



# Thermotropic Liquid Crystalline Polyesters using Aromatic Rigid Diols, Unsaturated Fumaric Acid and Flexible Sebacic Acid



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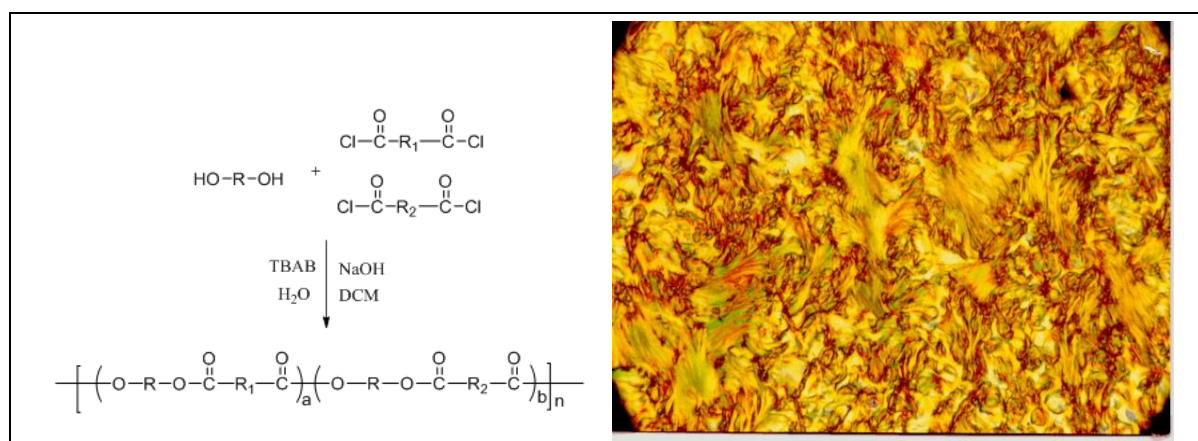
Liquid crystalline

Thermotropic

## ABSTRACT

In the present study, seven different series of thermotropic liquid crystalline polyesters (TLCPs) containing unsaturated fumaroyl chloride and flexible sebacoyl chloride were synthesized using the interfacial polymerization methodology. Homopolyesters prepared with saturated flexible spacer such as sebacoyl chloride were mesomorphic whereas homopolyesters synthesized using unsaturated aliphatic spacer such as fumaroyl chloride that was non-mesomorphic. Aromatic diad and triad based mesogenic diols were selected as rigid moiety for liquid crystalline phase formation. Within each series, copolyesters were synthesized by varying relative mole ratio of the above two aliphatic diacid chlorides. Most of the liquid crystalline polyesters showed solubility in phenol:tetrachloroethane (60:40) at 40 °C.

## GRAPHICAL ABSTRACT



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## Introduction

Liquid crystalline polymers (LCPs) are increasingly used worldwide in industrial and commercial applications as special materials in diverse fields such as delivery devices, ophthalmic devices and ink compositions for toner for photocopying, tissue engineering and other areas including biomedical applications [1-3]. However, properties related to orientation decreases considerably due to anisotropy. To overcome this problem introduction of reactive double bond into the polymer main chain was worked out. The literature on unsaturated polyesters describes extensive use of maleates whereas fumarates are rarely reported. The typical functional crosslinkable units in the main chain are cinnamoyl, *p*-phenylene, diacryl or stilbene. Functional end groups frequently used are maleimide, epoxy, vinyl, isocyanate, acetylene or acrylate [4]. The liquid crystalline polymers derived from fumarates and mesogenic methoxyphenyl azophenoxy resulting in formation of the enantiotropic nematic phase. Properties of liquid crystalline thermosets based on types of reactants and methods of synthesis were already described by many researchers [5-11].

The unsaturated polymers can be crosslinked thermally or photochemically. The network structure is based on rigid rod or extended chain segments that are crosslinked in three dimensions. The introduction of fumaroyl units into flexible spacer of liquid crystal polymers allows a structure fixing crosslinking reaction. Thus, unsaturated polyesters with liquid crystal elements can be synthesized by incorporating combination of rigid mesogenic unit with rigid fumarate units along the chain.

Liquid crystalline thermosets are a class of materials that combine properties typical of thermotropic liquid crystalline polymers with those of conventional thermosets. Mulani *et al.* [12] observed very large mesophasic

stability for new liquid crystalline polyesters consisting of bis-(4-hydroxybenzoyloxy)-2-methyl-1,4-benzene and aliphatic dicarboxylic acid chlorides [12]. Applications of liquid crystal thermosets include the advanced adhesives, new matrix materials for composites and variety of applications for microelectronics industry. These compounds have also been studied as optical materials and polarizers [13].

Thermotropic liquid crystalline polymers are exhibiting a class of high-performance polymers, because these polymers exhibit very good thermal and mechanical properties. Due to the attractive properties these polymers are applied in variety of fields such as electronic devices, protective coatings, sports equipment, and automotive part composites [14].

