

Thermotropic liquid crystalline polyesters derived from bis-(4-hydroxybenzoyloxy)-2-methyl-1,4-benzene and aliphatic dicarboxylic acid chlorides

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Abstract. A series of thermotropic liquid crystalline polyesters derived from bis-(4-hydroxybenzoyloxy)-2-methyl-1,4-benzene (BHBOMB) and aliphatic dicarboxylic acid chlorides were investigated. All these polyesters were synthesized by interfacial polycondensation method and characterized by differential scanning calorimetry and wide-angle X-ray diffractometer. These polyesters consist of BHBOMB as a mesogenic diol and aliphatic diacid chlorides were used as flexible spacers. The length of oligomethylene units in polymer was varied from the trimethylene to the dodecamethylene groups. The transition temperatures and thermodynamic properties were studied for all these polymers. All these polyesters were soluble in chlorinated solvents such as chloroform, dichloromethane, dichloroethane, etc. More importantly, all these polyesters exhibited very large mesophase stability.

Keywords. Liquid crystalline polyesters; thermotropic; interfacial polycondensation; rigid diol; dicarboxylic acid chloride.

1. Introduction

In the recent past, a branch of polymer chemistry, i.e., synthesis of liquid crystalline polymers (LCPs) has received more attention. LCPs are broadly divided into two main classes, namely thermotropic (TLCPs) and lyotropic (LLCPs) depending on the phenomena of formation of liquid crystalline phase. LLCPs exhibit liquid crystallinity in the solution, whereas TLCPs show liquid crystallinity in the melt.^{1,2} Researchers concentrate on modifying the structure and properties of liquid crystalline aromatic polymers.^{3–5} The thermotropic liquid crystalline behaviour of polymers is of strong interest among polymer scientists, because of their outstanding thermal and chemical resistance, high strength as well as low linear viscosity in liquid crystalline state.^{6–13} Particularly, these high-performance liquid crystalline aromatic polyesters have found wide range of applications in the variety of fields, such as, transportation industry, construction industry, food containers as well as electric and electronic industry and other applications, requiring chemical inertness and high strength.¹⁴ Due to low relative dielectric constants and low dissipation factors, these types of polyesters are specifically attractive for microwave frequency electronics.¹⁵ Broadly, TLCPs constitute from two different structural moieties: flexible and

rigid. Flexible aliphatic spacer groups are used to insulate the intramolecular interaction in the liquid crystalline portion, whereas rigid moiety incorporated in main chain as mesogen to exhibit liquid crystalline phase. In particular, flexible spacers are introduced into the polymer backbone to reduce the transition temperature as well as to improve processability.

In TLCPs the substituent effects are of special interest, as crystal–liquid crystal transition temperature of fully extended rigid rod polymers are extremely high. It is desirable to lower the crystal–liquid crystal temperature from the processing point of view. The effect of alkyl substitution on their glass transition temperature, melting temperature, melting points and thermal stabilities is discussed in detail somewhere.¹⁶ They also studied polymer with alkyl substitution more than eight carbon atoms and observed that longer alkyl substitution does not form a liquid crystalline phase. The effect of alkyl substitution on azoxy-based thermotropic liquid crystalline-ordered polyesters was examined and observed considerable decrease in the crystal–liquid crystal transition temperature.¹⁷

Several strategies have been used to decrease the liquid crystalline phase transition temperature. Substitution on mesogenic segment is one of the methodologies used for this purpose. As melting temperature of fully extended rigid rod polymers is very high, thus, majority of such polymers degrade before its isotropization temperature.

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Substitution lowers phase transition temperature substantially due to decrease in aspect ratio of rigid block. It is desirable to lower the melting temperature for processing through conventional methods. This could be accomplished by introducing substituent on the mesogenic unit of the polymer.¹⁸

The mesogen is referred as rigid moiety in liquid crystalline molecule. It is rod-like structure composed of two or more aromatic rings connected in one direction. Rigid part aligns molecule in one direction, whereas flexible part induces fluidity in the liquid crystal. Transition temperatures of mesomorphic polymers have been enhanced by an increase in the number of aromatic rings in the main chain.¹⁹ However, the presence of large number of aromatic rings results in non-melting polymers. Crystal-liquid crystal, liquid crystal-isotropic transition temperature and mesophase stability of these LCPs are higher. In the solution polycondensation method, mesogen and acid chloride lie in same phase, whereas in the interfacial polycondensation technique, acid chloride introduces in organic phase and diol is added into the aqueous phase and form two immiscible phases, and both phases were mixed together by introducing phase transfer catalyst. Polymerization conditions affect the polymer properties such as molecular weight, polydispersity and crystallinity.²⁰

