Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Novel photo-crosslinkable liquid crystalline polymers containing vanillylidene cycloalkanones and azobenzene units

D. Jayalatha[a]; R. Balamurugan[a]; P. Kannan[a]
[a] Department of Chemistry, Anna University, Chennai 600 025, India

To cite this Article Jayalatha, D. , Balamurugan, R. and Kannan, P.(2008) 'Novel photo-crosslinkable liquid crystalline polymers containing vanillylidene cycloalkanones and azobenzene units', Liquid Crystals, 35: 3, 275 — 285

To link to this Article: DOI: 10.1080/02678290701862256

URL: http://dx.doi.org/10.1080/02678290701862256

Liquid Crystals,
Vol. 35, No. 3, March 2008, 275–285

Novel photo-crosslinkable liquid crystalline polymers containing vanillylidene cycloalkanones and azobenzene units

D. Jayalatha, R. Balamurugan and P. Kannan*

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

(Received 22 April 2007; in final form 3 December 2007)

Two series of novel liquid crystalline photo-crosslinkable bis(vanillylidene-azobenzene) cycloalkanone containing polymers, namely poly(vanillylidene alkyloxy-4,4′-azobenzenedicarboxylic ester)s, have been synthesised from bis[*m*-hydroxyalkyloxy(vanillylidene)cycloalkanone] (m=6, 8, 10) with azobenzene dicarbonylchloride by solution polycondensation method at ambient temperature. Polymers with varying spacer lengths have been synthesised and characterised by spectroscopic techniques. These variations have been correlated with the thermal properties and transition temperatures. Thermal transitions were analysed by differential scanning calorimetry (DSC) and the mesophases were identified by hot stage optical polarised microscopy (HOPM). All of the polymers were found to exhibit liquid crystalline properties. Transition temperatures were observed to decrease with increasing spacer length. The thermogravimetric analysis reveals that all of the polymers were stable up to 280°C undergo two-stage decomposition. Using the UV–visible photolysis studies we investigated the simultaneous behaviour of reactivity rates of crosslinking in the vanillylidene unit and isomerisation caused by the azobenzene unit in the photo-crosslinkable main chain liquid crystalline polymers. The photolysis of liquid crystalline bis(vanillylidene)cycloalkanone-based polymers reveals that there are two kinds of photoreactions in these systems: the EZ photoisomerisation of azobenzene unit and 2p+2p addition by vanillylidene units. The EZ photoisomerisation in the liquid crystal phase disrupts the parallel stacking of the mesogens, resulting in the transition from the liquid crystal phase to isotropic phase. The photoreaction involving 2p+2p addition of the bis(vanillylidene)cycloalkanone units in the polymers results in the conjoining of the chains. The cyclopentanone polymers exhibited a faster rate of photolysis than the cyclohexanone polymers.

Keywords: liquid crystalline polymers; photo-crosslinking; azobenzene; thermal properties

1. Introduction

Liquid crystalline polymers (LCPs) have attracted considerable interest in recent years owing to the unique combination of the polymers with specific properties and the anisotropic behaviour of liquid crystals (LCs) (*1–5*). Among these polymers, photo-crosslinkable LCPs have generated special attention as they have both mesogens and photoactive groups in their structure (*6–10*). The former incorporates LC properties into the polymer and the latter facilitates crosslinking of the chains under the influence of UV or visible radiation. This class of polymers is useful in fabricating anisotropic networks and thin films (*7*), information storage devices (*11, 12*), non-linear optical devices (*13, 14*) and aligned membranes for the permeation of gases and drugs (*15, 16*). The photochemistry of these polymers is interesting from a topochemical point of view since the photoreaction take place in ordered LC media (*17, 18*). All of the photo-crosslinkable LCPs reported so far contain the cinnamate ester group as a photoactive centre, which undergoes photodimerisation on irradiation leading to the crosslinking of the polymer chains (*19–22*). Chalcone has been widely used as a mesogen in the LCPs and it is also a well-known photosensitive chromophore, which undergoes photo-crosslinking and thermal crosslinking (*23*). Azo groups are sensitive to various stimuli, namely light or heat, and it is a basic condition for these polymers to be utilised in communication technologies (*24*). In general, when the flexible spacer (alkyl chain) linking the azobenzene unit and the chain backbone is sufficiently long, the polymer may display the liquid crystallinity with the azobenzene groups forming the mesophases. The main feature of azobenzene polymers is the photo-chemically induced LC–isotropic phase transition that occurs when the rod-like *trans* isomer is converted into the contracted *cis* isomer as the later destabilises the LC phase (*25*). This phenomenon has been used to record volume holographic gratings and to realise optical switching when combined with the thermally or visible-light-induced *cis–trans* back isomerisation (*26*).

There are two major classes of LCPs, namely, the main chain LCPs and the side chain LCPs. The chemical structure of the mesogenic groups of the polymer backbone, the nature and length of the flexible spacer all play an important role in the type

---

*Corresponding author. Email: pakannan@annauniv.edu

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290701862256
http://www.informaworld.com

and thermal stability of the mesophase formation. In this paper, we present a new class of photo-crosslinkable main chain liquid crystalline polymers (PMCLCPs) based on the bis(vanillylidene)cycloalkanone unit with photoactive azobenzene unit.

α,β-Unsaturated ketone functionality of the bis(vanillylidene)cycloalkanone has the capacity to undergo photoisomerisation (*27–30*), photodimerisation (*31–34*) and photopolymerisation reactions (*35*). The latter two reactions in the polymer can lead to the crosslinking in the chains. The present study describes the synthesis, structural characterisation, liquid crystalline property and photo-crosslinking behaviour of the polymers containing photoreactive bis(vanillylidene)cycloalkanone units.

2. Experimental details

2.1. *Materials and methods*

Cyclohexanone, cyclopentanone, vanillin (SRL, India), boron trifluoride diethyl etherate (Fluka) and thionyl chloride (Spectrochem, India) were used as received. All of the solvents were purified and dried before use following the procedures reported in (*36, 37*). 6-Bromo-1-hexanol, 8-bromo-1-octanol, 10-bromo-1-decanol (*38*), 2,6-bis[vanillylidene] cyclohexanone (BVCH) and 2,5–bis[vanillylidene]cyclopentanone (BVCP) were prepared following the procedure reported in (*39*).

2.2. *Synthesis of monomers*

2.2.1. *2,5-Bis[4-(m-hydroxyalkyloxy)vanillylidene] cyclopentanone (m=6,8,10).*

The synthesis of 2,5-bis[4-(6-hydroxyhexyloxy(vanillylidene)]-cyclopentanone (BHHVCP) is as follows. BVCP (13.52 g, 10 mmol) was dissolved in dry dimethyl formamide (20 ml). Potassium carbonate (4.95 g, 50 mmol) was then added and an instant change in colour from yellow to red was observed as an indication of the formation of anions. Then, 6-bromo-1-hexanol (3.36 ml, 30 mmol) was added dropwise to the reaction mixture with constant stirring for 24 h at 90°C. At the end of the reaction, the mixture was cooled and poured over crushed ice to obtain a yellow precipitate; the product was washed with excess of distilled water, followed by *n*-hexane to remove unreacted 6-bromo-1-hexanol; the crude precipitate thus obtained was recrystallised from the ethanol–water mixture (50:50) and dried in a vacuum oven at 50°C for 6 h (yield 85%; melting point 168°C). All of the other monomers such as 2,5-bis[4-(8-hydroxyoctyloxy(vanillylidene)]-cyclopentanone (BHOVCP) and 2,5-bis[4-(10-hydroxydecyloxy(vanillylidene)]-cyclopentanone (BHDVCP), were synthesised by adopting a similar procedure wherein 1-bromo-8-octanol or 1-bromo-10-decanol was used, respectively, rather than 1-bromo-6-hexanol.

