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LIQUID CRYSTALLINE POLYURETHANE. POLYURETHANES CONTAINING BIS-(*p*-OXYMETHYLPHENYL) TEREPHTHALATE

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ABSTRACT

Several polyurethanes based on bis-(*p*-oxymethylphenyl) terephthalate (BOPT) were synthesized and studied with respect to some of their thermal properties. BOPT exhibits a mesomorphic phase at 252-264°C. Polymerization was carried out by equimolar reaction with hexamethylene diisocyanate (HDI), 4,4-dicyclohexylmethane diisocyanate ($H_{12}MDI$) α,α'-diisocyanate-1,3-dimethylcyclohexane (H_6XDI), 4,4′-diphenylmethane diisocyanate (MDI), 2,4-tolylene diisocyanate (TDI), and phenylene diisocyanate (PDI). It became clear that polyurethanes obtained from BOPT with HDI, $H_{12}MDI$, H_6XDI, and TDI have mesomorphic phases at 243-291, 214-250, 172-229, and 180-234°C, respectively, as determined by DSC and polarized microscopy, and that all polyurethanes are crystalline as evidenced by x-ray diffraction.

INTRODUCTION

Several research groups have reported the preparation of liquid-crystal polymers such as polyesters, polyamides, and vinyl polymers, which form mesophases in the melt [1, 2]. The liquid-crystalline polymers may be oriented under shear to yield fibers with unusually high strength and modulus. But many of them have high transition temperatures and low molecular weight, so that the processability and the mechanical properties of the products manufactured from these polymers are far from ideal. Attention has turned to the synthesis of polymers with low transition temperatures and high molecular weights. Since only a few liquid-crystal polyurethanes have been reported [3], our attention was directed to the synthesis of these compounds by reacting a low molecular weight liquid-crystal compound, bis-(*p*-oxymethylphenyl) terephthalate (BOPT) with diisocyanates. Some of the polyurethanes obtained have relatively low transition temperatures and low molecular weight.

EXPERIMENTAL

Materials

DMSO, HDI, TDI, MDI, PI, and BI were from Wako Chemicals Co. and were purified by vacuum distillation. H_{12}MDI, H_6XDI, and PDI were supplied by Takeda Yakuhin Co. *p*-Hydroxybenzyl alcohol was from Aldrich Chemical Co.

BOPT

BOPT was prepared by the Schotten-Baumann reaction. Into a 500-mL three-necked round-bottomed flask, equipped with a mechanical stirrer, thermometer, and dropping funnel, were placed 24.8 g (0.2 mol) *p*-hydroxybenzyl alcohol and a solution of 8.8 g (0.22 mol) sodium hydroxide in 79 mL distilled water. After cooling the solution at 10°C, 20.3 g (0.3 mol) terephthaloyl chloride in 180 mL of acetone was added slowly to the stirred solution, which caused the product to precipitate from the solution. The reaction mixture was maintained at 10-15°C during the addition and then allowed to rise to room temperature. After being kept at this temperature for 2 h, the precipitate was filtered and washed well with 1% aqueous sodium hydroxide to remove the unreacted species and the by-products. The residue was recrystallized three times from methyl acetate. T_m, 252°C; T_i, 264°C; yield, 12.5 g (33%); IR (KBr): 3310 cm^{-1} (–OH), 1735 cm^{-1} (=CO); ^{1}H NMR (DMSO-d_6): δ 4.16 ppm (*d*; $-CH_2-$, 4H), 5.31 ppm (*t*; –OH, 2H), 7.27 ppm (*s*; Ar–H, 8H), 8.30 ppm (*s*; Ar–H, 4H).

Analysis. Calculated for $C_{22}H_{18}O_6$ (378.4): C, 69.83; H, 4.80%. Found: C, 69.62; H, 4.89%.

