

Effect of Ethylphosphate on Azobenzene-Containing Thermotropic Liquid-Crystalline Polymers

S. Kumaresan, P. Kannan

Department of Chemistry, Anna University, Chennai 600 025, India

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ABSTRACT: A new series of liquid-crystalline polymers with azobenzene mesogens and an even number of methylene spacers along with phosphorus heterogeneity were synthesized. The structures of the monomers and polymers were characterized with various spectral techniques. The thermal analyses were performed with thermogravimetric analysis and differential scanning calorimetry (DSC). The formation of the liquid-crystalline phase was confirmed with hot-stage optical polarizing microscopy. All the polymers exhibited grainy and nematic textures during melting; this was confirmed by DSC analysis. The char yield of the polymers was quite high and was related to the formation of

phosphoric acid. The glass-transition temperature, melting temperature, and isotropization temperature were quite low. The reduction in the transition temperature could be attributed to the incorporation of the phosphorus heterogeneity and pendant ethyl group. Molecular modeling studies supported the experimental data obtained. The suitability of these polymers for optical data storage was studied with ultraviolet spectroscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 455–462, 2004

Key words: liquid-crystalline polymers (LCP); molecular modeling; azobenzene; phosphate esters

INTRODUCTION

The miniaturization of electrical and electronic equipment has led to potential materials for high-technology applications such as displays,¹ light-emitting diodes,² and information storage systems.³ Azobenzene-containing amorphous polymers are being studied as suitable materials for reversible optical data storage.⁴ Liquid-crystalline solutions have not yet found any commercial use, but highly orientated liquid-crystalline-polymer (LCP) films have found applications for information storage.³ The incorporation of a photochromic moiety into polymers is attractive for creating new light-sensitive materials and optical devices. Thin films containing photoisomerizable moieties are excellent materials for control in liquid-crystalline molecules, optical storage media,⁴ holographic surface relief gratings,⁵ photonic device applications,^{6,7} and so forth.

Azobenzene is a potentially useful photoisomerizable moiety that has been studied exhaustively by the doping of the dye into polymer matrices or the azo chromophores covalently bonded to the backbones of LCPs. The main advantage of these LCPs is the low glass-transition temperature (T_g).⁸ Azobenzene-containing side-chain LCPs have been extensively studied. However, only a few reports are available on

main-chain LCPs containing azobenzene units.^{9,10} There are three factors affecting the properties of azobenzene-based LCPs: the structure of the polymer backbone, the azo chromophore, and the linkage between the terminal groups and the substituents. These variables provide an excellent platform for preparing tailor-made azo-containing polymers.¹¹

Phosphorus-containing polymers are gaining recognition for their plasticizing and adhesive¹² characteristics as well as their flame-retardant¹³ properties. Being a nonmetal, phosphorus will impart special features such as adhesion, flexibility, and increased polarization effects when it is incorporated into a polymer backbone.¹⁴ The polarity of phosphorus could play a vital role in physical properties, such as stability, solubility, and film formation. Unlike azobenzene-containing liquid crystals, limited reports are available on phosphorus-containing LCPs.^{15–17}

In a continuation of our research in this area,^{12–16} this article deals with the synthesis and characterization of hitherto unreported thermotropic liquid-crystalline main-chain polymers containing azobenzene and phosphorus moieties.

EXPERIMENTAL

Materials

p-Nitrophenol, 1,2-dichloroethane, methanol, and ethanol (SRL, India) were purified by the usual methods.¹⁸ Phosphorus oxychloride, 2-bromoethanol (Fluka, Switzerland), and 1,6-hexane diol (Riedel, GmbH, Germany) were used as received.

Correspondence to: P. Kannan (pakannan@annauniv.edu).

Synthesis of the monomers

4,4'-Dihydroxyazobenzene was prepared by the reduction of *p*-nitrophenol in the presence of potassium hydroxide with a procedure reported elsewhere.¹⁹

mp: 220°C. ¹H-NMR [400 MHz, dimethyl sulfoxide-*d*₆ (DMSO-*d*₆), δ]: 6.94 (4H, d), 7.71 (4H, d) 10.14 (2H, s, OH).

4-Bromobutylacetate,²⁰ 6-bromo-1-hexanol, 8-bromo-1-octanol, 10-bromo-1-decanol,²¹ and ethylphosphorodichloridate²² were prepared according to a procedure reported in the literature.