Thermotropic liquid crystalline polymers are usually based on type of polyesters, because these polymers possess free hydrogen bond linkages. The polymers such as poly(4-oxybenzoyl), poly(4-phenylene terephthalate) and poly(4-phenylene naphthalene-2,6-dicarboxylate) melt at very high temperature. From the technological point of view, polyesterification of these polymers is carried out by melt polycondensation method and processing temperature is above 400 °C. As high processing temperature number of side reactions takes place; it affects the quality of the final product. Another major drawback of fully aromatic TLCPs is insolubility in common organic solvents namely chloroform, dichloromethane, tetrahydrofuran, ethyl acetate, acetone, toluene, and aprotic solvents such as NMP, DMF, DMSO, and DMAc. This insolubility exhibited due to high axial ratio and highly crystalline nature of the polymers; as they are difficult to process [15].

To enhance the processability of these TLCPs, various approaches have been

performed to reduce the crystal perfection and the crystal lattice energy include : i) insertion of flexible spacer into the main chain of polymer to reduce axial ratio of the mesogen; ii) introduction of substitution on aromatic ring of mesogenic moiety to disturb regularity of the repeating unit; iii) addition of cycloaliphatic monomer or kink into the main chain of polymer backbone; iv) incorporating crank-shaft monomers; and v) copolymerisation of different mesogens. Random arrangement of repeating units also lowers the transition temperature [16].

In the present work, series of main chain homo and copolyesters based on thermotropic liquid crystalline polymeric nature were synthesised by interfacial polycondensation method. Rigid mesogenic diols were condensed in combination with fumaroyl chloride and sebacoyl chloride. Fumaroyl chloride acts as rigid unsaturated aliphatic diacid whereas sebacoyl chloride performs as flexible aliphatic diacid.

## Experimental

### *Materials and methods*

Solvents such as dichloromethane, methanol, chloroform, dichloromethane, dichloroethane, tetrachloroethane, and tetrahydrofuran were procured from Merck and used as received. The chemicals such as phenol, sodium hydroxide and 4,4'-biphenol (BP) were purchased from Merck and were used as received. The diacid chlorides were obtained from Aldrich chemical company and were used as such. Aromatic diols *e.g.* 4,4'-dihydroxyazobenzene (AZ), 4,4'-dihydroxyazoxybenzene (AX), 4,4'-dihydroxy-3,3'-dimethylazoxybenzene (AXM), 2,6-bis(4-hydroxy benzylidene) cyclohexanone (BC), 2,6-bis(4-hydroxy benzylidene)-4-methyl cyclohexanone (BM), bis (4-hydroxy benzoyloxy) 2-chloro-1,4-benzene (BHOC) were synthesized by established procedures [17].

### *Synthesis of polyesters by interfacial polymerization*

Stock solutions of diacid chlorides were prepared by accurately weighing 0.001 mole of each acid chloride in 100 mL volumetric flask and making volume up to the mark with dry distilled 1,2-dichloroethane. To 50 mL erlenmeyer flask, 0.002 mol of diol was accurately weighed, dissolved in 20 mL of 0.2 N sodium hydroxide solution and transferred into reactor using 20 mL of distilled water. Tetrabutyl ammonium bromide (TBAB), a phase transfer catalyst (4 wt.% of diol) was then added, followed by 40 mL of 1,2-dichloroethane. Then required amount of the diacid chlorides was added and the reactants were vigorously stirred for 5 min. Subsequently 500 mL methanol was added to precipitate the polymer. Polymer obtained was filtered and dried under the reduced pressure at 40 °C for 8 h. Schematic representation of interfacial polymerization is shown in Scheme 1. Synthesized homo and copolyesters were characterized by infrared spectroscopy (IR), differential scanning calorimetry (DSC), and polarizing optical microscopy.

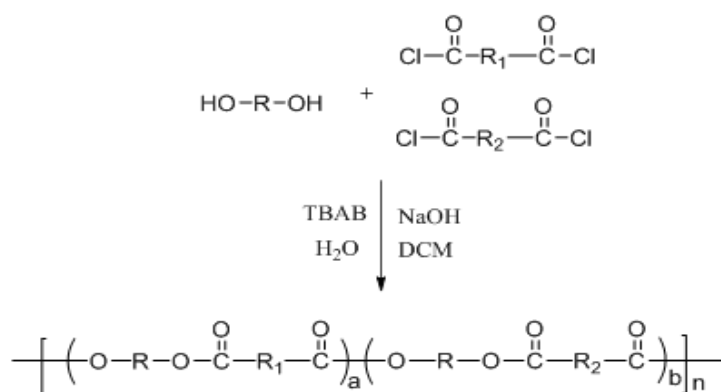
### *Solubility of polyesters*

Solubility of the polyesters was tested in organic solvents such as chloroform, carbon tetrachloride, 1,2-dichloroethane, dichloromethane, 1,1,2,2-tetrachloroethane, tetrahydrofuran, acetone, methanol and phenol:1,1,2,2-tetrachloroethane (60:40, v/v). Into 10 mL volumetric flask, 20 mg of polymer and 10 mL of desired solvent were added and kept aside for 3 days at ambient temperature with intermittent stirring. To avoid possibility of crosslinking through olefinic double bond of fumaroyl moiety, the solutions were not heated [18]. The intrinsic viscosity ( $\eta$ ) of selected polymers was estimated using an Ubbelohde viscometer using 0.5 g/dL solution prepared in

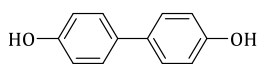
phenol:tetrachloroethane (60:40, v/v) mixture, kept for 24 h for complete

dissolution, filtered and then viscosity was measured.