Reaction of BOPT with PI

Into a 100-mL round-bottom flask equipped with a reflux condenser with a drying tube were placed 5.000 g BOPT, 3.148 g PI, 80 mL DMSO, and a Teflon-coated magnetic stirring bar. The mixture was stirred at 140°C for 1 h. At the end of reaction the mixture was concentrated to one-third of its original volume. The concentrate was poured into 200 mL water. The precipitate was filtered and washed with methanol and purified by three recrystallizations from acetic acid. T_m, 225°C; yield, 4.8 g (59%); IR (KBr): 3350 cm^{-1} (–NH–), 1735 cm^{-1} (=CO); ^1H NMR (DMSO-d_6): δ 4.21 ppm (*s*; $-CH_2-$, 4H), 7.20 ppm (*s*; Ar–H, 10H), 7.27 ppm (*s*; Ar–H, 8H), 8.30 ppm (*s*; Ar–H, 4H).

Analysis. Calculated for $C_{36}H_{28}N_2O_8$ (616.6): C, 70.12; H, 4.58; N, 4.54%. Found: C, 69.90; H, 4.68; N, 4.71%.

Reaction of BOPT with BI

BOPT (5.000 g) and 2.620 g BI were reacted. The method of reaction was similar to that described in the reaction of BOPT with PI. T_m, 233°C; yield, 4.2 g (55%); IR (KBr): 3350 cm^{-1} (–NH–), 1735 cm^{-1} (=CO), 1710 cm^{-1} (=CO); ^1H NMR (DMSO-d_6): δ 0.96 ppm (*t*; $-CH_3-$, 6H), 1.27-1.73 ppm (*m*; $-CH_2-$, 8H), 3.36 ppm (*t*; $-CH_2-$, 4H), 4.23 (*s*; $-CH_2-$, 4H), 7.27 ppm (*s*; Ar–H, 8H), 8.30 ppm (*s*; Ar–H, 4H).

Analysis. Calculated for $C_{32}H_{36}N_2O_8$ (576.5): C, 66.65; H, 6.29; N, 4.86%. Found: C, 66.95; H, 6.18; N, 4.77%.

Polymer

Into a 100-mL round-bottom flask equipped with a reflux condenser with a drying tube were placed equimolar quantities of BOPT and diisocyanate in 80 mL DMSO. The mixture was concentrated to one-third of its original volume. The concentrate was poured into 200 mL water, filtered, and washed with methanol. Intrinsic viscosities and T_m of the polymers are shown in Tables 1 and 2. IR (KBr): 3350 cm^{-1} (–NH–), 1735 cm^{-1} (=CO), 1710 cm^{-1} (=CO).

TABLE 1. Polyaddition Reaction of BOPT with Diisocyanates[a]

Polymer	Diisocyanate,	g	Polymerization time, h	Yield, %	$[\eta]$, dL/g
BOPT-HDI	HDI	0.444	1.5	95	0.16
BOPT-H_{12}MDI	H_{12}MDI	0.693	1.5	85	0.12
BOPT-H_6XDI	H_6XDI	0.513	1.5	80	0.10
BOPT-TDI	TDI	0.463	1.5	90	0.12
BOPT-MDI	MDI	0.660	1.5	90	0.20
BOPT-PDI	PDI	0.423	1.5	–	–

[a] Temperature, 140°C; BOPT, 1.00 g.

TABLE 2. The Transition Temperature of Polyurethanes Measured by Polarized Microscopy

