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Amorphous and Crystallizable Thermoplastic Polyureas Synthesized through a One-pot Non-isocyanate Route

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 Electronic Supplementary Information

Abstract A simple one-pot non-isocyanate route for synthesizing thermoplastic polyureas is presented. *In situ* urethanization was conducted from the ring-opening reaction of ethylene carbonate with poly(propylene glycol) bis(2-aminopropyl ether) and hexanediamine, *m*-xylylenediamine, or diethylene glycol bis(3-aminopropyl) ether at 100 °C for 6 h under normal pressure. Melt transurethane polycondensation was successively conducted at 170 °C under a reduced pressure of 399 Pa for different time periods. A series of non-isocyanate thermoplastic polyureas (NI-TPUreas) were prepared. The NI-TPUreas were characterized by gel permeation chromatography, FTIR, ¹H-NMR, differential scanning calorimetry, thermogravimetric analysis, wide-angle X-ray diffraction, atomic force microscopy, and tensile test. NI-TPUreas exhibited M_n of up to 1.67×10^4 g/mol, initial decomposition temperature over 290 °C, and tensile strength of up to 32 MPa. Several crystallizable NI-TPUreas exhibited T_m exceeding 98 °C. NI-TPUreas with good thermal and mechanical properties were prepared through a green and simple one-pot non-isocyanate route.

Keywords Non-isocyanate route; Thermoplastic polyureas; One-pot method; Sustainable synthesis; Transurethane polycondensation

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INTRODUCTION

Polyurethanes (PUs) are important commercial polymers that are widely used as foams, fibers, films, adhesives, and coatings because of their outstanding mechanical properties and abrasion resistance.^[1] PUs are currently prepared from diisocyanates, polyols, and low molecular-weight diols or diamines chain extenders.^[2–7] Polyureas (PUreas), which constitute an important analogue of PUs, are prepared from diisocyanates and polyamines,^[8–10] and are typically used as two-component protective coatings. Urea linkages evidently improve mechanical properties. Meanwhile, flame-retarding phosphorous-containing PUreas were also reported.^[11]

Recent efforts have been made to develop non-isocyanate PUs (NIPUs) to replace highly toxic diisocyanates. Related research focused on two routes: (a) reaction of bis- or multi-cyclic carbonates with diamines,^[12–16] and (b) transurethane polycondensation of diurethanes.^[17]

Transurethane polycondensation is an appropriate route to synthesize non-isocyanate thermoplastic polyurethanes (NI-TPUs), including amorphous^[18] or crystallizable^[19,20] PUs, alternating or segmented poly(amide urethane)s,^[21,22] and

non-isocyanate thermoplastic polyureas (NI-TPUreas).^[23–25] These NI-TPUs or NI-TPUreas are all synthesized from diurethanes, which must be prepared previously from the reaction of dimethyl carbonate, diphenyl carbonate, or ethylene carbonate (EC) with diamines (DAs), and transurethane polycondensation follows to synthesize NI-TPUs or NI-TPUreas. Dai *et al.* recently reported a method to synthesize NI-TPUreas through the direct solution-free polycondensation of DAs with diphenyl carbonate.^[26]

In the present work, a series of NI-TPUreas were synthesized through a one-pot non-isocyanate method by direct reaction of DAs with much greener EC. In the synthesis reaction, urethane groups were first formed from the *in situ* ring-opening reaction of EC with DAs. Then, urea linkages were formed from the reaction of urethane groups with the remaining amino groups. NI-TPUreas were prepared directly through the *in situ* bulk urethane-forming reaction followed with melt transurethane polycondensation. The obtained NI-TPUreas were characterized by gel permeation chromatography (GPC), Fourier transform infrared (FTIR), proton nuclear magnetic resonance (¹H-NMR), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide angle X-ray diffraction (WAXD), polarizing microscopy, atomic force microscopy (AFM), and tensile testing.

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EXPERIMENTAL

Materials

EC was purchased from Alfa Aesar Co. Ltd., and 1,6-hexanediamine (HDA) was purchased from Shanghai Reagent Plant, China. Poly(propylene glycol) bis(2-amino-propyl ether) (D230) was supplied by BASF Co. *m*-Xylylene-diamine (MXDA) was purchased from Sigma-Aldrich Company. Diethylene glycol bis(3-aminopropyl) ether (DGBAE) was purchased from TCI. Other materials, such as *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO), were obtained as reagent grade and used directly.

Synthesis of NI-TPUreas

In a 100 mL three-necked flask, 5.06 g (0.022 mol) of D230 and 1.94 g (0.022 mol) of EC were added and mechanically stirred under N₂ atmosphere at 100 °C for 6 h. Then, the mixture was reacted at 170 °C under a reduced pressure of 3990 Pa for 0.5 h. Finally, the pressure in the flask was reduced to 399 Pa for different periods until Weissenberg effect occurred.^[24] NI-TPUrea-1 was obtained from the reaction of D230 with EC. It was constructed only with D230 urea (D230U) segments.

Similarly, NI-TPUrea-2, NI-TPUrea-3, NI-TPUrea-4, NI-TPUrea-5, and NI-TPUrea-6 were prepared at a DA/EC molar ratio of 1/1 and a D230/HDA molar ratio of 7/3, 6/4 or a D230/MXDA molar ratio of 8/2, 7/3, and 6/4 (Table 1). They were constructed with D230U segments and hexamethylene urea (HU) or *m*-xylylene urea (MXU) segments. NI-TPUrea-7 to NI-TPUrea-11 were prepared at a DA/EC molar ratio of 1/1 and a DGBAE/D230 molar ratio of 1/0, 9/1, 7/1, 5/1, or 3/1. NI-TPUrea-7 was constructed with diethylene glycol bis(3-propylene) ether urea (DGBEU) segments only. NI-TPUrea-8 to NI-TPUrea-11 were constructed with DGBEU and D230U segments.

