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Thermotropic liquid crystalline-*cum*-photocrosslinkable poly(benzylidene arylphosphate ester)s containing the cyclopentanone moiety

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A new class of linear unsaturated polyarylphosphate esters based on dibenzylidene cyclopentanone, possessing liquid crystalline-cum-photocrosslinkable properties has been synthesized from 2,5-bis(*m*-hydroxyalkyloxybenzylidene)cyclopentanone (m=6,8,10) with various aryl phosphorodichloridates (aryl=phenyl, naphthyl, biphenyl) in chloroform at ambient temperature. Their chemical structures were confirmed by FTIR, and ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. Intrinsic viscosity showed that all the polymers were materials of moderate molecular mass. Phase behaviour was investigated with differential scanning calorimetry and hot stage polarizing optical microscopy, under which all the polymers showed anisotropic behaviour. The T_{m} and T_{i} of the polymers decreased with the increasing flexible methylene chain in the polymer backbone. The thermal behaviour of the polymers was studied by thermogravimetric analysis, and their photocrosslinking properties investigated by UV spectroscopy. The crosslinking proceeds via 2π–2π cycloaddition reactions of the dibenzylidene exocyclic double bond of the polymer backbone. The pendant biphenyloxy-containing polymers show faster crosslinking than the pendant naphthyloxy- and phenyloxy-containing polymers. The rate of crosslinking increases as the methylene chain lengthens in the polymer backbone.

1. Introduction

Chalcone has been widely used as a mesogen in liquid crystalline polymers (LCPs) [1]; it is a well-known photosensitive chromophore, which undergoes photocrosslinking and thermal crosslinking [2]. The bis(benzylidene) group has been utilized for its dual functionality as a mesogen-*cum*-photocrosslinkable segment in polymers. The anisotropic properties of liquid crystalline-*cum*-photocrosslinkable polymer films find applications in the fields of optical photolithography, fabrication of anisotropic networks and thin films, optical data storage and information display [3–7]. Nayef synthesized an interesting new class of linearly unsaturated polyesters and copolyesters based on bis(benzilidenecycloalkanones) by a high yield interfacial polycondensation at ambient temperature [8].

A flexible photocrosslinkable main chain liquid crystalline polymer consists of mesogenic units separated by flexible spacers, which usually consist of polymethylene chains [9]. These polymers have been the focus of considerable research interest, not only for their technical potential but also on a more fundamental level, because they exhibit a range of unusual liquid crystalline behaviour. Kricheldorf reported the thermotropic liquid crystalline poly(arylphosphate esters) for use in high performance fibres, and it was observed that the T_{g} of the polymers decreased with increase in the phosphorus content [10]. In earlier studies, we demonstrated that the introduction of the phosphate group into the polymer backbone improved their solubility due to its polarity and high char yield [11–13].

A literature survey reveals that investigations on the synthesis of photocrosslinkable liquid crystalline polymers are scarce [14]. The liquid crystalline-*cum*-photocrosslinkable polyarylphosphate esters containing the cyclopentanone moiety are hitherto unreported. In the present work, we proposed to synthesize and characterize new liquid crystalline-*cum*-photocrosslinkable benzylidene-containing poly(arylphosphate ester)s directly attached through a flexible spacer. The arylphosphate esters impart improved solubility and flame retardant properties. The effect of the methylene spacer and pendant aryl group in the polymers with respect to the rate of photocrosslinking was evaluated.

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2. Experimental

2.1. *Materials and methods*

Cyclopentanone (Merck), vanillin (Merck), boron triflouride diethyl etherate (Fluka), phosphorus oxychloride (Fluka), triethylamine (TEA), and phenol, 1-naphthol and 4-phenylphenol (SRL) were used without further purification. Methanol, ethanol, chloroform, dimethylformamide, dimethylsulphoxide and other solvents were purified by reported procedures [15]. *m*-Bromoalkanols ($m=6,8,10$) were prepared according to the reported procedure [16, 17]. 2,5-Bis(benzylidene)cyclopentanone (BVCP) was synthesized by the reaction of vanillin with cyclopentanone in the presence of acid catalysts in absolute ethanol [18].

2.2. *Synthesis of monomers*

2.2.1. 2,5-Bis[4-(*m*-hydroxyalkyloxy)benzylidene]cyclopentanone (*m*=6,8,10). All the title monomers were synthesized by condensation reactions. In a typical Williamson aryl ether procedure for the synthesis of 2,5-bis[4-(6-hydroxyhexyloxy)benzylidene]cyclopentanone (BHHVCP), BVCP (3.52 g, 10 mmol) was dissolved in dry dimethylformamide (20 ml), and potassium carbonate (4.95 g, 50 mmol) added. Bromohexanol (3.33 ml, 30 mmol) was then added dropwise and the reaction mixture was stirred for 24 h at 90°C; the formation of alkylated product was monitored by TLC (chloroform/methanol, 90/10). At the end of the reaction, the mixture was cooled and poured over crushed ice to obtain a yellow precipitate. The product was recrystallized from ethanol/water mixture (50/50); yield 85%, m.p.155°C. The other homologous diols were prepared in a similar manner. IR (KBr): 1678 (cyclopentanone C=O), 3395 (OH) and1585 cm^{-1} (exocyclic C=C). ^{1}H NMR: δ 7.5(s, 2H, OH), 6.7–7.3(m, 6H, aromatic), 6.0(s, 2H, –CH=CH–), 3.9(s, 6H, OCH_3), 3.5(t, 8H, OCH_2 spacer), 2.8(s, 4H, CH_2), 1.8–2.5(m, 16H, CH_2). ***m*=8** (HOVCP): yield 82%, m.p.149°C. IR (KBr): 1675 (cyclopentanone C=O), 3400 (OH) and 1583 cm^{-1} (exocyclic C=C). ^{1}H NMR: δ 8.2(s, 2H, OH), 6.9–7.5(m, 6H, aromatic), 6.0(s, 2H, –CH=CH–), 3.9(s, 6H, OCH_3), 3.4(t, 8H, OCH_2 spacer), 2.9(s, 4H, CH_2). 1.6–2.4(m, 24H, CH_2). ***m*=10** (HDVCP): yield 80%, m.p.144°C. IR (KBr): 1670 (cyclopentanone C=O), 3406 (OH) and 1578 cm^{-1} (exocyclic C=C). ^{1}H NMR: δ 6.9–7.3(m, 6H, aromatic), 7.9(s, 2H, OH), 5.8(s, 2H, –CH=CH–), 3.9(s, 3H, OCH_3), 3.1(t, 8H, OCH_2 spacer), 2.9(s, 4H, CH_2). 1.8–2.6(m, 32H, CH_2).

