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Stilbene-based liquid crystalline and photocrosslinkable polynaphthylphosphate esters

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Abstract A series of liquid crystalline and photocrosslinkable polymers were synthesized from 4,4′-bis (m-hydroxyalkyloxy)stilbene ($m = 2, 4, 6, 8, 10$) with naphthylphosphorodichloridate. The synthesized polymers were characterized by spectroscopic techniques. Thermogravimetric analysis revealed that the polymers were stable between 283 and 341 °C, then underwent two-stage decomposition, and char yield increased with decreasing spacer length. DSC and HOPM analysis disclosed that the polymers **III**–**V** ($m = 6, 8, 10$) exhibited LC phases wherein flexible methylene spacer separates mesogenic alignment and reduces overall rigidity of polymers, while polymers **I** and **II** are unable to show LC phase. The photolysis was studied by UV–visible and fluorescence spectroscopy. The rate of photocrosslinking increases with increase in methylene chain. The fluorescence property decreased with successive UV irradiation in the polymers.

Introduction

The reversible and irreversible photochromic or thermochromic liquid crystalline polymers winning much concern for various applications such as photoresists [1–3], data-storage materials [4], non-linear optics [5, 6], luminescent polymeric sensors [7] and in self-assembled layers [8, 9]. The anisotropic property comprising materials can be obtained by photo polymerization of liquid crystal (LC) molecules with reactive end groups in the macroscopically oriented state. The azobenzene and stilbene chromophores containing polymers possess very good anisotropic property attributed to *cis*–*trans*-isomerization under the influence of UV irradiation [10]. As a result of transformation of stilbene group from *trans* to *cis* form, under UV irradiation, the polarizability of the stilbene molecules were altered, leading to decrease in the birefringence of the anisotropic network [11]. A series of planar and non-planar stilbene derivatives were synthesized by Young et al. [12] and reported that the derivatives of non-planar *trans*-stilbenes possess lower melting points than the planar stilbenes. Rameshbabu et al. [13] synthesized the polymers containing 4,4′-dihydroxystilbene, exhibiting liquid crystalline-cum-photocrosslinking properties. Thermal stability and solubility of the polymers were much altered by introducing various methylene chain lengths along the polymer backbone [14, 15].

On the other hand, solubility, flexibility, stability, flame retardancy, adhesive properties of the polymers may be altered by introducing phosphate group into the polymer backbone [16, 17]. Organophosphorus molecules demonstrated their good ability in flame retardancy and proved to generate less toxic gases and low smoke during combustion for environmental and health consideration than the halogen-containing counterparts [18–21]. The shrinkage during crosslinking was also found to be lower for polyphosphate moieties [22].Our earlier studies described that the incorporation of phosphate units into polymer backbone improved their char yield, flame retardancy, thermal stability with reduced T_g [23, 24].

The combination of liquid crystalline and photocrosslinkable polyphosphate esters, containing stilbene is hitherto unreported in the literature. The present work involves synthesis and characterization of polynaphthylphosphate esters containing *trans*-stilbene moiety. The 4,4′-bis(m-hydroxyalkyloxystilbene) acts as a mesogen-

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cum-photocrosslinkable segment in the polymer and naphthylphosphate esters impart improved solubility, flame retardancy and char yield. The effects of methylene spacers in the polymer backbone with respect to rate of photocrosslinking were investigated.

Experimental

Materials

Bromoacetaldehyde diethylacetal, 1,4-chlorobutanol, 1,6-hexanediol, 1,8-octanediol, 1,10-decanediol (Aldrich), 2-chloroethanol, 47% HBr, anhydrous potassium carbonate, 1-naphthol (SRL), potassium iodide and anhydrous sodium sulphate (Merck) were used as received. Diethyl ether, methanol, chloroform, tetrahydrofuran (THF), dimethylformamide (DMF), acetone, ethylene glycol, acetic acid, benzene, toluene were purified and dried by usual methods before use [25].

Synthesis of *trans*-4,4′-dihydroxystilbene (DHS)

DHS was synthesized from bromoacetaldehyde diethylacetal and phenol by the reported procedure [26]. To a solution of phenol (0.12 mol) and bromoacetaldehyde diethylacetal (0.06 mol) in 25 mL of glacial acetic acid, concentrated sulphuric acid (13 mL) in glacial acetic acid (15 mL) was added drop wise at 0–5 °C with constant stirring for 45 min. The concentrated solution was then poured into crushed ice and extracted with diethyl ether. The ether solution was washed with water and dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure, resulting in an oily residue. The oily residue was refluxed in a solution of 22.5 g of KOH and 50 mL of ethylene glycol for 1 h. It was then cooled to 60 °C, poured into ice water and acidified with 2 N sulfuric acid. The precipitated product was extracted with ether, washed with water and then extracted with 20% KOH solution. The aqueous layer was acidified with 2 N sulfuric acid and again extracted with ether. The organic layer was then washed with water, dried over anhydrous sodium sulfate and evaporated by vacuum distillation. The residue was recrystallized from acetic acid to give white crystals. Yield: 65%, m.pt. 290–293 °C.

