

# Synthesis and Properties of Main-Chain Liquid Crystalline Polyurethane Elastomers with Azoxybenzene

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## SYNOPSIS

Liquid crystalline polyurethane elastomers (LCPUE) were synthesized by a two-step block copolymerization reaction. The main-chain LCPUE were based on two azoxybenzene-type mesogenic diol chain extenders ( $HA_2$  and  $HA_6$ ), a poly(tetramethylene oxide) (PTMO) soft segment, and different diisocyanates, including 4,4'-diphenylmethane diisocyanate (MDI), toluene diisocyanate (TDI), and hexamethylene diisocyanate (HDI). The polyurethanes were characterized by FTIR, DSC, DMA, WAXD, UV, and polarized optical microscopy. Most of the polyurethane samples exhibited nematic thermotropic liquid crystal behavior and had physical properties typical of thermoplastic elastomers. The liquid crystal properties were strongly related to the interaction between the hard and soft segments of the polyurethane. As the compatibility of the soft and hard segments increased, the thermal stability of the liquid crystal phase and the transition temperatures decreased and the range of the transition became narrower. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Introducing liquid crystalline mesogenic diols as a part of hard segment to the segment polyurethane elastomers has received considerable attention recently due to the anisotropic behavior of liquid crystalline polyurethane elastomers (LCPUE) imparts unique physical properties to the polymer in terms of its mechanical, optical, and electrical characteristics. Thus, the interest in the field of LCPUE increased.

Macknight (see Tang et al.<sup>1</sup> and Wedler et al.<sup>2</sup>) obtained an enantiotropic LCPUE from 4,4'-bis(6-hydroxyhexoxy) biphenyl with toluene diisocyanate and poly(tetramethyleneoxides) (PTMO) and studied their structures and rheology properties. In our previous studies, we synthesized LCPUE based on biphenyl-type mesogenic diol chain extenders with different diisocyanates and different soft segments, such as PTMO and polydimethylsiloxane.<sup>3,4</sup> Most of the polyurethane samples exhibited nematic thermotropic liquid crystal behavior and had physical properties of typical thermoplastic elastomers.

The liquid crystal properties were strongly related to the interaction between the hard and soft segments of the polyurethane.

Organic azoxy-dye is a type of material that has recently become important in modern technologies, due structurally to its specific visible spectra absorption, strong chromophore orientation and photo-thermal isomerization, which cause azoxy-dye to be able to used as dye lasers, nonlinear optics, and liquid crystallines in academic as well as industry applications. The polyurethane elastomer incorporated the azoxy-dye as part of the backbone may possess both characteristics of dye and thermoplastic elastomer properties. Imura<sup>5</sup> reported the synthesis of thermotropic liquid crystalline polyester with azoxy group. However, few publications have so far been concerned with azoxy-dye LCPUE.

In this paper, a series of azoxybenzene mesogenic diol chain-extended polyetherurethanes were synthesized. The hard segments consisted of different diisocyanates and either 4,4'-bishydroxyethyloxy-azoxybenzene ( $HA_2$ ) or 4,4'-bishydroxyhexyloxy-azoxybenzene ( $HA_6$ ). The soft segment was based on PTMO. Several polymers of different segment content were prepared. The purpose of this work was to study further the effects of mesogenic chain

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extenders on the microphase morphology and physical and thermal anisotropic properties of these LCPUE, as compared with our previous work, and to describe the azoxybenzene *cis-trans* isomerization in LCPUE.

