

# Functional Polyesters and Copolyesters Based on the 4,4'-Dihydroxy- $\alpha$ -methylstilbene

JONGGEON JEGAL,<sup>1</sup> ALEXANDRE BLUMSTEIN<sup>2</sup>

<sup>1</sup> Membrane and Separation Lab., Korea Research Institute of Chemical Technology, P.O. Box 107, Daedeog-Danji, Taejeon, South Korea

<sup>2</sup> Polymer Science Program, Department of Chemistry, University of Massachusetts at Lowell, Lowell, MA 01854

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**ABSTRACT:** Liquid crystalline (LC) thermotropic main-chain polyesters and copolyesters based on 4,4'-dihydroxy- $\alpha$ -methylstilbene (mesogen) and azelaoyl chloride (flexible spacer) and 10,12-docosadiynedioyl chloride [ultraviolet (UV)-crosslinkable moiety] were synthesized by interfacial polymerization. Improvement of molecular weight was achieved by the modification of interfacial polymerization. Molecular weights of the LC polymers ranged from 13,000 to 56,500 g/mol<sup>-1</sup>, depending on composition of the LC polymers. Mesomorphic properties of these polymers were studied, and phase diagrams were established. Polymers showed nematic and smectic mesophases, depending on the flexible spacer composition. UV-crosslinking of the LC polymers containing UV-sensitive diacetylenic groups was attempted, and crosslinked LC polymer films were obtained. Mechanical properties of LC polymer films were also studied with a dynamic mechanical analyzer. The storage moduli of the polymer films, depending on the molecular weight of the polymers, increased by the UV-crosslinking. Higher molecular weights and crosslinking were favorable for the higher storage moduli of the films. The effect of orientation on the mechanical properties was also studied, and it was found that orientation induced the increase of the moduli of the films. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 387–393, 1998

**Key words:** LC thermotropic main chain polyesters; 4,4'-dihydroxy- $\alpha$ -methylstilbene; 10,12-ducosadiynedioyl chloride; UV-sensitive; orientation

## INTRODUCTION

Thermotropic liquid crystalline (LC) main-chain polymers have attracted considerable attention due to their ease in the melting process and expected good mechanical properties. These polymers have potential application as high-modulus fibers and molding.<sup>1–6</sup>

Because of this potential application, some articles were already published about the fibers spun from the nematic mesophase of thermotropic LC

polymers. Muller and coworkers<sup>4</sup> and Blumstein and coworkers<sup>5</sup> have attained tensile moduli of 10–20 GPa with nematic thermotropic rigid-flexible polyether and 1–10 GPa with nematic thermotropic flexible polyesters and polyethers, respectively.

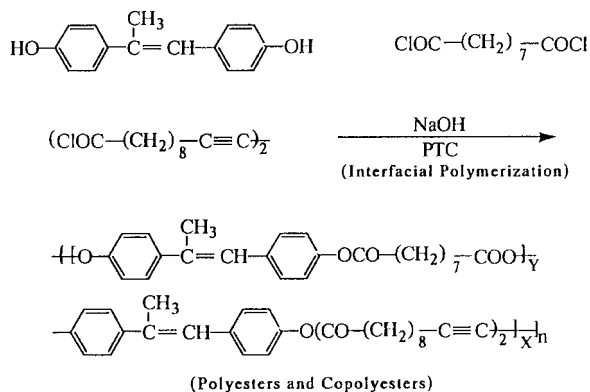
The spun fibers from the nematic melts of flexible thermotropic polyesters have high modulus ( $E$ ) significantly above the one expected of flexible polyesters spun from the isotropic phase due to the higher orientational order of individual chains.<sup>6</sup> The difficulty encountered with fibers spun from the nematic mesophase of such flexible polymers, however, is the lack of lateral strength. Because of this phenomenon, the chain experi-

Correspondence to: J. Jegal.

