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polyurethane materials



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## Shining a new light on the structure of polyurea/polyurethane materials†

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Polyurea and polyurethane containing urea bonds are widely used in the preparation of coatings, foams, and micro- and nanocapsules. The molecular structures of such materials are typically difficult to characterize quantitatively due to their poor solubility and because mixtures with strong acids tend to hydrolyze the polymers. In a mixture of trifluoroacetic acid (TFA) and acetone, a very strong hydrogen bonding occurs between the carbonyl oxygen of acetone and the proton of TFA, which leads to its deshielding. This peculiar mixture of solvent was used for the quantitative characterization of polyurethane/urea coatings, microcapsules, and nanocapsules by NMR spectroscopy. By using aromatic and aliphatic diisocyanates, diamines, and diols, the extent of urea groups, and hence hydrolyzed isocyanates, in the polymer can be determined. This method is shining light on materials that were not yet quantitatively characterized such as polyurea nanocapsules prepared by interfacial polymerization in miniemulsion.

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### Introduction

Polyurethanes and polyureas are polymers which are typically prepared by the reaction between isocyanates and molecules containing hydroxyl or amine groups.<sup>1</sup> While polyurethanes are ubiquitous in our daily life,<sup>2</sup> polyureas have more limited applications due to their difficult processibility. Polyureas were used to prepare coatings for antifouling,<sup>3</sup> antibacterial<sup>4</sup> and anti-icing applications.<sup>5</sup> Moreover, due to the hydrophobic nature of isocyanates and the hydrophilicity of many diols and diamines, interfacial polyaddition in emulsion were performed to fabricate nanocapsules or nanoparticles for the encapsulation of catalysts,<sup>6–9</sup> fragrances,<sup>10</sup> phase change materials,<sup>11</sup> pesticides,<sup>12</sup> dyes,<sup>13</sup> corrosion inhibitors,<sup>14</sup> contrast agents for magnetic resonance imaging,<sup>15,16</sup> self-healing agents,<sup>17–20</sup> and drugs.<sup>21</sup>

The presence of urea bonds in polyurethanes can be beneficial for the fabrication of intrinsic self-healing materials which can be remedied due to the presence of strong hydrogen bonds.<sup>22–24</sup> Moreover, the addition of controlled and low amounts of water to isocyanates was found to generate aerogels with high porosity.<sup>25</sup> However, the concurrent reaction between water and isocyanates in the synthesis of poly-

urethanes and polyureas is often not controlled, leading to the hydrolysis of isocyanates to carbamic acids. The latter are unstable and yields CO<sub>2</sub> and an amine, which can react with isocyanates to form unwanted urea groups in the structure of the main polymer. This fact has led various research groups to use anhydrous oil-in-oil emulsions for the fabrication of polyurethane particles without urea bonds.<sup>26,27</sup> Indeed, polymers containing many urea groups tend to become intractable and are difficult to process. This is due to the formation of abundant and strong intermolecular hydrogen bonding,<sup>28</sup> which can form readily ordered structures at room temperature.<sup>29</sup> For example, the presence of urea segments in polyurethane foams can lead to phase separation and the creation of fibril structures.<sup>30</sup>

Urea groups are typically detected by Fourier-transform infrared spectroscopy (FTIR) because the vibration of the carbonyl bond in urea is significantly different from the vibration of the carbonyl in urethane groups.<sup>31–39</sup> Nuclear magnetic resonance (NMR) spectroscopy can be performed but usually lead to weak signals due to the limited solubility of polyureas in conventional deuterated solvents such as DMSO-d<sub>6</sub>,<sup>40,41</sup> or require a high-resolution magic angle spinning (HR-MAS) setup and a large quantity of material to be measured.<sup>28,42</sup>

Herein, we aim to determine quantitatively the extent of formation of urea groups in polyurea and polyurethane, with a focus on the groups formed after hydrolysis of isocyanates. Recently, the mixture acetone/TFA was used for dissolving polyamides for the preparation of transparent and homogenous films.<sup>43</sup> Inspired by this finding, we dissolved polyureas and polyurethanes in this mixture and studied their struc-

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ture by  $^1\text{H}$  NMR spectroscopy. This investigation is particularly relevant for nanoparticles and nanocapsules prepared by interfacial polymerization and for coatings.

## Experimental section

### Materials

Polyglycerol polyricinoleate (PGPR, Danisco) was purified by washing with hexane before use. 1,6-Hexanediamine (HMDA, 99.5%, Acros Organics), 1,6-hexanediol (HDO, >97%, TCI chemicals), 1,3-bis(aminoethyl)-cyclohexane (BAC, >98%, TCI chemicals), *m*-xylylenediamine (XDA, >99%, TCI chemicals), 2,4-toluene diisocyanate (TDI, 80%, Acros Organics), hexamethylene diisocyanate (HMDI,  $\geq$ 98%, Sigma-Aldrich), cyclohexane ( $\geq$ 99.8%, Carlo Erba), sodium chloride (NaCl, 99%, Carlo Erba), calcium chloride dried granular ( $\text{CaCl}_2$ , 90%, Carlo Erba), acetone (99.8%, Carlo Erba), hexane (99.97%, Honeywell), resorcinol (>99%, TCI), sodium dodecyl sulfate (SDS, 99%, Acros), tetrahydrofuran (THF, 99.99%, Honeywell), xylene (mixture of isomers, 98.5%, RCI Labscan), isophorone diisocyanate (IPDI, 98%, Acros Organics) dimethyl sulfoxide (DMSO, 99%, Loba Chemie), trifluoroacetic acid (TFA, 99%, Acros Organics), and acetone- $\text{d}_6$  (99.8%, Eurisotop) were used as received. Deionized water was used throughout this work.

