

Aliphatic Thermoplastic Poly(ether urethane)s Having Long PEG Sequences Synthesized through a Non-isocyanate Route^{*}

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Abstract A non-isocyanate route for synthesizing thermoplastic polyurethanes with excellent thermal and mechanical properties was described. Melt transurethane polycondensation of 1,6-bis(hydroxyethyloxy carbonyl amino)hexane with four poly(ethylene glycol)s (PEGs), *i.e.* PEG400, PEG600, PEG1000, or PEG1500, was conducted at different molar ratios. A series of thermoplastic poly(ether urethane)s (TPEUs) with long PEG sequences were prepared. The TPEUs were characterized *via* gel permeation chromatography, FTIR, ¹H-NMR, differential scanning calorimetry, thermogravimetric analysis, wide-angle X-ray scattering, and tensile tests. The TPEUs exhibit *T_g* between 12.4 °C and −40.4 °C, *T_m* of up to 149.8 °C, and initial decomposition temperature over 239.4 °C. The tensile strength of the TPEUs reaches 38.39 MPa with a strain at break of 852.92%.

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

INTRODUCTION

Polyurethanes are important commercial polymers that are widely used as foams, adhesives, coatings and medical materials because of their outstanding mechanical properties, abrasion resistance, high elasticity and favorable biocompatibility^[1–4]. However, most commercial polyurethanes are prepared from highly toxic diisocyanates, whose major synthesis precursor 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 study polyurethanes^[5–7]. Most current investigations on non-isocyanate polyurethanes (NIPUs) focus on cross-linked polyurethanes, which are prepared from cyclic carbonates and diamines or multi-amines^[8–15]. Meanwhile, Loontjens *et al.* synthesized NIPUs from carbonyl biscaprolactamate^[16–18].

Transurethane polycondensation of diurethanes has been developed to synthesize linear or thermoplastic polyurethanes (TPUs). Tang *et al.* synthesized TPUs containing different multi-urea segments from solution polycondensation of dimethyl dicarbamates with amino-terminated poly(propylene glycol)^[19]. Deepa *et al.* synthesized a series of amorphous TPUs from transurethane polycondensation of dimethyl 1,6-hexamethylene dicarbamate and dimethyl isophorone dicarbamate with glycol oligomers, 1,4-cyclohexanedimethanol, 1,4-cyclohexanediol or isosorbide^[20, 21]. 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^[22]. Ochiai *et al.* studied the self-polycondensation of 1,6-bis(hydroxyethyloxy carbonyl

^{*} This work was financially supported by the National Natural Science Foundation of China (Nos. 21244006 and 50873013).

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Received October 9, 2014; Revised December 29, 2014; Accepted December 30, 2014

doi: 10.1007/s10118-015-1638-7

amino)hexane (BHCH) and used the obtained polyurethane to synthesize methacrylate macromolecular monomers^[23]. Meanwhile, Sharma *et al.* synthesized a series of α -hydroxy- ω -amino-amides 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^[24–26]. In our previous work, we synthesized aliphatic thermoplastic poly(amide urethane)s with short nylon-6 segments^[27], poly(ether amide urethane)s with poly(ethylene glycol) (PEG) sequences and short nylon-6 segments^[28] and poly(ether urethane)s with short PEG segments^[29]. The thermoplastic poly(ether urethane)s (TPEUs) were prepared *via* a simple melt transurethane polycondensation of BHCH with ethylene glycol oligomers, *e.g.* triethylene glycol and tetraethylene glycol. These TPEUs are tough thermoplastics with tensile strength of up to 32.82 MPa and strain at break of up to 151.82%.

As polyurethanes with excellent mechanical properties are normally prepared from polyether glycols, such as PEGs with high molecular weight in the common isocyanate route, introducing long PEG sequences into non-isocyanate TPEUs might also further increase the toughness and tensile strength of these TPEUs. In this study, we synthesized a series of TPEUs through melt transurethane polycondensation of BHCH with PEGs having high molecular weight, *i.e.* PEG400, PEG600, PEG1000, and PEG1500. The obtained TPEUs were characterized *via* gel permeation chromatography (GPC), FTIR and ¹H-NMR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray scattering (WAXS) and tensile testing.