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**Figure 1** Synthesis of the LC polyesters and copolyesters based on the 4,4'-dihydroxy- $\alpha$ -methylstilbene and azelaoyl chloride and/or 10,12-docosadiyne diol chloride by interfacial polymerization. (Polymer 1p:  $x = 0.0$ ,  $y = 1$ ; polymer 2p:  $x = 0.5$ ,  $y = 0.5$ ; polymer 3p:  $x = 0.7$ ,  $y = 0.3$ ; polymer 4p:  $x = 1.0$ ,  $y = 0.0$ ).

ences creep and relaxation of orientation under stress. Blumstein and colleagues tried to circumvent this weakness by incorporation into the main chain of functional groups and crosslinking.<sup>6</sup>

In this work, diacetylenic moieties as ultraviolet (UV)-crosslinkable parts were incorporated into the main chain of the LC polyester containing an azelaoyl chloride as a flexible spacer and the 4,4'-dihydroxy- $\alpha$ -methylstilbene as a mesogen. Films of flexible thermotropic LC polyesters were prepared, oriented, and subjected to UV irradiation. Mechanical properties of these films were studied.

## EXPERIMENTAL

### Materials

4,4'-Dihydroxy- $\alpha$ -methylstilbene was prepared by the reductive coupling of phenol and  $\alpha$ -chloro-

acetone at a low temperature,<sup>7</sup> followed by recrystallization from a water-ethanol mixture. Azelaoyl chloride, obtained from Aldrich Chemical Company (Milwaukee, WI), was fractionally distilled under vacuum. Before distillation, the equipment was carefully flame-dried and cooled under dry argon. 10,12-Docosadiynedioyl chloride was prepared by the reaction of 10,12-docosadiynedioic acid (Farchan Laboratories) with oxalyl chloride at a room temperature. 1,2-Dichloroethane was obtained from Aldrich Chemical Co. and distilled under argon before use.

### Polymerization

#### Poly( $\alpha$ -methylstilbeneazelate) (1p)

Conventional liquid-liquid phase transfer-catalyzed interfacial polyesterification was used for the synthesis of the poly( $\alpha$ -methylstilbeneazelate): 1.13 g (0.005 mol) of 4,4'-dihydroxy- $\alpha$ -methylstilbene was dissolved into 20 mL of 0.5N aqueous sodium hydroxide solution and added into the blender that contained a mixture solution of 31 mL of ice-cold distilled water and 47 mL of 1,2-dichloroethane containing 0.352 g (0.0016 mol) of benzyltriethyl ammonium chloride as a phase transfer catalyst. Freshly distilled 1.125 g (0.005 mol) of azelaoyl chloride in 31 mL of 1,2-dichloroethane was then added to the mixture with high-speed stirring. Then, the mixture solution was stirred with the highest speed stirring of the blender for 10 min. After polymerization, as described previously, the prepared polymer was precipitated into an excess amount of ethanol under moderate stirring and washed with a large amount of ethanol three times. It was then purified by repeated dissolution in chloroform and pre-

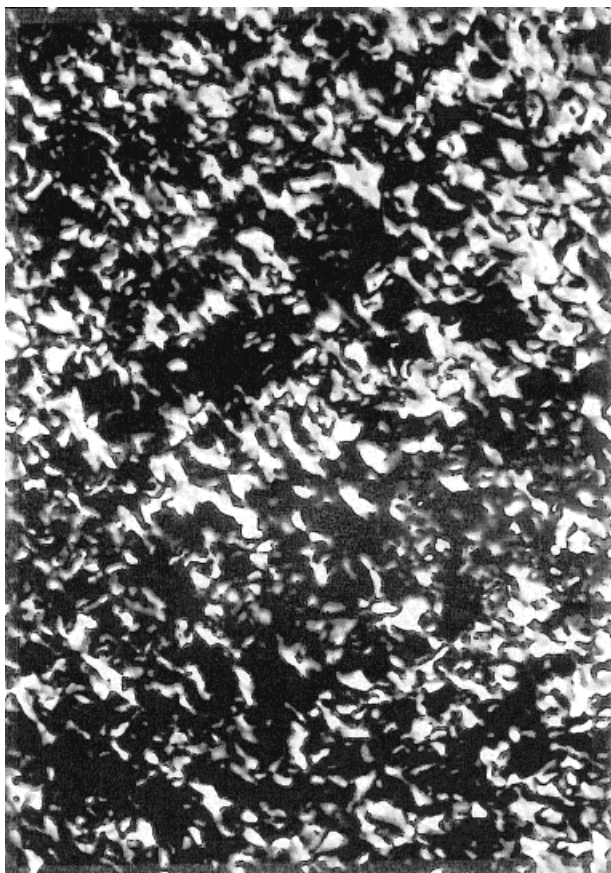
**Table I** Physical Properties of Thermotropic LC Polymers

