

NMR Analysis to Identify Biuret Groups in Common Polyureas

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Abstract Polyureas (PU) are well known as a class of high impact engineering materials, and widely used also in emerging advanced applications. As a general observation, most of them are only soluble in a very limited number of highly protonic solvents, which makes their chemical structure analysis a great challenge. Besides the presence of abundant hydrogen bonding, the poor solubility of PU in common organic solvents is often ascribed to the formation of biuret crosslinking in their molecular chains. To clarify the presence of biuret groups in PU has been of great interest. To this end, two samples, based on hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI) respectively, were synthesized by precipitation polymerization of each of these diisocyanates in water-acetone at 30 °C. Their chemical structures were analyzed by high resolution magic angle spinning (HR-MAS) NMR, and through comparison of their NMR spectra with those of specially prepared biuret-containing polyurea oligomers, it was concluded that biuret group was absent in all the PU prepared at 30 °C. In addition, this NMR analysis was also applied to a PU obtained by copolymerization of TDI with ethylene diamine (EDA) and water at 65 °C in EDA aqueous solution. It was confirmed that biuret unit was also absent in this PU and that EDA was more active than water towards TDI. The presence of EDA was crucial to the formation of uniform PU microspheres. This study provides therefore a reliable method for the analysis of PU chemical structure.

Keywords Diisocyanate; Polyurea; Chemical structure; Biuret; NMR spectroscopy

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INTRODUCTION

As a class of high impact engineering materials with good thermal shock and abrasion resistance, good flexibility and fast cure, polyureas (PU) have been known for a long time, and have been used in early days mainly as protective coatings for different structural materials^[1–3]. Nowadays, PU are also used in emerging technologies, including catalyst support^[4–6], controlled release^[7, 8], phase change material^[9], self-healing material *etc*^[10, 11]. As a general observation, most of PU are only soluble in a very limited number of highly protonic solvents^[12–14], which makes their chemical structure analysis a great challenge. For the poor solubility of PU in common organic solvents, the presence of abundant hydrogen bonding has been widely accepted as one of the causes. Besides this, the formation of biuret crosslinking in their molecular chains is also often believed to be the cause^[15–17]. Despite continuous studies over more than 5 decades^[14–20], the presence of biuret units in different types of PU remains debatable. In some reports, it is claimed that biuret is not formed unless at high temperature above 110 °C^[18–20]; in other reports, use of catalyst with excessive isocyanate is described as prerequisite for biuret formation^[18, 21, 22]. While biuret formation has been also

mentioned to occur without specific experimental conditions^[19, 21, 23], Suzuoki *et al.*^[16] reported the formation of biuret at 85 °C when conducting in bulk the polymerization of ethylene diamine (EDA) with diphenylmethane diisocyanate and a prepolymer with terminal isocyanate, and biuret was detected when the same polymerization was done in dimethylacetamide at 20 °C.

Synthesis and characterization of different PU have been one of our research focuses, different PU polymers under different forms, including uniform microspheres^[6, 12, 13, 24], core-shell and hollow PU microspheres^[25], porous PU^[5, 23, 26, 27] and PU nanofibers^[28]. The characterization of the chemical structures of these PU materials is of great importance and wide interest. To this end, two biuret-containing PU oligomers, denoted as BPU, were synthesized by a specially chosen process, on the one hand; and on the other hand, another two PU polymers, based on hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI), were synthesized by precipitation polymerization of each of these diisocyanates in water-acetone at 30 °C. Their chemical structures were analyzed by NMR for the BPU samples and by high resolution magic angle spinning (HR-MAS) NMR for PU polymers because of their poor solubility. HR-MAS NMR has been developed to analyze materials with their rheological feature in between those of liquids and solids, including for instances, gels, ionic liquid, liquid crystals *etc*^[29]. Through their comparison, it was concluded that biuret group was absent in all the PU

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prepared above. In addition, this analysis was also used for investigating PU prepared by TDI polymerization with EDA and water in EDA aqueous solution at 65 °C; accurate information on the chemical structure and on the formation of PU microspheres was obtained. This study provides therefore a reliable method for chemical structure analysis for all types of PU materials.

