



ISSN: 0976-3031

Available Online at <http://www.recentscientific.com>

CODEN: IJRSFP (USA)

*International Journal of Recent Scientific Research*  
Vol. 9, Issue, 3(J), pp. 25340-25344, March, 2018

**International Journal of  
Recent Scientific  
Research**

DOI: 10.24327/IJRSR

## Research Article

# SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE RANDOM COPOLYESTER

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DOI: <http://dx.doi.org/10.24327/ijrsr.2018.0903.1841>

### ARTICLE INFO

#### Article History:

Received 15<sup>th</sup> December, 2017  
Received in revised form 25<sup>th</sup>  
January, 2018  
Accepted 23<sup>rd</sup> February, 2018  
Published online 28<sup>th</sup> March, 2018

#### Key Words:

Copolyesters, Poly[oxy-(1,4-naphthalene)-oxy-co-(1,3-benzenoyl)-co-oxy-(1,4-benzene)-oxy], 1,4-Naphthalenediol, Quinol.

### ABSTRACT

Copolyesters are one of the most important class of polymers with repeating carboxylate group in their backbone. In the present work, copolyesters based on isophthaloyl chloride with aromatic diols were synthesized by solution polycondensation method. A copolyester was synthesized using 1,4-Naphthalenediol as one of the diols with isophthaloyl chloride as Diacid chloride. Quinol was used as another diols for the synthesis of random copolymer. The obtained polymer (P9NIQ) was identified and confirmed by various spectral studies like FTIR, NMR and UV spectroscopy. The thermal stability of the polymer was studied by TGA and DSC. The texture morphology and crystallinity of the polymer was monitored using SEM and XRD. Elemental analysis further confirms the formations for the copolymer. Results of the investigation confirm a relatively new entry copolymer in the family of liquid crystalline copolymers.

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## INTRODUCTION

A new technological application of liquid crystalline polymer has recent attention for their good thermal stability, excellent mechanical properties<sup>1</sup>. The texture, mechanical strength and thermal stability of the polymer was completely dependent the chemical structure and molecular weight of the monomers, thus fully aromatic monomers show good liquid crystalline property<sup>2</sup>. In the past decades many researchers have developed many LCP's with considerable efforts on modification the monomeric structure to reach more practical usage in industries<sup>3-5</sup>.

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. Reported the liquid crystalline copolyester compositions based on hydroxy benzoic acid, hydroquinone, 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.<sup>6</sup> The structural characteristics associated with liquid crystalline behavior have been reviewed by Gray<sup>7</sup>. Several thermotropic highly aromatic liquid crystalline polyesters such as Vectra and Xydar have been commercialized. These polyesters are thermally stable and possess high tensile strength and modulus. The application of liquid crystal polymers are in the area of fibres, films, plastics, holography, photocross linkages and as information storage devices.

## MATERIALS AND METHODS

1,2-dichlorobenzene (MerkLR), 1,4-Naphthalenediol (Loba), quinol (Loba), Isophthaloylchloride (Loba). Analarsamples of CHCl<sub>3</sub>, DMSO, DMF, Acetone, Methanol, Ether is used as such.

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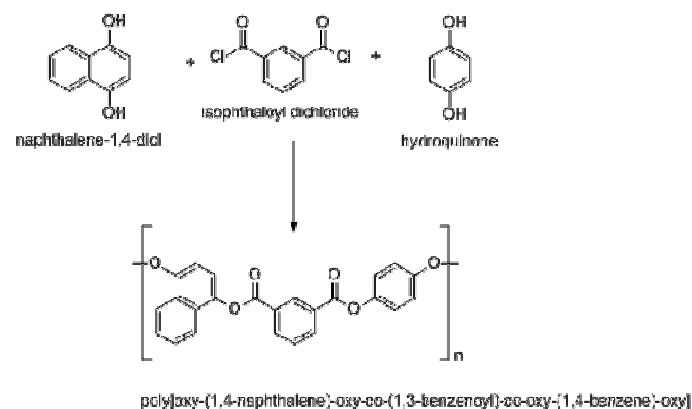
## Polymer Synthesis

### Preparation of Random Copolyester

Synthesis of Poly[oxy-(1,4-naphthalene)-oxy-co-(1,3-benzenoyl)-co-oxy-(1,4-benzene)-oxy]

The above co-polyester was prepared by the condensation of diols with diacid chloride in 1,2-dichlorobenzene. The reaction flask made up of pyrex glass. It was charged with 1 mole of 1,4-Naphthalenediol, 2 moles of quinol, 3 moles of Isophthaloylchloride and 150 mL of 1,2-dichlorobenzene. The mixture was heated to reflux for 65 hrs at 140-160 °C in nitrogen atmosphere with constant stirring and cooled to get pure copolyester. The yield was 80%.

