

A Non-isocyanate Route to Poly(ester urethane) with High Molecular Weight: Synthesis and Effect of Chemical Structures of Polyester-diol

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Abstract A series of non-isocyanate linear high molecular weight poly(ester urethane)s (PETUs) were prepared through an environmentally-friendly route based on dimethyl carbonate, 1,6-hexanediol and 1,6-hexanediamine. In this route, the polyurethane diol was first prepared by the reaction between bis-1,6-hexamethylencarbamate (BHC) and 1,6-hexanediol. A series of polyester soft segments of polyurethane have been synthesized from the polycondensation of adipic acid and different diols, including butanediol, hexanediol, octanediol and decanediol. The subsequent polycondensation of polyurethane diol and polyester diol led to linear PETUs. The resultant polymers were characterized by GPC, FTIR, ¹H-NMR, ¹³C-NMR, DSC, WAXD, TGA and tensile test. The results indicated that PETUs possess weight-average molecular weights higher than 1×10⁵ and the tensile strength as high as 10 MPa. The thermal properties, crystallization behavior, microphase separation behavior and morphology were studied by DSC and AFM, and the results indicated that the degree of phase separation was affected by two factors, the crystallization and hydrogen bonding interaction between soft segment and hard segment.

Keywords Non-isocyanate; Poly(ester urethane); Polyester-diol

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INTRODUCTION

Polyurethane (PU) has macromolecular chains, which can be rigid, semi-rigid or flexible, and versatile material properties, due to the adjustable structures. Therefore, polyurethane is one of the most important polymers that have widespread applications in various areas including construction, package, ship industry, health sector, automotive or bedding as thermoplastic elastomers, foams, coatings, paints, adhesives, and etc.^[1–3] The global production of polyurethane was close to 20 Mt in 2014, which is among the 6 most produced polymers.^[1]

Traditionally, the industrial synthesis of polyurethanes is based on polyaddition reaction between a diisocyanate, a polyol and a small molecular diol. The merit of this means is the high reactivity of diisocyanate. However, this approach has a main disadvantage of the involvement of the high lethal and unstable isocyanate as well as its raw material phosgene.^[4]

Therefore, developing green routes of nonisocyanate polyurethane (NIPU) using non-hazardous materials is attracting

more and more interest from both academic researchers and industries. One of the most developed synthetic routes is the step-growth polyaddition reaction between a five-membered bicyclocarbonate (multicyclocarbonate) and a diamine.^[3,5–10] However, the chemical structure of polyurethane synthesized by this route is different from that of traditional polyurethane due to the presence of —OH. The obtained polyurethane is called polyhydroxyurethanes (PHUs). As compared with conventional polyurethane, microphase separation behavior of PHUs is evidently different as the additional hydroxyl groups on the hard segment can form intersegmental hydrogen bonding with hydrogen bond acceptors in the soft segment and cause major phase mixing.^[11,12] Consequently, the mechanical properties, such as tensile strength and tensile modulus of NIPUs, are substantially inferior to those of conventional polyurethanes.^[11,13–15] As a result, this kind of NIPUs has been frequently crosslinked to be coatings,^[16–18] adhesives,^[19] foams,^[20] rather than elastomers or other structure materials.

Transurethane polycondensation of diurethanes is another useful method for achieving non-isocyanate polyurethane.^[21,22] Especially, it can be applied to synthesize PUs with structures similar to those of traditional ones.^[21,22]

Generally, cyclic ethylene carbonates, aliphatic carbonates, or their derivatives, have been employed to synthesize diur-

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ethanes, which can act as substitutions of diisocyanates.^[21–26] Typically, dihydroxyl or dimethyl terminated diurethanes or their oligomers have been synthesized first. Polycondensation of synthesized diurethanes with polyols and small molecule diols or dicarboxylic acids results in polyurethanes. Zhao *et al.* have performed much significant work on cyclic ethylene carbonate based polyurethane.^[27–39] Up to now, aliphatic thermoplastic poly(ether urethane), poly(amide urethane)s, poly(ether amide urethane)s, polyurethane-ureas and poly(ester urethane) (PTEU) with various structures and properties based on different soft segments have been synthesized using cyclic ethylene carbonate or linear dimethyl carbonate as the starting materials.^[21,27–40]

As compared to cyclic ethylene carbonate, the cost of non-toxic dimethyl carbonate (DMC) is much lower. But only very few groups reported the synthesis of PUs based on DMC.^[22,24,26,41–45] We synthesized polycarbonate based PUs and polyether based PUs from DMC.^[22,45] It should be mentioned that both the thermal and mechanical properties of DMC derived poly(carbonate urethane) are comparable with those isocyanate counterparts due to their similar chemical structures.^[22] However, up to now, there are no industrialized non-isocyanate products. The main reason lies in the prominently higher cost of non-isocyanate polyurethanes. Therefore, the low-cost DMC derived nonisocyanate polyurethanes are very promising. Another reason that restricts the application and industrialization of non-isocyanate polyurethanes is correlated with the side reactions due to the evidently higher polycondensation temperature needed to remove the side products so as to achieve high molecular weight, as compared with traditional isocyanate routes. The side reactions, such as tail-biting side reaction of the $\text{—HNCOOCH}_2\text{CH}_2\text{OH}$ terminal groups, which not only cause a lower molecular weight, but also led to the formation of more urea units in the main chains of polyurethanes, which interrupts the regularity of macromolecular chain and reduces the degree of microphase separation, resulting in loss of mechanical properties.^[38,45]

Polyester diol based PETU possesses good biodegradability, biocompatibility and mechanical properties. They can be applied to prepare vascular stent, and are considered as one of the medical materials with bright prospect.^[46,47]

