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Water-based Non-Isocyanate Polyurethanes-Polyureas (NIPUUs)

Boris Bizet,^{ab} Étienne Grau,^a Henri Cramail ^{*a} and José M. Asua ^{*b}

Non-isocyanate polyurethane-ureas (NIPUUs) are a greener alternative to the traditional isocyanate-based polyurethane-ureas. These materials are synthesized by transurethanization and aminolysis of cyclic carbonate, commonly performed in solvents and in bulk. For several reasons including scalability, properties and environmental impact, there is a growing interest in developing water-based NIPUUs. This review aims at discussing the achievements and the remaining challenges in the development of water-soluble NIPUUs, NIPUUs-based hydrogels as well as water-borne NIPUU dispersions.

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 foams, packaging, automotive, construction, textile industry, adhesives and coatings.²⁻⁶

Polyurethanes are also used for biomedical applications⁷ including long-term implants and scaffolds,^{8,9} bone repair,¹⁰ tissue engineering of cardiovascular system¹¹ as well as 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 and elasticity.¹⁴ Variations of the type and proportion of the diisocyanate, polydiol and chain extender allow 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 polymers,¹⁵ graphene,¹⁶ cellulose nanocrystals,¹⁷ clays¹⁸ 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 been used in this purpose²⁰⁻²⁸ and some of these products 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, dermatitis 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 is a strong

incentive to develop isocyanate-free pathways for the synthesis of PUs and PUreas. Several reviews focusing on the synthesis and process optimization for the formation of non-isocyanate polyurethanes, NIPUs, are available.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).

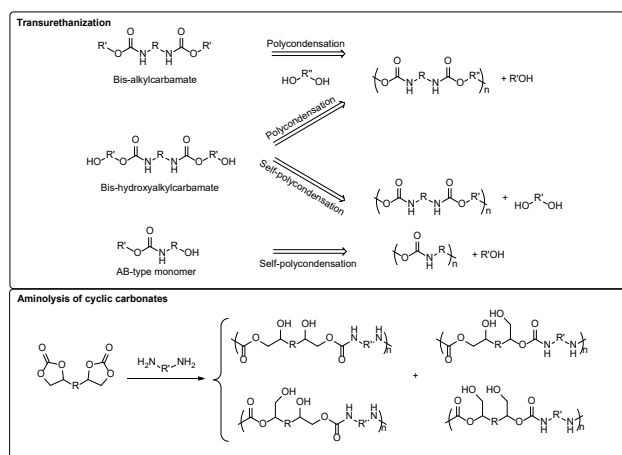


Figure 1 Transurethanization vs Aminolysis of cyclic carbonate compounds

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 biomedical 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 it leads 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 thus to summarize this emerging field.

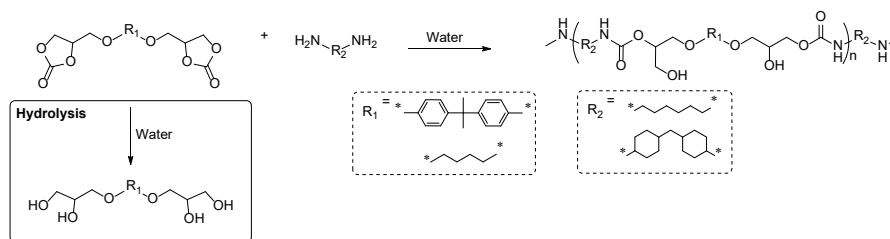
Water-soluble NIPUs

NIPU synthesis using water as reaction medium

The very first example of NIPU synthesis using water as reaction medium was published by Endo and coworkers⁴⁷ who

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 bisphenol 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 50°C.⁴⁸ These authors showed that the longer the length of the reactive aliphatic amine, the lower



Scheme 1 Preparation of poly(hydroxyurethane)s in water – adapted from Endo and coworkers⁴⁷

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 them more “dispersion-like”. Moreover, the structure of the diamine, and its water solubility influenced the kinetics of the reactions: the cycloaliphatic diamine yielded a diffusion-limited process, mostly due to the high hydrophobicity and the weak nucleophilicity of the diamine, whereas for the more nucleophilic aliphatic hexamethylene diamine, the efficiency of the reaction was found to rely on both the temperature and the reaction time.

