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Development of Mesomorphic Poly(methyl methacrylate)

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ABSTRACT

Methacrylate monomers were synthesized in four steps based on methacrylic acid and substituted phenols in the present investigation. In the first step, 4-(ω-hydroxy alkoxy) benzoic acids with ω = 2 and 6 were synthesized with the reaction of 4-hydroxy benzoic acid (PHB) and ω-chloroalkanol. The products were refluxed with methacrylic acid for 20 h to obtain the products of the type 4-(ω-methacryloyloxy alkoxy) benzoic acid. The products were chlorinated with thionyl chloride to obtain 4-(ω-methacryloyloxy alkoxy) benzoyl chloride. Finally, the chlorinated products were reacted with 4-methoxy and 4-hexyloxy phenols in dry benzene with triethylamine as catalyst at 0-5°C in nitrogen atmosphere for 3 h to obtain the methacrylate monomers. These monomers have been polymerized by free-radical polymerization technique at 50-60°C. The viscosity-average molecular weight ($\bar{M}_V$) of the synthesized polymers was calculated by Mark-Houwink's equation with K and α values 3.87×10^{-3} dL/g and 0.42, respectively. Finally, the phase transitions and the transition enthalpies of polymers from the dynamic scans by differential scanning calorimetric analysis (DSC) gave an inference about the presence of nematic-isotropic and smectic-isotropic transitions in polymers. These liquid crystalline orders were further confirmed by X-ray diffraction analysis.

Key Words:
substituted benzoic acid;
substituted phenol;
mesomorphic poly (methyl methacrylate);
viscosity-average molecular weight;
differential scanning calorimetry;
X-ray.

INTRODUCTION

Liquid crystals [1-4] are highly anisotropic fluids that exist between the boundaries of the solid and conventional isotropic liquid phase and they are formed as a consequence of molecular asymmetry. This intermediate or mesomorphic state of a substance results from a long-range orientational ordering among the constituent molecules that occur within certain range of temperature, in melts [4] (thermotropic) or in a solutions (lyotropic).

Thermotropic liquid crystalline

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polymers are most widely accepted in view of its inherent property-application relationship. LCPs are mostly based on low molecular mesogenic groups. The mesogenic groups are formed by *p*-substituted rigid-rod groups. These mesogenic groups are incorporated in two ways [3]: (a) direct incorporation of mesogenic groups into the main-chain either through flexible spacers or without flexible spacers which results in main-chain LCPs, and (b) incorporation of mesogenic groups as side groups to the main polymer chain resulting side-chain LCPs. Side-chain LC polymers have been considered due to its resemblance with low molecular weight liquid crystals.

In our present study four polymers and their monomers have been synthesized by free-radical polymerization technique. The monomers and polymers were characterized by spectral analysis. The liquid crystalline behaviour was inferred by DSC and they were further confirmed by powdered X-ray diffraction analysis.

EXPERIMENTAL

Materials

Para-hydroxy benzoic acid (PHB) (Loba Chemie, India), 4-methoxy phenol, *p*-toluene sulphonic acid (PTSA), methacrylic acid (all from E. Merck, Germany), 2-chloroethanol, 6-chlorohexanol, 4-hexyloxy phenol (all from Aldrich, USA), ethanol, isopropyl alcohol, etc. were the basic reagents and chemicals used during the syntheses of monomers and polymers.

Synthesis of Monomers

Synthesis of monomers involved the following four steps :

1. Synthesis of 4-(ω-hydroxy alkoxy) benzoic acid
2. Synthesis of 4-(ω-methacryloyloxy alkoxy) benzoic acid
3. Chlorination of the products from step 2
4. Synthesis of esters from chlorinated products of step 3 and 4-alkoxy phenols

The first step involved the reaction of 1.0 mol of 4-hydroxy benzoic acid (PHB) and 1.1 mol of ω-chloro alkanol in basic medium at 120□C with 0.5g of KI. The reaction mixture was refluxed for 24 h, the solvent was evaporated and the solid residue was dissolved in 1 L of water. The final solution obtained after reflux was precipitated with HCl and then dried. The precipitate was re-crystallized thrice with ethyl acetate/ethanol mixture. In this step the following two products were synthesized:

