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Synthesis and Liquid Crystalline Properties of Thermotropic Polyurethanes Prepared from 1,4-Diisocyanates and 4,4′-Bis(ω-hydroxyalkoxy)biphenyls

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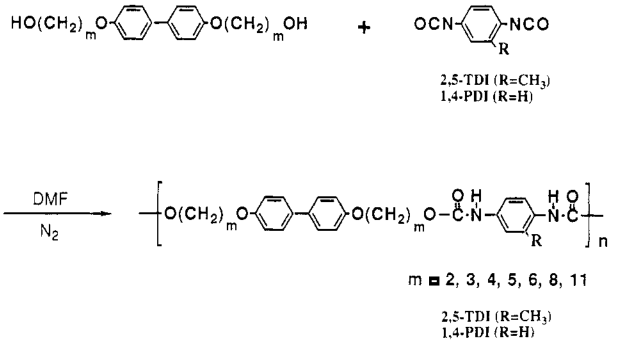
ABSTRACT: A new series of thermotropic polyurethanes was synthesized by reacting such para-substituted diisocyanate monomers as 2,5-tolylene diisocyanate (2,5-TDI) and 1,4-phenylene diisocyanate (1,4-PDI), with 4,4′-bis(ω-hydroxyalkoxy)biphenyls (BP*m*: $HOC_mH_{2m}OC_6H_4C_6H_4OC_mH_{2m}OH$; *m* is the carbon number of the hydroxyalkoxy group) in DMF. Intrinsic viscosities of the polymers were in the range of 0.41–0.99 dL/g. DSC thermograms for these polymers exhibited two endothermic peaks corresponding to phase transitions of melting and isotropization. Mesomorphic behavior of the polyurethanes was also observed under a polarizing microscope. For example, polyurethane 1,4-PDI/BP6 with $[\eta] = 0.77$ prepared from 1,4-PDI and 4,4′-bis[(6-hydroxyhexyl)oxy]biphenyl (BP6) exhibited a liquid crystalline phase from 247 to 259 °C. Infrared study indicated that the hydrogen bonding between urethane linkages affected the mesomorphism. Thermogravimetric analysis of 1,4-PDI/BP*m* showed that no weight loss of the polymer occurred up to 300 °C under an air atmosphere.

Introduction

Intensive work has been focused on main-chain thermotropic liquid crystalline polymers.[1,2] In particular, considerable attention has been paid to thermotropic polyesters.[3-7] For polyurethanes, Iimura and co-workers first reported thermotropic polyurethanes which were prepared by polyaddition of 3,3′-dimethyl-4,4′-biphenyldiyl diisocyanate with α,ω-alkanediols.[8] Later, polyurethanes with various molecular structures have been synthesized.[9-19] Recently, MacKnight and co-workers prepared liquid crystalline thermotropic polyurethanes from 2,4-tolylene diisocyanate (2,4-TDI) and 4,4′-bis[(6-hydroxyhexyl)oxy]biphenyl.[9-12] In this case, 2,4-TDI having two isocyanate groups in a meta position on the benzene ring was used as a monomer, which introduced a nonlinear structure to the polyurethane.

The purpose of the present paper is to report the synthesis and thermotropic properties of a new series of liquid crystalline polyurethanes by the reaction of para-substituted diisocyanate monomers, i.e., 2,5-tolylene diisocyanate (2,5-TDI) and 1,4-phenylene diisocyanate (1,4-PDI), with 4,4′-(ω-hydroxyalkoxy)biphenyl (BP*m*: $HOC_mH_{2m}OC_6H_4C_6H_4OC_mH_{2m}OH$; *m* is the carbon number of the hydroxyalkoxy group). The polymers were prepared by solution polyaddition in DMF. Diol monomers BP*m*'s contain a mesogenic biphenylene group and flexible spacers. These para-substituted monomers afford an overall linear structure of the polyurethane. Effects of the length of the alkylene spacers and the methyl substituent of the phenylene unit on thermal properties were examined for the series of polyurethanes.

Scheme I



Experimental Section

Materials. Diisocyanate monomers, 2,5-tolylene diisocyanate (2,5-TDI) and 1,4-phenylene diisocyanate (1,4-PDI), were kindly supplied by Mitsui Toatsu Co., Ltd. These compounds were used without further purification.

