Electronic Supplementary Material (ESI) for Biomaterials Science.
This journal is © The Royal Society of Chemistry 2016

Supporting information

Synthesis and characterization of biodegradable lysine-based waterborne polyurethane for soft tissue engineering applications

Hongye Hao, Jingyu Shao, Ya Deng, Shan He, Feng Luo, Yingke Wu, Jiehua Li, * Hong Tan,* Jianshu Li and Qiang Fu

College of Polymer Science and Engineering, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610065, China

Characterize

1. Fourier transform infrared spectroscopy

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) infrared data were obtained from a Nicolet-560 spectrophotometer (Thermo Electron Corporation, Nicolet, America) between 4000 and 6000 cm^{-1} equipped with a Geprism with an incident angle of 45°. Fifty scans were averaged for each sample.

2. Differential scanning calorimetry (DSC)

To characterize the thermal behavior of LWPUs, The DSC analysis was performed with a differential scanning calorimeter (TA instrument 2910 thermal analyzer, America) to measure the heat variation at a heating rate of 10 °C/min. The measuring range of this analysis was set between -150 and 150°C.

Results and Discussion

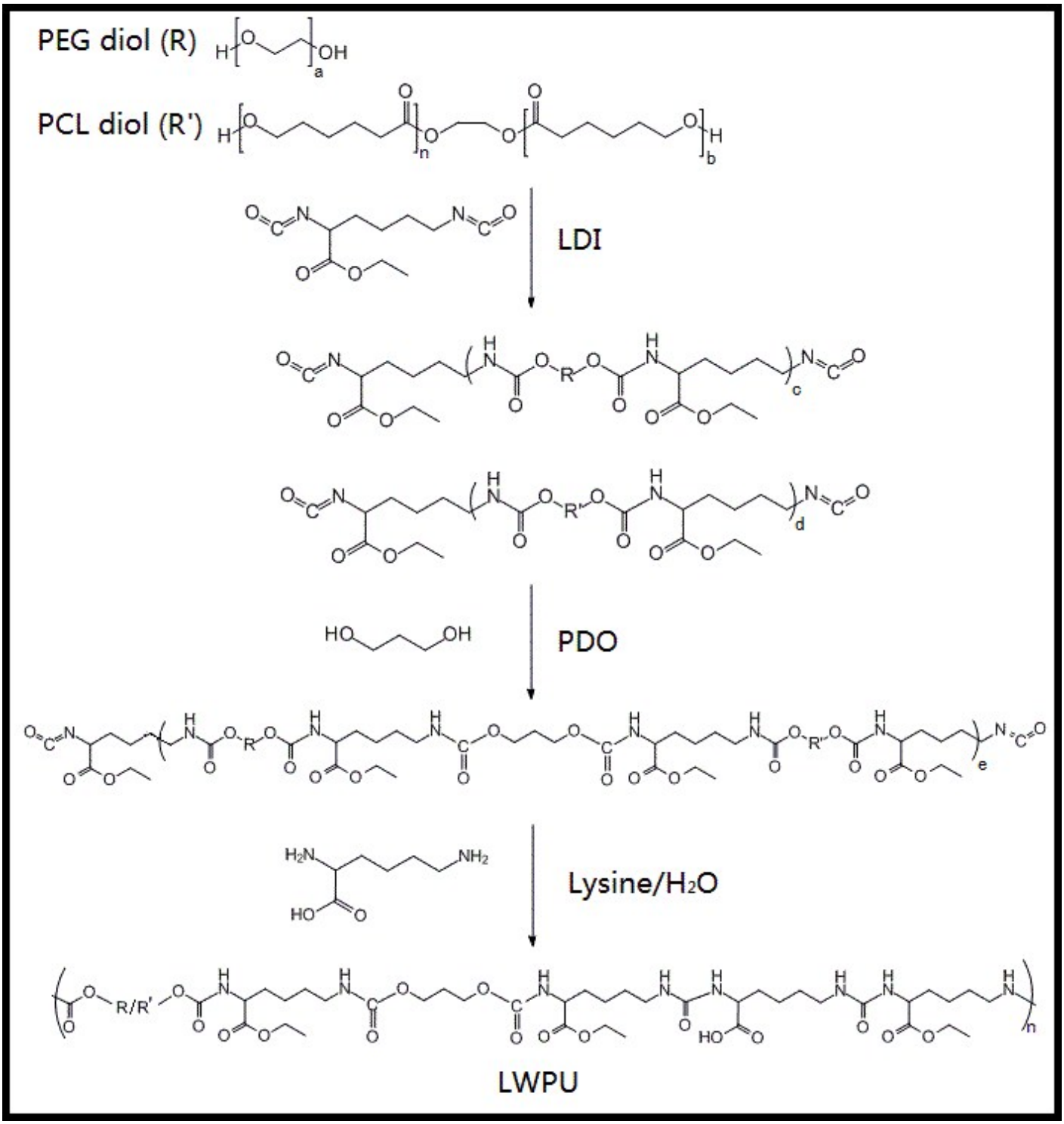

Figure S1.The chemical structure and synthetic procedure of LWPUs.

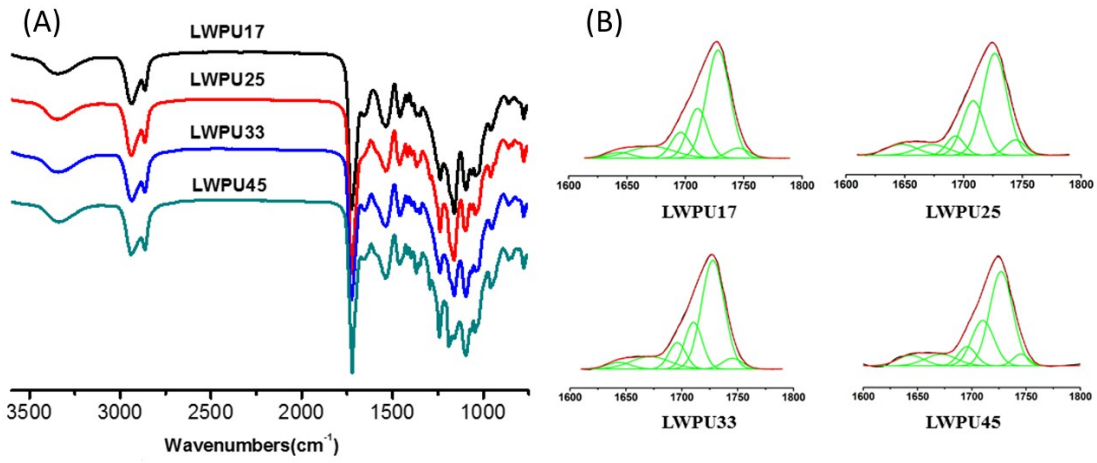

Figure S2. (A) ATR-FTIR spectra curves of LWPUs; (B) A split of carbonyl region between 1600 and 1850 cm^{-1} of LWPUs.

