

Synthesis and Characterization of Crystallizable Aliphatic Thermoplastic Poly(ester urethane) Elastomers through a Non-isocyanate Route^{*}

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Abstract A simple non-isocyanate route is developed for synthesizing crystallizable aliphatic thermoplastic poly(ester urethane) elastomers (TPEURs) with good thermal and mechanical properties. Three prepolymers of 1,6-bis(hydroxyethyloxycarbonylamino) hexane (BHCH), *i.e.* PrePBHCHs, were prepared through the self-transurethane polycondensation of BHCH. A poly(butylene adipate) prepolymer (PrePBA) with terminal HO— groups was prepared and used as a polyester glycol. A series of TPEURs were prepared by the co-polycondensation of the PrePBHCHs with PrePBA at 170 °C under a reduced pressure of 399 Pa. The TPEURs 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. The TPEURs exhibited M_n up to 23300 g/mol, M_w up to 51100 g/mol, T_g ranging from –33.8 °C to –3.1 °C, T_m from 94.3 °C to 111.9 °C, initial decomposition temperature over 274.7 °C, tensile strength up to 18.8 MPa with a strain at break of 450.0%, and resilience up to 77.5%. TPU elastomers with good crystallization and mechanical properties were obtained through a non-isocyanate route.

Keywords: Non-isocyanate route; Thermoplastic polyurethane elastomers; Diurethanediol; Transurethane polycondensation; Poly(ester urethane)s.

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INTRODUCTION

Polyurethanes (PUs) as the important commercial polymers are widely used in many fields, including foams, adhesives, coatings and medical materials because of their outstanding mechanical properties, abrasion resistance, and good biocompatibility^[1]. However, most of the commercial available PUs are prepared from highly toxic diisocyanates, a major precursor of which is the extremely toxic phosgene. Hence, non-isocyanate synthesis has attracted increasing attention for the researchers who are working on PUs^[2–4]. Currently, the study of non-isocyanate PUs (NIPUs) are mostly focused on the cross-linked PUs prepared from cyclic carbonates and diamines or multi-amines^[5–12]. An example was reported by Loontjens *et al.*, who synthesized NIPUs from carbonyl biscaprolactamate^[13, 14].

Recently, transurethane polycondensation of diurethanes has been developed to synthesize linear or thermoplastic PUs (TPUs). Tang *et al.* synthesized TPUs having different multi-urea segments *via* the solution polycondensation of dimethyl dicarbamates with amino-terminated poly(propylene glycol)^[15]. Deepa *et al.*

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synthesized a series of amorphous TPUs through the transurethane polycondensation of dimethyl 1,6-hexamethylene dicarbamate and dimethyl isophoronedicarbamate with glycol oligomers, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol or isosorbide^[16]. Rokicki *et al.* synthesized two α,ω -bis(hydroxyethyloxy carbonyl amino) alkanes and studied their solution transurethane polycondensation with 1,6-hexanediol or 1,10-decanediol^[17]. Ochiai *et al.* studied the self-polycondensation of 1,6-bis(hydroxyethyloxy carbonyl amino) hexane (BHCH), and used the homopolymer of BHCH (PBHCH) to synthesize methacrylate macromolecular monomers^[18]. Moreover, Sharma *et al.* synthesized α -hydroxy- ω -amino-amides through the ring-opening reaction from caprolactam with excessive aminoalcohol, and turned 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^[19]. Zhao *et al.* synthesized a series of aliphatic segmented poly(amideurethane)s having short nylon-6 segments^[20], poly(ether amideurethane)s having poly(ethylene glycol) (PEG) sequences and short nylon-6 segments^[21], and poly(ether urethane)s having short and long PEG segments^[22, 23]. All of the obtained polymers are crystallizable thermoplastics with good thermal and mechanical properties.

Thermoplastic polyurethane elastomers or rubber (TPURs) usually play an important role in the common isocyanate TPUs. However, up to now, no effective way is reported to synthesize non-isocyanate TPURs with good thermal and mechanical properties. In our previous work, we established a simple method to synthesize non-isocyanate thermoplastic poly(ether urethane) (TPEU) elastomers *via* the co-polycondensation of di(hydroxyethyl) isophorone biscarbamate with different PEGs^[24]. The TPEU elastomers exhibited good mechanical properties but the polymers were amorphous with low T_g , which confined their usage in the low temperature range because of the low thermal deformation temperature.

In this paper, three prepolymers of BHCH, *i.e.* PrePBHCHs, were prepared through the self-transurethane polycondensation of BHCH. A poly(butylene adipate) prepolymer (PrePBA) with terminal HO— groups, *i.e.* HO-PBA-OH, was prepared and used as a polyester glycol. A series of aliphatic thermoplastic poly(ester urethane) elastomers or rubbers (TPEURs) were prepared through the co-polycondensation of the PrePBHCHs with PrePBA. The TPEURs are composed of PBHCH hard segments (HSs) and flexible poly(butylene adipate) (PBA) soft segments (SSs). As the PBHCH HSs are the easily crystallizable sequences, introducing them into the polymer main chains might result in crystallizable TPURs with a high melting temperature (T_m) as well as good thermal and mechanical properties. The obtained TPEURs were characterized by gel permeation chromatography (GPC), FTIR and ¹H-NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD), atomic force microscope (AFM), and tensile testing.

EXPERIMENTAL

Materials

Ethylene carbonate was purchased from Alfa Aesar Co. Ltd. 1,6-Hexanediamine was purchased from Shanghai Reagent Plant, China. Butanediol (BD) and adipic acid (AA) were purchased from Tianjin Fuchen Reagent Co. Ltd., China. BD was redistilled under reduced pressure before use, and AA was purified by crystallization in de-ionized water. SnCl₂·2H₂O was purchased from Beijing Shuanghuan Weiyi Reagent Co. Ltd, China. Other materials such as *N,N'*-dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) were all obtained as reagent grade and used directly. BHCH was prepared from the reaction of ethylene carbonate with 1,6-hexanediamine according to the literature^[17, 20]. Its melting point was 94 °C.

Synthesis of PrePBA

In a 250 mL three-necked flask, 36.38 g (0.25 mol) of AA, 33.75 g of (0.375 mol) BD and SnCl₂ (0.2 wt%) were added and mechanically stirred. The reaction mixture was gradually heated from 150 °C to 200 °C under N₂ atmosphere in 6 h. Then, the pressure in the flask was gradually reduced to 3990 Pa in 4 h. Finally, the pressure in the flask was further reduced to 399 Pa and maintained for 4 h. A PrePBA with an acid value (A_v) of 1.91 mgKOH/g and a hydroxyl number (Q_v) of 68.54 mgKOH/g was obtained.

