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Polyether-polyester and HMDI Based Polyurethanes: Effect of PLLA Content on Structure and Property

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Electronic Supplementary Information

Abstract Thermoplastic poly(ether-ester-urethane)s were synthesized from poly(L-lactide) diols (PLLA diols), polytetrahydrofuran diol (PTMG diols), 4,4'-dicyclohexylmethane diisocyanate (HMDI), and 1,4-butanediol (BDO) by a two-step reaction, and the morphology and property of the resultant TPU could be adjusted by varying the PLLA contents. The soft segment was composed of PLLA and PTMG diols. By controlling the percentage of PLLA in the soft segment, the glass transition temperature and mechanical properties of the polyurethanes could be regulated. Based on the FTIR spectrum, we found that two kinds of hydrogen bonding existed individually in soft matrix and hard domain. The hydrogen bonding in soft matrix was unstable, which could be destroyed during elongation. With *in situ* stretching WAXS and SAXS experiments, we found that the PLLA crystal was destroyed and the PLLA domain oriented along the stretch direction. Finally, we proposed a schematic model to illustrate the microstructures of these elastomers before and after stretch.

Keywords Poly(L-lactide) diol; Polyurethane; Mechanical property; Hydrogen bonding

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INTRODUCTION

Thermoplastic elastomers (TPE) are block copolymers of which the microphase can be separated into hard and soft domains. The hard segments aggregate to form the hard phase or hard domain. The soft matrix provides elasticity, while the hard phase, in glass or crystalline state, acts as the physical crosslinking site.^[1] Thermoplastic polyurethane (TPU), a sub-category of TPEs, exhibits excellent flexibility, good abrasion and tear resistance, high strain to failure, and moderate tensile properties. The aggregated hard segments play the role in physical crosslinking point, and the free hard segment acts as the high modulus filler in the soft matrix. Like other TPEs, the soft matrix provides extensibility.^[2–5] The mechanical properties of TPUs mainly depend on the chemical species of soft and hard segments, the molar ratio between soft and hard components, and the microphase separated morphology. In fact, the mechanical behavior of TPU varies from soft elastomer to hard plastic.^[6–11]

Aromatic polyurethanes are widely used because of their

high elastic modulus, strong tensile strength, and good recoverability. The good mechanical properties derive from the deep microphase separation and the strong hydrogen bonding interaction between the hard segments.^[12] Unfortunately, the aromatic units would be activated by the ultraviolet (UV) light and decomposed into carcinogenic byproducts, such as 4,4'-methylene dianiline (MDA).^[13] Transparent TPU would become yellowish after such decomposition and the color could restrict their applications in some areas like biomedical and medical. On the contrary, aliphatic polyurethanes do not have such disadvantage. However, they suffer from the troubles like low elastic modulus, weak tensile strength, and poor recovery ratio. The relatively poor mechanical property could be attributed to the lack of rigid chemical unit and the absence of strong hydrogen bonding interaction.^[14] For example, polytetrahydrofuran (PTMG) and 4,4'-dicyclohexylmethane diisocyanate (HMDI) based PU is usually soft and flexible. This is because the aliphatic PUs are commonly lack of rigid chemical units and deep microphase separation.^[15] In order to solve the problems above, it is a worthwhile attempt to embed polyester component into the soft segment of polyurethane.

Poly(L-lactide) (PLLA),^[16–20] an aliphatic polyester derived from renewable resources like corn, can be degraded into carbon dioxide and water. Simultaneously, PLLA shows good mechanical strength that facilitates its application as

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bio-assimilable sutures and drug-loading devices.^[21–24] Considering the above advantages, the addition of PLLA diol may endow the aliphatic polyurethane with improved mechanical strength and degradability. However, the PLLA diol alone is probably not suitable as the soft segment in polyurethane. For example, Gu *et al.*^[25] synthesized PLLA-based polyurethanes with HMDI as the hard segment, and the obtained sample showed high elastic modulus (around 850 MPa) but low elongation at break of 4%. Clearly, single PLLA diol as the soft segment could not balance the mechanical strength and elasticity, and the resultant polyurethane was not an elastomer at all. It seems that the simultaneous use of rigid PLLA segment and flexible component may be a good option for the preparation of polyurethane elastomer. At room temperature, low molecular weight PLLA segments are in glass state. The glass state PLLA segment could play the role of high modulus filler and support good mechanical property. In this way, the mechanical properties can be adjusted by varying the molar ratio between the two different soft segments.^[26]

In this study, we synthesized a series of thermoplastic polyether-polyester-based polyurethane elastomers by using PLLA diol and PTMG as the soft segments, while HMDI and the chain extender 1,4-butanediol (BDO) acted as the hard segments. With such molecular selections, PTMG soft segment could provide flexibility and PLLA segment could endow the polyurethane with additional strength. The mechanical properties and the recovery capability of the resultant polyurethanes could be adjusted by varying the molar ratios of PLLA to (PLLA + PTMG), and the effect of soft segment composition on the morphology of PU was discussed. It indicated that the simultaneous use of flexible and relatively rigid components as the soft segment was an efficient way to balance the properties of aliphatic diisocyanate-based polyurethane.

EXPERIMENTAL

Materials

Commercially available reagents were used without further purification unless otherwise stated. L-lactide (L-LA) was purchased from Shenzhen Esun Industrial Co., Ltd. and was recrystallized in ethyl acetate before use. Stannous octoate (Sn(oct)₂, 95%) and HMDI were purchased from TCI-China Co., Ltd. BDO and PTMG diol ($M_n = 650 \text{ g}\cdot\text{mol}^{-1}$) were purchased from Aladdin Industrial Corporation, China. Toluene and ethyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. Toluene was distilled before use.

Synthesis of PLLA Diol

PLLA diol was prepared *via* ring-open polymerization.^[27] L-LA and BDO (L-LA:BDO = 23:1, mol:mol) were added into a 250 mL, four-necked flask under dry nitrogen atmosphere. Then, they were heated from room temperature to 125 °C with mechanical stirring and kept at 125 °C until the mixture was completely melted. Later, Sn(oct)₂ (0.3 mol% of the L-LA) was added as the catalyst. After that, the reactants were heated to 160 °C and kept for 2 h. The resultant product was purified by dissolving in chloroform and precipitation in excess and cold methanol. The purified product was dried in a vacuum oven to yield white powders at 70 °C for 48 h. Molecular weight of PLLA diol was characterized by ¹H-NMR and GPC.