In the present study, we report the synthesis and characterization of thermotropic LCPs prepared from bis-(4-hydroxybenzoyloxy)-2-methyl-1,4-benzene (BHBOMB) mesogenic moiety and diacid chloride is used as flexible spacer to dissociate the disorder of the main chain from the greater order of mesogenic group and decouple the motion of mesogenic moiety from polymer backbone. Flexible spacers such as glutaryl, adipoyl, pimeloyl, suberoyl, azeloyl, sebacoyl and decanedioyl chlorides have been used to separate mesogenic group in the main chain from each other. In this article, the thermal transition temperatures, liquid crystallinity and crystallinity of the mesophasic polymers are also described.

2. Experimental

2.1 Materials

Briefly, 2-methyl hydroquinone and 4-hydroxybenzoic acid were purchased from Aldrich and purified by recrystallization from acetone and hot distilled water, respectively. Acetic anhydride, dichloromethane, methanol,

pyridine, chloroform and potassium hydroxide were procured from Merck and used as-received. All acids used for synthesis of acid chlorides were purchased from Aldrich and used without purification.

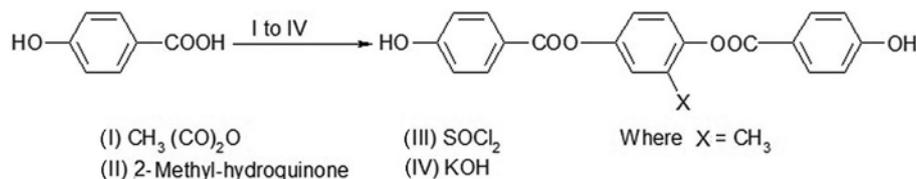
2.2 Synthesis of BHBOMB

Trimesogenic diol BHBOMB was synthesized using *p*-hydroxybenzoic acid as starting material and 2-methyl hydroquinone as central moiety.²¹ The synthesis route of BHBOMB is depicted in scheme 1. The detailed procedure is as follows.

2.2a Synthesis of 4-acetoxybenzoic acid [4-ACBA]: 4-Hydroxybenzoic acid, 13.81 g (0.1 mol) and 250 ml distilled water were added in 500 ml beaker and stirred to make uniform slurry. Into another beaker, 4.4 g of sodium hydroxide (0.11 mol) was dissolved in 50 ml distilled water, added to the slurry, and stirred to dissolve 4-hydroxybenzoic acid as to form sodium salt. Distilled acetic anhydride, 11.23 g (0.11 mol) was then added and stirred for 4 h at room temperature to obtain a precipitate of 4-acetoxybenzoic acid. The precipitate was filtered, washed several times with cold dilute hydrochloric acid and distilled water. The crude product was recrystallized from methanol and dried under reduced pressure. Yield: 80%. Melting point: 190°C (observed); 190–192°C (reported).²¹ IR (KBr, cm^{-1}): 1730 (C=O). ¹H NMR (400 MHz, DMSO- d_6): δ 8.00 [2H, d], 7.30 [2H, d], 2.30 [3H, s], 10.10 [1H, s].

2.2b Synthesis of 4-acetoxybenzoyl chloride: 4-Acetoxybenzoic acid, 9.0 g (0.05 mol), was charged into a single-necked 100 ml round bottom flask. Thionyl chloride, 5 ml (0.07 mol), was added drop wise to the reaction flask and reaction mixture refluxed gently for 8 h. The initial heterogeneous mass homogenized to give a yellowish fluid. Excess thionyl chloride was removed by normal distillation. The crude acid chloride was purified by double distillation under reduced pressure to get colourless liquid. Yield: 90%. Melting point: 29–30°C (observed); 29–30°C (reported).²¹ IR (KBr, cm^{-1}): 1780 (COCl), 1730 (C=O) and 1370 (–CH, bending). ¹H NMR (400 MHz, CDCl_3): δ 2.1 [3H, s], 7.1 [2H, d] and 8.0 [2H, d].