Synthesis of 4,4′-Bis(ω-hydroxyalkoxy)biphenyls (BP*m*; *m* = 2, 3, 5, 6, 8, 11). 4,4′-Bis(ω-hydroxyalkoxy)biphenyls (BP*m*: *m* = 2, 3, 5, 6, 8, 11), except for BP4, were synthesized by the

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

	carbon number of alkylene chain *m*	2,5-TDI, g (mmol)	BP*m*, g (mmol)	time, h	yield, %	[η],[b] dL/g
2,5-TDI/BP2	2	0.613 (3.52)	0.97 (3.52)	12	90	insoluble
2,5-TDI/BP3	3	0.610 (3.50)	1.06 (3.50)	20	92	0.41
2,5-TDI/BP4	4	0.600 (3.44)	1.14 (3.45)	20	90	0.53
2,5-TDI/BP5	5	0.600 (3.44)	1.23 (3.45)	20	92	0.44
2,5-TDI/BP6	6	0.600 (3.44)	1.33 (3.45)	20	94	0.82
2,5-TDI/BP8	8	0.610 (3.50)	1.55 (3.50)	24	93	0.47
2,5-TDI/BP11	11	0.611 (3.51)	1.85 (3.51)	24	95	0.99

[a] Solvent: DMF (15 mL). [b] Intrinsic viscosity measured in a 1,1,2,2-tetrachloroethane–phenol (1:1, v/v) solution at 30 °C.

Table II. Polyaddition Reaction[a] of 1,4-Phenylene Diisocyanate (1,4-PDI) with 4,4′-Bis(ω-hydroxyalkoxy)biphenyls (BP*m*)

	carbon number of alkylene chain *m*	1,4-PDI, g (mmol)	BP*m*, g (mmol)	time, h	yield, %	[η],[b] dL/g
1,4-PDI/BP2	2	0.512 (3.20)	0.87 (3.20)	20	90	insoluble
1,4-PDI/BP3	3	0.598 (3.74)	1.13 (3.74)	20	94	0.50
1,4-PDI/BP4	4	0.601 (3.76)	1.24 (3.76)	20	92	0.55
1,4-PDI/BP5	5	0.603 (3.77)	1.35 (3.77)	20	96	0.42
1,4-PDI/BP6	6	0.586 (3.66)	1.42 (3.66)	20	95	0.77
1,4-PDI/BP8	8	0.607 (3.79)	1.67 (3.79)	24	96	0.58
1,4-PDI/BP11	11	0.605 (3.78)	1.99 (3.78)	24	96	0.69

[a] Solvent: DMF (15 mL). [b] Intrinsic viscosity measured in a dichloromethane–trifluoroacetic acid (4:1, v/v) solution at 30 °C.

reaction of 4,4′-dihydroxybiphenyl with ω-halogenated alkanols. Sodium hydroxide (4.8 g, 0.12 mol), 4,4′-dihydroxybiphenyl (5.5 g, 0.029 mol), and ω-bromo- or chloro-1-alkanol (0.12 mol) in 100 mL of ethanol were refluxed for 24 h and then poured into cold water. The precipitate was filtered and recrystallized from a mixture of ethanol and DMF (3:1, v/v). Yield: 52–90%.

Synthesis of 4,4′-Bis(4-hydroxybutoxy)biphenyl (BP4). BP4 was prepared by deprotection of 4,4′-bis[[(tetrahydro-2-pyranyl)oxy]butoxy]biphenyl which was obtained from 4-[(tetrahydro-2-pyranyl)oxy]-1-chlorobutane and 4,4′-dihydroxybiphenyl.[20] 4-(Tetrahydro-2-pyranyloxy)-1-chlorobutane (108–109 °C, 8 mmHg) was prepared from 4-chloro-1-butanol and 3,4-dihydro-2*H*-pyran. To the methanol solution (400 mL) of 4,4′-bis[[(tetrahydro-2-pyranyl)oxy]butoxy]biphenyl (32.0 g, 6.4 × 10^{-2} mol) was added dropwise concentrated H_2SO_4 (5 mL). The mixture was refluxed with stirring for 0.5 h. After cooling to room temperature, the precipitate was filtered and successively washed with ethanol and water. The final product was recrystallized from isopropyl alcohol. Yield: 18 g (85%). Mp: 196–197 °C.

