

1, 4-BUTANE DIOL BASED LIQUID CRYSTALLINE RANDOM COPOLYESTER - SYNTHESIS AND CHARACTERIZATION**N. Mahadevan¹, G. Annamalai¹, S. Guhanathan² and G. Elango^{1*}**

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ABSTRACT

A copolyester was synthesized using 2,5-Ditertiarybutrylquinol 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.

KEYWORDS: Copolyester, ultravioletspectroscopy, infraredspectroscopy, nuclearmagnetic resonance, scanning electron microscope, X-ray Diffraction, characterization.

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, 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.^[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 thermally 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.

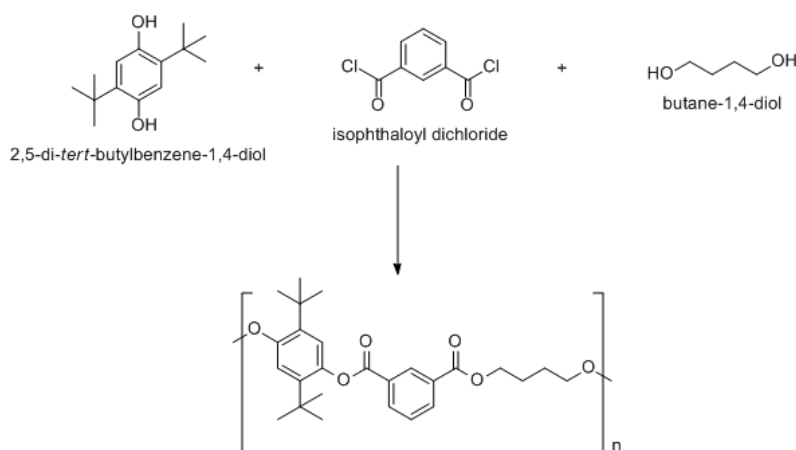
MATERIALS AND METHODS

1,2-dichlorobenzene (MerkLR), 1,4-ButaneDiol (Loba), 2,5-Ditertiarybutrylquinol (Loba), Isophthaloylchloride (Loba). Analytical samples of CHCl_3 , DMSO, DMF, Acetone, Methanol, Ether is used as such.

POLYMER SYNTHESIS

Preparation of Random Copolyester P2BID

A 250ml three necked round bottomed flask equipped with a mechanical stirrer, a nitrogen inlet, a reflux 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 2,5-Ditertiarybutrylquinol 2.2g (0.01mole). The mixture was stirred for 20 minutes and temperature was gradually increased to 120°C. To this reaction mixture, added isophthaloyl chloride 6g (0.03mole). Then the whole mixture was maintained with further stirring and heating 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 filtration, 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-(2,5-ditertiarybutyl- 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 $4000\text{--}500\text{ cm}^{-1}$. 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 $\text{C}=\text{O}$ 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. P2BID 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} , 1821 cm^{-1} and 873 cm^{-1} are due to $\text{--CH}_2\text{--}$ stretching and bending vibration. The absorption band at 1608 cm^{-1} is due to the arylidene keto group present in copolyester. The vibrational frequencies assigned for the copolyesters P2BID are summarized in Tables 1.

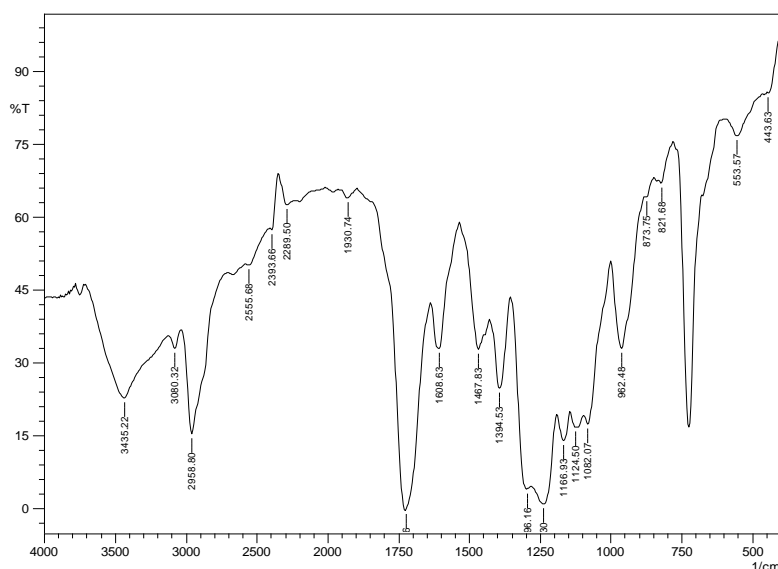


Figure. 1: FTIR Spectram of P2BID.

