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Research Article

1,4-NAPTHALENE DIOL BASED LIQUID CRYSTALLINE RANDOM COPOLYESTER-SYNTHESIS AND CHARACTERISATION

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ABSTRACT

A copolyester was synthesized using 1,4-Napthalene diol as one of the diols with isophthaloyl chloride as an Acidchloride. In addition, 1,4-Butanediol, have also been used as another comonomer for the synthesis of random copolymer. Formation of copolyester have been confirmed using various spectral techniques viz., Ultraviolet (UV), Fourier Transform Spectroscopy Infrared (FTIR), Nuclear Magnetic Resonance (NMR) spectral techniques. Thermal studies were also carried out using Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA). Elemental analysis further supports the formations for the copolymer. Morphology of the copolyester has also been characterized using Scanning Electron Microscope (SEM) and X-ray Diffraction (XRD) Method. Results of the investigation reveals that a relatively new entry of copolymer has been suggested into the family of liquid crystalline copolymers.

INTRODUCTION

The importance of thermotropic random copolyester has been recognized and several workers have reported the synthesis and characterization of various copolyester which exhibit different mesophase in the melt. Calundann [1] reported the liquid crystalline copolyester compositions based on hydroxy benzoic acid, hydroquione, 2,6 naphthalene diol, and 4,4'-biphenol and also granted a patent for this preparation. Liquid crystalline polyesters have positional and orientational molecular order which is intermediate between that of molecular crystals and of liquids. The liquid crystalline polyesters do not melt directly to a liquid phase, but first pass through a mesomorphic state, which at a higher temperature forms a clear liquid. The moieties which generate the liquid crystalline organization are called the mesogenic moieties and can be found either in main or side groups. Polymers which exhibit liquid crystalline nature in solution are termed as lyotropic and those that exhibit in melt are called thermotropic [2]. The structural characteristics associated with liquid crystalline behavior have been reviewed by Gray[3]. Several thermotropic highly aromatic liquid crystalline polyesters such as Vectra and Xydar have been commercialized. These polyesters are thermaly stable and possess high tensile strength and modulus. The application of liquid crystal polymers are in the area of fibres, films, plastics, holography, photocrosslinkages and as information storage devices.

MATERIALS AND METHODS

1,2dichlorobenzene (MerkLR), 1, 4-ButaneDiol (Loba),1,4-Napthalene diol (Loba), Isopthaloylchloride (Loba). Analarsamples of $CHCl_3$, DMSO, DMF, Acetone, Methanol, Ether is used as such.

Polymer Synthesis

Preparation of Random Copolyester P3BIN

A 250ml three necked round bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, a reflex condenser and a thermometer was used. To the flask added O-dichlorobenzene(150ml), then added 1,4-Butane diol 1.76ml(0.02 mole) followed by 1,4-Napthalene diol 2.2g(0.01mole). The mixture was stirred for 20 minutes and temperature was gradually increased to 120°C. To this reaction mixture, added isopthaloyl chloride 6g (0.03mole). Then the whole mixture was maintained with further stirring and heating

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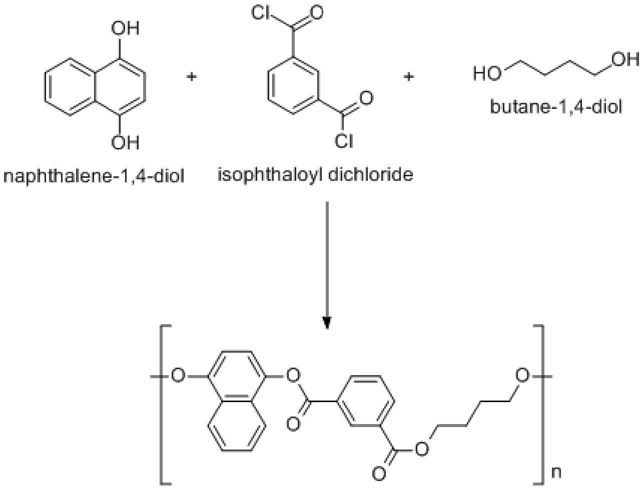
at 120°C-160°C for 52 hours. The reaction mixture was poured into ether with stirring to precipitate the polymer. The precipitated polymer was separated by filteration, recrystallized by dissolving in acetone and poured in water, filtered and then dried. The copolyester was obtained as a white colour solid.

