NOTES

Preparation and Properties of Polyurethanes Containing Mesogenic Units

Kazuo SUGIYAMA*, Kohei SHIRAISHI, and Koichi KATO

*Department of Industrial Chemistry, Faculty of Engineering, Kinki University,
Takaya, 1 Umenobe, Higashihiroshima 729-17, Japan*

(Received June 18, 1992)

KEY WORDS Polyurethane / Thermotropic Liquid Crystalline Polymer /
Hydrogen Bonding / X-Ray Diffraction /

Polymers in which the mesogenic moieties with flexible segments are incorporated into the backbone are known to have strongly ordered structures in the solid state and often exhibit a thermotropic liquid crystalline phase. These main-chain types of thermotropic liquid crystalline polymers (TLCPs) are mainly achieved in a variety of polyesters, polyamides, and polyethers.^{1–5} Not so many urethane based TLCPs have been reported on the synthesis and their thermal and rheological properties.^{6–11} In the previous paper,¹² a terminal-terminal type of compound **1** was synthesized as a model for urethane based TLCPs and we understood how the hydrogen bonding interaction affects the formation of mesophase in low molecular weight liquid crystalline di[urethane]s. In the present note thermotropic liquid crystalline polyurethanes, poly{(S)-2-hydroxypropyl 4[4-(11-hydroxy)benzylideneamino]cinnamate substituted diisocyanates}, **3a–e** were prepared from the polyaddition of (S)-2-hydroxypropyl 4[4-(11-hydroxyundecanoxy)benzylideneamino]cinnamate **2** with a series of diisocyanates.

EXPERIMENTAL

Diol

α , ω -Diol **2** was synthesized by the

condensation of 4(11-hydroxyundecanoxy) benzaldehyde with (S)-2-hydroxypropyl 4-aminocinnamate according to the method described previously¹³ and had the following: ¹H NMR (CDCl₃): 0.80–1.56 (m, 18H), 1.60–1.90 (m, 3H), 3.28–3.56 (t, 3H), 3.68–4.08 (m, 4H), 6.16–6.44 (d, *J* = 16Hz, 1H), 6.68–7.76 (m, 9H), 8.22 (s, 1H).

Polyaddition

Into a 100 ml three-necked round bottomed flask, equipped with a magnetic stirrer, N₂ inlet tube and dropping funnel, were placed a known amount of **2** in dry anisole. At the first step, 95% of the required amount of diisocyanate was slowly added to the stirred solution over a period of 2 h 155°C. After being kept at this temperature for 2 h, 5% of residual diisocyanate was added at once and the mixture was stirred for another 4 h. After polyaddition, the content of the reaction vessel was poured into a large amount of methanol to precipitate the solid. Polymers **3a–e** were purified by removing low molecular weight compounds by use of a Soxhlet extractor with ethanol as solvent for 20 h.

Characterization

¹H NMR measurements were carried out with a 100 MHz JEOL JNM-MH100 spectrom-

eter. IR measurements were carried out with a JASCO IR 810 spectrometer, with a heating plate made of aluminum attached to a temperature controller. For thermal processing IR studies, 5% (w/v) of sample were dissolved in spectrograde chloroform and poured onto KBr plates and the solvent removed *in vacuo*. The sample was sandwiched between two KBr plates and was used for the IR measurements. The phase transition temperature was determined by differential scanning calorimetry (DSC), using a Rigaku Thermoflex apparatus DSC-8230B. Sample quantity was 10 mg with $10^{\circ}\text{C min}^{-1}$ of heating and cooling rate. Pyrolysis was carried out with a Rigaku TG-DSC instrument standard type CN8076 E1. Polarized optical microscopy (POM) of thin samples, which were sandwiched between two glass slides (spacing, $25\ \mu\text{m}$), was performed using as Olympus microscope BH-2 with a heating stage attached to a temperature controller. Gel permeation chromatography (GPC) measurements were carried out in THF solution with TSK-G2000HXL/TSK-G3000-

HXL/TSK-G4000HXL at room temperature, using a TOSOH HLC-8020 GPC apparatus. The degree of crystallinity was measured on powder samples by a diffraction of Macscience Co. type MXP 18V using Cu-K_{α} radiation. The scattering intensity was registered at $2^{\circ}\text{ min}^{-1}$ for values of 2θ ranging from 4° to 40° . The small-angle X-ray diffraction pattern of **3e** was taken in the solid phase, that prepared from quenching rapidly to liquid nitrogen just after annealed at 170°C for 30 min. The X-ray diffraction pattern was recorded with a Rigaku RINT-1500/2203E1, E5.

