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Aliphatic thermoplastic polyurethane-ureas and polyureas synthesized through a non-isocyanate route†

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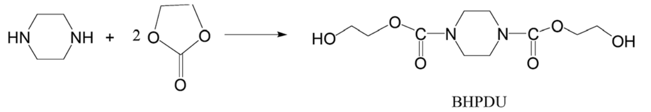
A simple non-isocyanate route for synthesizing aliphatic thermoplastic polyurethane-ureas (TPUUs) and thermoplastic polyureas (TPUreas) is presented. Melt transurethane polycondensation of isophorone diamine or diethylene glycol bis(3-aminopropyl) ether with bis(hydroxyethyl) hexanediurethane, bis(hydroxyethyl) isophoronediurethane or bis(hydroxyethyl) piperazinediurethane was conducted at 170 °C under a reduced pressure of 3 mmHg. A series of thermoplastic TPUUs and TPUreas were prepared, and were characterized by gel permeation chromatography, FT-IR, ^{1}H-NMR, differential scanning calorimetry, thermogravimetric analysis, and tensile testing. The TPUUs and TPUreas have an M_n up to 14 900 g mol^{-1}, an M_w up to 43 700 g mol^{-1}, T_g between −18.6 °C and 116.8 °C, and an initial decomposition temperature of over 222.3 °C. A flexible TPUU exhibits a melting temperature of 77.7 °C, a tensile strength of 6.46 MPa, and an elongation at break of 180.20%.

Introduction

Polyurethanes (PUs) are important commercial polymers that are widely used as foams, fibers, adhesives, coatings, and medical materials because of their outstanding mechanical properties, abrasion resistance, and good biocompatibility.[1] Almost all the commercial polyurethanes are currently prepared from diisocyanates and polyols with low molecular-weight diols or diamines as chain extenders. Polyurethane-ureas (PUUs) are prepared when diamines are used as the chain extenders.[2–7] Polyureas (PUreas), which are usually used as two-component systems in protective coating/lining industry, are prepared normally from diisocyanates and polyamines.[8–11] The urea linkages introduced provide many hydrogen bonds, and improve the mechanical properties of PUUs and PUreas evidently compared to those of common PUs. However, in the preparation of PUs including PUUs and PUreas, the starting raw materials, diisocyanates, are highly toxic, and the major synthesis precursor of them is the extremely toxic phosgene. Non-isocyanate synthesis is becoming a promising alternative for the isocyanate route, and is attracting increasing attention from academic and industrial researchers who are working on polyurethanes.[12–14] Most investigations on non-isocyanate polyurethanes (NIPUs) are currently focused on cross-linked PUs prepared from cyclic carbonates and diamines or multiamines.[15–22] Meanwhile, Loontjens *et al.* synthesized NIPUs from carbonyl biscaprolactamate.[23–25]

Transurethane polycondensation of diurethanes has been developed to synthesize linear or thermoplastic polyurethanes (TPUs). Deepa *et al.* synthesized a series of amorphous TPUs from the transurethane polycondensation of dimethyl 1,6-hexamethylene dicarbamate and dimethyl isophorone dicarbamate with glycol oligomers, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol and isosorbide.[26,27] Rokicki *et al.* synthesized two α,ω-bis(hydroxyethyloxy carbonyl amino)alkanes and studied their solution polycondensation with 1,6-hexanediol or 1,10-decanediol.[28] Ochiai studied the self-polycondensation of 1,6-bis(hydroxyethyloxy carbonyl amino)hexane and used the obtained polyurethane to synthesize methacrylate macromolecular monomers.[29] Sharma *et al.* synthesized a series of α-hydroxy-ω-amino-amides and transformed them into α-hydroxy-ω-*O*-phenyl urethanes or α-hydroxy-ω-*O*-hydroxyethyl urethanes, from which several alternating poly(amide urethane) s were prepared.[30–32] In our previous work, we synthesized aliphatic thermoplastic poly(amide urethane)s having short nylon-6 segments,[33] poly(ether amide urethane)s having short



Scheme 1 Synthesis of BHPDU through the ring-opening reaction of EC with PIP.

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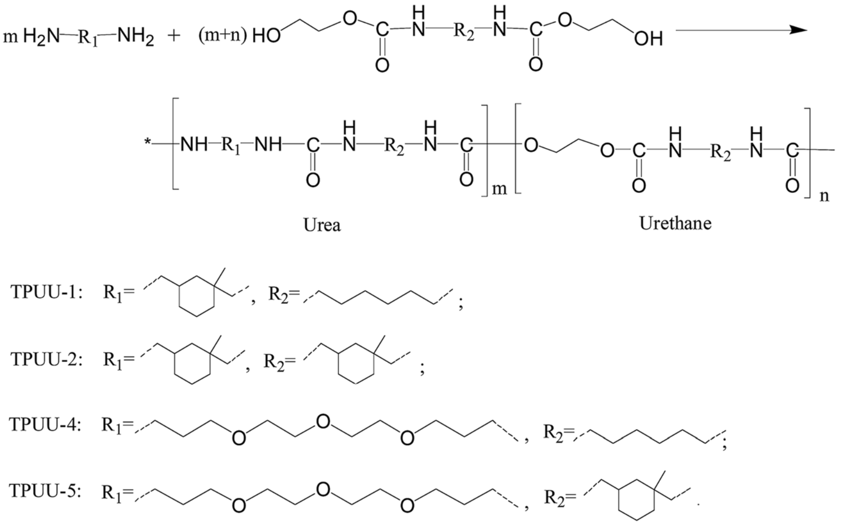
Table 1 Synthesis of TPUUs

TPUUs[a]	Diamine	Diurethanediol	Reaction time[b] (h)	M_n[c] (g mol^{-1}) (GPC)	M_w[c] (g mol^{-1}) (GPC)	PDI[c] (GPC)	T_g (°C)	T_i (°C)
TPUU-1	IPDA	BHHDU	5.0	6000	7100	1.17	75.3	222.3
TPUU-2		BHIDU	2.5	4800	5500	1.13	116.8	232.3
TPUU-3		BHPDU	5.5	3300	4400	1.34	113.3	239.1
TPUU-4[d]	DGBAE	BHHDU	2.1	—	—	—	—	—
TPUU-5		BHIDU	2.5	14 900	43 700	2.93	51.5	297.6
TPUU-6		BHPDU	11.0	12 100	25 000	2.07	−18.6	274.0

