

Synthesis and Mesogenic Behavior of Metal-Containing Liquid Crystalline Networks

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SYNOPSIS

A new hydroxy functionalized liquid crystalline (LC) polyazomethine has been synthesized by the solution polycondensation of a dialdehyde with a diamine. The polymer was characterized by IR, ^1H -, and ^{13}C -NMR spectroscopy. Studies on the liquid crystalline properties reveal the nematic mesomorphic behavior. This polymer functions as a polymeric chelate and forms a three-dimensional network structure through the metal complexation. Influence of various metals and their concentration on the liquid crystalline behavior of the network has been studied. Networks up to 30 mol % of the metal show LC phase transitions; above this the transitions are suppressed and the network behaves like an LC thermoset. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The liquid crystalline behavior of organometallic compounds is attracting increased attention as the combination of metal-based coordination chemistry and the unusual physical properties exhibited by liquid crystals may result in novel substances for molecular electronics, electrical and magnetic switches, conductors, and new optical devices.¹ Polarizability, one of the most important attributes of molecules that form liquid crystals, is increased with metal atoms having polymerizable electron density, which has a profound effect on the physical characteristics resulting from the possibility of unexpected but useful macroscopic properties. These properties make the metal-containing liquid crystals promising candidates for applications in devices requiring ferroelectric and nonlinear optical behavior.¹

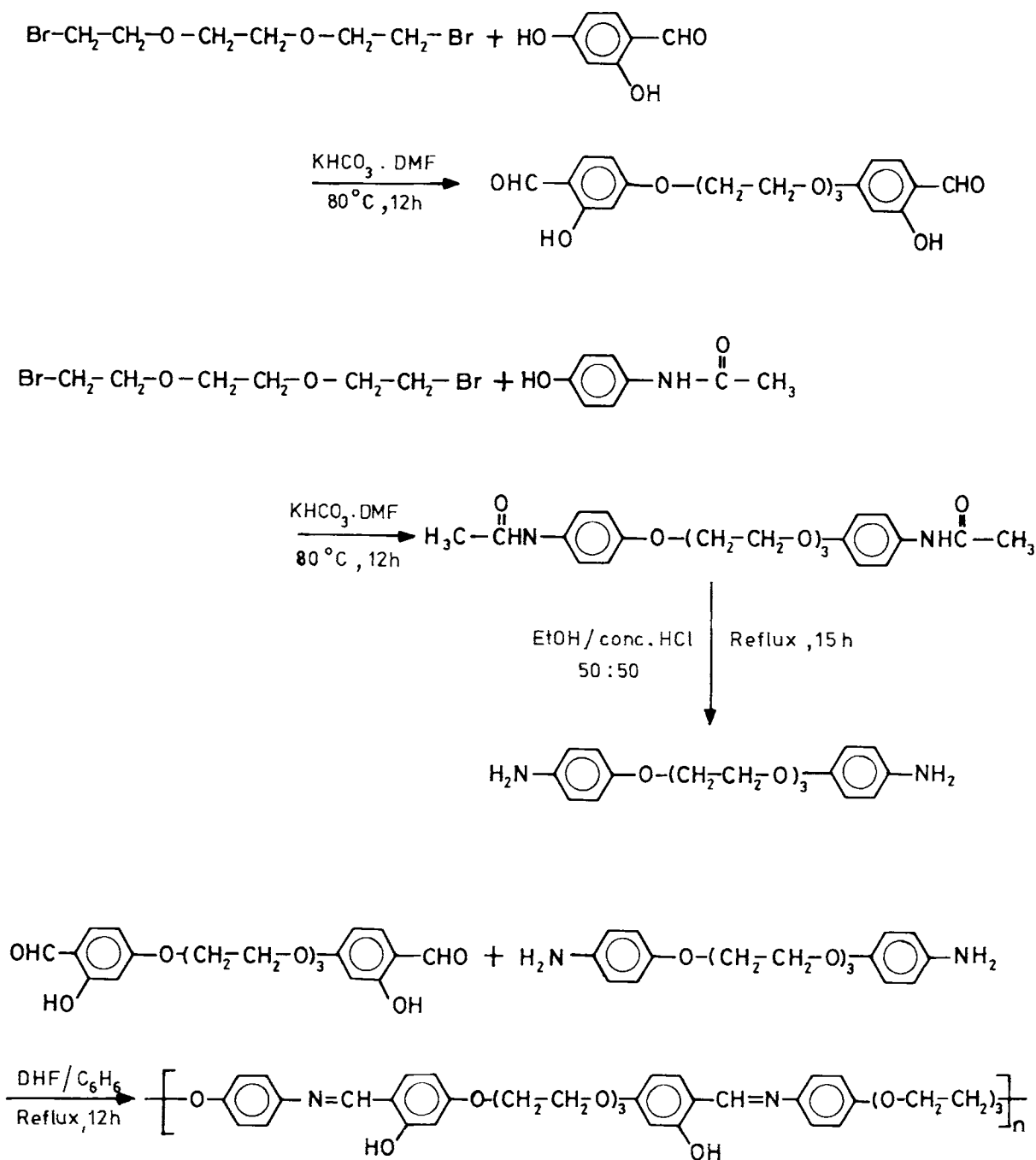
Metal-containing LC materials can also be designed easily to exhibit paramagnetic behavior, which is generally difficult to achieve in organic liquid crystals.² This may help in designing optical display devices based on magnetic fields instead of electric fields. Moreover, the choice of the correct metal ion can introduce unusual electrooptic and

