

*Full Length Research Paper*

## **2,3-butanediol based liquid crystalline random copolyester, synthesis and characterisation**

**G. Elango<sup>1\*</sup>, S. Guhanathan<sup>1</sup> and T. Venkataraman<sup>2</sup>**

<sup>1</sup>Department of Chemistry, Government Arts College, Tiruvannamalai -3, Tamil Nadu.

<sup>2</sup>Sri Venkateswara College of Engineering and Technology, Thirupachur, Thiruvallur – 631 203, Tamil Nadu.

Accepted 1 June, 2010

**A copolyester was synthesized using 2,3-butanediol as one of the diols with phthaloyl chloride as Diacid chloride. 2,5-ditertiary butyl quinol, was used as another diols for the synthesis of random copolymer. A formation of copolyester was confirmed using Ultraviolet (UV), Fourier Transform Spectroscopy Infrared (FTIR), Nuclear Magnetic Resonance (NMR) spectral techniques. Thermal studies were carried out using Differential Scanning Calorimetry (DSC) and Thermo Gravimetric Analysis (TGA). Hot Stage Optical Polarising Microscope (HOPM) was studied to confirm the existences of mesophase. Elemental analysis further confirms the formations for the copolymer. Morphology of the copolyesters was also characterized using Scanning Electron Microscope (SEM). Results of the investigation confirms a relatively new entry copolymer in the family of liquid crystalline copolymers.**

**Key words:** Copolyester, thermo gravimetric analysis, differential scanning calorimetry, infrared spectroscopy, nuclear magnetic resonance, scanning electron microscope, characterization.

### **INTRODUCTION**

Macromolecules are large molecule built up by repetition of smaller chemical units. This repetition may be linear or branched or interconnected to form three dimensional networks. These repeated units are derived from monomers, 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 which was first obtained in the year 1833 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.

The vast interest in commercial utilization of copolyesters has necessitated the determination of composition and microstructure as an important adjunct to polymer technology Immergut et al. (1956). Copolyesters can be represented in different aspects viz., random copolyesters, alternating copolyesters, block copolyesters and graft copolyesters etc. These distinctions are relevant to the formation and structural integrity of the linear polyesters as well as to the infrared properties and their uses Goodman and Rhys (1965). Linear polyesters derived from dicarboxylic acids and diols can be of four categories (Nicholas, 1989) in Table 1.

\*Corresponding author. Email: [sai\\_gugan@yahoo.com](mailto:sai_gugan@yahoo.com).

**Table 1.** Types of polyesters.

Monomers		
Diols	Diacids	Polymers
Aliphatic	Aliphatic	Aliphatic polyesters
Aliphatic	Aromatic	Aliphatic aromatic polyesters
Aliphatic	Aromatic	Aliphatic polyacrylates
Aromatic	Aromatic	Aromatic polyacrylates

Polyarylates are the class of high performance engineering plastics (Seymour and Krishenbaum, 1986; Cassidy, 1980). A number of aromatic polyacrylates have been synthesized to date in various combinations of bisphenol with different aromatic acids. Polyesters of this category are associated with many valuable properties such as high glass transition temperatures, a good dielectric constant and capability of forming strong films and mouldings (Liou et al., 1994). Goodman et al. (1965); Reiji et al. (2006) synthesized 1,4 phenylene terephthalate polyesters bearing a methyl, methoxy or halogen substituents on one or both aromatic rings of the repeat units. These polymers were reported to have melting temperature in excess of 350°C. Extensive studies (Ki and Park, 2001; Harris, 1981) have been done on fully aromatic thermotropic polyesters based on the hydroquinone or terephthalic acid monomers with aromatic substituent's. A few investigations have been carried out on fully aromatic thermotropic polyesters based on 3,4'-benzophenone dicarboxylic acid.

Skovby et al. (1990) investigated a series of copolyesters based on phenyl hydroquinone with mixture of terephthalic acid and 3,4'-benzophenone dicarboxylic acid. Jackson (1983) investigated a series of copolyesters of the naphthalene diol (1,4-, 1,5-, 2,6-naphthalene derivative) isomers with terephthalic acid and 4-hydroxybenzoic acid and found that 2,6-, isomer has lower  $T_m$  than corresponding 1,4- and 1,5- copolyesters. Recently polyesters have been synthesized by polycondensation of terephthaloyl chloride or isophthaloyl chloride with hindered biphenols and hydroquinone which contains bulky substituents on the arylene ring (Whan-Gi and Hay, 1994). 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.

## EXPERIMENTAL

### Materials

The basic materials required for the synthesis and their methods are listed in Tables 1 - 3.

### 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, m-cresol, o-chlorophenol, dimethyl sulphoxide, and methanol were used as such for the determination of solubility of the polymers. Special grade acetone-d6 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 sulphur dioxide. 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 (Table 2).

### 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 4.

### Characterization of random copolyesters

Table 3 summarizes the characterization of the random copolyester viscosity measurements, solubility studies and spectral data. Thermal studies were also performed on the polyester. The liquid crystalline properties were determined by optical polarizing microscopy coupled with X-ray diffraction studies. The morphology of the polyester film was investigated by Scanning Electron Microscope (SEM).

### 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

**Table 2.** List of monomers.

S/N	Monomers	Physical properties (M.Pt/B.Pt) °C	Make
1.	Phthaloyl chloride	135	Lancaster
2.	2,3 butane diol	203	Sigma
3.	2,5 ditertiary butylquinol	212	BDH