However, as far as we know, there are very limited references focusing on the non-isocyanate poly(ester urethane). Zhang *et al.*^[21] and Zhu *et al.*^[48] prepared polyurethane diol from biobased diamine and cyclic carbonate or ethylene carbonate, which was subsequently polycondensed with biobased dicarboxylic acid to introduce short ester bond to poly(urethane). Regrettably, the molecular weight of the synthesized polyurethane is lower than 3×10^4 , and they are frequently been applied as coating after thermosetting with ultraviolet light. Recently, Zhao *et al.* first synthesized 1,6-bis(hydroxyethyloxycarbonylamino) hexane (BHCH) from ethylene carbonate and 1,6-hexanediamine. Subsequent self-transurethane polycondensation of BHCH gave the BHCH prepolymers. The polycondensation of BHCH prepolymer with poly(butylene adipate) prepolymer achieved the polyester based polyurethane with good mechanical properties.^[38]

Up to now, no work has been reported on preparing thermoplastic polyester-based poly(urethane) from dimethyl car-

bonate or systematic work on their relationship between the structures and properties.

In this work, a new non-isocyanate strategy to PETUs from dimethyl carbonate has been reported for the first time. The hard segment of polyurethane was prepared from dimethyl carbonate, 1,6-hexanediamine and 1,6-hexanediol. The soft segment of polyester diol was synthesized from polycondensation of adipate acid and various diols (butanediol, hexanediol, octanediol and decanediol). Subsequent polycondensation of polyurethane diol and polyester diol led to linear PETUs. The chemical structures of polymers were characterized by FTIR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and GPC. The crystallization behavior, microphase separation behavior and morphology were studied by DSC, WAXD, and AFM. The mechanical properties were studied by tensile test. It should be noted that the PETUs possess weight-average molecular weights higher than 8×10^4 g/mol.

EXPERIMENTAL

Materials

DMC was used as received from Shandong Shida Shenghua Chemical (China). 1,6-Hexanediamine (HDA), CH_3COONa , and deuterated methyl sulfoxide were bought from Beijing InnoChem Science & Technology Corp. (China) and used without purification. Methanol, tetrabutyl titanate (TBT) and K_2CO_3 were purchased from Beijing Chemical Reagents Corp. (China) and used without purification. All the other reagents in analytical grade, were bought from J&K Chemicals (China) and used without purification.

Synthesis of Polyurethane Diol (PUDL)

Bis-1,6-hexamethylencarbamate (BHC) was synthesized from DMC and HDA according to the reference using DMC as the solvent.^[36] Crude yield: 84%. $^1\text{H-NMR}$ data (400 MHz, DMSO-d_6 , δ , ppm): 7.06 (br, 2H, NH); 3.50 (s, 6H, OCH_3); 2.97–2.92 (q, 4H, CH_2NH); 1.38–1.35 (m, 4H, $\text{CH}_2\text{CH}_2\text{NH}$); 1.24–1.20 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$).

PUDL was synthesized following our previous procedure.^[22] $^1\text{H-NMR}$ data (400 MHz, DMSO-d_6 , δ , ppm): 7.02 (NH); 4.34–4.30 (OH); 3.92–3.88 (NHC(O)OCH_2); 3.39–3.35 (CH_2OH); 2.95–2.91 (CH_2NH); 1.51 ($\text{CH}_2\text{CH}_2\text{NH}$); 1.40–1.36 ($\text{NHC(O)OCH}_2\text{CH}_2$); 1.29 ($\text{NHC(O)OCH}_2\text{CH}_2\text{CH}_2$); 1.22 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}$).

The polymerization degree was calculated to be 5.38 by comparing the integral area of protons at 2.95–2.91 ppm ($\text{—CH}_2\text{NH—}$) to those at 3.39–3.35 ppm ($\text{—CH}_2\text{OH}$). The M_n of the obtained PUDL was 1656 g/mol as calculated from the $^1\text{H-NMR}$ data.

Synthesis of Polyester Soft Segment (PEDL)

PEDL in Table 1 was synthesized from adipic acid and different diols in bulk by a two-step process, *i.e.*, esterification and polycondensation. Generally, adipic acid and diols were fed at 120 °C into a four-neck round-bottom flask in a 1:2 molar ratio and then the temperature was gradually increased to 150 °C and maintained for 5 h under nitrogen atmosphere until theoretical amount of water was separated which means the esterification was complete. Subsequently, the pressure of the reaction system was gradually reduced to 5–20 Pa, and maintained for 4–8 h to synthesize dihydroxyl-terminated PEDL-diol. All the prepolymers were purified by repeatedly

reprecipitation from hot $\text{CHCl}_2\text{CHCl}_2$ solution by cold methanol, and dried for 12 h at 40 °C. Their chemical structures were characterized by NMR spectra. The polymerization degree was deduced from ^1H -NMR spectrum by comparing the integral area of protons at 4.09 ppm ($-\text{C}(\text{O})\text{OCH}_2-$) to those at 3.67 ppm ($-\text{CH}_2\text{OH}$).