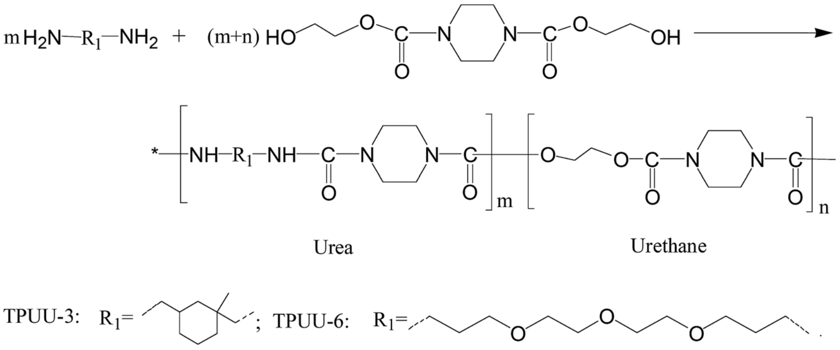
[a] Reaction conditions: diamine–diurethanediol = 1 : 1 (molar ratio); reaction temperature, 170 °C; 30 mmHg, 0.5 h. [b] Reaction time under a reduced pressure of 3 mmHg. [c] GPC data detected in DMF containing 10 mM LiBr with PS as the standard. [d] TPUU-4 is in solid state up to 220 °C and cannot dissolve in DMF.



Scheme 2 Synthesis of TPUUs from the polycondensation of IPDA or DGBAE with BHHDU or BHIDU.

nylon-6 segments and poly(ethylene glycol) (PEG) sequences,[34] and poly(ether urethane)s having short PEG segments.[35] Meanwhile, Tang *et al.* synthesized thermoplastic polyureas (TPUreas) from solution polycondensation of the dimethyl dicarbamates, which contained different multi-urea segments, with amino-terminated poly(propylene glycol).[36]

In this paper, several aliphatic thermoplastic polyurethane-ureas (TPUUs) and TPUreas were directly prepared through the transurethane polycondensation of diamines with different diurethanediols. Melt transurethane polycondensation of isophorone diamine (IPDA) and diethylene glycol bis(3-aminopropyl) ether (DGBAE) with bis(hydroxyethyl) hexanediurethane (BHHDU), bis(hydroxyethyl) isophoronediurethane (BHIDU) or bis(hydroxyethyl) piperazinediurethane (BHPDU) were conducted at 170 °C under reduced pressure. The obtained TPUUs or TPUreas were characterized by gel



Scheme 3 Synthesis of TPUUs from the polycondensation of IPDA or DGBAE with BHPDU.

Table 2 Different vibration modes in the FT-IR spectra of TPUUs[a]

TPUUs	νN–H	νC–H	νC=O	δN–H	νC–O	νC–N	νC–O–C
TPUU-1	3340.3 (s, b)	2931.1 (s), 2857.5 (s)	1707.3 (s), 1627.4 (vs)	1568.7 (vs)	1253.2 (s)	1143.9 (w)	—
TPUU-2	3359.1 (s, b)	2951.4 (s), 2915.3 (s)	1702.0 (s), 1644.8 (s)	1557.6 (vs)	1242.5 (s)	1143.9 (w)	—
TPUU-3	3368.8 (s, b)	2950.5 (s), 2914.4 (s)	1643.6 (vs)	1556.4 (vs)	1241.1 (s)	1132.8 (w)	—
TPUU-5	3363.5 (s, b)	2930.2 (s), 2868.7 (s)	1639.6 (vs)	1567.4 (vs)	1253.0 (s)	—	1113.1 (s)
TPUU-6	3327.5 (s, b)	2924.9 (sh), 2873.0 (s)	1747.5 (m, sh), 1618.0 (vs)	1566.1 (s)	1261.4 (s)	—	1118.3 (vs)

[a] (sh) shoulder, (b) broad, (vs) very strong, (s) strong, (m) medium, (w) weak.

permeation chromatography (GPC), FT-IR, ^{1}H-NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and tensile test.

