Liquid Crystallinity of Thermotropic Para-Type Homo- and Copolyurethanes Containing Biphenylene Mesogen and Their Blends

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ABSTRACT: High-molecular-weight para-type homopolyurethanes prepared by polyaddition of 2,5-tolylene diisocyanate with 4,4′-bis(ω-hydroxyalkoxy)biphenyls showed monotropic liquid crystallinity, when measurements were performed under shearing. For example, a polyurethane PU6T having [η] 0.82 which was obtained from 4,4′-bis(6-hydroxyhexyloxy)biphenyl showed T_{I-LC} of 201 °C and T_{LC-K} of 181 °C. In addition, thermotropic liquid-crystalline para-type copolyurethanes PU*mn*T (*m* and *n* denoting carbon number in alkylene moiety: 2, 6, 8, and 11) were synthesized by polyaddition of the diisocyanate with two 4,4′-bis(ω-hydroxyalkoxy)biphenyls having different alkylene lengths. For example, PU68T(75/25) had T_{I-LC} of 188 °C and T_{LC-K} of 173 °C. Blends of two para-type homopolyurethanes also exhibited monotropic liquid crystallinity. The liquid crystallinity was examined by differential scanning calorimetry measurement, polarized optical microscope observation, and X-ray diffractometry.

Introduction

A number of papers concerning the preparation and physical properties of thermotropic polyurethanes have been reported,[1−10] since thermotropic polyurethanes were first reported by Iimura and co-workers.[11] Although MacKnight and co-workers reported that a meta-type polyurethane has enantiotropic liquid crystallinity, they later published that an almost similar polyurethane has monotropic liquid crystallinity.[12−15]

It was reported that para-type polyurethanes containing biphenylene moiety as a mesogen and alkylene spacer showed thermotropic liquid crystallinity.[16] In addition, several para-type polyurethanes were found to exhibit the liquid crystallinity without containing the mesogen.[17,18] In the latter polyurethane, it was concluded that intermolecular hydrogen bondings between NH and C═O induced the liquid crystallinity by orienting the polyurethane backbone. A para-type polyurethane, especially a biphenylene-containing one, had a tendency to highly orient the backbone in a rigid rodlike manner, forming crystalline regions rather than liquid crystals.

An importance of the orientation formed by intermolecular or intramolecular interaction was also found out in the case of main-chain[19−21] and side-chain liquid-crystalline polymers.[22−25] It was revealed that the orientation of the polymer chains assisted by electron donor−acceptor interactions as well as by intermolecular hydrogen bonds plays an important role in the stability of LC mesophases.

In this study, we wish to report the synthesis of monotropic liquid-crystalline para-type homo- and copolyurethanes and homopolyurethane blends which contain a biphenylene mesogen and alkylene spacers. Although several para-type homopolyurethanes containing the biphenylene mesogen were previously reported by us to have enantiotropic liquid crystallinity,[16] we report that the liquid crystallinity depends on the molecular weight of the polyurethanes and that high molecular weight ones exhibit monotropic liquid crystallinity rather than enantiotropic using a detecting method suitable for such polymers as polyurethanes possessing a high rate of chain orientation. Thermal properties and structure of the polyurethanes and polymer blends were characterized by ^{1}H and ^{13}C NMR spectroscopies, FT-IR spectroscopy, polarized optical microscope observation, differential scanning calorimetry (DSC), and X-ray diffraction measurement.

Experimental Section

Materials. 2,5-Tolylene diisocyanate (2,5-TDI) kindly supplied by Mitsui Toatsu Co., Ltd., was used as a diisocyanate monomer as received. 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*m*; *m* = 2, 6, 8, 11). The reaction of 4,4′-dihydroxybiphenyl with ω-halogenated alkanols is described in detail elsewhere.[16]

Homopolymers. The homopolyurethanes were synthesized by a polyaddition reaction as described in the previous paper.[16] The solution of BP*m* (3.5 mmol) in 10 mL of dry DMF was placed in a three-neck round-bottomed flask. The diisocyanate 2,5-TDI solution dissolved in 5 mL of dry DMF was added dropwise to the BP*m* solution under nitrogen atmosphere at room temperature, followed by stirring at 80 °C for 24 h. The solution was poured into cold methanol to precipitate the polymer. The solid product was filtered and washed with methanol, followed by drying under vacuum at 70 °C for 24 h. Yield: 88−97%.

Copolymers. The copolymers with different compositions were prepared using the same method described for the homopolymers.