### Scheme



### Characterization of random copolyesters

The FTIR spectra of copolyesters were reported using Perkin-Elmer spectrophotometer. IR Spectrophotometer with the samples incorporated in KBr pellets

The UV- spectral analysis was performed on Shimadzu-uv-160A spectrophotometer using acetone solution.

The <sup>1</sup>H NMR spectra were recorded using JEOL GSX 400 FT-NMR spectrometer operating at room temperature. Samples for analysis were prepared by dissolving about 10mg of the copolyester in 5ml of spectral grade CDCl<sub>3</sub> solvent.

XRD patterns of samples were recorded using XPERT -PRO, Philips, operating at voltage of 40 kV, current -30 mA; scanning speed - 7.5·10<sup>-3</sup> °/s. The applied radiation from target CuK $\alpha$  was nickel filtered ( $\lambda=1.540 \text{ \AA}$ ).

### Solubility

The 10mg of copolyester was taken in small stopper test tube which contains 5ml of the solvent and was kept for 24 h with occasional shaking. If the polyester was insoluble in cold, the mixture was slowly heated up to boiling point of the solvent. Thus the polymer was dissolved or swell in solvent was noted. The process was done with various solvent qualitatively.

## RESULTS AND DISCUSSION

### FTIR spectrum

The FTIR spectra of the synthesized polyester showed the following characteristic absorption bands as shown in fig-1. The band assigned at 1747.51 cm<sup>-1</sup> for ester C=O stretching, a band at 1020, 1057 and 1217 cm<sup>-1</sup> due to ester C-O stretching and bending indicate the ester linkage present in the polymer.

The complete analysis of IR spectra of polymer has been engaged with detailed structure information given by several workers<sup>10-11</sup>. The data are tabulated in table 1.

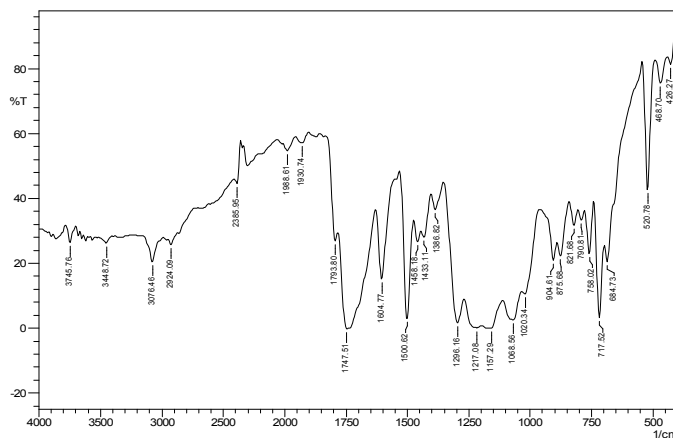


Figure 1 FTIR Spectrum of P9NIQ

Table 1 FTIR spectral data of P9NIQ random copolyester

Absorption frequency (cm <sup>-1</sup> )	Assignment
1058	Stretching vibration of C-O
1747	Carbonyl stretching
1604	Meta substituted aromatic ring
2924	Aromatic C-H stretching
3076	Para substituted aromatic ring

### UV-visible spectra

The UV-Visible spectrum of Polyesters show a high intensity band, there are two positively electronic transitions occurs, namely  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  which is due to carbonyl group and is shown in fig.

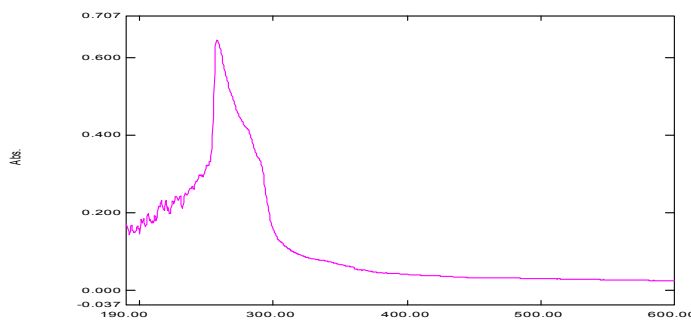


Figure 2 UV Spectrum of P9NIQ

### <sup>1</sup>H NMR spectral analysis

A PMR spectrum of the polyester was obtained in CDCl<sub>3</sub> solution with TMS as reference in Figure 3. The spectra show the aromatic proton in the range of 6.8 -8.7ppm. 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.

