

## Synthesis and Study of Oxygen Bridged Liquid Crystalline Copolyesters

D. ROOPSINGH<sup>1,\*</sup>, N. MALATHY<sup>1</sup>, P. SATHYAMURTHY<sup>1</sup> and V. KANNAPPAN<sup>2</sup>

<sup>1</sup>Post-Graduate & Research Department of Chemistry, Presidency College, Chennai-600 005, India

<sup>2</sup>Post-Graduate & Research Department of Chemistry, Loyola College, Chennai-600 034, India

\*Corresponding author: Tel: +91 44 22670644; E-mail: roopsingh@hotmail.com

(Received: 24 November 2009;

Accepted: 21 August 2010)

AJC-8992

Six new thermotropic liquid crystalline random copolyesters with ethereal linkages were prepared from mesogenic 4,4'-oxybis(benzoic acid) by direct polycondensation with different aromatic diols in pyridine solution. Diphenylchlorophosphate (DPCP) was employed as the condensation agent. The solution viscosity numbers ranged from 0.41-0.81 dL/g. The glass transition temperature of these polymers were determined by thermal studies (DSC and optical polarizing microscopy) and found to lie between 41.4 and 61.5 °C. Spectral studies (<sup>1</sup>H, <sup>13</sup>C NMR and FT IR) gave an insight about the microstructure and copolymer compositions. The polyester composite film was exposed to UV irradiation to find changes in morphology by SEM analysis.

**Key Words:** Polycondensation, Thermotropic liquid crystalline polyesters, Diphenylchlorophosphate, Arylidene diols.

### INTRODUCTION

Liquid crystal technology has had a major effect on many areas of science and engineering, as well as device technology. Applications for this special kind of material are still being discovered and continue to provide effective solutions to many different problems. Thermotropic polymeric liquid crystals consisting of alternating arrangement of mesogens and flexible spacers in the main-chain have been extensively investigated<sup>1-3</sup>. Mesomorphic property of a polymer is mainly attributed to the molecular shape. Anisotropic orientation dependent, polar and steric interactions also contribute to the stability of the mesophase. This can be achieved by introducing a suitable mesogen in the polymer backbone, incorporating flexible spacers or introducing lateral substituents or molecular kinks by copolymerization technique. These factors impart stiffness to the polymer chain and make the polymers liquid crystalline. Rigid chains are preferred for fibre formation, while flexible chains make better elastomers. It has been found that liquid crystal polyesters possessing low glass transition temperatures ( $T_g$ ) and exhibiting nematic phase can be used in reprographic applications<sup>4-7</sup>. The presence of ether group either in the diol or in the dicarboxylic acid as part of the polyester normally enhances the solubility and the ease of processing<sup>8</sup>. There are several reports<sup>9,10</sup> on thermotropic liquid crystal polyesters containing non-linear monomers<sup>11-14</sup>. A few documented reports<sup>13,14</sup> suggest that 4,4'-oxybis(benzoic acid) (OBBA) is a potential non-linear mesogen to lower the mesophase tempe-

rate effectively. However, this mesogen is seldom experimented in the preparation of thermotropic liquid crystalline polyesters (TLCPs). In this investigation, we have synthesized six new thermotropic liquid crystalline polyesters with a common monomer 4,4'-oxybis(benzoic acid) and analyzed their special properties.

### EXPERIMENTAL

Pyridine (Merck, 99 % pure), was refluxed over potassium hydroxide pellets and distilled (b.p. 115 °C). Lithium chloride anhydrous (SDS, AnalaR) was dried at 130 °C under vacuum for 4 h and at 180 °C for 10 h. Methanol (BDH, LR) was purified by refluxing over quick lime for 6 h and distilled three times to get dry methanol. The fraction distilling at 65 °C was collected and used. N,N-Dimethylacetamide (DMAc) (BDH, AnalaR) was dried over anhydrous copper sulphate and distilled under reduced pressure (b.p. 65 °C/10 mm). Spectral grade DMSO-*d*<sub>6</sub> and CDCl<sub>3</sub> (Aldrich) containing TMS as internal standard was used as such for recording NMR spectra. 9,10-Diketooanthracene 1,8-diol (AQ) (BDH, m.p. 193 °C) was recrystallized from ethanol. Aldrich samples of 4,4'-biphenyldicarboxylic acid (98 %), 4,4'-oxybis(benzoic acid) (99 %), vanillin (CDH, AnalaR), 4-hydroxybenzaldehyde (Fluka, 98 %), cyclopentanone (Fluka, 99 %), cyclohexanone (BDH, AnalaR) and bis(4-hydroxy-3-methoxybenzylidene ketone) were used without further purification in the preparation of random copolyesters.