Characterization

M_n , M_w and dispersity ($\bar{D}$) of NI-TPUreas were determined through GPC by using an Agilent-2600 system equipped with a PL gel 5- μ m 1000 Å column and a refractive index detector at 25 °C. DMF containing 10 mmol/L LiBr was used as the eluent at a flow rate of 1 mL/min, and polystyrene (PS) was used as the standard. The intrinsic viscosity ($[\eta]$) of NI-TPUreas was determined at 30 °C using Ubbelohde

viscometer with DMSO as the solvent.

The FTIR spectra were acquired by a NICOLET 60SXB FTIR spectrometer. ¹H-NMR spectra were obtained in deuterated DMSO on a Bruker 400 AVANCE spectrometer with tetramethylsilane as internal standard. ESI-MS spectra were recorded on Waters Quattro Premier XE mass spectroscope with methanol as solvent. The second-heating DSC curves were measured with a TA Q200 differential scanning calorimeter in N₂ atmosphere through heating (40 °C/min)-cooling (40 °C/min)-heating (10 °C/min) process.^[27] TGA was performed using a TGA Q50 analyzer at a heating rate of 10 °C/min in N₂ atmosphere.

Spin-coated films were used in the polarizing microscopy and AFM detection. The spin-coated films were prepared according to the literature^[24] and annealed in a vacuum oven from T_m to a crystallization temperature of 60 °C for 30 min. Photographs of NI-TPUrea-5 and NI-TPUrea-8 were captured on an OLYMPUS BX51 polarizing microscope. Tapping mode AFM was conducted with a Dimension FastScan atomic force microscope.

All polymer films used in the WAXD measurements and tensile tests were prepared by the same hot-press method.^[27] WAXD measurements were recorded on a Rigaku D/Max 2500 VB2+/PC diffractometer with Cu K α radiation. Mechanical analysis was conducted on a LLOYD LR30K tensile testing machine with dumbbell-shaped polymer bars^[27] at a crosshead speed of 50 mm/min at 25 °C.

RESULTS AND DISCUSSION

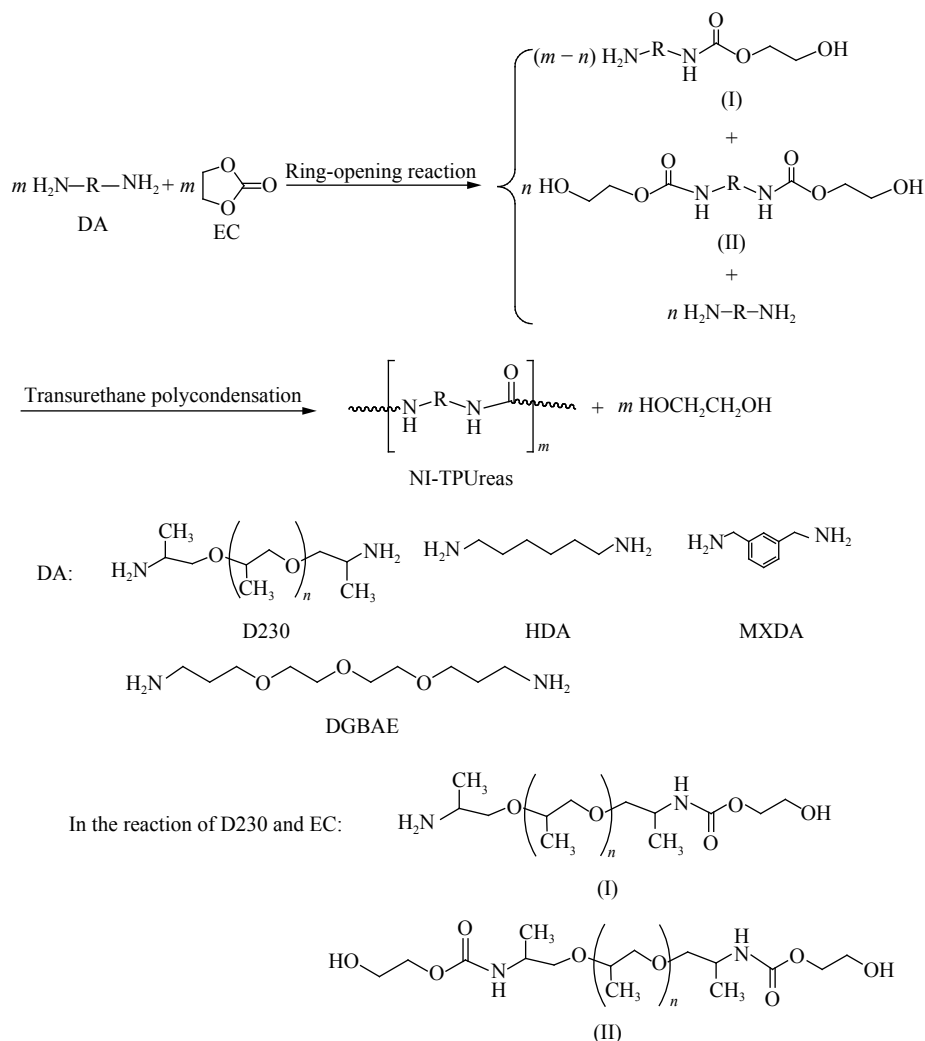
Synthesis of NI-TPUreas

NI-TPUreas were synthesized through the direct reaction of EC with DAs (Scheme 1). The bulk *in situ* ring-opening reaction between EC and DAs was conducted at 100 °C under normal pressure. Urethane formation was monitored through IR characterization during the *in situ* ring-opening reaction between D230 and EC in the synthesis of NI-TPUrea-1. Fig. 1 clearly shows the evidence of urethane formation. When D230 and EC were mixed at 100 °C (0 h), ring-opening reaction between them occurred immediately, and a peak corresponding to the C=O stretching vibration of urethane groups emerged at 1710.6 cm⁻¹. Meanwhile, some fraction EC was left because a peak related to the C=O