2.2.2. Arylphosphorodichloridates (aryl=phenyl, biphenyl, naphthyl). In a typical preparation of the phenyl derivative, freshly distilled phenol (0.1 mol, 9.5 g) was added to phosphorus oxychloride (0.3 mol, 46 g) and the mixture slowly heated to 50°C with stirring. The reaction was continued at that temperature, with evolution of HCl for 1 h; the temperature was then slowly raised to a gentle reflux and held until the HCl evolution ceased. Excess phosphorus oxychloride was distilled off under reduced pressure to leave a crude oily product. This was redistilled under reduced pressure to give a pure colourless liquid, b.p.104–106°C/2 mm Hg [19]. It was used immediately in the polymerization reaction.

2.3. *Synthesis of poly{2,5-bis[4-(m-alkyloxy)benzylidene]cyclopentanone arylphosphate ester}s(m=6,8,10; aryl=phenyl, naphthyl, biphenyl)*

All the photoreactive polymers were synthesized by solution polycondensation at ambient temperature. A typical procedure, for the preparation of poly{2,5-bis[4-(6-alkyloxy)benzylidenecyclopentanone phenylphosphate ester} (Ia) is as follows: BHHVCP (0.256 gm, 10 mmol) was dissolved in chloroform (20 ml) under nitrogen; TEA (20 mmol) was added and the mixture stirred. Phenylphosphorodichloridate (0.9 g, 10 mmol) was dissolved in the same solvent (20 ml), and the solution added dropwise to the reaction mixture; stirring was continued for 24 h at ambient temperature. The formation of products was monitored by TLC (chloroform/methanol, 90/10). At the end of the reaction, the mixture was concentrated to 10 ml, cooled and the polymer solution poured into excess of methanol. The yellow precipitate thus formed was purified by reprecipitation using chloroform/methanol and washed with *n*-hexane; the solid polymer material was then filtered and dried in a vacuum oven at 50°C to give 70% yield. The remaining homologous polymers (**Ib–IIIc**) were prepared in a similar manner.

2.4. *Characterization*

The infrared spectra were obtained with a Brucker IFS 66V Fourier transform spectrophotometer using KBr pellets. High resolution ^{1}H and ^{13}C spectra were recorded on a Brucker spectrometer of 300 MHz and 75.4 MHz for proton and carbon-13, respectively in $CDCl_3$; TMS was used as internal standard. ^{31}P NMR spectra were recorded on the same instrument (300 MHz) in $CDCl_3$ under broadband ^{1}H decoupling conditions. D_2O and phosphoric acid (85%) were used as an external lock and external standards, respectively.

Viscosity was measured using an Ubbelohde viscometer in a constant temperature bath at 30°C ± 0.5°C, with attached timer to measure the time needed for the solvent and polymer solution to flow through the capillary tube. The polymer solutions were prepared with concentrations around 0.5 g dl^{-1} in chloroform.

Thermogravimetric analysis was performed on a Mettler TA3000 thermal analyser under nitrogen at a heating rate of 20°C min^{-1}, and with a sample weight of 3–5 mg. DSC measurements were performed on a Mettler Toledo STAR^{e} system; all the synthesized polymers were scanned using unsealed aluminium pans under dry nitrogen, with an empty aluminium pan as reference. The scans were carried out at a heating rate of 10°C min^{-1}. The second DSC heating cycle was recorded for all the polymers.

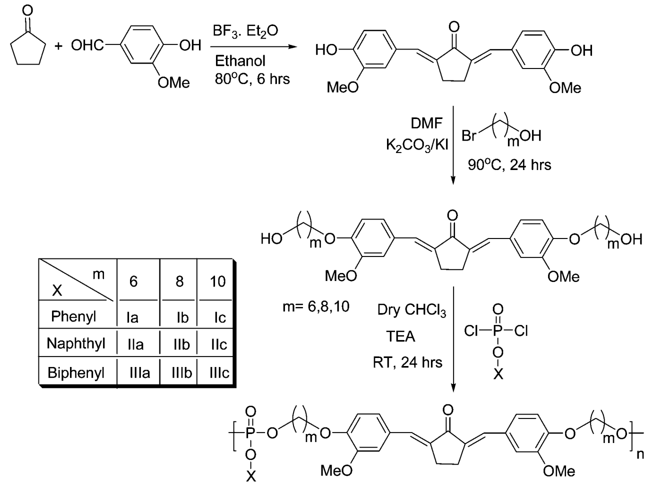
The textures of all the prepared samples were studied using a Euromax polarizing microscope equipped with a Linkam HFS91 heating stage and a TP-93 temperature programmer. Samples were prepared by melting a small quantity of the material between two thin glass cover slips to give a uniform film, and the anisotropic behaviour was observed while heating or cooling at 5°C min^{-1}. Photomicrographs were taken with a Nikon FM10 camera using Konica film.

The photocrosslinking ability of the polymers was investigated on film samples, observing the absorption in the range of 370–408 nm on a Hitachi U2000 UV spectrophotometer. In a typical procedure, a thin film was formed on the outer surface of a 1 cm quartz cuvette using 10^{-2} M chloroform solution. The photochemical studies were carried out in a discontinued mode, i.e. the sample was exposed to UV irradiation from a 125 W medium pressure mercury lamp held at a distance of 10 cm from the sample at various intervals of time. Subsequently, the irradiated film was subjected to spectral analysis. The procedure was repeated until there was no reduction in absorbance.