EXPERIMENTAL

Materials

Hexamethylene diisocyanate (HDI, AR) was purchased from Aladdin Chemicals and kept at 2 °C before use to prevent dimer formation. Toluene diisocyanate (TDI, industrial grade, a mixture of 2,6- and 2,4-isomers at 20% and 80% ratio) was from Beijing Keju New Materials Co. Ltd. Ethylene diamine (EDA, AR) was from Fuyu Fine Chemicals, Tianjin. Acetone (AR) was from Tianjin Damao Chemicals. Deuterated dimethyl sulfoxide (DMSO- d_6 , 99.9%) was from Sigma-Aldrich. All the chemicals were used as received. Ultrapure water (Millipore, US) was made in the laboratory.

Preparation of BPU and PU Samples

Two BPU samples (Table 1), specially designed to have biuret units, were prepared at 130 °C with excessive isocyanate (molar ratio of NCO/H₂O at 10/1), following a reported procedure^[20]. For a typical run, HDI (16.82 g, 100.0 mmol) was added in a three-necked flask located in an oil bath at 130 °C, and H₂O (0.36 g, 20.0 mmol) was added dropwise during 2 h under strong stirring with refluxing. To assure the full conversion of HDI, the system was kept at 130 °C for another 6 h after completion of H₂O addition. A yellow and viscous liquid (BPU-HDI) was obtained and stored at –20 °C for subsequent test. HDI was replaced by TDI to prepare biuret-containing BPU-TDI. The chemical reactions and the chemical structures of the resulting materials are given in Fig. 1.

Two PU samples (Table 1) were prepared at 30 °C by polymerization of diisocyanate with their corresponding

amine *in situ* formed through the reaction of the diisocyanate with water^[13, 24]. As a typical protocol for the preparation, a mixture of H₂O/acetone at mass ratio of 3/7 was first charged into a glass bottle of 120 mL capacity, followed by addition of 5.0 g of HDI. The bottle was sealed off immediately, hand-shaken for about 10 s to make the mixture homogeneous, located into a water bath at 30 °C under quiescent condition (standing still without shaking or stirring)^[24] and allowed for polymerizing for 4 h. At the end of the process, samples were taken and centrifuged for 5 min at 1.2×10^4 r/min. The polymer obtained was washed twice with acetone prior to drying up at 80 °C for 12 h under vacuum. The chemical reactions and the chemical structure of the PU are also given in Fig. 1.

PU Preparation by Interface Polymerization of TDI Droplets in EDA Aqueous Solution

An aqueous solution of EDA (0.3 g, 4.99 mmol) in 400 g of water was first introduced into a glass reactor located in a water bath at 65 °C. TDI (6.10 mL, 35.02 mmol), filled in a syringe, was added drop-wise at a rate of 130 mL/h with help of a pump, through a fine silicone pipeline with one end connected to the syringe, and with the other end connected to a needle of pore size of 260 μ m. Special care was taken with TDI addition so that the tip of the needle was immersed in the EDA aqueous solution to assure that TDI droplets were kept well in spherical shape and not splashing on the solution surface. The glass reactor was mounted on top of a mobile plate-rotor allowing the reactor to horizontally rotate in order to protect TDI droplets from eventual aggregation. After completion of TDI addition, the reaction was allowed to run for 5 h. At the end of polymerization, well formed PU microspheres were separated by filtration, and dried up at 70 °C for about 6 h under vacuum.

NMR Analysis of PU and BPU Samples

HR-MAS spectra of PU samples were recorded on a Brüker instrument (Advance III), operated at frequencies of 599.90, 150.86, and 60.79 MHz for ¹H, ¹³C and ¹⁵N, respectively. PU

Table 1 Reagents and their amounts used in preparation of BPU and PU samples

Samples	HDI (g, mmol)	TDI (g, mmol)	H ₂ O (g, mmol)	Acetone (g)
BPU-HDI	16.82, 100.0	–	0.36, 20.0	–
BPU-TDI	–	20.00, 114.8	0.41, 22.8	–
PU-HDI	5.00, 29.7	–	28.5, 1583.3	66.5
PU-TDI	–	5.00, 28.7	28.5, 1583.3	66.5