Synthesis of PLLA-PU Pre-polymer

The pre-polymer was synthesized as follows. Under dry nitrogen atmosphere, PTMG diol, PLLA diol, Sn(oct)₂, and toluene were mixed with mechanical stirring in a flask for 1 h at 70 °C. Then, HMDI was added and the reaction was continued with stirring for another 2 h at 70 °C to afford the pre-polymer. HMDI was added in the weight ratio of 0.7:1 with (PLLA diol + PTMG diol).

Chain Extension of Polyurethane

A chain-extension reaction was carried out to prepare high M_w PLLA-PU, and BDO was used as the chain extension diol. BDO, with molar amount equal to the molar number of isocyanate group in the pre-polymer, was added into the flask. The reaction mixture was stirred at 80 °C for 5 h under dry nitrogen atmosphere. After the reaction was completed, the polymer solution was collected and poured into excess and cold methanol to obtain precipitated polyurethane. At last, the sample was dried in a vacuum oven at 45 °C for 48 h to remove the residue solvent.

Five different PLLA-PU samples were obtained with different weight ratios of PLLA diol to PTMG. They were named as 0%-PU, 9%-PU, 23%-PU, 34%-PU, and 41%-PU, respectively. *x*%-PU means that the weight ratio of PLLA in the soft segment was *x*%. The compositions and molecular weights of the PUs are summarized in Table 1. In order to study the effect of PLLA content on the properties and morphology of polyurethane, the hard segment contents of all samples were controlled in the range of 44 wt%–46 wt%. A 0.5 mm thick film prepared by solvent evaporation was used in all the tests in this work.

Characterization

The number-average molecular weight (M_n) and the molecular weight distribution (PDI) were measured at 40 °C by

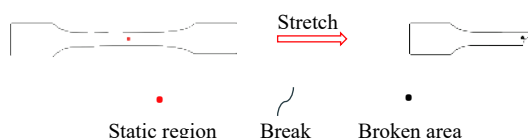
Table 1 Characteristics of the PLLA-PU polymers in this study

Sample	Hard segment content (wt%)	PLLA:(PLLA + PTMG) ^a (<i>W:W</i>)	$M_n^a \times 10^{-4}$ (g·mol ⁻¹)	$M_n^b \times 10^{-4}$ (g·mol ⁻¹)	$M_w^b \times 10^{-4}$ (g·mol ⁻¹)	PDI ^b
PLLA	—	—	0.32	0.36	0.43	1.2
0%-PU	44.1	0	—	2.4	5.0	2.1
9%-PU	44.6	8.51	—	4.0	8.9	2.2
23%-PU	45.3	22.8	—	3.1	5.7	1.8
34%-PU	45.7	34.1	—	3.0	6.3	2.1
41%-PU	46.1	40.9	—	2.8	5.0	1.8

^a Characterized by ¹H-NMR; ^b Characterized by GPC

GPC (Agilent PL-GPC220). 10 mg of PLLA-PU sample was dissolved in 10 mL of tetrahydrofuran to prepare a solution with concentration of $1 \text{ mg} \cdot \text{mL}^{-1}$. Tetrahydrofuran was used as the mobile phase at a flow rate of $1 \text{ mL} \cdot \text{min}^{-1}$. Polystyrene standards ($3070\text{--}258000 \text{ g} \cdot \text{mol}^{-1}$) were adopted for calibration.

As illustrated in Scheme 1, a dumbbell-shaped specimen of PLLA-TPU will break when the strain is large enough. Since we are interested in samples in both static region and broken area, the thermal and structural characterizations were carried out for the two types of samples.



Scheme 1 Samples in static and fracture areas of dumbbell-shaped specimens

Thermal behavior was recorded by a differential scanning calorimeter (PerkinElmer Diamond DSC) equipped with a liquid nitrogen cooling accessory under a nitrogen flow of $50 \text{ mL} \cdot \text{min}^{-1}$. The heating rate for all the experiments was fixed at $10 \text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$, and the samples were heated from $-60 \text{ }^{\circ}\text{C}$ to $200 \text{ }^{\circ}\text{C}$ in the first heating scan.

Tensile tests were performed on dumbbell-shaped specimens ($35 \text{ mm} \times 2 \text{ mm} \times 0.5 \text{ mm}$) using Instron 5567 tensile testing machine under room temperature. The crosshead speed was set at $100 \text{ mm} \cdot \text{min}^{-1}$. At least five specimens were tested for each sample according to GBT 528-2009.

Cyclic tensile test was performed by manipulating a sample in a cyclic way with a maximum deformation of 500%. The dumbbell-shaped splines were stretched at a rate of $100 \text{ mm} \cdot \text{min}^{-1}$ and retracted at a rate of $50 \text{ mm} \cdot \text{min}^{-1}$ for five cycles. At least five specimens were tested for each sample.

FTIR spectra were recorded on an attenuated total reflect-

ance-Fourier transform infrared (ATR-FTIR) (Agilent Cary 600 Series FTIR) spectrometer. The scan range was set from 500 cm^{-1} to 4000 cm^{-1} and each sample was scanned for 32 times. The static region before elongation and the broken area after stretch of PLLA-PU samples were examined to explore the effect of macroscopic breakage on the microstructure. Using a base-line technique, the peak absorbance A at the frequency of maximum absorption is given by:

$$A = I/I_0 \quad (1)$$

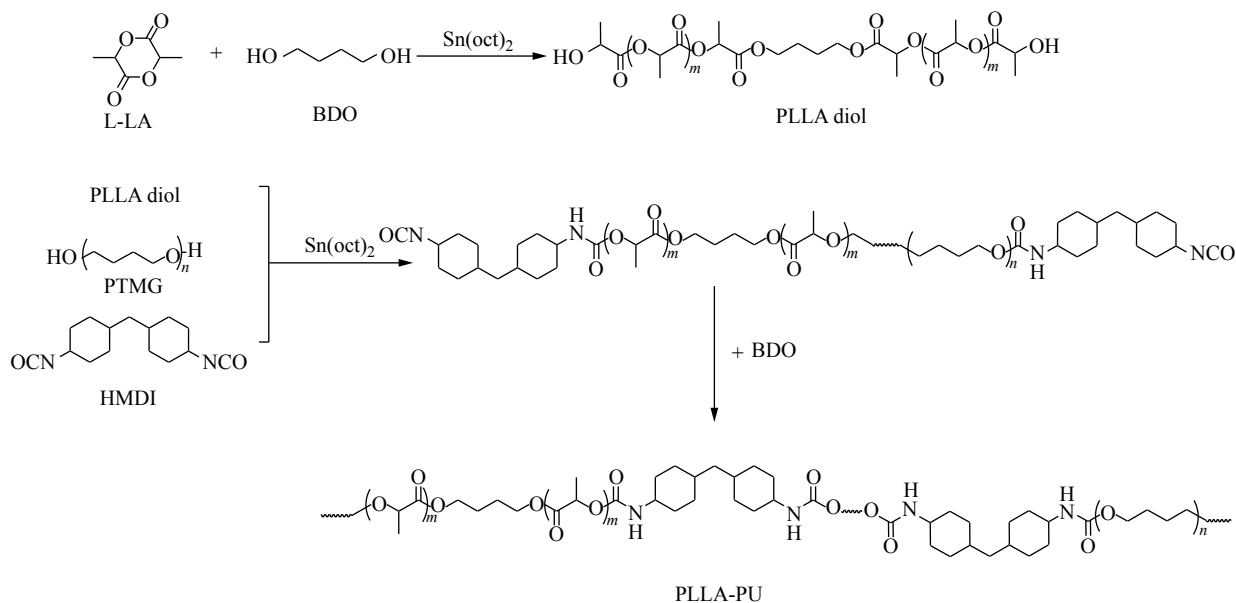
where I_0 is the base-line intensity and I is the intensity of the transmitted radiation.

Small angle X-ray scattering (SAXS) and wide angle X-ray scattering (WAXS) experiments were conducted at the beamline BL16B1 of Shanghai Synchrotron Radiation Facility with X-ray wavelength of 0.124 nm . For recording of the two-dimensional patterns, Mar 165 CCD detector (pixel size = $80 \text{ }\mu\text{m}$) was used. The distances between detector and sample were 2000 mm for SAXS and 164.43 mm for WAXS. All data were corrected for the air scattering and the background scattering.

RESULTS AND DISCUSSION

Synthesis of PLLA Diol and PLLA-PU

A series of PLLA-PU polymers containing PLLA diol and PTMG diol as the soft segment were prepared *via* a two-step reaction (Scheme 2). PLLA diol was synthesized by the ring-open polymerization method using BDO as the initiator and $\text{Sn}(\text{oct})_2$ as the catalyst. The pre-polymers were synthesized through the reaction between PLLA ($M_n = 3600 \text{ g} \cdot \text{mol}^{-1}$) and PTMG diols ($M_n = 650 \text{ g} \cdot \text{mol}^{-1}$) with HMDI, and PLLA-TPUs were subsequently obtained by a chain extension reaction using BDO as the chain extender. The weight ratio of PLLA diol to (PLLA + PTMG) diol was systematically changed from 0% to 41%, which facilitated to study the effect of soft segment composition on the physical properties



Scheme 2 Synthesis of PLLA-PU from PLLA diol, PTMG diol, HMDI, and BDO

of PLLA-PU samples. At the same time, the weight ratio of hard segment was controlled between 44% and 46% in all samples. Table 1 summarizes the molecular information of the PLLA-PU polymers. Clearly, high molecular weight PLLA-PU were successfully obtained. Fig. S1 (in the electronic supplementary information, ESI) presents GPC curves of the polymers, while Figs. S2 and S3 (in ESI) show the ^{13}C -NMR and ^1H -NMR spectra of PLLA diol and PLLA-PU, demonstrating the successful synthesis of the PLLA-PU.

Thermal Properties of PLLA-PU

Thermal properties of the PLLA diol and the PLLA-PU, obtained from the 1st DSC heating scan, are summarized in Table 2. The glass transition temperature (T_g) and the melting temperature (T_m) monotonically increased with the increasing content of PLLA and gradually approached the corresponding temperatures of neat PLLA diol. Such phenomenon implied good microphase separation between PLLA segment and other components.^[28] The glass transition temperature of hard domain was not found in DSC experiment, which might imply the weak microphase separation of hard segments.^[29] ΔH_m^1 was the melting enthalpy of PLLA-PU before stretch, including the enthalpy of the melting of PLLA crystals and the destruction of hard segments aggregation. As presented by the 1D-WAXS curves in Fig. S4(d) (in ESI), there were no PLLA crystals in the broken area of PLLA-PU. Therefore, ΔH_m^2 was just the enthalpy of the hard segment aggregation.^[30]

The uniaxial stretch could destroy the PLLA crystal and hard domain in PLLA-PU, but it had limited effect on the degree of hydrogen bonding association. In other words, the degree of microphase separation kept almost the same even if the domain structure was altered. Therefore, the melting enthalpy of PLLA could be calculated by subtracting ΔH_m^2 from ΔH_m^1 , and the crystallinity (X_c) of PLLA could be obtained according to the following equation:^[31]

$$X_c = \frac{\Delta H_m^1 - \Delta H_m^2}{100 \text{ J} \cdot \text{g}^{-1}} \times 100\% \quad (2)$$

The fusion enthalpy of PLLA crystals having infinite crystal thickness was taken as $100 \text{ J} \cdot \text{g}^{-1}$.^[19] It can be seen from Table 2 that the crystallinity also increased with the content of PLLA. Nevertheless, the crystallites in PLLA-PU were vulnerable and could be destroyed easily after large strain stretch.

