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Synthesis of Enantiotropic Liquid Crystal Copolyurethanes Containing Para- and Meta-Type Diisocyanate Units in the Backbone

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ABSTRACT: Enantiotropic liquid crystal (LC) polyurethanes were synthesized for the first time. Thermotropic LC copolyurethanes PU*n*T(*m*/*p*)s (*n*, the number of methylene unit, 6, 8, and 11; m, meta-type unit; p, para-type unit) were synthesized by polyaddition of 4,4′-bis(ω-hydroxyalkoxy)biphenyls (BPn) with two kinds of diisocyanates, that is, meta-type 2,4- and para-type 2,5-tolylene diisocyanates (2,4- and 2,5-TDI). The liquid crystallinity was examined by differential scanning calorimetry (DSC), polarized optical microscopy, and X-ray diffractometry. All copolyurethanes consisting of PU6T(*m*/*p*)s and PU8T-(*m*/*p*)s with all *m*/*p* ratios showed liquid crystallinity in the cooling stage under shear. Of them, six PU*n*T(*m*/*p*)s ($n = 6$ and 8; $m/p = 80/20$, 60/40, and 50/50) showed enantiotropic liquid crystallinity on both heating and cooling stages. However, copolyurethane PU11T(*m*/*p*)s having the undecamethylene spacer did not exhibit any liquid crystallinity at the *m*/*p* ratio from 100/0 to 20/80, although PU11T(0/100) was monotropic. For example, a copolyurethane PU6T(80/20) exhibited enantiotropic liquid crystallinity in the temperature ranges from 156 to 164 °C on the heating stage and from 147 to 138 °C on the cooling stage.

Introduction

Owing to their outstanding properties, thermotropic liquid crystalline polymers such as polyesters, polyamides, polycarbonates, poly(ester-imide)s, and polyurethanes have been studied as hopeful high-performance materials with unique thermal and mechanical properties. Because of the very high melting temperatures and low solubilities of thermotropic liquid crystalline polymers, many studies have been devoted to decreasing the melting point to a melt processable temperature range as well as to improving the solubility without destroying the liquid crystal formation.[1−16]

For polyurethanes, it was very difficult to synthesize thermotropic liquid crystalline polyurethanes because of the strong intermolecular interactions resulting from the hydrogen bonding of the urethane linkages. Many studies were devoted to minimizing the hydrogen-bonding effects using chain modifications.[17−19]

We have been studying the synthesis of thermotropic para-type aromatic polyurethanes containing alkylene spacers.[20−23] The para-type polyurethanes had a tendency to readily crystallize both by mesogenic interactions and by the intermolecular hydrogen bondings. Thus, first, to examine the effects of the mesogenic interactions, para-type polyurethanes without any mesogen were prepared.[21,22] Those polyurethanes exhibited monotropic liquid crystallinity induced by the intermolecular hydrogen bondings alone. Next, to decrease the intermolecular hydrogen bondings, para-type mesogen-containing copolyurethanes including two alkylene spacers with different lengths were synthesized.[23] It was revealed that the copolyurethanes also showed the monotropic nature. However, so far, there is no report on the synthesis of enantiotropic polyurethanes representing liquid crystallinity in both heating and cooling stages.

In this study, we wish to report that enantiotropic liquid crystalline copolyurethanes were successfully synthesized by copolyaddition of both meta- and para-type diisocyanates with 4,4′-bis(ω-hydroxyalkoxy)biphenyls. In addition, the relationship between the polyurethane structure and the monotropic or enantiotropic liquid crystallinity was examined in detail. Thermal properties and structure of the polyurethanes were characterized by ^{1}H and ^{13}C NMR spectroscopies, FT-IR spectroscopy, polarized optical microscope observation, differential scanning calorimetry, and X-ray diffraction measurements.

Experimental Section

Materials. 2,4- and 2,5-tolylene diisocyanates (2,4- and 2,5-TDI) kindly supplied by Mitsui Toatsu Co., Ltd. were used as diisocyanate monomers. ω-Halogenated alkanols (Aldrich Co.) were used without further purification. *N*,*N*′-Dimethylformamide (DMF) was purified by distillation under reduced pressure before use.

Synthesis of 4,4′-Bis(ω-hydroxyalkoxy)biphenyls (BP*n*; $n = 6, 8, 11$). The reaction of 4,4′-dihydroxybiphenyl with ω-halogenated alkanols is described in detail elsewhere.[20,23]

Copolyurethanes. The copolyurethanes with different compositions were prepared by polyaddition of 4,4′-bis(ω-hydroxyalkoxy)biphenyls (BPn) with different molar ratios of both diisocyanates, that is, 2,4- and 2,5-tolylene diisocyanates (2,4- and 2,5-TDI) using the same method described in the previous paper.[20,23]

Characterization. ^{1}H and ^{13}C NMR spectra of polymers and their intermediates were measured on the sample solutions in DMSO-d_6 using 3-(trimethylsilyl)propanesulfonic acid sodium salt (DSS) as an internal standard at 70 and 50 °C, respectively, with a JEOL Lambda-400 spectrometer. FT-IR spectra ranging from 4600 to 400 cm^{-1} of the polymers were measured with a Perkin-Elmer FT-IR 1600 spectrometer by the potassium bromide (KBr) method. Viscosities were measured with an Ubbelohde viscometer in 1,1,2,2-tetrachloroethane-phenol (1/1, v/v) mixture solutions at 30 °C. The thermal properties of the polymers were examined using a Mettler DSC 30 differential scanning calorimeter. The scanning rate was 10 °C/min. The maximum point of the peak was taken as the transition temperature. All samples were heated to a temperature above the isotropic temperature to eliminate thermal history, then cooled to room temperature

