

2, 5-Hexanediol Based Liquid Crystalline Random Copolyester Synthesis and Characterization

G. Annamalai,¹ N. Mahadevan¹, S. Guhanathan², G. Elango^{1*}

¹Department of Chemistry, Government Arts College, Tiruvannamalai-606603, Tamil Nadu, India.

²PG & Research Department of Chemistry, Muthurangam Government Arts College, Vellore -632002, Tamilnadu, India.

*Corresponding Author: G. Elango

Abstract: A copolyester was synthesized using 2,5-hexanediol as one of the diols with isophthaloyl chloride as another monomer. In addition, 1,4-dihydroxy naphthalene, 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). Results of the investigation reveals that a relatively new entry of copolymer has been suggested into the family of liquid crystalline copolymers.

Keywords: Copolyester, ultraviolet spectroscopy, infrared spectroscopy, nuclear magnetic resonance, scanning electron microscope, characterization.

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I. Introduction

Polymers are natural or synthetic chemical materials with long, linear or branched chains consisting of about 10^2 to 10^4 repeating monomer units. Polymers can be divided according to various criteria such as their occurrence, composition of polymer molecules, polymerisation types, physical properties, and chemical properties. These repeated units are derived from mono-mers, which combine together to form macromolecules. The process of formation of a macromolecule is termed as polymerization. The number of repeat units in the chain specifies the length of the polymer chain which implies degree of polymerization. Copolymerization technology has been developed in recent years as desirable properties that can be achieved by changing the chemical composition and microstructures of the resulting polymer. It can be used to blend the properties of homopolymers.

A synthetic polymer was first obtained by Gay-Lussac and Pelouze (1833) on heating lactic acid. Carothers created the modern chemistry and technology of polyesters James et al., (2003). Polyesters attract significant interest, despite inferior mechanical properties. Transition temperature and properties of copolyesters can be varied by alternating the comonomer composition. Polyesters are the most important and widely used classes of polymers which fall under heterochain macro molecular compounds possessing carboxylate esters as a part of the repeating unit. They are distinguished from other esters in which carboxylate ester group forms a part of substituent moiety attached to the backbone structure. Polyesters are usually prepared by the condensation of a diacid or its derivatives with diols. After careful analysis of literature, the scope of the present investigation aims to synthesis thermo-tropic liquid crystalline random copolyester with aliphatic and aromatic group in the main chain

II. Experimental

Materials

The basic materials required for the synthesis and their methods are listed in Table-1

Table-1 List of monomers

S.NO	Monomers	Physical properties (°C)	Make
1	Isophthaloyl chloride	M.pt 276	Merck
2	2,5 hexanediol	B.pt 223	Merck
3	1,4-dihydroxynaphalene	M.pt 191	Merck

Purifications of solvents

1,2-dichlorobenzene was kept over anhydrous calcium chloride overnight, filtered and purified by fractional distillation. The fraction distilling at 180°C was collected and used as a medium for polymerization. Petroleum ether was dried over anhydrous calcium chloride, distilled and used. Analar samples of acetone, chloroform, carbon tetrachloride, o-chlorophenol, dimethyl sulphoxide, and methanol were used as such for the determination of solubility of the polymers. Special grade CDCl₃ was used for recording Nuclear Magnetic Resonance (NMR) spectra of these polyesters.

Preparation of random copolyesters

The reaction vessel was a 250 ml three-necked round bottomed flask made of pyrex glass. It was equipped with a magnetic stirrer, a nitrogen inlet, a thermometer, a reflux condenser and a potassium hydroxide trap. The experiments were conducted in an oil bath thermostat. The bath was heated by immersion resistance coil and the temperature of the bath was controlled by a dimmerstat. A magnetic stirrer was used to maintain a uniform temperature. Nitrogen used for the deaeration was freed from traces of oxygen by passing through Fieser's solution. Fieser's solution was prepared by dissolving 20 g of sodium hydroxide in 100 ml of water and adding 2 g of sodium anthraquinone-2-sulphonate and 15 g of sodium dithionate to the warm solution and stirring until it dissolved. After cooling to room temperature the solution becomes blood red and was used. The gas was then passed through saturated lead acetate solution to free it from hydrogen sulphide and sulphurdioxide. It was then passed through vanadyl chloride solution and washed by passing through distilled water. The gas was then dried by passing through a bottle containing anhydrous calcium chloride.

