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Synthesis of novel liquid crystalline polymers with cross-linked network structures

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Abstract

Liquid crystalline (LC) polymers with cross-linked network structures containing azobenzene mesogens were synthesised from cardanol, the unsaturated C_{15} hydrocarbon side chain of which is utilised for cross-linking reactions. The azobenzene group was introduced by the diazo coupling reaction between cardanol and 4-aminobenzoic acid. The resulting monomer, 4-[(4-cardanyl)azo]benzoic acid (**I**) was polymerised by self-polycondensation using thionyl chloride and pyridine to get poly[4-[(4-cardanyl)azo]benzoic acid] (**III**). (**I**) was also converted to poly[4-[(4-acryloyloxycardanyl)azo]benzoic acid](**IV**) through acryloylation of (**I**) followed by free radical polymerisation. Cationic polymerisation of (**I**) gave poly {4-[(4-cardanyl)azo]benzoic acid} (**V**). The monomers and polymers were characterised using elemental analysis, IR, ^{1}H and ^{13}C NMR and UV–visible spectroscopy. Polymer (**III**) was neither soluble in any solvent nor fusible. Polymer (**IV**) was also insoluble, but swelling was observed with many solvents and polymer (**V**) was soluble in polar solvents. On slow heating, polymers **IV** and **V** also got converted to totally insoluble products. IR spectra indicated involvement of side chain unsaturation in bond formation leading to cross-linking. Threaded nematic textures were obtained when polymer (**III**) was heated to below 200°C and rapidly quenched to room temperatures and observed under PLM. Otherwise, on heating polymer (**III**) started decomposing near 200°C as observed by an exotherm in DSC and confirmed by TGA. Polymers (**IV**) and (**V**) exhibited schlieren nematic textures under PLM. Polymer (**V**) gave cross-linked transparent film when cast from a solvent and cured by slow heating.

Keywords: Liquid crystalline polymers; Cross-linked network structure; Azobenzene mesogen

1. Introduction

Liquid crystalline (LC) polymers with cross-linked networks are becoming attractive due to possibilities for freezing the LC phase [1–20]. These cross-linked polymers pass through a mesophase during curing and retain a mesophase in the final state [1]. LC main chain/side chain polymers with cross-linked networks can be prepared by chemical/thermal/photo- cross-linking of reactive double bonds in the chain or by reaction with a cross-linking agent or by copolymerisation [2,4,6–12,14–19]. In one of our earlier works on the synthesis of poly (cardanyl acrylate) from cardanol, a naturally occurring monomer, it was observed that cardanyl acrylate on suspension polymerisation gives cross-linked beads directly [21,22]. The formation of the cross-linked polymer has been explained as due to the auto cross-linking of the unsaturated side chain of cardanyl unit [22]. This property of the cardanyl side chain can be used to form cross-linked network structures for LC polymers. We have earlier shown that cardanol possesses special structural features that allow it to be transformed into high performance polymers including LCPs [23–25]. Thus, we showed that poly[4-[hydroxy-2-pentadecyl)azo]benzoic acid] derived from 3-*n*-pentadecyl phenol, the hydrogenated derivative of cardanol, is liquid crystalline and is potentially a non-linear optical (NLO) material [25,26]. Azobenzene derivatives and polymers containing donor–acceptor groups in conjugation are known for their NLO activity [27–36]. To retain the NLO property in a polymer, it is, however, important to prevent the dipole reversal or relaxation from their dipolar alignment. One of the methods recommended to arrest the relaxation is by introducing cross-links during poling which “lock in” dipole alignment due to the restricted molecular mobility [35]. We have now synthesised novel LC polymers with cross-linked network structures containing azobenzene mesogen based on cardanol, the unsaturated C_{15} hydrocarbon side chain of which is utilised for cross-linking reactions. The preliminary results are presented in this communication.

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2. Experimental

2.1. Synthesis of monomers

*4-[(4-Cardanyl)azo]benzoic acid (**I**)*: *p*-aminobenzoic acid (13.71 g, 0.1 mol) (Aldrich Co., Milwaukee, USA) was dissolved in dilute HCl and diazotised with sodium nitrite (6.90 g, 0.1 mol in 20 ml of water) solution at 0°C with stirring. Cardanol (30.05 g, 0.1 mol)(obtained by distillation of cashewnut shell liquid under vacuum [26]) dissolved in a chilled solution of potassium hydroxide (10.77 g, 0.19 mol) in methanol (100 ml) was added dropwise to the above solution diluted with chilled methanol (400 ml). The red dye formed was stirred for further 2 h and poured into dilute HCl solution with stirring. The red solid separated was filtered, washed thoroughly with water, and dried. The dye was then purified by column chromatography on silica gel (100–200 mesh) using chloroform as eluent. The solvent was removed and recrystallised from a methanol–water mixture.