Polymers	$\eta_{inh}$ (dL g <sup>-1</sup> )	$M_n^a$ (g mol <sup>-1</sup> )	Transition Temperature (°C) <sup>b</sup>	
			Heating	Cooling
1p	1.90	56,500	C174.5N215.4I	I200.6N13C
2p	1.60	45,000	C <sub>3</sub> 120.8C <sub>2</sub> 130N161I	I150N92C
3p	0.62	13,000	C120N139.5I	I127.2N98C
4p	0.62	13,000	C <sub>1</sub> 100.4C <sub>2</sub> 126.7S139.3I	I126.2S101.7C

<sup>a</sup> Calculated from the intrinsic viscosities by using the equation as:

$$[\eta] = 4.65 \times 10^{-4} M_n^{0.76}$$

<sup>b</sup> All values were taken from the second scan of DSC at 10°C min<sup>-1</sup> of heating and cooling rates.



**Figure 2** “Schlieren” nematic textures of polymer 1p at 190°C.

precipitation in ethanol (three times). The polymer was a white fibrous solid and readily soluble in chloroform, 1,2-dichloroethane, and other organic solvents: Yield 92%; infrared (IR) ( $\text{cm}^{-1}$ ) 1753 (C=O stretching), 1600 (conjugated C—H stretching), 2931 and 2852 (aliphatic C—H stretching);  $\eta_{\text{inh}}$  ( $\text{dL g}^{-1}$ ) 1.90. Elemental analysis, Calcd: C, 75.79; H, 7.37; O, 16.84. Found: C, 75.52; H, 7.49; O, 16.99.

***Poly( $\alpha$ -methylstilbeneazelaate-co- $\alpha$ -methylstilbene-10,12-docosadiyndioate) (2p, 3p)***

These copolymers consisting of a different ratio of azelaoyl chloride to 10,12-docosadiyndioyl chloride in composition were synthesized by the same method as the case of polymer 1p, except the composition of the monomers as follows: for synthesis of polymer 2p (ratio of azelaoyl chloride to 10,12-docosadiyndioyl chloride was 1 : 1); 1.13 g (0.005 mol) of 4,4'-dihydroxy- $\alpha$ -methylstilbene, 0.563 g (0.0025 mol) of azelaoyl chloride and 0.905 g

(0.0025 mol) of 10,12-docosadiyndioyl chloride. The yield of copolymer 3p was 94%. This product was a white fibrous solid and readily soluble in chloroform, 1,2-dichloroethane and other organic solvents: IR ( $\text{cm}^{-1}$ ) 1753 (C=O stretching), 1600 (conjugated C—H stretching), 2931 and 2852 (aliphatic C—H stretching);  $\eta_{\text{inh}}$  ( $\text{dL g}^{-1}$ ) 1.60. Elemental analysis, Calcd: C, 78.54; H, 7.73; O, 13.73. Found: C, 78.23; H, 7.94; O, 13.83.