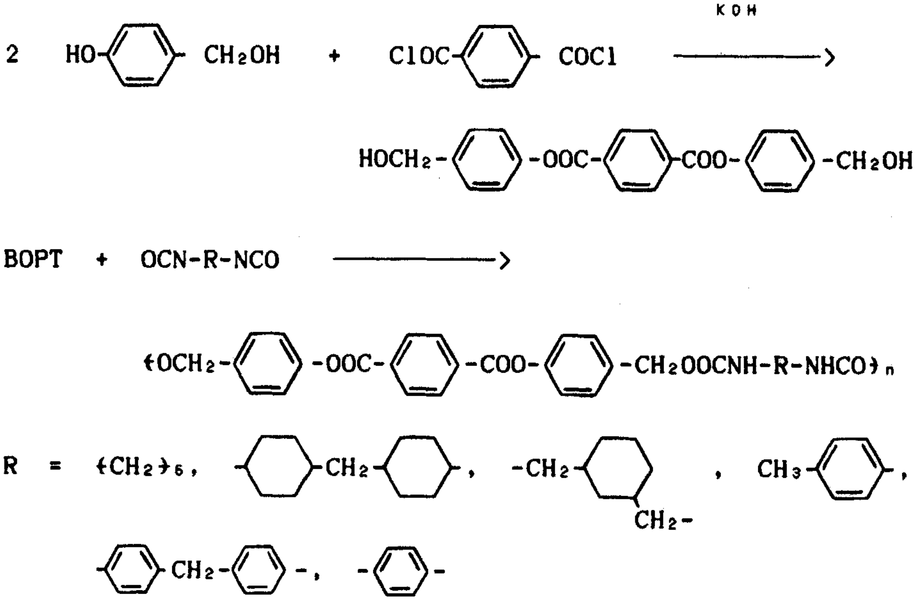
Polymers	T_m, °C	T_i, °C
BOPT-HDI	243	291
BOPT-H_{12}MDI	214	250
BOPT-H_6XDI	172	229
BOPT-TDI	185	234
BOPT-MDI	–	–
BOPT-PDI	–	–

Physical Measurements

IR spectra were recorded on a Jasco Model IR-G spectrometer and are reported in cm^{-1}. Thermal analysis was performed by using the differential scanning calorimetry (DSC) mode of the Rigaku Thermoflex model. The samples, weighing 0.01 g, were heated at 5°C/min from room temperature to 400°C. The wide-angle x-ray diffraction patterns of a powder were recorded with the JEOL Model DX-GE-2F. The intrinsic viscosity of polymers in DMSO at 30°C was measured with a Ubbelohde viscometer.

RESULTS AND DISCUSSION

The synthesis route leading to polyurethanes containing BOPT is outlined in



BOPT was prepared by condensing 2 mol *p*-hydroxybenzyl alcohol with 1 mol terephthaloyl chloride according to the Schotten-Baumann reaction. BOPT was obtained in 40% yield, and its structure was confirmed by elemental analysis, IR, and NMR data (see Experimental section). The IR spectrum (Fig. 1) indicates peaks at 3310 cm^{-1} due to OH groups and at 1715 cm^{-1} due to ester groups adjacent to benzene rings. The ^{1}H-NMR spectrum in DMSO-d_6 (Fig. 2) shows two peaks centered at 4.2 ppm due to methylene protons adjacent to the oxygen atom, at 5.3 ppm due to the protons of OH groups, and at 7.27 and 8.30 ppm due to the protons of benzene rings. The observed area ratio of the peaks is nearly equal to the calculated value.

The addition reaction of BOPT with monoisocyanates, such as phenylisocyanate (PI) and *n*-butylisocyanate (BI), was examined as a model reaction.