## EXPERIMENTAL

### Materials

4,4'-Diphenylmethane diisocyanate (MDI) was purified by vacuum distillation (0.3 mm Hg) until the boiling point was reached at 170°C. Hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI) (unspecified isomers) were purchased from Aldrich Chemical Co. Dimethylsulfoxide (DMSO) and N,N-dimethyl formamide (DMF) were dried over molecular sieves (5 Å). 1,6-Hexanediol and 1,2-diethanol were purchased from E. Merck and were used as received. The synthesis of 1-bromohexanol was according to the procedure described by Crivello et al.<sup>6</sup>

### Mesogenic Diol

The diol, 4,4'-bishydroxyhexyloxyazoxybenzene (HA<sub>6</sub>), was prepared as follows: 11.5 g 4,4'-dihydroxyazoxybenzene, 0.1 g of triethylbenzyl ammonium bromide, 10 g of potassium hydroxide, and 60 g of potassium carbonate were stirred into 150 mL DMF. The resulting slurry was heated to 100°C, and 6-bromohexanol was added dropwise. The reaction mixture was reacted for 24 h and poured into cold water. The precipitated solid was filtered and recrystallized twice from ethanol to give 6.5 g (30% yield) of HA<sub>6</sub>, mp 114–115°C. This compound was synthesized previously with a reported melting point of 114°C.<sup>7</sup> <sup>1</sup>H-NMR and element analysis of HA<sub>2</sub> and HA<sub>6</sub> revealed the following data [<sup>1</sup>H-NMR (DMSO-*d*<sub>6</sub>)]:

HA<sub>2</sub>: δ = 3.7–4.0 ppm (—CH<sub>2</sub>, 8H); 4.7–4.9 ppm (—OH, 2H);  
7.0–7.1 ppm (Ar—H, 4H); 7.7–7.8 ppm (Ar—H, 4H).

HA<sub>6</sub>: δ = 3.7–4.1 ppm (—CH<sub>2</sub>, 24H); 4.7–4.9 ppm (—OH, 2H);  
7.0–7.1 ppm (Ar—H, 4H); 7.7–7.8 ppm (Ar—H, 4H).

Anal: Calcd for HA<sub>2</sub>: C, 60.37%; H, 5.70%;  
N, 8.80%

Found: C, 60.77%; H, 5.45%;  
N, 9.09%.

Calcd for HA<sub>6</sub>: C, 66.95%; H, 7.96%;  
N, 6.51%.

Found: C, 67.13%; H, 7.57%;  
N, 6.65%.

### Liquid Crystalline Polyurethanes

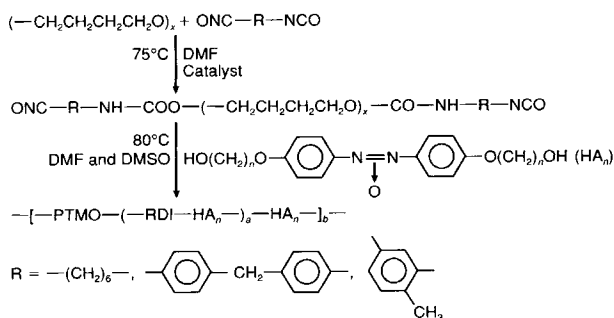
The LC polyurethanes were synthesized by the two-step condensation reaction (shown in Scheme 1). 1.37 g of HDI and 2 drops of stannous octoate were dissolved in 15 ml of DMF in a heat-dried four-neck round-bottom flask fitted with a reflux condenser, mechanical stirrer, thermometer, and addition funnels with 10 mL of DMF and 2.54 g of PTMO (*M<sub>w</sub>* = 981). Nitrogen was kept flowing through the system. The PTMO solution was added dropwise at 60°C, and the temperature was raised to 75°C. After 1.5 h, a solution of 2.22 g HA<sub>6</sub> in 20 ml DMSO was added dropwise to the above solution, and the temperature was raised to 80°C and kept there for 10 h. As the reaction proceeded, a mixed solvent system (DMF and DMSO) was added as needed to keep the solution clear throughout the reaction. By the end of the reaction period, the solution was poured into cold water to precipitate the polymer in the form of a yellow elastomeric material. The polymer was filtered, washed with fresh ethanol, and subsequently dried under vacuum at 60°C for 72 h.

