Front. Chem. China (2006) 4: 479–483
DOI 10.1007/s11458-006-0055-4

RESEARCH ARTICLE

Xin Haobo, Zhang Yunfeng, Xing Zheng

Synthesis and properties of liquid crystalline polyurethanes

Abstract 1,4-Bis(*p*-hydroxybenzoate)phenylene was prepared using 1,4-bis(trimethylsiloxy)benzene and *p*- hydroxybenzoyl chloride as starting materials. A series of novel 1,4-bis(*p*-hydroxyalkoxybenzoate)phenylene were synthesized by reaction of 1,4-bis(*p*-hydroxybenzoate) phenylene with 3-bromopropanol and 4-bromobutanol, respectively. The liquid crystal polyurethanes were prepared by 1,4-bis(*p*-hydroxyalkoxybenzoate)phenylene with MDI (*p*-methylene diphenylenediisocyanate) and 2,4-TDI(2,4-toluenediisocyanate), respectively. The thermotropic properties, the melting point (T_m) and the isotropization temperature (T_i) of the synthesized polyurethanes were characterized by DSC, IR and POM. It showed that all of the polyurethane polymers exhibited thermotropic liquid crystalline properties between 144°C and 260°C. The transition temperature (T_m and T_i) decreased with an increase in the length of the methylene spacer.

Keywords liquid crystal polyurethane, thermotropic, phase transition temperature

In recent years, researchers have paid much attention on main chain liquid crystalline polymers with mesogen hard blocks and flexible soft blocks, especially polyester and polyamide type liquid crystalline polymers [1-4]. But little attention has been paid on the synthesis of liquid crystalline polyurethane, even less attention on the synthesis of polyester polyurethane liquid crystals and the influence of polyester hard block and methylene flexible block on liquid crystalline property[5,6]. In this research, 1,4-bis(*p*-hydroxy benzoate)phenylene (**I**) was synthesized by reacting 1,4-bis (trimethylsiloxy)benzene with *p*-hydroxybenzoyl chloride. **I** was then reacted with 3-bromopropanol,4-bromobutanol and 6-bromohexanol respectively to synthesize a series of 1,4-bis(*p*- hydroxyalkoxybenzoate) phenylene (II). Compound II was then reacted with 2,4-toluenediisocyanate (2,4-TDI) and *p*-methylene diphenylenediisocyanate (MDI) respectively to prepare liquid crystalline polyurethane with polyester hard block and flexible methylene block. The liquid crystalline properties such as the thermotropic properties, the melting point (T_m) and the isotropization temperature (T_i) of the synthesized polyurethanes were characterized by DSC,IR and POM. The influence of the length of methylene spacer was investigated.

Translated from *Journal of Qingdao University of Science and Technology*, 2006, 27(1) (in Chinese)

Xin Haobo(✉), Zhang Yunfeng, Xing Zheng
Key Lab of Rubber-Plastics, Ministry of Education, Institute of Functional Polymers, Qingdao University of Science and Technology, Qingdao 266042, China
E-mail: xin_dengyu@163.com

1 Experimental

1.1 Reagents

2,4-toluenediisocyanate(2,4-TDI), *p*-methylene-diphenylene-diisocyante (MDI), 1,4-bis(trimethylsiloxy) benzene, *N*,*N*-dimethylformamide(DMF), *p*-hydroxy benzoyl- chloride, 3-bromopropanol, 4-bromobutanol, 6-bromohexanol, 1-butanol, ethanol, 1,1,2,2- tetrachloroethane and sodium carbonate are all commercial reagents.

1.2 Instruments

Magna-750 Fourier Transfer Infrared Spectroscopy (Nicolet Company, USA), DSC-204 differential Scanning Calorimetry (NETZSCH, Germany), BX51-P Polarized Optical Microscopy (POM) (Olympus, Japan).

1.3 Experiment

1.3.1 Synthesis of 1,4-bis(p-*hydroxybenzoate*)*phenylene* (***I***)

The synthesis of Compoand **I** follow Morman's procedure [7]. A 500 mL three-neck flask was equipped with a mechanical stirrer, a thermometer, and a condenser. 25.430g

(0.10 mol) 1,4-bis(trimethylsiloxy)benzene and 31.314g (0.20 mol) *p*-hydroxybenzoyl chloride and 50.0 mL 1,1,2,2-tetrachloroethane were added, the reaction mixture was heated to 165°C for 10 h under stirring. The reaction mixture was cooled to room temperature, filtered, washed with tetrachloroethane, and recrystalized in 1-butanol to give 30.1 g of Compound **I**.

