



Synthesis and Characterization of Thermotropic Liquid Crystalline Copolyesters with Quasi- Rigid Cyclohexyl and Biphenyl Moieties

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Abstract : Quasi-rigid random copolyesters with cyclohexyl and biphenyl moieties were synthesized via polycondensation with diphenyldichlorophosphate as the condensing agent. The cyclohexyl units have both cis and trans configuration in the polymer backbone. The phenyl rings in 2,2'-biphenyl dicarboxylic acid are forced into a non-coplanar conformation thus decreasing the interchain interaction. Copolymerization of 2,2'-biphenyldicarboxylic acid and 1,4-cyclohexanediol with specific monomers namely terephthalic acid, 4,4'-oxybis(benzoic acid) and 2,6-naphthalene dicarboxylic acid yielded thermotropic liquid crystalline polymers. The structural features of the three random copolyesters were investigated by FT IR, ¹H NMR, and ¹³C NMR spectroscopy. The polymer properties were characterized by thermal analysis, optical microscopy and wide-angle X-ray diffraction. All of the copolyesters exhibited a nematic mesophase. These polymers may emerge as components of photo-optic devices due to the presence of noncoplanar biphenyl unit.

Keywords : 2,2'-biphenyl dicarboxylic acid, diphenic acid, 1,4-cyclohexanediol, diphenyldichlorophosphate.

1. Introduction

Liquid crystalline polymers are a subject area of the great upsurge of interest for having potential applications in various fields, including optics, optical data storage, optoelectronic and non-linear optic devices [1-6]. Polyarylates are one of the most important types of liquid crystalline polymers possessing good thermal stability and excellent mechanical properties [7]. Rigid polyarylates like poly (hydroquinone terephthalate) and poly (hydroxybenzoate) are insoluble and exhibit high melting temperatures. They are nonmesomorphic with decomposition temperature greater than 500 °C and are not melt processable [8]. Under thermodynamic considerations high melting temperatures are the result of high melting enthalpies and low melting entropies. The melting entropies can be increased with a controlled decrease of the symmetry, along the polymer backbone thus reducing interchain interactions without destroying the formation of liquid crystalline phases [9]. One of the approaches to improve the processability would be the incorporation of non-coplanar 2,2'-biphenylene unit. 2,2'-Biphenylene acts as a kink mesogen of collinear orientation required for liquid crystalline polymers. Only 2,2'-biphenylene containing aromatic polyesters have been reported [10-17]. There are few reports on investigation of 2,2'-biphenylene containing alicyclic polyesters. Earlier studies have shown that 1,4-cyclohexane diol with a lateral substituent depress the melting point below 300 °C [18]. Moreover, liquid crystalline polymers prepared from cyclohexanediols are less toxic compared to hydroquinone and other phenolic alcohols. Cyclohexanediols have the added advantage of being less corrosive and less expensive.

With this perspective a set of three novel random, liquid crystalline polyesters was tailor made using 2,2'-biphenyl dicarboxylic acid as monomer and comonomers namely 1,4-cyclohexanediol with various aromatic dicarboxylic acids such as terephthalic acid, 4,4'-oxybis(benzoic acid) and 2,6-naphthalene dicarboxylic acid.

2. Experimental details

2.1 . Materials

Terephthalic acid (TA) (98%), 4,4'-oxybis(benzoic acid) (OBBA) (99%), 2,6-naphthalene dicarboxylic acid (NDA) (99%), diphenic acid (DA) (97%), diphenylchlorophosphate (DPCP) (99%), 1,4-cyclohexanediol (99%) (CHD) purchased from Sigma Aldrich were used as received. Lithium chloride anhydrous (Merck, India) was dried at 130 °C under vacuum for 4 h and at 180°C for 10 h. Pyridine was distilled before use.