Synthesis of PrePBHCHs

In a 100 mL 3-necked flask, 20.45 g (0.070 mol) of BHCH and SnCl_2 (0.2 wt%) were added and mechanically stirred. The reaction mixture was heated to 170 °C under a reduced pressure of 3990 Pa for 0.5 h. Then, the pressure in the flask was gradually reduced to 399 Pa and maintained for another 1.5 h. A PrePBHCH-1 with Q_v of 103.51 mg KOH/g was obtained.

Similarly, PrePBHCH-2 and PrePBHCH-3 with different Q_v values were prepared *via* the self-polycondensation of BHCH under a reduced pressure of 399 Pa for 2.3 h and 7.2 h, respectively.

Synthesis of TPEURs

In a 100 mL 3-necked flask, 4.00 g (0.0025 mol) of PrePBA, 2.72 g (0.0025 mol) of PrePBHCH-1 and SnCl_2 (0.2 wt%) were added and reacted at 170 °C under a reduced pressure of 3990 Pa for 0.5 h. Then, the pressure in the flask was gradually reduced to 399 Pa for different periods until Weissenberg effect took place. TPEUR-1 was prepared with the molar ratio of PrePBA/PrePBHCH-1 at 1:1. It was poured and cooled at room temperature.

Similarly, TPEUR-2 and TPEUR-3 were prepared at a PrePBA/PrePBHCH-1 molar ratio of 1:2 and 1:3, respectively. TPEUR-4 and TPEUR-5 were synthesized from the co-polycondensation of PrePBA with PrePBHCH-2 or PrePBHCH-3 at a PrePBA/PrePBHCH molar ratio of 1:1.

Characterization

Q_v and A_v were determined by titration as described in the literature^[21, 25, 26]. M_n , M_w and polydispersity index (PDI) of TPEURs were determined by GPC with Waters Agilent-2600 Series equipped with a PLgel 5 μm 100 nm column and a refractive index detector at 25 °C. The DMF containing 10 mmol/L LiBr was used as the eluent with a flow rate of 1 mL/min, and the polystyrene (PS) was used as the standard.

Polymer samples for FTIR and ^1H -NMR characterization were purified by three cycles of dissolution-precipitation using DMSO as the solvent and ether as the nonsolvent. FTIR spectra were acquired on a NICOLET 60SXB FTIR spectrometer. ^1H -NMR spectra were obtained in deuterated DMSO (DMSO-d_6) on a Bruker 400 AVANCE using tetramethylsilane as the internal standard.

WAXD measurements were taken on a Rigaku D/Max 2500 VB2+/PC diffractometer with $\text{Cu K}\alpha$ radiation. Samples were continuously scanned over the 2θ range from 5° to 50°.

DSC scans of the polymers were measured with a TA Q200 differential scanning calorimeter in N_2 atmosphere. The second heating DSC scans were conducted *via* a heating (40 K/min)-cooling (40 K/min)-heating (10 K/min) process. The samples were first heated from room temperature to 200 °C at a heating rate of 40 K/min and kept for 5 min to eliminate thermal history, and then cooled to -80 °C at a rate of 40 K/min. In the second heating scans, the samples were heated from -80 °C to 200 °C at a rate of 10 K/min. A series of heating DSC scans were measured *via* a cooling (40 K/min)-heating (10 K/min) process. TGA was performed on a TGA Q50 analyzer with a heating rate of 10 K/min from 25 °C to 600 °C in N_2 atmosphere.

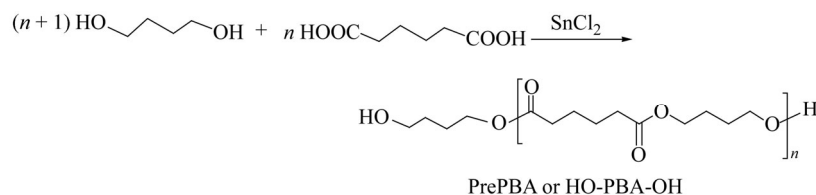
Tapping mode AFM was used to visualize the images of TPEURs on a Dimension FastScan Atomic Force Microscope. The sample was first dissolved in DMF (1 wt%). Then, the solution was dropped onto a silicon plate of 2 cm $\times$ 2 cm and spun *via* a WS-400B-6NPP-LITE spin coater at 2000 r/min for 130 s. The spin-coated films were annealed in a vacuum oven from their T_m to a crystallization temperature of 60 °C for 30 min.

The polymer films (50 mm $\times$ 50 mm $\times$ 1 mm) for tensile tests were prepared by a 70911-24B powder press machine (Tianjin New Technical Instrument Com., China). The samples were heated to the temperature higher than their melting point 20 °C, kept for 5 min under 15 MPa, cooled naturally to room temperature with the pressure unchanged, and then cut into dumbbell-shaped bars (50 mm $\times$ 4 mm $\times$ 1 mm). Mechanical analysis was conducted on a LLOYD LR30K tensile testing machine at a crosshead speed of 200 mm/min at 25 °C. The resilience of TPEURs was detected as follows: first, the testing bars were held by splints and stretched to a fixed-length; second, the splints were loosened, and the bars were restored naturally in 3 min; third, the final length of bars was measured. Five measurements were performed for each sample, and the results were averaged to obtain a mean value.

RESULTS AND DISCUSSION

Synthesis of PrePBA and PrePBHCHs

PrePBA was synthesized from AA and BD with the molar ratio of $-\text{COOH}/-\text{OH}$ at 1:1.5 (Scheme 1). PrePBA is mainly terminated with $\text{HO}-$ groups at both ends; it exhibits an A_v of 1.91 mgKOH/g, a Q_v of 68.54 mgKOH/g (Table 1), and the molecular weight of 1592.62 g/mol calculated from the A_v and the Q_v (M_{det}).