Table 1: FTIR spectral data of P2BID random copolyester.

Absorption frequency (cm ⁻¹)	Assignment
1082,1124,1166,	Stretching vibrations of the ester C-O
1740	Carbonyl stretching of the ester group
1276	CH ₂ – Wagging
720	AliphaticC-H bending
2958,873,821	CH ₂ - Stretching
3080	Characteristic absorption of para substituted benzene ring
3435	Free –OH group

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 P2BID show a The random copolyester reported in the present investigation contains substituted benzene Chromophore. Therefore, there are two possible electronic transitions, namely $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. 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.

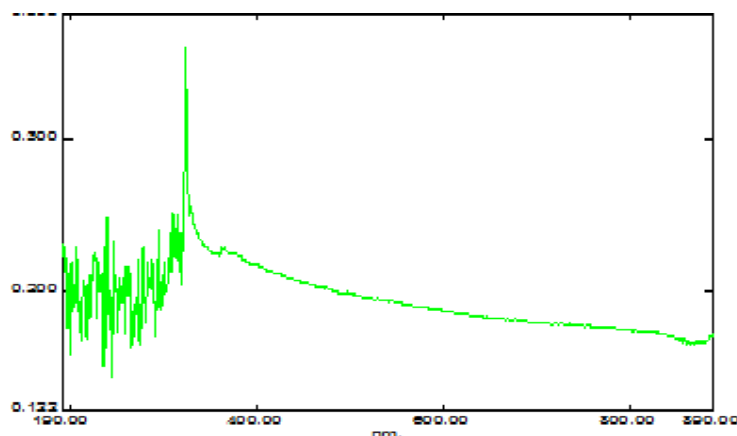


Figure 2: UV Spectrum of P2BID.

^1H 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.

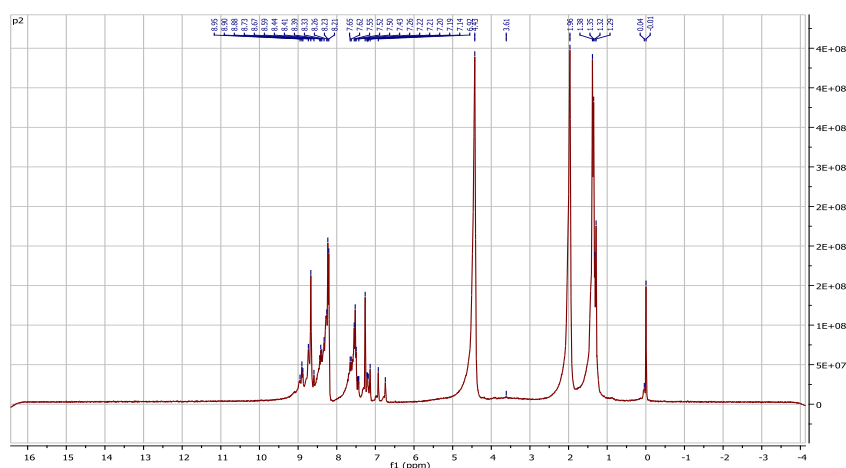


Figure 3: ^1H NMR Spectrum of P2BID.

Table 3: 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

Thermo gravimetric analysis (TGA)

TGA analysis of the polyester P2BID was carried out in SDT Q600V20.9. The experiment were done in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$. 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 P2BID degraded at lower temperature may be due to the presence of aliphatic mesogens.

Table 4: Thermal stability of copolyester.

Copolyesters	5%	18%	30%	80%	90%
P2BID	300	380	400	450	500

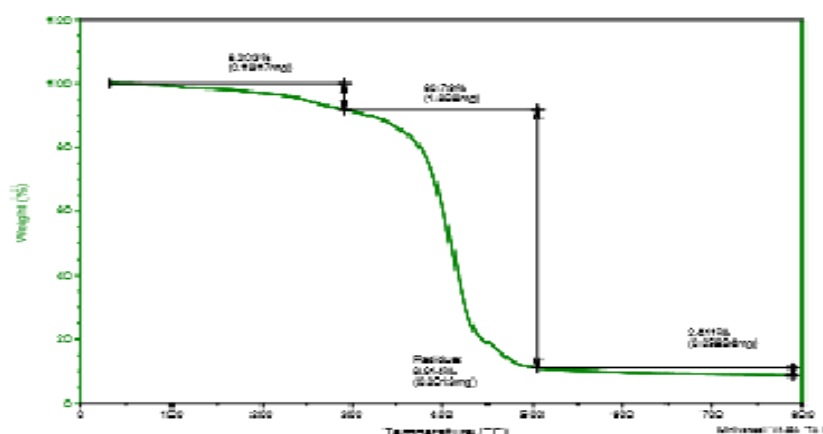


Figure 4: TGA thermograms of random copolyester P2BID.