3. Results and discussion

3.1. *Synthesis*

The synthesis and molecular structure of the polymers are shown in scheme 1. The bisbenzylidene moiety, as a photosensitive group, was prepared by the reaction of cyclopentanone and vanillin in absolute ethanol using an acid catalyst. The chain-extended chalcone derivative containing the even number (6–10) methylene spacer group was prepared by the nucleophilic displacement of the potassium salt of BVCP with *m*-bromoalkanols in DMF. All the polymers were prepared by polycondensation of the benzylidenealkyloxy mesogen-containing diol and arylphosphorodichloridates (aryl=phenyl, naphthyl, biphenyl) in chloroform solution at room temperature with good yields. All the polymers are yellow and powdery.



X \ m	6	8	10
Phenyl	Ia	Ib	Ic
Naphthyl	IIa	IIb	IIc
Biphenyl	IIIa	IIIb	IIIc

Scheme 1. Synthesis of monomers and polymers **Ia**–**IIIc**.

The solubility of the polymers is an important requirement for the particular use of these polymers; the solubility of the prepared polymers in various solvents was therefore tested. All the polymers were freely soluble in chlorinated solvents such as $CHCl_3$, CH_2Cl_2 and chlorobenzene, and in polar aprotic solvents such as DMF, DMSO, THF and *N*-methylpyrrolidene. They were insoluble in alcohols such as methanol, ethanol and 2-propanol, and in hydrocarbons such as benzene and toluene. The good solubility in polar organic solvents may be attributed to the polarity and flexibility of the phosphorus linkage and methylene spacer, respectively in the polymer backbone [20]. The intrinsic viscosity of the polymers was determined using an Ubbelohde viscometer with chloroform as a solvent at 30°C. The results are shown in figure 1 and the data are given in table 1. The intrinsic

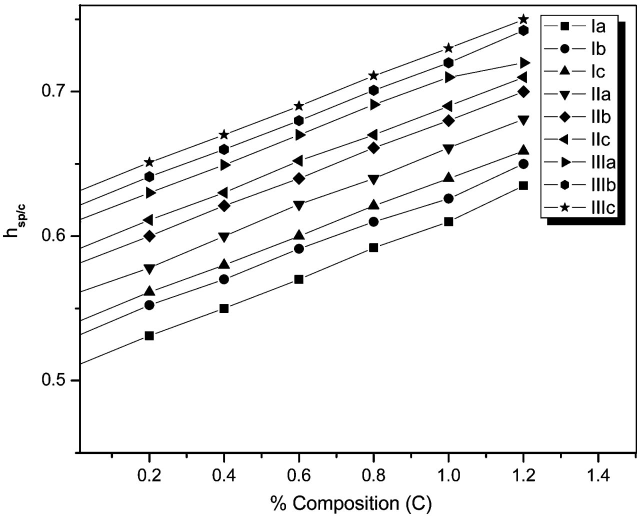


Figure 1. Viscosity plots of polymers **Ia**–**IIIc**.

Table 1. Yield, viscosity and TGA data of polymers **Ia**–**IIIc**.

Polymer	*m*	[η] (dLg^{-1})	Temperature for % weight loss °C 5%	50%	Total weight loss at 500°C %	Char yield at 500°C %
Ia	6	0.51	260	343	76	24
Ib	8	0.53	255	334	78	22
Ic	10	0.54	240	313	82	18
IIa	6	0.56	343	420	74	26
IIb	8	0.58	324	410	75	25
IIc	10	0.59	311	396	79	21
IIIa	6	0.61	347	438	73	27
IIIb	8	0.62	328	433	74	26
IIIc	10	0.63	315	425	78	22

viscosity results reveal that all the polymers are of moderate molecular mass.

The infrared spectra of the polymers **Ia**–**IIIc** showed characteristic bands around 1650–1689 and 1564–1596 cm^{-1}, pertaining to the keto carbonyl and exocyclic double bond of the polymer backbone, respectively. The characteristic –CH$_2$– stretching bands appeared in the range 2816–2855 and 2901–2934 cm^{-1}. In addition, the absorption bands of P=O stretching appeared in the range 1268–1299 cm^{-1}. Aryl and alkyl ether stretching appeared around 1239–1251 cm^{-1} [21]. A representative IR spectrum of polymer Ib is shown in figure 2.

In the ^{1}H NMR spectra of the polymers, the benzylidene aromatic proton appeared as a multiplet in the region 6.91–7.1 ppm; the pendant aryl group in the phosphate ester appeared as a multiplet in the region 7.11–7.6 ppm, the olefinic protons resonating as a singlet at 7.81δ. The O–CH$_2$– linked with a phenyl ring appeared as a triplet around 4.1 ppm, the resonance signal for methoxy protons of the dibenzylidene mesogen appeared as a singlet at 3.91 ppm. The –OCH$_2$– connected to phosphorus resonated as a triplet at 3.6 ppm, while the methylene protons of the spacers appeared as a multiplet in the region 1.31–1.59 ppm [22]. A representative ^{1}H NMR spectrum of the polymer IIc is shown in figure 3.