2.2c Synthesis of bis-(4-acetoxybenzoyloxy)-2-methyl-1,4-benzene: 2-Methyl hydroquinone (4.4 g, 0.04 mol)



Scheme 1. Synthesis of bis-(4-hydroxybenzoyloxy)-2-methyl-1,4-benzene (BHBOMB) mesogen.

and 25 ml pyridine (0.3 mol) were charged into 500 ml three-necked round bottom flask equipped with magnetic stirrer, nitrogen inlet and calcium chloride guard tube. Into another flask, 23.82 g of 4-acetoxybenzoyl chloride (0.12 mol) and 300 ml of dry 1,2-dichloroethane were taken. The acid chloride solution was added to the 2-methyl-hydroquinone solution. This reaction mixture was stirred under nitrogen blanket for 48 h at room temperature. The reaction mixture was then washed sequentially with 5% sodium carbonate solution, 5% hydrochloric acid and distilled water. 1,2-Dichloroethane layer was evaporated to dryness on rotavapor. Crude product was recrystallized from chloroform/petroleum ether (60:80) solvent mixture. The product was filtered and dried in vacuum oven at 80°C for 4 h. Yield: 90%. Melting point: 108°C (observed);⁶ IR (KBr, cm⁻¹): 1720 (C=O stretching) and 820 (C-CH₃). ¹H NMR (400 MHz, CDCl₃): δ 2.2 (3H, s), 2.3 (6H, s), 7.4 (8H, d) and 8.4 (3H, d).

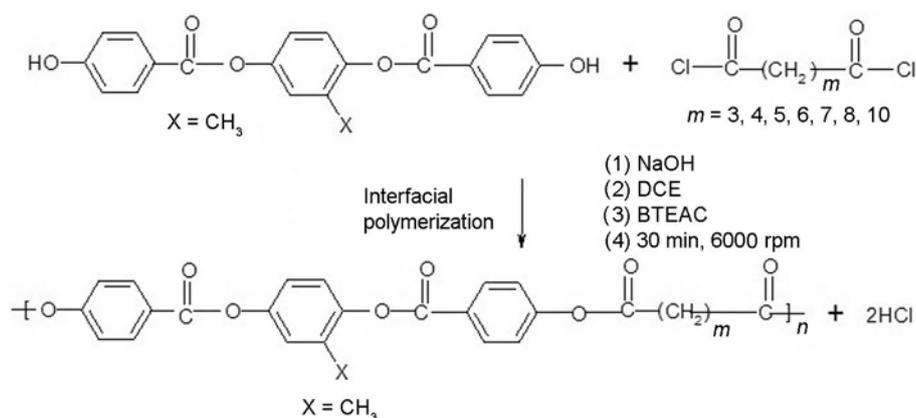
2.2d Synthesis of BHBOMB: Potassium hydroxide (1.32 g, 0.02 mol) and 100 ml methanol were charged into 250 ml single-necked round bottom flask equipped with magnetic stirrer and kept in ice bath and stirred till it dissolved completely. Alcoholic potassium hydroxide solution was cooled to 0–5°C. Into reaction flask, 4.34 g (0.01 mol) of bis-(4-acetoxybenzoyloxy)-2-methyl-1,4-benzene was added and stirred at 0–5°C for 4 h. Reaction mixture was acidified with 4 N hydrochloric acid. Methanol was removed under reduced pressure. The crude product was dissolved in 400 ml ethyl acetate and solution washed three times with distilled water. Ethyl acetate was distilled off and the solid was extracted with chloroform. Distilled off the chloroform to get purified product. The solid crude product was washed with methanol and dried in vacuum oven at 80°C for 4 h. Yield: 75%. Melting point: 280 ± 1°C (observed); 280°C (reported).⁶ IR (KBr, cm⁻¹): 3390 (–OH stretching), 1700 (C=O) and 820

(C-CH₃). ¹H NMR (400 MHz, DMSO₆): δ 2.2 (3H, s), 6.9 (4H, d), 7.2 (3H, s) and 8.0 (4H, dd) and 10.6 (2H, s).

2.2e Preparation of aliphatic diacid chlorides: Glutaryl chloride, adipoyl chloride, pimeloyl chloride, suberoyl chloride, azeloyl chloride, sebacoyl chloride and dodecanedioyl chloride were synthesized from the parent diacids using thionyl chloride. The aliphatic diacids were gently refluxed with thionyl chloride at 80°C for 4 h to get clear solution. This acid chloride solution was initially distilled with lower reduced pressure (100–150 mmHg) to remove the excess of thionyl chloride and was double distilled under reduced pressure (1–2 mmHg) at 150°C till get colourless product, prior to use.