IR (KBr, cm^{-1}): 3400 (phenolic OH), 1600 (*trans* ethylene), 1500 (–CH_2–); ^{1}H-NMR ($DMSOd_6$): 9.4 ppm (s, 2H), 7.42 ppm (d, 4H), 6.93 ppm (s, 2H), 6.85 ppm (d, 4H).

Synthesis of *m*-bromo-1-alkanols

The *m*-bromo-1-alkanols were synthesized by the reported procedures [27, 28]. A typical procedure for the synthesis of 6-bromo-1-hexanol is as follows: 1,6-hexane diol (0.1 mol) and 47% HBr (0.05 mol) solution in 250 mL of benzene were distilled azeotropically until the water was completely removed. Then the benzene layer was washed with 250 mL of 6 N NaOH solution followed by 250 mL of 10% HCl solution and finally with 250 mL of saturated brine solution. The benzene layer was dried with anhydrous sodium sulphate. Benzene was removed by vacuum distillation to yield crude brown-coloured viscous liquid, which on distillation under reduced pressure gave 6-bromo-1-hexanol as colourless oily liquid (yield: 60%). Similarly 8-bromo-1-octanol and 10-bromo-1-decanol were synthesized from the corresponding diols, but toluene was used as solvent instead of benzene.

Synthesis of 4,4′-bis(*m*-hydroxyalkyloxy)stilbene

The monomers were synthesized by the procedure reported elsewhere [13]. A typical procedure for the synthesis of 4,4′-bis(6-hydroxyhexyloxy)stilbene is given bellow. *Trans* 4,4′-dihydroxystilbene (0.05 mol) was dissolved in dry DMF (20 mL). Anhydrous potassium carbonate (0.20 mol) and calculated amount 5 wt% of potassium iodide were added to it. The mixture was heated to 90 °C with constant stirring, 6-bromo-1-hexanol (0.10 mol) was added drop wise to the reaction mixture and allowed to stir for 2 days. The reaction mixture was then cooled to room temperature and poured into ice-cold dilute hydrochloric acid. The precipitated product was filtered, washed and dried in vacuum; yield: 65%. In the similar manner, the remaining monomers were prepared.

Synthesis of 1-naphthylphosphorodichloridate

1-Naphthol (0.1 mol) was refluxed with freshly distilled phosphorusoxychloride (0.3 mol) for 1 h until the HCl evolution ceased. Excess phosphorusoxychloride was distilled off under reduced pressure to get a crude product. Finally the residue was washed with dry hexane to get a brown coloured solid (m.pt. 40 °C; lit. m.pt. 39 °C) [29].

Polymerization

The polymers **I**–**V** were prepared by solution polycondensation method using triethylamine (TEA) as an acid scavenger. A typical procedure for the synthesis of polymer **III**, polybis[4,4′-stilbeneoxy] hexylnaphthylphosphate is as follows: 4,4′-bis(6-hydroxyhexyloxy)stilbene (0.05 mol) was dissolved in dry chloroform (25 mL). Dry triethylamine (0.1 mol) was added under nitrogen atmosphere with constant stirring at room temperature. 1-Naphthylphosphorodichloridate (0.05 mol), dissolved in chloroform (20 mL), was added drop wise to this reaction mixture for a period of 30 min. The solution became homogeneous and the reaction was allowed to continue for 24 h. The reaction mixture was then refluxed for 2 h, concentrated, cooled and poured into excess methanol. The precipitate, thus formed was filtered, dried and reprecipitated in methanol.

Similar procedure was used for the synthesis of other polymers, viz. polybis[4,4′-stilbeneoxy]ethylnaphthylphosphate ester, polybis[4,4′-stilbeneoxy]butylnaphthylphosphate ester, polybis [4,4′-stilbeneoxy]octylnaphthylphosphate ester, polybis[4,4′-stilbeneoxy]decylnaphthylphosphate ester.