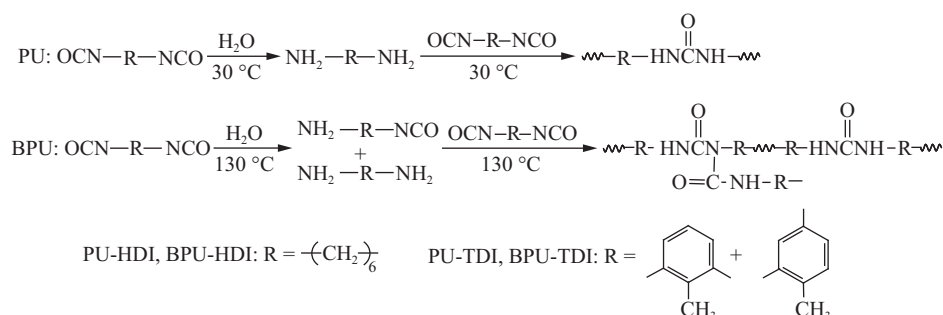


Fig. 1 Schematic illustrations of the reactions in the preparation of PU and biuret-containing BPU samples

samples were dispersed in DMSO- d_6 (60 mg/100 μ L), and the dispersion was thoroughly vortexed to ensure a complete wetting of the polymers. After a mild centrifugation, the resulting slurries were placed in 4 mm MAS rotors with 50 μ L inserts to obtain an optimal RF and magnetic field homogeneity. The samples were spun at 10 kHz using a 4 mm HR-MAS indirect-detection double resonance probe. The temperature was raised to 60 $^{\circ}$ C in order to improve spectral resolution and the field was locked using the DMSO- d_6 signal with the samples manually shimmed. ^{1} H, ^{13} C and ^{1} H- ^{15} N HSQC spectra were acquired under the same conditions as the liquid-state spectra, except that the pulse length in ^{13} C and ^{15} N at 90 $^{\circ}$ was reduced to 5 and 10 μ s respectively. For BPU samples (20 mg/100 μ L in DMSO- d_6), their analyses were operated at frequencies of 400, 100, and 50 MHz for ^{1} H, ^{13} C and ^{15} N, respectively.

RESULTS AND DISCUSSION

As described above, the formation of biuret in PU materials has been debatable for a long while. In order to clarify this point, the two PU samples (Table 1) as described above were subjected to the NMR analysis, along with the two biuret-containing BPU oligomers, *i.e.* BPU-HDI and BPU-TDI. Their structure analysis by NMR is given in accordance with the monomer used.

HDI-based Polyureas

The ^{1} H spectra, ^{13} C spectra and ^{1} H- ^{15} N HSQC of HDI-based PU and BPU are all given in Fig. 2. It is to note that only the part of the spectra concerning the urea region is given because it is where the main information about biuret and urea is better reflected. Little change was observed for the peaks appearing in the low chemical shifts of 2–4 ppm