In the ^{13}C NMR spectra of all the polymers, the C=O group located in the cycloalkanone moiety resonates at 188–196.6 ppm; the exocyclic carbon–carbon double bond appeared at 149 and 150 ppm; aromatic carbons in the pendant units resonated in the regions 129–135 ppm;

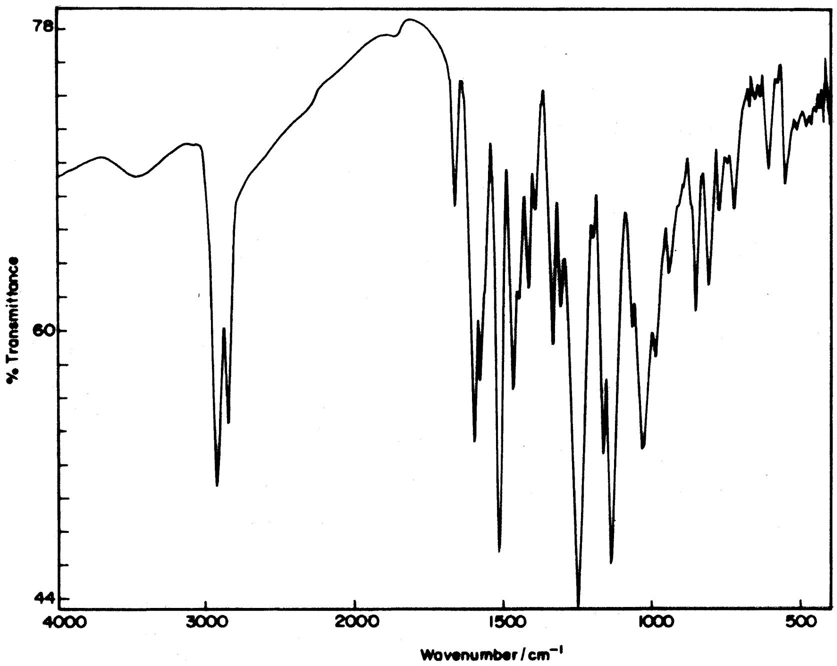


Figure 2. IR spectrum of polymer **Ib**.

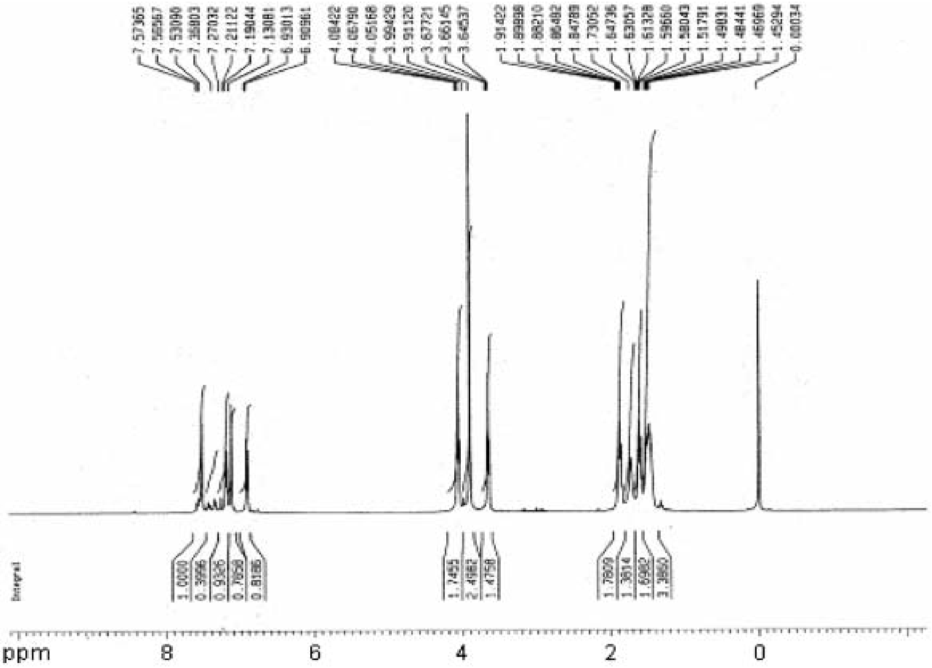


Figure 3. ^{1}H NMR spectrum of polymer **IIc**.

aromatic carbons in the mesogenic units appeared in the region 113–121 ppm, –OCH$_3$ appeared at 55 ppm, and the P–OCH$_2$ and –OCH$_2$ spacer groups resonated at 63 ad 69 ppm respectively. The resonance signal for methylene carbon in the spacer (–CH$_2$–) appeared in the region 21–39 ppm [23]. A representative ^{13}C-NMR spectrum of the polymer IIIa is shown in figure 4.

^{31}P NMR spectra of all the polymers were recorded using triphenylphosphine as an internal standard. All the polymers show two signals due to two different environments of the phosphate group, as there is a possibility of forming copolymer terminated with phosphate ester. Hence the terminal phosphate linkage in the main chain will experience and resonate at two different environments. The phosphorus atom in the

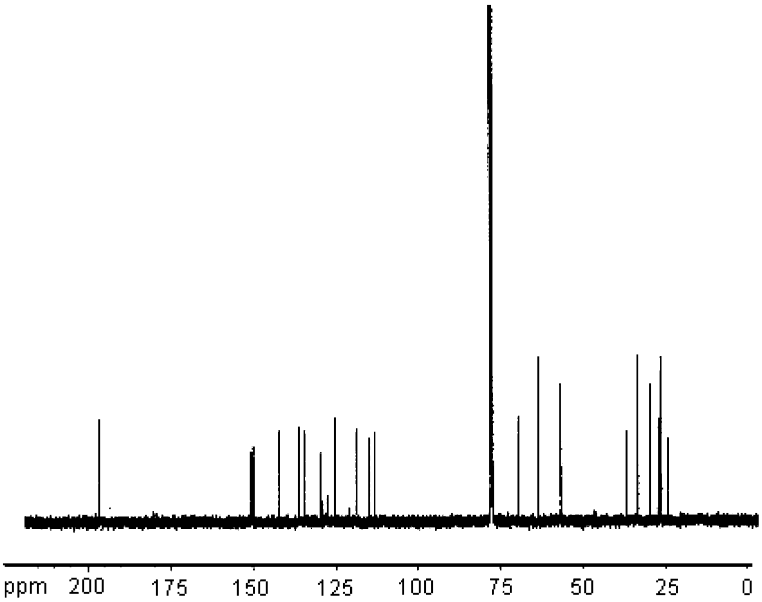


Figure 4. ^{13}C NMR spectrum of polymer **IIIa**.

