. This may be due to the lack of vinyl moiety in BAc. In this way, the diamine remained available for the reaction with bisCC-C_{10}.

To support this hypothesis, P1075 was dissolved in BAc without the presence of bisCC-C_{10} and left at 70°C during 19h, and then at 90°C for 25h. The ^{1}H-NMR follow-up is presented in Figure S5 and clearly demonstrates that the amine did indeed not react with BAc.

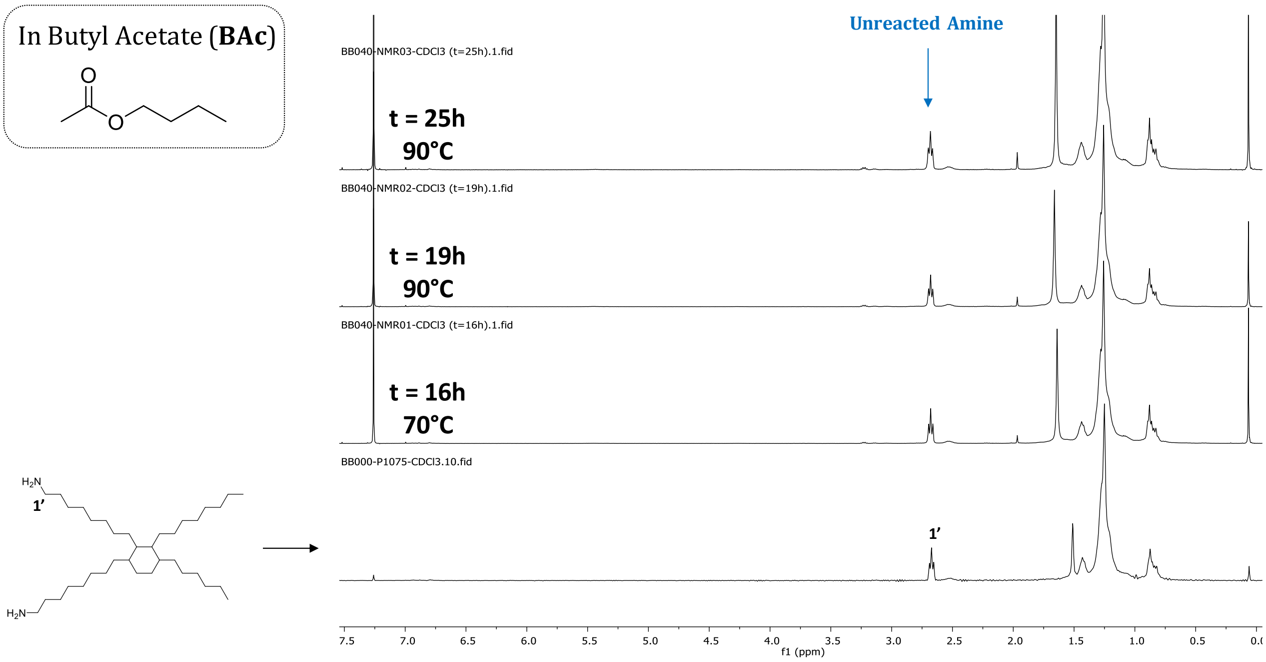


Figure S4: ^{1}H-NMR reaction follow-up (in $CDCl_3$) of P1075 in BAc

These results showed that acrylic monomers cannot be used as solvents for the synthesis of PHUs through aminolysis, because amines and acrylates undergo side-reactions. As methacrylates are in general less reactive than acrylates, it was decided to check if the side reactions could be avoided or at least minimized by using butyl methacrylate (BMA) instead of BA. The process was carried out under the same conditions than the ones utilized in the BA system (reaction at 70°C during 19h, and then further heating at 90°C during 23h). Figure S5 presents the evolution of the ^{1}H-NMR spectra.

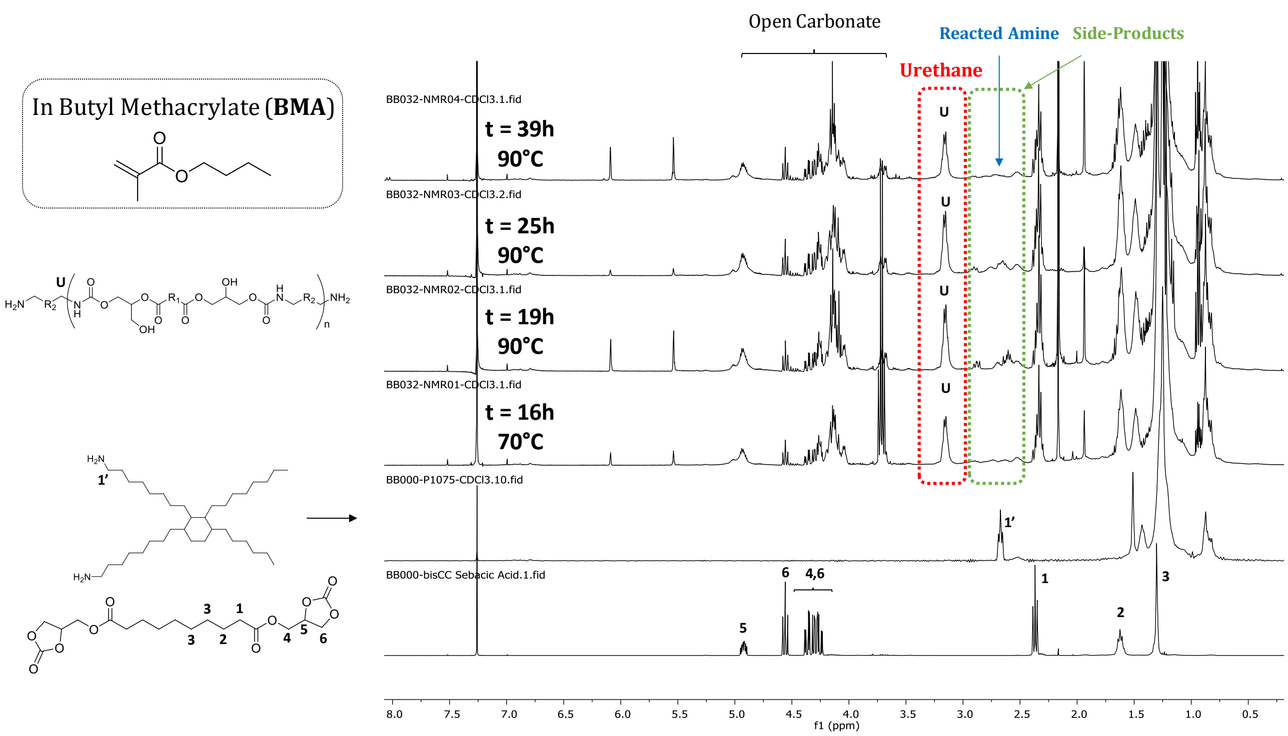


Figure S5: ^{1}H-NMR reaction follow-up (in CDCl$_3$) of the stoichiometric mixture of bisCC-C$_{10}$ and P1075 in BMA

Figure S5 shows that the amine peak at 2.6 ppm disappeared and that the peak corresponding to the urethane at 3.2 ppm appeared, which are the fingerprints of the formation of PHU. The reaction kinetics was relatively fast (less than 24h) and side reactions were not significant. This suggests that the extent of side reactions (and in particular *aza*-Michael addition) is strongly diminished when methacrylates are used, which is in accordance with the results reported by Schimpf *et al.*[5] They quantified the extent of the *aza*-Michael addition up to 10% (and 90% of hydroxyurethane) in the bulk reaction of stoichiometric amounts of glycerol carbonate methacrylate with primary amines at temperatures ranging from 60 to 100°C.

To further test these results, P1075 alone was put to react in BMA to see whether any trace of side reaction could be noticed (17h at 70°C followed by 22h at 90°C). The ^{1}H-NMR follow-up of the reaction is presented in Figure S6. It can be seen that almost no reaction was observed and the amine remained unreacted for 16h at 70°C followed by 9h at 90°C (t=25h). After such a time, traces of new forming products could be identified in the NMR spectra around 2.5 and 2.8 ppm ranges. Nevertheless, as the formation of PHU occurs at shorter process times and lower reaction temperatures, methacrylates could be safely used as solvents in the formation of PHU by aminolysis reaction between diamines and cyclic carbonates.

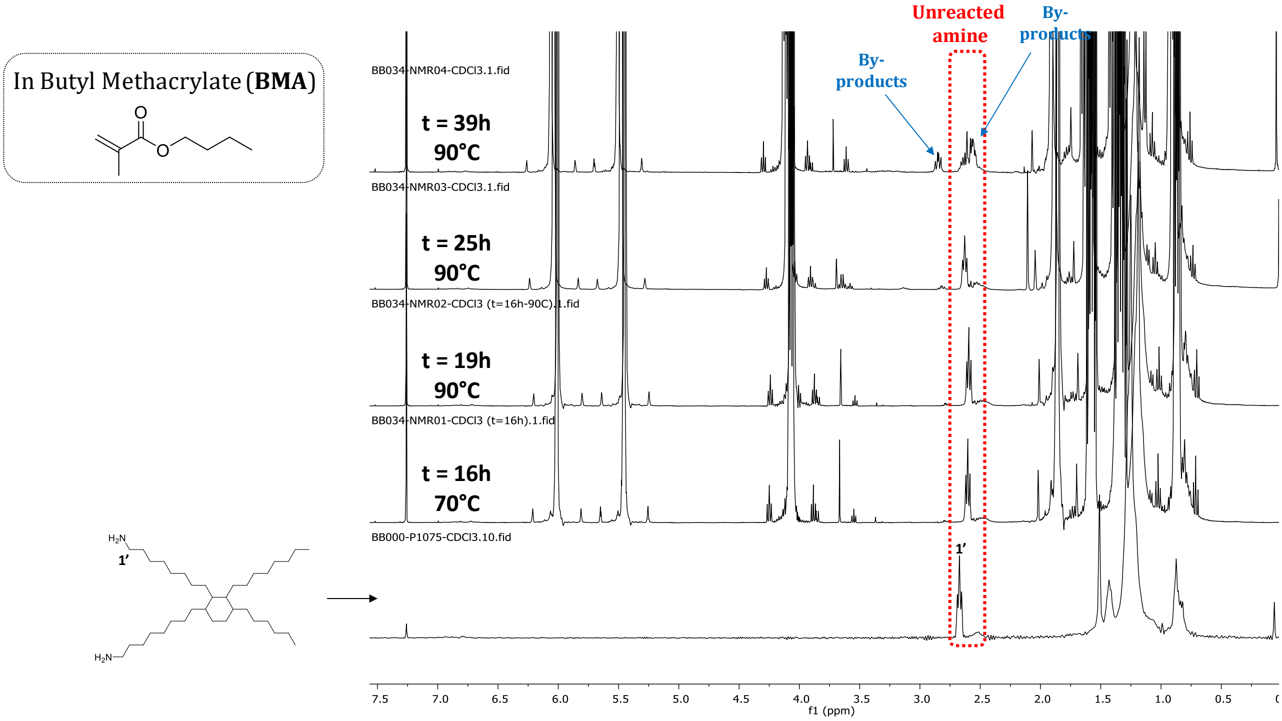


Figure S6: ^{1}H-NMR reaction follow-up (in $CDCl_3$) of P1075 in BMA

7.2. Solubility

As the aminolysis reaction could be carried out in BMA without occurrence of side reactions, the solubility of bisCC-C_{10}, diamines and the resulting PHUs in BMA was determined. The diamines used were 1,4-butanediamine (4DA), 1,6-haxanediamine (6DA), 1,10-diaminodecane (10DA), 1,12-diaminododecane (12DA), 1,3-cyclohexanebis(methylamine) (CycloDA), Priamine™ 1075 (P1075) (Scheme S3).

The solubility of the NIPU monomers and that of the resulting PHU was determined. For this, the diamines were pre-heated in BMA during 30 min before the bisCC-C_{10} was added. The monomers were added so that the total concentration of PHU monomers reached 10wt% of the resulting mixture. The reaction was then left to proceed at 80°C during 24h under magnetic stirring.

The influence of the targeted polymer chain length was also investigated by varying the cyclic carbonate/diamine ratio. Polymerizations involving stoichiometric amounts of monomers were also performed and will be labeled DP ∞. According to Carother's theory,[7] deviations from the stoichiometric ratio reduces the degree of polymerization (DP) of the resulting PHU chain. An excess of diamine was used in order to target DPs of 2 and 5. According to Carother's theory, the degree of polymerization, DP, is given by

$$\mathrm{DP} = \frac{1 + \mathrm{r}}{1 + \mathrm{r} - 2\mathrm{rp}} \tag{1}$$

where p is the conversion and r is the stoichiometric ratio between A-A and B-B reactants

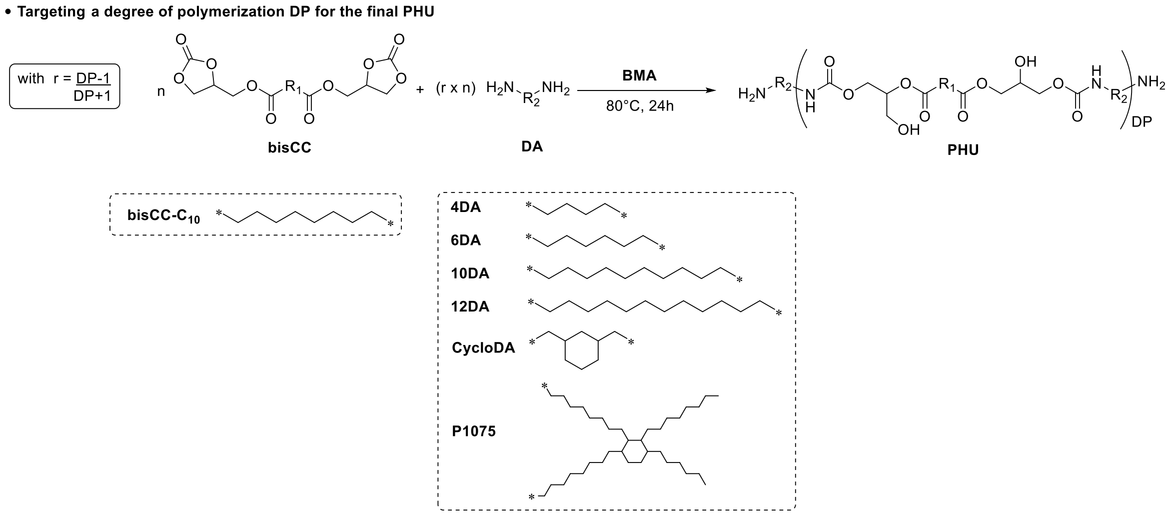
$$r = \frac{n_{\mathrm{CyclicCarbonate}}}{n_{\mathrm{NH2}}} \tag{2}$$

At complete conversion (p = 1), eq. 1 reduces to

$$\mathrm{DP} = \frac{1 + r}{1 - r} \tag{3}$$

Which allows the calculation of the excess of diamine to achieve a given degree of polymerization.

$$r = \frac{\mathrm{DP} - 1}{\mathrm{DP} + 1} \tag{4}$$



Scheme S3: Synthesized NIPUs in BMA for solubility studies (10wt% of PHU monomers, T=80°C, 24h reaction)

It is firstly important to mention that in the utilized conditions, only partial solubility of the monomers could be obtained.

Regarding the diamines, the aliphatic diamines (4DA, 6DA, 10DA, 12DA), which are white powders, were not fully soluble after pre-heating during 30 min (time at which the bisCC was added). After adding bisCC-C_{10}, the reactions were left at 80°C to react during 24h to see whether the polymerization would occur by progressive consumption of the monomers (note that bisCC-C_{10} is soluble is these conditions after 30 min at 80°C in BMA).

After reaction, the vials were removed from the oil bath and the solubility of the resulting polymer was checked. Table S1 summarizes the results and Figure S7 displays pictures of the vials in the case in which bisCC-C_{10} was copolymerized with different diamines using a stoichiometric ratio of the reactive moieties. As can be observed, only the formulation involving the branched P1075 led to a soluble polymer at 80°C, a result that was already known from Section 7.1. The solubility was maintained at room temperature (RT).

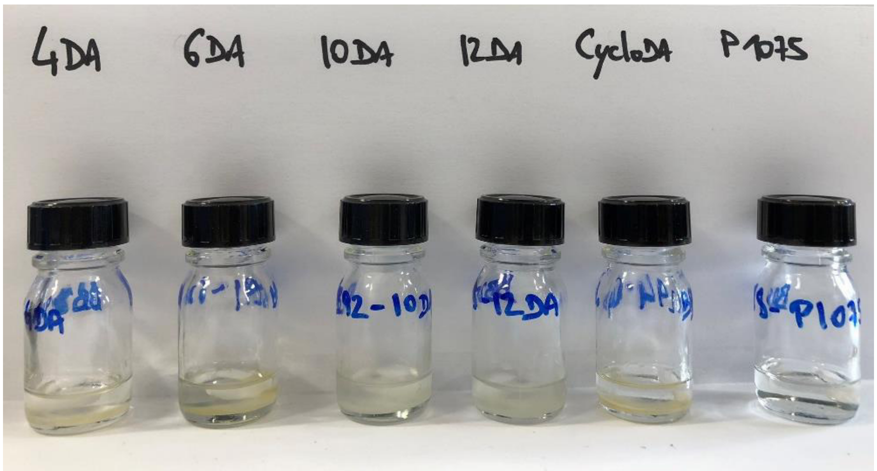


Figure S7: Typical resulting mixtures after PHU formation (10 wt% solids) in BMA

Table S1: PHU solubilities in BMA depending on their chemical structures and targeted DPs (10wt% PHU, 24h reaction, T = 80°C)

	bisCC-C_{10}		
	Targeted DP 2	Targeted DP 5	Targeted DP ∞
4DA	✗	✗	✗
6DA	✗	✗	✗
10DA	✗	✗	✗
12DA	✗	✗	✗
CycloDA	✗	✗	✗
P1075	✓	✓	✓

✓ : soluble
✗ : not soluble

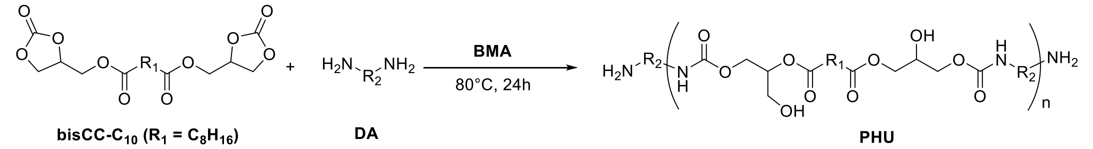
The reason for the solubility of the PHUs with the branched P1075 may be that this monomer provided very high flexibility to the resulting PHU.

Regarding the other formulations, none of them yielded a soluble product, whatever the targeted polymer structure or targeted degree of polymerization. No further characterization was undertaken because those products could not be of use for the formation of NIPU-Acrylic hybrids.

Building upon those outcomes, it appeared quite clear that the introduction of a branched structure was essential in order to achieve solubility of the PHU in BMA, necessary condition for the synthesis of H-NIPUs. However, ‘classical’ polyurethanes are segmented materials that are nano-phase segregated. This is done by copolymerizing altogether hard and soft segments (namely short and long comonomers). As a consequence, the introduction of aliphatic segments in the PHU formulation could be of interest in order to access H-NIPU of various properties.

Different PHU structures were targeted by copolymerization of bisCC-C_{10} with different ratios of 4DA, 10DA and P1075. In all the cases, the total concentration of PHU was 10 wt% and stoichiometric ratio of the reactive moieties was used. Table S2 summarizes these PHUs and their solubility in BMA at 80°C right after reaction and after cooling at room temperature.

Table S2: PHU copolymers' solubilities in BMA depending on their chemical structures (10wt% PHU, Targeted stoichiometric ratio of the reactive moieties, 24h, T = 80°C)



Ref	PHU		PHU	
	Aliphatic DA	P1075[a]	Soluble at RT	Soluble at 80°C
1	**4DA**	0%	✗	✗
2	**4DA**	25%	✗	✗
3	**4DA**	50%	✗	✗
4	**4DA**	75%	✗	✓
5		100%	✓	✓
6	**10DA**	0%	✗	✗
7	**10DA**	25%	✗	✗
8	**10DA**	50%	✗	✓
9	**10DA**	75%	✗	✓
10		100%	✓	✓

✓ : soluble

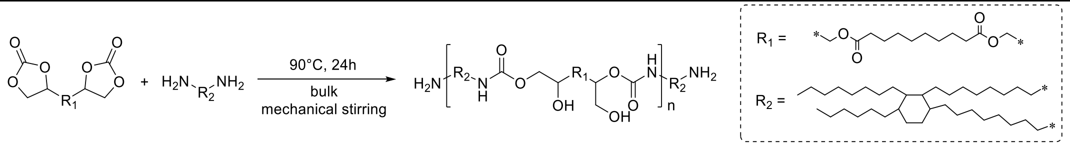
✗ : not soluble

[a] the molar fraction of **P1075** is provided as percentage of the total amount of diamine that has to be added for the stoichiometric ratio to be respected

Table S2 shows that at least 75mol% of P1075 is necessary for the PHU to be soluble in BMA at 80°C. It could also be noticed that the length of the aliphatic DA had almost no effect.

The solubility experiments detailed above were restricted to 10 wt%. However, in many cases, higher concentrations of PHU may be desired. Therefore, the solubility of PHU synthesized in Chapter 2 by reacting bisCC-C_{10} with P1075 in bulk was determined. To do so, the monomers were added in stoichiometric amounts in a Schlenk vessel and left under mechanical stirring at 90°C during 24h. The resulting PHU were then incorporated into BMA and left under magnetic stirring for 1h. The results are presented in Table S3.

Table S3: Solubility of the PHU (made of stoichiometric amounts of bisCC-C_{10} and P1075) in BMA depending on the concentration and the temperature



Concentration (PHU/BMA)	**50wt%**			**40wt%**	
Temperature	80°C	40°C	RT	40°C	RT
Solubility	✓	✗	✗	✓	✗

✓ : soluble

✗ : not soluble

Interestingly, it can be noticed that high concentrations of PHU in BMA could be reached in this way. Up to 50wt% of PHU could be solubilized provided the temperature was high enough (80°C in this case).

