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Investigation on thermotropic liquid crystalline and photocrosslinkable polyarylidene arylphosphate esters containing cyclohexanone units

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Abstract

Two series of novel liquid crystalline-cum-photocrosslinkable divanillylidene cyclohexanone containing polymers have been synthesized from 2,6-bis[*m*-hydroxyalkyloxy(vanillylidene)]cyclohexanone [$m=6, 8, 10$] with different arylphosphorodichloridates (naphthyl, biphenyl) by solution polycondensation method at ambient temperature. Their chemical structures were confirmed by FT-IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The intrinsic viscosity values were measured to find out molecular weight of the synthesized polymers. The mesogenic properties and phase behaviors were investigated with differential scanning calorimetry and hot stage optical polarized microscopy. The experimental results demonstrated that the mesogenic transition and isotropization temperature gradually decreases with increase in even number of methylene spacer of the polymer chain. All the polymers showed anisotropic behavior under hot stage optical polarized microscope (HOPM). The thermal behaviors of the polymers were studied by thermogravimetric analysis and stable between 292 and 330 °C. The photocrosslinking of the polymers was investigated in thin film by UV light/UV spectroscopy and the cyclobutane ring formation via 2π–2π cycloaddition reactions of the divanillylidene exo-cyclic double bond of the polymer backbone. The pendant naphthyloxy containing polymers show faster crosslinking than the pendant biphenyloxy containing polymers.

Keywords: Polyvanillylidene arylphosphate esters; Liquid crystalline polymers; Photocrosslinking polymers

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1. Introduction

Twin function polymers such as liquid crystalline-cum-photocrosslinkable polymers (LC-PCPs) have generated special attention due to the presence of mesogen and photoactive group in the polymer backbone. The former one contributes to the LC properties and the later one facilitates crosslinking of the polymer under the influence of UV irradiation [1]. In recent years, much attention has been paid to reversible and irreversible photochromic or thermochromic liquid crystalline polymers for potential applications such as data-storage materials [2], non-linear optics [3–5], photorefractive materials [6], intermediate for the drug synthesis [7] and photoresists [8,9]. The anisotropic properties of LC-PCPs exhibit thermally stable molecular reorientation structure and useful in the birefringent optical devices, such as optical retarders, polarization converters and interference filters [10]. The polarization converter films find applications in the field of optical photolithography, fabricating anisotropic networks, LC elastomers, LC thermosets and LCD [11–15]. A flexible photocrosslinkable main chain liquid crystalline polymer consists of mesogenic units separated by flexible alkyl spacers [16,17]. These polymers have been the focus of considerable research interest not only for the technical potential but also on a more fundamental level because they exhibit a range of unusual liquid crystalline behaviors. The poly [bis(benzylidene ester)s] containing LC-PCPs have been synthesized and exhibited good solubility in common organic solvents and this class of polymers were useful for information storage devices [18]. On the other hand, phosphorus possesses well-known peculiar characteristics such as fire retardancy, and adhesive properties to the polymers when incorporated in it [19,20]. Kricheldorf reported the thermotropic liquid crystalline poly(arylphosphate ester)s for the use of high performance fibers and observed that the T_g of the polymers decreases with increase

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in the phosphorus content [21]. In our earlier studies, we have demonstrated that the introduction of phosphate group into the polymer backbone improved their solubility due to its polarity and high char yield [22–26]. The literature survey reveals that the investigations on the synthesis of liquid crystalline and photocrosslinkable polymers (LC-PCPs) were scarce [18]. The present work involves hitherto unreported synthesis and characterization of new liquid crystalline-cum-photocrosslinkable divanillylidene containing arylpolyphosphate esters. The 2,6-bis[*m*-hydroxyalkyloxy(vanillylidene)]cyclohexanone group to act as a mesogen-cum-photocrosslinkable segment in the polymer and arylphosphate esters impart improved solubility and flame retardant properties. The effect of methylene spacer and pendant group in the polymers with respect to the rate of photocrosslinkability was described.

2. Experimental

2.1. Materials

Cyclohexanone (Merck), vanillin (Merck), boron trifluoride diethyl etherate (Fluka), phosphorusoxychloride (Fluka), anhydrous potassium carbonate (Merck) 1-naphthol, 4-phenylphenol (SRL) were used as supplied. Methanol, ethanol, chloroform, *N*,*N*-dimethylformamide, dimethylsulphoxide and other solvents were purified by reported procedures [27]. *m*-Bromoalkanols ($m=6$, 8, 10) were prepared according to the reported procedures [28,29]. 2,6-Bis[vanillylidene]cyclohexanone (BVCH) were prepared by the procedure reported elsewhere [30].

2.2. Synthesis of monomers

2.2.1. 2,6-Bis[4-m-hydroxyalkyloxy)vanillylidene]cyclohexanone ($m=6$, 8, 10)

All the monomers were synthesized by condensation reactions. A typical Williamson aryl ether procedure for the synthesis of 2,6-bis[6-hydroxyhexyloxy(vanillylidene)] cyclohexanone (BHHVCH) is as follows: A *N*,*N*-dimethylformamide (25 ml) solution of BVCH (3.66 g, 10 mmol) and potassium carbonate (4.95 g, 50 mmol) was stirred for 30 min at 90 °C. Then, bromohexanol (3.36 ml, 30 mmol) was added drop wise to the reaction mixture and stirred for 24 h at that temperature. The formation of 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 get yellow colored precipitate; the product was washed with distilled water, followed by *n*-hexane, recrystallized from ethanol water mixture (50:50) and dried in vacuum oven at 50 °C for 6 h (yield 85%; mp 168 °C). All the other monomers were synthesized by an analogous procedure [30].