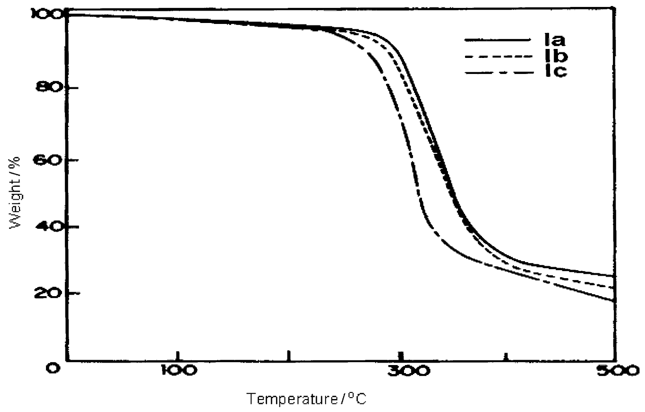


Figure 5. Thermogravimetric traces of polymers **Ia**–**c**.

main chain deshielded and gave one intense signal at −20.15 ppm; another weak resonance signal at −13.30 ppm is due to terminal –P–OH of the polymers [24].

3.2. *Thermal and polarizing microscope studies*

Thermogravimetric analysis was performed on a Mettler TA3000 thermal analyser under nitrogen at a heating rate of 10°C min^{-1}. The TGA traces of the polymers are shown in figures 5–7 and the data are given in table 1. The thermal stability of the polymers was evaluated from 5% weight loss at minimum temperature. The thermogram revealed that all the polymers were stable in the range 240–347°C. A 50% weight loss of the polymers was observed at 313–445°C for all the polymers; decomposition was almost complete around 500°C, after which no weight loss was observed. The data reveal that the thermal stability decreases with increasing methylene chain length [25]. On the other hand, thermal stability increased with increasing size and rigidity of the pendant aromatic groups attached through the phosphorus atom in the polymeric chain. It follows the trend: phenyloxy< 1-naphthyloxy<biphenyloxy.

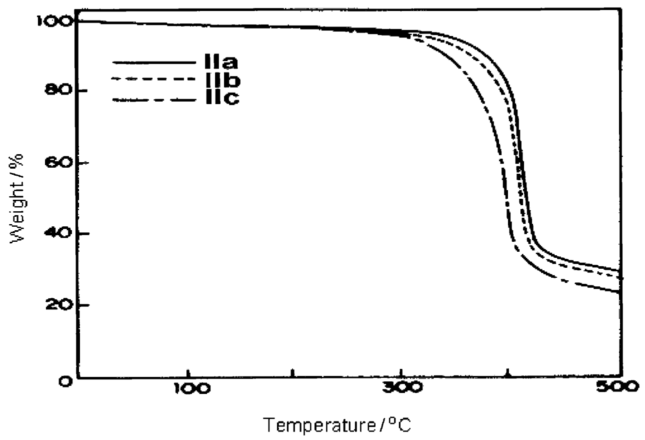


Figure 6. Thermogravimetric traces of polymers **IIa**–**c**.

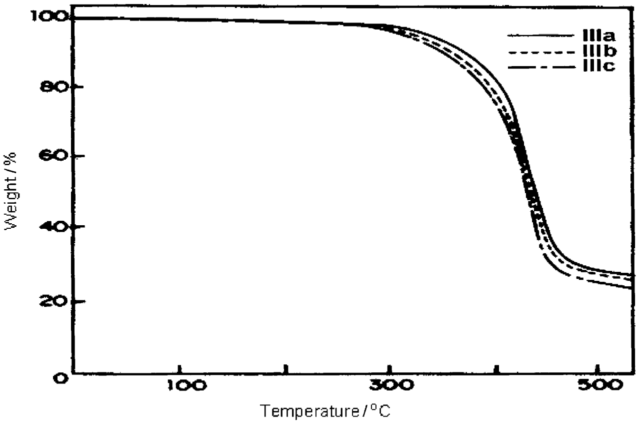


Figure 7. Thermogravimetric traces of polymers **IIIa**–**c**.

It is noteworthy that 1-naphthyloxy- and biphenyloxy-containing polymers were more stable than phenyloxy-containing polymers (table 1), due to the increase in size and number of aromatic rings. It is interesting to note that although the 1-naphthyloxy- and biphenyloxy-containing polymers vary considerably in size, aromaticity and number of carbons, little variation is seen in the initial decomposition temperature. The 1-naphthyloxy-containing polymers are less stable (**IIa**=343°C) than biphenyloxy-containing polymers (**IIIa**=347°C). This may be ascribed to the steric hindrance offered by the *peri*-hydrogen in the 1-naphthyl groups, which disrupts the close packing in the crystal lattice of the polymer chain and causes a lowering in thermal stability.

The char yield was calculated from the weight of residual substance present during TGA analysis. The char yield increased with decreasing spacer length (hexamethylene>octamethylene>decamethylene) [26, 27]. Char yield of all the polymers is given in table 1. The pendant group played an important role in the char yield, leading to the trend: biphenyloxy>1-naphthyloxy> phenyloxy.