magnetic properties. Unfortunately, there are very few reports with regard to the liquid-crystal polymers containing metallic mesogens.²⁻⁹ Liquid crystalline networks provide objects for investigating the mechanical properties of self-ordering systems and specifically with coupling between ordering and mechanical action.

Compared to organic LCs such as polymeric LCs may provide additional features such as mechanical strength, stability, enhanced processability, and other interesting structural and physical properties. Hanabusa et al. reported thermotropic LC polyesters with mesogenic bipyridinediyl units.³ These polymers form complexes with Fe(II) and Cu(II) and the LC transition temperatures are not changed either by the nature or quantity of the metal in the polymers. Depending upon the metal and its oxidation states as much as 35% of the metal could be incorporated into the polymer, while still retaining its LC properties. Higher metal content is found to suppress the mesogenic transitions in these polymers. Caruso et al. reported the synthesis of LC organometallic polymers containing a square planar [Cu(II)] Schiff base complex, a hydroxy polyazomethine joined by polymethylene spacers of varying length.^{2,8-10}

We describe here the preliminary results of an attempt made to synthesize and study the properties of a three-dimensional LC polymer network con-

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Scheme 1 Synthesis of hydroxy functionalized polyazomethine.

taining transition metals. The hydroxy functionalized polyazomethine exhibits thermotropic liquid crystalline properties and complexes with various metals such as Cu(II), Fe(II), Co(II), and Ni(II). Oligoethylene spacers are introduced into the chain so as to reduce the transition temperature. Sirigu et al. recently reported on similar work, which was published during the preparation of this manuscript.¹⁰ However, in our polymers, the spacers are

different, which provides more flexibility to the chain.

EXPERIMENTAL

Materials

p-Aminophenol (Aldrich), triethyleneglycol (Merck-Schuchart), resorcinol (Ranbaxy), and