Preparation of Polymer Blends. The polymer blends of PU*m*T and PU*n*T were prepared by blending in DMF. Preparation of polymer blend PU6T/PU8T (50/50) is described as a representative case. Equimolar amounts of polymers PU6T and PU8T (0.091 mmol) were mixed in a DMF solution (5 mL)

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Table 1. Polyaddition Reactionof 2,5-Tolylene Diisocyanate (2,5-TDI) with 4,4′-Bis(6-hydroxyhexyoxy)Biphenyls (BP6)[a]

PU designation	BP6, g (mmol)	2,5-TDI, g (mmol)	yield, g (%)	[η], dL/g
PU6T-1	0.883 (2.29)	0.398 (2.29)	0.814 (64)	0.23
PU6T-2	0.442 (1.14)	0.205 (1.18)	0.559 (86)	0.64
PU6T-3	0.338 (0.87)	0.153 (0.88)	0.475 (97)	0.77
PU6T-4	1.330 (3.44)	0.600 (3.45)	1.812 (94)	0.82

[a] Solvent, DMF; reaction time, 24 h; temperature, 80 °C.

Table 2. Copolyaddition Reaction of 2,5-Tolylene Diisocyanate (2,5-TDI) with Two Kinds of 4,4′-Bis(ω-hydroxyalkoxy)biphenyls (BP*m*)[a]

PU*mn*T (composition) (*m*/*n* mol %)	diol BP*m*, g (mmol)	diol BP*n*, g (mmol)	diisocyanate 2,5-TDI, g (mmol)	copolyurethane yield, g (%)	copolyurethane [η],[b] dL/g
PU68T (100/0)	0.338 (0.87)	0	0.153 (0.88)	0.475 (97)	0.77
PU68T (75/25)	0.338 (0.87)	0.129 (0.29)	0.203 (1.17)	0.634 (95)	0.92
PU68T (50/50)	0.225 (0.58)	0.258 (0.58)	0.203 (1.17)	0.635 (93)	0.41
PU68T (25/75)	0.085 (0.22)	0.290 (0.66)	0.153 (0.88)	0.499 (95)	0.89
PU68T (0/100)	0	0.258 (0.58)	0.102 (0.59)	0.316 (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) solution at 30 °C.

Table 3. Copolyaddition Reaction of 2,5-Tolylene Diisocyanate (2,5-TDI) with Two Kinds of 4,4′-Bis(ω-hydroxyalkoxy)biphenyls (BP*m*)[a]

PU*mn*T (composition) (*m*/*n* mol %)	diol BP*m*, g (mmol)	diol BP*n*, g (mmol)	diisocyanate 2,5-TDI, g (mmol)	copoluurethane yield, g (%)	copoluurethane [η],[b] dL/g
PU211T (100/0)	0.320 (1.17)	0	0.203 (1.17)	0.501 (96)	
PU211T (75/25)	0.288 (1.05)	0.184 (0.35)	0.244 (1.40)	0.617 (86)	1.08
PU211T (50/50)	0.160 (0.58)	0.307 (0.58)	0.203 (1.17)	0.592 (88)	0.52
PU211T (35/65)	0.096 (0.35)	0.343 (0.65)	1.740 (1.00)	0.527 (86)	0.44
PU211T (25/75)	0.096 (0.35)	0.553 (1.05)	0.244 (1.40)	0.865 (97)	0.83
PU211T (0/100)	0	0.461 (0.88)	0.153 (0.88)	0.580 (95)	0.99
PU611T (100/0)	0.338 (0.87)	0	0.153 (0.88)	0.475 (97)	0.77
PU611T (75/25)	0.406 (1.05)	0.184 (0.35)	0.244 (1.40)	0.763 (92)	0.91
PU611T (50/50)	0.270 (0.70)	0.369 (0.70)	0.244 (1.40)	0.795 (90)	0.77
PU611T (25/75)	0.135 (0.35)	0.553 (1.05)	0.244 (1.40)	0.902 (97)	0.61
PU611T (0/100)	0	0.461 (0.88)	0.153 (0.88)	0.580 (95)	0.99
PU811T (100/0)	0.258 (0.58)	0	0.102 (0.59)	0.316 (88)	0.47
PU811T (75/25)	0.290 (0.66)	0.115 (0.22)	0.153 (0.88)	0.469 (84)	0.63
PU811T (50/50)	0.194 (0.44)	0.231 (0.44)	0.153 (0.88)	0.532 (92)	0.72
PU811T (25/75)	0.097 (0.22)	0.346 (0.66)	0.153 (0.88)	0.521 (88)	0.55
PU811T (0/100)	0	0.461 (0.88)	0.153 (0.88)	0.580 (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) solution at 30 °C.

by stirring at 90 °C in an oil bath under nitrogen atmosphere, and then DMF was removed under reduced pressure on a rotary evaporator. The resulting product was dried under vacuum.