1.3.2 Synthesis of 1,4-bis(p-hydroxyalkoxybenzoate) phenylene (***II***)

The synthesis of Compound **II** follow Li's procedure [8]. 0.2 mol Compound **I** in 60 mL DMF was added to a 500 mL three-neck flask, followed by 0.45 mol Na_2CO_3 and 400 ml 0.001 mol/L 3-bromopropanol (or 4-bromobutanol or 6-bromohexanol) (the number of $-CH_2-$ unit is 3,4,6 respectively) in DMF. The mixture was stirred under 120°C for 12 h, then cooled to room temperature, washed with water, dried at 70°C under vacuum for 12 h. The product was recrystalized with 1:1 (*v*/*v*) DMF/butanol [9], washed with ethyl acetate, dried at 90°C under vacuum for 24 h to get Compound **II**. The yields and melting points of different Compound **II** are in Table 1.

Table 1 Yields and melting points of synthesized monomers

Monomers (**II**)	*n*	Yield/%	Melting point T_m/°C
(**II**)-1	3	45	219–223
(**II**)-2	4	65	200–212
(**II**)-3	6	51	182–189

1.3.3 Synthesis of liquid crystalline polyurethane

The synthesis of liquid crystalline polyurethane follow He's procedure [10]. In a 500 mL three-neck flask, 0.02 mol diisocyanates (TDI or MDI) and 100 mL DMF were added, then 0.02 mol Compound **II** in DMF solution was dropped in. The mixture was stirred for 1 h at 60°C and then was allowed to react for 12 h at 100°C. The reaction mixture was then precipitated into distilled water, washed with methanol 3–4 times, and dried at 80°C under vacuum for 12 h to get the polyurethane.

2 Results and discussion

2.1 The synthesis and physics of liquid crystalline polyurethane

The synthesis of different chain structure polyurethane liquid crystals (PU-1–PU-6) [11, 12] using different diisocyanates and different **II** with different length of flexible methylene group in the main chain was achieved. The results are shown in Table 2.

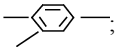
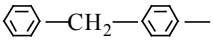
The T_m and T_i were measured with DSC. It can be seen that all the polyurethane samples show liquid crystalline properties in a certain temperature range. The melting temperature and isotropic transition temperature decrease with the increase of the length of soft methylene in the main chain.

2.2 The IR analysis of liquid crystalline polyurethane

The IR spectra of PU-4, PU-5, PU-6 are shown in Fig.1. The absorbance in 3300–3400 cm^{-1} is from the –NH- group, which is broadened due to the formation of hydrogen bond with a carbonyl group [13]. The absorbance between 1600–1720 cm^{-1} is from the carbonyl group. The absorbances between 2800–2955 cm^{-1} are from methylene groups, among which 2938, 2953 and 2955 cm^{-1} are the unsymmetrical stretch vibration, 2852, 2855 and 2859 $cm^{-1}$are the symmetrical stretch vibration of methylene groups. Hence the structures of the liquid crystalline polyurethane are proved by IR spectra.

Table 2 Preparation condition and properties of polyurethanes

Polymer	Polymeric structure※		Reaction temperature/°C	Time/h	Yield/%	Crystalline phase/°C	Transition temperature	
	n	R					T_m / °C	T_i /°C
PU-1	3	R_1	87	15	93	240～260	240	260
PU-2	3	R_2	96	10	88	233～253	231	253
PU-3	4	R_1	87	8	91	160～229	161	230
PU-4	4	R_2	96	15	86	207～240	200	249
PU-5	6	R_1	87	15	87	144～227	144	228
PU-6	6	R_2	96	8	92	197～229	197	230