Synthesis of Polyurethanes 2,5-TDI/BP*m* and 1,4-PDI/BP*m*. The polyurethanes were synthesized by a polyaddition reaction according to the method described in the literature.[9] 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 or 1,4-PDI (3.5 mmol) solution dissolved in 5 mL of dry DMF was added dropwise to the BP*m* solution under a nitrogen atmosphere at room temperature. Then, the reaction mixture was stirred 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: 90–96%. Anal. Calcd for 2,5-TDI/BP6 $(C_{33}H_{38}N_2O_6)_n$: C, 70.95; H, 6.86; N, 5.01. Found: C, 70.64; H, 7.05; N, 5.30. Calcd for 1,4-PDI/BP6 $(C_{32}H_{36}N_2O_6)_n$: C, 70.57; H, 6.66; N, 5.14. Found: C, 70.83; H, 6.91; N, 5.26.

Characterization. NMR spectra were recorded by a JEOL JNM-GX270 spectrometer. Samples were measured on a DMSO-d_6 solution at 70 or 130 °C. TMS was used as an internal reference. Viscosities were measured with an Ubbelohde viscometer in a 1,1,2,2-tetrachloroethane–phenol (1:1, v/v) or dichloroethane–trifluoroacetic acid (4:1, v/v) mixture solution at 30 °C. DSC measurements were conducted with a Mettler DSC 30. The scanning rate was 20 °C/min. The maximum point of the endotherm was taken as the transition temperature. A polarizing microscope (Olympus BH2) equipped with a Mettler FP84 hot stage was used for visual observation. Infrared spectra at various temperatures were obtained by a Jasco Micro FT/IR-200 spectrometer equipped with a Mettler FP84 hot stage at a heating rate of 10 °C/min. The resolution was 4 cm^{-1}. The sample between two KBr crystal plates was pressed to provide the disk for the measurement. The thickness of the KBr disk was less than 1 mm. Samples that were heated to 30 °C higher than the melting point and then cooled to room temperature were used for the measurements. Thermogravimetry measurements were performed on a Shimadzu DT-40 at a heating rate of 10 °C/min in air. Wide-angle X-ray diffraction measurements were carried out by use of a Rigaku X-ray Rad 2B system using Ni-filtered Cu Kα radiation. Samples placed on a Mettler FP 52 hot stage were used for the X-ray measurement.

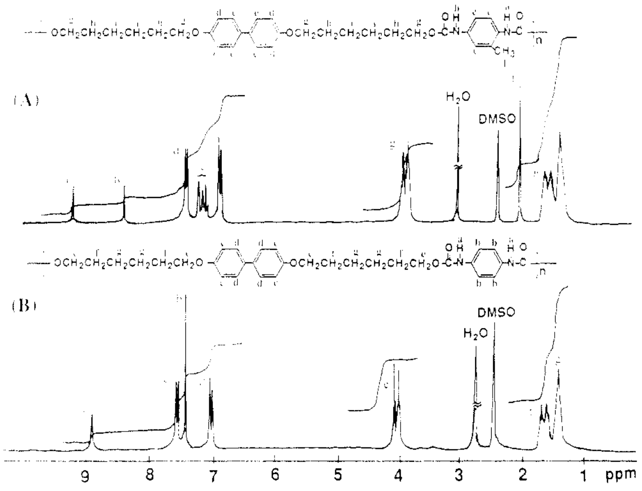


Figure 1. ¹H-NMR spectra of polyurethanes: (A) 2,5-TDI/BP6 in DMSO-d_6 at 70 °C; (B) 1,4-PDI/BP6 in DMSO-d_6 at 130 °C.

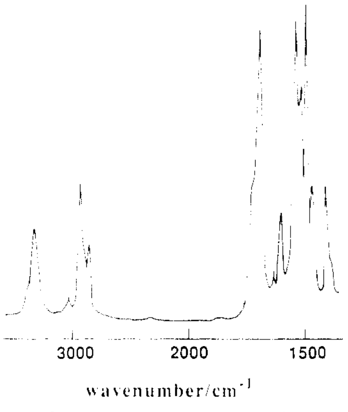


Figure 2. Infrared spectrum of polyurethane in the range of 1350–3600 cm^{-1}.