7.3. Miniemulsion polymerization using thermal initiators

7.3.1. Formulations with thermal initiators

Table S4: Formulation used in the Run S1

	Reference	**S1**	
	N2-flushing Time	**40 min**	
		Before Initiation	***After Initiation***
Basic recipe	PHU	0.961 g	
	(/PHU+BMA)	***10.0 wt%***	***9.0 wt%***
	BMA	8.652 g	
	(/PHU+BMA)	***90.0 wt%***	***91.0 wt%***
	SA	0.401 g	
	wbo	***4.0 wt%***	***3.63 wt%***
	Dowfax™ 2A1	0.100 g	
	wbo	***1.00 wt%***	***0.91 wt%***
	Water	9.897 g	
Post-Stabilization	Dowfax™ 2A1	0.100 g	
	wbo	***1.00 wt%***	***0.91 wt%***
	Water	0.832 g	
Initiation	BPO		0.045 g
	(/ BMA+SA)		***0.46 wt%***
	BMA		1.040 g
	TOTAL	22.028 g	
Solid Content (wt%)		**51.3**	

Table S5: Formulation used in the Run S2

	Reference	**S2**	
	N2-flushing Time	**40 min**	
		Before Initiation	***After Initiation***
Basic recipe	PHU	0.947 g	
	(/PHU+BMA)	***10.0 wt%***	***9.1 wt%***
	BMA	8.526 g	
	(/PHU+BMA)	***90.0 wt%***	***90.9 wt%***
	SA	0.395 g	
	wbo	***4.0 wt%***	***3.64 wt%***
	Dowfax™ 2A1	0.101 g	
	wbo	***1.02 wt%***	***0.93 wt%***
	Water	9.904 g	
Post-Stabilization	Dowfax™ 2A1	0.099 g	
	wbo	***1.01 wt%***	***0.92 wt%***
	Water	0.835 g	
Initiation	AIBN		0.046 g
	(/ BMA+SA)		***0.46 wt%***
	BMA		0.985 g
	TOTAL	21.838 g	
Solid Content (wt%)		**50.8**	

Table S6: Formulation used in the Run S3

	Reference	**S3**	
	N2-flushing Time	**25 min**	
		Before Initiation	***After Initiation***
Basic recipe	PHU	0.820 g	
	(/PHU+BMA)	***10.0 wt%***	***8.7 wt%***
	BMA	7.376 g	
	(/PHU+BMA)	***90.0 wt%***	***91.3 wt%***
	SA	0.342 g	
	wbo	***4.0 wt%***	***3.49 wt%***
	Dowfax™ 2A1	0.100 g	
	wbo	***1.17 wt%***	***1.02 wt%***
	Water	9.901 g	
Post-Stabilization	Dowfax™ 2A1	0.100 g	
	wbo	***1.18 wt%***	***1.03 wt%***
	Water	0.857 g	
Initiation	AIBN		0.043 g
	(/ BMA+SA)		***0.48 wt%***
	BMA		1.248 g
	TOTAL	22.028 g	
Solid Content (wt%)		**51.3**	

Table S7: Formulation used in the Run S4

	Reference	**S4**	
	N2-flushing Time	**30 min**	
		Before Initiation	***After Initiation***
Basic recipe	PHU	0.966 g	
	(/PHU+BMA)	***10.0 wt%***	***9.1 wt%***
	BMA	8.670 g	
	(/PHU+BMA)	***90.0 wt%***	***90.9 wt%***
	SA	0.402 g	
	wbo	***4.0 wt%***	***3.64 wt%***
	Dowfax™ 2A1	0.100 g	
	wbo	***1.00 wt%***	***0.91 wt%***
	Water	9.903 g	
Post-Stabilization	Dowfax™ 2A1	0.201 g	
	wbo	***2.00 wt%***	***1.82 wt%***
	Water	1.283 g	
Initiation	AIBN		0.043 g
	(/ BMA+SA)		***0.43 wt%***
	BMA		1.001 g
	TOTAL	22.569 g	
Solid Content (wt%)		**50.4**	

Table S8: Formulation used in the Run S5

	Reference	**S5**	
	N2-flushing Time	**25 min**	
		Before Initiation	***After Initiation***
Basic recipe	PHU	0.887 g	
	(/PHU+BMA)	***10.0 wt%***	***9.0 wt%***
	BMA	7.965 g	
	(/PHU+BMA)	***90.0 wt%***	***90.9 wt%***
	MAAc	0.104 g	
	wbo	***1.12 wt%***	***1.01 wt%***
	SA	0.369 g	
	wbo	***4.0 wt%***	***3.58 wt%***
	Dowfax™ 2A1	0.100 g	
	wbo	***1.07 wt%***	***0.97 wt%***
	Water	9.898 g	
Post-Stabilization	Dowfax™ 2A1	0.100 g	
	wbo	***1.08 wt%***	***0.97 wt%***
	Water	0.843 g	
Initiation	AIBN		0.043 g
	(/ BMA+SA)		***0.46 wt%***
	BMA		0.709 g
	TOTAL	25.588 g	
Solid Content (wt%)		**38.0**	

Table S9: Formulation used in the Run S6

	Reference	**S6**	
	N2-flushing Time	**20 min**	
		Before Initiation	***After Initiation***
Basic recipe	PHU	0.844 g	
	(/PHU+BMA)	***10.0 wt%***	***9.2 wt%***
	BMA	7.585 g	
	(/PHU+BMA)	***90.0 wt%***	***90.8 wt%***
	SA	0.352 g	
	wbo	***4.0 wt%***	***3.71 wt%***
	Dowfax™ 2A1	0.099 g	
	wbo	***1.13 wt%***	***1.05 wt%***
	Water	14.901 g	
Post-Stabilization	Dowfax™ 2A1	0.100 g	
	wbo	***1.14 wt%***	***1.05 wt%***
	Water	0.965 g	
Initiation	AIBN		0.043 g
	(/ BMA+SA)		***0.39 wt%***
	BMA		1.004 g
	TOTAL	21.314 g	
Solid Content (wt%)		**49.6**	

7.3.2. Results and discussion

Table S10 summarizes the experiments carried out using the thermal initiators (benzoyl peroxide, BPO; and azobisisobutyronitrile, AIBN). In all cases, the initiators were added as a shot after the miniemulsion prepared by sonication had been flushed with nitrogen and equilibrated at a temperature of 70°C. BPO and AIBN were solubilized in a small amount of neat BMA, as described in the formulations below. The targeted solids content was 50 wt.%, with a NIPU content of 10 wt%, based on monomers. After adding the initiator, regular sampling was performed in order to monitor the conversion (by gravimetry) as well as the evolution of the particle size, polydispersity index (PDI) and number of particles (by DLS).

Table S10: Miniemulsion polymerizations carried out using thermal radical initiators

Ref.	**Solid Content [wt%]**	**% NIPU [wt%]**	**Initiator** (wt%)	**Post-Stab. [wt%]**	**Meth. Acid [wt%]**	**Reaction Time [h]**	**Conv.[a] [%]**	**Coagulation [a] [wt%]**	**Particle Size[b] [nm]**
S1	47.8	10	**BPO** (0.5)	1	-	5h30	45	0	195
S2	47.4	10	**AIBN** (0.5)	1	-	5h30	>99	31	170
S3	47.2	10	**AIBN** (0.5)	1	-	1h30	>99	12.7	155
S4	49.1	10	**AIBN** (0.5)	2	-	1h30	>99	12.2	150
S5	48.7	10	**AIBN** (0.5)	1	1	1h30	>99	21.9	148
S6	37.2	10	**AIBN** (0.5)	1	-	3h	>99	2.1	130

[a] Measured by gravimetry

[b] Determined by DLS

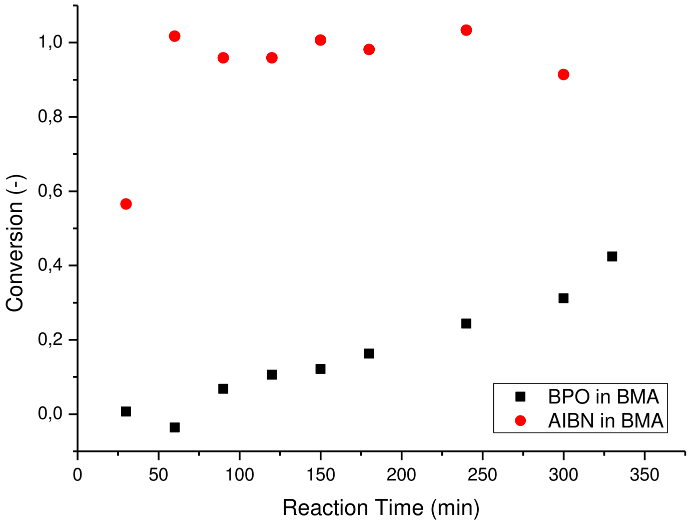


Figure S8: Conversion of BMA obtained by gravimetry upon polymerization with different radical initiators (BPO, run S1; AIBN, run S2). NIPU content: 10wt%. Solids content: 50wt%.

Figure S8 shows that the polymerization carried out with BPO presented a long inhibition period and only reached 45% after 5.5 hours. This is likely due to the difficulties encountered by the very hydrophobic BPO to reach the miniemulsion droplets/particles. The oil soluble AIBN reached complete conversion in less than 1 hour. The significant solubility of AIBN in water (0.04g/100g H_2O [8]) was the likely reason for the fast transfer of this initiator to the droplets. However, a severe coagulation was observed. Comparison between experiments S2 and S3 shows that for AIBN a substantial fraction of the coagulum was formed during the long time in which the latex was kept at the reaction temperature (70°C). Attempts to improve the colloidal stability of the dispersion were carried out by increasing the amount of surfactant used in the post-stabilization (run S4) and by using methacrylic acid (MAA) in the formulation (run S5). MAA is highly hydrophilic and upon polymerization tends to concentrate on the surface of the particles increasing the colloidal stability. However, although the reactions proceed fast (Figure S9), no improvement in colloidal stability was observed.

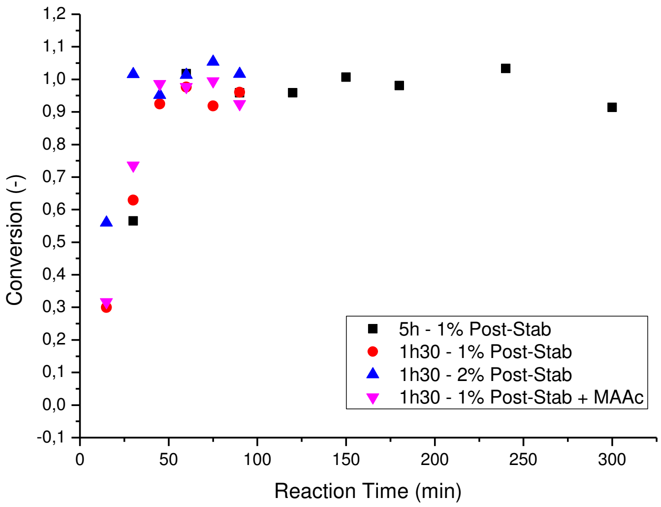


Figure S9: Evolution of the BMA conversion in runs S3-5. NIPU content: 10 wt.%. Solid content: 50 wt.%.

7.4. Formulations with redox initiators

For feeding purposes, aqueous solutions of TBHP (0.0157 g.mL^{-1}) and AsA (0.0151 g.mL^{-1}) solution were prepared.

Table S11: Formulations used in the series containing 0wt% NIPU (based on BMA)

	N2-Flushing Time	**40 min**	**35 min**	**25 min**
	Feeding Time	**2h**	**2h30**	**3h**
Basic recipe	PHU	0 g	0 g	0 g
	(/PHU+BMA)	***0 wt%***	***0 wt%***	***0 wt%***
	BMA	7.709 g	11.519 g	7.585 g
	(/PHU+BMA)	***100 wt%***	***100 wt%***	***100.0 wt%***
	SA	0.321 g	0.480 g	0.316 g
	wbo	***4.0 wt%***	***4.0 wt%***	***4.0 wt%***
	Dowfax™ 2A1	0.080 g	0.120 g	0.079 g
	wbo	***1.00 wt%***	***1.00 wt%***	***0.99 wt%***
	Water	11.923 g	17.881 g	11.773 g
Post-Stabilization	Dowfax™ 2A1	0.081 g	0.119 g	0.079 g
	wbo	***1.00 wt%***	***0.99 wt%***	***1.00 wt%***
	Water	0.595 g	0.648 g	0.545 g
Initiation	TBHP	0.0038 g	0.0057 g	0.0038 g
	(/ BMA+SA)	***0.05 wt%***	***0.05 wt%***	***0.05 wt%***
	AsAc	0.0037 g	0.0056 g	0.0037 g
	(/ BMA+SA)	***0.05 wt%***	***0.05 wt%***	***0.05 wt%***
	Water	0.492 g	0.734 g	0.492 g
	TOTAL	21.209 g	31.512 g	20.877 g
Solid Content (wt%)		**37.9**	**37.2**	**37.0**

Table S12: Formulations used in the series containing 10wt% NIPU (based on the mixture NIPU+BMA)

	N2-Flushing Time	**60 min**	**40 min**	**35 min**
	Feeding Time	**2h**	**2h30**	**3h**
Basic recipe	PHU	0.768 g	1.163 g	0.772 g
	(/PHU+BMA)	***10.0 wt%***	***10.1 wt%***	***10.0 wt%***
	BMA	6.914 g	10.369 g	6.953 g
	(/PHU+BMA)	***90.0 wt%***	***89.9 wt%***	***90.0 wt%***
	SA	0.320 g	0.481 g	0.322 g
	wbo	***4.0 wt%***	***4.0 wt%***	***4.0 wt%***
	Dowfax™ 2A1	0.080 g	0.120 g	0.080 g
	wbo	***1.00 wt%***	***1.00 wt%***	***0.99 wt%***
	Water	11.927 g	17.881 g	11.924 g
Post-Stabilization	Dowfax™ 2A1	0.081 g	0.120 g	0.081 g
	wbo	***1.01 wt%***	***1.00 wt%***	***1.00 wt%***
	Water	0.695 g	0.766 g	0.670 g
Initiation	TBHP	0.0038 g	0.0058 g	0.0038 g
	(/ BMA+SA)	***0.05 wt%***	***0.05 wt%***	***0.05 wt%***
	AsAc	0.0037 g	0.0056 g	0.0037 g
	(/ BMA+SA)	***0.05 wt%***	***0.05 wt%***	***0.05 wt%***
	Water	0.492 g	0.739 g	0.492 g
	TOTAL	21.280 g	31.650 g	21.302 g
Solid Content (wt%)		**37.6**	**38.0**	**37.8**

Table S13: Formulations used in the series containing 20wt% NIPU (based on the mixture NIPU+BMA)

	N2-flushing time	**60 min**	**60 min**	**60 min**
	Feeding Time	**2h**	**2h30**	**3h**
Basic recipe	PHU	2.112 g	3.070 g	2.117 g
	(/PHU+BMA)	***20.0 wt%***	***20.0 wt%***	***20.0 wt%***
	BMA	8.427 g	12.309 g	8.444 g
	(/PHU+BMA)	***80.0 wt%***	***80.0 wt%***	***80.0 wt%***
	SA	0.439 g	0.640 g	0.440 g
	wbo	***4.0 wt%***	***4.0 wt%***	***4.0 wt%***
	Dowfax™ 2A1	0.110 g	0.160 g	0.110 g
	wbo	***1.00 wt%***	***1.00 wt%***	***1.00 wt%***
	Water	16.397 g	23.853 g	16.387 g
Post-Stabilization	Dowfax™ 2A1	0.105 g	0.160 g	0.111 g
	wbo	***0.96 wt%***	***1.00 wt%***	***1.00 wt%***
	Water	0.638 g	1.101 g	0.650 g
Initiation	TBHP	0.0042 g	0.0077 g	0.0042 g
	(/ BMA+SA)	***0.05 wt%***	***0.06 wt%***	***0.05 wt%***
	AsAc	0.0041 g	0.0075 g	0.0041 g
	(/ BMA)	***0.05 wt%***	***0.06 wt%***	***0.05 wt%***
	Water	0.542 g	0.985 g	0.542 g
	TOTAL	28.778 g	42.293 g	28.809 g
Solid Content (wt%)		**38.1**	**37.9**	**38.1**

Table S14: Formulations used in the series containing 30wt% NIPU (based on the mixture NIPU+BMA)

	N2-flushing time	**60 min**	**90 min**	**45 min**
	Feeding Time	**2h**	**2h30**	**3h**
Basic recipe	PHU	2.206 g	3.354 g	2.162 g
	(/PHU+BMA)	***30.0 wt%***	***30.0 wt%***	***30.0 wt%***
	BMA	5.152 g	7.831 g	5.048 g
	(/PHU+BMA)	***70.0 wt%***	***70.0 wt%***	***70.0 wt%***
	SA	0.307 g	0.466 g	0.301 g
	wbo	***4.0 wt%***	***4.0 wt%***	***4.0 wt%***
	Dowfax™ 2A1	0.076 g	0.116 g	0.075 g
	wbo	***0.99 wt%***	***1.00 wt%***	***1.00 wt%***
	Water	11.327 g	17.370 g	11.177 g
Post-Stabilization	Dowfax™ 2A1	0.077 g	0.117 g	0.075 g
	wbo	***1.01 wt%***	***1.00 wt%***	***1.00 wt%***
	Water	0.620 g	0.851 g	0.677 g
Initiation	TBHP	0.0038 g	0.0049 g	0.0038 g
	(/ BMA+SA)	***0.07 wt%***	***0.06 wt%***	***0.07 wt%***
	AsAc	0.0037 g	0.0048 g	0.0037 g
	(/ BMA+SA)	***0.07 wt%***	***0.06 wt%***	***0.07 wt%***
	Water	0.492 g	0.630 g	0.492 g
	TOTAL	20.265 g	30.745 g	20.015 g
Solid Content (wt%)		**38.8**	**37.9**	**38.5**

7.5. SEC-MALLS Traces

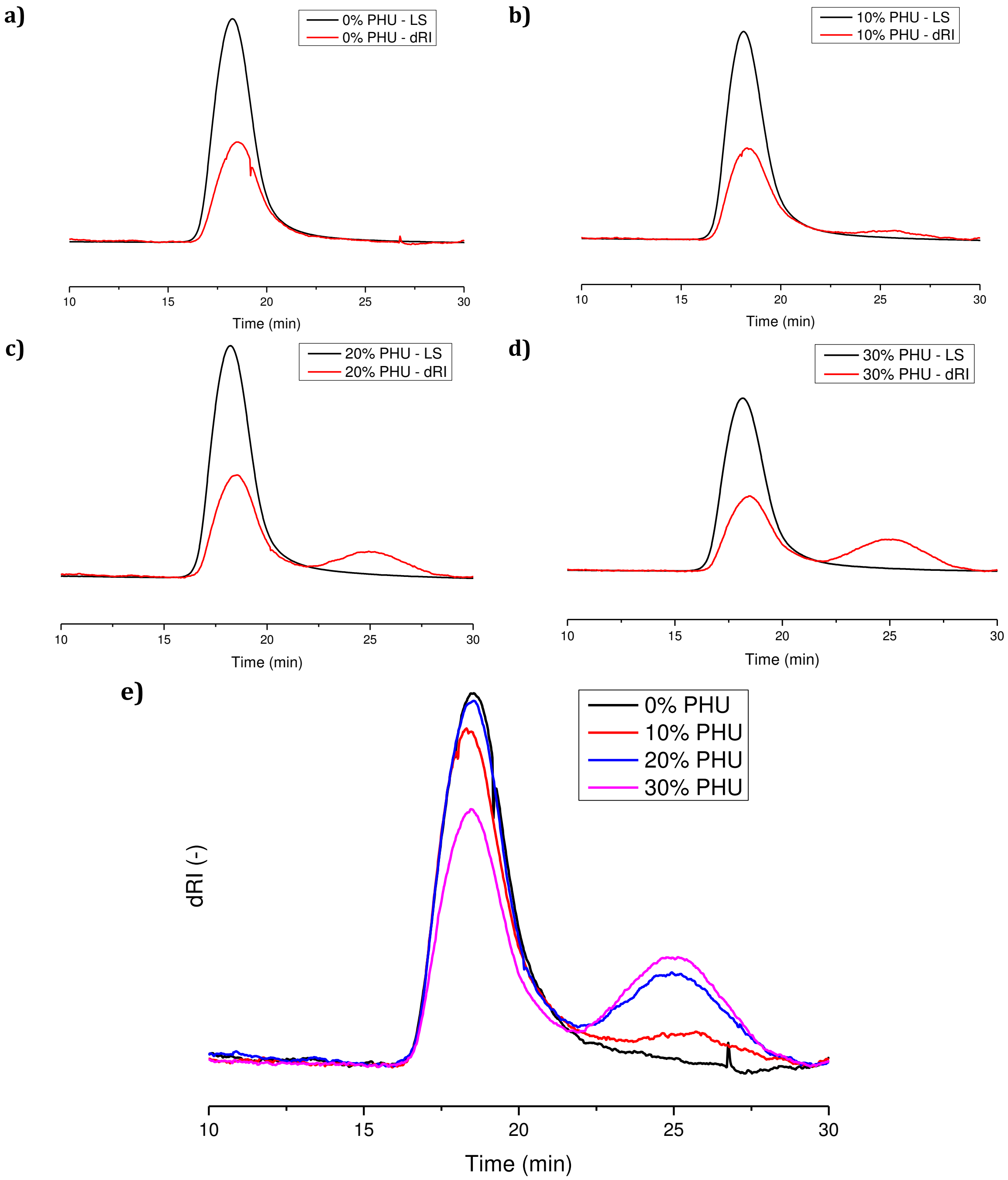


Figure S10: SEC-MALLS traces of the non cross-linked hybrids containing a) 0% PHU, b) 10% PHU, c) 20% PHU and d)30% PHU. e) provides the stacked traces obtained from the refractive index signal for hybrids containing 0% to 30% PHU

7.6. DSC Traces

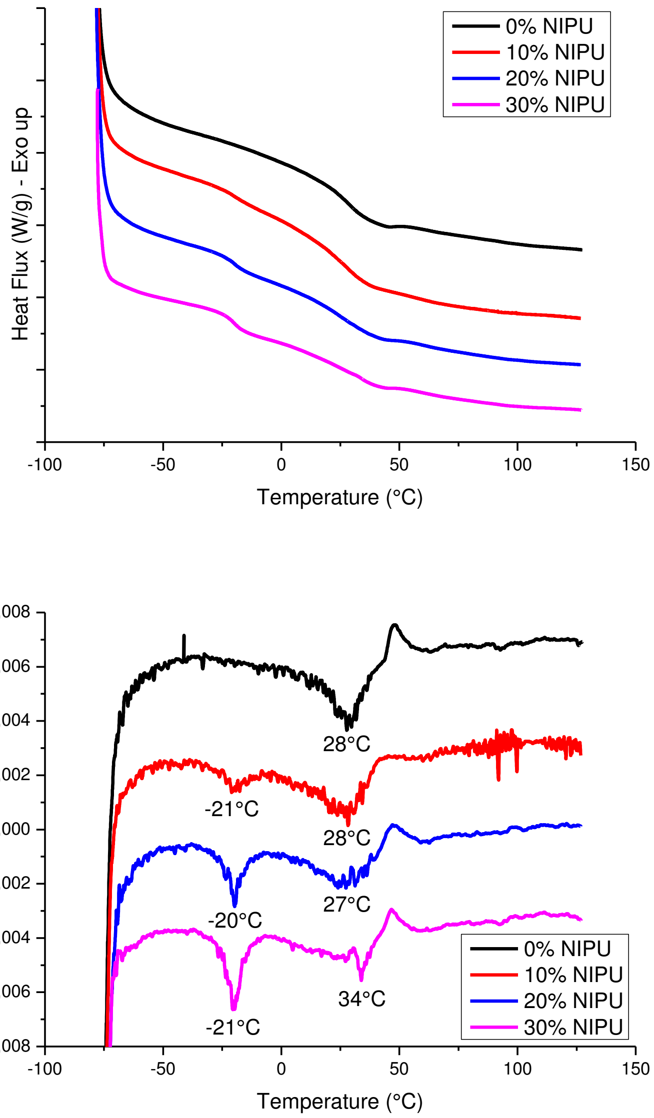
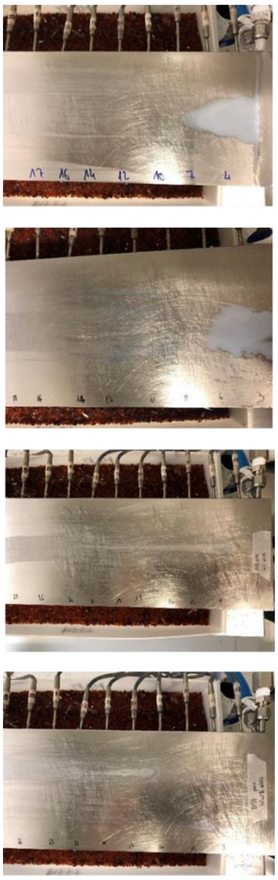


Figure S11: DSC traces (top) and first derivative of the DSC traces (bottom) of the films cast from the latexes fed during 2h30 with AsAc – 1st heating ramp (10°C.min^{-1})

7.7. Minimum Film Forming Temperature (MMFT)



	0% NIPU	10% NIPU	20% NIPU	30% NIPU
MMFT_NoCut[a]	20°C	24°C	15°C	< 7°C
MFFT_Cut[b]	30°C	24°C	15°C	< 7°C

Plasticizing effect of PHU on the final film

[a] Measured staight after drying – when a clear coat is observed

[b] Measured after cutting the film until it was not powdery anymore

Figure S12: Measurement of the MFFT of the latexes fed during 2h30 with AsAc

CHAPTER 4

THE ROLE OF GRAFTING IN THE SYNTHESIS OF ISOCYANATE-FREE POLY(HYDROXY URETHANE)S -POLYMETHACRYLATE HYBRID MATERIALS *VIA* MINIEMULSION

Keywords: Poly(Hydroxy)urethanes - PHUs
Bio-based Polymers
Crosslinking
PU-Acrylic Hybrid
Miniemulsion
Coatings

Table of content

1. Introduction 205
2. Experimental 206
   2.1. Materials and methods 206
   2.2. Synthesis of waterborne grafted PHU-(meth)acrylic hybrids 206
   2.3. Characterization 211
   2.4. Film casting 213
3. Results and discussion 213
   3.1. Synthesis of the functionalized PHUs 213
   3.1.1. Methacrylate-terminated PHUs 213
   3.1.2. Methacrylate groups distributed along the PHU chains (multifunctionalized) 218
   3.2. Synthesis of the hybrid latexes 221
   3.3. Film properties 225
4. Conclusions 230
5. References 232
6. Shortened forms 235
7. Supporting Information 236
   7.1. monoCC-GMA – Carbonated Glycidyl Methacrylate 236
   7.2. Telechelically-functionalized PHUs 236
   7.2.1. Formulations 236
   7.2.2. NMR Spectra 240
   7.3. Multi-functionalized PHUs 244
   7.4. Formulations used for the miniemulsions 245

1. Introduction

Polymer-polymer hybrids are used to access materials that present superior performance due to the synergistic combination of the properties of the constitutive polymers.[1–4]

Hybrid polyurethane-poly(meth)acrylic waterborne dispersions is one industrially relevant example of these materials. PUs provide the material superior mechanical properties such as toughness, flexibility and abrasion resistance[5–7] whereas the relatively low cost poly(meth)acrylics increase the outdoor and alkali resistance, as well as the pigment compatibility.[8–10] These dispersions find applications in interesting areas such as adhesives[11–13] and/or coatings.[14,15] The field has been reviewed recently.[16] This review shows that the main strategies available to synthesize these hybrids are blending of PU and poly(meth)acrylic dispersions[17–21] and the synthesis of bi-phasic particles of complex architectures providing intimate contact and interaction between the two polymer materials.[19,20,29,21–28] However, blends yield films with poor mechanical properties because of the strong phase segregation, whereas engineered bi-phasic particles form films with better properties due to a more homogeneous distribution of the two polymers.