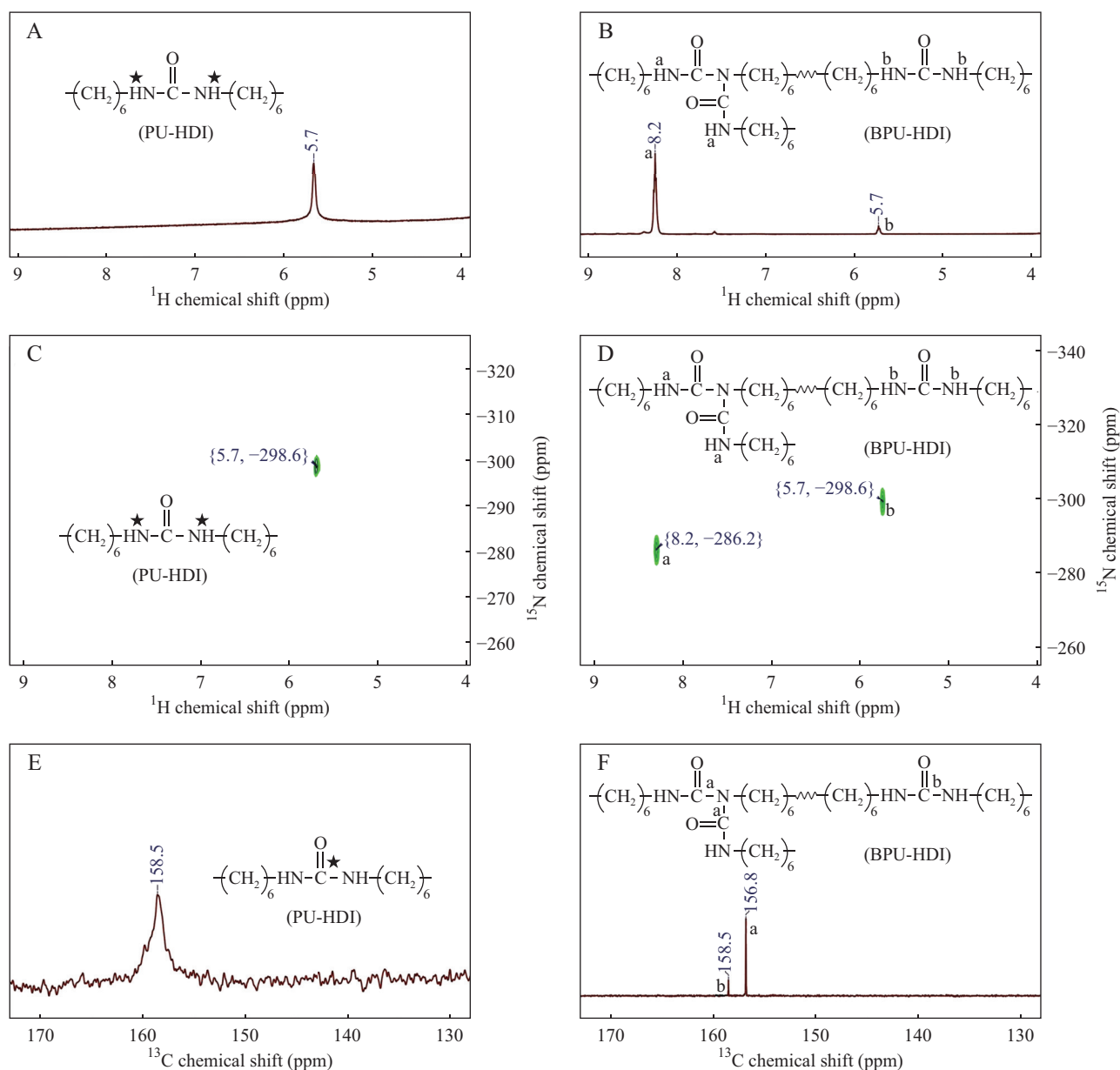


Fig. 2 NMR spectra of PU and BPU samples: (A) ^{1} H-NMR spectrum of PU-HDI; (B) ^{1} H-NMR spectrum of BPU-HDI; (C) ^{1} H- ^{15} N HSQC of PU-HDI; (D) ^{1} H- ^{15} N HSQC of BPU-HDI; (E) ^{13} C-NMR spectrum of PU-HDI; (F) ^{13} C-NMR spectrum of BPU-HDI

corresponding to the methylene hydrogen atoms, regardless of the tested samples being with or without designed biuret units.

For ^1H spectrum of PU-HDI (Fig. 2A, carbonyl region), besides the resonance peaks of the methylene protons at right side of the spectra (< 4 ppm, not shown here), there appeared only one single resonance peak at 5.7 ppm. This is expected since the two protons on the two amides at each side of the carbonyl share exactly the same chemical environment. The same peak at exactly the same position was reported by Sumi *et al.* for a PU with alkyls at both side of the urea unit^[14]; there were also studies reporting the same peaks at chemical shifts of 5.71 and 5.73 ppm^[20, 30]. To further confirm this assignment, ^1H - ^{15}N HSQC was carried out for PU-HDI (Fig. 2C). Knowing that the two nitrogen atoms on two sides of the carbonyl share exactly the same chemical environment, there has to be one single peak for N resonance, which appeared at -298.6 ppm, and therefore one single H-N coherence spot (5.7, -298.6) as seen in Fig. 2(C), which affirmed this assignment.

With regard to the oligomer sample BPU-HDI (chemical structure given in Fig. 1), its ^1H spectrum given in Fig. 2(B) showed 2 well separated peaks at 5.7 and 8.2 ppm. With the former ascribed in Fig. 2(A), the peak at 8.2 ppm was believed to be the resonance from the proton of NH neighboring the carbonyl of biuret unit, which was known to exist in this BPU specially prepared. In fact, this chemical shift was previously assigned to the same protons for biuret-containing polyurea at the same position by Zhang^[20], and in another report with various organic model compounds, this peak appeared in the chemical shift zone of 5.7~8.2 ppm^[14]. To further confirm this chemical shift, ^1H - ^{15}N HSQC was carried out for this biuret-containing BPU-HDI (Fig. 2D), which indicated that the assignment was correct, where two correlation spots of ^1H - ^{15}N (5.7, -298.6 ; 8.2, -286.2) were detected.

