



# Design, synthesis and characterization of novel poly(urethane-urea) based on a macrodiol from poly(lactic acid) and poly(*p*-dioxanone)

Yan Feng Luo<sup>a,b,\*</sup>, Mei Na Huang<sup>a,b</sup>, Su Jun Wang<sup>a,b</sup>, Ya Fu<sup>a,b,c</sup>, Yuan Liang Wang<sup>a,b,\*</sup>

<sup>a</sup> Key Lab of Biorheological Science and Technology (Chongqing University), Ministry of Education, College of Bioengineering, Chongqing University, Chongqing 400030, China

<sup>b</sup> Research Center of Bioinspired Material Science and Engineering, College of Bioengineering, Chongqing University, Chongqing 400030, China

<sup>c</sup> Department of Biology, Chongqing University of Science and Technology, Chongqing 401331, China

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## Abstract

A series of novel poly(urethane-urea) (PUU) was synthesized from poly(lactide-*co-p*-dioxanone) macrodiol (HO-P(LA-*co*-PDO)-OH), hexamethylene diisocyanate (HDI) and butanediamine (BDA). The obtained PUU, which is recorded as P(LA-*co*-PDO)-PUU here, may demonstrate enhanced phase separation and thus improved shape memory property. FTIR was employed to characterize the copolymers, and the effects of NCO/OH molar ratios on  $T_g$  of PUU was investigated by means of differential scanning calorimetry (DSC). The results revealed the successful synthesis of P(LA-*co*-PDO)-PUU. In addition, the  $T_g$  of P(LA-*co*-PDO)-PUU increased from 37.9 °C to 44.2 °C with the increase NCO/OH ratios from 1.1 to 1.2. The P(LA-*co*-PDO)-PUU with  $T_g$  close to body temperature will have potential applications as shape memory polymers in biomedical fields, especially in minimally invasive surgery.

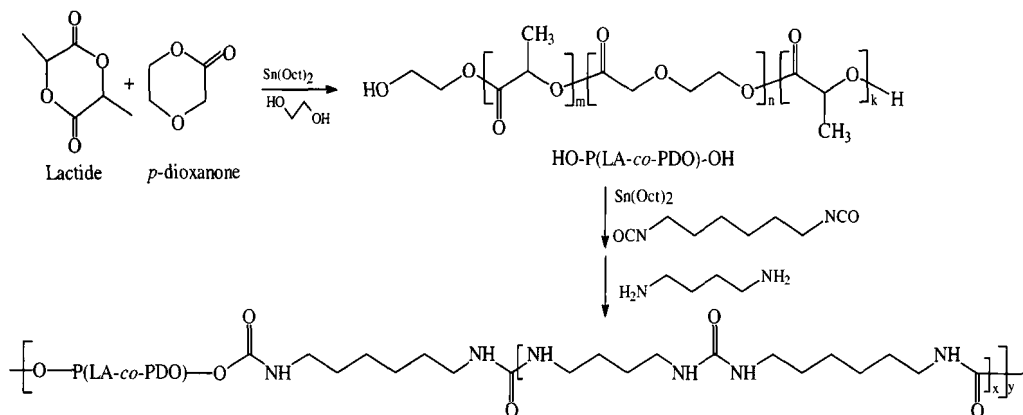
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**Keywords:** Poly(urethane-urea); Polylactic acid; *p*-Dioxanone; Butanediamine; Shape memory polymer

Biodegradable shape memory polyurethane (SMPU) has attracted growing research interests in biomedical fields, especially in the area of minimally invasive surgery due to its biodegradability and biocompatibility [1–4]. SMPU is composed of two types of segments, *i.e.* soft and hard segments. Soft segments are generally macrodiols, and hard segments are urethanes obtained from diisocyanate and small diol. The thermodynamic incompatibility of soft and hard segments produces phase separation and the extent of phase separation determines the shape memory behaviors of SMPU [1,5]. For SMPU, the factors impacting phase separation at least include the flexibility of soft segments and the strength of hydrogen bonding between urethane groups [6,7]. We have ever designed and synthesized a macrodiol HO-P(LA-*co*-PDO)-OH containing polylactic acid (PLA) and poly(*p*-dioxanone) (PPDO) [8], which is supposed to exhibit improved flexibility compared to PLA macrodiol (HO-PLA-OH) [9], because of the introduction of ether