IR (KBr): 1674 cm^{-1} ($\nu_{C=O}$), 1581 cm^{-1} ($\nu_{C=C}$ exocyclic). ^{1}H-NMR (CDCl$_3$, TMS): 7.4 (s, 2H, OH), 6.8–7.2 (m, 6H, Aromatic), 6.2 (s, 2H, –CH=CH–), 3.8 (s, 6H, OCH$_3$), 3.4 (t, 8H, OCH$_2$ spacer), 2.7 (s, 4H, βCH$_2$), 1.7 (s, 2H, γCH$_2$), 1.9–2.4 (m, 16H, CH$_2$ spacer). ^{13}C NMR (CDCl$_3$) δ: 25–29 (Ar–O–CH$_2$–$\underline{\mathrm{C}}$H$_2$–), 64 (Ar–O–$\underline{\mathrm{C}}$H$_2$–), 129 (aromatic carbons), 58.02 (ArC–O$\underline{\mathrm{C}}$H$_3$).

2.2.2. *Synthesis of BHOVCP.*

Yield 82%; melting point 148°C. IR (KBr): 1674 ($\nu_{C=O}$), 1582 cm^{-1} ($\nu_{C=C}$ exocyclic). ^{1}H-NMR (CDCl$_3$) δ: 8.1 (s, 2H, OH), 6.8–7.4 (m, 6H, Aromatic), 3.7 (s, 6H, OCH$_3$), 3.5 (t, 8H, OCH$_2$ spacer), 2.9 (s, 4H, βCH$_2$). 1.6 (s, 2H, γCH$_2$), 1.7–2.4 (m, 24H, CH$_2$). ^{13}C NMR (CDCl$_3$) δ: 26–29 (Ar–O–CH$_2$–$\underline{\mathrm{C}}$H$_2$–), 65 (Ar–O–$\underline{\mathrm{C}}$H$_2$–), 127 (Aromatic Carbon), 57–58 (ArC–O$\underline{\mathrm{C}}$H$_3$).

2.2.3. *Synthesis of BHDVCP.*

Yield 80%; melting point 145°C. IR (KBr): 1672($\nu_{C=O}$), 1579 cm^{-1} ($\nu_{C=C}$ exocyclic). ^{1}H-NMR δ: 6.9–7.3 (m, 6H, Aromatic), 7.8 (s, 2H, OH), 4.0 (s, 3H, OCH$_3$), 3.2 (t, 8H, OCH$_2$ spacer), 2.9 (s, 4H, CH$_2$), 1.7 (s, 2H, γCH$_2$), 1.8–2.5 (m, 32H, CH$_2$). ^{13}C NMR (CDCl$_3$) δ: 27–29 (Ar–O–CH$_2$–$\underline{\mathrm{C}}$H$_2$–), 66 (Ar–O–$\underline{\mathrm{C}}$H$_2$–), 129 (Aromatic Carbon), 57.6 (ArC–O$\underline{\mathrm{C}}$H$_3$).

2.2.4. *Synthesis of 2,6-bis[4-(m-hydroxyalkyloxy) vanillylidene]cyclohexanone (m=6, 8 and 10).*

A similar procedure to that followed for the synthesis of BHHVCP was adopted for the preparation of 2,6-bis[4-(*m*-hydroxyalkyloxy)vanillylidene)] cyclohexanone (*m*=6, 8 and 10).

2.2.5. *Synthesis of 2,6-bis[4-(6-hydroxyhexyloxy) vanillylidene)]cyclohexanone (BHHVCH).*

Yield 74%; melting point 171°C. IR (KBr): 1684 ($\nu_{C=O}$), 3376 (spacer OH) and 1569 cm^{-1} ($\nu_{C=C}$ exocyclic). ^{1}H-NMR δ: 9.0 (s, 2H, OH), 7.5 (s, 2H, CH=), 6.9–7.3 (m, 6H, Aromatic), 3.9 (s, 6H, OCH$_3$), 3.0 (s, 4H, βCH$_2$), 1.6 (s, 2H, γCH$_2$), 2.1–2.5 (m, 16H, CH$_2$ spacer), 3.8 (t, 8H, –OCH$_2$). ^{13}C NMR (CDCl$_3$) δ: 25–28 (Ar–O–CH$_2$–$\underline{\mathrm{C}}$H$_2$–), 64–67 (Ar–O–$\underline{\mathrm{C}}$H$_2$–), 126–129 (Aromatic Carbon), 57–58 (ArC–O$\underline{\mathrm{C}}$H$_3$).

2.2.6. *Synthesis of 2,6-bis[4-(8-hydroxyoctyloxy) vanillylidene)]cyclohexanone (BHOVCH).*

Yield 78%; melting point 151°C. IR (KBr): 1679 ($\nu_{C=O}$), 3396 (spacer OH) and 1592 cm^{-1} ($\nu_{C=C}$ exocyclic). ^{1}H-NMR δ: 8.5 (s, 2H, OH), 7.8 (s, 2H, CH=), 7.0–7.4 (m, 6H, Aromatic), 3.9 (s, 6H, OCH_3), 2.6 (s, 4H, βCH_2), 1.9 (s, 2H, γCH_2), 2.4–2.7 (m, 24H, CH_2spacer), 3.9 (t, 4H, $–OCH_2$). ^{13}C NMR ($CDCl_3$) δ: 26–29 (Ar–O–CH_2–$\underline{C}H_2$–), 69 (Ar–O–$\underline{C}H_2$–), 137–130 (Aromatic Carbon), 59.7 (ArC–O$\underline{C}H_3$).

2.2.7. *Synthesis of 2,6-bis[4-(10-hydroxydecyloxy) vanillylidene)]cyclohexanone (BHDVCH).*

Yield 83%; melting point 147°C. IR (KBr): 1683 ($\nu_{C=O}$), 3395 (spacer OH) and 1592 cm^{-1} ($\nu_{C=C}$ exocyclic). ^{1}H-NMR δ: 9.0 (s, 2H, OH), 7.4 (s, 2H, CH=), 6.8–7.4 (m, 6H, Aromatic), 3.9 (s, 6H, OCH_3), 3.0 (s, 4H, βCH_2), 1.8 (s, 2H, γCH_2), 1.8–2.5 (m, 32H, CH_2 spacer), 3.6 (t, 8H, $–OCH_2$). ^{13}C NMR ($CDCl_3$) δ: 26–30 (Ar–O–CH_2–$\underline{C}H_2$–), 69 (Ar–O–$\underline{C}H_2$–), 129 (Aromatic Carbon), 59.2 (ArC–O$\underline{C}H_3$).

2.2.8. *Synthesis of 4, 4′-Azobenzenedicarboxylic acid (ABDA).*

ABDA was synthesised as follows using the procedure reported in (*40*). 4-Nitrobenzoic acid (13 g, 77.8 mmol) was added to sodium hydroxide solution (50 g in 250 ml, 1250 mmol) at 50°C. To this, a solution of α-D-glucose (100 g in 150 ml of water, 555 mmol) was added slowly at this temperature with occasional shaking over a period of 1 h. The light brown coloured reaction mixture was then cooled to ambient temperature and aerated for 12 h with vigorous stirring to give a viscous dark brown mixture. The mixture was slowly acidified with glacial acetic acid to pH 6 and a mud-like precipitate thus obtained was collected by filtration. The solid was recrystallised from hot aqueous K_2CO_3 giving 8.0 g of bright orange coloured needles. Yield 59%, melting point over 300°C.