All materials studied are described in Table I. A polymer made from 1 mol of 981 *M<sub>w</sub>* PTMO, 3 mol of HDI, and 2 mol of HA<sub>6</sub> is designated as PHA<sub>6</sub>-9-58. The code indicates that this polymer contains 58 wt % hard segment.

### Polymer Characterization

The intrinsic viscosities of the polymers were determined at 30°C in DMSO using a Cannon Ubbelohde viscometer.

Thermal analysis was carried out on a Perkin-Elmer DSC-2C interfaced with a Model 3600 data station using TADS software. Temperature and enthalpy calibration were carried out using indium and mercury as standards. A heating rate of 20 K/min under a 20 ml/min flow of dry air as the purge gas



Scheme I Synthesis of liquid crystalline polyurethane.

**Table I** Properties of LCPUE

No.	Sample Code	PTMO Molecular Weight	RDI	PTMO : RDI : HAn	Yield (%)	$[\eta]$ (dL/g)	$T_g$ (°C)	$T_m$ (°C)	$T_i$ (°C)
1	PHA <sub>6</sub> -9-58 <sup>a</sup>	981	HDI	1 : 3 : 2	88	0.72	-58.1	156	198
2	PHA <sub>6</sub> -6-66	685	HDI	1 : 3 : 2	85	0.61	-45.9	159	226
3	PHA <sub>2</sub> -9-54	981	HDI	1 : 3 : 2	90	0.63	-56.2	171	221
4	PTA <sub>6</sub> -9-58	981	TDI	1 : 3 : 2	60	0.10	-32.5	79	118
5	PMA <sub>6</sub> -9-62	981	MDI	1 : 3 : 2	70	0.69	-57.2	137	227

<sup>a</sup> P refers to PTMO; H to HDI; A<sub>6</sub> to HA<sub>6</sub> (A<sub>2</sub> to HA<sub>2</sub>); 9 to 981 of PTMO molecular weight; and 58 to hard-segment content (%).

was used in samples of  $10 \pm 3$  mg. The data processing unit allowed automatic substration of the base line and normalization of the thermogram for the sample weight.

Nuclear magnetic resonance experiments were carried out on a JEOL JNM-PMX COSI using tetramethylsilane (TMS) as an internal standard with the samples held at room temperature. All samples were prepared by dissolving about 5 mg of copolymer in 0.2–0.3 ml of deuterated chloroform.

Wide-angle X-ray diffraction (WAXD) measurements were made by means of monochromatic CuK $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) and a Nicolet Xenonics two-dimensional position sensitive and data system. Data were collected for 20 min, and background scans of equivalent duration were subtracted to remove background scatter. The two-dimensional data were then azimuthally averaged to generate intensity versus  $2\theta$  scans.

Infrared (IR) survey spectra were recorded with a Nicolet 170SX Fourier transform infrared (FTIR) spectrophotometer. One hundred scans at a resolution of  $2 \text{ cm}^{-1}$  were signal averaged before Fourier transformation. All IR spectra covered the range  $400\text{--}4000 \text{ cm}^{-1}$ .

Dynamic mechanical data were obtained using a DDV-II-C apparatus that was controlled by a computer. All measurements were carried out under a nitrogen purge at a frequency of 110 Hz with a constant heating rate of  $2 \text{ K/min}$ .

Optical texture was studied with a Leitz-350 polarizing optical microscope equipped with a Linkam hot stage and a polaroid camera. The sample was molten in thin layers between slide glasses and heated to the isotropic melt, and the slides were then sheared to produce a thin layer of melted polymer. The sample was then cooled at  $10^\circ\text{C/min}$  to room temperature and observed or photographed at that temperature.