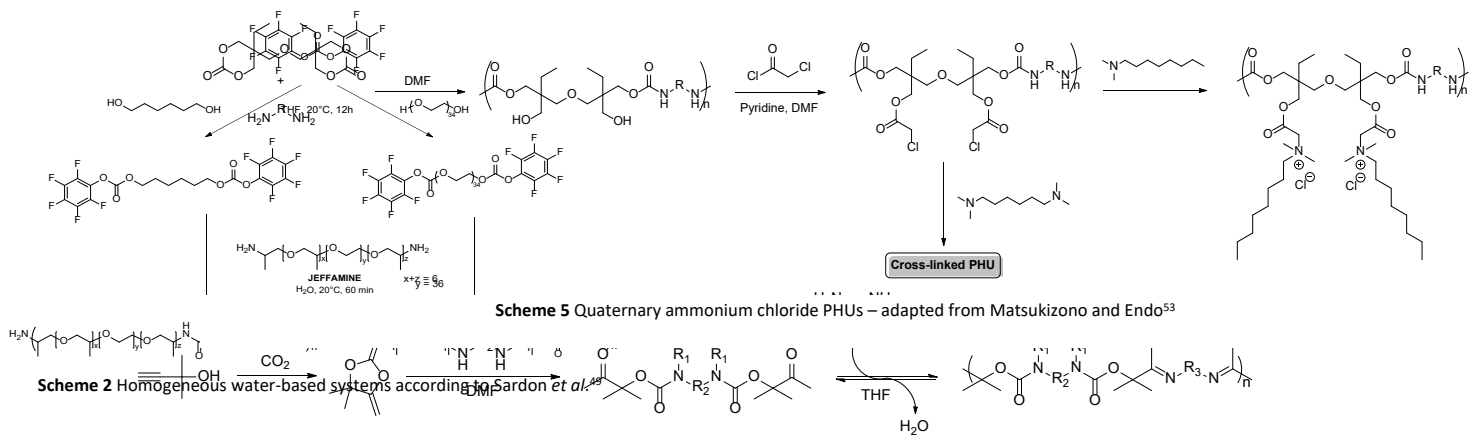
In order to avoid the drawbacks associated with the use of cyclic carbonates in water, Sardon *et al.*⁴⁹ explored a transesterification-like route. The authors designed bis-carbonates based on poly(ethylene glycol) - PEG, or hexanediol that were functionalized with bis(pentafluorophenyl)carbonate that 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. The copolymer structure (balance between hard and soft segments) was tuned by varying the monomer ratio. High conversions (>98%) and polymers with molar masses ranging from 15 to 16 kDa (\bar{M}_w/\bar{M}_n close to 2, according to SEC in THF) were

obtained. The polymers exhibited melting behaviors 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.

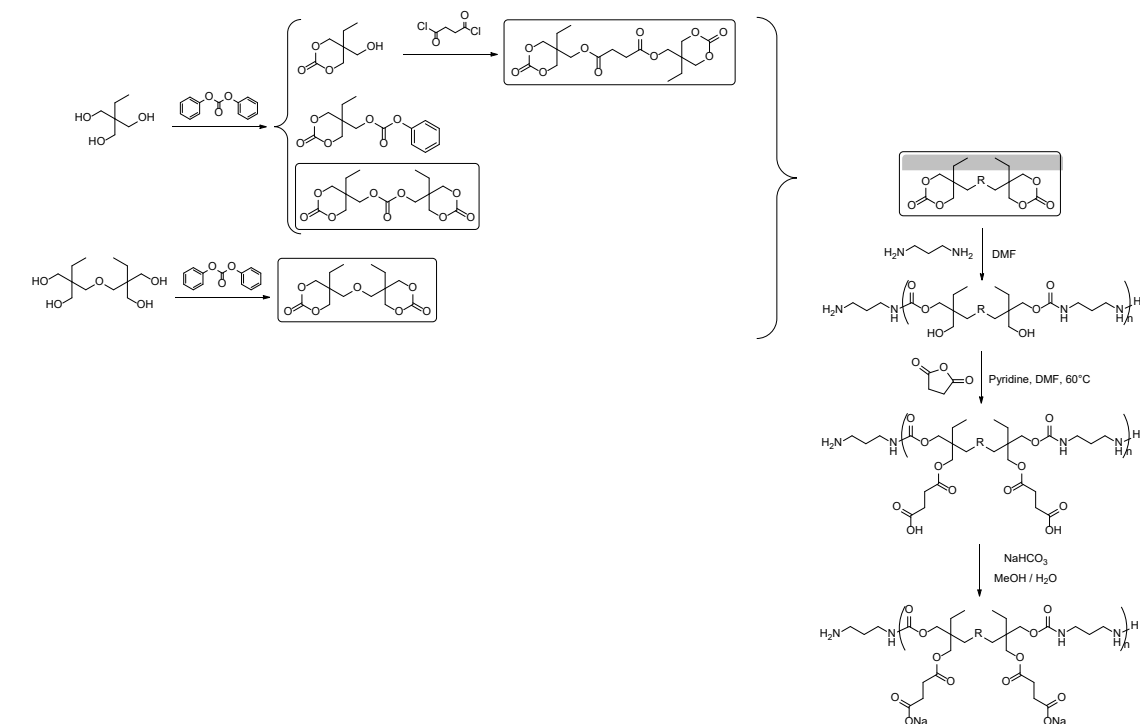
Modification of NIPUs synthesized in organic solvents

Detrembleur *et al.* introduced imine linkages within the polymer backbone in order to induce acid-sensitivity and hence to influence its final hydrolytic behavior.⁵⁰ This was achieved by reacting 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 the water formed 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 molar masses ranging from 3000 to 8500 Da after quenching and removal of the Lewis acid. The low molar masses obtained can be explained by the dynamic nature of the imine bond that may be hydrolyzed during the quenching step. The authors 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 synthesized in organic solvents 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 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 pH = 10.6 (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. Water soluble carbonate-based PHUs were extended with α,α -diisothiocyanate-p-xylene, forming thio-urea bridges⁵² and it was 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 hydrophobic xylene moiety of the chain extender was assumed to play also a role in this reduced water sensitivity.

Functionalization of the pendant OH-groups into quaternary ammonium chloride moieties also gave water-soluble PHU salts.⁵³ The 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 molar masses ranging from 3800 to 6300 Da 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.