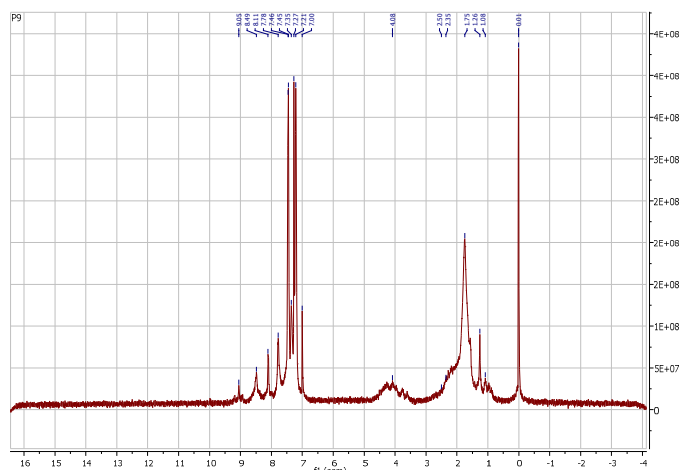


Figure 3 <sup>1</sup>H NMR Spectrum of P9NIQ

Table 2 PMR spectral data of random copolyester

Chemical Shift ( $\delta$ ) (ppm)	Type of protons
2.3	Protons of the ester group
6.5 – 8.0	1,3 – phenylene 1,4 – phenylene

**Thermo gravimetric analysis (TGA)**

TGA analysis of the polyester P9NIQ was carried out in SDT Q600V20.9. The experiment were done in nitrogen atmosphere at a heating rate of 20°C/min. About 2.3mg of powdered sample was used with close packing. It can also be used to determine the kinetic parameters of degradation of copolyester. The continuous weight loss curve for the thermal degradation of the co polyester was provided in Figures 4. The degradation of the copolyester was carried out in nitrogen atmosphere at a heating rate of 20°C/min.

The thermogram suggests that the copolyester was thermally stable up to 300°C with five stage degradation. The first degradation stage starts around 300°C with 5% of degradation. The second stage of degradation starts around 380°C with approximately around 18% of the copolyester gets degraded. Third stage of degradation starts around 400°C with 30% of degradation. Fourth stage of degradation starts around 450°C with 80% of degradation. Fifth stage of degradation starts around 500°C with 90% of degradation. Table show that around 5% of the copolyester degraded at about 300°C For 80% degradation was observed at 450°C. This may be due to the presence of rigid rod and crank shaft mesogens. It is evident from the degradation temperature of copolyesters that the copolyester P9NIQ degraded at lower temperature may be due to the presence of Aromatic mesogens.

Table 3 Thermal stability of copolyester.