Ultraviolet (UV) visible absorption spectra were recorded with a Shimadzu UV-240 spectrophotometer. The pure solvent was placed in the reference

beam. Thin polyurethane elastomer film was cast from a 1% DMF solution in quartz glass. The photoisomerization of azoxybenzene in polyurethane elastomer film was performed by a long wavelength UV lamp ( $\lambda_{\text{max}} = 380 \text{ nm}$ ) with an intensity of  $10 \text{ mw/cm}^2$ . Polyurethane elastomer film was irradiated by UV lamp for 2 h at room temperature.

## RESULTS AND DISCUSSION

### Polymer Synthesis

The polymers were prepared in a mixed solvent system of DMF and DMSO. The solvent was crucial in determining whether a high molecular weight sample could be obtained by a two-step condensation reaction because of the large differences in the solubility parameters of the soft and hard segments. It was found that a 5 : 4 ratio of DMF to DMSO could be used satisfactorily to prepare all the samples except those prepared using TDI. Relatively low molecular weight polyurethanes were obtained when the mixed TDI isomer was used as part of the hard segment. The reasons for these results are not clear, but similar observations have been reported in the literature.<sup>8</sup>

### IR Spectroscopy

A typical IR spectrum PHA<sub>6</sub>-6-66 is illustrated in Figure 1. The bands near  $3330 \text{ cm}^{-1}$  (N—H stretch),  $1700 \text{ cm}^{-1}$  (C=O stretch),  $1540 \text{ cm}^{-1}$  (C—N—H bending), and  $1280 \text{ cm}^{-1}$  (N—C—O stretch) are attributed to the polyurethane hard segments.

Based on NH band in the region of  $3200\text{--}3500 \text{ cm}^{-1}$ , the PHA<sub>6</sub>-6-66 material appears to be primarily hydrogen-bonded because the bonded NH peak at  $3310 \text{ cm}^{-1}$  predominates; whereas the free (nonhydrogen-bonded) NH peak at  $3460 \text{ cm}^{-1}$  is detectable only as a very small shoulder. In the carbonyl region between  $1650\text{--}1750 \text{ cm}^{-1}$ , the peak due

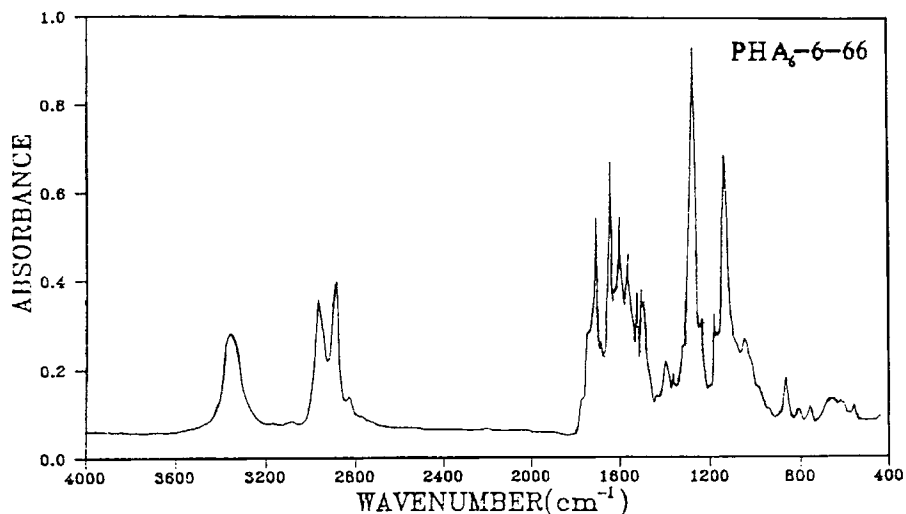


Figure 1 IR spectra of segmented polyurethane PHA<sub>6</sub>-6-66.

to bonded C=O stretching centered at 1700 cm<sup>-1</sup> predominates, and that due to free C=O stretching appears as a shoulder at 1730 cm<sup>-1</sup>. If it is assumed that the extinction coefficients of free and bonded C=O are approximately the same in polyurethanes,<sup>9,10</sup> the dominance of the bonded C=O peak indicates that a large fraction of the hard segments are hydrogen-bonded. This interurethane bonding is considered to occur in the interior of the hard domains. The intense H bonds form physical cross-links in the samples, which is one of the reasons that the samples exhibit thermally reversible rubber elasticity.