2.3 Interfacial polycondensation

The combined type polyester was synthesized according to scheme 2. Mole ratios of rigid diol BHBOMB and different aliphatic diacid chlorides for interfacial polycondensation are represented in table 1. BHBOMB (1.4573 g, 0.04 mol), sodium hydroxide (0.008 mol) and benzyl triethyl ammonium chloride (BTEAC) (0.02 g) were charged into two-necked 100 ml round bottom flask equipped with mechanical stirrer, nitrogen inlet, and calcium chloride guard tube, and stirred till it dissolved completely in 15 ml aqueous phase. Into another stoppered flask, organic layer consisting of 0.04 mol of acid chloride in 15 ml dry 1,2-dichloroethane (DCE) was added. The reaction mixture was vigorously stirred using 6000–7000 rpm for 30 min at 0–5°C. The polyester was precipitated by pouring into 500 ml methanol. It was filtered, washed with 5 wt% sodium carbonate solution, dilute hydrochloric acid and distilled water. The soxhlet extraction was carried out with methanol and followed by drying in vacuum oven at 80°C for 8 h.



Scheme 2. Synthesis pathway of polyesters using BHBOMB and aliphatic diacid chlorides.

Table 1. Mole ratio of BHBOMB and aliphatic diacid chlorides for interfacial polycondensation.

Polymer code	BHBOMB		Aliphatic diacid chloride			Polyester (mru ⁻¹)*
	Mole	g	Name	Mole	g	
PE-101	0.04	1.4573	Glutaryl	0.4	0.6760	460.41
PE-102	0.04	1.4573	Adipoyl	0.4	0.7321	474.44
PE-103	0.04	1.4573	Pimeloyl	0.4	0.7882	488.46
PE-104	0.04	1.4573	Suberoyl	0.4	0.8443	502.49
PE-105	0.04	1.4573	Azeloyle	0.4	0.9004	516.52
PE-106	0.04	1.4573	Sebacoyl	0.4	0.9565	530.54
PE-107	0.04	1.4573	Dodecane	0.4	1.0687	558.59

*Mole per repeat unit.

Table 2. Transition and thermodynamic data of BHBOMB polyester synthesized by interfacial polycondensation (first heating cycle).

Polymer code	K–N (°C)	N–I (°C)	ΔT (°C)	ΔH , K–N	ΔH , N–I	K–N	ΔS , N–I	[CH ₂] _n	DOC %
PE-101	208.3	355.2	146.9	9.58	0.28	19.20	0.44	3	54.60
PE-102	186.4	349.5	163.1	3.75	–	8.15	–	4	42.93
PE-103	173.3	327.5	154.2	6.55	1.54	14.67	2.57	5	37.15
PE-104	199.1	325.7	126.6	4.07	4.88	8.62	8.14	6	44.44
PE-105	164.3	289.9	125.6	12.35	5.17	28.23	9.18	7	40.60
PE-106	182.8	291.0	108.2	3.02	7.69	6.63	13.64	8	38.60
PE-107	184.6 ^a	274.4 ^b	89.8	5.92 ^a	6.93 ^b	12.94 ^a	12.65 ^b	10	46.15

K–N (°C): Crystal–liquid crystal transition temperature, N–I (°C): Liquid crystal–isotropic transition temperature, ΔT (°C): Temperature range of metaphase stability, ΔH (K–N) and ΔH (N–I): Enthalpy change in kJ mol⁻¹ of repeat unit (mru), ΔS (K–N) and ΔS (N–I): Entropy change in J mru⁻¹ (K), DOC: Percent degree of crystallinity.

^aCrystal to smectic transition and ^bSmectic to isotropic transition.

2.4 Characterization

Synthesized polyesters were soluble in typical organic solvents such as chloroform, carbon tetrachloride, dichloromethane, dichloroethane, 4-chlorophenol or phenol: tetrachloroethane (50 : 50 v/v) mixture. The thermal behaviour was determined with a Mettler DSC-30 thermal analyser under nitrogen atmosphere. Indium and zinc standards were used to calibrate the DSC temperature and enthalpy scale. The endotherm peak maxima were selected as phase transition temperatures. The enthalpies and entropies of liquid crystalline phase transitions were determined. A Leitz Ortholux polarizing microscope with a Mettler FP-52 hot stage controlled by Mettler FP-5 temperature controller was used for visual examination of phase changes in the polymers. Wide-angle X-ray diffractometer was used to determine the degree of crystallinity at room temperature. Inherent viscosities were determined with 0.5% solution in chloroform at 30°C.