2.2. Polymerization

All the three polymers were prepared by direct polycondensation [19] of two diacids and one diol in the respective molar ratio 1:1:2 as shown in the Table 1. A typical procedure for the synthesis of random copolyester DTCH (figure 1) is as follows: To a four-necked 250 mL round bottomed flask fitted with a condenser, thermometer, mechanical stirrer and an oil bath, 2.5 mmol of TA, 2.5 mmol of DA, 10mL pyridine and 13 mmol DPCP were added. After stirring for 20 min, 10 mmol of LiCl in 10 mL pyridine was added and stirring was continued at room temperature for 30 min. The reaction mixture was slowly heated and maintained at 120°C for 20 min. To this mixture 5 mmol of diol CHD in 5 mL pyridine was added drop wise at 120°C for 20 min and the whole solution was further stirred under the same condition for 3 h. The solution was cooled to room temperature and poured into 500 mL water/methanol (1:1 v/v). The product was filtered, washed with hot methanol and dried in vacuum oven at 50°C.

The other two polyesters were prepared in the same manner with the same feed ratio.

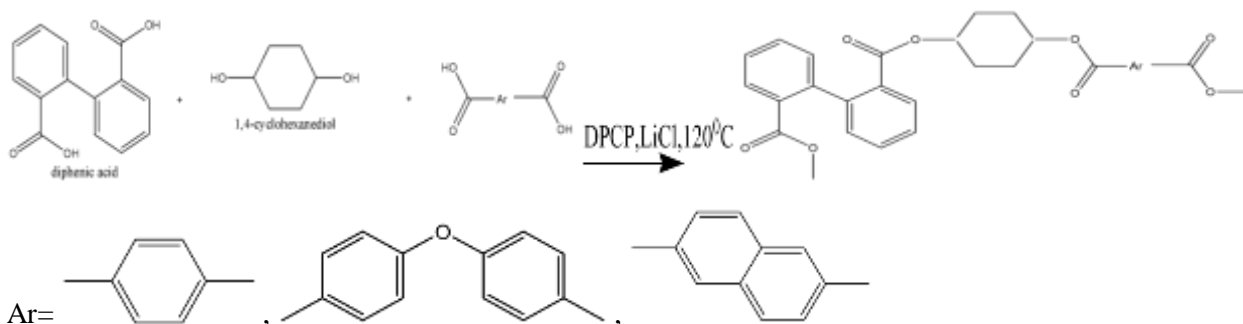


Figure 1. Scheme of synthesis of random copolyesters with 1,4-cyclohexanediol.

Table 1. Physical properties of random copolyesters and their IR data.

Polym er code	Monomer*	Inherent Viscosity g dL ⁻¹	Yield %	FT-IR Data (cm ⁻¹)				
				Aromatic C-H stretching	Aliphatic C-H stretching	C=O stretch ing	C=C aromatic stretching	C-O-C stretching
DTCH	DA+CHD+TA	1.24	64	3064.06	2950.25	1718.65	1594.23	1272.11
DOCH	DA+CHD+OBBA	1.20	70	3058.27	2943.5	1713.83	1594.23	1257.64
DNCH	DA+CHD+NDA	1.17	82	3063.09	2948.32	1715.76	1594.23	1280.79

* DA: 2,2'-biphenyldicarboxylic acid ,TA: terephthalic acid ,OBBA: 4,4'-oxybis(benzoic acid), NDA : 2,6-naphthalenedicarboxylic acid ,CHD: 1,4-cyclohexanediol

2.3 Characterization

The solubility of the polymers was determined using 0.005 g of the polymer in 1 mL of the solvent. The inherent viscosities of the copolyesters were determined with an Ubbelohde Viscometer at a concentration of 0.1 g dL⁻¹ in N, N-dimethylformamide. Infrared spectra from 4000–600 cm⁻¹ of solid samples of the synthesized polymers were obtained by the KBr pellet method using a Shimadzu, IR Affinity 1, Japan spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded at the scan rate of 10⁰⁰⁰ /min on a NETZSCH DSC 200F3 under nitrogen atmosphere. Samples of about 2 mg were employed. High resolution ¹H NMR spectra were recorded on a BrukerAvace III 500 MHz NMR for ¹H and 125 MHz for ¹³C nucleus in DMSO-d₆ solvent with TMS as an internal reference. X-ray diffraction measurements on powder samples were taken using Bruker D8 advance x-ray diffractometer with a source of Cu K- alpha radiation. The optical textures were examined on a hot stage polarizing microscope (Olympus BX 51) for the polymer samples pressed between a glass slide and a cover slip.