The ATR-FTIR spectra of LWPUs shows that free (not hydrogen-bonded) N–H stretching absorption bands at 3450 cm^{-1} are weak in Figure S2A, demonstrating that most of N-H formed hydrogen bond with C=O groups[1] . And the carbonyl groups in urethane and urea at stretching band from 1850-1600 cm^{-1} are mainly overlapped by the stretching band of carbonyl in urethane, urea, ester carboxyl groups of PCL and LDI[2] . In this region, the stretching bands of LWPUs are mainly comprised of the free carbonyl of hard segments at 1730 cm^{-1}, 1700 cm^{-1},1676 cm^{-1} due to the absorption of the free carbonyl of PCL, urethane linkage and urea groups, respectively. The hydrogen-bonded carbonyl absorption between hard segments and soft segments is at 1720 cm^{-1} [3], while the hydrogen-bonded carbonyl absorption among hard segments is at 1690 cm^{-1} for the carbonyl absorption of urethane linkage and 1645 cm^{-1} for urea groups. Herein, the carbonyl adsorption regions were fit to subpeaks of relevant

groups for investigation of the microphase separation degree of LWPUs (Figure S2B). The percentages of hydrogen bonded carbonyl in urethane and urea groups to total carbonyl groups are listed in Table S1. These percentage of hydrogen bonded carbonyl in LWPU45 (14.2%) is higher than those of LWPU17 (12.8%), LWPU25 (10.6%) and LWPU33 (13.1%), indicating that the microphase separation degree of LWPU45 is superior to that of other samples. These results suggest that LWPUs are successfully synthesized with various degree of microphase separation.