(a) 4-(2-Hydroxy ethoxy) benzoic acid (A_1)
(b) 4-(6-Hydroxy hexyloxy) benzoic acid (A_2)

In the step 2, a mixture of 4-(ω-hydroxy alkoxy) benzoic acid, methacrylic acid, dry benzene, PTSA, hydroquinone (HQ) and boric acid was refluxed for 20 h in a Dean-Stark apparatus. The cooled reaction mixture was diluted with large excess of ether and finally, the ether was evaporated to obtain the concentrated solution. This was washed with warm water and dried to obtain the following products:

(a) 4-(2-Methacryloyloxy ethoxy) benzoic acid (B_1)
(b) 4-(6-Methacryloyloxy hexyloxy) benzoic acid (B_2)

Substituted benzoic acids (B_1 and B_2) were dissolved in 20 mL of dry benzene. The solution was mixed with small amount of hydroquinone and few drops of DMF. Thionyl chloride, diluted with dry benzene was poured into the reaction mixture. The reaction mixture was stirred for 1 h at room temperature and the thionyl chloride was removed afterwards. The following chlorinated products were obtained :

(a) 4-(2-Methacryloyloxy ethoxy) benzoyl chloride (C_1)
(b) 4-(6-Methacryloyloxyl hexyloxy) benzoyl chloride (C_2)

In the final step, the chlorinated products were reacted with proper amounts of 4-methoxy phenol or 4-hexyloxy phenol in dry benzene with triethylamine catalyst at 0-5□C in nitrogen atmosphere for 3 h. After the completion of reaction, the solvent was evaporated in vacuum and finally the residue was dried over Na_2SO_4 to obtain the followings:

(a) 4-Methoxy phenyl-4′-methacryloyloxy ethoxy benzoate (D_1)
(b) 4-Hexyloxy phenyl-4′-methacryloyloxy ethoxy benzoate (D_2)
(c) 4-Methoxy phenyl-4′-methacryloyloxy hexyloxy benzoate (D_3)
(d) 4-Hexyloxy phenyl-4′-methacryloyloxy hexyloxy benzoate (D_4)

In each step, the purity of the product was checked by TLC.

The melting points, elemental analysis, infra-red (IR) and nuclear magnetic resonance (NMR) spectro-

Table 1. Elemental analysis, percent yield, melting point and expected molecular formula of liquid crystalline monomers (D_1-D_4) .

Sample	Approx. yield (%)	Melting point (°C)		Elemental analysis				Expected molecular formula
		Experimental	Literature	Calculated		Found		
				C (%)	H (%)	C (%)	H (%)	
D_1	30.0	178	180	67.42	5.62	67.11	5.29	$C_{20}H_{20}O_6$
D_2	41.0	138	140	70.42	7.04	70.18	6.89	$C_{25}H_{30}O_6$
D_3	39.0	130	134	69.90	6.80	69.43	6.67	$C_{24}H_{28}O_6$
D_4	39.0	90	91	72.19	7.88	72.01	7.79	$C_{29}H_{38}O_6$

Table 2. Infra-red band assignment for monomers D_1-D_4.

Wavenumber range	Monomer samples				Functional group	Vibration mode
	D_1	D_2	D_3	D_4		
3010			x		Sharp and weak, broad, C-H stretch of aromatic ring	$\nu_{(C-H)}$
3020	x	x		x		
3030			x			
3040		x		x		
2940-2900			x		Small and sharp C-H stretch of methylene	$\nu_{(C-H)}$
2990-2850	x	x	x	x		
1759-1730	x	x	x	x	Strong, broad with weak band, stretch of C=O group	ν (C=O)
1600-1500	x	x	x	x	Sharp, stretch of C=C aromatic ring	
1659-1630	x	x	x	x	Sharp, stretch of C=C	ν (C=C)
1490-1480	x	x	x	x	Methyl linked with olefin	Symm.
1230-1210	x	x	x	x	Stretch of C-O-C	Asymm.
1180-1160	x	x	x	x	Stretch of O-C=C-	
1090-1070	x		x		Stretch of C-O-C	Symm.
1060-1040		x		x	Stretch of C-O-C	Symm.
1000-980	x	x	x	x	Out-of-plane bending of C-H	$\nu_{(C-H)}$
910-900	x	x	x	x	Out-of-plane bending of aromatic C-H	$\nu_{(C-H)}$
770-760	x	x	x	x	Out-of-plane bending of olefinic C-H	ν (C-H)
730		x	x	x	Methylene	