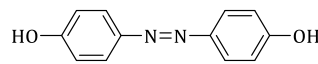
**Scheme 1.** Schematic representation for synthesis of polyesters



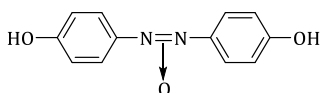
Where R:



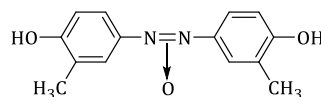
4,4'-Biphenol (BP)



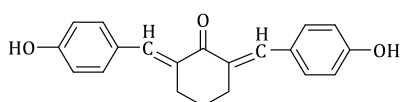
4,4'-Dihydroxyazobenzene (AZ)



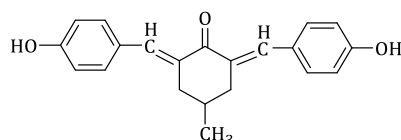
4,4'-Dihydroxyazoxybenzene (AX)



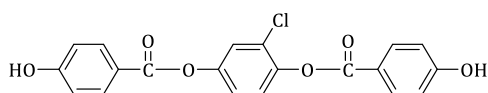
4,4'-Dihydroxy-3,3'-dimethylazoxybenzene (AXM)



2,6-Bis(4-hydroxy benzylidene) cyclohexanone (BC)



2,6-Bis(4-hydroxy benzylidene)-4-methyl cyclohexanone (BM)



Bis (4-hydroxy benzoyl oxy) 2-chloro-1, 4-benzene (BHOC)

Where R1: Fumaroyl chloride and R2: Sebacoyl chloride

### Thermal analysis

DSC analysis of the synthesized polyesters was conducted using Mettler-4000 thermal analyzer and DSC-30 cell. Temperature calibration was made by using Indium-Lead-Zinc standards. All samples were heated from room temperature to 300 °C at a rate of 10 °C/min (first heating cycle) after that sample was heated for 5 min isothermally at same temperature then cooled back to room

temperature at the cooling rate of 10 °C/min (first cooling cycle). After that the same sample was reheated from room temperature to 450 °C at a rate 10 °C/min to evaluate glass transition temperature and melting temperatures of polymers (second heating cycle). Thermal transitions were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. For DSC analysis, 4-9 mg of

sample was weighed. Empty pans were weighed to match within a deviation of  $\pm 0.002$  mg.

#### *Optical polarizing microscopy*

Optical polarizing microscopic study was conducted under the crossed polarized light with Carl Zeiss microscope equipped with hot stage and Leitz 350 hot stage coupled to Leitz Laborlux 12 POLs microscope. Photographs were taken using Leica wild MP SSZ/46 photoautomat system. The polymer grains were held between cover slip and glass plate and heated gradually (5-10 °C) to desire temperature (selected from thermal transitions observed in DSC thermogram). Morphology of thin layer of material, which formed above glass transition and melting temperature, was studied visually during heating as well as cooling with optical polarizing microscope.

### **Results and discussion**

Rigid rod-flexible spacer based thermotropic liquid crystalline polyesters were synthesized by interfacial polymerization methodology and its monomer compositions are presented in Table 1. In these series, seven different types of aromatic rigid diols were used namely 4,4'-biphenol (BP), 4,4'-dihydroxyazobenzene (AZ), 4,4'-dihydroxyazoxybenzene (AX), 4,4'-dihydroxy-3,3'-dimethylazoxybenzene (AXM), 2,6-bis(4-hydroxy benzylidene) cyclohexanone (BC), 2,6-bis(4-hydroxy benzylidene)-4-methyl cyclohexanone (BM), and bis (4-hydroxy benzoyloxy)-2-chloro-1, 4-benzene (BHOC).

#### *Solubility of polyesters*

Solubility study of all synthesized thermotropic liquid crystalline polyesters was checked in organic solvents such as

chloroform, carbon tetrachloride, 1,2-dichloroethane, dichloromethane, tetrahydrofuran, acetone, methanol and phenol/1,1,2,2-tetrachloroethane mixture (60:40, v/v) and are presented in Table 2. Into 10 mL volumetric flask, 20 mg of polymer and 10 mL of desired solvent were added and kept aside for 3 days at ambient temperature with intermittent stirring. To avoid possibility of crosslinking through olefinic double bond of fumaroyl moiety, the solutions were not heated [18]. All these polyesters were insoluble in almost all chlorinated solvents such as chloroform, carbon tetrachloride, dichloromethane and 1,2-dichloroethane and also in acetone and tetrahydrofuran. But all these liquid crystalline polyesters showed solubility in phenol:tetrachloroethane (60:40, v/v) solvent system at 40 °C.