The final outlook of the review of Mehravar *et al.* highlights the challenge of reducing the environmental impact of the current industrial processes (based on the use of isocyanates) by developing isocyanate-free synthetic methods.[16] The field of water-based non-isocyanate poly(urethanes) (NIPUs) has been reviewed in Chapter 1. That review shows that in contrast with the field of classical PUs, the literature dealing with hybrid NIPU waterborne dispersions is very limited.[30–32] For the specific case of the NIPU-(meth)acrylic hybrids, only two articles where urethane functionalities are incorporated as pendant groups in the (meth)acrylic backbone (namely these polymers did not contain any polyurethane) have been reported.[30,31] Nevertheless, the incorporation of the pendant urethane moieties led to a remarkable simultaneous increase of Young modulus, tensile strength and elongation at break.

In the previous chapter, we developed a synthetic strategy to prepare waterborne PU/(meth)acrylic hybrids. Two complementary strategies were explored. The first one involved the formation of the isocyanate-free poly(hydroxy urethane)s (PHU) by aminolysis of cyclic-carbonate derivatives using (meth)acrylic monomers as reacting media, followed by the miniemulsification of the PHU/(meth)acrylatic solution in water. The final step of this process was the free radical polymerization of the (meth)acrylic monomers. However, this route was hampered by the *aza*-Michael reaction of the acrylates with the amines. Attempts to use methacrylates that are much less affected by this side reaction failed due to the low solubility of the cyclic carbonates and diamines in butyl methacrylate. In the second strategy, PHUs were first formed by bulk aminolysis of cyclic carbonates and a vegetable oil-based diamine (Priamine™ 1075). The PHUs were dissolved in (meth)acrylic monomers and the solution miniemulsified. The hybrid dispersion was obtained by polymerizing the monomers using tert-butyl hydroperoxide and ascorbic acid (TBHP/AsAc) as redox initiator system. The hybrid particles had a core-shell morphology with the PHU in the shell. The performance of these latexes was studied finding that the Young's modulus and stress at break decreased with the PHU content, but the strain at break and the toughness increased. TEM and AFM images of the films showed that a substantial phase segregation occurred with the formation of large PHU domains.

A way to avoid phase segregation is by grafting the PHU and the (meth)acrylic polymer, however, the effect on the performance is unknown. Thus, although in classical PU-(meth)acrylic hybrids the effect of grafting has been frequently studied the overall effect of grafting seems to be system dependent.[16] Although there are many examples showing an improvement of the mechanical properties with grafting,[22,33] there are also others where grafting has little effect.[14,15,34]

Therefore in this chapter, waterborne grafted PHU-poly(meth)acrylate hybrid dispersions were synthesized and the effect of grafting on the particle and film morphologies as well as on the mechanical properties of the films was investigated.

2. Experimental

2.1. Materials and methods

Butyl Methacrylate (BMA, 99%), Stearyl Acrylate (SA, 97%), tetrabutylammonium bromide (TBABr), glycidyl methacrylate (GMA, >97%) and methacrylic anhydride (94%) were obtained from Sigma. tert-butyl hydroperoxide (TBHP, >98%) was purchased at Panreac. Ascorbic acid (or Vitamin C, AsAc, >99.5%) was obtained from Fluka. Hydrochloric acid (HCl) in isopropanol (0.1 mol.L^{-1}) was purchased at Panreac. Croda kindly provided Priamine™ 1075 (P1075). Dow kindly provided Alkyl diphenyl oxide disulfonate (Dowfax™ 2A1, D2A1). Acetone was obtained from VWR Chemicals. All products and solvents (reagent grade) were used as received unless otherwise mentioned. Deionized water was used.

2.2. Synthesis of waterborne grafted PHU-(meth)acrylic hybrids

The synthesis of the waterborne grafted PHU-(meth)acrylic hybrids was carried out by dissolving poly(hydroxy urethane)s containing methacrylic groups in a mixture of BMA and SA (the PHU was 20wt% based on BMA, and SA was 4wt% based on the total organic phase), dispersing the solution in an aqueous solution of Dowfax 2A1 using sonication, and polymerizing the resulting miniemulsion employing a redox initiator system (TBHP/AsAc). Two different kinds of methacrylic functionalized PHUs were used.

The first one was telechelically modified with the methacrylic functionality. The synthesis is summarized in Scheme 1. The formulations used are given in Table S1 – S3 (Supporting Information). Amine-terminated poly(hydroxy urethane)s (PHUs) were synthesized by aminolysis between bisCC-C_{10} and P1075 using an excess of diamine, targeting a specific degree of polymerization. The reactions were performed at 90°C in bulk in a Schlenk tube using a helical shaped mechanical stirrer specifically designed to fit in the Schlenk vessel. The amount of NH_2-moieties was then measured by titration with HCl in isopropanol. The amine terminated PHUs were then reacted with the mono-carbonate derivative of glycidyl methacrylate (monoCC-GMA). The amount of monoCC-GMA added was half of the amine groups when a mono-functionalized PHU was aimed and the same quantity as the amine for the di-functionalized PHU (details in Tables S1 to S3). No catalyst was added for the polymerization reactions. No purification of the PHUs was performed after reaction.

In the case of mono-functionalized PHUs (labeled Batch #1), bisCC-C_{10} and P1075 reacted during 25.5h at 90°C. A degree of polymerization of 6 was targeted (Step #1). After titration of the excess-NH_2, a quantity of monoCC-GMA corresponding to half of the amount of this excess-NH_2 was added in the bulk and it was left to react during 21h at 90°C (Step #2).

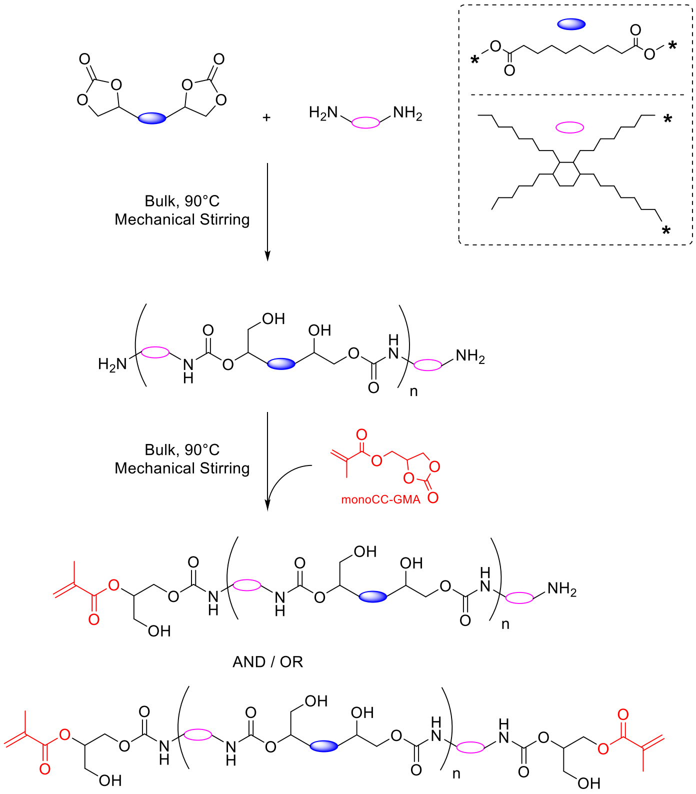
In the case of acryloyl-telechelic PHUs, two experimental protocols were implemented. In the first one (labeled Batch #2), bisCC-C_{10} and P1075 reacted during 27h at 90°C. A degree of polymerization of 6 was targeted (Step #1). After titration of the excess-NH_2, a quantity of monoCC-GMA corresponding to this excess-NH_2 was added in the bulk and it was left to react during 21h at 90°C (Step #2). In the second one (labeled Batch #3), bisCC-C_{10} and P1075 reacted during 4h at 90°C. A degree of polymerization of 10 was targeted (Step #1). A quantity of monoCC-GMA corresponding to the theoretical excess-NH_2 was added in bulk and it was left to react during 20h at 90°C (Step #2).

The reason for the difference in the experimental protocol is that the degree of polymerization of the NH_2-terminated PHUs (Step #1) was not well controlled in Batch #1 and Batch #2. Indeed, titration of the excess-NH_2 indicated that the excess of NH_2 moieties at the end of Step #1 was lower than expected, suggesting that the NH_2 moieties had disappeared, probably due to side-reactions. During Batch #3, the reaction time of Step #1 was reduced to avoid the occurrence of side reactions. Moreover, monoCC-GMA was added at a quantity corresponding to the theoretical excess-NH_2 to make sure all of them could react.

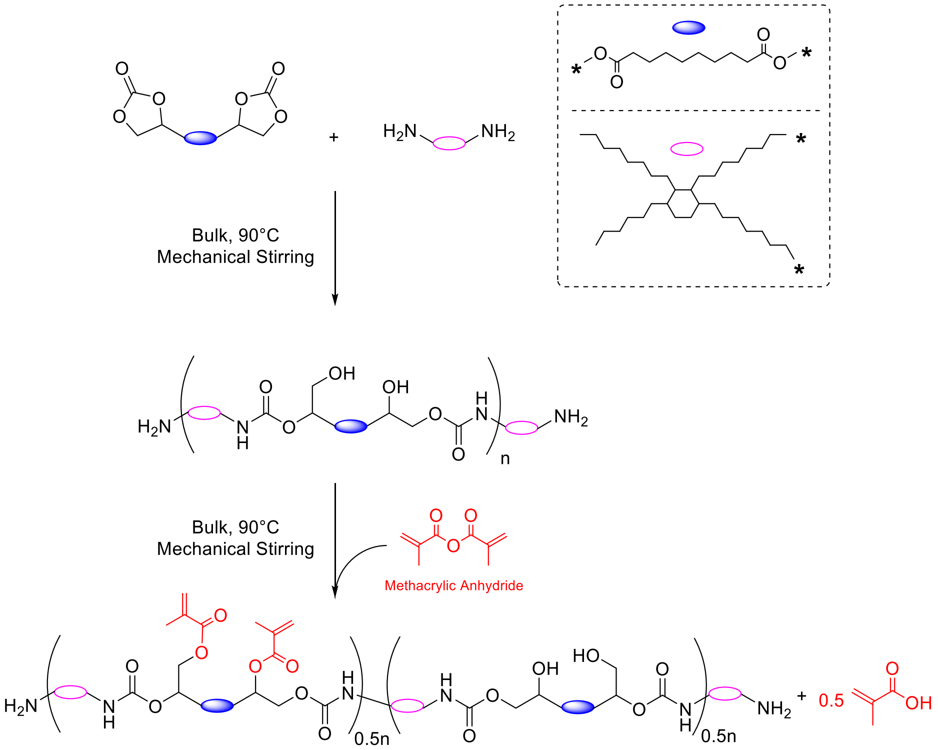
The second type of methacrylic functionalized NIPUs contained the methacrylic groups distributed along the PHU chain and was synthesized as depicted in Scheme 2. The formulation used is given in Table S4 (Supporting Information). In this case, the amine functionalized PHU was prepared by aminolysis between bisCC-C_{10} and P1075 using an excess of diamine at 90°C for 4 hours in bulk in the Schlenk tube described above. A degree of polymerization of 10 was targeted (Step #1). Then, methacrylic anhydride was added and the system was kept for 20h at 90°C. The amount of methacrylic anhydride was half of the theoretical amount of OH-moieties produced during PHU synthesis (assuming complete conversion of the cyclic carbonate groups). No catalyst was added for the polymerization reactions. No purification of the PHUs was performed after reaction.

The monoCC-GMA used to incorporate the methacrylic groups into the PHU was synthesized by reacting glycidyl methacrylate (GMA) with carbone dioxide (CO_2) in acetone under pressure using tetrabutylammonium bromide (TBABr) as catalyst – Scheme 3. Typically 1 eq. of glycidyl methacrylate (9.5 g, 66.83 mmol) and 0.013 eq. of tetrabutylammonium bromide (TBABr) (0.285 g, 0.88 g) were mixed together and diluted in 50 mL acetone. 3 wt% of TBABr with respect to the amount of epoxy moiety were utilized. The mixture was placed at 80°C under 30 bars of CO_2 in a reactor and left under mechanical stirring during 5 days. Full conversion was obtained according to ^{1}H-NMR analysis. Removal of the acetone solvent under reduced pressure allowed recovering the final product that was utilized without any further purification. The ^{1}H-NMR spectra of the obtained monoCC-GMA is given in Supporting Information (Figure S1).

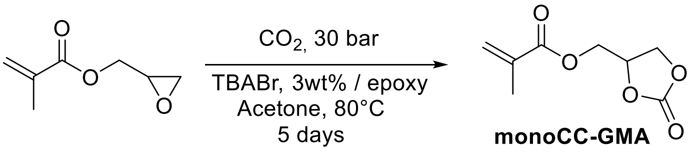
For the sake of comparison non functionalized poly(hydroxy)urethanes (PHUs) were synthesized through the aminolysis reaction between bisCC-C_{10} and P1075 using a stoichiometric ratio for the reactive moieties (refer to Chapter 2). The reactions were performed in bulk at 90°C for 24h in the Schlenk tube described above. No catalyst was added for the polymerization reactions. No purification of the PHUs was performed after reaction. (The molecular weights measured by SEC in DMF were: M_n = 2,2.10^4 g.mol^{-1}, M_w = 4,1.10^4 g.mol^{-1} and Đ = 1.9).



Scheme 1: 1 pot – 2 step synthesis of methacryloyl-telechelic poly(hydroxy urethane)s



Scheme 2: Synthesis of reactive PHUs containing methacrylic groups along the chain (50% functionalization)

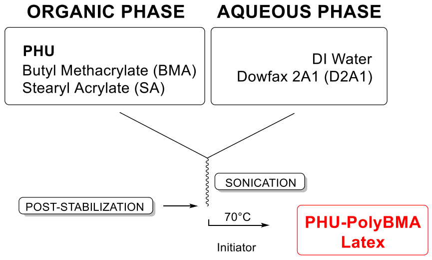


Scheme 3: Carbonation reaction of glycidyl methacrylate to its corresponding mono-cyclic carbonate (monoCC-GMA)

The formulations used for the synthesis of the waterborne PHU-(meth)acrylates hybrids by miniemulsion polymerization are summarized in Table 1 and further details are given in the Supporting Information (Table S5). In order to prepare the miniemulsion, the functionalized PHUs (20 wt% based on BMA) were dissolved in a mixture of BMA and SA (SA being 4 wt% based on organic phase) at 80°C. The organic phase was added drop-wise into the aqueous phase formed by a solution of Dowfax 2A1 (1 wt% based on organic phase) in deionized water under vigorous magnetic stirring. The resulting coarse emulsion was sonicated for 30 min in a Hielscher Ultrasonics GmbH (ref UIS250V; 100% amplitude, 0.8s duty cycle). After miniemulsification, another 1 wt% (based on organic phase) of Dowfax 2A1 was added to the miniemulsion. The reason for this post-stabilization step is that for this system, the droplet size was controlled by the available surfactant, and therefore the droplets were sparingly covered by the surfactant, namely close to the stability limit.[35] The resulting mini-emulsion was then transferred into a 3-neck round-bottom flask. An aqueous solution of TBHP was then added as a shot so that it had enough time to partition between the aqueous and the organic phase. After the nitrogen flushing (at least 50 min at 70°C), an aqueous solution of AsAc was fed during 2.5h. Note that, as mentioned in Chapter 3, TBHP does not suffer any significant decomposition at 70°C.

The reaction mixture was left under magnetic stirring at 70°C during the entire period of feeding (as well as 1h more at the end of the feeding of AsAc in the case of the mono-functionalized PHU). Regular sampling was performed in order to gauge the conversion (by gravimetry) and the particle size (by DLS). At the end of the process, the latex was cooled down to room temperature and filtered through an 85 µm mesh in order to collect and measure the amount of formed coagulum (if any).

Table 1: Formulations used in the miniemulsion polymerizations (detailed SI – Table S5)

			Composition			
	Basic recipe	PHU	20	wt%	96wt%	40 wt% solids
		BMA	80	wt%		
		SA	4	wt%		
		Dowfax™ 2A1	1	wt% (wbo)		
		Water				
	Post-Stabilization	Dowfax™ 2A1	1	wt% (wbo)		
		Water	< 1g			
	Initiation	TBHP	0.05 or 0.1	wt% (wbo)		
		AsAc	0.05 or 0.1	wt% (wbo)		
		Water	<1g			

2.3. Characterization

A Bruker Avance 400 spectrometer (400.20 MHz or 400.33 MHz) was used to record ^{1}H-NMR spectra. The samples were dissolved in DMSO-d6 at room temperature for the analyses. The conversion into the urethane and the Amide : Urea : Urethane ratios were calculated according to the equations presented in Chapter 2.

A dynamic light scattering (DLS) monitoring of the monomer droplets and particle sizes was performed upon polymerization. The measurements were performed in a Zetasizer Nano Z (Malvern Instruments). The reported values are the average of three repeated measurements of the z-average values, measured at 25°C after 15 sec equilibration time, of a sample of the latex that had previously been diluted in deionized water.

The molar mass distributions of the PHU pre-polymers (functionalized and non-functionalized) were measured by size exclusion chromatography in DMF with LiBr salts according to the description provided in Chapter 2.

The molar mass distribution and the distribution of the radius of gyration of the whole polymer swelling degree were measured by asymmetric-flow field-flow fractionation (AF4, Wyatt Eclipse 3) with multiangle light scattering (MALS) and refractive index (RI) detectors and using THF as the solvent. The setup consisted of a pump (LC-20, Shimadzu) coupled to a DAWN Heleos multiangle light scattering laser photometer (MALS, Wyatt) equipped with a He–Ne laser (λ = 658 nm) and an Optilab Rex differential refractometer (λ = 658 nm) (RI, Wyatt Technology). In AF4, the separation is based on the interplay between the flows of the carrier and the Brownian motion of the macromolecules occurring in an open channel in which one of the walls is a membrane.[36] The sample is first fixed against the membrane using a cross-flow. The interplay between the cross-flow and the diffusion creates a profile of macromolecular sizes such as the large sizes are closer to the membrane wall. The parabolic flow along the cell makes that the macromolecules that are further away from the membrane (i.e., the smaller ones) are eluted first. The main advantage of AF4 is that due to the lack of stationary phase very large macromolecules can be analyzed. The data collection and treatment were carried out by ASTRA 6 software (Wyatt Technology). The samples were prepared by dispersing the latexes directly in THF (5 mg of polymer latex in 1 mL of THF). The molar mass was calculated from the RI/MALS data using the Debye plot (with second-order Berry formalism).

Titration of the formed polymers was performed by dosing the excess of NH_2-moieties (chain-ends) with HCl in isopropanol, using bromocresol green as a color indicator. The reported values are an average of 3 replicates.

Transmission electron microscopy (TEM) was used in order to study the particle and film morphologies. The device was a TECNAI G^2 20 TWIN microscope operated at 200 kV and equipped with LaB6 filament, and high angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM). The particle and film morphologies were studied using the same protocols described in Chapter 3 (phosphotungstic acid – PTA – was used as a staining agent for the particles and ultra-thin sections of the films – about 80 nm – were analyzed without any staining).

Differential Scanning Calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA Instruments. For each film sample, the following temperature program was applied: from -80°C to 130°C at 10°C.min^{-1} and from 130°C to -80°C at 10°C.min^{-1}. The glass transition temperatures (T_gs) were calculated from the first heating ramp so that the properties of the films after casting are obtained.

The minimum film formation temperature (MFFT) was measured by applying a thin layer of latex (60 µm thickness) onto a steel bar with a temperature gradient. After the water evaporated and the film formed, thermocouples located at regular distances allowed for the measurement of the MFFT, which was defined in this work as the temperature at which both a clear coat was observed and a clear cut could be made with a knife without the film becoming a powder.

Tensile stress-strain measurements were carried out from the cast rectangular films (10 x 10 x 0.5 mm^3) with a texture analyzer (Stable Micro Systems Ltd., Godalming, UK). The reported results were the average of at least 3 different specimens measured at a constant velocity of 0.42 mm.s^{-1}. The Young's modulus was determined as the slope of the stress-strain curve before the yield point (elactic region) and the toughness was determined as the area under the obtained curve.

The gel content was measured gravimetrically after 24 h of Soxhlet extraction in technical-grade tetrahydrofuran (THF). 10 to 15 latex drops were deposited on glass fiber square pads of and dried overnight at 60 °C. After Soxhlet extraction under reflux at 200 ºC, the pads were dried again at 60 °C overnight. The gel content was calculated as according to previously reported methods.[14]

2.4. Film casting

Films were cast from the latexes in silicon molds. Rectangular specimens were cast for tensile tests (10 x 40 x 0.3 mm^3) at 30°C, 55% relative humidity for 48h. Square samples were cast for TEM (10 x 10 x 0.5 mm^3) at RT, 55% relative humidity for 48h. Those samples were cut thanks to the help of a cryo-microtome device.

3. Results and discussion

3.1. Synthesis of the functionalized PHUs

3.1.1. Methacrylate-terminated PHUs

Three different methacrylate terminated PHUs were prepared using the formulations summarized in Table S1 to S3. Some of the characteristics of the PHUs synthesized are given in Table 2. In each case, Step #1 corresponded to the formation of the NH_2-terminated PHU by reaction of bisCC-C_{10} and P1075 and Step #2 is the functionalization of the NH_2-terminated PHU with monoCC-GMA. In the case of Batch #1 and #2, a DP of 6 was targeted by adjusting the excess of diamine in the formulation.

The excess of diamine was calculated according to Carother's theory.[37] According to this theory, the degree of polymerization, DP, is given by

$$\mathrm{DP} = \frac{1 + \mathrm{r}}{1 + \mathrm{r} - 2\mathrm{rp}} \qquad (1)$$

where p is the conversion and r is the stoichiometric ratio between A-A and B-B reactants

$$\mathrm{r} = \frac{\mathrm{n_{CyclicCarbonate}}}{\mathrm{n_{NH2}}} \qquad (2)$$

At complete conversion, (p = 1) eq. 1 reduces to

$$\mathrm{DP} = \frac{1 + \mathrm{r}}{1 - \mathrm{r}} \qquad (3)$$

which allows the calculation of the excess of diamine to achieve a given degree of polymerization (eq. 4)

$$r = \frac{DP - 1}{DP + 1} \qquad (4)$$

Step #1 was performed in bulk by reacting together bisCC-C_{10} with the corresponding excess of P1075 at 90°C during more than 24h (Table 2, S1 and S2). In all the cases, the formation of the urethane moiety was confirmed by the appearance of a peak corresponding to the $-CH_2-$ moiety in alpha-position of the urethane peak at 2.9 ppm in the ^{1}H-NMR analysis (Figure 1, S2 and S3). Unfortunately, the spectra were not resolved enough to allow for the calculation of the conversion. In order to further characterize the product, titration of the NH_2 moieties with HCl was performed in isopropanol, using bromocresol green as color indicator. If full conversion of the reactive moieties is achieved (meaning that 100% cyclic carbonate has reacted), there is no free diamine, and if no side-reaction occurs during polymerization, it would allow to get an insight on the apparent degree of polymerization (DP_{app}). There were calculated to be 34 and 50. These DP_{app}s were much higher than expected and suggest that NH_2-moieties have disappeared during the PHU formation. This also infers that the corresponding molecular weights (Mn_{app}) are overestimated. The formation of amide- and urea- by-products, observed by ^{1}H-NMR, can be a potential explanation for the low amount of observed amine moieties. Indeed, peaks corresponding to the labile protons of those moieties were observed in the range 6.5 to 8.0 ppm (Figures 1, S1, S2, S3). Urea and amide moieties are respectively originating from the reaction between an NH_2-terminated compound (supposedly any diamine or NH_2-terminated growing PHU chain) with the urethane or the ester moieties that are contained within the PHU backbone. The suggested mechanism of the reaction is provided in Scheme 4. The calculations of the Amide : Urea : Urethane ratios (as described in Chapter 2) allowed to see that those side-products accounted for about 40% of the obtained products. Even if the values are indicative because of the low resolution of the NMR spectra, such an amount of side-reaction is very high when compared with a published example in which the extent of side-reaction (including both urea and amide) did not exceed 15% with ester-activated bisCCs.[38] The fact that the reaction in taking place in bulk (and not in solvent[38]) in addition to the very high excess of diamine introduced are potential explanations for this outcome.

