Supporting Information

High Recoverable Rosin-based Shape Memory Polyurethanes

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Materials

Rosinmaleopimaric acid anhydride (RMA) was purchased from the Research Institute of Chemical Processing and Utilization of Forest Products (Nanjing, China). It was recrystallized from glacial acetic acid before using. All reagents and solvents of analytical grade were purchased from Aladdin and used as received. Polytetramethylene-ether-glycol diol (PTMG) with the number-average molecular weight (M_n) 2000 was bought from Bayer (Germany). Petroleum-based chain extender hydroquinone bis(2-hydroxyethyl)ether (HQEE) was kindly supplied by Yantai Yusheng Chemical Company (Yantai, China).

Synthesis of rosin-based chain extender and SMPUs

Rosin–maleic anhydride imidodicarboxylic acid (RMID) was synthesized according to previous work of Liu and coworkers.[1-3] In a 100 mL three necked

round-bottomed flask with magnetic stirrer, charged RMID (5.1926 g, 10 mmol), then thionyl dichloride (20 mL) and DMF (0.5 mL) used as catalyst were added by using a constant pressure funnel in 30 min. After kept the mixture at 85 ^{o}C for 5 h, the extra thionyl dichloride was removed through reducing pressure distillation and the RMID acyl chloride was obtained. Then toluene (20 mL) was charged to dissolve the RMID acyl chloride, and after that pyridine (2 mL) and ethylene glycol (2.48 g, 40 mmol) were added. The pyridine served as the acid binding agent here. After the mixture was heated to 110 ^{o}C and was then maintained at this temperature for another 5 h, it was cooled down to room temperature. Finally, distilled water was used to wash the organic layer to eliminate the excess ethylene glycol, pyridine and the pyridine hydrochloride. At last, we removed the solvent and got the desired product.

Shape memory polyurethanes (SMPUs) were synthesized by a two-step polymerization process.[4]The polyurethane film was cast from 30% solutions into a rectangular polytetrafluoroethene (PTFE) mold. Different SMPUs were synthesized as listed in Table S1

Characterization

^{1}H spectrum was recorded on a Bruker 400 AVANCE III spectrometer operating at 400.23MHz at 25^{o}C and using $CDCl_3$ as solvents. Fourier transform infrared (FTIR) characterization was performed on a Thermo Nicolet 6700 Fourier transform infrared (FTIR) spectrometer from Thermo-Fisher Scientific, scanning from 500 to 4000 cm^{-1}, 32 scans were collected for each sample. The number-average molecular weights (M_n) and weight-average molecular weights (M_w) were measured by a Waters-2414 GPC.

Chloroform was used as mobile phase at a flow rate of 1 mL/min and mono-dispersed commercial polystyrene was used as the calibration standard.

The samples were cast from 20% chloroform solutions onto Si plates and atomic force microscopy (AFM) scanning was performed to detect the phase morphology of these samples at room temperature with a scanning probe microscope (SPM) (Nanoscope IIIa, Multimode from Digital Instruments) operating in tapping mode. The set point amplitude, which is used in feedback control, was adjusted to 40-70% of the free amplitude for moderate force image mode data. All images are presented without any image processing except in some cases where horizontal leveling and contrast enhancement were used.

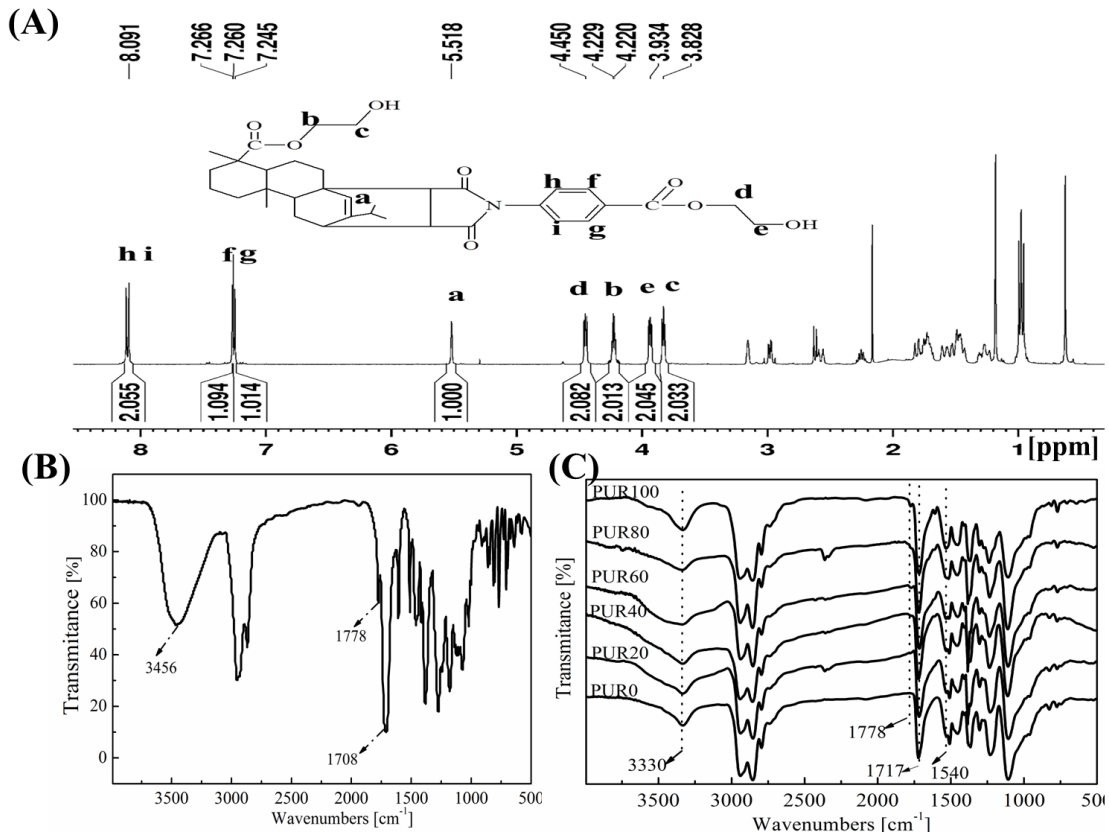

Figure S1. (A) The ^{1}H-NMR spectrum of R-CE, (B) the FTIR spectrum of R-CE, (C)

the FTIR spectra of synthesized polyurethanes

Table S1. Designation, molar ratio, molecular weight and hard segment content of the synthesized SMPUs

SMPUs	PTMG :IPDI:CE [molar ratio]	R-CE [mol]	HQEE [mol]	HS [wt.%]	M_w /10^4	M_n /10^4
PUR0	1:2:1	0	1.0	24.3	7.0	3.2
PUR20	1:2:1	0.2	0.8	26.6	10.6	5.0
PUR40	1:2:1	0.4	0.6	28.7	9.8	5.1
PUR60	1:2:1	0.6	0.4	30.8	9.8	3.8
PUR80	1:2:1	0.8	0.2	32.7	9.1	4.8
PUR100	1:2:1	1.0	0	34.5	10.7	5.7

[1] X. Liu, C. Li, D. Zhang, Y. Xiao, G. Guan, *Polym. Int.* **2006**, *55*, 545.
[2] X. Liu, W. Xin, J. Zhang, *Bioresour. Technol.* **2010**, *101*, 2520.
[3] H. Wang, X. Liu, B. Liu, J. Zhang, M. Xian, *Polym. Int.* **2009**, *58*, 1435.
[4] L. S. T. J. Korley, B. D. Pate, E. L. Thomas, P. T. Hammond, *Polymer* **2006**, *47*, 3073.