Copolyesters	5%	18%	30%	80%	90%
P9NIQ	300	380	400	450	500

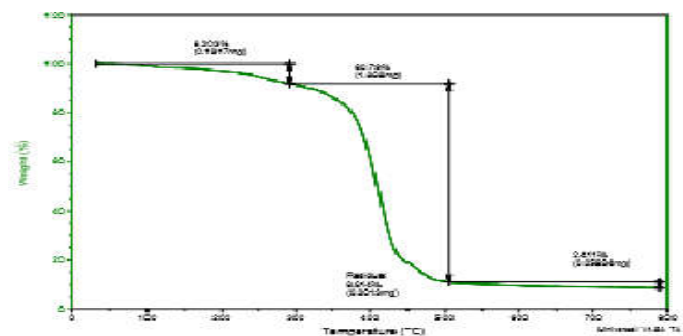


Figure 4 TGA thermograms of random copolyester P9NIQ

**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.

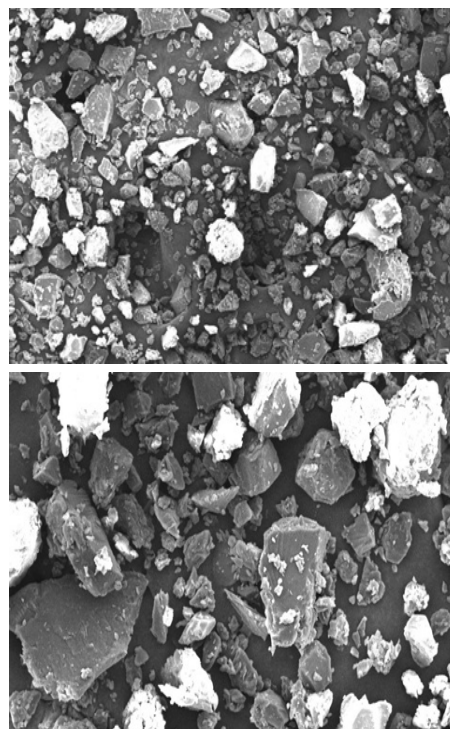


Figure 5 (a). P9NIQ(5 Kv), 10(b). P9NIQ(15 Kv)

## X-ray Diffraction

The powder X-ray diffraction pattern of P9NIQ. The pattern shows many high intensity peaks. At  $2\theta = 21.5^\circ$  the peak intensity is maximum. The  $2\theta$  values are from  $17-25^\circ$  with intermolecular spacing of 4.5 to 4.8 Å have been reported for nematic texture.

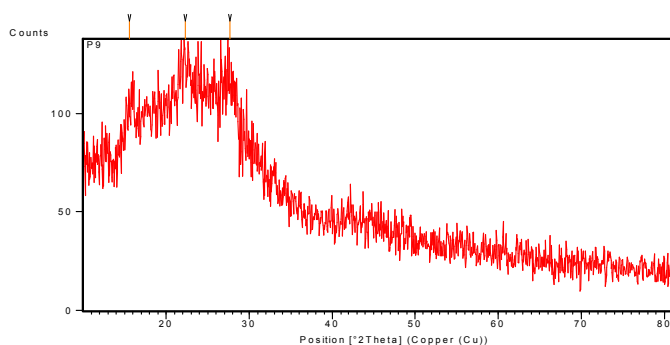


Figure 6 X-ray Diffraction of P9NIQ

Table 4 X-ray Diffraction valu of P9NIQ

Pos. [ $2\theta$ .]	Height [cts]	FWHM Left [ $2\theta$ .]	d-spacing [Å]	Rel. Int. [%]
15.6018	32.23	1.1808	5.67990	53.18
22.2957	60.61	1.1808	3.98744	100.00
27.6661	54.06	1.5744	3.22441	89.19

## CONCLUSION

Synthesize of high molecular weight aromatic polyester was obtained by simple polycondensation and transesterification process was further analyzed by different techniques. The copolyesters was soluble in acetone, chloroform etc., the chemical structure of the synthesized polyester was confirmed by IR and NMR spectral values are in accordance with ester linkage and protons of the polymer. The thermal data i.e. degradation of the polyester was investigated the liquid crystalline state of the polyester was further proved by SEM micrograph and XRD pattern of the LC polymer film provides useful information about film surface of the polymer structure. The thermo topic liquid crystalline random copolyester may be potential candidate for future device technology.