3. Results and discussion

The random copolyesters described in this work were synthesized by a direct polycondensation method using DPCP as condensing agent. Higashi method [19] is mainly used for the polycondensation of aromatic dicarboxylic acids and aromatic diols. Synthesis of polyesters with aromatic dicarboxylic acid and alicyclic diols demonstrates the extended applicability of Higashi method. The risk of degradation of the monomers especially 1,4-cyclohexanediol is greatly reduced because of the low temperature and shorter time required for polymerization. All the polymers obtained are semicrystalline and obtained in good yield. The copolyesters synthesized are soluble in organic solvents such as DMSO, acetone, N,N-dimethylformamide, NMP, sulphuric acid and insoluble in chlorinated solvents. The increase in the solubility of all the polyesters is attributed to the presence of 2,2'-biphenylene moiety in the polymer backbone [12]. Because of the rigidity of the naphthalene structures the polyester containing naphthalene segments showed poor solubility. Polyester containing oxybis(benzoic acid) showed enhanced solubility due to the presence of the flexible ether linkage. The Fourier transform infrared spectra of the synthesized copolyesters indicate, the formation of ester in the products (Table 1). The infrared spectrum shown in figure 2 exhibits peaks at 3058 cm⁻¹ and 2944 cm⁻¹ which are characteristic of aromatic C-H stretch and aliphatic C-H stretch respectively. The peak at 3411.26 cm⁻¹ is due to the overtone of the C=O group from ester [20]. C=C stretching vibration of aromatic ring is observed at 1594 cm⁻¹. Band characteristics of aromatic esters (aryl conjugation with carbonyl group) are observed at 1714 cm⁻¹ (C=O stretching) [21] and 760 cm⁻¹ (out-of-plane C-H bend of aromatic ring). Strong vibrational modes observed at 1257 cm⁻¹ and 1017 cm⁻¹ are associated with C-O-C stretching modes of the copolyester. The repeat unit in the copolyester was identified by ¹H NMR and ¹³C NMR spectra. For illustration purposes, the ¹H and ¹³C NMR spectra of polymer DOCH with respective chemical assignments are shown in figure 3 and figure 4 respectively. The peak positions in both ¹H NMR and ¹³C NMR studies validate the structure of the repeat unit in the synthesized copolyester as expected. In ¹H NMR of DOCH peaks from δ 1.44 ppm to 5.06 ppm are due to cis and trans isomers of cyclohexyl moiety. Four different kinds of aromatic protons at δ 8.03 (H_g), δ 7.8 (H_f), δ 7.42 (H_e) and δ 7.25 (H_d) can be distinguished for 2,2'-biphenyl dicarboxylate moiety and the oxybis benzoate moiety resonates at δ 7.19 (H_c) and δ 8.04 (H_d) [22]. Commercially available 1,4-cyclohexanediol is a mixture of cis and trans isomers in the ratio 1:1 [18]. The polymer obtained using this sample possesses both the configurations in the chain. ¹³C NMR of DOCH also showed peaks due to the cis and trans isomers at δ 27.5, 28.9, 70.9 and 71.4 ppm as reported by Malcolm in the model compounds [23]. The resonances associated with the aromatic ring carbons of oxybis benzoate moiety occur at δ 119.3 ppm (C-3), δ 124.48 ppm (C-4), δ 132.18 ppm (C-5), δ 160.15 ppm (C-6) and the carbonyl carbon at δ 164.82 ppm (C-7) [24,25]. The aromatic carbons of diphenate moiety showed signals at δ 127.74 ppm (C-8), δ 129.3 ppm (C-9), δ 130.54 ppm (C-10), δ 132.18 ppm (C-11), δ 149.85 ppm (C-12) and the carbonyl carbon at δ 166.68 ppm (C-13) [26]. The presence of two different ester carbonyls in the polymer backbone was confirmed by the appearance of more than two different carbonyl absorptions at δ 166.88, 166.59, 164.91 and 164.82 ppm, which in turn indicates that both the monomeric units are incorporated into the polymeric backbone.