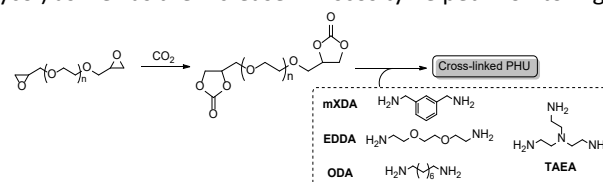
NIPU-based hydrogels

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 hydrogel was synthesized by reacting a carbonated polyethylene glycol diglycidylether with various polyamines in bulk. Three diamines were tested: 2,2'-(ethylenedioxy)diethyl-amine (EDDA), *m*-xylylenediamine (m-XDA) and 1,8-diaminooctane (ODA) and a triamine, acting as crosslinking agent: tris(2-aminoethyl)amine (TAEA) – Scheme 6. 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 bis-cyclic 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 absorptions 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 between the last two diamines 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) resulted in a higher compression stress of 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 PEG bis-carbonate, 0.2 eq. of triamine and 0.7 eq. of mXDA, (loadings from 1wt% up to 15wt% of clay were studied). It was however demonstrated that it had an effect on the compression properties. When the nanoclay loading was varied from 2 and 5 wt%, 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).

NIPU-based water-borne dispersions

The very first example of NIPU water-based dispersion was published in 1996 by Blank *et al.*,⁵⁸ who investigated the properties of cross-linked polyurethane dispersions. They used the transesterification 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



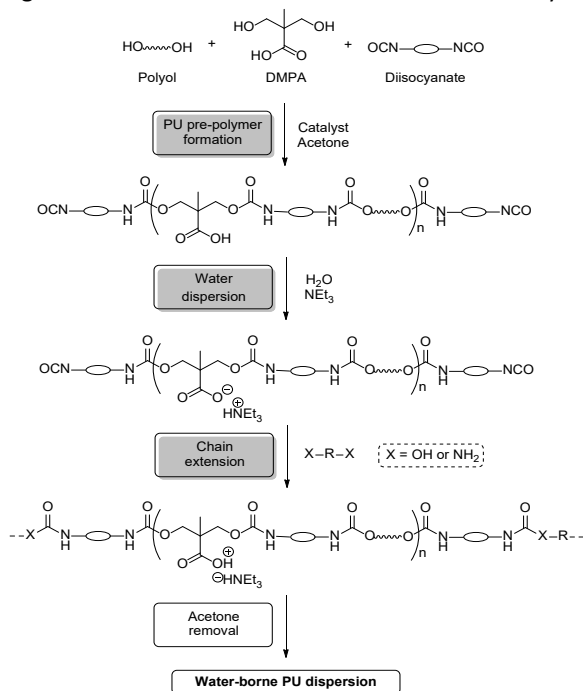
Scheme 6 Preparation of cross-linked PHUs for the formation of hydrogels – adapted from Detrembleur and coworkers⁵⁷

extent of polymerization. Carboxyl functionality was brought by reacting an anhydride onto the OH chain-ends. Two types of waterborne dispersions were prepared: a first one at 41 wt% solids content, neutralized with diisopropanolamine and a second one at 35 wt% solids content, neutralized with a mixture of diisopropanolamine/trimethylamine. No co-solvent was used in both cases. The particle size, measured by DLS, was found to depend on the solids content of the DLS sample. In the first formulation, no DLS signal was observed below 41 wt% solids and particles of 12.2 nm were measured. In the second formulation, the particle size was of 60.7 nm at 0.1 wt% solids and it shifted towards lower diameters (around 30 nm) with a tail as large as 0.3 µm at 15 wt% solids. The authors interpreted that such a change was due to the aggregation of smaller (non-observed) primary particles. Further cross-linking was performed by addition of water dispersible

hexa(methoxymethyl)melamine. The dispersions were used in coating applications and paints.

Acetone-like processes

Dispersions of polyurethanes are very important products in the coating and adhesive markets due to the relatively easy



Scheme 7 Water-borne PUs through the acetone process

synthesis and good performance. PUs are usually synthesized through the so-called acetone process – Scheme 7.^{15,59} 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 a diamine and after acetone removal, the PU dispersion is finally obtained.

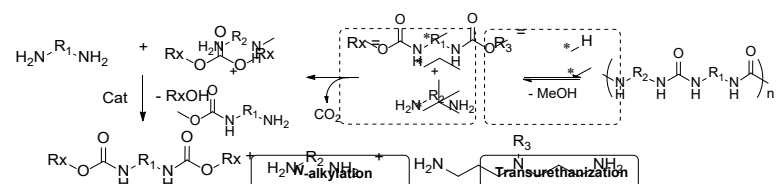
Most of the published examples of isocyanate-free PUs or PUreas dispersions are inspired by the acetone process, namely the copolymerization of three monomers, including an internal dispersing agent is done in a low boiling point solvent or in bulk and then dissolved in an organic solvent. The subsequent 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.

NIPUs dispersion by acetone-like transesterification processes.