The IR spectra of other samples, which are not presented here, are very similar and indicate that nearly all the NH and C=O groups are hydrogen-bonded. It implies that the presence of LC brought about more aggregation of the hard segments, i.e., better microphase separation in LCPUE than those in more conventional segmented polyurethanes.

### Optical Texture Analysis

Figure 2 shows polarizing optical microphotographs of the polymer samples, in which the thread texture shown for PHA<sub>2</sub>-9-54 is typical of a nematic LC polymer. It is noticeable that the increased of shear will result in the formation of a mesophase of a higher degree of order; i.e., a marble texture instead of a thread texture may be formed. Similar textures were observed in the other samples.

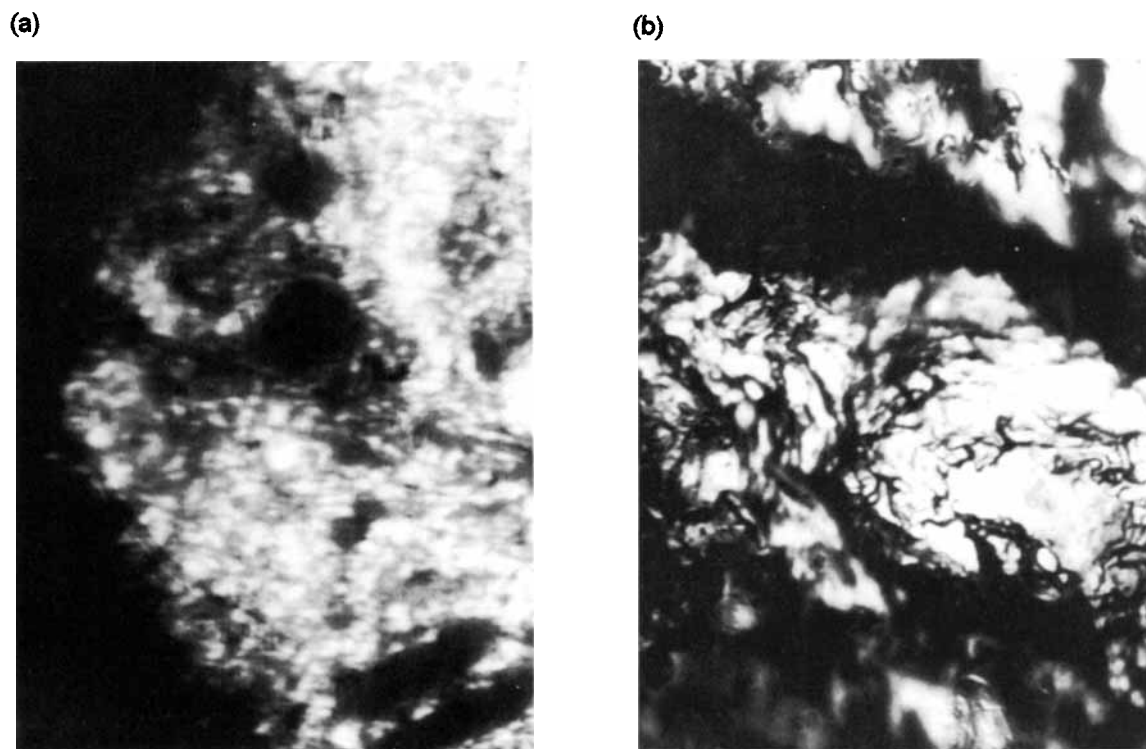
As compared with LCPUE of PHB series we studied previously,<sup>3</sup> the PHA series had strong nematic tendency. This may be due to the linking units

containing azoxy bond that maintained the rigidity and linearity of the molecules.