4,4'-Bis(*n*-hydroxyalkyloxy)azobenzene (*n* = 2, 6, 8, or 10)

The title compounds were prepared with a modified procedure reported in the literature.²³ A typical procedure for the preparation of 4,4'-bis(2-hydroxyethyl-oxy) azobenzene was as follows. 4,4'-Dihydroxyazobenzene (0.01 mol) was dissolved in ethanol (100 mL), and potassium hydroxide (0.2 mol) dissolved in water (10 mL) and KI (100 mg) were added. The mixture was refluxed, and 2-bromoethanol (0.05 mol) was added dropwise to the refluxing mixture. The reaction was continued for 15 h, and the excess ethanol was removed under reduced pressure. The remaining solution was cooled and poured into ice-cold diluted HCl with stirring, and the precipitated product recrystallized in ethanol.

Yield: 60%. mp: 142°C. IR (KBr, cm⁻¹): 3458 (OH), 2930 (CH₂), 1477 (N=N), 1253 (Ar—O—C). ¹H-NMR (400 MHz, DMSO-*d*₆, δ): 10.1 (2H, s, OH) 7.51 (2H, d), 6.99 (2H, d), 4.2 (2H, t), 3.5 (2H, t), 1.7 (5H, m), 1.5 (5H, m).

The other homologues (*m* = 6, 8, or 10) were prepared with a similar procedure.

4,4'-Bis(4-hydroxybutyloxy)azobenzene

4,4'-Dihydroxyazobenzene (0.01 mol) was dissolved in dry dimethylformamide (30 mL), and anhydrous potassium carbonate (0.1 mol) and KI (100 mg) were added. The mixture was heated around 90–95°C, 4-bromobutylacetate was added dropwise with stirring, and the reaction was continued at that temperature for 12 h; the mixture was cooled and poured into a diluted HCl solution. A waxy product that precipitated out was extracted with ether, washed with water, and dried over sodium sulfate. Ether was removed *in vacuo* to obtain the bisester (70% yield). The bisester was dissolved in ethanol (100 mL), an aqueous sodium hydroxide solution (0.25 mol, in 10 mL of water) was added, and the mixture was refluxed for 6 h. The product was cooled and neutralized with diluted HCl, and this afforded a yellow and spongy precipitate. It

was recrystallized in hot water to give the title compound.

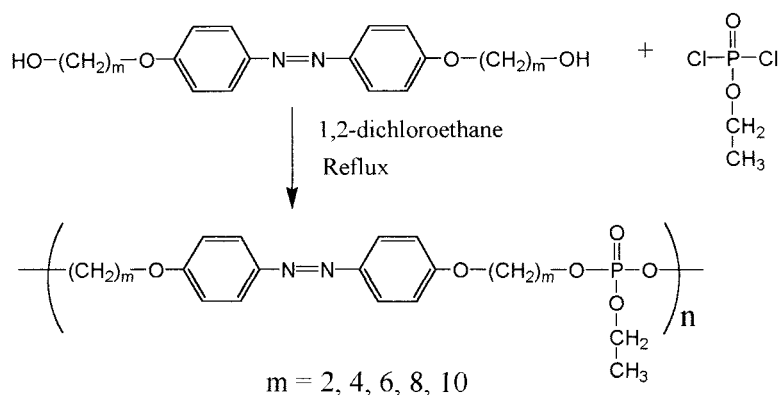
Yield: 72%. mp: 121°C. IR (KBr, cm⁻¹): 3458 (OH), 2930 (CH₂), 1477 (N=N), 1253 (Ar—O—C). ¹H-NMR (400 MHz, DMSO-*d*₆, δ): 10.0 (2H, s, OH) 7.43 (2H, d), 6.99 (2H, d), 4.4 (2H, t), 3.5 (4H, m), 1.68 (5H, m), 1.6 (5H, m).

