

# Investigation on Stilbene- and Azobenzene-Based Liquid Crystalline Organophosphorus Polymers

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**ABSTRACT:** Two series of combined liquid crystalline polyphosphates bearing dual photoreactive mesogenic units (stilbene and azobenzene/ $\alpha$ -methylstilbene and azobenzene) were synthesized by solution polycondensation method. The structures of the synthesized polymers were confirmed by various spectroscopic techniques. Thermogravimetric analysis reveals that they are stable between 230 and 320°C. Differential scanning calorimetry studies were done to study the liquid crystalline property, and glass-transition, melting, and isotropization temperatures for all the polymers. Polarizing optical microscope shows the birefringent melt for all the polymers exhibiting liquid crystalline property. The photochemical response was

studied by UV-visible and fluorescence spectroscopy for all the polymers. The photocrosslinking reaction of the stilbene containing polymers was ascertained by spectroscopic and photolysis studies. The rate of the switching time for the conversion of trans to cis form of azobenzene unit was investigated by UV spectroscopy. The terminal substituents in the side chain affects the texture of liquid crystalline phase for all the polymers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2760–2768, 2007

**Key words:** liquid crystalline polymers; stilbene;  $\alpha$ -methylstilbene; azobenzene; fluorescence; polarizing optical microscope

## INTRODUCTION

Photoresponsive materials have gained unabated attention in recent years. Among the photoresponsive materials belonging to the thermotropic vicinity, stilbene-based polymers are scarcely exploited. Stilbene derivatives have been used as conducting materials and possess novel features, for example artificial hormones,<sup>1</sup> photochemical interlocked systems applicable in rotaxane,<sup>2</sup> laser dyes,<sup>3</sup> mesogenic properties,<sup>4</sup> etc. It has been reported that the introduction of photoresponsive moieties into the liquid crystalline polymers is a useful method to afford the liquid crystal materials photoresponsive property.<sup>5</sup> Stilbene- and azobenzene-based materials are useful for nonlinear optical properties such as photoinduced poling<sup>6</sup> and frequency doubling<sup>7</sup> in second-order phenomena and degenerate four wave mixing<sup>8</sup> and photo refractivity<sup>9</sup> in third-order phenomena. Consequently, by combining both the stilbene and azobenzene moieties, the trans isomer is mesogenic because of its rod-like shape, while the cis

isomer obtained by photoisomerization is nonmesogenic because of its bent shape and acts as an impurity, which perturbs the orientational order. The two photoresponsive chromophores are incorporated with phosphorus unit through decamethylene spacer affords the polymer. These combined LC polymers of stilbene ( $-\text{C}=\text{C}-$ ) and azobenzene ( $-\text{N}=\text{N}-$ ) photoresponsive groups are obviously of interest.<sup>10,11</sup> On the other hand, phosphorus being a nonmetal that can perform as bridging unit to the dual mesogens, imparts characteristic properties such as flame-retardancy, binding properties, increased polarity, and plasticizing properties, in addition to models for natural biopolymers.<sup>12–14</sup> The phosphate esters show better resistance to extraction, migration, and volatile loss, thus assembling them is more attractive.<sup>15</sup> In this work, we have studied the comparison of the synthesis and photophysical properties of photoresponsive dual mesogenic liquid crystalline polymers containing two main chain (stilbene and  $\alpha$ -methylstilbene) chromophores with similar terminally substituted azobenzene units. Stilbene-containing polymers (I series) undergo photocrosslinking process, whereas the  $\alpha$ -methylstilbene polymers (II series) experienced only isomerization. The terminal substituents in the side chain influence the LC properties. Further, the rate of switching property of the polymers was studied by UV and fluorescence spectroscopy.

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## EXPERIMENTAL

### Reagents and solvents

Bromoacetaldehyde diethyl acetal (Merck, Germany), chloroacetone (Fluka, Swiss), 1,10-decanediol (E-Merck, Germany), phosphorus oxychloride (Spectrochem, India), substituted anilines (E-Merck), hydrobromic acid (40%) (Spectrochem), and fluoroaniline, chloroaniline, bromoaniline, nitroaniline, toluene, and 4-methoxyaniline (E-Merck) were purchased and used as received. Phenol, chloroform, diethyl ether, dichloromethane, glacial acetic acid, triethyl amine, ethanol, methanol, ethylene glycol, dimethylformamide, ethyl acetate, and toluene were of analytical grade and purified before use.<sup>12,16</sup> 4,4'-Dihydroxy- $\alpha$ -methylstilbene was prepared by a procedure reported elsewhere.<sup>1,17-19</sup> Potassium carbonate, potassium iodide, and sodium sulfate were purchased (Qualigens, India) and used as received.