Scheme 1 The synthetic route of PrePBA

Table 1. The properties of PrePBA and PrePBHCHs

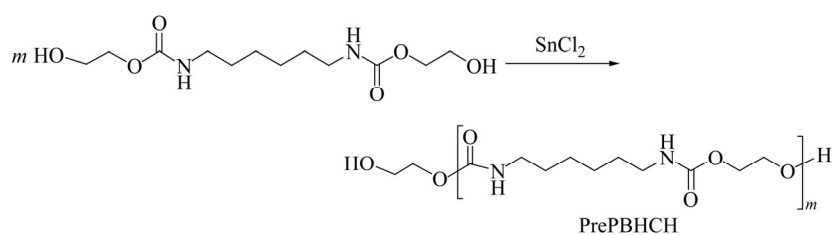
Prepolymers	Reaction conditions ^c		A_v (mgKOH/g)	Q_v (mgKOH/g)	M_{det}^d (g/mol)
	Temperature (°C)	Time (h)			
PrePBA ^a	200	4.0	1.91	68.54	1592.62
PrePBHCH-1 ^b	170	1.5	—	103.51	1083.95
PrePBHCH-2 ^b	170	2.3	—	55.60	2017.99
PrePBHCH-3 ^b	170	7.2	—	37.69	2976.92

^a Reaction conditions for PrePBA: SnCl_2 , 0.2 wt%; 150–200 °C (gradually raised), 1.01×10^5 Pa, 6 h; 200 °C, 3990 Pa, 4 h; ^b Reaction conditions for PrePBHCHs: SnCl_2 , 0.2 wt%; reaction temperature: 170 °C; reaction time: 3990 Pa, 0.5 h;

^c Reaction time under a reduced pressure of 399 Pa; ^d M_{det} , molecular weight calculated from the A_v and Q_v :

$$M_{\text{det}} = \frac{56.1 \times 2 \times 1000}{(A_v + Q_v)}, \text{ in which } 56.1 \text{ represents the molecular weight of KOH.}$$

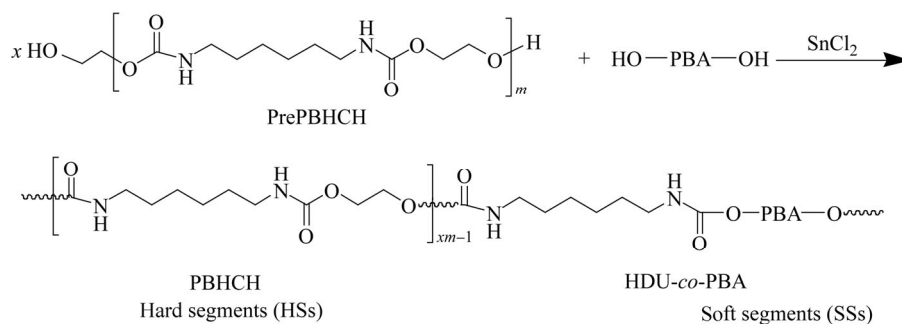
Three PrePBHCHs with different molecular weight were prepared *via* the self-polycondensation of BHCH at 170 °C under a reduced pressure of 399 Pa for different times (Scheme 2). It was found that the molecular weight increased in a longer reaction time because of the removal of the by-product of ethylene glycol. The resulting PrePBHCHs show the Q_v values of 103.51, 55.60 and 37.69 mgKOH/g, respectively (Table 1). Their M_{det} are from 1083.95 g/mol to 2976.92 g/mol.



Scheme 2 The synthesis of PrePBHCHs from the self-polycondensation of BHCH

Synthesis of TPEURs

PrePBHCHs contain terminal hydroxyethyl carbamate (HC) or $-\text{HNCOOCH}_2\text{CH}_2\text{OH}$ groups at both ends, which make the self-polycondensation of the HC groups and the co-polycondensation of them with the terminal $\text{HO}-$ groups of PrePBA concurrently to take place in the synthesis of TPEURs. A series of TPEURs were prepared by the melt transurethane polycondensation of the PrePBHCHs with PrePBA at different molar ratios (Scheme 3). We observed that the molecular weight increased when the vacuum was higher up to 399 Pa due to the removal of by-product of ethylene glycol. TPEUR-1 was prepared at a PrePBA/PrePBHCH-1 molar ratio of 1:1. The co-polycondensation between PrePBHCH-1 and PrePBA generated hexanediurethane-*co*-polybutylene adipate (HDU-*co*-PBA) segments with PBA SSs introduced in the polymer structure. Meanwhile, PBHCH



The obtained TPEURs were characterized by FTIR and ^1H -NMR measurements. Figure 1 shows the FTIR spectrum of TPEUR-1 with the major vibration peaks marked. It can be seen that the absorption peaks appear at 1734.9 and 1256.5 cm^{-1} , which are correspond to the C=O and C—O stretching vibration of the ester groups in the PBA segments and those in the hexanediurethane (HDU) units or the PBHCH segments. It also shows the

peaks that correspond to the C—N stretching vibration (1138.0 cm^{-1}), N—H bending stretching of the HDU units (1538.9 cm^{-1}), and that relates to the C—O stretching vibration in the terminal $-\text{CH}_2\text{OH}$ groups (1063.3 cm^{-1}). The $-\text{CH}_2\text{OH}$ groups derive from PrePBHCH-1 or PrePBA and are left in TPEUR-1 as terminal groups. TPEUR-1 is constructed with PBA SSs and HDU units or PBHCH HSs. Similar structure characteristics of TPEUR-2, TPEUR-3, TPEUR-4, and TPEUR-5 were also verified by the FTIR spectra (Supporting information, Fig. S1 to Fig. S4).

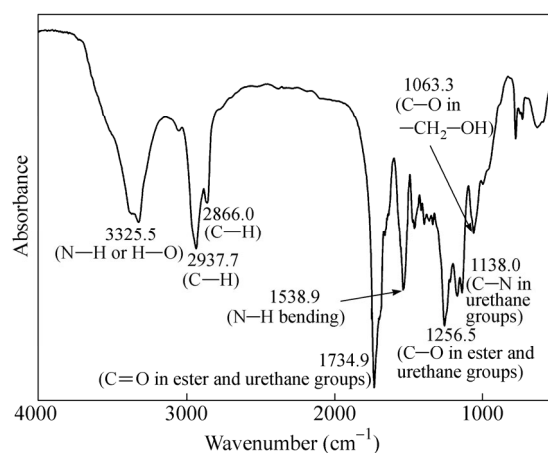


Fig. 1 FTIR spectrum of TPEUR-1

Figure 2 shows the ^1H -NMR spectrum of TPEUR-1^[17, 18, 22, 25]. It clearly shows the proton signals that correspond to the PBHCH segments, HDU-co-PBA segments and the terminal groups of $-\text{HNCOOCH}_2\text{CH}_2\text{OH}$. Some urea units were observed in the TPEUR-1 alongside, which resulted from the tail-biting side reaction of the $-\text{HNCOOCH}_2\text{CH}_2\text{OH}$ terminal groups during the synthesis reaction of PrePBHCH-1 (Scheme 4). Similar structures of TPEUR-2, TPEUR-3, TPEUR-4 and TPEUR-5 were also verified by the ^1H -NMR measurement (Supporting information, Fig. S5 to Fig. S8).