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Scheme 1. Synthesis of Copolyurethanes Containing Para-Type and Meta-Type Units in the Polymer Chains

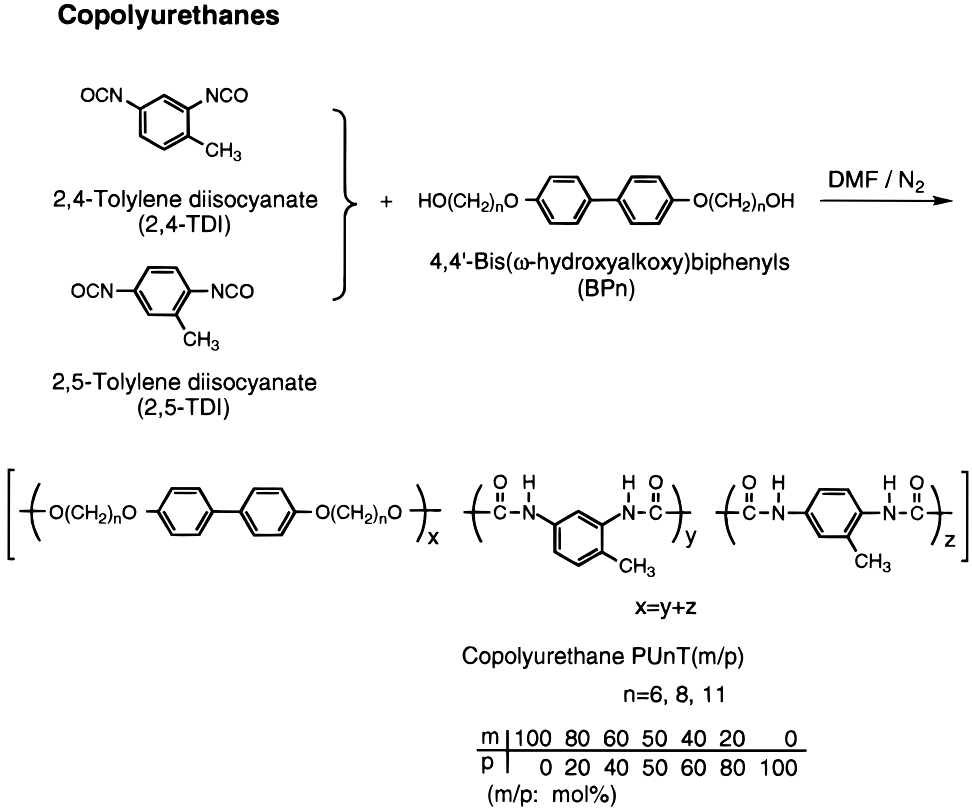

Table 1. Copolyaddition Reaction of Two Kinds of Tolylene Diisocyanates (TDI) with 4,4′-Bis(ω-hydroxyhexoxy)biphenyls (BPn)[a]

copolyurethane	diisocyanate		diol	copolyurethane	
PU6T (*m*/*p*) [*m*/*p*: mol %]	2,4-TDI [mg (mmol)]	2,5-TDI [mg (mmol)]	BPn [mg (mmol)]	yield [mg (%)]	[η][b] [dL/g]
PU6T(100/0)[c]	124.0 (0.71)		275.2 (0.71)	342.0 (86)	0.37
PU6T(80/20)	114.7 (0.66)	28.7 (0.17)	318.2 (0.82)	328.9 (71)	0.62
PU6T(60/40)	79.9 (0.46)	53.3 (0.31)	295.7 (0.77)	365.5 (85)	0.49
PU6T(50/50)	77.0 (0.44)	77.0 (0.44)	341.7 (0.88)	361.2 (73)	0.50
PU6T(40/60)	54.1 (0.31)	81.2 (0.47)	300.3 (0.78)	339.3 (78)	0.36
PU6T(20/80)	24.9 (0.14)	99.6 (0.57)	276.4 (0.72)	273.8 (68)	0.40
PU6T(0/100)		153.0 (0.88)	338.0 (0.88)	475.0 (97)	0.67

[a] Solvent: DMF. Reaction time: 24 h. Temperature: 80 °C. [b] Measured in 1,1,2,2-tetrachloroethane−phenol (1:1 v/v) solutions at 30 °C. [c] The numbers in parenthesis designate mole ratios in the meta- and para-diisocyanates in the feed.

and scanned for the second time. All DSC data listed in Tables refer to the second run. The optical textures of the mesophases were observed using an Olympus BH2 polarizing microscope equipped with a Mettler FP84 hot stage. Measurements on the thermal stability of polymers were carried out with a TG8120 thermogravimeter at a heating rate of 5 °C/min under nitrogen atmosphere. X-ray diffraction measurements were performed with a Rigaku RINT 1500 X-ray diffractometer.