### Measurements

The FTIR and NMR spectra were recorded on a Perkin-Elmer 300 spectrophotometer and Joel 400 MHz for all the precursors and polymers respectively. The inherent viscosity of the polymers ( $\eta_{inh}$ ) was measured at 30°C using chloroform as solvent in an Ubbelohde viscometer. The thermal behavior of the polymers was investigated using Mettler-Toledo STAR systems of thermogravimetry (TGA) and differential scanning calorimeter (DSC) under nitrogen atmosphere. The heating rate for TGA and DSC was 10°C/min, with a nitrogen flow of 20 mL/min. Polarizing optical microscopy (POM) was performed with a Euromex polarizing microscope attached with a Linkam HFS 91 heating stage and a TP-93 temperature programmer. The optical textures of mesophase of the polymers were observed with program mode. The photomicrographs were taken from Nikon FM10 camera and printed on a Konica 400 film. Fluorescence spectra of the polymers were obtained on a Hitachi model F2000 spectrofluorimeter with excitation near and absorption maximum of the stilbene moiety, using 5 nm of resolution for both excitation and emission. The photoisomerization studies of the polymers were carried out by UV irradiation between 350 and 500 nm wavelengths. Trans-cis photochemical isomerization of polymers was investigated by irradiated with Spectroline (New York) low-pressure mercury pencil lamp in dichloromethane solution taken in a 1-cm Quartz cuvette for 1 min and the UV absorption measured immediately on a Shimadzu UV-1610 spectrophotometer. The experiment was repeated until no change in absorbance was noted.

### Synthesis of precursors and monomers

#### 4,4'-Dihydroxystilbene

4,4'-Dihydroxystilbene was prepared from phenol and bromoacetaldehyde diethyl acetal. Concentrated sulfuric acid (25 mL) in glacial acetic acid (30 mL) was added dropwise and stirred for 1.5 h to a solution of phenol (0.12 mol) and bromoacetaldehyde diethyl acetal mixture (0.06 mol) in glacial acetic acid (150 mL) at 0°C. Stirring was continued at 0–3°C for 6 h. The concentrated solution was poured into ice and extracted with diethyl ether. The ether extracts were washed with water and dried with sodium sulfate, and the solvent was removed under reduced pressure below 35°C, resulting in a white solid.

Sodium (0.2 mol) was dissolved in methanol (500 mL) and ethylene glycol (250 mL). The mixture was distilled until the bulb temperature reached 190°C. The white precipitate in ethylene glycol (100 mL) was then added dropwise under nitrogen atmosphere to the hot sodium glycolate solution within 1 h. Stirring was continued for 45 min at 190–195°C. The yellow fluorescent mixture was cooled to 60°C and poured into ice/water (1000 mL). The precipitated product on acidifying with 2N sulfuric acid (100 mL) was extracted with 7:3 ratio of diethyl ether/acetone and twice with diethyl ether. The extracts were washed with water and the solvent was evaporated below 35°C. The residual solid was boiled in diethyl ether (100 mL), filtered, and washed with diethyl ether. Crystallization from acetic acid and ethanol mixture gave pure 4,4'-dihydroxystilbene (DHS). The yield was 60%, mp 283°C (Lit. mp 283–285°C).<sup>3</sup>

FTIR (KBr,  $\text{cm}^{-1}$ ): 3450  $\text{cm}^{-1}$  (phenolic OH), 1690  $\text{cm}^{-1}$  (*trans*-ethylene), 1471  $\text{cm}^{-1}$  ( $\text{CH}_2$ ). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>,  $\delta$ ): 6.77 (d, 2H), 6.99 (s, C=C) 7.31 (d, 2H).

#### 4,4'-Bis(10-hydroxydecyloxy)- $\alpha$ -methylstilbene

4,4'-Dihydroxy- $\alpha$ -methylstilbene (DHAMS) was dissolved in dry DMF (25 mL). Anhydrous potassium carbonate (0.10 mol) and a calculated amount of 5 wt % of potassium iodide were added to it. The mixture was heated to 90°C, with constant stirring. 10-Bromo-1-decanol (0.05 mol) was added dropwise to the reaction mixture and the reaction continued for 2 days. The reaction mixture was cooled to room temperature and poured into ice-cold dilute hydrochloric acid solution. The precipitated product was filtered, washed with water until neutral, and then dried *in vacuo*. A similar procedure was adopted for the decylated product of the 4,4'-dihydroxystilbene to get 4,4'-bis(10-hydroxydecyloxy)stilbene (BHDS).

Yield: 50%, mp 182°C (Lit. mp 182–183°C). IR (KBr): 1260  $\text{cm}^{-1}$  (C—O—C *asymmetric stretch*), 1471  $\text{cm}^{-1}$  ( $\text{CH}_2$ ), 1680  $\text{cm}^{-1}$  (*trans* C=C), 3445  $\text{cm}^{-1}$  (*phenolic OH*).  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ -TMS,  $\delta$ ): 1.24 (s, *alpha CH*<sub>3</sub>), 4.9 (s, *trans-ethylene*) 6.68 (d, 2H, *aromatic meta to C—CH*<sub>3</sub>), 6.73 (d, 2H *aromatic meta to CH*), 6.95 (d, *aromatic ortho to CH*<sub>3</sub>), 7.09 (m, *aromatic ortho to CH*).

4-[10-(Hydroxydecyloxy)-4'-substituted (X) azobenzene](X = H, F, Cl, Br, CN, and NO<sub>2</sub>)

4-Hydroxy-4'-substituted (X) azobenzene (X = H, F, Cl, Br, CN, and NO<sub>2</sub>) monomers were synthesized as per the procedure reported elsewhere.<sup>20</sup> The title precursors were prepared using a similar procedure adopted for the synthesis of BHDMS and BHDS.

X = H: Yield, 85–90%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 1.2–1.4 (m,  $\text{CH}_2$ ), 3.5 (t, *heteroatom O—CH*<sub>2</sub>), 7.7 (d, *meta to azo*), 7.85 (d, *ortho to azo*), 7.4–7.8 (m, 5H, *aromatic benzene*).