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

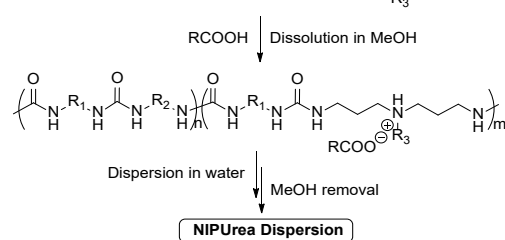
further dissolved in methanol. After neutralization, usually with the help of acetic acid, the mixture was slowly added into water. The removal of methanol gave the final dispersion – Scheme 8. The authors demonstrated that during the preliminary transurethanization-based step, the nature of the alkyl-leaving group of the bis-carbamate as well as the process conditions (such as high vacuum) were of outmost importance to obtain polyureas of high molar masses.^{60,61}

The successful implementation of this process thus 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 molar masses.



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



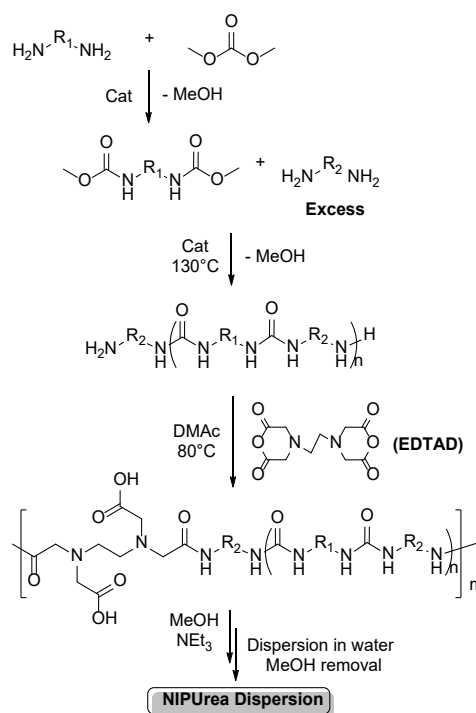
Scheme 8 Preparation of water-borne non-isocyanate polyureas – adapted from Ma *et al.*^{60,61}

Ma *et al.* 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 the rate of reaction; 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 generated alcohol (R_xOH in Scheme 8), for example thanks to a high vacuum in addition to a dynamic argon flow rate, favored the transurethanization reaction and the generation of higher molar mass polyureas. In general, relatively high molar masses (16 to 65 kDa according to SEC in HFIP with PMMA standards) were obtained.^{60,61}

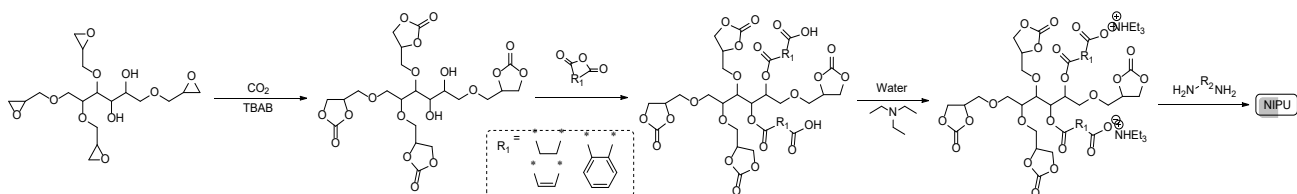
In order to disperse the formed polyurea chains, internal dispersing agents (IDA) were used. Their subsequent neutralization allowed for the polymer chains to form nanoparticles in water. 10 to 30 mol% based on diamine of IDA were used.^{60,61} The higher surface-charge density on the particles led to smaller particles. Thus, in the case of a series of copolymers composed of isophorone dimethylcarbamate, 4,7,10-trioxa-1,13-tridecanediamine and 3,3'-diamino-*N*-methyldipropylamine used as IDA, the particle diameters varied from 280 nm for 10 mol% IDA to 44 nm for 30 mol% IDA).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 molar masses of the polymer influenced the entanglement densities of the polymer chains and it was observed that polyurea coatings with molar masses lower than 30 kDa exhibited poorer impact resistance than coatings with higher molar masses. Moreover, longer monomers that increase the distance between urea moieties tended to decrease the H-bond density resulting in softer coatings.

Ma *et al.* also 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. 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 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 (NEt₃, TEA) allows 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 NEt₃ was added prior to dispersion. When increasing the TEA/COOH ratio, the particle size dramatically decreased and the viscosity of the



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

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 molar mass of the diamino prepolymer. Prepolymer molar masses 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 ($M_{n,prepolymer} = 950$ Da) to 61 nm ($M_{n,prepolymer} = 4750$ 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. The curing temperature was found to be very important since higher



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

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.

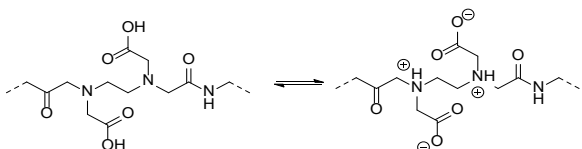
NIPUs dispersion by acetone-like aminolysis processes.

