

Main-Chain Liquid Crystalline Poly(ester-amide)s Containing Lithocholic Acid Units

V. A. E. Shaikh,^{1*} V. P. Ubale,¹ N. N. Maldar,¹ S. V. Lonikar,¹ C. R. Rajan,² S. Ponrathnam²

¹Shivaji University Centre for Postgraduate Studies, Opp. Octroi Naka, Solapur-Pune Road, Kegaon, Solapur 413002, India

²Division of Chemical Engineering, National Chemical Laboratory, Pune 411008, India

Received 30 July 2004; accepted 12 December 2004

DOI 10.1002/app.22286

Published online 9 January 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of poly(ester-amide)s based on an ester group containing lithocholic acid derivative [3-(3-carboxypropionyl) lithocholic acid] and several aromatic diamines (naphthalene-1,5-diamine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylsulfone, benzidine, *m*-phenylenediamine, *p*-phenylenediamine, and tetraphenylthiophene diamine) was synthesized and characterized by solubility, viscosity, IR, differential scanning calorimetry, thermogravimetric analysis, and optical microscopy. The polymers were soluble in most of the organic solvents and had inherent viscosities in the range of 0.21–0.38 dL/g. All the polymers exhibited a nematic me-

sophase, but only on shearing. Thermal transitions due to mesophase formation were not seen in the differential scanning calorimetry thermograms. However, the liquid crystalline character of the polymers was observed under an optical microscope. Thermogravimetric analyses revealed the maximum decomposition temperature was 390–435°C for these polymers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 73–80, 2006

Key words: lithocholic acid; main-chain liquid crystalline polymers; poly(ester-amide)s

INTRODUCTION

The present day industrial and academic interest in liquid crystalline polymers is due to their remarkable mechanical, optical, and thermal properties.^{1–3} Since the development and commercialization of the lyotropic liquid crystalline polyamide Kevlar (Du Pont) and the thermotropic liquid crystalline polyester Vectra (Celanese),^{4–11} liquid crystalline main-chain aromatic polycondensation polymers have been the focus of much interest. Formation of liquid crystalline phases in polymers allows the fabrication of ultrahigh strength and ultrahigh modulus fibers or high strength engineering plastics from concentrated solutions or from the melt. Polymers forming organized phases in common organic solvents or with lower thermotropic liquid crystal transition temperatures are desirable to facilitate fabrication and processing. Introduction of suitable bulky substituents, molecular

kinks, flexible spacers, and copolymerization, and so forth may bring about desirable changes so that the processability and solubility of the polymer are improved.¹²

This article describes the synthesis of a dicarboxylic mesogen using a compound of biological origin and subsequent utilization of this mesogen along with diamine monomers in the synthesis of main-chain liquid crystalline poly(ester-amide)s. The dicarboxylic mesogen 3-(3-carboxypropionyl) lithocholic acid [lithocholic acid monosuccinate (LAMS)] is bulky and somewhat flexible because of the aliphatic side chain. Because derivatization of LA involves esterification, the mesogen contains an ester linkage. LAMS was reacted with a series of aromatic diamines to yield poly(ester-amide)s. Yamazaki's phosphorylation reaction¹³ formed the basis of the polycondensation reactions. To our knowledge, there has been no published report thus far on main-chain liquid crystalline polymers containing an LA moiety. We opted for an LA derivative as a monomer in the synthesis of polymers for two reasons. First, the LA derivative acts as both a mesogen and a bulky, flexible spacer, which results in improved solubility compared to the polymers containing rigid mesogenic units. Second, we anticipated that these polymers based on a steroid moiety and capable of mesophase formation may be useful in biomedical applications.

Correspondence to: V. A. E. Shaikh (shaikh_vasi@yahoo.com).

*Present address: Polymer Engineering Department, Maharashtra Institute of Technology, Sr. No. 124, Paud Road, Kothrud, Pune 411038, India.

Contract grant sponsor: Department of Science and Technology, New Delhi, India; contract grant number: SP/S1/G-72/90.

EXPERIMENTAL

Materials

Naphthalene-1,5-diamine, 4,4'-diaminodiphenyl ether, 4,4'-diaminodiphenylmethane, 4-4'-diaminophenylsulfone, benzidine, *m*-phenylenediamine, and *p*-phenylenediamine were obtained from commercial sources and recrystallized prior to use. Tetraphenylthiophene diamine and succinic anhydride were prepared according to known procedures.^{14,15} Triphenyl phosphite, pyridine, *N*-methylpyrrolidinone, and lithium chloride were purified before use.¹⁶ LA was purchased from Aldrich Chemical Co. and used as received.