IR (KBr): 1685 (cyclohexanone C=O), 3375 (spacer OH) and 1568 cm^{-1} (exo-cyclic C=C) ^1H NMR-δ: 8.9 (s, 2H, OH), 7.6 (s, 2H, CH=), 6.9–7.4 (m, 6H, Aromatic), 3.9 (s, 6H, OCH_3), 2.9 (s, 4H, βCH_2), 1.7 (s, 2H, γCH_2), 2.1–2.6 (m, 16H, CH_2spacer), 3.2 (t, 8H, $-OCH_2$).

2.2.2. Arylphosphorodichloridate (aryl = naphthyl, biphenyl)

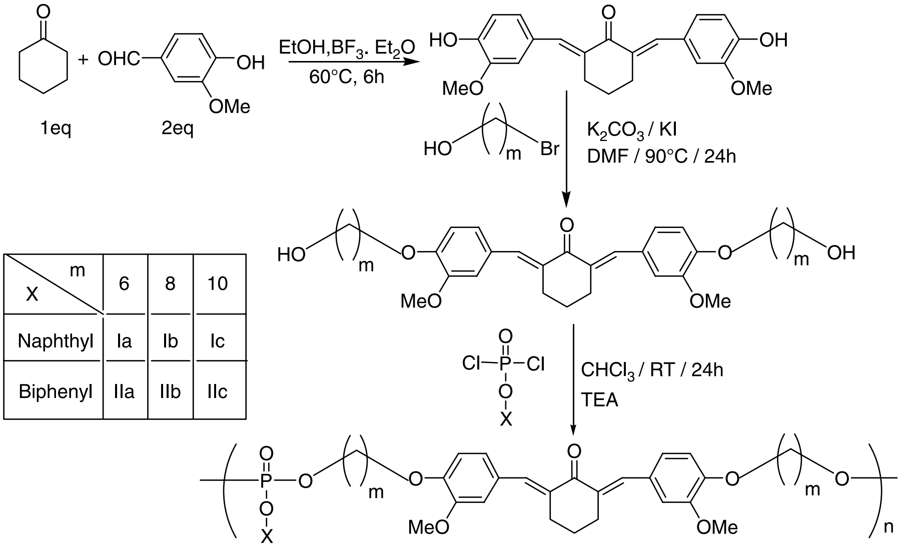
The arylphosphorodichloridates were prepared by reacting 1-naphthol and 4-phenylphenol, respectively, with excess of phosphorusoxychloride and the corresponding dichloridates obtained in pure form under vacuum distillation. The typical procedure for the synthesis of naphthyl phosphorodichloridate is as follows: 1-Naphthol (0.1 mol, 26 g) was added to freshly distilled phosphorusoxychloride (0.5 mol, 46.5 g) placed in a round-bottomed flask fitted with condenser and guard tube. The reaction mixture was slowly heated to 50 °C with stirring. The temperature was maintained for 1 h and then slowly raised to gentle reflux. The reaction mixture was maintained at that temperature until the HCl evolution ceased. Excess phosphorusoxychloride was distilled under reduced pressure. The residue was washed with dry hexane. A white solid obtained was immediately used without further purification mp 39 °C. The biphenyl phosphorodichloridate was synthesized in a similar manner [31].

2.3. Poly{2,6-bis[4-(alkyloxy)vanillylidene]cyclohexanone arylphosphate ester}s [$m=6$, 8, 10; aryl = naphthyl, biphenyl]

The polymers (Ia–IIc) were synthesized by solution polycondensation method at ambient temperature, using an acid acceptor (TEA). The typical procedure for the synthesis of poly{2,6-bis[4-(hexyloxy)vanillylidene]cyclohexanone naphthylphosphate ester}s (Ia) is as follows: BHHVCH (0.534 g, 1 mmol) was dissolved in 20 ml of chloroform under nitrogen atmosphere, TEA (20 mmol) added to it and stirred for 15 min at room temperature. The naphthyl phosphorodichloridate (0.26 g, 1 mmol) was dissolved in chloroform and added drop wise to the reaction mixture at ambient temperature and the reaction continued for 24 h. TLC was performed [chloroform:methanol (90:10)] until the monomer was completely disappeared. At the end of the reaction, the excess solvent was distilled, and the residue was cooled and poured into excess of methanol. A yellow colored precipitate thus obtained was purified by reprecipitation using chloroform–methanol and dried in a vacuum oven at 50 °C (yield 85%). All other homologous polymers (Ib–IIc) were prepared in a similar manner.