Measurements

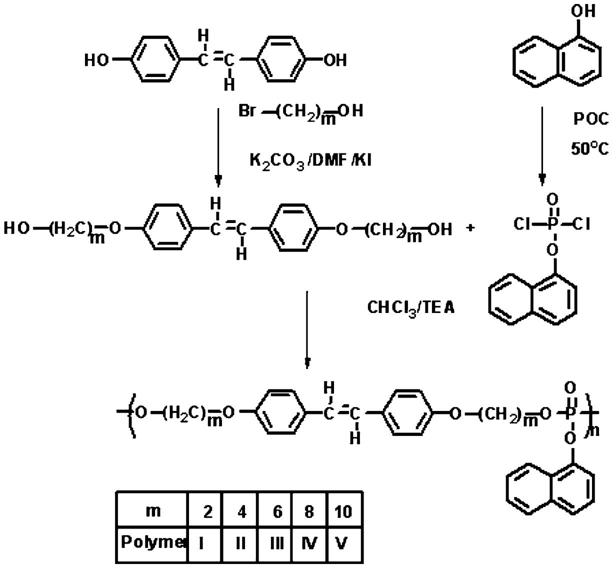
FT-IR spectra of the polymers (**I**–**V**) were recorded on Brucker IFS 66 V Fourier Transform spectrophotometer using KBr pellet. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Brucker spectrometer of 300 and 75.4 MHz, respectively, in DMSO-d_6 using TMS as an internal standard. ^{31}P-NMR spectra were recorded in the same instrument (300 MHz) in DMSO-d_6 under broadband ^{1}H decoupled conditions using D_2O and phosphoric acid (85%) as an external lock and external standards, respectively. The inherent viscosities of the polymers were measured in chloroform (0.5 g/dL) at 30 °C using an Ostwald's viscometer. Thermogravimetric analysis was performed on a mettler TA 3000 thermal analyzer in a dry nitrogen atmosphere at a heating rate of 10 °C min^{-1} with a sample weight of 3–5 mg. The DSC measurements were performed on a mettler Toledo STAR^{e} system for all the polymers in sealed aluminium pans with an empty aluminium pan as a reference under nitrogen atmosphere. The scans were carried out at a heating rate of 10 °C min^{-1}. The LC textures of all the polymers were examined by using Euromex polarizing microscope equipped with a Linkem HFS91 heating stage and a TP-93 temperature programmer. All the polymer samples were placed between two thin microscopic slides. The textures were investigated during heating and cooling at the rate of 5 °C min^{-1}. The photographs were taken with a Nikon FM 10 camera and printed on a Konica film. The photocrosslinking abilities of the polymers were examined in thin film by irradiating under UV light at 260 nm wavelength on a Hitachi U2000 UV spectrophotometer. A typical procedure is as follows. A thin film was formed on the outer surface of a 1 cm quartz cuvette using 10^{-2} M chloroform solution. The photocrosslinking abilities were studied by exposing the film to UV irradiation from a 125 W medium pressure mercury lamp kept at a distance of 10 cm from the sample at various time intervals until the reduction in absorbance was completed. Fluorescence spectra of the polymers were recorded on a Hitachi (Tokyo, Japan) model F2000 spectrofluorimeter with excitation near the absorption maxima of the stilbene moiety, with a resolution of 5 nm for both excitation and emission.

Results and discussion

Synthesis of polymers

Synthesis of polymers is depicted in Scheme 1. The photosensitive *trans* 4,4′-dihydroxy stilbene was synthesized by condensation reaction [26]. 4,4′-bis(*m*-hydroxyalkyloxy)stilbenes, containing even number (m = 2, 4, 6, 8, 10) methylene spacers, were prepared by reacting dihydroxystilbene with *m*-bromo-1-alkanols in DMF. All the polymers obtained by solution polycondensation method at ambient temperature and were solid and powdery. The intrinsic viscosities of the polymers were examined using suspended level Ostwald's viscometer in chloroform at 30 °C and the results are shown in Table 1. The results revealed that all the polymers have moderate molecular masses.

The structure of the polymers was confirmed spectroscopically. The representative IR spectrum of polymer **III** is shown in Fig. 1. The characteristic absorption band at 2937 cm^{-1} is due to the –CH$_2$– stretching. The absorption band at 1607 cm^{-1} is due to the C=C stretching of *trans*-exocyclic double bond. Aryl and alkyl ether stretchings appeared at 1270 cm^{-1} [30, 31]. The absorption bands of P=O stretching and P–O–C aliphatic stretchings appeared at 1271 and 1474 cm^{-1}, respectively. The representative ^{1}H-NMR spectrum of polymer **I** is shown in Fig. 2. The aromatic protons of the stilbene in polymer **I** appeared as multiplets in the region of 6.78–6.86 ppm, the pendant



m	2	4	6	8	10
Polyme	I	II	III	IV	V

Scheme 1 Synthesis of monomers and polymers

Table 1 Yield, viscosity and TGA data of the polymers **I**–**V**

PIolymer	Yield (%)	η [dlg^{-1}]	Temperature for % weight loss		Char yield at 600 °C (%)
			5%	50%	
I	61	0.56	341	465	33
II	64	0.58	319	455	32
III	63	0.60	304	448	28
IV	62	0.62	292	432	26
V	71	0.64	283	425	23