**Table 3.** Materials and method.

S/N	Instruments used	Make	Method
1.	IR	Bio- rad (FTS 6000 spectrometer).	IR spectra photometer with samples incorporated in KBR pellets
2.	NMR ( <sup>1</sup> H and <sup>13</sup> C)	Varian 500 MHZ	Deuterioacetone (acetone- d6) contains 1% TMS. Chemical shifts are reported in ppm from Tetramethylsilane (TMS) @zero ppm.
3.	TGA	Perkin-Elmer thermogravimetric analyser (TGA-7).	Heating rate of 10 °C/min was maintained over a temperature range of 50 to 550 °C.
4.	DSC	Perkin - Elmer Differential Scanning Calorimeter (DSC-204)	Heating rate of 10 °C/min was maintained over a temperature range of 50 to 550 °C.
5.	Hot stage optical polarising microscope	Perkin-Elmer (LEICA DMLP model)	Uniform heating rate of 5 °C/minute was maintained.
6.	Gel permeation chromatography and HPLC	Waters (Waters 510 HPLC pump, Waters 717 autosampler)	Polystyrene standard was used for calibration. Tetrahydrofuran eluent was used (flow rate = 1.0 ml/min).
7.	Scanning electron microscope	SEM Leica Cambridge stereoscan -440	Gold-amalgam sputtering
8.	UV- Visible	Hewlett Packard (HP model # 8453) spectrometer	Spectra of all the polyesters were recorded with. Ethanol was used as solvent

**Table 4.** Comonomers used for P3BPD random copolyester synthesis.

S/N	Polymer	Diol-1	Diol-2	Diacid chloride	% of yield
1.	P3BPD	2,5-ditertiary butyl quinol	2,3 -Butane diol	Phthaloyl chloride	60

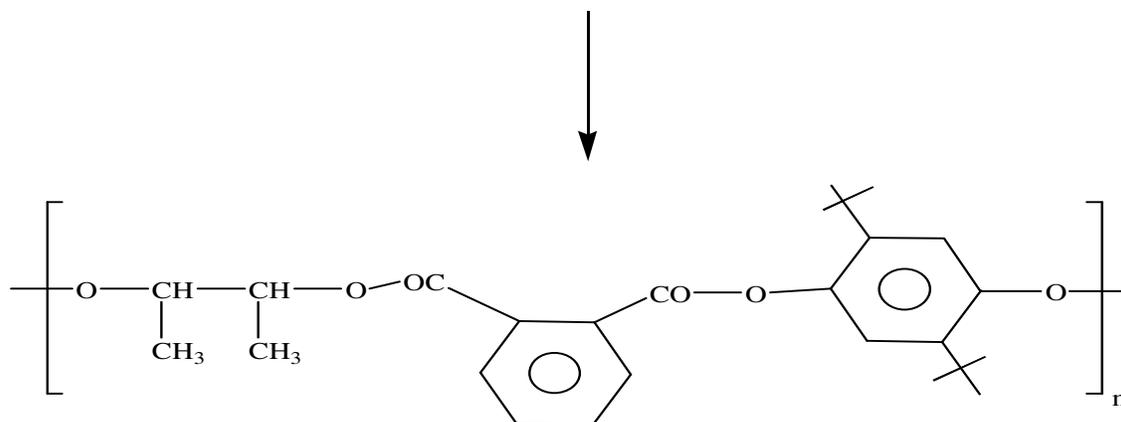
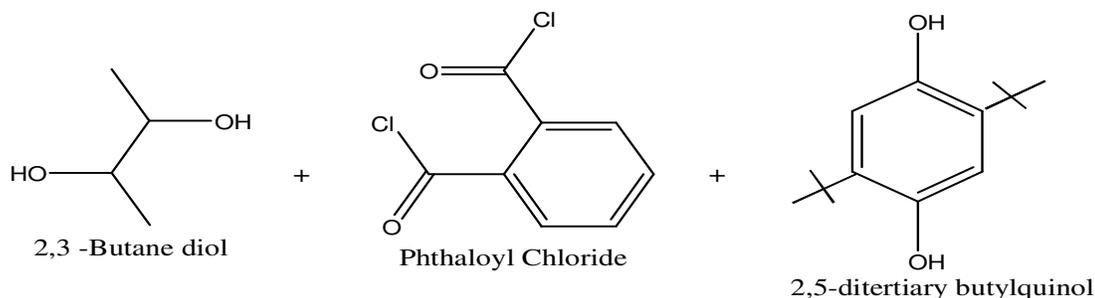
whether the polymers dissolved or swell in the solvent was noted.

## RESULTS AND DISCUSSION

Results of the present investigation were listed in Tables 4 - 15.

## Elemental analysis

The formula of the repeating unit in the copolyester can be inferred from the percentage composition. Scheme 1 describes the copolyester synthesis. The percentage of carbon and hydrogen were determined using a carbon, hydrogen analyzer. The results obtained are given in



**Poly[oxy-(2,3-butane)-oxy-co-(1,2-benzenoyl)-co-oxy-(2,5-ditertiary butyl-1,4-benzene)-oxy]**

**Scheme 1.** P3BPD.

**Table 5.** Elemental analysis data of P3BPD random copolyester.

S/N	Polyester	Molecular formula	Percentage composition			
			Carbon		Hydrogen	
			Calculated	Observed	Calculated	Observed
1	P3BPD	(C <sub>26</sub> H <sub>32</sub> O <sub>6</sub> ) <sub>n</sub>	73.2	73.1	7.51	7.53

Table 5. The data provide supporting evidence for the correctness of the structural units randomly distributed in the polymer chains of the copolyester.

### Gel permeation chromatography and high performance liquid chromatography

Gel permeation chromatography (GPC) has its greatest value for measuring the molecular weight and polydispersity of synthetic polymers. A closely related method, High-Performance Liquid Chromatography (HPLC) is more useful for polymers containing functional groups (Zbinden, 1964). Both of these methods depend on distribution coefficients, relating the selective distribution of an analyte between the mobile phase and stationary phase. The auto-scaled chromatogram was presented

in Figure 1. These chromatograms show Mn, Mw values. They are tabulated (Table 6) with  $\eta_{inh}$  values.

### Infrared spectroscopy spectra

Infrared spectroscopy (IR) 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 Figure 2. The characteristic absorptions of the polyesters and its assignments are summarized in Table 7. The IR

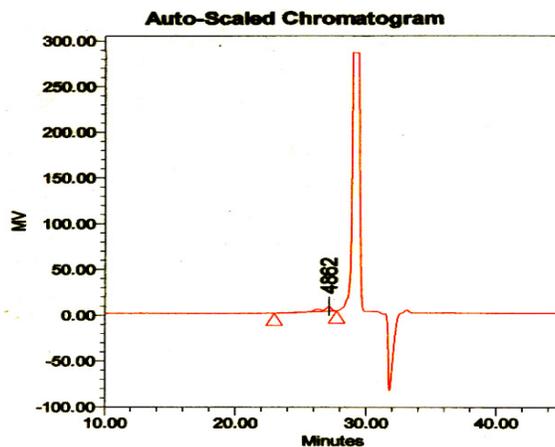


Figure 1. GPC Calibration curve of P3BPD.