Polymerization process

The copolyester was prepared by the condensation of diols with diacid chloride in o-dichlorobenzene. The reaction flask was charged with the required amount of diol. About 150 ml of o-dichlorobenzene was added followed by the diacid chloride in the appropriate proportion. The mixture was then refluxed for 25 to 36 h at 130 to 150°C in nitrogen atmosphere with constant stirring. The contents were cooled and poured into about 250 ml of petroleum ether. The mixture was kept in refrigerator overnight and filtered. The polyester was dissolved in a minimum amount of acetone and the solution was evaporated to get the pure polyester. It was dried in vacuum over phosphorous pentoxide. The diols and the diacid chlorides used in the preparation of the polyesters along with their yields are given in Table 2

Scheme

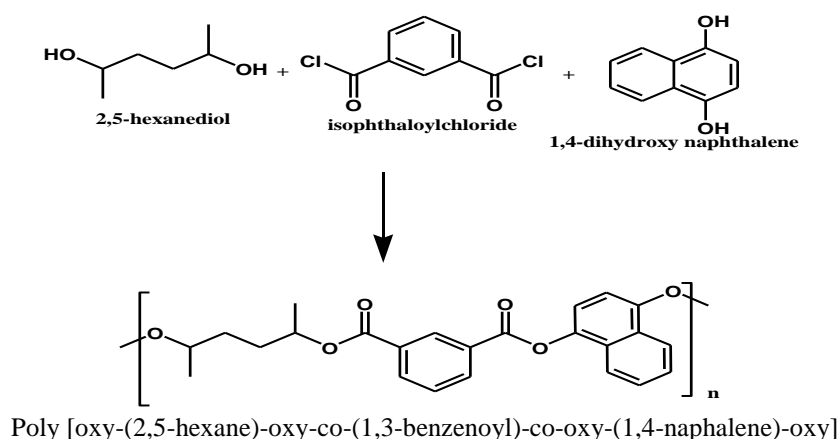


Table 2. Common momers used for P4DIH random copolyester synthesis.

S/N	Polymer	Diol-1	Diol-2	Diacid chloride	% of yield
1	P4DIH	1-4-dihydroxynaphthalene	2,5-hexanediol	Isophthaloyl chloride	68

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.

Solubility

Solubility of all the random copolyester was determined in various solvents qualitatively. About 10 mg of the polyester was taken in small stopper test tubes containing 5 ml of the solvent. The mixture was kept for 24 h with occasional shaking. If insoluble in cold, the mixture was slowly heated up to the boiling point of the solvent and whether the polymers dissolved or swell in the solvent was noted

Fourier Transform Infrared spectroscopy spectra

Fourier Transform Infrared spectroscopy (FTIR) has been employed extensively for the investigation of the structure and composition of high molecular weight compounds. The complete analysis of the complex IR spectra of polymer is difficult and several workers have been engaged in obtaining detailed structural information on polymers from IR spectroscopy (Bellamy, 1975; Yiwang et al., 2007; Krighaum et al., 1982). The IR spectral data have been recorded for the random copolyester was given in Figure1. The IR spectrum of random copolyester showed characteristic absorption at 1710 cm⁻¹ due to ester C = O stretching, 1031, 1074 and 1212 cm⁻¹ due to the ester -C-O stretching and bending indicating that the polyester chain is present in all the polymer.