#### *Intrinsic viscosity*

Intrinsic viscosity of the thermotropic liquid crystalline polyesters was determined at a concentration of 0.5 g/dL in phenol:tetrachloroethane (60:40, v/v) using an Ubbelohde viscometer at 40 °C and are presented in Table 2. Polyesters coded as 5BP, 5AX and 4AX showed lower viscosity whereas polyester coded as 5BC and 5BM showed considerable good viscosities such as 0.56 and 0.49 dL/g respectively. It indicates that polyesters prepared from cyclohexanone based diols showed higher viscosity than biphenol and azoxy based diols.

#### *IR spectroscopy*

IR spectral measurements of powder polymer samples embedded in potassium bromide disc were carried out with Shimadzu IR-470 spectrophotometer. The discs were prepared using 1-2 mg of dried sample and 100 mg of spectroscopic grade sieved (200 mesh) potassium bromide.

**Table 1.** Monomer composition for synthesis of LCPs by interfacial polycondensation

Sr. No.	Polymer Code	Aromatic diols		Aliphatic diacid chloride			
		Mole	g	Fumaroyl chloride		Sebacoyl chloride	
				Mole	g	Mole	g
1	1BP			0.002	0.3059	0	0
2	2BP			0.0015	0.2293	0.0005	0.1125
3	3BP	0.002	0.3724	0.001	0.1529	0.001	0.2251
4	4BP			0.0005	0.0764	0.0015	0.3376
5	5BP			0	0	0.002	0.4502
6	1AZ			0.002	0.3059	0	0
7	2AZ			0.0015	0.2293	0.0005	0.1125
8	3AZ	0.002	0.4284	0.001	0.1529	0.001	0.2251
9	4AZ			0.0005	0.0764	0.0015	0.3376
10	5AZ			0	0	0.002	0.4502
11	1AX			0.002	0.3059	0	0
12	2AX			0.0015	0.2293	0.0005	0.1125
13	3AX	0.002	0.4604	0.001	0.1529	0.001	0.2251
14	4AX			0.0005	0.0764	0.0015	0.3376
15	5AX			0	0	0.002	0.4502
16	1AXM			0.002	0.3059	0	0
17	2AXM			0.0015	0.2293	0.0005	0.1125
18	3AXM	0.002	0.5165	0.001	0.1529	0.001	0.2251
19	4AXM			0.0005	0.0764	0.0015	0.3376
20	5AXM			0	0	0.002	0.4502
21	1BC			0.002	0.3059	0	0
22	2BC			0.0015	0.2293	0.0005	0.1125
23	3BC	0.002	0.6122	0.001	0.1529	0.001	0.2251
24	4BC			0.0005	0.0764	0.0015	0.3376
25	5BC			0	0	0.002	0.4502
26	1BM			0.002	0.3059	0	0
27	2BM			0.0015	0.2293	0.0005	0.1125
28	3BM	0.002	0.6407	0.001	0.1529	0.001	0.2251
29	4BM			0.0005	0.0764	0.0015	0.3376
30	5BM			0	0	0.002	0.4502
31	1 BHOC			0.002	0.3059	0	0
32	2BHOC			0.0015	0.2293	0.0005	0.1125
33	3 BHOC	0.002	0.7735	0.001	0.1529	0.001	0.2251
34	4 BHOC			0.0005	0.0764	0.0015	0.3376
35	5 BHOC			0	0	0.002	0.4502

**Table 2.** Solubility and viscosity data of polyesters

Polyester	a	b	c	d	e	f	g	h	Viscosity* (dL/g)
5BP	x	x	x	x	x	x	x	√	0.20
5AZ	x	x	x	x	x	x	x	√	---
5AX	x	x	x	x	x	x	x	√	0.07
4AX	x	x	x	x	x	x	x	√	0.12
5AXM	x	x	x	x	x	x	x	√	---
5BC	x	x	x	x	x	x	x	√	0.56
5BM	x	x	x	x	x	x	x	√	0.49

Where, a: chloroform, b: carbon tetrachloride, c: 1,2-dichloroethane, d: dichloromethane, e: tetrahydrofuron, f: acetone, g: methanol, h: phenol:tetrachloroethane (60:40);

\* intrinsic viscosity determined in phenol:tetrachloroethane (60:40, v/v) at 40 °C

IR spectra of rigid diol BP, homopolyester (1BP) based on 4,4'-dihydroxy biphenyl (BP) with 100% fumaroyl chloride (unsaturated rigid aliphatic spacer) and homopolyester (5BP) based on 4,4'-dihydroxy biphenyl (BP) with 100% sebacoyl chloride (saturated flexible spacer) are depicted in Figure 1.

