Synthesis and Thermotropic Properties of Polyurethanes Prepared from 2,5-Tolylene Diisocyanate and 2,6-Bis(ω -hydroxyalkoxy)naphthalenes

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ABSTRACT: A series of thermotropic polyurethanes containing no mesogenic unit were synthesized by polyaddition of a *para*-type diisocyanate such as 2,5-tolylene diisocyanate (2,5-TDI) with 2,6-bis(ω -hydroxyalkoxy)naphthalenes (BHN*m*: $\text{HO}(\text{CH}_2)_m\text{OC}_{10}\text{H}_6\text{O}(\text{CH}_2)_m\text{OH}$; *m* is the carbon number in the hydroxyalkoxy group). Intrinsic viscosities of the polymers were in the range of 0.27–0.48 dL g⁻¹. The thermal properties of these polymers were studied by differential scanning calorimetry, thermogravimetric analysis, polarizing microscopy, and X-ray diffractometry. Polyurethane 2,5-TDI/BHN*m*'s (*m* = 5, 6, 8, 11) prepared from BHN*m* and 2,5-TDI having methyl substituent on the phenylene unit exhibited monotropic liquid crystallinity. For example, polyurethane 2,5-TDI/BHN8 with $[\eta] = 0.30$ exhibited a mesophase from 139 to 111°C on cooling. However, in the series of polyurethanes prepared by polycondensation of 1,4-phenylene diisocyanate (1,4-PDI) with BHN*m*, no explicit mesomorphic behavior was observed by DSC measurement and polarizing microscopic observation.

KEY WORDS Thermotropic Polyurethane / 2,5-Tolylene Diisocyanate / 1,4-Phenylene Diisocyanate / Hydrogen Bonding /

Polyurethanes are a distinct class of materials with industrial importance.¹ Induction of mesomorphic behavior for polyurethanes have attracted much attention. Iimura and co-workers first reported thermotropic polyurethanes prepared by polyaddition of 3,3'-dimethyl-4,4'-biphenyldiyl diisocyanate with α,ω -alkanediols.² Tanaka and Nakaya synthesized several polyurethanes by polyaddition of diols containing mesogenic units with various diisocyanates.^{3,4} MacKnight and coworkers reported thermotropic properties of polyurethanes based on meta-type 2,4- or 2,6-tolylene diisocyanate.^{5–12} Other research groups have also reported the preparation and the physical properties of liquid-crystalline polyurethanes consisting of rigid or mesogenic units in the main chain.^{13–20}

In the previous paper, we reported the synthesis and thermotropic properties of a series of liquid-crystalline polyurethanes by polyaddition reaction of such para-substituted diisocyanates as 2,5-tolylene diisocyanate (2,5-TDI) and 1,4-phenylene diisocyanate (1,4-PDI) with 4,4'-bis(ω -hydroxyalkoxy)biphenyl or 1,4-bis(ω -hydroxyalkoxy)benzene.^{21,22}

In this study, we synthesized a new series of polyurethanes by the polyaddition of para-substituted diisocyanate monomers, *i.e.*, 2,5-TDI and 1,4-PDI, with 2,6-bis(ω -hydroxyalkoxy)naphthalenes. Thermal properties were examined for these polyurethanes using differential scanning calorimetry (DSC), X-ray diffractometry and polarizing microscopy.

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EXPERIMENTAL

Materials

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

Monomer Synthesis

2,6-Bis(ω -hydroxyalkoxy)naphthalenes (BHN m ; $m=2, 3, 5, 6, 8, 11$) were synthesized by the reaction of 2,6-dihydroxynaphthalene with ω -halogenated alkanols. A mixture of sodium hydroxide (5.4 g, 0.13 mol), 2,6-dihydroxynaphthalene (5.1 g, 0.032 mol), and ω -bromo- or chloro-1-alkanol (0.13 mol) in 150 mL of ethanol was refluxed for 12 h, and then poured into cold water. The precipitate was filtered and recrystallized from isopropyl alcohol. Yield 50–86%. mp: 187–189°C ($m=2$), 148–150°C ($m=3$), 126–127°C ($m=5$), 125–126°C ($m=6$), 117–119°C ($m=8$), 121–123°C ($m=11$). ^1H NMR (dimethyl sulfoxide- d_6): BHN2, δ 3.72 (4H, m), 4.02 (4H, t), 4.82 (2H, t), 7.72–7.03 (6H, m); BHN3, δ 1.89 (4H, m), 3.56 (4H, m), 4.07 (4H, t), 5.54 (2H, t), 7.70–7.01 (6H, m); BHN5, δ 1.82–1.37 (12H, m), 3.39 (4H, m), 4.00 (4H, t), 4.32 (2H, t), 7.71–7.00 (6H, m); BHN6, δ 1.80–1.22 (16H, m), 3.36 (4H, m), 4.00 (4H, t), 4.21 (2H, t), 7.70–7.00 (6H, m); BHN8, δ 1.79–1.20 (24H, m), 3.37 (4H, m), 4.02 (4H, t), 4.16 (2H, t), 7.72–7.02 (6H, m); BHN11, δ 1.80–1.09 (40H, m), 3.32 (2H, t), 4.00 (4H, t), 7.68–7.01 (6H, m).