When the reaction time of Step #1 was reduced to 4h (Batch #3), the DP_{app} (28) was found to be closer to the targeted DP (10), suggesting that the side reactions occurred due to the prolonged contact of PHUs and diamines.

Table 2: Characteristics of the synthesized radical-reactive PHU pre-polymers

Batch	**Targeted DP**[a]	**Reaction Step**	**Reaction Time**	**Conversion**[b]		**Amide : Urea : Urethane Ratio**[e]	**M_n**[f] **[g.mol]**	**Đ**[f]	**Titration**[g]		
				U[c]	F[d]				**$[NH_2]_{app}$** [$mol.g^{-1}$]	**Mn_{app}** [$g.mol^{-1}$]	**DP_{app}**
#1 (mono)	6	#1	25.5h	n.d.	-	13 : 14 : 73	9900	2.3	$1,25.10^{-4}$	16000	34
		#2	21h	89%	100%	19 : 16 : 64	10200	2.3	$6,95.10^{-5}$	-	-
#2 (telech)	6	#1	27h	86%	-	23 : 17 : 60	10000	2.2	$8,38.10^{-4}$	23900	50
		#2	21h	84%	100%	15 : 20 : 65	11600	2.8	$2,87.10^{-5}$	-	-
#3 (telech)	10	#1	4h	n.d.	-	25 : 13 : 65	11600	1.8	$1,51.10^{-4}$	13350	28
		#2	20h	66%	60%	18 : 17 : 65	13400	1.9	$2,42.10^{-5}$	-	-

[a] Calculated according to Carother's theory

[b] Calculated *via* ^1H-NMR when possible

[c] Conversion of the carbonate moiety into urethane

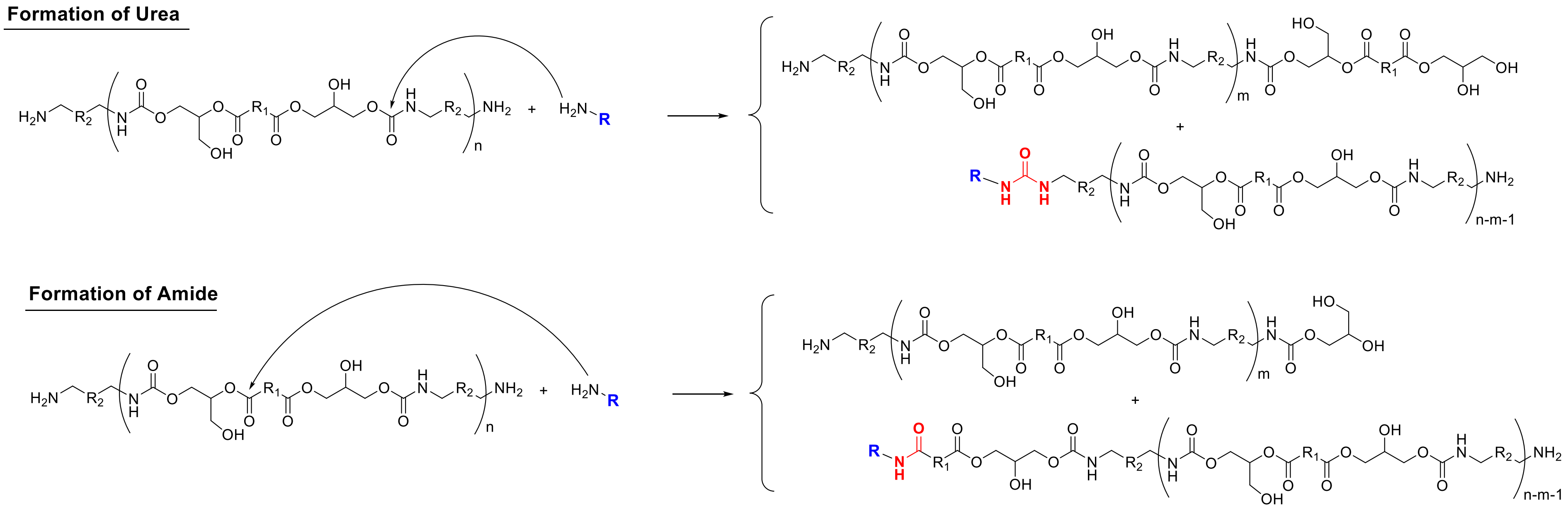
[d] Conversion of the methacrylic protons of monoCC-GMA into methacrylic protons attached to the PHU backbone

[e] Calculated from the labile proton zone according to the description provided in Chapter 2

[f] Performed in DMF with LiBr salts according to the description provided in Chapter 2

[g] Performed with HCl in Isopropanol with bromocresol green as color indicator

n.d. not determined



R can in principle be any diamine or growing PHU which is NH_2-terminated at least on 1 chain-end

Scheme 4: Suggested mechanism of the reaction between any NH_2-terminated compound and the urethane or the ester moieties contained in the backbone of the growing PHUs to yield urea- and amide-containing side-products respectively.

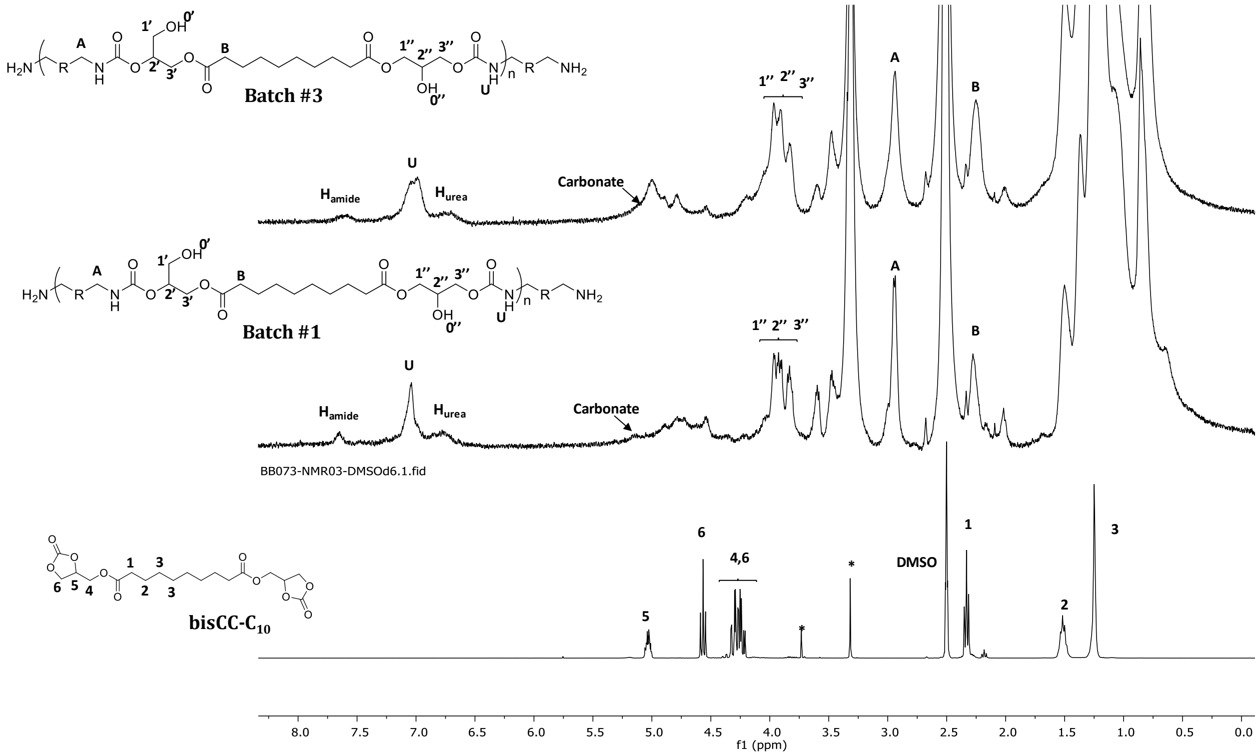


Figure 1: Stacked ^{1}H-NMR Spectra of bisCC-C$_{10}$, the NH$_2$-terminated PHU from Batch #1, and the NH$_2$-terminated PHU from Batch #3 in DMSO-d6.

These results show that the synthesis and the characterization of NH$_2$-terminated PHU pre-polymers of controlled chain length is challenging. Two main limitations can be mentioned: the reaction does not reach full conversion (Batch #2, Table 3) and side-reactions occur with the formation of amide and urea by-products. The extent of side-reactions is confirmed by both ^{1}H-NMR analyses and the fact that the calculated molecular weights by titration of the NH$_2$-moieties are overestimated. The excess of diamine utilized in the synthesis probably plays an important role in the occurrence of the side-reactions. Interestingly, by decreasing the reaction time from 24h to 4h, a better control of the chain length was obtained according to titration, suggesting that the extent for disappearance of the amine moieties had decreased.

The amine-terminated PHUs were functionalized with monoCC-GMA. In Batches #1 and #2, the amount of monoCC-GMA was adapted according to the measured concentration of NH$_2$. In Batch #1, the formation of a mono-functional PHU was targeted, and therefore amount of monoCC-GMA added was half of the measured NH$_2$. In Batch #2, bi-functional telechelic PHUs were targeted and the amount of monoCC-GMA added was that of the measured amines. In Batch #3 the amount of monoCC-GMA was that of the theoretical amount of the excess-NH$_2$ introduced at the beginning of the reaction. This was done to make sure that a majority of the amine moieties got functionalized by monoCC-GMA. In all the cases, the reactions were carried out in bulk during 20h to 21h (see Tables S1, S2 and S3 for details) at 90°C. The shifts of the peaks corresponding to the acrylic protons at 5.68 and 6.06 ppm (noted F2 in Figure 2) in the ^{1}H-NMR spectra confirmed the incorporation of monoCC-GMA. In addition, no NH_2 moieties were detected when the resulting PHUs were titrated with HCl in isopropanol.

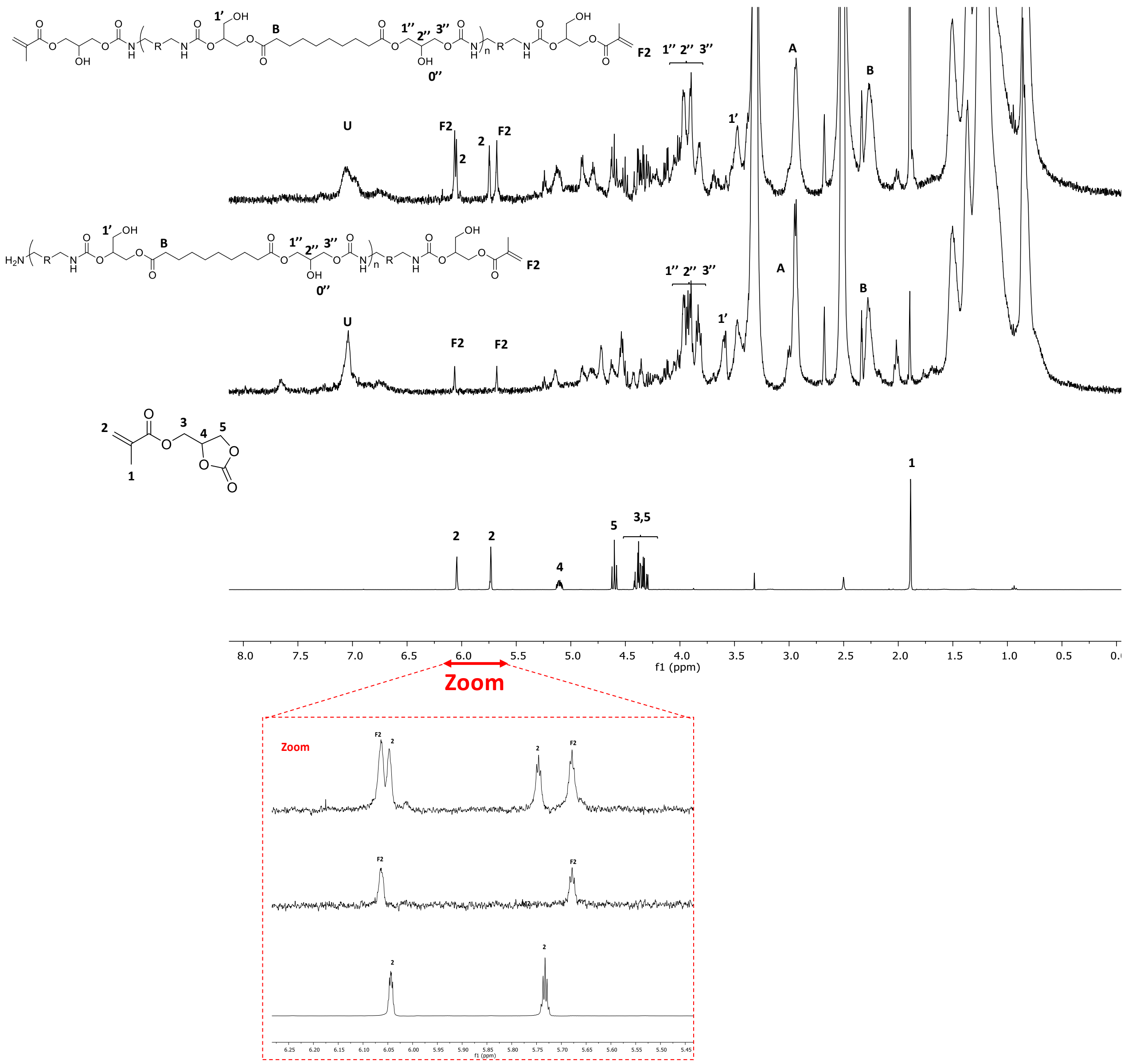


Figure 2: Stacked ^1H-NMR Spectra of bisCC-C_{10}, the NH_2-terminated PHU from Batch #1, and the NH_2-terminated PHU from Batch #3 in DMSO-d6.

3.1.2. Methacrylate groups distributed along the PHU chains (multifunctionalized)

Methacrylate groups were placed along the PHU chain by reacting the OH-groups of the PHUs with methacrylic anhydride using the formulation in Table S4 (Scheme 2). In this case, an amino-telechelic PHU prepolymer with a targeted DP of 10 was first synthesized in bulk at 90 °C during 4 h. Then, methacrylic anhydride was added and the reacting mixture was kept at 90 °C during 20h under mechanical stirring. The resulting ^1H-NMRs are shown in Figure 3 and some characteristics are listed in Table 3.

The peak at 2.9 ppm in the ^{1}H-NMR spectrum of the NH_2-terminated PHU pre-polymer confirmed the formation of the urethane moiety. However, it is remarkable that some characteristic peaks of the PHUs such as the one corresponding to the CH_2 moiety in alpha position of the ester-groups of the bisCC-C_{10} (usually showing at chemical shifts closed to 2.1-2.2 ppm) could not be observed. This was due to a poor solubility of the sample in DMSO-d6 and in DMF, since small white agglomerates could be observed. Nevertheless, after functionalization with methacrylic anhydride, no problems of solubility were observed and the conversion of the cyclic carbonate moiety could be measured to reach the value of 66%.). For the attribution of the peaks of the methacrylate functionalized amine-terminated PHUs we followed the recent work of Mülhaupt and coworkers.[39] Interestingly, when analyzing the peaks of the methacrylic protons (zoom in Figure 3) it was found that about 60% of the methacrylic anhydride had reacted with pendant OH-groups of the PHU backbone. The resulting peaks **F2** (at 5.61 and 5.98 ppm) appeared at higher chemical shifts than the ones of methacrylic acid. The peak at 5.28 ppm (**F3**) was attributed to the quaternary proton attached to the functionalized pendant OH-groups. All this information indicated that the PHU was functionalized with methacrylic groups in the backbone. Moreover, labile protons of amide and urea moieties could be noticed, suggesting the occurrence of side-reactions as described above. Finally, it was surprising to observe the appearance of a broad peak at 7.83 ppm (circled in red in Figure 3), that could unfortunately not be identified. Because of its proximity with the amide labile proton, it could be assumed that NH_2 moieties (from free P1075 or NH_2-terminated growing chains of PHU) reacted with methacrylic anhydride to form the corresponding amide, following a similar mechanism to the one described in Scheme 4, but further investigation would be needed in order to confirm this outcome.

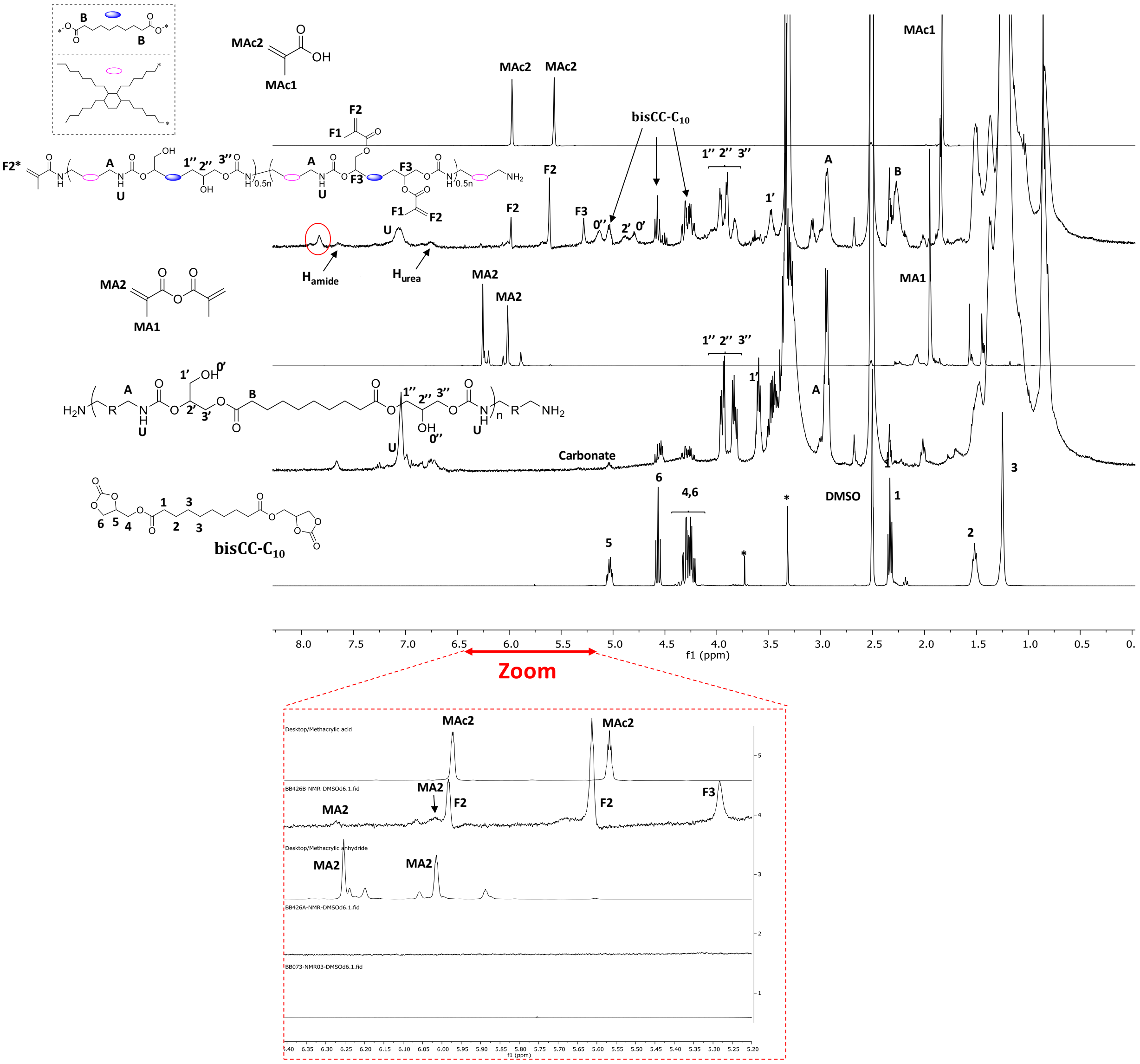


Figure 3: 1H-NMR spectra of **bisCC-C$_{10}$**, the NH$_2$-terminated PHU from Step 1, Methacrylic Anhydride, the OH-functionalized PHU from Step 2 and Methacrylic Acid (from bottom to top) in DMSO-d6

Table 3: Characteristics of the multifunctionalized radical-reactive PHU pre-polymer

Batch	Targeted DP[a]	Reaction Step	Reaction Time	Conversion[b]		Amide : Urea : Urethane Ratio[e]	M_n[f] [g.mol]	Đ[f]
				U[c]	F[d]			
Multi	10	#1	4h	n.d.	-	n.d.	4100*	1.1*
		#2	20h	66%	60%	19 : 19 : 62	7500	1.4

[a] Calculated according to Carother's theory

[b] Calculated *via* ^{1}H-NMR when possible

[c] Conversion of the carbonate moiety into urethane

[d] Conversion of methacrylic protons of monoCC-GMA into methacrylic protons attached to the PHU backbone

[e] Calculated from the labile proton zone according to the description provided in Chapter 2

[f] Performed in DMF with LiBr salts according to the description provided in Chapter 2

* An insoluble fraction in DMF was noticed

n.d. not determined

3.2. Synthesis of the hybrid latexes

The hybrid latexes were prepared by miniemulsion polymerization. 40 wt% solids content mini-emulsions containing butyl methacrylate (BMA), stearyl acrylate (SA) (4 wt% of organic phase) and PHU (20 wt% based on BMA) were prepared as detailed in the experimental section. The end-chain modified Batch#1 (mono-functionalized PHU) and Batch #3 (bi-functionalized PHU), as well as the multi-functionalized PHU were used.

The free radical polymerization was initiated with the tert-butyl hydroperoxide / ascorbic acid (TBHP/AsAc) redox pair. TBHP was added as a shot after post-stabilization of the miniemulsion prior to flushing with nitrogen for at least 50 min at 70°C. An aqueous solution of AsAc was fed during 2h30min. 70°C were used to make sure that the PHU was soluble in BMA, and hence that the droplets were homogeneous. As substantial retardation periods were observed when copolymerizing the mono-functional PHU and BMA with 0.05wt% (wbo) of AsAc, a higher concentration of initiator was used for the bi-functional and the multifunctionalized PHUs (Table S5).

Figure 4 presents the evolution of the gravimetric conversion for the three different methacrylic functionalized PHUs. It can be seen that in all the cases, induction periods were observed, although they were shorter than those in Chapter 3, or in the case of the mono-functional PHU, due to the higher concentration of initiator used. Conversions approaching 100% at the end of the process were obtained.

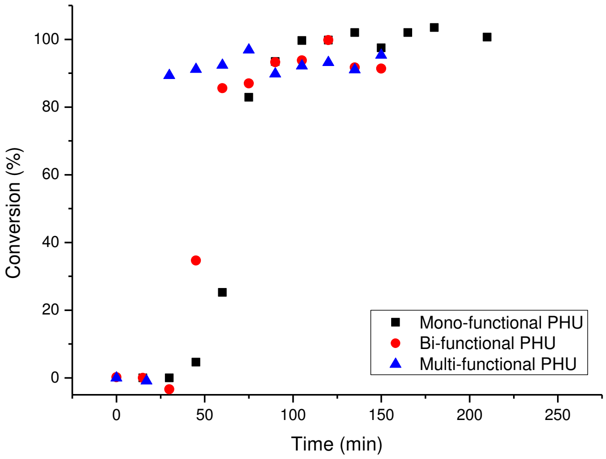


Figure 4: Conversion of BMA obtained by gravimetry upon polymerization with different functionalized PHUs (a) mono-functional, b) bi-functional, c) multi-functional PHU).

Figure 5 depicts the evolution of the particle size (z-average), polydispersity index (PDI) and the number of particles per liter upon polymerization. The number of particles was calculated from the measured diameter by DLS. Their evolutions are thus linked because as the solids content was the same in all reactions, an increase in the particle diameter directly results in a decrease in the number of particles. It can be seen that the number of particles remained constant during the whole process, which indicates an efficient nucleation of the miniemulsion droplets and an absence of significant secondary nucleation. On the other hand, the particle diameters, and thus the number of particles, were similar for the mono- and telechelically-functionalized PHUs, but much lower particle diameters were obtained in the case of the multifunctionalized PHUs. This can be explained by the presence of methacrylic acid that was formed upon functionalization and not purified before dissolving the reactive PHU into BMA. When the methacrylic acid was copolymerized with the PHU and BMA, the charge density on the surface of the particles increased, resulting in a decrease in the particle diameter. The higher number of particles resulted in a shorter inhibition period.