EXPERIMENTAL

Materials

Ethylene carbonate, PEG400, PEG600, PEG1000 and PEG1500 were purchased from Alfa Aesar, United Kingdom, and were used as received. 1,6-Hexanediamine was purchased from Shanghai Reagent Plant, China. 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 were used directly. BHCH was prepared from the reaction of ethylene carbonate with 1,6-hexanediamine according to literature^[22]. The melting point of BHCH is 94 °C.

Synthesis of the TPEUs

In a 100 mL three-necked flask, different amounts of BHCH, PEG400 and 0.2 wt% SnCl₂ were added at a BHCH/PEG molar ratio of 5:1. The mixture was stirred at 170 °C for 2 h under a nitrogen atmosphere and was reacted under a reduced pressure of up to 3990 Pa for another 4 h. Subsequently, the pressure in the flask was gradually reduced to 399 Pa and was maintained for 8 h until no further increase in viscosity was observed. The obtained faint polymer was poured out and cooled at room temperature. This polymer was designated as TPEU-1.

Similarly, TPEU-2, TPEU-3 and TPEU-4 were synthesized at a BHCH/PEG molar ratio of 5:1 through melt polycondensation of BHCH with PEG600, PEG1000 and PEG1500, respectively. TPEU-5, TPEU-6, TPEU-7, and TPEU-8 were synthesized at a BHCH/PEG molar ratio of 9:1 at reaction conditions similar to those of TPEU-1 through the melt polycondensation of BHCH with PEG400, PEG600, PEG1000, or PEG1500.

Characterization

The M_n , M_w , and polydispersity index (PDI) of the TPEUs were determined *via* GPC at 25 °C using Waters Agilent-2600 Series equipped with a PLgel 5 μ m 1000 Å column and a refractive index detector. DMF was used as the eluent with a flow rate of 1 mL/min, and polystyrene (PS) was used as the standard.

The polymer samples for the FTIR and ¹H-NMR characterization were purified thrice through dissolution-precipitation cycles by using DMSO as solvent and ether as nonsolvent. The FTIR spectra were acquired using a Nicolet 60SXB FTIR spectrometer. The ¹H-NMR spectra were obtained using deuterated DMSO (DMSO-*d*₆) as solvent on a Bruker 400 AVANCE with tetramethylsilane as the internal standard.

WAXS measurements were taken on a Rigaku D/Max 2500 VB2+/PC diffractometer with Cu K α radiation. The samples were continuously scanned over a 2θ range from 5° to 50°.

^c GPC data detected in DMF with PS as the standard

FTIR and ^1H -NMR Characterization

The obtained TPEUs were characterized *via* FTIR and ^1H -NMR spectra. Figure 1 shows the FTIR spectrum of TPEU-1. Absorption peaks corresponding to the PEG sequences and the hexanediurethane (HDU) units derived from BHCH are evidently found. TPEU-1 possesses these HDU units and long PEG sequences.

Figure 2 shows the ^1H -NMR spectrum of TPEU-1 and the chemical shifts of different hydrogen atoms. Signals are assigned according to several literatures^[22, 23, 28, 29]. Signals corresponding to the EHDU segments and the HDU-co-PEG sequences (in Scheme 2) are clearly found. The ^1H -NMR spectrum verifies the TPEU-1 structure. TPEU-1 has $-\text{HNCOOCH}_2\text{CH}_2\text{OH}$ terminal groups remaining. Meanwhile, a little portion of urea units was formed during the synthesis reaction. Tail-biting side reaction of the $-\text{HNCOOCH}_2\text{CH}_2\text{OH}$ terminal groups caused the formation of urea units (Scheme 3).