Results and Discussion

Preparations of Copolyurethanes. The previous paper revealed that copolyurethanes containing biphenylene mesogen, two different alkylene moieties, and a para-type diisocyanate exhibit monotropic liquid crystallinity.[23] Thus, in this study, copolyurethanes containing the biphenylene mesogen, an alkylene moiety, and two different diisocyanates, that is, meta- and para-type tolylene diisocyanates, were synthesized in order to induce enantiotropic liquid crystallinity by decreasing to some extent both intermolecular hydrogen bondings and mesogenic interactions, as shown in Scheme 1.

Results of copolymerizations and intrinsic viscosities are shown in Tables 1, 2, and 3. Copolyurethane PU6T(*m*/*p*)s having different compositions were obtained by polyaddition of equimolar amounts of diisocyanates and the diol. Those had fairly high molecular weights indicated by intrinsic viscosities of 0.36−0.67 dL/g. In addition, copolyurethane PU8T(*m*/*p*)s and PU11T(*m*/*p*)s also exhibited fairly high intrinsic viscosities of 0.33−0.99 dL/g.

The formation of copolyurethanes was confirmed by ^{1}H and ^{13}C NMR and IR spectra. As shown in Figure 1, a ^{1}H NMR spectrum for a copolyurethane PU8T(40/60) indicated that there are four NH proton absorptions due to the urethane linkage at 8.41, 8.49, 9.24, and 9.26 ppm the nonequivalency of which was caused by the existence of two kinds of methyl groups in the meta- and para-tolylene groups. Absorptions assignable to biphenylene protons at 6.91 and 7.41 ppm also appeared. The ^{13}C NMR spectrum showed the signals for the aromatic rings at 116.5−159.5 ppm, the carbonate C═O at 155.2−156.3 ppm, and the aliphatic chains at 26.9−69.5 ppm. In the IR spectrum, absorptions due to NH and C═O bonds of urethane linkages were seen at 3310 and 1700 cm^{-1}, respectively. Therefore, the

Table 2. Copolyaddition Reaction of Two Kinds of Tolylene Diisocyanates (TDI) with 4,4′-Bis(ω-hydroxyoctoxy)biphenyls (BPn)[a]

copolyurethane	diisocyanate		diol	copolyurethane	
PU8T (m/p) [m/p: mol %]	2,4-TDI [mg (mmol)]	2,5-TDI [mg (mmol)]	BPn [mg (mmol)]	yield [mg (%)]	$[\eta]^b$ [dL/g]
PU8T(100/0)[c]	124.7 (0.72)		316.9 (0.72)	386.1 (87)	0.47
PU8T(80/20)	107.3 (0.62)	26.8 (0.15)	340.9 (0.77)	386.7 (81)	0.61
PU8T(60/40)	82.2 (0.47)	54.8 (0.32)	348.2 (0.79)	374.2 (77)	0.63
PU8T(50/50)	66.8 (0.38)	66.8 (0.38)	339.6 (0.77)	370.1 (78)	0.53
PU8T(40/60)	60.1 (0.35)	90.2 (0.52)	381.9 (0.86)	393.4 (74)	0.61
PU8T(20/80)	23.4 (0.13)	93.6 (0.54)	297.5 (0.67)	321.8 (78)	0.33
PU8T(0/100)		102.0 (0.58)	258.0 (0.58)	316.0 (88)	0.47

[a] Solvent: DMF. Reaction time: 24 h. Temperature: 80 °C. [b] Measured in 1,1,2,2-tetrachloroethane−phenol (1:1 v/v) solutions at 30 °C. [c] The numbers in parenthesis designate mole ratios in the meta- and para-diisocyanates in the feed.

Table 3. Copolyaddition Reaction of Two Kinds of Tolylene Diisocyanates (TDI) with 4,4′-Bis(ω-hydroxyundecoxy)biphenyls (BPn)[a]

copolyurethane	diisocyanate		diol	copolyurethane	
PU11T (m/p) [m/p: mol %]	2,4-TDI [mg (mmol)]	2,5-TDI [mg (mmol)]	BPn [mg (mmol)]	yield [mg (%)]	$[\eta]^b$ [dL/g]
PU11T(100/0)[c]	115.3 (0.66)		348.7 (0.66)	402.7 (87)	0.70
PU11T(80/20)	106.4 (0.61)	26.6 (0.15)	402.3 (0.76)	472.0 (88)	0.55
PU11T(60/40)	78.3 (0.45)	52.2 (0.30)	394.7 (0.75)	446.0 (85)	0.64
PU11T(50/50)	57.3 (0.33)	57.3 (0.33)	346.6 (0.66)	405.4 (88)	0.59
PU11T(40/60)	54.7 (0.31)	82.1 (0.47)	413.7 (0.79)	419.5 (88)	0.90
PU11T(20/80)	23.7 (0.14)	94.8 (0.54)	358.5 (0.68)	402.7 (87)	0.69
PU11T(0/100)		153.0 (0.88)	461.0 (0.88)	580.0 (95)	0.99

[a] Solvent: DMF. Reaction time: 24 h. Temperature: 80 °C. [b] Measured in 1,1,2,2-tetrachloroethane−phenol (1:1 v/v) solutions at 30 °C. [c] The numbers in parenthesis designate mole ratios in the meta- and para-diisocyanates in the feed.

copolyurethanes were obtained as designed.