Mechanical Behaviors of PLLA-PU

Typical tensile curves of PLLA-PU are displayed in Fig. 1, and the tensile properties of PLLA-PU are summa-

rized in Table 3. The PLLA content affected Young's modulus and tensile strength of the polyurethanes significantly. 41%-PU displayed the highest elastic modulus of 110 MPa and tensile strength of 38 MPa among all the samples. PLLA amorphous region, which possessed much higher T_g than that of PTMG, together with PLLA crystals acted as the filler in the soft matrix and improved the modulus and strength of elastomers. Interestingly, the elongation at break decreased drastically when the PLLA content was as low as 9%. The elongation at break for 0%-PU was ~1300%, but it decreased sharply to 670% for 9%-PU. The PLLA domains acted as the cross-link points as well, which constrained the mobility of flexible chains and reduced the elongation at break drastically. Another interesting fact was that when the PLLA content was higher than 9%, the elongation at break became insensitive to the composition of PLLA. It seemed that the cross-linking density in PLLA-PU grew slowly with the PLLA content. Such fact might imply that the number of PLLA domains remained almost unchanged even with the increasing content of PLLA.

Another noteworthy observation was the double yielding phenomenon during the elongation process. When the content of PLLA was higher than 9% in the soft segment, a second yielding point appeared. The first yielding point could be related to the destruction of PLLA crystals, as reported by Mandelkern *et al.*^[32,33] With the increasing PLLA content and PLLA crystallinity, the yielding stress at the first yielding point became higher and higher. As discussed above, the strain-induced crystallization of PLLA did not happen in these elastomers. Therefore, it was possible that the second yielding point might relate with the orientation of chain segment and PLLA domains.

Cyclic stretch experiment was helpful in getting more structure-property information about these elastomers. Fig. S5 (in ESI) and Table 4 show the cyclic tensile behaviors of the five polyurethanes. Five cycles of stretch and recovery were applied to each sample with strain of 500%, strain rate of $100 \text{ mm} \cdot \text{min}^{-1}$, and recovery rate of $50 \text{ mm} \cdot \text{min}^{-1}$. The recovery ratio was calculated according to Eq. (3):

$$R_n = \frac{(l_n - l'_n)}{l_n} \times 100\% \quad (3)$$

where R_n is the recovery ratio of the n^{th} cycle tensile, l_n is the maximum strain of the n^{th} cycle tensile, and l'_n is the minimum strain of the n^{th} cycle tensile at zero stress in the unloading cycle.

As can be seen from Fig. 1, except 0%-PU and 9%-PU, 500% strain was already beyond the second yielding point of

Table 2 Thermal properties of PLLA-PU

Sample	T_g (°C)	T_m (°C)	ΔH_m^1 (J·g ⁻¹)	ΔH_m^2 (J·g ⁻¹)	T_g^{DMA} (°C)	X_c (%)
PLLA	60	130	—	—	—	—
0%-PU	-17	82	2.57	2.36	8.3	0
9%-PU	-4	95	4.08	2.46	13.7	1.62
23%-PU	7	99	5.98	2.31	26.9	3.67
34%-PU	23	118	7.28	2.33	40.8	4.95
41%-PU	36	115	9.13	2.50	45.9	6.63

ΔH_m^1 : The enthalpy of the melting of PLLA crystals and the destruction of hard segments aggregation; ΔH_m^2 : The enthalpy of the destruction of hard segments aggregation; T_g^{DMA} : glass transition temperature obtained from DMA analysis

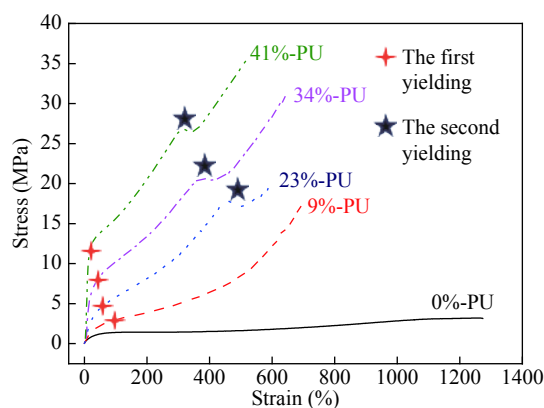


Fig. 1 Stress-strain curves of the PLLA-PU samples

the rest three samples. It meant that eternal destructions in PLLA-PU had already happened in the first cycle. Therefore, the recoverability of 23%-PU, 34%-PU, and 41%-PU was poor as shown in Fig. S5 (in ESI) and Table 4. 9%-PU showed the best recoverability, because the stretch process only destroyed the PLLA crystals and left the well-maintained PLLA amorphous phases, which could solidify the microstructure. Such results also implied that the PLLA amorphous phases were more important than the PLLA crystals in keeping the network of PLLA-PU. This was understandable since the number of PLLA lamellar or spherulite was very limited due to the low crystallinity. The above results also indicated that the PLLA domain would deform after the second yielding point and might not be restored at the experimental temperature. These deductions were partially verified by the multiple cyclic elongation and recovery. The recovery ratio in the cycles 2–5 was tremendously improved in all the samples, meaning that the deformation or destruction of microstructures in the first cycle was almost complete and irreversible.^[34,35]

FTIR Analysis

FTIR spectra of PLLA diol and PLLA-PU are displayed in Figs. 2(a) and 2(b), respectively. The characteristic OH stretching band at 3500 cm^{-1} of PLLA diol disappears after the polymerization, which implies the complete depletion of PLLA diol in the system. Instead, a new NH stretching band at 3322 cm^{-1} emerges, which proves the successful poly-

merization of monomers. Hydrogen bonds could form between NH and C=O groups in the hard domains of PLLA-PU. The characteristic frequency and intensity of the NH stretching vibration and C=O stretching vibration could be strongly perturbed by the hydrogen bonds in hard phases. As shown in Figs. S6(a) and S6(b) (in ESI), absorption band of NH group at 3450 cm^{-1} can be assigned to those free of hydrogen bonding while the absorption band of NH group at 3320 cm^{-1} was associated with hydrogen-bonded ones. Fig. 2(c) shows that there are four types of absorption peaks that corresponded to the C=O stretching of PLLA-PU samples in the static state. They are peak I at 1757 cm^{-1} , peak II at 1715 cm^{-1} , peak III at 1694 cm^{-1} , and peak IV at 1660 cm^{-1} . For 0%-PU, only peak II and peak III appear, which should be assigned to the free carbonyl group and the hydrogen-bonded carbonyl group in the hard domains, respectively. In Figs. 2(c) and 2(d), the intensity of peak II is slightly weakened and the intensity of peak III is slightly enhanced for 23%-PU, 34%-PU, and 41%-PU. This is because the degree of hydrogen bond association in the hard phase was improved during the stretching process. With the addition of PLLA diol, peak I and IV appear and the intensities of the absorption peaks increase with the increasing content of PLLA. Interestingly, peak IV disappears after the tensile break of PLLA-PU in Fig. 2(d). With the above observations, the analysis of the C=O group of PLLA soft segment became possible.