X = F: Yield, 80–89%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 1.3–1.6 (m,  $\text{CH}_2$ ), 3.4 (t, *heteroatom O—CH*<sub>2</sub>), 6.9 (d, *ortho to azo*), 7.18 (d, *meta to azo*), 7.18–7.2 (m, 5H, *aromatic benzene*).

X = Cl: Yield, 78–89%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 1.1–1.8 (m,  $\text{CH}_2$ ), 3.23 (t, *heteroatom O—CH*<sub>2</sub>), 6.9 (d, *ortho to azo*), 7.3 (d *meta to azo*), 7.4–7.8 (m, 5H, *aromatic benzene*).

X = Br: Yield, 86–95%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 1.3–1.9 (m,  $\text{CH}_2$ ), 3.3 (t, *heteroatom O—CH*<sub>2</sub>), 7.0 (d *meta to azo*), 7.6 (d, *ortho to azo*), 7.3–8.1 (m, 5H, *aromatic benzene*).

X = CN: Yield, 84–90%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 1.2–1.8 (m,  $\text{CH}_2$ ), 3.45 (t, *heteroatom O—CH*<sub>2</sub>), 6.8 (d, *ortho to azo*), 7.1 (d *meta to azo*), 7.7–8.0 (m, 5H, *aromatic benzene*).

X = NO<sub>2</sub>: Yield, 81–90%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 1.2–1.6 (m,  $\text{CH}_2$ ), 3.55 (t, *heteroatom O—CH*<sub>2</sub>), 6.9 (d, *ortho to azo*), 7.5 (d *meta to azo*), 7.8–7.9 (m, 5H, *aromatic benzene*).

4-Substituted (X) phenylazo-4'-phenyloxydecylphosphorodichloridates (side chain mesogen)

4-[10-(Hydroxydecyloxy)-4'-azobenzene] (0.02 mol) was dissolved in dry chloroform (25 mL) and freshly distilled phosphorus oxychloride (0.04 mol) was added dropwise. The reaction mixture was slowly heated to 60°C with constant stirring for an hour and then raised to reflux condition. The reaction was continued until the HCl evolution ceased. Excess phosphorus oxychloride was distilled under reduced pressure and the residue was connected to high vacuum for several hours. The dark reddish brown solid thus obtained was used immediately for the polymerization reaction without further purification.

## Synthesis of polymers

The stilbene (I series) and  $\alpha$ -methylstilbene (II series) containing polymers were prepared by solution polycondensation reaction at room temperature using triethylamine (TEA) as an acid scavenger. The typical procedure for the preparation of polymer Ia is as follows:

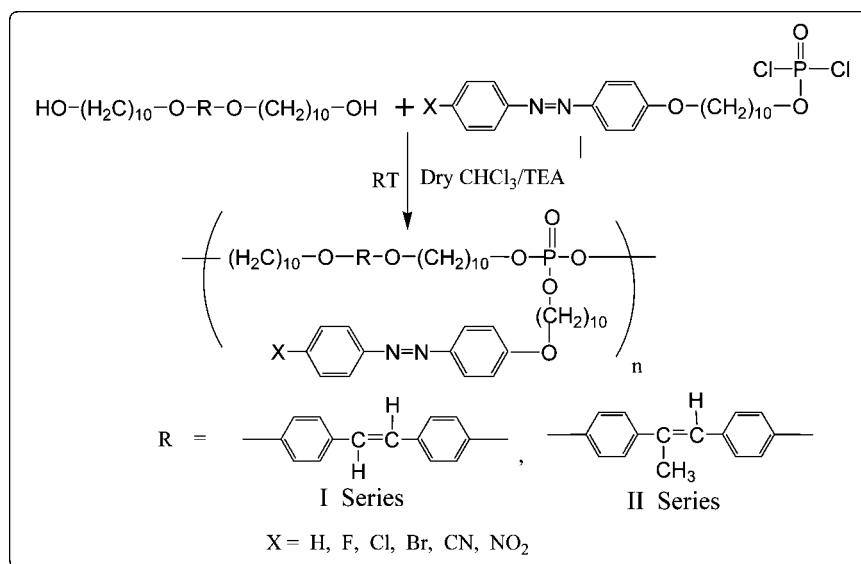
4,4'-Bis(hydroxydecyloxy)stilbene (0.1 mol) was dissolved in dry chloroform (20 mL). Dry TEA (0.14 mol) was added under nitrogen atmosphere and stirred at room temperature. Individually, to the above-mentioned reaction mixture, 4-phenylazo-4'-phenyloxydecylphosphorodichloridate (0.05 mol) dissolved in chloroform was added dropwise for a period of 30 min. During addition, the solution became homogeneous and the reaction continued for 24 h. Then the above-mentioned solution was refluxed for 2 h, concentrated, cooled, and poured into excess methanol. The dark reddish brown precipitate thus formed was filtered and dried in a vacuum oven at 50°C. All other polymers (Ib–Iif) were prepared in the similar method.