Only three examples of poly(hydroxy urethane) dispersions have been reported. The first example dates back to 2008 with a patent from Rhodia⁶³ that 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 formed 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

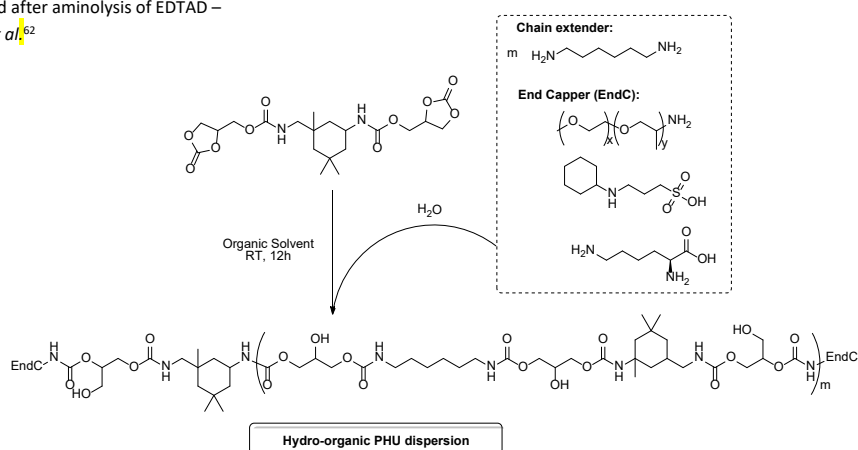
synthesis. To counter-balance this, in some examples, the PHU chains were crosslinked with water-soluble polyisocyanates.

In the second example, Wu *et al.* designed in 2018 a sorbitol-based multi-carbonate capable of being water dispersible.⁶⁴ A glycidyl-derivative sorbitol was carbonated and subsequently derivatized with succinic, maleic or *o*-phthalic anhydride. After addition of acetone to reduce the viscosity, the formed monomers were neutralized with NEt₃ and dispersed in water to obtain an aqueous cyclic carbonate dispersion with 30 to 40 wt% solids content after removal of the acetone – Scheme 13. The authors only characterized the succinic anhydride-based carbonate dispersion, that was further used for the formation of water-borne PHUs. The particle diameters according to DLS varied from 63 nm to 174 nm with the variation of the acid value from 45 to 30 mg KOH/g. A similar strategy was also patented, in which the formation of gas barrier films from PHU dispersions is claimed.⁶⁵

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 diamines led to more flexible films with higher impact resistance. When mixtures of IPDA and HMDA at different ratios were used, 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_g*s were in the range of 59 to 103°C.

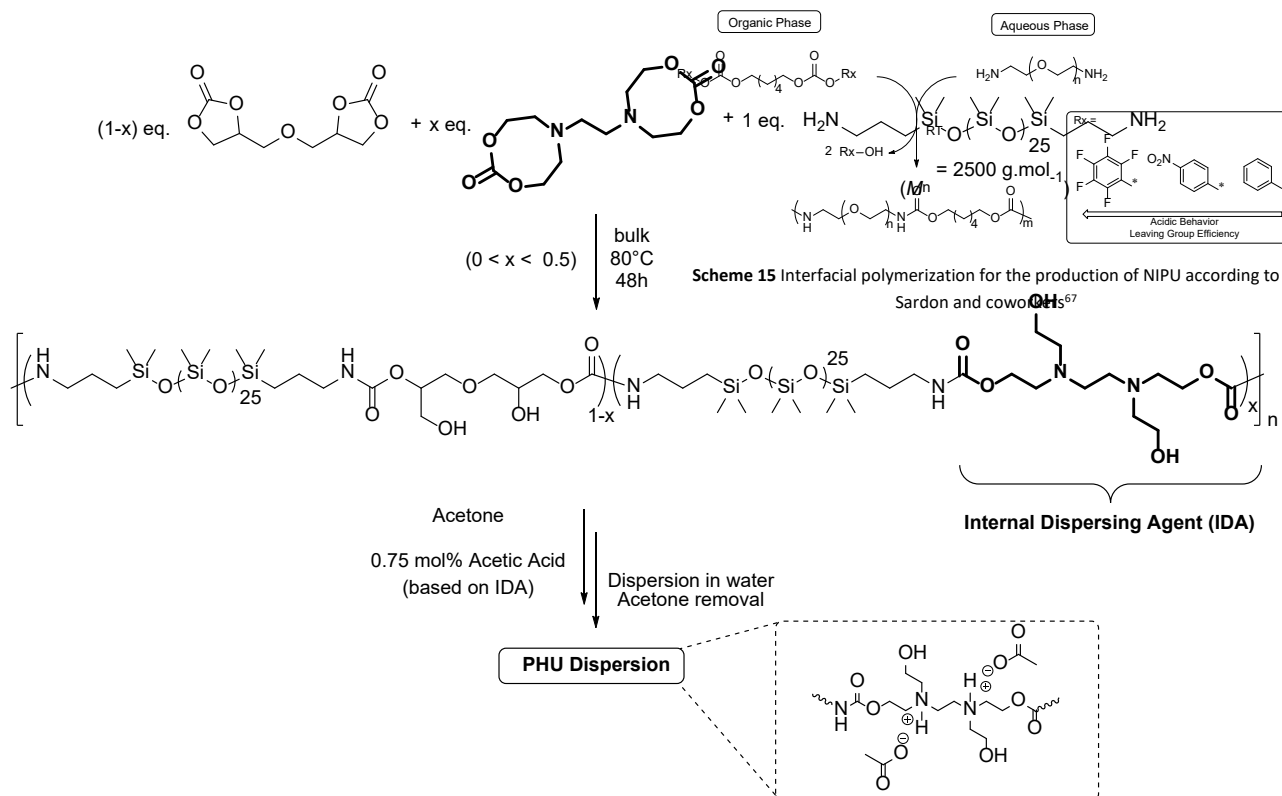


Scheme 11 Zwitterionic form of the amic acid after aminolysis of EDTAD – adapted from Ma *et al.*⁶²



