Thermotropic Polyurethanes Prepared from 2,5-Tolylene Diisocyanates and 1,4-Bis(ω-hydroxyalkoxy)benzenes Containing No Mesogenic Unit

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ABSTRACT: Thermotropic liquid-crystalline polyurethanes were synthesized by the polyaddition reaction of para-substituted 2,5-tolylene diisocyanate (2,5-TDI) with 1,4-bis(ω-hydroxyalkoxy)benzenes (BHB*m*: $HO(CH_2)_mOC_6H_4O(CH_2)_mOH$; *m* is the carbon number of the hydroxyalkoxy group). Intrinsic viscosities of the polymers were in the range of 0.22−0.41 dL/g. Polyurethanes 2,5-TDI/BHB*m*'s (*m* = 3, 5, 6, 8) prepared from BHB*m* and 2,5-TDI, exhibited monotropic liquid crystallinity, although these polyurethanes contained no mesogenic core unit. For example, polyurethane 2,5-TDI/BHB5 with $[\eta] = 0.33$ prepared from 1,4-bis(5-hydroxypentoxy)benzene (BHB5) and 2,5-TDI exhibited an anisotropic phase from 119 to 51 °C. In contrast, for the series of 1,4-PDI/BHB*m* (*m* = 2, 3, 5, 6, 8, 11) having no substituent in a phenylene unit, no explicit mesomorphic behavior was observed by DSC measurement and polarized microscopic observation.

Introduction

Thermotropic liquid-crystalline polymers having mesogenic units in the main chain have attracted attention for the demand of high-performance materials.[1−4] Intensive work has focused on syntheses and properties of thermotropic all-aromatic and semiflexible polyesters.[1−4] More recently, a variety of semiflexible thermotropic main-chain polymers such as polyethers, polycarbonates, polyesteramides, and polyurethanes have been studied extensively.[1]

For polyurethanes, a number of mesogenic molecular structures have been reported by several groups.[5−24] MacKnight and co-workers reported thermotropic properties of polyurethanes based on 2,4- or 2,6-tolylene diisocyanate.[9−14] Mormann prepared liquid-crystalline polyurethanes based on diad and triad para-linked aromatic diisocyanate esters.[19−21] We reported that polyurethanes obtained by polyaddition of para-substituted diisocyanates such as 2,5-tolylene diisocyanate (2,5-TDI) and 1,4-phenylene diisocyanate (1,4-PDI) with 4,4′-bis(ω-hydroxyalkoxy)biphenyl showed thermotropic liquid crystallinity.[22] In this case, the polymers had a biphenylene mesogenic unit which was responsible for the mesogenic behavior. Intermolecular hydrogen bonds also played an important role in the emergence of the liquid-crystalline properties of these polyurethanes.

The objective of the present paper is to report the synthesis and thermotropic properties of a new series of mesogenic polyurethanes by the polyaddition reaction of 2,5-TDI, which is para-substituted diisocyanate monomers, with 1,4-bis(ω-hydroxyalkoxy)benzene (BHB*m*: $HO(CH_2)_mOC_6H_4O(CH_2)_mOH$; *m* is the carbon number of the hydroxyalkoxy group) which has no mesogenic core group. In addition, for polyurethanes obtained by polyaddition of 1,4-PDI with BHB*m*, their thermal properties were examined without observing conventional thermotropic liquid crystallinity. The polymers were characterized by differential scanning calorimetry (DSC), X-ray diffraction, and infrared spectroscopy.

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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 1,4-Bis(ω-hydroxyalkoxy)benzenes (BHB*m*; *m* = 2, 3, 5, 6, 8, 11). 1,4-Bis(ω-hydroxyalkoxy)benzenes (BHB*m*; *m* = 2, 3, 5, 6, 8, 11) were synthesized by the reaction of 1,4-dihydroxybenzene with ω-halogenated alkanols. Sodium hydroxide (7.7 g, 0.19 mol), 1,4-dihydroxybenzene (9.0 g, 0.045 mol), and ω-bromo- or -chloro-1-alkanol (0.19 mol) in 100 mL of ethanol were refluxed for 24 h. In the case of *m* = 2, 3, 5, the reaction mixture was then poured into water and extracted twice with chloroform. The organic layer was washed with water, separated, and evaporated. The residual product was recrystallized from ethyl acetate. As for the case of *m* = 6, 8, 11, the resulting precipitate was directly filtered after pouring the reaction mixture into cold water, and then also recrystallized from ethyl acetate. Yield: 40−85%.

Synthesis of Polyurethanes 2,5-TDI/BHB*m* and 1,4-PDI/BHB*m*. The polyurethanes were synthesized by a polyaddition reaction according to the method described in the literature.[9,22] The solution of BHB*m* (2.87 mmol) in 10 mL of dry DMF was placed in a three-neck round-bottom flask. The diisocyanate 2,5-TDI or 1,4-PDI (2.87 mmol) dissolved in 10 mL of dry DMF was added dropwise to the BHB*m* solution under a dry nitrogen atmosphere at room temperature. Then, the reaction mixture was stirred at 80 °C for 20 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 12 h. Yield: 88−94%. Anal. Calcd for 1,4-PDI/BHB5 $(C_{24}H_{30}N_2O_6)_n$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.18; H, 6.82; N, 6.40.