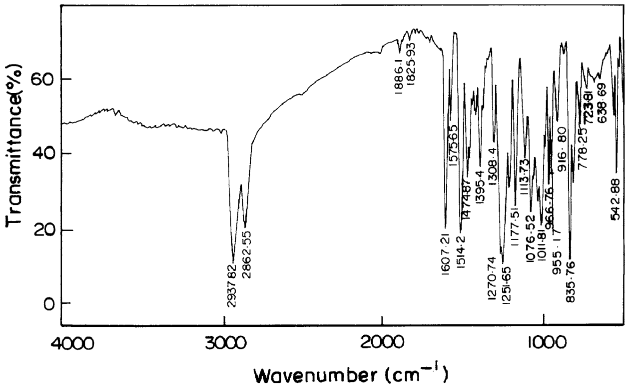


Fig. 1 FT-IR spectrum of polymer **III**

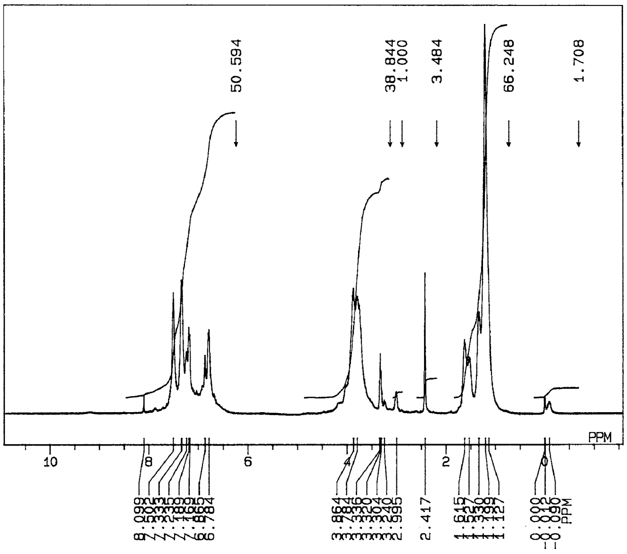


Fig. 2 ^{1}H-NMR spectrum of polymer **I**

naphthyloxy group in the phosphate ester appeared as multiplets in the region of 7.16–8.09 ppm. The ethylenic protons appeared as a singlet in the region of 6.7 ppm [26]. The Ar–O–CH_2 protons appeared as triplet between 3.30 and 3.33 ppm.

P–O–CH_2– protons appeared as triplet between 3.78 and 3.86 ppm. The methylenic protons of the spacers appeared as multiplets in the region of 1.1–1.61 ppm [32]. The representative ^{13}C-NMR spectrum of polymer **IV** is shown in Fig. 3. The aromatic carbons in mesogenic unit appeared in the region of 120–125 ppm, but the same in pendant units resonated in the region of 126–129 ppm. The resonance signal for the methylene carbon (–CH_2–) in spacer appeared in the region of 25–32 ppm. The methylene carbon of P–O–CH_2 and Ar–O–CH_2 resonated at 60 and 67 ppm, respectively [33]. The ^{31}P-NMR spectra of all the polymers showed two signals, the resonance signal corresponding to −20.0 ppm is due to the P atom in the main chain, the signal at −13.0 ppm is due to P atom at the end of the chain [24], which confirmed the incorporation of phosphorus in the polymer backbone.

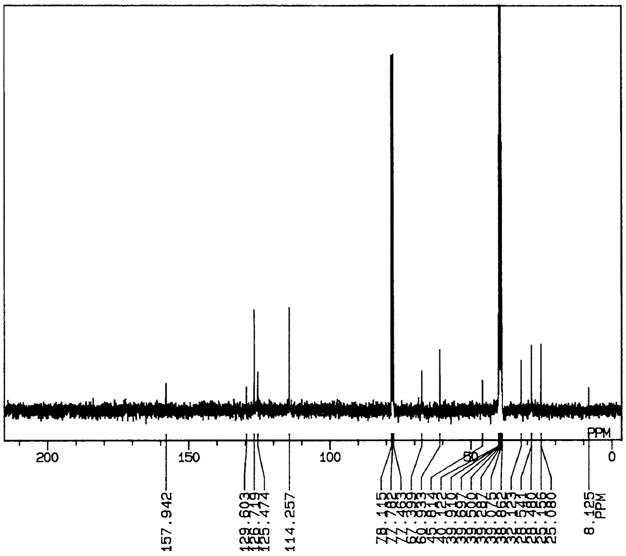


Fig. 3 ^{13}C-NMR spectrum of polymer **IV**

Thermal stability

The thermal stabilities of polymers **I**–**V** were investigated by thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} under nitrogen atmosphere. TGA traces of polymers are shown in Fig. 4. The TGA data are listed in the Table 1. The data revealed that they were stable in between 283 and 341 °C and underwent two-stage decomposition. The first stage decomposition took place in the range of 330 to 370 °C, which is ascribed to cleavage of phosphate esters combined with aliphatic spacers. The second stage