Yield 36.16 g (80%); red flakes; m.p. 134–135°C. Anal. Calcd. for $C_{28}H_{37}N_2O_3$: C, 74.80; H, 8.29; N, 6.23. Found: C, 75.10; H, 8.25; N, 6.10. m.p. 134–135°C. UV–vis ($\lambda_{\max}$): 372 nm ($\epsilon_{max} = 13{,}862\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). IR (KBr; cm^{-1}): 3320 (Ar–OH), 2920, 2860 ($-CH_2-$), 1690(Ar–COOH), 1610, 1580 (Ar, C=C),3020, 790 (*cis* –CH=CH–), 1155 (–N=N–). ^{1}H NMR (acetone-d_6): δ(0.7–3.3 (~27H, m, $-CH_2-$), 5.0–5.6 (m, –CH=CH–), 6.7–8.3 (7H, m, Ar) ppm. ^{13}C NMR (acetone-d_6): δ(13.2, 22.1, 28.5, 29.0, 29.3, 30.9, 31.4, 31.9, 114.6, 113.9, 116.2, 116.8, 121.9, 129.4, 130.5, 131.4, 143.5, 146.6, 155.5, 161.5, 166.4 ppm.

*4-[(4-Acryloyloxycardanyl)azo]benzoic acid (**II**)*: Acryloyl chloride (0.41 g; 4.5 mmol) (prepared by the procedure of Stempel et al. [37]) was added in drops to cold potassium salt of **I** (1 g; 2.2 mmol) in DMAc solution with stirring. The solution was poured into ice water (500 ml) after stirring for 1 h. The precipitated product was filtered and washed thoroughly with cold water, then dissolved in ether, dried using anhydrous sodium sulphate and filtered. Ether was removed under reduced pressure and the product was chromatographed on silica gel (100–200 mesh) using chloroform as eluent. Chloroform was removed under reduced pressure.

Yield 0.89 g (79.6%); red solid; m.p. 118–120°C. Anal. Calcd. for $C_{31}H_{38}N_2O_4$: C, 74.08; H, 7.62; N, 5.57. Found: C, 74.11; H, 7.74; N, 5.30. UV–vis ($\lambda_{\max}$) 347 nm ($\epsilon_{max} = 19{,}319\ \mathrm{M}^{-1}\ \mathrm{cm}^{-1}$). IR (KBr; cm^{-1}): 2932, 2860 ($-CH_2-$); 1742 (CH_2:CH–COOAr); 1694 (ArCOOH); 1662 (acrylic CH_2:CH–); 1609, 1585 (Ar; C=C); 3016, 780 (olefinic –CH:CH–); 1151 (–N=N–). ^{1}H NMR (DMSO-d_6): δ(7.7–8.3 (7H, m, Ar); 6.1–6.6 (3H, m, CH_2:CH); 0.7–2.9 (~27H, m, $-CH_2-$). ^{13}C NMR (DMSO-d_6): δ = 166.6, 163.5, 154.5, 153.0, 147.2, 144.7, 132.8, 130.5, 129.4, 127.8, 127.4, 123.1, 122.4, 120.1, 116.3, 31.4, 31.1, 30.9, 30.4, 29.0, 28.6, 28.2, 26.5, 25.1, 22.0, 13.7, 13.4 ppm.

