



Synthesis and Characterization of Certain Photoactive Liquid Crystalline Poly(ester amides) from 2,5-Pyridine Dicarboxylic Acid

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A new series of four photo-crosslinkable thermotropic liquid crystalline poly(ester amides) were synthesized by direct polycondensation of 2,5-pyridine dicarboxylic acid with two different varying diols and diamines. Two diamines employed in the synthesis were 4,4'-diaminodiphenyl methane and 1,4-diaminobenzene. The arylidene diols 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone and 2,6-bis(4-hydroxy-3-methoxybenzylidene)cyclohexanone were also used. The synthesized poly(ester amides) were characterized by qualitative solubility test, FT-IR, ¹H and ¹³C NMR spectra. The monomeric moieties were found to be well incorporated in the polymer backbone. The molecular weight of the polymer was assessed by gel permeation chromatography (GPC). The thermal phase transition behavior and liquid crystallinity of the poly(ester amides) were investigated by differential thermogravimetry (DTG) and hot stage optical polarized microscopy (HOPM), respectively. Interestingly, these poly(ester amides) in dimethylacetamide were found to possess photo-crosslinking characteristics when irradiated by UV light. These polymeric materials may find utility value in optical information storage devices.

Keywords: Arylidene diols, Poly(ester amides), Liquid crystals, Photocrosslinking.

INTRODUCTION

Poly(ester amides) are considered to be important class of polymeric materials in recent years as they possess polyester and polyamide building blocks in a single molecule. Poly(ester amides) form strong intermolecular hydrogen bonding which can enhance the limited mechanical and thermal properties of the materials [1]. The polymers incorporated arylidene diol moiety find uses in many fields such as surgical devices, thermo-plastic materials, scaffolds in tissue engineering, cell encapsulation and injectable drug delivery [2-5]. Sudha [6] has synthesized certain thermotropic liquid crystalline aromatic-aliphatic poly(ester-amide)s from amido diol.

Abdolmaleki *et al.* [7] reported the synthesis of novel nano-structured aromatic optically active poly(ester amides) derived from biodegradable polymers containing S-tyrosine amino acids. Song *et al.* [8] have been investigated the synthesis of electroactive and biodegradable multiblock copolymers based on poly(ester-amide) and aniline oligomers. Pinilla *et al.* [9] evidenced that high molecular weight poly(ester amides) can be prepared from carbohydrates bearing methoxyl groups

along the polymer backbone. Synthesis of novel biodegradable poly(ester amides) having ether linkages in the backbone chain by ring-opening copolymerization was studied by Li *et al.* [10]. The difference in the thermal properties of segmented poly(ester amides) has been evaluated. Generally, thermal properties were dependent on the microstructure of polymers. The structure-property relationship is essential for designing polymeric materials [11]. The photo-crosslinkable thermotropic liquid crystalline polymers containing bis(benzylidene)cycloalkane groups have also been extensively studied [12]. Shibaev [13] found applications in the field of developing optical information storage devices and non-linear optical materials.

Murali and Samui [14] reported an excellent review concerning bisbenzylidene cycloalkane as a polymer building block and its significance in various fields. Ankushrao *et al.* [15] recently reported the synthesis of novel aromatic poly(ester amides) containing cyclopentylidene moiety in the polymer backbone to improve the solubility and processability of polymers.

Synthesis of poly(ester amides) from wide range of monomers can lead to linear or hyper branched molecular arrangements [16]. Many synthetic methods to produce poly(ester

amides) have been proposed. But one of the easiest and most studied methods is direct polycondensation. In this study, we report on the synthesis and characterization of photocross-linkable liquid crystalline poly(ester amides) obtained from a common diacid namely 2,5-pyridine dicarboxylic acid with two different diamines and two different *bis*(benzylidene)-cycloalkanone diols using diphenylchlorophosphate (DPCP) as polycondensation agent in pyridine medium. From the data, a correlation between optical properties and polymeric structure is discussed.