## Methods

**Preparation of arylidene diols:** Arylidene diols used as varying diols in the synthesis of random polyesters were prepared by the condensation of the respective carbonyl compounds and aromatic hydroxy aldehydes in the mole ratio 1:2 (Table-1).

TABLE -1  
MONOMERS USED IN THE SYNTHESIS  
OF RANDOM COPOLYESTERS

| Polymer code | Diol I                         | Diol II   |
|--------------|--------------------------------|---|
| EQBA         | 9,10-Diketoanthracene 1,8-diol | <i>Bis</i> (4-hydroxybenzylidene)-acetone                 |
| EQBP         | 9,10-Diketoanthracene 1,8-diol | <i>Bis</i> (4-hydroxybenzylidene)-cyclopentanone          |
| EQBH         | 9,10-Diketoanthracene 1,8-diol | <i>Bis</i> (4-hydroxybenzylidene)-cyclohexanone           |
| ETVA         | 2,5-Ditertiarybutylquinol      | <i>Bis</i> (4-hydroxy-3-methoxybenzylidene)acetone        |
| ETVP         | 2,5-Ditertiarybutylquinol      | <i>Bis</i> (4-hydroxy-3-methoxybenzylidene)cyclopentanone |
| ETVH         | 2,5-Ditertiarybutylquinol      | <i>Bis</i> (4-hydroxy-3-methoxybenzylidene)cyclohexanone  |

Different methods have been reported<sup>15-18</sup> in literature for the synthesis of arylidene diols. *Bis*(4-hydroxybenzylidene)-acetone (BHAC) and *bis*(4-hydroxy-3-methoxybenzylidene)-acetone (BVAC) were prepared by the method of McGookin and Sinclair<sup>15</sup>. Dry hydrogen chloride gas was passed through a solution containing 4-hydroxybenzaldehyde (0.206 mol) and acetone (0.103 mol) in dry methanol (100 mL). The solution turned dark pink and green precipitate was obtained after the addition of water. It was further purified by crystallization from aqueous methanol. Yield: 90 % (m.p. 236 °C). *Bis*(4-hydroxybenzylidene)cycloalkanones and *bis*(4-hydroxy-3-methoxybenzylidene)cycloalkanones were synthesized by the method adopted by Arumugasamy and coworkers<sup>17,18</sup>. This method yielded the arylidene diols quickly and in high yield. The synthesis of a typical diol, namely, *bis*(4-hydroxybenzylidene)-cyclopentanone (BHCP) is described here. A solution containing 4-hydroxybenzaldehyde (0.2 mol) in 100 mL of dry methanol was taken in a 250 mL conical flask. Cyclopentanone (0.1 mol) was added drop wise and the mixture was shaken well. Fuming sulphuric acid (5 mL) was added drop wise with external cooling in an ice bath. An exothermic reaction took place and the reaction mixture turned bright yellow, dark green and finally pink. The precipitated diol was filtered and washed with aqueous methanol. It was filtered and recrystallized from aqueous methanol. Yield: 93 % (m.p. > 300 °C). All the other arylidenediols derived from cycloalkanones were prepared by a similar procedure and their yield and m.p. are given in Table-2.

**Synthesis of copolyesters:** All the six copolyesters were prepared by direct polycondensation of two diols and one diacid in the respective mole ratio 1:1:2 in pyridine solution using diphenylchlorophosphate (DPCP) as the condensation agent. This method was extensively used by Chang and

TABLE-2  
ARYLIDENE DIOLS SYNTHESIZED  
WITH YIELD AND MELTING POINTS

| Arylidene diol   | Yield (%) | m.p. (°C) |
|--|-----------|-----------|
| <i>Bis</i> (4-hydroxybenzylidene)acetone (BHAC)*                   | 90        | 236       |
| <i>Bis</i> (4-hydroxy-3-methoxybenzylidene)acetone (BVAC)*         | 85        | 160       |
| <i>Bis</i> (4-hydroxybenzylidene)cyclohexanone (BHCH)#             | 90        | 280       |
| <i>Bis</i> (4-hydroxybenzylidene)cyclopentanone (BHCP)#            | 93        | >300      |
| <i>Bis</i> (4-hydroxy-3-methoxybenzylidene)-cyclohexanone (BVCH)#  | 95        | 180       |
| <i>Bis</i> (4-hydroxy-3-methoxybenzylidene)-cyclopentanone (BVCH)# | 90        | 212       |

\*Dry HCl gas was used; #Fuming sulphuric acid was used.

coworkers<sup>19,20</sup> in the synthesis of several polyesters. The reaction set up consists of a 250 mL round bottomed flask equipped with a stirrer, a condenser with calcium chloride trap and a thermometer.