※ R_1: CH_3—  —; R_2: —  —

2.3 Liquid crystalline polyurethane properties

The liquid crystalline properties of the synthesized polyurethane samples were characterized with DSC (temperature increase at 10°C /min). Figure 2 shows the DSC curves of PU-4, PU-5 and PU-6. It can be seen that all the sampleshave two endothermic peaks (T_m and T_i, PU-4: 200.3°C, 250.3°C; PU-5: 144.3°C, 228.3°C; PU-6: 197.5°C, 230.6°C) from all the curves. The exothermic peaks between T_m and T_i are due to hydrogen bond formation arising from the rearrangement of segments, which are attributed to the symmetric structures of the polymers [14]. Therefore, the changes in the relative molecular weights of the polyurethane only affect T_m and the entropy of the phase transition, but have almost no influence on T_i. The T_m decreases with the increase of the methylene length in the main chain. The tendency is because with the increase of the number of methylene group, the length of the flexible segment increases, which decreases the intermolecular force or the interchain attraction and increases the interchain distances. As a result, the polymer cannot pack very tightly, causing low crystallinity and T_m. In the same way, T_i also decreases with the length of methylene group.

2.4 POM analysis of liquid crystalline polyurethane

Figure 3 shows the orthogonal polarized optical microscopy (POM) image of liquid crystal polyurethane PU-4, PU-5 and PU-6. POM is an effective tool to characterize liquid crystal behavior [15]. The polyurethane samples synthesized have no dual reflectivity at room temperature.