Scheme 12 PHU preparation for further water dispersion by neutralization according to Rhodia⁶³

synthetic approach lies in the short oligomers formed upon



Scheme 14 Preparation of waterborne PHUs using the acetone process and a tertiary amine-containing bis-cyclic carbonate as an internal dispersing agent – adapted from Bossion *et al.*⁶⁶

The last example was published in 2019 by Bossion *et al.*⁶⁶ They describe the copolymerization of diglycerol dicarbonate (DGC), with an aminoalkyl-terminated polydimethylsiloxane (PDMS-diamine, $M_n = 2500$ Da) and a tertiary amine-containing 8-membered bis-cyclic carbonate, used as an internal dispersing agent (IDA) – Scheme 14. The PHU was first synthesized in bulk prior to being dissolved in acetone and dispersed in water by neutralization with acetic acid. It was found that 30 mol% of IDA (relative to DGC and IDA) gave the most stable dispersion when targeting a solid content of 60 wt%, with an average particle diameter of around 200 nm (PDI of 0.25 after acetone removal) according to DLS when full quaternization of the tertiary amino groups was achieved. Interestingly, the authors proved that by decreasing the degree of neutralization to 75% of acetic acid (compared to the concentration of the IDA), it was still possible to obtain stable dispersion with particles exhibiting similar characteristics (around 216 nm, PDI of 0.01 after acetone removal). The subsequent addition of adipic or citric acids to quaternize the remaining tertiary amino-groups allowed to obtain supramolecular ionic structures. The obtained films exhibited self-healing characteristics.

NIPU dispersions through interfacial polymerization

In 2017, Sardon and coworkers used surfactant-assisted interfacial polymerization for the synthesis of non-isocyanate polyurethane soft nanoparticles.⁶⁷ To do so, they extended the work undertaken in 2013 on water-soluble NIPUs⁴⁹ based on the design of aromatic leaving groups. In this process, the hexanediol-based activated bis-cyclic carbonates were

dissolved 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 15.

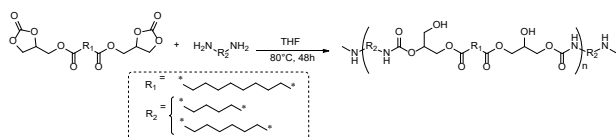
The reaction kinetics was fast, especially in the case of the pentafluorophenolate-activated bis-cyclic carbonate and full conversion was achieved in reaction times as short as 10 min. The lower basicity of the pentafluorophenol-based monomer enhanced its ability to act as a leaving group while reacting with a diamine. 2.5 and 5 wt% of sodium dodecyl sulfate (SDS) allowed the formation of stable dispersions with particle sizes of 274 and 162 nm, respectively. Molar masses of 23000 to 27000 Da and polydispersities ranging from 1.22 to 1.63 were determined by SEC in DMF. These polydispersities 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 (particle diameters went from 274 to 3222 nm and from 162 to 1910 nm respectively). To counterbalance this effect, the polymer was cross-linked with tris(2-aminoethyl)amine (TAEA). With 20 mol% of TAEA, more stable particles were obtained (the particle diameter was 148 nm before DCM evaporation and 298 nm after). 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.

NIPU dispersions by miniemulsion polymerization

The only example of mini-emulsion of NIPUs has been reported by Cramail and coworkers in 2016 (Scheme 16). The authors used fatty acid-based bis-cyclic carbonates that reacted with the commercially available Priamine™ 1075 (dimer diamine) at 60°C during 24h in order to form poly(hydroxyurethane)s.⁶⁸ Tween® 80 was found to be a suitable surfactant in the case of the thiol-containing bis-cyclic carbonate (bisCC-S). The very high hydrophobicity of the fatty acid-based monomers allowed the polymerization to proceed in miniemulsion without requiring the use of an additional co-stabilizer to avoid Ostwald ripening.⁶⁹ The molar mass (in weight) according to SEC in THF (PS calibration) was of 11.2 kDa ($\bar{D} = 1.7$). Particles of 100 nm were measured by DLS for a surfactant concentration of 10 wt% (of the aqueous phase). Similar feature was noticed in the case of fatty acid-based water-borne 'classical' PUs.⁷⁰ However, in the case of monomers with longer linear aliphatic chain, the use of sodium dodecyl sulfate as surfactant (1.2 wt% of the aqueous phase) in combination with hexadecane as co-stabilizer (3.3 wt% of the organic phase) led to better performances in terms of colloidal stability. In the case of bisCC-C36, an M_w of 7.1 kDa ($\bar{D} = 1.55$) and a particle diameter of 116 nm by DLS were measured. For bisCC-C1450, the M_w was of 6.6 kDa ($\bar{D} = 1.8$) and the particle diameter of 53 nm.