Characterization. The structure analysis of the polymers and their intermediates was performed by ^{1}H and ^{13}C NMR spectroscopy using a JEOL Lambda-400 spectrometer with 3-(trimethylsilyl)propanesulfonic acid sodium salt (DSS) as an internal standard. Samples were measured on a DMSO-d_6 solution at 70 °C. FT-IR spectra ranging from 4600 to 400 cm^{-1} of the synthesized polymers were measured with a Perkin-Elmer FT-IR 1600 spectrometer by the KBr method. Viscosities were measured with an Ubbelohde viscometer in 1,1,2,2-tetrachloroethane−phenol (1:1, v/v) solution at 30 °C. The thermal properties of the polymers were investigated using a Mettler DSC 30 differential scanning calorimeter. The scanning rate in all cases 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 and then cooled to room temperature and scanned for the second time. All DSC data listed in tables refer to the second run. The optical

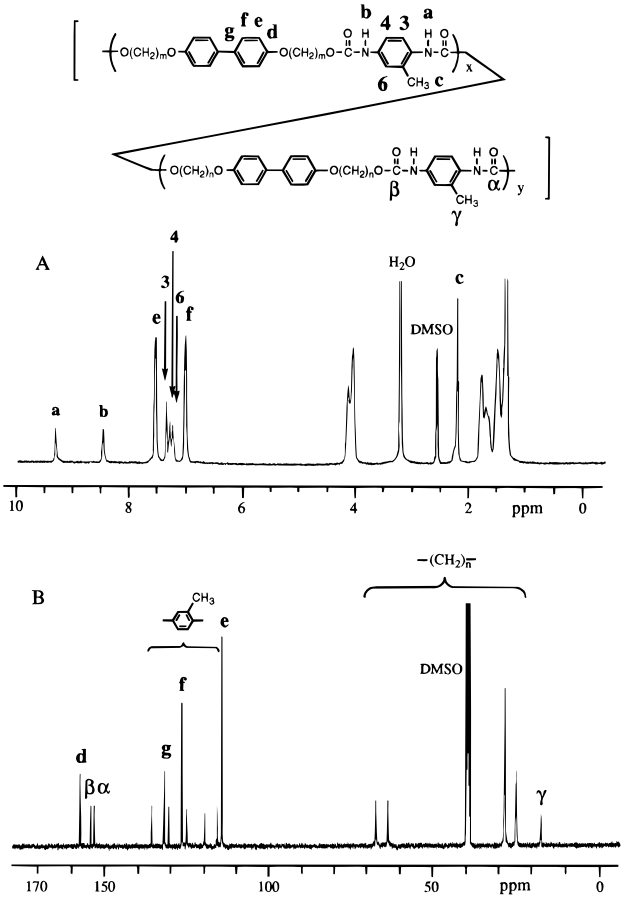

Figure 1. 400 MHz NMR spectra of copolyurethane PU611T (50/50) in DMSO-d_6 at 70 °C: (A) ^{1}H and (B) ^{13}C.

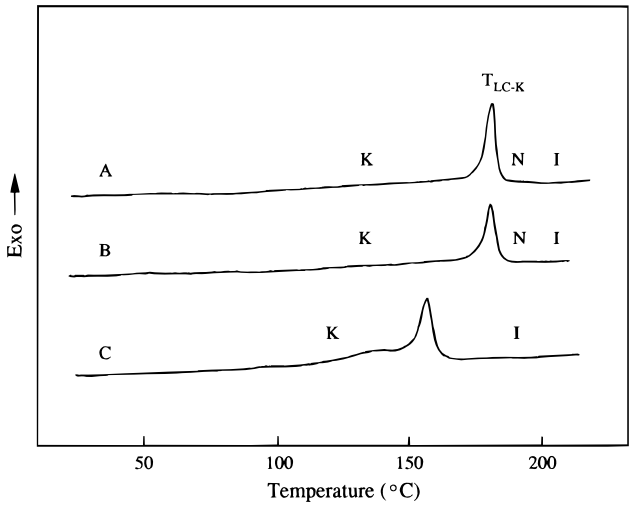

Figure 2. DSC thermograms of PU6Ts in the cooling stage: (A) PU6T-3, (B) PU6T-2, and (C) PU6T-1. The cooling rate was 10 °C/min.

textures of the mesophases were observed using Olympus BH2 polarizing microscope equipped with a Mettler FP84 hot stage. The measurements of thermostability were obtained on a TG8120 thermogravimeter at a heating rate of 5 °C/min under nitrogen atmosphere. X-ray diffraction measurements were carried out by a MAC Science MXP^3 X-ray diffractometer equipped with a Model 5310 thermal controller.

Results and Discussion

Preparations of Para-Type Homo- and Copolyurethanes. Homopolyurethanes were prepared by