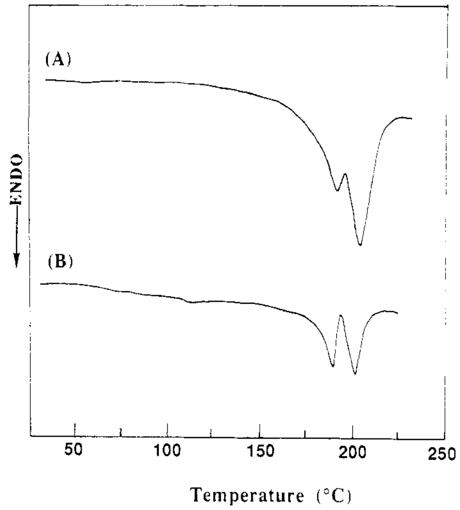


Figure 3. DSC curves of polyurethanes: (A) 2,5-TDI/BP5; (B) 2,5-TDI/BP6 on the second heating at a rate of 20 °C/min.

Table III. Thermal Properties[a] of Thermotropic Polyurethanes

	carbon number of alkylene chain m	T_m, °C	T_i, °C	T_i-T_m, °C	ΔH_m, J/g	ΔH_i, J/g
2,5-TDI/BP2	2	256	279	23	15.2	47.4
2,5-TDI/BP3	3	227	245	18	7.5	33.5
2,5-TDI/BP4	4	214	232	18	6.0	34.8
2,5-TDI/BP5	5	194	205	11	5.6	15.6
2,5-TDI/BP6	6	191	204	13	13.3	14.6
2,5-TDI/BP8	8	152	172	20	6.4	34.5
2,5-TDI/BP11	11	156	173	17	16.3	43.5

[a] Transition temperatures were determined by DSC measurements with a heating rate of 20 °C/min.

Table IV. Thermal Properties[a] of Thermotropic Polyurethanes

	carbon number of alkylene chain m	T_m, °C	T_i, °C	T_i-T_m, °C	ΔH_m, J/g	ΔH_i, J/g
1,4-PDI/BP2	2	[b]				
1,4-PDI/BP3	3	255	272	17	21.6	13.8
1,4-PDI/BP4	4	245	261	16	32.4	7.1
1,4-PDI/BP5	5	252	268	16	10.4	37.7
1,4-PDI/BP6	6	247	259	12	17.3	41.4
1,4-PDI/BP8	8	225	235	10	26.1	18.8
1,4-PDI/BP11	11	177	205	28	12.9	45.0

[a] Transition temperatures were determined by DSC measurements with a heating rate of 20 °C/min. [b] Decomposition occurs at approximately 340 °C before melting.

Results and Discussion

Polyurethanes 2,5-TDI/BP*m*'s and 1,4-PDI/BP*m*'s were synthesized by the polyaddition reaction of equimolar amounts of diisocyanates and 4,4'-bis(ω-hydroxyalkoxy)biphenyls as shown in Scheme I. The diisocyanate monomers, 2,5-TDI and 1,4-PDI, have the functional group at the para position. A series of 4,4'-bis(ω-hydroxyalkoxy)biphenyl BP*m* with m = 2–6, 8, 11 was used as diol monomers having a biphenyl mesogen. The effect of the length of alkylene spacers on thermal properties of polyurethanes was examined. The reaction was performed in DMF for 24 h under a dry nitrogen atmosphere.

The results of polymerization for 2,5-TDI/BP*m* and 1,4-PDI/BP*m* are given in Tables I and II, respectively. The yields were over 90%. The molecular weights of these polymers were relatively high. Intrinsic viscosities for 2,5-TDI/BP*m* polymers with m = 3–11 were in the range of 0.41–0.99 dL/g. 2,5-TDI/BP2 and 1,4-PDI/BP2 polymers were insoluble in solvents with high dissolving strengths such as a 1,1,2,2-tetrachloroethane–phenol mixture (1:1, v/v) and a dichloroethane–trifluoroacetic acid mixture (4:1, v/v). For the series of 1,4-PDI/BP*m*, the intrinsic viscosities were between 0.42 and 0.77 dL/g.