Polymer Iie: Yield: 70–88%. IR (KBr) ( $\text{cm}^{-1}$ ): 763 (P—O), 1244 (P=O), 1251 (Ar—O—C), 1500 (—N=N—), 1588 (C=C), 2924 ( $\text{CH}_2$ ), 3441 (P—OH).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 1.29, 1.55 (m, O— $\text{CH}_2$ ), 1.66 (s, =CH, *alpha CH*<sub>3</sub>), 4.0 (m, *aromatic O—CH*<sub>2</sub>), 6.5 (d, *azo aromatic ortho to O—CH*<sub>2</sub>), 6.9–7.0 (d, *aromatic ortho to O—CH*<sub>2</sub>), 7.2 (d, *aromatic ortho to —CH*<sub>3</sub>), 7.4 (d, *aromatic ortho to =CH*), 7.8 (d, *azo aromatic meta to O—CH*<sub>2</sub>), 7.9 (d, *azo aromatic meta to X*), 8.0 (d, *trans-ethylene*,  $J = 15$  Hz).  $^{31}\text{P NMR}$ :  $-6.7$   $\delta$  and  $-14.5$   $\delta$ .

## RESULTS AND DISCUSSION

### Synthesis

Two series of photopolymers were prepared by solution polycondensation reaction at room temperature with good yield (Scheme 1 and Table I). All the synthesized polymers are soluble in organic polar solvents. Inherent viscosity measurements for all the polymers were carried out in chloroform solution at 30°C and the results are presented in Table I. I series of (DHS) polymers showed a narrow range of viscosities than that of the II series (DHAMS). This may be due to the structural variations in the main chain of the stilbene units. All the polymers were characterized by IR spectroscopy. The absorption around 919 and 2924  $\text{cm}^{-1}$  corresponds to P—O—C aliphatic stretching and aliphatic  $\text{CH}_2$  stretching respectively. The absorption band around 1508  $\text{cm}^{-1}$  represents the *trans*-exocyclic double bond.<sup>21</sup> All the polymers showed absorption around 1016, 1141, and 1251  $\text{cm}^{-1}$  due to P=O stretching. The  $^1\text{H NMR}$



Scheme 1 Synthesis of polymers.

spectrum of aromatic protons of polymer in the main chain stilbene appeared in the region of 6.5–6.9 ppm. The side chain aromatic protons of all the polymers are resonated in the downfield region around 7.2–7.9 ppm. The <sup>31</sup>P NMR spectra of the polymer show two signals; the resonance signal corresponds to  $-6.7 \delta$  owing to the P in the main chain and the other at  $-14.5 \delta$  is the P at the chain ends, which confirmed the incorporation of phosphorus in the polymer backbone.<sup>22,23</sup>

### Thermal and optical properties

The TGA traces of stilbene (I series) and  $\alpha$ -methylstilbene (II series) containing polymer is shown in Figure 1. The thermal stability of polymers (I and II series) is investigated by TGA at a heating rate of 10°C/min under nitrogen atmosphere and the data are summarized in Table I. Both series of polymers

exhibited a three-stage decomposition pattern. Initial decomposition may be ascribed to evolution of nitrogen gas by the cleavage of side chain azo group.<sup>24</sup> The second decomposition around 335–410°C may be attributed to the cleavage of phosphate esters combined with aliphatic spacers. The final decomposition around 402–490°C may be due to the pyrolytic cleavage of ether linkage of the aromatic backbone. The decomposition of I and II series of polymer was almost complete at 600°C and no further weight loss was observed in both the series. On the basis of the structural changes, the thermal crosslinking of stilbene (I series) containing polymers shows higher char yield than that of noncrosslinkable  $\alpha$ -methylstilbene (II series) containing polymers. I series polymers showed higher char yield than did II series of polymers. The high percentage of char yield for these polymers may be attributed to the formation of phosphoric acid as the final product.

TABLE I  
Yield, Inherent, TGA, and UV Data of the Polymers Ia–If (DHS) and IIa–IIf (DHAMS)

Polymer	Yield (%)	$\eta_{inh}$ (dL g <sup>-1</sup> )	Thermal decomposition			Maximum weight loss (%)	Char yield at 600°C	$\lambda_{max}$ (trans azo nm)
			I	II	III			
DHSH (Ia)	65	0.55	260	360	440	22	78	350
DHSF (Ib)	68	0.62	290	400	460	25	75	349
DHSCl (Ic)	60	0.69	300	400	460	27	73	354
DHSBr (Id)	70	0.72	320	410	490	28	72	353
DHSCN (Ie)	63	0.75	280	392	471	31	69	380
DHSNO <sub>2</sub> (If)	67	0.78	263	370	450	33	67	377
DHAMSH (IIa)	68	0.35	262	362	480	17	83	385
DHAMSF (IIb)	66	0.41	240	360	465	20	80	349
DHAMSCl (IIc)	62	0.46	242	385	450	21	79	360
DHAMSBBr (IId)	73	0.50	230	335	420	22	78	353
DHAMSCN (IIe)	68	0.62	230	350	402	33	67	380
DHAMSN <sub>2</sub> (IIIf)	64	0.65	238	380	440	31	69	377

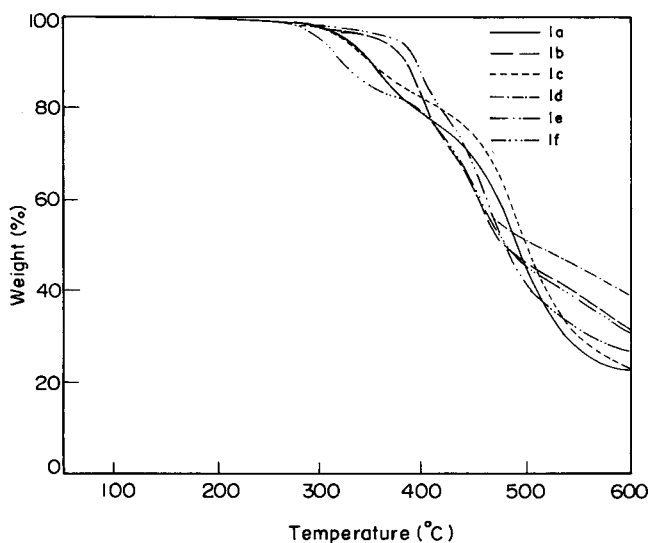


Figure 1 TGA thermogram of polymer Ia–If.