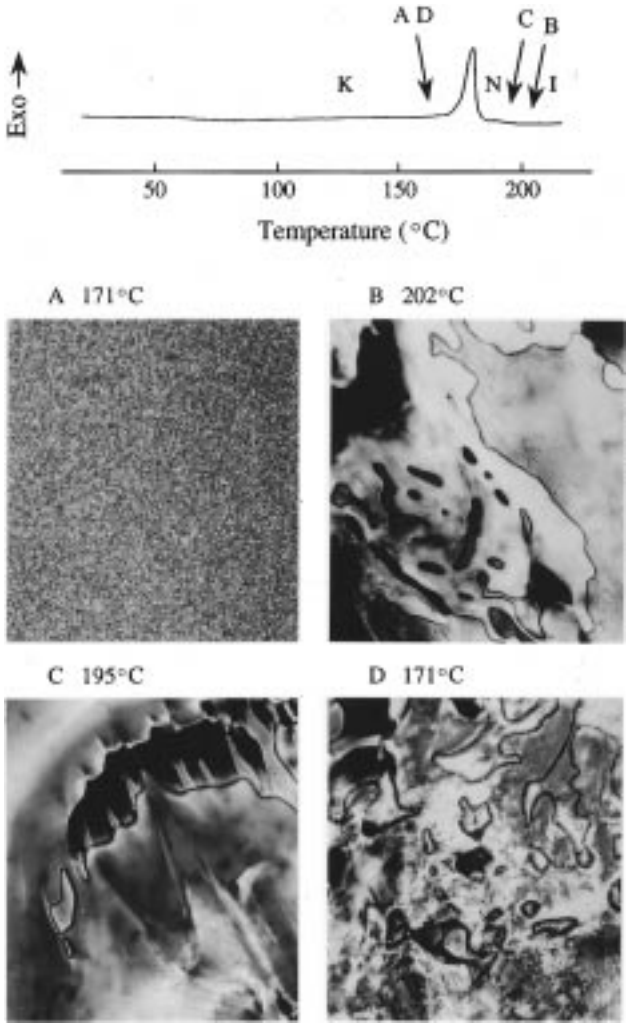

Figure 3. Polarized microphotographs of PU6T-4 on cooling: (A) a threaded crystalline morphology taken at 171 °C without shearing; (B) a isotropic phase taken at 202 °C with shearing; (C) a nematic phase taken at 195 °C; (D) a nematic crystalline phase taken at 171 °C.

polyaddition of 4,4′-bis(ω-hydroxyalkoxy)biphenyls (BP*m*) with a para-type 2,5-tolylene diisocyanate (2,5-TDI). Four kinds of copolyurethanes (PU*mn*T), i.e., PU68T, PU211T, PU611T, and PU811T, were synthesized by polyaddition of two different BP*x* ($x = m, n$) with 2,5-TDI. As a representative case, PU68T is a copolyurethane consisting of $m = 6$ and $n = 8$ in which both 4,4′-bis(6-hydroxyhexyloxy)biphenyl (BP6) and 4,4′-bis(8-hydroxyoctyloxy)biphenyl (BP8) were used as diols. Furthermore, polyurethane blends prepared by mixing homopolymers PUmT and PUnT were designated as PUmT/PUnT (mol %/mol %).

Table 4. Thermal Properties of Homopolyurethane PU6Ts[a]

PU designation	phase transition temperature 2nd cooling T_{I-LC},[b] °C	T_{LC-K}, °C	T_K, °C	ΔH_{LC-K}, J/g	phase transitin temperature 2nd heating T_g, °C	T_{m1}, °C	T_{m2}, °C	ΔH_{m1}, J/g	ΔH_{m2}, J/g
PU6T-1			158	33.5	75	151	173	9.7	20.0
PU6T-2	197	182		35.5	88	202		35.2	
PU6T-3	202	183		32.2	89	198	206	3.6	19.9
PU6T-4	201	181		36.3	86	191	204	13.3	14.6

[a] Determined by DSC at a heating or cooling rate of 10 °C/min under nitrogen atmosphere. [b] Determined by polarized microscopic observation.

First, to examine liquid crystallinity of para-type homopolyurethanes containing biphenylene mesogen, the polyurethanes with different molecular weights were prepared. Results of polymerizations and intrinsic viscosities of the polyurethanes are summarized in Table 1. High molecular weight homopolyurethanes having [η] 0.64−0.82 were prepared using a little excess equivalent of 2,5-TDI (PU6T-2 to -4), while a low molecular weight polyurethane (PU6T-1) with [η] 0.23 was obtained by equimolar amounts of the two reagents.

As shown in Table 2, copolyurethane PU68Ts having different compositions were synthesized by copolyaddition of equimolar amounts of diols and the diisocyanate in high yields. PU68Ts had fairly high molecular weights indicated by intrinsic viscosities of 0.41 to 0.92 dL/g. Similarly, other para-type copolyurethanes having high molecular weights, i.e., PU211Ts, PU611Ts, and PU811Ts, were also obtained in high yields (Table 3).

The formation of copolyurethanes was confirmed by ^{1}H and ^{13}C NMR and infrared spectroscopies. Figure 1 shows ^{1}H and ^{13}C NMR spectra for a copolyurethane PU611T (50/50), which were taken in a DMSO-d_6 solution at 70 °C. The ^{1}H NMR spectrum indicated that there were two NH proton absorptions due to the urethane linkage at 8.42 and 9.26 ppm the nonequivalency of which was caused by the existence of a methyl group in the tolylene group. Absorptions assignable to biphenylene protons at 6.91 and 7.41 ppm also appeared. 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, para-type polyurethanes were obtained as designed.