The method employed in the synthesis of typical polyester is described here. Diphenylchlorophosphate (12 mmol) in pyridine (10 mL) was added to a solution containing LiCl (10 mmol) and oxybis(benzoic acid) (5 mmol) in pyridine (10 mL) taken in a reaction vessel. The mixture was continuously stirred at room temperature for 0.5 h. The temperature was raised to 120 °C and stirred at this temperature for 10 min. A solution containing the diol *bis*(4-hydroxybenzylidene)acetone (BHAC) (2.5 mmol) and 9,10-diketoanthracene-1,8-diol (2.5 mmol) in pyridine (10 mL) was added drop wise over a period of 10 min with constant stirring. The mixture was maintained at 120 °C with continuous stirring for 3 h. The reaction mixture was cooled and poured into 300 mL of methanol when the polymer was precipitated. It was filtered, washed repeatedly with acetone, methanol and water and dried at 80 °C in vacuum.

**Characterization of random copolyesters:** All the polyesters synthesized were characterized by viscosity measurements and spectral data (UV-visible, FTIR, <sup>1</sup>H and <sup>13</sup>C NMR). Thermal investigations (DSC) were made on the polyesters. The liquid crystalline properties were determined by optical polarizing microscopy (OPM). The morphology of the polymer composite film was investigated by scanning electron microscopy (SEM). Photo-cross linking studies were carried out by UV irradiation on both solution and composite film of typical polyesters.

## RESULTS AND DISCUSSION

All the polyesters synthesized had a common monomer, namely, 4,4'-oxybis(benzoic acid) which possesses an oxygen bridge in the middle. The presence of ether group in the main chain of the polyester enhances the solubility in organic solvents and hence eases processing<sup>8</sup>.

The percentage yield of the polyesters and their inherent viscosity values determined in N,N-dimethylacetamide (DMAc) solution at 30 °C are given in Table-3. It is worth mentioning that the yield of the copolyesters synthesized by the diphenylchlorophosphate method<sup>19,20</sup> are relatively high and this method bypasses the tedious preparation of diacid chlorides. All the copolyesters are coloured, amorphous solids at room temperature.

TABLE-3  
YIELD (%) AND INHERENT VISCOSITIES OF RANDOM COPOLYESTERS IN DMAc SOLUTION AT 30 °C

| Polymer | Yield (%) | $\eta_{inh}$ (dL/g) |
|---------|-----------|---------------------|
| EQBA    | 68        | 0.41                |
| EQBP    | 70        | 0.72                |
| EQBH    | 73        | 0.60                |
| ETVA    | 65        | 0.49                |
| ETVP    | 69        | 0.81                |
| ETVH    | 73        | 0.60                |

**Spectral characterization:** The FT IR spectra of all the random copolyesters showed ester carbonyl absorption at  $\bar{\nu} = 1730 - 1750 \text{ cm}^{-1}$ . The carbonyl stretching frequency of the arylidene keto group is slightly greater in the polyester than that in the monomeric diols which may be ascribed to the rigidity of the arylidene keto moiety in the polymer chain.

The structural units in the polymer chain were identified by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral data. The methoxy protons in the vanillin moiety are indicated by the signal at  $\delta = 3.4$  ppm while methylene protons of cycloalkanone absorbed at 2 ppm. The aromatic protons and the olefinic protons of arylidene group showed signals around 6.8-7.5 ppm. The signals at 160-170 ppm in the  $^{13}\text{C}$  NMR spectra of all the polyesters indicated the carbonyl carbon of the ester group. The carbonyl carbon of the arylidene moiety is highly deshielded and absorbed at 190 ppm. The methylene carbon atom of the aliphatic diacid could be seen at  $\delta = 40$  ppm.

**Thermal characterization:** DSC thermograms of the polyesters from vanillin based arylidene diols are presented in Fig. 1. The thermal transition temperatures of all the polyesters synthesized are presented in Table-4. It is worthwhile to compare the transition temperatures of the random copolyesters obtained in the present investigation with that of the polyesters reported by earlier workers. Arumugasamy and Kannappan<sup>17,18</sup> have identified nematic mesophase in certain copolyesters with low  $T_g$ ,  $T_m$  and  $T_{cl}$  values containing arylidene keto diols with aliphatic diols. The data in the present investigation suggest that copolymerization significantly reduced  $T_g$  values which in turn indicates that processing of these polymers will be easier.