2.2.9. *4,4′-Azobenzenedicarbonylchloride (ABDCC).*

ABDCC was prepared from ABDA using a modified procedure as reported by Petersen (*41*). ABDA (10 mmol) was taken in a 100 ml round-bottomed flask immersed in an oil bath. To this, 25 ml of dry benzene was added with stirring. Next, thionyl chloride (40 mmol) was added dropwise with stirring. At the end of addition, one drop of DMF was added and the bath temperature was slowly raised to about 70°C. As the reaction proceeded, dispersed ABDA was slowly dissolved in benzene solution; after complete dissolution the reaction mixture was refluxed for 4 h. Benzene and excess thionyl chloride were removed by vacuum distillation. The red powder thus obtained was recrystallised in dry hexane (95% yield, melting point 164°C).

2.3. *Polymerisation of poly(vanillylidenealkyloxy -4,4′-azobenzenedicarboxylic ester)s*

All of the photoreactive polymers were prepared using the solution polycondensation method at ambient temperature using an acid acceptor as a catalyst (*42*). The typical procedure for the synthesis of poly{2,5-bis{4-(6-hydroxyhexyloxy)-vanillylidene] cyclopentanone azo-benzenedicarboxylic ester}s (**Ia**) is as follows: BHHVCP (10 mmol) was dissolved in dry chloroform (20 ml). TEA (20 mmol) was added to and the mixture was stirred for 5 min. ABDCC (10 mmol) was dissolved in chloroform (20 ml) and added dropwise to the reaction mixture at ambient temperature and the reaction was continued for 24 h. The formation of product was monitored by thin layer chromatography (TLC; chloroform:methanol ratio 90:10). At the end of the reaction, the reaction mixture was concentrated to 10 ml, cooled and the polymer solution was poured into excess methanol. The yellow precipitate thus obtained was purified by reprecipitation using chloroform–methanol, washed successively with *n*-hexane, filtered and then dried in a vacuum oven at 50°C to give ~85% yield. All of the other polymers (**Ib**–**IIc**) were prepared in an analogous manner.

IR (KBr): 1684 ($\nu_{C=O}$), 1569 cm^{-1} ($\nu_{C=C}$ exocyclic), 1725 cm^{-1} (ester –C=O). ^{1}H-NMR δ: 7.5 (s, 2H, CH=), 6.9–7.3 (m, 6H, Aromatic), 3.9 (s, 6H, OCH_3), 3.0 (s, 4H, βCH_2), 1.6 (s, 2H, γCH_2), 2.1–2.5 (m, 16H, CH_2 spacer), 3.8 (t, 8H, $–OCH_2$). ^{13}C NMR ($CDCl_3$) δ: 25–28 (Ar–O–CH_2–$\underline{C}H_2$–), 64–67 (Ar–O–$\underline{C}H_2$–), 126–129 (Aromatic Carbon), 57–58 (ArC–O$\underline{C}H_3$), 169.3 (ester –C=O).

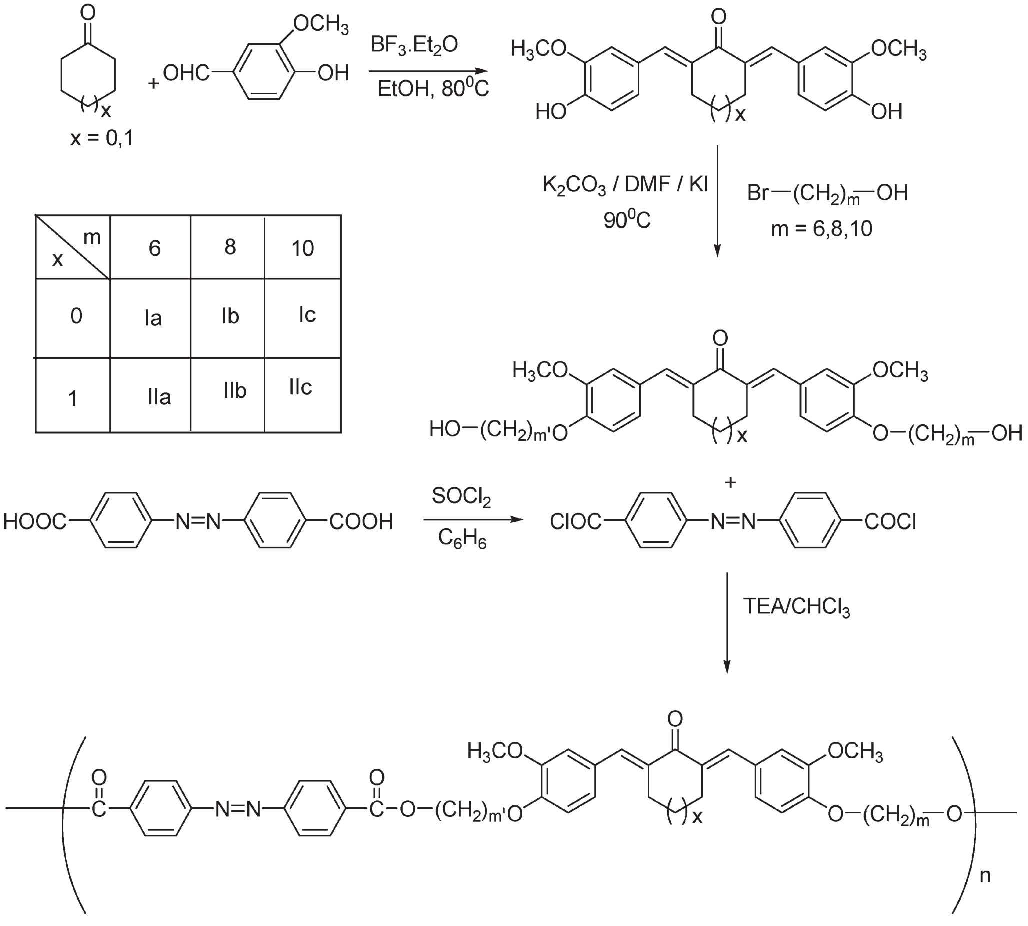
2.4. *Characterisation*

The inherent viscosity measurements were carried out with Ubbelohde viscometer thermostated at 30°C. In each case, a solution of 100 mg of polymer in $CHCl_3$ was used for measurements. Infrared spectra were obtained on the Thermomattson Satellite Model FTIR spectrophotometer using KBr pellets. High-resolution ^{1}H and ^{13}C NMR spectra were recorded on a Bruker spectrometer at 300 and 75.4 MHz for proton and carbon-13, respectively, on $CDCl_3$. Tetramethylsilane (TMS) was used as an internal standard. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) thermograms were recorded on the NETZSCH-Gerâtebau Gmbh Thermal analysis system. All of the synthesised polymers were scanned in a DTA/TGA Al_2O_3 crucible in a dry nitrogen atmosphere at 30°C/ 10.0 (K/m) up to 700°C. The phase transitions were ascertained using the heating rate of the endotherm with a Mettler Toledo (USA) STAR differential scanning calorimeter at a scanning rate of $20°C\,min^{-1}$ with a nitrogen flow of $20\,ml\,min^{-1}$. Polarising microscopy studies were performed with a Euromex polarising microscope equipped with a Linkem HFS 91 heating stage and a TP-93 temperature programmer. Small quantities of the samples were placed between two thin glass cover slips and the anisotropic behaviour was observed by heating and cooling at a rate of $5°C\,min^{-1}$. Photographs were taken with a Nikon FM10 camera and printed on Konica 200 films. The isomerisation and photo-crosslinking ability of the polymers was investigated by observing the absorptions between 350 and 420 nm, on a Shimadzu UV-160A UV visible recording spectrophotometer. The typical procedure adopted is as follows. The polymer solutions were prepared (10^{-2} M) in chloroform, taken in a 1 cm quartz cuvette and irradiated by UV light emanating from a 125 W medium pressure mercury lamp kept at a distance of 10 cm from the samples at various intervals of time and immediately the UV absorption of the medium was measured on the spectrophotometer. This procedure was repeated until the reduction in absorption was complete.