Polymerization

All the polymers (I–V) were prepared by a solution polycondensation method. A typical procedure for the preparation of poly[4,4'-phenyloxyazoalkyl(ethylphosphate)] was as follows. 4,4'-Bis(2-hydroxyethyl-oxy)azobenzene (0.01 mol) was dissolved in dry 1,2-dichloroethane (25 mL) with stirring and refluxed under a nitrogen atmosphere. Ethyl phosphorodichloridate (0.01 mol), dissolved in 1,2-dichloroethane (25 mL), was added dropwise under those conditions, and the reaction was continued for 12 h more. At the end of the reaction, the solution was concentrated to 10 mL, cooled, and poured into methanol. A yellow precipitate that formed was reprecipitated and purified with 1,2-dichloroethane and methanol. (60% yield). The remaining polymers—poly[4,4'-phenyloxyazobutyl(ethyl phosphate)], poly[4,4'-phenyloxyazohexyl(ethylphosphate)], poly[4,4'-phenyloxyazo-octyl(ethylphosphate)], and poly[4,4'-phenyloxyazodecyl(ethyl phosphate)]—were prepared with a similar procedure.

Characterization

The molecular weight distribution was investigated with a Waters 85C (Germany) gel permeation chromatograph with a Styragel column and with tetrahydrofuran as a solvent. The column was calibrated with polystyrene standards (molecular weight = 5000–25,000). High-resolution ¹H-NMR, ¹³C-NMR, and ³¹P-NMR spectra were recorded on a Bruker (Germany) spectrometer (400 MHz). A mixture of CDCl₃ and DMSO-*d*₆ was used as a solvent to record the spectra. IR spectra were recorded on a Nicolet IR (USA) (Impact 440) spectrometer with KBr pellets. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies were carried out on a Mettler-Toledo STAR^e (USA) system under a nitrogen atmosphere. TGA was performed at a heating rate of 20°C min⁻¹ under a nitrogen flow of 20 mL min⁻¹. The polarizing microscopy studies were performed with a Euromax (Holland) polarizing microscope equipped with a Linkam HFS 91 heating stage and a TP-93 temperature programmer. Samples were made by the melting of a small quantity of the material between two thin glass coverslips for a uniform film at heating and cooling rates of 5°C/min. The photographs were taken with a Nikon FM10 camera and



Scheme 1 Synthesis of polymers I-V.

were exposed on Konica film. X-ray diffraction (XRD) measurements were performed with a Rigaku (Germany) R axis IIC powder diffractometer. A monochromatized X-ray beam from nickel-filtered Cu K α radiation with a wavelength of 0.15406 nm was used. Molecular modeling studies were performed with the Chem 3D Pro computer program. The structures were initially minimized with Molecular Mechanics 2 (MM2) to a minimum root-mean-square gradient of 0.100. The structure was further resolved with Molecular Orbital Package (MOPAC) with Hamiltonian AM1 as a semiempirical wave function. The polymer was dissolved in 1,2-dichloroethane (30 mg/L), studied for trans-cis-trans photoisomerization with ultraviolet (UV) light at 366-nm irradiation, and monitored at regular intervals on a Shimadzu 1601 (Japan) ultraviolet-visible spectrophotometer.

RESULTS AND DISCUSSION

4,4'-Dihydroxyazobenzene was alkylated with ω -bromoalkanol based on the Williamson ether synthesis method. Ethylphosphorodichloridate was prepared by the reaction of 1 mol of ethanol with 5 mol equiv of phosphorus oxychloride. The synthesis of phosphorus-incorporated polymers was achieved by the reaction of azobenzene-containing mesogenic diols and ethylphosphorodichloridate by a solution polycondensation method (Scheme 1). These polymers were soluble in 1,2-dichloroethane, dimethylacetamide, DMSO, and dimethylformamide and were insoluble in common organic solvents such as methanol and acetone. The number-average molecular weights obtained by gel permeation chromatography analysis for all the polymers were in the range of 3100–4500 (Table I).