Experiment section

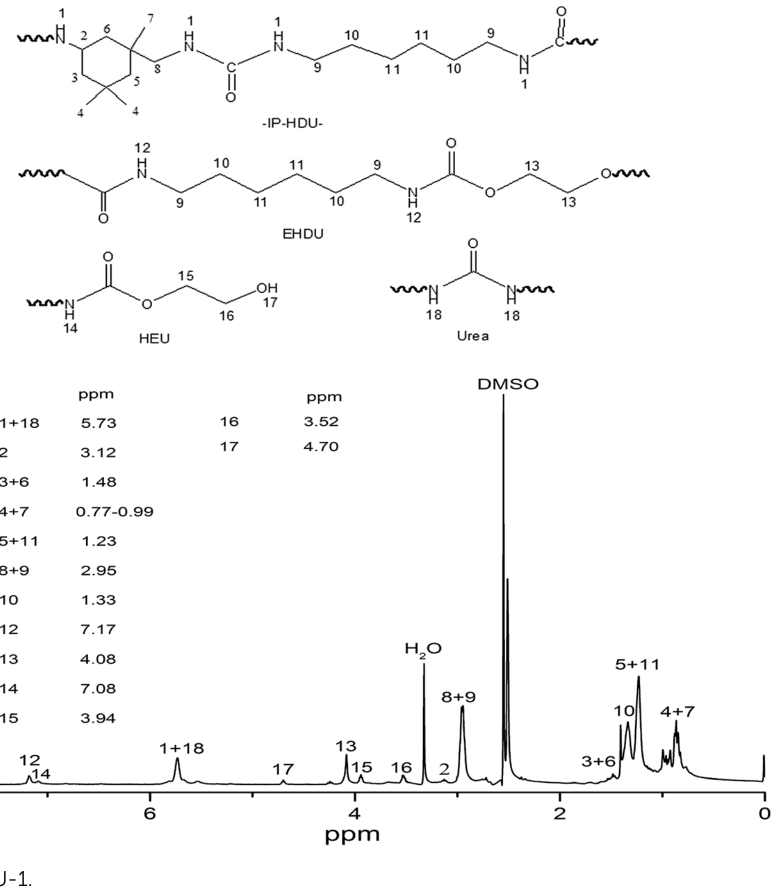
Materials

IPDA and DGBAE were purchased from TCI Japan. Piperazine hexahydrate (PIP) and ethylene carbonate (EC) were purchased from Alfa Aesar UK. 1,6-Hexanediamine (HAD) was purchased from Shanghai Reagent Plant, China. Other materials, such as ethanol, *N*,*N*′-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), were all obtained as reagent grades and used directly. BHHDU (^{1}H-NMR spectrum, Fig. S1†) was prepared from the reaction of EC with HAD according to the literatures.[28,33] Its melting point was 94 °C. BHIDU (^{1}H-NMR spectrum, Fig. S2†) was prepared similarly from the reaction of EC with IPDA.

Synthesis of BHPDU

17.76 g (0.21 mol) PIP and 38.16 g (0.42 mol) EC were added to a 100 mL 3-necked flask. The mixture was mechanically stirred and heated under N_2 atmosphere to 80 °C for 7 h. The resulting solution was cooled to room temperature. White crystals were obtained and recrystallized with ethanol. After filtration and drying, 41.86 g BHPDU (yield: 78.95%) was obtained. Its melting point is 105 °C.

FT-IR, cm^{-1} (KBr): 3375.2 (–OH), 2876.2 (–CH_2–), 1699.1 (–O–C=O), 1661.7 (amide I), 1445.3 (–CH_2–), 1243.9 (–C–O in carbamate group), 1075.2 (–C–O in –CH_2–OH).



	ppm		ppm
1+18	5.73	16	3.52
2	3.12	17	4.70
3+6	1.48		
4+7	0.77-0.99		
5+11	1.23		
8+9	2.95		
10	1.33		
12	7.17		
13	4.08		
14	7.08		
15	3.94		

Fig. 1 ^{1}H-NMR spectrum of TPUU-1.

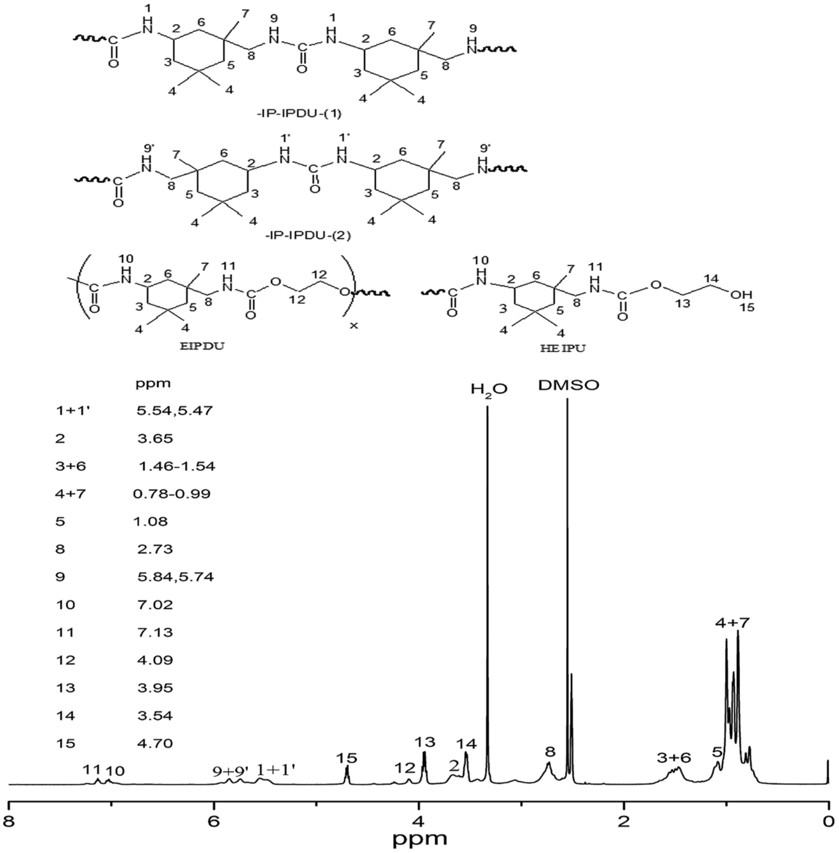


Fig. 2 ^{1}H-NMR spectrum of TPUU-2.

^{1}H-NMR, ppm (400 MHz, DCCl$_3$): 2.51 (2H, –OH), 3.52 (8H, 4 × ring CH$_2$), 3.84 (4H, 2 × –CH$_2$OH), 4.29 (4H, 2 × –OCH$_2$).

Synthesis of TPUUs

3.40 g (0.02 mol) IPDA and 5.84 g BHHDU (0.02 mol) were added to a 100 mL 3-necked flask equipped with a distilling adapter, a condenser, and a receiver. The mixture was melt and stirred at 170 °C under a nitrogen atmosphere, and was reacted under a reduced pressure of 30 mmHg for 0.5 h. Then, the pressure in the flask was gradually reduced to 3 mmHg for different periods until no further increase of viscosity was observed. The obtained TPUU-1 was poured and cooled at room temperature.

Similarly, TPUU-2 and TPUU-3 were prepared from the melt polycondensation of IPDA with BHIDU and BHPDU at a diamine–diurethanediol molar ratio of 1 : 1, respectively. TPUU-4, TPUU-5 and TPUU-6 were prepared from the melt polycondensation of DGBAE with BHHDU, BHIDU or BHPDU at a diamine–diurethanediol molar ratio of 1 : 1.

Characterization

The M_n, M_w and polydispersity index (PDI) of TPUUs were determined *via* GPC by using an Agilent-2600 system (Agilent Technologies, Inc., USA) equipped with a PLgel 5 μm 1000 Å column and a refractive index detector at 25 °C. The DMF containing 10 mM LiBr was used as an eluent with a flow rate of 1 mL min^{-1}, and polystyrene (PS) was used as the standard.