It is natural that the hydrogen bonded carbonyls have less vibration energy than those of the free ones. Correspondingly, the characteristic band of the C=O group would shift to the low wavenumber side. Therefore, peak I at 1757 cm^{-1} can be assigned to those free of hydrogen bonding while peak IV at 1660 cm^{-1} is associated with hydrogen-bonded ones. Under the static condition, the free hard segment might disperse in the soft matrix and form hydrogen bonding with the C=O group of PLLA component, which is manifested by peak IV. However, the compatibility between the hard segment and PLLA domain was very limited, and a lot of C=O groups remained free. Interestingly, this type of physical interaction that connected PLLA and the hard segments was destroyed during the mechanical stretch, as revealed by the disappearance of peak IV. It seemed that the macroscopic elongation of specimen drew the hard segment from the

Table 3 Mechanical properties of PLLA-PU at 20 °C

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Yield strength (MPa)	Elongation at break (%)
0%-PU	4.5 ± 0.4	3.6 ± 0.9	1.4 ± 0.3	1300 ± 100
9%-PU	7.6 ± 0.1	17 ± 0.9	3.2 ± 0.1	670 ± 30
23%-PU	15.1 ± 1.4	20 ± 2.2	4.6 ± 0.1	590 ± 30
34%-PU	68 ± 3.6	31 ± 3.8	7.4 ± 0.5	610 ± 30
41%-PU	110 ± 10	38 ± 3.0	12.2 ± 1.2	530 ± 30

Table 4 Cycle tensile properties of PLLA-PU at 20 °C

Sample	Recovery ratio (%)				
	1 st cycle	2 nd cycle	3 rd cycle	4 th cycle	5 th cycle
0%-PU	74.7 ± 1.4	83.3 ± 0.9	96.8 ± 0.5	97.3 ± 1.0	98.1 ± 0.4
9%-PU	83.9 ± 1.4	98.3 ± 0.6	98.7 ± 0.5	99.1 ± 0.3	99.4 ± 0.5
23%-PU	64.4 ± 3.7	95.0 ± 1.9	96.9 ± 1.9	96.9 ± 0.2	98.7 ± 0.6
34%-PU	25.3 ± 2.3	89.1 ± 0.1	91.6 ± 1.1	95.3 ± 2.2	94.9 ± 0.5
41%-PU	22.8 ± 1.2	87.6 ± 1.5	92.7 ± 0.3	93.4 ± 0.8	95.1 ± 0.6

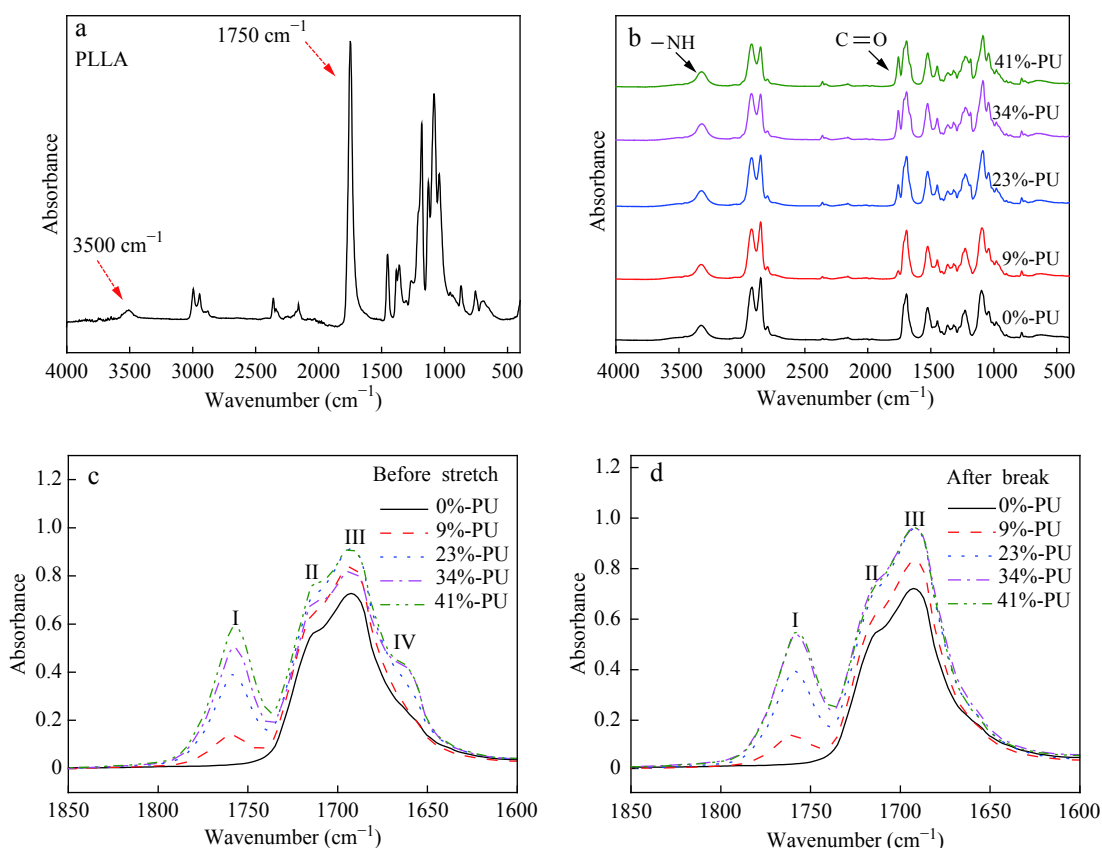


Fig. 2 Typical FTIR spectra of (a) PLLA diol and (b) PLLA-PU; FTIR spectra of the C=O region for PLLA-PU (c) before stretch and (d) after break

PLLA domain. Nevertheless, more work is needed to clarify such interesting phenomenon.