Scheme



Poly[oxy-(1,4-benzene)oxy-co-(1.3-benzenoyl)-co-oxy-(1,4-butane)-oxy]

RESULTS AND DISCUSSION

Characterization of random copolyesters

The characterization of the random copolyester viscosity measurements, solubility studies and spectral data. Thermal studies were also performed on the polyester

Fourier Transform Infrared spectroscopy spectra

The IR spectra of copolyesters were recorded using Perkin-Elmer spectrophotometer in the frequency region 4000-500 cm^{1}. KBr pellet technique was employed for recording the IR spectra of copolyester. The IR Spectrum of random copolyester showed characteristic absorption at 1740 cm-1 due to ester C = 0 stretching, 1020, 1080 and 1200 cm-1 due to the ester – C-O stretching and bending indicating that the polyester chain is present in all the polymer. The –OH absorption at 3435 cm-1 due to end – OH groups is very weak since the hydroxyl groups are present at the end of long chains. It has been shown that the polymer with stiff chains attached to a flexible backbone exhibit thermotropic liquid crystalline behaviour. P3BIN contain stiff chains with rigid spacer. This suggests that the ester carbonyl bond strength decreases with increase in the length of the spacer group and hence rigidity of the polymer chain decreases. The strong bands at 1082 cm-1,1124 cm-1,1166 cm-1 is due to the carbonyl stretching of ester group. The three bands at 2958 cm-1,821 cm-1 and 873cm-1 are due to –CH2- stretching and bending vibration.

Table 1 FTIR spectral data of P3BIN random copolyester

Absorption frequency (cm^{-1})	Assignment
1082,1124,1166,	Stretching vibrations of the ester C-O
1716	Carbonyl stretching of the ester group
1276	CH2 – Wagging
720	AliphaticC-H bending
2958,873,821	CH2- Stretching
3080	Characteristic absorption of para substituted benzene ring
3435	Free –OH group

The absorption band at 1608cm-1 is due to the arylidene keto group present in copolyester. The vibrational frequencies assigned for the copolyesters P3BIN are summarized in Tables 1.

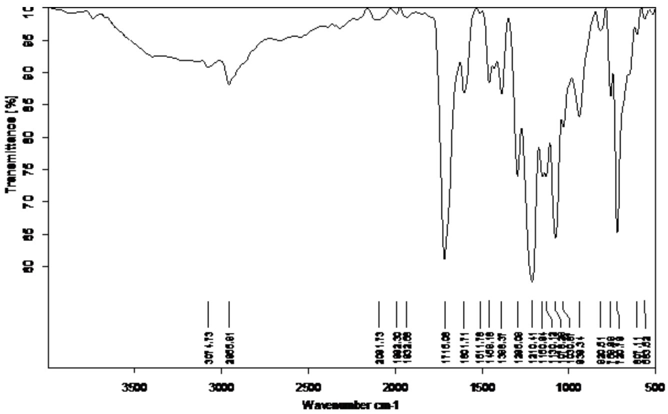


Figure 1 FTIR Spectram of P3BIN

UV – VISIBLE Spectrum

The UV-Visible spectra of these polyesters were recorded in Shimadzu-uv-160A spectrophotometer using acetone as solvent. The UV –Visible spectrum of P3BIN show a The random copolyester reported in the present investigation contains substituted benzene Chromophore. Therefore, there are two possible electronic transitions, namely π → π* and n → π*. On the There are two absorption maxima was noted for the copolyester (Figure 2). It may be pointed out that the value corresponding to both the absorption maxima are not influenced by the length of the spacer in the polymer chain, but influenced by the number of condensed rings present in the polymer chain

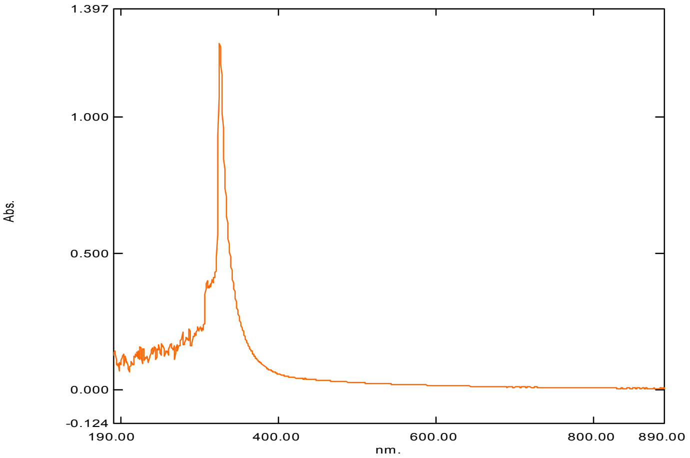


Figure 2 UV Spectrum of P3BIN

^{1}H NMR spectral analysis

A PMR spectrum of the polyester was obtained in $CDCl_3$ solution with TMS as reference in Figure 3. The peak positions in the spectrum were listed in Table 2. The chemical shift values can be explained on the basis of structural units present in the polyester