Both samples, PU-HDI and BPU-HDI, were subsequently subjected to NMR ^{13}C analysis. The corresponding spectra are given, for the carbonyl region only, in Figs. 2(E) and 2(F), respectively. For PU-HDI, there appeared only one peak at 158.5 ppm, which has been recognized as that of the carbonyl carbon^[22, 31], whereas for BPU-HDI, besides the one at 158.5 ppm, there appeared a new peak at 156.8 ppm. Edwards *et al.*^[32] in their study on biuret adduct resins of HDI, observed a peak at 156.5 ppm and ascribed it to the urea carbonyl C with its one of the two NH turned biuret, just as illustrated in Fig. 2(F). This peak was also reported at 156.4 ppm with CDCl_3 as the solvent^[33]. Based on these reports, the peak at 156.8 ppm was ascribed to the carbonyl C in biuret unit. The fact that this peak was absent in ^{13}C spectrum of PU-HDI (Fig. 2E) provided also a solid support that there was no biuret formation in PU-HDI prepared by

HDI reaction with water at 30°C .

It is to note that, for the two peaks shown in Fig. 2(B), the peak intensity of the one at 8.2 ppm was much larger than that at 5.7 ppm, an indication that the number of biuret groups was significantly larger than that of the urea groups. This confirms that the synthesis process of biuret-containing BPU was reliable. All these chemical shifts are summarized in Table 2.

TDI-based Polyureas

To clarify whether there are biuret units in TDI-based PU is more difficult in comparison to the HDI-based PU because of the following reasons: (1) TDI molecule is asymmetric, and the PU-TDI made wherefrom is of different structure since TDI monomers may be connected differently (head-head, head-tail *etc.*); (2) TDI used for PU preparation is a mixture of its 2,4- and 2,6-isomers, which rendered the chemical structure of PU-TDI more complexity; (3) Knowing that PU-TDI was prepared through TDI reaction with water, the main chain of PU-TDI is consisting of two basic chemical groups (urea— HN—CO—NH— , and methyl substituted phenylene— $\text{C}_6\text{H}_4(\text{CH}_3)—$), as depicted in Fig. 1. There are strong interactions between the electrons on the phenylene ring and those on the adjacent urea, which makes their NMR spectra very complicated. It is to remind that the focus here is to check out the presence of biuret formation in PU-TDI, rather than a full analysis of the chemical structure. In an early study on NMR analysis for PU-TDI, quite detailed information has been provided, by comparing NMR spectra of TDI and TDA to that of PU-TDI^[23]. With the effect of the protons on the aromatic rings and that of the substituents all taken into account, we have concluded that the protons of the urea unit in PU-TDI (—NH—CO—NH—) should have their chemical shifts between 6.5 and 9.2 ppm, as shown in Fig. 3(A) (urea region only). This was further confirmed by the spectra of ^1H - ^{15}N HSQC given in Fig. 3(B), which demonstrates that the chemical shifts of N atoms in PU-TDI (—NH—CO—NH—) appeared between -276.4 and -273.3 ppm. Based on this conclusion, we can now examine the ^1H -NMR spectrum of biuret-containing sample BPU-TDI, shown in Fig. 3(C). By simply comparing this spectrum with that of PU-TDI (Fig. 3A), one can observe the appearance of new peaks at larger chemical shifts beyond 9.2 ppm, spreading from 9.6 ppm to 10.3 ppm. The same or very similar peaks have been observed in reported studies. In one study on aromatic urea of small model compounds similar to PU-TDI, Sumi *et al.* ascribed ^1H peaks located in 9.6 ppm to 10.2 ppm to the protons of NH neighboring a biuret bonding^[14]; in the other, Okuto assigned ^1H peaks in between 9.2 ppm and 10.2 ppm to the same protons in a biuret bonding^[18]. In addition, this was also well supported by ^1H - ^{15}N HSQC test of BPU-TDI (Fig. 3D), where two new H-N coherence spots (9.7, -265.8 ; 9.9, -266.4) were

Table 2 Chemical shifts of ^1H and ^{13}C atoms of urea and biuret in different polyureas