scopic analysis, etc. were performed to check the formation of exact products. These data for monomeric benzoates, D_1-D_4, are presented in Tables 1-3.

Synthesis of Polymers

The synthesized benzoates in the above steps 4 were polymerized, in solution, in the temperature range 50-60□C in an inert atmosphere for 6-10 h of reaction with AIBN initiator. The viscous mass was precipitated in a suitable solvent and finally the precipitated polymer was vacuum dried (Table 4).

Characterization of Polymers

The polymer formation was confirmed by several characterization methods viz., elemental analysis (Perkin Elmer 240-C), infra-red (Perkin Elmer 599-B) and NMR (Jeol FX 90Q FT-NMR) spectroscopic analysis were employed. The viscosity-average molecular weight ($\overline{M}_V$) of the synthesized polymers were calculated by Mark-Houwink□s equation [5] with K and α values 3.87×10^{-3} dL/g and 0.42, respectively.

Finally, the liquid crystalline behaviour of the polymers was investigated by differential scanning calorimetric (DSC)(DuPont 910) analysis which was further confirmed by X-ray diffraction (Siefert-2002) analysis emitting CuK_a radiations.

RESULTS AND DISCUSSION

Synthesis of Monomers

The syntheses of various intermediate products for the

Table 3. ^{1}H-NMR Band assignments for monomers D_1-D_4.

Sample No.	Functional group	Peak	Sample			
			D_1	D_2	D_3	D_4
1	$C_6\underline{H}_5$ - (or Ph)	A	6.73-7.10 m	6.90-7.22 m	6.93-7.02 m	6.65-7.02 m
2	- $C\underline{H}_2OPh$	B	3.13-3.33 t	3.13-3.27 t	3.67-3.83 t	3.72-3.93 t
3	- $(C\underline{H}_2)_4$	C	-	-	1.07-1.50 m	1.10-1.50 m
4	$C\underline{H}_3$ - C=C-	D	1.28 s	1.90 s	1.90 s	1.79 s
5	- C=$C\underline{H}_2$	E	5.38 s	5.60 s	5.43 s	5.73 s
6	- $OC\underline{H}_3$	F	3.80-4.03 m	-	3.14-3.34 m	-
7	- O $(C\underline{H}_2)_5$	G	-	2.02-2.51 m	-	1.95-2.38 m
8	-$CC\underline{H}_3$	I	-	1.82 s	-	1.63 s
9	-$C\underline{H}_2$ - C - ‖ O	J	3.47-3.68 t	3.37-3.58 t	4.00-4.17 t	4.03-4.22 t

s: singlet; m: multiplet; t: triplet .

preparation of monomers followed the mechanism similar to the mechanism given by Srivastava and Mathur [6] for their work on mesomorphic polyacrylates. The ether group was introduced through etherification reaction resulting 4-(ω-hydroxy alkoxy) benzoic acids (A_1 and A_2) followed by the introduction of ester group through an esterification reaction giving 4-(ω-methacryloyloxy alkoxy) benzoic acids B_1 and B_2. A small amount of boric acid increased the yield of the products in this step. This might be due to the production of more hydrogen ions which slowed down the reverase reaction. Thionyl chloride was used for the chlorination of the compounds B_1 and B_2. Distillation and the remaining traces might be absorbed in DMF which could separate the excess thionyl chloride from the products (C_1 and C_2).

Compounds synthesized in the last step have been used as monomers for the synthesis of polymers.