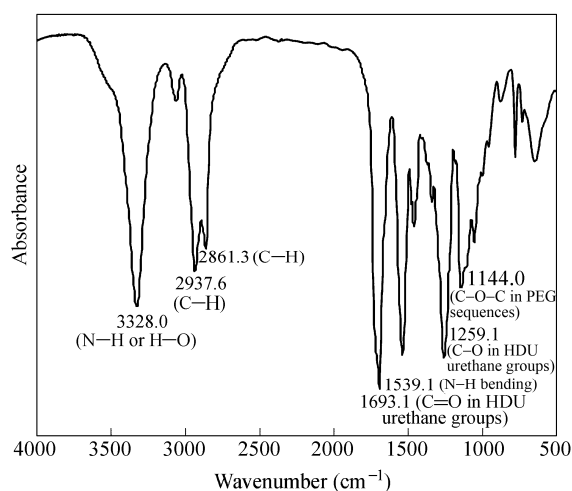


Fig. 1 FTIR spectrum of the TPEU-1

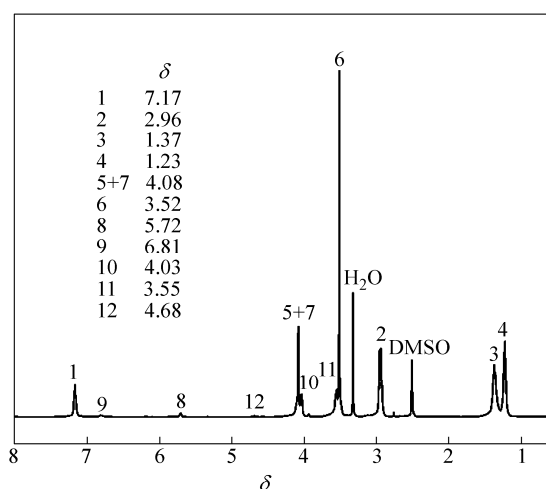
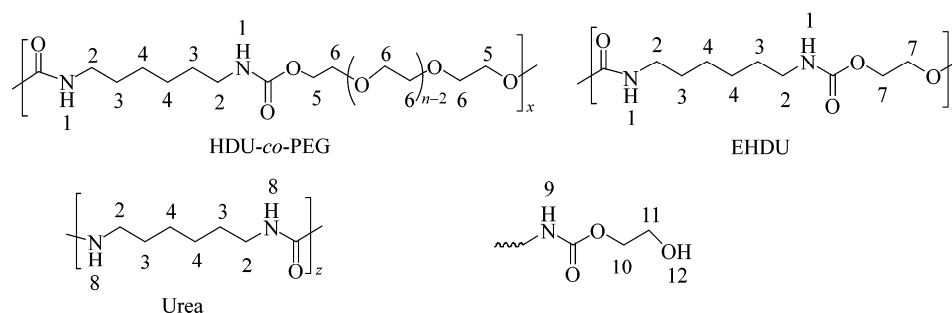
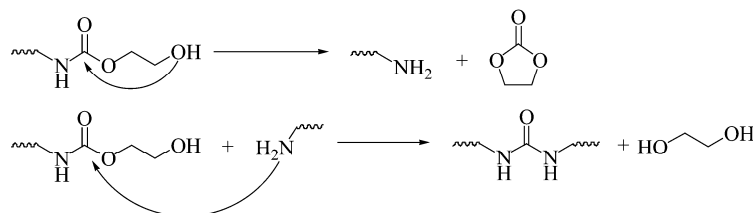


Fig. 2 ^1H -NMR spectrum of the TPEU-1



Scheme 2 Structural units in the TPEU-1



Scheme 3 Formation of the urea units in the polycondensation of BHCH with PEG

Table 2 shows the compositions of the TPEUs detected from ^1H -NMR spectra. The detected BHCH:PEG molar ratios in TPEUs are close to the BHCH:PEG feed ratios. TPEUs exhibit urea percentage ranging from

3.26 mol% to 8.50 mol%. The M_n detected from the $^1\text{H-NMR}$ spectra is obviously lower than that detected from GPC method, probably because GPC method provides relative molecular weight which is calculated with PS as standard. The difference is also attributed to the low accuracy of $^1\text{H-NMR}$ characterization. Unlike the $^1\text{H-NMR}$ spectra of small organic molecules, which can show exact molar ratios between different hydrogens, the $^1\text{H-NMR}$ spectra of polymers merely exhibit exact chemical shifts, but their area ratios often deviate from the actual molar ratios of different hydrogens, particularly for the copolymers with complicated structure and for the terminal groups of polymers with high molecular weight.