Liquid Crystallinity and Thermal Properties of Copolyurethanes. DSC measurement was carried out for copolyurethane PUnT(m/p)s. As shown in Figures 2 and 3, DSC thermograms for PU8T(m/p)s observed without shearing exhibited individually two peaks due to thermal transitions. Peaks corresponding to thermal transitions were also showed for PU6T(m/p)s and PU11T(m/p)s. Since, in thermotropic polyurethanes, the liquid crystalline orientation is induced under shearing, the origins of these peaks could not be decided with the DSC thermograms alone. After they were combined with data from the polarized microscope observations mentioned below, the DSC thermograms were analyzed below.

Polarized microscope observation was performed on the PUnT(m/p)s under shearing. Polarized microphotographs for a copolyurethane PU6T(80/20) are shown in Figure 4. The photos A and B are ones taken in the first cooling stage from the isotropic state under shearing. This is a typical texture for the para-type polyurethane in the liquid crystalline state.[21−23] Since the samples representing the photos A and B taken at 146 and 145 °C, respectively, possessed mobility, it is clear that they were in the liquid crystalline state. In this study, the liquid crystalline state was defined as the state having both liquid crystalline texture and mobility.

On the other hand, although the photos C and D represent colored patterns similar to those in the liquid crystalline, the samples at these temperatures did not possess the mobility, indicating that they were in the crystalline state.

It is noteworthy that the photos E, F, and G observed in the second heating stage at 145, 156, and 159 °C, respectively, are combinations of patterns A and C. Moreover, in this temperature range, the samples possessed the mobility. This sample was subjected to shearing in the mesophase temperature range when it was cooled. Thus, it was discovered that the copolyurethane PU6T(80/20) had enantiotropic liquid crystallinity.

For copolyurethanes containing the meta component 2,4-TDI more than 50 mol %, that is, PUnT(m/p)s (n = 6 and 8; m/p = 80/20, 60/40, and 50/50), the enantiotropic behaviors were observed. On the other hand, copolyurethanes containing the meta component less than 50 mol % exhibited the monotropic nature.

Transition temperatures of copolyurethane PU6T(m/p)s and PU8T(m/p)s consisting of the meta- and para-type components with different compositions are summarized in Tables 4 and 5. The copolyurethane PU8T(40/60) exhibited liquid crystallinity in the temperature range from 153 to 146 °C on cooling, while on heating it melted at 160 °C to show an isotropic phase without representing any mesophase. Accordingly, the sample was monotropic.

The induction of the enantiotropic liquid crystallinity might be caused by the following reason. In the copolyurethanes containing both meta and para units in random distribution, the decrease in regularity of distributions of the mesogenic units and urethane linkages in the polymer backbone must have caused the decrease in persistence length and effective axial ratio, resulting in the decrease in both mesogenic interactions and intermolecular hydrogen bondings. Thereby, an appropriate magnitude of the intermolecular interactions to cause the enantiotropic liquid crystallinity might be attained, because in the para-type polyurethanes containing biphenylene mesogen, strong intermolecular interactions readily caused the crystallization but not the liquid crystallization.[21−23]

There are a number of studies which dealed with the introduction of nonlinear monomer units into thermotropic aromatic polyesters.[7,14,24−27] In general, when the proportion of nonlinear monomers in the polyesters increased beyond a certain critical value, the liquid