The IR spectra of the polymers showed absorptions around 2935 and 1496 cm^{-1} corresponding to $-\text{CH}_2-$ stretching and $-\text{N}=\text{N}-$, respectively. The incorporation of ethyl phosphate groups was confirmed by the absorptions around 1381, 1096, and 912 cm^{-1} corresponding to $\text{P}-\text{O}-\text{C}$ stretching. All the polymers showed absorptions around 1150 cm^{-1} due to $\text{P}=\text{O}$ stretching; the absorption around 1254 cm^{-1} corresponded to an aryl-alkyl ether linkage.²⁴

A representative $^1\text{H-NMR}$ spectrum of polymer IV is shown in Figure 1. All the spectra showed 2H doublets appearing at $\delta = 7.0$ (meta to $-\text{N}=\text{N}-$) and $\delta = 7.75$ (ortho to $-\text{N}=\text{N}-$) for the unsubstituted aromatic ring protons in azobenzene (which has a planar structure). A signal resonating at $\delta = 4.1$ corresponded to the $\text{Ar}-\text{O}-\text{CH}_2$ methylene proton. The methylene proton of the pendant ethyl group and methylene proton attached to the phosphate moiety merged together and appeared as a broad multiplet around δ

TABLE I
GPC and TGA Data of Polymers I-V

Polymer	M_n	M_w	M_w/M_n	Weight loss corresponds to (°C)		Weight loss at 600°C (%)	Char yield at 600°C (%)
				2%	50%		
I	3128	3300	1.05	250	494	44	56
II	3400	3550	1.04	249	450	60	40
III	4080	4210	1.03	249	400	63	37
IV	4397	4545	1.03	248	390	70	30
V	4230	4402	1.04	260	368	72	28

M_n = number-average molecular weight; M_w = weight-average molecular weight.

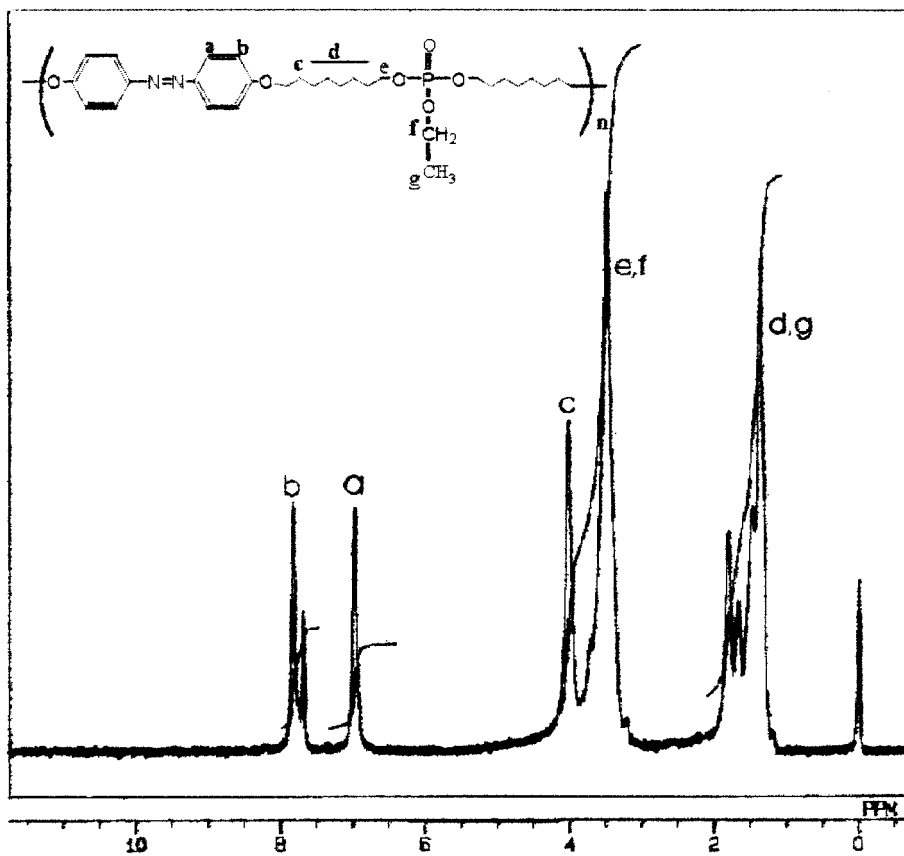


Figure 1 ^1H -NMR spectrum of polymer IV.

= 3.5. The pendant methyl proton and the remaining methylene protons in the main chain merged together and resonated around $\delta = 1.5$ as multiplet.