Characterization. ^{1}H NMR spectra were recorded by a JEOL JNM-GX270 spectrometer. Viscosities were measured with an Ubbelohde viscometer in dichloromethane−trifluoroacetic acid (4:1, v/v) mixture solution at 25 °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. In case of T_g, the half point was taken. A polarizing microscope equipped with a Mettler FP82 hot stage was used for visual observation. Infrared spectra at various temperatures were obtained by a Jasco Micro FT/IR-200 spectrophotometer 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

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Scheme 1

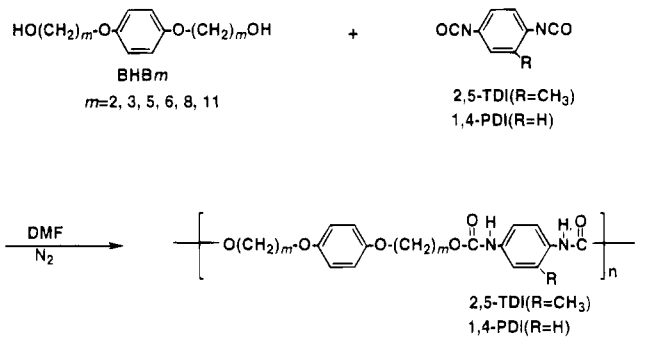

Table 1. Polyaddition Reaction of 2,5-Tolylene Diisocyanate (2,5-TDI) with 1,4-Bis(ω-hydroxyalkoxy)benzenes (BHB*m*)[a]

polymer	carbon number of alkylene chain *m*	diisocyanate, g (mmol)	BHB*m*, g (mmol)	yield, %	$[\eta]$,[b] dL/g
2,5-TDI/BHB2	2	0.500 (2.87)	0.568 (2.87)	91	0.22
2,5-TDI/BHB3	3	0.500 (2.87)	0.649 (2.87)	88	0.41
2,5-TDI/BHB5	5	0.500 (2.87)	0.809 (2.87)	89	0.33
2,5-TDI/BHB6	6	0.500 (2.87)	0.890 (2.87)	89	0.40
2,5-TDI/BHB8	8	0.500 (2.87)	1.050 (2.87)	92	0.37
2,5-TDI/BHB11	11	0.500 (2.87)	1.292 (2.87)	88	0.27

[a] Conditions: 80 °C; 24 h. Solvent: DMF (20 mL). [b] Intrinsic viscosity measured in a dichloromethane–trifluoroacetic acid (4:1, v/v) solution at 25 °C.

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. X-ray diffraction measurements were carried out by a Rigaku X-ray Rad 2B system using Ni-filtered Cu Kα radiation. Samples placed on a Mettler FP52 hot stage were used for the X-ray measurement.

Results and Discussion

Preparation of Para-type Polyurethane. The structure and the reaction scheme for the polyurethanes of 2,5-TDI/BHB*m*'s and 1,4-PDI/BHB*m*'s are given in Scheme 1. The polyurethanes were obtained by the polyaddition reaction of equimolar amounts of the diisocyanate of 2,5-TDI or 1,4-PDI, and the diol of BHB*m* (m = 2, 3, 5, 6, 8, 11). The diisocyanate monomers have the functional groups at the para position. These polymers have no mesogenic core unit in the main chain. The polymerization was performed in dry DMF at 80 °C for 24 h under a dry nitrogen atmosphere.

The results of the polymerization for 2,5-TDI/BHB*m* and 1,4-PDI/BHB*m* are given in Tables 1 and 2, respectively. The yields were 88–94%. The intrinsic viscosities of polymers were measured in the mixture of dichloromethane and trifluoroacetic acid (4:1, v/v) except for 1,4-PDI/BHB2 which was insoluble in such solvent. The viscosities for 2,5-TDI/BHB*m* and 1,4-PDI/BHB*m* were in the range of 0.22–0.41 and 0.31–0.52 dL/g, respectively.

^{1}H NMR and infrared spectra confirmed the formation of the structure of the polyurethanes shown in Scheme 1. Figure 1 shows ^{1}H NMR spectra for the polymers of 1,4-PDI/BHB5 (A) and 2,5-TDI/BHB5 (B). For 1,4-PDI/BHB5 (Figure 1A), the singlet N–H proton peak was observed at 9.09 ppm because of the symmetric molecular structure. The aromatic proton (H_b) of the phenylene group of the diisocyanate was also seen at 7.29

Table 2. Polyaddition Reaction of 1,4-Phenylene Diisocyanate (1,4-PDI) with 1,4-Bis(ω-hydroxyalkoxy)benzenes (BHB*m*)[a]

polymer	carbon number of alkylene chain *m*	diisocyanate, g (mmol)	BHB*m*, g (mmol)	yield, %	$[\eta]$,[b] dL/g
1,4-PDI/BHB2	2	0.500 (3.13)	0.620 (3.13)	92	insoluble
1,4-PDI/BHB3	3	0.500 (3.13)	0.703 (3.13)	91	0.52
1,4-PDI/BHB5	5	0.500 (3.13)	0.883 (3.13)	93	0.35
1,4-PDI/BHB6	6	0.500 (3.13)	0.970 (3.13)	92	0.46
1,4-PDI/BHB8	8	0.500 (3.13)	1.146 (3.13)	90	0.40
1,4-PDI/BHB11	11	0.500 (3.13)	1.409 (3.13)	94	0.31