Monomer

LAMS was prepared by reacting LA (10 g) and succinic anhydride (10 g) in the presence of dry pyridine as a solvent. The reaction was allowed to proceed at 110°C for 24 h. The product was precipitated in warm distilled water, filtered, and purified by Soxhlet extraction and subsequent recrystallization from acetone.

Polymers

The polymers were synthesized according to Yamazaki's phosphorylation reaction.¹³ LAMS (1 mmol) and the desired diamine (1 mmol) in a mixture of pyridine (0.5 mL) and *N*-methylpyrrolidinone (2 mL) containing 8% lithium chloride were added to a 50-mL three-necked round-bottomed flask equipped with a reflux condenser, calcium chloride guard tube, nitrogen inlet, and heating bath. Triphenyl phosphite (0.766 g) was added under a nitrogen atmosphere. The reaction mixture was stirred at 100°C for 3 h. The polymer was isolated by pouring the mixture into methanol. The obtained precipitate was filtered and washed several times with methanol and boiling distilled water to remove impurities and traces of salt. The polymer was dried in a vacuum at 80–85°C for 6 h.

Methods

IR spectra were recorded on a Perkin–Elmer 883 IR spectrophotometer calibrated with polystyrene, using KBr pellets as the dispersion medium. Proton NMR spectra were recorded with a Bruker 200-MHz NMR spectrometer at 303 K in CDCl₃ (4 mg/mL concentration).

The thermal properties were studied by using Leitz Laborlux 11 POL microscope equipped with a Leitz 350 microheating stage and a Wild MPS 0.32X camera. Each sample was heated to isotropization, cooled to room temperature, and reheated to isotropization in a single checking. The heating and cooling rate was 10°C/min. Sample preparation involved sandwiching

a very small amount of powdered compound in between a clean glass slide and a thin cover glass. The lyotropic properties of the polymers were studied using solutions of the polymers at various concentrations.

The polymers were further characterized by differential scanning calorimetry (DSC) with a Mettler TA 4000 series instrument. It consists of a DSC 30 cell coupled to a Mettler TC 11 TA processor. Three runs (heating, cooling and second heating) were performed for all the samples at a heating and cooling rate of 10°C/min.

Viscosity measurements were carried out with a 0.1% (w/v) solution of polymers in dimethylacetamide using an Ubbelohde suspended level viscometer.

RESULTS AND DISCUSSION

Monomer

LAMS was obtained in 63.2% yield by refluxing LA and succinic anhydride in pyridine. The microanalysis data for C and H were in agreement with the calculated values (Calcd: C, 70.58; H, 9.24. Found: C, 70.53; H, 8.82). The IR spectrum of LAMS showed peaks at 3300–3400, 1700–1710, and 1730 cm⁻¹, which may be attributed to —OH and C=O stretching vibrations of —COOH groups and the C=O of ester linkage, respectively. The peak at 1730 cm⁻¹ confirms the presence of ester linkage in LAMS. A proton NMR spectrum in CDCl₃ showed a multiplet at δ 2.5 (4H, —OOCCH₂CH₂COO—); other peaks were similar to those for LA. The mass spectrum of LAMS confirmed the structure unambiguously. The *m/e* ratio in each step was in conformity with the expected fragmentation pattern. The first fragmentation (*m/e* 476–358) could be attributed to the removal of the side-chain substituent from C-3 as succinic acid with abstraction of hydrogen from C-4 and simultaneous formation of a double bond between C-3 and C-4. The fragmentation of *m/e* 118 confirms the presence of a succinoyl moiety as a side chain at the C-3 position.