## References

- Calundann., U.S.Pat.4,067,852(1978)
- Winderlich.B., "Macromolecular Physics", Vol.1. (1973)
- Gray, G.W., Academic press(1978) Butzbach GD, Wendorff JH, Zimmermann HJ (1985). "Pressure dependence of free radical decay gamma –irradiated main-chain liquid crystalline polymers" *Makromol. Chem. Rapid Commun.*, 6:
- .U. Witt, R. J. Muller and W. D. Deckwar, *Pure Appl. Chem.*, 4, 851 (1995).
- F. Alasandra, Daldiserra, E. S. Carlos, Valerio, Nara. R. de S., Basso, Farnando Guaragna e Sandra Einloft, *Quim Nova*, 2, (2005).
- W. O. Jackson, Jr. and H. F. Kuhfuss, *J. Polym. Sci.*, 14, 2043 (1976).
- James J, Malley O, Walter JS (2003). Synthesis and characterization of isomeric polyesters based on sebacic acid and hexanediols. J.
- 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 moieties", *Reactive Functional Polymers*, 67(5): 396-407.
- Bellamy LJ (1975). *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London. P.217
- 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.
- Windle AH, Viney C, Golombok R, Donald AM, Mitchell GR (1985). *Sequencesegregation in molten liquid crystalline random copolymers*, *Faraday Dis., Chem. Soc.*, 79: 55.
- Lin YG, Winter H (1988). "High temperature recrystallisation and rheology of thermotropic liquid crystalline polymers" *Macromolecules*, 21: 2439.
- Cheng SZD (1988). "Electrochemical formation of chiral polyaniline colloid codoped polymers" *Macromolecules*, 21: 2475.
- Butzbach GD, Wendorff JH, Zimmermann HJ (1985). "Pressure dependence of free radical decay gamma – irradiated main-chain liquid crystalline polymers" *Makromol. Chem. Rapid Commun.*, 6: 821.
- 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
- Ki HC, Park Ok O (2001). *Synthesis, characterization and biodegradability of the biodegradable aliphatic–aromatic random copolyesters*, *Polymer*, 42(5): 1849-1861.
- 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*.
- Liou GS, Kakimoto MA, Imai Y (1994). *Thermally stable organosoluble binaphthylene based polymers*, *J. Polym. Sci: Part A. Polym. Chem.*, 32: 597.
- Nicholas PC (1989). "Handbook of Polymer science and Technology; Synthesis and properties", 1: 177.
- Padmanabha N, Arumugasamy E, Ravichandran E, Kannappan EV, Varma IK (1996). *Formation and characterization of fibres and films*, *Mol. Cryst. Liq. Cryst.*
- 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.
- Roviello A, Sirigu A (1979). *Advances in macromolecules- perspectives and applications*" *Makromol. Chem.*, 183: 895.
- Sachindrapal P, Ramasamy S, Nanjan MJ (1981). *unsaturated polyamide from 3 amino or 4 – carboxycinnamic acid*, *Polymer Bull.*, 5: 417.
- Seymour BR, Krishenbaum GS (1986). "High performance polymers: Their origin and development", New York, p. 147.
- Shibaev VP (1980). *Advances in Liquid Crystals*, Bata, L., Ed., Oxford Bergamon Press, Budapest, 2: 869.

26. Shibaev VP, Kostromin SG, Plate NA (1982). sidechain liquid crystalline polymers, *Europ. Polym. J.*, 8: 651.
27. Skovby MHB, Heilmann CA, Kops J (1990). In liquid crystalline polymers, weiss. R.A., Oba.
28. C.K., Eds., ACS symposium series 435; American chemical Society, Washington, DC p.46.
29. Whan-Gi K, Hay AS (1994). Random block copolyester – characterization, *J. Polym. Sci. Part A. Polym. Chem.*, 32: 97-103
30. Wendorff IH, Finkelmann H, Ringsdorf H (1978). "liquid-crystalline polymethacrylates –by atom transfer radical polymerization" *J.Polym.Sci. Polym. Symp.*, 63, 245.
31. Zbinden R (1964). IR Spectra of High Polymers, Academic Press, New York. p. 59.
32. Robinson C (1958). "Heterogeneous network polymers- 7. cholestric liquid cryslline polymers"
33. Trans. Faraday Soc., 1956, 52: 571 & Robinson, C., Ward, J.C. and Beevers, R.B., Discuss. Faraday Soc., pp. 25-29.
34. Werbowyi RS, Gray DG (1976). "Liquid crystalline state of concentrated solution cyanoethyl derivatives" *Mol.Cryst. Liq. Cryst. Lett.*, 34: 97.
35. Lenz RW, Jin JI (1985). Liquid Crystals and Ordered Phases, Griffin, and Johnsons, J., Ed., Plenum Press, New York, p. 328.
36. Strzelecki L, Van Luyen D (1980). "Orientation dynamics of main chain liquid crystalline polymers" *Eur. Polym. J.*, 16: 299.
37. Halina Kaczmarek(2013) Crosslinked blends of poly(lactic acid) and polyacry
38. Annamalai.G, Elango.G DJ *journal of Engineering chemistry and Fuel*, vol,3(1) 2018,1-5
39. Annamalai.G. Elango.G. *IOSR Journal of Applied Chemistry* vol,10(9)2017,11-17.

**How to cite this article:**

Annamalai G and Elango G.2018, Synthesis And Characterization of Liquid Crystalline Random Copolyester. *Int J Recent Sci Res.* 9(3), pp. 25340-25344. DOI: <http://dx.doi.org/10.24327/ijrsr.2018.0903.1841>

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