3. Results and discussion

3.1. *Synthesis*

The synthetic routes for the bis(vanillylidene)cycloalkanone and azobenzene based monomers and polymers are shown in Scheme 1. The photosensitive chalcone group was obtained by reacting the corresponding cycloalkanone and vanillin in absolute ethanol with an acid catalyst. Furthermore, the chalcone was alkylated under Williamson aryl–alkyl ether synthesis conditions using various α-haloalkanols by the nucleophilic displacement reaction in DMF. The other photoreactive monomer, i.e. ABDCC was prepared from the reaction of ABDA



Scheme 1. Synthesis of monomers and polymers (**Ia**–**IIc**).

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

Polymer	*m*	Yield	$[\eta]^{a}$ ($g\,dl^{-1}$)	Weight loss[b] corresponding to (°C) 5%	50%	Char yield[c] at 600°C (%)
Ia	6	70	0.53	290	558	48
Ib	8	80	0.57	295	570	46
Ic	10	93	0.61	300	650	39
IIa	6	80	0.55	280	470	45
IIb	8	75	0.59	282	565	43
IIc	10	72	0.62	290	430	40

[a] Measured at a concentration of $0.5\,g\,dl^{-1}$ in chloroform at 30°C. [b] Error ± 2%. [c] Error ± 1%.

with thionyl chloride. This polymerisable carbonyl moiety was then linked to the bis(vanillylidene)cycloalkanone unit and then polymerised using a solution polycondensation method at ambient temperature. All of the polymers were soluble in DMF and chlorinated solvents such as $CHCl_3$, CH_2Cl_2 and chlorobenzene and insoluble in methanol, ethanol, 2-propanol, benzene and toluene.

The intrinsic viscosity of the polymers was determined using a Ubbelohde viscometer with chloroform as a solvent at 30°C and the data are given in Table 1. The inherent viscosity of the polymers was in the range of 0.53–$0.62\,dl\,gm^{-1}$. The data reveals that these polymers are of moderately high molecular weight. All of the polymers were structurally characterised by UV–visible, IR and NMR spectroscopic techniques. The representative IR spectral data of polymer **Ib** is shown in Figure 1. The strong absorption bands at 1683 and $1590\,cm^{-1}$ correspond to the carbonyl (C=O) and the olefinic exocyclic double bond (C=C), respectively.

The bands appearing at 2929 and $2852\,cm^{-1}$ were a result of the asymmetric stretching of the methylene spacers. The aryl and alkyl ether stretching appeared around 1241–$1263\,cm^{-1}$. The absorption of the ester carbonyl appeared between 1720 and $1716\,cm^{-1}$ and the aromatic ring vibrations were observed within the range 782–$700\,cm^{-1}$. In addition to these vibrations, all polymers showed an absorption band around 3412–$3431\,cm^{-1}$ owing to the azo linkage.

A typical ^{1}H-NMR spectrum for polymer **Ic** is shown in Figure 2. The vanillylidene aromatic protons appeared as multiplet in the region of 6.9–7.5 ppm. The aromatic protons of the azobenzene unit resonated at 7.9 and 8.3 ppm. The methylene proton attached to the ester group of the azobenzene unit appeared at 4.3 ppm. The methylene proton attached to the chalcone unit resonates at 3.7 ppm. The methylene proton nearer to the exocyclic double bond of the chalcone unit appeared at 3.0 ppm. The olefinic protons for all polymers appeared as a singlet at 7.5–7.7 ppm.

The representative ^{13}C NMR spectrum of polymer **IIa** is shown in Figure 3. The resonance signals corresponding to the aromatic carbons of azobenzene unit appeared at 112–113 ppm. The methylene carbon in the spacer (CH_2) resonated in the range 28–29ppm,

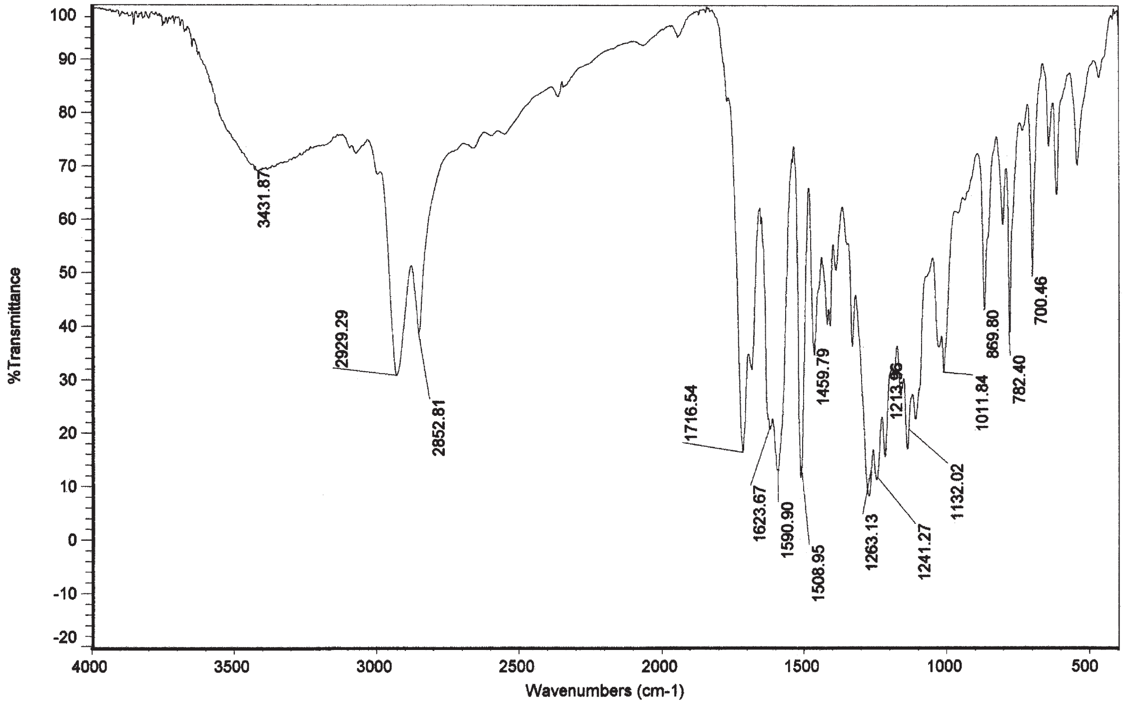


Figure 1. IR spectrum of polymer **Ib**.

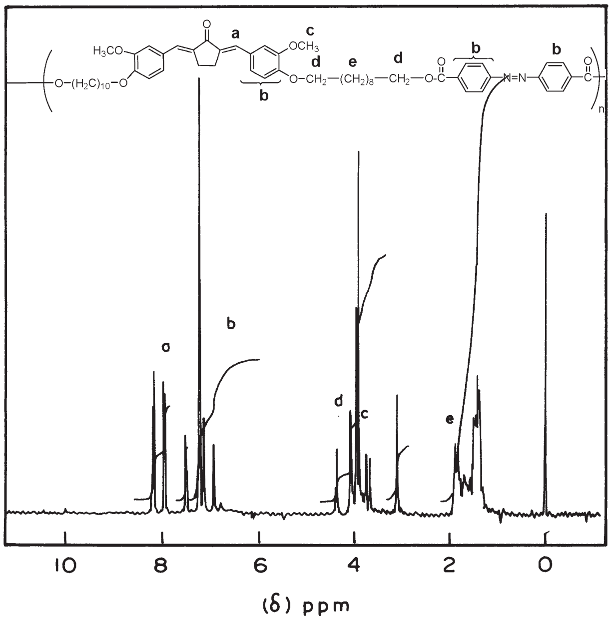


Figure 2. ^{1}H-NMR spectrum of polymer **Ic**.