3. Results and discussion

3.1 General properties

The transition temperatures and thermodynamic properties are presented in tables 2 and 3. These polymers were

soluble in all chlorinated solvents, namely chloroform, dichloromethane, dichloroethane, 4-chlorophenol, phenol: tetrachloroethane (50 : 50, v/v) solvent mixture. Main chain thermotropic liquid crystalline polyesters exhibit complex and sometimes uninterpretable thermograms for crystal–liquid crystal transitions.^{17,22} The factors responsible for such complex thermal behaviour are solid–solid transitions, melting of crystals/recrystallization of new ones, formation in rapid succession and more than one liquid crystalline phase. All polyesters exhibited a rather narrow endothermic transition for the mesophase at the isotropization temperature, which suggests that polydispersity were rather narrow.

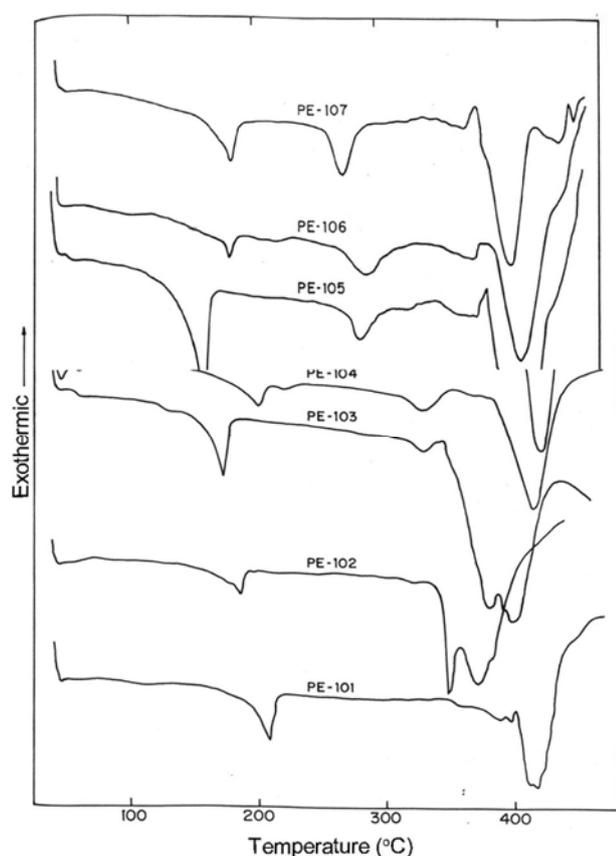
DSC thermograms of first heating cycle of BHBOMB homopolyesters are presented in figure 1, whereas DSC thermograms of second heating cycle of BHBOMB homopolyesters are depicted in figure 2. The melting endotherms were pleasingly simple (unstructured). In general, the nature of thermograms of first and second heating cycles is almost similar, when compared, respectively. Transition temperatures of second heating cycles are slightly higher than first heating cycle. This is due to annealing of crystals in crystal to liquid crystal transition as well as liquid crystal to isotropic. Mesophase stability was also higher in second heating cycle compare to first heating cycle. The polyesters synthesized are well

Table 3. Transition and thermodynamic data of BHBOMB polyester synthesized by interfacial polycondensation (second heating cycle).