DSC thermograms of all the polymers are shown in figures 8 and 9, and their phase transition temperatures are summarized in table 2. The DSC thermograms confirm the formation of liquid crystalline phases for all the polymers **Ia**–**IIIc**. All the polymers showed two endothermic peaks in the range 72–170°C and one broad exothermic peak around 300°C. The two endothermic peaks correspond to the crystalline–liquid crystalline (T_m) and liquid crystalline–isotropic (T_i) transition temperatures, respectively. The melting transition temperature (T_m) was obtained in the range

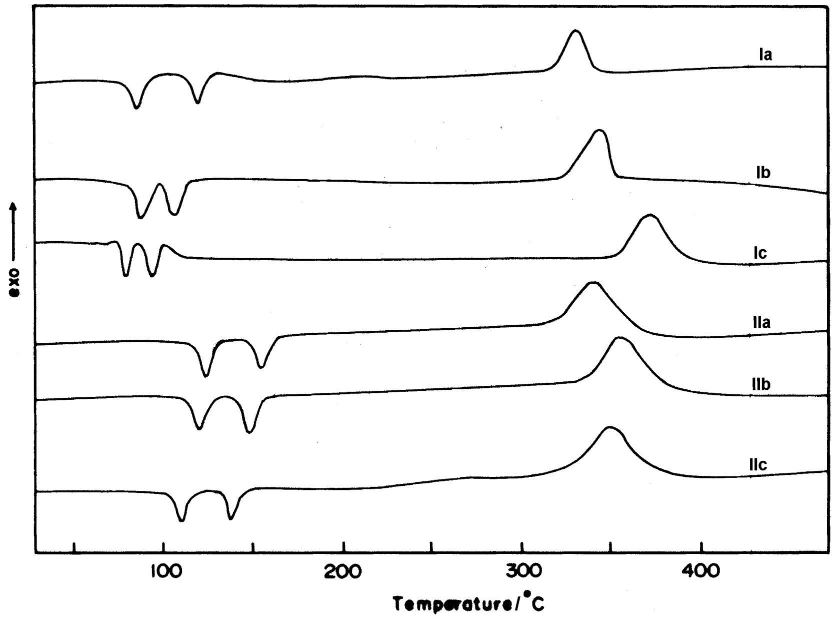


Figure 8. DSC curves of polymers **Ia**–**IIc**.

76–144°C and isotropic transition temperatures in the range 94–170°C. The ΔT data indicated that the polymers exhibit a stable mesophase. In general, T_m and T_i values of LCPs are strongly influenced by the polymeric chain flexibility [28, 29]. The data obtained from DSC thermograms for all our polymers showed that the T_m and T_i decrease as the flexible methylene chain length increases from six to ten methylene units (table 2). In addition, the phase range also decreased with increasing spacer length.

Among the three pendant arylphosphate ester-containing polymers, the naphthyloxy- and biphenyloxy-containing polymers showed higher transition temperature than phenyloxy-containing polymers. While the naphthyloxy- and biphenyloxy-containing polymers have the same number of aromatic rings, the naphthyloxy-containing polymers showed lower T_m and T_i. This may be ascribed to the presence of the more bulky naphthyl group leading to increasingly disordered arrangement, and hence lower phase transition temperatures. All the polymers showed broad exothermic peaks beyond 300°C. This might be attributed to thermal crosslinking leading to cyclobutane ring formation [30, 31].

Representative photomicrographs taken by polarizing optical microscopy (POM) during the first cooling

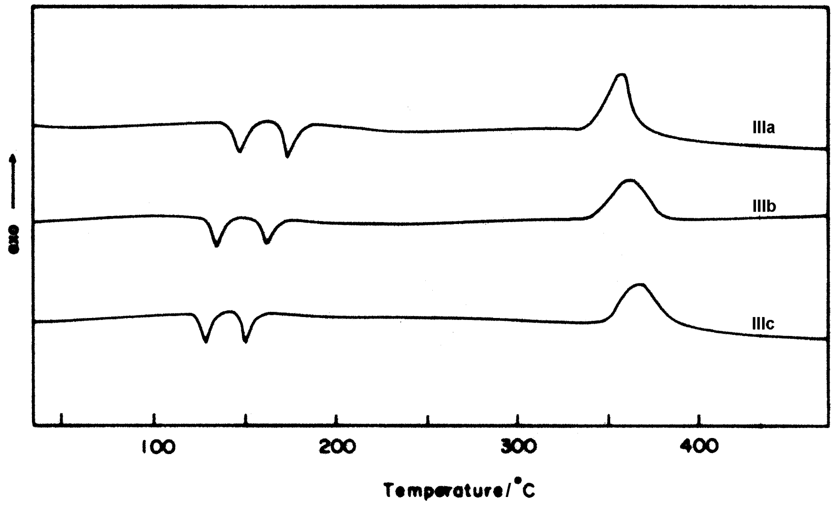


Figure 9. DSC curves of polymers **IIIa**–**c**.

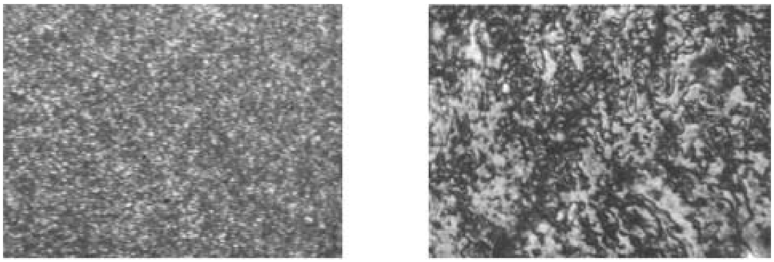
Table 2. Transition temperature (°C) from DSC and POM data for polymers **Ia**–**IIIc**.

		DSC			POM			
Polymer	*m*	T_m	T_i	ΔT	T_m	T_i	ΔT	Type of mesophase
Ia	6	89	112	23	88	113	25	Grainy
Ib	8	80	101	21	80	102	22	Nematic
Ic	10	76	94	18	75	95	20	Nematic
IIa	6	120	151	31	118	150	32	Grainy
IIb	8	118	148	30	117	146	29	Nematic
IIc	10	111	140	29	113	139	26	Nematic
IIIa	6	144	170	26	145	169	24	Grainy
IIIb	8	133	158	25	136	159	23	Nematic
IIIc	10	128	151	23	129	152	23	Nematic