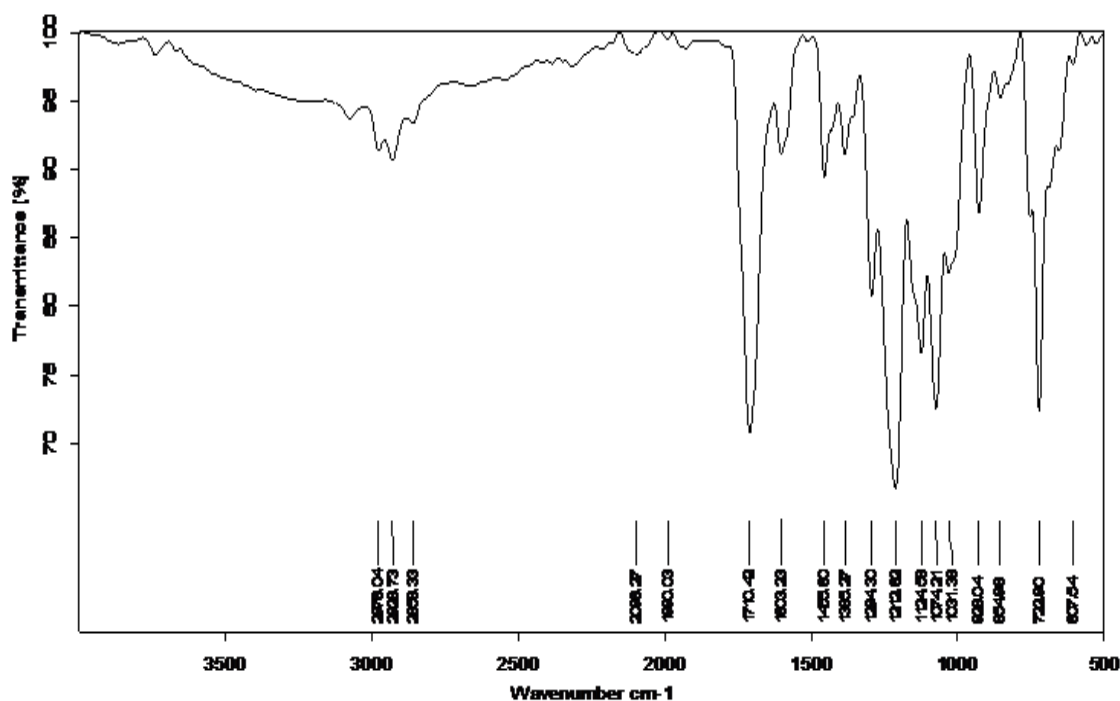


Figure.1 FTIR Spectram of P4DIH

Table 3- FTIR spectral data of P4DIH random copolyester.

Absorption frequency (cm ⁻¹)	Assignment
1074	Stretching vibrations of the ester C-O
1710	Carbonyl stretching of the ester group
1294	CH ₂ – Wagging
1603	Characteristic absorptions of meta substituted benzene rings
722	Aliphatic C-H bending
2848	C – H Stretching
3435	Characteristic absorptions of naphthalene moiety
2976	Aromatic C-H stretching
3080	Characteristic absorption of para substituted benzene ring

UV-visible spectra

The random copolyester reported in the present investigation contains substituted benzene Chromophore. Therefore, there are two possible electronic transitions, namely $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The uv – visible spectrum of the polyester has been recorded in acetone solution. 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.

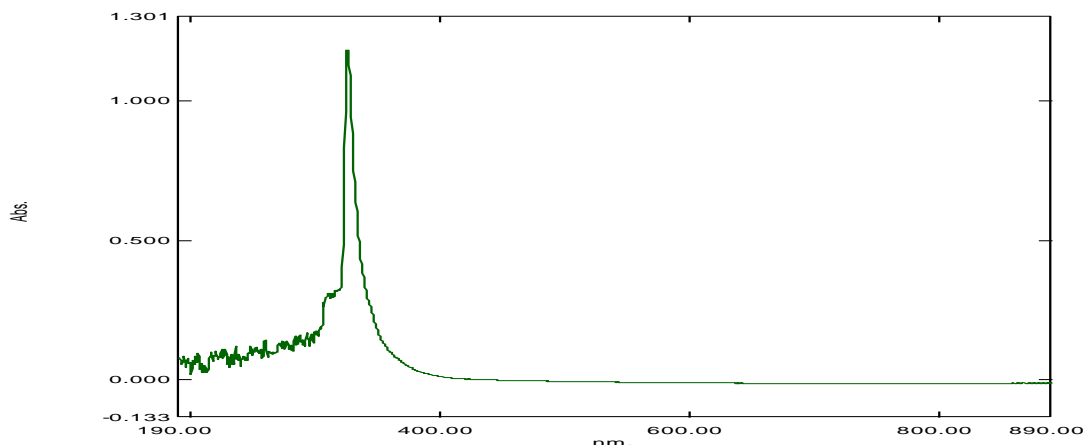


Figure 2. UV Spectrum of P4DIH

¹H NMR spectral analysis

A PMR spectrum of the polyester was obtained in CDCl₃ solution with TMS as reference in Figure 3. The peak positions in the spectrum were listed in Table 4. The chemical shift values can be explained on the basis of structural units present in the polyester.