### Thermal Analysis

Differential Scanning Calorimetry (DSC) curves for the LCPUE are shown in Figure 3, and the thermal properties are summarized in Table I. All DSC data are for the first heating of the samples. The DSC scans show that the LCPUE samples based on HDI and MDI have wider LC transition region than the polymer based on TDI. The melting point order is PU<sub>HDI</sub> > PU<sub>MDI</sub> > PU<sub>TDI</sub>. The LC phase transition region ( $T_i - T_m$ ) or mesophase interval order is PU<sub>MDI</sub> > PU<sub>HDI</sub> > PU<sub>TDI</sub>. This can be explained as due to the fact that hard segments of the TDI-based polyurethane have a lower order than that of HDI- and MDI-based polyurethanes. The better compatibility between the hard and soft segments results in a decrease in the melting point. The higher melting point of the HDI series polymers is due to the better order of the rigid chain that approaches the decomposition temperature of the polyurethane. It can be observed that  $T_i$  and  $T_m$  decrease with increasing length of the spacer in the LC extenders by comparing the transition temperatures in PHA<sub>6</sub>-9-58 and PHA<sub>2</sub>-9-54. The complexity of multien-dotherms in the HDI and MDI is due to the short-range ordering of the hard segments due to room temperature annealing.

It can be seen from the transition temperatures of PHA<sub>6</sub>-9-58 and PHA<sub>6</sub>-6-66 that an increase in the molecular weight of the soft segment results in a lower  $T_g$ , better separation, and high  $T_i$  and  $T_m$ .

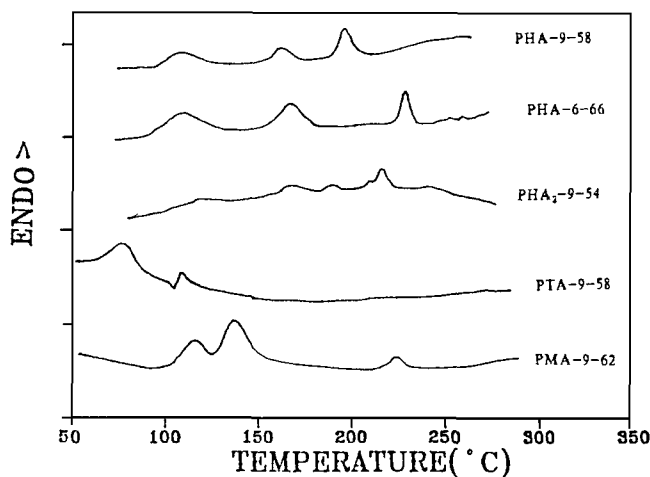


**Figure 2** Textures of the nematic phase: (a) PTA<sub>6</sub>-9-58,  $T = 110^{\circ}\text{C}$ ; (b) PHA<sub>2</sub>-9-54,  $T = 193^{\circ}\text{C}$ .

Compared to LCPUE of PHB series, most LCPUE of PHA series showed high  $T_{N-I}$  values. This is also contributed to the rigid azoxybenzene segment.

#### Dynamic Mechanical Thermal Analysis

Rheovibron dynamic mechanical testing was used to study the dynamic moduli ( $E'$ ,  $E''$ ) and internal