Thermal Properties of Homopolyurethanes. DSC thermograms of the second cooling stage of homopolyurethane PU6Ts with different molecular weights were measured. As shown in Figure 2, the thermograms for high molecular weight PU6Ts exhibited a single peak ascribable to a transition from crystal to liquid-crystalline state. On the other hand, in the thermogram for the low molecular weight PU6T, there was another peak

Table 5. Thermal Properties of Para-Type Copolyurethane PU*mn*Ts[a]

PU*mn*T (composition) (*m*/*n* mol %)	phase transition temperature 2nd cooling T_{I-LC},[b] °C	T_{LC-K}, °C	T_K, °C	mesophase temp range, deg	ΔH_{LC-K}, J/g	phase transition temperature 2nd heating T_g, °C	T_{m1}, °C	T_{m2}, °C	ΔH_{m1}, J/g	ΔH_{m2}, J/g
PU68T (100/0)	202	183		19	32.2	89	198	206	3.6	19.9
PU68T (75/25)	188	173		15	31.7	73	186	195	9.2	11.9
PU68T (50/50)	171	157		14	31.2	79	176		31.2	
PU68T (25/75)	169	158		11	31.3	76	173		30.5	
PU68T (0/100)	170	151		19	24.3	81	152	171	6.2	15.4

[a] Determined by DSC at a heating or cooling rate of 10 °C/min under nitrogen atmosphere. [b] Determined by polarized microscopic observation.

at lower temperature, but no peak due to the transition from crystal to liquid-crystalline state.

These polyurethanes exhibited unique thermal behaviors. When the sample was cooled from the isotropic state without shearing, it showed no light transmission under the polarized microscope until T_{LC-K} where the sandlike texture appeared. On the other hand, a monotropic polyurethane exhibited a bright liquid-crystalline texture, when it was sheared in the mesophase temperature range, that is, the upper cover glass inserting the sample was slid horizontally. In this temperature range, the sample kept mobility. Alternatively, when the sample was sheared in the isotropic state near T_{I-LC}, it kept the liquid-crystalline texture until it was solidified at T_{LC-K}. Accordingly, the liquid-crystalline state was defined as a state keeping both the mobility and the texture. The detection of the liquid-crystalline state was performed in several minute cycles by cooling from the isotropic state to a temperature within mesophase range, followed by shearing.

As a representative case, polarized microphotographs of a high molecular weight homopolyurethane are shown in Figure 3. Photo A is a microphotograph taken on the sample cooled from the isotropic state without shearing. This is a typical texture for para-type polyurethanes in the crystalline state but not in the liquid-crystalline state. Photo B was taken at the isotropic state at 202 °C under shearing. In photo C taken at 195 °C, a nematic pattern was acquired on this sample cooled from the isotropic state where the sample shearing was carried out. In photo D, a pattern indicating the crystalline state was obtained for the solidified sample possessing no mobility.

The thermal properties of homopolyurethanes containing biphenylene mesogen are summarized in Table 4. The high molecular weight polyurethane with intrinsic viscosity of 0.82 had a transition from isotropic to liquid crystal at 201 °C and that from liquid crystal to crystal at 181 °C, and it did not show liquid-crystalline state in the heating stage. Therefore, it was concluded that the high molecular weight homopolyurethanes have monotropic liquid crystallinity. On the contrary, the low molecular weight homopolyurethane did not have any liquid crystallinity.

Para-type polyurethanes have high crystallizability originating from intermolecular hydrogen bondings.[17,18] Since low molecular weight polyurethanes have relatively high molecular motions, the crystallization might occur in the cooling stage even under shearing. On the other hand, it is assumed that since high molecular weight polyurethanes possess restricted molecular motions, partial molecular orientations take place along the sheared direction in the cooling stage, remaining ordered and disordered regions which align in the sheared direction and form layered structure so as to induce a liquid-crystalline state.

Previously, although we reported that para-type polyurethanes containing the biphenylene mesogen which had low to high molecular weights showed enantiotropic liquid crystalliniy,[16] several high molecular weight samples should have exhibited monotropic liquid crystallinity if more cautious measurements have been performed.

Liquid Crystallinity and Thermal Properties of Copolyurethanes. Liquid crystallinity of para-type homopolyurethanes seemed to be caused by disordering in the orientation of segments in high molecular weight polymers. It is supposed that such disordering can be produced by formation of copolyurethanes.