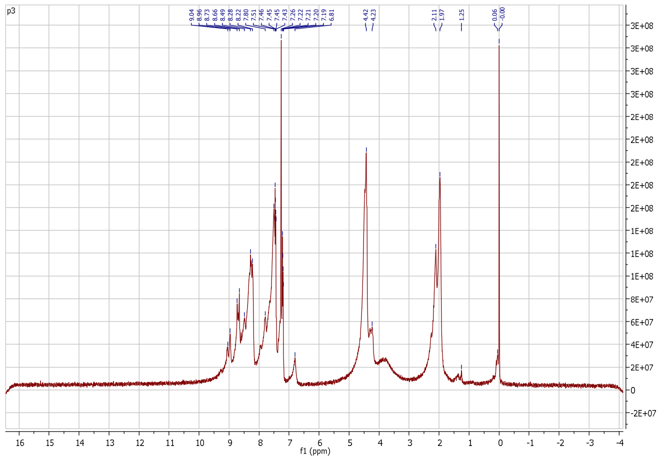


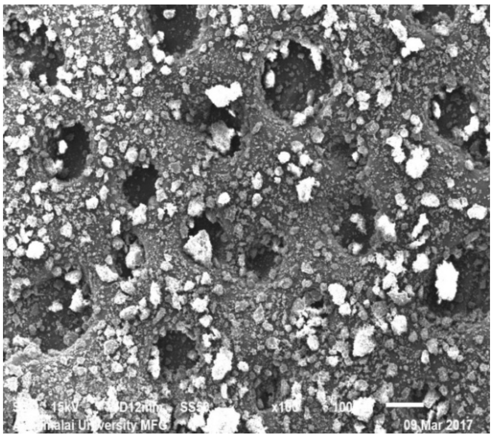
Figure 3 ^{1}H NMR Spectrum of P3BIN

Table 2 PMR spectral data of random copolyester

Chemical Shift (δ) (ppm)	Type of protons
2.1	Protons of the ester group
3.6	- CH_3 group
6.5 – 8.0	1,3 – phenylene 1,4 – phenylene

Scanning electron microscopic studies

The characterization of LC polyester by optical polarizing microscopy is the most straight forward method available and the use of the technique in TLC polymer is limited, because polymeric materials take longer time to show the recognizable textures at moderately high temperatures and during that period, the polymers may decompose. In such cases SEM micrograph of the LC polyester film pro-vides useful information regarding the structure of the film surface. SEM investigations have been made for polyester at different places on the surface of the film with varying magnifications. The SEM photographs of the random copolyester were depicted in Figure 5. The rigid and long range orientational order is evident from the SEM micrographs of the polyester. It has been suggested that the microstructure of TLC polymeric materials have some evidences of crystallinity embedded within extended chain structure of the mesophase (Windle *et al*., 1985; Lin and Winter, 1988; Blundell, 1982; Kaito *et al*., 1988; Cheng, 1988; Butzbach *et al*., 1985). This crystallinity has been described as a non –periodic layer structure which propagates among adjacent oriented chains. The SEM photographs of the random copolyester show such crystallinity on their film surface indicating long range orientational order.



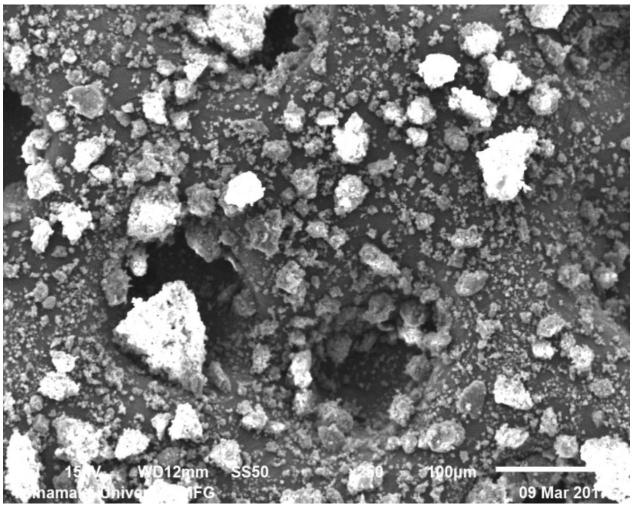


Figure 4 (a). P3BIN(5 Kv), (b). P3BIN(15 Kv).