IR spectrum of biphenol (BP) showed characteristic peaks at 3500-3600  $\text{cm}^{-1}$  (primary O-H stretching), 2900-3000  $\text{cm}^{-1}$  (C-H stretching), 1600  $\text{cm}^{-1}$  (aromatic C=C stretching), 1200  $\text{cm}^{-1}$  (C-O-C stretching), and 800  $\text{cm}^{-1}$  (1,4-disubstitution). IR spectrum of homopolyester (1BP) prepared from biphenol and 100% fumaroyl chloride exhibited characteristic peaks at 3400-3500  $\text{cm}^{-1}$  (O-H stretching), 2900-3000  $\text{cm}^{-1}$  (C-H stretching), 1730-1760  $\text{cm}^{-1}$  (ester carbonyl), 1220  $\text{cm}^{-1}$  (O-H bending, phenolic), 1100-1150  $\text{cm}^{-1}$  (C-O-C stretching), 900-1000  $\text{cm}^{-1}$  (C=C bending) and 720  $\text{cm}^{-1}$  (long chain). IR spectrum of homopolyester (5BP) prepared from biphenol and 100% sebacoyl chloride displayed characteristic peaks at 3400-3500  $\text{cm}^{-1}$  (O-H stretching), 2900-3000  $\text{cm}^{-1}$  (C-H stretching), 1730-1760  $\text{cm}^{-1}$  (ester carbonyl), 1220  $\text{cm}^{-1}$  (O-H bending, phenolic), 1100-1150  $\text{cm}^{-1}$  (C-O-C stretching) and 720  $\text{cm}^{-1}$  (long chain).

Copolyesters prepared within series using rigid diols, unsaturated rigid aliphatic spacer and flexible aliphatic spacers differ only in composition relative to the mole fraction of rigid aliphatic spacer to flexible aliphatic spacer. It shows almost identical overall IR spectra but differs in the intensity of characteristic peaks. Major difference between the rigid and flexible spacer is unsaturated double bond present in fumaroyl chloride appeared at 900  $\text{cm}^{-1}$  to 1000  $\text{cm}^{-1}$ . Spectroscopic data obtained was in good agreement with the proposed structure [10, 19].

#### *Thermal analysis*

Thermal analysis data measured by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) are

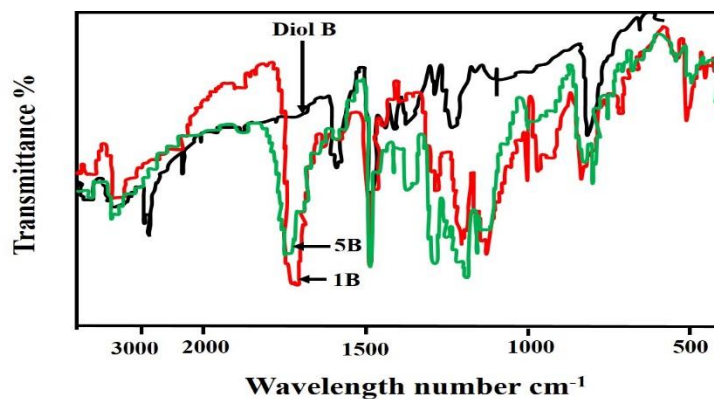
presented in Table 3 and discussion about behaviors of individual series is as follows.

#### *DSC analysis of BP series*

Thermal properties of the thermotropic liquid crystalline polyesters were determined using the DSC analysis. The results are presented in Table 3. DSC thermograms of the liquid crystalline polyesters of 1BP and 5BP are depicted in Figure 2. The homopolyester 1BP, no change in baseline was observed till 250 °C. It showed two transitions at 270 °C and >300 °C which corresponds to glass transition temperature and decomposition respectively. No exotherm was observed in the first cooling cycle. It indicates that mesophasic phase was not formed, thus, it did not show any characteristics of liquid crystalline phase. DSC thermogram of 1BP is depicted in Figure 2a. Copolyester 2BP, exhibited two transition temperatures at 260 °C and >300 °C which corresponds to glass transition temperature and decomposition respectively and was not showing any characteristics of liquid crystalline phase. Copolyester 3BP also displayed two transition temperatures particularly at 210 °C and >300 °C, which correspond to glass transition temperature and decomposition respectively. This copolyester also did not show any characteristics of mesophase formation. Copolyester 4BP also allowed two transition temperatures particularly at 170 °C and >300 °C which corresponds to glass transition temperature and decomposition respectively. The copolyester 5BP revealed two transitions at 115 °C and 185 °C which correspond to glass transition temperature and melting temperature respectively. This copolyester showed liquid crystalline phase in the range of 220-260 °C. The copolyester 5BP expressed two endothermic transitions in the first heating cycle and these were retained in the second heating. On cooling, two exotherms were observed at 166 °C and 106 °C. DSC thermogram of 5BP is depicted in Figure 2b. Typical polarizing optical micrograph of 5BP at 246 °C

during heating depicted in Figure 3 and showed smectic batonnet texture.