Polymer Synthesis

The polyurethanes were synthesized by a polyaddition reaction according to the method described in the literature.^{21,22} The solution of BHN m (2.87 mmol) in 15 mL of dry *N,N*-dimethylformamide (DMF) was placed in a three-neck round bottom flask. The diisocyanate, 2,5-TDI or 1,4-PDI (2.87 mmol), dissolved in 15 mL of dry DMF was added

dropwise to the BHN m solution under a dry nitrogen atmosphere at room temperature. Then, after the reaction mixture was stirred at 80°C for 24 h, it was poured into methanol to precipitate the polymer. The precipitated polymer was treated with boiling methanol, filtered, and then dried under vacuum at 60°C overnight. Yield: 85–93%.

Anal. Calcd for 1,4-PDI/BHN5 ($\text{C}_{28}\text{H}_{32}\text{N}_2\text{O}_6$) $_n$: C, 68.28; H, 6.55; N, 5.68. Found: C, 68.25; H, 6.56; N, 5.65. Calcd for 2,5-TDI/BHN2 ($\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_6$) $_n$: C, 65.39; H, 5.24; N, 6.63. Found: C, 65.34; H, 5.20; N, 6.65.

Measurements

^1H NMR spectra were obtained in dimethyl sulfoxide- d_6 (DMSO- d_6) by a JEOL JNM GX-270 spectrometer. Infrared spectra were obtained by a Perkin Elmer FT/IR 1600 spectrometer. Viscosities were measured on the polymer solution in dichloromethane–trifluoroacetic acid (4:1, v/v) mixture with an Ubbelohde viscometer at 25°C. Differential scanning calorimetry (DSC) measurements were performed on a Mettler DSC 30 at a scanning rate of 20°C min⁻¹. The maximum point of the endotherm was taken as the transition temperature. A polarizing microscope equipped with a Mettler FP82 hot stage was used for visual observation. X-ray diffraction measurements of the samples placed on a CN2311B1 thermal control were carried out with a Rigaku RINT X-ray 2000 system using Ni-filtered Cu- K_α radiation. The thermogravimetric analysis was performed by a Shimadzu DT-40 at a heating rate of 10°C min⁻¹ in air.

RESULTS AND DISCUSSION

The general synthetic route and the structure of 2,5-TDI/BHN m and 1,4-PDI/BHN m polyurethanes are given in Scheme 1. A series of polyurethanes 2,5-TDI/BHN m 's and 1,4-PDI/BHN m 's were synthesized by the polyaddition reaction of equimolar amounts of diisocyanates and 2,6-bis(ω -hydroxyalkoxy)-

Scheme 1. Synthetic route of 2,5-TDI/BHN m and 1,4-PDI/BHN m polyurethanes.

naphthalenes. These polyurethanes contained no mesogenic core unit in the main chain like the thermotropic polyurethanes prepared from 2,5-TDI and 1,4-bis(ω -hydroxyalkoxy)benzenes.²² The reaction was allowed to proceed in dry DMF at 80°C under a dry nitrogen atmosphere for 24 h.

The results of the polymerization for 2,5-TDI/BHN m and 1,4-PDI/BHN m are given in Tables I and II, respectively. The yields were 87–92%. The intrinsic viscosities of the polymers were measured in the mixture of dichloromethane and trifluoroacetic acid (4:1, v/v) except for 1,4-PDI/BHN2 which was insoluble in the mixture solvent. The viscosities for 2,5-TDI/BHN m and 1,4-PDI/BHN m were in the range of 0.27–0.42 dL g⁻¹ and 0.31–0.48 dL g⁻¹, respectively.