### Preparation of polyurea/polyurethane nanocapsules

HMDA or BAC or HDO (0.1 g) and 30 mg NaCl or  $\text{CaCl}_2$  were mixed in 1.3 g of water or DMSO. These solutions were mixed at 1000 rpm for 1 h at 27 °C with a solution of 75 mg of PGPR in 7.5 g cyclohexane. Afterwards, the obtained emulsion was further emulsified with an ultrasonicator (Hielscher UP200St, diameter 7 mm) for 6 min in a pulse mode (1 s on, 1 s off) at 50% amplitude in an ice bath. Then, known amounts of TDI and 35 mg PGPR in 5 g cyclohexane were slowly dropped in the miniemulsion for 5 min, which were stirred at 500 rpm at 27 °C for polyurea or 60 °C for polyurethane nanocapsules. The reactions were further stirred for 2 h to complete the reaction. The dispersions (2 g) were then added into 20 g water and the mixture was centrifuged (2-16KL model from Sigma) at 2655 g and 25 °C for 5 min. Phase separation occurred to facilitate the purification of the polymers. The pellets were re-dispersed in 2 mL cyclohexane. The process was repeated 2 more times by changing the precipitation solvent to acetone and then hexane. Finally, the pellets were dried in a vacuum desiccator.

For the determination of the completion of reaction, dispersions of polyurea and polyurethane nanocapsules (2 g) (P2, P5–7) were added to 20 g hexane. The dispersions were then centrifuged (2-16KL model from Sigma) at 2655 g and 25 °C for 5 min. The supernatants were collected and filtered through a filter paper and the filtrate were evaporated with a rotary evaporator at 40 °C. Around 10 mg of the resulting product was dissolved in 700  $\mu\text{L}$  DMSO- $\text{d}_6$  containing 2 mg of ethylene carbonate as internal standard.

### Preparation of polyurea microcapsules

Polyurea microcapsules were synthesized following a slightly modified procedure.<sup>20</sup> A 1.0 wt% aqueous solution (50 mL) of SDS was added into a 100 mL beaker. Then, IPDI (1.63 g) was dissolved into 10 mL of xylene and added to the beaker. The mixture was homogenized with a high-speed disperser (Ultraturrax T18) at 5000 rpm at 28 °C for 5 min to obtain a stable emulsion. Then, XDA (1 g) in 10 mL of a 1.0 wt% aqueous solution of SDS was added dropwise to the emulsion for 5 min, stirred at 300 rpm for 30 min at 28 °C, and further stirred 1.5 h at 50 °C. The obtained suspension (2 g) was added in 20 g water and then centrifuged (2-16KL, Sigma) at 2655 g at 25 °C for 5 min. The pellets were re-dispersed in 2 mL cyclohexane. The process was repeated 2 more times by changing the precipitation solvent to acetone and then hexane. Finally, the pellets were dried in a vacuum desiccator.

### Preparation of the polyurethane coating

Resorcinol (500 mg) was dissolved in a mixture of 400  $\mu\text{L}$  THF and 4  $\mu\text{L}$  water. HMDI (750.5 mg) was added in the aforementioned solution and stirred at 500 rpm for 5 min. Then, the mixture was drop-cast on a glass slide and cured 24 h at 28 °C, followed by 24 h at 60 °C. A transparent coating with a thickness of 170  $\mu\text{m}$  was obtained. The coating was peeled off and dissolved in 1 mL DMSO. The solution was precipitated in 10 mL methanol and then centrifuged (2-16KL, Sigma) at 2655 g for 10 min at 25 °C. The pellet was dissolved and reprecipitated two more times and dried in a vacuum oven at 60 °C 24 h.