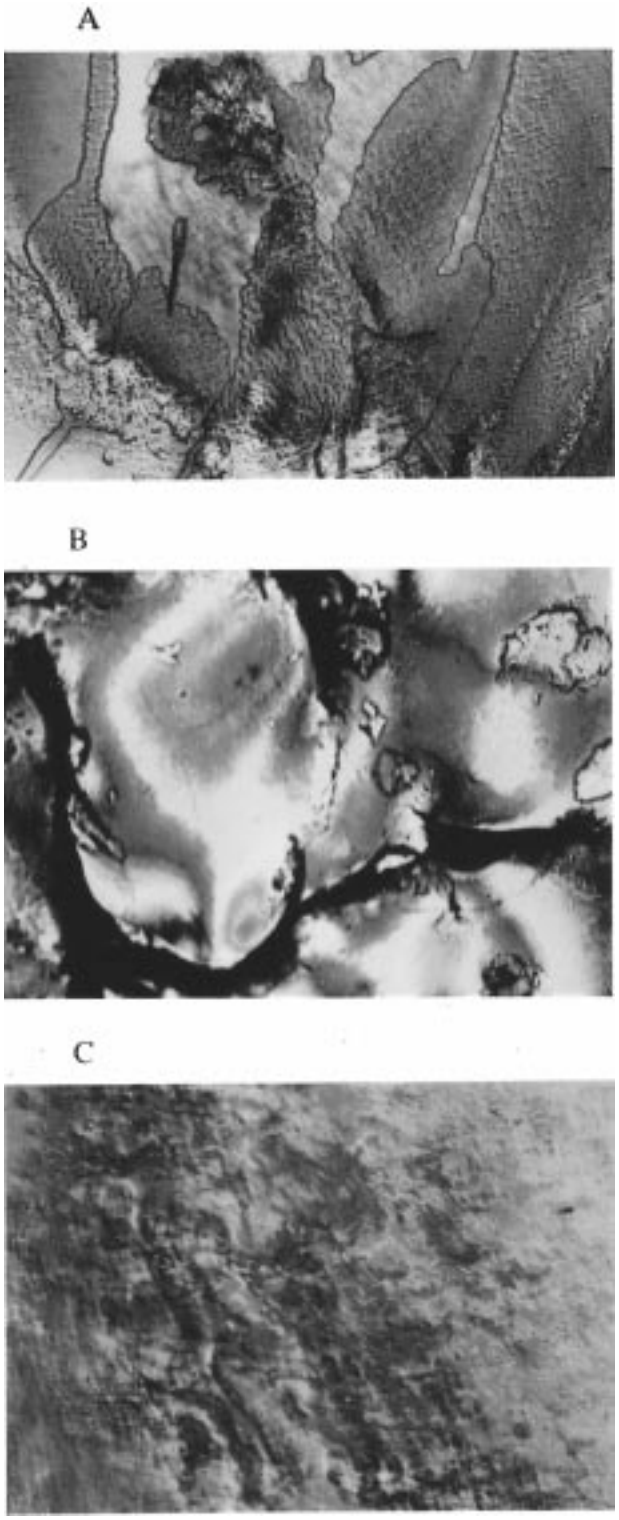

Figure 4. Polarized microphotographs of (A) copolyurethane PU68T (50/50) at 167 °C, (B) copolyurethane PU611T (50/50) at 152 °C, and (C) blend PU6T/PU8T (40/60) at 165 °C on cooling.

For copolyurethane PU68Ts and PU811Ts composed individually of two different alkylenes as well as of different compositions, DSC measurements were carried out. Only liquid crystal-to-crystal transition (T_{LC-K}) peaks appeared in the cooling stage for both copolyurethanes. Although in the heating stage there were

Table 6. Thermal Properties of Para-Type Copolyurethane PU*mn*Ts[a]

PU*mn*T (composition) (*m*/*n* mol %)	phase transition temperature 2nd cooling					phase transition temperature 2nd heating				
	T_{I-LC},[b] °C	T_{LC-K}, °C	T_K, °C	mesophase temp range, deg	ΔH_{LC-K}, J/g	T_g, °C	T_{m1}, °C	T_{m2}, °C	ΔH_{m1}, J/g	ΔH_{m2}, J/g
PU211T (100/0)			243			122	279		68.1	
PU211T (75/25)			229			88	267	271	28.1	9.1
PU211T (50/50)			214			70	190	255	4.2	9.6
PU211T (35/65)			181			63	146	191	8.8	9.3
PU211T (25/75)	161	140		21	11.4	58	162	192	2.9	6.7
PU211T (0/100)	171	155		16	48.9	77	156	173	16.3	43.5
PU611T (100/0)	202	183		19	32.2	89	198	206	3.6	19.9
PU611T (75/25)	184	167		17	31.2	71	177	192	8.1	21.1
PU611T (50/50)	157	137		20	28.9	64	165		31.6	
PU611T (25/75)	151	141		10	30.7	63	144	160	11.6	22.3
PU611T (0/100)	171	155		16	48.9	77	156	173	16.3	43.5
PU811T (100/0)	170	151		19	24.3	81	152	171	6.2	15.4
PU811T (75/25)	163	143		20	35.8	67	169		39.5	
PU811T (50/50)	158	142		16	30.0	74	162		32.2	
PU811T (25/75)	160	141		19	27.3	72	162		27.3	
PU811T (0/100)	171	155		16	48.9	77	156	173	16.3	43.5

[a] Determined by DSC at a heating or cooling rate of 10 °C/min under nitrogen atmosphere. [b] Determined by polarized microscopic observation.

peaks around 170−200 °C, those were assigned to be possibly due to a melting and recrystallization process.