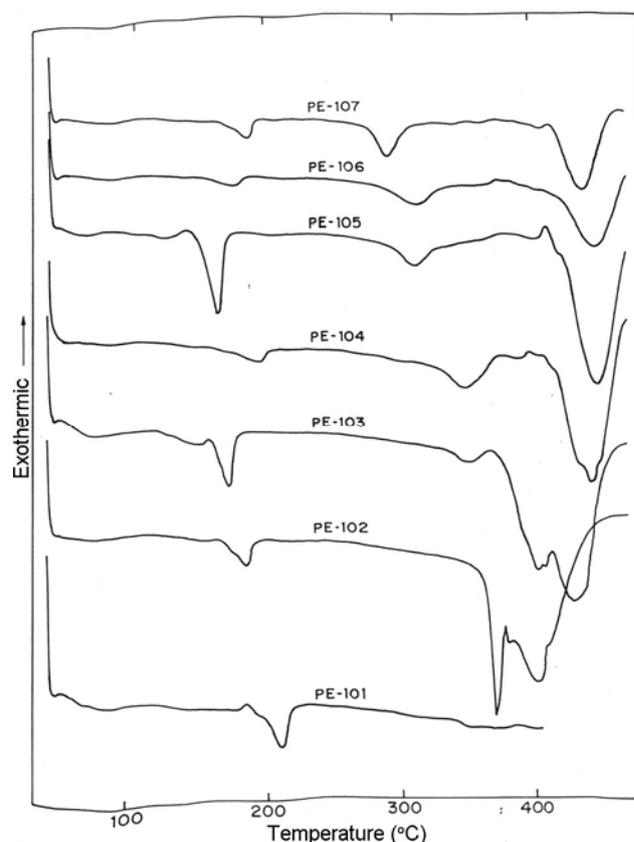
Polymer code	K-N (°C)	N-I (°C)	ΔT (°C)	ΔH , K-N	ΔH , N-I	ΔS , K-N	ΔS , N-I	$[\text{CH}_2]_n$	IV
PE-101	210.6	350.3	139.7	4.42	1.24	11.43	1.99	3	0.97
PE-102	186.3	369.5	183.2	3.84	—	8.37	—	4	0.93
PE-103	173.3	351.4	178.1	3.81	1.66	8.54	2.66	5	1.46
PE-104	195.5	349.5	154.0	2.71	7.24	5.79	11.62	6	1.10
PE-105	164.1	311.0	146.9	8.73	5.68	19.97	8.70	7	1.03
PE-106	177.2	312.9	135.7	2.86	6.74	6.36	11.50	8	0.98
PE-107	188.2 ^a	294.6 ^b	106.4	6.31 ^a	8.94 ^b	8.24 ^a	15.75 ^b	10	1.05

K-N (°C): Crystal–liquid crystal transition temperature, N-I (°C): Liquid crystal–isotropic transition temperature, ΔT (°C): Temperature range of metaphase stability, ΔH (K–N) and ΔH (N–I): Enthalpy change in kJ mol^{-1} of repeat unit (mru), ΔS (K–N) and ΔS (N–I): Entropy change in $\text{J mru}^{-1} (\text{K})$, IV: Intrinsic viscosity (at 30°C in CHCl_3).

^aCrystal to smectic transition and ^bSmectic to isotropic transition.

**Figure 1.** DSC thermograms of first heating cycle of BHBOMB homopolyesters.

chemically ordered. A broadening of isotropic transition would be expected for polydisperse samples, as indeed observed for the polyesters based on unsubstituted trimesogen, wherein insolubility intervened. The peak maxima was selected to make comparative estimates of structure–property relationship. We were unable to study the transition from isotropic to the liquid crystal state (deisotropization process) as the isotropizations in most samples in this series are rapidly followed by decomposition. It is

**Figure 2.** DSC thermograms of second heating cycle of BHBOMB homopolyesters.

known that deisotropization in main liquid crystalline polyesters exhibit a smaller degree of super cooling. In other words, isotropization is thermodynamically more of an equilibrium (reversible) process, rather than crystal to liquid crystal transition. The crystallization in these polyesters, when cooled at the rate of $10^\circ\text{C min}^{-1}$ from 250°C , showed moderate supercooling of about 50°C .

All polyesters formed a turbid melt showing a strong stir-opalescence up to the isotropization or clearing temperature (T_i). Thin films of polymer melts were examined on

the hot stage of a polarizing microscope for optical textures. Polyesters other than PE-107 showed characteristic features pertaining to the nematic mesophase, i.e., threaded-schlieren texture. Polyesters with longer ($n = 10$) flexible spacers, such as PE-107, showed focal conic texture typical of smectic mesophase prior to the isotropic transition and is depicted in figure 3. Photomicrograph of PE-107 was observed at 152.4°C during cooling cycle. Thus, the longest flexible spacer in this series ($n = 10$) allowed the rigid mesogenic unit to align more readily in two-dimensional layers giving rise to a smectic mesophase.