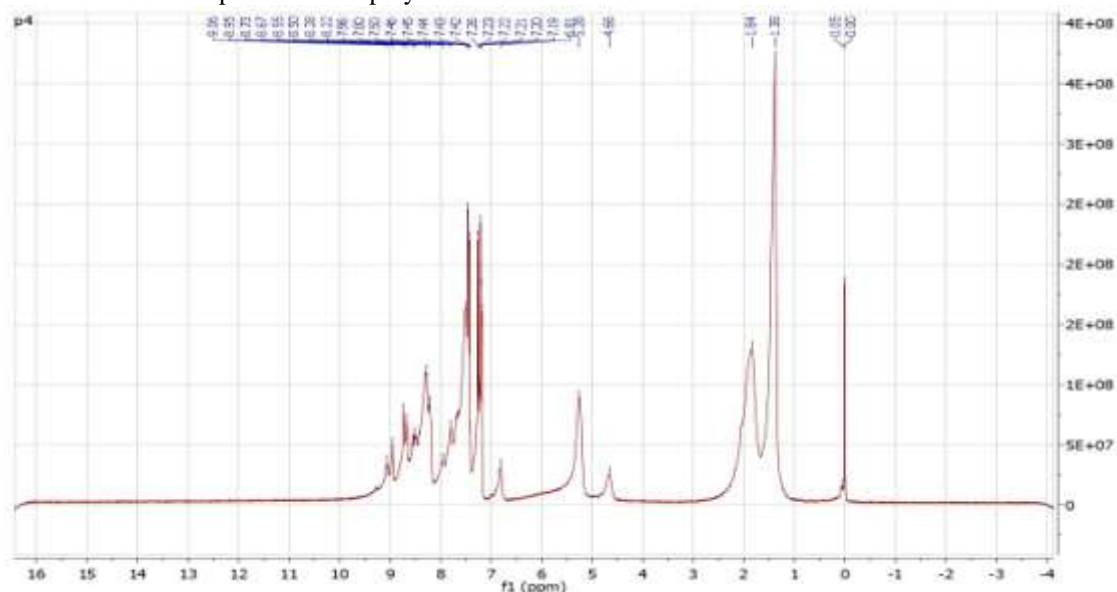


Figure 3. ¹H NMR Spectrum of P4DIH

Table 4: PMR spectral data of random copolyester.

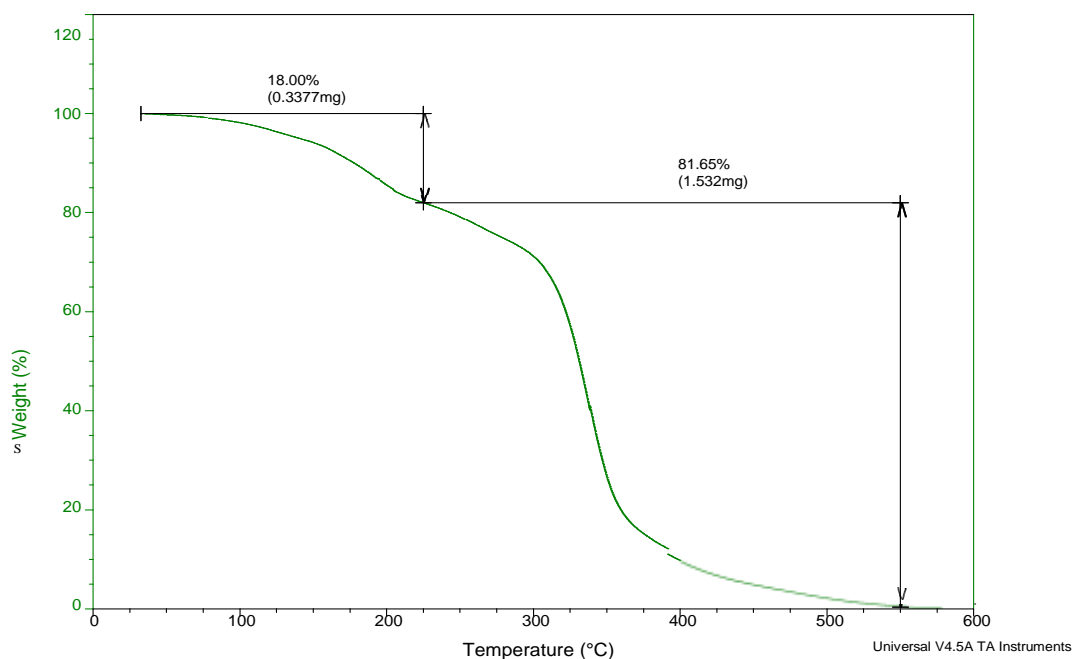
Chemical Shift (δ) (ppm)	Type of protons
2.3	Protons of the ester group
3.7	- CH ₃ group
6.5 – 8.0	1,3 – phenylene 1,4 – phenylene

Thermo gravimetric analysis (TGA)

The thermal stability of the copolyester can be determined by TGA. 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 copolyester 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 230°C with four stage degradation. The first degradation stage starts around 230°C with 18% of degradation. The second stage of degradation starts around 340°C with approximately around 40% of the copolyester gets degraded. Third stage of degradation starts around 380°C with 80% of degradation. Fourth stage of degradation starts around 550 0°C with 100% of degradation Table show that around 10% of the copolyester degraded at about 150 For 80% degradation was observed at 380°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 P4DIH degraded at lower temperature may be due to the presence of aliphatic mesogens.