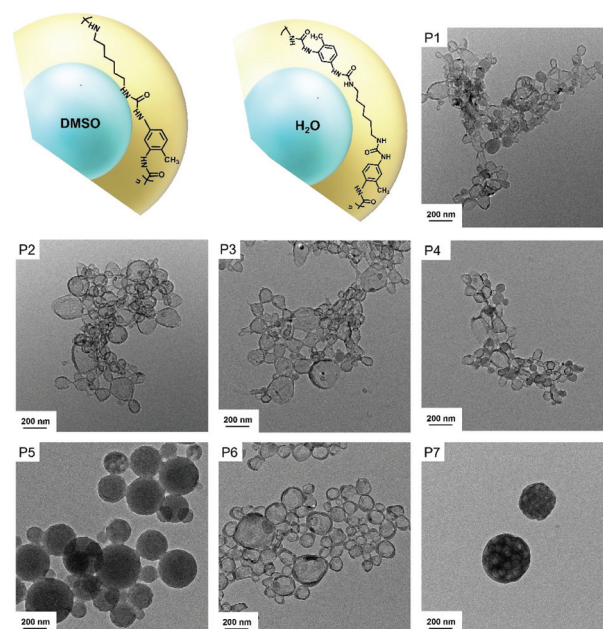
### Analytical tools

$^1\text{H}$  NMR spectra of polyurea/polyurethane nanocapsules were recorded on a Bruker 600 MHz NMR spectrometer. Dried polyurea/polyurethane (4–6 mg) of nanocapsules were dissolved in a mixture of 300  $\mu\text{L}$  acetone- $\text{d}_6$  (40% mol) and 460  $\mu\text{L}$  TFA (60% mol) for NMR experiments, which were acquired with a 5 mm double resonance broad band probe equipped with a z-gradient on a 600 MHz console (Bruker AVANCE III HD System). For the calculation of the molar ratios of monomer units in the polymers, the integral associated with the signals given by the 4 protons of the 2 methylene groups neighbouring the urea or urethane groups was compared with the aromatic protons. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) measurements were performed on a Frontier FTIR spectrometer (PerkinElmer) between 400 to 4000  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$ . Dispersions of polyurea or polyurethane nanocapsules (50  $\mu\text{L}$ ) were diluted with 3 mL cyclohexane for measuring the hydrodynamic diameter by dynamic light scattering (DLS, NanoPlus, Particulate systems). The morphologies of nanocapsules were observed with a transmission electron microscope (TEM, JEM-ARM200F, JEOL). Dispersions of polyurea microcapsules (5  $\mu\text{L}$ ) were diluted with 5 mL cyclohexane and dropped on silicon wafers and left for drying. The morphology of polyurea microcapsules were observed with a scanning electron microscope (SEM, JSM-7610F, JEOL).

## Results and discussion

Polyureas, because of the high density of hydrogen bonding inside their structures, are difficult to dissolve. Even the presence of alkali halide salts such as LiCl, LiBr<sub>2</sub>, or CaCl<sub>2</sub> in organic solvents, typically used for dissolving polyamides, are often not sufficient to dissolve them. Solvents such as sulfuric acid or formic acid at high temperatures are required for protonating the carbonyl bond and breaking hydrogen bonding between polymer molecules, which limit their characterization in the liquid state. Recently, the mixture of trifluoroacetic acid (TFA) and acetone was used to dissolve polyamide 66<sup>44,45</sup> and polyamide 11 at room temperature to prepare composites and ferroelectric coatings.<sup>43</sup> The TFA/acetone mixture allowed the formation of smooth homogeneous films with polyamide 11 crystallizing in the  $\delta'$  phase. <sup>1</sup>H NMR spectroscopy investigations have shown that the acidic proton of TFA was shared with acetone.<sup>43</sup> Whereas no intermolecular hydrogen bonding was detected in pure TFA or pure acetone, strong hydrogen bonding occurred between the oxygen of acetone and the proton in TFA, which is one of the hydrogen bonds with the largest enthalpy ( $-10 \text{ kcal mol}^{-1}$ ).

We investigated herein the structure of polyurea and polyurethane containing urea groups by <sup>1</sup>H NMR spectroscopy in a TFA/acetone-*d*<sub>6</sub> mixture. First of all, we prepared polyurea and polyurethane nanocapsules by interfacial polymerization in inverse miniemulsions. The process involves the reaction between diamines or diols that are dissolved in water or a polar solvent and subsequently emulsified in an apolar solvent (here cyclohexane).<sup>14,46–48</sup> After addition of diisocyanates through the continuous phase of the miniemulsions, nanocapsules are formed (see Fig. 1). Water and DMSO were used as dispersed phase for the dissolution of diols and diamines so that polyurethanes, polyureas, and polyurethane/ureas materials were obtained (Table 1). After the interfacial polymerization, colloids with a hydrodynamic diameter of 150–500 nm were obtained. The morphology of the colloids varied from nanocapsules (P1–4, 6) to nanoparticles (P5), and multi-hollow nanoparticles (P7), as observed by transmission electron microscopy (see Fig. 1). Derivatives of this procedure have been widely used and reported by several groups in the literature.<sup>49–55</sup> We collected polyurea/polyurethane nanocap-



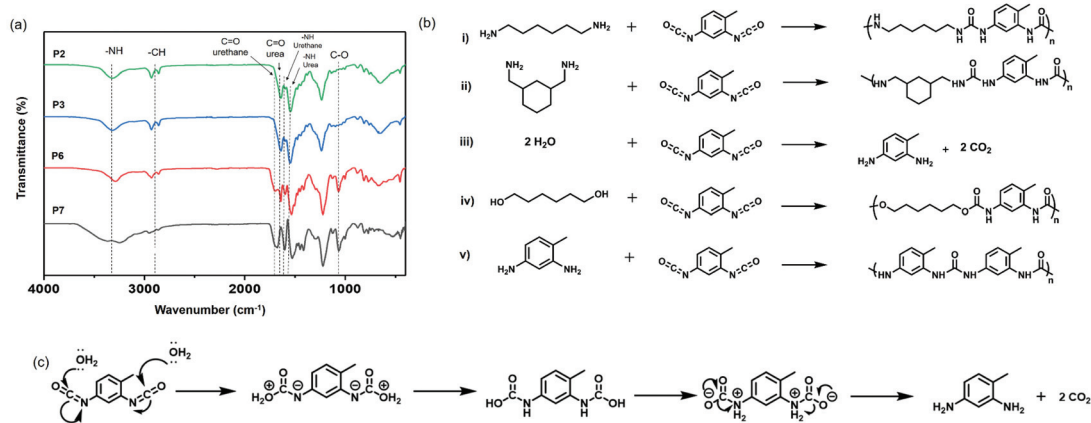
**Fig. 1** Scheme for the preparation of polyurea nanocapsules with either DMSO or water as core and transmission electron micrographs of polyurea (P1–5) and polyurethane (P6–7) nanocapsules and nanoparticles.