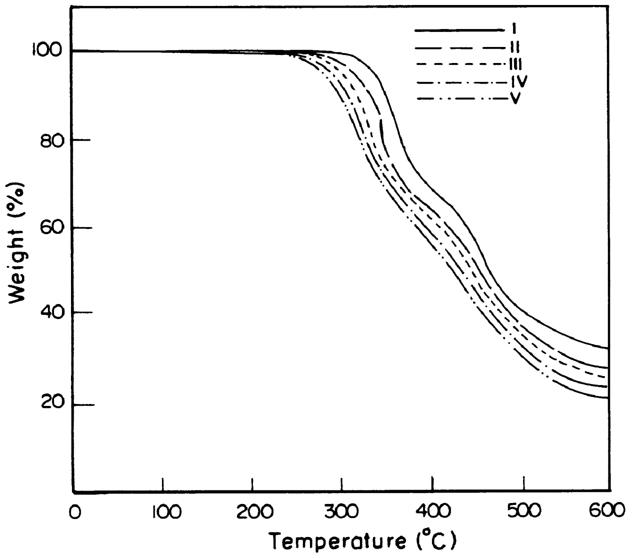


Fig. 4 TGA thermo grams of polymers **I**–**V**

decomposition took place in the range of 375 to 405 °C, attributed the breaking of ether linkage in the aromatic backbone [13, 27]. The decomposition was completed at 600 °C and no further weight loss was observed. In addition, the data indicate that thermal stability decreases with increasing methylene chain length [34].

$$\text{Ethylene} < \text{tetramethylene} < \text{hexamethylene} < \text{octamethylene} < \text{decamethylene}$$

The char yield was calculated from the weight of residual substance present during the TGA analysis. The char yields are given in Table 1, which shows that the char yield increases with decreasing spacer length [35, 36].

$$\text{Ethylene} > \text{tetramethylene} > \text{hexamethylene} > \text{octamethylene} > \text{decamethylene}$$

The char percentage of all the polymers at 600 °C is in the range of 23–33%, is an indication of their flame retardant characteristics. The phosphorus polymers follow condensed phase mechanism by way of leaving large amount char on the surface in the actual fire environment [37]. When the material starts burning, the phosphorus segment decomposes in the initial stage and then form a phosphorus-rich residue as a char layer on the material that prevent further decomposition. The formation of high char yield during combustion of materials can usually limit the production of combustible carbon-containing gases and flow of oxygen and decrease the thermal conductivity of the burning materials, thus the flammability gets reduced.

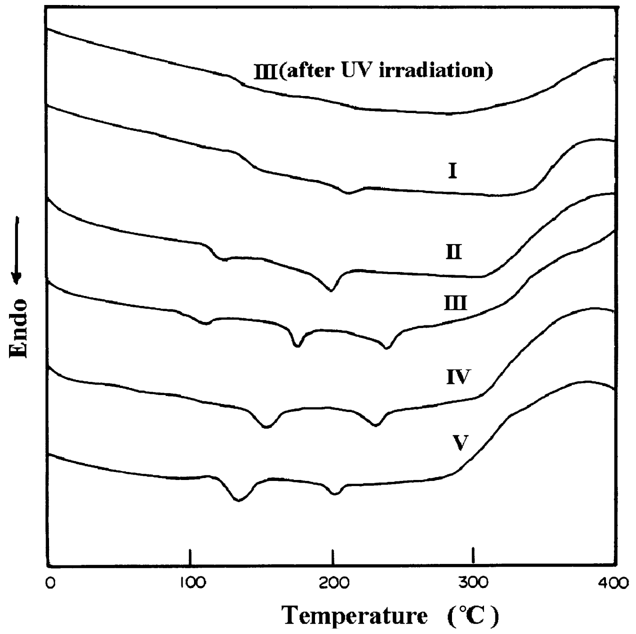


Fig. 5 DSC thermo grams of polymers **I**–**V**

Table 2 DSC and HOPM data of the polymers **I**–**V**

Plolymer	*m*	DSC/°C				HOPM/°C			Types of mesophase
		T_g	T_m	T_i	ΔT	T_m	T_i	ΔT	
I	2	135	210	–	–	211	–	–	–
II	4	123	192	–	–	195	–	–	–
III	6	102	175	238	63	174	239	65	Grainy
IV	8	–	150	227	77	150	229	79	Grainy
V	10	–	129	203	74	131	208	77	Nematic

Thermal and liquid crystalline properties

DSC thermograms of the polymers are shown in Fig. 5 and their phase transition temperatures listed in Table 2. The DSC thermograms confirm the formation of liquid crystalline phases for the polymers **III**–**V**. They showed three endothermic peaks in the range of 102 to 238 °C of T_g, T_m and T_i. The melting transition temperature (T_m) was obtained in the range of 129 to 175 °C and isotropic transition temperature (T_i) in the range of 203 to 238 °C. The ΔT ranges between 63 and 74 °C suggested the stable mesophase of the polymers **III**–**V**. An exothermic peak beyond 350 °C showed the thermal crosslinking of the olefinic bond, which was recognized by stilbene moiety of main chain as reported in the literature [26]. The effect of various methylene spacers on T_g, T_m, T_i are shown in Fig. 6. It shows that the T_g, T_m and T_i decreases with increase in spacer length. The photomicrographs taken on a hot stage optical polarizing microscope (HOPM), during the cooling cycle at 20× are shown in Fig. 7 and observed that lower methylene chain containing polymers **III** and **IV**, exhibited grainy textures while polymer **V** displayed nematic texture. The transition temperatures (T_m and T_i),