3.2 Substitution effect

The liquid crystalline behaviour of low-molecular mass liquid crystals with different substituents on mesogenic units has been systematically studied by Gray^{23,24} and others.^{25–27} In general, the influence of substitution is complicated by both steric and polar effects. The steric effect, which leads to a less thermally stable mesophase, may involve in following contribution: (i) a broadening of the mesogenic groups by the substituent and therefore, a decrease in the overall length to diameter ratio; (ii) a decrease in the coplanarity of adjacent mesogenic moieties due to steric interaction between substituents and (iii) a tendency for the substituent to force apart mesogenic groups in neighbouring polymer chains due to spatial requirements. On the other hand, substituent that imparts an increased polarizability and stronger dipolar interaction between the mesogenic groups acquire stronger intermolecular attractions. This leads to higher thermal stabilities for both crystalline and liquid crystalline phases and results in higher crystal–liquid crystal and isotropization temperatures.

In TLCs, the substituent plays an important role to reduce the transition temperature, as crystal–liquid

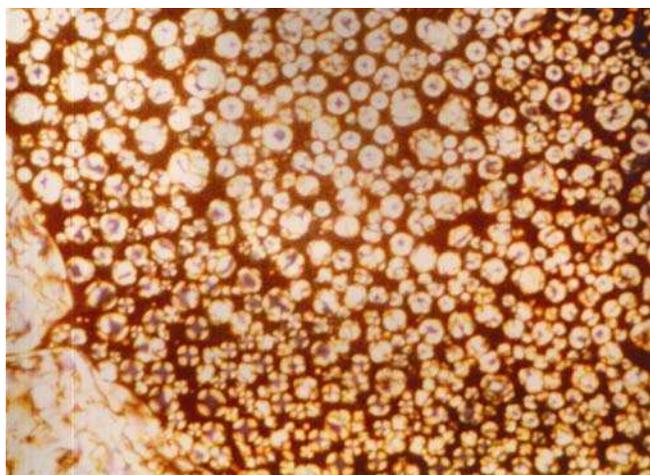


Figure 3. Texture of polyester PE-107 at 152.4°C.

crystal transition temperature of fully extended rigid rod polymers are extremely high. It is desirable to lower the crystal–liquid crystal temperature for processing from liquid crystalline melts. It is apparent that this could be accomplished by introducing substituent into the mesogenic units of the polymer.²⁶ The use of monosubstituted hydroquinone in random copolyesters results in a considerable decrease in the crystal–liquid crystal transition temperature and permit melt spinning from the liquid crystalline states.²⁸

3.3 Thermodynamics of LC states

The transition temperatures, thermodynamic properties as determined by DSC and first heating cycle thermodynamic properties are presented in table 2. In TLCs, the crystal and isotropic transition temperatures are dependent on molecular weight till a critical value is attained. The polyesters of this series were soluble and hence it is believed that these had attained sufficiently high molecular weights to enable a meaningful comparison of the thermal and thermodynamic properties.

In these series, all polyesters display moderate, though not very precise, odd–even fluctuation in the crystal–liquid crystal transition temperatures T_m , relative to methylene unit length except first and last polyesters (PE-101 and PE-107). This odd–even effect seems to suggest that the spacer part of the polymer backbone is largely in its most extended (trans) conformation. In this conformation, even numbered methylene spacers can retain their co-linearity with mesogenic parts, while the odd numbered methylene spacers cannot retain their co-linearity with mesogenic parts. It must be mentioned that the odd–even effect in T_m is not universal in homologous LCPs. The off-equilibrium nature of the crystal to liquid crystal transition can mark this odd–even effect to some extent. The isotropization temperature (T_i) showed more tendency towards a continued decrease rather than an odd–even fluctuation. Unlike liquid, crystal transition of isotropization is a near-equilibrium process. But very often, isotropization reaction occurs at high temperatures with polyesters and risks of concurrent or imminent degradation are not entirely avoidable. The problem of degradation can impair the actual effect in T_i . In the present series, the isotropization temperature decreases continuously with the spacer length.

3.4 Mesophase stability (ΔT)

Mesophase stability ($\Delta T = T_i - T_m$) of polyesters decreases with the increase in methylene units in the flexible spacer. It is due to the dilution of mesogen, indirect reduction in rigidity of polymeric structure. Odd–even effect was also observed in almost all polymers. Even number of methylene units showed higher mesophase stability than

odd number of methylene units. It is due to even number of methylene units allowed trans–trans conformation, whereas odd number of methylene dictates gauche conformation. The mesophase stability of these polyesters were found to be quite high ($> 100^\circ\text{C}$).