The DSC thermograms of LAMS showed a sharp endotherm at 235–237°C during the first heating run. No apparent changes were observed on cooling and second heating in contrast to the observation under a microscope, which showed a texture indicative of a liquid crystalline phase. Hot-stage coupled polarizing optical microscopic observation with crossed polars showed direct melting at about 235°C on first heating, and there was slight brightness just before melting. Highly colored birefringence was observed from 170 to 167°C during the cooling run. A comparison of this texture with standard plates¹⁷ suggests that it is probably a smectic G mosaic texture [Fig. 1(a)]. This texture changes into an unidentifiable texture below 135°C

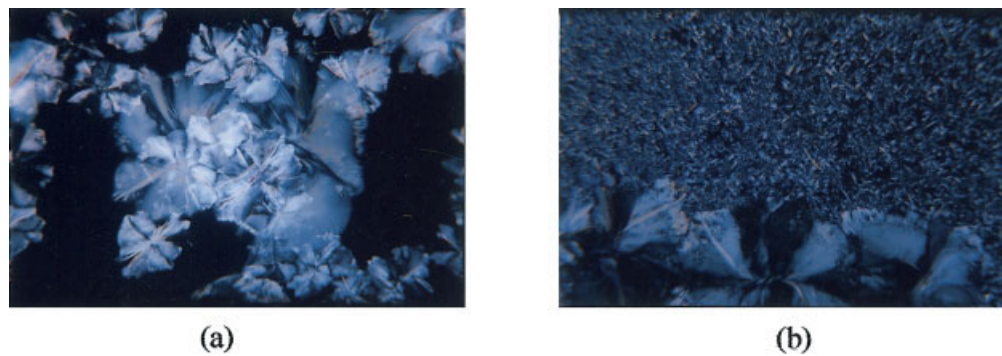
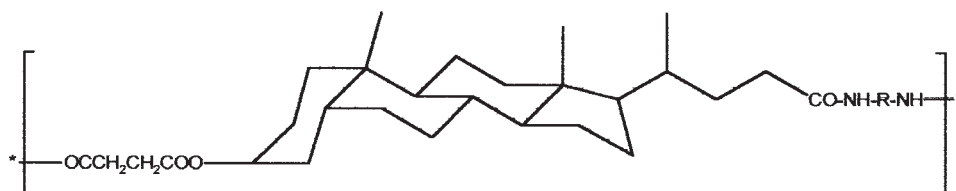


Figure 1 Microphotographs (crossed polars) of LAMS at (a) 165°C (cooling run) and (b) 120°C (second heating run). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



R =

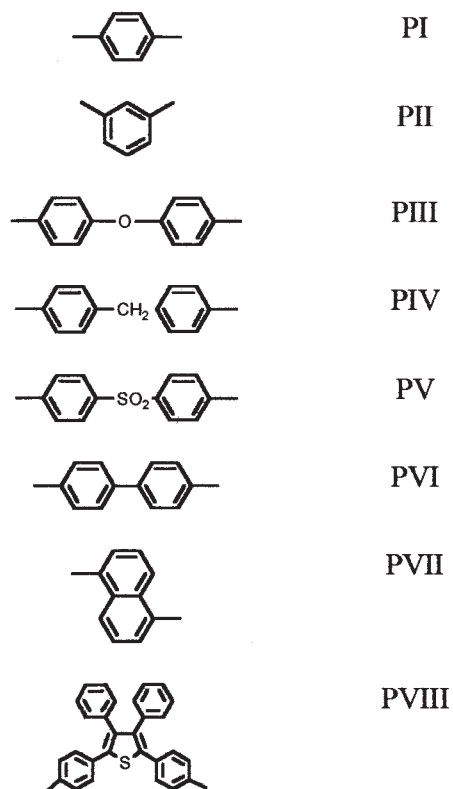


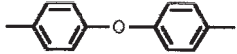
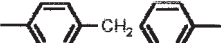
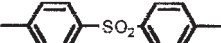

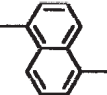
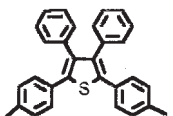


Figure 2 The structure of poly(ester-amide)s.

TABLE I
Yield and Inherent Viscosity of Polymers

Polymer code	Diamine	Yield (%)	η_{inh} in DMAc (dL/g)
PI		98	0.242
PII		99	0.279
PIII		97	0.304
PIV		98	0.309
PV		98	0.210
PVI		98	0.380
PVII		97	0.342
PVIII		99	0.250

DMAc, dimethylacetamide.

and remains up to room temperature. On second heating a texture similar to smectic A batonnets was observed [Fig. 1(b)] from 120°C onward. The birefringence disappeared to give an isotropic melt at 236°C.

Polymers

Figure 2 displays the structures of the various poly(ester-amide)s synthesized by polycondensation of aromatic diamines with LAMS. The polymers were obtained in quantitative yield. The yield and inherent viscosity of the polymers are recorded in Table I. All polymers had inherent viscosities in the range of 0.21–0.38 dL/g. The low viscosity for PV may be due to the lower reactivity of the amine because it contains an electron withdrawing sulfone group.