Table S1. Absorption band assignments between 1600 and 1850 cm^{-1} and their respective integration areas of LWPUs.

Frequency (Cm^{-1})	Absorption band assignment	Integration area (%)			
		LWPU17	LWPU25	LWPU33	LWPU45
1744	(C=O) of ethyl ester groups of LDI	4.5	3.0	4.6	4.2
1727	carbonyl(C=O) in ester group of soft segments	51.8	49.0	53.9	49.9
1700	(C=O) free carbonyl in urethane linkage	20.1	29.5	17.9	23.2
1690	(C=O) hydrogen bonded carbonyl in urethane linkage	9.9	8.2	9.7	7.8
1676	(C=O) free carbonyl in urea groups	10.8	7.9	10.5	8.4
1645	(C=O) hydrogen bonded carbonyl in urea groups	2.9	2.4	3.4	6.4
	The percentage of hydrogen bonding between hard segments	12.8%	10.6%	13.1%	14.2%

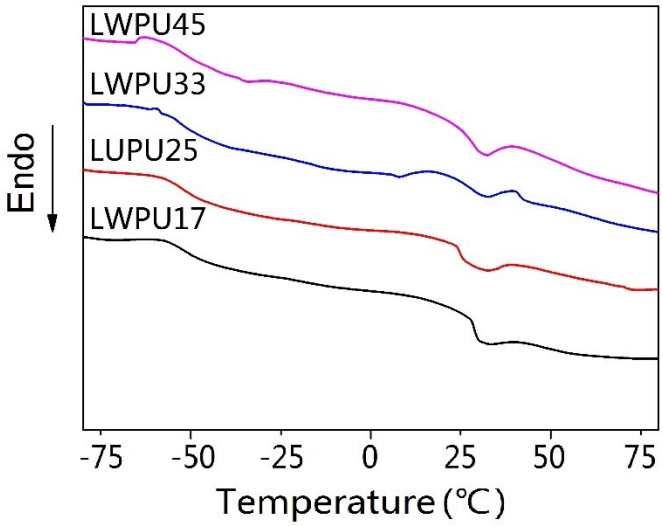

Figure S3. DSC curves of LWPU, the heating rate of 10 °C/min.

Table S2, Glass transition temperatures and enthalpies of LWPUs by DSC test.

Sample	Tg (ºC)	ΔH (J/g)
LWPU17	-51.61	0.62
LWPU25	-52.40	1.05
LWPU33	-53.14	0.80
LWPU45	-53.22	0.56

DSC experiment was carried out to measure the thermal properties of LWPUs. The results are shown in Figure S3, and the data are summarized in Table S2. For polyurethane materials, the glass transition temperature (T_g) of the soft segments has been used as an indicator of the degree of microphase separation[4] . As shown in Figure S3, no obvious thermal transition related to hard segment was observed in all

DSC curves of LWPUs. And T_gs of the LWPUs soft segments from -53 °C to -51 °C are higher than that of pure PCL (T_g = -60 °C) , indicating that these obtained polyurethanes have a certain degree of hard and soft segment mixing. Different melting endotherm could be observed between 25 and 50 °C, which should be attributed to different degree of crystallinity and crystal size of soft segment. However, the increase of PEG content promoted the phase separation for thermodynamic incompatibility between hard and soft segment increasing[5], which is in good agreement with results of ATR-FTIR analysis.

References

1. Li, G.; Li, P.; Qiu, H.; Li, D.; Su, M.; Xu, K. *J. Biomed. Mater. Res., Part A* 2011**,** 98a, (1), 88-99.
2. Li, J.; Tan, D.; Zhang, X.; Hong, T.; Ding, M.; Wan, C.; Qiang, F. *Colloids Surf., B* 2010**,** 78, (2), 343–350.
3. Zhou, L.; Yu, L.; Ding, M.; Li, J.; Tan, H.; Wang, Z.; Fu, Q. *Macromolecules* 2011**,** 44, (4), 857-864.
4. Furukawa, M.; Kojio, K.; Kugumiya, S.; Uchiba, Y.; Mitsui, Y. *Macromol. Symp.* 2008, 9-15.
5. Cao, J.; Cheng, F.; Cao, H.; Lu, A.; Cai, M.; Chen, Y.; He, B.; Gu, Z.; Luo, X., *Colloids Surf., B* 2015**,** 125c, 213–221.