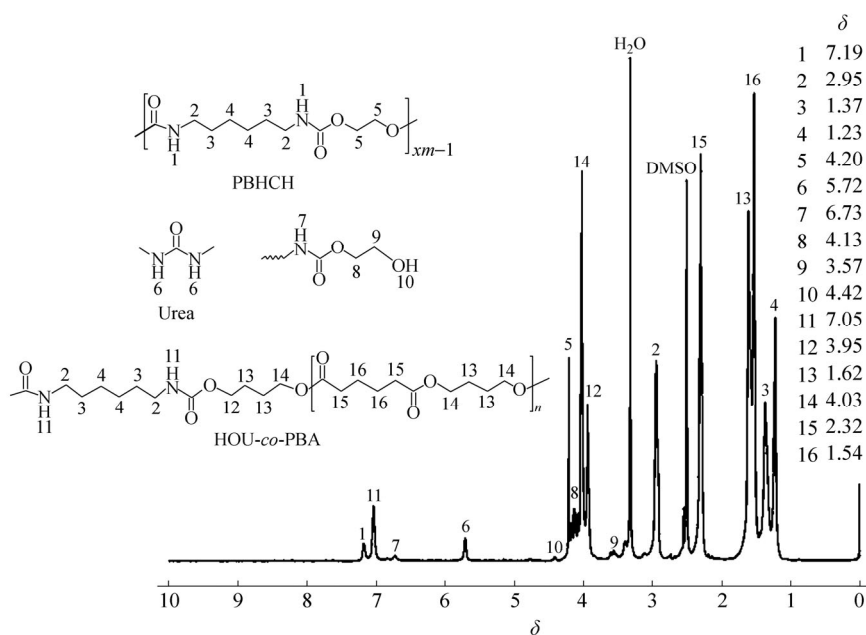
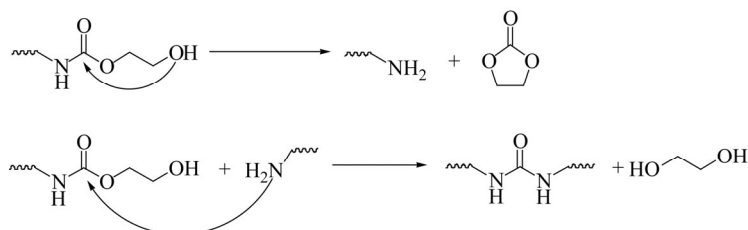


Fig. 2 ^1H -NMR spectrum of TPEUR-1



Scheme 4 The formation of the urea units in the reaction of PrePBHCH-1 and TPEUR-1

The molar percentage of HS (HS%) in TPEURs and the molar percentage of urea (Urea%) in HSs are calculated from $^1\text{H-NMR}$ spectra and the results are shown in Table 3. Although TPEUR-1, TPEUR-2, and TPEUR-3 were synthesized from the same PrePBHCH-1, their HS% increased from 38.73% to 65.61% as the PrePBA/PrePBHCH-1 molar ratio changed from 1:1 to 1:3. In addition, when the length of PrePBHCHs increased from PrePBHCH-1 to PrePBHCH-3, the HS% also increased. TPEURs exhibit the Urea% ranging from 14.81% to 32.36%. TPEUR-1, TPEUR-2, and TPEUR-3 contained almost the same Urea% in HSs because they were synthesized from the same PrePBHCH-1. TPEUR-4 showed the lowest Urea% possibly because of less urea units' formation in the synthesis of PrePBHCH-2. TPEUR-5 contained the highest Urea% up to 32.36% because more urea linkages formed in the long reaction period of PrePBHCH-3 synthesis.

Table 3. HS% and Urea% in the TPEURs calculated from $^1\text{H-NMR}$ spectra

Polymer	A_6^a	A_2^a	A_{15}^a	A_1^a	A_{11}^a	HS% ^b	Urea% ^c
TPEUR-1	1.00	10.16	16.07	0.73	2.56	38.73	23.31
TPEUR-2	1.00	10.15	8.29	1.44	2.06	55.04	22.22
TPEUR-3	1.00	9.71	5.09	2.14	1.19	65.61	23.09
TPEUR-4	1.00	14.83	13.58	2.42	3.33	52.20	14.81
TPEUR-5	1.00	6.85	4.31	0.95	1.14	61.38	32.36

^a Area of different hydrogens; ^b HS% = $\frac{A_2}{A_2 + A_{15}} \times 100$; ^c Urea% = $\frac{A_6}{A_6 + A_1 + A_{11}} \times 100$

DSC Characterization

Figure 3 shows the second heating DSC curves of PrePBA and PrePBHCHs detected in a heating (40 K/min)-cooling (40 K/min)-heating (10 K/min) cycle. The glass transition temperature (T_g), crystallization temperature (T_c), enthalpy of crystallization (ΔH_c), T_m , and enthalpy of melting (ΔH_m) of them are listed in Table 4. For PrePBA, its ΔH_m , T_m are 73.61 J/g and 45.9 °C, respectively, no T_g is found because its very fast crystallization. The T_g of PrePBHCHs rises in the range of 29.4 °C to 34.5 °C as the molecular weight increased. PrePBHCHs are all crystallized polyurethanes with a T_m ranging from 151.9 °C to 165.0 °C. PrePBHCH-1 and PrePBHCH-2 show a sharp T_c at 81.9 °C and 93.5 °C, respectively. It means that they cannot crystallize completely in the fast cooling period. The crystallization still progressed in the second heating scan. Figure 4 shows the DSC curves of TPEURs in the second heating (40 K/min)-cooling (40 K/min)-heating (10 K/min) cycle. Their T_g , T_c , ΔH_c , T_m , and ΔH_m are listed in Table 4. The T_g of TPEURs ranges from -33.8 °C to -3.1 °C, which is between the T_g of PBA (-76 °C)^[27] and that of PrePBHCHs. TPEURs have the higher T_g than PBA because of the PBHCH segments in the main chains. PBHCH segments contain many carbamate groups which can easily form hydrogen bonding each other, or with the PBA segments. Partial solubilization between the PBHCH segments and the PBA segments might occur, and affected the T_g of TPEURs. The T_g of TPEURs is lower than that of the PrePBHCHs and higher than that of PBA, which is the reason that TPEURs have the T_g between the PrePBHCHs and PBA. TPEUR-1, TPEUR-2 and TPEUR-3 were synthesized at a PrePBA/PrePBHCH-1 molar ratio from 1:1 to 1:3. As the amount of the PBHCH segments increases, the T_g increases. TPEUR-4 and TPEUR-5 have the higher T_g than TPEUR-1 because they have longer PBHCH segments. TPEURs are all crystallized poly(ester