The IR spectra of the poly(ester-amide)s are shown in Figure 3. All polymers show peaks at 3280–3300, 2850–2950, and 1720–1730 cm^{-1} and a couple of peaks around 1510, 1560, 1620–1650, and 1680–1690 cm^{-1} , corresponding to amide absorption (N—H), C—H stretching of the steroid moiety, ester carbonyl, and amide I and amide II bands, respectively. In addition, one peak at 1250 cm^{-1} in the 4,4'-diaminodiphenylether containing polymer (PIII) and another in the range of 1440–1445 cm^{-1} in the tetraphenylthiophene diamine containing polymer (PVIII) are characteristic features of the respective compounds.

The solubility characteristics of the polymers in various solvents are presented in Table II. A 1% solution

was taken as a criterion for solubility. All polymers were clearly soluble in most of the solvents with few exceptions. The good solubility behavior of all the polymers can be attributed to the bulky nature of LAMS. This was further confirmed by our work on copolymers prepared by using a nonbulky diacid (terephthalic acid) as the comonomer.¹⁸ We found that as the fraction of the bulky diacid monomer (LAMS) decreased, the solubility also decreased. Moreover, the aliphatic nature of LAMS probably helps to improve the solubility of the polymers.

The mesomorphic behavior of the polymers, on heating as well as in solutions, was studied by observations under crossed polarizers on an optical microscope. Microscopic observation did reveal textures indicative of a liquid crystalline phase when the cover glass was pressed slightly. Mesophase formation under shear was reported earlier.^{19,20}

All the polymers were slightly yellowish nonbirefringent powders at room temperature. Polymer PI starts softening at about 215°C, as judged by pressing the cover glass slightly. The softening became promi-

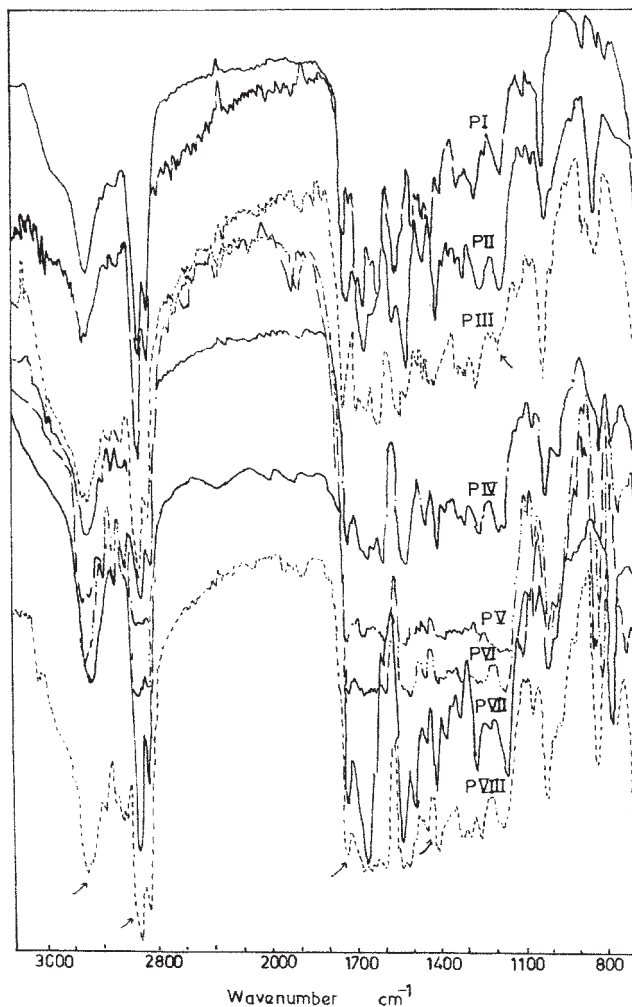


Figure 3 IR spectra of the polymers.