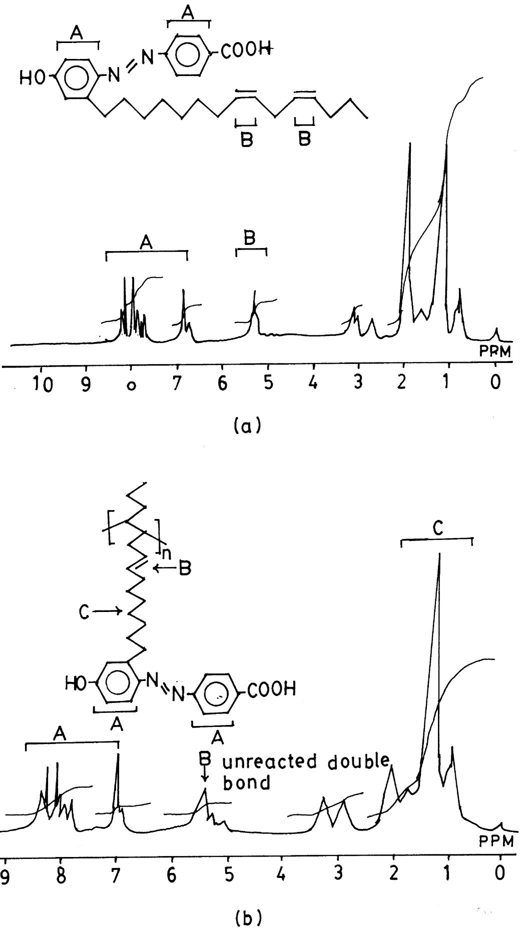


Fig. 1. ^{1}H NMR spectra of (a) 4-[(4-cardanyl)azo]benzoic acid (monomer **I**) and (b) polymer **V**.

2.2. Synthesis of polymers

*Poly[4-[(4-cardanyl)azo]benzoic acid] (**III**)*: Monomer **I** (1.0 g; 4.1 mmol) was refluxed (1 h) with an excess of thionyl chloride (1 ml) in a two necked round bottom flask attached with a condenser and a gas purge tube and the excess thionyl chloride was distilled off in a nitrogen stream. *o*-Dichlorobenzene was added to dissolve the acid chloride and a few drops of pyridine was added. The polymerisation was continued for 12 h at 80°C and the polymer was precipitated in excess methanol and dried.

Yield 0.85 g (89%); red–orange powder. Anal. Calcd. for $C_{28}H_{34}N_2O_2$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.29; H, 8.12; N, 6.58. IR (KBr; cm^{-1}): 1745 (ArCOOAr); 1620, 1590, 1560 (Ar; C=C); 2925, 2860, 1485, 1465, 1430 ($-CH_2-$); 1150 (–N=N–).

*Poly[4-[(4-acryloyloxycardanyl)azo]benzoic acid] (**IV**)*: To 1 g of monomer **II** dissolved in 10 ml *o*-dichlorobenzene, 10 mg (1 wt%) of benzoyl peroxide was added with stirring in a reaction flask which was then corked with rubber septum and purged with pure dry nitrogen gas for 30 min. The reaction mixture was heated to 85°C on an oil

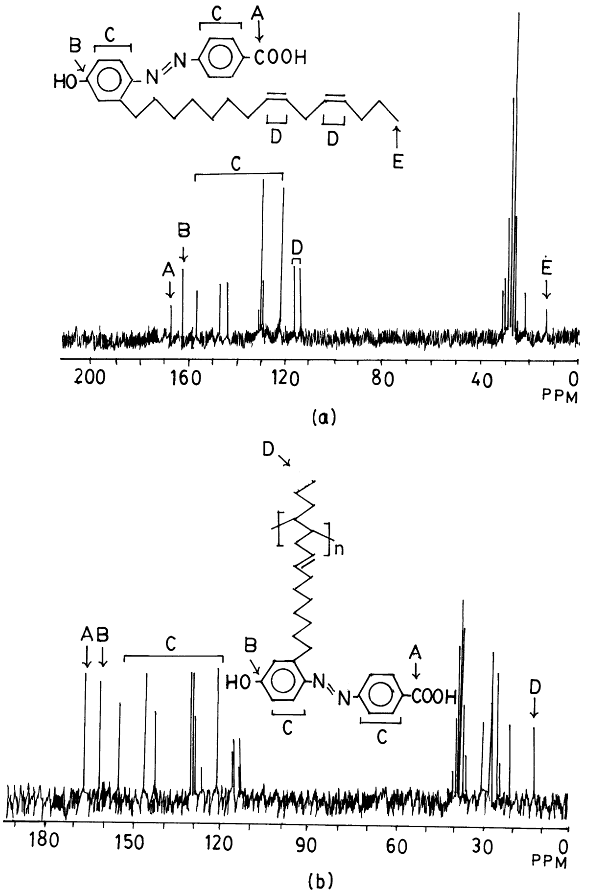


Fig. 2. ^{13}C NMR spectra of (a) 4-[(4-cardanyl)azo]benzoic acid (monomer **I**) and (b) polymer **V**.

bath with stirring. The polymer formed was precipitated after 12 h of polymerisation, filtered and dried.