urethane)s with a T_m between 94.3 °C and 111.9 °C due to the PBHCH segments functioned as the HSs in the structure. The PBA segments act as the SSs with an amorphous phase in TPEURs. Partial solubilization between the HSs and SSs leads to the decrease of T_m and ΔH_m of TPEURs as compared to those of PrePBHCHs. Some TPEURs also show an obvious T_c , implying that they cannot crystallize completely and the crystallization still progressed in the second heating scan. TPEUR-1, TPEUR-4, and TPEUR-5 were synthesized with the same PrePBA/PrePBHCH molar ratio of 1:1. Although PrePBHCH-2 has higher molecular weight than PrePBHCH-1, it exhibits lower T_m and ΔH_m or crystallinity than PrePBHCH-1. This is because PrePBHCH-2 contains less urea% (Table 3), which lowers the intermolecular interactions and crystallization. TPEUR-4 was synthesized from PrePBHCH-2, so it crystallized slowly with a big T_c peak emerged.

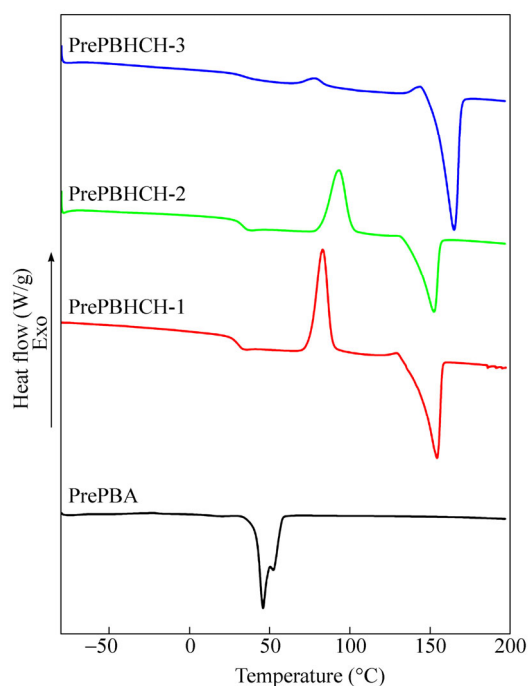


Fig. 3 The DSC thermograms of the second heating of PrePBHCHs and PrePBA detected in the heating (40 K/min)-cooling (40 K/min)-heating (10 K/min)

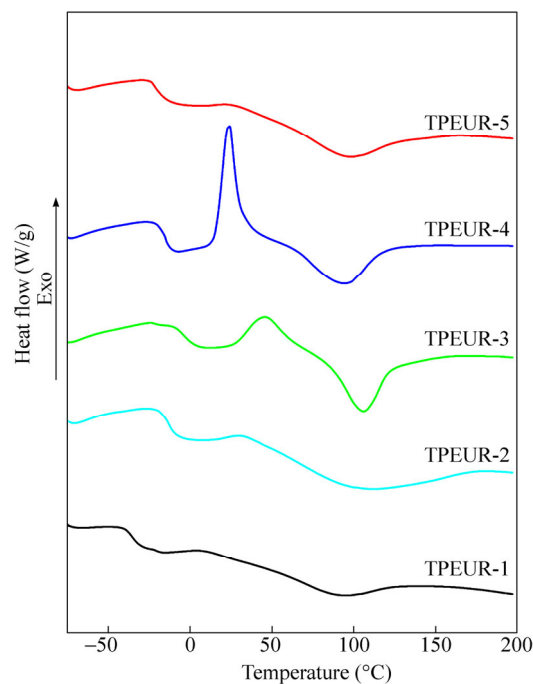


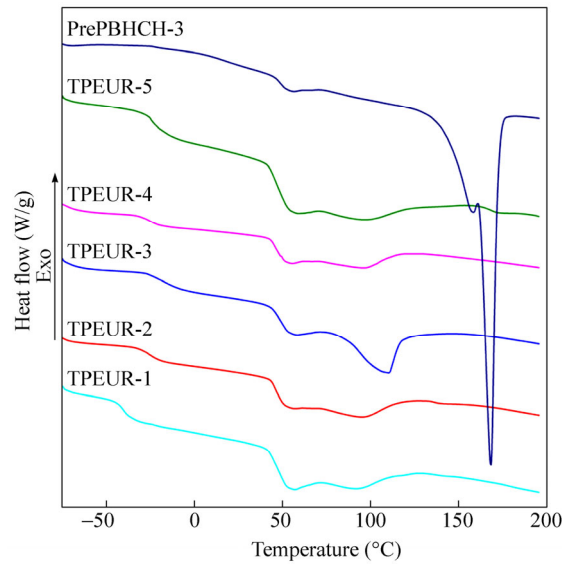
Fig. 4 The DSC thermograms of the second heating of TPEURs detected in the heating (40 K/min)-cooling (40 K/min)-heating (10 K/min)

Figure 5 shows the DSC heating scans of TPEURs and PrePBHCH-3 detected in the cooling (40 K/min)-heating (10 K/min) cycle. The T_g s, T_m , and ΔH_m of them are listed in Table 5. Different from the results in Fig. 4, TPEUR-1 to TPEUR-5 show two T_g and the obviously lower ΔH_m . The reason might be that TPEURs crystallized slowly at room temperature. The PBHCH-rich HS phase crystallized partially with an obvious HS T_g and lower ΔH_m . Meanwhile, the PBA-rich SS phase exhibited a T_g that was lower than that obtained in the heating (40 K/min)-cooling (40 K/min)-heating (10 K/min) cycle (Table 4). Obvious phase separation occurred during the natural cooling process. In the heating (40 K/min)-cooling (40 K/min)-heating (10 K/min) detection, the PBHCH HS phase nearly crystallized completely because high cooling rate led to high crystallization rate of HSs^[28], such the higher ΔH_m or crystallinity was observed. Merely one T_g related to the PBA-rich SS phase was observed.