–OCH_3 resonated at 54 ppm and the –OCH_2 spacer group resonated between 62 and 68 ppm. The exocyclic (C=C) appeared between 130 and 149 ppm. The methylene protons of cyclopentanone and cyclohexanone resonated at 29 and 22 ppm, respectively.

3.2. *Thermal analyses*

TGA was performed on a NETZSCH-Gerâtebau Gmbh thermal analyser under a nitrogen atmosphere at a heating rate of 10°C min^{-1}. The thermogravimetric traces of the various polymers are shown in Figure 4 and the data are given in Table 1. The temperatures corresponding to 5% and 50% weight loss and the char remaining at 600°C are also given in Table 1. All of the polymers are stable up to 280°C and start degrading thereafter in nitrogen. The degradation occurs in a two-step manner; the first step around 300°C corresponds to the pyrolytic cleavage of azo groups and thus leads to evolution of nitrogen gas in the main chain. The second step around 420°C may be a result of the cleavage of aryl–alkyl–ether linkage present in the polymer chain. The char yield of all of the polymers were measured at 600°C and the data revealed that it increases with decreasing spacer length (**Ia**>**Ib**>**Ic** and **IIa**>**IIb**, **IIc**).

The phase transitions were ascertained using a Mettler Toledo (USA) STAR differential scanning calorimeter at a scanning rate of 20°C min^{-1} with a nitrogen flow of 20 ml min^{-1}. The DSC thermograms of all of the polymers are shown in Figure 5 and their phase transition temperatures are summarised in Table 2. The DSC thermograms confirm the formation of liquid crystalline phases for all of the polymers

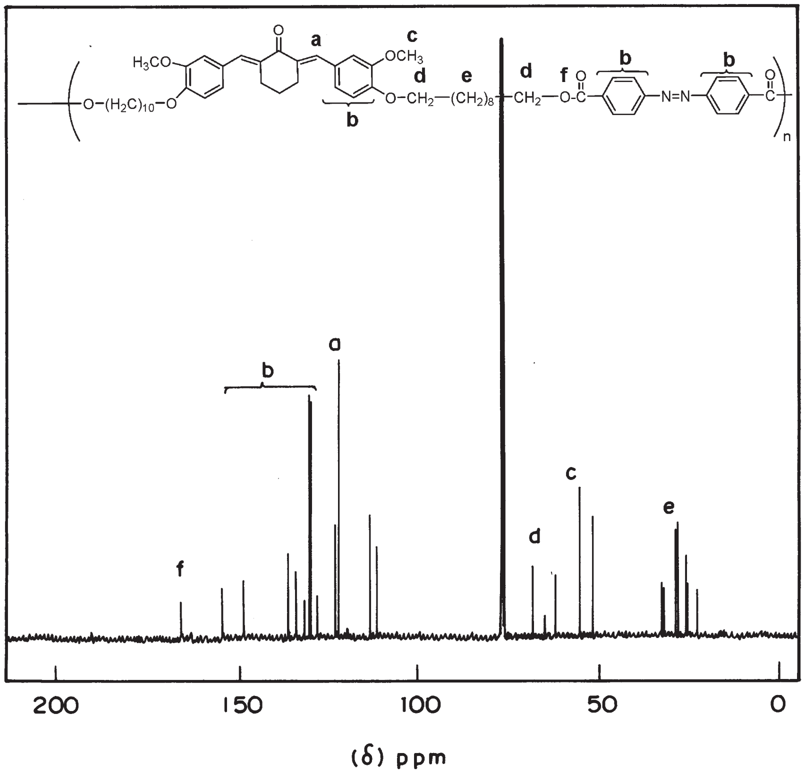


Figure 3. ^{13}C-NMR spectrum of polymer **IIa**.

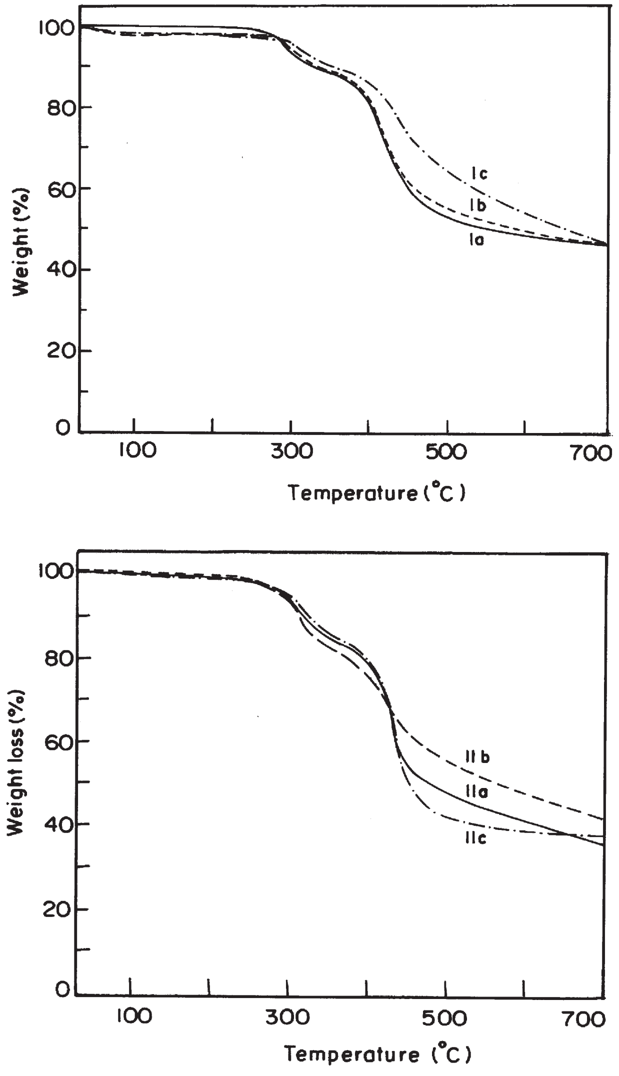


Figure 4. TGA traces of the polymers **Ia**–**IIc**.

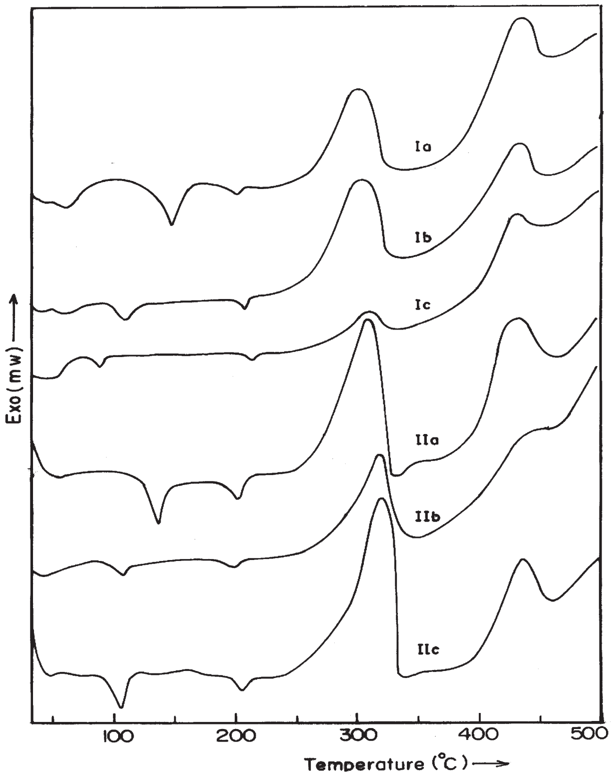


Figure 5. DSC traces of the polymers **Ia**–**IIc**.