sules prepared in water-in-oil or DMSO-in-oil miniemulsions just after (start of the reaction) and 2 h (end of the reaction) after ultrasonication. Whereas signals for the isocyanate groups at  $2265 \text{ cm}^{-1}$  were observed by Fourier transform infrared (FTIR) spectroscopy directly after ultrasonication, no signals were observed after 2 h of the reaction (Fig. S1, ESI†). Furthermore, the dispersion of nanocapsules after 2 h reaction was added to hexane, centrifuged, and the supernatant was concentrated by evaporation of hexane. The remaining liquid was dissolved in a solution of ethylene carbonate (internal standard) in DMSO-*d*<sub>6</sub>. As shown in Fig. S2, ESI†, no signals that could be assigned to TDI were found, confirming that the isocyanates were not present in significant amounts after reaction.

The qualitative analysis of the chemical structure of these compounds was usually reported by measuring them by

**Table 1** Solvents in the dispersed phase, molar ratio between monomers and monomer units, and hydrodynamic diameter of polyurea and polyurethane nanocapsules prepared in inverse miniemulsion

Entry	Dispersed phase	Polymer	Polar monomer	M : TDI ratio		$D_h$ nm	PDI
				Feed	Polymer		
P1	Water	Polyurea	HMDA	1 : 0.9	1 : 1.3	243	0.300
P2	Water	Polyurea	HMDA	1 : 1	1 : 1.3	276	0.194
P3	Water	Polyurea	HMDA	1 : 1.1	1 : 1.5	245	0.307
P4	Water	Polyurea	1,3-BAC	1 : 1	1 : 1.9	173	0.187
P5	DMSO	Polyurea	HMDA	1 : 1	1 : 1.2	319	0.264
P5'	Anh. DMSO	Polyurea	HMDA	1 : 1	1 : 1.1	301	0.216
P6	Water	Polyurethane/urea	HDO	1 : 1	1 : 2.8	490	0.308
P7	DMSO	Polyurethane	HDO	1 : 1	1 : 2.1	386	0.084



**Fig. 2** (a) FT-IR spectra of the polyurea (P2–3) and polyurethane/urea (P6–7) nanocapsules. (b) Scheme for the reactions between the diamines monomers and from hydrolyzed diisocyanates, water, and diols with the toluene-2,4-diisocyanate (TDI) (c) Mechanism of the hydrolysis of isocyanate and decarboxylation of the carbamic acid in the presence of water.

Fourier transform infrared spectroscopy.<sup>14,56</sup> As expected, vibrations from carbonyl groups of urea at  $1634\text{ cm}^{-1}$  and for  $-\text{NH}$  bending at  $1548\text{ cm}^{-1}$  were observed for polyurea nanocapsules (P1–5), as shown in Fig. 2a and Fig. S3, ESI† For the polyurethane specimen (P6–7), vibrations associated to the carbonyl groups of urethane groups at  $1710\text{ cm}^{-1}$ ,  $1600\text{ cm}^{-1}$  for the  $-\text{NH}$  bending,  $\sim 1510\text{ cm}^{-1}$  for amide II band<sup>57</sup> and  $1066\text{ cm}^{-1}$  for C–O bonds were detected (Fig. 2a). Furthermore, a small signal for the polyurethane P6 at  $1634\text{ cm}^{-1}$  indicated the presence of urea groups.

The urea groups produced during the reactions in the presence of isocyanates, amines, and water (P1–4) originated from the reaction between diisocyanates and diamines (i and ii in Fig. 2b) or from the reaction between diisocyanates and hydrolyzed diisocyanates. Indeed, isocyanates react with water to form unstable carbamic acid compounds, which are subsequently decomposed in amines and carbon dioxide (iii) (Fig. 2c). The rate of the reaction between isocyanates with water is typically around  $\sim 10^{-3}$  less than for the reaction between isocyanates and primary amines,<sup>58</sup> meaning that diamines are primarily consumed, even in the presence of water. The hydrolyzed diisocyanate can react with non-hydrolyzed diisocyanates to yield new urea segments in the polymer (v). Finally, diisocyanates react with diols (iv), with a kinetic constant in the absence of catalyst typically estimated as similar as for the reaction between water and isocyanates.<sup>58</sup>