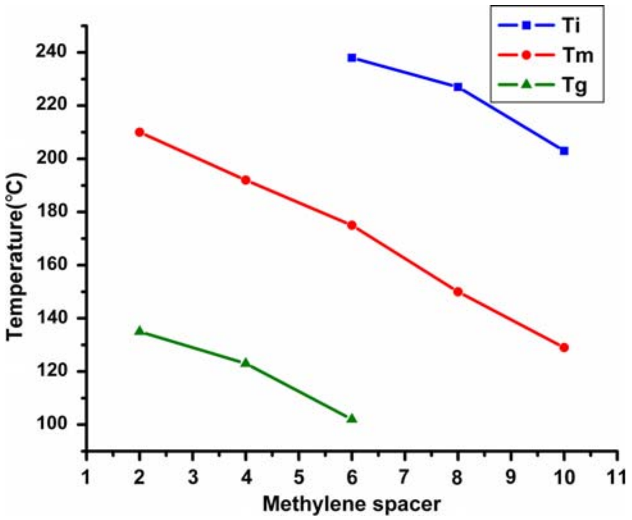


Fig. 6 Effect of methylene spacer on transition temperatures of the polymers **I**–**V**

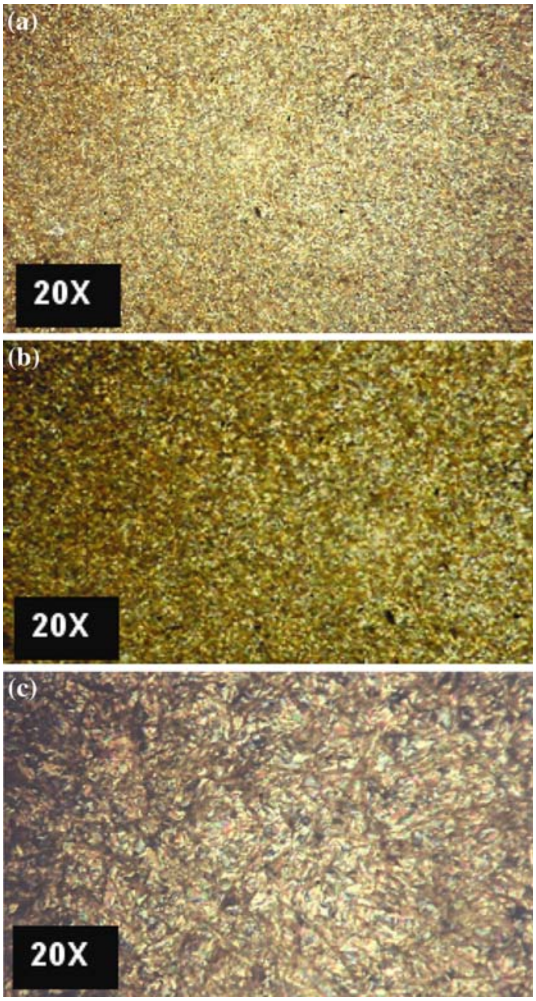


Fig. 7 LC photographs (taken at 20× resolution) of **a** Grainy texture of polymer **III** at 195 °C, **b** Grainy texture of polymer **IV** at 172 °C, **c** Nematic texture of polymer **V** at 153 °C

observed in HOPM, are closely related to the transition temperatures (T_m, T_i) observed in DSC.

The DSC and HOPM studies resolved that the order of liquid crystalline mono domains was increased from the hexamethylene- to decamethylene-containing polymers [37]. The flexible methylene spacer group separates the mesogenic alignment and reduces the overall rigidity of the polymers. Apart from this, incorporation of phosphate ester group also provides extra flexibility to the polymer chain. Thus the polymers **I** and **II** have not exhibited LC property, while **III**, **IV** and **V** exhibited LC textures.

Photo-crosslinking studies

Photocrosslinking abilities of the polymers **I**–**V** were studied in thin films using UV spectrophotometer. Changes in the UV spectral pattern during the photolysis of representative polymers **IV** and **V** are shown in Fig. 8. The absorption bands around 245–280 nm corresponds to π–π^* transition of the olefinic double bond of the mesogenic unit in the polymer backbone. During the successive irradiations, a decrease in intensity of the absorbance was observed. This is due to the photocrosslinking of the olefinic bond of the polymer chains, which involves $2\pi + 2\pi$ cycloaddition reaction leading to the formation of cyclobutane ring [38] as shown in Fig. 9. The relative rates of photocrosslinking of polymers **I**–**V** are shown in Fig. 10. The relative reactivity $(A_0 - A_t)/A_0$ is plotted against the time 't' of irradiation, where A_0 is absorbance before irradiation and A_t is the absorbance after irradiation for time 't'.