A typical broadband ^1H -decoupled ^{13}C -NMR spectrum of polymer III is illustrated in Figure 2. A tertiary carbon linked with nitrogen of an azo group and another tertiary carbon attached to an ether linkage resonated at $\delta = 159.98$ and $\delta = 145.53$, respectively. The unsubstituted aromatic carbons in the azobenzene moiety resonated in the region of $\delta = 123.15$ (ortho to $-\text{N}=\text{N}-$) and $\delta = 113.59$ (meta to $-\text{N}=\text{N}-$). A methylene carbon attached to aryl-alkyl ether resonated at $\delta = 69.44$. Methylene carbons in the main chain and side chain attached to phosphate groups resonated at $\delta = 69.44$ and $\delta = 66.98$, respectively. Methyl carbon in the pendant chain appeared at $\delta = 24.81$. All the remaining main-chain aliphatic carbons resonated between $\delta = 27.95$ and $\delta = 29.00$.²⁴

The ^{31}P -NMR spectra of all the polymers showed two signals at $\delta = -20.12$ and $\delta = -19.64$ as a result of two different phosphorus atmospheres. P surrounded by alkyloxy groups was more shielded and appeared at $\delta = -20.12$ for the repeat unit, whereas end-group P appeared at $\delta = -19.64$.²⁵

Thermogravimetric data of the polymers are summarized in Table I. The TGA pattern is shown in

Figure 3. The thermal stability was evaluated by a 2% weight loss at the minimum temperature under a nitrogen atmosphere. TGA revealed that the polymers were stable up to 200–320°C. The 40% weight loss of the polymers took place in a regularly decreasing order with an increase in the spacer length and fell between 368 and 494°C. The decomposition of the polymers was almost complete around 600°C, and no further weight loss was observed thereafter. The char yield of the polymers at 600°C increased as the spacer length decreased. This may be attributed to fact that the polymers with longer alkyl spacers had more carbons per repeating unit and thus experienced greater mass loss by the degradation of C—C bonds at 600°C. The maximum char yield was obtained for polymer I (56%), and the minimum was obtained for polymer V (28%). The data suggested that the char yield of the polymer decreased with the ratio of the single mesogen as the spacer increased. The decomposition of the polymers probably occurred through the pyrolytic cleavage of the phosphate ester group and the breaking of the linkage between the mesogenic groups with different methylene units. The higher char yield may also be attributed to the formation of phosphoric acid during the breakage of the phosphorus segment in the polymer chain.

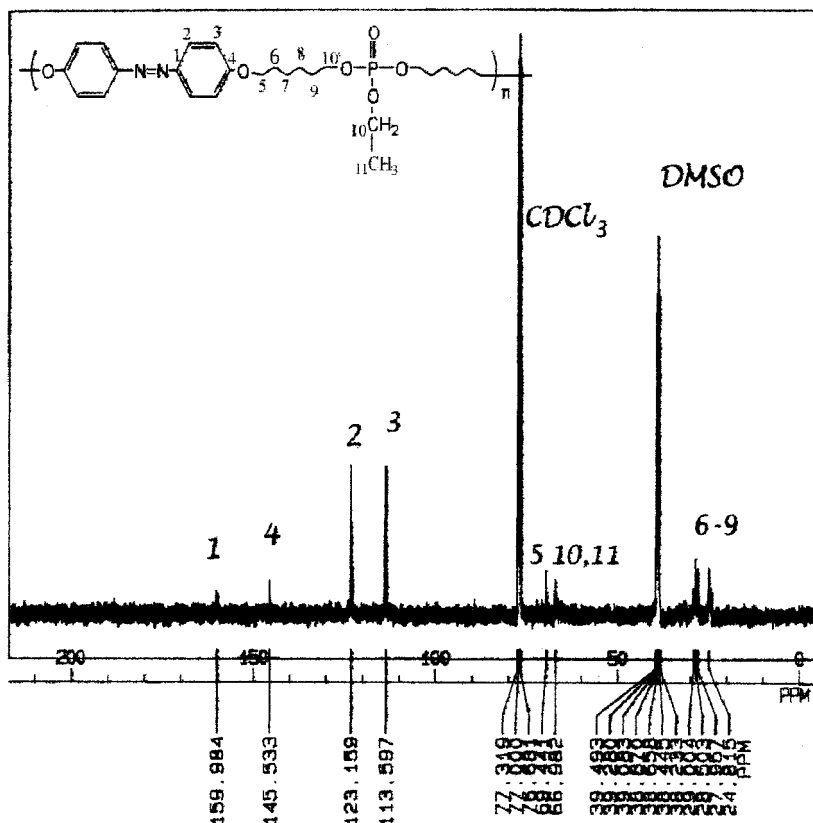


Figure 2 ¹³C-NMR spectrum of polymer III.