RESULTS AND DISCUSSION

α , ω -Diol **2** used in this work exhibits the ferroelectric liquid crystalline phase: $K\ 57\ S_{\text{H}}^* 112\ S_{\text{C}}^* 132\ S_{\text{A}} 147\ I$.¹³ Diisocyanates used were 1,6-hexamethylene (HMDI), 4,4'-diphenylmethane (DPMDI), 1,3-phenylene (1,3-PDI), toluene 2,4- (2,4-TDI), and toluene 2,6-diisocyanate (2,6-TDI). Table I shows the results of the polyaddition of diol to

Table I. Polyaddition^a of diols **1** to diisocyanates (DI) and characterization of polyurethanes **3**

Polymer 3	1	DI	Anisole	Yield	$^1\text{H NMR}^b$	Elemental analysis			M_w^c	M_w/M_n	Crystallinity ^d
	mmol	mmol	ml	%	$-\text{CH}=\text{N}-$ ppm	C	H	N			%
a	4.92	HMDI 4.92	12	90.6	8.88	$\text{C}_{38}\text{H}_{53}\text{N}_3\text{O}_7$ (663.862)			15300	1.52	10.9
						Calc.	68.75	8.05			
						Found	69.05	8.01			
b	0.98	DPMDI 0.98	40	61.1	8.20	$\text{C}_{45}\text{H}_{51}\text{N}_3\text{O}_7$ (745.924)			7400	1.05	10.0
						Calc.	72.46	6.89			
						Found	72.73	6.70			
c	3.94	1,3-PDI 3.94	20	51.1	8.80	$\text{C}_{38}\text{H}_{45}\text{N}_3\text{O}_7$ (655.798)			5800	1.02	8.5
						Calc.	69.60	6.92			
						Found	70.05	6.97			
d	3.94	2,4-TDI 3.94	20	62.9	8.96	$\text{C}_{39}\text{H}_{47}\text{N}_3\text{O}_7$ (669.825)			20700	1.67	8.1
						Calc.	69.93	7.07			
						Found	69.61	6.91			
e	1.97	2,6-TDI 1.97	20	78.7	8.54	$\text{C}_{39}\text{H}_{47}\text{N}_3\text{O}_7$ (669.825)			6200	1.08	8.5
						Calc.	69.93	7.07			
						Found	70.06	7.17			

^a Polyaddition was carried out in anisole at 155°C .

^b Measured in CDCl_3 .

^c Measured by GPC with tetrahydrofuran (THF) as an eluent and calibrated with standard polystyrenes.

^d Determined by X-ray diffraction analysis.

Figure 1. Structures of twin models, diol, and polyurethanes.

diisocyanates in anisole at 155°C and characterization of resulting polymer. Polyurethanes **3** are soluble in chloroform with small insoluble part and the chloroform soluble fractions were discussed in this note. The structure of **3** shown in Figure 1 was identified by $^1\text{H-NMR}$, IR spectroscopy and elemental analyses. IR spectra showed N-H stretch in 3320–3340 cm^{-1} and C=O stretch of urethane linkage 1960–1720 cm^{-1} . The peaks which appeared at 8.20–8.96 ppm in the ^1H NMR were attributed to the Schiff base protons. The elemental analysis data matched the theoretical values within the limits of experimental error. From GPC measurements, the molecular weight of **3** was found to be 4900–20700. The thermal properties of the polymers were studied by DSC and POM. Figure 2 depicts the DSC traces of **3** with heating and cooling at 5°C min $^{-1}$. The melting process of **3a**, for instance, indicated by two strong endothermic peaks at 124.6°C (crystal-

Figure 2. DSC traces of polyurethanes **3**.

line-crystalline transition) and 144.6°C (melting points) with a small peak at 198°C (isotropization transition) is followed by

decomposition that began at 257°C.

After annealed at the temperature below decomposition for 2 h, **3a** and **3e** exhibit a broad exothermic peak due to crystallizing transition on cooling, while **3d** shows no peak. DSC traces of **3b** and **3c** were in a similar

Figure 3. POM photograph of polyurethane **3e** at 74°C on cooling cycle, $\times 150$.

pattern as that of **3d**. POM of **3e** reveals birefringence, which is retained even at 0°C as shown in Figure 3. Similar textures, frozen in the state by fairly low temperature, were observed on the other polyurethanes. The small-angle X-ray diffraction pattern scanning for $2\theta = 0.150$ – 10.000° for the annealed sample of **3e** at room temperature shows a broad peak at $2\theta = 3.88^\circ$ corresponding to an interplanar spacing of $d = 22.7 \text{ \AA}$ as shown in Figure 4. This is assigned to the layer spacing in a smectic mesophase.¹⁴

At present, it is not known to which smectic mesophase **3** belongs. Low molecular weight compounds composed of two terminal mesogenic groups interconnected by a flexible spacer group may be taken as models for main-chain type of TLCs which contain core units interconnected through spacer groups.^{15–18} The relationship between structure and property of the twin models is known to parallel that of analogous TLCs. We have already prepared twin model **1a–e** as the prototype of urethane-based TLCs. Table II tabulates the phase transition temperature of **3** together with that of their twin models **1**. In twin models it was found that intra- and intermolecular interaction due to the hydrogen bonding play an important role in formation of mesophase.¹² In twin models **1c** and **1d**, the rigid core unit tends to self-associate by a relatively strong in-

Figure 4. Small-angle X-ray diffraction scans for the annealed sample of **3e** at room temperature.