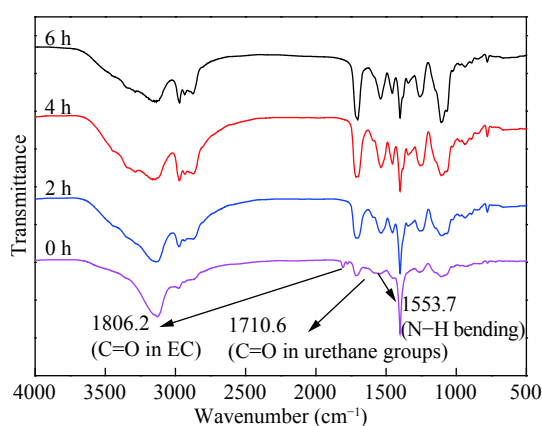
Table 1 Syntheses and properties of NI-TPUreas

NI-TPUreas	Molar ratio				Reaction time ^a (h)	GPC			$[\eta]$ (dL/g)	T_i ^b (°C)	Tensile strength (MPa)	Strain at break (%)
	DGBAE	D230	HDA	MXDA		$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	$\bar{D}$				
NI-TPUrea-1	—	1	—	—	14.0	1.04	1.43	1.38	0.58	303	2	1330
NI-TPUrea-2	—	7	3	—	13.5	1.12	1.98	1.77	0.60	309	9	842
NI-TPUrea-3	—	6	4	—	8.0	—	—	—	0.83	290	16	315
NI-TPUrea-4	—	8	—	2	11.0	0.95	1.24	1.31	0.39	299	10	419
NI-TPUrea-5	—	7	—	3	10.0	0.86	1.09	1.27	0.46	306	22	284
NI-TPUrea-6	—	6	—	4	5.0	0.92	1.37	1.49	0.41	311	32	9
NI-TPUrea-7	1	0	—	—	13.0	0.84	1.17	1.39	0.33	315	14	13
NI-TPUrea-8	9	1	—	—	5.6	—	—	—	0.78	315	20	42
NI-TPUrea-9	7	1	—	—	6.0	—	—	—	0.80	314	17	91
NI-TPUrea-10	5	1	—	—	6.5	1.15	5.71	4.97	0.61	324	15	333
NI-TPUrea-11	3	1	—	—	7.0	1.67	6.53	3.91	0.81	313	8	244

^a Reaction time under a reduced pressure of 399 Pa; ^b T_i : initial decomposition temperature



Scheme 1 Synthesis of NI-TPUreas from DAs and EC

Fig. 1 FTIR monitoring spectra during the *in situ* ring-opening reaction between D230 and EC in the synthesis of NI-TPUrea-1

stretching vibration of EC was found at 1806.2 cm^{-1} . After 2 h, the peak at 1710.6 cm^{-1} became strong and steady, while the peak at 1806.2 cm^{-1} disappeared, indicating that the reaction of EC was nearly complete and urethane groups formed swiftly. The *in situ* ring-opening reactions between

DAs and EC were all conducted for 6 h in the synthesis of NI-TPUreas to obtain the entire urethane formation.

The components formed during the *in situ* ring-opening reaction between D230 and EC in NI-TPUrea-1 synthesis were also monitored by ESI-MS spectra (Fig. 2). Scheme 1 shows the structures of the components. Their molecular weight (M) and m/z values (Figs. 2a and 2b) are compiled in Table 2. The detected n values in D230 were mainly 1, 2, 3, and 4. The reaction between D230 and EC after 2 h mainly resulted in α -amino- ω -urethane (I), with low amount of bis(hydroxyethyl)diurethane (II) formed and small portion of D230 left untouched (Scheme 1). In ESI detection, components usually show different detection sensitivity, and ESI-MS cannot be used directly as a quantitative method to analyze component content. However, the height or intensity of the peaks can reflect the amount of components qualitatively. Higher intensity means higher amount of the component. Extended reaction time (4 h to 2 h) led to formation of additional α -amino- ω -urethane (I) and bis(hydroxyethyl)diurethane (II), with less D230 remaining.

Transurethane polycondensation between the NH_2 - and urethane groups was further preformed under a reduced pres-

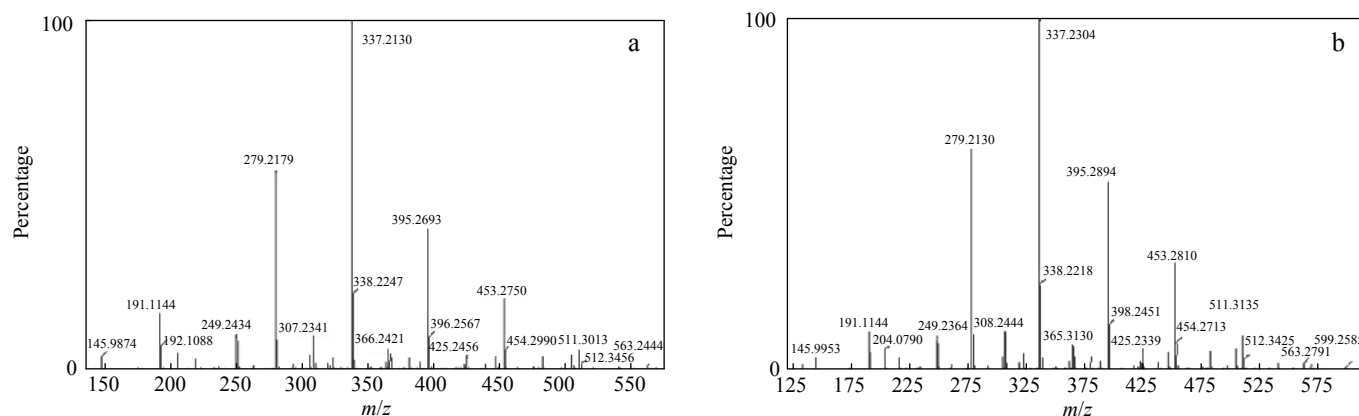


Fig. 2 ESI-MS monitoring spectra during the *in situ* ring-opening reaction between D230 and EC in the synthesis of NI-TPUrea-1 at (a) 2 h and (b) 4 h