Table I. Polyaddition reaction of 2,5-tolylene diisocyanate (2,5-TDI) with 2,6-bis(ω -hydroxyalkoxy)naphthalenes (BHN m)^a

Polymer	Carbon number of alkylene chain m	Diisocyanate	BHN m	Yield	$[\eta]^b$
		g (mmol)	g (mmol)	%	dL g ⁻¹
2,5-TDI/BHN2	2	0.500 (2.87)	0.712 (2.87)	87	0.27
2,5-TDI/BHN3	3	0.510 (2.93)	0.808 (2.93)	90	0.25
2,5-TDI/BHN5	5	0.508 (2.92)	0.968 (2.92)	87	0.32
2,5-TDI/BHN6	6	0.500 (2.87)	1.033 (2.87)	92	0.32
2,5-TDI/BHN8	8	0.506 (2.91)	1.209 (2.91)	89	0.30
2,5-TDI/BHN11	11	0.500 (2.87)	1.435 (2.87)	88	0.42

^a 80°C, 24 h, solvent: DMF (20 mL). ^b Intrinsic viscosity measured on dichloromethane–trifluoroacetic acid (4:1, v/v) solution at 25°C.

Table II. Polyaddition reaction of 1,4-phenylene diisocyanate (1,4-PDI) with 2,6-bis(ω -hydroxyalkoxy)naphthalenes (BHN m)^a

Polymer	Carbon number of alkylene chain m	Diisocyanate	BHN m	Yield	$[\eta]^b$
		g (mmol)	g (mmol)	%	dL g ⁻¹
1,4-PDI/BHN2	2	0.500 (3.13)	0.775 (3.13)	92	Insoluble
1,4-PDI/BHN3	3	0.506 (3.16)	0.873 (3.16)	88	0.33
1,4-PDI/BHN5	5	0.505 (3.16)	1.048 (3.16)	91	0.36
1,4-PDI/BHN6	6	0.508 (3.18)	1.143 (3.18)	89	0.31
1,4-PDI/BHN8	8	0.500 (3.13)	1.300 (3.13)	90	0.35
1,4-PDI/BHN11	11	0.500 (3.13)	1.563 (3.13)	91	0.48

^a 80°C, 24 h, solvent: DMF (20 mL). ^b Intrinsic viscosity measured on dichloromethane–trifluoroacetic acid (4:1, v/v) solution at 25°C.

Figure 1. ^1H NMR spectrum for polyurethanes: (A) 2,5-TDI/BHN8 in $\text{DMSO}-d_6$ at 30°C ; (B) 1,4-PDI/BHN5 in $\text{DMSO}-d_6$ at 80°C .

The structure of polyurethanes was confirmed by ^1H NMR and infrared spectra. Figure 1 shows ^1H NMR spectra of 2,5-TDI/BHN8 (A) and 1,4-PDI/BHN5 (B) polymers obtained in a $\text{DMSO}-d_6$ solution at 30 and 80°C , respectively. For 2,5-TDI/BHN8, two N–H proton absorptions of the urethane linkage were observed at 8.61 and 9.42 ppm (Figure 1(A)). The methyl group on the phenylene unit caused a non-equivalency of the N–H protons. The naphthalene protons resonated at 7.04, 7.18, and 7.62 ppm. On the other hand, for 1,4-PDI/BHN5, a singlet N–H proton absorption of the urethane linkage was observed at 9.02 ppm because of the symmetric

molecular structure. The naphthalene protons resonated at 7.01, 7.21, and 7.78 ppm. The aromatic proton of the phenylene group was seen at 7.31 ppm as a singlet resonance.