2.4. Measurements

The infrared spectra were obtained by using Brucker IFS 66V Fourier transform spectrophotometer using KBr pellet. High-resolution ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Brucker spectrometer of 300 and 75.4 MHz, respectively, for proton and carbon-13 in $CDCl_3$. TMS was



Scheme 1. Synthesis of monomers and polymers Ia–IIc.

used as an internal standard. ^{31}P NMR spectra were also recorded on the same instrument (300 MHz) in $CDCl_3$ under broadband ^{1}H decoupled conditions. D_2O and phosphoric acid (85%) were used as an external lock and external standards, respectively. Viscosity was measured by using Ubbelohde viscometer at a constant temperature bath at 30 °C with ±1 °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 various concentrations range (0.5 g dl^{-1}) in chloroform. Thermogravimetric analysis was performed on a Mettler TA3000 thermal analyzer in 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 used to scan all synthesized polymers in unsealed aluminium pan in a dry nitrogen atmosphere with an empty aluminium pan as reference. The scans were carried out at a heating rate of 10 °C min^{-1}. The second heating cycle was recorded for all the polymers in the DSC. The texture of all the prepared polymer samples were observed by using Euromax polarizing microscope equipped with a Linkam HFS91 heating stage and a TP-93 temperature programmer. A small quantity of the sample being melted between two thin glass cover slips to get uniform film and the anisotropic behavior was observed by heating and cooling at the rate of 5 °C min^{-1}. The photographs were taken with a Nikon FM10 camera and exposed on a Konica film. The photocrosslinking ability of the polymers were investigated in the form of films and monitored the absorption between 390 and 408 nm regions on a Hitachi U2000 UV spectrophotometer. A typical procedure of photolysis 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 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 kept at a distance of 10 cm from the sample at various intervals of time. Subsequently, the irradiated film was subjected to spectral analysis.

3. Results and discussion

3.1. Synthesis

The synthetic route for the target polymers is shown in the Scheme 1. The chalcone was used as a photosensitive group and prepared by the reaction with cyclohexanone and vanillin in absolute ethanol using an acid catalyst. The chain extended chalcone derivative containing methylene spacer

Table 1
Yield, viscosity and thermogravimetric analysis of polymers Ia–IIc

Polymer	*m*	Yield (%)	[η] (dl g^{-1})	Weight loss corresponding to (°C) 10%	Char yield at 600 °C
Ia	6	85	0.66	298	34
Ib	8	80	0.68	294	32
Ic	10	83	0.69	292	31
IIa	6	75	0.72	330	39
IIb	8	79	0.73	316	37
IIc	10	80	0.75	309	36

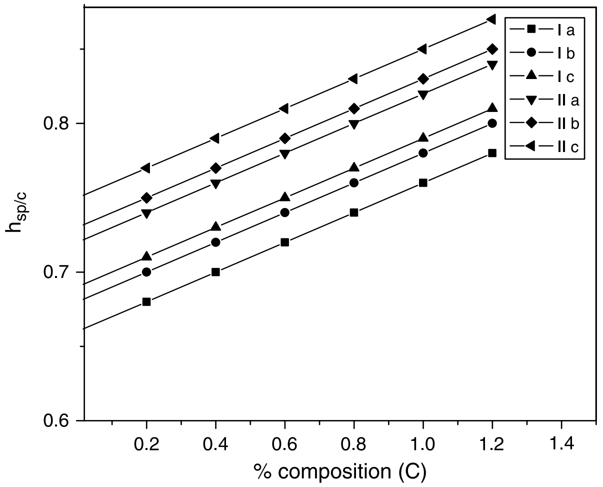


Fig. 1. Intrinsic viscosity plots of polymers Ia–IIc.

group was prepared by the nucleophilic displacement of potassium salt of BVCH with *m*-bromoalkanols ($m=6$, 8, 10) in DMF. All the polymers were prepared by polycondensation of divanillylidenealkyloxy mesogen containing diol and arylphophorodichloridates in chloroform solution at room temperature with good yield (Table 1). They are yellow in color and powdery. They are soluble in $CHCl_3$, CH_2Cl_2, chlorobenzene, DMF, DMSO, THF, dioxane and *N*-methylpyrrolidone and insoluble in methanol, ethanol, 2-propanol, benzene and toluene. The intrinsic viscosity data of the polymers are listed in the Table 1 and shown in Fig. 1. The results reveal that all the synthesized polymers are moderate molecular weight materials.

The IR spectra of the polymers showed characteristic absorption band at 1670 and 1560 cm^{-1}, attributed to the keto carbonyl and exo-cyclic double bond of the polymer backbone, respectively. The characteristic CH_2–O–CH_2 stretching bands appeared at 2884 and 2980 cm^{-1}. In addition, the absorption of P=O and aromatic stretching appeared at 1249 and 1528 cm^{-1} [32]. The representative ^1H NMR spectrum of polymer Ic is exposed in Fig. 2. The vanillylidene aromatic protons appeared as two doublets in the region 6.9–7.1 ppm, the pendant naphthyloxy group in the phosphate ester appeared as a multiplet in the region of 7.2–7.6 ppm. The methoxy protons of the divanillylidene mesogen appeared as a singlet at 3.9 ppm. The OCH_2– connected to phosphorus of the spacer resonate as a triplet at 3.6 ppm and O–CH_2– linked with phenyl ring of the spacer appeared as triplet around 3.9 ppm, while the methylene