Groups	^1H chemical shift (ppm, carbonyl region)		^{13}C chemical shift (ppm, carbonyl region)		^{15}N chemical shift (ppm, urea region)	
	HDI	TDI	HDI	TDI	HDI	TDI
Biuret	8.2	9.6~10.3	156.8	—	-286.2	$-265.8 \sim -266.4$
Urea	5.7	6.5~9.2	158.5	—	-298.6	$-276.4 \sim -273.3$

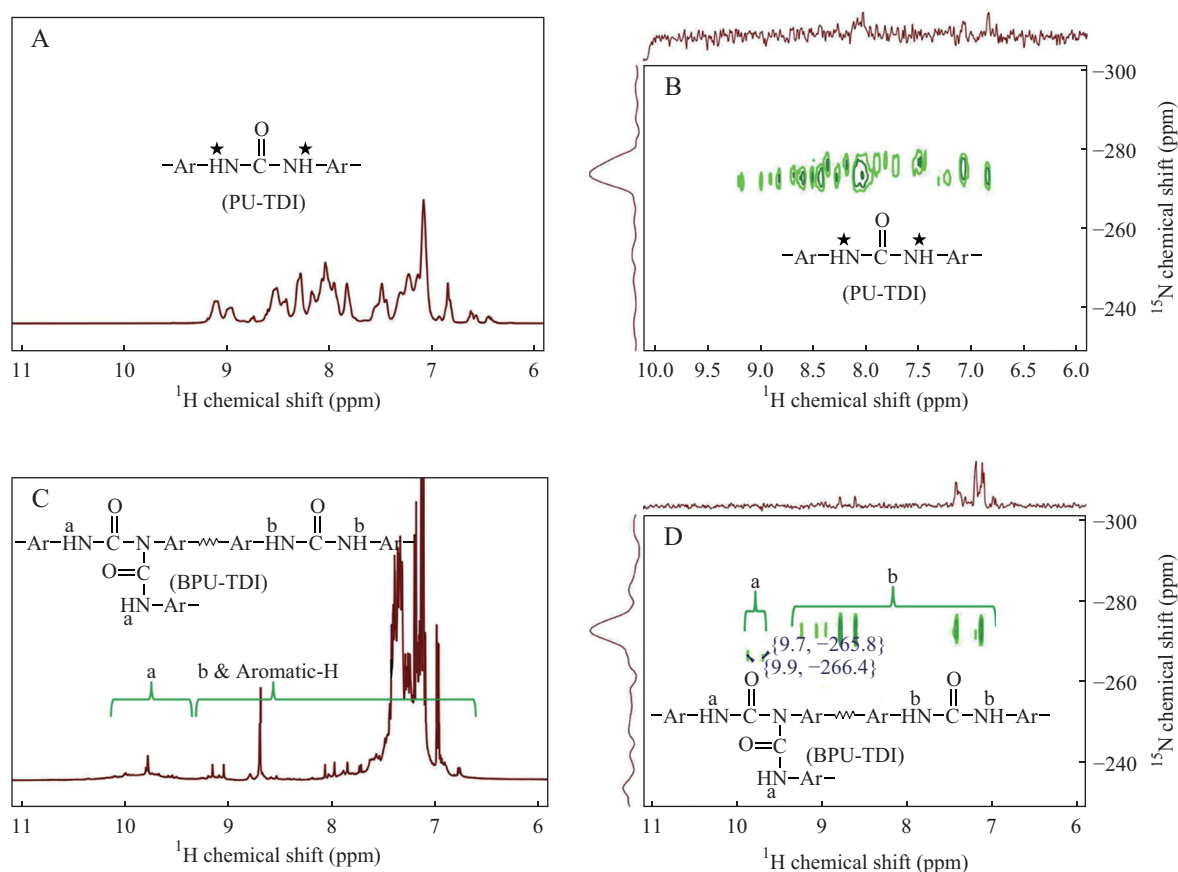


Fig. 3 NMR spectra of PU and BPU samples: (A) ^1H -NMR spectrum of PU-TDI; (B) ^1H - ^{15}N HSQC of PU-TDI; (C) ^1H -NMR spectrum of BPU-TDI; (D) ^1H - ^{15}N HSQC of BPU-TDI

detected in comparison with ^1H - ^{15}N HSQC of PU-TDI shown in Fig. 3(B). Based on these results, one is assured that the peaks from 9.6 ppm to 10.3 ppm were due to the biuret groups, known to be present in the sample BPU-TDI, and that biuret bonding was absent in PU-TDI.