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 provides 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.

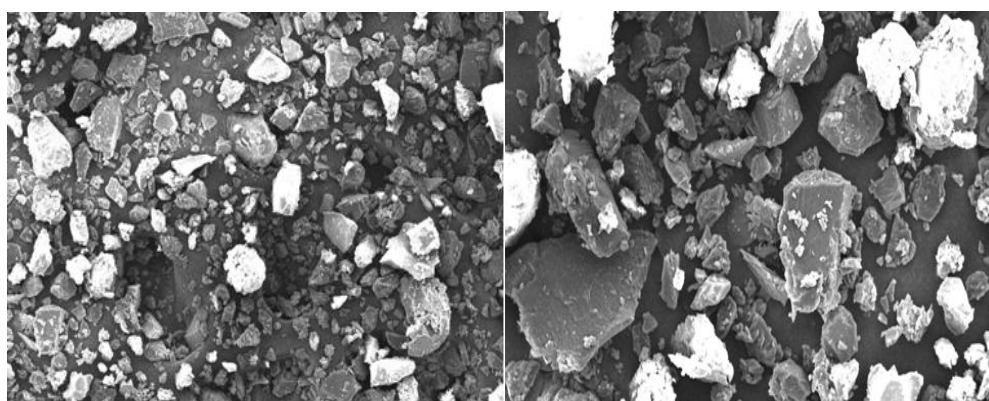


Figure 5: (a). P2BID(5 Kv), 10(b). P2BID (15 Kv).

X-ray Diffraction

XRD patterns of samples were recorded using XPERT -PRO, Philips, operating at voltage of 40 kV, current -30 mA; scanning speed - $7.5 \cdot 10^{-3}$ °/s. The applied radiation from target CuK α was nickel filtered ($\lambda = 1.540$ Å). The range of scattering angles (2θ) was 5–40°. The obtained curves have been mathematically elaborated using Hpert High Score soft-ware. X-ray diffraction patterns were obtained at room temperature.

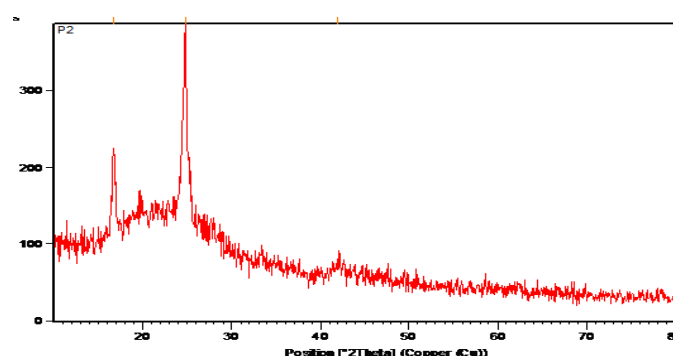


Figure 6: X-ray Diffraction of P2BID.

Table 5: X-ray Diffraction Value of P2BID.

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 CCl₄. 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.

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REFERENCES

1. Calundann., U.S. Pat., 1978; 4: 067-852.
2. Winderlich. B., "Macromolecular Physics", 1973; 1.
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., 1981; 26: 441
6. U. Witt and R. J. Muller, W. D. Deckwar, Macromol. Chem. Phys., 1996; 197: 1525.
7. G. Odian, Principles of Polymerization, Mc Graw Hill, New York., 1970.
8. W. O. Jackson, Jr. and H. F. Kuhfuss, J. Polym. Sci., 1976; 14: 2043.