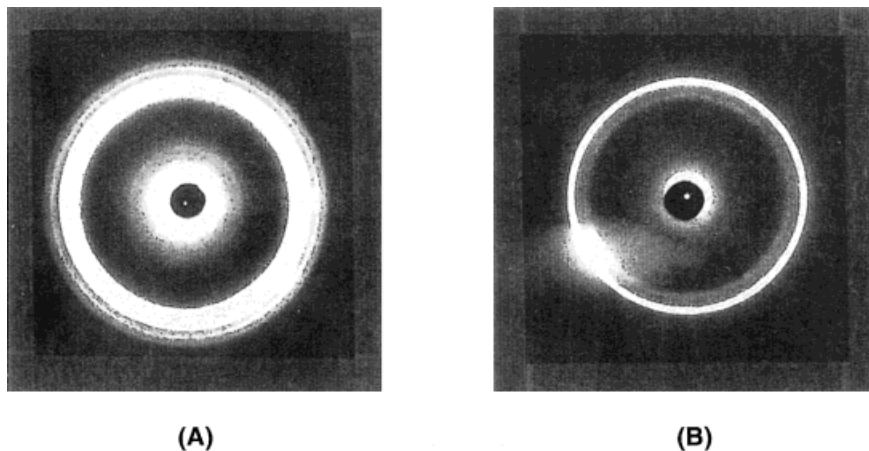
For the synthesis of polymer 3p (ratio of azelaoyl chloride to 10,12-docosadiyndioyl chloride was 3 : 7); 1.13 g (0.005 mol) of 4,4'-dihydroxy- $\alpha$ -methylstilbene, 0.338 g (0.0015 mol) of azelaoyl chloride, and 1.267 g (0.0035 mol) of 10,12-docosadiyndioyl chloride. The yield of the copolymer 4p was 94%. This product was a white fibrous solid and readily soluble in chloroform, 1,2-dichloroethane, and other organic solvents: IR ( $\text{cm}^{-1}$ ) 1753 (C=O stretching), 1600 (conjugated C—H stretching), 2931 and 2852 (aliphatic C—H stretching);  $\eta_{\text{inh}}$  ( $\text{dL g}^{-1}$ ) 0.62. Elemental analysis, Calcd: C, 79.38; H, 7.83; O, 12.79. Found: C, 79.21; H, 7.92; O, 12.87.

***Poly( $\alpha$ -methylstilbene-10,12-docosadiyndioate) (4p)***

This polymer was synthesized by the same method as the case of polymer 1p, except the composition of the monomers as follows: 1.13 g (0.005 mol) of 4,4'-dihydroxy- $\alpha$ -methylstilbene and 1.81 g (0.005 mol) of 10,12-docosadiyndioyl chloride. This product was a white fibrous solid and readily soluble in chloroform, 1,2-dichloroethane, and other organic solvents: Yield, 94%; IR ( $\text{cm}^{-1}$ ) 1753 (C=O stretching), 1600 (conjugated C—H stretching), 2931 and 2852 (aliphatic C—H stretching);  $\eta_{\text{inh}}$  ( $\text{dL g}^{-1}$ ) 0.62. Elemental analysis, Calcd: C, 80.43; H, 7.97; O, 11.59. Found: C, 80.45; H, 7.78; O, 11.76.

**Film Preparation and Crosslinking**

To study the UV-crosslinking mechanism and the mechanical properties of the LC polymers containing UV-sensitive diacetylenic groups, films were prepared by casting the polymer solutions in chloroform on Teflon plates (for free-standing films) or on quartz plates (for very thin films). Film thicknesses were controlled from a submicron to about 10  $\mu\text{m}$  according to different purposes. The films so prepared were crosslinked by UV irradiation at  $\lambda_{\text{max}}$ , 254 nm, and with an inten-



**Figure 3** Wide-angle XRD patterns of polymer 4p (A) at room temperature and (B) at mesophase (109°C).

sity of  $2.53 \text{ mW cm}^{-2}$  (high-pressure mercury arc lamp).

### Characterization

#### FTIR

To study the chemical structures of the polymers, a Perkin-Elmer 1600 series Fourier transform infrared spectrophotometer was used. Samples used were in film state, and their thickness was about  $10 \mu\text{m}$ .

#### UV

UV-visible spectrophotometer (IBM 9420) was used to study the UV-crosslinking of the LC polymer films. Thickness of the samples was about  $10 \mu\text{m}$ .

#### Differential Scanning Calorimetry (DSC)

Thermal properties of the LC polymers were determined by DSC (Perkin-Elmer 2C differential scanning calorimeter). Heating and cooling were at a rate of  $10^\circ\text{C min}^{-1}$ . All reported transition temperatures correspond to the peak maximum of the trace obtained from the intersection points of the tangents drawn to the peak.

#### Optical Microscopy

Mesophase textures of the LC polymers were observed with the polarizing optical microscope (Leitz Ortholux polarizing microscope) equipped with a mettler FP2 heating stage.

#### X-ray Diffraction (XRD)

XRD patterns of the LC polymers were studied with a Warhus flat plate camera using Ni-filtered  $\text{Cu}_\alpha$  radiation. The samples used were three different types: unoriented powders, unoriented just cast film, and oriented film.

#### Viscosity

Inherent viscosities of the polymers were obtained from the polyester solutions ( $1 \text{ g dL}^{-1}$ ) in chloroform by using Ubbelohde viscometer at  $25^\circ\text{C}$ .