Table 2 Molecular weights and m/z values of the D230, α -amino- ω -urethanes (I), and bis(hydroxyethyl)diurethane (II) components

n	M_{D230}	$M_{D230} + 1$ (m/z)	$M_{(I)}$	$M_{(I)} + 1$ (m/z)	$M_{(II)}$	$M_{(II)} + 1$ (m/z)
1	190	191	278	279	—	—
2	248	249	336	337	424	425
3	306	307	394	395	—	—
4	364	365	452	453	—	—

sure of 399 Pa, and a series of NI-TPUreas were prepared (Scheme 1). As the urethane groups in α -amino- ω -urethane (I) and bis(hydroxyethyl)diurethane (II) have similar reactivity, condensation between the remaining NH_2 groups and the urethane groups formed caused the decrease of both α -amino- ω -urethane (I) and bis(hydroxyethyl) diurethane (II), with urea unit formation. The prepared NI-TPUreas were all soluble in DMSO, whereas some NI-TPUreas were insoluble in DMF. DMF-soluble NI-TPUreas exhibited an M_n of 8.4×10^3 – 1.67×10^4 g/mol and an M_w of 1.09×10^4 – 6.53×10^4 g/mol (Table 1). The molecular weight of DMF-insoluble NI-TPUreas was determined using Ubbelohde viscometer. The NI-TPUreas exhibited $[\eta]$ of 0.33–0.83 dL/g.

Synthesis of NI-TPUreas was conducted under reduced pressure until Weissenberg effect took place (polymer climbed onto the stirrer blades). Due to a small amount (about 7 g) of sample synthesized in one reaction and the limits of present set-up (glass equipments, air-sealing limit between the stirrer and the stopper, and determination of the accurate reaction termination point), it was difficult to get the same extent of polymerization every time. The M_n , M_w and D of NI-TPUreas obtained were different and random. We re-synthesized NI-TPUrea-10 and NI-TPUrea-11, *i.e.* NI-TPUrea-10' and NI-TPUrea-11', at the same reaction conditions. Lower M_n , M_w and narrow D were obtained (Table S1 and Fig. S1 in electronic supplementary information, ESI). Random factors influenced the synthesis reaction to some extent.

FTIR and ^1H -NMR Characterization

Fig. 3 shows the FTIR spectrum of NI-TPUrea-2. Absorption bands corresponding to the C–H stretching vibration, C–O–C stretching vibration, and C–H bending vibration of the $-\text{CH}_3$ in D230 segments were clearly found. The bands corresponding to the N–H stretching vibration,

C=O stretching vibration, and N–H bending vibration of urea groups were also shown. A weak shoulder peak at 1707.5 cm^{-1} was ascribed to the C=O stretching vibration of urethane groups in $-\text{HNCOOCH}_2\text{CH}_2\text{OH}$ or hydroxyethyl urethane (HEU) terminal groups. FTIR characterization confirmed that NI-TPUrea-2 mainly derived from D230 and contained numerous urea linkages. The HEU groups were formed in the *in situ* ring-opening reaction between EC and D230 or HDA, and remained as terminal groups of NI-TPUrea-2.

Fig. 4 shows the ^1H -NMR spectrum of NI-TPUrea-2 and the chemical shifts of different hydrogen atoms.^[19,20,28] Signals corresponding to HU segments, D230U segments, and HEU groups were clearly found. ^1H -NMR characterization verified the structure of NI-TPUrea-2, which were terminated with HEU groups.