[a] Conditions: 80 °C; 24 h. Solvent: DMF (20 mL). [b] Intrinsic viscosity measured in a dichloromethane–trifluoroacetic acid (4:1, v/v) solution at 25 °C.

ppm as a singlet resonance. On the other hand, for 2,5-TDI/BHB5, two N–H proton absorptions of the urethane linkage were observed at 8.62 and 9.42 ppm (Figure 1B). The methyl group on the phenylene unit caused nonequivalency of the N–H protons. The infrared spectrum of 1,4-PDI/BHB5 obtained at room temperature is shown in Figure 2. The N–H stretching band of the urethane group in the region of 3200–3600 cm^{-1} and the carbonyl stretching in the region of 1690–1720 cm^{-1} appeared in the spectrum. The C=O peak had a shoulder at a higher wave number, which will be discussed in more detail below.

Liquid Crystallinity of Poly(2,5-TDI/BHB*m*). DSC Thermograms of 2,5-TDI/BHB5 in the first cooling and second heating stages are shown in Figure 3A. The first cooling thermogram was measured on the sample which was melt at an isotropic temperature, followed by cooling at the rate of 20 °C/min.

A broad exothermic peak possibly due to crystallization appears at 96 °C. In addition, a faint exothermic peak is seen at 119 °C. The latter peak was concluded to be due to an isotropic-to-liquid crystalline transition in combination with the result of microscopic observation mentioned later. The T_g appeared at 51 °C. Unlike other thermotropic polyurethanes, this polyurethane kept its softness in the temperature range of 96–51 °C, and thus the mesophase temperature range of this polymer was concluded to be from 119 to 51 °C (= T_g).

In the second heating stage, first, the T_g peak is seen at 58 °C, and an exothermic peak due to crystallization appears at 109 °C, followed by a melting peak at 145 °C. The microscopic observation revealed that there is no liquid-crystalline state in the heating stage. The 2,5-TDI/BHB5 polyurethane was a polymer which keeps its hardness above T_g and is subject to ready crystallization even in the fast heating stage. It is assumed that since the polyurethane has a high proportion of the oriented region and strong intermolecular interactions even above T_g, it did not exhibit liquid-crystalline state in the heating stage. Therefore, the 2,5-TDI/BHB5 was a monotropic liquid-crystalline polymer.

As shown in Figure 3B, a DSC thermogram in the first cooling of 2,5-TDI/BHB6 exhibits a large sharp peak due to crystallization at 96 °C. Although the first cooling stage did not show a clear peak, the second cooling stage gave a small peak at 119 °C due to $T_{I\text{-}LC}$ transition. In the second heating, the polyurethane shows a small endothermic peak at 105 °C and a large one at 145 °C both of which are possibly due to melting. Below 96 °C, the polymer was hard and had no fluidity. Accordingly, the polyurethane was a monotropic liquid-crystalline polymer with the mesophase temperature range of 119–96 °C (= T_m).

Similarly, 2,5-TDI/BHB3 had $T_{I\text{-}LC}$ at 175 °C and $T_{LC\text{-}K}$ at 133 °C in the first cooling. 2,5-TDI/BHB8

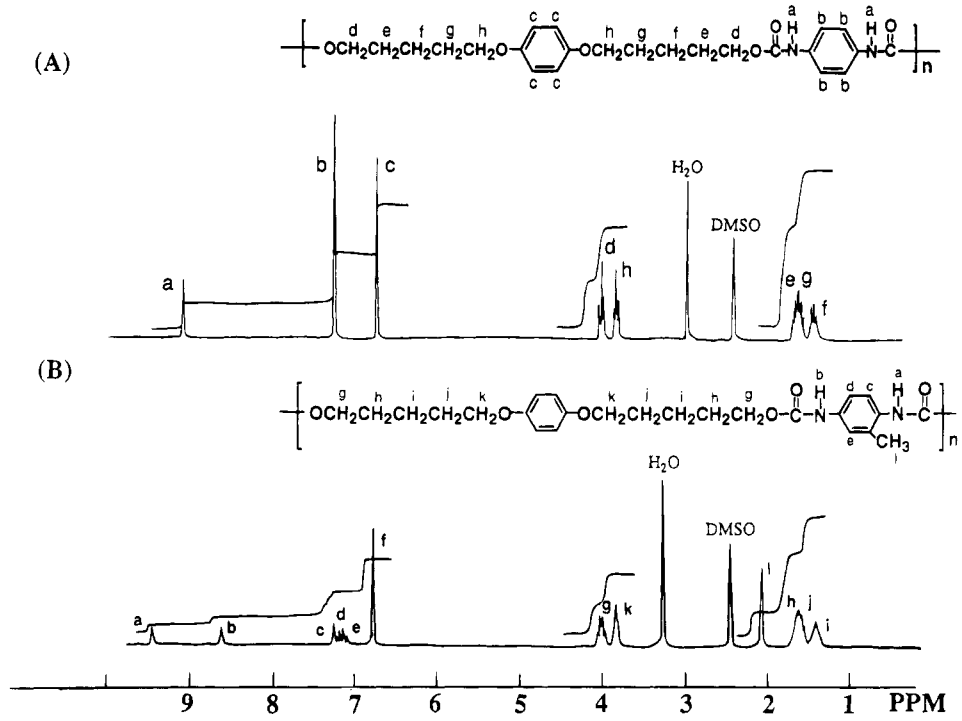

Figure 1. ^{1}H NMR spectra of polyurethanes: (A) 1,4-PDI/BHB5 in DMSO-d_6 at 80 °C and (B) 2,5-TDI/BHB5 in DMSO-d_6 at 30 °C.