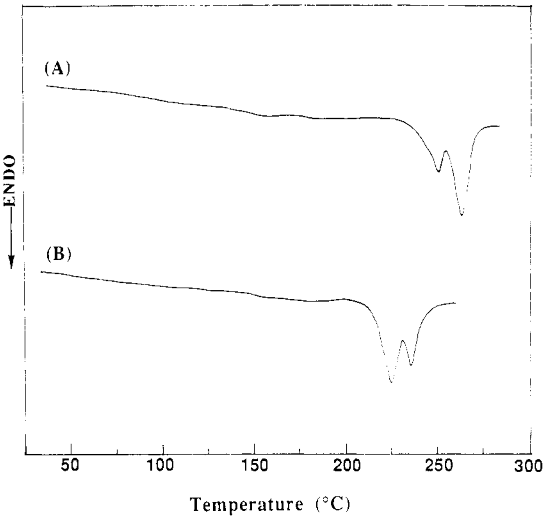


Figure 4. DSC curves of polyurethanes: (A) 1,4-PDI/BP6; (B) 1,4-PDI/BP8 on the second heating at a rate of 20 °C/min.

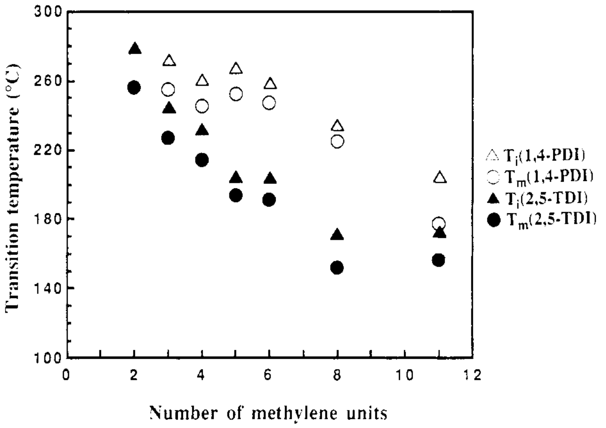
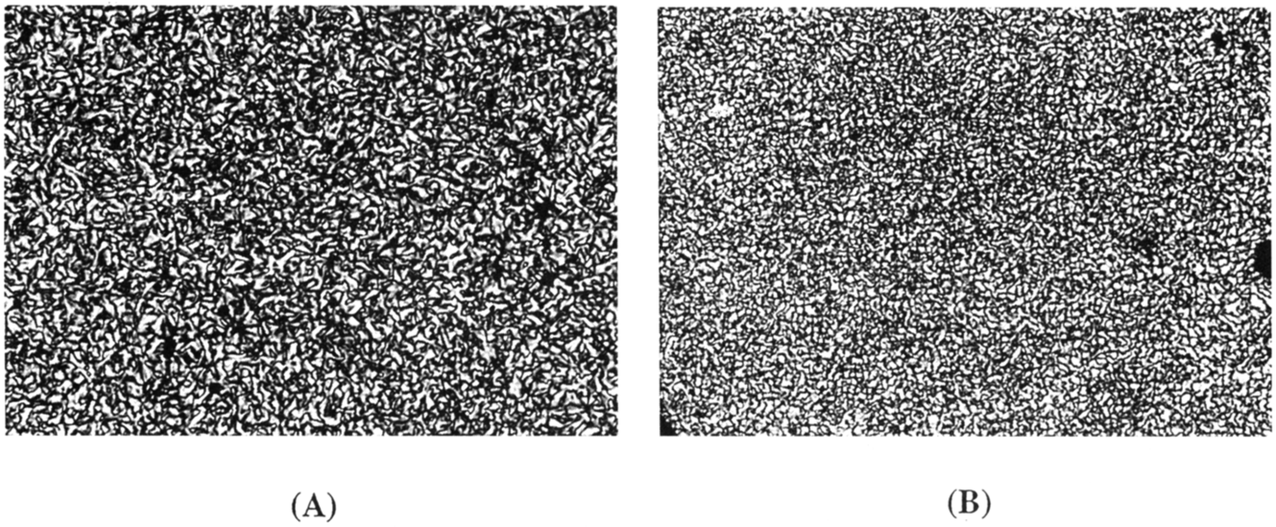


Figure 5. Dependence of the temperature of melting (T_m) and isotropization (T_i) on the methylene chain length.