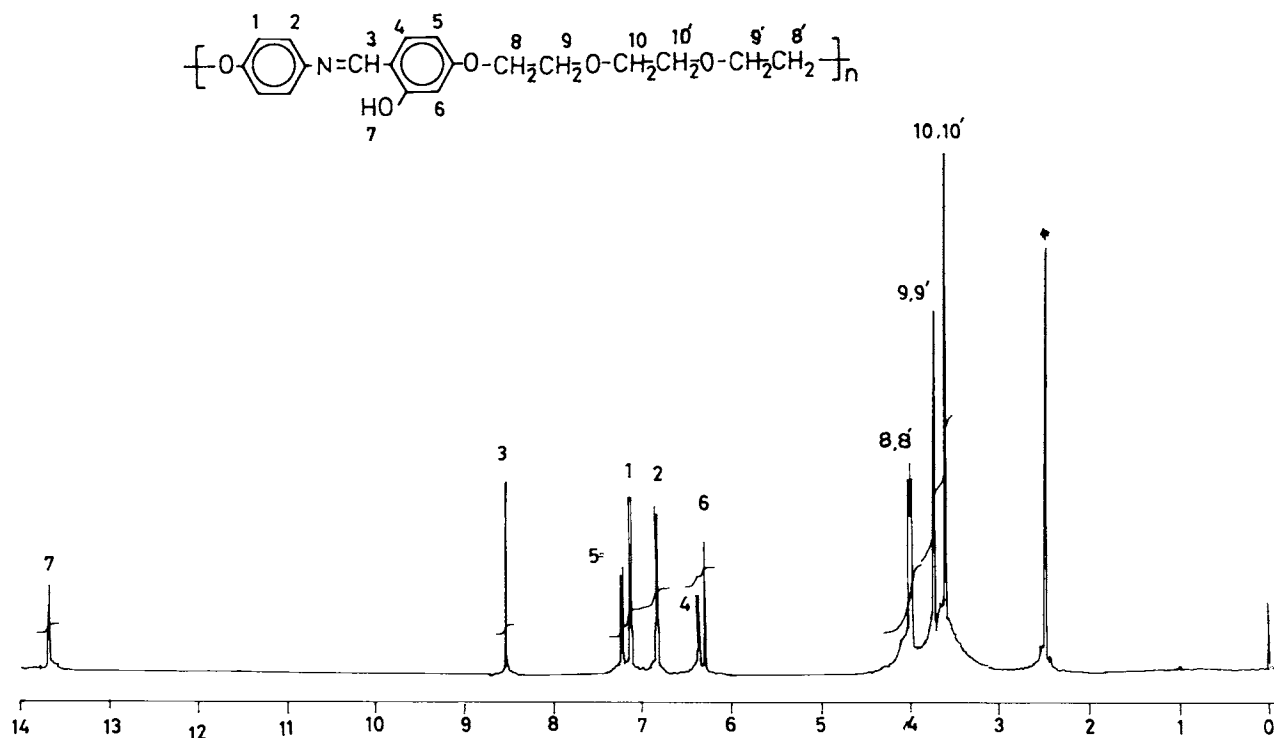


Figure 1 400 MHz $^1\text{H-NMR}$ spectrum of polyazomethine in $\text{DMSO-}d_6$.

phosphorous tribromide (Fluka) all were used without further purification. Solvents were purified by distillation.

4-Hydroxysalicylaldehyde

4-Hydroxysalicylaldehyde was prepared according to the reported procedure.¹¹

Triethylene Glycol Dibromide

Triethylene glycol dibromide was prepared from triethylene glycol as follows. A mixture of 50 g (0.33 mol) of triethylene glycol and 110 mL of pyridine was taken in a 500-mL conical flask and cooled to 0°C . The mixture was stirred and 180 g (0.67 mol) of PBr_3 was added dropwise so that the temperature always remained below 10°C . When the addition was complete, the mixture was further stirred at room temperature overnight. Unreacted PBr_3 was destroyed by dropwise addition of ice-cold water. Triethylene glycol dibromide, separated as a yellowish oil, was extracted with 250 mL of ether, which was subsequently dried over Na_2SO_4 . The product was isolated by evaporating ether; yield 75 g (89%). IR (KBr): 2860 cm^{-1} ($\nu_{\text{C-H}}$), 1113 cm^{-1} ($\nu_{\text{O-C}}$), 570 cm^{-1} ($\nu_{\text{C-Br}}$); $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 3.46

(t, 4H, $\text{OCH}_2\text{-CH}_2\text{-Br}$), 3.82 (t, 4H, $\text{O-CH}_2\text{-CH-Br}$), 3.68 (s, 4H, $\text{-OCH}_2\text{-CH}_2\text{O-}$).

Triethylene Glycol Di(4-salicylaldehyde) Ether

Seven grams (0.051 mol) of 4-hydroxysalicylaldehyde was dissolved in 50 mL of dry DMF and 4.57 g (0.056 mol) of KHCO_3 was added and stirred at 80°C for about 1 h. A CaCl_2 guard tube was used to prevent moisture from entering the reaction system. This mixture was then cooled to room temperature and 7.0 g (0.025 mol) of triethylene glycol dibromide was added dropwise for 15 min. After complete addition, the temperature was raised to 80°C and stirring was continued for another 12 h. The reaction mixture was cooled to room temperature and poured into 150 mL of cold water. The product, separated as a light brown solid, was extracted with 100 mL of ether and dried over Na_2SO_4 for 24 h. Triethylene glycol di(4-salicylaldehyde) ether was then isolated by evaporating ether and was purified by recrystallization from ether; yield 12.3 g (62%), m.p. 82°C . IR (KBr): 3268 cm^{-1} ($\nu_{\text{O-H}}$), 2908 cm^{-1} ($\nu_{\text{C-H}}$), 1608 cm^{-1} ($\nu_{\text{C=O}}$), 1245 cm^{-1} ($\nu_{\text{C-O}}$); $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 4.09 (t, 4H, $\text{-CH}_2\text{CH}_2\text{-OAr}$), 3.80 (m, 4H, $\text{-CH}_2\text{-CH}_2\text{-OAr}$), 3.70 (s, 4H, $\text{CH}_2\text{O-CH}_2\text{-OCH}_2$), 6.48 (d, 2H, aro-