EXPERIMENTAL

Aldrich samples of 2,5-pyridine dicarboxylic acid, 4,4'-diaminodiphenyl methane, 1,4-diaminobenzene, diphenylchlorophosphate (99 %) and anhydrous lithium chloride (99 %) were used as received. Cyclopentanone and cyclohexanone were purchased from SRL and freshly distilled in the laboratory. Merck sample of pyridine was refluxed over KOH pellets and distilled (115 °C). It was preserved in amber coloured bottles over KOH pellets. Merck samples of other solvents such as tetrahydrofuran and methanol were distilled at their boiling point before use. Spectral grade DMSO-*d*₆ (Aldrich) containing TMS as internal standard was used as such for recording NMR spectrum.

Preparation of arylidene diol: The synthesis of arylidene diol, namely, 2,5-*bis*(4-hydroxy-3-methoxy benzylidene)cyclopentanone was carried out according to the procedure as reported by Mayavathi *et al.* [17]. Briefly, a mixture of 18.5 g (0.15 mol) 4-hydroxy-3-methoxybenzaldehyde and 6.31 g (0.075 mol) cyclopentanone was dissolved in 75 mL of dry methanol and maintained in ice cold condition. To this mixture, catalytic amount of conc. sulphuric acid was added slowly dropwise and kept for 24 h. The product was filtered, washed several times with distilled water and dried. The crude monomer was recrystallized twice from methanol to yield yellowish green crystals. m.p. 212 °C. Yield: 85 % FT-IR (KBr, ν_{\max} , cm^{-1}): 2923 (CH₂), 1674 (cyclopentanone C=O), 3338 (OH) and 1593 (C=C).

The other arylidenediol, 2,6-*bis*(4-hydroxy-3-methoxybenzylidene)cyclohexanone was also synthesized as above mentioned procedure.

Synthesis of poly(ester amides): The polymers (Table-1) were prepared by direct polycondensation as according to the following procedure.

In a three necked 250 mL round bottomed flask equipped with a condenser, thermometer and mechanical stirrer (400 rpm/min) in an oil bath, 0.835 g (5 mmol) of 2,5-pyridine dicarboxylic acid in 10 mL pyridine and 2.694 mL (13 mmol) diphenylchlorophosphate (DPCP) were added. After stirring for 20 min, 0.4250 g (10 mmol) of LiCl in 10 mL pyridine

TABLE-1
POLYMER CODE, MONOMERS USED, YIELD,
INHERENT VISCOSITY AND COLOUR

Polymer code	Monomers	Yield (%)	Inherent viscosity (dL/g)	Colour
PAPM	PD + AP + DM	84	1.16	Grey
PAPB	PD + AP + DB	65	1.20	Black
PAHM	PD + AH + DM	78	1.18	Black
PAHB	PD + AH + DB	80	1.23	Brown

PD: 2,5-pyridine dicarboxylic acid; AP: 2,5-*bis*(4-hydroxy-3-methoxy benzylidene)cyclopentanone; AH: 2,6-*bis*(4-hydroxy-3-methoxybenzylidene)cyclohexanone; DM: 4,4'-diamino diphenyl methane; DB: 1,4-diamino benzene.

was added and the stirring was continued at room temperature for 30 min. The reaction mixture was slowly heated and maintained at 120 °C for 20 min. To this mixture, 0.88 g (2.5 mmol) of 2,5-*bis*(4-hydroxy-3-methoxybenzylidene)cyclopentanone in 5 mL pyridine and 0.495 g (2.5 mmol) of 4,4'-diaminodiphenyl methane in 5 mL pyridine were added dropwise simultaneously at 120 °C and the whole solution was further stirred under the same condition for 3 h. The solution was cooled to room temperature and poured into 500 mL water/methanol (1:1 v/v) mixture. The product was filtered, washed with hot methanol and dried in sunlight. Similarly, all the other poly(ester amides) were prepared in the same method having same monomer feed ratio.

RESULTS AND DISCUSSION

Solubility of poly(ester amides): The solubility of all the synthesized poly(ester amides) are listed in Table-2. The poly(ester amides) derived from aromatic dicarboxylic acid were found to be easily soluble in highly polar solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc) dimethyl sulphoxide (DMSO) and tetrahydrofuran (THF) partially soluble in acetone, chloroform and sparingly soluble in common organic solvents like methanol, benzene and hexane.