Table II. Phase transition temperature of twin models **1** and polyurethanes **3**

1, 3	X ^a	Twin model 1 ^b Phase transition/°C				Polyurethane 3 ^c Phase transition/°C		
		<i>K</i>	<i>S_X</i>	<i>S_A</i>	<i>I</i>	<i>T_m</i>	<i>T_i</i>	<i>T_d</i>
a	$-(\text{CH}_2)_6-$	123	—	—	·	144	198	257
b		120	—	—	·	159	207	267
c		84	—	105	·	97	192	224
d		54	65	99	·	71	233	257
e		102	—	—	·	145	159	228

^a See Figure 1.^b Reference 12.^c *T_m*, *T_i*, and *T_d* represent melting points, phase transition temperature from nematic phase to isotropic melt on heating cycles, and initial decomposition temperature, respectively. **Figure 5.** Temperature dependence of C=O (left) and N-H (right) stretching band for polyurethanes **3a**, **3d**, and **3e**.

tramolecular hydrogen bonding and a reasonably long aliphatic chain contributes to formation of the smectic A (*S_A*) phase. Since the intermolecular hydrogen bonding is a dominant factor for the crystallization, other twin models **1a**, **1b**, and **1c** exhibits the

transition of crystalline-isotropic melt. In order to know how the hydrogen bonding interaction affects the formation of mesophases in polyurethanes **3**, thermal processing IR measurements were carried out. Figure 5 shows the frequency shift in IR spectra of **3a**, **3d**, and **3e**

as a function of temperature in the range of 20 to 250°C, including the N–H stretch and the C=O stretch of which frequencies and relative intensities are characteristic of hydrogen bond formation.⁹ It was found that the stretches regarded as hydrogen bonding C=O as well as N–H vibration of polyurethanes gradually shift to higher frequency region with increasing temperature around their melting points. These facts suggest that the hydrogen bonding plays an important role in the development of mesophases in **3**.⁹

All of **3** having structure corresponding to **1** showed a smectic phase since the mesogenic groups in the main chains are restricted to align by intermolecular interaction.

Acknowledgments. The authors thank Mr. T. Ohashi of Western Industrial Research Institute of Hiroshima for the determination of degree of crystallinity. Thanks are also due to Mr. T. Sakatani of Rigaku X-ray diffract application center for the measurements of small-angle X-ray diffraction.

REFERENCES

1. T. Uryu and T. Kato, *Macromolecules*, **21**, 378 (1988).
2. W. H. Chen, T. C. Chang, and F. Higashi, *J. Polym. Sci., A: Polym. Chem. Ed.*, **26**, 3269 (1988).
3. B. C. Auman and V. Percec, *Polymer*, **29**, 938 (1988).
4. M. Marcos, F. Navarro, L. Oriol, and J. L. Serrano, *Makromol. Chem.*, **190**, 305 (1989).
5. M. Schmucki and A. D. Jenkins, *Makromol. Chem.*, **190**, 1303 (1989).
6. W. Mormann and M. Brahm, *Makromol. Chem.*, **190**, 631 (1989).
7. H. R. Kricheldorf and J. Awe, *Makromol. Chem.*, **190**, 2597 (1989).
8. M. Tanaka and T. Nakaya, *J. Macromol. Sci. Chem.*, **A26**, 1655 (1989).
9. S. K. Pollack, D. Y. Shen, S. L. Hsu, Q. Wang, and H. D. Stidham, *Macromolecules*, **22**, 551 (1989).
10. P. J. Stenhouse, E. M. Valles, S. W. Kantor, and W. J. MacKnight, *Macromolecules*, **22**, 1467 (1989).
11. F. Papadimitrakopoulos, S. W. Kantor, and W. J. MacKnight, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, **31**(1), 486 (1990).
12. K. Sugiyama, K. Kato, and K. Shiraishi, *Bull. Chem. Soc. Jpn.*, **65**, 2259 (1992).
13. K. Sugiyama, K. Kato, and K. Shiraishi, *Bull. Chem. Soc. Jpn.*, **64**, 1652 (1991).
14. G. Smyth, S. K. Pollack, W. J. MacKnight, and S. L. Hsu, *Liq. Cryst.*, **7**, 839 (1990).
15. R. B. Blumstein, M. D. Poliks, E. M. Stickles, A. Blumstein, and F. Volino, *Mol. Cryst. Liq. Cryst.*, **129**, 375 (1985).
16. H. Toriumi, H. Furuya, and A. Abe, *Polym. J.*, **17**, 895 (1985).
17. P. Esnault, D. Galland, F. Volino, and R. B. Blumstein, *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.*, **157**, 409 (1988).
18. G. S. Attard, S. Garnett, C. G. Hickman, C. T. Imrie, and L. Taylor, *Liq. Cryst.*, **7**, 495 (1990).