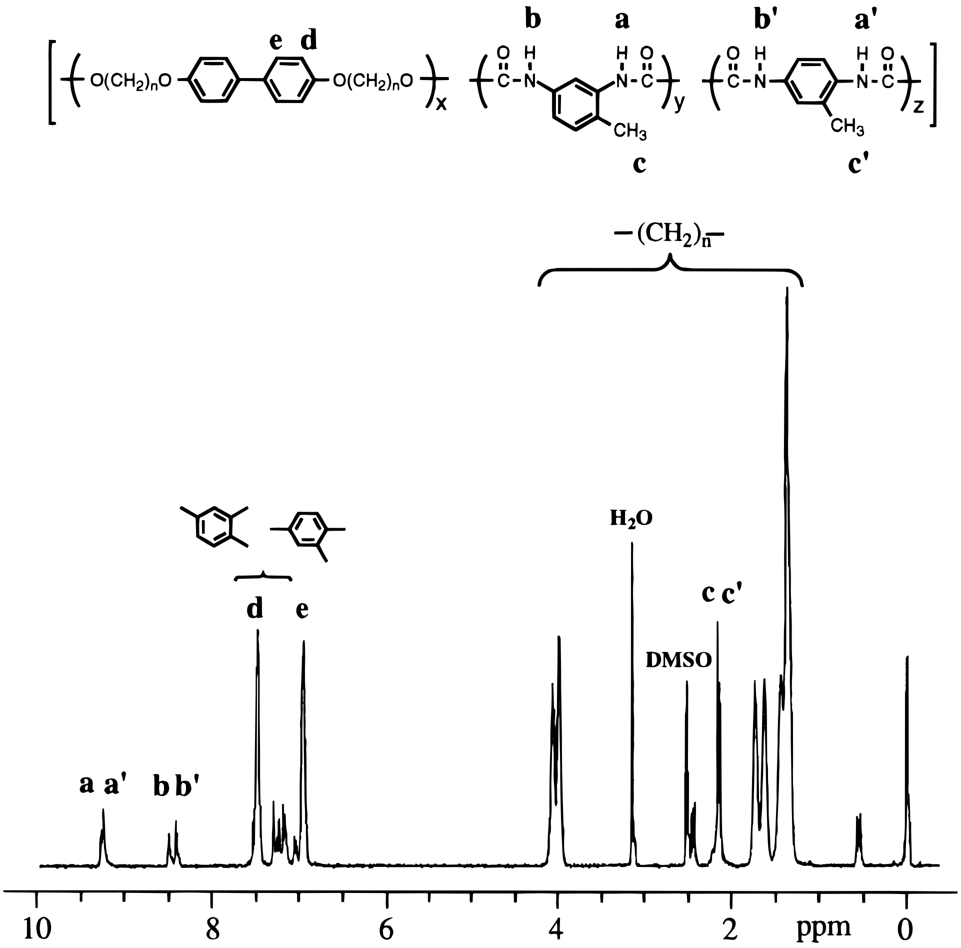

Figure 1. ^{1}H NMR spectrum (400 MHz) of a copolyurethane PU8T(40/60) in DMSO-d_6 at 70 °C.

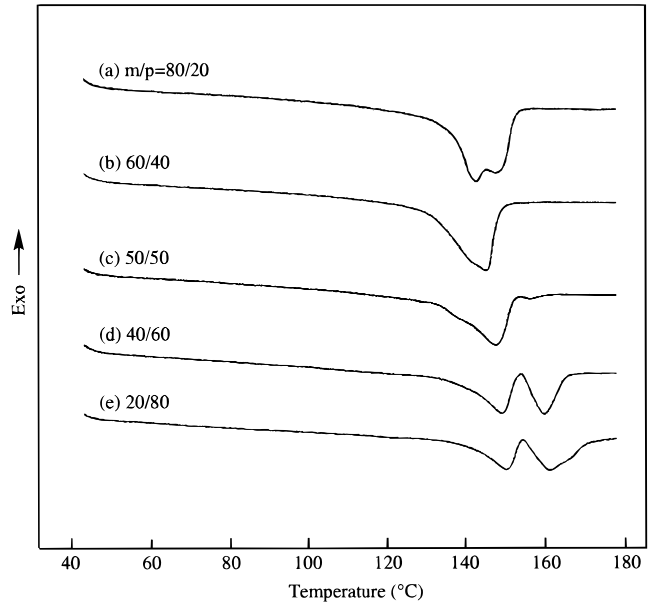

Figure 2. DSC thermograms of PU8T(*m*/*p*)s on heating scan: (a) $m/p = 80/20$, (b) $m/p = 60/40$, (c) $m/p = 50/50$, (d) $m/p = 40/60$, and (e) $m/p = 20/80$. The cooling rate was 10 °C/min.

crystallinity was not induced. However, the present results indicate that although the incorporation of nonlinear meta units in the polyurethanes decreased the T_m and the liquid crystalline temperature range, the liquid crystallinity was induced with high proportions of the nonlinear units.

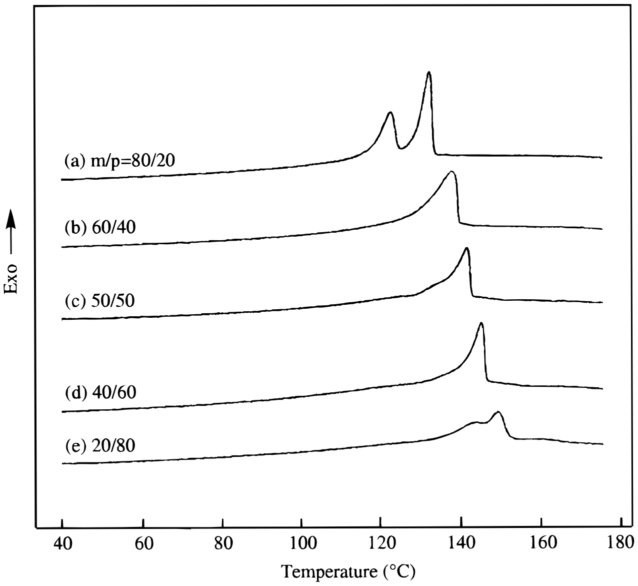

Figure 3. DSC thermograms of PU8T(*m*/*p*)s on cooling scan: (a) $m/p = 80/20$, (b) $m/p = 60/40$, (c) $m/p = 50/50$, (d) $m/p = 40/60$, and (e) $m/p = 20/80$. The heating rate was 10 °C/min.