DSC thermograms of the polymers (II series) are shown in the Figure 2. The DSC data of the polymers are given in Table II. The I series of polymers exhibit the softening point between 50 and 60°C. The melting and isotropic transition temperature was obtained in the range of 110–152°C and 205–321°C respectively. The glass transition temperatures for II series of polymers are in the range of 60–70°C. The melting and isotropic transition temperatures were observed in the region of 112–150°C and 148–173°C respectively. The transition temperature data revealed that the I series of polymers exhibit fairly high clearing temperature while II series showed lower clearing temperature attributed to the unsymmetry of the  $\alpha$ -methylstilbene molecule.<sup>25</sup> In addition, the Ia–f polymers involving crosslinkable olefinic group could be crosslinked by the central ethylenic linkage of the stilbene unit, forming thermally stable three-dimensional network confirmed by DSC analysis. On the other hand, the IIa–f series of polymers show lower melting and isotropic transition temperatures. It is believed that the methyl substitution in the ethylenic linkage of stilbene moiety affects the cross dimension of the mesogen and presumably improves the solubility. Therefore the substituted  $\alpha$ -methyl stilbene shows lower melting transition temperature. The  $\Delta T$  (phase duration) values of both the series reveal that I series of polymer display mesophase stability between 95 and 169°C whereas II series of polymers exhibit the same between 18–54°C. This indicates that a simple substitution of a methyl group in olefinic bond by lateral fashion produces drastic reduction of mesophase stability. It is also noteworthy to mention that I series polymers can undergo thermal crosslinking while the II series polymers cannot.

The optical textures of mesophase were observed for the polymer melt through the POM. The photomicrographs of the polymer DHS (I) and DHAMS (II) series are shown in Figure 3. The main chain monomer containing decyloxy stilbene and decyloxy- $\alpha$ -methylstilbene and their polymers (I and II series) exhibited the enantiotropic mesomorphism of textures. The photomicrographs were taken during the cooling cycle and were held for 1 h with a sensitivity of  $\pm 3^\circ\text{C}$ . In I series of polymers, the electron withdrawing substituents exhibit marblelike texture (polymer Ie) and mosaiclike texture for polymers Ib, Ic and Id having electron-releasing nature.<sup>26</sup> In DHAMS (II) series of polymers (IIa–i), the glass transition temperature is around 50–70°C and the polymer exhibits melting between 109 and 150°C. The isotropic transition temperature is observed between 150 and 170°C. In this series, the polymers exhibit two types of textures: mosaic and unidentified smectic.<sup>27</sup> The polymers II d (bromo), II e (cyano), and II f (nitro) show unidentified textures whereas all the remaining polymers show mosaiclike textures. Accordingly, the intermolecular interaction, dipole interactions play a vital role in determining the type of mesophase texture of the terminal substituents. These terminal substituents of the mesomorphic nature vary with one another. In the case of polar group such as cyano and nitro containing polymers, the interaction of permanent and induced dipoles plays a remarkable role. The strong terminal dipole moment (calculated to be 8.8 D) introduced by the nitro groups increases the polarizing nature of rotational barrier about a long axis of the mesogens. The results emphasize the fact that the type of the texture, growth of the domain, and transparency of the phases depend not only on the length of the alkyl

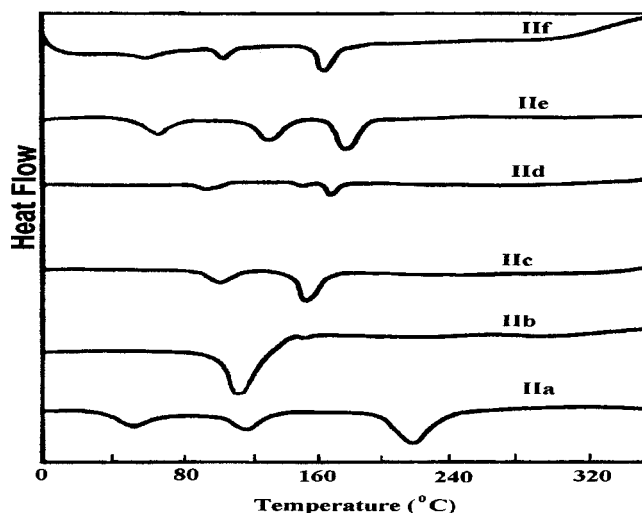


Figure 2 DSC thermograms of second heating cycle of polymer IIa–IIf.