9. H. G. Elias, New Commercial Polymers, Garden and Branch Science Publishers, New York., 1977.
10. Abe A “Isotropic (Ni) transitions –contribution in entropy” *Macromolecules*, 1984; 17: 2280.
11. Lussac JG, Pelouze J Advances in the synthetic macromolecular compounds, *Ann.*, 1833; 7: 40.
12. James J, Malley O, Walter JS Synthesis and characterization of isomeric polyesters based on sebacic acid and hexanediols. *J.*, 2003.
13. Yiwang C, Yan Y, Jiying S, Licheng T, Yan W “Preparation and characterization of aliphatic/aromatic copolyesters based on bisphenol-A terephthalate, hexylene terephthalate and lactide moieties”, *Reactive Functional Polymers*, 2007; 67(5): 396-407.
14. Bellamy LJ *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London. P., 1975; 217.
15. Krigbaum WR, Asrar J, Toriumi H, Ciferri A, Presten J Thermotropic Homopolymers III. Preparation and properties, *J. Polym. Sci. Polym. Lett. Ed.*, 1982; 20: 109.
16. Windle AH, Viney C, Golombok R, Donald AM, Mitchell GR Sequencesegregation in molten liquid crystalline random copolymers, *Faraday Dis., Chem. Soc.*, 1985; 79: 55.
17. Lin YG, Winter H “High temperature recrystallisation and rheology of thermotropic liquid crystalline polymers” “*Macromolecules*, 1988; 21: 2439.
18. Blundell DJ “Variation of crystallographic parameters in PEEK with heat” *Polymer*, 1982; 23: 359.
19. Cheng SZD “Electrochemical formation of chiral polyaniline colloid codoped polymers” *Macromolecules*, 1988; 21: 2475.
20. Butzbach GD, Wendorff JH, Zimmermann HJ “Pressure dependence of free radical decay gamma –irradiated main-chain liquid crystalline polymers” *Makromol. Chem. Rapid Commun.*, 1985; 6: 821.
21. Kaito A, Kyotani M, Nakayana K “Effects of shear rate on the molecular orientation in extruded rods of a thermotropic liquid crystalline polymers” *Macromolecules*, 1988; 23: 1035.
22. Ki HC, Park Ok O Synthesis, characterization and biodegradability of the biodegradable aliphatic–aromatic random copolyesters, *Polymer*, 2001; 42(5): 1849-1861.
23. Licheng T, Yiwang C, Yang W, Weihua Z, Xiaohui H “Melt reaction and structural analysis based on poly(butylene terephthalate) and oligo(lactic acid) with addition of butanediol” *J. Ther. Anal. Calorimetry- in Press.*, 2010.

24. Liou GS, Kakimoto MA, Imai Y Thermally stable organosoluble binaphthylene based polymers, *J. Polym. Sci. Part A. Polym. Chem.*, 1994; 32: 597.
25. Nicholas PC 'Handbook of Polymer science and Technology; Synthesis and properties', 1989; 1: 177.
26. Padmanabha N, Arumugasamy E, Ravichandran E, Kannappan EV, Varma IK Formation and characterization of fibres and films, *Mol. Cryst. Liq. Cryst.*, 1996.
27. Reiji M, Kei W, Takashi O, Yasunari N "Development of novel multifunctional cosmetic raw materials and their applications. novel emulsifying method with random copolymer of polyoxyethylene / polyoxypropylene" *J. Oleo Sci.*, 2006; 55(8): 403-411.
28. Roviello A, Sirigu A Advances in macromolecules- perspectives and applications" *Makromol. Chem.*, 1979; 183: 895.
29. Sachindrapal P, Ramasamy S, Nanjan MJ unsaturated polyamide from 3 amino or 4 – carboxycinnamic acid, *Polymer Bull.*, 1981; 5: 417.
30. Seymour BR, Krishenbaum GS 'High performance polymers: Their origin and development', New York, p., 1986; 147.
31. Shibaev VP Advances in Liquid Crystals, Bata, L., Ed., Oxford Bergamon Press, Budapest, 1980; 2: 869.
32. Shibaev VP, Kostromin SG, Plate NA sidechain liquid crystalline polymers, *Europ. Polym. J.*, 1982; 8: 651.
33. Skovby MHB, Heilmann CA, Kops J In liquid crystalline polymers, weiss. R.A., Oba., 1990.
34. C.K., Eds., ACS symposium series American chemical Society, Washington, DC., 435: 46.
35. Whan-Gi K, Hay AS Random block copolyester – characterization, *J. Polym. Sci. Part A. Polym. Chem.*, 1994; 32: 97-103.
36. Wendorff IH, Finkelmann H, Ringsdorf H "liquid-crystalline polymethacrylates –by atom transfer radical polymerization" *J. Polym. Sci. Polym. Symp.*, 1978; 63: 245.
37. Zbinden R IR Spectra of High Polymers, Academic Press, New York., 1964; 59.
38. Robinson C "Heterogeneous network polymers-7. cholestric liquid cryslline polymers" 1958.
39. Trans. Faraday Soc., 571 & Robinson, C., Ward, J.C. and Beevers, R.B., Discuss. Faraday Soc., 1956; 52: 25-29.
40. Werbowyi RS, Gray DG "Liquid crystalline state of concentrated solution cyanoethyl derivatives" *Mol. Cryst. Liq. Crys. Lett.*, 1976; 34: 97.

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