The liquid-crystalline properties of the polymers (I-V) were studied with hot-stage optical polarized microscopy (HOPM). All the polymers formed an entiotropic birefringence melt on heating. The reproducibility of the formation of the liquid-crystalline phases for all the polymers was satisfactory. All the photographs were taken during the first cooling cycle at a magnification of 20× (Fig. 4). The microscopic observations of the polymers showed that the liquid-crystalline monodomain size was increasing while the methylene spacer was increasing. Polymers I and II

exhibited grainy textures between the melting temperature (T_m) and isotropization temperature (T_i). The size was not increased with further heating, and it moved to an isotropic liquid state at T_i ; on cooling, it regained its grainy texture. Polymers III-V, however, exhibited a nematic texture during the first cooling cycle from the isotropic-transition state. They formed nematic droplets upon cooling and agglomerated to form well-structured nematic threads. The phases were identified and compared with previously ob-

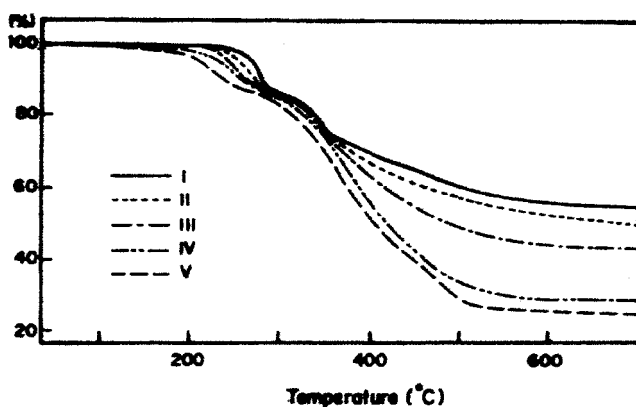


Figure 3 TGA traces of polymers I-V.

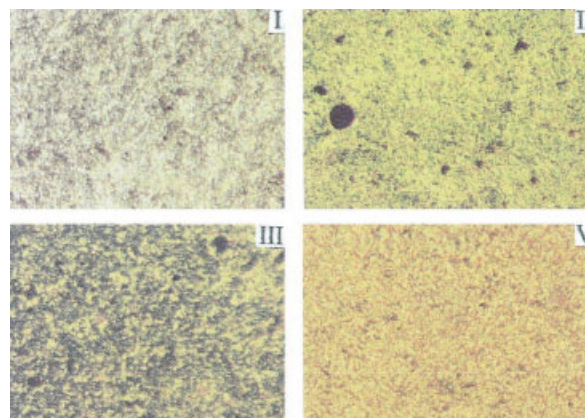


Figure 4 Thermal polarized optical micrograph (20×) of polymers I, II, III, and V.

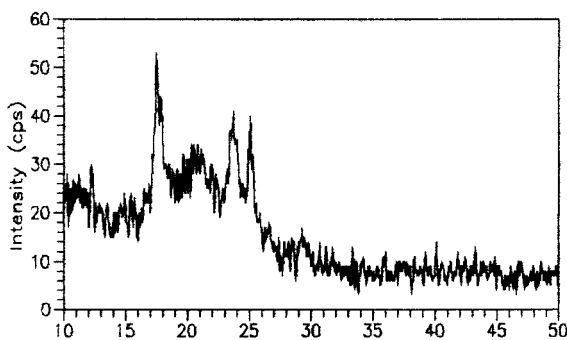


Figure 5 XRD pattern of polymer II.

served phases reported in the literature.²⁶ To confirm the identity of the mesophase texture, we performed representative XRD measurements for polymer II. The XRD pattern for polymer II is shown in Figure 5. A sharp diffuse peak was observed at $d \sim 5.0$ Å and $d \sim 4.96$ Å, indicating a liquidlike ordering of the molecule. Moreover, two peaks at $d \sim 3.74$ Å and $d \sim 3.54$ Å corresponded to lateral substituents of the side-chain moiety. Also, a broad region at $2\theta = 22^\circ$ represented alkyl chain melting.²⁷ The results revealed that the texture of polymer II was nematic and corresponded to the formation of small monodomains that were grainy in nature.