The challenge of this process relies in getting latexes of high solids content. Unfortunately, in the case of bisCC-S, latexes with solids contents higher than 20 wt%, although stable, presented a secondary population of larger size and a very broad distribution (around 500-800 nm in the case of 30 wt% solids content). The molar masses obtained in miniemulsion were lower than in bulk (for bisCC-S: $M_w = 19.6$ kDa ($\bar{D} = 1.9$), for bisCC-C36: $M_w = 14.2$ kDa ($\bar{D} = 2$) and for bisCC-C1450: $M_w = 12.1$ kDa ($\bar{D} = 1.8$)). Partial hydrolysis of the bis-cyclic carbonate monomers was assumed to be the reason for this phenomenon.

NIPU dispersions by nano-precipitation



Scheme 17 PHU formation before subsequent nanoprecipitation – adapted from Qu  rette *et al.*⁷¹

Nanoprecipitation basically consists in a solvent shifting or solvent displacement. A pre-formed polymer – in this case a

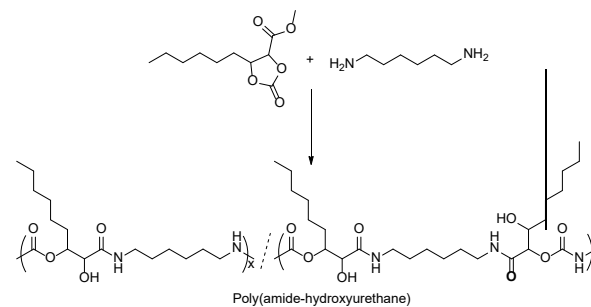
PHU – is synthesized or solubilized in a semi-polar organic solvent and this solution is added to a non-solvent of the polymer (usually water).

The organic solvent and the non-solvent are mutually miscible. Since the polymer is not soluble in the mixture, precipitation occurs forming nanoparticles.

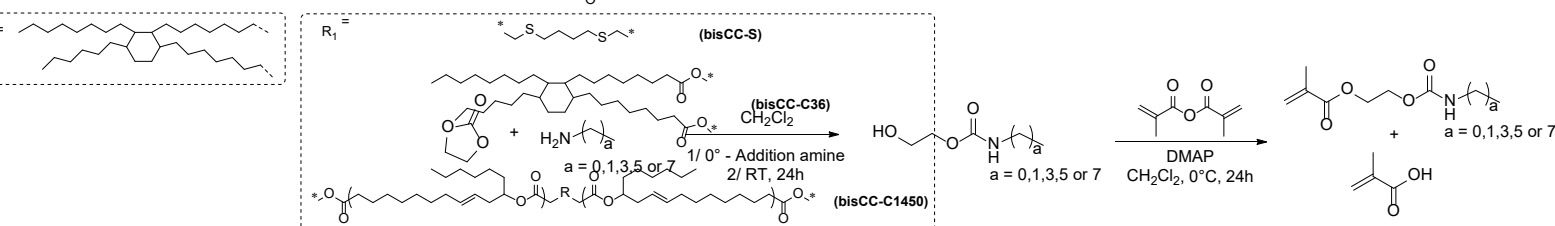
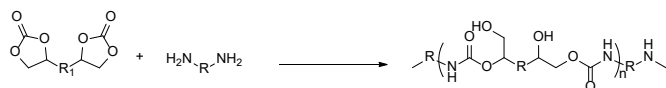
This process was applied to poly(hydroxyurethane)s synthesized by aminolysis of sebacic acid derived bis-cyclic carbonate with tetramethylene diamine (TMDA) and hexamethylene diamine (HMDA) – Scheme 17.⁷¹

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 molar masses (between 2.4 and 9.7 kDa according to ¹³C-NMR). The T_g s 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,⁶⁷ showing that some water-based NIPU processes are very sensitive to the specific structure of the monomers.

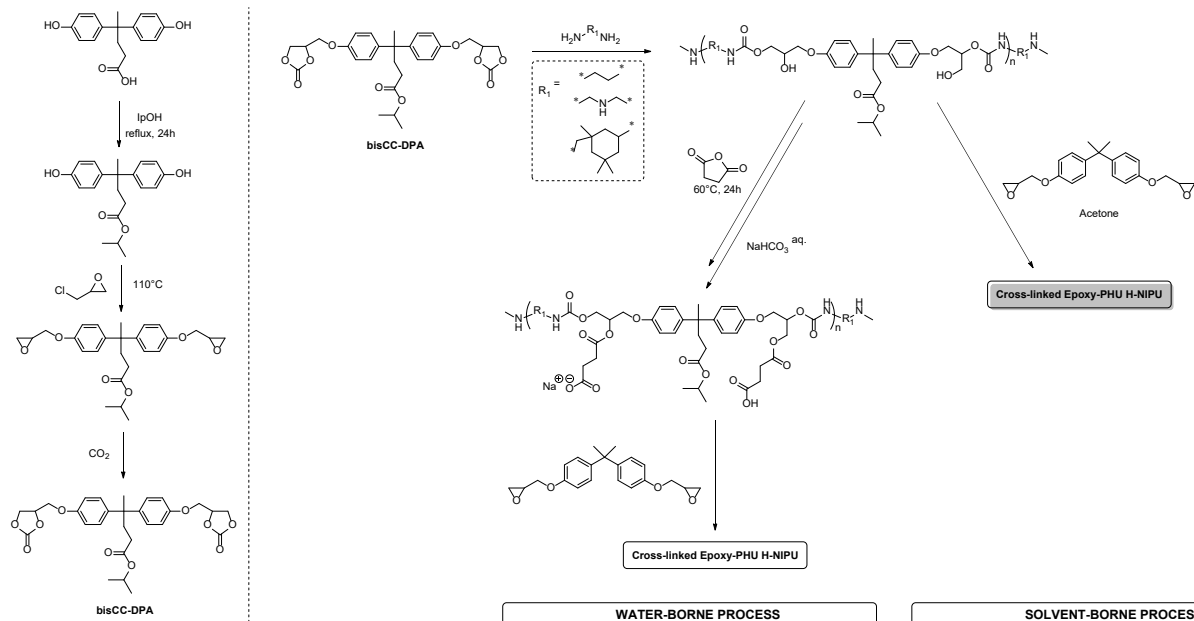
Ethanol and DMSO were suitable solvents for the nanoprecipitation of the HMDA-based PHU (molar mass: 6.8 kDa), and smaller particles were formed in ethanol (particle diameter of about 90 nm in ethanol and particle diameter of about 135 nm in DMSO according to DLS). When increasing the polymer concentration 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.⁷² The aqueous to organic phase ratio did not exhibit any influence on the nanoparticle size. Ageing by aggregation was found to occur in