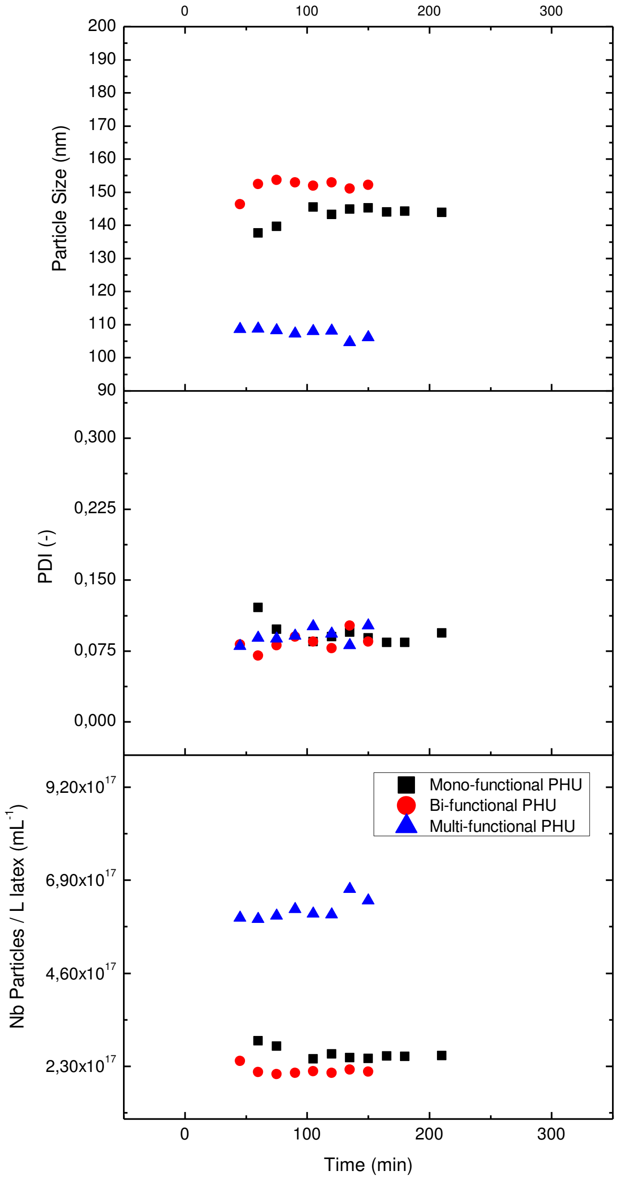


Figure 5: Evolution of the particle size, the polydispersity index (PDI), and of the number of particles upon free radical polymerization of cross-linked H-NIPUs

The characteristics of the synthesized latexes are listed in Table 4. For comparison purposes this table also includes the latex synthesized with a non-functionalized PHU in

Chapter 3, although it should be kept in mind that the comparison is not straightforward as in that experiment the concentration of initiator was lower. The same remark goes for the latex originating from the mono-functional PHU. Asymmetric flow field flow fractionation (AF4) was utilized in order to measure the molecular weight of the obtained products. AF4 uses an open channel for separation and therefore large molecular weights and even cross-linked particles can be measured. In the case of the mono-functionalized PHU a bimodal distribution was obtained (Figure 6), the small molecular weight peak corresponding to free PHU and the large one to the poly(BMA-co-SA) with included grafted PHU. It should be pointed out that the reported molecular weights of the small molecular weight peaks are uncertain because they are not detected by the light scattering detector and therefore no direct measurement of the molecular weights of these peaks was possible. The values provided were obtained by using an extrapolation of the molecular weight vs. retention time plot obtained from the LS detector at higher molecular weights. The fraction of PHUs grafted was estimated from the relative areas of these two peaks in the RI chromatogram finding that 42% of the PHU was grafted. On the other hand, the molecular weight of the methacrylic polymer is smaller than the one obtained with the non-functionalized PHU suggesting that the methacrylic groups on the PHU interfere with the polymerization of BMA either by increasing the chain transfer to monomer or reducing the overall propagation rate coefficient.

The molecular weight distribution (actually the trace) of the telechelic (bi-functionalized) PHU also presented two peaks clearly indicating that there was some PHU that was not grafted to the (meth)acrylic polymer (the estimated grafted fraction of PHU was about 65%). Possible reasons are the existence of a fraction of non-functionalized PHU and/or the slower reactivity of the telechelic methacrylic groups (it is known that macromonomers are less reactive than regular monomers.[40,41] On the other hand, the telechelic PHU formed gel as examplified by Soxhlet extraction, which indicated that a substantial fraction was really telechelic. The swelling degree, determined by AF4 from the radius of gyration and the molecular weight was 32.5.

The multifuctionalized PHU gave a single molar mass distribution with a large molecular weight (Figure 6) showing a complete incorporation of the PHU into the (meth)acrylic polymer and the formation of a crosslinked structure that was evidenced by the measured gel content by Sohxlet extraction in THF. The swelling degree obtained in the AF4 was 43.3. It is somehow surprising that this network was less crosslinked that the one obtained with the telechelic PHU, but it may be the result of incorporating most of the PHU into the methacrylic polymer. The molecular weight obtained for the multifunctionalized PHU was lower than for the telechelic one because the size of the particle was smaller and for highly crosslinked systems, the molecular weight is limited by the size of the particle. Nevertheless, higher differences were expected considering only the particle sizes, which suggests a stronger grafting for the multifunctional PHU.

This hypothesis is supported by the shift of the T_g of the PHU towards higher temperatures (see below in Figure 9).

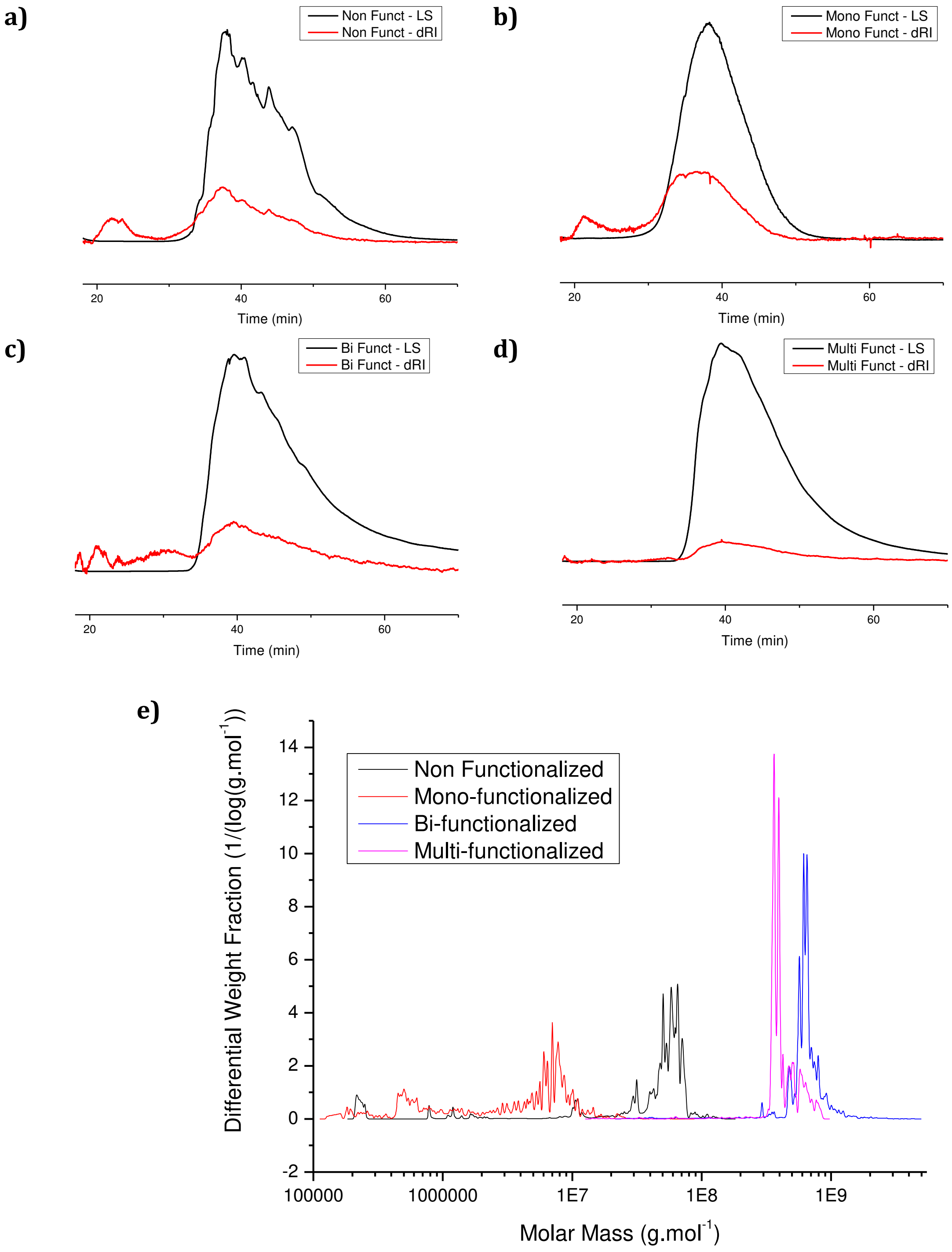


Figure 6: AF4 traces of the latexes (a) Non functionalized PHU, b) mono-functionalized PHU, c) bi-functionalized PHU and d) Multi-functionakized PHU) and
e) Molecular Weight Distributions as obtained by means of AF4

Table 4: Characteristics of the synthesized latexes (20wt% NIPU, 2h30 feeding)

Type of reactive PHU	Coagulation [wt%]	Particle Size[a] [nm]	M_ns[b] [g.mol^{-1}]	M_Ws[b] [g.mol^{-1}]	Đ[b]	Gel Content [%][c]	T_gs[d] [°C]	MFFT [°C]
Non-functionalized[e]	2.1	138	*$4,1.10^4$* $1,7.10^7$	*$7,2.10^4$* $5,0.10^7$	*1.8* 3.0	0	-20/24	15
Mono-functionalized	4.7	144	*$2,6.10^5$* $1,8.10^6$	*$2,8.10^5$* $5,7.10^6$	*1.1* 3.3	0	-19/24	< 9
Bi-functionalized	2.2	152	- $5,0.10^8$	- $6,6.10^8$	- 1.3	84	-13/25	18
Multi-functionalized	2	106	$3,6.10^8$	$4,3.10^8$	1.2	84	-12/26	27

[a] Measured by DLS
[b] Determined by AF4 (Asymmetric Flow Field Flow Fractionation)
[c] Measured by Soxhlet extraction of the latexes
[d] Measured by DSC of the dried films
[e] Latex from Chapter 3, 20wt% PHU, fed during 2h30 with AsAc
-: not determined because of a too low LS signal

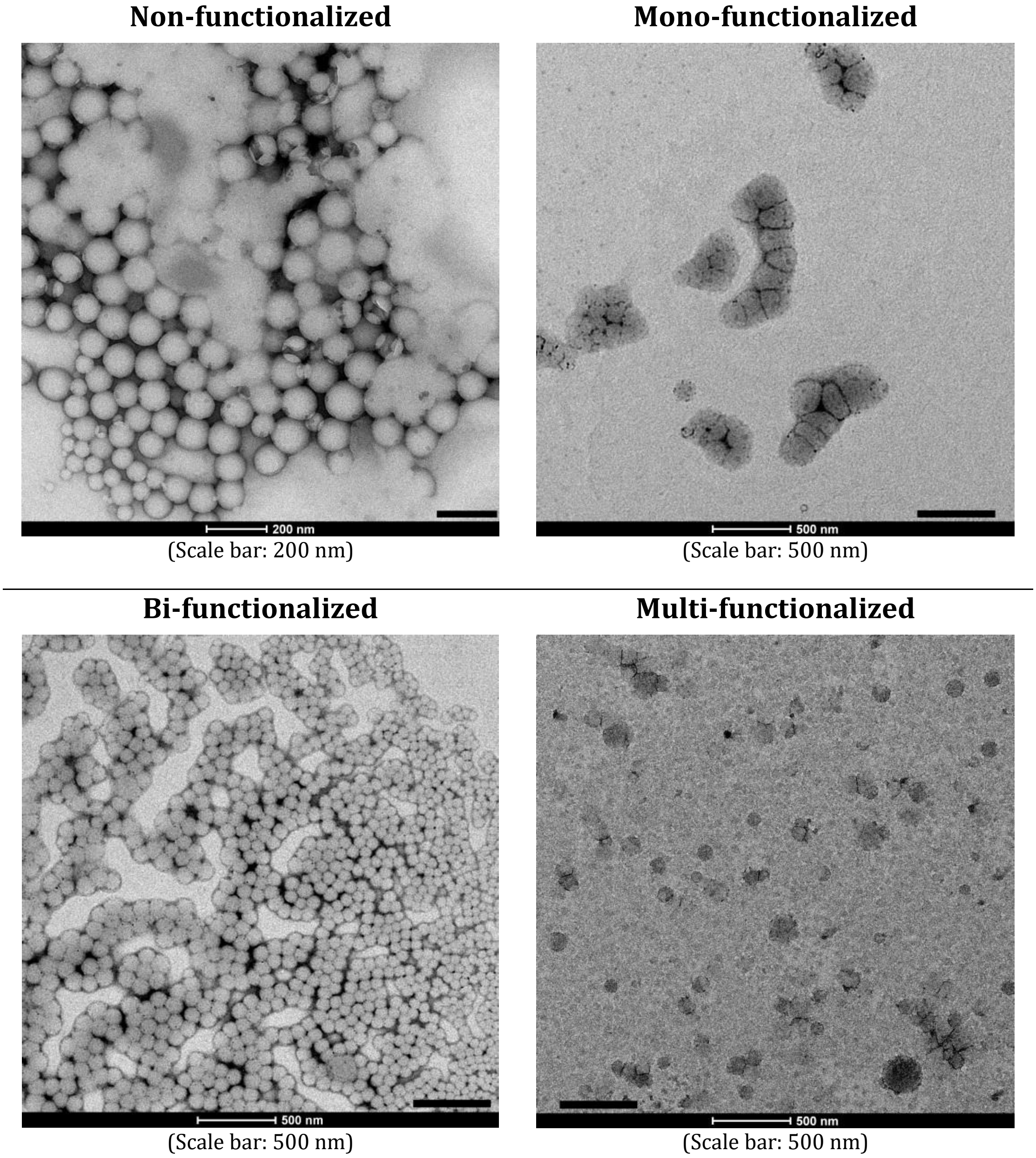
An attempt to determine the morphology of the hybrid particles was carried out by means of TEM using PTA as staining agent. The resulting pictures are provided in Figure 7. It can be seen that no evidence of presence of different phases was obtained. However, this does not mean that the particles were homogeneous due to grafting as even with the non-functionalized PHU, the particles looked homogeneous. As discussed in Chapter 3, the reason was that the amount of PHU (20 wt%) was not enough to see the PHU that was located at the surface of the particle. On the other hand, the TEM analyses confirmed the particle sizes observed by DLS, with much smaller particle diameters for the multifunctional PHU.

3.3. Film properties

Clear films were prepared at room temperature (Figure 8). On the other hand, Table 4 shows that for the functionalized PHUs, the minimum film forming temperature (MFFT) increased with the crosslinking density. On the other hand, the MFFT of the monofunctionalized hybrid was lower than that of the non-functionalized one whereas those of the telechelic and multi-functionalized ones were higher.

These effects should be the result of the different polymer structure caused by the functionalized PHU. These effects were also observed in the T_gs (Figure 9). It can be seen that all the hybrids presented two T_gs, one corresponding to the (meth)acrylic polymer and another one to the PHU. However, the differences between them were also significant. Whereas the T_g of the (meth)acrylic part was roughly unaffected (about 24-27°C), that of the PHU varied from -20°C for the non-functionalized and mono-functionalized PHU to -12°C for the multifunctionalized one, which is a strong proof of grafting.

Therefore, the increase in MFFT with the extent of grafting/crosslinking can be attributed to the decrease of the fraction of free soft PHU and the stronger mechanical properties of the crosslinked particles. Comparison with the results obtained with the non-functionalized PHU show that in the absence of crosslinking, some grafting helps in the mobility of the polymer during film formation.



Non-functionalized

(Scale bar: 200 nm)

Mono-functionalized

(Scale bar: 500 nm)

Bi-functionalized

(Scale bar: 500 nm)

Multi-functionalized

(Scale bar: 500 nm)

Figure 7: TEM images of the hybrid particles.

Figure 8: Pictures of the cast films at RT and 30°C of hybrid-PHUs of different architectures (20wt% PHU in all the cases)

In order to shed some light on these results, the morphology of the films cast at room temperature and 50% relative humidity was studied. Figure 10 presents the TEM images of the cross-sections of the films. The film prepared with the mono-functionalized PHU showed a clear phase separation with formation or rather large PHU-rich clusters. These clusters are not visible for the films containing telechelic and multifunctional PHUs. Actually, in the telechelic film the presence of particles with a PHU-rich shell were evident. This kind of particles could also been seen in the case of the multifunctionalized PHU, although in this case they are not as evident, in part due to the smaller particle size. The fact that the non-functionalized PHU presented less defined clusters than the mono-functionalized is interesting because at first sight the opposite would be expected. The reason perhaps was that the incorporation of a fraction of PHU into the poly(methacrylate) resulted in a softer system (the MFFT was substantially lower) that allowed an easier flow of the free PHU.

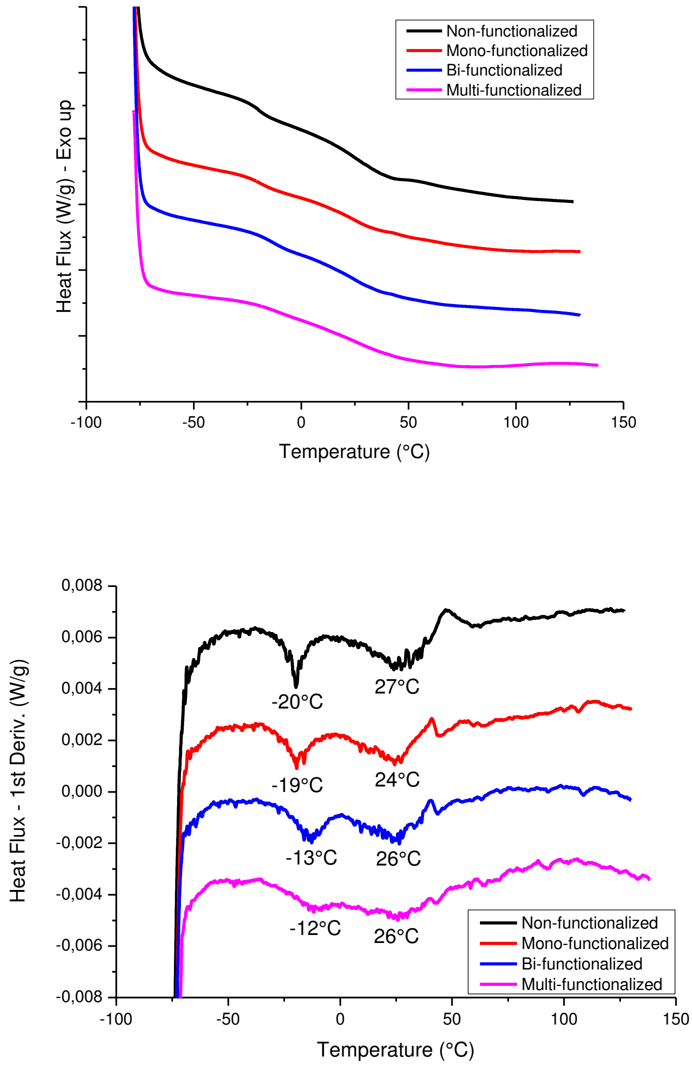
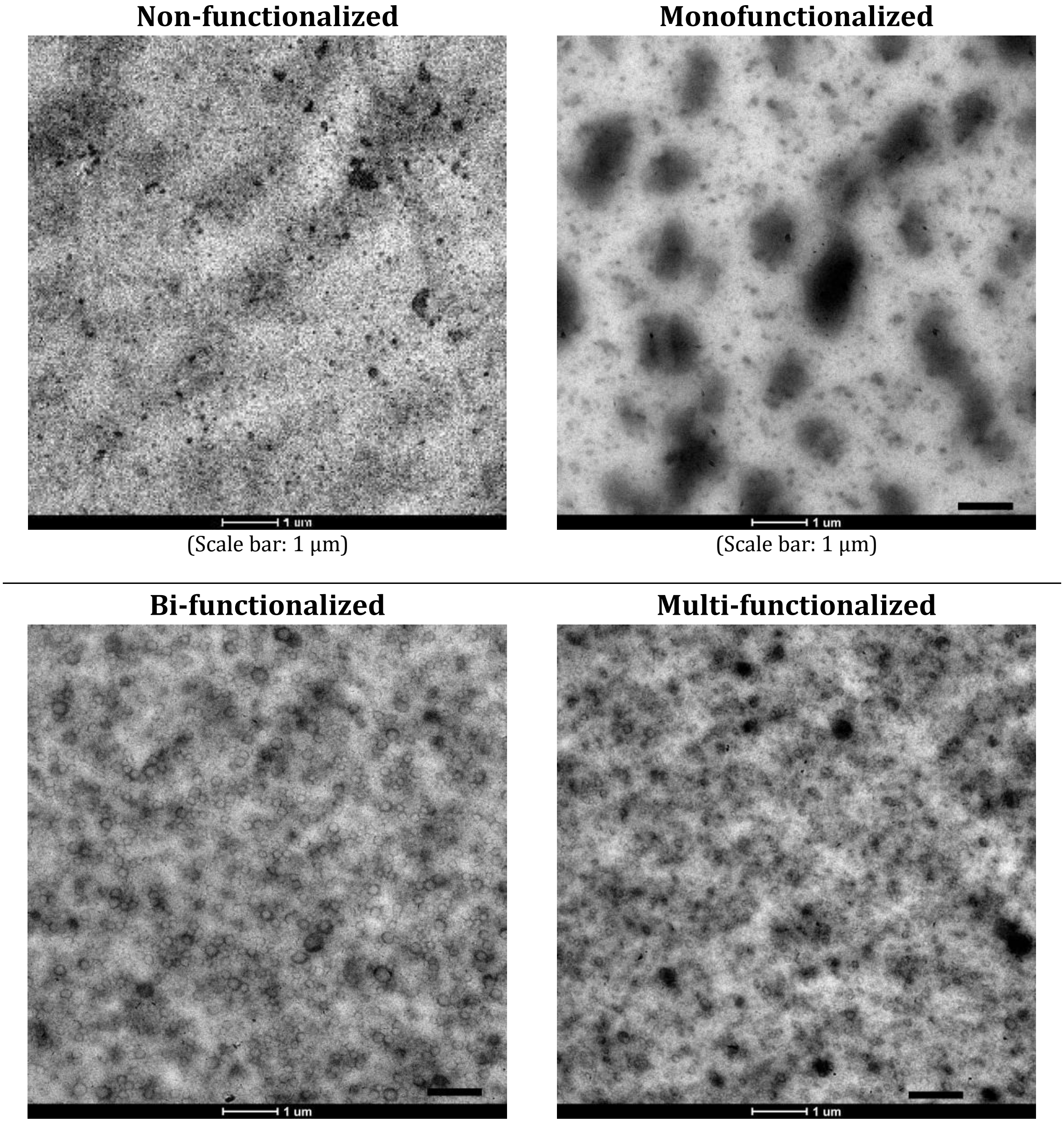


Figure 9: DSC curves of the cast films (left) and their first derivatives (right) depending on the chemical composition (1st heating ramp – 10°C/min)



Non-functionalized

(Scale bar: 1 µm)

Monofunctionalized

(Scale bar: 1 µm)

Bi-functionalized

(Scale bar: 1 µm)

Multi-functionalized

(Scale bar: 1 µm)

Figure 10: TEM pictures of cryo-microtome cuts of the cast films made from hybrids of different architectures (20wt% PHU, room temperature, 55% relative humidity). No staining was performed and the phase contrast is only due to the latex composition.

Figure 11 presents the stress-strain curves obtained in tensile experiments. Films were cast in silicon molds at 30°C and a relative humidity of 55% in a humidity chamber. A 1wt% of wetting agent was used to reduce the surface tension of the dispersion and allow good wetting of the silicon. Transparent and good quality films were obtained in the case of non-functionalized, mono-functionalized and telechelic-hybrids. However, multifunctionalized PHUs formed films prone to crack. The mechanical properties are listed in Table 5. It can be seen that the Young's modulus followed a similar trend as the MFFTs in Table 2. The incorporation of some PHU into the polymethacrylic chains reduced the stiffness of the polymethacrylate initially lowering the Young's modulus. The formation of crosslinks counteracted the softening effect of the PHU leading to a clear increase of the Young's modulus. A similar trend was found for the stress at break. The strain at break showed the opposite behavior with the longest one corresponding to the softest mono-functional PHU containing latex. The toughness, which represents the compromise between stress and strain at break, was maximum for mono-functional NIPU containing latex.