Yield 0.68 g (68%); red solid. Anal. Calcd. for $C_{31}H_{38}N_2O_4$: C, 74.08; H, 7.62; N, 5.57. Found: C, 74.22; H, 7.75; N, 5.46. IR (KBr; cm^{-1}): 2960, 2880 (–CH$_2$–); 1740 (>CHCOOAr); 1700(ArCOOH);1620, 1600 (Ar; C=C); 1420 (–CH$_2$–);1156 (–N=N–); 3020, 780 (*cis* –CH=CH–).

*Cationic polymerisation of [4-[(4-cardanyl)azo]benzoic acid] (**V**)*: To 1 g of monomer **I** dissolved in *o*-dichlorobenzene, 10 mg (1 wt%) of $BF_3 \cdot OEt_2$ was added. The reaction was continued for 2 h at 100°C under nitrogen atmosphere on an oil bath. The polymer was precipitated in excess carbon tetrachloride, filtered and washed thoroughly with chloroform and dried at 80°C for 12 h in a vacuum oven.

Yield 0.80 g (80%); dark red solid. Anal. Calcd. for $C_{28}H_{37}N_2O_3$: C, 74.8; H, 8.29; N, 6.23. Found: C, 75.34; H, 7.3; N, 7.12. UV–vis ($\lambda_{\max}$): 371 nm ($\epsilon_{max} = 21,783\ M^{-1}\ cm^{-1}$). IR (cm^{-1}): 3320 (Ar–OH); 3020, 790 (*cis* –CH=CH–); 2960, 2880 (–CH$_2$–); 1700 (ArCOOH); 1620, 1600 (Ar; C=C); 1440 (–CH$_2$–); 1158 (–N=N–). ^{1}H NMR (DMSO-d$_6$): δ(0.7–3.3 (–CH$_2$–); 4.9–5.5 (–CH=CH–); 6.7–8.3 (Ar). ^{13}C NMR (DMSO-d$_6$): δ(166.8, 161.6, 155.1, 146.3, 143.0, 131.6, 130.4, 129.8, 129.4, 121.9, 116.8, 116.2, 114.6, 114.1, 31.6, 31.1, 30.8, 29.1, 28.7, 28.6, 28.3, 26.9, 26.6, 25.8, 25.1, 22.1, 13.8 ppm.

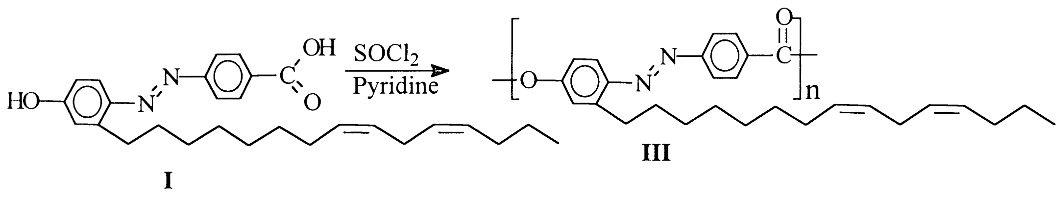
Elemental analysis was performed using Perkin–Elmer 2400 CHN Elemental Analyser. Molecular mass of the monomers was obtained from GC-MS (5890 Series II GC connected to 5970 Mass Detector). IR spectra were recorded using Perkin–Elmer 882 infrared spectrometer and ^{1}H and ^{13}C NMR from Jeol JNM-EX 90 FT NMR spectrometer. UV–vis spectra were obtained in DMF using Shimatzu UV-160A spectrophotometer. The phase behaviour of the polymers was observed under Nikon Optiphot polarised light microscope equipped with Linkam THMS 600 heating stage. DSC scans were performed using Du Pont DSC 2010 Differential Scanning Calorimeter attached to Thermal Analyst 2100 data station under nitrogen and TGA using Du Pont 951 Thermogravimetric Analyser under air and nitrogen. The heating rate used was 20°C/min.