Transition temperatures of PU68Ts are shown in Table 5. Three copolyurethanes having different compositions in addition to a homopolyurethane PU68T(0/100) were monotropic liquid crystals. For example, PU68T(75/25) consisting of 75% hexamethylene and 25% octamethylene exhibited an isotropic-to-liquid crystal transiton at 188 °C and a liquid crystal-to-crystal transition at 173 °C. The mesophase temperature range was narrow in the range of 11 to 19°.

Polarized microscope observation was performed on the PU68Ts and PU811Ts under shearing, as shown in Figure 4. Both copolyurethanes demonstrated nematic liquid-crystalline texture in the cooling stage from isotropic state where the shear was applied, but not in the heating stage.

Para-type polyurethanes have a tendency to be easily crystallized by both intermolecular hydrogen bonds and mesogenic interactions, when those were subjected to cooling from the isotropic state. However, irregularities included in the copolyurethane backbone might help for the polymer chains to remain unoriented segments among oriented crystalline segments by which the liquid-crystalline (LC) state was induced. Once the crystallized solid is formed, it is assumed that the state is not broken until melting.

For three other copolyurethanes composed of undecamethylene as one of the two alkylenes, i.e., PU211Ts, PU611Ts, and PU811Ts, thermal properties are summarized in Table 6. Since a homopolyurethane PU211T-(100/0) was not a liquid crystal, copolyurethanes containing an ethylene component in the proportion more than 35% were not liquid crystals. On the other hand, copolyurethanes containing the ethylene component less than 25% were monotropic liquid crystals. All other copolyurethanes were monotropic liquid crystals, as phase diagrams are shown in Figure 5.

One of the reasons that these para-type copolyurethanes clearly demonstrated the monotropic liquid crystallinity is supposed to be due to their considerably high thermal stability. For four copolyurethanes composed of 50/50 alkylenes, 5% weight loss temperatures ranged from 271 to 291 °C which were much higher than the isotropic temperatures.

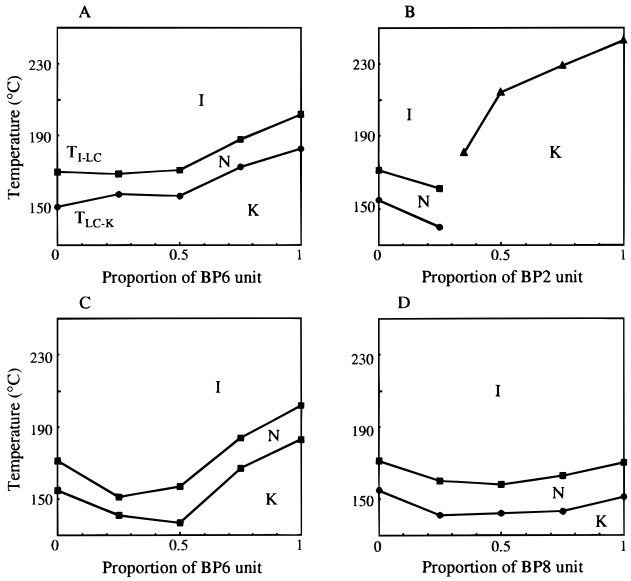

Figure 5. Phase diagrams on cooling for copolyurethanes (A) PU68T, (B) PU211T, (C) PU611T, and (D) PU811T.

Thermal Properties of Polymer Blends. Since irregularities in the polymer structure leading to the formation of liquid crystals are assumed to be caused by blending of two kinds of polymers,[23] thermal behaviors for blends of homopolyurethanes PU6T and PU8T were examined. In DSC diagrams, a single liquid crystal-to-crystal transition peak was observed for all blends composed of different compositions, revealing that the blends were also monotropic liquid crystals and that the transition temperature depended on the blend composition. A polarized microphotograph of a polymer blend is shown in Figure 4C which exihibits a typical bright nematic texture. Thermal properties of the polyurethane blends are summarized in Table 7. The PU6T−PU8T blends exhibited T_{I-LC} of 165−202 °C and T_{LC-K} of 151−183 °C. The mesophase temperature range was narrow in the range of 8−21 °C.

X-ray Diffraction Measurements. X-ray diffraction patterns for a copolyurethane PU68T (50/50) were taken in the cooling stage from the isotropic state in which the shear was subjected (Figure 6A). At 176 °C of the isotropic state, a pattern due to an amorphous