FTIR analysis: The representative FT-IR spectrum of poly(ester amide) (PAPM) is shown in Fig.1. The vibration at 1740 cm^{-1} is attributed to C=O ester linkage which confirms the completion of polymerization. The characteristic carbonyl stretching frequency of cyclopentanone ring appeared at 1673 cm^{-1} . The aromatic C=C is shown at 1520 cm^{-1} . The absorption due to NH bond of amide linkage is observed at 3338 cm^{-1} . In addition, absorption at 1265 cm^{-1} was observed. This vibration is attributed to C-O-C of ester group and other characteristic absorptions appeared in the IR spectra indicate that the monomers are well incorporated into the polymer backbone of poly(ester amides). Similar FT-IR spectra with characteristic absorptions were also obtained for the other three poly(ester amides).

NMR analysis: The chemical repeat units in poly(ester amides) were identified by ¹H and ¹³C NMR spectra. The typical

TABLE-2
SOLUBILITY OF THE POLY(ESTERAMIDES)

Polymer	Hexane	Benzene	CHCl ₃	THF	Acetone	CH ₃ OH	DMF	DMAc	DMSO
PAPM	–	–	±	+	±	–	+	+	+
PAPB	–	–	±	+	±	–	+	+	+
PAHM	–	–	±	+	±	–	+	+	+
PAHB	–	–	±	+	±	–	+	+	+