The formation of a polyurethane structure was confirmed by ^{1}H-NMR and infrared spectra. Figure 1 shows ^{1}H-NMR spectra of polymers of 2,5-TDI/BP6 (A) and 1,4-PDI/BP6 (B). The spectra of 2,5-TDI/BP6 (A) and 1,4-PDI/BP6 (B) were obtained in a DMSO-d_6 solution at 70 and 130 °C, respectively. For 2,5-TDI/BP6, two N-H proton absorptions of the urethane linkage were observed at 8.32 and 9.16 ppm (Figure 1A). The methyl group on the phenylene unit caused a nonequivalency of the N-H protons. The biphenyl protons resonated at 6.91 and 7.41 ppm. On the other hand, for 1,4-PDI/BP6 (Figure 1B), the singlet N-H proton peak was observed at 8.70 ppm because of the symmetric molecular structure. The aromatic proton (H_b) of the phenylene group was also seen at 7.30 ppm as a singlet resonance.

Figure 2 shows the infrared spectrum of 1,4-PDI/BP6 in the solid state at room temperature. Absorption peaks were characteristic of polyurethanes. The carbonyl band due to the formation of a urethane linkage was observed at 1700 cm^{-1}. The peak had a shoulder at a higher wavenumber, which will be discussed later. The N-H band of the urethane group was seen at 3310 cm^{-1}. In Figure 3, DSC thermograms of 2,5-TDI/BP5 (A) and 2,5-TDI/BP6 (B) of heating scans are shown, which were repre-


(A)

(B)

Figure 6. Polarizing optical photomicrographs of thermotropic polyurethanes: (A) 2,5-TDI/BP8 taken at 165 °C; (B) 1,4-PDI/BP6 taken at 244 °C.

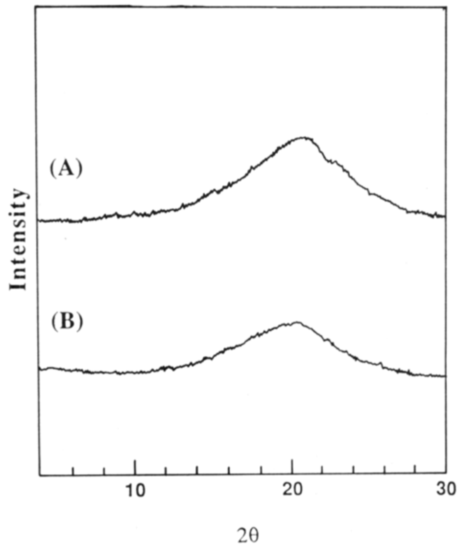


Figure 7. Wide-angle X-ray diffraction patterns of polyurethanes: (A) 2,5-TDI/BP6 at 199 °C; (B) 1,4-PDI/BP6 at 255 °C.

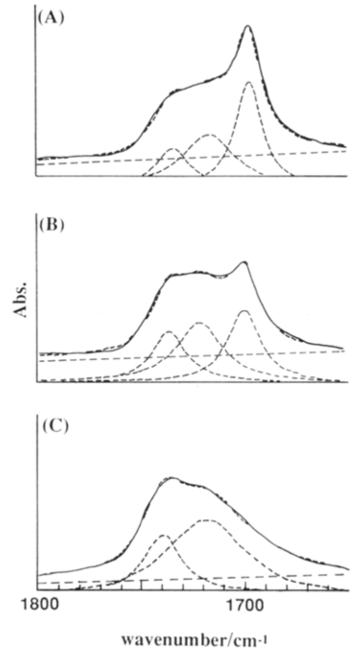


Figure 8. Curve-fitting results of the carbonyl bands of the infrared spectra for 2,5-TDI/BP6 at (A) 170, (B) 195, and (C) 250 °C.

Table V. Curve-Fitting Results of the Carbonyl Peak of 2,5-TDI/BP6 at Various Phases

	hydrogen-bonded C═O bands		free C═O band	
	ν (cm^{-1})	fraction of area	ν (cm^{-1})	fraction of area
crystalline (170 °C)	1717	0.39	1734	0.19
	1698	0.42		
liquid crystalline (195 °C)	1719	0.39	1736	0.26
	1700	0.35		
isotropic (250 °C)	1717	0.73	1739	0.27