^1H -NMR data (400 MHz, CDCl_3 , δ , ppm): poly(butylene adipate): 4.09 ($-\text{C}(\text{O})\text{OCH}_2-$); 3.67 ($-\text{CH}_2\text{OH}$); 2.32 ($-\text{CH}_2\text{C}(\text{O})\text{O}-$); 1.69–1.65 ($-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{OCH}_2\text{CH}_2-$); poly(hexamethylene adipate): 4.05 ($-\text{C}(\text{O})\text{OCH}_2-$); 3.64 ($-\text{CH}_2\text{OH}$); 2.31 ($-\text{CH}_2\text{C}(\text{O})\text{O}-$); 1.65 ($-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{OCH}_2\text{CH}_2-$); 1.36 ($-\text{C}(\text{O})\text{OCH}_2\text{CH}_2\text{CH}_2-$); poly(octylene adipate): 4.04 ($-\text{C}(\text{O})\text{OCH}_2-$); 3.63 ($-\text{CH}_2\text{OH}$); 2.30 ($-\text{CH}_2\text{C}(\text{O})\text{O}-$); 1.64 ($-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{OCH}_2\text{CH}_2-$); 1.30 ($-\text{CH}_2-$); polydecamethylene adipate: 4.03 ($-\text{C}(\text{O})\text{OCH}_2-$); 3.63–3.61 ($-\text{CH}_2\text{OH}$); 2.30 ($-\text{CH}_2\text{C}(\text{O})\text{O}-$); 1.64 ($-\text{CH}_2\text{CH}_2\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})\text{OCH}_2\text{CH}_2-$); 1.28 ($-\text{CH}_2-$).

Synthesis of PETU

PETUs were synthesized by the polycondensation of PEDL and PUDL, using TBT (0.3 wt%) as the catalyst in a 250 mL four-necked flask equipped with a nitrogen inlet and a fractionating column. PEDL and PUDL were fed at a weight ratio of 70:30, and they were heated at 180 °C until they completely melt under mechanical stirring. Then the pressure of the system was gradually reduced to 20 Pa and maintained for 4–8 h to eliminate the side product diol. In order to obtain the PETU with similar molecular weight, the polycondensation lasted until the stirring rate decreased to 10 r/min under 125 V. The products were named as PETU6-4, PETU6-6, PETU6-8 and PETU6-10, respectively. The first number 6 in the nomenclature represents the carbon chain length of the dicarboxylic acid, adipic acid, and the second number indicates carbon chain length of diols employed to synthesize the PEDL soft segments.

^1H -NMR data (400 MHz, CDCl_3 , δ , ppm): (400 MHz, $\text{DMSO}-d_6$, δ , ppm): 7.02 ($-\text{NHC}(\text{O})\text{O}-$); 4.03 ($-\text{C}(\text{O})\text{OCH}_2-$); 3.92 ($-\text{NHC}(\text{O})\text{OCH}_2-$); 2.94–2.92 ($-\text{CH}_2\text{NH}-$); 2.29 ($-\text{CH}_2\text{C}(\text{O})\text{O}-$); 1.60–1.21 ($-\text{CH}_2-$).

Characterizations

The chemical structures of PETUs were characterized by NMR spectrometer (Bruker DMX-400) at a concentration of 10 mg/mL at ambient temperature, using $\text{DMSO}-d_6$ as the solvent.

The ATR-FTIR spectra of PETUs were recorded on a Thermo Nicolet Avatar 6700 FT-IR equipped with an attenuated total reflectance device (Smart Orbit). The samples were scanned 32 times with a resolution of 4 cm^{-1} from 400 cm^{-1} to 4000 cm^{-1} at room temperature.

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and dispersity ($\bar{D}$) were determined by GPC (Waters 2414). The measurements were taken at 45 °C, using DMF as eluent at a flow rate of 1.0 mL/min. The M_n was calculated by using a calibration curve with monodisperse polystyrene as standards.

A TA Instruments differential scanning calorimeter (Perkin-Elmer Pyris Diamond DSC Q200) was used for the thermal properties characterization of prepolymers and PETUs. The samples (3–5 mg) were first heated to 180 °C under N_2 atmosphere and held for 5 min to eliminate the thermal history. Then the samples were cooled to -70 °C at a rate of 200 °C/min. Thereafter, the samples were reheated to 180 °C at a rate of 10 °C/min and held for 5 min, then cooled to

-120 °C at the same rate to obtain heating and cooling curves.

Both wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) were tested with a Xeuss 2.0 system of Xenocs (France) using a Cu K α source ($\lambda=1.54$ Å). The sample to detector distance was 140.2 mm and 2500 mm for WAXD and SAXS test, respectively. Scattering patterns were collected by a semiconductor detector (Pilatus 300K, DECTRIS, Swiss). Each pattern was collected for 30 min. The samples were heated to 180 °C at a rate of 10 °C/min and held for 5 min under N_2 atmosphere to eliminate thermal history. Thereafter, the samples were naturally cooled to room temperature for WAXD and SAXS test. The cooling rate was estimated to be 3 °C/min.

Mechanical properties of PETUs were tested with a universal tester (Instron 1122, UK). The tensile strength and elongation at break of the specimens (75 mm $\times$ 4 mm $\times$ 2 mm) were measured according to ISO 527-5A at a crosshead speed of 50 mm/min. Each measurement was performed on five separate samples. The value was reported as the average of the five measurements. The specimens for these tests were prepared on an injection moulding machine (Haake Minijet, German). The temperatures of melting chamber and mould were set at 180 °C and 30 °C, respectively.

Atomic force microscope (AFM) measurements were carried out on a Digital Instrument Multimode Nanoscope adopting Scan Asyst mode. The PETUs solution (1 wt%) in formic acid were prepared to cast films. The films were heated to 180 °C at a rate of 10 °C/min and kept there for 5 min under N_2 atmosphere to eliminate thermal history before they were naturally cooled to room temperature for AFM experiments.