In order to assess the proportion of urea groups in the synthesized nanocapsules,  $^1\text{H-NMR}$  spectroscopy of polyurea and polyurethane nanocapsules after purification and dissolved in TFA–acetone- $d_6$  was performed. Solutions of polyurea and polyurethane in acetone- $d_6$ /TFA (40 : 60 mol%) were transparent until a concentration of  $\sim 42$  and  $13\text{ mg ml}^{-1}$ , respectively (Fig. S4, ESI†). Then, we verified that the mixture TFA–acetone- $d_6$  was not degrading the polymers during at least the time of measurements by using Diffusion Ordered Spectroscopy (DOSY) technique. DOSY is a 2D NMR spectroscopy technique displaying chemical shifts and self-diffusion coefficients of

dissolved molecules. The loss of magnetization/resonance intensity of molecules during with time yields information about their diffusion coefficient. The diffusion coefficient  $D$  is related to molecular weight  $M$  by the following equation:<sup>59</sup>  $D = AM^a$  where  $A$  and  $a$  are constants specific to the polymer. High polydispersity in molecular weight hence leads to widening of the values of diffusion coefficient. As examples, poly(ethylene oxide) with molecular weights of  $85\,000\text{ g mol}^{-1}$  and  $90\,000\text{ g mol}^{-1}$  displayed coefficients of diffusion measured by  $^1\text{H DOSY NMR}$  spectroscopy in  $\text{D}_2\text{O}$  of  $2.4 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$  and  $2.2 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$ , respectively.<sup>60</sup> Besides, coefficients of diffusion of  $6.5 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$  and  $5.4 \times 10^{-11}\text{ m}^2\text{ s}^{-1}$  were measured for poly(ethylene terephthalate) with weight-average molecular weights of  $18\,000\text{ g mol}^{-1}$  and  $25\,000\text{ g mol}^{-1}$ .<sup>61</sup>  $^1\text{H DOSY NMR}$  was employed for monitoring the hydrolysis and degradation of nylon 11.<sup>43</sup>  $^1\text{H-NMR DOSY}$  spectra of polyurethane and polyurea from dissolved nanocapsules showed that the coefficient of diffusion of the polymer was constant (Fig. S5, ESI†), hereby indicating that no significant decomposition occurred. In the  $^1\text{H-NMR}$  spectra, the signal from the proton of TFA was indeed detected at around 12.5 ppm in every  $^1\text{H NMR}$  spectra (Fig. S6, ESI†). The signal appears at very high chemical shift (downfield) because of the strong electron withdrawing group in TFA, which decreases the electron density around the proton nucleus. The integral of the signal associated to the methylene proton near the nitrogen of the urea group at 3.1 ppm or near the oxygen of the urethane group at 4.0 ppm was compared with the integral of the signal associated to the protons of the aromatic rings (7.0–7.2 ppm). Because the latter solely originated from the TDI, this method allows to estimate the amount of TDI that was hydrolyzed and reacted with itself after hydrolysis.

For the preparation of polyurea nanocapsules from hexamethylene diamine (HMDA) and toluene-2,4-diisocyanate (TDI), the feed molar ratio HMDA:TDI was varied to 1:0.9, 1:1, 1:1.1 (entries P1–3 in Table 1). Integration of the  $^1\text{H-NMR}$  spectra (Fig. S7, ESI†) showed that the ratio between HMDA

and TDI monomer units in the polyurea were 1:1.3, 1:1.3, 1:1.5, respectively. This increase of TDI units in the polymer compared to the feed ratio indicates that TDI was partially hydrolyzed and reacted with non-hydrolyzed, participating in the formation of polyurea nanocapsules. Replacing HMDA with 1,3-bis(aminoethyl)cyclohexane (BAC) led to nanocapsules with more TDI units inside the polymer (Table 1, Fig. S7, ESI†), implying that HMDA displayed a higher reactivity than BAC.<sup>2</sup>

Published literature mention the replacement of water by aprotic polar solvents such as DMSO for water-sensitive reactions or when the encapsulated payload is not water-soluble.<sup>26,62,63</sup> As expected, the polymerization with DMSO (P5) (Fig. 3a) as dispersed phase instead of water (P2) yielded a polyurea with less aromatic units. Using anhydrous DMSO (P5') further decreased the content of TDI monomer units in the polyurea shell, yielding a HMDA:TDI composition in the polymer close to the feed molar ratio. The very small discrepancy was attributed to the fact that moisture can be absorbed by DMSO during the ultrasonication of the samples. The polymerization between diols and diisocyanates is slower than the polymerization between diamines and diisocyanates, especially in the absence of catalyst. It is then inferred that the extent of side-reactions, such as hydrolysis of isocyanates, in the former reaction increases. Indeed, larger amounts of TDI was incorporated in the polyurethane/urea (P6 and P7) than their comparable polyurea counterparts (P2 and P5), both with water (P2 and P6) or DMSO as dispersed phase (P5 and P7). In the light of this study, we can conclude that polyurethane and polyurea nanocapsules prepared with a similar procedure contain substantial amounts of TDI units in their structure,