Table 2. Compositions of the TPEUs detected from $^1\text{H-NMR}$ spectra

	TPEU-1	TPEU-2	TPEU-3	TPEU-4	TPEU-5	TPEU-6	TPEU-7	TPEU-8
n^a	9	13	22	34	9	13	22	34
A_{12}^b	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
A_1^b	41.52	20.94	15.58	23.09	26.53	29.96	32.21	21.59
A_{5+7}^b	52.75	45.63	38.63	37.63	55.63	48.21	62.54	42.15
A_6^b	146.04	125.76	157.83	404.41	56.32	105.40	184.39	196.75
A_8^b	4.76	2.11	2.36	3.76	3.79	5.87	3.70	1.56
A_9^b	1.21	1.51	1.05	1.55	1.03	1.62	1.96	1.58
x^c	9.13	5.24	3.76	6.13	3.52	4.39	4.39	2.98
y^c	17.25	17.58	15.56	12.69	24.30	19.71	26.88	18.09
z^c	4.76	2.11	2.36	3.76	3.79	5.87	3.70	1.56
M_n^d	10163	8522	8458	13966	8383	8904	11982	9605
BHCH/PEG ^e	5.34	4.98	5.33	4.89	9.20	8.90	9.07	8.83
Urea, mol% ^f	5.28	4.49	6.63	7.09	6.43	8.50	5.14	3.26

^a Polymerization degree of PEG;

^b Area of different hydrogens;

^c The $x:y:z$ molar ratios between the HDU-co-PEG, EHDU, and urea units. They were calculated by the following

$$\text{equations: } x = \frac{A_6/4(n-1)}{A_{12}/2}; y = \frac{A_{5+7}/4}{A_{12}/2} - x; z = \frac{A_8/2}{A_{12}/2};$$

^d Number-average molecular weight, $M_n = (186 + 44n)x + 230y + 142z + 2 \times 104$, in which 186, 44, 230, 142, and 104 represent the molecular weight of the HDU, $(-\text{CH}_2\text{CH}_2\text{O}-)$, EHDU, urea units, and the $-\text{HNCOOCH}_2\text{CH}_2\text{OH}$ terminal groups described in Scheme 2;

$$\text{The BHCH:PEG molar ratio: } \text{BHCH/PEG} = \frac{A_1/2 + A_8/2 + A_9}{A_6/4(n-1)};$$

$$\text{Content of urea, Urea\%} = \frac{A_8/2}{A_1 + A_9 + A_8/2}$$

WAXS Characterization

Figure 3 shows the WAXS patterns of TPEUs. TPEUs are all crystallized polymers. PBHCH is a crystallizable TPU, which exhibits a series of diffraction peaks at 2θ of 6.69° , 19.74° , 21.00° , 22.33° , 24.10° and 26.09° , respectively^[27]. TPEU-1, TPEU-2, TPEU-3, and TPEU-4 were synthesized at a BHCH/PEG molar ratio of 5:1. TPEU-1, TPEU-2, and TPEU-3 crystallize similarly as PBHCH. The short PBHCH segments in the main chains are the crystallization source of the TPEUs. Although PEG with molecular weight above 1000 can crystallize by themselves, the PEG segments in TPEU-3 hardly crystallize. Introducing PEG segments into TPEU-3 lowers the regularity of the main chains. Therefore, no crystallization peaks corresponding to the PEG segments are found. TPEU-4 was prepared from PEG1500. The PBHCH segments in TPEU-4 have lower molecular weights (M_n of about 1150 g/mol) than those of the PEG sequences (M_n of about 1500 g/mol). The short PBHCH segments

merely form a small portion, which cause the poor crystallization of TPEU-4. A peak at 21.08° corresponds to the crystallization of the PBHCH segments in TPEU-4. Meanwhile, two peaks at 19.28° and 23.33° , which correspond to the PEG crystallization^[30], are found. The PEG segments in the TPEU-4 amount for the major portion and their crystallization becomes easier. TPEU-5, TPEU-6, TPEU-7, and TPEU-8 were synthesized at a BHCH/PEG molar ratio of 9:1. Longer PBHCH segments in the main chains provide the TPEUs with excellent crystallization. As the PEG segments merely account for a small portion, they do not crystallize also because introducing PEG segments into TPEUs lowers the regularity of the main chains in TPEU-5, TPEU-6, TPEU-7, and TPEU-8.