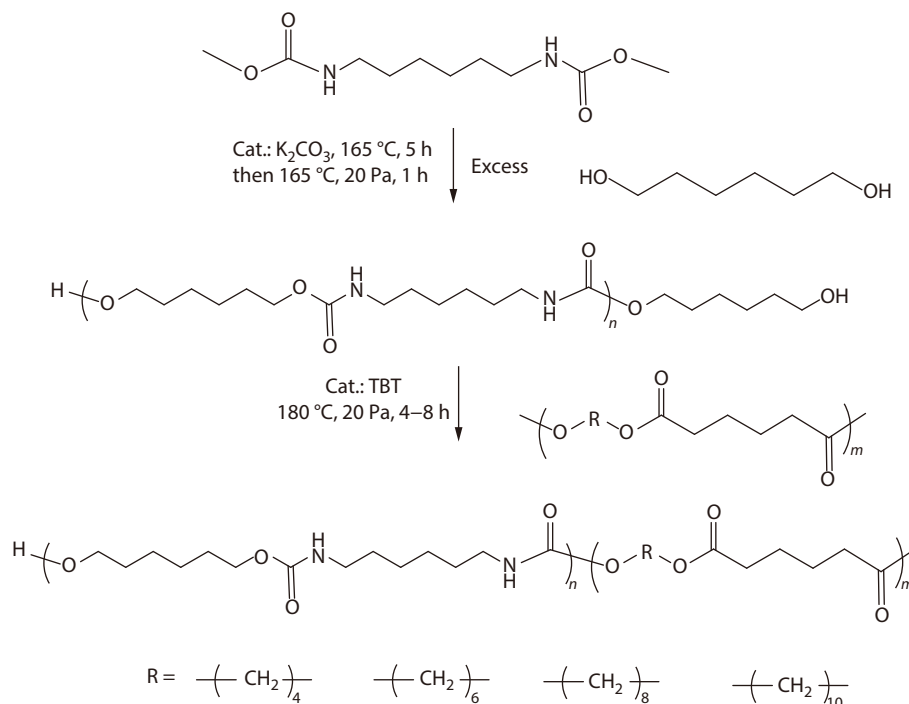
RESULTS AND DISCUSSION

Synthesis and Structural Characterization of PETUs

The synthetic route to non-isocyanate PETU is shown in Scheme 1. Firstly, bis-1,6-hexamethylencarbamate (BHC) reacted with excess HDO to obtain the hydroxyl-terminated PUDL, the hard segment of PETU. The chemical structures of PUDL were characterized by ^1H -NMR, and the polymerization degree was calculated to be 5.4.

Polyester soft segments of poly(butylene adipate) (PEDL6-4), poly(hexylene adipate) (PEDL6-6), poly(octylene adipate) (PEDL6-8) or poly(decylene adipate) (PEDL6-10) were synthesized from adipic acid and the corresponding diols with different carbon chain lengths. The chemical structures of polyester prepolymers were characterized by ^1H -NMR, and the polymerization degree was calculated from ^1H -NMR. Their molecular weight ranges can be calculated from the gross mass of end chains, mass of repeating unit and polymerization degree. The molecular weight of polyester prepolymers is listed in Table 1. It can be found that their molecular weights range from 1600 g/mol to 2000 g/mol.

The content of soft segment for the subsequent polymerization was set to be 70 wt%, and the feed ratio was calculated according to the polymerization degree of the soft segment and hard segment. PETU6-4 was set as an example to interpret the calculation of feed. The polymerization degree, repeating unit mass, and gross mass of end chains of PUDL are 5.4, 286 g/mol and 118, respectively. The polymerization

**Scheme 1** Synthesis routes.**Table 1** Molecular weight of prepolymers and polymers.

Sample	M_{nh} (g/mol) (PUDL)	M_{ns} (g/mol) (PEDL)	Weight fraction of hard segment	M_n (g/mol)	M_w (g/mol)	$\bar{D}^a$
PETU6-4	1656	1630	30%	4.1×10^4	8.6×10^4	2.1
PETU6-6	1656	1826	30%	3.5×10^4	8.1×10^4	2.3
PETU6-8	1656	1728	30%	4.2×10^4	1.09×10^5	2.6
PETU6-10	1656	1524	30%	3.6×10^4	1.08×10^5	3.0

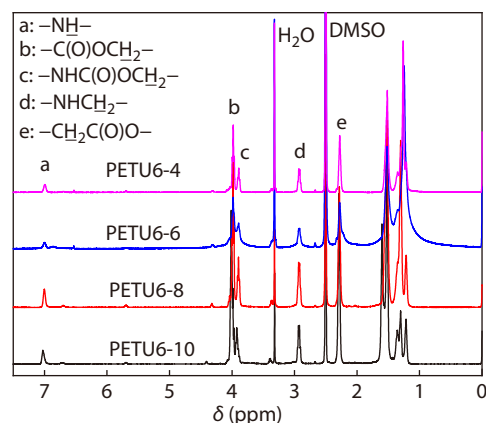
^a Dispersity values.

degree and repeating unit mass of PEDL6-4 are 7.7 and 200 g/mol. For synthesizing 40 g of PETU6-4, $\frac{40 \times 0.3}{286 \times 5.4} = 0.0078$ mol of hard segment should be fed. As the M_n of PUDL is deduced to be 1656 g/mol from $5.4 \times 286 + 118$, the feed amount of hard segment is $1656 \times 0.0078 = 12.9$ g. Similarly, feed amount of PEDL6-4 is calculated to be 29.6 g.

With the proceed of polycondensation of hard segment and soft segment at high temperature and high vacuum, the polymer chain length and molecular weight grow gradually along with the removal of the small diols. To synthesize PETUs with similar molecular weight, the polycondensation is stopped when the stirring rate achieves 10 r/min under 125 V. The obtained PETUs were named as PETU6-4, PETU6-6, PETU6-8, PETU6-10, respectively, in which the first number indicates the carbon chain length of adipic acid, while the second number represents the carbon chain length of diols employed to synthesize the polyester soft segments.