Table 6. Comparison of Mn, Mw,  $\eta_{inh}$  values of P3BPD random copolyester.

S/N	Polymer	Mn	Mw	$\eta_{inh}$
1	P3BPD	5341	5429	0.23

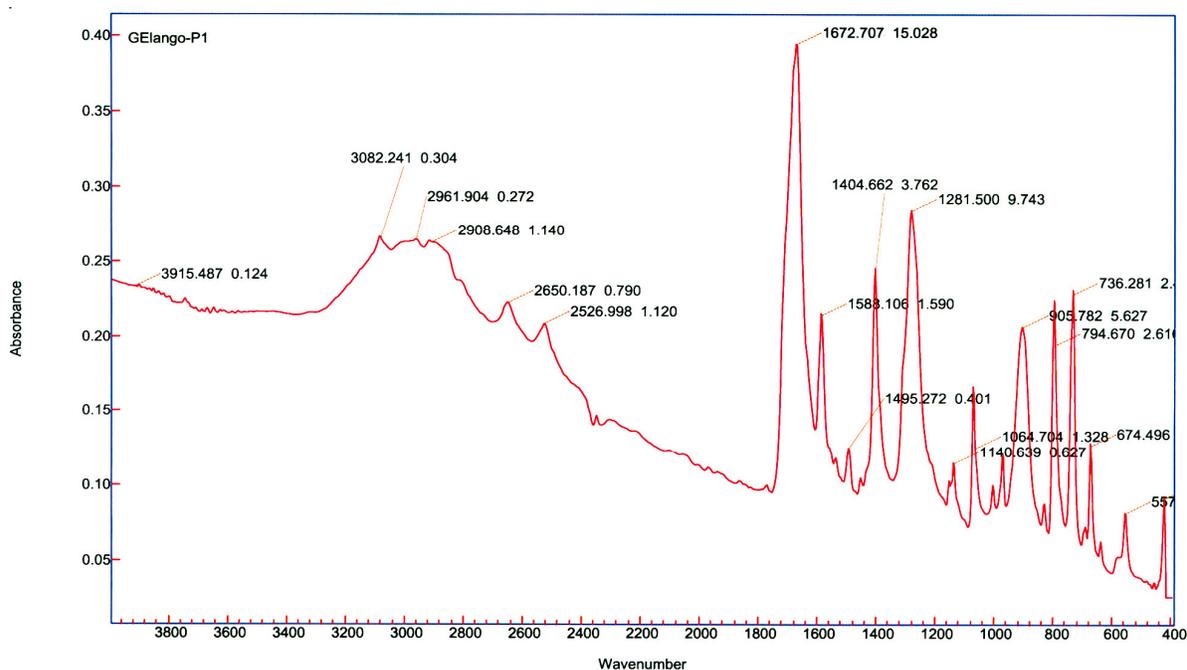


Figure 2. IR Spectrum of P3BPD.

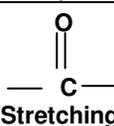
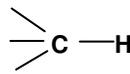
spectrum of random copolyester showed characteristic absorption at 1740  $\text{cm}^{-1}$  due to ester  $\text{C}=\text{O}$  stretching, 1020, 1080 and 1200  $\text{cm}^{-1}$  due to the ester  $-\text{C}-\text{O}$  stretching and bending indicating that the polyester chain is present in all the polymer. The  $-\text{OH}$  absorption at 3450

$\text{cm}^{-1}$  due to end  $-\text{OH}$  groups is very weak since the hydroxyl groups are present at the end of long chains (Edlund and Albertsson, 2003; Coats and Redfern, 1964). It has been shown that the polymer with stiff chains attached to a flexible backbone exhibit thermotropic liquid

**Table 7.** IR spectral data of P3BPD random copolyester.

Absorption frequency (cm <sup>-1</sup> )	Assignment
1020, 1080, 1120, 1200	Stretching vibrations of the ester C-O
1650 – 1750	Carbonyl stretching of the ester group
1180 – 1345	- CH <sub>2</sub> - Wagging
1200, 1450, 1600, 2750	Characteristic absorptions of meta substituted benzene rings
700 – 900	Aliphatic C-H bending
2600 – 2700	Ortho disubstituted benzene ring
2840 – 3000	 C – H Stretching
3500 – 3200	H – bonding
3400-3440	Characteristic absorptions of naphthalene moiety
2900 – 3000	Aromatic C-H stretching
3650 – 3600 (Sharp)	free – OH
3000 – 3100	Characteristic absorption of para substituted benzene ring

**Table 8.** Stretching frequencies of random copolyester.

Polymer	Group frequencies in IR spectra (cm <sup>-1</sup> )					
	 Stretching	 C – O Stretching	Phthaloyl moiety	Naphthalene moiety	 CH <sub>2</sub> –	 C – H
P3BPD	1672	1064	2650	-	-	2908

crystalline behaviour (Licheng et al., 2010). P3BPD contain stiff chains with rigid spacer was shown in Table 8. 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.

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

A PMR spectrum of the polyester was obtained in acetone-d<sub>6</sub> solution with TMS as reference in Figure 3. The peak positions in the spectrum were listed in Table 9. The chemical shift values can be explained on the basis of structural units present in the polyester.

### <sup>13</sup>C NMR spectra

The structural units present in the polymer chain of the polyester can be identified by <sup>13</sup>C NMR spectra. The basis of spectral analysis, it is possible to infer the structural units which are randomly distributed in the copolyester. The structural units thus inferred are listed in Table 11.

### 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. proton decoupled <sup>13</sup>C NMR spectrum of the polyester has been obtained in acetone – d<sub>6</sub> solution with TMS as the internal reference. The <sup>13</sup>C NMR spectrum of polyester was described in Figure 3. The down field peaks at 160 – 170 ppm correspond to the ester carbonyl carbon atoms of the ester group. The absorptions at 115 – 130 ppm are due to the carbon atoms of the aromatic ring. The methylene carbon atoms of the dicarboxylic acid part in the polymer absorb at  $\delta = 20 – 40$  ppm (Table 10). On the There are two absorption maxima was noted for the copolyester (Figure 4). 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.