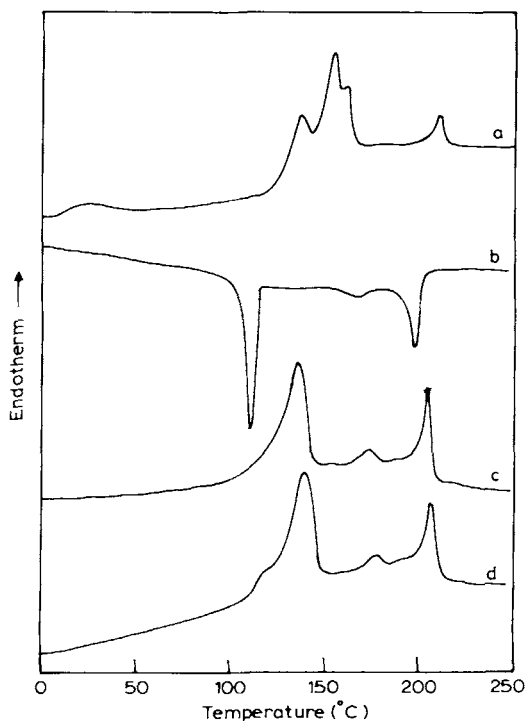


Figure 2 DSC thermograms of polyazomethine: (a) first heating scan, (b) first cooling scan, (c) second heating scan, and (d) third heating scan.

matic), 7.33 (d, 2H, aromatic), 6.34 (s, 2H, aromatic), 9.62 (s, 2H, —CHO), 11.38 (s, 2H, —OH).

4-Hydroxyacetanilide

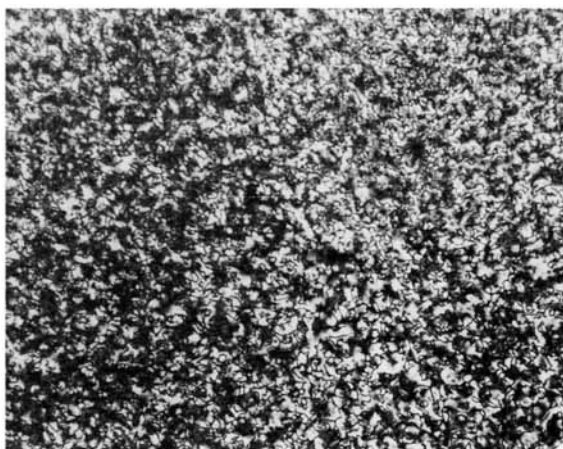
This compound was prepared from *p*-aminophenol and acetic anhydride by the reported procedure.¹²

Triethylene Glycol Di(4-acetanilide) Ether

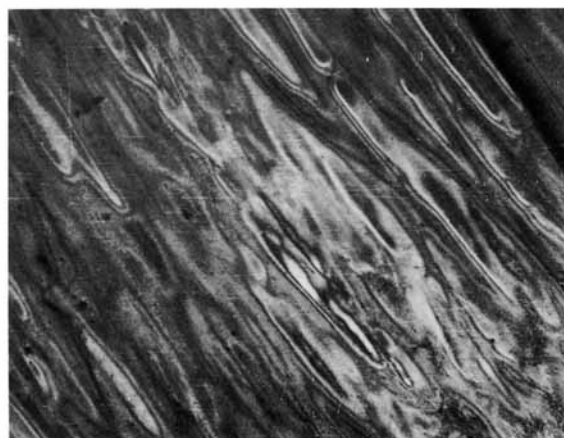
Sixteen grams (0.105 mol) of 4-hydroxyacetanilide was dissolved in 50 mL of dry DMF and to this solution was added 10.0 g (0.10 mol) of KHCO_3 in one lot. The reaction mixture was stirred while temperature was raised to 80°C . After an hour, the reaction temperature was brought down to room temperature and 12.8 g (0.05 mol) of triethylene glycol dibromide was added dropwise for 15 min. The temperature was then once again raised to 80°C and stirred for 12 h. After the completion of the reaction, the mixture was poured into 150 mL of cold water; the separated white solid was collected by filtration and dried at 60°C for 24 h in vacuum. Yield 20.8 g (76%), m.p. 123°C , $^1\text{H-NMR}$ ($\text{DMSO-}d_6$, TMS, ppm, δ): 2.02 (s, 2H, —NH—CO— CH_3), 4.04 (t, 4H, — CH_2 — CH_2 —OAr), 3.76 (m, 4H, — CH_2 — CH_2 —OAr), 3.65 (s, 4H, $\text{CH}_2\text{O—CH}_2$ — CH_2 — OCH_2), 6.83 (d, 4H, aromatic), 7.45 (d, 4H, aromatic), 9.76 (s, 2H, —NH—CO—).

