



2,5-Ditertiary Butyl Quinol based Liquid Crystalline Random Copolyester – Synthesis and Characterisation

¹G. Elango, ²N.Mahadevan, ³K. Annamalai and ⁴S. Guhanathan

^{1,2,3}PG and Research Department of Chemistry, Government Arts College, Tiruvannamalai .

⁴PG & Research Department of Chemistry, Muthurangam Government Arts College. (Autonomous), Vellore- 632 002.
Email: sai_gugan@yahoo.com

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ABSTRACT - A copolyester was synthesized using 2,3 butane diol 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 UV, FTIR, NMR spectral techniques. Thermal studies were carried out using DSC and 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 SEM. Results of the investigation confirms a relatively new entry copolymer in the family of Liquid crystalline copolymers.

Keyword: Copolyester –TGA, DSC – IR, NMR – SEM–characterization.

I. 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 repeat 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 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 [1] on heating lactic acid. Carothers created the modern chemistry and technology of polyesters [2]. Polyesters attract significant interest, despite inferior mechanical properties. Transition temperature and properties of copolyesters can be varied by altering 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 [3].

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 [4]. Linear polyesters derived from dicarboxylic acids and diols can be of four categories [5] in Table 1. Polyarylates are the class of high performance engineering plastics [6-7]. 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 [8].

Goodman, McIntyre and Alred [9] 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 [10,11] have been done on fully aromatic thermotropic polyesters based on the hydroquinone or terephthalic acid monomers with aromatic substituents. A few investigations have been carried out on fully aromatic thermotropic polyesters based on 3,4'-benzophenone dicarboxylic acid. Skovby et al.,[12] investigated a series of copolyesters based on phenyl hydroquinone with mixture of terephthalic acid and 3,4'-benzophenone dicarboxylic acid. Jackson[13] 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 [14]. After careful analysis of literature, the scope of the present

investigation aims to synthesis thermotropic liquid crystalline random copolyester with aliphatic and aromatic group in the main chain.

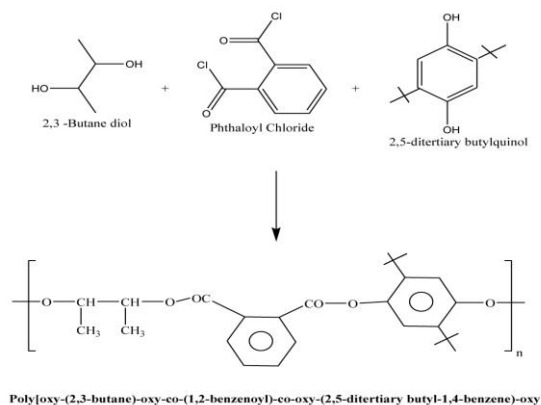
II. EXPERIMENTAL

2.1 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 20g of sodium hydroxide in 100 ml of water and adding 2g of sodium anthraquinone-2-sulphonate and 15g 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.

2.2 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 150ml of *o*-dichlorobenzene was added followed by the diacid chloride in the appropriate proportion. The mixture was then refluxed for 25 to 36 hours at 130°C to 150°C in nitrogen atmosphere with constant stirring. The contents were cooled and poured into about 250ml 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.



2.3 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 SEM.

III. RESULTS AND DISCUSSION

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

3.2 Gel Permeation Chromatography and High Performance Liquid 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. Both of these methods depend on distribution coefficients, relating the selective distribution of an analyte between the mobile phase and stationary phase.

3.3 IR Spectra

Infrared spectroscopy 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. 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 $-\text{C}-\text{O}$ stretching and bending indicating that the polyester chain is present in all the polymer. The $-\text{OH}$ absorption at 3450 cm^{-1} due to end $-\text{OH}$ 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. 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.

3.4 ^1H NMR Spectral Analysis

A PMR spectrum of the polyester was obtained in acetone- d_6 solution with TMS as reference in Figure 1. The chemical shift values can be explained on the basis of structural units present in the polyester.

3.5 ^{13}C NMR Spectra

The structural units present in the polymer chain of the polyester can be identified by ^{13}C NMR Spectra. The proton decoupled ^{13}C NMR spectrum of the polyester has been obtained in acetone – d6 solution with TMS as the internal reference. The ^{13}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.

3.7 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 degradation of the copolyester was carried out in nitrogen atmosphere at a heating rate of $20^\circ\text{C}/\text{min}$.

The thermogram suggests that the copolyester was thermally stable upto 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. 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.

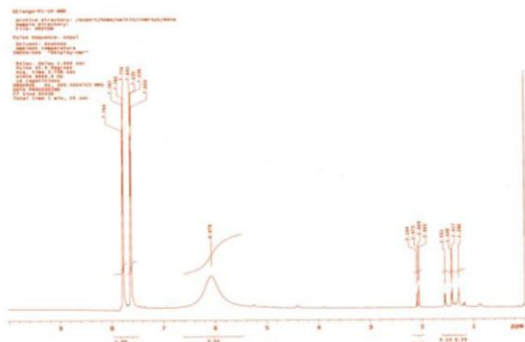


Figure 1. ^1H NMR Spectrum of P3BPD

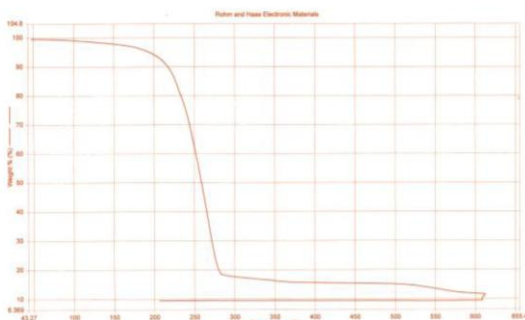


Figure 2. TGA Thermograms of Random Copolyesters P3BPD

3.9 Scanning electron microscopic studies

The characterization of LC polyester by optical polarising 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 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. 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.

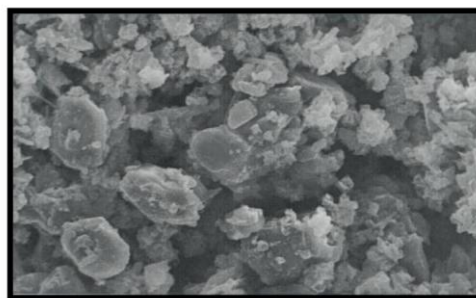


Figure 3(a). P3BPD (2.5 KX)

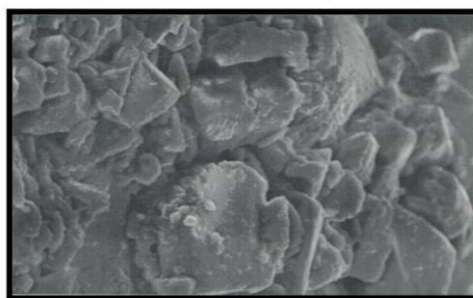


Figure 3(b). P3BPD (5 KX)

IV. CONCLUSION

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 fibers 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. The kinetics of thermal degradation of copolyesters were studied using Murray and White method, Coats and Redfern method and Doyle method for the copolyesters.

V. ACKNOWLEDGEMENT

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