Photolysis studies of the polymers, containing various methylene spacers, showed that the rate of photocrosslinking increases in the following order.

$$\begin{aligned}&\text{Ethylene} < \text{tetramethylene} < \text{hexamethylene}\\&\quad < \text{octamethylene} < \text{decamethylene}.\end{aligned}$$

It is interesting to note that the rate of reduction of exocyclic double bond during the photolysis is faster for longer methylene chain than the shorter methylene chain bearing polymers [24]. Thus the rate of crosslinking was slower for the polymer **I**, containing ethylene unit, and the absorption band at 280 nm completely disappeared in 20 min. But, the rate of crosslinking was faster for the polymer **V**, containing decamethylene unit, and the absorption band at 245 nm was completely disappeared within 10 min. After completion of the photolysis study, the film was insoluble in chloroform solvent. The irradiated samples were further subjected for HOPM and DSC analysis and found that they lost their LC properties with increase in transition temperatures. The DSC thermogram of irradiated polymer **III** is depicted in Fig. 5. It was noticed that the T_g of the polymer was shifted to higher

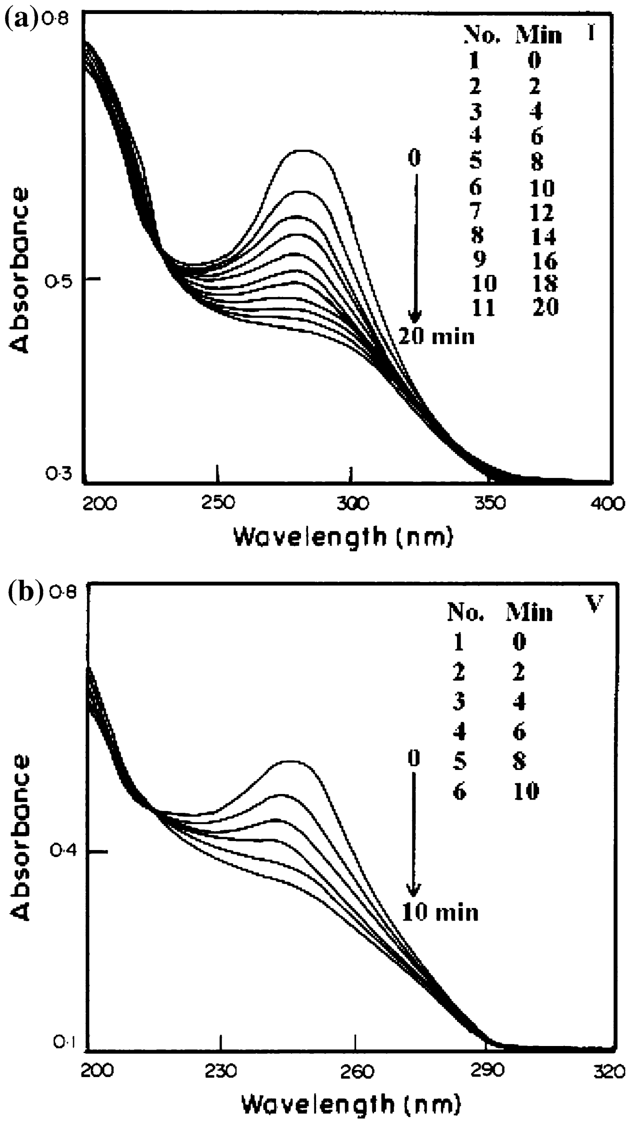


Fig. 8 UV spectral changes during the photolysis of polymers **I** (**a**) and **V** (**b**) irradiated by 260 nm of UV light at various time intervals

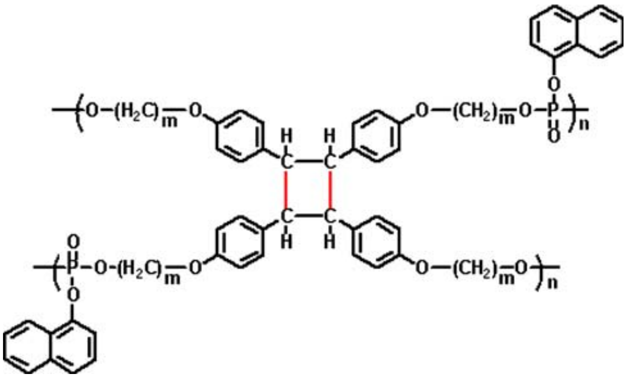


Fig. 9 Schematic representation of the chemical structure of the polymer main chain after ($2\pi + 2\pi$) cycloaddition reaction involves cyclobutane formation