Figure 2 shows the infrared spectrum of 1,4-PDI/BHN5 in the range of $500\text{--}4000\text{ cm}^{-1}$ measured at room temperature. Absorption peaks were characteristic of polyurethanes. The N–H stretching band of the urethane group appeared at 3339 cm^{-1} . The peak at 1696 cm^{-1} was ascribed to the hydrogen bonded C=O peak.^{12,21,22} The shoulder peak due to free carbonyl group was observed at 1732 cm^{-1} .^{12,21,22}

The thermal properties of these polymers

Figure 2. Infrared spectrum of 1,4-PDI/BHB5 in the range of 500–400 cm^{-1} .

were studied by DSC and polarizing microscopy. DSC thermograms of 2,5-TDI/BHN8 (A) and 2,5-TDI/BHN11 (B) in the 1st cooling and heating scan are shown in Figure 3. These curves are representative of 2,5-TDI/BHN m polymers. The DSC measurements of the polymer samples were carried out in the range from 30 degrees above melting temperature to 0°C. The DSC curves of the 2,5-TDI/BHN8 and 2,5-TDI/BHN11 in the 1st cooling showed two exothermic. The two peaks which occurred at 139° and 111°C were responsible for isotropic-liquid crystalline transition and crystallization, respectively, as shown in Figure 3(A). T_g peak and two endotherms were observed at 55°C, 130°C, and 142°C in the 2nd heating scan. But, the microscopic observation revealed that there is no liquid-crystalline state in the heating scan. Therefore, the 2,5-TDI/BHN8 was a monotropic liquid-crystalline polymer.

As shown in Figure 3(B), DSC thermogram of 2,5-TDI/BHN11 exhibits two exothermic peaks due to isotropic-liquid crystalline transition at 125°C and crystallization at 111°C in the 1st cooling. In the 2nd heating scan the 2,5-TDI/BHN11 shows two endotherms corresponding to meltings at 122°C and 137°C. Accordingly, the polyurethane was a monotropic liquid-crystalline polymer with the mesophase range from 125 to 111°C. The thermal properties of 2,5-TDI/BHN m and 1,4-PDI/BHN m obtained from DSC and microscopic observations are summarized in

Figure 3. DSC curves of polyurethanes: (A) 2,5-TDI/BHN8; (B) 2,5-TDI/BHN11 on the 1st cooling and 2nd heating stages (rate, 20°C min^{-1}).

Tables III and IV. Similarly, 2,5-TDI/BHN5 had isotropic-liquid crystalline transition at 152°C and crystallization at 133°C in the 1st cooling as shown in Table III. 2,5-TDI/BHN8 behaved similarly, representing its monotropic liquid crystallinity.

On the other hand, in the series of 1,4-PDI/BHN m ($m=2, 3, 5, 6, 8, 11$) without methyl substituent on the phenylene unit, no explicit mesomorphic behavior was observed by DSC measurement and polarizing microscope. They showed a colored sand-like texture characteristic of highly crystalline para-linked polyurethanes.²² The reason that the para-

Table III. Thermal properties of 2,5-TDI/BHN m polyurethanes^a

Polymer	Phase transition behavior second heating					Phase transition behavior first cooling				
	T_g	T_{m1}	T_{m2}	ΔH_{m1}	ΔH_{m2}	T_{1-LC}	T_{LC-K}	T_g	ΔH_{1-LC}	ΔH_{LC-K}
	°C	°C	°C	J g ⁻¹	J g ⁻¹	°C	°C	°C	J g ⁻¹	J g ⁻¹
2,5-TDI/BHN2	97	220°	244	8.7	11.9	—	—	96	—	—
2,5-TDI/BHN3	81	216	—	21.0	—	—	—	81	—	—
2,5-TDI/BHN5	65	179	—	33.1	—	152 ^b	133	65	—	32.6
2,5-TDI/BHN6	71	183	—	37.9	—	153 ^b	142	67	—	39.8
2,5-TDI/BHN8	55	130	142	17.1	16.9	139	111	35	3.1	17.3
2,5-TDI/BHN11	46	122	137	13.9	29.1	125	111	44	5.9	40.4

^a Transition temperatures were determined by DSC measurement with the heating and cooling rates of 20°C min⁻¹.^b Determined by microscopic observation. ° Might be crystal-to-crystal transition.**Table IV.** Thermal properties of 1,4-PDI/BHB m polyurethanes^a

Polymer	Polymer transition behavior second heating					Phase transition behavior first cooling		
	T_g	T_{m1}	T_{m2}	ΔH_{m1}	ΔH_{m2}	T_m	ΔH_m	T_g
	°C	°C	°C	J g ⁻¹	J g ⁻¹	°C	J g ⁻¹	°C
1,4-PDI/BHN2	— ^b	—	—	—	—	—	—	—
1,4-PDI/BHN3	51	273	—	39.3	—	245	39.9	52
1,4-PDI/BHN5	76	241°	253	25.1	35.9	213	63.2	69
1,4-PDI/BHN6	71	225	—	41.5	—	198	45.8	110
1,4-PDI/BHN8	59	192	—	36.4	—	173	34.4	50
1,4-PDI/BHN11	46	142°	178	6.2	34.2	152	40.6	42