(**Ia**–**IIc**). All of the polymers showed three endothermic peaks and two exothermic peaks. The three endothermic peaks correspond to the glass transition temperature (T_g), the crystalline–liquid crystalline (T_m) and liquid crystalline–isotropic (T_i) transition temperatures. The glass transition temperature was obtained in the range of 52–75°C, the melting transition temperature (T_m) was obtained in between 89 and 146°C and the isotropic transition temperature was obtained in the range of 198–219°C. The large ΔT data indicate that the polymers exhibit a stable mesophase. In general, the T_m and T_i values of the LCPs are strongly influenced by the polymeric chain flexibility (*43, 44*). The data obtained from the DSC thermogram in all of the polymers revealed that the T_m of the polymers decrease as the flexible methylene chain length increases from six to ten methylene units (see Figure 6 and Table 2). The two exothermic transitions are taking place at almost the same temperature for all of the polymers at around 310 and 433°C. The former exotherm may be ascribed to nitrogen evaluation owing to thermal cleavage of azo linkage in azobenzene unit and the latter may be attributed to thermal crosslinking leading to cyclobutane ring formation (*45, 46*).

Table 2. DSC and HOPM data of polymers **Ia**–**IIc**

		DSC (°C)				HOPM (°C)			
Polymer	*m*	T_g	T_m	T_i	ΔT	T_m	T_i	ΔT	Type of LC textures
Ia	6	63	146	202	56	147	204	57	Grainy
Ib	8	56	105	208	103	108	207	99	Nematic
Ic	10	52	89	219	130	88	219	131	Nematic
IIa	6	75	136	204	68	135	205	70	Grainy
IIb	8	74	108	198	90	110	197	87	Nematic
IIc	10	73	105	207	102	106	209	103	Nematic

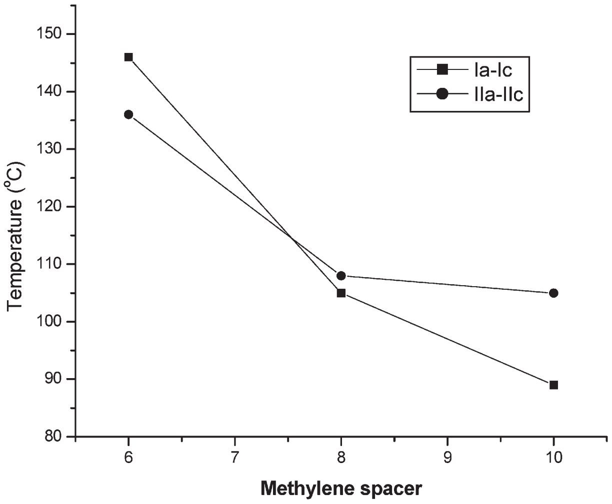


Figure 6. Correlation between the melting transition temperatures (T_m) obtained in DSC and spacer length.

3.3. *Liquid crystalline properties*

All of the polymers show birefringent melt and exhibited the LC behaviour under hot stage optical polarised microscopy (HOPM), and representative photographs of the polymers are shown in Figure 7. The type of mesophase is displayed in Table 2. The melting points of all of the polymers were between 88 and 147°C and the isotropic transition temperatures were between 197–219°C. On cooling from isotropic melt (T_i), the reproducibility of the grainy and nematic textures was satisfactory. The phase transition temperature values noted in DSC thermograms are closer to that of the mesogenic transition temperatures observed from HOPM. The hexamethylene spacer containing polymers (**Ia** and **IIa**) exhibited grainy textures owing to their restricted mesogenic movement, whereas the octamethylene and decamethylene spacer containing polymers (**Ib**, **Ic**, **IIb** and **IIc**) showed nematic textures. The HOPM results revealed that, when the methylene spacer length was increased, the polymers grew as large mono-domains by forming nematic textures (*47, 48*) possibly ascribed to the high segmental mobility that leads to the separation of mesogens.

3.4. *Photolysis studies*

It is noteworthy to mention that the polymers reported herein contain dual chromophores, namely, divanillylidene and azobenzene moieties. *Cis-trans* isomerisation takes place in the ln azobenzene segment, while exposing the polymers to UV light

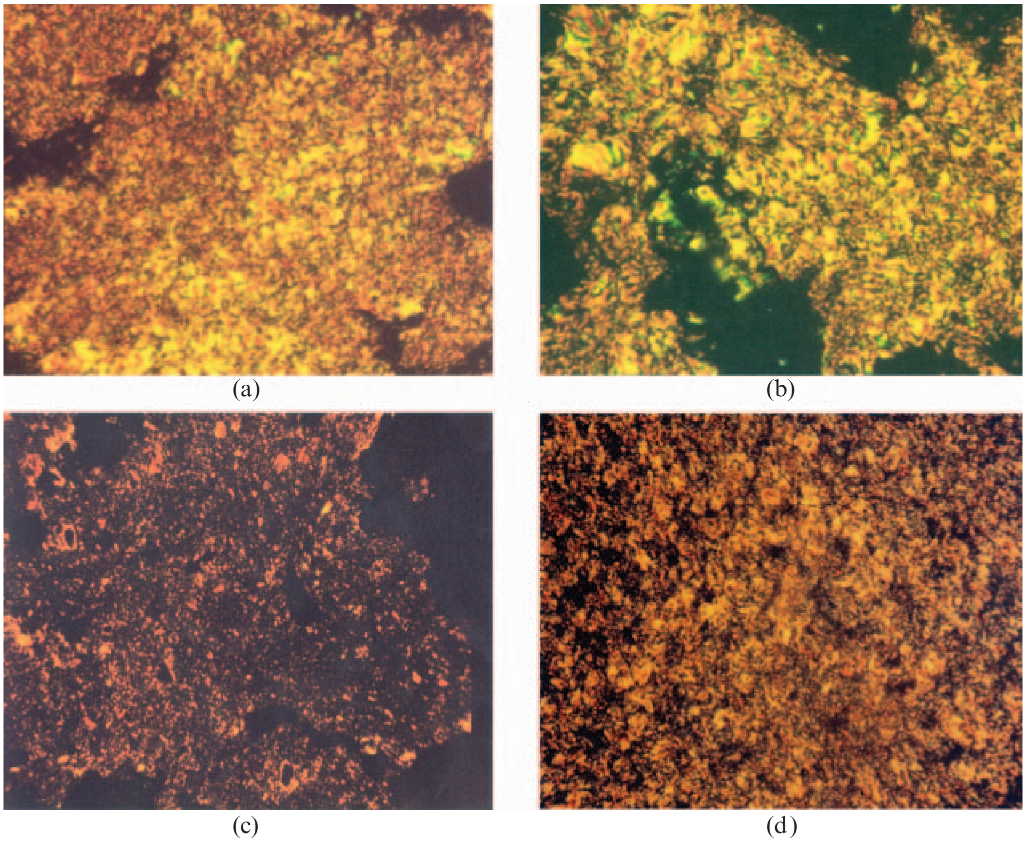

(a) (b) (c) (d)

Figure 7. Optical polarised photographs of polymers **Ia** (a), **Ib** (b), **IIa** (c) and **IIc** (d) at a magnification of 200×.