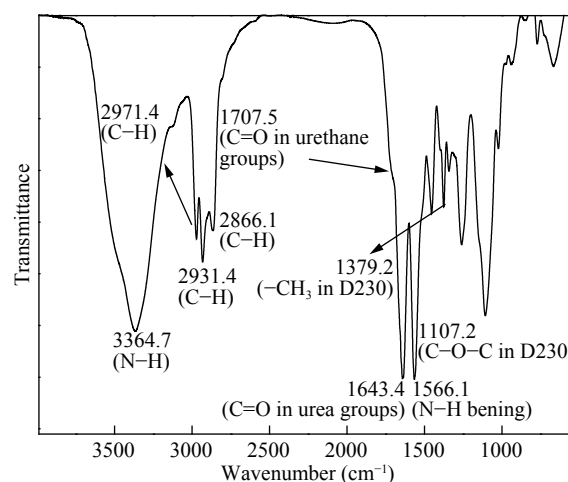


Fig. 3 FTIR spectrum of NI-TPUrea-2

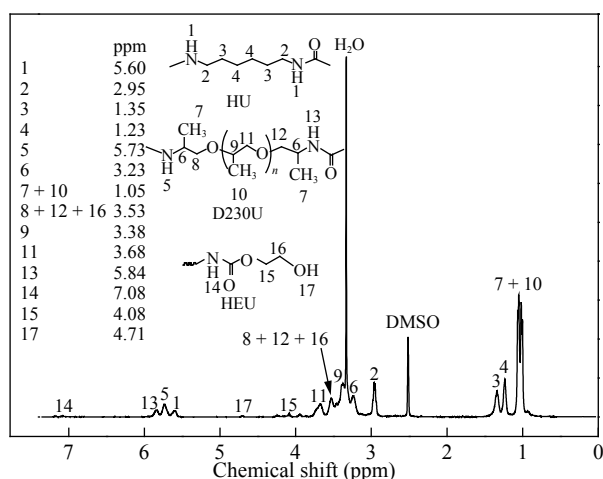


Fig. 4 ^1H -NMR spectrum of NI-TPUrea-2

WAXD Characterization

Fig. 5 shows the WAXD patterns of NI-TPUreas from NI-TPUrea-1 to NI-TPUrea-6. These NI-TPUreas, except NI-TPUrea-3, showed only one big blunt peak. NI-TPUrea-1 was constructed only with irregular D230U segments. NI-TPUrea-2 was constructed mainly with irregular D230U segments and small part of HU segments. NI-TPUrea-1 and NI-TPUrea-2 were both amorphous polyureas. NI-TPUrea-3 showed two diffraction peaks at 2θ of 20.6° and 23.7° , which correspond to intramolecular spacing and intermolecular spacing,^[24,29,30] respectively. NI-TPUrea-3 was synthesized from D230 and HDA at a D230/HDA molar ratio of 6/4. Regular HU segments at increased amount led to the crystallization of NI-TPUrea-3. Thus, crystallized NI-TPUrea-3 was prepared. NI-TPUrea-4, NI-TPUrea-5, and NI-TPUrea-6 were all constructed with irregular D230U and MXU segments and exhibited amorphous characteristics.

Fig. 6 shows the WAXD patterns of NI-TPUreas from NI-TPUrea-7 to NI-TPUrea-11 which were all crystallized poly-

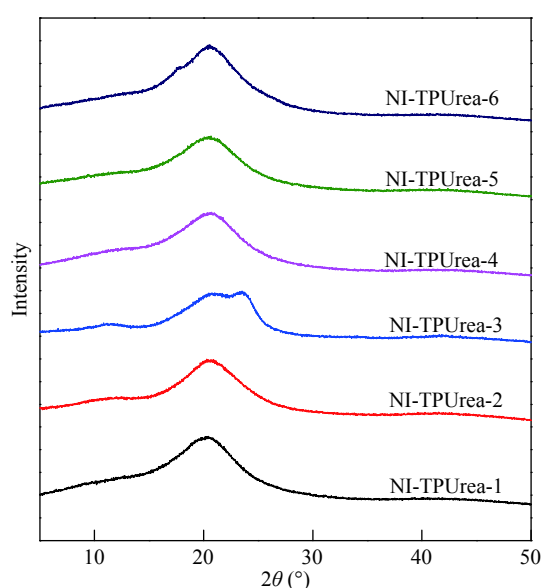


Fig. 5 WAXD patterns of NI-TPUrea-1 to NI-TPUrea-6

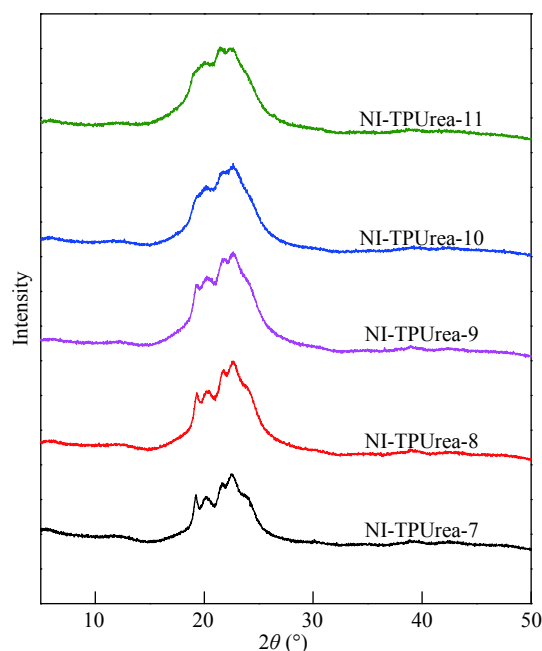


Fig. 6 WAXD patterns of NI-TPUrea-7 to NI-TPUrea-11

ureas. NI-TPUrea-7 clearly showed five diffraction peaks. Among them, two peaks at 2θ of 19.3° and 20.2° corresponded to the intramolecular spacing, whereas two peaks at 21.6° and 22.6° , and a shoulder peak at 23.9° corresponded to intermolecular spacing.^[24,29,30] NI-TPUrea-7 contained long regular and easily crystallizable DGBEU segments, because it was prepared merely from linear DGBAE with EC. NI-TPUrea-8 and NI-TPUrea-9 showed similar diffraction peaks to NI-TPUrea-7 because they also contained long DGBEU sequences. NI-TPUrea-10 and NI-TPUrea-11 showed weak diffraction peaks especially at 2θ of 19.3° and 23.9° . In their main chains, short DGBEU sequences were formed because additional irregular D230U segments were introduced, lowering the regularity of the main chains. Thus, NI-TPUrea-10 and NI-TPUrea-11 with low crystallinity were prepared (Table 3).