Table 7. Thermal Properties of Para-Type Polyurethane Blends[a]

	phase transition temperature 2nd cooling					phase transition temperature 2nd heating				
PU (blend ratio) (mol %)	T_{I-LC},[b] °C	T_{LC-K}, °C	T_K, °C	mesophase temp range, deg	ΔH_{LC-K}, J/g	T_g, °C	T_{m1}, °C	T_{m2}, °C	ΔH_{m1}, J/g	ΔH_{m2}, J/g
PU6T/PU8T (100/0)	202	183		19	32.2	89	198	206	3.6	19.9
PU6T/PU8T (80/20)	191	172		19	25.8		191	201	4.1	17.8
PU6T/PU8T (60/40)	164	145		19	24.4	87	163	174	17.3	3.2
PU6T/PU8T (50/50)	174	155		19	20.2	86	177	193	1.2	10.1
PU6T/PU8T (40/60)	174	153		21	33.8	85	171	178	22.0	2.7
PU6T/PU8T (20/80)	177	160		17	37.8	83	174		34.4	
PU6T/PU8T (0/100)	170	151		19	24.3	81	152	171	6.2	15.4
PU8T/PU11T (100/0)	170	151		19	24.3	81	152	171	6.2	15.4
PU8T/PU11T (80/20)	172	164		8	32.3		175	182	25.5	3.5
PU8T/PU11T (60/40)	168	160		8	14.7	71	171	180	16.2	3.1
PU8T/PU11T (50/50)	165	153		12	41.0	68	170		36.1	
PU8T/PU11T (40/60)	166	153		11	13.4	69	174		29.0	
PU8T/PU11T (20/80)	167	156		11	42.0	68	143	159	6.8	12.0
PU8T/PU11T (0/100)	171	155		16	48.9	77	156	173	16.3	43.5

[a] Determined by DSC at a heating or cooling rate of 10 °C/min under nitrogen atmosphere. [b] Determined by polarized microscopic observation.

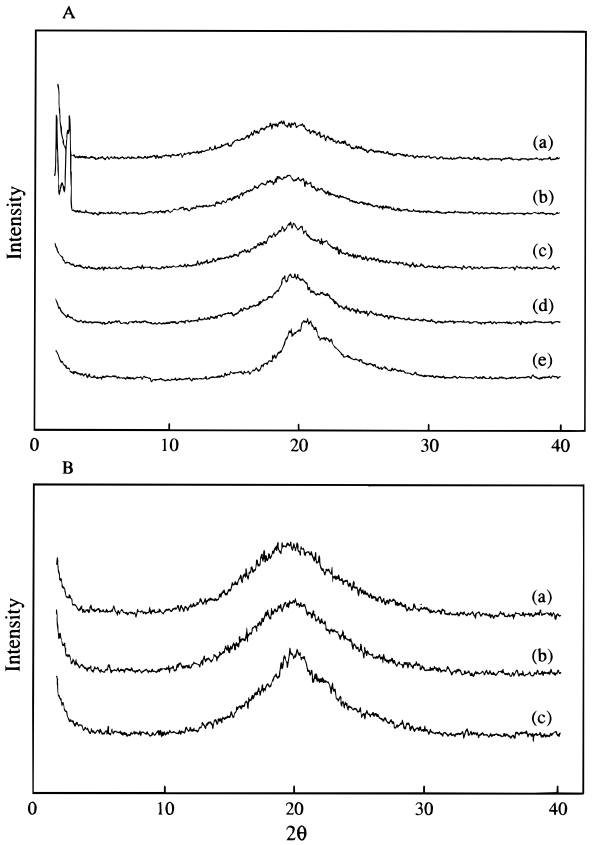

Figure 6. X-ray diffraction patterns of polyurethanes in different temperatures before and after shear was applied in the cooling stage: (A) PU68T (50/50) taken at (a) 176 °C, (b) 165 °C, (c) 160 °C, and (d) 150 °C, and (e) room temperature under shearing; (B) PU68T (50/50) taken at (a) 176 °C, (b) 165 °C, and (c) 160 °C without shearing.

state was observed. In the LC state at 165 °C, sharp peaks appeared at the small angle region around $2\Theta = 2.6°$, suggesting that an ordered structure was partially formed by the shearing. However, the sharp diffraction disappeared at 160 °C (LC). This phenomenon indicates that a layered structure such as pseudosmectic structure formed by shearing was rearranged into nematic structure during X-ray measurement. More detailed investigations might be necessary to elucidate such transition behaviors in the monotropic polymers. As the temperature was decreased to 150 °C of the solid state, a pattern due to the crystalline region began to appear. And, at room temperature, the observed pattern was the same as that due to conventional crystalline polymers. Similar behaviors were observed in para-type liquid-crystalline polyurethanes containing no mesogenic units.[17,18]

On the other hand, X-ray diffraction patterns measured on the same copolyurethane without shear exhibited a little different tendency (Figure 6B). The diffraction patterns measured without shear at 176−165 °C were almost identical with those measured under shear. However, at 160 °C of liquid-crystalline state, orientation of the polymer chains already occurred, showing a crystalline pattern which is the same as that measured under shear at room temperature. A similar tendency was also seen for other copolyurethanes.

The X-ray diffraction measurement revealed that as the sample under shear is cooled, orientation of the polymer chain gradually takes place in the liquid-crystalline state and finally induces a large quantity of crystalline regions. Stabilization of the state at each measuring temperature needed a considerably long time, probably because the polyurethane chain in the liquid-crystalline state has a long relaxation time.[26]

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