### 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 6-9. The

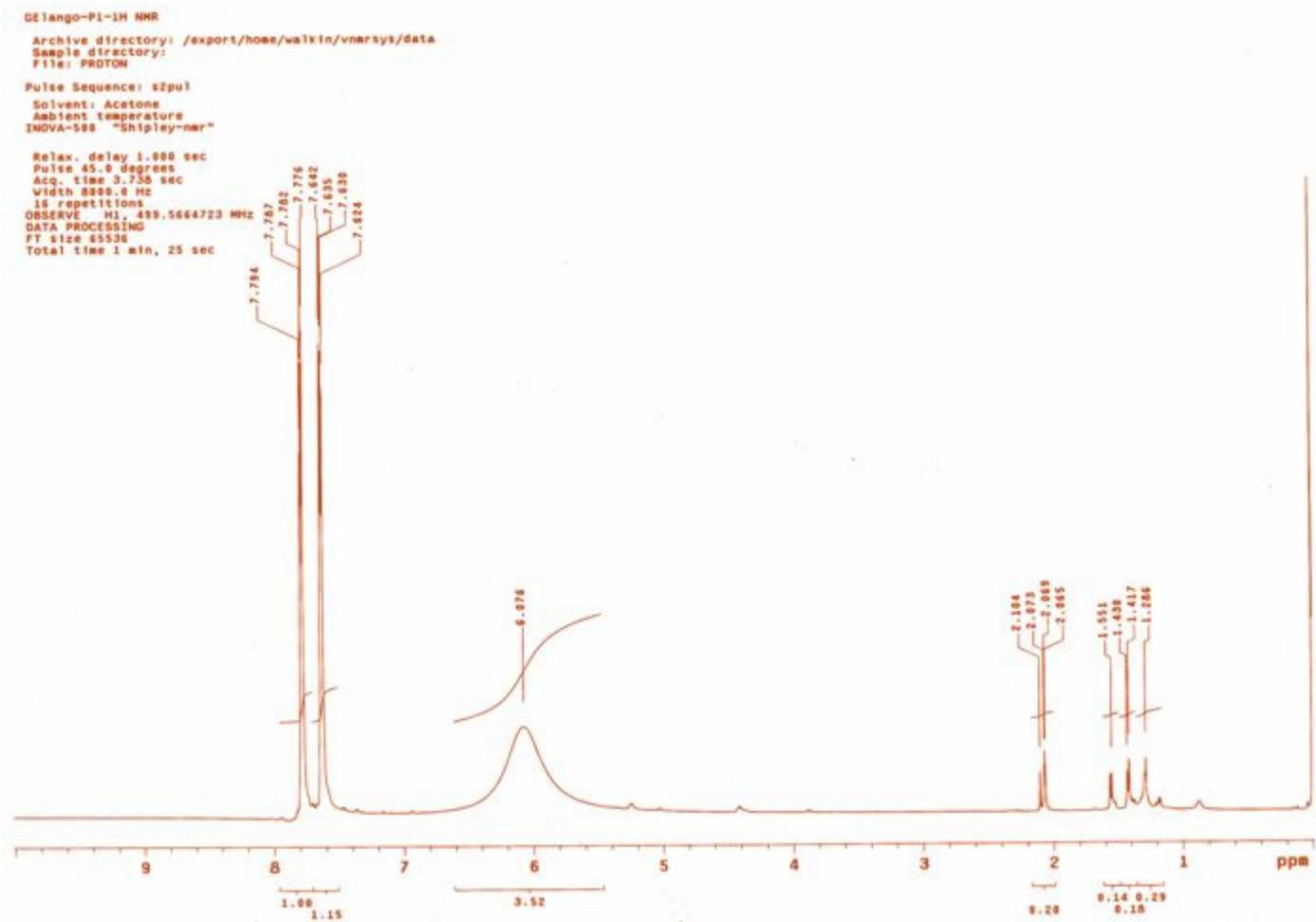


Figure 3. <sup>1</sup>H NMR Spectrum of P3BPD.

Table 9. PMR spectral data of random copolyester.

Chemical shift ( $\delta$ ) (ppm)	Type of protons
1.3	Tertiary butyl
1.6	Isopropylidene part of Bisphenol –A
2.3	Protons of the ester group
3	- CH <sub>2</sub> – group adjacent to carbonyl group
3.7	- CH <sub>3</sub> group
6.7 - 7.1	Bisphenol
6.5 – 6.8	2,5 – ditertiary butyl 1,4 – phenylene ring
6.5 – 8.0	1,2 – phenylene
	1,3 – phenylene
	1,4 – phenylene

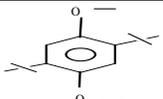
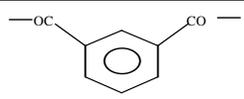
degradation of the copolyester was carried out in nitrogen atmosphere at a heating rate of 20°C/min. The thermogram suggests that the copolyester was thermally stable up to 225°C with two stage degradation. The first