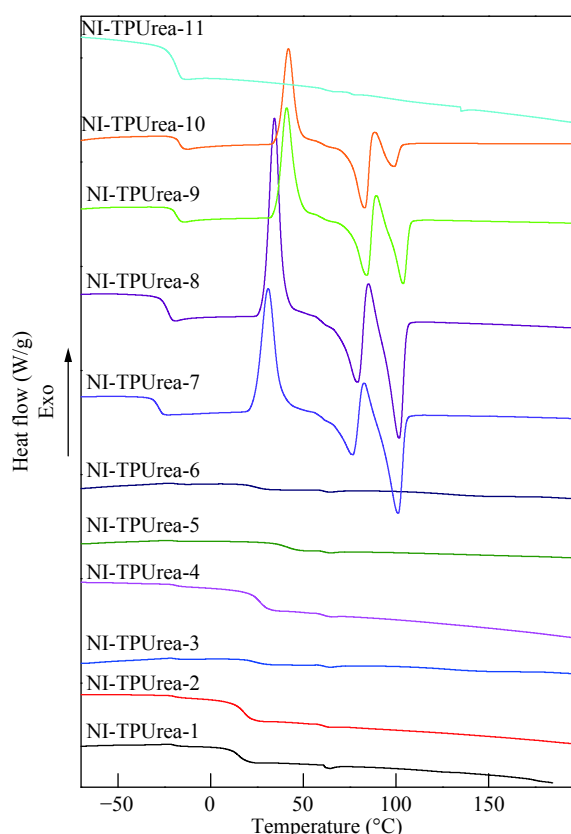
Thermal Properties

NI-TPUreas showed a T_g ranging from -28°C to 42°C (Fig. 7 and Table 3), which was confirmed by the evidence that their $\tan\delta$ curves showed only one peak (T_a) (Figs. S2 and S3, in ESI) in dynamic mechanical analysis (DMA). NI-TPUrea-1 was constructed only with irregular flexible poly(propylene glycol) segments and stiff urea units. It exhibited the T_g of 16°C . NI-TPUrea-2 and NI-TPUrea-3 were constructed with D230U and HU segments. With the increase in HU amount, T_g increased because additional short and stiff HU segments were introduced. NI-TPUrea-1 and NI-TPUrea-2 were amorphous polyureas because D230U segments were the major structural units. NI-TPUrea-3 exhibited a very weak melting peak (T_m) at approximately 145°C . NI-TPUrea-3 was a crystallized polyurea because it contained relatively high amount of regular and easily crystallizable HU segments. Other characteristics, such as insolubility in high polar DMF and two crystallization peaks in WAXD curve (Fig. 5), also confirmed that NI-TPUrea-3

Table 3 The second heating DSC data of NI-TPUreas (10 °C/min)

NI-TPUreas	DSC							T_a^a (°C)	X_c^b (%)
	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_{m1} (°C)	ΔH_{m1} (J/g)	T_{m2} (°C)	ΔH_{m2} (J/g)		
NI-TPUrea-1	16	—	—	—	—	—	—	—	0.9
NI-TPUrea-2	18	—	—	—	—	—	—	23	2.3
NI-TPUrea-3	24	—	—	—	—	145	—	32	6.1
NI-TPUrea-4	28	—	—	—	—	—	—	—	1.1
NI-TPUrea-5	42	—	—	—	—	—	—	46	1.3
NI-TPUrea-6	25	—	—	—	—	—	—	52	1.5
NI-TPUrea-7	−28	31	41	77	28	101	44	—	72.2
NI-TPUrea-8	−23	35	40	80	30	101	37	−9	50.1
NI-TPUrea-9	−19	41	39	85	27	104	28	−11	35.3
NI-TPUrea-10	−17	42	36	83	25	98	12	−10	29.7
NI-TPUrea-11	−18	—	—	—	—	—	—	−3	14.3

^a T_a was determined by DMA; ^b Crystallinity was determined by WAXD method

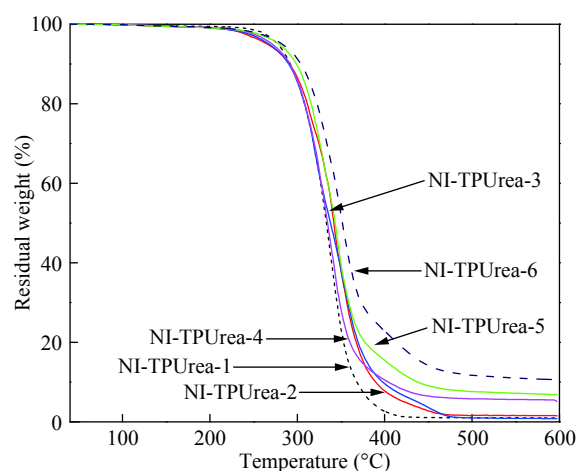
**Fig. 7** The second heating DSC scans of NI-TPUreas (10 °C/min)

was a crystallized polyurea. NI-TPUrea-4 to NI-TPUrea-6 were all amorphous polyureas because they were constructed with irregular D230U and MXU segments. These NI-TPUreas exhibited higher T_g than that of NI-TPUrea-1 because MXU segments are stiff urea units.

Fig. 7 also shows the second heating DSC curves of NI-TPUrea-7 to NI-TPUrea-11. Their T_g , crystallization temperature (T_c), enthalpy of crystallization (ΔH_c), T_m , and enthalpy of melting (ΔH_m) are compiled in **Table 3**. NI-TPUrea-7 exhibited one T_g at −28 °C and two T_m s at 77 °C (T_{m1}) and 101 °C (T_{m2}). Two T_m s or fusion peaks were associated with different populations of lamellar crystals.^[31] NI-TPUrea-7 was a semi-crystallized thermoplastic polyurea. A T_c at 31 °C indicated that NI-TPUrea-7 did not crystallize

sufficiently fast to complete crystallization after fast cooling period. Crystallization still progressed in the second DSC scan. NI-TPUrea-8 to NI-TPUrea-10 showed similar crystallization behavior to NI-TPUrea-7. In contrast to NI-TPUrea-7, which was constructed with DGBEU hard segments (HSs) only, NI-TPUrea-8 and NI-TPUrea-9 contained DGBEU HSs and D230U soft segments (SSs). From NI-TPUrea-7 to NI-TPUrea-9, T_{m1} and T_{m2} both increased as the amount of D230U SSs increased. This phenomenon is due to the introduction of an appropriate amount of flexible D230 segments, which benefited the crystallization of DGBEU HSs. NI-TPUrea-10 was synthesized at a DGBAE/D230 molar ratio of 5/1. Introduction of additional D230U SSs further shortened the length of DGBEU HSs, leading to the decrease in T_{m1} and T_{m2} of NI-TPUrea-10. NI-TPUrea-11 did not exhibit T_{m1} or T_{m2} because too short DGBEU HSs were introduced, and crystallization became difficult.