The synthesis of these esters (D_1 and D_2) from alkoxy phenols and the chlorinated products C_1 and C_2 might follow the substitution reaction. In this, the nucleophile alkoxy phenols were attached to the carbonyl carbon of the benzoyl chloride derivative which produced the tetrahedral intermediate, and it was decomposed with the elimination of HCl to give the desired monomers.

Synthesis of Polymers

Methacrylate monomers (D_1-D_4) were polymerized, in solution, in presence of free-radical initiator, AIBN. The polymerization proceeded through three basic steps of polymerization as given by Srivastava et al. [6]. The structures of the synthesized polymers are characterized further.

Characterization of Polymers

Elemental Analysis

Table 5 shows the percentage of carbon and hydrogen

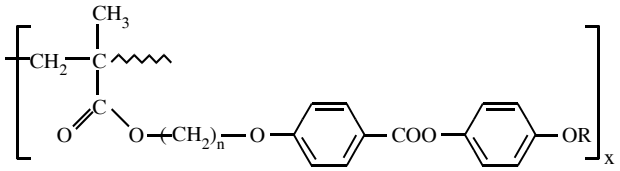
Table 4. Various parameters for the preparation of LC polymers (E_1-E_4).

Monomer code	Conc. of monomer (g)	Solvent used	Initiator conc. x 10^2 (g)	Polymization time (h)	Polymization temp. (°C)	Non-solvent used	Polymer code
D_1	1.0	Toluene	4.0	7	50	Diethyl ether	E_1
D_2	1.0	Chloroform	1.0	6	60	Diethyl ether	E_2
D_3	1.0	Toluene	0.5	8	55	Diethyl ether	E_3
D_4	1.0	Chloroform	0.5	10	50	Diethyl ether	E_4

Table 5. Elemental analysis, yield (%) and viscosity-average molecular weight ($\bar{M}_V$) for liquid crystalline polymers (E_1-E_4).

Sample code	Approx. yield (%)	Elemental analysis				η_{inh}	$\bar{M}_v$
		Calculated		Found			
		C(%)	H(%)	C(%)	H(%)		
E_1	41	67.42	5.62	67.32	5.57	0.262	22832
E_2	33	70.42	7.04	70.36	6.98	0.235	17623
E_3	39	69.90	6.80	69.68	6.77	0.283	27433
E_4	46	72.19	7.88	71.97	7.73	0.244	19273

present in the polymers (E_1-E_4). From these values, it is clear that they are in close agreement with their calculated values of carbon and hydrogen in the presumed structure of polymers (Scheme I).



Polymers: E_1 (n = 2 and R = CH_3);
E_2 (n = 2 and R = $(CH_2)_5CH_3$);
E_3 (n = 6 and R = CH_3);
E_4 (n = 6 and R = $(CH_2)_5CH_3$)
x = degree of polymerization

Scheme I

IR Analysis

Absorption bands sensitive to phase state of polymer E_1 (Figure 1) were mainly situated below 1500 cm^{-1} while those due to functional groups were situated above 1500 cm^{-1}. The polymer displayed an absorption band near 1600 cm^{-1} which might be attributed due to the stretching vibrations of C-C bonds of the benzene ring and the deformation of CCH and CCC angles. Small peaks near 3050 cm^{-1} and in the region of 2910-2840 cm^{-1} appeared due to C-H stretching vibrations of aromatic ring and methylene linkages, respectively (Figure 1). A peak appearance near 1750 cm^{-1} confirmed the presence of carbonyl type stretching (C=O) vibrations in polymer E_1. The overtone of these bands appeared near 890-860 cm^{-1}. Wavy bands appeared due to repetition of several functional groups such as ester and ether. The most intensive absorption bands displayed in the region of 1300-1100 cm^{-1} due to the skeletal vibrations of -C-C-O-C- fragment in the side-