\* Corresponding authors at: Key Lab of Biorheological Science and Technology (Chongqing University), Ministry of Education, College of Bioengineering, Chongqing University, Chongqing 400030, China.

E-mail addresses: [yfluo@cqu.edu.cn](mailto:yfluo@cqu.edu.cn) (Y.F. Luo), [wyl@cqu.edu.cn](mailto:wyl@cqu.edu.cn) (Y.L. Wang).



Scheme 1. Synthesis route of P(LA-co-PDO)-PUU.

bonds provided by PPDO. In addition, when small diol as chain extender for the hard segments is replaced by diamine, poly(urethane-urea) (PUU), which contains a large number of urea group in the hard segments, will be produced. The hydrogen bonding between urea groups is much stronger than that between urethane linkages due to two  $-\text{CONH}-$  groups in urea [10]. Because one of the driving forces for phase separation is strong hydrogen bonding between urethane and urea groups [6,7], the urea groups will produce the higher bond strength and a higher driving force for phase separation. As a result, it would result in increasing extent of phase separation, which significantly facilitates the better shape memory behaviors of PUU than PU [1,5]. Taking all above in mind, we hypothesize that the combination of  $\text{HO}-\text{P}(\text{LA-co-PDO})-\text{OH}$  as soft segments with urea as hard segments produced from diisocyanates and diamine will yield a novel shape memory polymer integrating such advantages as excellent shape recovery force, shape recovery rate together with biodegradability and biocompatibility.

In this work, a novel biodegradable shape memory poly(urethane-urea) was synthesized based on  $\text{HO}-\text{P}(\text{LA-co-PDO})-\text{OH}$  macrodiol, hexamethylene diisocyanate (HDI) and butanediamine (BDA) as a chain extender, which was referred as P(LA-co-PDO)-PUU. And the effect of the ratio of hard segments to soft segments, *i.e.*  $\text{NCO}/\text{OH}$ , on the shape memory temperature was also examined.

## 1. Experimental

The synthesis route of the P(LA-co-PDO)-PUU was illustrated in Scheme 1.  $\text{HO}-\text{P}(\text{LA-co-PDO})-\text{OH}$  macrodiol was prepared and characterized as described in our previous study [8]. For the synthesis of P(LA-co-PDO)-PUU, a predetermined amount of  $\text{HO}-\text{P}(\text{LA-co-PDO})-\text{OH}$  ( $\bar{M}_w = 5676$ ,  $\text{PDI} = 1.08$ , measured by gel permeation chromatography with multi-angle laser light scattering (laser photometer Dawn EOSTM, Wyatt Technology Corporation, USA)) was dissolved in dried toluene. Then  $\text{Sn}(\text{Oct})_2$  (0.75% with respect to  $\text{HO}-\text{P}(\text{LA-co-PDO})-\text{OH}$ , mol/mol) in dried toluene and HDI were added to the solution. After 3 h of stirring at  $70\text{--}75\text{ }^\circ\text{C}$ , the reaction mixture was cooled using ice bath, and subsequently BDA solution in isopropanol was added dropwise. Molar number of the added BDA is equal to the difference between the HDI moles and the macrodiol moles. The chain extending reaction was allowed to last for 2 h in ice bath. Thereafter, the obtained polymer was firstly isolated by precipitation in ethanol and then immersed in isopropanol which was refreshed once a day for 3 days to remove unreacted monomer. All solvents were dried using  $\text{CaH}_2$  and kept together with activated 4A molecular sieve before use.