The chemical structures of PETUs were characterized by $^1\text{H-NMR}$ spectra. As shown in Fig. 1, the $^1\text{H-NMR}$ spectra of the four samples are almost the same except the peaks at 1.60–1.21 ppm, arising from the $-\text{CH}_2-$ on the residue groups of diols in the repeating unit of soft segment. The resona-

nce signals at 7.02 ppm ($-\text{NHC(O)O}-$), 3.92 ppm ($-\text{NHC(O)OCH}_2-$) and 2.94–2.92 ppm ($-\text{CH}_2\text{NH}-$) are attributed to the repeating unit of hard segment; while the strong peaks at 4.03 ppm ($-\text{C(O)OCH}_2-$), 2.29 ppm ($-\text{CH}_2\text{C(O)O}-$) and 1.60–1.21 ppm ($-\text{CH}_2-$) belong to the methylene protons of the repeating unit of soft segment. Based on the above results, it can be safely concluded that PETUs possess the chemical structure of polyester soft segment and the urethane hard segment, and the polycondensation just proceeded in the way we designed.

**Fig. 1** $^1\text{H-NMR}$ spectra of PETUs.

Furthermore, two peaks at 5.7 and 6.7 ppm of $-\text{NH}-$ on urea can be observed from Fig. 1, suggesting the side reaction occurs under high temperature during the polycondensation. As reported in our previous study, there are two possible reasons for the formation of urea groups.^[45] First, during

the synthesis of PUDL, the terminal amine, resulting from the reaction between terminal hydroxyl and carbamate group on BHC, reacts with another carbamate group to form a urea group. Second, a urea group was formed by the carbamate metathesis polymerization of two dialkyl carbamate groups.^[44,45]

The chemical structures of PETUs are further characterized by ATR-FTIR spectra, and the results are presented in Fig. 2. All the four PETU samples display the two stretching vibration bands of N—H, at 3381 and 3324 cm^{-1} , respectively. As the free stretching vibration band of N—H is around 3450 cm^{-1} , these two peaks can be attributed to hydrogen bonded bands of N—H. The band at 3381 cm^{-1} is originated from the N—H that form hydrogen bonds with C=O on soft segment; 3324 cm^{-1} is attributed to the N—H that form hydrogen bond with C=O on hard segment. It should be noted that with the increase of carbon chain length of the repeating unit of soft segment, the band intensity at around 3381 cm^{-1} decreases gradually, which may be due to the reduction of the density of C=O of soft segment. The characteristic bands at 1726 and 1679 cm^{-1} arise from the C=O stretching of polyester soft segment and polyurethane hard segment (hydrogen bonded), respectively; while the bands at 1527 cm^{-1} can be ascribed to N—H bending vibration. The ATR-FTIR spectra also suggest that the synthesized PETUs possess the chemical structure of polyester soft segment and the urethane hard segment. A weak peak can be found around 1662 cm^{-1} , which is originated from the hydrogen bonded C=O of urea in ordered phase. As the peak of free C=O of urethane hard segment, at 1720 cm^{-1} , is very close to that of soft segment (1726 cm^{-1}), it is very difficult to separate from each other. Therefore, it is impossible to evaluate fraction of H-bonded urethane groups in hard segment and degree of the phase separation. PETU6-4 shows a most evident peak at 1662 cm^{-1} , implying the fact that it has the highest content of urea.

Molecular weight is a key parameter for polymers as it determines the mechanical properties, which is very important for the application of the end products. The molecular weight

of PETUs was tested on GPC, and the results are listed in Table 1. The molecular weight of polyester soft segment and the polyurethane hard segment, calculated from $^1\text{H-NMR}$, and the weight fraction of hard segment, are also given in Table 1. It should be noted that the weight average molecular weight of all the four PETU samples, ranging from 8.1×10^4 g/mol to 1.09×10^5 g/mol, is higher than 8×10^4 g/mol, and that of PETU6-8 and PETU6-10 is even higher than 1×10^5 g/mol, which is high enough to ensure the mechanical properties for the application. Generally, the low reactivity of cyclic carbonate and subsequent low molecular weight of synthesized PU are the major problems faced by the synthesis of NIPUs, which are the main reasons that prevent their true application and industrialization. The data in Table 1 suggest that DMC based non-isocyanate route is an effective strategy to achieve high molecular weight poly(ester urethane). Considering the low cost of DMC, the high molecular weight, and no solvent involved, this approach is very promising to be industrialized to replace the isocyanate route to synthesize polyurethane. In this work, the number average molecular weight of PETUs was controlled to be as close as possible, between 3.5×10^4 and 4.2×10^4 g/mol, to eliminate the effect of molecular weight on thermal properties and mechanical properties. As displayed in Table 1, dispersity value ($\bar{D}$) of PETUs lies between 2.1 and 3.0.

Thermal Properties and Crystallization Behavior of PETUs

Thermal properties of prepolymers and PETUs were studied by DSC, and the obtained heating curves and cooling curves are shown in Figs. 3 and 4, respectively. The basic parameters, including glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c), and enthalpy of crystallization (ΔH_c), were listed in Table 2. It can be found from Fig. 3 and Table 2 that both PUDL and PEDLs are crystallizable. The T_m of PEDL (T_{m1}) lies between 30 and 71 $^{\circ}\text{C}$, and increases steadily with increasing chain length of diols. The ester bonds in the polyester can be regarded as the defect and reduce the regularity of macromolecular chains, as compared with polyethylene. The higher melting point of polyesters with longer chain length of diols is due to the increased regularity of macromolecular chains. ΔH_c also follows the same trend, suggesting that their degree of crystallinity increases with increasing chain length of repeating unit. No glass transition can be observed except PEDL-4 in the heating curve, which is due to the fact the crystallization rate of the three other samples is so fast that they still have relatively high crystallinity degree after quenching. PEDL-4 has two melting points, which may be due to the presence of two types of crystals.^[49] On the other hand, the synthesized PUDL has a much higher melting temperature at 150 $^{\circ}\text{C}$ and T_g at 6 $^{\circ}\text{C}$ because of its inner rigidity of macromolecular chains. To sum up, both PEDL and PUDL employed to construct the soft segment and hard segment of PETUs are crystallizable prepolymers, and their T_g s are well below the room temperature.