3. Results and discussions

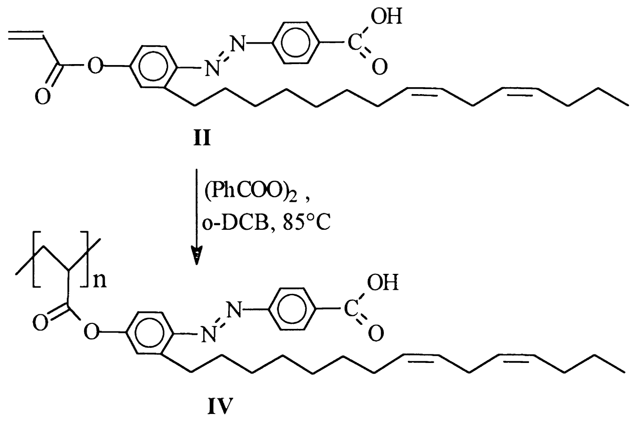
3.1. Synthesis of monomers and polymers

Azobenzene monomer **I** was synthesised by the diazo coupling reaction between cardanol and 4-aminobenzoic acid according to the procedure reported elsewhere for the synthesis of related compounds [16]. Elemental analysis, IR spectra, ^{1}H and ^{13}C NMR spectra (see Figs. 1 and 2) support the proposed structure of **I**. The UV–vis spectra of **I** have one absorption peak at 372 nm ($\epsilon_{\max} = 13,862\ M^{-1}\ cm^{-1}$) due to π–π^* transition of azobenzene.

Acrylate monomer **II** was synthesised from the potassium salt of **I** and acryloyl chloride in DMAc and the structure **II** was assigned using IR spectra, ^{1}H NMR (the multiplet of acrylic protons appeared in the region of δ 6.1–6.6 and ^{13}C NMR spectra (the acrylate ester carbonyl group appeared at δ 166.6 ppm with acrylic double bond carbons at δ 129.4 and 127.8 ppm) (Figs. 1 and 2). The UV–vis spectra of **II**



Scheme 1.



Scheme 2.

have one absorption peak at 347 nm ($\epsilon_{max} = 19,319\ M^{-1}\ cm^{-1}$) due to $\pi-\pi^*$ transition of azobenzene.

Polymer **III** was synthesised by self-polycondensation of **I** using thionyl chloride and pyridine. The polymer got precipitated during polymerisation. Polymer **III** was neither soluble in any solvent nor fusible. This behaviour may be explained on the basis of the formation of cross-links involving the side chain double bonds. A similar behaviour has been reported in the case of poly(cardanyl acrylate) where the unsaturated side chain gets cross-linked during polymerisation giving rise to insoluble polymer beads [12]. (Scheme 1 (Synthesis of poly[4-[(4-cardanyl)azo]benzoic acid]). The involvement of the unsaturated side chain in cross-link formation can be further inferred by comparing with the excellent solubility of poly[4-[(4-hydroxy-2-pentadecylphenyl)azo]benzoic acid], an LC azo polyester prepared from 3-pentadecylphenol, the saturated analogue of cardanol in polar solvents [25,26].

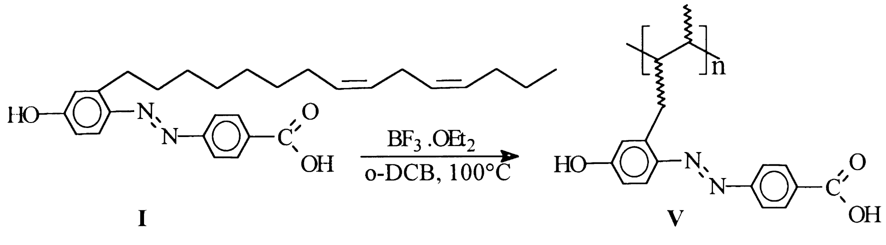
The IR spectra of **III** gave the characteristic vibrations of ester carbonyl (1745 cm^{-1}), C–H stretching of aliphatic pendant (2920 and 2860 cm^{-1}) and –N=N– stretching (1150 cm^{-1}). In addition, **III** showed disappearance of 3020 and 790 cm^{-1} peaks characteristic of the side chain olefinic unsaturation of cardanol. The disappearance of the unsaturation in the side chain of cardanol suggests the involvement of these carbon atoms in cross-link formation. This has been further confirmed by the DSC data.