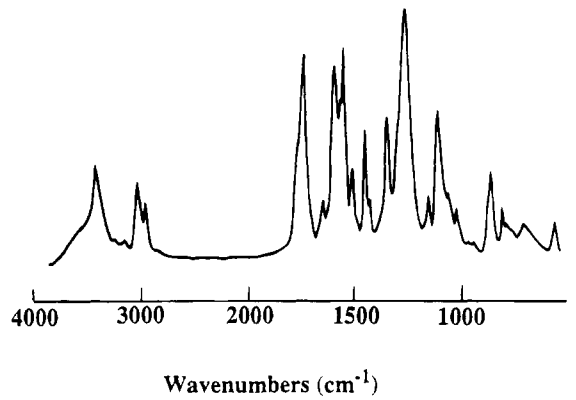

Figure 2. Infrared spectrum of 1,4-PDI/BHB5 in the range of 500–4000 cm^{-1}.

behaved similarly, representing its monotropic liquid crystallinity.

On the other hand, both 2,5-TDI/BHB2 with a shorter alkylene group and 2,5-TDI/BHB11 with a longer alkylene group did not show liquid crystallinity.

Liquid-crystalline patterns of 2,5-TDI/BHB5 and 2,5-TDI/BHB6 were viewed by the polarized microscopic observation, as shown in Figure 4. Since these polyurethanes were considerably stiff even in the liquid-crystalline state, the nematic patterns appeared by putting shear on the sample inserted between the cover glass.

The thermal properties of 2,5-TDI/BHB*m* series obtained from the DSC and microscopic observations are summarized in Table 3. The four polyurethanes having the alkylene group ranging from trimethylene to octamethylene were monotropic liquid-crystalline polymers with the nematic texture.

When the polarized microscopic observation was carried out on the oriented fiber of 2,5-TDI/BHB5 by changing the angle of observation, the brightest fibrous pattern was obtained at the angles of 45° and 135°. Accordingly, it was revealed that the polyurethane backbone is oriented in the direction of fiber axis.

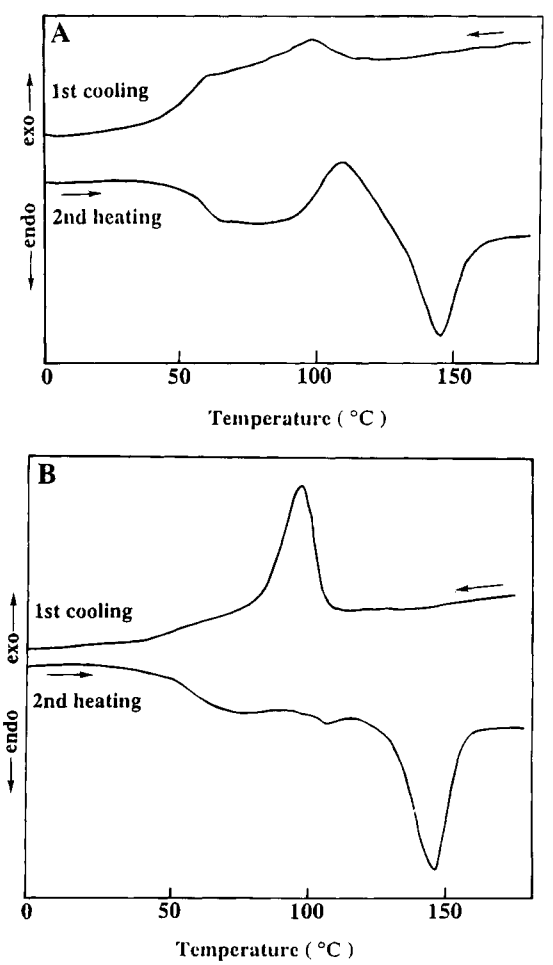

Figure 3. DSC thermograms of (A) 2,5-TDI/BHB5 and (B) 2,5-TDI/BHB6 on the first cooling and second heating stages: (Rate: 20 °C/min).

Next, 2,5-TDI/BHB*m* polyurethanes in isotropic, liquid-crystalline, and solid states were examined by X-ray