The second heating curves of the synthesized PETUs obtained from polycondensation of PEDL and PUDL is shown in Figs. 3 and 4. During the heating process, all the four PETU samples have one T_g and two T_m s, originating from the melting of soft segment and hard segment, respectively. A great part of melting peak of soft segment coincides with that of

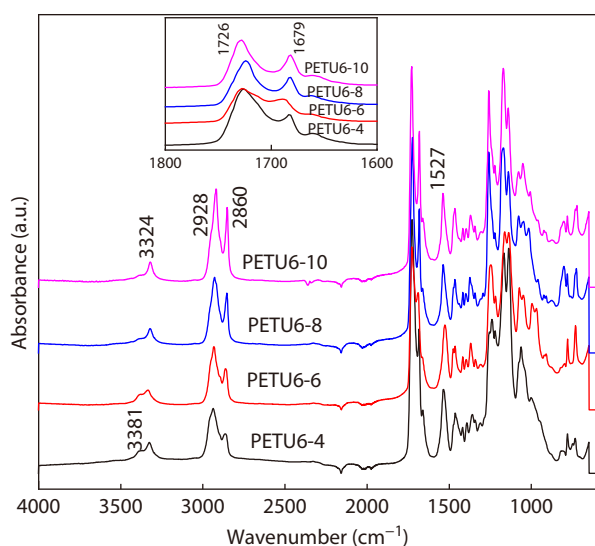


Fig. 2 ATR-FTIR spectra of PETUs.

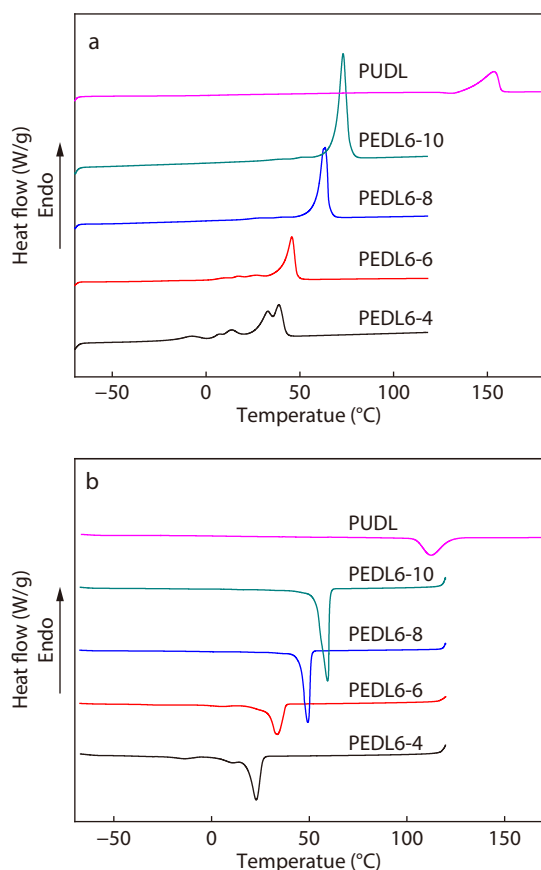


Fig. 3 DSC heating scans (a) and cooling scans (b) of PUDL and PEDLs.

hard segment. As far as glass transition is regarded, T_g of PETUs lies between -50 °C and -41 °C, which is well below the room temperature. Therefore, good properties of these PETUs under low temperature will be expected. The evidently higher T_g as compared with that of the prepolymers of the soft segment implies that part of hard segment is dissolved in the amorphous soft segment, which restricts the movement of the macromolecular chain of soft segment and increases the T_g . As compared with the prepolymers, the melting temperature of hard segment in PETUs decreased evidently, while that of the soft segment increase slightly. It is difficult to calculate the melting enthalpy of each segment as their peaks overlap largely. As far as PETU6-4 is regarded, a cold crystallization peak appears, and a very weak melting peak of hard segment appears due to its low crystallization rate and crystallinity.

The crystallization enthalpy of PETUs in Table 2 is substantially lower than that of PUDL or corresponding PEDL, implying the largely restricted crystallization of both segment and relatively high degree of phase mixing in the polymer.

Fig. 4(b) shows the cooling curves of the four PETU samples. No evident crystallization peak can be observed for PETU6-4. All the other three samples display an evident crystallization peak, and PETU6-6 has the highest crystallization temperature. It may be due to the fact that the hard segment and soft segment in PETU6-6 can form cocrystals as their chemical structure is similar to each other.

WAXD experiments were further performed to study the

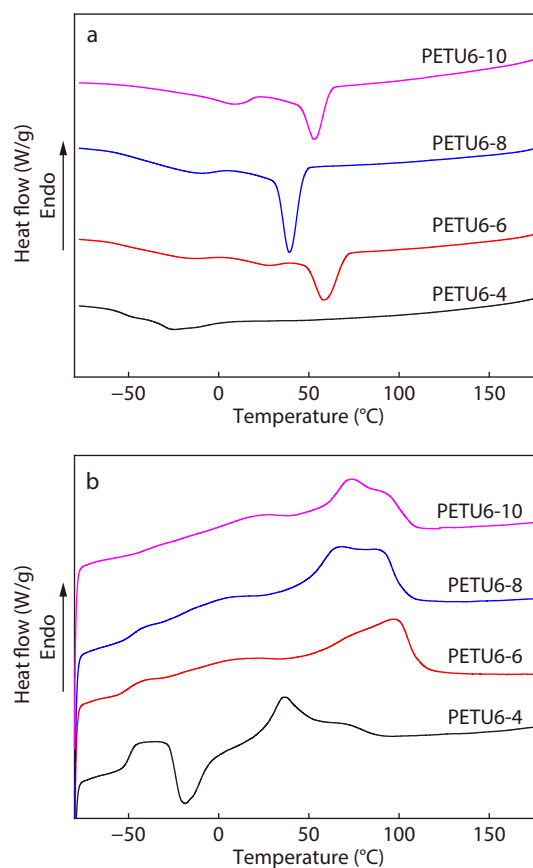


Fig. 4 DSC heating scans (a) and cooling scans (b) of PETUs.