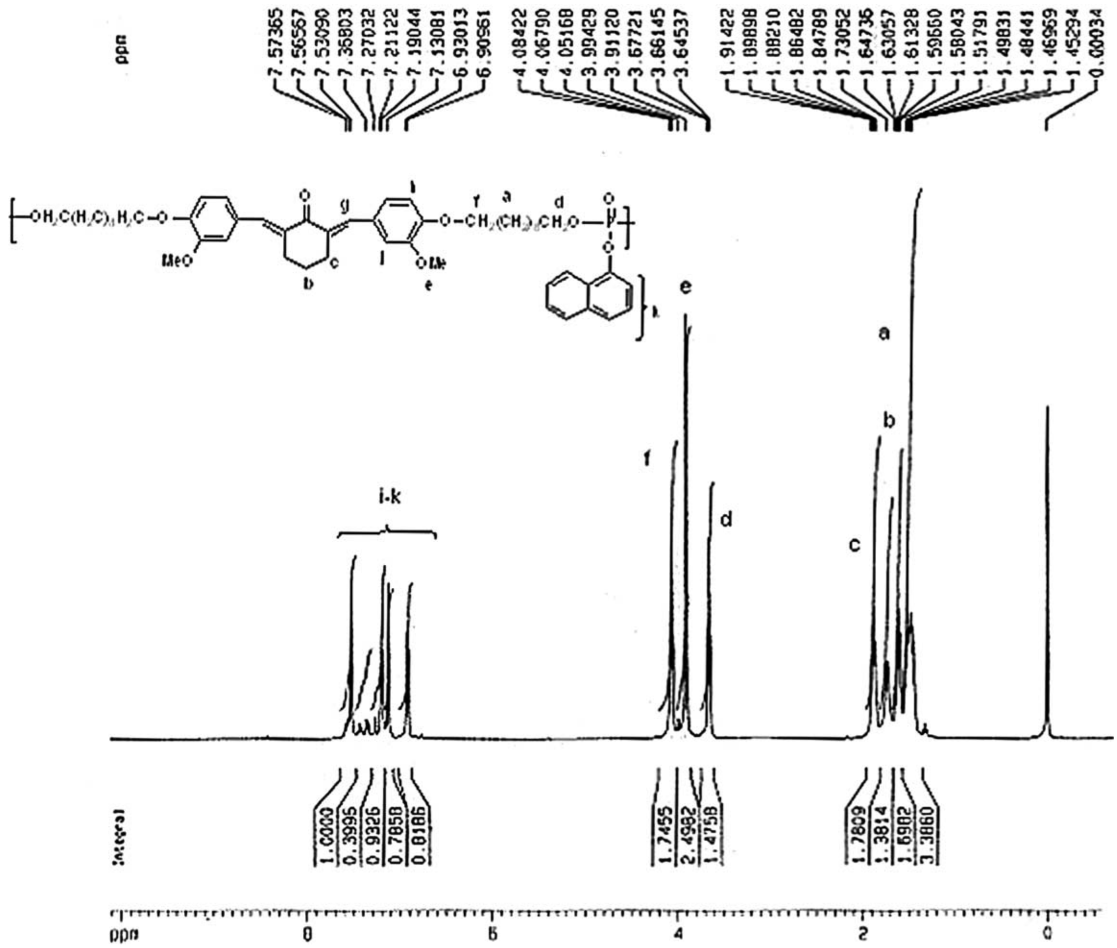


Fig. 2. ^1H NMR spectrum of polymer Ic.