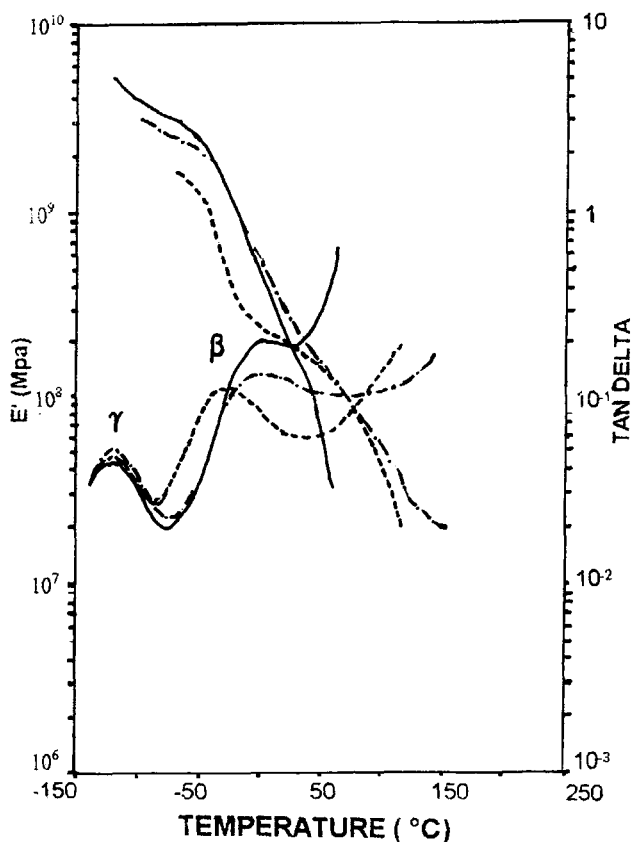


**Figure 3** DSC traces of polyurethanes at heating of 20 K/min.

friction ( $\tan \delta$ ) as a function of temperature for  $-150$  to  $150^{\circ}\text{C}$ . These typical samples, PMA<sub>6</sub>-9-62, PHA<sub>6</sub>-9-58, and PTA<sub>6</sub>-9-58, are illustrated in Figure 4. Two peaks designated  $\gamma$  and  $\beta$  appear in  $\tan \delta$  data. The  $\gamma$  peak relaxation at  $-125^{\circ}\text{C}$ , which is independent of sample composition, is a local mode motion of  $\text{CH}_2$  sequences in the polyether phase. The  $\beta$  peak corresponds to the glass transition of the polyether-rich soft-segment phase. Different diisocyanates cause the  $\beta$  peak to move to higher temperatures and become broader in the order of HDI, MDI and TDI. The result is in agreement with the DSC data. This indicates that compatibility between the hard and soft segments is in the order  $\text{PU}_{\text{MDI}} < \text{PU}_{\text{HDI}} < \text{PU}_{\text{TDI}}$ . The MDI and HDI hard segment exhibited a more symmetric and rigid structure than did the TDI hard segments, which is indicative of a high-domain cohesion. This is in accordance with our previous observation.

#### Phase Behavior in WAXD Measurements

Figure 5 represents the WAXD patterns at different temperatures during heating from  $20^{\circ}\text{C}$  at  $5^{\circ}\text{C}/\text{min}$  for sample PHA<sub>6</sub>-9-58. At  $20^{\circ}\text{C}$ , PHA<sub>6</sub>-9-58 exhibits three sharp peaks, respectively, located between  $2\theta = 10$  and  $25$  degrees. These peaks indicate that the

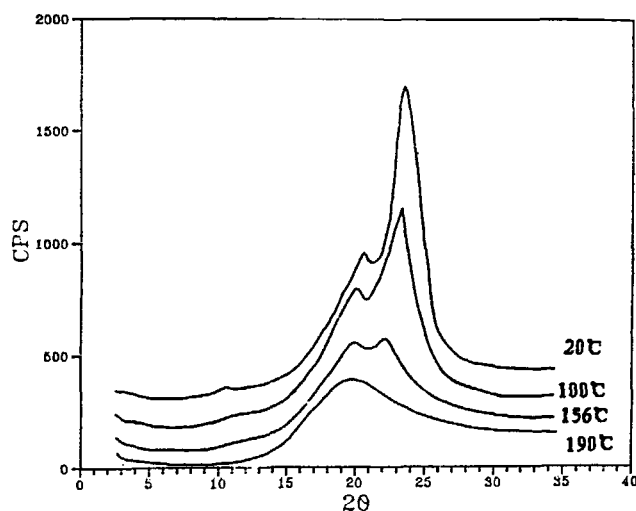


**Figure 4** Dynamic mechanical spectrum of LCPUE: (—) PTA<sub>6</sub>-9-58; (- - -); PMA<sub>6</sub>-9-62; (- · - ·) PHA<sub>6</sub>-9-58.