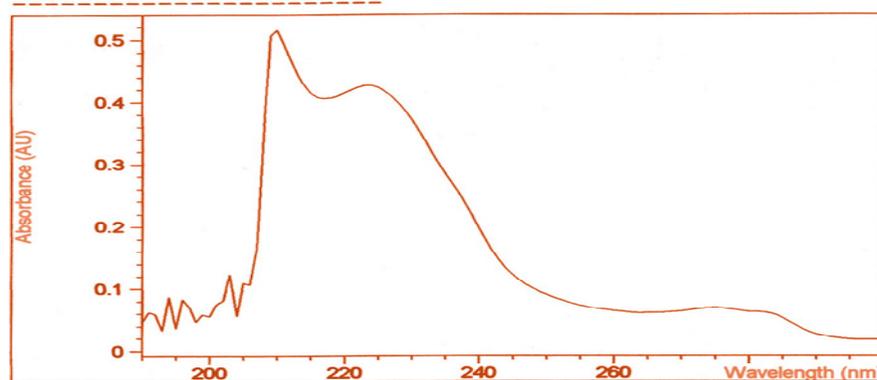
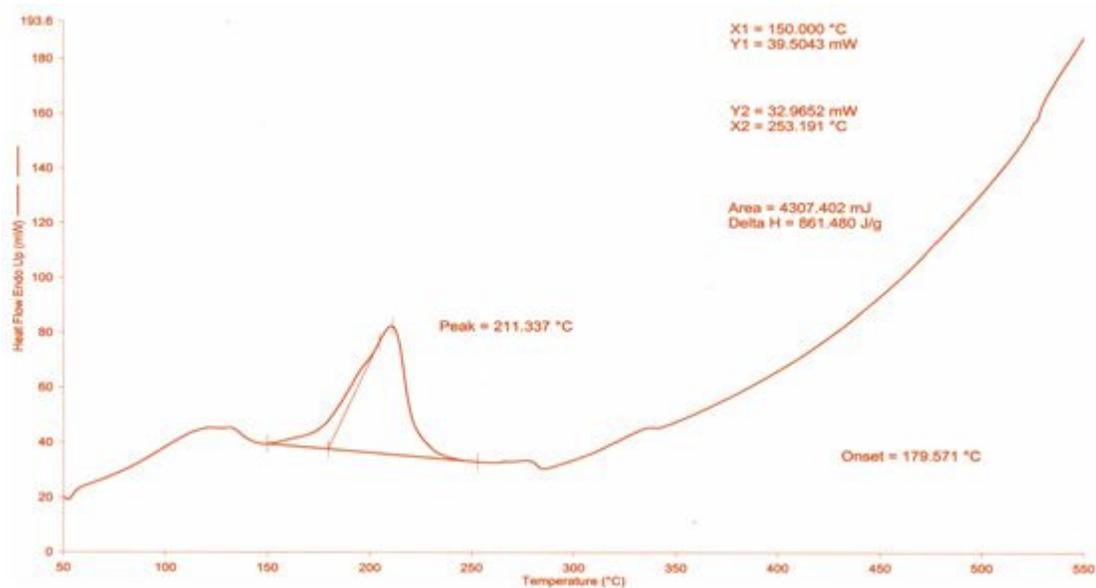
degradation stage starts around 225°C with 80% of degradation. The second stage of degradation starts around 275°C with approximately around 97% of the copolyester gets degraded. Table 12 show that around

**Table 10.**  $^{13}\text{C}$  NMR spectral data of random copolyester.

Chemical shift ( $\delta$ ) (ppm)	Type of carbons
20-40	Methylene carbon of the dicarboxylic acid
115-130	Carbon atoms of the aromatic ring
130-140	Carbon atoms of the naphthalene moiety.
160-170	Carbonyl carbon atoms of the ester group

**Table 11.** Structural units.

S/N	Polymer	Diol - 1	Diol - 2	Diacid Dichloride	Mole ratio
1.	P3BPD		$-\text{O}-\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{CH}}-\text{O}-$		1:2:3

**Overlaid Sample Spectra****Figure 4.** UV-visible spectra of random copolyester P3BPD.**Figure 5.** DSC Thermograms of Random Copolyesters P3BPD.

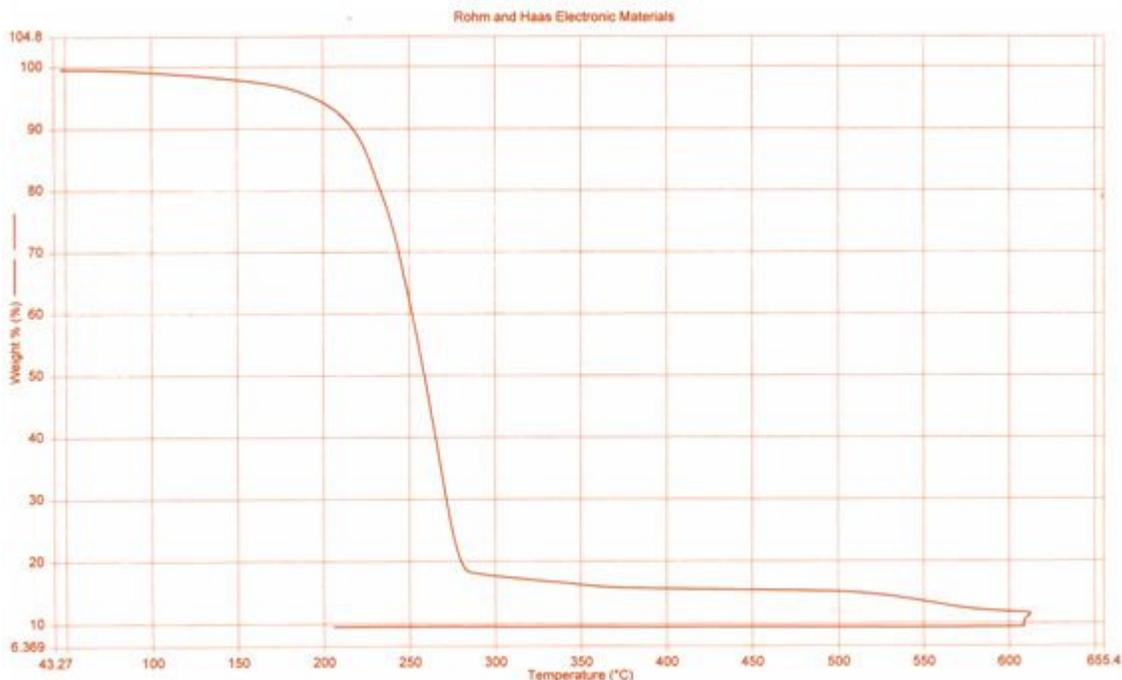


Figure 6. TGA thermograms of random copolyester P3BPD.