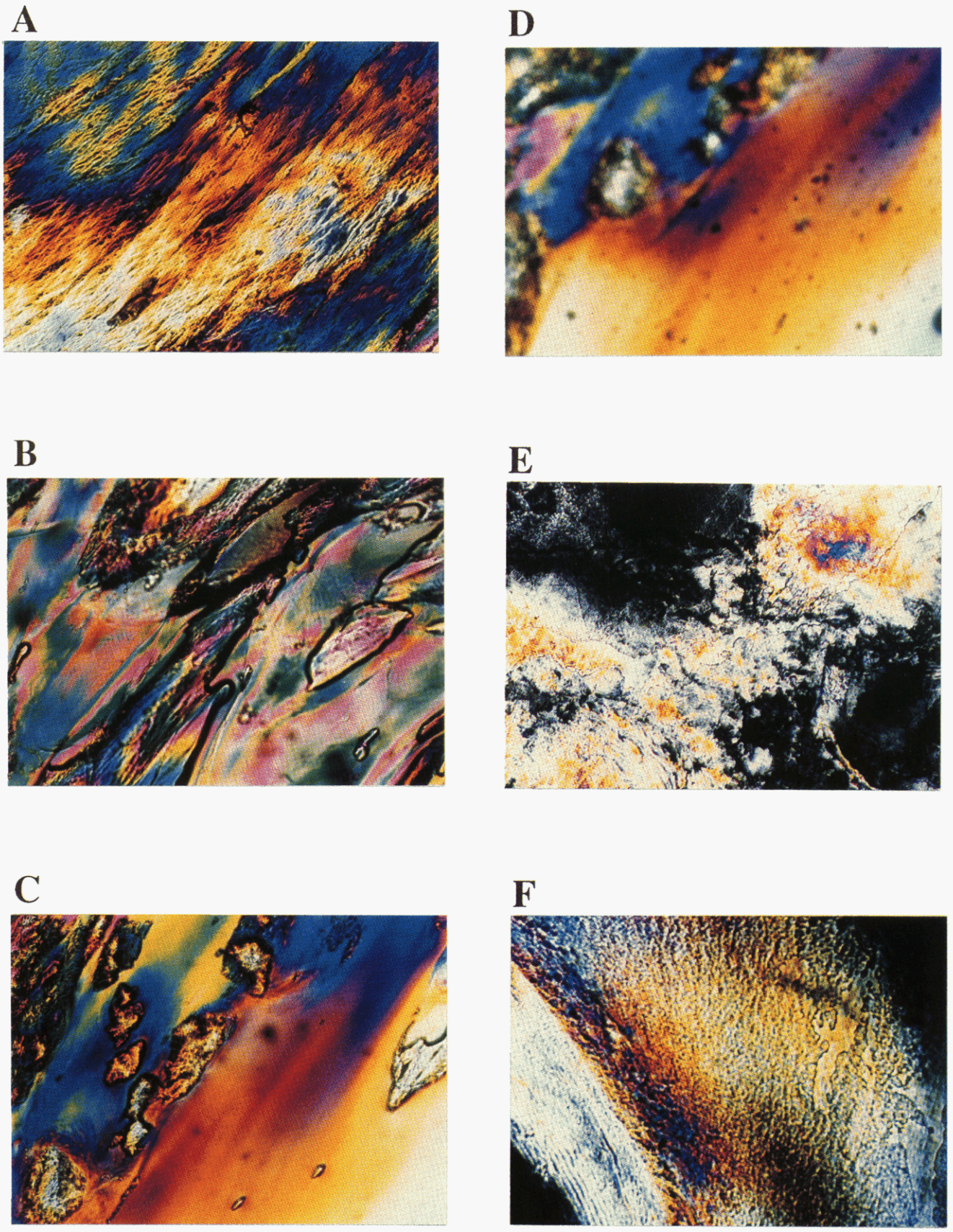

Figure 4. Polarizing optical photomicrographs of (A) 2,5-TDI/BHB5 at 115 °C, (B) 2,5-TDI/BHB5 at 96 °C, (C) 2,5-TDI/BHB6 at 115 °C, (D) 2,5-TDI/BHB6 at 110 °C, (E) 1,4-PDI/BHB5 at 207 °C, and (F) 1,4-PDI/BHB6 at 193 °C.

diffractometry. For 2,5-TDI/BHB5, X-ray diffraction patterns in different temperatures are shown in Figure 5A. In the isotropic state at 130 °C, a diffraction pattern characteristic of an amorphous polymer is displayed. In the liquid-crystalline state at 113 °C, the pattern is that of a little oriented polymer. And, in the mesophase state at 70 °C, X-ray pattern indicates that crystallization proceeded to a little extent, because it is close to the pattern measured at 30 °C where the solid polymer contained a considerable proportion of crystalline regions. By taking into account this result and other measurements taken on a different apparatus and in

Table 3. Thermal Properties of 2,5-TDI/BHBm Polyurethanes[a]

	phase transition behavior second heating					phase transition behavior first cooling				
polymer	T_g, °C	T_{m1}, °C	T_{m2}, °C	ΔH_{m1}, J/g	ΔH_{m2}, J/g	$T_{I\text{-}LC}$, °C	$T_{LC\text{-}K}$, °C	T_g, °C	$\Delta H_{I\text{-}LC}$, J/g	$\Delta H_{LC\text{-}K}$, J/g
2,5-TDI/BHB2	96	232[d]	253	12.1	51.7			91		
2,5-TDI/BHB3	83	209		34.7		175[b]	133	77		27.7
2,5-TDI/BHB5	58	145		21.9		119	96	51	0.1	3.5
2,5-TDI/BHB6	56	105[d]	145	0.3	23.0	119[c]	96	50	0.1	21.1
2,5-TDI/BHB8	33	90	114	11.0	11.2	108	75	25	2.7	10.3
2,5-TDI/BHB11	40	126		47.3				44		

[a] Transition temperatures were determined by DSC measurement with a heating and cooling rate of 20 °C/min. [b] Determined by microscopic observation. [c] Determined on the second cooling stage. [d] Might be crystal-to-crystal transition.