The copolyurethane PU6T(80/20) containing 80% meta units exhibited the isotropic-to-liquid crystal transition at 147 °C and the liquid crystal-to-crystal transition at 138 °C in the cooling stage, while it showed the crystal-to-liquid crystal transition at 156 °C and a liquid crystal-to-isotropic transition at 164 °C in the

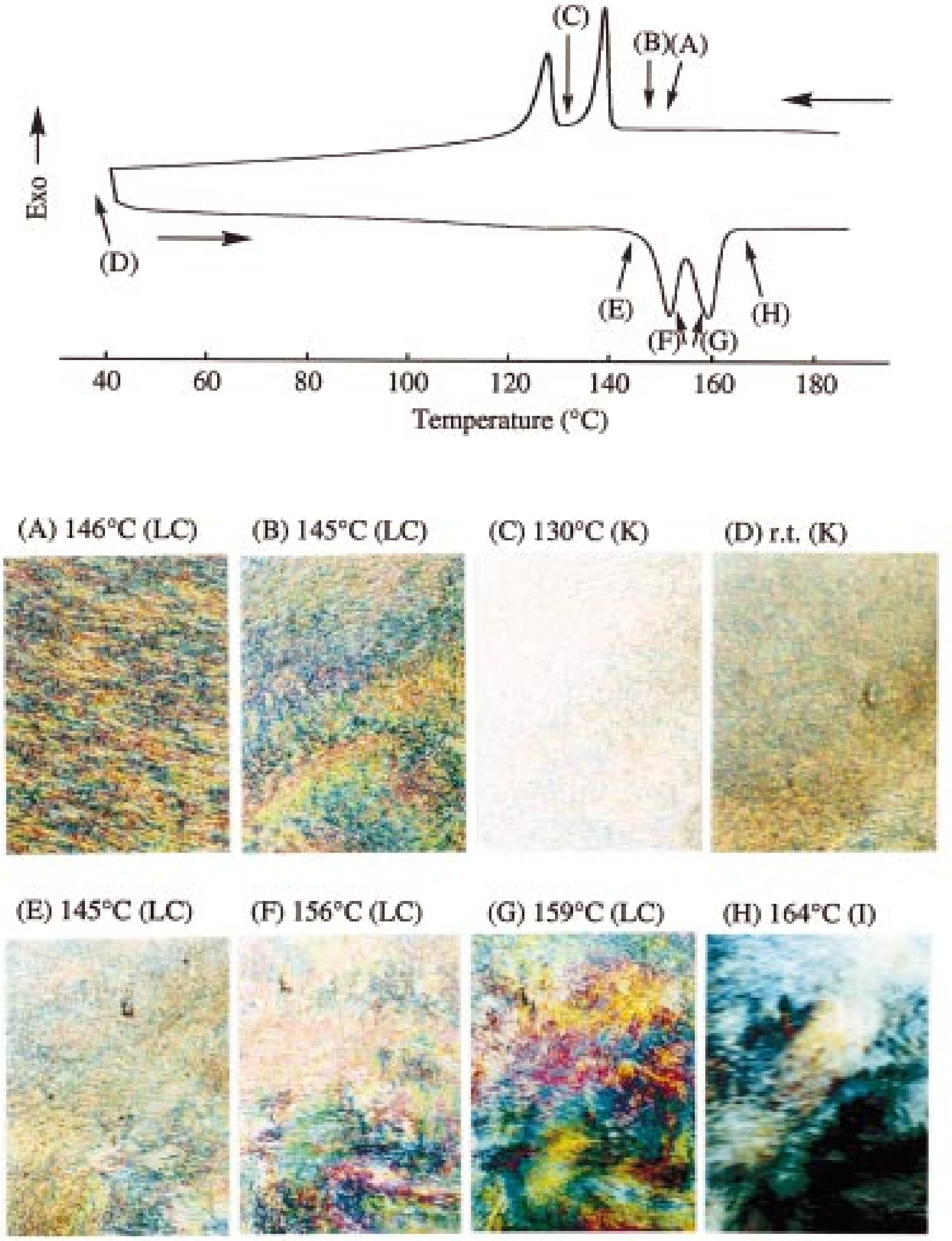

Figure 4. Polarized microphotographs of a copolyurethane PU6T(80/20): (A) a nematic phase taken at 146 °C, and (B) at 145 °C under shear; (C) a crystallized nematic morphology taken at 130 °C, and (D) at room temperature on cooling; (E) a nematic phase taken at 145 °C, (F) at 156 °C, and (G) at 159 °C; and (H) an isotropic phase taken at 164 °C on heating.

Table 4. Thermal Properties of Copolyurethane PU6T (*m*/*p*)s[a]

copolyurethane	phase-transition temperature											
	second heating							second cooling				
PU6T (*m*/*p*) [*m*/*p*: mol %]	T_g[b] [°C]	T_{K-LC}[c] [°C]	T_{LC-I}[c] [°C]	T_{m1}[d] [°C]	T_{m2}[d] [°C]	ΔH_{m1} [J/g]	ΔH_{m2} [J/g]	T_{I-LC}[c] [°C]	T_{LC-K1}[d] [°C]	T_{K2}[d] [°C]	ΔH_{LC-K1} [J/g]	ΔH_{K2} [J/g]
PU6T(100/0)	91			150	166	29.0	10.0	139	131		16.8	
PU6T(80/20)	85	156	164	153	160	19.2	19.8	147	138	126	20.6	20.1
PU6T(60/40)	90	134	144	136	143	20.4	7.8	141	134	115	16.8	8.6
PU6T(50/50)	88	133	146	145	155	24.2	2.7	145	139	119	19.1	7.2
PU6T(40/60)	86			151	162	24.8	8.4	151	143		34.2	
PU6T(20/80)	90			154	166	25.4	10.7	159	151	144	15.9	18.8
PU6T(0/100)	89			198	206	3.6	19.9	202	183		32.2	

[a] Determined by DSC at a heating or cooling rate of 10 °C/min under nitrogen atmosphere except for T_{K-LC}, T_{LC-I}, and T_{I-LC}. [b] Determined in the first heating scan of DSC. [c] Determined by polarized microscopic observation. [d] Determined by DSC measurement.

heating stage. This phenomenon was rather extraordinary.