X-ray Diffraction

XRD patterns of samples were recorded using XPERT -PRO, Philips, operating at voltage of 40 kV, current -30 mA; scanning speed - 7.5·10−3 °/s. The applied radiationfrom target CuKα was nickel filtered (λ=1.540 Å). The range of scattering angles (2θ) was 5–40°. The obtained curves havebeen mathematically elaborated using Hpert High Score soft-ware. X-ray diffraction patterns were obtained at room temperature.

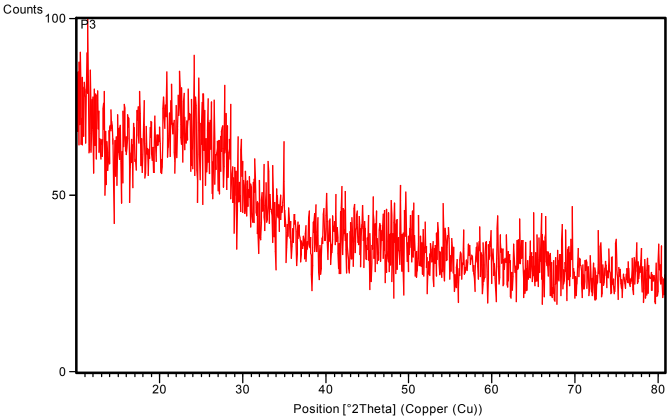


Figure 5 X-ray Diffraction of P3BIN

Table 4 X-ray Diffraction Value of P3BIN

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
16.6960	116.33	0.2460	5.31003	39.27
24.7679	296.20	0.1968	3.59475	100.00
41.9883	16.86	1.1808	2.15182	5.69

CONCLUSION

The reaction pathways for synthesis of high molar mass aliphatic-aromatic polyester were elaborated. Copolymers obtained by polycondensation process were characterized by a random chemical structure. The copolyester was soluble in common organic solvents such as acetone, chloroform and aprotic solvents such as DMF and CCl_4. The inherent viscosity is proportional to polymer molecular weight and molecular weight has a drastic influence on the phase transition temperature of the polyester. IR and NMR spectral values are in accordance with functional group and the nature of mesogens present. Thermal analysis infers the glass transition temperature, melting mesophase formation temperature and isotropisation temperature respectively. The transition temperatures are useful in determining the liquid crystalline state. Oriented fibres and plastic of high strength can be obtained at the liquid crystalline state, when copolyesters can be spun and injection moulded Molecular mass of liquid crystals have proved that LC state can be directly correlated with constitutions of the molecule.SEM micrograph of LC polyester film provides useful information regarding the structure of the film surface.