Table 4. DSC data of PrePBA, PrePBHCHs and TPEURs detected in the second heating (40 K/min)-cooling (40 K/min)-heating (10 K/min) cycle

Polymer	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c^a (%)
PrePBA	—	—	—	45.9	73.61	76.39
PrePBHCH-1	29.4	81.9	46.65	154.3	46.56	57.08
PrePBHCH-2	32.5	93.5	38.58	151.9	44.44	53.08
PrePBHCH-3	34.5	78.5	4.28	165.0	58.73	67.61
TPEUR-1	-33.8	—	—	94.3	8.29	8.62
TPEUR-2	-12.8	—	—	111.9	15.81	10.04
TPEUR-3	-3.1	46.17	11.66	105.5	25.83	37.53
TPEUR-4	-16.4	20.61	35.06	94.9	21.68	36.00
TPEUR-5	-18.8	—	—	99.3	28.71	39.50

^a The crystallinity (X_c) was determined by WAXD. X_c (%) = $\frac{A_c}{A_t} \times 100$, in which A_c and A_t represent the crystallization peak area and total area, respectively.

**Fig. 5** The DSC thermograms of PrePBHCH-3 and TPEURs detected in the cooling (40 K/min)-heating (10 K/min) process**Table 5.** The DSC data of PrePBHCH-3 and TPEURs detected in the cooling (40 K/min)-heating (10 K/min) process

Polymer	T_{g1} (°C)	T_{g2} (°C)	T_m (°C)	ΔH_m (J/g)
PrePBHCH-3	—	48.6	168.4	90.79
TPEUR-1	-40.2	47.9	92.8	3.86
TPEUR-2	-25.9	47.7	97.3	8.13
TPEUR-3	-18.2	48.1	110.2	19.34
TPEUR-4	-25.4	47.3	97.8	8.17
TPEUR-5	-20.1	48.3	98.7	4.52

WAXD Characterization

Figure 6 shows the WAXD patterns of PrePBHCHs and PrePBA. PrePBHCHs shows a series of diffraction peaks at the 2θ of 6.6°, 19.9°, 21.1°, 22.3°, 24.2° and 26.4°, while PrePBA exhibits the diffraction peaks at 2θ of 17.7°, 21.7°, 22.5°, 24.2° and 29.4°, respectively. These diffraction peaks are similar to those of PBHCH and PBA reported in the literature^[20, 25]. Figure 7 shows the WAXD patterns of TPEURs, which show the diffraction peaks at 2θ of 20.7°, 22.0° and 23.8°, respectively. TPEURs crystallize similarly to PrePBHCHs because all of them are synthesized from PrePBA and PrePBHCHs. The PBHCH HSs and PBA SSs segments are the crystalline phase and the amorphous phase in the TPEURs.

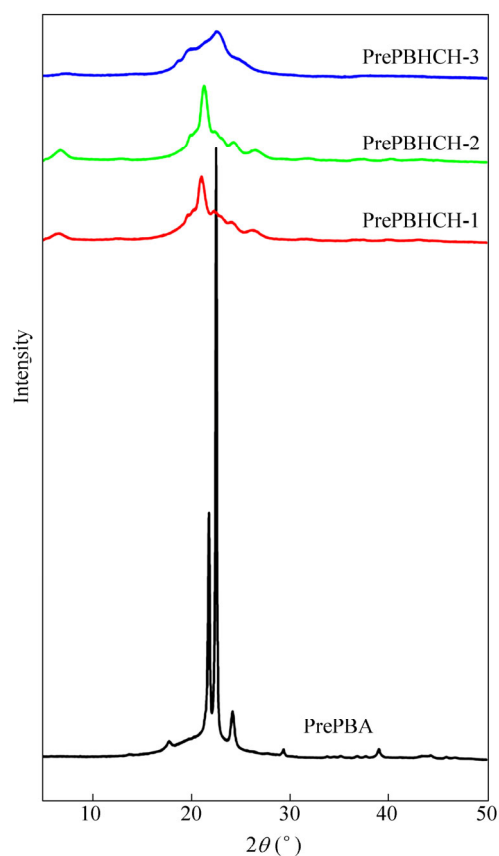


Fig. 6 The X-ray diffraction patterns of PrePBHCHs and PrePBA

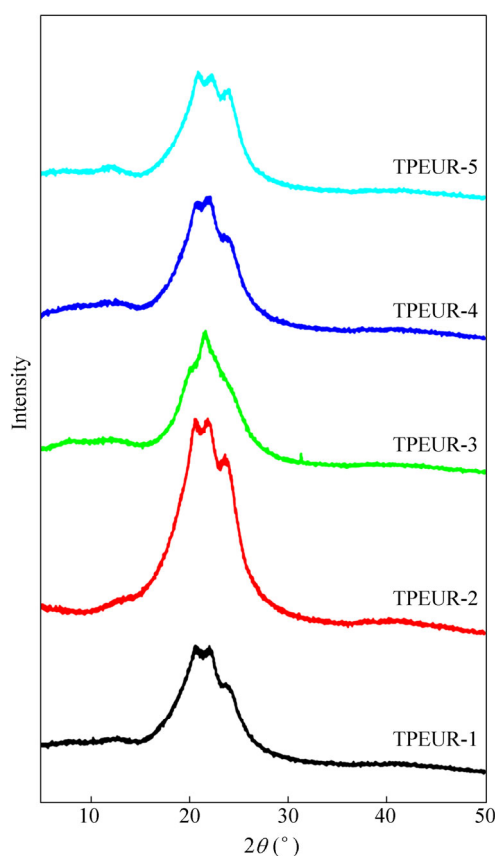


Fig. 7 The X-ray diffraction patterns of TPEURs

TGA Characterization

The thermal stability of TPEURs was characterized using TGA and the results are shown in Fig. 8. The initial decomposition temperature (T_i), 50% mass decomposition temperature (T_{50}), end decomposition temperature (T_{end}) and end mass loss are summarized in Table 6. TPEURs exhibit a T_i between 274.7 and 287.3 °C, which is obviously higher than T_i of PBHCH (262.8 °C) due to the PBA segments have higher thermal stability than PBHCH^[22, 25]. The T_i of TPEURs is about 170 °C that is higher than their T_m .