Table 2 Thermal properties of PEDLs, PUDL and PETUs.

	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	T_c (°C)	ΔH_c (J/g)
PEDL6-4	-73	30, 37	—	19	51
PEDL6-6	—	44	—	32	81
PEDL6-8	—	61	—	48	101
PEDL6-10	—	71	—	56	118
PUDL	6	—	150	112	70
PETU6-4	-50	37	73	—	—
PETU6-6	-49	—	99	60	21
PETU6-8	-49	66	92	39	23
PETU6-10	-41	73	95	54	27

crystal structure of PETUs. The WAXD patterns of prepolymers were also tested for comparison. Before the WAXD test, the samples were firstly heated to melting state and then cooled to room temperature naturally. As shown in Fig. 5, all the four PETU samples show similar diffraction peaks. The strongest diffraction peak appears at 21.5° , which is very close to one of the characteristic peaks of PUDL (21.9°). Another characteristic peak at 24.3° is also close to that of PUDL (24.3°). Due to the low crystallinity degree, the characteristic diffraction peaks of the soft segment cannot be observed, which may be because they are so weak that are overlapped by that of the hard segment.

Morphology of PETUs

SAXS is regarded to be a useful method to investigate the phase separated structure of PETUs. Herein, the hard segment of PETUs is PUDL, originated from BHC and chain extender HDO,

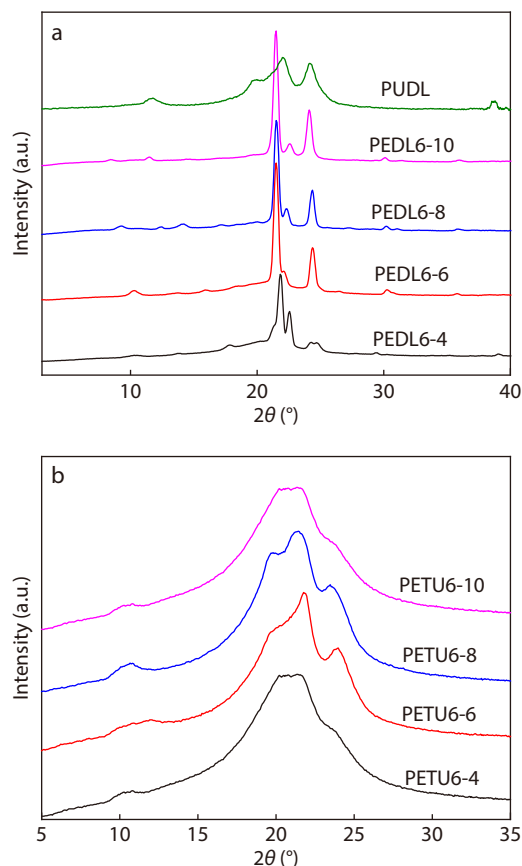


Fig. 5 WAXD patterns of PEDL, PUDL and PETUs.

and the soft segment is polyester diols of PEDL6-4, PEDL6-6, PEDL6-8 or PEDL6-10, derived from the polycondensation of adipic acid and different diols. As discussed above, the hydrogen bond can form between the —NH on hard segment and C=O on soft segment, besides the covalent bonds. Hydrogen bond density decreases gradually and the crystallizability increases from PETU6-4 to PETU6-10 with decreasing C=O density in soft segment. Theoretically, the reduction in hydrogen density between soft segment and hard segment is beneficial to the enhancement of phase separation between soft segment and hard segment. SAXS patterns of PETUs are shown in Fig. 6 and the obtained domain parameters are summarized in Table 3. As shown in Fig. 6, the characteristic scattering peak of PETU6-4 is weak, implying its low degree of phase separation, which arises from its highest degree of C=O in the soft segment and the strongest hydrogen interaction between the soft segment and hard segment. The three other samples show evidently stronger SAXS scattering peaks, suggesting higher degree of phase separation. As crystallinity also largely affects the phase separation degree besides the hydrogen interaction between soft segment and hard segment, there is no evident difference among the SAXS patterns of PETU6-6, PETU6-8 and PETU6-10.

The morphology of PETUs was further studied in real space by AFM, and the resulted height images of the PETU films are given in Fig. 7. Although both the soft segment and hard segment are crystallizable, no evident spherulitic structure can be found on the surface of PETU, lamellar morphology (part

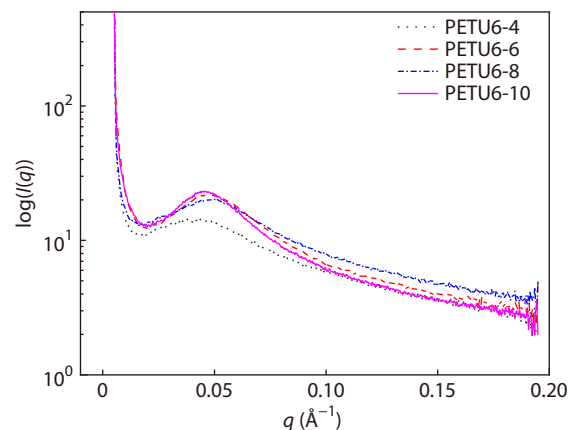


Fig. 6 SAXS patterns of PETUs

Table 3 Domain parameters of PETUs.