SAXS Analysis

The phase morphologies of PLLA-PU were analyzed by SAXS, and 2D scattering patterns are presented in Fig. 3. The 1D scattering profiles, with scattering intensity plotted versus the scattering vector ($q = 4\pi\sin\theta/\lambda$), along equatorial and meridional directions are shown in Figs. 4 and 5, respectively. The interdomain spacing (d) was calculated by Bragg's equation:

$$d = \frac{2\pi}{q_{\max}} \quad (4)$$

where $q_{\max}$ corresponds to the peak position of the scattering profile.

As can be seen in Fig. 3(a), the scattering halo could be discerned in 23%-PU, 34%-PU, and 41%-PU before stretch. However, no sign of microphase separation or crystallization can be found in 0%-PU and 9%-PU. It was possible that the content of PLLA component was too low to form phase domains, and the PLLA segment might disperse in PTMG matrix. With Figs. 4 and 5, the scattering peak positions of 23%-PU, 34%-PU, and 41%-PU can be identified. Their $q_{\max}$ s locate between 0.26 and 0.30 nm⁻¹, and correspond to 21–24 nm in real space. It is notable that most peaks were reserved after the shape recovery, implying that these structures were PLLA amorphous phase domains but not PLLA

crystals. This is because both WAXS and DSC data confirmed that almost all the crystals were destroyed during elongation. After shape recovery, the scattering profiles of 0%-PU and 9%-PU restored well, which means good stability of microstructures. Nevertheless, it is worth mentioning that the recoverability of 9%-PU seemed better than 0%-PU, probably due to the addition of a small amount of PLLA. On the other hand, the recoverability of 23%-PU, 34%-PU, and 41%-PU behaved differently and the microstructures became asymmetrical after shape recovery. For 23%-PU, when comparing the results of Figs. 4(c) and 5(c), we found that the microphase restored in meridional direction but not in the equatorial direction (perpendicular to the stretching direction in real space). Similar phenomenon can be observed for 41%-PU too, as illustrated in Figs. 4(e) and 5(e). Unfortunately, the tensile stress of 41%-PU became very high when the strain reached 270% and the fixture in our instrument could not hold the sample anymore. As a result, the dumb-bell-shaped specimen of 41%-PU slipped out of the fixture, and we could not observe the phase behavior of 41%-PU at higher strain under SAXS examination. In Fig. 3(b), the 2D SAXS pattern of 34%-PU displays a streak after shape recovery. Such image could be the representation of the irrecoverable and extremely elongated PLLA domain. The elliptical halo of 23%-PU and 41%-PU means irreversible orientation of PLLA domain. These microstructure variations during the stretch could be well correlated with the mechan-

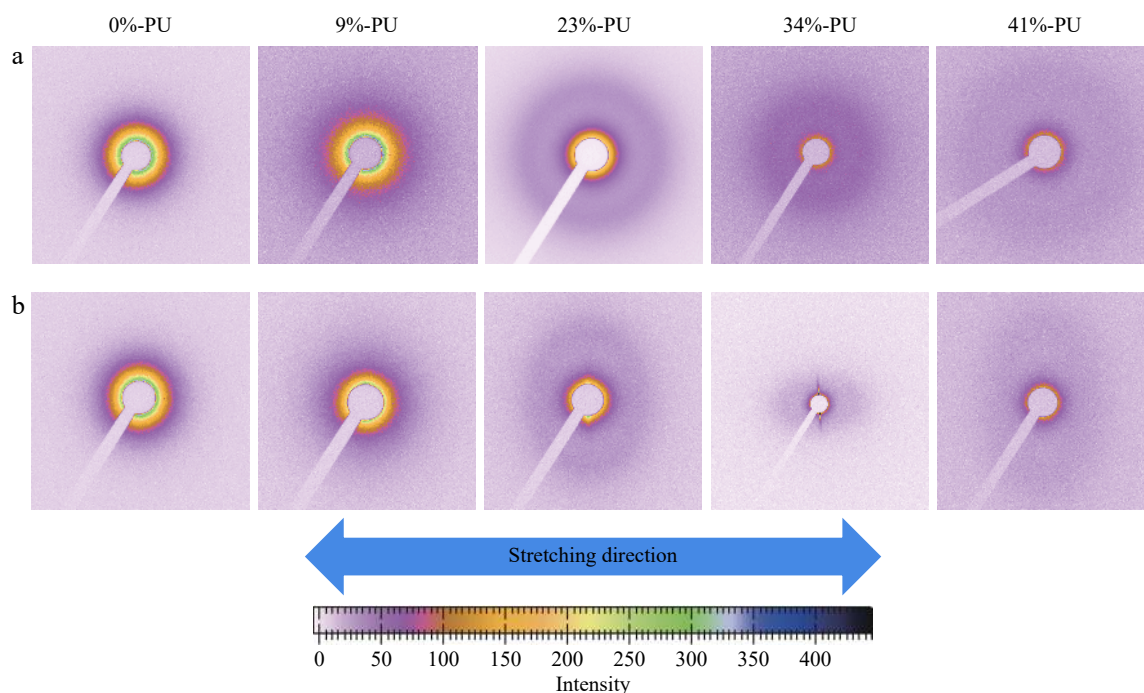


Fig. 3 2D SAXS patterns of PLLA-PU samples (a) before stretch and (b) after recovery