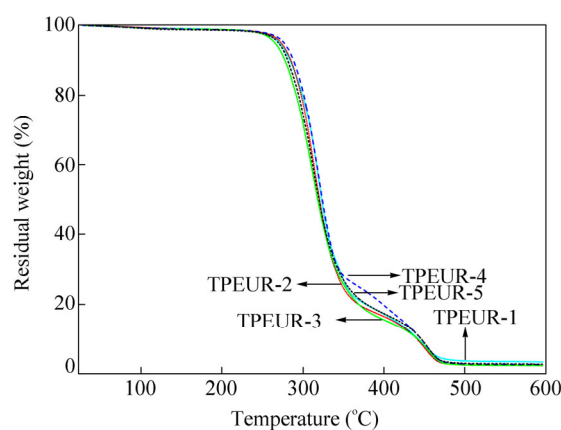


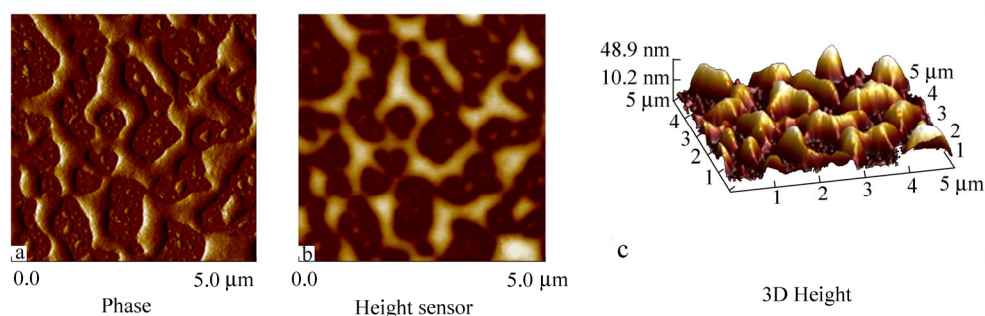
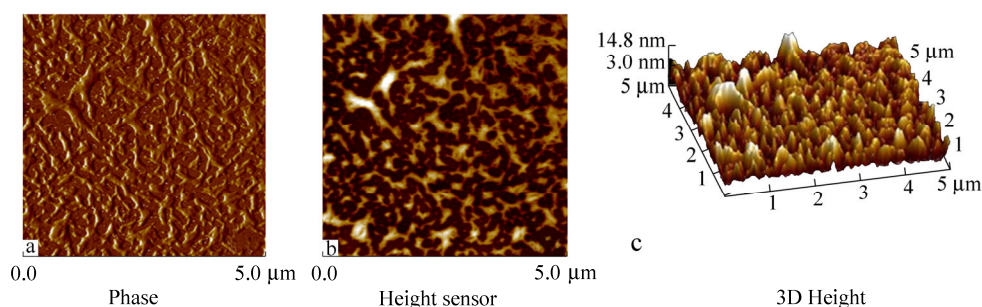
Fig. 8 The TGA curves of TPEURs (heating rate: 10 K/min; atmosphere: N₂)

Table 6. TGA^a and tensile testing data of TPEURs

Sample	T_i (°C)	T_{50} (°C)	T_{end} (°C)	End mass loss (%)	Tensile strength (MPa)	Strain at break (%)	Resilience at 100% fixed- length (%)	Resilience at 200% fixed- length (%)
TPEUR-1	282.0	323.4	508.5	96.70	16.5	471.8	77.5	62.7
TPEUR-2	284.6	320.2	503.1	97.40	14.0	362.4	68.6	44.4
TPEUR-3	274.7	318.6	510.6	97.40	14.3	246.3	60.4	—
TPEUR-4	287.3	326.1	507.4	97.20	14.5	629.4	75.3	57.4
TPEUR-5	278.9	319.6	514.4	97.10	18.8	450.0	67.1	52.1

^a Heating rate: 10 K/min**Phase Behavior**

AFM has proven to be an important tool to elucidate microphase separation of isocyanate TPURs^[29]. The morphology of the annealed TPEURs was measured by using a tapping-mode AFM, which allowed simultaneous detection of phase and height features. Figures 9–13 show the phase (a), 2D height (b), and 3D height (c) images of TPEURs. The bright regions are the hard phase (hard ordered domains or crystalline PBHCH HS regions), and the dark regions correspond to the soft phase (PBA regions or SSs)^[30]. In these images, visual evidences for the appearance of microphase separation are clearly shown in TPEURs. TPEUR-1 exhibits lower density of hard phases due to the shorter PBHCH segments. As the amount of the PBHCH HSs increases, the density of hard phases increases. Similar trend is also observed for TPEUR-1, TPEUR-4 and TPEUR-5 because they were synthesized from PrePBHCH-1, PrePBHCH-2, and PrePBHCH-3 with the same PrePBA/PrePBHCH molar ratio of 1:1. As the length of PBHCH HSs increases, the density of hard phases increases. The hard domains are formed with increased density when the amount of regular and crystallizable PBHCH segments increases. Phase morphology is an important factor for influencing the mechanical properties of the polymers^[31].

**Fig. 9** AFM images of TPEUR-1: (a) phase, (b) 2D height and (c) 3D height**Fig. 10** AFM images of TPEUR-2: (a) phase, (b) 2D height and (c) 3D height