## 2. Results and discussion

A series of P(LA-co-PDO)-PUU was synthesized through varying molar ratios of  $-\text{NCO}$  groups in HDI to  $-\text{OH}$  groups in  $\text{HO}-\text{P}(\text{LA-co-PDO})-\text{OH}$  ( $\text{NCO}/\text{OH}$ ). Comparing with forthcoming PUUs, the PUU has prominent characteristic, which can be attributed to the composition of its soft segment. The  $T_g$  of PPDO (the polymer of PDO) is

Table 1  
Effects of NCO/OH on  $T_g$  of P(LA-co-PDO)-PUU.

No	Polymers	NCO/OH (mol/mol)	$T_g$ (°C)
1	HO-P(LA-co-PDO)-OH	0	28.02
2	P(LA-co-PDO)-PUU 1.10	1.10	37.90
3	P(LA-co-PDO)-PUU 1.15	1.15	38.90
4	P(LA-co-PDO)-PUU 1.20	1.20	44.20

only about  $-10$  °C [11], while the  $T_g$  of PLA is about  $50$ – $60$  °C [12], which is beneficial to synthesize the copolymers with different  $T_g$ , and can regulate the shape memory temperature of PUUs (showed in the further study). Their glass transition temperature ( $T_g$ ) was detected by differential scanning calorimeter (DSC, PerkinElmer) under argon atmosphere with heating rate of  $10$  °C/min from  $-30$  °C to  $350$  °C.  $T_g$  values were taken as the midpoints of the transition zones and determined from the second heating scan. The obtained  $T_g$  values were listed in Table 1 and a typical DSC curve of P(LA-co-PDO)-PUU is illustrated in Fig. 1.

As shown in Table 1, the pure HO-P(LA-co-PDO)-OH exhibited a  $T_g$  of  $28.02$  °C. With the increase of NCO/OH from  $1.1$  to  $1.2$ ,  $T_g$  of the obtained P(LA-co-PDO)-PUU increased from  $37.90$  °C to  $44.20$  °C. This  $T_g$  increase is attributed to the increase of hard segments, *i.e.* the increase of polymerization degree  $x$  in P(LA-co-PDO)-PUU (Scheme 1). As shown in Scheme 1, the reaction between HDI and HO-P(LA-co-PDO)-OH should give rigid urethane groups, and that between HDI and BDA give more rigid urea groups. These rigid groups restrict the mobility of HO-P(LA-co-PDO)-OH soft segments, thus resulting in higher  $T_g$  than HO-P(LA-co-PDO)-OH. Moreover, the more rigid groups (or hard segments) exist, the higher  $T_g$  would be produced. Besides, some hydrogen bonds might also form between the carbonyl groups in HO-P(LA-co-PDO)-OH and the  $-NH-$  in urethane groups and urea groups, further hindering HO-P(LA-co-PDO)-OH diols chains rotation and increasing  $T_g$ . Those  $T_g$  values of P(LA-co-PDO)-PUU with NCO/OH more than  $1.2$  are not shown here since obvious crosslinking was observed and the obtained crosslinked polymers are beyond of this study.

In order to verify this explanation and have a clear picture on the chemical structure of P(LA-co-PDO)-PUU, the Fourier transform infrared (FTIR) spectrum of P(LA-co-PDO)-PUU 1.1 (B) compared to that of HO-P(LA-co-PDO)-OH (A) was recorded on a PerkinElmer Spectrum GX model by using thin films (Fig. 2).