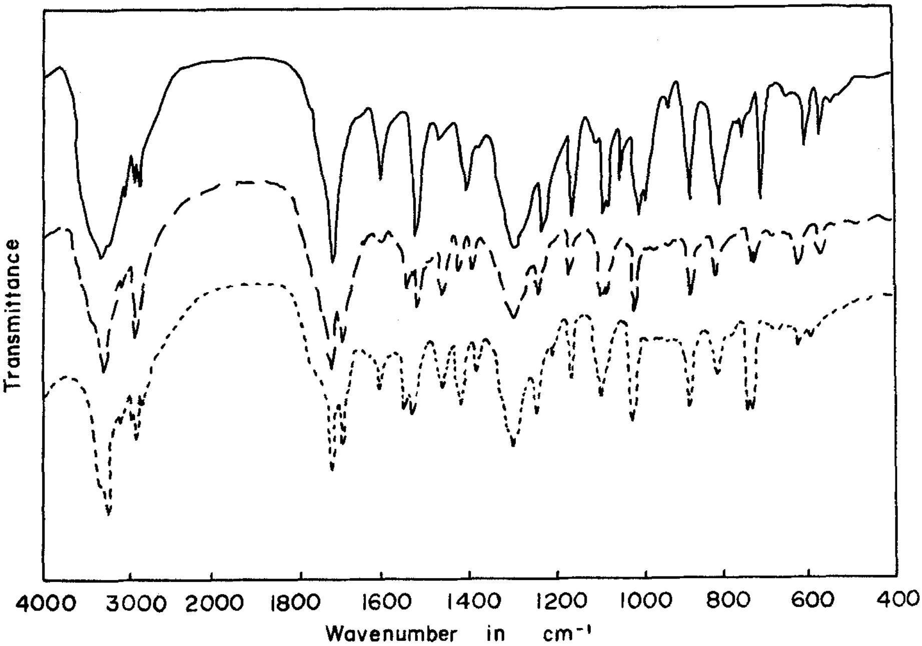


FIG. 1. IR spectra of BOPT (—), BOPT-PI (– –), and BOPT-BI (• • •).

The synthesis of addition products was achieved by reacting 1 mol BOPT with 2 mol PI or BI in dimethylsulfoxide (DMSO) for 1 h at 140°C. The products from PI and BI were obtained in 80 and 75% yield, respectively. Results of the polyaddition reaction of BOPT with diisocyanates in DMSO at 140°C are listed in Table 1.

All polyurethanes except BOPT-PDI are soluble in DMSO and in DMF. BOPT-PDI precipitates during the reaction and is not soluble in any solvent. As shown in Table 1, the polyurethanes have low intrinsic viscosities, suggesting that the polymer chains are not very long.

The thermal properties of the polymers were determined by DSC and polarized microscopy. Polymers BOPT-HDI, BOPT-H_{12}MDI, BOPT-H_6XDI, and BOPT-TDI exhibit two phase transitions, as shown by DSC measurements (Fig. 3). Two endothermic peaks, the transition temperature on melting (T_m) and that on forming the isotropic liquid (T_i), were observed on heating. The transition of polyurethanes measured by polarized microscopy is shown

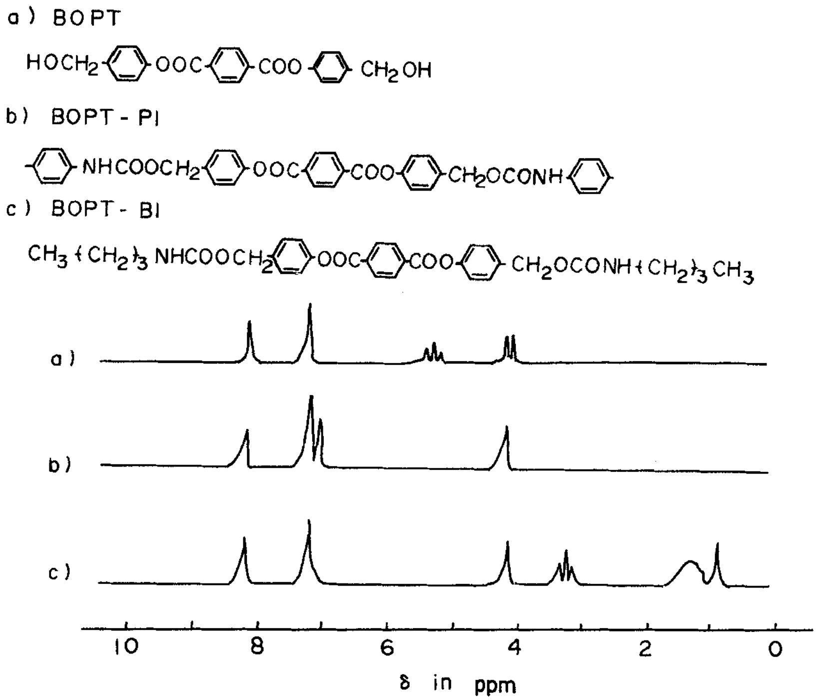


FIG. 2. ^{1}H-NMR spectra of BOPT, BOPT-PI, and BOPT-BI in DMSO-d_6.

in Table 2. Polymers BOPT-HDI, BOPT-H_{12}MDI, BOPT-H_6XDI, and BOPT-TDI exhibit two phase transitions by polarized microscopy as well as by DSC measurements (Fig. 3). Both measurements give approximately concordant results. By the observation of gas formation in the melt by microscopy and of the weight loss in the melt by TG, it was clear that the polymers decompose on melting. It was impossible to determine the transition temperature of BOPT-MDI and BOPT-PDI by polarized microscopy because of their high transition temperatures, and only one peak with a weight loss at 298-319°C was observed by DSC-TG in BOPT-MDI and at 314-335°C in BOPT-PDI.