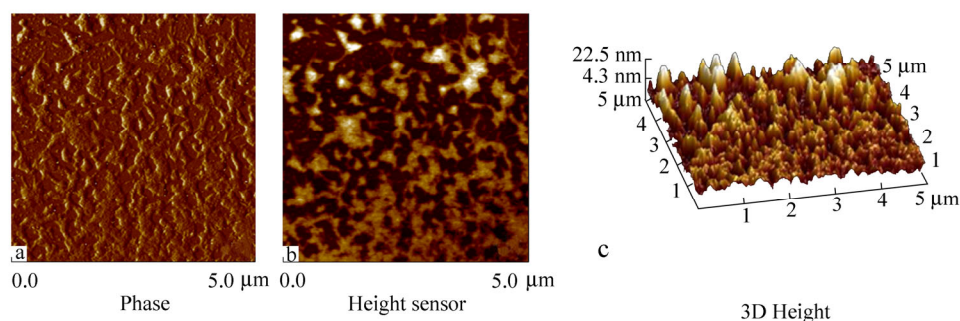


Fig. 11 AFM images of TPEUR-3: (a) phase, (b) 2D height and (c) 3D height

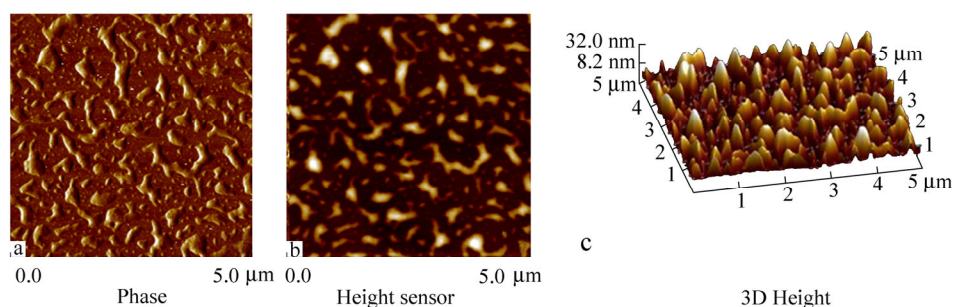


Fig. 12 AFM images of TPEUR-4: (a) phase, (b) 2D height and (c) 3D height

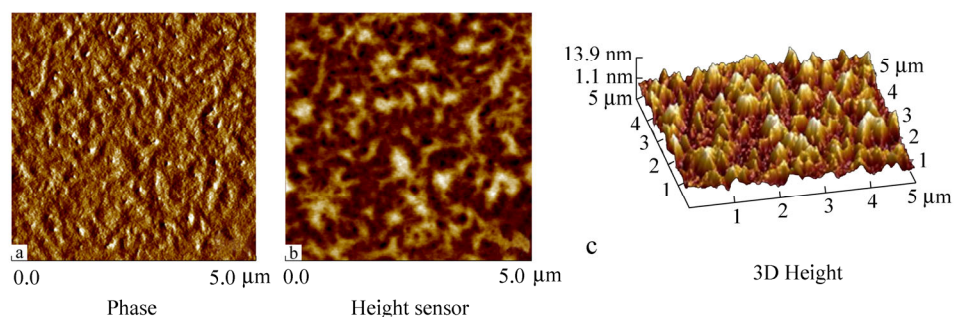


Fig. 13 AFM images of TPEUR-5: (a) phase, (b) 2D height and (c) 3D height

Tensile Testing

The tensile testing of TPEURs was conducted, and the stress-strain curves are shown in Fig. 14. The tensile strength and strain at break of TPEURs are summarized in Table 6. TPEUR-1 has a tensile strength of 16.5 MPa and a strain at break of 471.8%. Introduction of PBA SSs improves the flexibility of TPEUR-1 and endows the TPEUR-1 with moderate tensile strength and good toughness. The strain at break of TPEUR-2 and TPEUR-3 decreased obviously compared to that of TPEUR-1 due to the fact that the crystallinity (Table 4) increases because of more amount of the PBHCH HSs in the structure. Although the crystallinity of TPEUR-1 and TPEUR-2 are lower than 10.04%, TPEUR-1, TPEUR-2 and TPEUR-3 all form interconnected hard domains (Figs. 9–11) because the amount of HS% is higher than 38.73% (Table 3), which makes them with the similar tensile strength. The density of the hard domains further increases when increasing the amount of PBHCH HSs, such leading to the hard domains without enough toughness. Thus, the strain at break decreases and the tensile strength also slightly decreased as the amount of PBHCH HSs increases from TPEUR-1 to TPEUR-3. Although TPEUR-4 has higher crystallinity than TPEUR-1, TPEUR-4 forms small scattered HS granules in its AFM images (Fig. 12), which makes TPEUR-4 more flexible and show higher strain at break and lower tensile strength than TPEUR-1. TPEUR-5 was prepared from easily crystallized PrePBHCH-3. Longer HSs and higher

HS amount makes TPEUR-5 form less regular interfaces and interconnected fine crystallites of hard domains (Fig. 13). TPEUR-5 exhibits the highest tensile strength of 18.8 MPa and the lower strain at break of 450.0%. TPEURs are TPU elastomers. They exhibit resilience of up to 77.5% at 100% fixed-length and resilience of up to 62.7% at 200% fixed-length. As the length of HSs or HS amount increases, the SS amount decreases, resulting in the decrease of resilience.

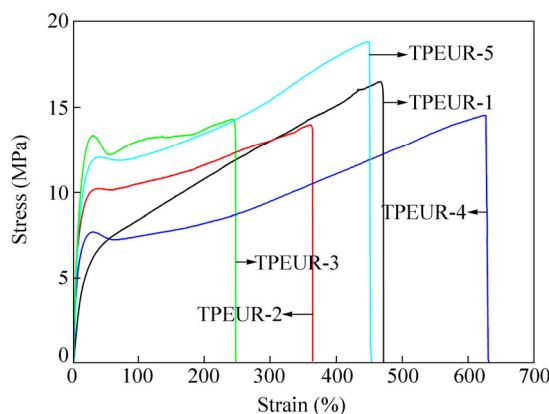


Fig. 14 The stress-strain curves of TPEURs

CONCLUSIONS

Three prepolymers, PrePBHCHs, were prepared through the self-transurethane polycondensation of 1,6-bis(hydroxyethyloxycarbonylamino) hexane, BHCH, at different reaction time. The co-polycondensation of the PrePBHCHs with a PrePBA, a poly(1,4-butylene adipate) was conducted, and the prepolymer was obtained *via* the polycondensation of adipic acid with butanediol. A series of aliphatic thermoplastic poly(ester urethane) elastomers, TPEURs, were synthesized. The TPEURs exhibit an M_n up to 23300 g/mol, M_w up to 51100 g/mol, T_g ranging from $-33.8\text{ }^{\circ}\text{C}$ to $-3.1\text{ }^{\circ}\text{C}$, T_m from $94.3\text{ }^{\circ}\text{C}$ to $111.9\text{ }^{\circ}\text{C}$, initial decomposition temperature over $274.7\text{ }^{\circ}\text{C}$, tensile strength up to 18.8 MPa with a strain at break of 450.0%, and resilience up to 77.5%. A simple non-isocyanate route for synthesizing crystallizable TPU elastomers with high T_m and good mechanical properties was established.

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