^a Transition temperatures were determined by DSC measurement with the heating and cooling rates of 20°C min⁻¹.^b Decomposition occurred at approximately 344°C before melting. ° Might be crystal-to-crystal transition.

linked polyurethanes containing 1,4-PDI units did not exhibit liquid crystallinity is assumed to be due to the formation of a highly crystalline region even in the cooling stage. This property might originate from ready orientation of the polymer chains by intermolecular hydrogen bonds between urethane linkages. Therefore, it is assumed that for the tolylene-containing polyurethanes, the methyl substituent in the ortho position of the phenylene group might diminish the formation of the intermolecular hydrogen bonding between the polymer chains and enable the polyurethane to exhibit the mesophase.

Liquid-crystalline patterns of 2,5-TDI/

BHN6 and 2,5-TDI/BHN8 were viewed by the polarizing microscope, as shown in Figure 4. Since these polyurethanes were considerably hard even in the liquid-crystalline state, the nematic patterns appeared by putting shear on the sample inserted between the cover glasses.

X-Ray diffractograms of 2,5-TDI/BHN8 and 1,4-PDI/BHN11 at different temperatures are shown in Figure 5. The X-ray diffractograms of 2,5-TDI/BHN8 on cooling show that no three-dimensional order existed at 123°C because a broad halo corresponding to $d = ca.$ 4.4 Å was only observed, as shown in Figure 5(A). A polarizing photomicrograph of 2,5-TDI/BHN8 taken at 123°C (Figure 4(B)) shows

Figure 4. Polarizing optical photomicrographs of (A) 2,5-TDI/BHN6 at 151°C and (B) 2,5-TDI/BHN8 at 123°C on cooling.

the existence of a mesophase at the temperature between two exothermic peaks. The results of the polarized microscopic observation and the X-ray measurement may suggest that a nematic-like ordering occurred between these two exothermic peaks. X-ray pattern at 70°C showed that crystallization occurred in the cooling process because of the existence of sharp wide angle reflection ($d=4.9$ Å). The X-ray pattern at 123°C on cooling showed only a broad halo corresponding to $d=ca.$ 4.5 Å (Figure 5(B)) which is similar to that of a nematic-like ordering but not a smectic order.^{23,24} The X-ray pattern at 30°C showed that crystallization ($d=4.8$, 4.2, and 3.6 Å) occurred in the cooling process.

Figure 5. X-ray diffraction patterns of (A) 2,5-TDI/BHN8 and (B) 2,5-TDI/BHN11 at various temperatures.

Thermogravimetric analysis was performed for the para-linked polyurethanes. For 1,4-PDI/BHN5 (T_{m2} , 253°C) and 2,5-TDI/BHN8 (T_{m2} , 142°C), the temperatures of 5% weight loss in air were 312°C and 300°C, respectively. No degradation phenomenon was observed in the heating at the liquid-crystalline state of the polymers.

Schematic illustration of an anisotropic state proposed for the thermotropic polyurethanes is shown in Figure 6. These polymers showed liquid-crystalline properties, though for every repeating unit they were composed of non-mesogenic naphthalene and tolylene units that are connected by alkylene spacers. In general, a separated naphthalene group is not rigid

Figure 6. Proposed structure of the anisotropic state for the thermotropic polyurethane containing no mesogenic group.

enough to form a mesogenic group for semi-rigid main-chain liquid-crystalline polymers. The lateral intermolecular hydrogen bonding between the urethane linkages may be responsible for the induction of liquid crystallinity of the polyurethanes examined in the present study, as was the case in the polyurethanes obtained from 2,5-TDI and 1,4-bis(ω -hydroxyalkoxy)benzenes.²²

In conclusion, new para-type polyurethanes were synthesized by the polyaddition of 2,5-TDI or 1,4-PDI having diisocyanate group at the para position with BHN m diols both of which contained no mesogenic unit. Of them, the 2,5-TDI/BHN m polyurethanes having m of 5 to 11 showed monotropic liquid crystallinity.

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