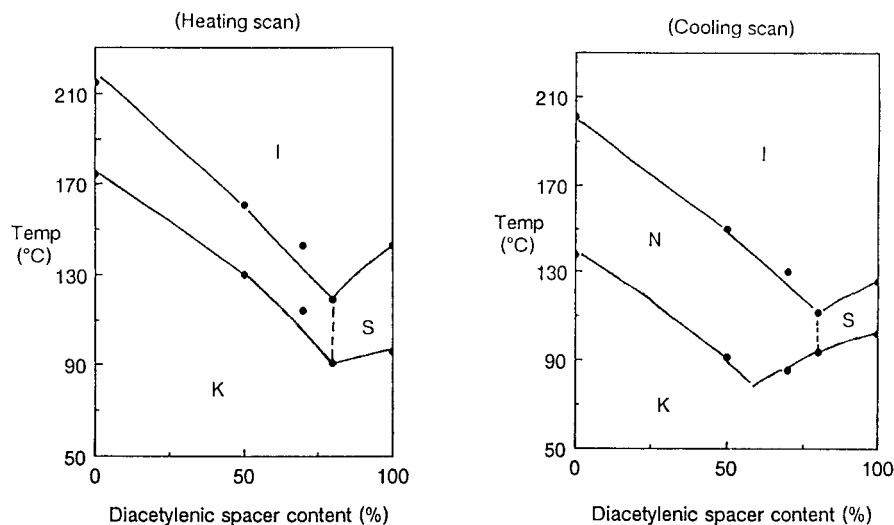
#### Dynamic Mechanical Analyzer (DMA)

Dynamic mechanical properties of films were measured by means of a DMA (model: Dupont, DMA 983). The sample dimension was as follows: (width: about  $2 \text{ mm}$ )  $\times$  (length: about  $10 \text{ mm}$ )  $\times$  (thickness: about  $0.01 \text{ mm}$ ). The distance between the sample holders was about  $1 \text{ mm}$ . The frequency was fixed at  $1 \text{ Hz}$  and the amplitude ( $p-p'$ ) was  $1.5 \text{ mm}$ .

## RESULTS AND DISCUSSION

### Synthesis

LC polyesters and copolyesters based on the 4,4'-dihydroxy- $\alpha$ -methylstilbene (mesogen) and azelaoyl chloride (flexible spacer) and 10,12-docosadienediyl chloride (UV-crosslinkable moiety) were synthesized by interfacial polymerization as shown in Figure 1. Improvement of the molecular



**Figure 4** Phase diagrams (data obtained from second heating and cooling scan at  $10^{\circ}\text{C min}^{-1}$ ).

weight was achieved by the modification of interfacial polymerization. To obtain high molecular weight, several experimental factors have to be considered. First, the *trans*-4,4'-dihydroxy- $\alpha$ -methylstilbene must be free of the *cis*-isomer. This is because the *cis*-isomer forms easily the 2+2 cyclo adduct in the presence of light.<sup>8</sup> A partially crosslinked polymer is then obtained during polymerization. The polymer has a soluble and insoluble fraction in 1,2-dichloroethane. The insoluble fraction is crosslinked. The soluble fraction is low molecular weight. Second, azelaoyl chloride and 10,12-docosadiynedioyl chloride should be completely water-free, because water can convert these chlorides to the corresponding acids that do terminate polymerization. Table I gives data of inherent viscosities for a number of polymers and copolymers, each of which was prepared according to two polymerization procedures. These procedures result in two widely different molecular masses: one very high and one significantly lower. It was also found that the inherent viscosities of the polymers decreased with the increasing ratio of 10,12-docosadiynedioyl chloride to azelaoyl chloride. This is probably due to the impurities contained in 10,12-docosadiynedioyl chloride, which are very difficult to remove because of their high boiling points. These impurities will probably be the mono-acid form or di-acid form of 10,12-docosadiynedioyl chloride. In this work, high molecular weight polymers were obtained from the polymerization of highly