Triethylene Glycol Di(4-aminophenyl) Ether

Five grams (0.01 mol) of triethylene glycol di(4-acetanilide) ether was dissolved in 25 mL of a 50/50 (v/v) mixture of ethanol and conc. HCl and the solution was refluxed for 1.5 h. The reaction mixture was then cooled and diluted with 100 mL of water and neutralized with saturated NaHCO_3 solution. The separated solid amine was extracted with ether, dried over Na_2SO_4 , and evaporated to yield a brown solid. Further purification was done by recrystallization; yield 20.8 g (86%) m.p. 92°C , IR (KBr):



(a)



(b)

Figure 3 Optical microphotographs of polyazomethine at (a) 158°C and (b) 147°C .

3310 cm^{-1} , ($\nu_{\text{N-H}}$), 2854 cm^{-1} ($\nu_{\text{C-H}}$), 1272 cm^{-1} ($\nu_{\text{C-N}}$), 1176 cm^{-1} ($\nu_{\text{C-O}}$), $^1\text{H-NMR}$ (CDCl_3 , TMS, ppm, δ): 4.03 (t, 4H, $-\text{CH}_2-\text{CH}_2-\text{OAr}$), 3.80 (m, 4H, $-\text{CH}_2-\text{CH}_2-\text{OAr}$), 3.72 (s, 4H, $\text{CH}_2\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_2$), 3.38 (s, 4H, $\text{Ar}-\text{NH}_2$), 6.60 (d, 4H, aromatic), 6.74 (d, 4H, aromatic).

Polymerization

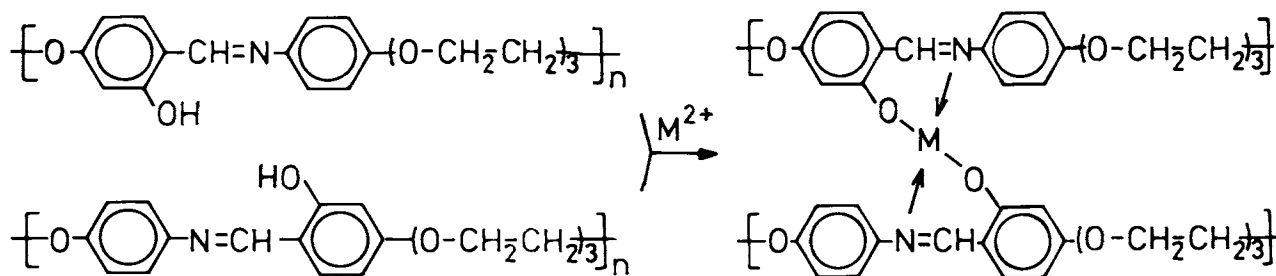
One gram (0.0025 mol) of triethylene glycol di(4-salicylaldehyde) ether was dissolved in 20 mL of dry DMF. To this solution was added dropwise 0.851 g (0.0025 mol) of triethylene glycol di(4-amino-phenyl) ether in 10 mL of dry benzene. The reaction mixture was refluxed for 12 h with stirring; water formed as a by-product was removed by azeotropic distillation using a Dean-Stark apparatus. When the polymerization was complete, the reaction mixture was cooled and poured into 100 mL of methanol. The polymer, precipitated as yellow solid, was separated by filtration, and dried at 60°C under vacuum; yield 1.8 g (93%). IR (KBr): 2866 cm^{-1} ($\nu_{\text{C-H}}$), 1617 cm^{-1} ($\nu_{\text{C=N}}$), 1245 cm^{-1} ($\nu_{\text{C-O}}$), $^1\text{H-NMR}$ ($\text{DMSO}-d_6$, TMS, ppm, δ): 4.02 (t, 4H, $\text{OCH}_2-\text{CH}_2-\text{OAr}$), 3.76 (m, 4H, $\text{O}-\text{CH}_2-\text{CH}_2-\text{OAr}$), 3.68 (m, 4H, $\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OCH}_2$).