sentative thermograms for a series of 2,5-TDI/BP*m* polymers. Polymer samples once heated to 30 °C above their melting temperatures and then cooled to room temperatures were used for DSC measurements. Two endothermic peaks were observed in the thermograms. The microscopic observation suggested that the two endotherms corresponded to melting and isotropization transitions, respectively. The mesomorphic state with birefringence was seen in the temperature range between two endothermic peaks. For the series of 2,5-TDI/BP*m*, the thermal behavior is summarized in Table III. All polymers exhibited liquid crystalline phases. The melting temperature (T_m) of 2,5-TDI/BP*m* decreased from 256 to 156 °C with increasing the length of the methylene spacer from $m = 2$ to 11. The isotropization temperature (T_i) also showed a similar tendency. The mesophase temperature range (T_i–T_m) was between 11 and 23 °C. The widest range (23 °C) was observed for 2,5-TDI/BP2. MacKnight and co-workers synthesized thermotropic polyurethanes from 2,4-TDI which had two isocyanate groups in a meta position and BP6 which contained the biphenylene group as a mesogenic group.[9] Polymer 2,4-TDI/BP6 with $[\eta] = 0.32$ exhibited a liquid crystalline phase between 152 and 166 °C. It was reported that monotropic mesomorphic behavior was observed for the polymer based on 2,4-TDI.[9] On the other hand, for polyurethane 2,5-TDI/BP6 the mesophase appeared between 191 and 204 °C on heating. These results suggest that the incorporation of the para-type urethane linkage increased the melting temperature and contributed to liquid crystallinity.

Table IV shows thermal properties of the series of 1,4-PDI/BP*m* that has no methyl substituent on the phenylene

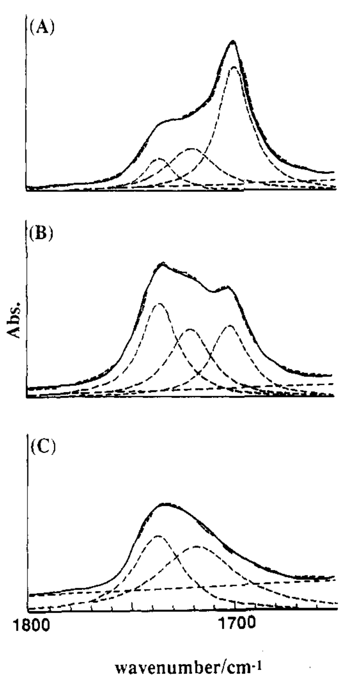


Figure 9. Curve-fitting results of the carbonyl bands of the infrared spectra for 1,4-PDI/BP6 at (A) 210, (B) 250, and (C) 290 °C.

Table VI. Curve-Fitting Results of the Carbonyl Peak of 1,4-PDI/BP6 at Various Phases

	hydrogen-bonded C=O bands		free C=O band	
	ν (cm^{-1})	fraction of area	ν (cm^{-1})	fraction of area
crystalline	1717	0.29	1736	0.14
(210 °C)	1700	0.57		
liquid crystalline	1719	0.32	1736	0.39
(250 °C)	1701	0.29		
isotropic	1719	0.56	1737	0.44
(290 °C)				

unit. Polyurethane 1,4-PDI/BP*m*'s (*m* = 3–6, 8, 11), except for 1,4-PDI/BP2, also exhibited liquid crystalline behavior. DSC thermograms for 1,4-PDI/BP6 (A) and 1,4-PDI/BP8 (B) on the second heating are shown in Figure 4. Polymer 1,4-PDI/BP2 decomposed at approximately 340 °C before melting. The melting and isotropization temperatures of the 1,4-PDI/BP*m* series showed a decreasing tendency with the increase of the aliphatic spacer length as was observed for the 2,5-TDI/BP*m* series. The mesophase range for the series of 1,4-PDI/BP*m* was between 10 and 28 °C. In Figure 5, transition temperatures (T_m and T_i) of 2,5-TDI/BP*m* and 1,4-PDI/BP*m* series were plotted against the carbon number (*m*) of the alkylene spacer, revealing the effects of the length of the flexible spacer and the methyl substituent on thermotropic properties. The introduction of the methyl group in the phenylene unit caused decreases in both T_m and T_i.

Polarizing optical photomicrographs shown in Figure 6 for 2,5-TDI/BP8 (A) and 1,4-PDI/BP6 (B) were representative textures for these series of polyurethanes. Threaded textures were observed for these polymers. MacKnight and co-workers also observed[9] a threaded texture for the mesophase of polyurethane 2,5-TDI/BP6.