**x-axis :**  $T^{-1} \times 10^3 (K^{-1})$

**y-axis :**  $\ln[\ln(1-c)] - 2\ln T$

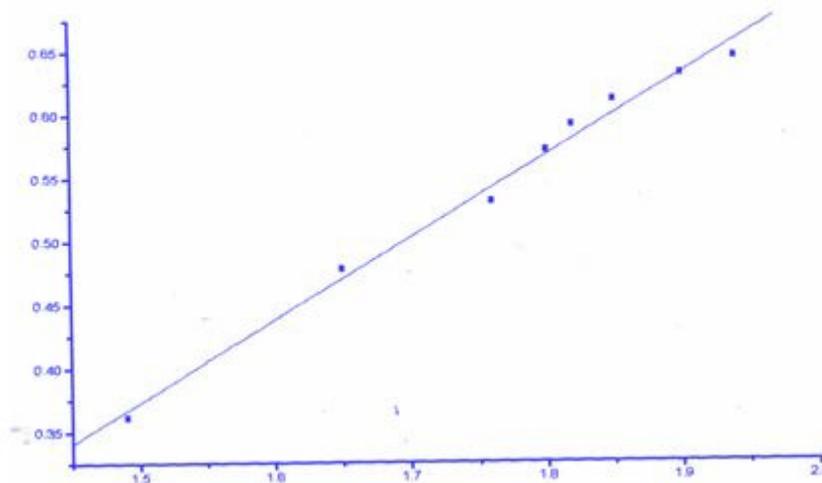


Figure 7. Arrhenius plots of degradation of random copolyester murray and white method.

10% of the copolyester degraded at about 220°C. For 80% degradation was observed at 285°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 P3BPD degraded at lower temperature may be due to the presence of aliphatic mesogens.

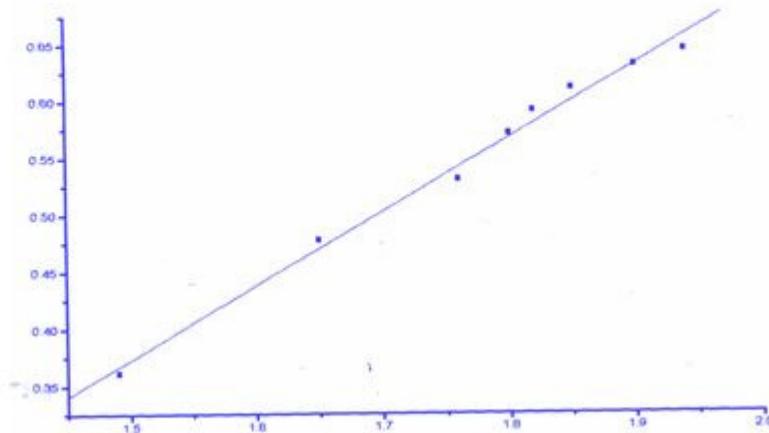
**Activation energies of degradation of random copolyester**

Activation energy calculations (Table 13) was made from TGA curves using Murray and White (Roviello and Sirigu, 1979), Coats and Redfern (Finkelmann and Rehage 1984) as well as Doyle (Balasubramanian et al., 1979)

**White method**

**x-axis :  $T^{-1} \times 10^3 (K^{-1})$**

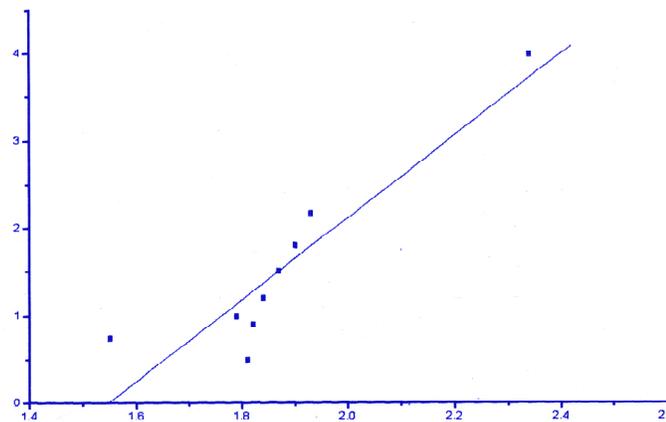
**y-axis :  $\ln[\ln(1-c)] - 2\ln T$**



**Figure 8.** Arrhenius plots of degradation of random copolyesters coats and redfern method.

**x-axis :  $T^{-1} \times 10^3 (K^{-1})$**

**y-axis :  $\log [\ln(1-c) / T^2]$**



**Figure 9.** Arrhenius plots of degradation of random copolyester.

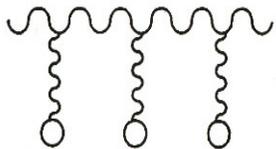
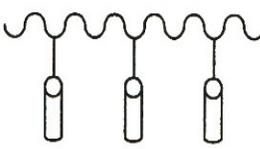
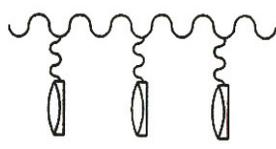
**Table 12.** Thermal stability of copolyester.

Copolyesters	Temperature (°C) corresponding weight loss								
	10%	20%	30%	40%	50%	60%	70%	80%	90%
P3BPD	222	238	248	250	263	270	275	285	-

**Table 13.** Transition parameters of random copolyester.

S/N	Polymer	Tg (°C)	Tm (°C)	Tcl (°C)	ΔT (°C)	Type of mesophase
1	P3BPD	130	211	266	55	D

**Table 14.** Different types of LC polymers.

	<i>Amphiphilic</i>	<i>Non-amphiphilic</i>	
		<i>Cylindric</i>	<i>Discotic</i>
Monomer unit			
Main chain polymer			
Side chain polymer			

methods. The slope of the curve was obtained by least square method and then activation energy was calculated.

### Differential scanning calorimeter (DSC)

Thermal analysis of polyesters is important because these investigations not only explain the behaviour of the copolyester when subjected to high temperatures but also aid in establishing uses. In the present investigation, DSC is used to detect the phase transitions in the random copolyester. DSC thermogram obtained in nitrogen atmosphere for the polyester was presented in Figure 5. Thermogram contains sharp as well as broad peaks at characteristic temperatures indicating phase transitions, before melting. The transition temperatures were calculated from the DSC thermogram and they are presented in Table 14 along with the type of mesophase detected in hot-stage polarising microscope. These transition temperatures are found to be in agreement with the transition temperatures for the formation of mesophase determined by polarizing optical microscopy. The  $T_g$  and  $T_m$  of the polymer could be precisely determined from heating curve of the differential scanning analysis. P3BPD was found to have lower  $T_g$  and  $T_m$  values. Such peculiar thermal behaviour may be due to the nature of the spacer which links the main chain.