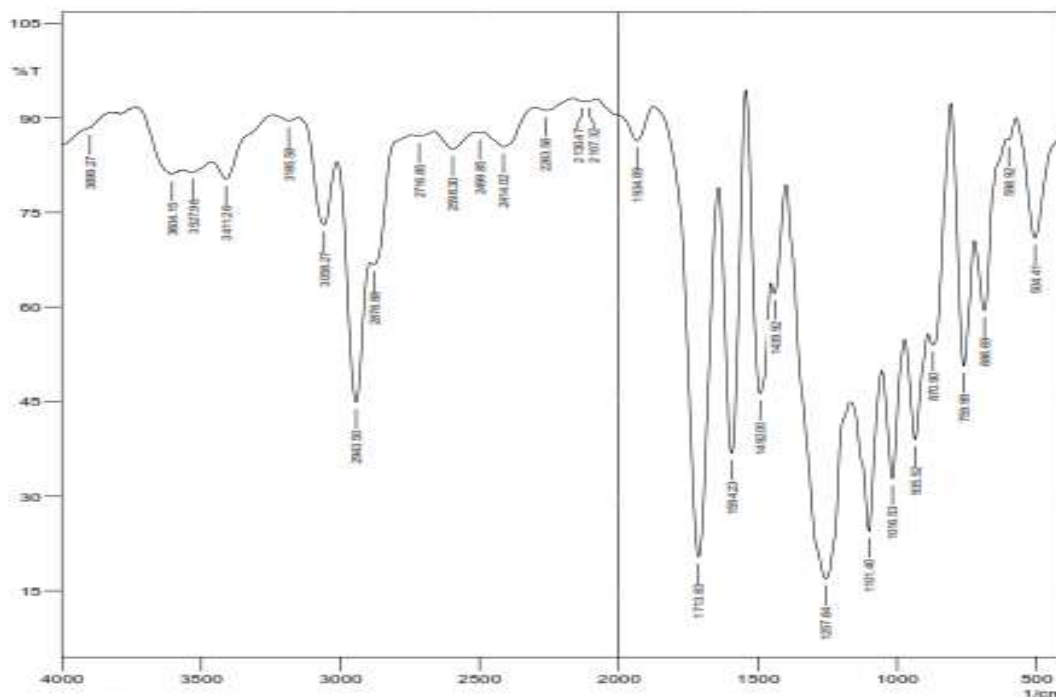


Figure 2: FT IR spectrum of DOCH

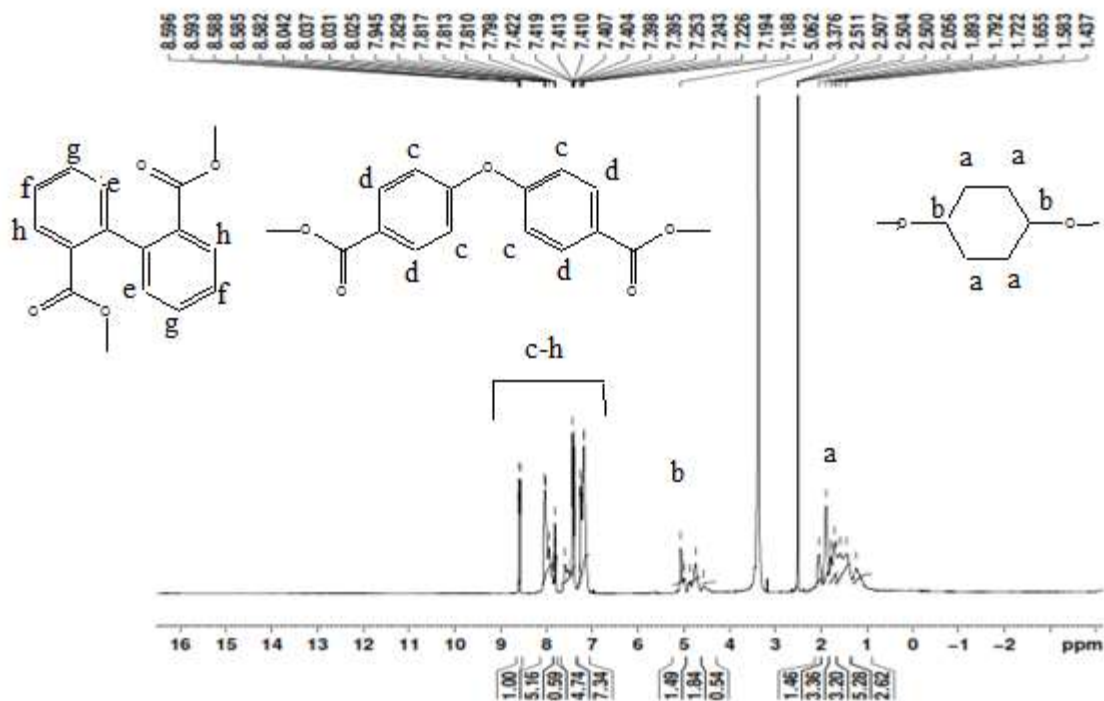


Figure 3. ¹H NMR spectrum of DOCH

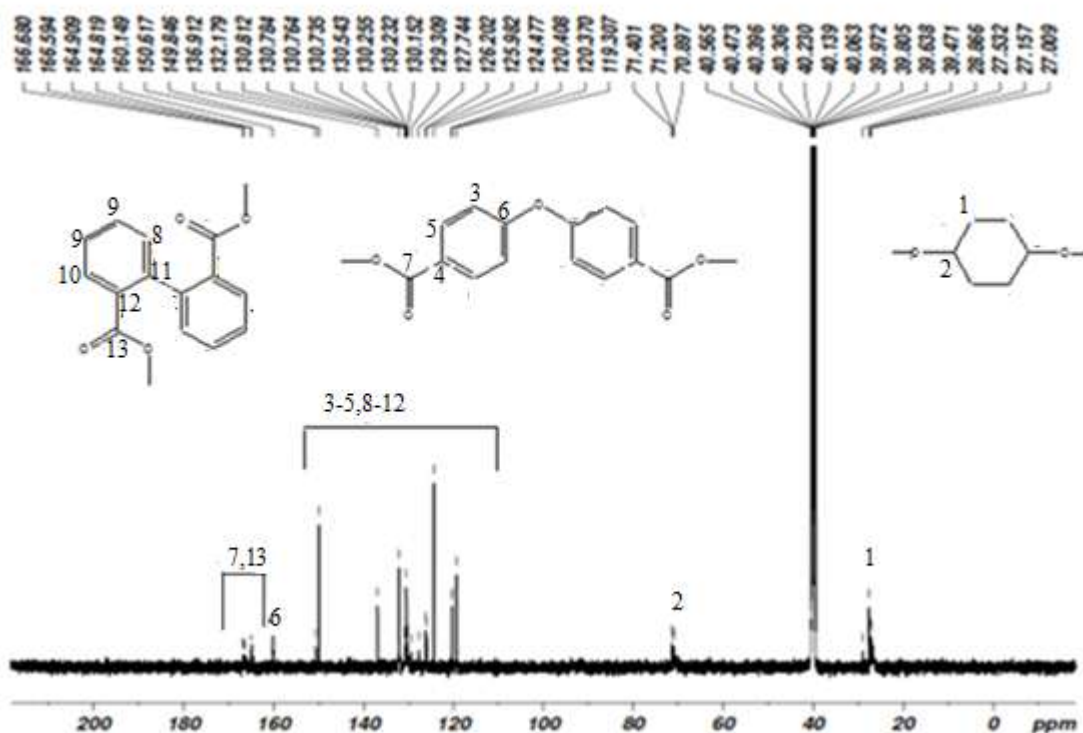


Figure 4. ^{13}C NMR spectrum of DOCH

3.1. Thermal studies and liquid crystalline properties

Several research papers have been published regarding the stereochemistry of 1,4-cyclohexanediol polymers [18,23,27,28]. In the present work three random copolyesters containing both cis and trans cyclohexanediol in the ratio 1:1 were subjected to thermal studies. The DSC thermograms of the polyesters are shown in figure 5 and their phase transition temperatures in the second scan with the heating rate of $10^\circ\text{C}/\text{min}$ are summarized in table 2. From the table it is evident that with increase in flexibility of the polymer backbone in the polyester prepared from 4,4'-oxybis(benzoic acid) and distortion in regular symmetry the glass transition temperature decreases. All these polymers exhibit two endothermic peaks. The endothermic peaks in the rigid terephthalate polymer are sharp whereas the endothermic peaks in the flexible oxybis(benzoate) and kink 2,6-naphthalate are broad. Two endothermic peaks separated by an exotherm may indicate polymorphism [29].