The wide-angle X-ray diffractograms of 2,5-TDI/BP6 at 199 °C (A) and 1,4-PDI/BP6 at 255 °C (B) are shown in Figure 7. These diffractograms obtained at temperatures between two endothermic peaks suggested the existence of mesomorphic states. Polymer 1,4-PDI/BP6 (B) showed only a broad reflection at *ca.* 4.4 Å. For 2,5-TDI/BP6, a broad reflection at *ca.* 4.2 Å was observed. These diffraction patterns showed that no three-dimensional crystalline order existed at a temperature between two endotherm temperatures.

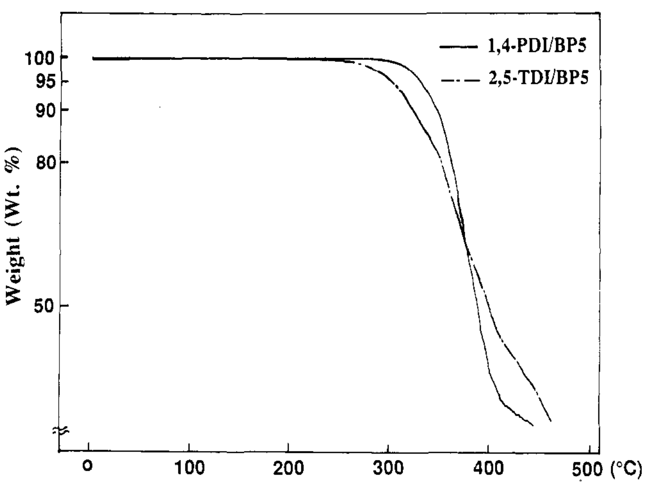


Figure 10. Thermogravimetry conducted at a heating rate of 10 °C/min in an air atmosphere.

The hydrogen bonding between the urethane linkages may play an important role for mesomorphic behavior. Induction of liquid crystallinity through intermolecular hydrogen bonds was observed for a few polymeric systems.[21-23] Infrared spectra were recorded for polyurethanes 2,5-TDI/BP6 and 1,4-PDI/BP6 at various phases to examine the states of hydrogen bonds. It was reported that the carbonyl band of polyurethanes was sensitive to hydrogen bonding.[14,24] Figure 8 and Table V show the curve-fitting results of the carbonyl band of 2,5-TDI/BP6 at 170 °C (crystalline), 195 °C (mesophase), and 250 °C (isotropic). In the crystalline state, the carbonyl band was separated into three bands at 1698, 1717, and 1734 cm^{-1}. Of them, the bands at 1698 and 1717 cm^{-1} were assigned to the hydrogen-bonded C=O groups in the ordered and disordered states, respectively. The 1734-cm^{-1} band was assigned to the non-hydrogen-bonded carbonyl group. The fraction of free C=O band increased in the liquid crystalline state at 195 °C. In the isotropic state, the band was separated into only two bands due to the H-bonded C=O group in the disordered state and the free C=O bands.

A similar tendency was observed for the curve-fitting results for the carbonyl bands of 1,4-PDI/BP6 shown in Figure 9 and Table VI.

These results suggest that the mesomorphic behavior of the polyurethanes is greatly dependent on the hydrogen bonds between the urethane linkage.

Thermogravimetry for polyurethanes of 2,5-TDI/BP5 (A) and 1,4-PDI/BP5 (B) is presented in Figure 10. The temperatures of 5% weight loss for 2,5-TDI/BP5 and 1,4-PDI/BP5 were 297 and 334 °C, respectively. For 1,4-PDI/BP5, no weight loss was observed up to 300 °C. Since intrinsic viscosities for these two polymers were almost the same (2,5-TDI/BP5, [η] = 0.44; 1,4-PDI/BP5, [η] = 0.42), 1,4-PDI/BP5 was more thermally stable than 2,5-TDI/BP5 having a methyl substituent. No degradation was observed in liquid crystalline states for both polymers, suggesting a processibility of these polyurethanes at molten states.

A new type of thermotropic liquid crystalline polyurethanes based on para-substituted monomers, 2,5-TDI and 1,4-PDI, was obtained by solution polyaddition. These polymers exhibited mesomorphic properties.

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