Table 4. Thermal Properties of 1,4-PDI/BHBm Polyurethanes[a]

	phase transition behavior second heating					phase transition behavior first cooling		
polymer	T_g, °C	T_{m1}, °C	T_{m2}, °C	ΔH_{m1}, J/g	ΔH_{m2}, J/g	T_m, °C	ΔH_m, J/g	T_g, °C
1,4-PDI/BHB2	71	249[b]	274	5.7	16.9	210	25.9	
1,4-PDI/BHB3	81	263[b]	271	53.3	30.9	230	77.1	
1,4-PDI/BHB5	65	207[b]	223	19.4	29.0	194	48.9	
1,4-PDI/BHB6	64	212		44.9		184	45.0	
1,4-PDI/BHB8	34	171	185	28.6	3.7	148	34.0	
1,4-PDI/BHB11	45	170		44.9		155	41.2	106

[a] Transition temperatures were determined by DSC measurement with a heating and cooling rate of 20 °C/min. [b] Might be crystal-to-crystal transition.

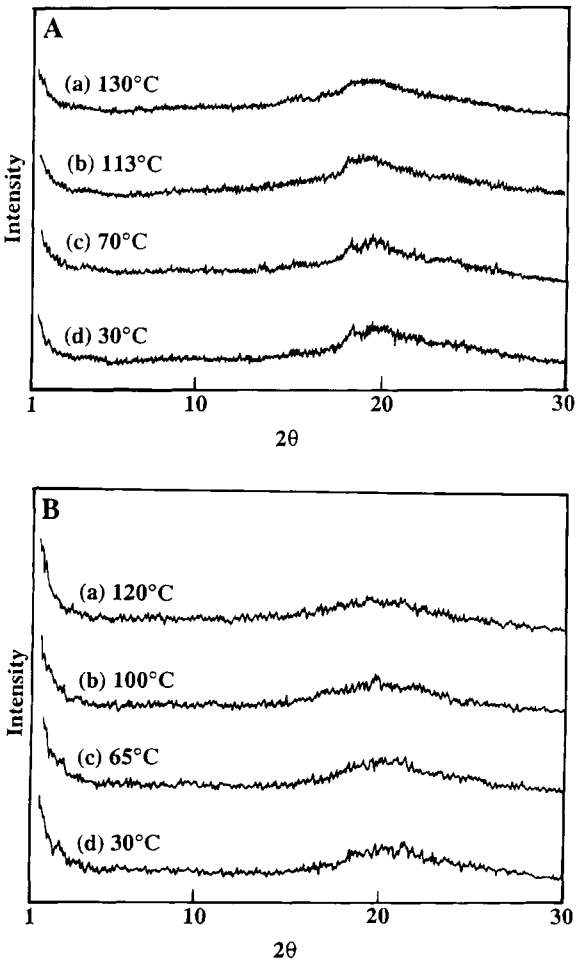

Figure 5. X-ray diffraction patterns of (A) 2,5-TDI/BHB5 and (B) 2,5-TDI/BHB8 in different temperatures.

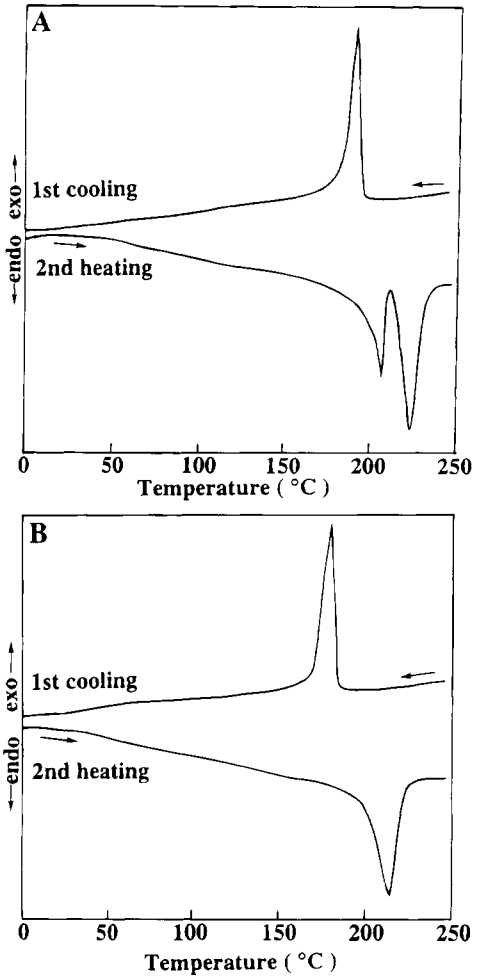

Figure 6. DSC thermograms of (A) 1,4-PDI/BHB5 and (B) 1,4-PDI/BHB6.

different conditions, the para-type polyurethane has a property that its crystallization is beginning even in the liquid-crystalline state.

A similar tendency was observed in X-ray measurements of a 2,5-TDI/BHB8 homologue (Figure 5B). In this case, a broad amorphous pattern is seen in the isotropic state at 120 °C, and a pattern similar to crystalline diffraction overlaps the amorphous pattern in the liquid-crystalline state at 100 °C, and then at 65 and 30 °C a crystalline diffraction pattern appears.