DSC analysis was performed under nitrogen at a heating rate of $10^\circ\text{C min}^{-1}$; the results are summarized in Table II, and the thermograms are shown in Figure 6. DSC showed three endotherms for polymers I–III but only two endothermic transitions for polymers IV and V. The first transition in polymers I–III was glass transition that was not observed for polymers IV and V. The other two transitions in the polymers confirmed the formation of a liquid-crystalline mesophase. T_g of the polymers decreased as the methylene chain increased. T_g was not observed for polymers IV and V. T_m and T_i decreased as the flexible chain length increased. T_m decreased from 84 (polymer I) to 50°C (polymer V). T_i also decreased from 170 to 105°C . The mesophase duration (ΔT) of the polymers was decreased as the methylene chain increased.

The energy-minimized structures were obtained for a model compound and polymer II initially with MM2, and the structures were further refined by

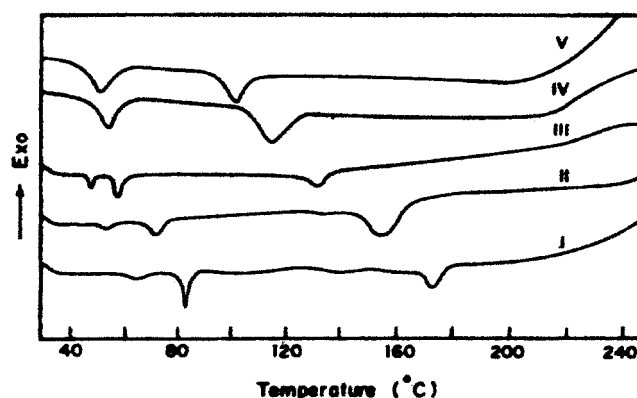


Figure 6 DSC traces of polymers I–V.

MOPAC with the AM1 semiempirical wave function. The model compound [Fig. 7(b)] was designed in such a way that the mesogen length and spacer length were the same, and it resembled the structure (repeating unit) of polymer II with a nonphosphorus moiety. The energy-minimized structures are depicted in Figure 7(a,c). The results revealed that, at the lowest potential energy, the model compound [Fig. 7(b)] was an almost straight-line structure, whereas the polymer [Fig. 7(a)] appeared to be a broad, coil-like structure. This indicated that the incorporation of a phosphorus moiety led to more coiling of the polymer chain and produced entanglements. This effect could seriously affect the transition temperatures of the polymers and the development of monodomain structures in the liquid-crystalline phase. The molecular modeling results agreed with our experimental results. Indeed, the T_g values observed for these polymers were below 65°C and even went below room temperature for polymers containing 8 and 10 methylene spacers. T_m was also quite low. This could be due to less packing and more coiling of the polymer chains, which led to a reduction in the transition temperatures. In addition, the pendant ethyl groups may have disturbed the packing of the chains. These explanations may also hold true for the formation of liquid-crystalline textures. Accordingly, the polymers containing shorter spacers (I and II) exhibited grainy textures, whereas those containing longer spacers (III–V) exhibited nematic textures.²⁸

To determine the suitability of these polymers for optical data storage systems, we performed UV studies; the UV spectral pattern is shown in Figure 8. The absorption maximum around 366 nm was due to the $\pi-\pi^*$ transition in the stable trans conformation of the azobenzene moiety. After the irradiation of the polymer solution with UV light, the absorbance around 366 nm decreased and a new absorption band around 430 nm increased with increasing exposure time. This may be due to the formation of an unstable cis conformation of the $n-\pi^*$ transition. The results agreed with the reports available in the literature²⁹ and

TABLE II
HOPM and DSC Analysis of Polymers I–V

Polymer	T_g ($^\circ\text{C}$)	T_m ($^\circ\text{C}$)	T_i ($^\circ\text{C}$)	ΔT ($^\circ\text{C}$)	Texture
I	65	84	175	91	Grainy
II	52	75	157	82	Grainy
III	50	59	140	81	Nematic
IV	Not observed	54	118	64	Nematic
V	Not observed	50	105	55	Nematic