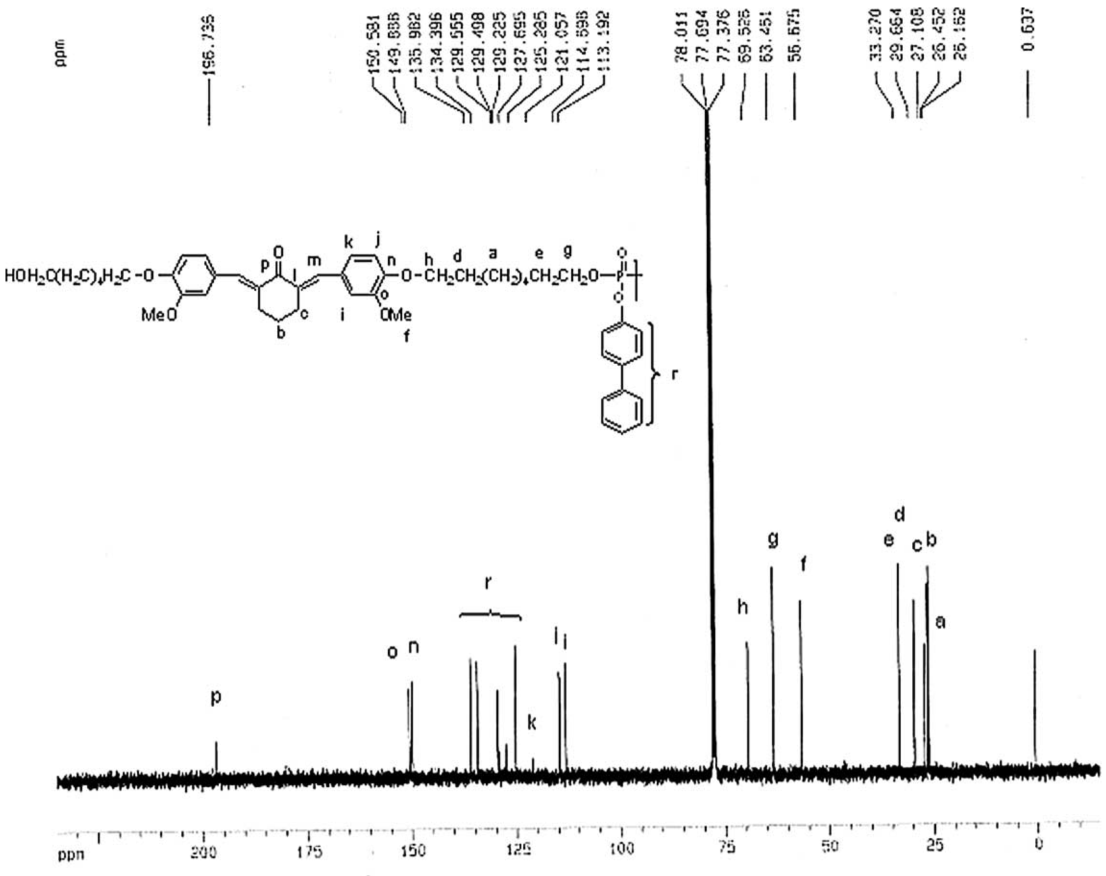


Fig. 3. ^{13}C NMR spectrum of polymer IIb.

protons of the spacers appeared as multiplet in the region of 1.4–1.9 ppm [33]. The representative ^{13}C NMR spectrum of the polymer IIb is shown in Fig. 3. The C=O group of the cyclohexanone moiety resonate at 197 ppm, aromatic carbons in the mesogenic units are resonated in the regions 113–121 ppm, aromatic carbons in the pendant units are resonates in the regions 129–135 ppm. The exo-cyclic carbon–carbon double bond (C=C) appeared at 149 and 150 ppm, methylene carbon in the spacer (–CH$_2$–) resonated in the range 26–33 ppm, –OCH$_3$ resonated at 75 ppm, the P–OCH$_2$ and –OCH$_2$ spacer group resonated at 63 ad 69 ppm, respectively, [34]. All the ^{31}P NMR spectra of the polymers

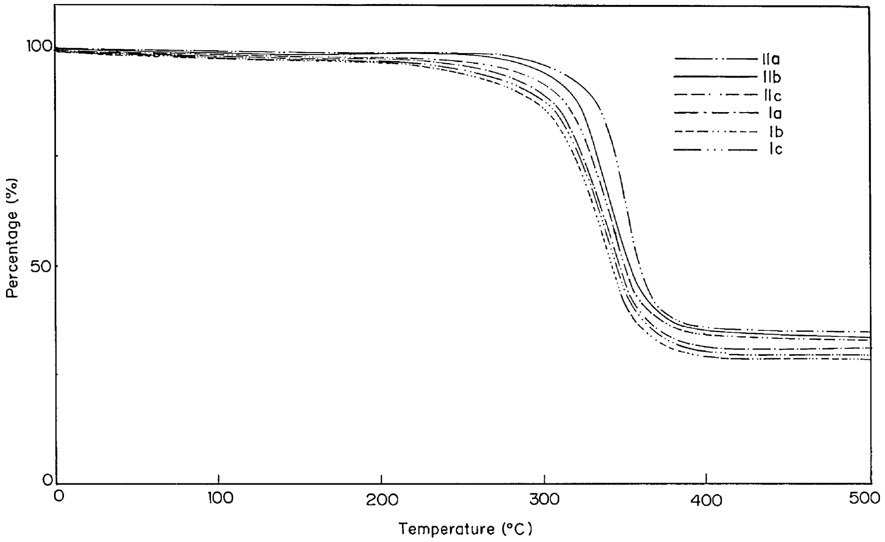


Fig. 4. Thermogravimetric traces of polymers Ia–IIc.

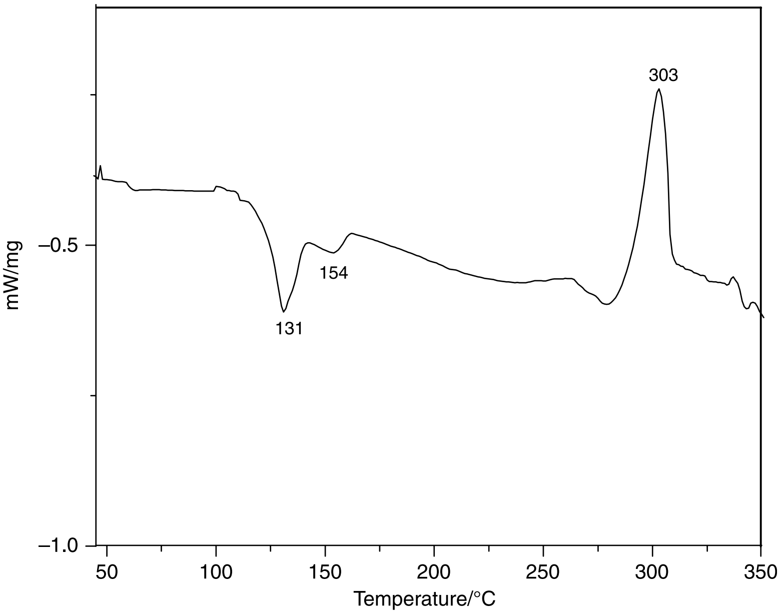


Fig. 5. DSC curve of polymer IIa.