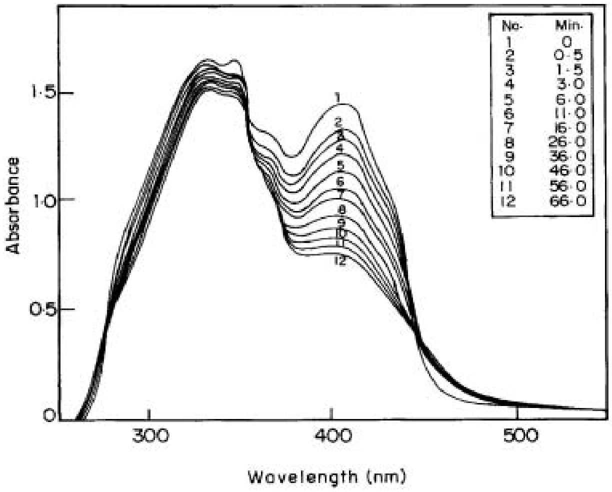


Figure 8. Changes in UV spectral characteristics during the photolysis of polymer **Ib** at various intervals of time.

at an appropriate wavelength, *trans-cis* conformational changes can be observed. The representative absorption spectra of polymer Ib are shown in Figure 8. The data revealed that on continuous irradiation in the UV light a decrease in absorbance was noticed in the π–π* transition of *trans* azobenzene at $\lambda_{\max}$=5354 nm.

During photolysis the absorbance maximum at 354 nm (*trans* isomer) was decreased while a new absorbance maxima arose at 365 nm (*cis* isomer) and increased with increasing irradiation. This may be a result of the *cis–trans* isomerisation of the azo group in the main chain (*49, 50*).

The mesogenic divanillylidene cyclohexanone and cyclopentanone contain the photosensitive α,β unsaturated ketones (chalcone) group that will undergo photodimerisation. The photo-crosslinking ability of the polymers was studied in solution, which was irradiated under UV light and monitored using a UV spectrophotometer. The changes in the photolysis of the polymers **Ib** is shown in Figure 8. The absorption band around 390–408 nm corresponds to the π–π* transition of the olefinic double bond of the mesogenic unit in the polymer backbone. During the successive irradiation a decrease in intensity of the absorption was observed, indicating that the cleavage of the unsaturated bond leads to the formation of a saturated bond. This may be a result of the dimerisation of the olefinic double bond of the polymer which involves the $2\pi+2\pi$ cycloaddition reactions leading to the formation of a cyclobutane ring (*51, 52*). It is interesting to note that the photolysis took place at a much faster rate and the absorption band at 390–408 nm completely disappeared within 50–60 min. The relative rates of photo-crosslinking of the polymers **Ia**–**Ic** and **IIa**–**IIc** are depicted in the Figure 9, where the relative reactivity A_0-A_t/A_0 is plotted against the time of irradiation (A_0 is the absorption before irradiation and A_t is the absorption after irradiation for time *t*).

It is evident that the rate of reduction of the exocyclic double bond during photolysis is faster for the longer carbon chain than the shorter carbon chain in the polymer. Among the cycloalkanone polymers, the cyclopentanone containing polymers showed a higher rate of crosslinking than the cyclohexanone polymers. This may be attributed to an increase in the unfavourable geometry for 2+2 cycloaddition reactions in cyclohexanone containing polymers (**IIa**–**IIc**).

The photolysis studies of various methylene spacer-containing polymers revealed that the rate of photo-crosslinking of exocyclic double bonds of the various methylene spacer-containing polymers is increasing in the following order:

hexamethylene < octamethylene < decamethylene.

The photo-crosslinking rate is faster as the number of methylene units increases from six to ten in the polymer chain. This may be attributed to the folding tendency of the methylene units present in the chain. The folding tendency normally increases with an increased number of methylene units in the polymer chain, which brings the vanillylidene units closer, therefore the photo-crosslinking reaction proceeded at a much faster rate.

After completion of the photolysis study, *in-situ* turbidity appeared in the solution and once it was set aside fine particles started to settle out in the cuvette, which was an indication of the sample's insolubility in chloroform solvent (*27*). In addition, after cross-linking, the polymers no longer displayed the liquid crystalline property attributed to the restricted molecular mobility and rigidity in the polymer backbone.

4. Conclusions

A new class of PMCLCPs containing the bis(vanillylidene)cycloalkanone group has been synthesised, where the structure was varied with the spacer length, using a polycondensation method and characterised spectroscopically. These variations have been correlated with the thermal properties and transition temperatures. The intrinsic viscosity of the polymer data reveals that these polymers are moderately high molecular weight materials. All of the polymers are stable up to 280°C and the degradation occurs in a two-step manner. All of the polymers showed a LC phase. The absorbance of all of the polymers occurred above 375–408 cm^{-1}; as the methylene chain

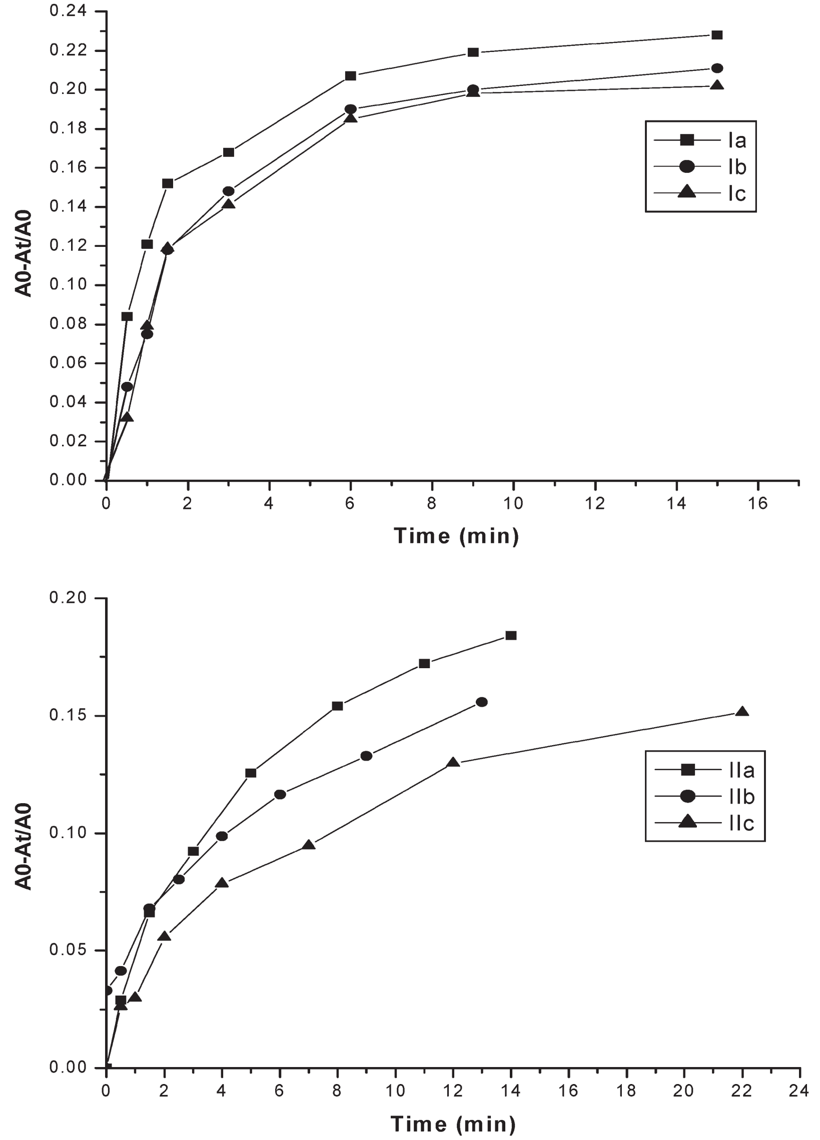


Figure 9. Dependence of photo-crosslinking rate on irradiation time for the polymers **Ia**–**Ic** and **IIa**–**IIc**.

increased the absorbance shifted to a bathochromic shift. All of the prepared polymers rapidly established crosslinking under UV irradiation. The higher methylene chain containing polymers showed a faster rate of photolysis than the lower methylene chain containing polymers. These dual properties of the liquid crystallinity and photo-crosslinking of these polymers might be exploited in non-linear optical applications.