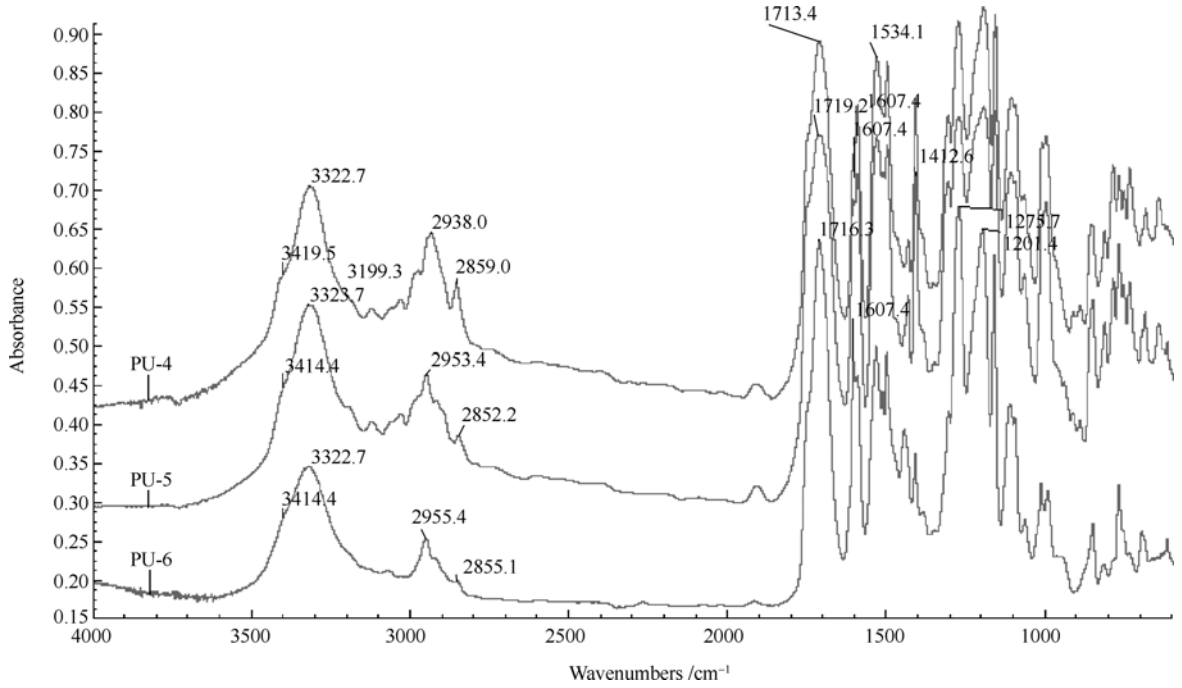


Fig. 1 IR spectra of liquid crystalline polyurethanes of PU-4, PU-5 and PU-6

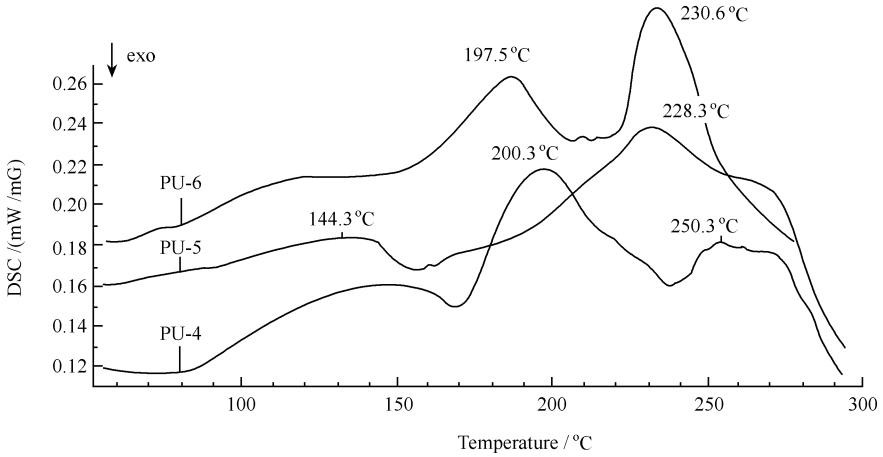
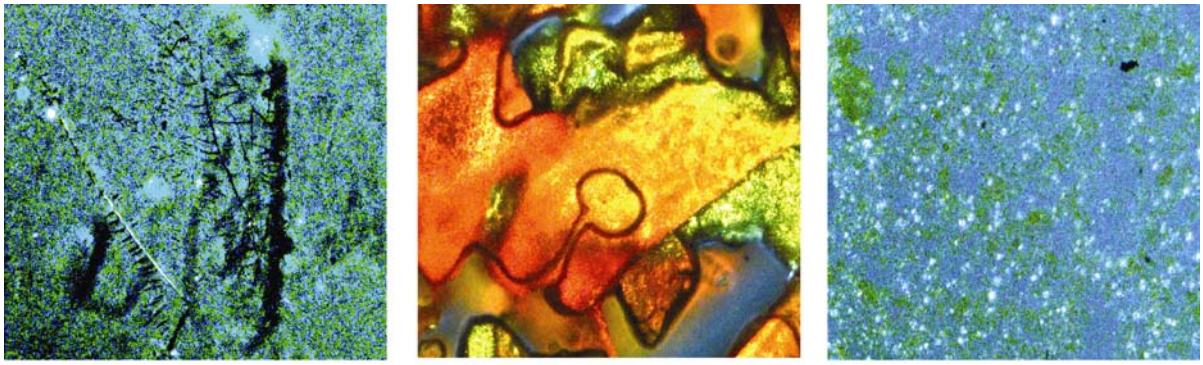


Fig. 2 DSC curves of polyurethanes for PU-4, PU-5 and PU-6 (heating at 10°C/min)



(a) for PU-4 at 200°C (b) for PU-5 at 190°C (c) for PU-6 at 210°C

Fig. 3 Textures of the nematic phase of polyurethanes of PU-4, PU-5 and PU-6(×200)

When the temperature increases, however, the samples first start to soften, and then change to molten liquid crystal state showing a lined or fibrous ordered structure. With the increase in the number of methylene group, the T_m of the polymers decrease and the mobility gradually increases showing a colored nematic structure. Therefore, the polymers can be classified as heat-induced nematic liquid crystals [16, 17]. When temperature goes over T_i, the dual reflective behavior disappears, entering into an isotropic state causing dark image [18]. When cooling the above sample slowly, the dual reflective phenomenon appears again proving that the liquid crystal behavior is heat induced.

3 Conclusion

A series of polyurethane samples with different main chain flexibility were synthesized and characterized by reacting diols having different lengths of flexible methylene with TDI and MDI. The experimental results showed that all the polymers had crystallinity behavior and dual reflective phenomena between T_m and T_i. The T_m and T_i decrease with the increase in the length of the flexible methylene group in the main chain. When the temperature increases, the polymers begin to melt and enter into the liquid crystal state, and dual reflectivity increases gradually showing a clear fibrous structure typical of heat-induced nematic liquid crystal polyurethanes.