Chemical Structure Analysis of Polyurea Obtained from TDI Reaction in EDA Aqueous Solution

In the preparation of PU microspheres through interface polymerization of TDI droplets in water, it was found that the presence of a diamine in water was crucial for the microsphere formation^[34]. With TDI droplets added into pure water without EDA, no microspheres were obtained, only polymer clumps were formed regardless of the polymerization process. It was believed then that the presence of EDA was to accelerate the polymerization, and therefore the formation of a hard shell on TDI droplets, since its reactivity towards isocyanate group is much greater than that of water^[24, 35]. To affirm that EDA reacted predominantly with TDI in the early stage of the process and was responsible for the quick formation of a hard shell on TDI droplets, samples were taken at early stage (10 min) and at end of the polymerization (2 h). The PU obtained, denoted as PU-EDA, was subjected to NMR analysis. Their ^1H -NMR spectra are given in Fig. 4. For comparison, the full spectrum of PU-TDI discussed above is also given (Fig. 4a). By comparing these spectra, a remarkable observation is that a distinct peak at chemical shift 3.2 ppm was seen for PU-EDA

at 10 min (Fig. 4b). This peak has previously assigned to the protons in ethylene units in PU main chains^[34], and reportedly appeared at 3.35 ppm with *N,N*-dimethylformamide as solvent^[36]. As expected, no any peak was observed around this region (3.20 ppm to 3.35 ppm) for PU-TDI, the sample prepared by reacting TDI with water, since no ethylene unit was involved in this sample as shown in Fig. 1. However, the spectrum of PU-EDA sample at 2 h (Fig. 4c) is very similar to that of PU-TDI (Fig. 4a) rather than to that of PU-EDA sample at 10 min (Fig. 4b), and the peak at 3.2 ppm was not seen. It is to remind that the amount

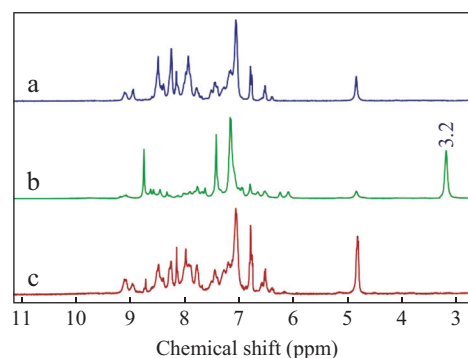


Fig. 4 ^1H -NMR spectra of PU samples prepared by: (a) TDI reaction with H_2O ; (b) TDI reaction in EDA aqueous solution sampled at 10 min; (c) TDI reaction in EDA aqueous solution sampled at 2 h

of EDA used was quite low, 3.8 wt% of EDA relative to the total weight of the monomers (EDA+TDI). TDI was copolymerized with EDA at very beginning of the process. At 10 min of the polymerization, it was detectable by NMR as shown by the presence of its ethylene segment at 3.2 ppm, whereas at 2 h of the polymerization, EDA had been fully exhausted long enough, and most of the PU was now consisting of the chains formed through TDI reaction with water, exactly the same chemical structure as PU-TDI, free of the ethylene units. The relatively low amount of PU chains containing ethylene units formed at the start of the polymerization was no more detectable. These results confirm that the reactivity of EDA towards TDI is much greater than water, and the presence of EDA is crucial for the formation of the microspheres.

Based on the mechanism of the polymerization, terminal $-NH_2$ groups are present at the end of the polymerization. The peak at 4.80 ppm was due to the protons of the terminal $-NH_2$ [23]. Among the three spectra shown in Fig. 4, the intensity of the peak was the lowest for the PU-EDA at 10 min, also an indication that amine of EDA quickly reacted with TDI, leaving the lowest amount of terminal groups in the dry polymer among all the three samples.

CONCLUSIONS

Specially designed biuret-containing polyurea (BPU) oligomers were prepared and the presence of biuret groups was clearly demonstrated by NMR analysis of ^1H , ^{13}C and ^{15}N spectra. By comparison of these spectra with those of PU materials prepared either through the reactions of diisocyanate with water or through that with diamine, it is concluded that biuret was not formed in all these PU prepared at 30 °C or 65 °C under ordinary experimental conditions. Therefore the poor solubility of PU in common organic solvents must be caused by the presence of abundant hydrogen bonding rather than by biuret crosslinking. This study provides a reliable method for the analysis of PU chemical structure.

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