As thermal properties of copolyurethane PU11T(*m*/*p*)s having undecamethylene spacer are summarized in

Table 5. Thermal Properties of Copolyurethane PU8T (*m*/*p*)s[a]

copolyurethane	phase-transition temperature											
	second heating							second cooling				
PU8T (*m*/*p*) [*m*/*p*: mol %]	T_g[b] [°C]	T_{K-LC}[c] [°C]	T_{LC-I}[c] [°C]	T_{m1}[d] [°C]	T_{m2}[d] [°C]	ΔH_{m1} [J/g]	ΔH_{m2} [J/g]	T_{I-LC}[c] [°C]	T_{LC-K1}[d] [°C]	T_{K2}[d] [°C]	ΔH_{LC-K1} [J/g]	ΔH_{K2} [J/g]
PU8T(100/0)	80			144	158	15.5	24.3	135	127	114	20.0	14.3
PU8T(80/20)	81	141	152	143	148	28.4	14.2	141	133	128	22.4	16.8
PU8T(60/40)	79	139	147	145		39.1		144	138		39.6	
PU8T(50/50)	80	137	147	148	156	36.9	1.0	148	142		40.1	
PU8T(40/60)	80			150	160	23.0	13.6	153	146		34.4	
PU8T(20/80)	88			151	162	15.4	15.9	158	150	145	11.6	12.4
PU8T(0/100)	81			152	171	6.2	15.4	170	151		24.3	

[a] Determined by DSC at a heating or cooling rate of 10 °C/min under nitrogen atmosphere except for T_{K-LC}, T_{LC-I}, and T_{I-LC}. [b] Determined in the first heating scan of DSC. [c] Determined by polarized microscopic observation. [d] Determined by DSC measurement.

Table 6. Thermal Properties of Copolyurethane PU11T (*m*/*p*)s[a]

copolyurethane	phase-transition temperature									
	second heating					second cooling				
PU11T (*m*/*p*) [*m*/*p*: mol %]	T_g[b] [°C]	T_{m1}[d] [°C]	T_{m2}[d] [°C]	ΔH_{m1} [J/g]	ΔH_{m2} [J/g]	T_{I-LC}[c] [°C]	T_{LC-K}[d] [°C]	T_K[d] [°C]	ΔH_{LC-K} [J/g]	ΔH_K [J/g]
PU11T(100/0)	88	143		45.7				129		55.3
PU11T(80/20)	88	141		42.2				130		48.9
PU11T(60/40)	88	142		42.1				133		49.4
PU11T(50/50)	84	144		42.9				137		49.3
PU11T(40/60)	88	146	156	43.9	2.9			139		54.7
PU11T(20/80)	83	145	161	20.7	24.0			145		56.7
PU11T(0/100)	77	156	173	16.3	43.5	171	155		48.9	

[a] Determined by DSC at a heating or cooling rate of 10 °C/min under nitrogen atmosphere except for T_{I-LC}. [b] Determined in the first heating scan of DSC. [c] Determined by polarized microscopic observation. [d] Determined by DSC measurement.

Table 6, all PU11T(*m*/*p*)s except for a PU11T(0/100) were not liquid crystalline.

For the two enantiotropic LC copolyurethanes PU6T and PU8T, phase diagrams are shown in Figure 5. The transition temperatures of the copolyurethane PU*n*T(*m*/*p*)s (n = 6 and 8) had a tendency to shift toward the high-temperature side with an increasing proportion of the meta-type unit in the heating stage.

To observe the liquid crystalline state in both heating and cooling stages, shear must be applied during the cooling stage. When copolyurethanes having the meta and para mixed compositions are in tension-free conditions, non-liquid-crystalline ordering structures might be easily formed. Therefore, it is assumed that the thermally equilibrated structures must be mechanically distorted in the liquid-crystalline state during the cooling stage to produce a quasi-stable mesophase.

One of the reasons that the copolyurethanes exhibited clear enantiotropic liquid crystallinity is their considerably high thermal stability. Thermogravimetry for three copolyurethanes, that is, PU6T(60/40), PU8T(60/40), and PU11T(50/50), is shown in Figure 6. Their 5% weight loss temperatures ranged from 277 to 310 °C, much higher than isotropic temperatures.

X-ray Diffraction Patterns. X-ray diffraction patterns were taken for a copolyurethane PU6T(60/40) quenched from the liquid crystalline state where the shear was subjected (Figure 7). This diffractogram showed a broad reflection at approximately 2θ of 20° (d = 4.38 Å) and a weak reflection at approximately 2θ of 6° (d = 15.68 Å), which suggests the existence of a layered structure. A similar tendency was also seen for other copolyurethanes.[23]