Fig. 8 shows the TGA curves of NI-TPUrea-1 to NI-TPUrea-6. The initial decomposition temperature (T_i) of NI-TPUreas was all above 290 °C (**Table 1**), evidently exceeding the previously reported value for NI-TPUs,^[32,33] possibly because urea linkages are more thermally stable than urethane groups. The introduction of aromatic units also led to the increase of T_i . NI-TPUrea-6 exhibited the highest T_i because it contained the highest MXU amount. NI-TPUrea-1

**Fig. 8** TGA thermograms of NI-TPUrea-1 to NI-TPUrea-6 (10 °C/min, N₂)

to NI-TPUrea-3 were aliphatic polyureas which decomposed approximately 98% at 500 °C and exhibited the low residue weight. NI-TPUrea-4 to NI-TPUrea-6 contained aromatic MXU units. As the MXU amount increased, residue weight increased because additional aromatic units caused the increased graphitization extent at high temperature. NI-TPUrea-7 to NI-TPUrea-11 (Fig. S4, in ESI) exhibited increased T_i because ethylene units in DGBEU segments were more thermally stable than the propylene units in D230U segments. NI-TPUreas were thermoplastics and suitable for processing with normal thermal processing machines at the temperatures above their T_m (98 °C to 145 °C) and below their T_i (290 °C).

Phase Behavior

Fig. 9 shows the photographs of NI-TPUrea-5 and NI-TPUrea-8 detected using polarizing microscopy. NI-TPUrea-5 exhibited amorphous characteristics, while NI-TPUrea-8 exhibited numerous crystalline globes. AFM, which can simultaneously detect phase and height features, is an important tool for elucidating the microphase separation of TPUs.^[34] The morphologies of the annealed NI-TPUrea-5 and NI-TPUrea-8 were imaged using tapping-mode AFM (Fig. 10). In the phase, 2D height, and 3D height images, the bright regions corresponded to hard phase (urea HS regions), whereas the dark regions corresponded to soft phase (D230U

SSs).^[35] NI-TPUrea-5 was an amorphous polyurea because of its irregular D230U and MXU segment content. Certain micro-separation still occurred given that different polar characteristics and intermolecular interaction remained between D230U SSs and MXU HSs. MXU HSs were the minor components. They formed scattered phases in the major D230U soft phase. NI-TPUrea-8 was synthesized from DGBAE and D230 at a DGBAE/D230 molar ratio of 9/1. Extended and crystallized DGBEU HSs were formed, with a small portion of flexible D230U SSs introduced. DGBEU HSs were regular and easily crystallizable segments. Thus, NI-TPUrea-8 showed numerous bundles of nano-fibrils in the DGBEU hard phase.

Tensile Testing

The stress-strain curves of NI-TPUreas are shown in Figs. 11 and 12. Their tensile strength and strain at break are listed in Table 1. NI-TPUrea-1 was constructed only with flexible D230U segments, exhibiting extremely low tensile strength of 2 MPa and high strain at break of 1330% because of the low portion of urea linkages. NI-TPUrea-2 and NI-TPUrea-3 were constructed with D230U and HU segments. As additional HU HSs were introduced, tensile strength increased, whereas the strain at break decreased because the introduction of more stiff HU HSs caused increasing intermolecular hydrogen bonding and stiffness. NI-TPUrea-4 to NI-TPUrea-6 were constructed with D230U and MXU segments. MXU segments also formed stiff HSs. As the amount of MXU segments increased, tensile strength increased while the strain at break decreased because more hydrogen bonds were formed, thereby increasing stiffness. At the same D230/HDA or D230/MXDA molar ratio, the tensile strength of aromatic NI-TPUreas was considerably higher than that of aliphatic NI-TPUreas, whereas the strain at break of aromatic NI-TPUreas was markedly lower than that of the aliphatic NI-TPUreas, such as in NI-TPUrea-2 to NI-TPUrea-5 and NI-TPUrea-3 to NI-TPUrea-6. MXU

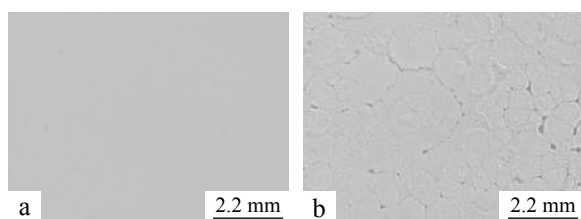


Fig. 9 Photographs detected using polarizing microscope: (a) NI-TPUrea-5; (b) NI-TPUrea-8