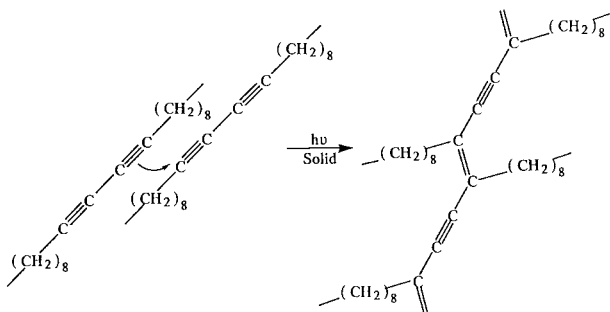
pure mesogenic compound, *trans*-4,4'-dihydroxy- $\alpha$ -methylstilbene, with a highly pure spacer, azelaoyl chloride. All polymers obtained in this polymerization procedure were in high yields (usually  $> 90\%$ ). Molecular weights, shown in Table I, were estimated from their intrinsic viscosities by using an equation ( $[\eta] = 4.60 \times 10^{-4} \text{Mn}^{0.76}$ ) obtained for rigid-flexible thermotropic polyesters based on the azoxybenzen mesogen of similar conformation in terms of length and rigidity of mesogen, as well as that of spacer.<sup>9</sup> These spanned an interval of molecular mass between 13,000 to 56,500  $\text{g mol}^{-1}$ .

### Characterization

Characterization of the mesophases of polymers was done by using DSC, polarizing microscope,

**Table II** Mechanical Properties of Thermotropic LC Polymer Films

Polymer	Storage Modulus ( $E'$ ) (GPa)		
	Unoriented Cast Film	Oriented Film (200% Elongation)	Crosslinked Film
1p	0.50	7.10	—
2p	0.36	6.38	—
3p	0.20	—	—
4p	0.16	—	0.28



**Figure 5** UV-crosslinking mechanism of the diacetylenic parts of the polymers.

and X-ray. Thermal transition temperatures of polymers shown in Table I were obtained from second heating and cooling DSC scans. A nematic “Schlieren” textures of polymer 1p at its mesophase transition temperature that was taken from the DSC second heating scan are shown in Figure 2. Polymers 2p and 3p also showed nematic “Schlieren” textures. From DSC data and “Schlieren” textures, one can infer that polymers 1p, 2p, and 3p exhibit enantiotropic nematic mesophases.

Polymer 4p showed an enantiotropic smectic mesophase. The XRD pattern taken at 109°C (at mesophase) shows clearly a small-angle ring and a diffuse wide-angle halo characteristic of a smectic mesophase of lower order ( $S_A$  or  $S_C$ ). Both high and room temperature XRD pattern are shown in Figure 3. From the X-ray picture, calculated layer distance was 24.3 Å ( $d = 24.3$  Å). The calculated length of repeating unit of this polymer is approximately 38.6 Å ( $L = 38.6$  Å). The tilted angle ( $\theta$ ) of the repeating unit in the layer can be calculated by using the following equation:

$$\theta = \cos^{-1}(dL^{-1})$$

where  $\theta$  is tilt angle of the repeating unit in the layer,  $d$  is layer distance (from X-ray) picture, and  $L$  is length of the repeating unit of the polymer. The obtained tilt angle was 56.3°. From this result, it was found that this mesophase is smectic C.

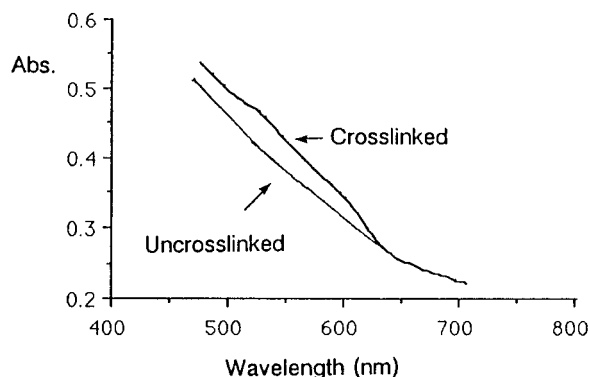
The phase diagrams shown in Figure 4 are from DSC and a polarizing microscope. One can see that the smectic mesophase is present only for compositions high in 10,12-docosadienediyl chloride and that only a nematic mesophase is present for all other compositions.