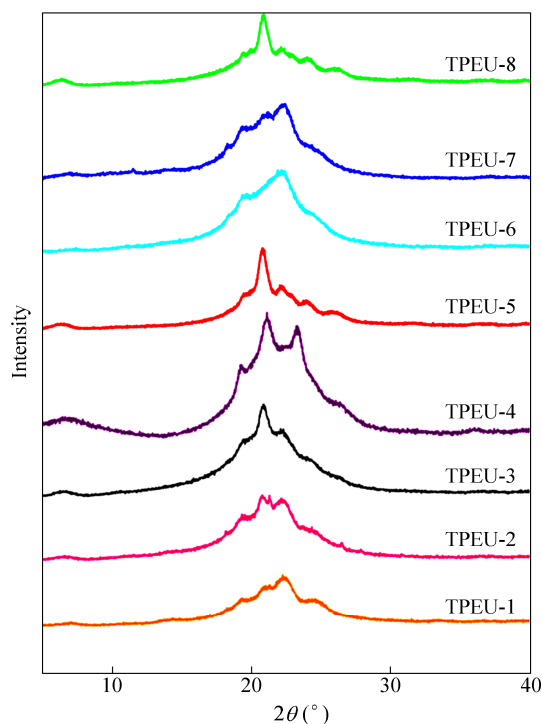


Fig. 3 X-ray diffraction diagrams of the TPEUs

DSC Characterization

Figure 4 shows the second heating DSC curves of the TPEUs. The glass transition temperature (T_g), crystallization temperature (T_c), crystallization enthalpy (ΔH_c), melting temperature (T_m), and melting enthalpy (ΔH_m) of the TPEUs are shown in Table 3. PBHCH is a semi-crystallized TPU with T_m at 154.31°C ^[27]. The TPEUs except TPEU-4, show crystallization behavior similar to that of PBHCH. TPEUs exhibit a T_m ranging from 101.3°C to 149.8°C , which is lower than the T_m of PBHCH and is probably because the PEGs have different structures from PBHCH. The introduction of PEG sequences lowers the regularity of TPEUs, which decreases the T_m . TPEU-1, TPEU-2, TPEU-3 and TPEU-4 were all synthesized at a BHCH/PEG molar ratio of 5:1. As TPEU-1, TPEU-2, TPEU-3, and TPEU-4 contain PBHCH segments with lower molecular weight of about 1150 g/mol , their T_m is easily influenced by the molecular weight of the PEG segments. The T_m of TPEU-1, TPEU-2, TPEU-3, and TPEU-4 is obviously lower than that of TPEU-5, TPEU-6, TPEU-7 and TPEU-8, which were synthesized at a BHCH/PEG molar ratio of 9:1. TPEU-4 shows a strong T_m peak at 27.7°C and a weak T_m at 101.3°C , which correspond to the T_m of the PEG sequences and that of the PBHCH segments. TPEU-4 is composed of long PEG segments (M_n of 1500 g/mol) and short PBHCH segments (M_n of about 1150 g/mol). The PBHCH segments in TPEU-4 merely account for a minor component. Crystallization of the PBHCH segments in TPEU-4 becomes weak, and that of the PEG segments becomes obviously strong. TPEU-4 shows obviously lower T_m than TPEU-1, TPEU-2 and TPEU-3, which contain shorter PEG sequences. Unlike

TPEU-4, the PBHCH segments in TPEU-1, TPEU-2 and TPEU-3 are the major crystallization source. TPEU-5, TPEU-6, TPEU-7, and TPEU-8 show obviously higher T_m than the corresponding TPEUs that were synthesized at a BHCH/PEG molar ratio of 5:1, because TPEU-5, TPEU-6, TPEU-7, and TPEU-8 contain longer and more easily crystallizable PBHCH segments in the main chains. TPEUs all exhibit a T_c , which means that these TPEUs did not crystallize fast enough to complete crystallization after the fast cooling period before the second heating started. Crystallization still progressed in the second DSC scans.