Sample	$q_{\max}$ ($\text{\AA}^{-1}$)	d (nm)
PETU6-4	0.0434	14.4
PETU6-6	0.0500	12.6
PETU6-8	0.0502	12.5
PETU6-10	0.0448	14.0

of the spherulite) can be observed for PETU6-4, PETU6-8 and PETU6-10. As these patterns are similar to the lamellar structure of aliphatic polyester observed by AFM and TEM in the references,^[50,51] they can be considered to be the lamellar crystals of the soft segment. As far as PETU6-6 is concerned, its height images displayed the fibrous patterns, which is similar to the morphology of hard segment observed by Wilkes *et al.*^[52] As analyzed before, as the soft segment can form cocrystals with hard segment in PETU6-6 due to their very similar chemical structures, the crystal structure of PETU6-6 is different from those of traditional aliphatic polyesters, and only the morphology similar to hard segment is displayed.

Tensile Strength of PETUs

The mechanical properties of PETUs are evaluated by tensile test. All the PETU samples showed good processability during injection molding. The tensile strength, tensile modulus and elongation at break are listed in Table 4. As displayed in Table 4, the tensile strength of PETUs ranges from 6.9 MPa to 10.1 MPa, while elongation at break lies between 137%–673%. PETU6-6 possesses the highest tensile strength and modulus due to the similar chemical structure of the soft segment and the hard segment, and the resulting cocrystals. PETU6-4 has the lowest tensile strength and the highest elongation at break due to its lowest crystallinity degree, which has been testified by the DSC data, and its highest content of phase mixing. For NIPUs, the PEG based NIPU has the highest extent of phase mixing and lowest mechanical properties and the tensile strength is undetectable.^[11] The lowest elongation at break of PETU6-10 is originated from its highest crystallinity degree, which can be evidenced by the highest ΔH_c .

Due to the good processability, mechanical properties and non-toxic substance or solvent involved during the synthesis, these PETUs in this work have great potential to be applied as biodegradable elastomers for medical implants such as vascular stents.

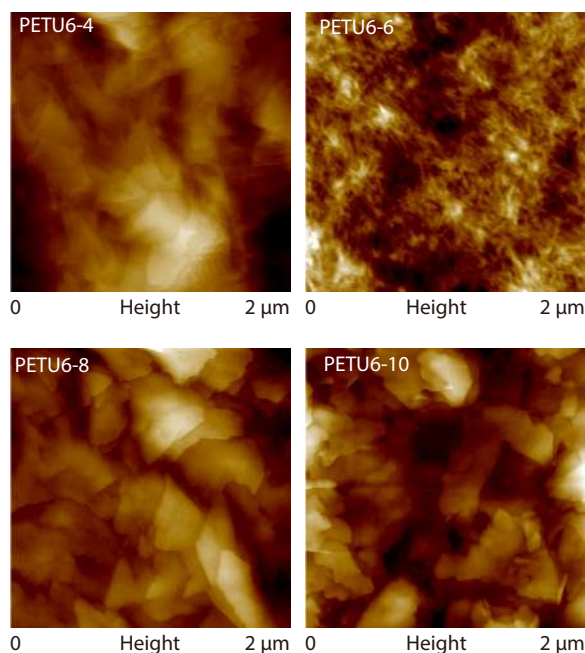


Fig. 7 AMF images of PETUs.

Table 4 Mechanical properties of PETUs.

Sample	σ_b (MPa)	E (MPa)	ε_b (%)
PETU6-4	6.9±1	36±8	673±35
PETU6-6	10.1±1	55±4	568±32
PETU6-8	9.0±0.8	47±4	551±25
PETU6-10	8.8±0.1	52±5	137±23

CONCLUSIONS

This study developed a novel non-isocyanate and solvent-free route for the synthesis of high molecular weight PETUs based on DMC for the first time. The hard segment of polyurethane is synthesized from dimethyl carbonate, 1,6-hexanediamine and 1,6-hexanediol. A series of polyester soft segments of polyurethane have been synthesized from the polycondensation of adipic acid and different diols, including butanediol, hexanediol, octanediol and decanediol. The subsequent polycondensation of polyurethane diol and polyester diol led to linear poly(ester urethane). It should be noted that the PETUs possess weight-average molecular weight higher than 1×10^5 and the tensile strength as high as 10 MPa. The thermal properties, crystallization behavior, microphase separation behavior and morphology were studied, and the results indicate that degree of phase separation is affected by two factors, the crystallization and hydrogen bonding interaction between soft segment and hard segment. As the C=O density on the soft segment of PETU6-4 is the highest among the four samples, C=O on the soft segment of PETU6-4 can form the strongest hydrogen with the hard segment. Therefore, both the crystallization of the soft segment and the hard segment are seriously restricted and the degree of phase separation of PETU6-4 is lowest among the four samples. As a result, PETU6-4 has the lowest melting temperature, lowest tensile strength and highest elongation at break. The three other samples of PETU6-6, PETU6-8 and PETU6-10, with reduced

C=O density on soft segment and relatively higher degree of phase separation, displayed relatively higher melting temperature and tensile strength. The elongation at break is mainly dominated by crystallinity degree. The PETU6-4 shows the highest elongation at break due to its poor crystallizability, while PETU6-10 possesses the lowest elongation at break due to its highest crystallinity degree.

NOTES

The authors declare no competing financial interest.

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