Polymer **IV** was prepared by radical polymerisation of **II** through the acrylate vinyl function. Polymer **IV** was also insoluble, but swelling was observed with all solvents tried. In contrast, poly[4-[(4-acryloyloxy-2-pentadecylphenyl)-azo]benzoic acid], a polymer with analogous structure except the side chain which is saturated was soluble in polar solvents [26]. The disappearance of the acrylate C=C vibration at 1662 cm^{-1} in the IR spectra of **IV** indicated polymerisation through the acrylate C=C (Scheme 2 (Synthesis of poly[4-[(4-acryloyloxycardanyl)azo]benzoic acid]). The ester peak of **IV** has been shifted by at least 10 cm^{-1} on polymerisation when compared to the monomer and the carboxylic acid hydrogen bonded dimer peak appeared at 1700–1690 cm^{-1}. The intensity of the peaks due to olefinic unsaturation of cardanol at 3020 and 790 cm^{-1} got reduced, but did not disappear completely indicating possibly a low level of cross-linking which is also clear from the swelling of **IV** in organic solvents.

Polymer **V** was prepared by cationic polymerisation (Scheme 3 (Cationic polymerisation of 4-[(4-cardanyl)azo]-benzoic acid (**V**)) of **I** using the procedure of Rosy et al. [38]. The polymer is soluble in polar solvents indicating that it is not cross-linked at this stage. The inherent viscosity (measured using Ubbelhode suspended level viscometer in a water bath at 28 ± 1°C) of **V** in *o*-dichlorobenzene at 28°C was found to be 0.74 dl/g (concentration: 0.5 g/dl).

The formation of polymer **V** was supported by elemental analysis, IR, ^1H and ^{13}C NMR spectroscopy.

It was noted that there is only a decrease in the intensity of *cis* olefinic peaks at 3020 and 790 cm^{-1} indicating that one of the double bonds is not used-up on polymerisation. The ^1H NMR peaks broadened on polymer formation but the olefinic resonance peaks did not vanish completely due to the presence of unreacted double bonds (Fig. 1). However, the conclusive evidence of polymer formation is provided by ^{13}C NMR spectroscopy. When compared to the ^{13}C NMR (Fig. 2) of **II**, polymer **V** has five new peaks in the region of 32–12 ppm indicating five different, new carbon centres have been produced on polymerisation. The increase in the number of carbon centres can be attributed to the formation of saturated carbon centres. Moreover, when compared to **I**, the unaltered aromatic carbon resonances indicates that there is no Friedel–Crafts type substitution



Scheme 3.

Table 1
Properties of polymers **III**–**V**

Polymer			DSC[a]		Polarised light microscopy[b] (°C)
Code	Yield (%)	η_{inh} (dl/g)	T_m (°C)	T_c (°C)	
III	89	Insoluble	–	dec. > 200	dec. > 200; (N)
IV	68	Swelling	151	258	K 153 N 260 I
V	80	0.74[c]	134	242	K 136 N 245 I

[a] First heating cycle; m: mesophase, c: clearing temperatures.

[a] K, crystalline; N, nematic; (N), nematic mesophase obtained on rapid melting and quenching.

[c] Measured at a concentration of 0.5 g/dl in *o*-dichlorobenzene at 28°C.

to aromatic ring under Lewis acidic condition. The UV–vis spectrum of polymer **V** has one absorption peak at 371 nm ($\epsilon_{max} = 21,783\ M^{-1}\ cm^{-1}$). Polymer (**V**) gave cross-linked transparent film when cast from a solvent and cured by slow heating.

3.2. Thermal and phase behaviour of the polymers

Prior to discussing the thermal properties and phase behaviour of the polymers (studied by a combination of DSC and hot stage polarised light microscope (PLM)), an understanding of the structural relations of polymers **III**–**V** is warranted. Polymer **III** is a main chain polyester with the azophenyl mesogen in the main chain and the C_{15} unsaturated hydrocarbon side chain as pendant. Polymer **IV** is a polyacrylate side chain polymer with the azophenyl group along with the unsaturated side chain as pendant. In polymer **V**, the polymerisation is carried out through the unsaturation of the hydrocarbon moiety with the azophenyl mesogenic moiety remaining as pendant. Hence, the side chain unsaturation in these polymers offers opportunities for introducing cross-linking and thus entrapping the mesogenic group in a cross-linked network. The results of DSC and PLM are summarised in Table 1.