Polymer samples for FT-IR and ^{1}H-NMR characterization were purified thrice through dissolution–precipitation cycles by using 20 mL DMSO as solvent and 200 mL ether as non-solvent. FT-IR spectra were acquired on a NICOLET 60SXB FTIR spectrometer (Nicolet Analytical Instruments, USA). ^{1}H-NMR spectra of the polymers were obtained in deuterated DMSO on a Bruker 400 AVANCE (Bruker Corporation, USA) by using tetramethylsilane as the internal standard.

The second heating DSC spectra were measured with a TA Q200 differential scanning calorimeter (TA Instruments, USA) in N$_2$ atmosphere. Samples were first heated from room temperature to 200 °C at a heating rate of 40 °C min^{-1} and maintained for 5 min to eliminate thermal history. The samples were then cooled to −80 °C at a rate of 40 °C min^{-1} or 10 °C min^{-1}. In the second heating scans, the samples were heated from −80 °C to 200 °C at a rate of 10 °C min^{-1}. TGA was performed on a TGA Q50 analyzer (TA Instruments, USA) with a heating rate of 10 °C min^{-1} from 25 °C to 600 °C in N$_2$ atmosphere.

Samples for tensile testing were processed by a heating compression molding method which was similar to that reported in the literature.[6] Polymer films (50 mm × 50 mm × 1 mm) were prepared by using a 70911-24B powder press machine (Tianjin New Technical Instrument Co. Ltd., China). Samples were heated to temperature 30 °C higher than their T_g or T_m, maintained for 5 min under 10 MPa, naturally cooled to room temperature with the pressure unchanged, and then cut into dumbbell-shaped bars (50 mm × 4 mm × 1 mm). Mechanical analysis was

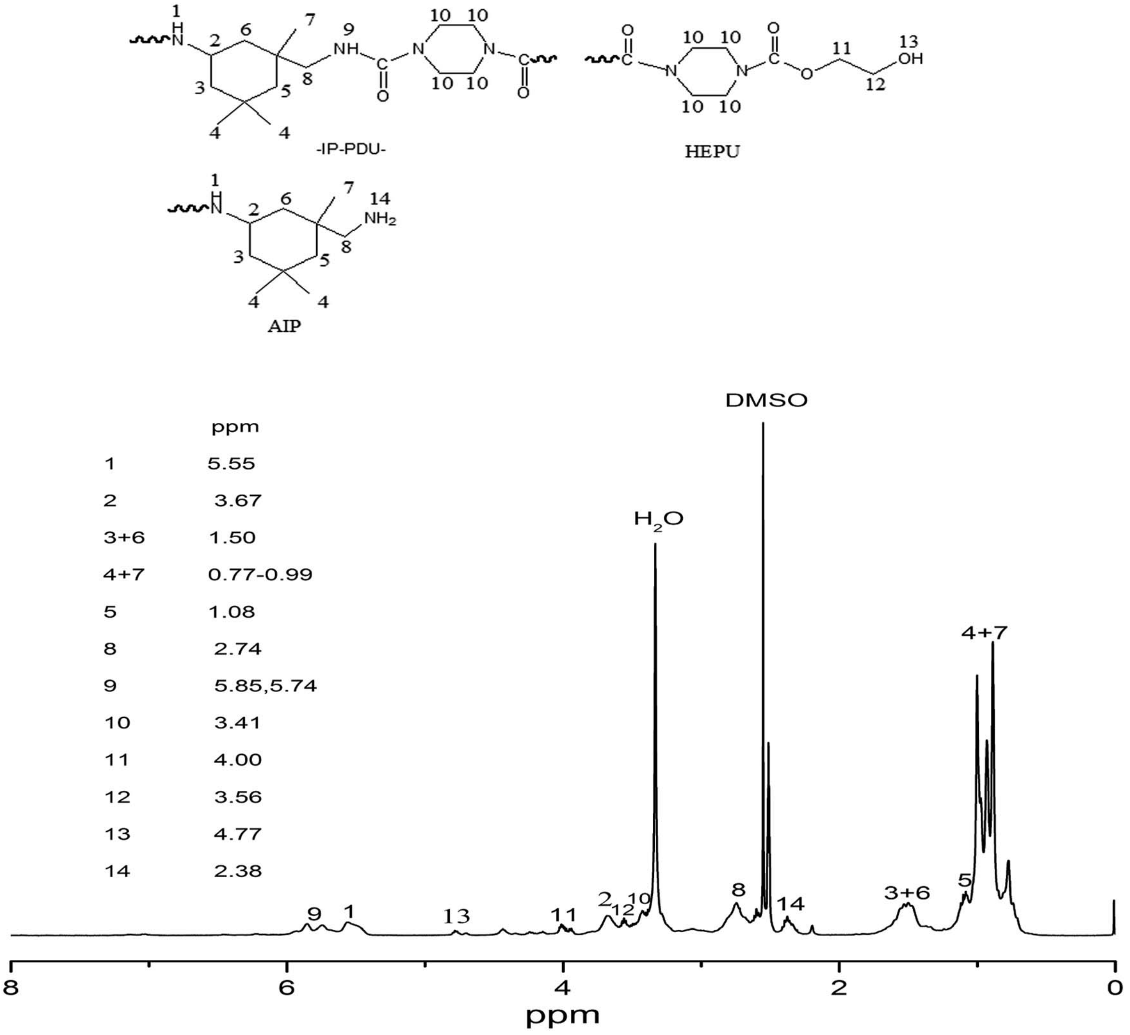


Fig. 3 ^{1}H-NMR spectrum of TPUU-3.

conducted on a LLOYD LR30K tensile testing machine (Lloyd Materials Testing, UK) at a crosshead speed of 200 mm min^{-1} at 25 °C. Five measurements were performed for each sample, and the results were averaged to obtain a mean value.

Results and discussion

Synthesis of BHPDU

Huang *et al.* synthesized BHPDU from the reaction of EC with PIP under the catalysis of cesium carbonate.[37] Li *et al.*[33] had synthesized BHHDU from direct melt reaction of EC with HAD. In this article, direct reaction of EC with PIP was conducted at 80 °C without any catalyst, and BHPDU with a yield of about 78.95% was prepared (Scheme 1). Its structure was verified by FT-IR and ^{1}H-NMR spectrum (Fig. S3†).