Network Formation through Metal Complexation

Polymer was mixed thoroughly with various amounts of metal acetates and pressed into pellets. The sample so prepared was heated isothermally in the liquid crystalline phase (175°C) for 15 min. The sample was then cooled and refluxed in DMF for 5 h. The insoluble part was separated and dried.

Characterization

$^1\text{H-NMR}$ spectra were recorded on a 400-MHz Bruker AMX-400 FTNMR spectrometer. The chemical shifts were calibrated from tetramethylsilane



Scheme 2 Crosslinking of polyazomethine by metal complexation.

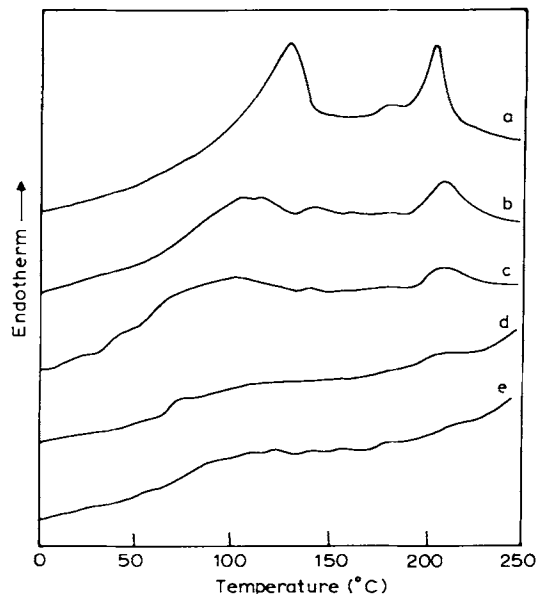


Figure 4 DSC thermograms of polyazomethine cross-linked with different mol % of Cu(II): (a) 10, (b) 20, (c) 30, (d) 40, and (e) 50.

(TMS). Infrared spectra were recorded on a Bio-Rad FTS 7 FTIR spectrophotometer using KBr pellets. A Du Pont TA9900 differential scanning calorimeter (DSC) was used to determine the thermal transitions. The glass transition temperature (T_g) was taken as the middle point of the heat capacity change. All the heating and cooling rates were 10°C/min and the sample weight was 30 mg. A Leitz optical polarized microscope model BK-2, equipped with hot stage, was used to observe the thermal transitions and to analyze the anisotropic textures.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization

The synthetic route followed for the synthesis of the monomers and the polymer is given in Scheme 1.

Two monomers, a dialdehyde and a diamine with oligoethylene oxide spacer, were prepared and polymerized by polycondensation in DMF/benzene (2 : 1) under refluxing condition. H₂O formed as a byproduct was continuously removed by azeotropic distillation. The polymer is yellow in color and soluble only in highly polar solvents. Monomers and the polymer were characterized by IR and ¹H- and ¹³C-NMR spectroscopy. Figure 1 shows the ¹H-NMR spectrum for the polymer.

Liquid Crystalline Properties

The liquid crystalline properties of the polymer have been studied by DSC and polarized light optical microscopy (POM). The DSC thermograms are shown in Figure 2. In the first heating cycle (curve a), there are four endotherms, the first three endotherms at 137°, 155°, and 162°C overlap each other with total enthalpy of 37.9 J/g. Examination of the sample in POM reveals that the first endotherm at 137°C corresponds to the melting from the crystalline to anisotropic field. Two endotherms at 155° and 162°C are assigned to the transition from one mesophase to another of lesser order. The last endotherm at 210°C ($\Delta H = 4.57$ J/g) corresponds to the transition from LC to the isotropic state. In the first cooling cycle (curve b), the isotropic to LC transition is observed at 196°C. The microphotograph of the polymer at 158°C, on cooling from the isotropic phase, is shown in Figure 3(a). The threaded texture in the figure confirms that the polymer exhibits nematic mesophase. A small exotherm observed at 167°C on cooling (Fig. 2, curve b) is probably a transition from the nematic to a higher order LC phase, perhaps a smectic phase. Figure 3(b) shows the microphotograph at 147°C. The texture in the photograph does not give any clear idea about the kind of mesophase at this temperature. An exotherm at 111°C is associated with the mesophase to crystalline transition. Unlike the first heating scan (curve a), in the