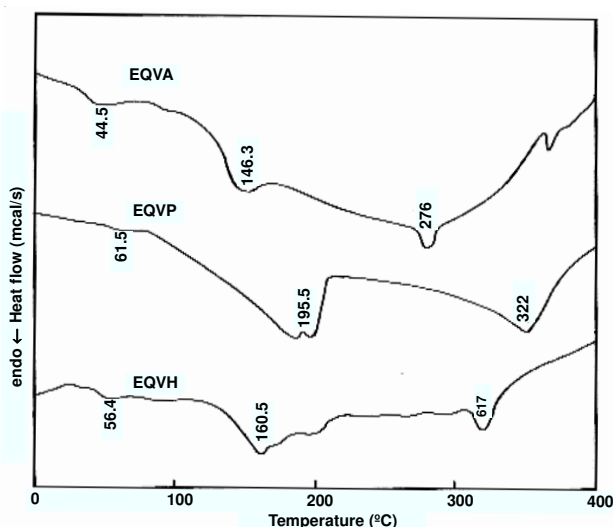


Fig. 1. DSC traces of random copolyesters recorded on heating (in nitrogen)

TABLE-4  
TRANSITION TEMPERATURES (°C) OF THE RANDOM COPOLYESTERS DEDUCED FROM DSC TRACES

| Polymer | Transition temperature (°C) |       |          | $\Delta T$ |
|---------|-----------------------------|-------|----------|------------|
|         | $T_g$                       | $T_m$ | $T_{cl}$ |            |
| EQBA    | 41.4                        | 118.2 | 265.3    | 147.1      |
| EQBP    | 55.0                        | 155.0 | 277.5    | 122.5      |
| EQBH    | 53.2                        | 152.8 | 275.0    | 122.2      |
| EQVA    | 44.5                        | 146.3 | 276.0    | 129.7      |
| EQVP    | 61.5                        | 195.3 | 322.0    | 126.7      |

**Optical polarizing microscopic studies:** The magnified photograph of the random copolyester EQBP taken at 158 °C during heating is given in Fig. 2. It has fine grain structure and greenish orange crystals which could be seen in the magnified photograph. This is indicative of nematic phase in this polymer. Fascinatingly, birefringent rod like texture could be seen in the polarized optical micrograph placed in Fig. 3 which shows characteristic of smectic mesophase at 183 °C for EQBH. The difference could be ascribed due to the rigidity of cyclohexanone based arylidene diol in EQBH.

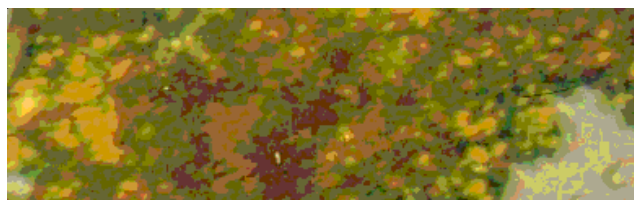


Fig. 2. Polarized optical micrograph of EQBP at 158 °C (X100)

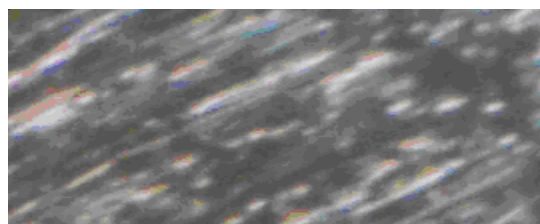


Fig. 3. Polarized optical micrograph of EQBH at 183 °C (X100)

**Photocrosslinking studies by SEM:** Arylidene keto group is photoactive one. SEM is used to find the topographical change by photocrosslinking on UV irradiation of these samples. The typical test was done with the composite film of EQBP obtained in tetrahydrofuran solution with PVC with the weight ratio 10:1 and was subjected to UV irradiation for 0.5 h. SEM micrographs taken before and after UV irradiation are placed in Figs. 4 and 5. These photographs show that there is difference in the morphology of the film after UV irradiation. This is the result of photocrosslinking which has increased the crystallinity of the surface by absorption of photoirradiation. Hence, the new polyesters synthesized in this investigation could be used as potential photoresists.