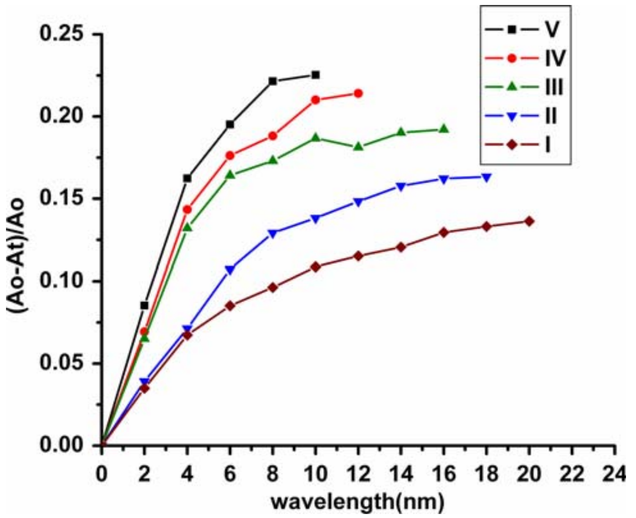


Fig. 10 Rate of photolysis on irradiation at different time intervals of polymers **I**–**V**

temperature. In addition to that, T_m observed for the same sample before irradiation was disappeared and T_i was observed at a higher temperature with decomposition. This confirms the photocrosslinking reaction of the LC polymers which indicates the formation of crosslinked product.

The fluorescence analysis is an important tool for investigating the structure of the polymers. It is acknowledged that the isomerization of *cis*-configuration causes loss of the fluorescence properties. Fluorescence spectra of the polymers **I**–**V** were investigated in thin films with constant excitation at 260 nm for various time intervals. The fluorescence emission was recorded at 350–550 nm. The representative fluorescence spectrum for the polymers **IV** and **V** are shown in the Fig. 11.

The decrease in intensity of emission, on successive irradiation shows that the effect of dimerization of the olefinic double bond and isomerization of *cis*-configuration. It has been designated that the degree of overlapping between two mesogen moieties depends on their spacer lengths. The polymer with longer spacer lengths shows larger red shifts in wave length for fluorescence than those for the polymer with shorter spacer lengths. This is due to the mobile packing structure with more flexible and longer spacer lengths. The degree of overlapping between two stilbene moieties for polymers **I**–**V** was confirmed to decrease with increasing methylene units [39].

Conclusion

A series of liquid crystalline and photocrosslinkable polymers with different methylene chain lengths were synthesized by solution polycondensation and characterized. The intrinsic viscosity data for all the polymers show that the

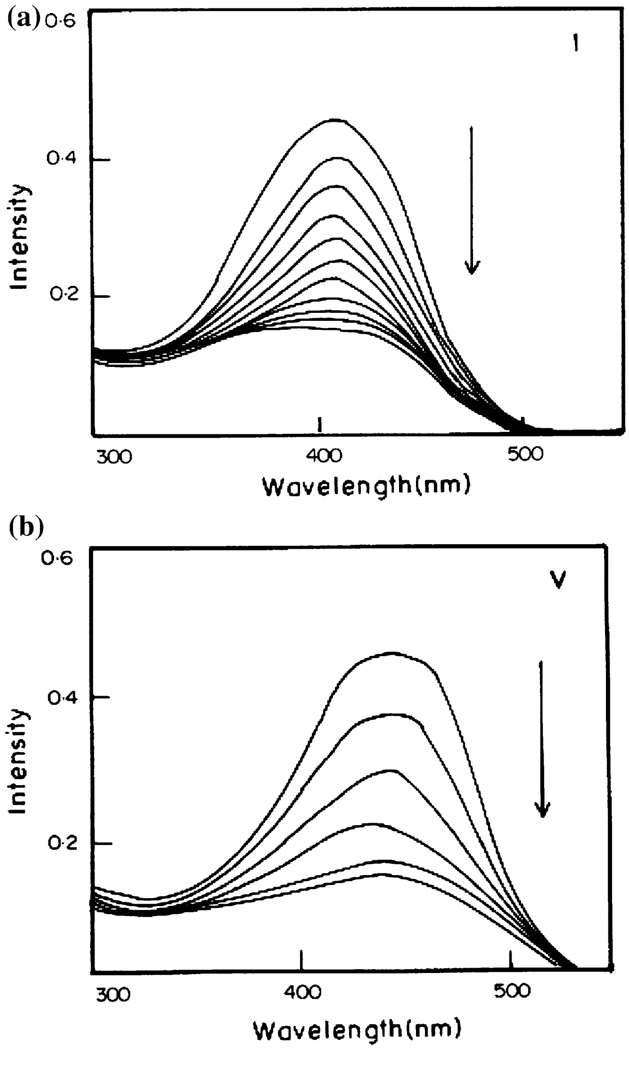


Fig. 11 Fluorescence spectra of the polymers **I** (**a**) and **V** (**b**) recorded at 300–550 nm with constant excitation at 260 nm

polymers have moderate molecular masses. Thermogravimetric analysis revealed that all the polymers were stable between 283 and 341 °C. The polymers **III**–**V** exhibited liquid crystalline behavior, which was confirmed by the DSC analysis. The thermal stability, T_m and T_i of the polymers were decreased with increase in number of methylene chain in the polymer backbone. The photocrosslinking property of all the polymers were examined by UV spectroscopy, the crosslinking proceeds through 2π–2π cycloaddition reaction of the olefinic group present in the mesogen. Fluorescence properties of all the polymers were confirmed and also the intensity of the emission spectra of all the polymers found to decrease at different interval of time.

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