TABLE II  
DSC and POM of Polymer Ia–If (DHS) and IIa–IIf (DHAMS)

Polymer	DSC				HOPM			Type of mesophase
	$T_g$ (°C)	$T_m$ (°C)	$T_i$ (°C)	$\Delta T$ (°C)	$T_m$ (°C)	$T_i$ (°C)	$\Delta T$ (°C)	
DHSH (Ia)	55	110	205	95	120	214	94	Unidentified smectic
DHSF (Ib)	–	120	230	110	122	225	103	Mosaic
DHSCI (Ic)	60	118	220	102	115	210	95	Mosaic
DHSBr (Id)	–	152	321	169	140	315	175	Mosaic
DHSCN (Ie)	60	125	243	118	124	240	116	Marble
DHSNO <sub>2</sub> (If)	50	135	250	115	130	238	108	Smectic E
DHAMSH (IIa)	60	150	173	23	150	170	20	Mosaic
DHAMSF (IIb)	–	130	148	18	135	150	15	Mosaic
DHAMSCI (IIc)	–	138	158	20	140	157	17	Mosaic
DHAMSBr (IId)	–	109	163	54	109	162	53	Unidentified smectic
DHAMSCN (IIe)	62	140	161	21	138	163	23	Unidentified smectic
DHAMSNO <sub>2</sub> (IIf)	70	112	160	48	115	160	45	Unidentified smectic

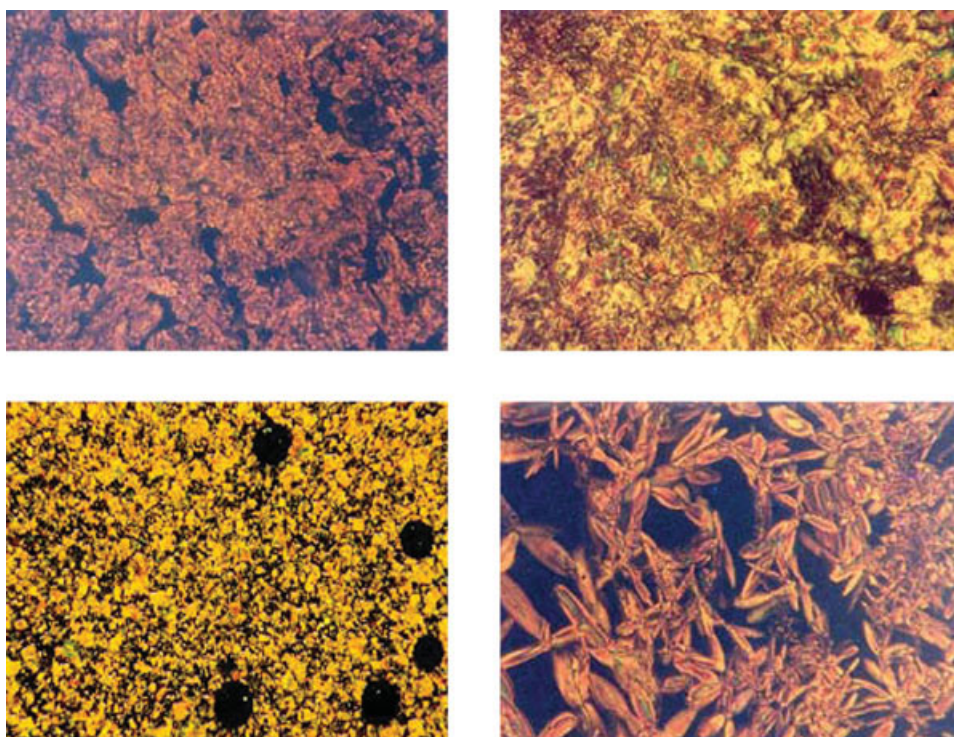
chain but also on the polarity and extend of conjugation and chemical nature of the substituents. If the conjugation is more (polymer Ie and If, and IIe and IIf) the textures are more clear and transparent. But polymers Ia and IIa (without any polar group substituent) exhibit poor domain formation and clarity.

#### Photolysis studies

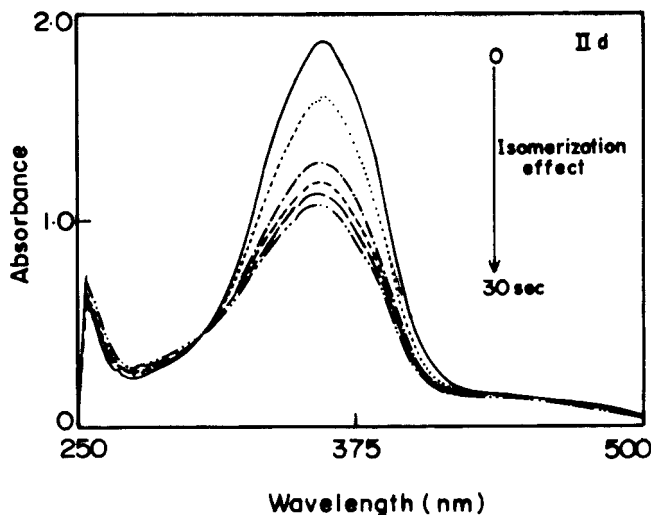
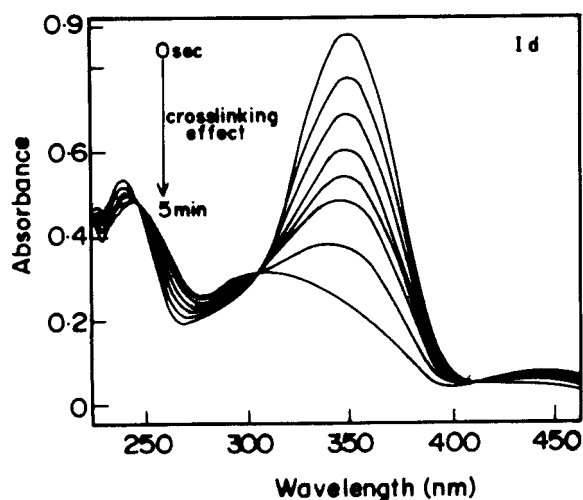
The photolysis studies were done for the two different types of photosensitive polymers. Both types of polymers contain MC (Stilbene derivative) and SC moieties (terminal substituted azobenzene) with pho-

tosensitive chromophores. To compare the two types of polymers, a model polymer (III) was synthesized with MC (bisphenol-A) and SC (azobenzene) moieties. The justification for the selection of bisphenol-A unit in the MC of model polymer is that the unit is insensitive with light. Obviously, the effect of the MC moiety (stilbene) could be clearly determined. The steady state photolysis of the two types of polymers were studied individually and compared with model polymer.