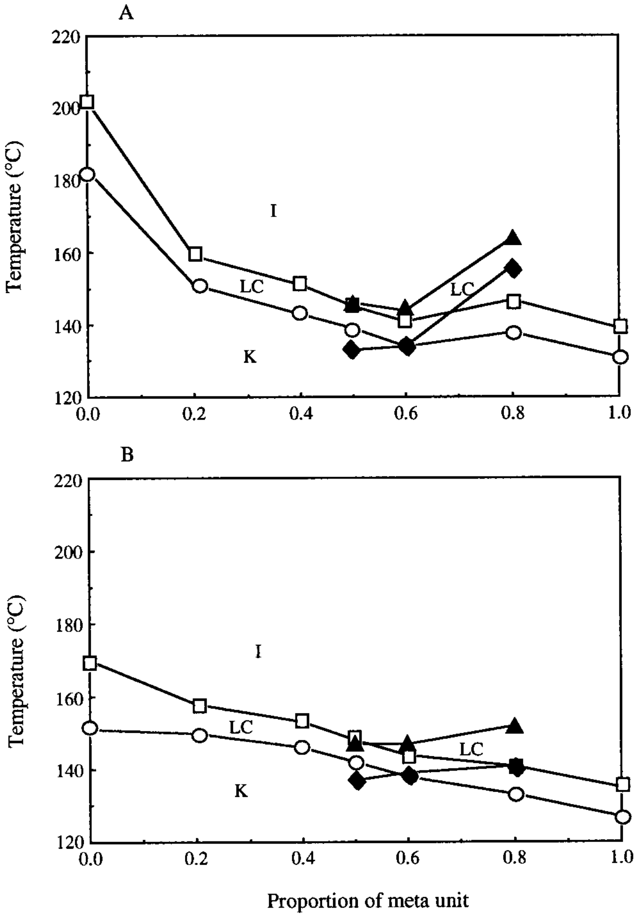

Figure 5. Phase diagrams of copolyurethane (A) PU6T(*m*/*p*)s and (B) PU8T(*m*/*p*)s: (□) T_{I-LC} on cooling; (○) T_{LC-K} on cooling; (◆) T_{K-LC} on heating; and (▲) T_{LC-I} on heating.

We intended to cause the irregularity in the structure of polyurethanes by random copolymerization. Because of incorporation of high proportions of the meta unit, both the decrease in the aspect ratio of rodlike sequences

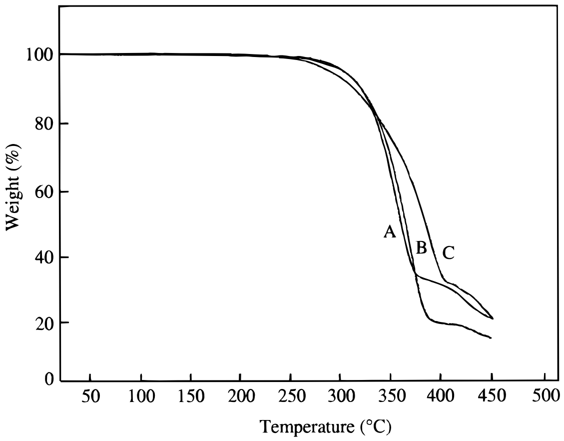

Figure 6. Thermogravimetry conducted with a heating rate of 5 °C/min under a nitrogen atmosphere: (A) PU6T(60/40), (B) PU8T(60/40), and (C) PU11T(50/50).

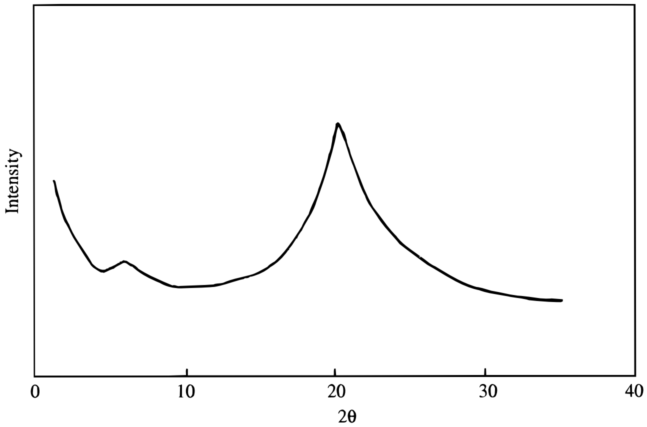

Figure 7. X-ray diffraction pattern of a copolyurethane PU6T-(60/40) quenched from the liquid-crystalline state where the shear was subjected.

and the lowering in the intermolecular interactions to some extent might occur. Especially, regulation of the quantity of the intermolecular hydrogen bondings which was otherwise impossible can be accomplished by this method. The introduction of nonlinear units in the backbone must have resulted in reduction of the chain packing. Upon shearing, the polymer domains are aligned in shear-applied direction, which can form a liquid-crystalline phase based on a kind of mechanical orientation. Accordingly, copolyurethanes containing both meta- and para-type units can form a monotropic mesophase, which is the case of those containing 2,4-TDI component in a proportion less than 50%. In the case of copolyurethanes containing 2,4-TDI component in a proportion more than 50%, an increase in the nonlinear unit resulted in the reduction of the lateral chain packing as well as the intermolecular interaction due to the hydrogen bonding between the urethane linkages to a certain critical level, and thereby these polymers showed LC mesophases with birefringence and fluidity on heating. Finally, these polymers can form an enantiotropic mesophase. This means that in the polyurethanes a combination of the shear and the introduction of nonlinear units played an important role in inducing the orientation of polymer chains so as to form the enantiotropic LC mesophases.

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