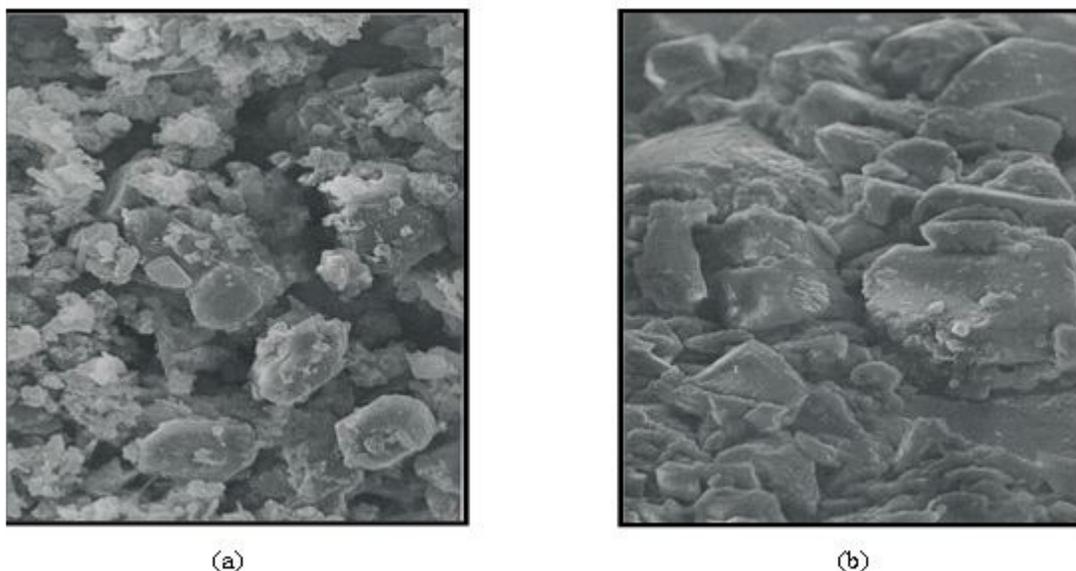
Polymer having low  $T_g$  and  $T_m$  contain flexible spacer which serves to dissociate the disorder of the main chain from the greater order of the mesogenic groups and to decouple the motions of the mesogenic moiety from those of the polymer backbone. The effect of increased polymethylene flexible spacer length on the liquid crystalline polymer was observed by Roviello and singu,

(1979); Sachindrapal et al. (1981).

### Optical polarizing microscopic studies

Figure 8 displays the characterization of liquid crystals by polarized light microscopy is the most useful for polymers possessing desired mechanical, thermal and optical properties (Cassidy, 1980; Liou et al., 1994; Reiji et al., 2006). Recently there has been considerable interest in Thermotropic Liquid Crystalline (TLC) polyesters with low  $T_g$  values followed by a sharp transition to a mesophase with as low  $T_m$  value as possible, since these polymers are used in reprographic applications (Jackson, 1983; Whan-Gi and Hay, 1994; Zbinden, 1964; Bellamy, 1975; Yiwang et al., 2007; Krighaum et al., 1982). The widely employed technique to identify the mesophase in TLC polyesters is by optical polarizing microscopic investigation (Gordon and Plate, 1984). The characterisation of thermographic melts by optical method has been the subject of much theoretical and experimental analysis (Shibaev, 1980; Shibaev et al., 1982; Abe, 1984; Wendorff et al., 1978). Extensive investigation on low molecular mass liquid crystals has proved that LC state can be directly correlated with the chemical constitution of the molecules (Kelkar, 1979; Gray, 1982; Gray, 1979; Robinson, 1958; Werbowyi and Gray, 1976). Owing to their chemical constitution, liquid crystalline phases having defined molecular organizations are formed. Gray and Windsor (Padmanabha et al., 1996) classified liquid crystals into two types, namely amphiphilic LC and non-amphiphilic liquid crystals (Figure 11).

Non amphiphilic liquid crystals can be further differentiated into LC molecules having a cylindrical molecular shape and those having a disc like shape. LC's



**Figure 10.** (a). P3BPD (2.5 KX), 10(b). P3BPD (5 KX).



**Figure 11.** Optical polarized micrographs of random copolyester

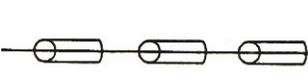
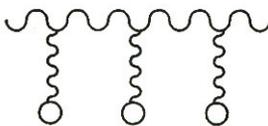
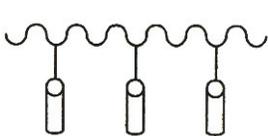
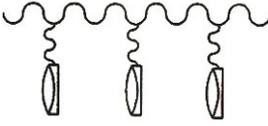
of molecules with cylindrical shape are long range positional and orientationally ordered in smectic phases and only orientationally ordered in nematic and cholesteric phases (Dewar and Griffin, 1975). In order to identify the existence of mesophase in the polyesters, magnified photographs have been taken for the copolyester in hot stage polarizing microscope equipped with a pentax camera attachment. The transition temperatures for the formation of mesophase and isotropisation have been determined. These thermal transition temperatures along with the type of mesophases are given in Table 15. The observed transition temperatures are also supported by

sharp endotherms in DSC thermograms of the random copolyester. The random copolyester containing unsubstituted phenylene groups and aliphatic groups in the polymer backbone usually exhibited nematic behaviour when longer spacer groups were present in the main chain (Lenz and Jin, 1985; Griffin and Havens, 1981; Strzelecki and Van, 1980).

### 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 10. 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

**Table 15.** Different types of LC polymers.

	<i>Amphiphilic</i>	<b>Non-Amphiphilic</b>	
		<b>Cylindric</b>	<b>Discotic</b>
Monomer unit			
Main chain polymer			
Side chain polymer			

range orientational order.