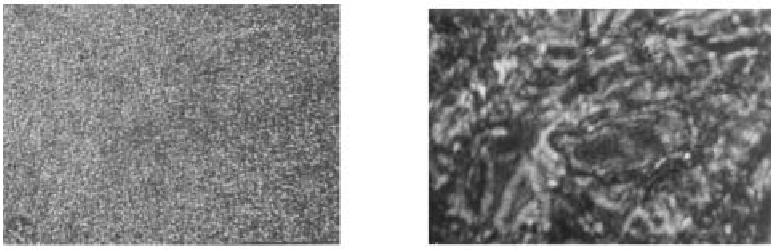
cycle at 20× are shown in figure 10; the type of mesophase is given in table 2. All the polymers exhibited a birefringent melt. The melting point of all the polymers was in the range 70–145°C, with isotropic transitions in the range 85–169°C. The textures were identified and compared with previously observed phases [32, 33]. On cooling from the isotropic melt, the reproducibility of the grainy and nematic textures was satisfactory. The phase transition temperature values noted in DSC thermograms are close to those of the observed in POM. The hexamethylene spacer-containing polymers (**Ia**, **IIa**, **IIIa**) exhibited grainy textures due to their restricted mesogenic movement; whereas, the octamethylene and decamethylene spacer-containing polymers (**Ib**, **Ic**, **IIb**, **IIc**, **IIIa**, **IIIc**) showed nematic textures. The POM results showed that, when the methylene spacer length was increased, they grew as large monodomains by forming nematic textures [34, 35], possibly ascribed to greater segmental mobility leading to separation of the mesogens, one from another.

3.3. *Photocrosslinking studies*

The mesogenic dibenzylidenecycloalkanones contain photosensitive α,β-unsaturated ketone (chalcone) groups that will undergo photocrosslinking; the photocrosslinking ability of the polymers was studied in thin film samples. Changes in the UV spectral pattern during photolysis of representative polymers are shown in



Polymer Ia Polymer IIb



Polymer IIIa Polymer IIIc

Figure 10. Representative liquid crystalline photomicrographs of polymers **Ia**, **IIb**, **IIIa** and **IIIc**, taken during the first cooling at a magnification of 20X.

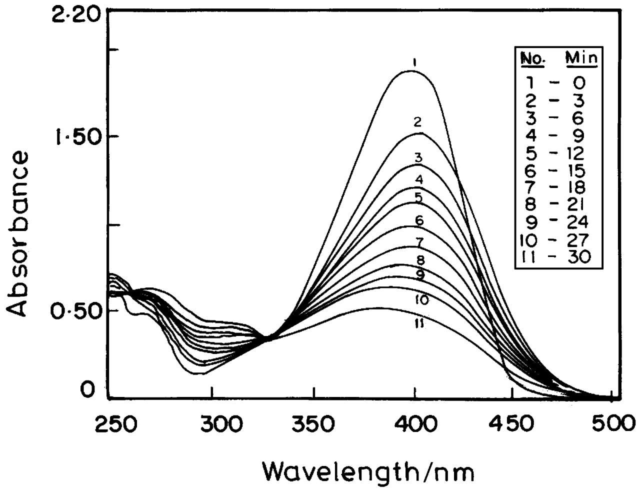


Figure 11. Changes in UV spectral characteristics during the photolysis of polymer Ia at various intervals of time.

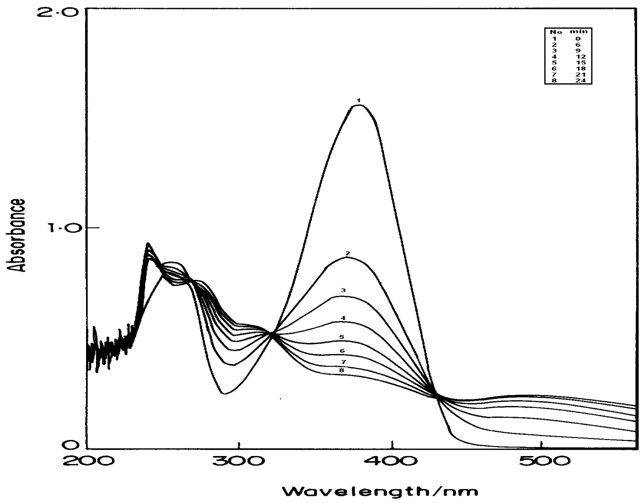


Figure 12. Changes in UV spectral characteristics during the photolysis of polymer IIIc at various intervals of time.

figures 11 and 12. The absorption band around 380–408 nm corresponds to the π–π* transition of the olefinic double bond of the mesogenic unit in the polymer backbone. During further irradiation a decrease in intensity of the absorption was observed. This may be due to dimerization of the olefinic double bond of the polymer chain, which involves 2π+2π cycloaddition reactions leading to the formation of the cyclobutane ring, shown in figure 13 [36, 37]. The relative rate of photocrosslinking of the polymers is shown in figures 14–16. The relative reactivity A_o-A_t/A_o is plotted against the time of irradiation (min), where A_o is the absorption before irradiation and A_t after irradiation, for time t. Photolysis studies of various methylene spacer-containing polymers showed that the rate of photocrosslinking of exocyclic double bonds of the various polymers increases in the following order: hexamethylene<octamethylene<decamethylene.

The photocrosslinking rate becomes greater with the increase in methylene units from six to ten in the polymer chain. This may be attributed to the folding tendency of the methylene units present in the chain, which brings the benzylidene units closer, leading to a faster photocrosslinking reaction. Polymer (**Ia**), containing the hexamethylene unit crosslinked at a slow rate, and the absorption band at 408 nm completely disappeared within 30 min (figure 10); on the other hand, polymer (**IIIc**), containing the decamethylene unit crosslinked at a much faster rate, and the absorption band at 380 nm completely disappeared within 24 min (figure 11).