Thermal Properties and Structural Characteristics of Poly(1,4-PDI/BHBm). DSC Thermograms of 1,4-PDI/BHB5 and 1,4-PDI/BHB6 in the first cooling and second heating stages are shown in Figure 6. In the first cooling thermogram of the former, a large exothermic peak due to crystallization appears at 194

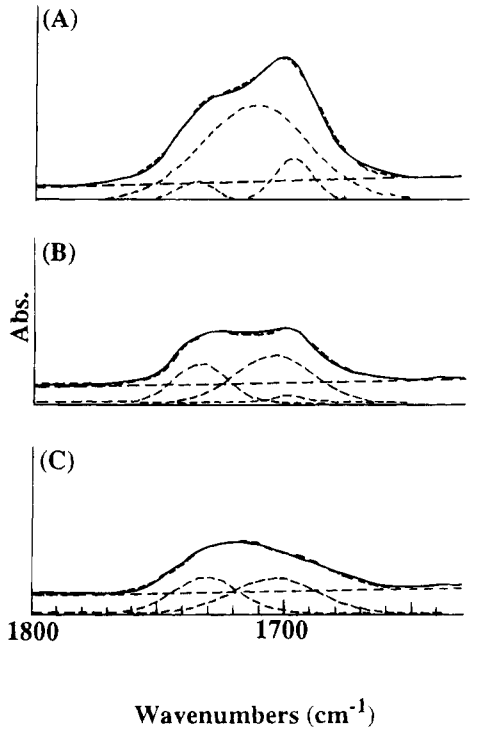

Figure 7. Curve-fitting results of the carbonyl bands of the infrared spectra for 1,4-PDI/BHB5 at (A) 173, (B) 214, and (C) 245 °C.

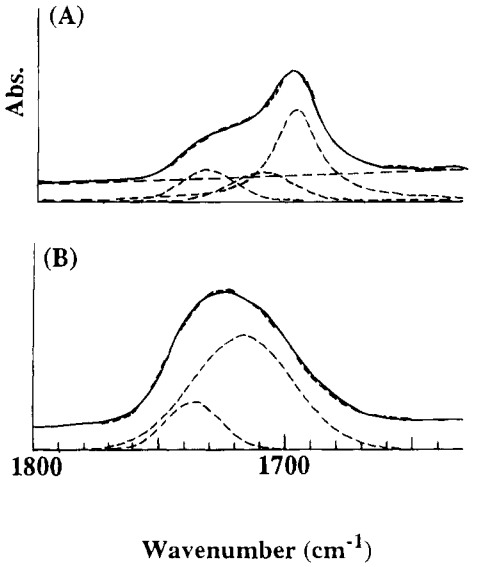

Figure 8. Curve-fitting results of the carbonyl bands of the infrared spectra for 2,5-TDI/BHB5 at (A) 110 and (B) 180 °C.

°C. In the second heating thermogram, there are two large endothermic peaks at 207 and 223 °C. A faint endothermic peak at 65 °C is probably ascribed to T_g.

Although the 1,4-PDI/BHB5 polyurethane was observed by a polarizing optical microscope in an unsheared or sheared condition, it showed only colored soil textures (Figure 4E). Moreover, in the cooling stage, the polyurethane was viewed by the microscopic observation in the temperature range from isotropic temperature to T_m or to lower temperatures in an unsheared or sheared condition. However, any conventional liquid-crystalline texture was not found. The observed state of 1,4-PDI/BHB5 changed from the isotropic melt to a hard solid containing possibly a large proportion of crystalline regions without passing soft liquid-crystalline state. In addition, a clear T_g peak was not observed in the cooling stage.

Table 5. Curve-Fitting Results of the Carbonyl Peak of 1,4-PDI/BHB5 at Various Phases[a]

	hydrogen-bonded C=O bands		free C=O band	
	ν, cm^{-1}	fraction of area	ν, cm^{-1}	fraction of area
173 °C	1698	0.13	1736	0.05
	1713	0.82		
214 °C	1700	0.05	1734	0.35
	1705	0.60		
245 °C	1703	0.56	1730	0.44

[a] Measured on the heating stage.

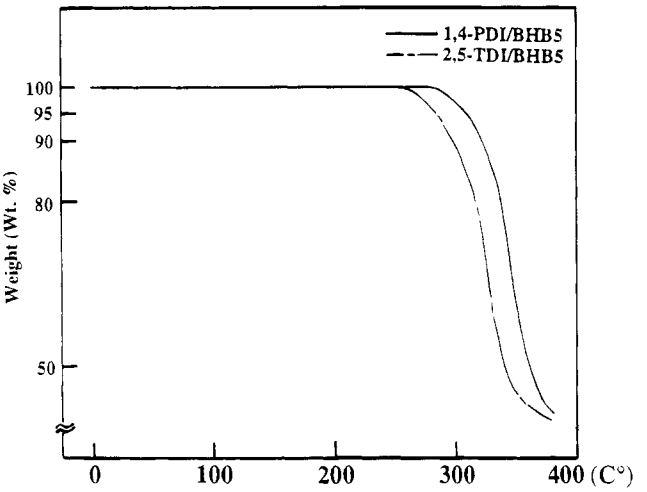

Figure 9. Thermogravimetry conducted at a heating rate of 10 °C/min in an air atmosphere.

Figure 4F shows a polarizing optical photomicrograph of 1,4-PDI/BHB6 with T_m of 180 °C which was taken at 193 °C in the first cooling stage. A colored fine sand texture is seen. This texture was also not classified into a conventional liquid-crystalline texture.