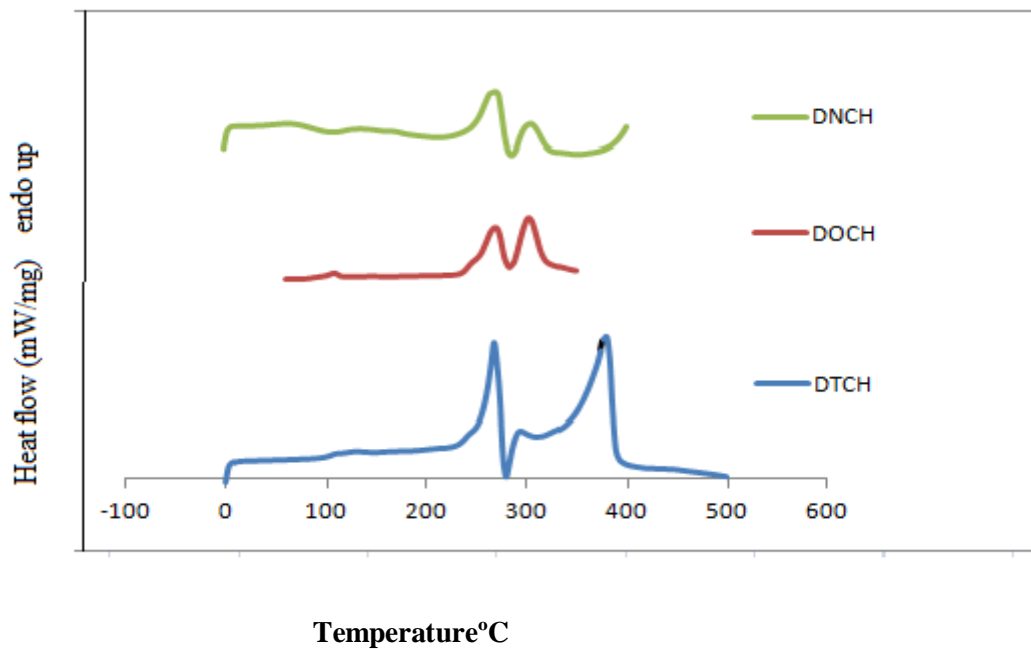


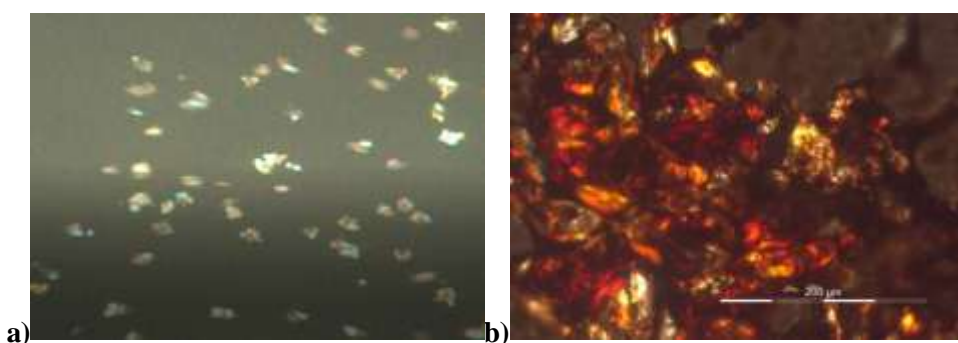
Figure 5. DSC thermogram of polyesters

Table 2. Transition temperatures of the random copolyesters from DSC traces

Polymer	T_g °C	T_m °C
DTCH	105	267.2
DOCH	98.9	265.8
DNCH	101.6	269.8

3.2. Polarizing microscopic studies

Mesophase identification was determined by optical polarized microscope observations. The optical properties of biphenyl based random copolyesters are quite interesting. Three random copolyesters with biphenyl moiety in the polymer chain are found to be thermotropic. Introduction of a flexible oxybis(benzoic acid) group in DOCH significantly lowers the liquid crystalline transition temperature and broadens the melting endotherm. In the polarizing microscope, an apparent melting of DOCH was observed to begin at 250 °C which corresponds to the lowest temperature endotherm in its thermogram. At 280 °C, threaded Schlieren texture characteristic of nematic mesophase appeared as shown in figure 6 (a) and (b) [30]. The polymer DTCH has a higher T_g than the polymers DOCH and DNCH. The rigidity of the terephthalate ring results in high T_g value. On the polarizing microscope, the onset of flow occurred at 144 °C and the birefringence intensity increased at about 192 °C. Figure 6 (c) shows the characteristic nematic Schlieren texture for DTCH [23]. In the thermogram of DNCH two broad endotherms at about 247 °C and 297 °C are seen. In the photomicrographs of DNCH, figure 6 (d), (e) and (f), the birefringent phase has the appearance of the threaded Schlieren texture, which is characteristic of the nematic mesophase [23,30].