+ = Highly soluble; ± = Partially soluble; – = Sparingly soluble

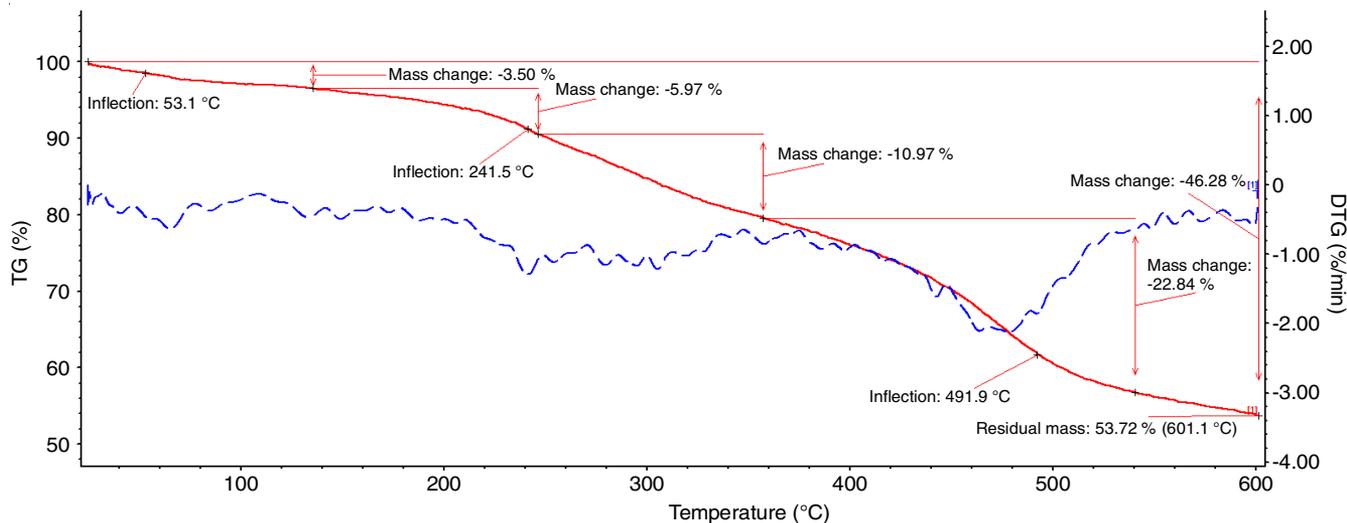


Fig. 4. DTG thermogram of PAPM

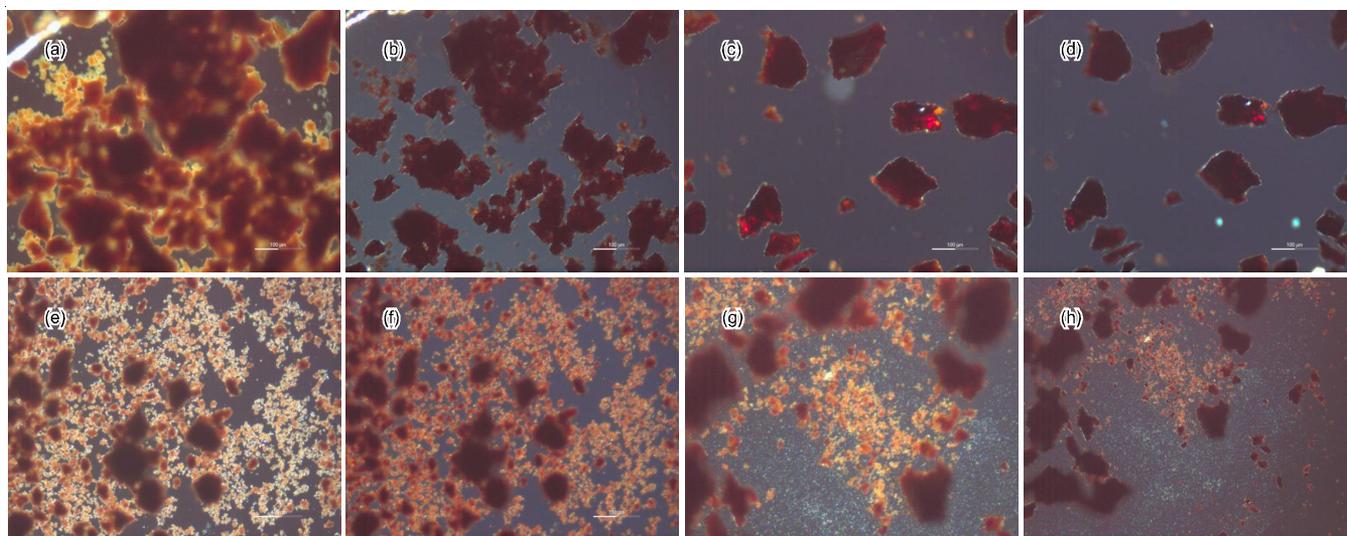


Fig. 5. OPM micrographs of (a) PAPM at 55 °C (b) PAPM at 260 °C (c) PAPB at 205 °C (d) PAPB at 283 °C (e) PAHM at 250 °C (f) PAHM at 400 °C (g) PAHB at 253 °C (h) PAHB at 395 °C

lamp at regular time intervals. The decrease in absorbance showed at different intervals of time of irradiation established that there is steady rate of photocrosslinking. The photocrosslinking ability of the polymer was followed by the rate of disappearance of C=C bond of photosensitive group in the UV spectrum (Fig. 6). When the polymers were irradiated with UV light, they undergo $2\pi+2\pi$ cycloaddition and form photodimers. The absorption intensity decreases rapidly with increasing irradiation time. The decrease in the UV absorption intensity due to photocrosslinking of polymer through $2\pi+2\pi$ cyclo-dimerization of carbon-carbon double bond in the arylidene moiety leads to formation of cyclobutane ring.

X-ray diffraction analysis: The powdered wide angle XRD patterns for four synthesized poly(ester amides) were studied at room temperature to examine the crystal behaviour of the polymers. A representative X-ray diffractogram of the polymer PAPM is shown in Fig. 7. The XRD spectrum showed diffraction peaks in the region $2\theta = 16-85^\circ$ indicate that these polymers are semi-crystalline in nature. This is due to the presence of methoxy substituent in arylidene diols caused some