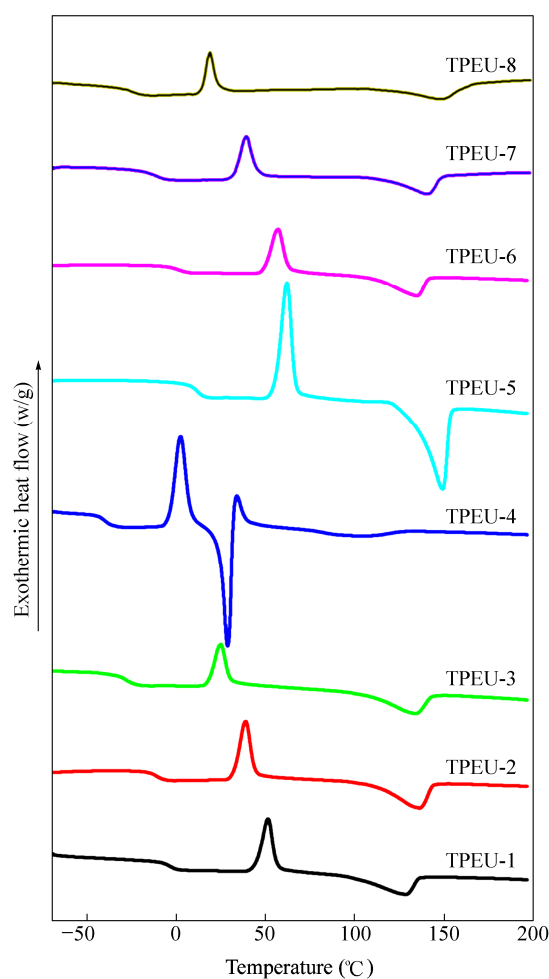


Fig. 4 Second heating DSC scans of the TPEUs (heating rate: 10 K/min)

Table 3. Second heating DSC data of the TPEUs (heating rate: 10 K/min)

TPEUs	T_g (°C)	T_c (°C)	ΔH_c (J·g ⁻¹)	T_m (°C)	ΔH_m (J·g ⁻¹)
TPEU-1	-3.2	51.4	24.30	128.5	20.60
TPEU-2	-11.9	38.8	24.69	136.5	30.25
TPEU-3	-28.7	24.8	16.71	134.2	26.20
TPEU-4	-40.4	2.2	40.41	28.8, 101.3	49.45, 12.55
TPEU-5	12.4	62.0	32.64	148.1	44.04
TPEU-6	1.5	57.0	29.18	135.1	28.71
TPEU-7	-11.2	39.0	22.52	140.9	38.60
TPEU-8	-25.6	18.6	16.73	149.8	26.25

TGA Characterization

The thermal stability of the TPEUs was characterized using TGA, as shown in Fig. 5. Table 4 summarizes the initial decomposition temperature (T_i), 50% mass decomposition temperature (T_{50}), end decomposition temperature (T_{end}), and end mass loss. TPEUs exhibit a T_i of between 239.4 and 254.9 °C, which is lower than the T_i (at 276.9 °C) of PBHCH^[24], probably because the PEG sequences are also low thermal stable units. TPEUs all exhibit T_i of above 239.4 °C, which is not too high because carbamate and ether linkages are only moderately thermally stable. Nevertheless, these TPEUs have T_i several tens degrees higher than their T_m . TPEUs are thermoplastics and are still suitable for processing using normal thermal processing machines.

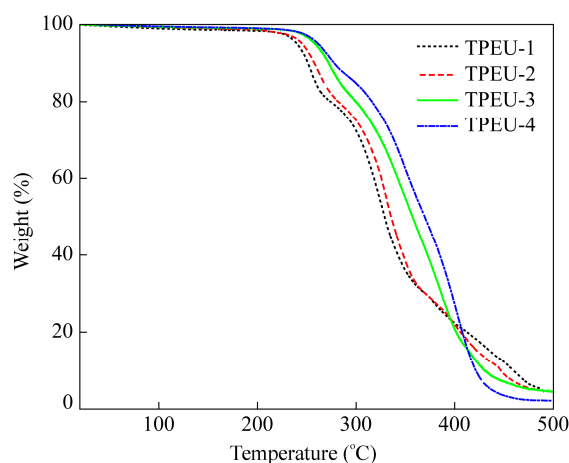


Fig. 5 TGA curves of the TPEUs (heating rate: 10 K/min; atmosphere: N₂)

Table 4. TGA data of the TPEUs (heating rate: 10 K/min under N₂)

TPEUs	T_i (°C)	T_{50} (°C)	T_{end} (°C)	End mass loss (%)
TPEU-1	239.4	329.0	491.5	95.5
TPEU-2	244.3	334.8	493.1	95.7
TPEU-3	254.9	375.2	487.7	95.7
TPEU-4	253.5	368.9	476.0	97.8