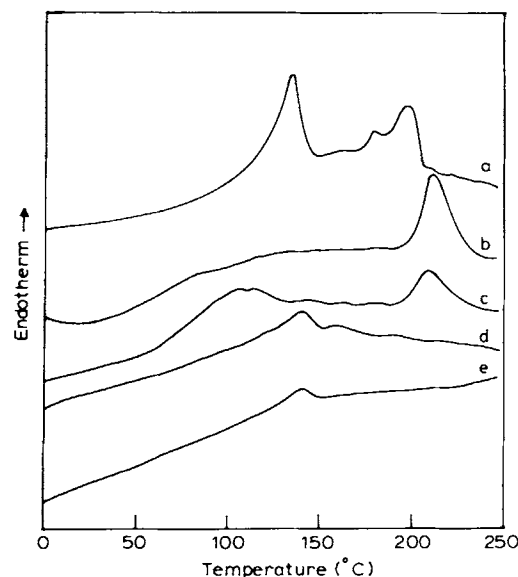


Figure 5 DSC thermograms of polyazomethine cross-linked with 20 mol % of different metals: (a) Cd(II), (b) Ni(II), (c) Cu(II), (d) Zn(II), and (e) Co(II).

second heating scan (Fig. 2, curve c) there is no overlap of the endotherms. The sample melts to mesophase at 136°C as confirmed by the birefringence observed in POM, but we were unable to identify the mesophase prevailing at this temperature. A small endotherm at 175°C ($\Delta H = 1.07$ J/g) is due to the transition to the nematic phase. Isotropization takes place at 205°C ($\Delta H = 3.91$ J/g). Subsequent heating thermograms are similar to the second heating thermogram.

Network Formation through Metal Complexation

It is well known that the Schiff bases (hydroxy functionalized azomethine) coordinate with metal ions [Cu(II), Co(II), Zn(II)] and form a metal complex with the general formula ML_2 , where M is the metal ion and L is the bidentate Schiff base ligand.¹³

Table I Temperature and Enthalpy of Transitions for the Liquid Crystalline Network Formed at Different Concentrations of Cu(II)

Amount of Cu(II) (mol %)	Temperature (°C) and Enthalpy (J/g) of Transition					
	T_m	ΔH_m	T_{1c-1c}	ΔH_{1c-1c}	T_i	ΔH_i
0	135	21.0	175	1.07	205	5.9
10	129	16.0	177	0.38	204	5.9
20	113	2.6	—	—	207	3.5
30	101	2.1	—	—	207	2.7
40	76	—	—	—	205	—

Table II Temperature and Enthalpy of Transitions for the Polymer Network Formed from Different Metals

Metal 20 mol %	Transition Temperature ($^{\circ}\text{C}$) and Enthalpy (J/g)					
	T_m	ΔH_m	T_{1c-1c}	ΔH_{1c-1c}	T_i	ΔH_i
Cd(II)	133	8.8	177	0.4	197	4.4
Ni(II)	—	—	—	—	209	10.0
Cu(II)	123	2.6	—	—	207	3.5
Zn(II)	139	1.7	—	—	—	—
Co(II)	139	1.2	—	—	—	—

On extending these reactions to polymeric Schiff bases, the complex formation establishes the inter-chain links leading to crosslinking. For the present polymer system, this reaction is as shown in Scheme 2. In the present investigation, this approach has been adopted to get the LC polymer network containing metals. Metal acetates and the polymer in varying ratios were powdered and mixed thoroughly. The complexation was effected in the LC state by isothermally heating the polymer and metal acetate mixture, at 175°C , for 15 min. The network thus formed was insoluble in any solvent and was studied by DSC. Figure 4 shows the DSC heating thermograms (second heating cycle) for the polymer network formed with different percentages of copper acetate. The transition temperatures and the corresponding enthalpy of transition are given in Table I. Compared to the uncrosslinked linear polymer (curve a), there is a steady decrease in the melting temperature with the increase in the metal content. However, the isotropization temperature does not vary significantly. The endothermic transitions are not seen for the network when the metal content exceeds 30%. The enthalpies associated with all the transitions are found to decrease with the increase in the metal content. This decrease in the enthalpy of transition together with the reduction in the melting temperature of the network, in comparison with the uncrosslinked linear polymer, could be due to the defects introduced by the metal at the crosslink sites. The networks, up to 30% of Cu(II) (curves b, c, and d), behave like LC elastomers. Above 30%, LC transitions are suppressed and the network becomes rigid and behaves like LC thermosets (curves e and f). Heating the network above 250°C results in endothermic degradation.