TABLE II
Solubility Characteristics of Polymers

Polymer	Solvents								
	DMAc	NMP	HMPA	<i>m</i> -Cresol	Pyridine	THF	DMF	DMSO	Nitrobenzene
PI	+	+	+	+	+	–	+	–sh	–sh
PII	+	+	+	+	+	s	–sh	–sh	–sh
PIII	+	+	+	+	+	s	–sh	–sh	–sh
PIV	+	+	+sh	+	+	s	–sh	–sh	–sh
PV	+	+	+	+	+	–	–sh	–sh	–sh
PVI	+	+	+	+	+	+	+	–sh	–sh
PVII	+	+	+	+	+	s	–sh	–sh	–sh
PVIII	+	+	+	+	+	+	+	–sh	+sh

+, Soluble at room temperature; –, insoluble; s, swelling; –sh, soluble when hot (reappears when cooling); +sh, soluble on heating (does not reappear on cooling); DMAc, dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; HMPA, hexamethyl phosphoramide; THF, tetrahydrofuran; DMF, dimethylformamide; DMSO, dimethylsulfoxide.

ment from 250 to 254°C onward and weak birefringence indicative of a nematic Schlieren texture was seen when pressed gently at this temperature. The birefringent structure disappeared when shearing force was released. Isotropization occurred in the range of 280–290°C. A birefringent structure was not observed until isotropization, except when the cover glass was pressed slightly at around 250°C. The sample was held at 295°C for 5 min and then cooled. No birefringence was observed while cooling the sample, unless sheared. During the second heating run, strong

birefringence was observed without applying pressure from 168 to 169°C onward. The texture was clearly identifiable and appeared to be close to the smectic G/nematic transition, showing a dendritelike pattern [Fig. 4(a)]. Above 235°C the birefringence showed considerable flow, but there was no change in the texture. However, the birefringent texture could be deformed if the cover glass was disturbed. The sample turned brownish above 300°C, indicating decomposition. Then, it was heated to 340°C. It was interesting to note that the birefringent structure remained intact,

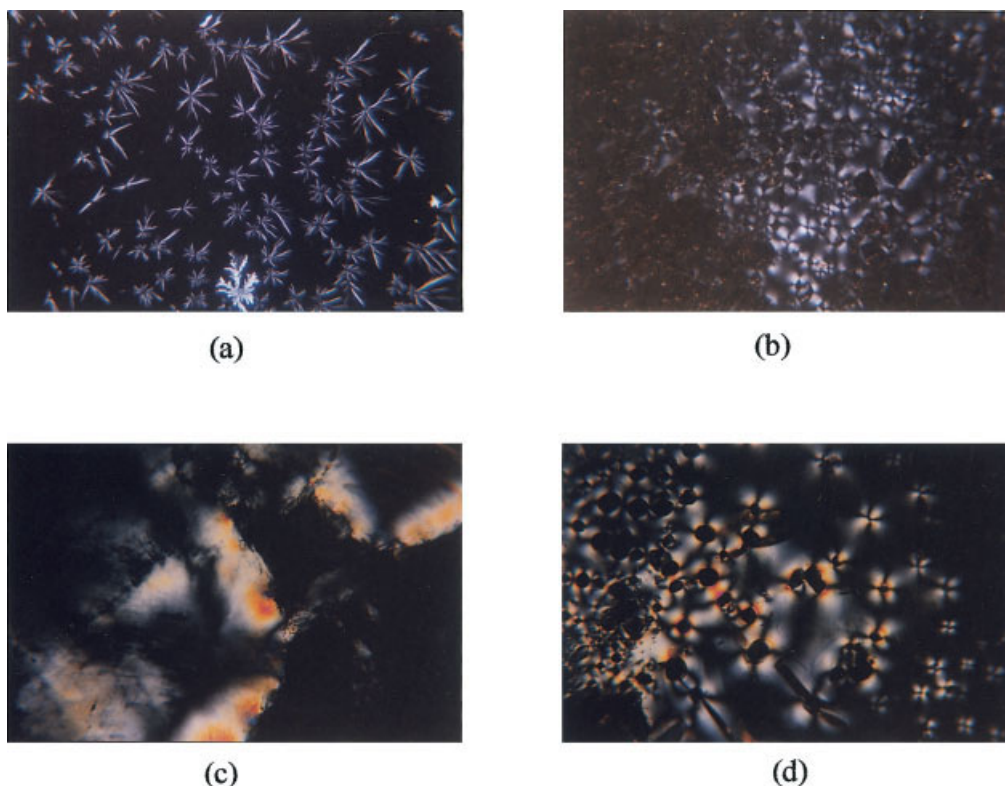


Figure 4 Microphotographs (crossed polars) of polymers taken during heating runs for (a) PI at 220°C, (b) PII at 250°C, (c) PVI at 240°C, and (d) PVI at 270°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]



Figure 5 Microphotographs (crossed polars) of polymers: (a) 70 wt % PI in *m*-cresol and (b) 80 wt % PIII in *m*-cresol.

even at a temperature as high as 340°C. The sample could not be heated above 340°C because of instrumental constraints.