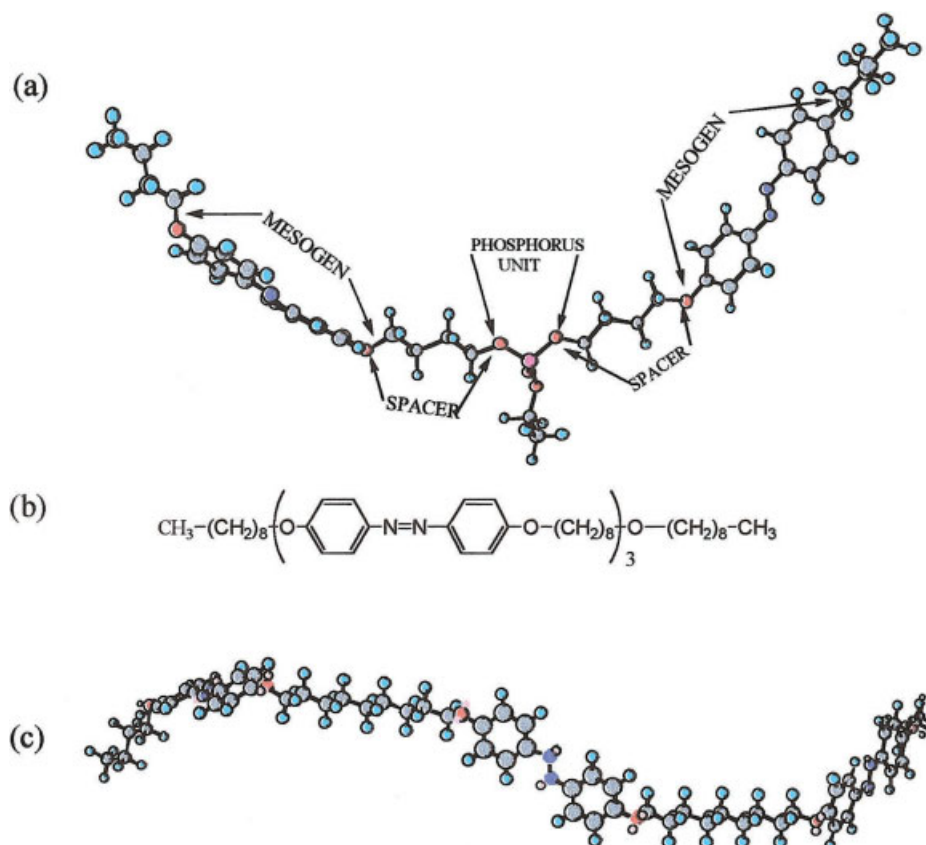


Figure 7 (a) Energy-minimized structure of polymer II, (b) structure of the model compound, and (c) energy-minimized structure of the model compound.

clearly indicated that these polymers could be suitably exploited for optical data storage devices.

CONCLUSIONS

A series of azobenzene-containing polyphosphates were synthesized by the solution polycondensation method.

The structures of the polymers were confirmed with various spectral techniques. HOPM studies revealed that all the polymers had liquid-crystalline properties, and this was further confirmed by DSC data. The TGA results showed that the polymers were stable up to 200–320°C. The char yield of polymers I–V was quite high and was related to the formation of phosphoric acid. The results derived from molecular modeling studies supported the experimental data. The UV irradiation analysis revealed the suitability of these polymers for optical data storage applications.

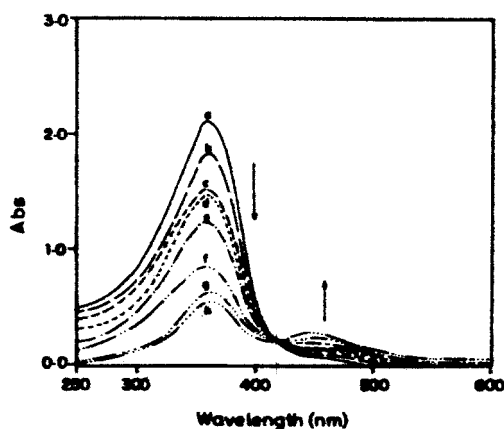


Figure 8 UV absorption spectra of polymer III before and after irradiation: (a) before irradiation, (b) after 20 s, (c) after 40 s, (d) after 60 s, (e) after 80 s, (f) after 100 s, (g) after 120 s, and (h) after 140 s.

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