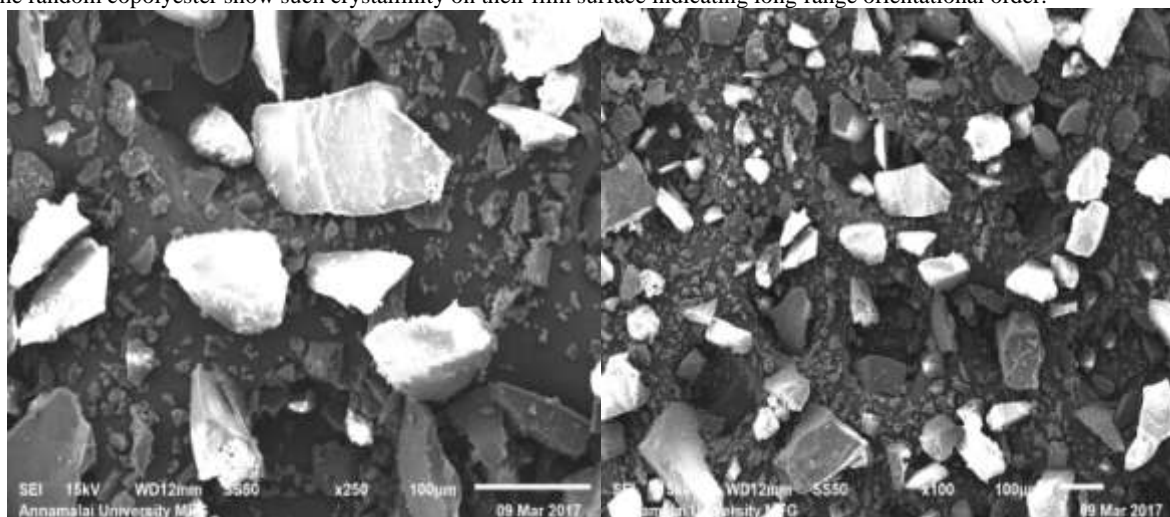
Table 5 . Thermal stability of copolyester.

Copolyesters	10%	20%	30%	40%	50%	60%	70%	80%	90%	100%
P4DIH	150	260	300	340	360	365	375	380	450	550

**Figure 4.** TGA thermograms of random copolyester P4DIH

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.



(a) (b)

Figure 5. (a). P4DIH(5 Kv), 10(b). P4DIH(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.

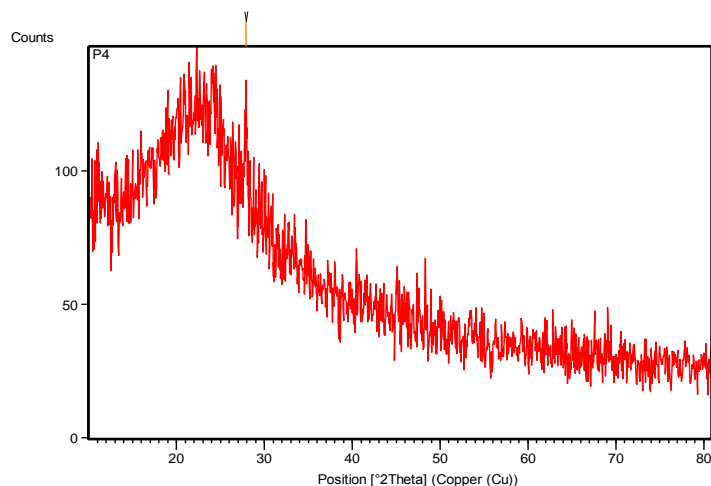


Figure 5. X-ray Diffraction of P4DIH

Table 6 .X-ray Diffraction Value of P4DIH

Pos. [°2Th.]	Height [cts]	FWHM Left [°2Th.]	d-spacing [Å]	Rel. Int. [%]
27.9152	23.89	0.7200	3.19356	100.00

III. 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.

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