Other 1,4-PDI/BHB*m* polyurethanes exhibited similar thermal behaviors. Their thermal behaviors obtained by the DSC observation are summarized in Table 4. All 1,4-PDI/BHB*m*'s had a single T_m peak in the cooling stage and one or two T_m peaks in the heating stage. The higher T_m in the heating stage was the isotropic temperature. In any case, an isotropic-to-liquid crystalline or melting-to-liquid crystalline transition was not observed. Therefore, the 1,4-PDI/BHB*m* polyurethanes in which *m* ranged from 2 to 11 were not conventional liquid-crystalline polymers. The reason that no liquid crystallinity was observed might be ascribed to extremely ready crystallization of the unsubstituted para-type polyurethanes.

Hydrogen Bonding as an Orienting Force of Polymer Backbone. To examine the effect of hydrogen bonds, infrared spectra were recorded for once-melted samples of 1,4-PDI/BHB5 (Figure 7) and 2,5-TDI/BHB5 (Figure 8) on the heating stage. Although these polyurethanes showed no liquid crystallinity, their structural characteristics were clearly different from those of non-liquid-crystalline polymers. It has been reported that for polyurethanes the carbonyl band of the urethane group is sensitive to the state of H-bonding and molecular aggregation.[14,26] MacKnight and coworkers studied liquid-crystalline polyurethanes by infrared spectroscopy.[14] They showed that the carbonyl band could be resolved into three bands, i.e., the H-bonded ordered peak at *ca.* 1697 cm^{-1}, the H-bonded disordered peak at *ca.* 1710 cm^{-1}, and the non-H-bonded peak at *ca.* 1740 cm^{-1}. For the polyurethane 1,4-PDI/BHB5, the curve-fitting results of the carbonyl bands

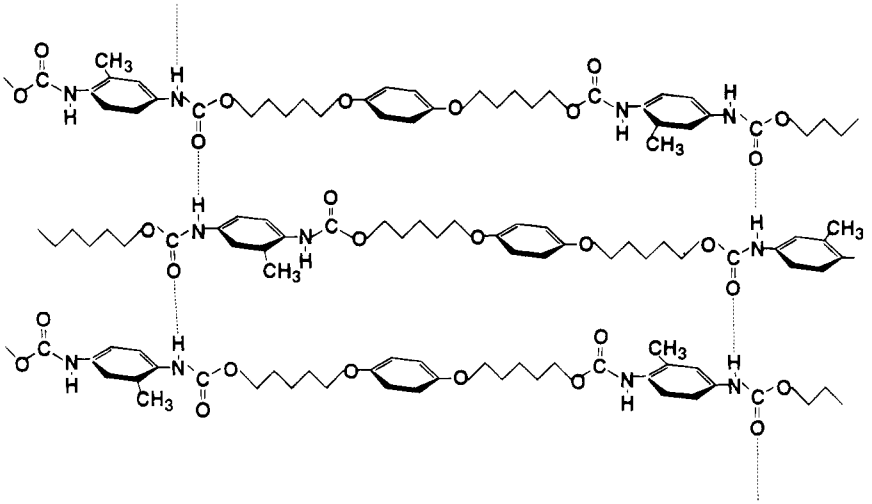

Figure 10. Proposed structure of the anisotropic state for the thermotropic polyurethane containing no mesogenic group.

Table 6. Curve-Fitting Results of the Carbonyl Peak of 2,5-TDI/BHB5 at Various Phases[a]

	hydrogen-bonded C=O bands		free C=O band	
	ν, cm^{-1}	fraction of area	ν, cm^{-1}	fraction of area
110 °C	1698	0.63	1732	0.18
	1711	0.19		
180 °C	1717	0.82	1736	0.18

[a] Measured on the heating stage.

at 173 and 214 °C also showed that the peaks consisted of three bands (Figure 7 and Table 5). In the crystalline state, the fraction of H-bonded band at 1698 cm^{-1} was 0.13. It decreased to 0.05 at 214 °C. In contrast, the fraction of the free C=O band at 1736 cm^{-1} increased from 0.05 to 0.35. In the isotropic state at 245 °C, only two peaks due to the disordered H-bonded peak at 1703 cm^{-1} and the non-H-bonded peak at 1730 cm^{-1} were obtained.

On the other hand, for 2,5-TDI/BHB5, the fraction of the free C=O band at 1732 cm^{-1} was 0.18 in the crystalline phase (Figure 8 and Table 6), which was larger than that for 1,4-PDI/BHB5. The methyl group of 2,5-TDI unit may hinder the formation of the hydrogen bond to some extent in the crystalline state. When the polymer directly melted to the isotropic phase, the fraction of the free carbonyl band did not change. The disordered H-bonded C=O band greatly increased in its fraction and shifted to higher frequency.

Thermogravimetric analysis was performed for the polyurethanes. The temperatures of 5% weight loss for 1,4-PDI/BHB5 (T_m 223 °C) and 2,5-TDI/BHB5 (T_m 145 °C) in air were 314 and 291 °C, respectively (Figure 9). It is known that urethane groups generally decompose at about 220 °C.[25] However, for 1,4-PDI/BHB5, no weight loss was observed up to 250 °C. The infrared study showed that the fraction of the hydrogen-bonded carbonyl group was 0.82 at 110 °C. This relatively large fraction of hydrogen bonding which forms a network structure as by the noncovalent bonding shown in Figure 10 may stabilize the orientation of liquid crystalline state and the chemical structure of 2,5-TDI/BHB5.[26,27]

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