Synthesis of TPUUs

Melt transurethane polycondensation of IPDA or DGBAE with BHHDU, BHIDU or BHPDU was conducted at 170 °C under reduced pressure. A series of TPUUs were prepared. Higher vacuum up to 3 mmHg favored the removal of by-product ethylene glycol, and led to the increase of molecular weight. TPUUs or TPUreas with M_n up to 14 900 g mol^{-1} and M_w up to 43 700 g mol^{-1} were prepared (Table 1). Scheme 2 shows the synthesis reaction of TPUU-1, TPUU-2, TPUU-4 and TPUU-5 from IPDA or DGBAE with BHHDU or BHIDU, respectively. Co-polycondensation of IPDA or DGBAE with BHHDU or BHIDU forms urea linkages. Meanwhile, self-polycondensation of BHHDU or BHIDU also occurs, resulting in the possible urethane units. Similarly, TPUU-3 and TPUU-6 were prepared from the co-polycondensation of IPDA or DGBAE with BHPDU (Scheme 3). TPUU-1 is an opaque polyurethane-urea. Other TPUUs such as TPUU-2, TPUU-3, TPUU-5, and TPUU-6 are all transparent polyurethane-ureas or polyureas.

FT-IR and ^{1}H-NMR characterization

The structures of TPUUs were characterized by FT-IR and ^{1}H-NMR spectra. The major vibrations in the FT-IR spectra of TPUUs are listed in Table 2. Based on the characteristic vibrations in FT-IR spectrum and the chemical shifts of different

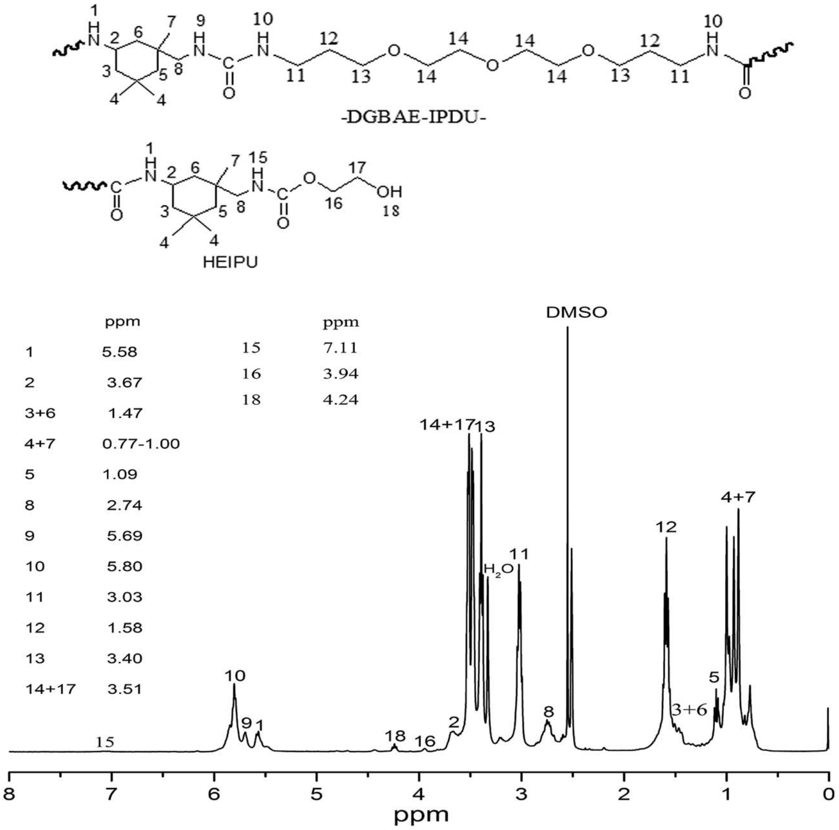


Fig. 4 ^{1}H-NMR spectrum of TPUU-5.

hydrogens in ^{1}H-NMR spectrum (Fig. 1), the structure of TPUU-1 is described. TPUU-1 is mainly constructed with isophorone hexanediurea (-IP-HDU-) segments and ethylene hexanediurethane (-EHDU) segments, which were formed from the co-polycondensation of IPDA with BHHDU and the self-polycondensation of BHHDU, respectively. Urea formation is the major reaction in TPUU-1 synthesis. Some hydroxyethyl urethane (HEU) or $-HNCOOCH_2CH_2OH$ groups were left as terminal groups, because the molecular weight of TPUU-1 was not too high. Meanwhile, some urea units were formed due to tail-biting side reaction of the $-HNCOOCH_2CH_2OH$ terminal groups.[28,29]

TPUU-2 shows almost the same intensities of FT-IR peaks at 1702.0 cm^{-1} and 1644.8 cm^{-1}, which correspond to the C=O stretching vibration of urethane groups and that of urea groups, respectively. The amount of urea groups is slightly higher. Combined the chemical shifts of different hydrogens in ^{1}H-NMR spectrum (Fig. 2), the structure of TPUU-2 is described. TPUU-2 is constructed with isophorone isophorone diurea (-IP-IPDU-) segments and ethylene isophoronediurethane (-EIPDU-) segments, which were formed from the co-polycondensation of IPDA with BHIDU and the self-polycondensation of BHIDU. Large steric hindrance between IPDA and BHIDU leads to lower amount of urea linkages (*i.e.* -IP-IPDU- segments) formed than TPUU-1, because IPDA and BHIDU all contain bulky trimethyl-substituted cyclohexylene units. Self-polycondensation of BHIDU was little influenced because of lower steric interaction, with higher amount of urethane units (*i.e.* -EIPDU- segments) formed in TPUU-2 than in TPUU-1. Some hydroxyethyl isophorone urethane (HEIPU) groups were left as terminal groups due to low molecular weight of TPUU-2. The -IP-IPDU- segments may also contains -IP-IPDU-(1) and -IP-IPDU-(2) segments, which derive from different connections between IPDA with BHIDU, *i.e.* head-to-tail connections and head-to-head connections. As H_2N- terminal groups are sensitive to the solvents used in NMR detection, and TPUU-2 has not very low molecular weight, the signal corresponding to H_2N- terminal groups was not found in Fig. 2.