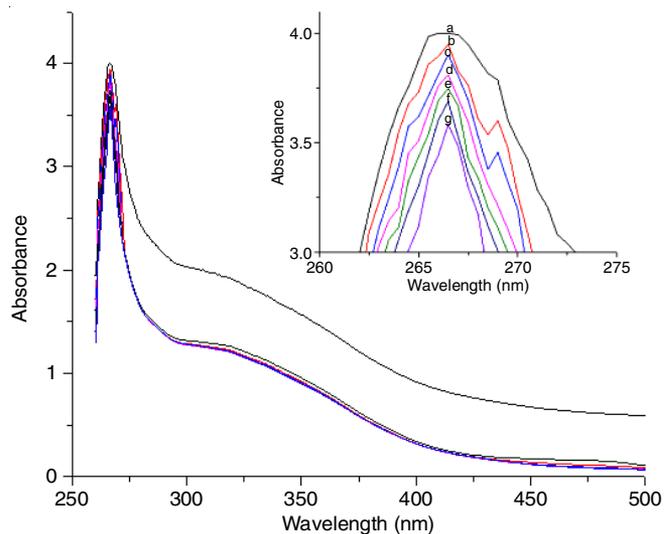


Fig. 6. UV spectrum of PAHB on irradiation of UV light at different time intervals: (a) 0 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 25 min, (f) 30 min and (g) 35 min

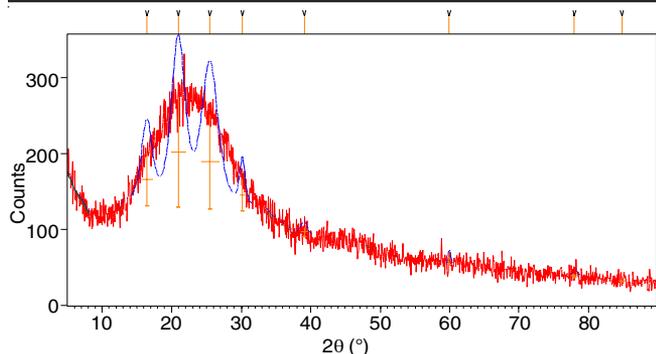


Fig. 7. XRD pattern of PAMM

hindrance between repeating units leading to unsymmetrical orientation and reduced the crystallinity. However, the presence of carbonyl group and carbon-carbon double bonds induces some degree of crystallinity.

Molecular weight determination by gel-permeation chromatography: The molecular weight and molecular weight distribution of polymer PAMM were monitored by gel permeation chromatography technique. Because of the solubility of poly(ester amide) viz. PAMM in THF, it was possible to measure their molecular weights using THF as carrier solvent at room temperature by GPC. The GPC plot of PAMM is shown in Fig. 8. The number average molecular weight (M_n), weight average molecular weight (M_w), and the polydispersity indices of this poly(ester amide) are listed in Table-4.

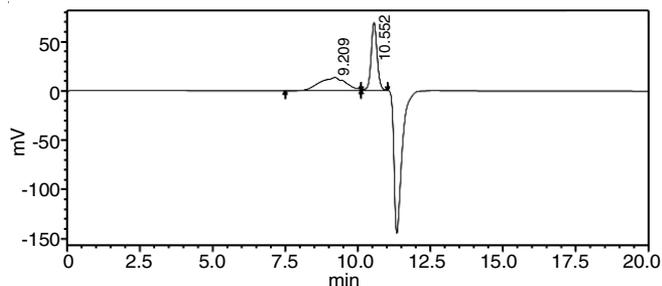


Fig. 8. GPC plot of PAMM

TABLE-4

NUMBER AVERAGE MOLECULAR WEIGHT (M_n),
WEIGHT AVERAGE MOLECULAR WEIGHT (M_w) AND
POLYDISPERSITY INDICES OF PAMM

Polymer code	M_n (g/mol)	M_w (g/mol)	PDI
PAMM	48,824	70,795	1.45

Conclusion

A series of four new photoactive liquid crystalline poly(ester amides) were synthesized and characterized. The spectral data supported the microstructure of polymer backbone. The resulting polymers showed good solubility in polar, aprotic solvents and the inherent viscosity data revealed that these

polymers are of high molecular weight. The TG-DTG thermograms indicated that all the poly(ester amides) are thermally stable. The display of nematic mesophase exhibited by these polymers was confirmed by hot stage optical polarizing microscopy (HOPM) observations. Arylidene cycloalkanones are photoactive chromophores as evidenced by experiments on photocrosslinking by UV irradiation. X-ray diffraction analysis of poly(ester amides) showed that they are semi-crystalline in nature. Considering the results of this work, these poly(ester amides) could be expected to be potential candidates for photoresists and in optical information technology.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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