The UV–visible spectra for I series polymers (Ia–i), in dichloromethane solution, are quantitatively measured and depend on the photoactive stilbene

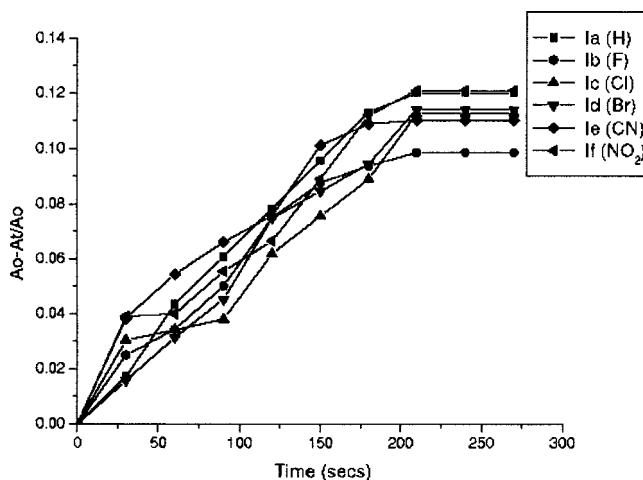


**Figure 3** Polarized optical photomicrograph of polymer Ib (DHSF), Ie (DHSCN), IIb (DHAMSF), and IId (DHAMSBr) during the first cooling cycle ( $\times 100$ ). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 4** Absorption spectrum of polymer Id (DHSBr) and IId (DHAMSBr) at different intervals of time in seconds.

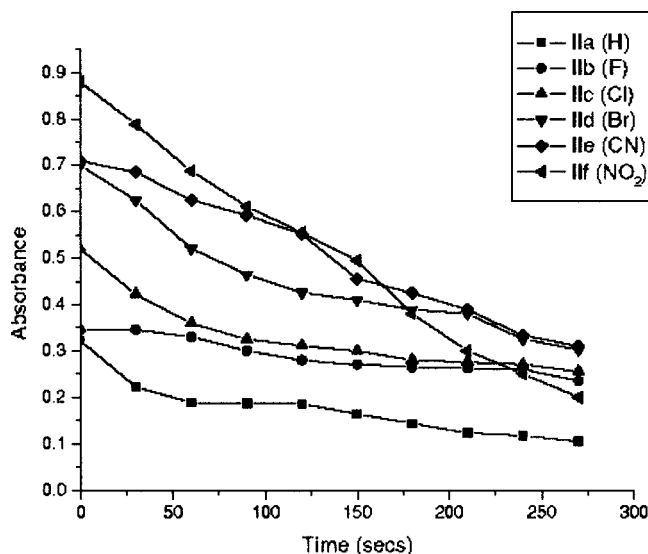
and azobenzene units. The absorption maxima for I series polymers are shown in Figure 4 and observed with four different wavelengths with intensity. The absorption of MC stilbene unit was found between 228 and 254 nm for trans and cis isomer. All the UV curves clearly represent the simultaneous observation of the crosslinking by stilbene unit and cis-trans isomerization process of SC azobenzene unit. The relative rates of photocrosslinking effect for I series polymers are shown in Figure 5. The relative reactivity ( $A_0 - A_t/A_0$ ) rate is plotted against the time  $t$  of irradiation, where  $A_0$  is the absorbance before irradiation and  $A_t$  is the absorbance after irradiation of time  $t$ . The intensity of  $\pi-\pi^*$  electronic transition of I series of stilbene polymers (224–254 nm) initially decreased in absorbance, gradually followed by no change in absorbance indicating the effect of cross-