Polymer PII softened at about 205°C onward and more so above 220°C, which was judged by pressing the cover glass slightly. Birefringence was observed in the 240–250°C range when pressed, which persisted for a short while after releasing the pressure. The texture seemed to be nematic Schlieren [Fig. 4(b)] and could be preserved if cooled from the same temperature under slight pressure. Birefringence could not be seen above 270°C and isotropization occurred at about 295–300°C. Birefringence was not observed during the cooling run unless pressed slightly in the same temperature range (at about 240°C). The heating and cooling cycles were repeated with similar results.

The observations for PIII, PIV, PV, and PVII were similar to those for PII, except for the temperature ranges. PIII softened at about 190°C onward and exhibited weak birefringence. Strong birefringence was observed above 230°C when sheared, and isotropization occurred at 295°C. The texture was a nematic Schlieren type. PIV softened at 180°C onward and displayed birefringence at about 200–205°C under shearing, which persisted for a short while after the shearing force was released. Isotropization occurred at 280–290°C. The temperatures for PV were 235, 260, and 295°C and for PVII were 210, 260, and 305°C.

PVI softened from 200 to 210°C onward. Birefringence was observed when sheared and persisted a little longer compared to that for other polymers. Highly colored birefringence was seen at about 230–235°C [Fig. 4(c)], a nematic Schlieren texture was exhibited upon shearing at 270–280°C [Fig. 4(d)], and it became isotropic at 296–300°C. Birefringence was observed upon cooling at about 270°C and remained up to room temperature if cooled under shearing.

Polymer PVIII softened from 200°C onward. Colored birefringence was observed when pressed slightly at this temperature, which persisted for a longer time compared to the other polymers. The pattern was indicative of a nematic Schlieren texture,

which was stable to 270°C; and isotropization occurred at 290°C. No birefringence was observed during cooling and the second heating run unless pressed slightly above the softening temperature.

Thus, the polymers exhibited a nematic Schlieren texture only on shearing and the texture remained stable under shearing force and disappeared either at high temperature or when the shearing force was released. The texture was seen only if sheared on cooling as well as on second heating at around the softening temperature of the polymer. Even though the birefringent phase was not highly colored, the textures observed in all the polymers were clear enough to suggest the nematic Schlieren type. However, in some cases colored textures were also observed. The softening temperatures for the polymers were 205–235°C whereas their isotropization temperatures were 295–305°C as observed under the optical microscope.

Polymers PI and PIII were evaluated for lyotropic mesophase formation in a concentration range of 20–80 wt % in solvents such as *m*-cresol and dimethylacetamide. Solutions were kept aside for 48 h and checked for mesophase formation. We observed that polymers with concentrations above 60 wt % in *m*-cresol exhibit birefringence upon shearing. Interestingly, the birefringent texture did not disappear upon releasing the shearing force. Similar observations were reported by Lin and Sherrington for an aromatic polyester–dimethylsulfoxide/water system.²⁰ Lyotropic mesophases also indicate a nematic Schlieren texture like thermotropic mesophases. Figure 5 shows optical micrographs of polymers PI and PIII in *m*-cresol (70 and 80 wt %, respectively).

Thus, the polymers studied in the present work exhibit thermotropic as well as lyotropic behavior. Formation of both types of mesophases is attributed to the limited flexibility of the polymer chain. Mesophase formation upon shearing (i.e., shear-induced mesophase formation upon heating as well as in solution) is a known phenomenon and has been reported by different groups. For example, polyamides containing diaza-18-crown-6-ether units¹⁹ show thermotropic