The wide-angle x-ray diffraction pattern (WAXD) for BOPT-HDI is shown in Fig. 4. The broad peaks at 2θ = 7-12 and 28.5-30.5° and the sharp peaks at 19.5, 22.0-23.0, and 27.5° indicate crystalline behavior.

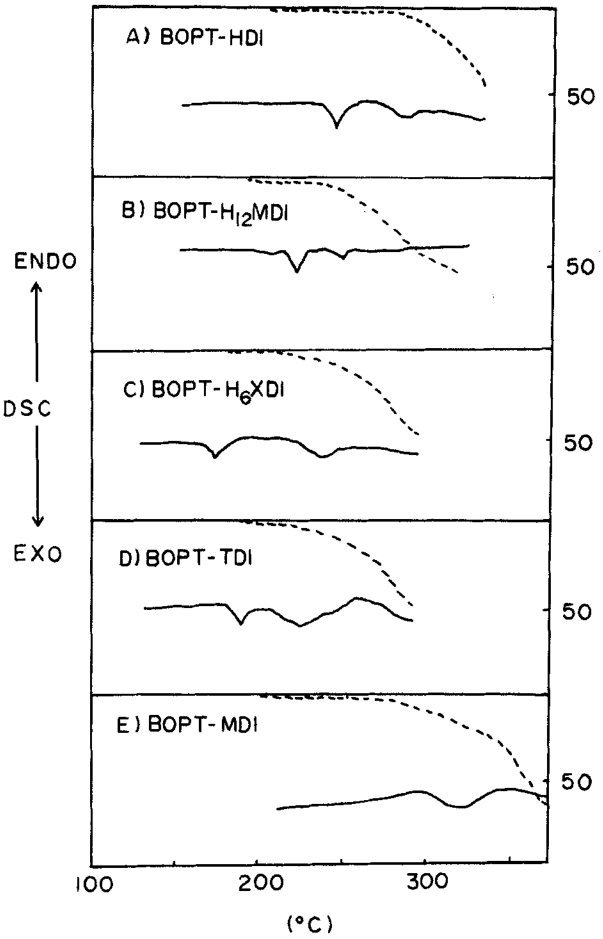


FIG. 3. DSC-TG curves of polyurethanes: (A) BOPT-HDI, (B) BOPT-H_{12}MDI, (C) BOPT-H_6XDI, (D) BOPT-TDI, (E) BOPT-MDI.

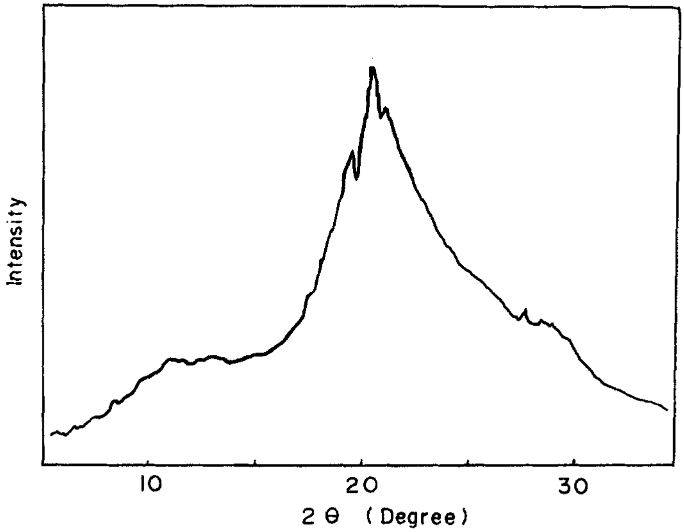


FIG. 4. Wide-angle x-ray diffraction scans of the polyurethane BOPT-HDI.

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