References

(1) Chapoy L.L. *Recent Advances in Liquid Crystalline Polymers*; Elsevier Applied Science: London, **1985**.

(2) McArdle C.B. *Side Chain Liquid Crystal Polymers*; Chapman and Hall: New York, **1989**.

(3) Noel C.; Navard P. *Prog. Polym. Sci.* **1991**, *16*, 55–110.

(4) Ober C.K.; Jin J.I.; Lenz R.W. *Adv. Polym. Sci.* **1984**, *59*, 103–146.

(5) Hani R.; Lenz R.W. *Silicone Based Polymer Science: A Comprehensive Resource* 1990 Advances in Chemistry 224, American Chemical Society: Washington, DC, **1990**. p 741.

(6) Creed D.; Griffin A.C.; Gross J.D.; Hoyle C.E.; Venkataram K. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 57–71.

(7) Ikeda T.; Itakura H.; Lee C.; Winnik F.M.; Mitchell S. *Macromolecules* **1988**, *21*, 3536–3537.

(8) Keller P. *Chem. Mater.* **1990**, *2*, 3–4.

(9) Whitcombe M.J.; Gilbert A.; Hirai A.; Mitchell G.R. *J. Polym. Sci. Polym. Chem. Ed.* **1991**, *29*, 251–259.

(10) Whitcombe M.J.; Gilbert A.; Hirai A.; Mitchell G.R. *Br. Polym. J.* **1990**, *23*, 77–83.

(11) Griffin A.C.; Hoyle C.E.; Gross J.R.D.; Venkataram K.; Creed D.; McArdle C.B. *Macromol. Chem.* **1988**, *9*, 463–477.

(12) Legge C.H.; Whitcombe M.J.; Gillbert A.; Mitchell G.R. *J. Mater. Chem.* **1991**, *1*, 303–304.

(13) Mohlmann G.R.; van der Vorst C.P.J. *Side Chain Liquid Crystal Polymers*; McArdle C.B. (Eds), Chapmann and Hall: New York, **1989**. p. 330.

(14) Marturunkakul S.; Chen I.J.; Li L.; Jeng R.J.; Kumar J.; Tripathy S.K. *Chem. Mater.* **1993**, *5*, 592–594.

(15) Koch T.; Ritter H.; Buchholz N. *Macromol. Chem.* **1989**, *190*, 1369–1377.

(16) Loth H.; Euschem A. *Macromol. Chem. Rapid Commun.* **1988**, *9*, 35–44.

(17) Creed D.; Griffin A.C.; Hoyle C.E.; Venkataram K. *J. Am. Chem. Soc.* **1990**, *112*, 4049–4050.

(18) Noonan J.M.; Caccamo A.F. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1984**, *30*, 501–504.

(19) Krigbaum W.R.; Ishikawa T.; Watanabe J.; Toriumi H.; Kubota K. *J. Polym. Sci. Polym. Chem. Ed.* **1983**, *21*, 1851–1856.

(20) Peter K.; Ratzsch M. *Makromol. Chem.* **1990**, *191*, 1021–1025.

(21) Whitcombe M.J.; Gilbert A.; Hirai A.; Mitchell G.R. *J. Polym. Sci. Polym. Chem.* Ed. **1992**, *30*, 1681–1691.

(22) Finkelmann H.; Ringsdorf H.; Wendorff J.H. *Makromol. Chem.* **1978**, *179*, 2541–2544.

(23) Kannan P.; Murugavel S.C. *Polym. Int.* **1996**, *40*, 287–293.

(24) Nuyken O.; Scherer C.; Baindl A.; Brenner A.R.; Dahn U.; Gartner R.; Kaiser-Rohrich S.; Kollefrath R.; Matusche P. *Prog. Polym. Sci.* **1997**, *22*, 93–183.

(25) Ikeda T.; Tsutsumi O. *Science* **1995**, *268*, 1873–1875.

(26) Kurihara S.; Sakamoto A.; Yoneyama D.; Nonaka T. *Macromolecules* **1999**, *32*, 6493–6498.

(27) Gangadhara; Kishore K. *Macromolecules* **1993**, *26*, 2995–3003.

(28) McArdle C.B. *Side Chain Liquid Crystal Polymers*; McArdle C.B. (Ed.), Chapman and Hall: New York, 1989. p 1.

(29) George H.; Roth H.J. *Tetrahedron Lett.* **1971**, *43*, 4057–4060.

(30) Wargnier F.B.; Feigenbaum A.; Muaart J. *J. Chem. Educ.* **1978**, *55*, 339–362.

(31) Forward G.C.; Whiting D.A. *J. Chem. Soc.* C. **1989**, 1868–1872.

(32) Frey H.; Behmann G.; Kaupp G. *Chem. Ber.* **1987**, *120*, 387–392.

(33) Kaupp G.; Zimmermann I. *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 1018–1019.

(34) Theocharis C.R.; Jones W.; Thomas M.J.; Molevalli M.; Hursthouse B.M. *J. Chem. Soc. Perkin Trans.* **1984**, *2*, 71–76.

(35) Aizeshtat Z.; Hausmann M.; Pickholts Y.; Tal D.; Blum J. *J. Org. Chem.* **1977**, *42*, 2386–2394.

(36) Furniss B.S.; Hannaford J.; Smith P.W.G.; Tatchill A.R. *Vogel's Text Book of Practical Organic Chemistry* **1994** 5th edition, ELBS: London, 1994.

(37) Perrin D.D.; Armarego W.L.F. *Purification of Laboratory Chemicals* 1988 3rd edition, Pergamon Press: New York, **1988**.

(38) Goldsmith D.J.; Kennedy E.; Campbell R.G. *J. Org. Chem.* **1975**, *40*, 3571–3574.

(39) Borden D.S. *J. Appl. Polym. Sci.* **1978**, *22*, 239–251.

(40) Tomlinson M.L. *J. Chem. Soc.* Part *2.* **1946**, *2*, 546–548.

(41) Petersen J.M. *Organic Synthesis*; Price C.C. (Ed.), Wiley: New York, **1953**. pp. 33–53.

(42) Sun S.J.; Schwarz G.; Kricheldorf R.; Chang T.C. *J. Polym. Sci. Polym. Part A: Polym. Chem.* **1999**, *37*, 1125–1133.

(43) Juan P.; Fernandez B.; Antonio B.; Ernesto P. *Macromolecules* **2004**, *37*, 9018–9026.

(44) Luping Y. *Macromolecules* **1995**, *28*, 6410–6415.

(45) Mallon P.E.; McGill W.J.; Shillington D.P. *J. Appl. Polym. Sci.* **1995**, *55*, 705–721.

(46) Ahmed R.; Nehal S. *Polymer* **1999**, *40*, 2197–2207.

(47) Ungar G.; Percec V.; Rodenhouse R. *Macromolecules* **1991**, *24*, 1996–2002.

(48) Kyung M.L.; Chang D.H. *Macromolecules* **2003**, *36*, 8796–8810.

(49) Dierking I. *Textures of Liquid Crystals*; Wiley-VCH: Weinheim, **2003**. p 51.

(50) Ichimura K. *Chem. Rev.* **2000**, *100*, 1847–1874.

(51) Thomas J.M. *Nature* **1981**, *289*, 633–634.

(52) Rehab A.; Salahuddin N. *Polymer* **1999**, *40*, 2197–2207.