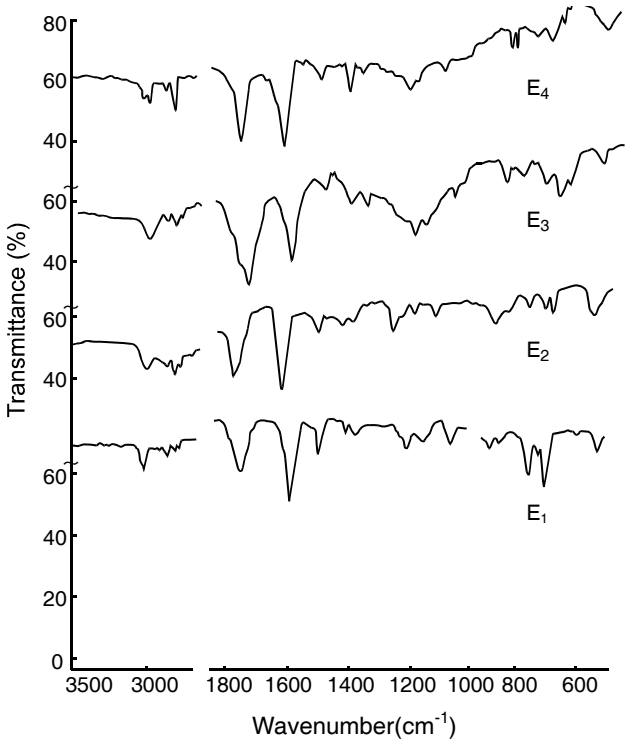


Figure 1. Infra-red spectra of LC polyesters (E_1-E_4).

chains (the main contribution being made by C-O vibrations). These vibrations are very sensitive to the conformational state of the ester group. A comparison of these polymers with the corresponding monomers [6] showed that the peaks near 1650 and 950 cm^{-1}, appeared in the spectrum of monomer for polymer E_1, i.e. D_1 (Table 2), disappeared in the spectrum of polymer E_1 (Figure 2). This clearly indicated the formation of polymer. All other vibrations in case of polymers showed a similar peak position as mentioned in the work of several researchers [4,7-10].

NMR Spectrum

The band assignments from ^1H NMR spectra of polymers E_1-E_4 are shown in Figure 2. These band assignments resemble the band assignments of different groups cited in the literature [4,12]. From Figure 2 it is clear that there appear two multiplets near 6.78-7.33 ppm, and 6.33-6.83 ppm, have been observed for polymer E_1 (Figure 2) and they might be due to the benzene rings present in the sample [6]. The appearance of two triplets in the region of 3.23-3.73 ppm and 3.67-4.13 ppm confirmed the presence of ether and ester linkages in E_1. The presence of methoxy protons, OCH_3, appeared as multiplets in the region of 3.07-3.37 ppm

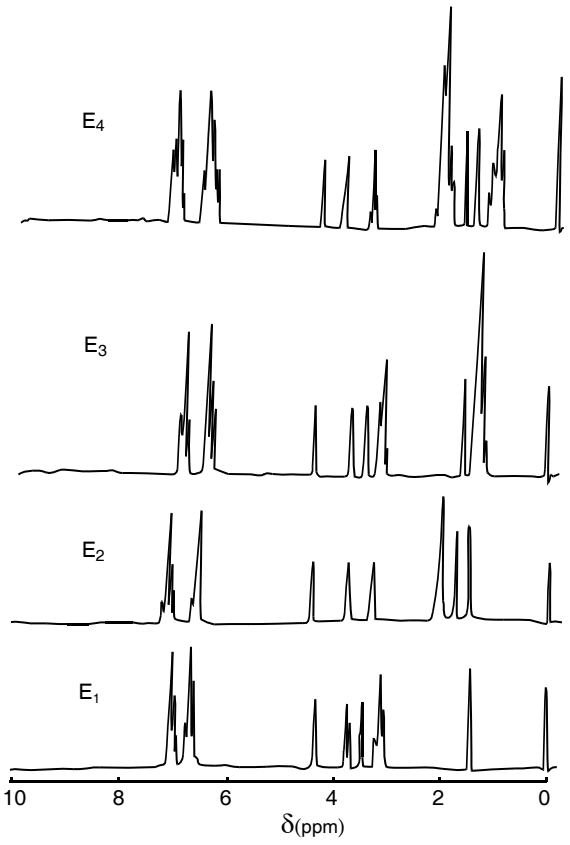


Figure 2. ^{1}H NMR Spectra of LC polyesters (E_1-E_4) in $CDCl_3$/TMS.