TPUU-3 exhibits a very strong peak corresponding to urea linkage at 1643.6 cm^{-1} in FT-IR spectrum. Fig. 3 shows the ^{1}H-NMR spectrum, the chemical shifts of different hydrogen atoms, and the major structural units in TPUU-3. TPUU-3 is mainly constructed with isophorone piperazinediurea (-IP-PDU-) segments, because of less steric interaction in the co-polycondensation of IPDA with BHPDU. As TPUU-3 had very low molecular weight, some hydroxyethyl piperazine urethane (HEPU) groups and amino isophorone (AIP) groups were left as terminal groups.

TPUU-5 also merely shows a very strong peak corresponding to urea linkages at 1639.6 cm^{-1} in FT-IR spectrum. Based on the chemical shifts of different hydrogens in ^{1}H-NMR spectrum, the structure of TPUU-5 is described in Fig. 4. TPUU-5 is mainly

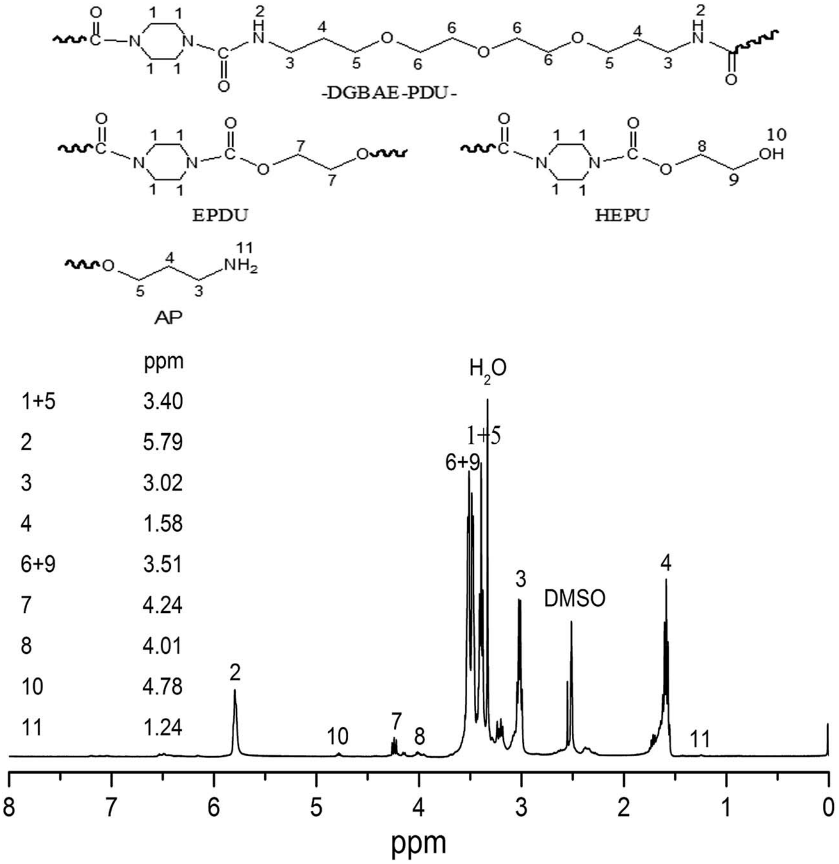


Fig. 5 ^{1}H-NMR spectrum of TPUU-6.

constructed with DGBAE isophorone diurea (-DGBAE-IPDU-) segments, which were formed from the co-polycondensation of DGBAE with BHIDU. Some HEIPU groups were left as terminal groups.

TPUU-6 shows a medium shoulder peak at 1747.5 cm^{-1} and a very strong peak at 1618.0 cm^{-1} in FT-IR spectrum, which correspond to the urethane groups and urea groups, respectively. Combined the chemical shifts in ^{1}H-NMR spectrum, the

Table 3 Urea/urethane ratios in TPUUs

			Urea/urethane			
TPUUs	Peak	Area	Calculation equation	Ratio	Urea (%)	Urethane (%)
TPUU-1	A_{17}	1.00	$\text{Urea/urethane} = \frac{(A_{1+18})/2}{A_{12} + A_{14}}$	1.60	61.54	38.46
	A_{1+18}	13.42				
	A_{12}	2.53				
	A_{14}	1.66				
TPUU-2	A_{15}	1.00	$\text{Urea/urethane} = \frac{(A_{1+1'} + A_{9+9'})/2}{A_{10} + A_{11}}$	1.43	58.85	41.15
	$A_{1+1'}$	1.82				
	$A_{9+9'}$	1.46				
	A_{10}	0.63				
	A_{11}	0.52				
TPUU-3	A_{13}	1.00	$\text{Urea/urethane} = \frac{A_1 + A_9}{A_{13}}$	13.29	93.00	7.00
	A_1	5.86				
	A_9	7.43				
TPUU-5	A_{18}	1.00	$\text{Urea/urethane} = \frac{A_{10}}{A_{15}}$	82.56	98.80	1.20
	A_{10}	28.07				
	A_{15}	0.34				
TPUU-6	A_{10}	1.00	$\text{Urea/urethane} = \frac{A_2}{\frac{A_7}{4}}$	25.78	96.27	3.73
	A_7	5.70				
	A_2	36.73				

structure TPUU-6 is described in Fig. 5. TPUU-6 is constructed with the major DGBAE piperazinediurea (-DGBAE-PDU-) segments and the minor ethylene piperazinediurethane (-EPDU-) segments, which were formed from the co-polycondensation of DGBAE with BHPDU and the self-polycondensation of BHPDU, respectively. Some HEPU groups derived from BHPDU and amino propyl (AP) groups from DGBAE were left as terminal groups.

Melt polycondensation of IPDA or DGBAE with BHHDU, BHIDU or BHPDU was conducted at a diamine–diurethanediol molar ratio of 1 : 1. In addition to the co-polycondensation between diamine and diurethanediol, which resulted in urea units, some self-polycondensation of diurethanediols also occurred, with some urethane units formed. Table 3 shows the urea/urethane ratios in TPUUs. The urea linkages are the major units, with urethane linkages ranging from 1.20% to 41.15% formed. Although the self-polycondensation of diurethanediols effects the stoichiometric reaction between diamines and diurethanediols, the molecular weight of TPUUs was not influenced, because the self-polycondensation of diurethanediols also results in high molecular polyurethanes.[33,35] All polycondensations were conducted until Weissenberg effect took place, *i.e.* the polymers formed finally climbed onto the stirrer blades.