## Conclusions

1. The copolyester was soluble in common organic solvents such as acetone, chloroform and aprotic solvents such as DMF and CCl<sub>4</sub>.
2. The inherent viscosity is proportional to polymer molecular weight and molecular weight has a drastic influence on the phase transition temperature of the polyester.
3. IR and NMR spectral values are in accordance with functional group and the nature of mesogens present.
4. 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.
5. Molecular mass of liquid crystals have proved that LC state can be directly correlated with constitutions of the molecule.
6. SEM micrograph of LC polyester film provides useful information regarding the structure of the film surface.
7. The kinetics of thermal degradation of copolyesters were studied using Murray and White method, Coats and Redfern method and Doyle method for the copolyesters.

## REFERENCES

Abe A (1984). "Isotropic (Ni) transitions –contribution in entropy" *Macromolecules*, 17: 2280.

- Balasubramanian M, Nanjan MJ, Santappa M (1979). Synthesis of aromatic –aliphatic polyamide containing azo linkages" *Makromol. Chem.*, 180(2517): 182-853.
- 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.
- Blundell DJ (1982). "Variation of crystallographic parameters in PEEK with heat" *Polymer*, 23: 359.
- Bellamy LJ (1975). *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London. P.217.
- Cassidy PE (1980). "Thermally stable polymers" *Dekker*, New York. p. 73.
- Cheng SZD (1988). "Electrochemical formation of chiral polyaniline colloid codoped polymers" *Macromolecules*, 21: 2475.
- Coats AW, Redfern JP (1964). Kinetics parameters from thermogravimetric analysis, *Nature*, London, 201, 68.
- Dewar MJS, Griffin AC (1975). The STO-3G transition structure of Diels- alder reaction, *J. Am. Chem. Soc.*, 97: 6662.
- Edlund U, Albertsson AC (2003). Polyesters based on diacid monomers, *Advanced Drug Delivery Reviews* 55: 4(1 2003): 585-609.
- Finkelmann H, Rehage G (1984). *Advances in Polymer Science Series 60/61*, Springer-Verlag, New York. pp. 99.
- Goodman I, Rhys JA (1965). "Saturated Polymers" (Published for the plastics Institute, London Illiffe Books Ltd.), New York, American Elsevier Publishing Company Inc.
- Gordon M, Plate NA (1984). *Liquid Crystal Polymers II/III*, Springer-Verlag, Berlin. p. 124.
- Gray GW (1979). *The Molecular Physics of Liquid Crystals*, Eds., Luckhurst, G.W. and Gray G.W., Academic Press, New York, p.126.
- Gray GW (1982). *Polymer Liquid Crystals*, Eds., Cifferri, A., Krigbaum, W.R. and Meyer, RB. Academic Press, New York.
- Harris JF Jr. (1981). NMR evidences for polymeric structure, *U.S. Pat.*, 4: 294-955.
- Immergut EH, Mark HF (1956). Investigation on copolymeric characterization, *Macromol. Chem.*, 18: 322.
- Jackson WJ Jr (1983). synthesis and characterization of block copolyesters, *Macromolecules*, 16: 1027.
- James J, Malley O, Walter JS (2003). Synthesis and characterization of isomeric polyesters based on sebacic acid and hexanediols. J.

- Polymer Sci., 12(4): 865-874.
- 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.
- Kelkar H (1979). Synthesis and mesomorphic behaviour of lithocholic acid derivatives, *Mol.Cryst. Liq. Cryst.*, 21: 1.
- Ki HC, Park Ok O (2001). Synthesis, characterization and biodegradability of the biodegradable aliphatic–aromatic random copolyesters, *Polymer*, 42(5): 1849-1861.
- 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.
- 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.
- Lin YG, Winter H (1988). "High temperature recrystallisation and rheology of thermotropic liquid crystalline polymers" *Macromolecules*, 21: 2439.
- Liou GS, Kakimoto MA, Imai Y (1994). Thermally stable organosoluble binaphthylene based polymers, *J. Polym. Sci: Part A. Polym. Chem.*, 32: 597.
- Lussac JG, Pelouze J (1833). *Advances in the synthetic macromolecular compounds*, Ann., 7: 40.
- 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.
- Shibaev VP, Kostromin SG, Plate NA (1982). sidechain liquid crystalline polymers, *Europ. Polym. J.*, 8: 651.
- Skovby MHB, Heilmann CA, Kops J (1990). In liquid crystalline polymers, weiss. R.A., Oba. C.K., Eds., ACS symposium series 435; American chemical Society, Washington, DC p.46.
- Whan-Gi K, Hay AS (1994). Random block copolyester – characterization, *J. Polym. Sci. Part A. Polym. Chem.*, 32: 97-103
- Wendorff IH, Finkelmann H, Ringsdorf H (1978). "liquid-crystalline polymethacrylates –by atom transfer radical polymerization" *J.Polym.Sci. Polym. Symp.*, 63, 245.
- Windle AH, Viney C, Golombok R, Donald AM, Mitchell GR (1985). Sequencesegregation in molten liquid crystalline random copolymers, *Faraday Dis., Chem. Soc.*, 79: 55.
- 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.
- Zbinden R (1964). *IR Spectra of High Polymers*, Academic Press, New York. p. 59.
- Robinson C (1958). "Heterogeneous network polymers-7. cholestric liquid cryslline polymers" *Trans. Faraday Soc.*, 1956, 52: 571& Robinson, C., Ward, J.C. and Beevers, R.B., *Discuss. Faraday Soc.*, pp. 25-29.
- Werbowyi RS, Gray DG (1976). "Liquid crystalline state of concentrated solution cyanoethyl derivatives" *Mol.Cryst. Liq. Cryst. Lett.*, 34: 97.
- Lenz RW, Jin JI (1985). *Liquid Crystals and Ordered Phases*, Griffin, and Johnsons, J., Ed., Plenum Press, New York, p. 328.
- Griffin AC, Havens S (1981). "Energy profile for nonconcerted SN2 reaction in solution" *J.Polym. Sci. Polym. Phys.Ed.*, 9,951.
- Strzelecki L, Van Luyen D (1980). "Orientation dynamics of main chain liquid crystalline polymers" *Eur. Polym. J.*, 16: 299.