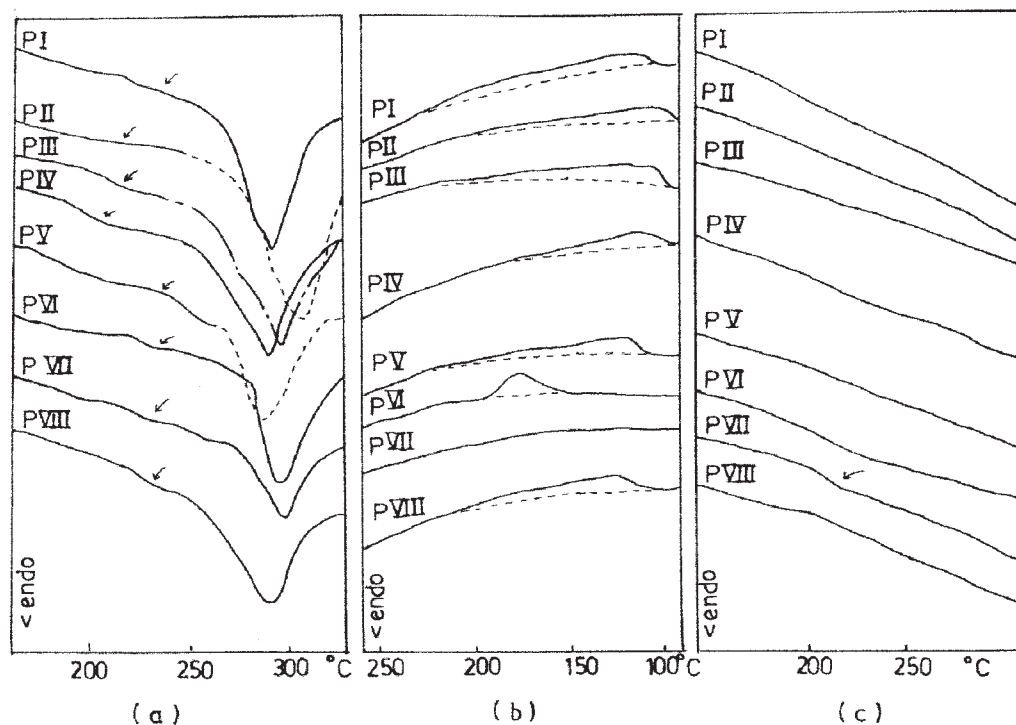


Figure 6 DSC thermograms of polymers in (a) first heating, (b) cooling, and (c) second heating modes.

mesophase formation upon shearing and wholly aromatic polyester²⁰ shows mesophase formation upon shearing in solution. The formed mesophases were clear enough to identify the texture.

DSC thermograms of the polymers are shown in Figure 6. Polymers PI–PVIII show a single broad endotherm and a glass-transition temperature [Fig. 6(a)], indicating the amorphous nature of the polymers. On cooling, DSC thermograms of polymers PI–PVIII show a broad exotherm at approximately 220–100°C, indicating formation of an organized structure. Note that optical microscope observations also suggest a birefringent structure upon shearing during the cooling run, but not at a temperature as low as 100°C. Therefore, the broad exotherm (220–100°C) may be ascribed to the process of organized structure formation leading to crystallization. This inference is further substantiated by the fact that nearly all of the polymers (except PVII) show a glass transition on second heating [Fig. 6(c)], indicating that crystallization had taken place during the cooling. Polymer PVII did not exhibit an exotherm in the cooling run and a transition due to the glass transition was seen in the second heating run, suggesting that the sample did not crystallize on cooling and remained amorphous; hence, it showed a glass-transition temperature in the second heating run. This is probably attributable to the “crank shaft” type of structure of the diamine (naphthalene-1,5-diamine) not allowing the polymer to crystallize.

Although observation under the polarizing optical microscope revealed mesophase formation in all polymers

with an identifiable nematic texture, the DSC thermograms did not show distinct transitions related to mesophase formation. As discussed earlier, the mesophase formation is shear induced, which might account for the absence of thermal transitions due to mesophase formation in the DSC thermograms of the polymers. Cowie and Wu¹⁹ reported similar observations in which the DSC thermograms did not reveal mesophase formation but optical studies showed the formation of a nematic phase when the polymer was sheared.

The diamines in this study are structurally different, but the softening and melting temperatures of the polymers were not considerably affected. However, the decomposition temperature was affected. The polymer derived from *p*-phenylenediamine (PI) was less stable toward decomposition compared to the polymer derived from tetraphenylthiophene diamine (PVIII). This may be explained on the basis of more aromatic or rigid ring structures of PVIII than that of PI. Thermogravimetric analysis of the polymers showed no weight loss below 280°C (Table III). The maximum decomposition temperature was in the range of 390–435°C.