Scheme 18 Preparation of poly(amide-hydroxyurethane)s – adapted from Ruiz *et al.*⁷³



Scheme 16 Mini-emulsion of fatty-acid based poly(hydroxy)urethanes, PHUs – adapted from Cramail and coworkers⁶⁸ apted from Meng *et al.*^{74,75}



Scheme 20 Preparation of water-borne diphenolic acid-based Epoxy-PHU hybrid NIPUs – adapted from Ma *et al.*⁷⁸

28 days, but ageing was significantly slower when DMSO was used as a solvent. This can be 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.

In another example, Ruiz *et al.*⁷³ self-assembled in water poly(amide-hydroxyurethane)s into nanoparticles. They investigated the polymerization of heptanal-based methyl 2,3-carbonyldioxynonanoate with 1,6-diaminohexane as depicted in Scheme 18. Polymers with molar masses up to 9800 Da ($\bar{M}_n = 1.5$) were synthesized. After dissolution in DMF, and dropwise addition into water under stirring, stable and monodispersed nanoparticles of diameters around 100 nm (PDI = 0.1) were obtained. The authors also demonstrated the possibility to encapsulate pyrene as a hydrophobic probe into these nanoparticles. This outcome was explained by the presence of hydrophobic cavities formed thanks to the pendant aliphatic chains.

Water-borne Hybrid-NIPUs (H-NIPUs)

NIPU-Acrylics-UMA dispersions

Meng *et al.* reported in 2017 two studies describing the use of urethane methacrylate (UMA) reactive diluents in water-borne systems.^{74,75} 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 19.⁷⁴

The copolymerization of these UMAs with MMA/BA was performed in seeded semi-batch emulsion polymerization, targeting a solid content of 30 wt%. The seed was a MMA/BA (70/30 wt/wt) copolymer 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. The particle diameters according to DLS were in the range 200-205 nm (PDI between 0.01 and 0.04). TEM images showed a unimodal and uniform spherical morphology. The T_{gs} and minimum film forming temperatures (MFFT) of the latexes decreased with the increasing chain length of the UMA. MFFT close to room temperature were obtained when the aliphatic pendant 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.⁷⁵ 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. Particles of diameters in the range 374-394 nm (PDI between 0.01 and 0.03) were measured by DLS. 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 semi-batch. The composition distribution strongly affected the mechanical properties and the batch latex presented higher Young's modulus and stress at break than the semi-continuous 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.

Some other examples, relying on the use of acetone-like processes, were patented in which polycarbonates were obtained by radical polymerization, dispersed in water and further cured with amine-containing resins.^{76,77}

NIPU-Epoxy dispersions

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.⁷⁸ To do so, the native DPA was modified with epichlorohydrin prior to carbonation with CO_2 . The protection of the pendent acid group during the esterification reaction was necessary to avoid unwanted side reactions. The formed bisCC-DPA was reacted in *N*-methyl pyrrolidone (NMP) or propylene glycol methyl acetate (PGMAC) with various diamines to yield the corresponding PHUs. Only short oligomers, with molar masses in the range 4300-4800 Da and dispersities close to 2 were obtained (by SEC in THF). The NIPUs were used as both solvent-based and in waterborne coatings. 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. 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 20. 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. (the particle diameter by DLS dropped from 321 nm to 78 nm with the increase of the NaHCO_3 concentration in the aqueous phase from 9.1 to 50 wt%). Surprisingly, the T_g of the cured polymer decreased from 63 to 35°C 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 from 68.4° to 35.6° with the NaHCO_3 content.

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 bis-cyclic 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. In addition, *tert*-butoxyl-group generates the *in situ* formation of an isocyanate moiety in the mechanism, which is questionable, if a full isocyanate-free process is desired. On the other hand, cyclic carbonates' aminolysis in aqueous media is challenging because the latter are prone to suffer hydrolysis. The only example is which it has been demonstrated to work so far is the case of very hydrophobic (vegetable oil-based) monomers, capable of forming miniemulsions.

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 NIPUs closer to industrial implementation.

Conflicts of interest

There are no conflicts to declare.

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