Figure 5 displays the DSC thermograms (second heating cycle) for networks made by crosslinking with 20 mol % of various metals, i.e., Cd, Cu, Ni, Zn, and Co. Table II summarizes the transition temperatures along with the enthalpy of transitions

for these networks. Comparing with the linear uncrosslinked polymer, there is a considerable change in the transition temperature of the network. The nature and extent of change depend upon the kind of the metal present. For the network with Cd(II) (curve a), all three endothermic transitions, observed for the linear polymers, are seen without much difference. In the case of a network with Cu(II) (curve b) the melting temperature is shifted toward a lower value (113°C) but the isotropic temperature remains unchanged. The network containing Ni(II) did not show any melting endotherm, but the endotherms for isotropic transition were seen at 210°C , close to the isotropic temperature of the uncrosslinked polymer. For the network with either Zn(II) or Co(II), the thermogram shows only one endotherm at 140°C (curves d and e) near the melting temperature of linear polymers. The isotropic transition endotherm seems to be suppressed in these cases.

CONCLUSION

An attempt has been made to synthesize metal-containing liquid crystalline polymer networks based on a new hydroxy functionalized thermotropic polymer, namely polyazomethine. This polymer exhibits nematic mesophase. Three-dimensional networks were formed in the liquid crystalline state through metal complexation. DSC studies show that the networks exhibit mesomorphic behavior up to 30 mol % of Cu(II). Similar networks are also formed by complexation of the polymer with various other metals like Co, Ni, Cd, and Zn.

The authors thank Prof. N. V. Madhusudana, Raman Research Institute, Bangalore, for his help in POM studies. This research was supported by the Department of Science and Technology, New Delhi.

REFERENCES

1. P. Espinet, M. A. Esteruelas, L. A. Oro, J. L. Serrano, and E. Sola, *Coordination Chem. Rev.*, **117**, 215 (1992).
2. U. Caruso, A. Roviello, and A. Sirigu, *Macromolecules*, **24**, 2606 (1991).
3. K. Hanabusa, J. Higashi, T. Koyama, H. Shirai, N. Hojo, and A. Karose, *Makromol. Chem.*, **190**, 1 (1989). 4. S. Takahashi, H. Morimoto, Y. Takai, K. Sonogoshira, and N. Hagihara, *Mol. Cryst. Liq. Cryst.*, **72**, 101 (1981).
5. K. Hanabusa, C. Kobayashi, T. Koyama, E. Masuda, H. Shirai, Y. Kondo, K. Takemoto, E. Iizuka, and N. Hojo, *Makromol. Chem.*, **187**, 753 (1986).
6. C. Carafagna, U. Caruso, A. Roviello, and A. Sirigu, *Makromol. Chem. Rapid Commun.*, **8**, 345 (1987).
7. L. Oriol, P. J. Alonso, J. I. Martinez, M. Pinol, and J. L. Serrano, *Macromolecules*, **27**, 1869 (1994).
8. U. Caruso, R. Centor, A. Roviello, and A. Sirigu, *Macromolecules*, **25**, 129 (1992).
9. U. Caruso, S. Pragliola, A. Roviello, and A. Sirigu, *Macromolecules*, **26**, 221 (1993).
10. U. Caruso, B. Panunzi, A. Roviello, and A. Sirigu, *Macromolecules*, **27**, 3513 (1994).
11. A. I. Vogel, *A Text Book of Practical Organic Chemistry*, 4th ed. ELBS and Longman Group Ltd., England, 1978, p. 760.
12. A. I. Vogel, *A Text Book of Practical Organic Chemistry*, 4th ed. ELBS and Longman Group Ltd., England, 1978, p. 753.
13. D. Wohrle and H. Bohlen, *Makromol. Chem.*, **184**, 763 (1983).

Received Feb. 23, 1995

Accepted Aug. 5, 1995