It can be concluded that grafting allowed fine tuning of the mechanical properties of the PHU containing hybrids and that a mild incorporation of the PHU into the polymethacrylic chains led to tougher coatings, whereas crosslinking increased the stiffness of the films.

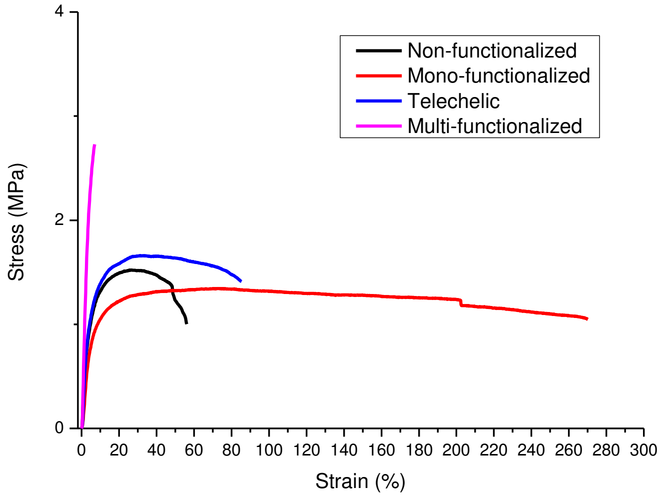


Figure 11: Stress-strain curves of the cast films (30°C, 55% humidity 1wt% wetting agent)

Table 5: Tensile test results of the cast films. The films were cast at 30°C, 55% humidity with 1wt% of wetting agent.

Temperature [°C]	Architecture	Young Modulus [MPa]	Strain at break [%]	Stress at break [MPa]	Toughness [MPa]
30	Non-funct.	52 ± 11	41.4 ± 6.1	1.5 ± 0.05	0.63 ± 0.10
30	Mono-funct.	32 ± 15	173.6 ± 64.1	1.3 ± 0.1	2.31 ± 0.83
30	Telechelic	46 ± 11	76.2 ± 9.2	1.3 ± 0.4	1.14 ± 0.15
30	Multi-funct.	86 ± 20	5.2 ± 4.0	2.2 ± 0.7	0.09 ± 0.07

4. Conclusions

In this chapter, waterborne grafted PHU-poly(meth)acrylate hybrid dispersions were synthesized and the effect of grafting on the particle and film morphologies as well as on the mechanical properties of the films was investigated. The dispersions were prepared by free radical polymerization of a miniemulsion in which the organic phase was a mixture of methacrylate functionalized PHU, BMA and SA. TBHP/AsAc was used a redox pair. Functionalized PHUs with different architectures were prepared. Telechelically modified PHUs were synthesized by reacting amine terminated PHUs with mono-carbonated glycidyl methacrylate (monoCC-GMA). The amount of monoCC-GMA was adjusted targeting mono and bifunctional methacrylate functionalized PHUs. A functionalized PHU having multiple methacrylic groups in the backbone was also prepared by reacting the OH groups of the PHU with methacrylic anhydride. A non-functionalized hybrid was prepared for comparative purposes.

The structure of the functionalized PHU had a substantial effect on the polymer hybrid. The hybrids prepared with both the non-functionalized and the functionalized PHUs presented two T_gs, one at about 24-27 °C that corresponded to the (meth)acrylic polymer and another one at a lower temperature for the PHU. This lower temperature increased from -20 °C for the hybrid containing non-functionalized and mono-functionalized PHUs to -12°C for the hybrid prepared with the multi-functionalized PHU, which indicates that grafting increased with the methacrylic functionalization. Functionalization had also a strong effect on the molecular weight distribution. AF4 measurements showed that all hybrids, with the exception of that prepared with the multifunctional PHU, presented two peaks, the small one corresponding to the ungrafted PHU and the large one to the poly(methacrylate) that included the PHU grafted. This result was expected for the non-functionalized and the mono-functionalized PHUs, but is was surprising for the dual functionalized telechelic PHU, because it indicates that some PHUs were not functionalized or were not reactive enough. Nevertheless, hybrids formed with this telechelic PHU as well as with the multifunctional PHU yielded macroscopic gel.

Clear films were cast from all the hybrids, although that of the multifunctional PHU was prone to crack. The structure of the hybrid had a strong influence on the minimum film forming temperature (MFFT), film morphology and mechanical properties of the film.

For the functionalized PHUs, MFFT increased with the crosslinking density. On the other hand, the MFFT of the monofunctionalized hybrid was lower than that of the non-functionalized one, whereas those of the telechelic and multi-functionalized ones were higher. These results were attributed to the decrease of the fraction of free soft PHU and the stronger mechanical properties of the crosslinked particles.

The film prepared with the mono-functionalized PHU showed a clear phase separation with formation or rather large PHU-rich clusters. These clusters were not visible in the films containing telechelic and multifunctional PHUs.

The incorporation of some PHU into the polymethacrylic chains reduced the stiffness of the polymethacrylate initially lowering the Young's modulus and stress at break. The formation of crosslinks counteracted the softening effect of the PHU leading to a clear increase of the Young's modulus and stress at break. The strain at break showed the opposite behavior with the longest one corresponding to the softest mono-functional PHU containing latex. The toughness, which represents the compromise between stress and strain at break, was maximum for mono-functional PHU containing latex.

The results presented in this chapter show that grafting allowed fine tuning of the mechanical properties of the PHU containing hybrids and that a mild incorporation of the PHU into the polymethacrylic chains led to tougher coatings, whereas crosslinking increased the stiffness of the films.

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6. Shortened forms

AFM:	Atomic Force Microscopy
AF4:	Asymmetric-flow field-flow fractionation
AsAc:	Ascorbic acid (or Vitamin C)
bisCC-C$_{10}$:	bis-cyclic carbonate derived from sebacic acid
BMA:	Butyl Methacrylate
CO$_2$:	Carbon Dioxide
Đ:	Polydispersity
DLS:	Dynamic Light Scattering
DMF:	Dimethylformamide
DMSO-d6:	Deuterated Dimethylsulfoxide
DP:	Degree of Polymerization
DSC:	Differential Scanning Calorimetry
D2A1:	alkyl diphenyl oxide disulfonate (Dowfax™ 2A1)
GMA:	Glycidyl methacrylate
HCl:	Hydrochloric acid
MALS:	Multi Angle Light Scattering
monoCC-GMA:	Cyclic carbonate methacrylate
Mn:	Molecular weight (in number)
MFFT:	Minimum Film Forming Temperature
Mw:	Molecular weight (in weight)
NIPU:	Non Isocyanate Polyurethane
NMR:	Nuclear Magnetic Resonance
PHU:	Poly(hydroxy)urethanes
PTA:	Phosphotungstic Acid
PU:	Polyurethane
P1075:	Priamine™ 1075
r:	Stoichiometric ratio according to Carother's theory
RI:	Refractive Index
SA:	Stearyl Acrylate
SEC:	Size Exclusion Chromatography
TBABr:	tetrabuytlammonium bromide
TBHP:	tert-butyl hydroperoxide
TEM:	Transmission Electron Microscopy
THF:	Tetrahydrofuran
T$_g$:	Transition Glass Temperature
wt%:	weight percent
^{1}H-NMR:	Proton- Nuclear Magnetic Resonance

7. Supporting Information

7.1. monoCC-GMA – Carbonated Glycidyl Methacrylate

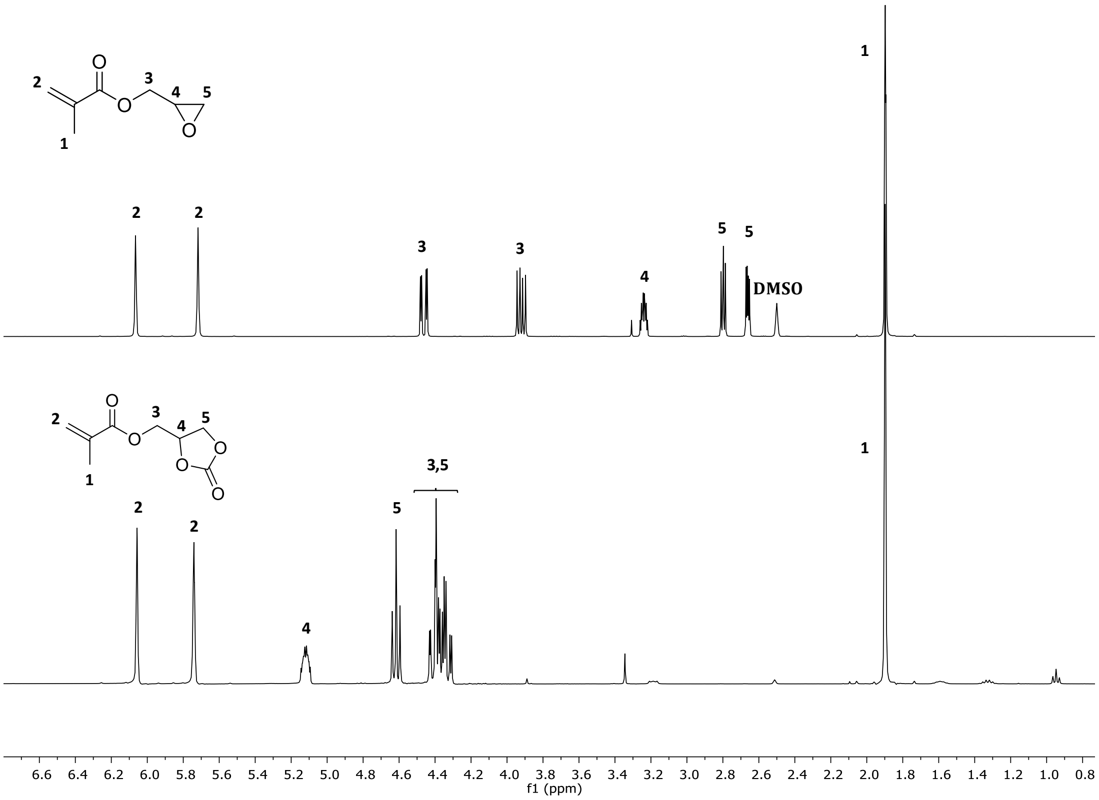


Figure S 1: ^{1}H-NMR of glycigyl methacrylate (top) and monoCC-GMA (bottom)

7.2. Telechelically-functionalized PHUs

7.2.1. Formulations

3 different functionalized PHUs were synthesized:

- **Batch#1** targeted the formation of NH_2-terminated PHU of DP 6, that was then mono-functionalized with monoCC-GMA (Table S1)
- **Batch #2** targeted the formation of NH_2-terminated PHU of DP 6, that was then telechelically-functionalized with monoCC-GMA (Table S2)
- **Batch #3** targeted the formation of NH_2-terminated PHU of DP 10, that was then telechelically-functionalized with monoCC-GMA (Table S3) with a change in the reaction kinetics as explained in the experimental section.

Table S1: Formulation used for Batch #1

Batch #1

Targeted DP: **6** (r = 0.714)

Step	Component		Theoretical	Experimental
Step #1 **(25h30)**	**bisCC-C$_{10}$**	**m_{bisCC} [g]**	**1.359**	**1.358**
		n_{bisCC} [mmol]	3.377	3.375
		$n_{\text{carbonate}}$ [mmol]	6.753	6.750
	P1075	**m_{P1075} [g]**	**2.570**	**2.570**
		n_{P1075} [mmol]	4.727	4.727
		n_{amine} [mmol]	9.454	9.454
	Excess Amine moiety	$n_{\text{amine}} - n_{\text{carbonate}}$ [mmol]	2.701	2.704
	Total PHU	**$m_{\text{PHU 1}}$ [g]**	**3.929**	**3.928**
Withdrawn Mass for sampling purposes		**$m_{\text{Sampling 1}}$ [g]**		**0.201**

For the calculations in Step #2, the concentration of NH_2 moiety obtained thanks to titration was used ($1,25.10^{-4}$ $mol_{NH2}/g_{NIPU}{}^{-1}$).

Step	Component		Theoretical	Titration	Experimental
Step #2 **(21h)**	**Remaining PHU**	**$m_{\text{PHU 1}} - m_{\text{Sampling 1}}$ [g]**			**3.727**
	Excess Amine moiety	$n_{\text{excess amine 2}}$ [mmol]	2.56	**0.466**	
	monoCC-GMA	n_{monoCC} [mmol]		0.233	
		m_{monoCC} [g]		**0.043**	**0.046**
	Total PHU	**$m_{\text{PHU 2}}$ [g]**			**3.773**
Withdrawn Mass for sampling purposes		**$m_{\text{Sampling 2}}$ [g]**			**0.123**
Remaining PHU for emulsion		**$m_{\text{PHU Final}}$ [g]**			**3.650**

Table S2: Formulation used for Batch #2

Batch #2

Targeted DP: **6** (r = 0.714)

Step	Component		Theoretical	Experimental
Step #1 **(27h)**	**bisCC-C10**	**m_{bisCC} [g]**	**0.800**	**0.801**
		n_{bisCC} [mmol]	1.988	1.991
		$n_{carbonate}$ [mmol]	3.976	3.981
	P1075	**m_{P1075} [g]**	**1.513**	**1.529**
		n_{P1075} [mmol]	2.783	2.812
		n_{amine} [mmol]	5.567	5.625
	Excess Amine moiety	$n_{amine} - n_{carbonate}$ [mmol]	1.590	1.643
	Total PHU	**$m_{PHU\,1}$ [g]**	**2.313**	**2.330**
Withdrawn Mass for sampling purposes		**$m_{Sampling\,1}$ [g]**		**0.150**

For the calculations in Step #2, the concentration of NH_2 moiety obtained thanks to titration was used ($8{,}38.10^{-5}$ $mol_{NH2}/g_{NIPU}{}^{-1}$).

Step	Component		Theoretical	Titration	Experimental
Step #2 **(21h)**	**Remaining PHU**	**$m_{PHU\,1} - m_{Sampling\,1}$ [g]**			**2.180**
	Excess Amine moiety	$n_{excess\ amine\ 2}$ [mmol]	1.49	**0.183**	
	monoCC-GMA	n_{monoCC} [mmol]		0.183	
		m_{monoCC} [g]		**0.034**	**0.038**
	Total PHU	**$m_{PHU\,2}$ [g]**			**2.218**
Withdrawn Mass for sampling purposes		**$m_{Sampling\,2}$ [g]**			**0.115**
Remaining PHU for emulsion		**$m_{PHU\,Final}$ [g]**			**2.103**

Table S3: Formulation used for Batch #3

Batch #3

Targeted DP: **10** (r = 0.818)

Step	Component		Theoretical	Experimental
Step #1 **(4h)**	**bisCC-C$_{10}$**	**m_{bisCC} [g]**	**0.800**	**0.802**
		n_{bisCC} [mmol]	1.99	1.99
		$n_{carbonate}$ [mmol]	3.98	3.98
	P1075	**m_{P1075} [g]**	**1.321**	**1.318**
		n_{P1075} [mmol]	2.43	2.42
		n_{amine} [mmol]	4.86	4.85
	Excess Amine moiety	$n_{carbonate} - n_{amine}$ [mmol]	0.884	0.862
	Total PHU	**$m_{PHU\ 1}$ [g]**	**2.121**	**2.120**
Withdrawn Mass for sampling purposes		**$m_{Sampling\ 1}$ [g]**		**0.079**

For the calculations in Step #2, the theoretical excess of amine moiety (0.884 mmol) was used.

Step #2 **(20h)**	**Remaining PHU**	**$m_{PHU\ 1} - m_{Sampling\ 1}$ [g]**		**2.041**
	Excess Amine moiety	$n_{excess\ amine\ 2}$ [mmol]	0.851	
	monoCC-GMA	n_{monoCC} [mmol]	0.851	
		m_{monoCC} [g]	**0.158**	**0.158**
	Total PHU	**$m_{PHU\ 2}$ [g]**		**2.199**
Withdrawn Mass for sampling purposes		**$m_{Sampling\ 2}$ [g]**		**0.054**
Remaining PHU for emulsion		**$m_{PHU\ Final}$ [g]**		**2.145**

7.2.2. NMR Spectra

Batch #1:

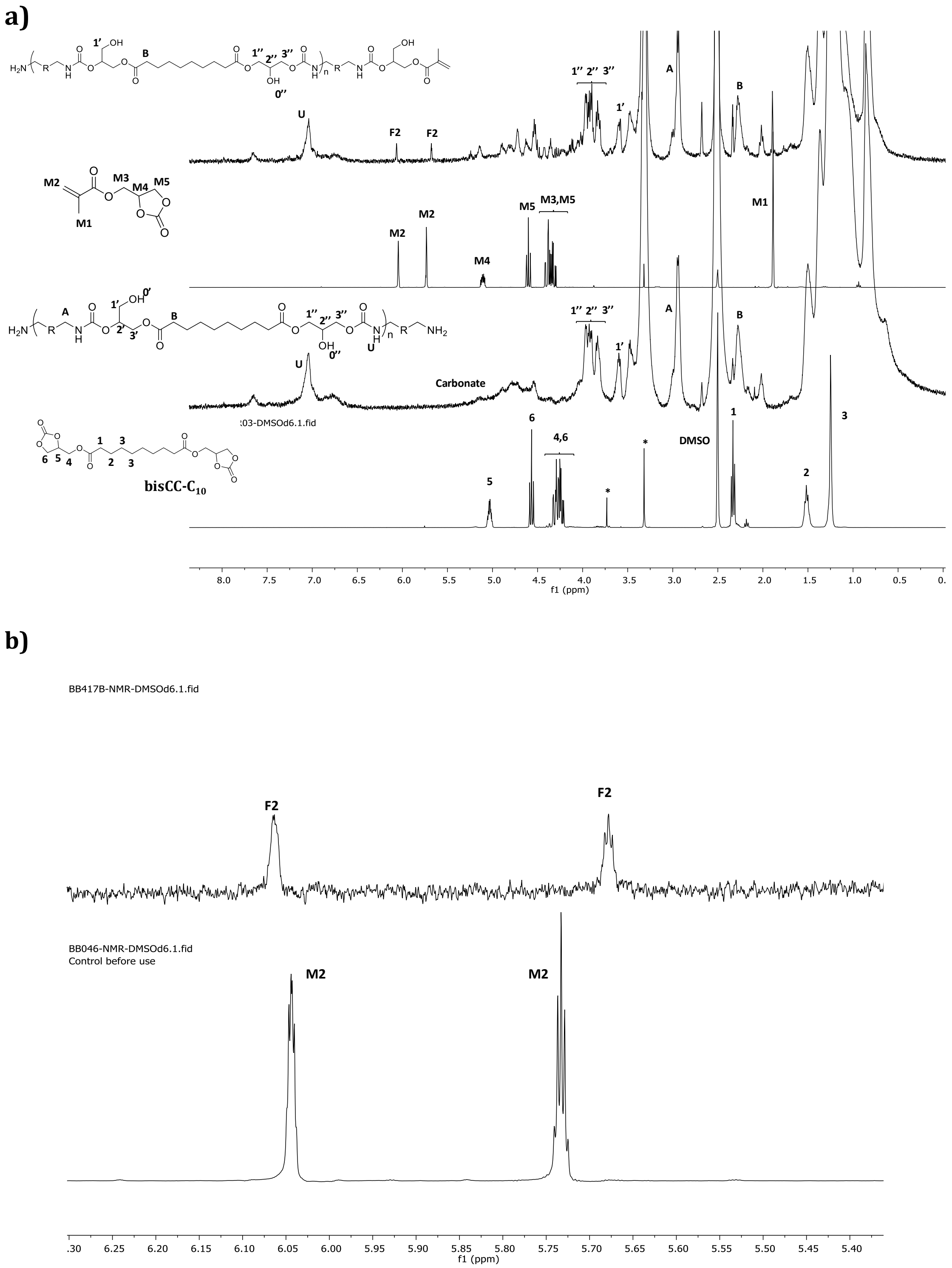
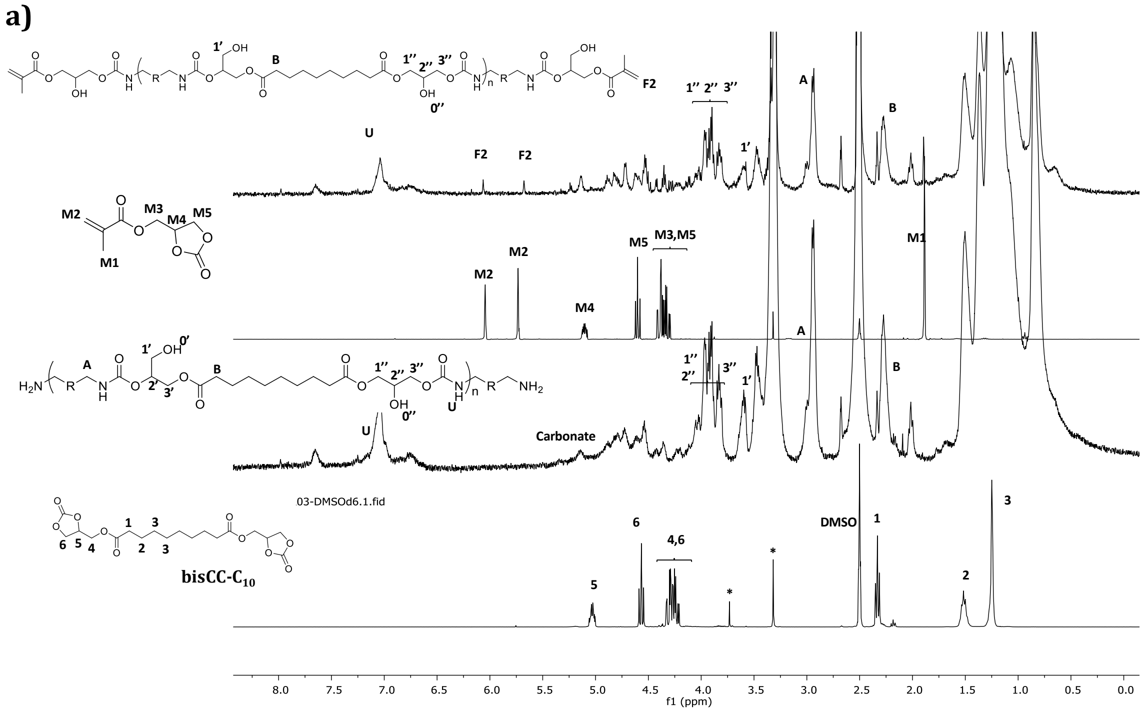


Figure S 2: ^{1}H-NMR of the prepolymers obtained during the preparation of the mono-functionalized PHU from Batch #1(a) Stack spectra of bisCC-C_{10}, the amine-terminated PHU, monoCC-GMA and the mono-methacrylate PHU (from bottom to top) and b) Zoom on the vinyl protons of monoCC-GMA (bottom) and the mono-functionalized PHU (top))

Batch #2:

a)



b)