for polymers E_1 and E_3. For polymers E_2 and E_4, the multiplets appeared in the region of 1.90-2.13 and 2.03-2.35, respectively (Figure 2) and for hexyloxy protons in polymers E_2 and E_4 (Figure 2) multiplets appeared in the region of 1.90-2.13 and 2.03-2.35 ppm. These band assignments were found to be in close resemblance to the band assignments given by various researchers while studying the phase behaviour of similar LC polymers [9,10-12].

Viscosity-average Molecular Weight ($\bar{M}_V$)

The viscosity and molecular weight of polymers E_1-E_4 are presented in Table 5. From the results it is clear that the values of viscosity increased as the spacer length was increased from n=2 to n=6 with the methoxy as the substituent group. This resulted in an increase of 16.8 % in molecular weight. The change of substituent group from methoxy (OCH_3) to hexyloxy (OC_6H_{13}) with n=2 decreased the value of viscosity, which finally decreased the molecular weight by 22.8 % (n=2) and 19.7 % (n=6).

The decrease in molecular weight with increase of spacer length (n=2 to n=6) might be due to the increase in free volume between the adjacent C-C linkages. This might increase the flexibility of the chain, which increased the number of chain end segments and hence, decreased the molecular weight. Several researchers [1,13] proposed a similar concept for decrease in molecular weight with spacer length and flexible spacers while working on similar systems. They also inferred that the reduction of the stereo-hindrance on main backbone on mesogenic cores was the major role of flexible spacer. Due to this and thermodynamical driving force, the change occurred in molecular weight which resulted in LC phase transitions, smectic or nematic [5,16-19]. The low values of viscosity, in the present study, might show the compactness of the polymer coils due to intra-molecular interactions of the side groups which might decouple the mesogenic side-group with the main-chain. A similar concept was given by Seiberle and his coworkers [20].

DSC Analysis

The phase transitions and the transition enthalpies of polymers E_1-E_4 from DSC are shown in Figure 3 and the results are summarized in Table 6. A broad endotherm peak appeared with a minimum of 120□C in polymer E_1 which corresponded to nematic-isotropic transition. In polymer E_3, nematic to isotropic transi-

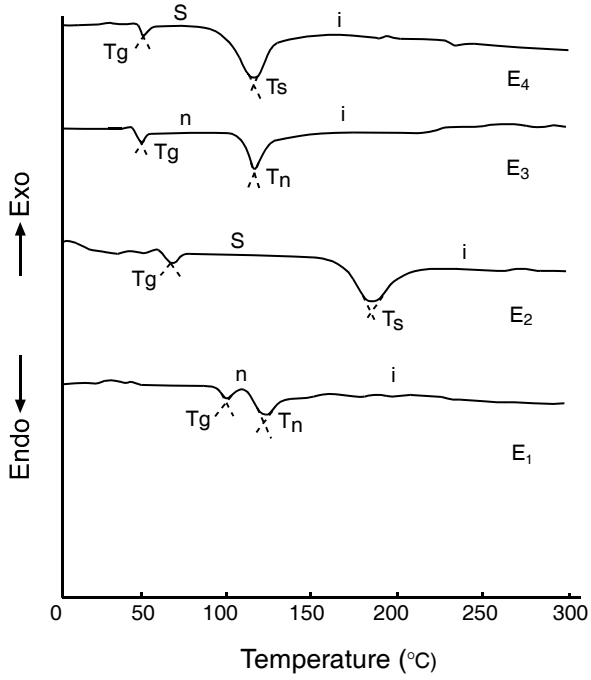


Figure 3. DSC Scans of LC polyesters (E_1-E_4).