References

1. Calundann., U.S.Pat.4,067,852(1978)
2. Winderlich.B., “Macromolecular Physics”,Vol.1. (1973)
3. Gray, G.W., Academic press(1978)
4. Billmeyer, F.W.Jr., “Text book of polymer science”, John Wiley and Son New York (1970)
5. Y. Tokiwa and T. Suzuki, *J. Appl. Polym. Sci*., 26, 441 (1981).
6. U. Witt and R. J. Muller, W. D. Deckwar, Macromol. *Chem. Phys.,* 197, 1525 (1996).
7. G. Odian, Principles of Polymerization, Mc Graw Hill, New York (1970).
8. W. O. Jackson, Jr. and H. F. Kuhfuss*, J. Polym. Sci*., 14, 2043 (1976).
9. H. G. Elias, New Commercial Polymers, Garden and Branch Science Publishers, New York (1977)
10. Abe A (1984). “Isotropic (Ni) transitions –contribution in entropy” *Macromolecules*, 17: 2280.
11. Lussac JG, Pelouze J (1833). Advances in the synthetic macromolecular compounds, Ann., 7: 40
12. James J, Malley O, Walter JS (2003). Synthesis and characterization of isomeric polyesters based on sebacic acid and hexanediols. J.
13. Yiwang C, Yan Y, Jiying S, Licheng T, Yan W (2007). “Preparation and characterization of aliphatic/aromatic copolyesters based on bisphenol-A terephthalate, hexylene terephthalate and lactide mioties”, *Reactive Functional Polymers*, 67(5): 396-407.
14. Bellamy LJ (1975). The Infrared Spectra of Complex Molecules, Chapman and Hall, London. P.217
15. Krighaum WR, Asrar J, Toriumi H, Ciferri A, Presten J (1982). Thermotropic Homopolymers III. Preparation and properties, *J. Polym. Sci. Polym. Lett.* Ed., 20: 109.
16. Windle AH, Viney C, Golombok R, Donald AM, Mitchell GR (1985). Sequencesegregation in molten liquid crystalline random copolymers, Faraday Dis., *Chem. Soc.,* 79: 55.
17. Lin YG, Winter H (1988). “High temperature recystallisation and rheology of thermotropic liquid crystalline polymers” “*Macromolecules*, 21: 2439.
18. Blundell DJ (1982). “Variation of crystallographic parameters in PEEK with heat” Polymer, 23: 359.
19. Cheng SZD (1988). “Electrochemical formation of chiral polyaniline colloid codoped polymers” *Macromolecules*, 21: 2475.
20. 20. Butzbach GD, Wendorff JH, Zimmermann HJ (1985). “Pressure dependence of free radical decay gramma –irradiated main-chain liquid crystalline polymers” Makromol. Chem. Rapid Commun., 6: 821.
21. Kaito A, Kyotani M, Nakayana K (1988). “Effects of shear rate on the molecular orientation in extruded rods of a thermotropic liquid crystalline polymers” *Macromolecules*, 23: 1035
22. Ki HC, Park Ok O (2001). Synthesis, characterization and biodegradability of the biodegradable aliphatic–aromatic random copolyesters, *Polymer*, 42(5): 1849-1861.
23. Licheng T, Yiwang C, Yang W, Weihua Z, Xiaohui H (2010). “Melt reaction and structural analysis based on poly (butylene terephthalate) and oligo(lactic acid) with addition of butanediol*” J. Ther. Anal. Calorimetry*- in Press.
24. Liou GS, Kakimoto MA, Imai Y (1994). Thermally stable organosoluble binaphthylene based polymers, *J. Polym, Sci: Part A. Polym. Chem*., 32: 597.
25. Nicholas PC (1989). ‘Handbook of Polymer science and Technology; Synthesis and properties”, 1: 177.
26. Padmanabha N, Arumugasamy E, Ravichandran E, Kannappan EV, Varma IK (1996). Formation and characterization of fibres and films, *Mol. Cryst. Liq.Cryst.*
27. Reiji M, Kei W, Takashi O, Yasunari N (2006). “Development of novel multifunctional cosmetic raw materials and their applications. Novel emulsifying method with random copolymer of polyoxyethylene / polyoxypropylene” *J. Oleo Sci.,* 55(8): 403-411.
28. Roviello A, Sirigu A (1979). Advances in macromolecules- perspectives and applications"“*Makromol. Chem*., 183: 895.
29. Sachindrapal P, Ramasamy S, Nanjan MJ (1981). unsaturated polyamide from 3 amino or 4 –carboxycinnamic acid, *Polymer Bull.,* 5: 417.
30. Seymour BR, Krishenbaum GS (1986). 'High performance polymers: Their origin and development', New York, p. 147.
31. Shibaev VP (1980). Advances in Liquid Crystals, Bata, L., Ed., Oxford Bergamon Press, Budapest, 2: 869.
32. Shibaev VP, Kostromin SG, Plate NA (1982). sidechain liquid crystalline polymers, *Europ. Polym. J.,* 8: 651.
33. Skovby MHB, Heilmann CA, Kops J (1990). In liquid crystalline polymers, weiss. R.A., Oba.
34. C.K., Eds., ACS symposium series 435; American chemical Society, Washington, DC p.46.
35. Whan-Gi K, Hay AS (1994). Random block copolyester – characterization, *J. Polym. Sci. Part A. Polym. Chem*., 32: 97-103
36. Wendorff IH, Finkelmann H, Ringsdorf H (1978). ”liquid-crystalline polymethacrylates –by atom transfer radical polymerization” *J.Polym.Sci. Polym. Symp*., 63, 245.
37. Zbinden R (1964). IR Spectra of High Polymers, Academic Press, New York. p. 59.
38. Robinson C (1958). “Heterogeneous network polymers-7. cholestric liquid cryslline polymers”
39. Trans. Faraday Soc., 1956, 52: 571& Robinson, C., Ward, J.C. and Beevers, R.B., Discuss. Faraday Soc., pp. 25-29.
40. Werbowyi RS, Gray DG (1976). “Liquid crystalline state of concentrated solution cyanoethyl derivatives” *Mol.Cryst. Liq. Crys. Lett*., 34: 97.

41. Lenz RW, Jin JI (1985). Liquid Crystals and Ordered Phases, Griffin, and Johnsons, *J., Ed., Plenum Press,* New York, p. 328.
42. Strzelecki L, Van Luyen D (1980). "Orientation dynamicsof main chain liquid crystalline polymers" *Eur. Polym. J.,* 16: 299.
43. Halina Kaczmarek (2013) Crosslinked blends of poly (lactic acid) and polyacrylates: AFM, DSC and XRD studies polymers 20:19.

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