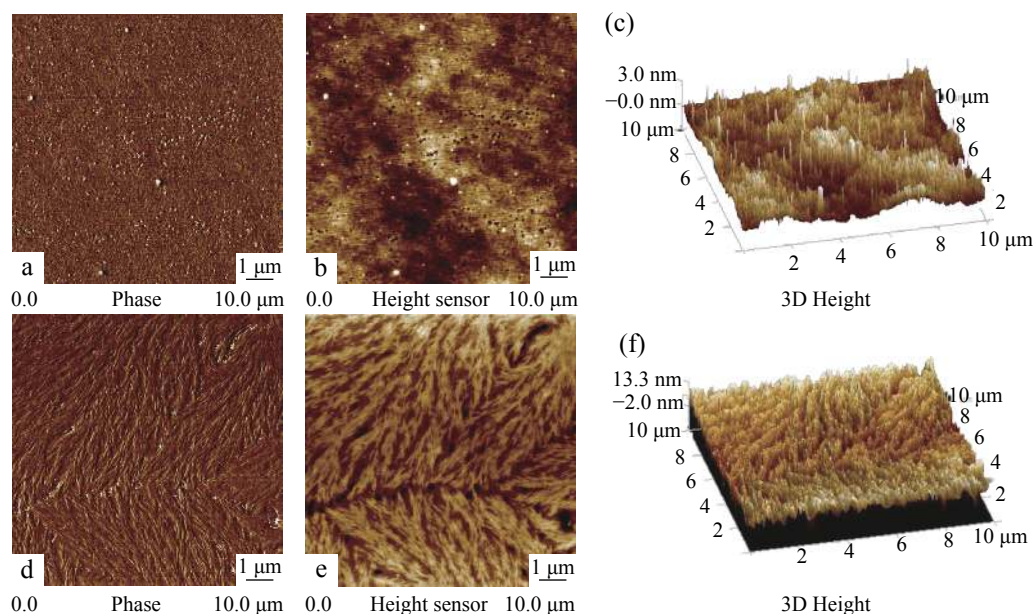


Fig. 10 AFM images of (a–c) NI-TPUrea-5 and (d–f) NI-TPUrea-8: (a, d) phase, (b, e) 2D height, (c, f) 3D height

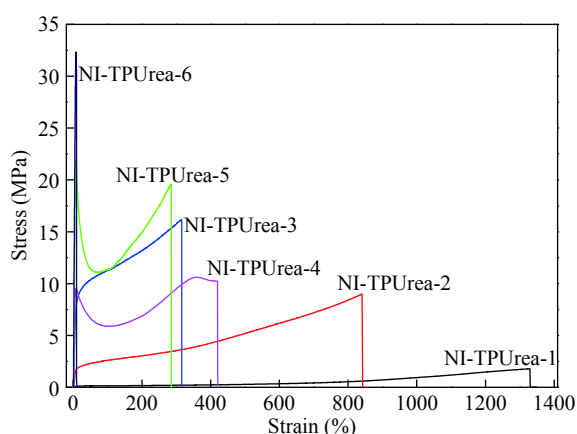


Fig. 11 Stress-strain curves of NI-TPUrea-1 to NI-TPUrea-6

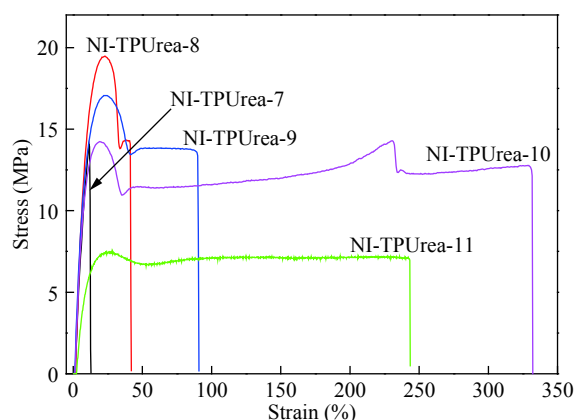


Fig. 12 Stress-strain curves of NI-TPUrea-7 to NI-TPUrea-11

segments are stiffer HSs than HU segments. Meanwhile, the aromaticity of MXU segments rendered the semi-aromatic NI-TPUreas considerably stronger nature than the respective aliphatic NI-TPUreas with the increase in tensile strength. NI-TPUrea-6, a strong but brittle polyurea, exhibited a maximal tensile strength of 32 MPa with a strain at break of 9%. NI-TPUrea-5 showed the best comprehensive mechanical properties among these NI-TPUreas, with a tensile strength of 22 MPa and a strain at break of 284%.

NI-TPUrea-7 exhibited a tensile strength of 14 MPa and a strain at break of 13%. This polyurea was slightly brittle with moderate tensile strength because NI-TPUrea-7 was constructed with DGBEU segments only. Short diethylene glycol ether units in DGBEU segments were connected directly through urea linkages. High urea density made NI-TPUrea-7 lack flexibility; thus, slightly brittle NI-TPUrea-7 was prepared. NI-TPUrea-8 was prepared from DGBAE and D230 at a DGBAE/D230 molar ratio of 9/1. The introduction of an appropriate amount of irregular and flexible D230 sequences in the main chains evidently improved the toughness of NI-TPUrea-8. Thus, NI-TPUrea-8 with increased tensile strength of 20 MPa and strain at break of 42% was obtained. From NI-TPUrea-8 to NI-TPUrea-10, the tensile strength decreased and the strain at break increased as the amount of D230 segments increased because the crystallinity of NI-TPUreas decreased (Table 3). NI-TPUrea-11 exhib-

ited low tensile strength of 8 MPa with the strain at break of 244% because of its low DGBEU amount and low crystallinity.

CONCLUSIONS

NI-TPUreas were successfully prepared through a one-pot non-isocyanate method by an *in situ* bulk reaction of diamines with ethylene carbonate followed with melt transurethane polycondensation. This route can avoid the previous preparation and purification of diurethanediols typically used in NI-TPU synthesis. NI-TPUreas exhibited initial decomposition temperature at over 290 °C and a tensile strength up to 32 MPa. The introduction of HU, MXU, and crystallizable DGBEU segments in the main chains considerably improved the mechanical properties of NI-TPUreas. Crystallized NI-TPUreas with good mechanical properties and T_m from 98 °C to 145 °C were prepared through a green and simple one-pot non-isocyanate method.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2165-0>.

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