sample possesses semicrystalline regions. Above 100°C, the peak ( $2\theta = 10$  degrees) disappears, and the peaks of 20 and 24 degrees become weak. Further heating to 156°C results in a diffuse equatorial reflection at 20 and 22.9 degrees, which are characteristic of a nematic LC phase. Increasing temperature to 190°C results in diffraction peak in PHA<sub>6</sub>-9-58 that are quite diffuse, with a maximum of about 20 degree, indicating a spacing of 4.5 Å, which is characteristic of an average distance between two neighboring chain molecules in the amorphous state. Similar results were obtained from a sample held in the melt for 10 h and then quenched into liquid nitrogen.

### Photoisomerization

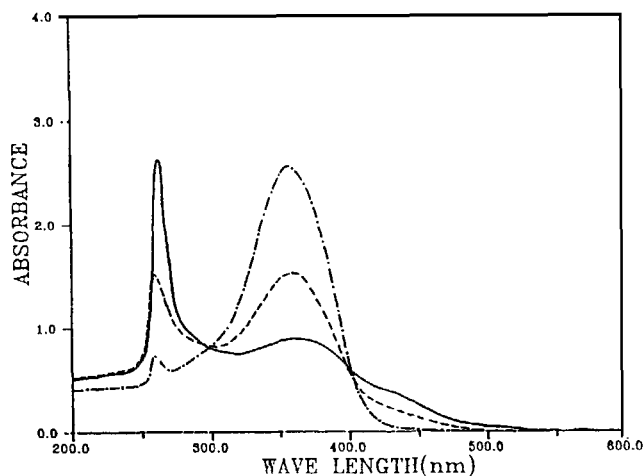
LC polymers containing azoxybenzene group have received considerable attention due to the UV induced *cis-trans* isomerization of the azoxy linkage.<sup>5</sup> PHA<sub>6</sub>-9-58 shows absorption maximum at approximately 365 nm (Figure 6), which is due to the  $\pi \rightarrow$



**Figure 5** WAXD scanning of PHA<sub>6</sub>-9-58 under different temperatures.

$\pi^*$  transition; therefore, all the azoxychromophores are in the *trans* state. As the solution is irradiated, the absorption at 380 nm decreases; while absorption at 262 nm, due to  $n \rightarrow \pi^*$  transition, increases. This photoisomerization cycle can be repeated without fading.

However, the UV-visible absorption spectra of PHA<sub>6</sub>-9-58 film before and after UV irradiation were not varied. This indicated that the intramolecular hydrogen bonds in polyurethane elastomer stabilized the azoxybenzene chromophores. The *trans*-form did not change to *cis*-form during UV irradiation.



**Figure 6** UV spectra of PHA<sub>6</sub>-9-58 in DMSO: (- · - ·) no irradiation; (- - -) after UV irradiation, 0.5 h; (—) after UV irradiation, 1 h.

## CONCLUSIONS

It has been possible to synthesize block polyurethanes that are nematic LC polymers or both smectic and nematic in some samples. The formation of the LC phase is strongly related to the interaction of the soft and hard segments.

The linking units containing azoxy bond that maintained the rigidity and linearity of molecules are more satisfactory in preserving high  $T_{N-I}$  values.

Greater compatibility between the hard and soft segments results in a decrease of the stability and the phase transition temperatures of LC phase, and the mesophase interval becomes narrower.

The intramolecular hydrogen bonds stabilized azoxybenzene chromophores in polyurethane elastomer film. The *cis-trans* isomerization of azoxybenzene in solution is observed.

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