Table 4 shows the degree of polymerization (X_n) calculated based on structural units, and the extent of reaction (P) in TPUU synthesis. TPUUs with P of above 86.38% were prepared. From FT-IR and ^{1}H-NMR characterization, the TPUU-1 and TPUU-2 are verified as polyurethane-ureas, and the TPUU-3, TPUU-5 and TPUU-6 are nearly polyureas. Polyurethane-ureas and polyureas are prepared directly through melt transurethane polycondensation of diamines with diurethanediols.

TPUUs resist common organic solvents. They are soluble in high polar solvents like DMF or DMSO, and are insoluble in common solvents such as ether, alcohol, ethyl acetate, acetone, and tetrahydrofuran. TPUU-1, TPUU-2 and TPUU-3 are inert to water and dilute HCl solution or NaOH solution in short time because they contain hydrophobic alkylenes. Their surface did not change after contact with drops of water, 0.1 M HCl solution or 0.1 M NaOH solution for 48 h. Drops of water, 0.1 M HCl solution or 0.1 M NaOH solution on the surface of TPUU-5 or TPUU-6 were absorbed in 48 h, and the surface became viscous, maybe because some hydrolysis took place. TPUU-5 and TPUU-6 exhibit poor resistance to water and dilute HCl solution or NaOH solution, because they contain hydrophilic short PEG segments.

Table 4 Extent of reaction in TPUU synthesis

			X_n[a]		
TPUUs	Peak	Area	Calculation equation	Value	P[b] (%)
TPUU-1	A_{17}	1.00	$X_n = \frac{1}{1-P} = \frac{\frac{A_{10}}{4} + \frac{A_{4+7}}{9}}{\frac{A_{17}}{2}}$	24.58	95.93
	A_{10}	25.49			
	A_{4+7}	53.26			
TPUU-2	A_{15}	1.00	$X_n = \frac{1}{1-P} = \frac{\frac{A_{4+7}}{9}}{\frac{A_{15}}{2}}$	7.92	87.37
	A_{4+7}	35.66			
TPUU-3	A_{13}	1.00	$X_n = \frac{1}{1-P} = \frac{\frac{A_{10}}{8} + \frac{A_{4+7}}{9}}{\frac{A_{13} + A_{14}/2}{2}}$	7.34	86.38
	A_{4+7}	103.92			
	A_{10}	7.53			
	A_{14}	4.81			
TPUU-5	A_{18}	1.00	$X_n = \frac{1}{1-P} = \frac{\frac{A_{11}}{4} + \frac{A_{4+7}}{9}}{\frac{A_{18}}{2}}$	61.34	98.37
	A_{4+7}	146.58			
	A_{11}	57.53			
TPUU-6	A_{10}	1.00	$X_n = \frac{1}{1-P} = \frac{A_2 + \frac{A_7}{4}}{\frac{A_{10} + A_{11}/2}{2}}$	56.73	98.24
	A_7	5.91			
	A_2	37.38			
	A_{11}	0.74			

[a] Degree of polymerization calculated based on structural units in TPUUs. [b] Extent of reaction in TPUU synthesis.

Thermal and mechanical properties

Fig. 6 shows the second heating DSC curves of TPUUs. Their glass transition temperature (T_g) is listed in Table 1. As TPUUs from TPUU-1 to TPUU-5 are random polyurethane-ureas or polyureas, they merely exhibit a T_g from −18.6 °C to 116.8 °C. TPUU-2 and TPUU-3, which were prepared from the co-polycondensation of IPDA with BHIDU or BHPDU, have higher stiff structural units and higher T_g than TPUU-1 that was prepared from IPDA and BHHDU with flexible structure. TPUU-6 was prepared from the co-polycondensation of DGBAE with BHPDU, and had symmetrical structural units. TPUU-6 is a

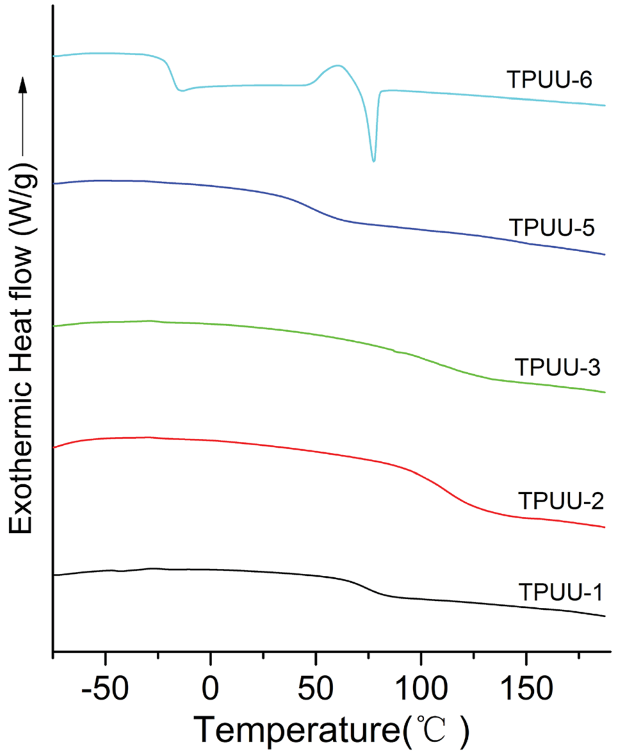


Fig. 6 Second heating DSC scans of TPUUs (cooling rate: 40 °C min^{-1}; heating rate: 10 °C min^{-1}).

crystallizable polyurethane–urea with a T_m at 77.7 °C and a T_c at 60.5 °C. A T_c meant that TPUU-6 did not crystallize fast enough to complete crystallization just after fast cooling period before the second heating started. Crystallization still progressed in the second DSC scan.