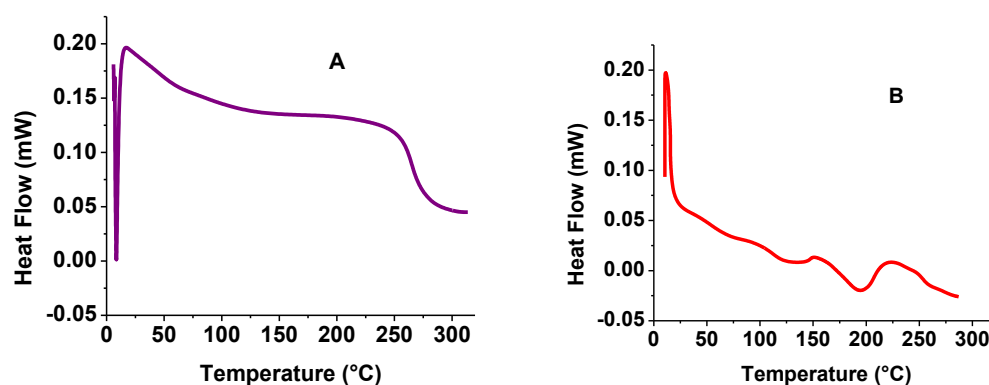
**Figure 1.** Superimposed Infra-red spectra of 1BP, 5BP and diol BP where 1B: 1BP, 5B: 5BP and B: BP



**Table 3.** Thermal properties of polyesters observed by DSC

Polymer code	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)	LC phase (°C)
1BP	270	>300 d	--
2BP	260	>300	--
3BP	210	>300 d	--
4BP	170	>300 d	--
5BP	115	185	220-260
1AZ	--	145	--
2AZ	161	208	210-236
3AZ	129	142, 158	209-250
4AZ	145	177, 201	194-265
5AZ	--	178, 207	190-246
1AX	--	143	--
2AX	--	140, 164	219-250
3AX	--	134, 150	200-255
4AX	145	156	190-265
5AX	--	143, 168	190-260
1AXM	--	--	--
2AXM	129	143	--
3AXM	133	143	145-175
4AXM	155	180	154-186
5AXM	118	143	130-150
1BC	--	200	--
2BC	--	150	--
3BC	48	128, 230	--
4BC	115	181	--
5BC	134	107, 146	170-196
1BM	--	115	--
2BM	--	144	--
3BM	--	130	--
4BM	134	146	--
5BM	--	124, 182	170-185
1 BHOC	--	145, 163, 174	--
2BHOC	--	335	--
3 BHOC	--	144, 250	--
4 BHOC	--	132	--
5 BHOC	--	206	216-285





**Figure 2.** A) DSC thermogram of 1BP during first heating; B) DSC thermogram of 5BP during first heating

**Figure 3.** Optical polarizing micrograph of 5BP showing Smectic batonnet texture at 246 °C during heating (Magnification 20X)



In general, DSC study of liquid crystalline polyesters based on BP diol with aliphatic diacid chlorides showed decrease in glass transition temperature with increase in sebacoyl chloride content. This trend is attributed to the content of fumaroyl chloride in polyester backbone. Basically fumaroyl chloride contains unsaturated double bond and this double bond forms continuous polarization with rigid diol BP *i. e.*,  $\pi$ - $\pi$  bond orientation which makes the entire structure more ordered. In case of homopolyester prepared from sebacoyl chloride with rigid diol BP (5BP), mesomorphic phase was observed in the range of 220-260 °C, because polyester content sebacoyl chloride forms more flexible structure [20-24]. Basic

requirement of the formation of mesophase in thermotropic liquid crystalline polymers is presence of rigid rod-flexible spacer system and sebacoyl chloride containing polyester follow the perfectly rigid rod – flexible spacer system.

#### *DSC analysis of AZ series*

The homopolyester, 1AZ, showed only one transition at 145 °C corresponds to melting transition temperature. No exotherm was observed in the first cooling cycle. It indicates that there is no formation of mesophasic phase, thus, it did not show any characteristics of liquid crystalline phase. The copolyester, 2AZ, manifested two transitions at 161 °C and 208 °C which correspond to glass and melting

transition temperatures. This copolyester exhibited liquid crystalline phase in the range of 210-236 °C. Typical polarizing optical micrograph of 2AZ during heating depicted in Figure 4 and it displayed smectic focal conic texture at 224 °C. Similarly, copolyester 3AZ showed three transitions at 129 °C, 142 °C and 158 °C. Glass transition temperature appears at 129 °C whereas two melting transition temperatures show at 142 °C and 158 °C. This copolyester allowed liquid crystalline phase in the range of 209-250 °C. Similarly, copolyester 4AZ showed three transitions at 145 °C, 177 °C and 201 °C. Glass transition temperature was appeared at 145 °C whereas two melting transition temperatures were observed at 142 °C and 158 °C. This copolyester showed liquid crystalline phase in the range of 194-265 °C. Copolyester 5AZ did not show glass transition temperature whereas it exhibited two melting peaks at 178 °C and 207 °C. It also showed the mesomorphic in the range of 190-246 °C.