Tensile Testing

The tensile testing of the TPEUs was conducted, and the stress-strain curves of the TPEUs are shown in Fig. 6. The tensile strength and strain at break of the TPEUs are listed in Table 1. PBHCH is a TPU with a tensile strength of 28.41 MPa and a strain at break of 3.91%^[24]. PBHCH has high tensile strength but is very brittle. Introducing PEG sequences in the main chains improves the toughness of the TPEUs. TPEU-1, TPEU-2, TPEU-3 and TPEU-4 were synthesized at a BHCH/PEG molar ratio of 5:1. TPEU-1 is constructed with short PBHCH segments (M_n of about 1150 g/mol) and PEG sequences (M_n of about 400 g/mol). The rigid PBHCH segments form the crystallized phase, and the flexible PEG sequences improve the toughness of TPEU-1. TPEU-1 exhibits a tensile strength of 31.77 MPa and a strain at break of 370.33%. TPEU-2 and TPEU-3 also show good tensile strengths and toughness. As TPEU-4 was prepared from PEG1500, the PBHCH segments in the main chains of TPEU-4 have lower molecular weights (about 1150 g/mol) than the PEG sequences (M_n of about 1500 g/mol). The PBHCH segments in TPEU-4 merely form a minor phase, and the PEG sequences form the major crystallized phase. TPEU-4 shows a tensile strength of 3.98 MPa and a strain at break of 118.87%. TPEU-4 is a tough TPU with low tensile strength. TPEU-5, TPEU-6, TPEU-7, and TPEU-8 were synthesized at a BHCH/PEG molar ratio of 9:1. Longer PBHCH segments in the main chains of these TPEUs form stronger intermolecular hydrogen bonding, which cause TPEU-5, TPEU-6, and TPEU-7 to have a tensile strength of up to 38.39 MPa and a strain at break ranging from 197.34% to 852.92%. TPEUs with high tensile strength and excellent toughness were prepared. In Fig. 6, the rise and fall in the stress-strain curves of TPEU-5 and TPEU-6

might arise from the orientation and re-crystallization along the stress direction. When TPEU-5 or TPEU-6 was stretched, the crystallizable PBHCH segments rearranged and crystallized, so the stress peak or wave emerged. TPEU-8 was prepared using PEG1500. Longer PBHCH sequences with a M_n of about 2070 g/mol and PEG sequences with a M_n of about 1500 g/mol in TPEU-8 form two different phases with poor interfacial interactions. Therefore, TPEU-8 merely shows a tensile strength of 9.54 MPa and a strain at break of 12.23%. TPEU-8 is a brittle TPU with low tensile strength. Appropriate flexibility is essential to these TPEUs allowing them to exhibit good mechanical properties. TPEU-7 which is composed of the PBHCH sequences with a M_n of about 2070 g/mol and the PEG sequences with a M_n of about 1000 g/mol shows relatively high T_m , the highest tensile strength and the longest strain at break.

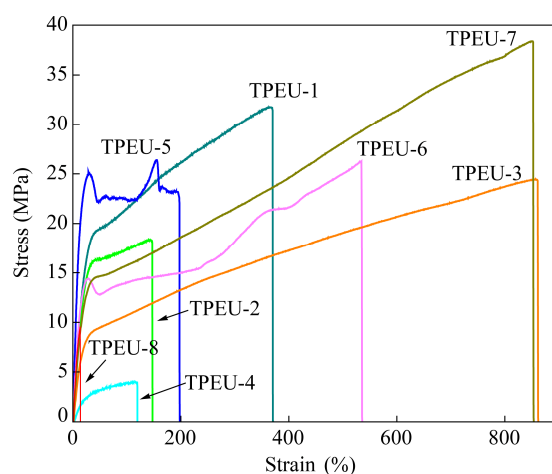


Fig. 6 Stress-strain curves of the TPEUs

CONCLUSIONS

Four PEGs with higher molecular weights were copolymerized with diurethanediol BHCH through melt transurethane polycondensation and a series of TPEUs were prepared. The TPEUs exhibit a T_m ranging from 101.3 °C to 149.8 °C, and initial decomposition temperature of over 239.4 °C. The tensile strength of the TPEUs reaches 38.39 MPa with a strain at break of 852.92%. High molecular weight aliphatic TPUs with excellent thermal and mechanical properties were prepared through the non-isocyanate route. These TPEUs with long PEG sequences exhibit better toughness and higher tensile strength than those prepared from ethylene glycol oligomers.