The second heating DSC scans in Fig. 6 were recorded *via* a heating–cooling–heating process: *i.e.* fast heating to 200 °C and maintaining for 5 min, fast cooling to −80 °C at a rate of 40 °C min^{-1}, and slow heating to 200 °C at 10 °C min^{-1}. Fast cooling in the second period is often adopted to evaluate the crystallization behavior of the crystallized polymers. If a polymer crystallizes very fast, its crystallization may have finished before the fast cooling period ends. A T_c of TPUU-6 in the second heating DSC curve meant that it did not crystallize fast enough and the crystallization did not finish after fast cooling. A slow cooling mode at 10 °C min^{-1} was also adopted, and the related second heating DSC curve of TPUU-6 is showed in Fig. 7(a). A weak T_c peak in this mode meant that the crystallization was nearly complete after the melt sample was cooled at a slow rate of 10 °C min^{-1}.

The initial decomposition temperature (T_i) of TPUUs or TPUreas is summarized in Table 1. All TPUUs or TPUreas exhibit T_i above 222.3 °C (Fig. 8), which is not too high because carbamate and urea linkages are only moderately thermally stable. TPUUs are thermoplastics still suitable for processing with normal thermal processing machines. TPUU-1, TPUU-2, TPUU-3 and TPUU-5 are very brittle polymers, and their tensile testing cannot be conducted. They lack any flexibility and elasticity. TPUU-6 exhibits an elongation at break of 180.20% and a tensile strength of 6.46 MPa (Fig. 9). TPUU-6 is a thermoplastic polyurethane-urea with appropriate tensile strength and good flexibility, but it has no elasticity. TPUU-6 shows similar tensile strength and elongation at break to the TPUUs prepared from poly(oxytetramethylene) glycol with 1,6-hexanediisocyanate,[5] but shows obviously lower tensile strength and elongation at break than the TPUUs prepared from polyester glycols with 1,6-hexanediisocyanate or 1,4-butane diisocyanate.[2,6] Maybe TPUUs with high tensile strength and long elongation at break can be prepared through the copolymerization of diurethanediols with long polyester glycols.

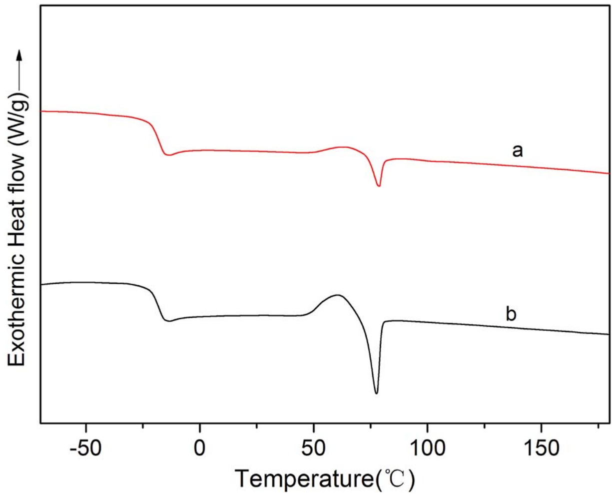


Fig. 7 Second heating DSC scans of TPUU-6 detected after different cooling period (cooling rate: (a) 10 °C min^{-1}; (b) 40 °C min^{-1}) (heating rate: 10 °C min^{-1}).

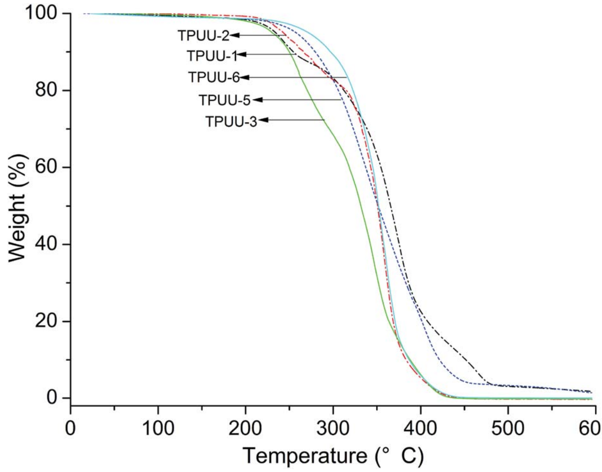


Fig. 8 TGA curves of TPUUs (heating rate: 10 °C min^{-1}; atmosphere: N_2).

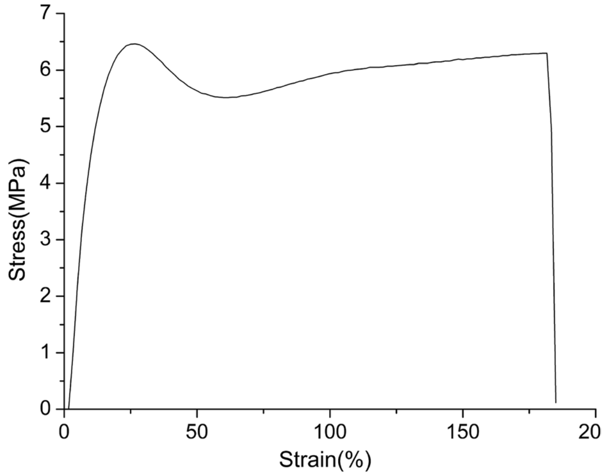


Fig. 9 Stress–strain curve of TPUU-6.

TPUU-1, TPUU-2 and TPUU-3 have low molecular weight. Their strength, flexibility and elasticity are poor. These properties are also influenced by the structural units in their main chains. TPUU-5 and TPUU-6 have similar molecular weight. As TPUU-5 is constructed with irregular trimethyl-substituted cyclohexylene units, it is a brittle polymer, and its tensile strength cannot be detected. Otherwise, TPUU-6 is composed of symmetric structural units, it is a polyurethane-urea with appropriate tensile strength and good flexibility.

Conclusion

This method provides a simple method to synthesize thermoplastic polyurethane-ureas and polyureas directly from melt transurethane polycondensation of diamines with simple diurethanediols. The diurethanediols can be easily prepared from diamines and ethylene carbonate. Polycondensation between diamines and diurethanediols with lower steric hindrance tends to formation of thermoplastic polyureas. This method can also be extended to synthesize thermoset polyurethane-ureas or polyureas from multi-amines and diurethanediols, and will change their synthesis method from an isocyanate and toxic route into a non-isocyanate and environment-friendly route.

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