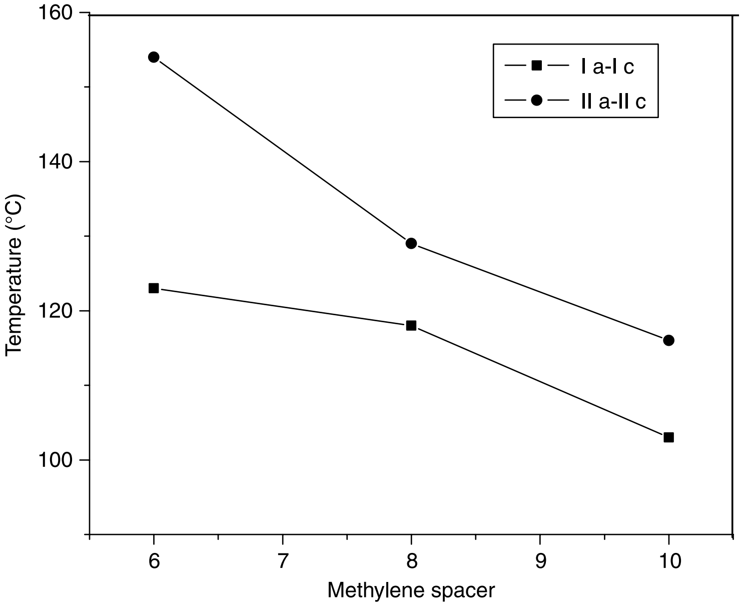
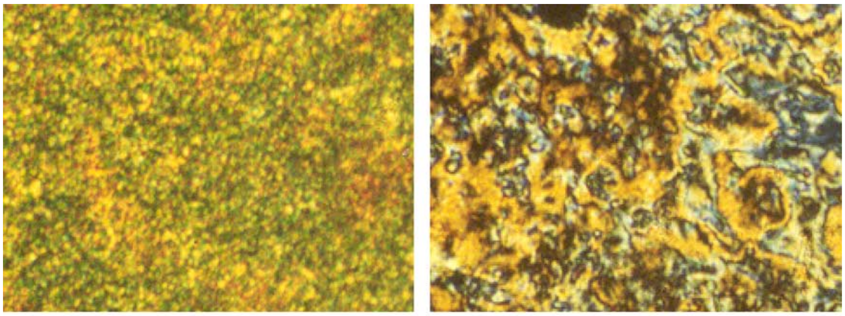


Fig. 6. Correlation between the isotropization temperatures and spacer length ($m=6$–10) obtained in DSC.

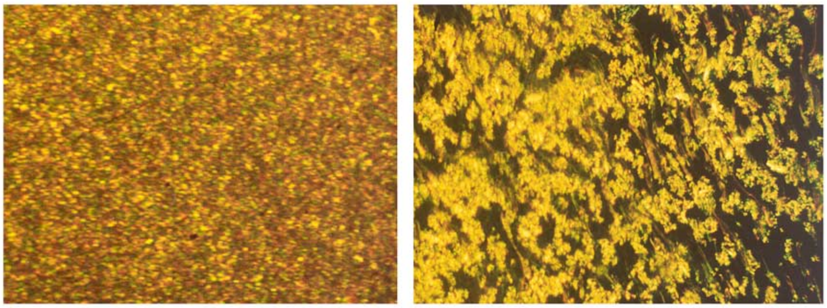
Table 2
DSC and HOPM data of the polymers Ia–IIc

Polymer	m	DSC			HOPM			Type of mesophase
		T_m (°C)	T_i (°C)	ΔT (°C)	T_m (°C)	T_i (°C)	ΔT (°C)	
Ia	6	97	123	26	95	122	27	Micro grainy
Ib	8	94	118	23	96	117	21	Nematic
Ic	10	84	103	19	82	104	22	Nematic
IIa	6	131	154	23	130	154	24	Micro grainy
IIb	8	108	129	21	107	127	20	Nematic
IIc	10	96	116	20	97	114	17	Nematic



Polymer Ia

Polymer Ic



Polymer IIa

Polymer IIc

Fig. 7. Representative liquid crystalline photographs of polymers (Ia, Ic, IIa and IIc). Photographs were taken during the first cooling at a magnification of 20×.

show one intense resonance signal at −20.15 ppm due to the main chain phosphorus atoms and another weak resonance at −13.30 ppm is due to terminal –P–OH of the polymers [35], which conformed the incorporation of phosphorus in the polymer backbone.

3.2. Thermal analyses

3.2.1. Thermogravimetric analysis (TGA)

The thermal behavior of the polymers was evaluated by TGA in nitrogen at heating rate 10 °C/min, the traces of polymers are shown in Fig. 4 and the data illustrated in Table 1. The thermal stability was evaluated by 10% weight loss at minimum temperature. TGA revealed that the polymers were stable up to 292–330 °C. It was observed that the II series of the polymers (330 °C) were more stable than that of I series polymers (292 °C). The ether linkage in the spacer units are expected to introduce greater flexibility to the polymer methylene chains and consequently bring down the thermal stability. In addition to that the pendant naphthyl containing polymers are less stable than pendant biphenyl containing polymer. This may be ascribed at the steric hindrance offered by the peri hydrogen in the naphthyl group disrupt the close packing in the crystal lattice of the polymer chain causing a depression on the thermal stability. The char yield was measured at 600 °C and the data reveal that it increases with decreasing the spacer length [Ia > Ib > Ic] [35]. The pendant group played an important role in the char yield and it follows the trend: Biphenyl > naphthyl containing polymers. The maximum char yield was noticed for polymer IIa (39%) and minimum obtained for polymer Ic (31%). The percentage of char yield reveals that the high char for these polymers is an indication to behave as fire-retardant polymeric materials via condensed phase mechanism [37]. The decomposition of the polymers probably occurred through pyrolytic cleavage of the polyphosphate ester group and linkage between divanillylidene mesogenic groups with different methylene units in the polymer chain.