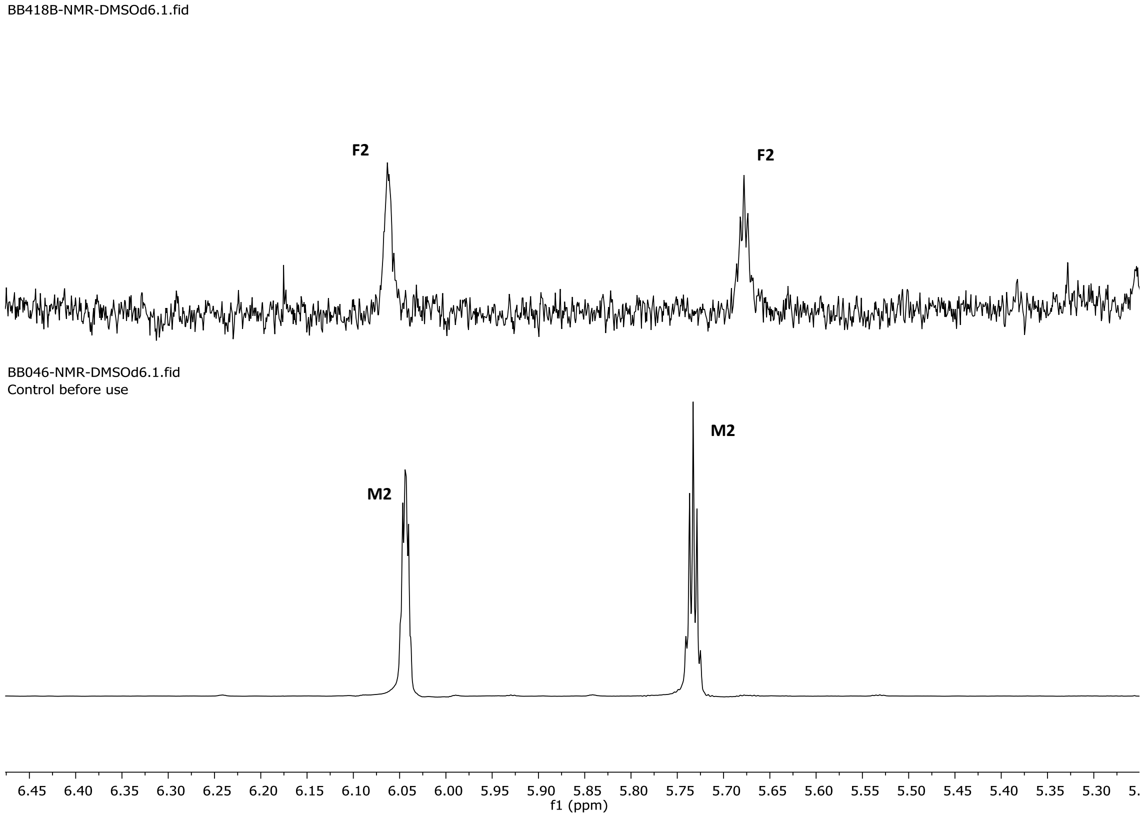


Figure S 3: ^{1}H-NMR of the prepolymers obtained during the preparation of the bifunctionalized PHU from Batch #2(a) Stack spectra of bisCC-C$_{10}$, the amine-terminated PHU, monoCC-GMA and the bifunctional PHU (from bottom to top) and b) Zoom on the vinyl protons of monoCC-GMA (bottom) and the bifunctionalized PHU (top))

Batch #3:

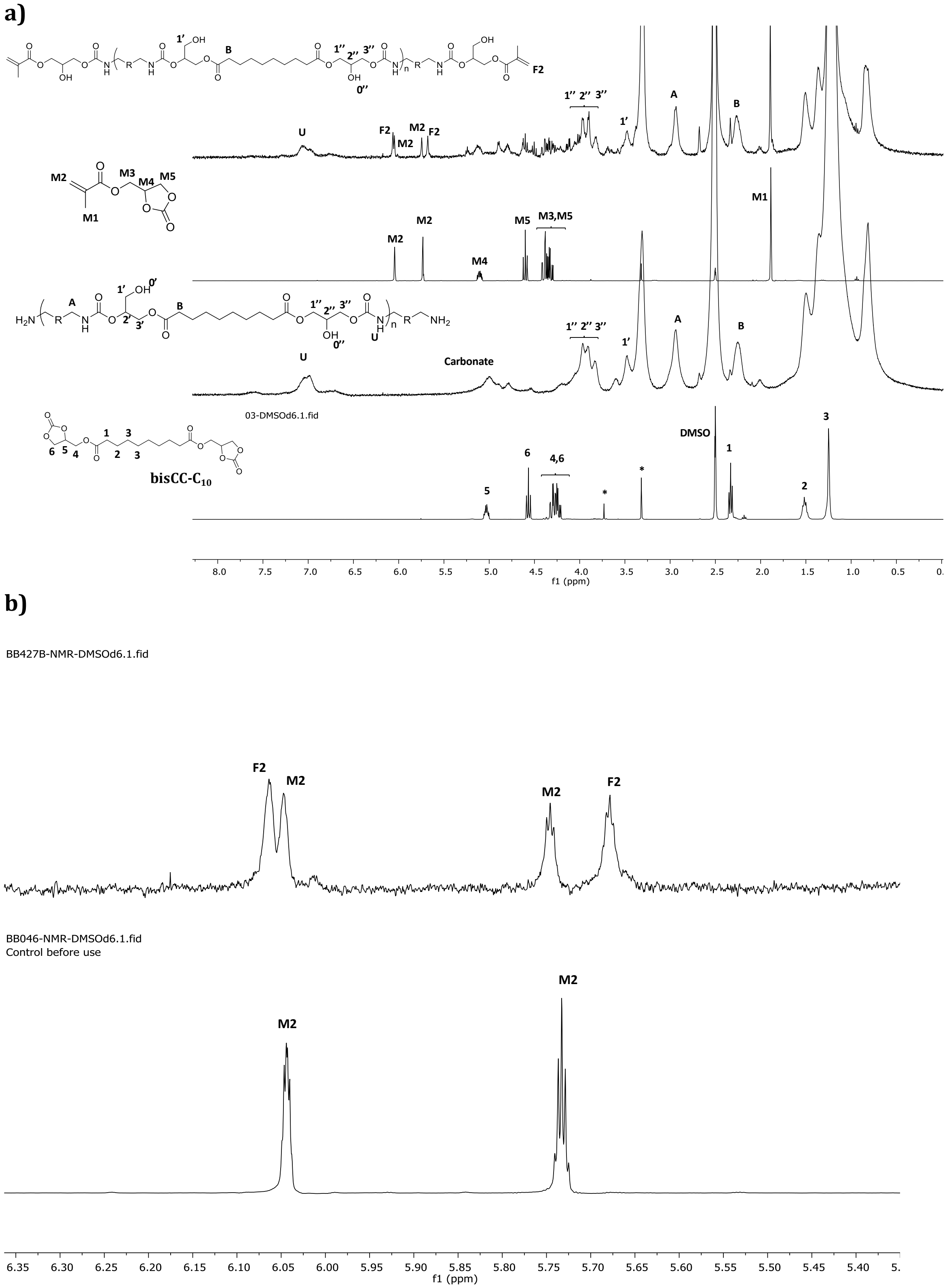


Figure S 4: ^{1}H-NMR of the prepolymers obtained during the preparation of the bifunctionalized PHU from Batch #3(a) Stack spectra of bisCC-C$_{10}$, the amine-terminated PHU, monoCC-GMA and the bifunctional PHU (from bottom to top) and b) Zoom on the vinyl protons of monoCC-GMA (bottom) and the bifunctionalized PHU (top))

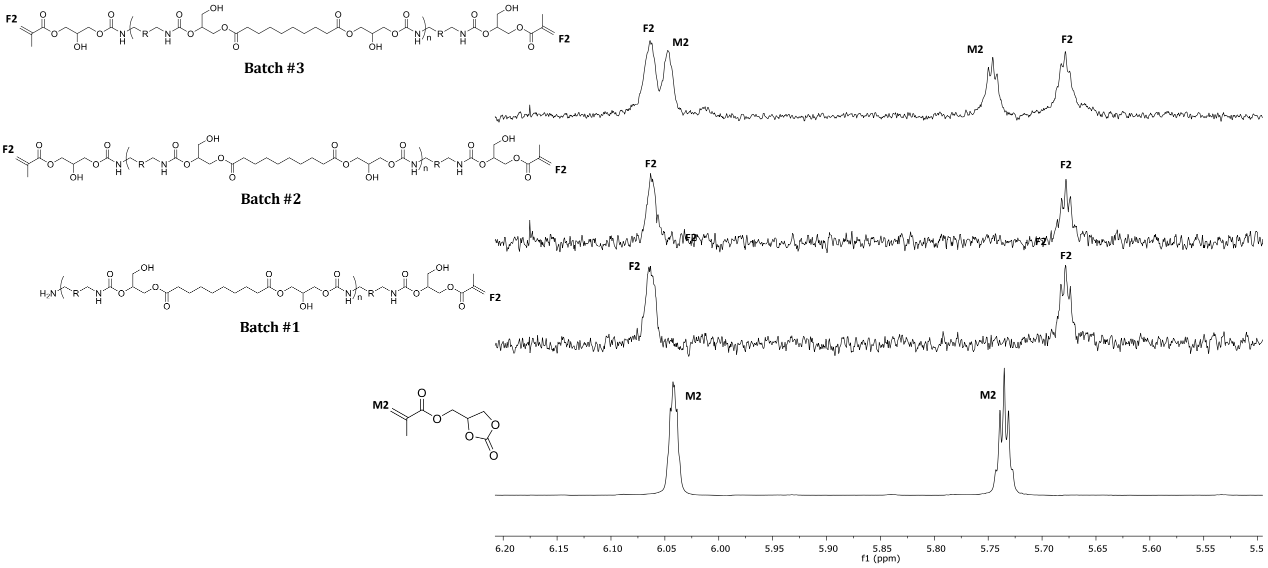


Figure S 5: ^{1}H-NMR (zoom in the range 5.5-6.2 ppm) of the prepolymers obtained during the preparation of the bifunctionalized PHU (Step #2). From bottom to top: monoCC-GMA, mono-functionalized PHU from Batch #1, telechelically-functionalized PHUs from Batch #2 and telechelically functionalized PHU from Batch #3

7.3. Multi-functionalized PHUs

Table S4: Formulation used for Multifunctionalized PHUs

Batch – Multifunctionalized PHU

Targeted DP: **10** (r = 0.818)

Step	Component		Theoretical	Experimental
Step #1 **(4h)**	**bisCC-C$_{10}$**	**m_{bisCC} [g]**	**0.800**	**0.800**
		n_{bisCC} [mmol]	1.99	1.99
		$n_{\text{carbonate}}$ [mmol]	3.98	3.98
	P1075	**m_{P1075} [g]**	**1.321**	**1.322**
		n_{P1075} [mmol]	2.43	2.43
		n_{amine} [mmol]	4.86	4.86
	Excess Amine moiety	n_{amine} [mmol]	0.884	0.887
	Total PHU	**$m_{\text{PHU 1}}$ [g]**	**2.121**	**2.122**
Withdrawn Mass for sampling purposes		**$m_{\text{Sampling 1}}$ [g]**		**0.101**
Remaining PHU		**$m_{\text{PHU 1}} - m_{\text{Sampling 1}}$ [g]**		**2.021**

For the calculations in Step #2, the theoretical amount of OH moieties before sampling was used. To do so, it was considered that 1 mol of carbonate moieties gives 1 mol of hydroxyl moiety after ring opening with an amine.

The amount of OH-moiety to functionalize, which equals the amount of methacrylic anhydride to add, is then given by the following equation:

$$n_{\text{OH}} = n_{\text{Methacrylic Anhydride}} = \frac{n_{\text{carbonate}}}{2}$$

Targeted Degree of functionalization: **50%**

Step #2 **(20h)**	OH to functionalize	n_{OH} [mmol]	1.99	
	Methyl Methacrylate Anhydride	n_{MeMeth} [mmol]	1.99	
		m_{MeMeth} [g]	**0.306**	**0.305**
	Total PHU	**$m_{\text{PHU 2}}$ [g]**		**2.326**
Withdrawn Mass for sampling purposes		**$m_{\text{Sampling 2}}$ [g]**		**0.068**
Remaining PHU for emulsion		**$m_{\text{PHU Final}}$ [g]**		**2.258***

* In this final weight, if we consider that methyl methacrylate has fully reacted in the functionalization step, it should have generated 1.99 mmol of methacrylic acid, corresponding to a weight of 0.199 g.

7.4. Formulations used for the miniemulsions

In the case of the mono-functionalized PHU, aqueous solutions of TBHP (0.0157 g.mL^{-1}) and AsA (0.0152 g.mL^{-1}) were used.

In the case of the bi-functionalized, and multi-functionalized PHUs, the concentrations of the aqueous solutions of TBHP (0.1997 g.mL^{-1}) and AsA (0.1992 g.mL^{-1}) were higher to increase the amount of redox-initiator in order to reduce the induction period and have a faster nucleation of the droplets.

Table S5: Formulation used for the synthesis of the different latexes

	Reference	**Mono-funct. (from Batch #1)**	**Bi-funct. (from Batch #3)**	**Multifunct. (from Batch Multi)**
	N2-Flushing Time	**50 min**	**50 min**	**90 min**
Basic recipe	PHU	2.619 g	2.145 g	2.059 g*
	(/PHU+BMA)	***20 wt%***	***20 wt%***	***18 wt%****
	BMA	10.463 g	8.569 g	9.24 g*
	(/PHU+BMA)	***80 wt%***	***80 wt%***	***82 wt%****
	SA	0.546 g	0.447 g	0.470 g
	wbo	***4.0 wt%***	***4.0 wt%***	***4.0 wt%***
	Dowfax™ 2A1	0.140 g	0.112 g	0.118 g
	wbo	***1.03 wt%***	***1.00 wt%***	***1.00 wt%***
	Water	20.856 g	16.626 g	17.562 g
Post-Stabilization	Dowfax™ 2A1	0.148 g	0.112 g	0.118 g
	wbo	***1.09 wt%***	***1.00 wt%***	***1.00 wt%***
	Water	0.828 g	0.636 g	0.664 g
Initiation	TBHP	0.0067 g	0.0342 g	0.0342 g
	(/ BMA+SA)	***0.06 wt%***	***0.38 wt%***	***0.35 wt%***
	AsAc	0.0066 g	0.0365 g	0.0365 g
	(/ BMA+SA)	***0.06 wt%***	***0.41 wt%***	***0.38 wt%***
	Water	0.863 g	0.369 g	0.369 g
	Feeding time	**2h30**	**2h30**	**2h30**
Post-polymerization		**1h**	**-**	**-**
	TOTAL	36.476 g	29.310 g	30.671 g
Solids Content (wt%)		**37.5**	**38.8**	**39.6**

CHAPTER 5

GENERAL CONCLUSIONS & PERSPECTIVES

The development of non–isocyanate polyurethanes (NIPU) has opened the possibility to access polyurethanes (PUs) without using toxic compounds such as phosgene-based isocyanates. Among NIPUs, poly(hydroxy urethane)s (PHUs) are particularly interesting because their inherent chemical structure includes inner OH pendant moieties, providing them with new ranges of properties when compared to their PU counterparts. However, PHUs still suffer from limitations the major one being the limiting reaction extents, which usually reach a plateau between 90 and 100%, hence preventing those materials to yield polymers of sufficiently high molecular weights to foster industrial implementation. In this Thesis, PHU-based polymer-polymer hybrids are developed in an attempt to overcome this limitation and to pave the way towards the valorization of PHUs.

Therefore, the purpose of this thesis was to synthesize novel waterborne hybrid-NIPU materials (H-NIPUs) by combining bio-based isocyanate-free poly(hydroxy urethane)s (PHUs) pre-polymers with (meth)acrylates. In order to fulfill this goal, several challenges should be overcome such as the synthesis of specific monomers (in this case bis-cyclic carbonates), the bulk polymerization of these monomers with diamines to form the PHUs, the selection of a suitable acrylic phase to dissolve these PHUs and finally the polymerization of the acrylic phase in a mini-emulsion process. As the characteristics and properties of the hybrids are expected to depend on the interaction between the PHU and the acrylic polymer, both grafted and non-grafted hybrids were synthesized and the properties of the resulting coatings investigated.

The aim of the thesis was to make use of PHUs in the development of water-borne PHU-Acrylics polymer-polymer hybrids, to be valorized as coatings, taking advantage of the synergistic combination of the properties of both constitutive polymers. This project thus targeted the design of bio-based PHU monomers capable of yielding PHU pre-polymers that could be compatibilized with a (meth)acrylic phase, dispersed in water and polymerized *via* free radical polymerization in a miniemulsion process to yield both grafted and non-grafted hybrids. The performance of the resulting latexes then had to be studied.

The synthesis of PHUs requires the design of bis-cyclic carbonate compounds (bisCCs), capable to ring open upon polymerization with diamines. The challenge of such syntheses lies in the design of monomers that can be produced at a sufficiently high scale to afford enough material to cast films at the end of the process. In this regard, two ester-activated bisCCs were targeted, one originating from sebacoyl chloride (bisCC-C_{10}) and another derived from succinic anhydride (bisCC-C_4). Both bisCCs were then copolymerized in bulk with various ratios of the aliphatic 1,10-decanediamine and the branched commercially available Priamine™ 1075. It allowed us to get access to PHUs of tunable thermal and viscoelastic properties. In particular, the use of Priamine™ 1075 was found to decrease the

T_g, to provide a better thermal resistance and yield very viscous polymers. On the other hand, the aliphatic 1,10-decanediamine yielded solid PHU materials exhibiting melting temperatures around 50°C (in the case of bisCC-C_4) and 90°C (in the case of bisCC-C_{10}). The bisCCs' aliphatic chain length has thus an influence on the material's resulting thermal and viscoelastic properties. Moreover, a mechanistic study, *via* DFT, allowed to potentially realize that potential tuning of the microstructure of the resulting PHUs might be possible in terms of a preferred formation of primary or secondary OHs, thus broadening the future opportunities for investigation.

With this in mind, PHU-(meth)acrylic waterborne dispersions were prepared by miniemulsion polymerization. Two complementary strategies were explored. The first one involved the formation of the isocyanate-free PHU by aminolysis of cyclic-carbonate derivatives using (meth)acrylic monomers as reacting media, followed by dispersion of the PHU/(meth)acrylates solution in water through a miniemulsification process, and polymerization the (meth)acrylic monomers by free radical polymerization. However, this strategy was hindered by the combined effect of the reaction of the amines with acrylic monomers by an *aza*-Michael-type mechanism with acrylates and the poor solubility of the PHU monomers (amines and cyclic carbonates) in butyl methacrylate. More success was obtained with the second strategy in which the PHU was first form by bulk aminolysis of cyclic-carbonate derivatives using bio-sourced vegetable oil-based diamines. Then, the PHU was dissolved in (meth)acrylate monomers and the solution used as the organic phase of a miniemulsion. The use of a plasticizing diamine was very important to confer the PHU the ability to be soluble in the (meth)acrylic phase. Subsequent free radical polymerization of the (meth)acrylic monomers led to the hybrid PU/(meth)acrylate waterborne dispersions. The choice of the initiator system (in this case the redox pair TBHP/ascorbic acid) was critical to achieve coagulum-free dispersions. Waterborne hybrid dispersions containing up to 30wt% of PHU were prepared and it was found that they were formed by core-shell particles with the PHU in the shell when sufficiently high amounts of PHU was incorporated within the formulation. Transparent films could be cast for all compositions, but some yellowing appeared as the PHU content increased. The minimum film formation temperature (MFFT) decreased with the increasing PHU content, whereas tensile tests showed that softer materials were obtained (clear decrease of both Young's modulus and stress at break, and an increase of the strain at break were observed). The mechanical properties were also affected by the casting temperature. By increasing the casting temperature from 30 to 45°C, the Young's modulus and in particular the strain at break increased, leading to a substantial increase in toughness, presumably due to a better film formation as a result of the better particle packing and perhaps polymer chains interdiffusion. However, further increase of the casting temperature to 60°C led to decrease in Young's modulus, strain at break and toughness, which was attributed to a strong phase separation caused by the migration of the soft phase (PHU).

Waterborne grafted PHU-poly(meth)acrylate hybrid dispersions were also synthesized and the effect of grafting on the particle and film morphologies as well as on the mechanical properties of the films was investigated. The dispersions were prepared by free radical polymerization of a miniemulsion in which the organic phase was a mixture of methacrylate functionalized PHU, BMA and SA. TBHP/AsAc was used as redox initiator. Functionalized PHUs with different architectures were prepared. Telechelic PHUs were synthesized by reacting amine terminated PHUs with carbonated glycidyl methacrylate (monoCC-GMA). The amount of monoCC-GMA was adjusted targeting mono and bifunctional methacrylate functionalized PHUs. A functionalized PHU having multiple methacrylic groups in the backbone was also prepared by reacting the OH groups of the PHU with methacrylic anhydride, thus taking advantage of the unique structure of PHUs. A non-functionalized hybrid was prepared for comparative purposes.

The structure of the functionalized PHU has a substantial effect on the polymer hybrid. The hybrids prepared with both the non-functionalized and the functionalized PHUs presented two T_gs. The one of the (meth)acrylic polymer was measured around 24-27 °C, another one was observed at a lower temperature, corresponding to the PHU. This lower temperature increased from -20 °C for the hybrid containing non-functionalized and mono-functionalized PHUs up to -12°C for the hybrid prepared with the multi-functionalized PHU, which indicates that grafting increased with the methacrylic functionalization. Functionalization has also a strong effect on the molecular weight distribution. AF4 measurements showed that all hybrids, with the exception of that prepared with the multifunctional PHU, presented two peaks, the small one corresponding to the ungrafted PHU and the large one to the poly(methacrylate) that included the PHU grafted. If this result was expected for the non-functionalized and the mono-functionalized PHUs, it was however surprising for the bifunctionalized PHU. This indicates that some PHUs were not functionalized or were not reactive enough. Nevertheless, hybrids formed with this telechelic PHU as well as with the multifunctional PHU yielded macroscopic gel.

Clear films were cast from all the hybrids, although that of the multifunctional PHU was prone to crack. The structure of the hybrid had a strong influence on the minimum film forming temperature (MFFT), film morphology and mechanical properties of the film. For the functionalized PHUs, MFFT increased with the crosslinking density, but the MFFT of the monofunctionalized hybrid was lower than that of the non-functionalized one. Moreover, the MMFT of the telechelic and multi-functionalized-PHU-based hybrids were higher. These results were attributed to the decrease of the fraction of free soft PHU and the stronger mechanical properties of the crosslinked particles. The film prepared with the mono-functionalized PHU showed a clear phase separation by TEM with formation or rather large PHU-rich clusters. These clusters were not visible in the films containing telechelic and multifunctional PHUs.

This research work addressed several challenges in the field of polymerization, and can call for future perspectives in different areas.

Regarding the PHU synthesis, it would be very interesting to explore more deeply the potential control of the PHU's microstructure due to the aliphatic chain length of the bisCC monomer. Moreover, a clear challenge, arising from Chapter 4, is the control of the chain length of the PHUs. A detailed investigation of the reaction kinetics, and maybe modeling could help design optimized processes in this purpose.

Regarding the formation of PHU-Acrylic hybrids, varying the acrylic phase composition could allow broadening the scope of resulting properties and access different end-uses (for example adhesives). Grafting was also found to strongly influence the microstructure as well as the mechanical properties of the resulting hybrids. Future work, notably on the tuning of the functionalization degree of the PHUs, could be of help to get a deeper insight into the structure-properties relationship of the final hybrids.

The process developed in this thesis is based on the use of conventional surfactants that can migrate during film formation and cause problems in gloss and adhesion of the coatings. The design of PHUs containing inner-surfactants will overcome this drawback. Additionally, they might reduce the need of a highly energetic-device to form the dispersion.

CHAPITRE 5

CONCLUSIONS GENERALES & PERSPECTIVES

Le développement des polyuréthanes sans isocyanates (NIPU) a ouvert la possibilité d'accéder aux polyuréthanes (PU) sans utiliser de composés toxiques tels que les isocyanates à base de phosgène. Parmi les NIPU, les poly (hydroxy uréthanes) (PHUs) sont particulièrement intéressants parce que leur structure chimique inhérente comprend des groupements OH internes pendants, leur fournissant de nouvelles gammes de propriétés par rapport à leurs homologues PU. Cependant, les PHU souffrent encore de limitations, la principale étant un l'avancement de réaction limité, qui atteint généralement un plateau entre 90 et 100%, empêchant ainsi ces matériaux de produire des polymères de masse molaire suffisamment élevée pour favoriser une mise en place industrielle. Dans cette thèse, des hybrides polymère-polymère à base de PHU sont développés dans le but de surmonter cette limitation et d'ouvrir la voie à la valorisation des PHU.

Par conséquent, le but de cette thèse était de synthétiser de nouveaux matériaux hybrides NIPU en dispersion aqueuse (H-NIPU) en combinant des prépolymères biosourcés poly(hydroxy uréthane)s sans isocyanate (PHUs) avec des (méth)acrylates. Afin d'atteindre cet objectif, plusieurs défis doivent être surmontés tels que la synthèse de monomères spécifiques (dans ce cas des carbonates bis-cycliques), la polymérisation en masse de ces monomères avec des diamines pour former les PHU, la sélection d'une phase acrylique appropriée pour dissoudre ces PHU et enfin la polymérisation de la phase acrylique dans un procédé de mini-émulsion. Comme les caractéristiques et les propriétés des hybrides devraient dépendre de l'interaction entre le PHU et le polymère acrylique, des hybrides greffés et non greffés ont été synthétisés et les propriétés des revêtements de surface résultants ont été étudiées.

L'objectif de la thèse était d'utiliser les PHU dans le développement d'hybrides polymère-polymère PHU-Acryliques en dispersion aqueuse, les valoriser en tant que revêtements de surface, en profitant de la combinaison synergique des propriétés des deux polymères constitutifs. Ce projet a ainsi ciblé la conception de monomères PHU biosourcés capables de produire des prépolymères PHU qui pourraient être compatibilisés avec une phase (méth)acrylique, dispersés dans l'eau et polymérisés par polymérisation radicalaire dans un processus de mini-émulsion pour produire à la fois des hybrides greffés et non-greffés. Les performances des latex résultants ont ensuite dû être étudiées.