Table 6. DSC Data for LC polymers (E_1-E_4).

Sample code	T_g (°C)	Phase transitions[a] (°C)	Transition enthalpies (ΔH)[b] (kJ/mol)		
			s-n	n-i	s-i
E_1	98	g 98 n 121 i	X	0.9	x
E_2	72	g 72 s 185 i	X	x	2.2
E_3	49	g 49 n 115 i	X	1.8	x
E_4	50	g 50 s 121 i	X	x	3.6

(a) Obtained from DSC thermograms; g: glass; s: smectic; n: nematic; i: isotropic.
(b) From area of under DSC peaks.

tion was observed, whereas, polymers E_2 and E_4 showed smectic-isotropic transitions (Figure 3). A shortening of the spacer length from n = 6 to n = 2 increased the value of T_g up to 48°C. With long spacer length (n = 6), i.e. polymer E_3 and E_4, the T_g values have been found to be 10-20°C higher than the corresponding polyacrylates [6,9,14,21]. The low values of transition enthalpies in all polymers (Table 6) further confirmed the formation of LC order in polymers [9,16].

Similar transition behaviour was also observed for LC polymers with a polysiloxane chain. These results allowed to test the working hypothesis of Finkelmann and his coworkers [22] that the flexible spacer decoupled the motions of the mesogenic side-groups and the polymer backbone and thus led to LC polymers. They concluded that the liquid crystalline behaviour was only governed by the mesogenic groups and the T_g only by the main chain [23,24]. This concept resembled our results of T_g. The results showed that the influence of the mesogenic groups on the polymer behaviour have been shown by the fact that the lowering of the T_g in LC polyacrylates, in our previous publication [6], was not as marked as for the unsubstituted polymers. In addition, LC polymers having identical main chains showed very different T_g-values depending on their mesogenic groups and the spacer length. The influence of the main chain on the LC phase has been shown by the fact that LC polyacrylates [6] and polymethacrylates, the present investigation, having the same mesogenic groups showed different types of LC phases. This could be due to the mobility of the chain backbone [23-25].

X-Ray Analysis

Figure 4 shows the powdered X-ray diffraction pattern for unoriented polymers E_1-E_4 and the results are summarized in Table 7. The diffused reflections are appeared (Figure 4) for all the polymers in the region of wide-angle scattering which corresponded to the average distance between side-branches of the macromolecules. The appearance of halos confirmed the formation of polymers [26,27]. Also, there occurred a slight reduction in diffraction interplaner spacing, d_d, with an increase in the aliphatic bond length, i.e. increase in the value of n from 2 to 6 (Table 7). In addition, a number of sharp low-angle reflections have been observed for polymers E_1-E_4, which corresponded to the inter-planer spacing, d_1, d_2 and d_3 (Figure 4). Only reflection d_1 corresponded to the distance between the layers while the other two, d_2 and d_3, corresponded to the ordered arrangement of the mesogenic groups. Such ordering have been observed in polymers E_2 and E_4.

The preceding results indicated a slight reduction in inter-planer spacing, d_d, with an increase in the length of methylene units, which might be due to intensification of the interaction between the side-groups. The