3.2.2. Differential scanning calorimetry (DSC)

DSC analysis investigated the mesogenic transitions. The DSC thermograms of the polymers were measured in the second scan with heating rate of 10 °C/min and a representative thermogram of polymer IIa is shown in Fig. 5 the phase transition temperatures of all the polymers are summarized in Table 2. The data reveal the formation of the liquid-crystalline phase and isotropization temperatures [34,38,39]. All the polymers showed two endothermic peaks, which correspond to the crystalline-liquid crystalline and liquid crystalline-isotropic transitions respectively. The Fig. 6 revealed that the isotropic temperature of the polymers (Ia–IIc) decreases with an increase in the flexible methylene chain from 6 to 10 in the polymeric backbone [40]. The T_m of the I and II series of polymers were in the range of 84–97 and 96–131 °C, respectively. The lower T_m values for I series of polymers may be attributed to the presence of more bulky naphthyl group leading to more disorder arrangements and exhibited lower phase transition temperatures. On the other hand, in the II series polymers (biphenyloxy) showed higher T_m values. This may be attributed to the biplanarity of the biphenyl ring, where the

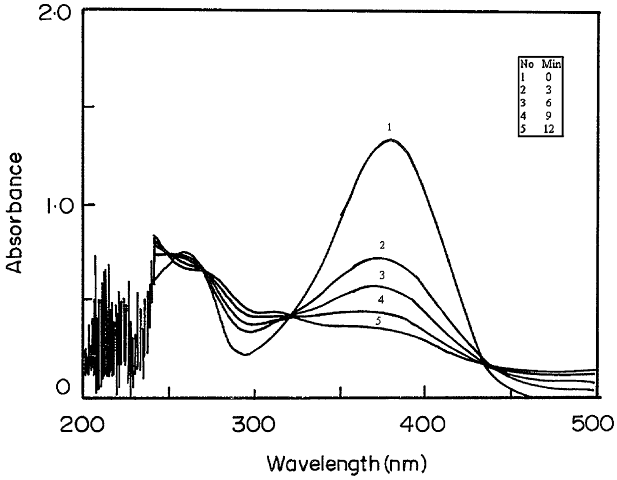


Fig. 8. Changes in UV spectral characteristics during the photolysis of polymer Ib at various intervals of time.

two phenyl rings are perpendicular to each other, thus allows the close packing of the chains through the higher π–π interaction of the two aromatic rings. Moreover, the phase stability was also decreased with increasing in spacer length. All the polymers showed broad exothermic peak beyond 300 °C, this might be attributed to thermal crosslinking leading to cyclobutane formation [20].

3.2.3. Texture analysis

The liquid crystalline textures of the polymers (Ia–IIc) were observed on hot stage optical polarized microscope in the range of 82–130 °C upon cooling cycle at 20×. The representative photographs were shown in Fig. 7, the type of mesophase is tabulated in Table 2. All the polymers exhibited the melting and isotropic transition temperatures. On cooling from isotropic melt (T_i), the reproducibility of the mesophase was satisfactory. The mesophase transition temperatures of the polymers were measured by DSC thermograms is in accordance with that of the transition temperatures observed in HOPM. The order of liquid crystalline mono domains increased from the lower methylene chain containing polymers to the higher methylene chain containing polymers. The flexible methylene spacer groups separate the mesogenic alignment, thereby reducing the overall rigidity. The lower methylene (6) chain containing polymers (Ia and IIa) showed grainy texture. Whereas the higher methylene (8 and 10) chain containing polymers (Ib, Ic, IIb and IIc) showed nematic texture. This may be ascribed to the incorporation of methylene spacer (8 and 10) in to the polymer chain that may be affect in the arrangement of the mesogenic core to form an orderly liquid crystalline state [30,36]. Apart from the methylene spacers, phosphate ester group also impart the dilution to the mesogenic segment and provide extra flexibility to the polymer chain. Lengthy flexible spacer units ($m=8$, 10) allow the mesogen to move freely, thus lead to the formation of nematic texture [41]. Hence, the rigidity of the mesogen was diluted and helps to produce large monodomain.