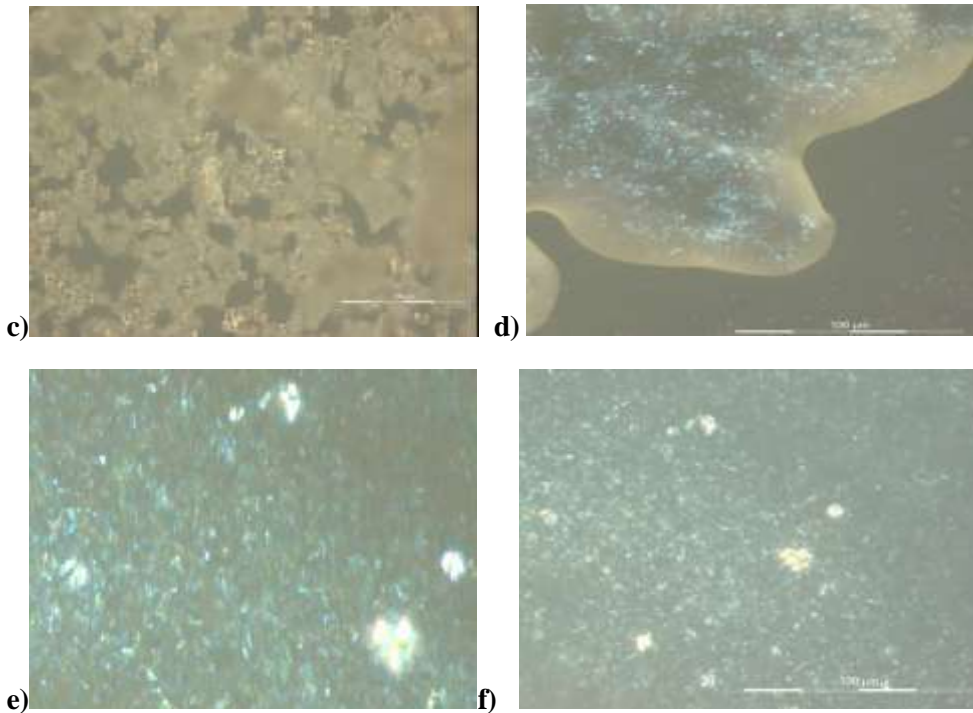


Figure 6 Optical polarized micrographs for a) DOCH at 258 °C heating b) DOCH at 280 °C heating c) DTCH at 188 °C heating d) DNCH at 180 °C (heating) e) DNCH at 248°C (heating) f) DNCH at 175°C (cooling)

3.3. X-ray diffraction studies

The X-ray diffraction analysis of the polymers was conducted at room temperature. These spectra suggest that there is some degree of crystallinity in these polymers. All the copolyesters exhibit main peak located around 20° belong to (110) crystallographic planes which is a typical feature peak of nematic liquid crystal polymer [31]. The polyester DTCH displayed a moderately high crystallinity due to the symmetric, rod-like benzene moiety. Introducing flexible oxybis(benzoate) moiety in DOCH decreased the crystallinity [30]. The crystallinity of DNCH is lowered by the linear offset motion of 2,6-naphthalene units [32].