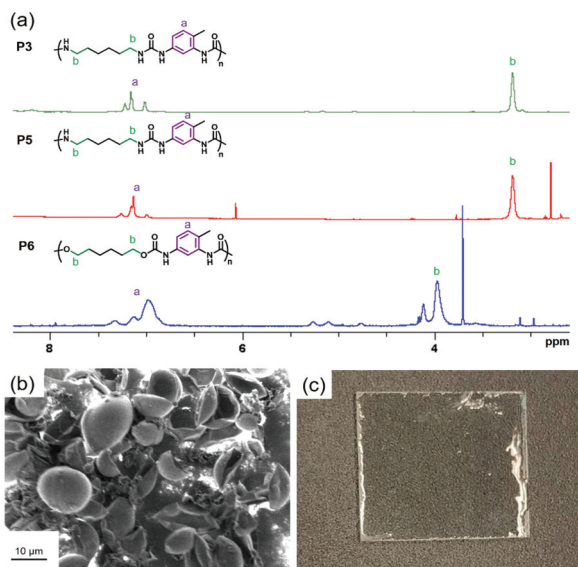
with amounts superior to their feed ratios. For biomedical applications, the presence of TDI units in the polymer is not suitable as its degradation products can be toxic. The concept of the study was then generalized to other systems such as microcapsules and coatings. Instead of preparing nanocapsules in water-in-oil miniemulsions, we prepared polyurea microcapsules in an oil-in-water process by suspension polymerization. Polyurea was produced by the reaction between equimolar amounts of IPDI and XDA. In principle, similar reactions are possible also in oil-in-water miniemulsions.<sup>64–66</sup> Microcapsules with an average diameter of  $12 \pm 2 \mu\text{m}$  were obtained (see Fig. 3b). In this system, the diamine was aromatic while the isocyanate was aliphatic. A ratio of IPDI:XDA units in the polyurea microcapsules of 1.6:1 was detected by <sup>1</sup>H NMR spectroscopy (Fig. S8a, ESI†). The larger amounts of aliphatic moieties compared with the feed ratio was attributed to the hydrolysis of IPDI, yielding a product that reacted with non-hydrolyzed IPDI concurrently to its reaction with XDA. The relative content of water in this experiment was much larger than for the nanocapsules because water was used as continuous phase. Besides, a polyurethane coating was prepared from the reaction between resorcinol and HMDI on a glass substrate, followed by thermal curing (Fig. 3c). The reaction took place in the presence of a small amount of water to simulate situations of high humidity or long storage in imperfectly sealed container. However, the content of water being however too low to allow foaming. The ratio between aliphatic (from the diisocyanate) and aromatic units (from the diol) was 1.1:1, hence suggesting that HMDI reacted partially with water (Fig. S8b, ESI†).

## Conclusions

Polyurethane/urea nanocapsules and coatings were characterized by nuclear magnetic resonance spectroscopy in a mixture of deuterated acetone and trifluoroacetic acid. The extent of monomeric units in the polymers was determined by comparing and quantifying aliphatic and aromatic protons. In water-in-oil miniemulsions, the hydrolysis of isocyanates and its subsequent reaction with non-hydrolyzed isocyanates was found to be very significant and led to the incorporation of large extent of urea units in the polymers. The concept was further extended to the analysis of microcapsules prepared in oil-in-water emulsions and to coatings. These findings show that assumption of composition based on starting monomers is not suitable and that the polymeric materials should be accurately characterized. This work has hence important implications for the design of formulations of polyurea and polyurethanes.

## Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.



**Fig. 3** (a) <sup>1</sup>H-NMR spectra of polyurea/urethane nanocapsules (entries P3, 5 and 6) in acetone-*d*<sub>6</sub>:TFA (40:60). (b) SEM micrograph of polyurea microcapsules prepared by interfacial polymerization in an oil-in-water emulsion. (c) Photograph of a polyurethane coating prepared by the reaction between resorcinol and HMDI.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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## Notes and references