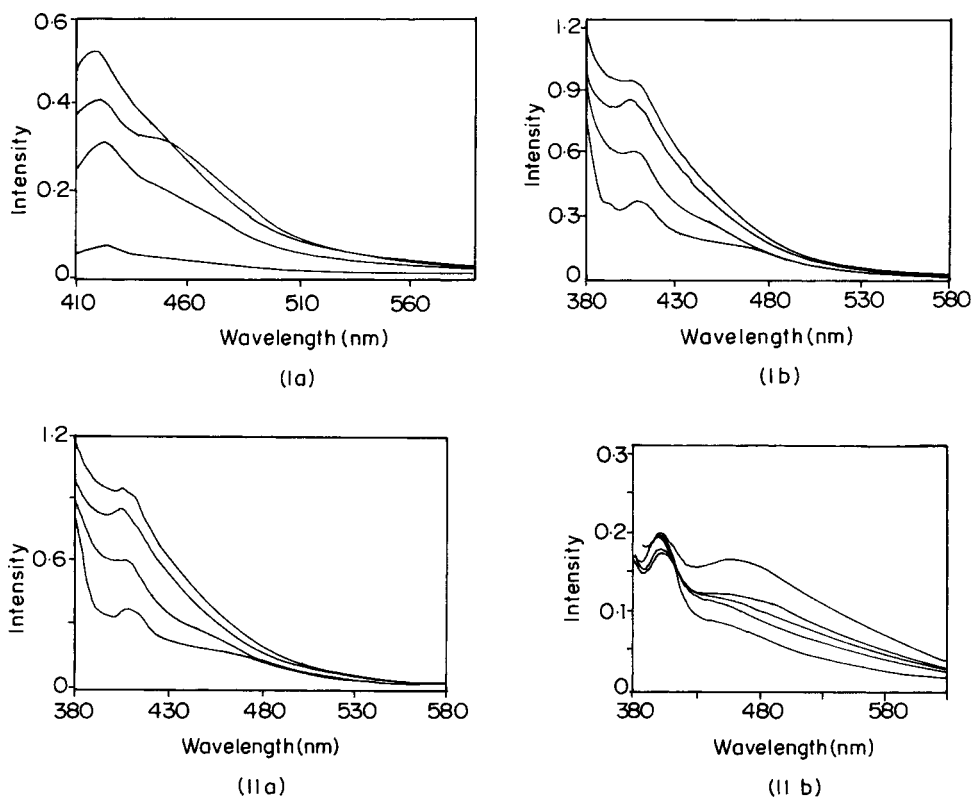
**Figure 5** Rate of photolysis of stilbene polymers (Ia-I f) at different intervals of time (30 s).

linking due to dimerization of the olefinic double bond of the stilbene unit, which involves the  $(2 + 2)\pi$  cyclization reaction of the same leading to the formation of the cyclobutane ring, a new type of crosslinked polymer materials is formed.<sup>28</sup> It was found that at the end of irradiation (5 min) the system did not show any further change.

In the case of SC-substituted azobenzene, the absorption maxima were observed around 349–380 nm and 430–463 nm relative to that of the trans and cis forms. On irradiation of the polymer solution with different interval of time, the azobenzene chromophores undergo trans-cis photoisomerization process.<sup>29</sup> While substituting the different terminal groups in the SC azobenzene moiety the shape, intensity and position of the UV absorption peak



**Figure 6** Photoisomerization of polymer I Ia-I f having a concentration of  $2 \times 10^{-5}$  mol.



**Figure 7** Fluorescence emission (EM) spectrum of the polymers Ia (DHS), Ib (DHSF), IIa (DHAMSA), and IIb (DHAMSF) excited at 350 nm at different interval of irradiation time (30 s).

change according to the nature of the substituents, as shown in Figure 6. In fact, the electron-withdrawing nature of the side chain azobenzene substituents showed higher wavelength than that of the electron-donating natures. A similar trend was observed in both (I and II) the series. This may be ascribed to the resonance effect and stability of the electron withdrawing substituents for higher wavelength. On the basis of the above-mentioned inference, I series of polymers (Ia-i) exhibit the simultaneous observations of crosslinking by MC stilbene unit along with the isomerization process of SC-substituted azobenzene moieties. The substituents effect plays a prominent role in determining the type of stability, crosslinking effect, and the type of mesophasic textures.

The fluorescence method is an effective tool for investigating the molecular level information of polymers. It is well known that the isomerization of *cis*-configuration causes loss of the fluorescence properties; no complete theory exists to explain how the photophysical and photochemical process is correlated to the polymer properties. Fluorescence spectra of polymers (Ia, Ib and IIa, IIb) with constant excitation (350 nm) of emission are shown in Figure 7. The fluorescence emission wavelengths in dichloromethane solution were observed in the range of 330, 410, and 580 nm. The fluorescence spectrum of *trans*- and *cis*-azobenzene was formed by rotation and

inversion mechanism. Emission spectrum was observed at 360 nm and more or less equal to that of absorption spectrum. Figure 7-Ia shows that I series of polymers exhibit the emission property in the range of 300–410 nm, whereas in II series of polymers the emission wavelength absorbed in the range of 350–450 nm. It has been known that the substituent, which enhances the electron mobility or reduces the activation energy through the resonance effect, brings about the shift in fluorescence maxima towards the longer wavelength region.

## CONCLUSIONS

Two series of liquid crystalline polymers containing stilbene and  $\alpha$ -methylstilbene in the main chain and terminally substituted azobenzene moiety in side chain were synthesized and characterized. The thermal stability of all the polymers was stable up to 230°C and three-stage decomposition temperatures are identified with good char yields, which is required for the polymers to act as flame-retardant materials. All the polymers showed melting and isotropization transition temperature in the range of 109–321°C. All the polymers exhibited the birefringent melt of the liquid crystalline properties with



mosaic and unidentified smectics. I series (DHS) of stilbene containing polymers observed simultaneous crosslinking/isomerization effect whereas the II series (DHAMS) exhibited the isomerization process alone. Photoisomerization kinetics of all the polymers by UV irradiation studies confirmed that the rate of switching time and the efficiency of terminal substituents for the side chain azobenzene moieties were observed. After completion of irradiation with visible light (365 nm), the stilbene and  $\alpha$ -methylstilbene of main chain mesogen exhibit thermally irreversible photochromic properties. The emission spectra of all the polymers excited at 350 nm at different interval of time (30 s) show a decrease in intensity.

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