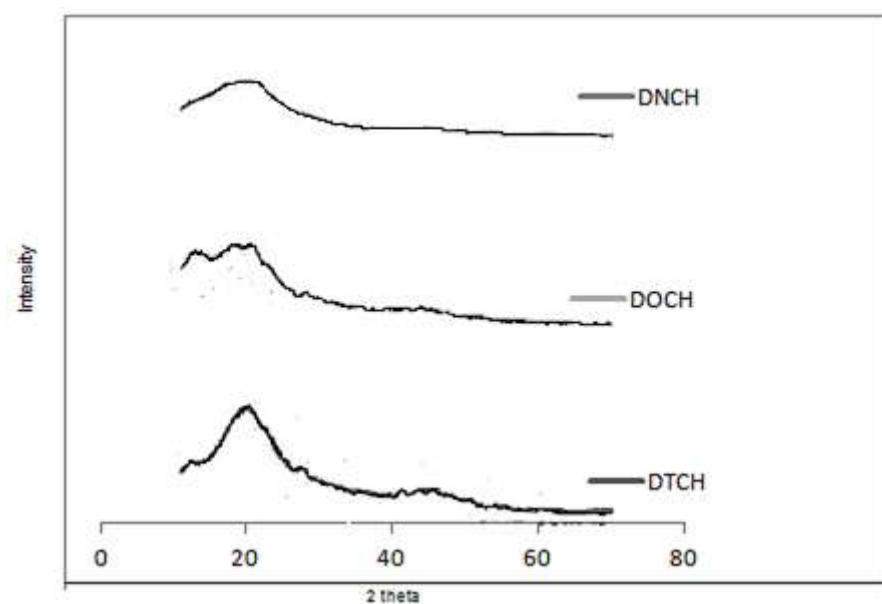


Figure 7. XRD patterns of the polyesters

4. Conclusion

Three thermotropic liquid crystalline polyesters were synthesized by polycondensation with diphenylchlorophosphate and characterized spectroscopically. The cyclohexyl units have both *cis* and *trans* configuration in the polymer backbone. The copolyesters based on 2,2'-biphenyldicarboxylic acid and 1,4-cyclohexanediol exhibit a nematic mesophase. Presence of 2,2'-biphenylene moiety in the polymer backbone increased the solubility. Two endothermic peaks separated by an exothermic peak may indicate polymorphism in these polyesters. These polyesters may emerge as potential candidates for photo-optic devices.

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