CONCLUSION

The synthesis and properties of new main-chain liquid crystalline poly(ester-amide)s based on an ester-containing diacid derivative of LA were described. Yamazaki's phosphorylation reaction formed the basis of the polycondensation reaction.¹³ The polymers had inherent viscosities in the range of 0.21–0.38

TABLE III
Thermal Stability of Polymers in Air

Polymer	Temperature (°C) for various decompositions					T_{\max}^a
	10%	20%	30%	40%	50%	
PI	325	360	380	396	405	390
PII	325	358	380	395	410	410
PIII	355	390	405	415	425	425
PIV	355	393	410	420	430	425
PV	320	375	395	406	415	415
PVI	345	390	405	417	427	425
PVII	340	370	385	400	415	405
PVIII	360	410	425	440	480	435

T_{\max} Temperature of the maximum rate of decomposition in the TGA curve.

dL/g. All the polymers were soluble in most of the organic solvents, could be cast into slightly yellow, transparent films, and exhibited mesophase formation under shearing. Polymers derived from *p*-phenylenediamine showed a smectic G/nematic transition with dendritic texture whereas other polymers exhibited a mesophase, suggesting a nematic Schlieren texture. The two polymers derived from *p*-phenylenediamine and 4,4'-diaminodiphenyl ether showed a nematic Schlieren texture when their solution in *m*-cresol at 60–80 wt % concentration was sheared. A thermal transition due to mesophase formation was not observed in the DSC thermograms, probably because the mesophase was observed only on shearing. The maximum decomposition temperature was 390–435°C for these polymers.

Three of the authors (V.A.E.S, N.N.M, and S.V.L.) thank the Department of Science and Technology, New Delhi, India, for financial assistance.

References

1. Ciferri, A.; Krigbaum, W. R.; Meyer, R. B. *Polymer Liquid Crystals*; Academic: New York, 1982.
2. Noel, C. *Makromol Chem Macromol Symp* 1988, 22, 95.
3. Donald, A. M.; Windle, A. H. *Liquid Crystalline Polymers*; Cambridge University Press: Cambridge, UK, 1992; p 310.
4. Preston, J. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Kroschwitz, J. L., Eds.; Wiley-Interscience: New York, 1988; Vol. 11, p 381.
5. Vollbracht, L. In *Comprehensive Polymer Science*; Allen, G.; Bevington, J. C.; Eastmond, G. C., Eds.; Pergamon: Oxford, UK, 1989; Vol. 5, p 375.
6. Reisch, M. S. *Chem Eng News* 1987, 65, 9.
7. Tanner, D.; Fitzgerald, J. A.; Philips, B. R. *Angew Chem Int Ed Engl Adv Mater* 1989, 28, 649.
8. Jin, J.-L.; Antoun, S.; Ober, C.; Lenz, R. W. *Br Polym J* 1980, 12, 132.
9. Chung, T.-S. *Polym Eng Sci* 1986, 26, 901.
10. Varshney, S. K. *J Macromol Sci Rev Macromol Chem Phys* 1986, C26, 551.
11. Kwolek, S. L.; Morgan, P. W.; Schaeffgen, J. R. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Kroschwitz, J. L., Eds.; Wiley-Interscience: New York, 1988; Vol. 9, p 1.
12. Ober, C. K.; Lin, J. L.; Lenz, R. W. *Adv Polym Sci* 1984, 59, 104.
13. Yamazaki, N.; Masumoto, M.; Higashi, F. *J Polym Sci Polym Chem Ed* 1975, 13, 1373.
14. Imai, Y.; Maldar, N. N.; Kakimoto, M. A. *J Polym Sci Polym Chem Ed* 1984, 22, 2189.
15. Furniss, B. S.; Hannaford, A. J.; Rogers, V.; Smith, P. W. G.; Tatchell, A. R. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed.; ELBS Longman: London, 1978; p 500.
16. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1980.
17. Demus, D.; Richter, L. *Texture of Liquid Crystals*; Verlag Chemie: New York, 1978.
18. Shaikh, V. A. E.; Ubale, V. P.; Maldar, N. N.; Lonikar, S. V. In *Polymers Beyond A.D. 2000*; Ghosh, A. K., Ed.; The Society for Polymer Science: New Delhi, India, 1999; p 174.
19. Cowie, J. M. G.; Wu, H. H. *Br Polym J* 1988, 20, 515.
20. Lin, J.; Sherrington, D. C. *Macromolecules* 1992, 25, 7107.