In Fig. 2(A), HO-P(LA-co-PDO)-OH demonstrates two strong characteristic peaks at  $3487\text{ cm}^{-1}$  and  $1754\text{ cm}^{-1}$ , which are assigned to the stretching vibrations of end OH groups and ester  $C=O$  groups, respectively. After chain extended by HDI and BDA, the peak at  $3487\text{ cm}^{-1}$  in Fig. 2(A) disappeared and new multiple peaks at  $3507\text{ cm}^{-1}$  and  $3330\text{ cm}^{-1}$  were presented in Fig. 2(B), which are typical peaks from N–H stretching vibration. In addition, there are another three new absorption bands at  $1675\text{ cm}^{-1}$ ,  $1618\text{ cm}^{-1}$  and  $1587\text{ cm}^{-1}$  in Fig. 2(B), which should be contributed by  $C=O$  stretching vibration and N–H bending vibration in urethane amide and urea amide groups. All these observations verified the successful synthesis of P(LA-co-PDO)-PUU with a chemical structure as indicated in Scheme 1.

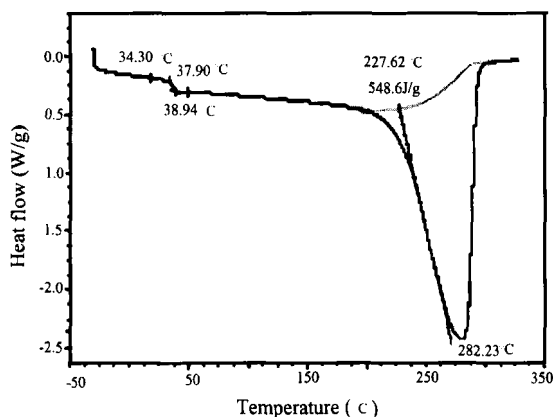


Fig. 1. Typical DSC curve of P(LA-co-PDO)-PUU with NCO/OH = 1.1.

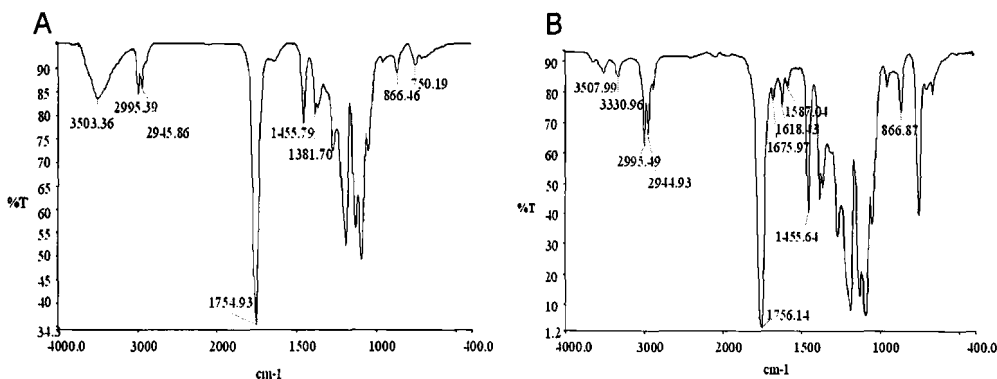


Fig. 2. FTIR spectrum of P(LA-co-PDO)-PUU1.1 (B) compared to that of HO-P(LA-co-PDO)-OH (A).

### 3. Conclusions

FTIR spectra revealed the successful synthesis of P(LA-co-PDO)-PUU using HO-P(LA-co-PDO)-OH as soft segments and HDI/BDA as hard segments. And the DSC detections demonstrated that the  $T_g$  values of P(LA-co-PDO)-PUU increased with increasing NCO/OH ratios. By controlling NCO/OH ratio,  $T_g$ , *i.e.* the shape memory temperature of P(LA-co-PDO)-PUU can be regulated so that it is close to body temperature, suggesting its potential application in biomedical fields. Theoretically, the increased flexibility of HO-P(LA-co-PDO)-OH as soft segments (compared to PLA macrodiol) and the incorporation of more rigid urea groups in hard segments (compared to pure urethane groups) will enhance the phase separation extent and result in better shape memory property. The phase separation detection by using atomic force microscopy and shape memory test will be carried out in further work.

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