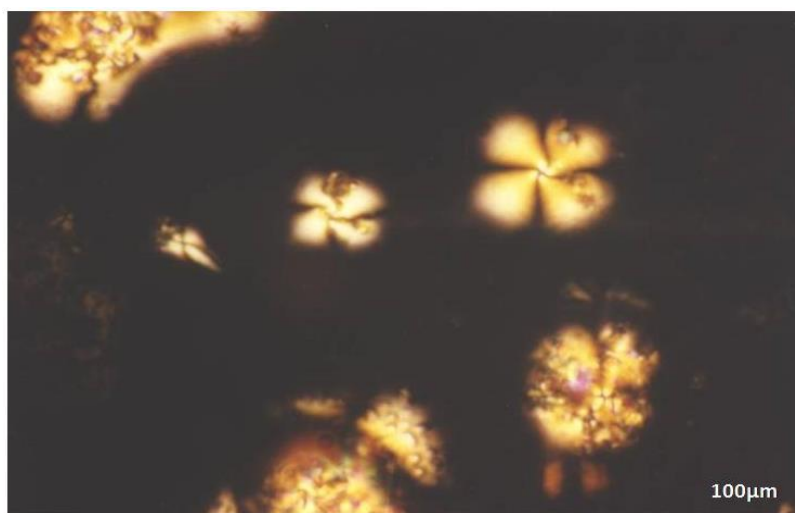
Almost all the polyesters of this series display glass transitions and melting transitions as well as two exotherms during cooling indicates that the samples maintain crystallinity even in cooling cycle. Mesomorphism was observed almost in all polyester samples namely 2AZ, 3AZ, 4AZ and 5AZ (except 1AZ) [25-28]. This series reveals that homopolyesters prepared by using fumaroyl chloride is non-

liquid crystalline while others are liquid crystalline.

#### *DSC analysis of AX series*

DSC data for the series of polyesters based on 4,4'-dihydroxyazoxybenzene (AX) is presented in Table 3. Homopolyester 1AX displayed melting transition at 143°C; however, in the corresponding cooling cycle no exotherm was noted. It demonstrates that no mesophasic phase formation takes place, thus, it did not show any characteristics of liquid crystalline phase. Copolyester 2AX allowed two transitions of melting at 140 °C and 164 °C. On cooling, large exothermic peak extending from 150-50 °C was recorded. On second heating it showed liquid crystalline phase in the range of 219-250 °C. Copolyester 3AX exhibited two melting transitions at 142 °C and 158 °C while on cooling exotherm was observed in the range of 160-170 °C. On second heating it manifested liquid crystalline phase in the range of 209-250 °C. The glass transition at 145 °C was observed in copolyester 4AX followed by melting transition at 156 °C. On second heating it revealed liquid crystalline phase in the range of 190-265 °C. The copolyester 5AX showed two transitions at 143 °C and 168 °C. On cooling, two exotherms were observed at 160 °C and 120 °C. On second heating it allowed liquid crystalline phase in the range of 190-260 °C.

**Figure 4.** Optical polarizing micrograph of 2AZ at 224 °C during heating (Magnification 32X)

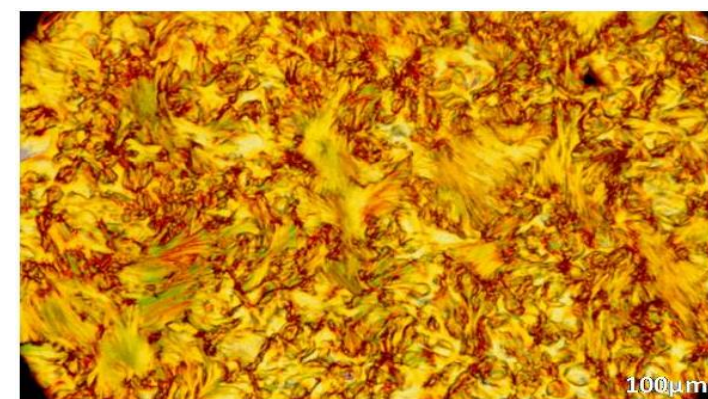


Mesomorphism was observed in homopolyester 5AX and was also marked in copolyesters 2AX, 3AX and 4AX. This series retained liquid crystallinity till incorporation of 75% of unsaturated fumaroyl chloride spacer with respect to sebacoyl chloride. This AX diol has been extensively studied earlier in the synthesis of thermotropic liquid crystalline polyesters [29-33]. Asrar *et al.* [34] discussed the structure-property relationship between replacements of central azo or azoxy as bridging group in mesogen along with other substituent at different positions. Azoxy polyesters were found to have higher transition temperature compared with their azo analogue. Polyester synthesized in present study reveals greatest tolerance towards stabilization of liquid crystalline phase even after incorporation of high mole ratio of rigid aliphatic spacer.

#### *DSC analysis of AXM series*

In the all polyesters of AXM series, no particular trend was observed. Mesomorphism was perceived in copolyesters when fumaroyl chloride content below 50% with respect to sebacoyl chloride. Thermotropic liquid crystallinity is observable over a wide temperature range in polyesters with azoxybenzene moiety in the main chain. AXM series showed lower liquid crystalline phase transition temperatures than AX series due to methyl substitution [16, 35, 36].