3.5 Enthalpy and entropy change

The enthalpy and entropy changes in the first and second heating cycle of polyesters are represented in tables 2 and 3, respectively. These data do not show any clear and regular trend for crystal to liquid crystal (K–LC) or for liquid crystal to isotropic (LC–I) transition in either first or second heating cycle. The enthalpy or entropy data for $n = 3$ –10 indicate a variable degree of supercooling of the nematic to crystal (N–K) transition, i.e., a variable degree of crystallinity in the supercooled sample prior to the second heating cycle. In other words, our attempts to maintain a constant thermal history in all these samples had not been successful.

The enthalpy and entropy change for the liquid crystal to isotropic transition (LC–I) are more or less comparable in both first and second heating cycles. The values of $\Delta H_{\text{K-LC}}$ and $\Delta S_{\text{K-LC}}$ observed in both cycles for all above polyesters discussed are comparable with those found normally in main chain liquid crystalline polyesters. The degradation in polyesters PE-104 to PE-107 generates somewhat elevated values of $\Delta H_{\text{LC-I}}$ and $\Delta S_{\text{LC-I}}$. Such elevated values of $\Delta H_{\text{LC-I}}$ and $\Delta S_{\text{LC-I}}$ are usually typical of transition from highly ordered smectic phase to the isotropic phase. We observed that the presence of smectic phase in PE-107 in which number of methylene units are 10, and hence the high values of $\Delta H_{\text{LC-I}}$ and $\Delta S_{\text{LC-I}}$ are expected in this case, provided the isotropic transition has occurred from the smectic phase. In other polyesters PE-104 to PE-106, textures corresponding only to the nematic phases were observable under hot stage coupled polarizing microscopy. The highest values of $\Delta H_{\text{K-LC}}$ and $\Delta S_{\text{K-LC}}$ point to some conformational ordering in the flexible spacer.

Our conclusion is reinforced when we find that $\Delta H_{\text{LC-I}}$ and $\Delta S_{\text{LC-I}}$ increase monotonously for the odd and even series of nematic polyesters. The increase for $\Delta H_{\text{LC-I}}$ is from 0.27 for $n = 3$ to 7.69 kJ mru⁻¹ for $n = 8$. Similarly, the increase for $\Delta S_{\text{LC-I}}$ is from 0.44 to 13.64 kJ mru⁻¹. The values coated are from the data of the first heating cycle. The increases of odd and even series do not precede with any uniform, average increment of $\Delta H_{\text{LC-I}}$ and $\Delta S_{\text{LC-I}}$ per methylene unit. However, the fact remains that there is significant, but not non-uniform, extension of the flexible spacer in the nematic phase of polyesters PE-104 to PE-106. The population of trans conformers in nematic phase could not be estimated due to lack of knowledge about the respective population of trans/gauche conformers in the pretransition state.

3.6 X-ray diffraction

The degree of crystallinity data from X-ray diffraction are not always concordance with the values of $\Delta H_{\text{K-LC}}$ from DSC data. Bragg's spacing's less than 5 Å that are seen in all polyesters arise mainly from proffered separation in the lateral packing of the polyesters chains. Spacing of 12 Å or higher indicate regularity of packing along the chain. Lateral packing can allow a regular arrangement of molecules along the chain in spite of the randomness arising out of the positional isomerization of the monosubstituent on the central unit of the trimesogen. The degree of crystallinity in one case overlooks any such order along the chain, because we have not been able to harness any reflection below $\Delta = 5^\circ$ due to instrumental limitations. It is likely that the crystallinity arising out of this order could have contributed to higher values of $\Delta H_{\text{K-LC}}$ for PE-103 and PE-105 with $n = 5$ and 7, respectively.

4. Conclusion

A series of new combined type liquid crystalline polyesters consisting of BHBOMB mesogen by varying length of flexible spacers have been successfully synthesized and characterized. These polyesters exhibit very large mesophasic stability ($> 100^\circ\text{C}$). The experimental data show that endotherms are rather sharp, indicating narrow molecular weight distribution. The polyesters display moderate odd–even fluctuation in liquid crystal transition temperature with the increase in flexible spacer length, while no such effect is observed for the isotropization temperatures. The mesophase stability ($\Delta T = T_i - T_m$) decreases regularly with the increase in methylene units. Also, degree of crystallinity decreases with the increase in molecular weights. However, no clear trends were observed for enthalpy and entropy changes with respect to spacer length for either liquid crystal or liquid crystal to isotropic transition due to inability to maintain constant thermal history in all samples. Interestingly, these values are depressed by unsymmetrical monomethyl substitution on the mesogenic core and points to greater disorder induced by the substitution.

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