References

1. Yu Haifeng, Jiang Hongzhou, Lian Yanqing, Wang Xiaogong and Liu Deshan, Synthesis and characterization of a novel polyurethane-based photo-alignment layer polymer for liquid crystal displays, Acta Polymerica Sinica, 2003, (1): 133–137 (in Chinese)
2. Iimura K., Koide N., Tanabe H. and Takeda M., Synthesis of Thermotropic liquid crystalline polymers 2 polyurethanes, Makromol Chem, 1981, 182 (10): 2569–2575
3. Stenhouse P. J.,Valles E. M., Kantor S. W. and Macknight W. J., Thermal and rheological properties of a liquid-crystalline polyurethanes. Macromolecules, 1989, 22(3): 1467–1473
4. Aharoni S. M., Hydrogen-Bonded highly regular strictly alternating aliphatic-aromatic liquid-crystalline poly(ester amides). Macromolecules, 1988, 21(6): 1941–1961
5. Osman M. A., Thermotropic liquid crystalline polymers with quasi-rigid chains: 2.chain flexibility, Polymer, 1987, 28(5): 713–715
6. Osman M. A., Thermotropic liquid crystalline polymers with quasi-rigid chains: 1.cyclohexyl moieties. Macromolecules, 1986, 19(7): 1824–1827
7. Mormann W. and Brahm M., Polymers from multifunctional isocyanates: 7. Synthesis and phase behavior of liquid-crystalline triad ester-group-containing diisocyanates, Polymer, 1993, 34(1): 187–194
8. Li C. H. and Chang T. C., Studies on the thermotropic liquid crystalline polymers:I. Synthesis and properties of poly (amide-azomethine-ether), J Polym Sci. Part A: Polym Chem, 1990, 28(13): 3625-3638
9. Soga Kazuo, Shiono Takeshi and Doi Yoshiharu, Influence of internal and external donors on activity and stereospecificity of Ziegler-Natta catalysts, Makromol Chem, 1988, 189(7): 1531–1541
10. He Shangjin, Song Moudao, Zhang Banghua and Zhang Baolong, Synthesis and characterization of liquid crystalline polyurethanes based on 4,4'-bis[p-(β-hydroxyethoxy)benzylideneamino] phenyl, Ion Exchange and Adsorption, 1999, 15(2): 109-114(in Chinese)
11. Takashi M. and Naoyuki K., Hydrogen bonding and mesomorphic properties for side chain type liquid crystalline polyurethanes containing rigid moieties in the polymer backbone, Polymer J, 1997, 29(2): 134–137
12. Takashi M Naoyuki K, The influence of hydrogen bonding on the mesomorphic properties of side chain type liquid crystalline polyurethanes with rigid moieties in the polymer backbone, Polymer J, 1997, 29(2): 138-141
13. Hsu T.-F. and Lee Y.-D., Properties of thermoplastic polyurethane elastomers containing liquid crystalline chain extender (I) synthesis and properties of hard segments, Polymer, 1999, 40(3): 577–587
14. You Yingcai, Jiao Hua, Hao Jiyuan, Zhang Baolong and Du Zongjie, Polycondensation of 4,4-terephthaloydioxybenzoyl chloride and aliphatic diols and studies on the liquid crystal behavior of the copolyesters, Ion Exchange and Adsorption, 1999, 15(2): 121–126(in Chinese)
15. Li Zifa, Guo Yinzhong, Zhang Chunxiao and Zhou Qifeng, Synthesis of a new kind of rigid side chain type liquid crystal polymers, Acta Polymerica Sinica, 1995, (4): 414–419 (in

Chinese)
16. Li Zifa, Zhang shuyuan, Zheng Shijun, Ning Chaofeng, Niu Mingjun and Zhou Qifeng, Synthesis of a new kind of liquid crystal copolymers, Polymeric Materials Science and Engineering, 1997, 13(1): 33−37 (in Chinese)
17. Lin Baoping, Onouchi Y. and Okamoto H., Study of main chain liquid crystalline polyurethane containing biphenyl unit, Journal of Southeast University, 1996, 26(2): 97−100 (in Chinese)
18. Zheng Shijun, Zhang Shuyuan, Li Yanhong, Yuan Jing and Li Zifa, Synthesis of thermotropic liquid crystalline aromatic-aliphatic poly(imide ester)s, Polymeric Materials Science and Engineering, 1997, 13(4): 53−58 (in Chinese)