## Mechanical Properties

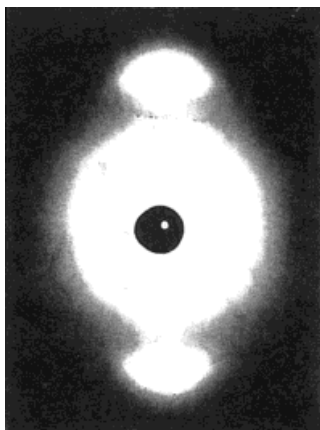
To study the mechanical properties of the LC polymers containing UV-crosslinkable groups, the polymer films prepared by the solution casting method were tested with a DMA. Table II shows the storage moduli of these films. The storage moduli of unoriented, solution cast films of the polymers were in the range of 0.5 GPa to 0.1 GPa, and varied with different molecular weights and different polymer compositions. The storage moduli increased with increasing molecular weights.

## Effect of Crosslinking

The effect of crosslinking on the mechanical properties was studied with a film of polymer 4p, which has UV-sensitive diacetylenic moiety incorporated into the spacer of the polymer backbone. This polymer was irradiated with UV under the condition described in the Experimental section. The film became insoluble in all solvents, and its color changed from colorless to light purple. This bathochromic absorption shift indicates crosslinking of the chains *via* an opening of the triple bond, resulting in an increase in the degree of conjugation (Fig. 5). The intensity of the absorption (intensity of the color) increased with exposure time. Figure 6 shows the visible range portion of the UV-visible spectrum of the crosslinked polymer 4p film (10  $\mu\text{m}$  thickness irradiated for 20 min). Because of the high absorbance at UV range of the film, absorbance was over-ranged and cut away from the UV-visible spectrum of the crosslinked film. This crosslinked film showed a very broad absorption from 500 to 650 nm, which the uncrosslinked film do not. This broad absorption



**Figure 6** Visible spectra of the polymer 4p film with a 10  $\mu\text{m}$  thickness before and after UV-crosslinking. Abs., absorbance.



**Figure 7** Wide-angle XRD pattern of the oriented film of polymer 1p at room temperature.

corresponds to an increase in the degree of conjugation of the acetylenic bond in the chain; however, no acetylenic absorption peak was apparent in the IR spectra, and no differences in IR spectra could be observed as a result of the UV irradiation process. The UV-crosslinked film showed an almost twofold increase of the storage modulus of the uncrosslinked polymer as shown in Table II.

#### Effect of Orientation

The effect of orientation on the mechanical properties of the films was studied with two polymers (polymers 1p and 2p) with relatively high molecular weights. The oriented samples were prepared as follows: cast films of these two polymers were heated to their nematic transition temperatures, such as 184°C for polymer 1p and 137°C for polymer 2p, and kept at these temperatures for 5 min, respectively. Almost transparent semicrystalline cast films became milky at their nematic mesophase without a substantial change in film dimension. The milky color at their nematic mesophases might be due to the light scattering from the nematic domains with different long axis orientation of each other. These films were quenched with dry ice and became milky nematic glassy films. These nematic glassy films were stretched at room temperature to orient. After stretching, 200% extension, films became transparent and wide-angle XRD pattern of these films (shown in Fig. 7) represented good orientation of molecules. The flex-

ural storage moduli ( $E'$ ) of these oriented films are higher than those of unoriented films (Table II). This flexural storage modulus ( $E'$ ) of polymer 1p increased from 0.499 GPa to 7.098 by the orientation, whereas the flexural storage modulus ( $E'$ ) of polymer 2p increased from 0.36 GPa to 6.38. The flexural storage modulus ( $E'$ ) of oriented polymer 1p film (7.098 GPa) was comparable with 8.02 GPa of the commercially available Vectran HC-100C.

## CONCLUSIONS

UV-crosslinkable LC polymers can be prepared by the interfacial polymerization of 4,4'-dihydroxy- $\alpha$ -methylstilbene with azelaoyl chloride and/or 10,12-docosadiynedioyl chloride. The molecular weights depend strongly on the purity of the monomers used. The LC polymer films containing UV-sensitive diacetylenic groups can be cross-linked by UV irradiation. UV-crosslinking of the diacetylenic groups are *via* the opening of the triple bonds and increases the degree of conjugation. Mechanical properties of the LC polymer films depend on the molecular weights of the polymers, and the UV-crosslinking affected positively on the mechanical strengths.

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