- 1 E. Delebecq, J.-P. Pascault, B. Boutevin and F. Ganachaud, *Chem. Rev.*, 2013, **113**, 80–118.
- 2 D. K. Chattopadhyay and K. V. S. N. Raju, *Prog. Polym. Sci.*, 2007, **32**, 352–418.
- 3 J. Fang, A. Kelarakis, D. Wang, E. P. Giannelis, J. A. Finlay, M. E. Callow and J. A. Callow, *Polymer*, 2010, **51**, 2636–2642.
- 4 L. A. T. W. Asri, M. Crismaru, S. Roest, Y. Chen, O. Ivashenko, P. Rudolf, J. C. Tiller, H. C. van der Mei, T. J. A. Loontjens and H. J. Busscher, *Adv. Funct. Mater.*, 2014, **24**, 346–355.
- 5 H. Yu, Z. He, G. Qian, X. Gong and X. Qu, *Constr. Build. Mater.*, 2020, **242**, 117793.
- 6 S. V. Ley, C. Mitchell, D. Pears, C. Ramarao, J.-Q. Yu and W. Zhou, *Org. Lett.*, 2003, **5**, 4665–4668.
- 7 H. Han, Y. Zhou, S. Li, Y. Wang and X. Z. Kong, *ACS Appl. Mater. Interfaces*, 2016, **8**, 25714–25724.
- 8 H. Sun, Y. Wei, X. Z. Kong and X. Jiang, *Polymer*, 2021, **216**, 123432.
- 9 Y. Sui, Y. Cui, G. Xia, X. Peng, G. Yuan and G. Sun, *Process Biochem.*, 2019, **87**, 73–82.
- 10 M. Jacquemond, N. Jeckelmann, L. Ouali and O. P. Haefliger, *J. Appl. Polym. Sci.*, 2009, **114**, 3074–3080.
- 11 C. Liang, X. Lingling, S. Hongbo and Z. Zhibin, *Energy Convers. Manage.*, 2009, **50**, 723–729.
- 12 L. Ren, B. Huang, W. Fang, D. Zhang, H. Cheng, Z. Song, D. Yan, Y. Li, Q. Wang, Z. Zhou and A. Cao, *ACS Appl. Mater. Interfaces*, 2021, **13**, 1333–1344.
- 13 S. Behzadi, C. Rosenauer, M. Kappl, K. Mohr, K. Landfester and D. Crespy, *Nanoscale*, 2016, **8**, 12998–13005.
- 14 K. Thongchaiwetcharat, R. Jenjob, F. Seidi and D. Crespy, *Carbohydr. Polym.*, 2019, **217**, 217–223.
- 15 K. Malzahn, S. Ebert, I. Schlegel, O. Neudert, M. Wagner, G. Schütz, A. Ide, F. Roohi, K. Münnemann, D. Crespy and K. Landfester, *Adv. Healthcare Mater.*, 2016, **5**, 567–574.
- 16 I. Schlegel, R. Muñoz-Espí, P. Renz, I. Lieberwirth, G. Floudas, Y. Suzuki, D. Crespy and K. Landfester, *Macromolecules*, 2017, **50**, 4725–4732.
- 17 M. M. Caruso, B. J. Blaiszik, H. Jin, S. R. Schelkopf, D. S. Stradley, N. R. Sottos, S. R. White and J. S. Moore, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1195–1199.
- 18 G. Wu, J. An, D. Sun, X. Tang, Y. Xiang and J. Yang, *J. Mater. Chem. A*, 2014, **2**, 11614–11620.
- 19 D. Sun, J. An, G. Wu and J. Yang, *J. Mater. Chem. A*, 2015, **3**, 4435–4444.
- 20 P. D. Tatiya, R. K. Hedao, P. P. Mahulikar and V. V. Gite, *Ind. Eng. Chem. Res.*, 2013, **52**, 1562–1570.
- 21 W. He, X. Gu and S. Liu, *Adv. Funct. Mater.*, 2012, **22**, 4023–4031.
- 22 H. Ying, Y. Zhang and J. Cheng, *Nat. Commun.*, 2014, **5**, 3218.
- 23 C. Liu, C. Ma, Q. Xie and G. Zhang, *J. Mater. Chem. A*, 2017, **5**, 15855–15861.
- 24 J. Xu, W. Chen, C. Wang, M. Zheng, C. Ding, W. Jiang, L. Tan and J. Fu, *Chem. Mater.*, 2018, **30**, 6026–6039.
- 25 N. Leventis, C. Sotiriou-Leventis, N. Chandrasekaran, S. Mulik, Z. J. Larimore, H. Lu, G. Churu and J. T. Mang, *Chem. Mater.*, 2010, **22**, 6692–6710.
- 26 C. Herrmann, D. Crespy and K. Landfester, *Colloid Polym. Sci.*, 2011, **289**, 1111–1117.
- 27 K. Müller, M. Klapper and K. Müllen, *Colloid Polym. Sci.*, 2007, **285**, 1157–1161.
- 28 W.-G. Qiu, F.-L. Zhang, X.-B. Jiang and X.-Z. Kong, *Chin. J. Polym. Sci.*, 2018, **36**, 1150–1156.
- 29 J. Mattia and P. Painter, *Macromolecules*, 2007, **40**, 1546–1554.
- 30 R. Neff, A. Adedeji, C. W. Macosko and A. J. Ryan, *J. Polym. Sci., Part B: Polym. Phys.*, 1998, **36**, 573–581.
- 31 B. Di Credico, G. Griffini, M. Levi and S. Turri, *ACS Appl. Mater. Interfaces*, 2013, **5**, 6628–6634.
- 32 P. Scarfato, E. Avallone, P. Iannelli, V. De Feo and D. Acierno, *J. Appl. Polym. Sci.*, 2007, **105**, 3568–3577.
- 33 W. Chen, X. Liu and D. W. Lee, *J. Mater. Sci.*, 2012, **47**, 2040–2044.
- 34 J.-S. Cho, A. Kwon and C.-G. Cho, *Colloid Polym. Sci.*, 2002, **280**, 260–266.
- 35 G. Li, Y. Q. Feng, X. G. Li, P. Gao, J. Wang and J. Y. Xie, *J. Mater. Sci.*, 2007, **42**, 4838–4844.
- 36 S.-K. Wang and C. S. P. Sung, *Macromolecules*, 2002, **35**, 883–888.
- 37 P. W. Loscutoff, H. Zhou, S. B. Clendenning and S. F. Bent, *ACS Nano*, 2010, **4**, 331–341.
- 38 S. Lu, T. Shen, J. Xing, Q. Song, J. Shao, J. Zhang and C. Xin, *Mater. Lett.*, 2018, **211**, 36–39.
- 39 S. Park, Y. Lee, Y. S. Kim, H. M. Lee, J. H. Kim, I. W. Cheong and W.-G. Koh, *Colloids Surf., A*, 2014, **450**, 46–51.
- 40 J. Xu, H. Han, L. Zhang, X. Zhu, X. Jiang and X. Z. Kong, *RSC Adv.*, 2014, **4**, 32134–32141.
- 41 H. Han, S. Li, X. Zhu, X. Jiang and X. Z. Kong, *RSC Adv.*, 2014, **4**, 33520–33529.
- 42 X. Jiang, X. Zhu, A. A. Arnold, X. Z. Kong and J. P. Claverie, *Ind. Eng. Chem. Res.*, 2017, **56**, 2993–2998.
- 43 S. Anwar, D. Pinkal, W. Zajaczkowski, P. von Tiedemann, H. Sharifi Dehsari, M. Kumar, T. Lenz, U. Kemmer-Jonas, W. Pisula, M. Wagner, R. Graf, H. Frey and K. Asadi, *Sci. Adv.*, 2019, **5**, eaav3489.