**Figure 5.** Optical polarizing micrograph of 5BC at 191 °C during heating (Magnification 10X)



#### *DSC of BC series*

BC copolyester series shows decreasing order in melting temperatures ( $T_m$ ) except 4BC. In general, glass transition temperature decreases with increase in content of flexible spacer (sebacoyl chloride). Copolyesters 1BC, 2BC, 3BC and 4BC manifested melting transitions at 200, 150, 128 and 181 °C, respectively, whereas homopolyester 5BC displayed two melting transitions at 107 °C and 146 °C. In addition to that it showed liquid crystalline phase in the temperature range of 170-196 °C. Homopolyester 5BC marked two transitions as mentioned above and were retained in the second heating cycle. On cooling, exotherm was observed at 102 °C.

During heating BC polyesters appear to be easily cured which prevents flow and formation of liquid crystalline phase. High performance polymers and photo crosslinkable liquid crystalline polymers prepared by using diols applied in electro optical devices were already known [37-39]. Alternatively, the mesogen may be highly extended due to fumaroyl unit, which leads to highly rigid non-melting polyester. Typical polarizing optical micrograph of 5BC (during heating) depicted in Figure 5 and shows marble texture at 191 °C.

#### *DSC of BM series*

BM copolyester series did not show glass transition temperatures except 4BM and also did not demonstrate any definite trend in melting temperature.



Homopolyester 5BM displayed two melting transitions at 124 °C and 182 °C. In addition, it revealed short liquid crystalline phase at the temperature ranging from 170 to 185 °C.

Even in the absence of fumaroyl chloride, for 5BM and 5BC, crosslinking took place during heat treatment while observing mesomorphism. To overcome this drawback, we use to keep hot stage at predetermined temperatures and checked the samples. After many trials we were successful in observing the liquid crystalline temperature range for said polyesters. This result itself indicates that apart from fumaroyl chloride's double bond, the double bonds present in diol itself play a role in crosslinking mechanism. Methyl substitution to bis(benzylidene) cyclohexanone diol did not play the significant change in behavior of homo and copolyesters as observed from BM series.

#### *DSC analysis of BHOC series*

BHOC polyester series did not reveal any glass transition temperature but it showed melting transitions. The homopolyester 1BHOC allowed three melting transitions at 145, 163 °C and 174 °C whereas copolyester 2BHOC showed only one melting transition at 335 °C, which could be decomposition. On the contrary, copolyester 3BHOC exhibited two melting transitions at 144 °C and 250 °C whereas copolyester 4BHOC showed only one melting transition at 132 °C. Copolyester 5BHOC displayed glass transition temperature at 206

°C. It allows liquid crystalline phase in the temperature range of 216-285 °C. Homopolyester 5BC marked two transitions as mentioned above and were retained in the second heating cycle. On cooling, exotherm was observed at 102 °C. Schlieren nematic texture collected from optical polarizing micrograph of 5BHOC during heating at 227 °C (Figure 6).

To summaries, total seven rigid diols were used for the synthesis of homo and copolyesters in which fumaroyl chloride was used as rigid aliphatic spacer whereas sebacoyl chloride was utilized as flexible aliphatic spacer. In the present research study, total 35 polyesters were synthesized by interfacial polymerization method and out of that fifteen polyesters show liquid crystalline phase. Copolyester series based on AZ and AX showed almost two melting transitions whereas rest of the polyesters showed mostly only one melting transition. Comparative study of aromatic rigid diols with respect to liquid crystalline nature indicates that azoxy based copolyester systems containing sebacoyl chloride (AX, AZ and AXM) manifests liquid crystalline phase.

It is interesting to note that copolyester 5BP shows smectic batonnet texture at 246 °C whereas copolyester 2AZ allows smectic focal conic texture at 224 °C. Copolyester (5BC) derived from cyclohexanone exhibits marvelous marble texture at 191 °C whereas 5BHOC displays normal schlieren nematic texture at 227 °C.

**Figure 6.** Optical polarizing micrograph of 5BHOC at 227 °C during heating (Magnification 10X)



## Conclusion

The incorporation of flexible aliphatic sebacoyl spacer partially into the rigid fumaroyl aliphatic spacer upto 75% did not form mesophasic character of the polyester based on 4,4'-dihydroxy biphenyl. BP diol showed liquid crystallinity when 100% of flexible sebacoyl chloride is present in the main chain. The effect of rigid and flexible spacer also depends on the type of mesogenic moiety along the main chain. In corporation of fumaroyl chloride into the aromatic rigid main chain did not show liquid crystallinity. It might be due to the extended  $\pi - \pi$  orientation along the main chain, as it formed more rigid structure. To observe liquid crystalline phase in thermotropic system, rigid-flexible system is essential. Thus, almost all the homopolyesters prepared from the sebacoyl chloride with rigid aromatic diols displayed liquid crystalline phase. From the thermotropic liquid crystal point of view, azo and azoxy systems showed better bridging groups for the formation of liquid crystalline phase.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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