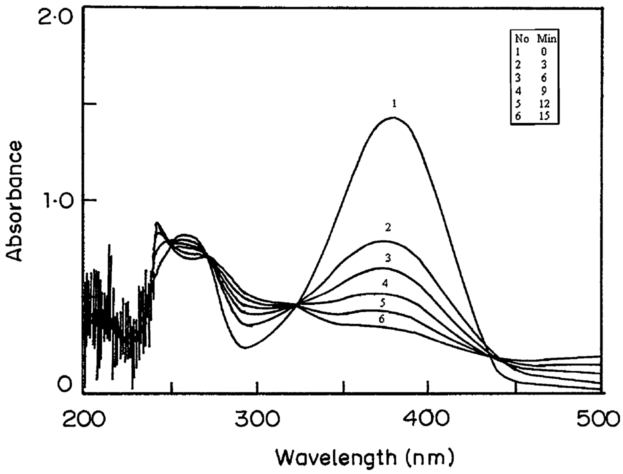


Fig. 9. Changes in UV spectral characteristics during the photolysis of polymer IIc at various intervals of time.

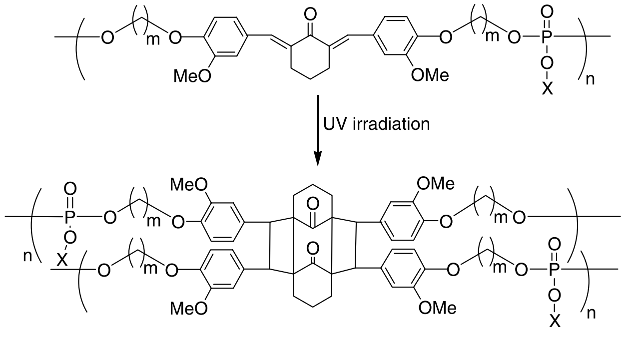


Fig. 10. Photocrosslinking reactions (2π+2π cycloaddition) of polymers.

3.2.4. Photophysical studies

The polymers containing the mesogenic divanillylidene cyclohexanone will undergo photocrosslinking by UV irradiation. The structural changes were monitored by UV spectroscopy. The photocrosslinking ability of the polymers was studied in the form of a thin film, which was irradiated under UV light. The changes in the photolysis of the representative polymers Ib and IIc are shown in the Figs. 8 and 9. The absorption band around 385 nm corresponds to π–π* transition of the olefinic double bond of the mesogenic unit in the polymer backbone. During the successive irradiation of UV light a decrease in intensity of the absorption was observed, this is attributed to the formation of cyclobutane ring through 2π+2π cycloaddition of carbon–carbon double bond in the chalcone unit [42,43] and it is shown in Fig. 10. It is noteworthy to mention that the photolysis took place in a much faster rate for naphthyl containing polymer and absorption band at 385 nm

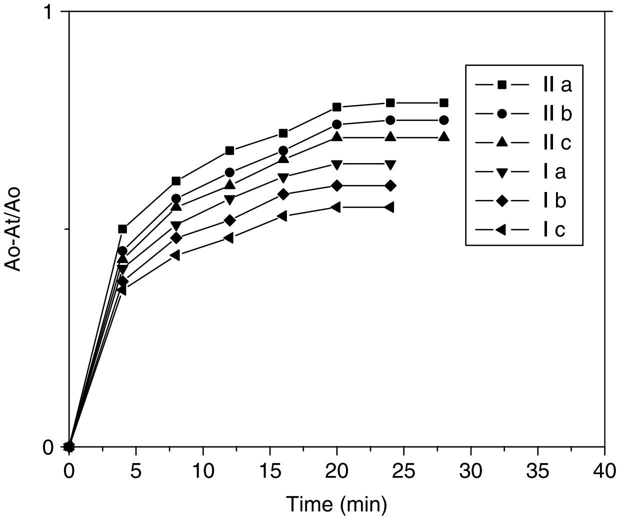


Fig. 11. Dependence of photocrosslinking rate on irradiation time of polymers Ia–IIc.

completely disappeared with in12–25 min. The relative rate of photocrosslinking of the polymers (Ia–IIc) are shown in the Fig. 11, relative reactivity $A_0 - A_t/A_0$ is plotted against the time of irradiation. Where A_0 is the absorption before irradiation and A_t is after irradiation for time t. It is interesting to note that the rate of reduction of exo-cyclic double bond during photolysis is faster for longer methylene chain than the shorter methylene chain in the polymer. Similarly, the pendant naphthyloxy-containing polymer showed faster crosslinking than that of pendant biphenyloxy containing polymers. After completion of the photolysis study the film was insoluble in chloroform solvent [30] as well as the polymers did not show liquid crystalline property attributed to restricted molecular mobility in the polymer backbone.

4. Conclusions

Photocrosslinkable arylphosphate esters were synthesized and characterized spectroscopically. The spectral data supported the structural assignment for the polymers. The intrinsic viscosity of the polymer data reveals that these polymers are moderate molecular weight materials. Thermal stability was better for the pendant biphenyloxy containing polymer IIa–IIc than that of naphthyloxy containing polymer Ia–Ic due to the increased coplanarity of the pendant group (Fig. 11). The pendant biphenyloxy containing polymers showed higher char yield than naphthyloxy containing polymer. T_m and T_i of the polymers decreases with increase in even number of methylene spacer. The HOPM studies indicated that all the prepared polymers show LC properties with micro grainy and nematic textures. All the polymers showed photocrosslinking behaviour under UV irradiation and the photolysis reaction completed with in 12–25 min. Here again, the higher methylene chain containing polymers showed faster photolysis than that of lower methylene chain containing polymers. Similarly, the pendant naphthyloxy containing polymers show faster crosslinking than the biphenyloxy containing polymers.

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