La synthèse des PHU nécessite la conception de composés carbonates bis-cycliques (bisCC), capables de s'ouvrir lors de la polymérisation avec des diamines. Le défi de telles synthèses réside dans la conception de monomères qui peuvent être produits à une échelle assez élevée pour fournir suffisamment de matière pour produire des films à la fin du processus. À cet égard, deux bisCC activés par des fonctions esters ont été ciblés, l'un provenant du chlorure de sébacoyle (bisCC-C_{10}) et l'autre dérivé de l'anhydride succinique (bisCC-C_4). Les deux bisCCs ont ensuite été copolymérisés en masse avec divers ratios de la 1,10-décanediamine aliphatique et de la Priamine™ 1075 branchée commerciale. Cela nous a permis d'accéder à des PHU de propriétés thermiques et viscoélastiques modulables. En particulier, l'utilisation de Priamine™ 1075 s'est avérée diminuer la température de transition vitreuse (T_g), pour fournir une meilleure résistance thermique et donner des polymères très visqueux. D'autre part, la 1,10-décanediamine aliphatique a donné des matériaux PHU solides présentant des températures de fusion autour de 50°C (dans le cas du bisCC-C_4) et 90°C (dans le cas du bisCC-C_{10}). La longueur de la chaîne aliphatique des bisCC a donc une influence sur les propriétés thermiques et viscoélastiques résultantes du matériau. De plus, une étude mécanistique, via DFT, a permis de réaliser qu'éventuellement, une modulation potentielle de la microstructure des PHUs résultants pourrait être possible en termes de formation préférée de groupements OH primaires ou secondaires, élargissant ainsi les futures opportunités de recherche.

En prenant ceci en compte, des dispersions aqueuses de PHU-(méth)acrylique ont été préparées par polymérisation en mini-émulsion. Deux stratégies complémentaires ont été explorées. La première impliquait la formation de PHU sans isocyanate par aminolyse de dérivés de carbonate cyclique en utilisant des monomères (méth)acryliques comme milieu de réaction, suivie de la dispersion de la solution de PHU/(méth)acrylates dans l'eau par un procédé de mini-émulsification et de polymérisation des monomères (méth)acryliques par polymérisation radicalaire. Cependant, cette stratégie a été entravée par l'effet combiné de la réaction des amines avec les monomères acryliques par un mécanisme de type aza-Michael avec les acrylates et la mauvaise solubilité des monomères PHU (amines et carbonates cycliques) dans le méthacrylate de butyle. Plus de succès a été obtenu avec la deuxième stratégie dans laquelle le PHU a été formé par aminolyse en masse de dérivés de carbonate cyclique en utilisant des diamines bio-sourcées à base d'huile végétale. Ensuite, le PHU a été dissous dans des monomères (méth)acrylates et la solution a été utilisée comme phase organique d'une mini-émulsion. L'utilisation d'une diamine plastifiante était très importante pour conférer au PHU la capacité d'être soluble dans la phase (méth)acrylique. La polymérisation radicalaire subséquente des monomères (méth)acryliques a conduit aux dispersions aqueuse d'hybrides PU/(méth)acrylate. Le choix du système initiateur (dans ce cas, la paire redox TBHP/acide ascorbique) était essentiel pour obtenir des dispersions sans coagulum. Des dispersions aqueuses d'hybrides contenant jusqu'à 30% (en masse) de PHU ont été préparées et il s'est avéré qu'elles étaient formées par des particules de type cœur-coquille avec le PHU dans la coquille lorsque des quantités suffisamment élevées de PHU ont été incorporées dans la formulation. Des films transparents pouvaient être formés pour toutes les compositions, mais un certain jaunissement est apparu au fur et à mesure que la teneur en PHU augmentait. La température minimale de formation de film (MFFT) a diminué avec l'augmentation de la teneur en PHU, tandis que les tests de traction ont montré que des matériaux plus souples étaient obtenus (une nette diminution du module de Young et de la contrainte à la rupture, et une augmentation de la déformation à la rupture ont été observées). Les propriétés mécaniques ont également été affectées par la température de formation des films. En augmentant la température de coulée de 30 à 45°C, le module d'Young et en particulier la déformation à la rupture ont augmenté, conduisant à une augmentation substantielle de la ténacité, probablement en raison d'une meilleure formation de film grâce à un meilleur empilement des particules et peut-être l'interdiffusion des chaînes polymères. Cependant, une nouvelle augmentation de la température de formation des films à 60°C a entraîné une diminution du module de Young, de la déformation à la rupture et de la ténacité, ce qui a été attribué à une forte séparation de phases provoquée par la migration de la phase molle (PHU).

Des dispersions aqueuses de polymères méthacryliques greffés avec des PHU hybrides ont également été synthétisées et l'effet du greffage des particules sur la morphologie des films ainsi que sur leurs propriétés mécaniques a été étudié. Ces dispersions ont été préparées par polymérisation radicalaire en mini-émulsion dont la phase organique est un mélange de PHU fonctionnalisé méthacrylate, BMA et SA avec un initiateur redox, le couple TBHP/AsAc. Des PHUs fonctionnalisés avec différentes architectures macromoléculaires ont été préparés. Des PHUs téléchéliques ont été synthétisés en faisant réagir des PHUs terminés par un groupement amine avec du méthacrylate de glycidyle carbonaté (monoCC-GMA). La quantité de monoCC-GMA a été ajustée de façon à obtenir un PHU soit mono soit di-fonctionnalisé méthacrylate. Un PHU avec de nombreux groupes méthacryliques greffés a aussi été préparé en faisant réagir les groupements OH du PHU avec de l'anhydride méthacrylique, tirant ainsi profit de la structure remarquable des PHUs. Un hybride non fonctionnalisé a aussi été préparé à des fins de comparaison.

La structure des PHUs fonctionnalisés a un effet non négligeable sur le polymère hybride. Les hybrides préparés soit avec un PHU non fonctionnalisé soit avec un PHU fonctionnalisé présentent deux T_gs distinctes. Celle attribuée au polymère méthacrylique est mesurée autour de 24-27°C et une autre, correspondant au PHU, est observée à plus basse température. Cette dernière augmente de -20°C à -12°C en passant d'un hybride non fonctionnalisé ou mono-fonctionnalisé à un hybride multi-fonctionnalisé, indiquant que le taux de greffage a augmenté lors de la fonctionnalisation des OH en groupement méthacrylique. Le fait de fonctionnaliser a également un grand effet sur la distribution des masses molaires. Des mesures en AF4 ont montré que pour tous les hybrides, à l'exception de ceux préparés avec le PHU multi-fonctionnalisé, deux pics étaient obtenus, le petit correspondant au PHU non greffé et le gros correspondant au poly(méthacrylate) greffé PHU. Bien que ce résultat ait été attendu pour les PHUs non fonctionnalisés et mono-fonctionnalisés, il se révèle surprenant pour le PHU di-fonctionnalisé. Cela indique que certains PHUs n'ont pas été fonctionnalisés ou n'étaient pas assez réactifs. Des gels macroscopiques ont tout de même été obtenus avec les hybrides formés avec le PHU téléchélique ou le PHU multifonctionnel.

Des films transparents ont été obtenus à partir des hybrides bien que ceux obtenus à partir du PHU multifonctionnel cassaient facilement. La structure des hybrides a eu un impact considérable sur la température minimale de formation de film (MFFT), la morphologie du film et les propriétés mécaniques du film. La MFFT des PHUs fonctionnalisés augmente avec le degré de réticulation mais celle des hybrides mono-fonctionnalisés est plus faible que celle des hybrides non fonctionnalisés. De plus, la MFFT des hybrides faits à partir de PHUs téléchéliques ou multi-fonctionnalisés est plus élevée. Cela est attribué à la diminution de la fraction libre de PHU, mou, et aux meilleures propriétés mécaniques des particules réticulées. Une nette séparation de phase a été observée en TEM pour les films préparés à partir de PHU mono-fonctionnalisé, avec la formation de clusters relativement gros riches en PHU. Ces derniers ne sont pas visibles dans les films contenant des PHUs téléchéliques ou multi-fonctionnels.

De nombreux enjeux dans le domaine de la polymérisation ont été abordés au cours de ces travaux de thèse et permettent ainsi d'envisager plusieurs perspectives dans différents thèmes.

Dans le cas de la synthèse des PHUs, il serait très intéressant d'explorer de manière plus approfondie le contrôle potentiel de la microstructure du PHU selon la taille de la chaine aliphatique du monomère bisCC, comme suggéré par des calculs DFT. De plus, un enjeu principal, qui émerge du chapitre 4, est le contrôle de la longueur de chaine des PHUs. Dans ce sens, une analyse détaillée de la cinétique de réaction, voire même une modélisation, pourraient permettre de créer un procédé optimisé.

Concernant la formation des hybrides entre le PHU et les acryliques, la variation de la composition de la phase acrylique pourrait permettre d'étenddre le portfolio des propriétés mécaniques obtenues ainsi que d'avoir accès à de nouveaux domaines d'utilisation (par exemple les adhésifs). Il apparait que la microstructure et les propriétés mécaniques sont fortement influencées par le greffage. Un travail futur concernant, notamment, le degré de fonctionnalisation des PHUs pourrait être d'intérêt pour obtenir des une meilleure compréhension de la relation structure-propriétés des hybrides résultants.

Le procédé développé dans cette thèse est basé sur l'utilisation de surfactants conventionnal qui peuvent migrer durant la formation des films et faire émerger des problèmes en terme de brillance et d'adhésion des revêtements de surface. La conception de PHU contenant des agents de dispersion internes contrerait cet inconvénient. Il se pourrait de plus que cela permette de réduire le besoin d'un équipement à haute énergie afin de former la dispersion.

CAPÍTULO 5

RESUMEN, CONCLUSIONES & PERSPECTIVAS

El desarrollo de poliuretanos sin isocianatos (NIPU) ha abierto la posibilidad de acceder a poliuretanos (PUs) sin la presencia de compuestos tóxicos como los isocianatos a base de fosgeno. Entre los principales NIPU, los poli-hidroxi uretanos (PHUs) son particularmente interesantes ya que dentro de su estructura química incluye grupos colgantes de hidroxilo, los cuales proporcionan nuevas propiedades en comparación con sus análogos de PUs. Sin embargo, los PHUs presentan ciertas limitaciones, entre las que se destacan una conversión limitada, que usualmente es de 90 y 100%. Debido a esto no es posible alcanzar materiales con pesos moleculares suficientemente altos para su posible uso en la industria. En esta tesis, se desarrollaron híbridos polímero-polímero basados en PHUs con el objetivo de superar esta limitación y simplificar el camino hacia la valorización de los PHUs.

Así, el propósito de esta tesis ha consistido en la síntesis de nuevos materiales híbridos de NIPU a base de agua (H-NIPUs) mediante la combinación de prepolímeros de poli-hidroxi uretano (PHUs) libres de isocianato, con (met)acrilatos como base. Para cumplir este objetivo, se han debido superar varios desafíos, entre ellos, la síntesis de monómeros específicos (en este caso, carbonatos bicíclicos), la polimerización en masa de dichos monómeros en presencia de diaminas para formar los PHUs, la selección de una fase acrílica adecuada para la disolución de los PHUs y, finalmente, la polimerización de la fase acrílica mediante la técnica de miniemulsión. Debido a que las características y propiedades de los híbridos poliméricos dependen de la interacción entre el PHU y el polímero acrílico, se sintetizaron híbridos, tanto injertados como no injertados, y se investigaron las propiedades de los recubrimientos resultantes.

El objetivo de la tesis fue utilizar PHUs en el desarrollo de híbridos polímero-polímero de PHUs-Acrílicos a base de agua, para ser desarrollados como recubrimientos, aprovechando la combinación sinérgica de las propiedades de ambos polímeros constitutivos. Por lo tanto, este proyecto se centró en el diseño de monómeros de PHUs como base biológica capaces de producir prepolímeros de PHUs que podrían compatibilizarse con una fase metacrílica, dispersarse en agua y polimerizarse mediante polimerización por radicales libres utilizando la técnica de miniemulsión para producir tanto híbridos poliméricos injertados como no injertados. Y posteriormente, se estudió el rendimiento de los látex resultantes.

La síntesis de PHUs requiere del diseño de compuestos de carbonato biscíclico (bisCCs), capaces de abrir el anillo tras la polimerización con diaminas. El desafío de estos métodos sintéticos radica en el diseño de monómeros que pueden producirse a una escala lo suficientemente alta para obtener suficiente cantidad de material explotable para la formación de las películas poliméricas al final del proceso. Para lograr esto, se seleccionaron dos bisCCs activados con un grupo éster, uno de ellos procedente del cloruro de sebacoilo (bisCC-C_{10}) y el otro derivado del anhídrido succínico (bisCC-C_4). Ambos bisCCs se copolimerizaron en masa en varias proporciones de 1,10-decanodiamina alifática y Priamine™ 1075 ramificada disponible comercialmente. Esto permite modular las propiedades térmicas y viscoelásticas de los PHUs. En particular, se encontró que el uso de

Priamine™ 1075 disminuye la temperatura de temperatura de transición vítrea(Tg), produciendo polímeros altamente viscosos y con una mejor resistencia térmica. Por otro lado, al utilizar la 1,10-decanodiamina alifática se pueden producir materiales sólidos de PHUs con puntos de fusión alrededor de 50°C (en el caso de bisCC-C_4) y 90°C (en el caso de bisCC-C_{10}). La longitud de la cadena alifática de los bisCCs influye en las propiedades térmicas y viscoelásticas resultantes del material. Además, un estudio teórico, utilizando DFT, permitió ver que el potencial ajuste de la microestructura de los PHUs resultantes, podrían ser posibles en términos de la formación preferentemente de los grupos OH primarios o secundarios, ampliando así las oportunidades de investigación en un futuro.

Debido a esto, se prepararon dispersiones de PHU-metacrilato a base de agua por polimerización en miniemulsión; y se exploraron dos estrategias complementarias. La *primera* implicaba la formación del PHU libre de isocianato por aminólisis de derivados de carbonato cíclico utilizando monómeros metacrílicos como medios de reacción, seguido de la dispersión de la mezcla PHU/metacrilatos en agua a través de un proceso de miniemulsificación, lo que provoca la polimerización por radicales libre de los monómeros metacrílicos. Sin embargo, esta estrategia se vio obstaculizada por el efecto combinado de la reacción de las aminas con los monómeros acrílicos por un mecanismo de tipo aza-Michael con acrilatos, además de la escasa solubilidad de los monómeros de PHU (aminas y carbonatos cíclicos) en metacrilato de butilo. En la *segunda estrategia* se formó por primera vez el PHU mediante aminólisis en masa de derivados de carbonato cíclico, utilizando diaminas basadas en aceite vegetal de origen biológico. Posteriormente, el PHU se disolvió en monómeros acrílicos para utilizarse después como fase orgánica de la miniemulsión. Para poder solubilizar el PHU en monómeros acrílicos es necesaria la adición de una diamina plastificante. La polimerización por radicales libres de estos monómeros dio como resultado dispersiones acuosas de híbridos de PU/metacrilato. La selección del sistema del iniciador (en este caso el par redox TBHP/ácido ascórbico) fue crítica para lograr dispersiones sin coágulos. Se prepararon dispersiones híbridas a base de agua que contenían hasta 30% en peso de PHU y se observó que estaban formadas por partículas *core-shell*. Se observó que al incorporar cantidades suficientemente altas de PHU dentro de la formulación se puede observar el PHU en la superficie de las partículas. También se pudieron formar películas transparentes con las diferentes composiciones experimentales; sin embargo, al aumentar el contenido de PHU la apariencia de las películas comenzó a tomar un aspecto amarillento. La temperatura mínima de formación de la película (MFFT) disminuyó con el aumento del contenido de PHU, mientras que las pruebas de tracción mostraron que se obtuvieron materiales más blandos (demostrado por la clara disminución tanto del módulo de Young como de la tensión de rotura, así como el aumento de la elongación de rotura). Las propiedades mecánicas también se vieron afectadas por la temperatura de formación de las películas poliméricas. Al aumentar la temperatura de 30 a 45°C, el módulo de Young y, en particular, la tensión de rotura, aumentan. Esto causo un incremento sustancial de la tenacidad lo cual está relacionado probablemente a un mejor empaquetamiento de partículas, y a la interdifusion de las cadenas poliméricas. Sin embargo, el aumento adicional de la temperatura para la formación de la película a 60°C condujo a una disminución en el módulo de Young, la tensión de rotura y la tenacidad, que se atribuyó a una fuerte separación de fases causada por la migración de la fase blanda constituida por PHU.

También se sintetizaron dispersiones acuosas de polímeros híbridos de PHU-polimetacrilato injertados, se investigó el efecto del injerto sobre la morfología de las partículas y películas, así como las propiedades mecánicas de estas. Las dispersiones se prepararon por polimerización por radicales libres de una miniemulsión en la que la fase orgánica era una mezcla de metacrilato funcionalizado con PHU, BMA y SA. El par TBHP/AsAc se utilizó como iniciador redox. Se prepararon PHUs funcionalizadas con diferentes arquitecturas. Los PHUs telequelicas se sintetizaron haciendo reaccionar estos PHUs con grupos terminales tipo amina con metacrilato de glicidilo carbonatado (monoCC-GMA). La cantidad de monoCC-GMA se ajustó a los PHUs mono y bifuncionales, funcionalizados con metacrilato. Igualmente, se preparó un PHU funcionalizado con múltiples grupos metacrílicos en la cadena haciendo reaccionar los grupos hidroxilo del PHU con anhídrido metacrílico, aprovechando así la estructura única de los PHUs. De forma complementaria, se preparó un híbrido no funcionalizado con fines comparativos.

La estructura del PHU funcionalizado tiene un efecto sustancial sobre el híbrido polimérico. Los híbridos preparados con los PHUs no funcionalizados y funcionalizados presentaron dos temperaturas de transición vítreas (T_gs). La primera T_{g1} se observó alrededor de 24-27ºC correspondiente al polímero metacrílico y la segunda T_{g2} se observó a una temperatura menor a la anterior, la cual corresponde al PHU. Esta T_{g2} aumentó de -20°C para el híbrido que contiene PHUs no funcionalizados y mono-funcionalizados, hasta -12°C para el híbrido preparado con el PHU multifuncionalizado. Este hecho indica que el injerto aumentó con la funcionalización metacrílica. La funcionalización también tiene un fuerte efecto sobre la distribución del peso molecular. Las mediciones de AF4 (Asymetric field flow-field fractionation) mostraron que todos los híbridos, con excepción de los preparados con el PHU multifuncional, presentaron dos señales: el menor pico correspondiente al PHU no injertado y el mayor al polimetacrilato que incluía el PHU injertado. Este resultado no era sorprendente para los PHUs no funcionalizados y mono funcionalizados; sin embargo, no se esperaba para el PHU bifuncionalizado. Esto indica la no funcionalización de algunos PHUs o una limitada reactividad. No obstante, los híbridos formados con el PHU telequelico así como el PHU multifuncional, produjeron un gel macroscópico.

En conclusión, se formaron películas transparentes de todos los híbridos, aunque la película correspondiente al PHU multifuncional era propenso a la formación de grietas. La estructura del híbrido tuvo una fuerte influencia en la temperatura mínima de formación de la película (MFFT), así como la morfología de la película y las propiedades mecánicas de esta. Para los PHUs funcionalizados, la MFFT aumentó con la densidad de reticulación, pero la MFFT del híbrido monofuncionalizado fue menor que la del híbrido no funcionalizado.

Además, el MMFT de los híbridos basados en PHU telequélicos y multifuncionalizados fue mayor. Estos resultados se atribuyeron a la disminución de la fracción de PHU libre y a las mejores propiedades mecánicas de las partículas reticuladas. El estudio por TEM de la película preparada con el PHU monofuncionalizado mostró una clara separación de fase con la formación de aglomerados constituidos de PHU. Estos grupos no eran visibles en las películas que contenían PHU telequelicos y multifuncionales.

Este trabajo de investigación abordó varios desafíos en el campo de la polimerización, y puede requerir futuras perspectivas en diferentes áreas de la ciencia.

Con respecto a la síntesis de PHU, sería interesante explorar de manera más exhaustiva el posible control de la microestructura de PHU debido a la longitud de la cadena alifática del monómero bisCC. Además, el trabajo del Capítulo 4 sugiere un claro desafío ya que consiste en el control de la longitud de la cadena de los PHUs. Una investigación detallada de la cinética de reacción, y tal vez un trabajo de modelización, podrían ayudar a diseñar procesos optimizados

Con respecto a la formación de híbridos entre PHUs y acrílicos, la variación de la composición de la fase acrílica permitiría ampliar el alcance de las propiedades resultantes y acceder a diferentes aplicaciones, como los adhesivos, entre otros. Por otra parte, en este trabajo se demostró que los injertos influyen fuertemente en la microestructura, así como en las propiedades mecánicas de los híbridos resultantes. Como trabajo futuro, el ajuste del grado de funcionalización de las PHU podría ayudar a la obtención de una visión más profunda de la relación estructura-propiedades de los híbridos finales.

Por último, el proceso desarrollado en esta tesis se basa en el uso de tensoactivos convencionales que pueden migrar durante la formación de la película, trayendo consigo algunos inconvenientes relacionados con el brillo y la adhesión de los recubrimientos. El diseño de las PHU que contienen tensoactivos internos superará este problema. Además, podrían reducir la necesidad de un dispositivo menos energívoro para formar la dispersión.

Design of Waterborne Isocyanate-free Poly(Hydroxy Urethane)s– Poly(Butyl Methacrylate) Hybrids *via* Miniemulsion and Properties of the Cast Films

Abstract: The objective of this thesis consists in the development of waterborne hybrid polymers composed of vegetable oil-based poly(hydroxy urethane) – PHU – and poly(butyl methacrylate) – polyBMA. To do so, the design of fatty-acid based bis-cyclic carbonates, as well as their behavior in the bulk polymerization with fatty-acid based diamines was firstly studied. The bis-cyclic carbonate structure was found to influence the microstructure of the formed poly(hydroxy urethane)s as well as the properties of the resulting poly(hydroxy urethane)s. Secondly, the design of waterborne PHU-PolyBMA polymer-polymer hybrids was performed using a miniemulsion process. Both non-crosslinked and crosslinked formulations were developed and compared with respect to kinetics, particle morphology, film formation ability and film morphology. On the one hand, in the case of non-crosslinked hybrids, the ratio between the PHU and the acrylic phase was found to have a strong impact onto the film casting ability as well as the extent of phase segregation. On the other hand, the influence of grafting was analyzed and it was shown to be a potential solution towards the formation of more homogeneous films, exhibiting tunable mechanical properties.

Keywords: Non-isocyanate Polyurethanes, Poly(hydroxy urethane)s, Fatty acids, PHU-Acrylic hybrids, Miniemulsion, Waterborne, Grafting

Conception d’Hybrides Poly(Hydroxy Uréthane)s sans Isocyanate – Poly(Méthacrylate de Butyle) en Mini-émulsion et Propriétés des Films Résultants

Résumé : L’objectif de cette these consiste au développement de polymères hybrides en dispersion aqueuse composés de poly(hydroxy uréthane)s – PHUs – issus d’huile végétale, et de poly(méthacrylate de butyle) – PolyBMA. La synthèse de bis-carbonates cycliques issus d’acides gras, ainsi que leur comportement en polymérisation en masse avec des diamines également issues d’acides gras, ont été étudiés dans un premier temps. Il a été montré que la structure du bis-carbonate cyclique influence la microstructure du poly(hydroxy uréthane) formé ainsi que les propriétés des poly(hydroxy uréthane)s résultants. Dans un second temps, la conception de dispersions aqueuses d’hybrides polymère-polymère PHU-PolyBMA a été réalisée *via* l’utilisation d’un procédé de miniémulsion. Des formulations à la fois non-réticulées et réticulées ont été développées et comparées en termes de cinétique, morphologie des particles, capacité à former des films et morphologie des films. D’une part, dans le cas des hybrides non-réticulés, il a été trouvé que le ratio entre le PHU et la phase acrylique jouait un rôle important dans la possibilité de former des films ainsi que la tendance à la ségrégation de phase. D’autre part, l’influence de la réticulation a été analysée et il a été montré qu’elle pouvait être une solution potentielle pour la conception de films plus homogènes, aux propriétés mécaniques modulables.

Mots clefs: Polyuréthanes sans isocyanates, Poly(hydroxy uréthane)s, Acides gras, Hybrides PHU-Acrylique, Mini-émulsion, Dispersion aqueuse, Réticulation