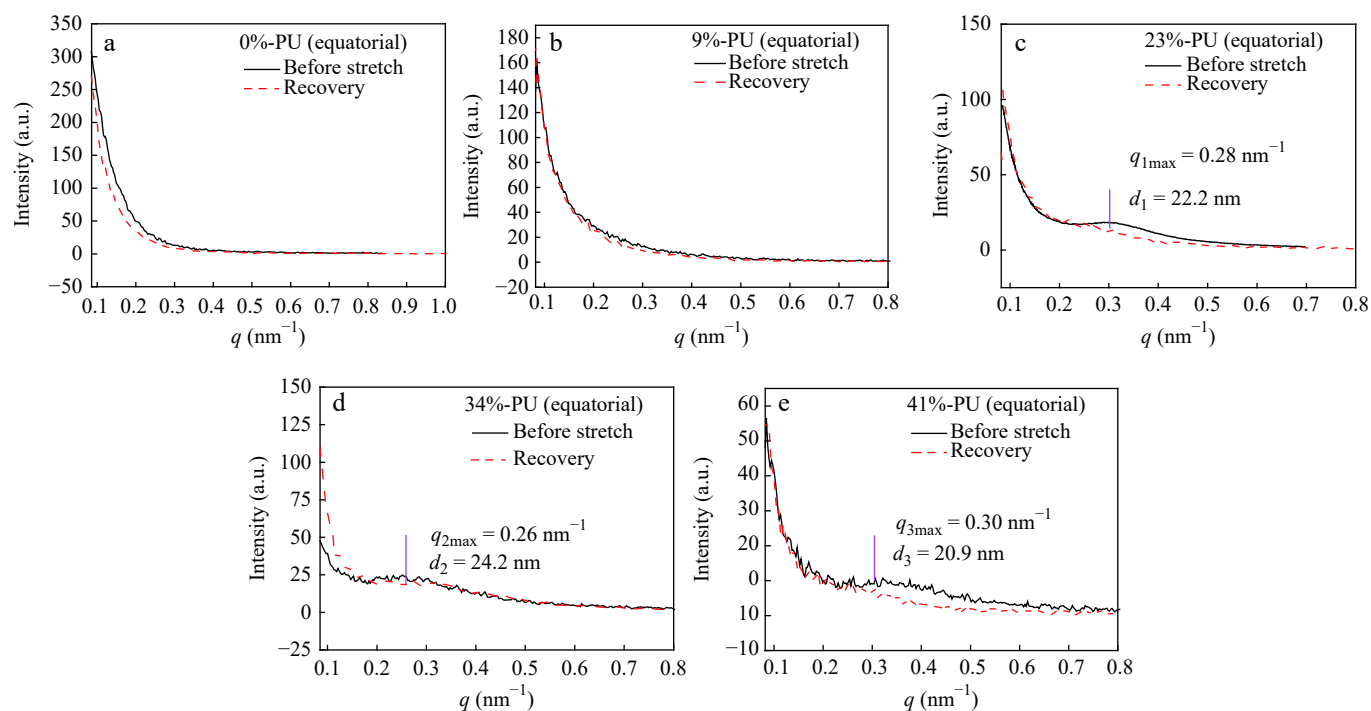


Fig. 4 1D SAXS profiles along the equatorial direction for PLLA-PU samples before stretch and after recovery: (a) 0%-PU, (b) 9%-PU, (c) 23%-PU, (d) 34%-PU, and (e) 41%-PU. The scattering peak before stretch is marked by a vertical solid line.

ical behavior and shape recovery described capability above.

Schematic Illustration of Microstructures of PLLA-PUs before Stretch and after Recovery

Based on the structural information above, we propose a microstructure model, describing the microstructures of PLLA-PUs before stretch and after recovery, as shown in Scheme 3. With the SAXS results, we knew that the microphase separation

between hard segment and soft segments was not obvious. The aggregation of hard segments was weak, probably due to the relatively steric hindrance between HMDI units. Instead, when the content of PLLA was higher than 23% in the soft segment, the PLLA domain appeared and a microphase separated structure formed. Therefore, as illustrated in Scheme 3(a) under the static condition, typical PLLA-PUs contained several structural elements, including PLLA amor-