REFERENCES

- 1 Delebecq, E., Pascault, J.P., Boutevin, B. and Ganachaud, F., *Chem. Rev.*, 2013, 113: 80
- 2 Ling, J., Rong, M.Z. and Zhang, M.Q., *Chinese J. Polym. Sci.*, 2014, 32(10): 1286
- 3 Liu, C.C., Zhang, A.Y., Ye, L. and Feng, Z.G., *Chinese J. Polym. Sci.*, 2013, 31(2): 251
- 4 Yu, R.L., Zhang, L.S., Feng, Y.H., Zhang, R.Y. and Zhu, J., *Chinese J. Polym. Sci.*, 2014, 32(8): 1099
- 5 Guan, J., Song, Y.H., Lin, Y., Yin, X.Z., Zuo, M., Zhao, Y.H., Tao, X.L. and Zheng, Q., *Ind. Eng. Chem. Res.*, 2011, 50: 6517
- 6 Ochiai, B. and Endo, T., *Prog. Polym. Sci.*, 2005, 30: 183
- 7 Kathalewar, M.S., Joshi, P.B., Sabnis, A.S. and Malshe, V.C., *RSC Adv.*, 2013, 3: 4110
- 8 Tamami, B., Sohn, S. and Wilkes, G.L., *J. Appl. Polym. Sci.*, 2004, 92: 88
- 9 Brocas, A.L., Cendejas, G., Deffieux, A. and Carlotti, S., *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49: 2677

- 10 Diakoumakos, C.D. and Kotzev, D.L., *Macromol. Symp.*, 2004, 216: 37
- 11 Ochiai, B., Inoue, S. and Endo, T., *J. Polym. Sci., Part A: Polym. Chem.*, 2005, 43: 6613
- 12 Annunziata, L., Diallo, A.K., Fouquay, S., Michaud, G., Simon, F., Brusson, J.M., Carpentier, J.F. and Guillaume, S.M., *Green Chem.*, 2014, 16: 1947
- 13 Moritz, B., Alexandro, B. and Rolf, M., *Green Chem.*, 2012, 14: 1447
- 14 Moritz, B. and Rolf, M., *Green Chem.*, 2012, 14: 483
- 15 Besse, V., Auvergne, R., Carlotti, S., Boutevin, G., Otazaghine, B., Caillol, S., Pascault, J.P. and Boutevin, B., *React. Funct. Polym.*, 2013, 73: 588
- 16 Maier, S., Loontjens, T., Scholtens, B. and Mulhaupt, R., *Macromolecules*, 2003, 36: 4727
- 17 Maier, S., Loontjens, T., Scholtens, B. and Mulhaupt, R., *Angew. Chem. Int. Ed.*, 2003, 42: 5094
- 18 Zimmermann, J., Loontjens, T., Scholtens, B.J.R. and Mulhaupt, R., *Biomaterials*, 2004, 25: 2713
- 19 Tang, D.L., Mulder, D., Noordover, B.A.J. and Koning, C.E., *Macromol. Rapid Commun.*, 2011, 32: 1379
- 20 Deepa, P. and Jayakannan, M., *J. Polym. Sci., Part A: Polym. Chem.*, 2008, 46: 2445
- 21 Deepa, P. and Jayakannan, M., *J. Polym. Sci., Part A: Polym. Chem.*, 2007, 45: 2351
- 22 Rokicki, G. and Piotrowska, A., *Polymer*, 2002, 43: 2927
- 23 Ochiai, B. and Utsuno, T., *J. Polym. Sci., Part A: Polym. Chem.*, 2013, 51: 525
- 24 Sharma, B., Ubaghs, L., Keul, H., Höcker, H., Loontjens, T. and van Benthem, R., *Polymer*, 2004, 45: 5427
- 25 Sharma, B., Ubaghs, L., Keul, H., Höcker, H., Loontjens, T. and van Benthem, R., *Macromol. Chem. Phys.*, 2004, 205: 1536
- 26 Sharma, B., Ubaghs, L., Keul, H., Höcker, H., Loontjens, T. and van Benthem, R., *Polymer*, 2005, 46: 1775
- 27 Li, C.G., Li, S.Q., Zhao, J.B., Zhang, Z.Y., Zhang, J.Y. and Yang, W.T., *Acta Polymerica Sinica (in Chinese)*, 2014, (11): 1486
- 28 Li, S.Q., Zhao, J.B., Zhang, Z.Y., Zhang, J.Y. and Yang, W.T., *RSC Adv.*, 2014, 4: 23720
- 29 Deng, Y., Li, S.Q., Zhao, J.B., Zhang, Z.Y., Zhang, J.Y. and Yang, W.T., *RSC Adv.*, 2014, 4: 43406
- 30 Shi, Q.S. and Liu, T.Q., *Adv. Mater. Res.*, 2011, 284–286: 1983