- 44 E. L. Papadopoulou, J. A. Heredia-Guerrero, M. I. Vázquez, J. Benavente, A. Athanassiou and I. S. Bayer, *Polymer*, 2017, **120**, 255–263.
- 45 E. L. Papadopoulou, F. Pignatelli, S. Marras, L. Marini, A. Davis, A. Athanassiou and I. S. Bayer, *RSC Adv.*, 2016, **6**, 6823–6831.
- 46 D. Crespy, M. Stark, C. Hoffmann-Richter, U. Ziener and K. Landfester, *Macromolecules*, 2007, **40**, 3122–3135.
- 47 W. He, M. Parowatkin, V. Mailänder, M. Flechtner-Mors, R. Graf, A. Best, K. Koynov, K. Mohr, U. Ziener, K. Landfester and D. Crespy, *Biomacromolecules*, 2015, **16**, 2282–2287.
- 48 Q. Luo, Y. Wang, Z. Chen, P. Wei, E. Yoo and E. Pentzer, *ACS Appl. Mater. Interfaces*, 2019, **11**, 9612–9620.
- 49 D. Crespy and K. Landfester, *Beilstein J. Org. Chem.*, 2010, **6**, 1132–1148.
- 50 A. Elzayat, I. Adam-Cervera, O. Álvarez-Bermúdez and R. Muñoz-Espí, *Colloids Surf., B*, 2021, **203**, 111764.
- 51 S. K. Pramanik, U. Pal, P. Choudhary, H. Singh, R. J. Reiter, A. Ethirajan, S. Swarnakar and A. Das, *ACS Appl. Bio Mater.*, 2019, **2**, 5218–5226.
- 52 O. Álvarez-Bermúdez, I. Adam-Cervera, A. Aguado-Hernández, K. Landfester and R. Muñoz-Espí, *ACS Sustainable Chem. Eng.*, 2020, **8**, 17956–17966.
- 53 S. Seneca, S. K. Pramanik, L. D'Olieslaeger, G. Reekmans, D. Vanderzande, P. Adriaensens and A. Ethirajan, *Mater. Chem. Front.*, 2020, **4**, 2103–2112.
- 54 E. P. Barros Silva Soares de Souza, G. Trindade, M. V. Lins Dantas Gomes, L. A. Santos Silva, R. Grespan, L. J. Quintans Junior, R. L. Cavalcanti de Albuquerque Júnior, S. Shanmugan and A. Antunes de Souza Araújo, *Food Chem. Toxicol.*, 2020, **135**, 110958.
- 55 D. Bresolin, V. Mazurek, A. Valério, C. Sayer, P. H. H. de Araújo and D. de Oliveira, *Eur. Polym. J.*, 2018, **108**, 529–535.
- 56 F. Wang and C. E. Diesendruck, *Polym. Chem.*, 2017, **8**, 3712–3720.
- 57 P. J. Peruzzo, P. S. Anbinder, O. R. Pardini, J. R. Vega and J. I. Amalvy, *Polym. J.*, 2012, **44**, 232–239.
- 58 W. D. Vilar, *Chemistry and Technology of Polyurethanes*, Rio de Janeiro Vilar Consultoria Tecnica Ltd, 2002.
- 59 A. Chen, D. Wu and C. S. Johnson, *J. Am. Chem. Soc.*, 1995, **117**, 7965–7970.
- 60 M. Urbańczyk, D. Bernin, A. Czuroń and K. Kazimierczuk, *Analyst*, 2016, **141**, 1745–1752.
- 61 J.-G. Rosenboom, J. De Roo, G. Storti and M. Morbidelli, *Macromol. Chem. Phys.*, 2017, **218**, 1600436.
- 62 D. Crespy and K. Landfester, *Soft Matter*, 2011, **7**, 11054–11064.
- 63 C. Bohlender, K. Landfester, D. Crespy and A. Schiller, *Part. Part. Syst. Charact.*, 2013, **30**, 138–142.
- 64 M. Takasu and H. Kawaguchi, *Colloid Polym. Sci.*, 2005, **283**, 805–811.
- 65 Q. Zhang, Y. Shi, X. Zhan and F. Chen, *Colloids Surf., A*, 2012, **393**, 17–26.
- 66 L. Torini, J. F. Argillier and N. Zydowicz, *Macromolecules*, 2005, **38**, 3225–3236.