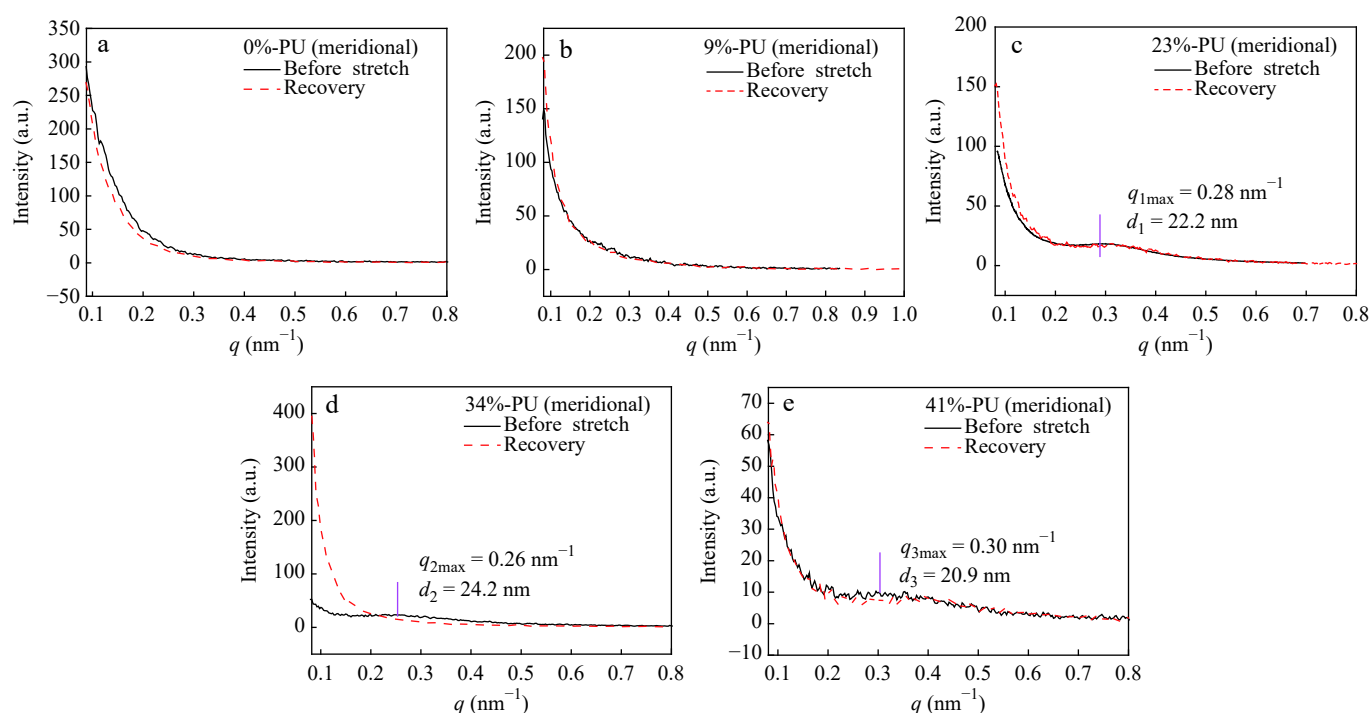
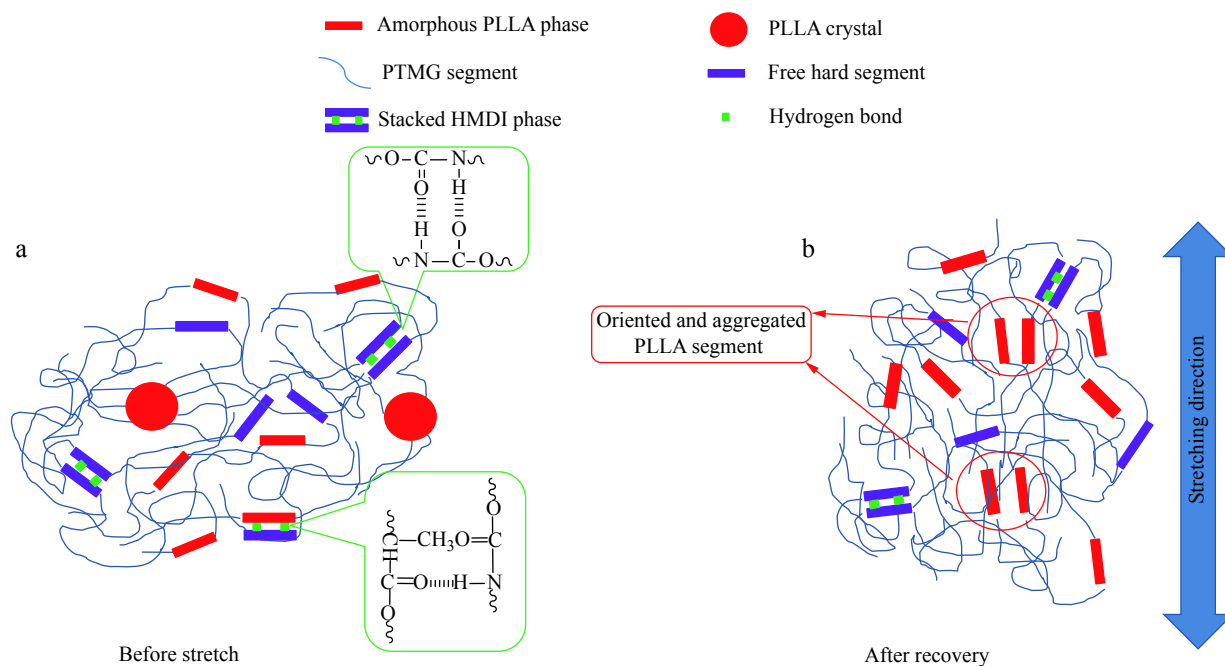


Fig. 5 1D SAXS profiles along the meridional direction for PLLA-PU samples before stretch and after recovery: (a) 0%-PU, (b) 9%-PU, (c) 23%-PU, (d) 34%-PU, and (e) 41%-PU. The scattering peak before stretch is marked by a vertical solid line.



Scheme 3 Illustration of microstructures of PLLA-PU (a) before stretch and (b) after recovery

phous and crystalline regions, hard segment phase immersed in the soft matrix, the free hard segment dispersed in the soft domain, and the amorphous PTMG domain. With the increasing PLLA content in the soft segment, the crystallinity of PLLA and the size of PLLA amorphous phase increased. Such deduction was reflected by the enhanced T_g in the high PLLA content samples. As a result, the modulus and strength of the elastomers monotonically increased with the increasing PLLA content. After shape recovery, as shown in

Scheme 3(b), the breakage of hydrogen bonds between PLLA and hard segment was observed by FTIR experiment. WAXS results revealed the destruction of PLLA crystals after the large strain stretch, which is manifested as the first yielding point in stress-strain curve. From the 2D WAXS patterns in Fig. S4(b) (in ESI), we can see that the PLLA segment is slightly oriented along the stretching direction. SAXS results show the deformation of PLLA domain during the stretch, which corresponded to the second yielding point

in the tensile experiment. The unrecoverable shape and orientation of the PLLA phase could be proved by the SAXS patterns. The cyclic mechanical stretch experiment with strain up to 500% also confirmed the above physical image.

CONCLUSIONS

In this work, we synthesized a series of HMDI-based polyurethane elastomers, containing different amounts of PLLA diols and PTMG as the soft components. As the PLLA content increased in the soft segment, T_g s and T_m s of PLLA-PU increased. At the same time, the Young's modulus and tensile strength of PLLA-PU increased with the increasing PLLA content as well. 9%-PU exhibited the best recoverability among all the samples. With PLLA content higher than 23%, two yielding points appeared, representing the destruction of PLLA crystal and the eternal orientation of PLLA amorphous phase, respectively. The elongation process not only changed the phase structure of PLLA but also destroyed the hydrogen bonding between PLLA and the hard segments. The fact of the unrecoverable microstructures could partially explain the hysteresis in cyclic tensile test. In all, the PLLA and PTMG based polyurethane elastomer displayed many interesting properties. This work opened a window to observe some attractive phenomena in PLLA-PTMG-based polyurethanes. Many questions, including the variation of T_g with PLLA content and molecular weight, the recovery ratio of PLLA domain, and the nature of debonding between PLLA and hard segment during the stretch, etc., are worth of investigation in the future research.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-019-2283-3>.

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