The photolysis studies of arylphosphate ester-containing polymers showed a decreasing that the photocrosslinking rate in the following order: biphenyloxy>1-naphthyloxy>phenyloxy. It showed be noted that the photocrosslinking is much faster for the biphenyloxy-containing polymer than for the

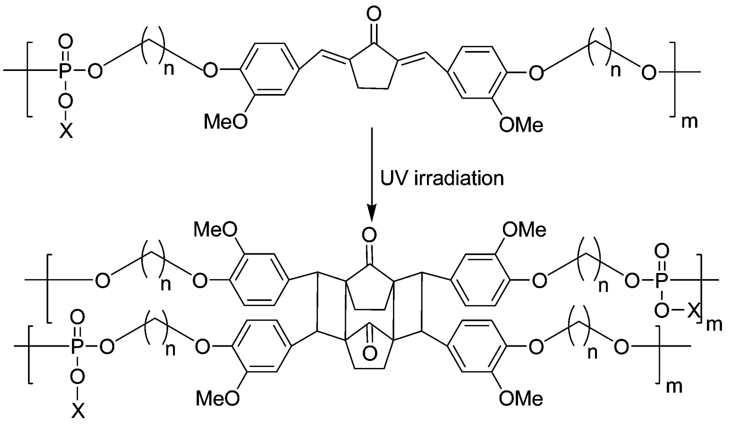


Figure 13. Photochemical reactions (2π+2π cycloaddition) of polymers.

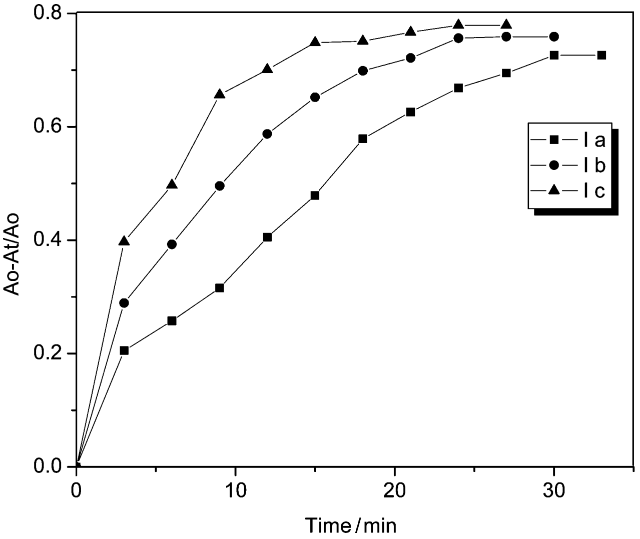


Figure 14. Rate of photolysis vs irradiation time for polymers **Ia–c**.

naphthyloxy- and phenyloxy-containing polymers. This may be due to the biplanarity of the biphenyl ring, where the two phenyl rings are perpendicular to each other, thus allowing closer packing of chains (through higher π–π interactions of the two aromatic rings) than in the naphthyloxy- and phenyloxy-containing polymers. The naphthyloxy-containing polymers showed faster crosslinking than phenyloxy-containing polymers.

4. Conclusions

Three series of polybenzylidene arylphosphate esters, with varying methylene chain length (6,8,10) and pendant aryl group, were synthesized and characterized spectroscopically. Data for intrinsic viscosity shows that these polymers are moderately high molecular mass materials. All the polymers showed an LC phase. Monodomain size increased with increase in length of the methylene spacer. These polymers exhibited moderate thermal stability with good char yield, which is a criterion for the polymers to act as fire retardants. The T_m and T_i of the polymers were much reduced, ascribed to the incorporation of methylene spacer and phosphate ester linkage in the polymer backbone. The absorbance of all the polymers occurred above 375–408 cm^{-1}; as the methylene chain increased, the absorbance exhibited a bathochromic shift. All the prepared polymers rapidly established crosslinking under UV irradiation. Here again, the polymers with the longer methylene chain showed faster photolysis than the shorter chain materials.

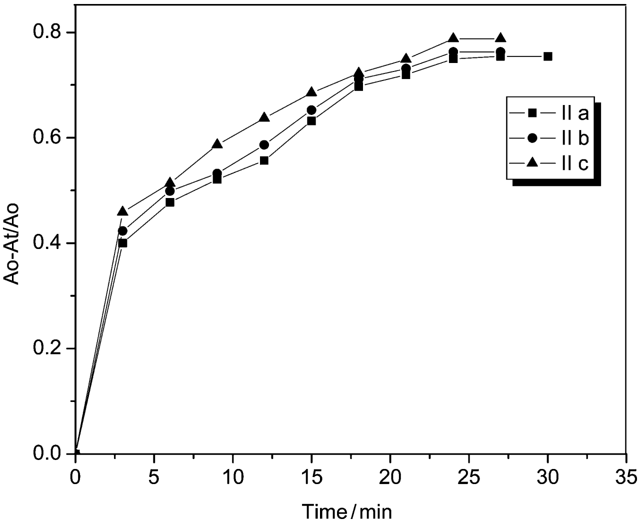


Figure 15. Rate of photolysis vs irradiation time for polymers **IIa–c**.

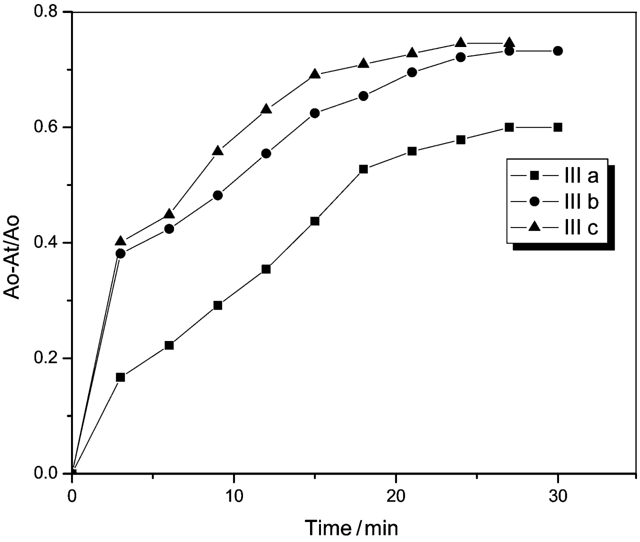


Figure 16. Rate of photolysis vs irradiation time for polymers **IIIa–c**.

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