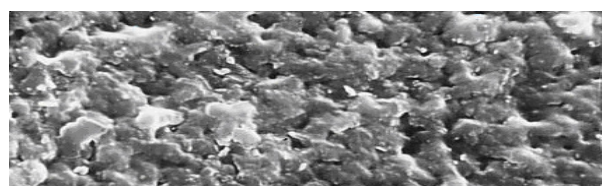


Fig. 4. SEM of composite film of EQBP before UV irradiation (X5000)

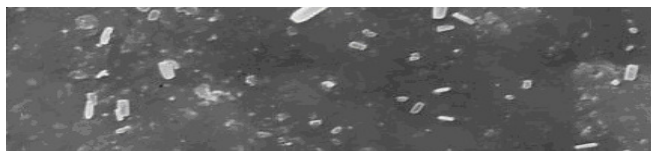


Fig. 5. SEM of composite film of EQBP after UV irradiation (X5000)

### Conclusion

Six new thermotropic liquid crystalline polyesters with oxygen bridge of 4,4'-oxybis(benzoic acid) were synthesized by solution polycondensation using diphenylchlorophosphate. Oxybiphenylene group is a bent and flexible group and this may be the reason for the nematic behaviour of the polyesters derived from OBBA except EQBH. Interestingly, due to the rigidity of cyclohexanone based arylidene diol in EQBH smectic mesophase was observed at 183 °C. Arylidene keto moiety is a photoactive chromophore and hence they can be photocrosslinked by UV irradiation. This is established SEM studies on UV irradiated composite films of these polyesters. It opens the possibilities of using these polyesters and their composite films as photoresists.

### ACKNOWLEDGEMENT

The authors are thankful to the University Grants Commission of India for permitting and supporting research by Faculty Development Program.

### REFERENCES

1. R. Roviello and A. Sirigu, *Eur. Polym. J.*, **15**, 61 (1979).
2. R.B. Blumstein, E.M. Stickles, M.M. Gauthier and A. Blumstein, *Macromolecules*, **26**, 1205 (1993).
3. T. Shaffer and V. Pearce, *J. Polym. Sci. Polym. Lett. Ed.*, **23**, 185 (1985).
4. R.A.M. Hikmet, J. Lub and D.J. Broer, *Adv. Matter.*, **3**, 392 (1991).
5. G.G. Barclay, S.G. McNamee, C.K. Ober, K.I. Parathomas and D.W. Wang, *J. Polym. Sci. Polym. Chem. Ed.*, **30**, 845 (1992).
6. J. Schatzle, W. Kaufhold and H. Finkelman, *Makromol. Chem.*, **190**, 3269 (1989).
7. J. Beeckman, R. James, F. Fernandez, W. De Cort, P. Vanbrabant and K. Neyts, *J. Lightwave Tech.*, **27**, 3812 (2009).
8. P.K. Bhowmik, D. Edward, T. Atkins and R.W. Lenz, *Macromolecules*, **29**, 3778 (1996).
9. A.B. Erdemir, D.J. Johnson, I. Karacan and J.G. Tomka, *Polymer*, **29**, 597 (1988).
10. S.N. Magonov and D. Reneker, *Ann. Rev. Mater. Sci.*, **27**, 175 (1997).
11. R. Pearce and J. Vansco, *Polymer*, **39**, 1237 (1998).
12. D.W. Schwark, D.L. Vezie, J.R. Reffiner, E.L. Thomas and B.K. Annis, *J. Mater. Sci. Lett.*, **11**, 352 (1992).
13. H.D. Sikes and D.K. Schwartz, *Science*, **278**, 1604 (1997).
14. E.-J. Choi, B.-K. Choi, J.-H. Kim and S.-C. Lee, *Korean Polym. J.*, **8**, 12 (2000).
15. A. McGookin and D.J. Sinclair, *J. Chem. Soc.*, 1170 (1928).
16. Gangadhara and K. Kishore, *Polymer*, **36**, 1903 (1995).
17. V. Kannappan, E. Arumugasamy, E. Ravichandran and B. Baskar, *J. Polym. Mater.*, **17**, 4 (2000).
18. E. Arumugasamy, Ph.D. Thesis, University of Madras, Chennai, India (1998).
19. C.P. Chen, S.J. Sun and T.C. Chang, *J. Polym. Res.*, **2**, 187 (1995).
20. S.J. Sun, Y.C. Liao and T.C. Chang, *J. Polym. Sci. A: Polym. Chem.*, **38**, 1852 (2000).