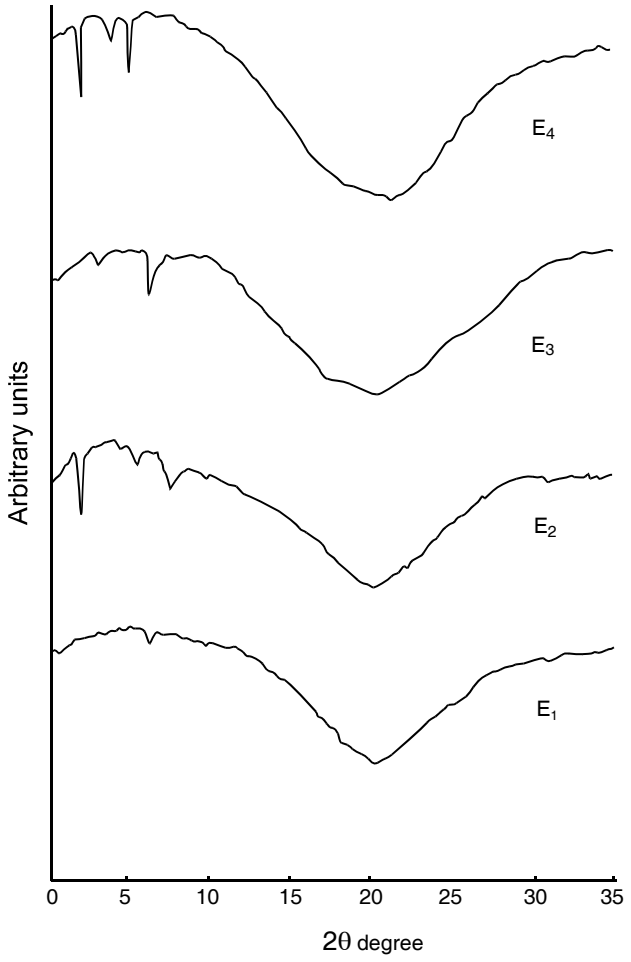


Figure 4. X-Ray diffraction pattern of LC polyesters (E_1-E_4).

Table 7. X-Ray diffraction data for LC polymers E_1-E_4.

Sample code	X-ray Data[a]												
	Reflection angle								Interplanar spacing				Type of mesophase
	Small angle						Wide angle (halo)		Small angle			Wide angle diffusion halo	
	d_1		d_2		d_3		d_d		d_1	d_2	d_3		
	2q	q	2q	q	2q	q	2q	q	d_1	d_2	d_3	d_d	
E_1	-	-	-	-	6.30	3.15	20.20	10.10	-	-	14.0 w.d.	4.4	Nematic
E_2	2.25	1.13	5.80	2.40	7.00	3.80	20.60	10.30	40.0 st	15.2 w	11.7 m.d.	4.3	Smectic
E_3	3.26	1.63	-	-	6.50	3.25	20.20	10.10	27.0 w.d.	-	13.6 m.d.	4.4	Nematic
E_4	2.40	1.20	4.20	2.10	5.48	2.74	21.10	10.25	37.0 st	21.0 m	16.1 st	4.2	Smectic

w.d. : wide & diffuse; m.d. : medium & diffuse; st. : strong; w : wide; m : medium. (a) Obtained from X-ray diffractograms.

side-chain might be packed anti-parallel so that the methylene chains might surround the mesogenic groups of one macromolecule to the neighbouring molecules. The side branches might be arranged pre-dominantly at right angles to axis of the main-chain. Such layered ordering of the mesogenic groups suggested the occurrence of an LC structure of the smectic type [10,14,15,18,19,27,28-35]. In case of polymer E_1 (Figure 4), only one sharp reflection occurred at small angle side, which might suggest the random formation of side-chains without any layer ordering. This type of arrangement of mesogenic groups suggested the occurrence of an LC structure of the nematic type [14,27]. Hartshorne [36] gave the parallel interpretation for the formation of nematic and smectic mesophases by polarized light optical microscopic analysis which was further confirmed by similar results, as in our case, from X-ray and DSC analysis.

CONCLUSION

The present work allows us to conclude the followings:

- The addition of boric acid increased the yield of the monomers and polymers.

- Spectral analysis viz. infra-red and NMR confirmed the product formation.

- The viscosity-average molecular weight increased with spacer length and decreased with the substituent group.

- The glass-transition temperatures (T_gs) have been found to be strongly influenced by the mesogenic side-groups and the length of the spacer group. Shortening of the spacer group increased the value of T_g. The low values of transition enthalpies in all polymers confirmed the presence of liquid-crystalline order in polymers.

- Some polymers showed nematic-isotropic transitionds, whereas, others showed smectic-isotropic transitions as inferred by DSC analysis.

- Powdered X-ray analysis supported the results obtained by DSC. The presence of halos in the wide and small angle side confirmed the nematic and smectic type ordering in polymers even at room temperature.

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