The DSC scan of main chain polymer **III** showed an unidentified endotherm at 70°C and an exotherm at 138°C. Above 200°C the polymer started decomposing as indicated by the steep rise of the base line. When observed under PLM, **III** did not show melting to form mesophase, but started decomposing above 200°C. On the contrary, the polymer sample prepared by rapid melting below the decomposition temperature and quenching to room temperature within a few seconds showed threaded nematic texture (Fig. 3) under PLM. Recent findings indicate that large flexible alkyl side chains stabilise the mesophase [29,39] by adopting a conformation that are nearly parallel to the basic molecule. We have observed such behaviour with a number of LC polymers containing azophenyl mesogen and a $C_{15}H_{31}$ side chain [25,26]. As the side chain in the present case is unsaturated, it undergoes cross-linking to give three-dimensional network structure without affecting the LC behaviour. The PLM observation was supported by TGA results where initial decomposition temperature (T_i) of **III** was observed at 209 and 221°C under air and nitrogen, respectively.

In contrast to the behaviour of polymer **III**, polymer **IV** melted at 153°C exhibiting a clear schlieren texture (Fig. 4) characteristic of nematic phase under PLM. These findings were confirmed by DSC (Table 1). Although there was no exotherm of cross-linking observed for polymer **IV** under the normal conditions of DSC measurement, further cross-linking was observed when heating was carried out at a slow rate. A fully cross-linked product (the IR peak at 3020 cm^{-1} totally disappeared) insoluble in all the solvents was

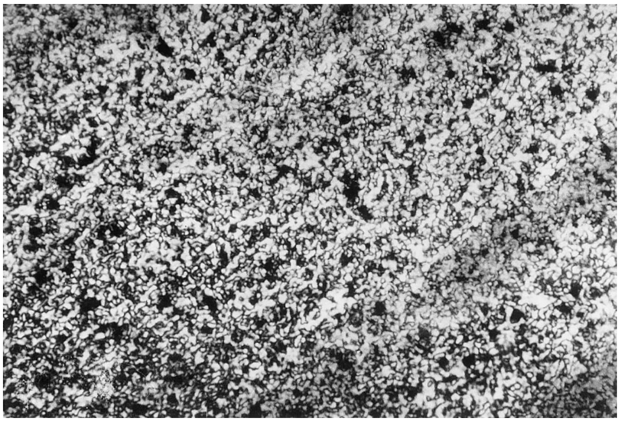


Fig. 3. PLM of polymer **III** showing threaded nematic texture.

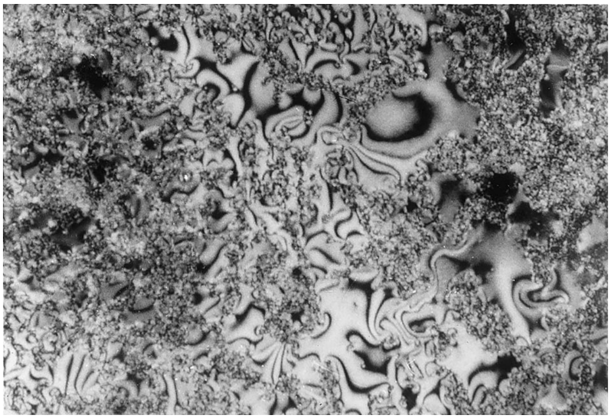


Fig. 4. PLM of polymer **IV** showing schlieren nematic texture.

Fig. 5. PLM of polymer **V** showing schlieren nematic texture.

obtained. Polymer **V** melted at 134°C exhibiting a clear schlieren texture (Fig. 5) characteristic of nematic phase under PLM. The polymer isotropised at 236°C and darkened soon after isotropisation. DSC confirmed these observations. On slow heating, polymer **V** also got converted to an insoluble product (cross-linking through one double bond remaining after polymerisation).

In short, solubility studies and IR spectra have indicated that polymer **III** is a fully cross-linked polymer. On slow heating, polymers **IV** and **V** also get converted to fully cross-linked products. While polymer **III** gave a nematic phase with threaded texture, polymers **IV** and **V** exhibited nematic phases with schlieren textures. Polymer **V** was soluble (prior to slow heating) in many common solvents. The significance of polymer **V** lies its capability to be cast into a film from solution and later thermally converted to an insoluble transparent film that retains the LC phase. It should be noted that these polymers cannot be compared to rigid rods thermosets [1] because the cross-linking in this case is developed from an unsaturated hydrocarbon side chain. Because of the same reason, it also differs from the semi-rigid rod diacrylates with densely cross-linked LC network structures [1,9] or the semi-rigid rod diacrylates with loosely cross-linked anisotropic gels [40]. Hence, this is the first of the kind of network developed through a side chain containing unsaturation.

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