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Molecular engineering of liquid crystal polymers by living polymerization

XXII. Synthesis and characterization of binary copolymers of 11-[4-cyano-4′-biphenyl)oxy]undecanyl vinyl ether with (2*S*, 3*S*)-(+)-2-chloro-3-methylpentyl 4′-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate, and of (2*S*, 3*S*)-(+)-2-chloro-3-methylpentyl 4′-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate with 3-[4-cyano-4′-biphenyl)oxy]propyl vinyl ether†

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The synthesis and characterization of poly{11-[(4-cyano-4′-biphenyl)oxy]undecanyl vinyl ether-co-(2*S*, 3*S*)-(+)-2-chloro-3-methylpentyl 4′-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate}X/Y {poly[(6-11)-co-(15-8)]X/Y} (where X/Y represents the molar ratio of the two structural units) and poly {(2*S*, 3*S*)-(+)-2-chloro-3-methylpentyl 4′-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate-co-3-[(4-cyano-4′-biphenyl)oxy]propyl vinyl ether}X/Y poly[(15-8)-co-(6-3)]X/Y} with degree of polymerization of about 20 and molecular weight distribution of about 1·1 are described. The mesomorphic behaviour of all copolymers determined from both first, second and subsequent DSC scans was discussed as a function of composition. As determined from the second DSC scans, poly(6-11) exhibits enantiotropic smectic A (S_A) and S_X (unidentified smectic), poly(6-3) enantiotropic nematic, while poly(15-8) exhibits enantiotropic S_A, chiral smectic C (S_C^*) and S_X (unidentified smectic) mesophases. Poly[(6-11)-co-(15-8)]X/Y exhibit a S_A phase over the entire range of compositions and a new induced S_X phase for $X/Y = 8/2$ to 4/6. The S_A phase displays a continuous dependence of copolymer composition with an upward curvature. Poly[(15-8)-co-(6-3)]X/Y with X/Y from 10/0 to 3/7 displays an enantiotropic S_A mesophase with an upward curvature as their highest phase, while those with X/Y from 2/8 to 1/9 an enantiotropic cholesteric mesophase.

1. Introduction

Copolymerization provides the most effective method for the molecular engineering of side chain liquid-crystalline polymers [1, 2]. Copolymerization of monomer pairs each containing mesogenic units [1–10] can be classified into at least four different groups: (1) copolymers from monomer pairs containing identical mesogens and polymerizable groups but different spacer lengths; (2) copolymers from monomer pairs containing identical mesogens and spacer lengths but different polymerizable groups; (3) copolymers from monomer pairs containing dissimilar mesogens but either

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similar or different spacer lengths and polymerizable groups; (4) copolymers from monomer pairs containing constitutional isomeric units and similar or dissimilar spacers and polymerizable groups [2].

For a quantitative approach to the understanding of side chain liquid-crystalline copolymers, molecular weight, molecular weight distribution and copolymer composition should be well-defined [11]. Copolymers synthesized by chain copolymerization reactions exhibit a heterogeneous composition since the copolymer composition differs from that of the monomer feed in the initial reaction mixture, exception being the azeotropic copolymerizations. Furthermore, the temperature and the nature of the mesophase are molecular weight [12–16] and molecular weight distribution dependent [15, 17]. Therefore, for a quantitative investigation of side chain liquid-crystalline copolymers it is essential that these factors are well-defined. The ideal solution to the synthesis of copolymers by chain reactions would be to select monomer pairs that can be copolymerized by an azeotropic living mechanism [18].

Several previous publications [19, 20] from our laboratory have investigated the first series of quantitative experiments on statistical binary copolymers with well-defined composition, molecular weight and molecular weight distribution by living cationic polymerization corresponding to class 1, i.e. copolymers from monomer pairs containing identical mesogenic units and polymerizable groups but different spacer lengths. The general trend observed from these investigations is that over the entire range of copolymer compositions where the two structural units of the copolymer are isomorphic within a certain mesophase, both the phase transition temperatures and the enthalpy changes associated with this mesophase follow a continuous dependence of copolymer composition. The dependence of isotropization temperature on composition can also be predicted by the Schroeder–van Laar equation [21] when the isomorphic structural units of the copolymer behave like an ideal solution of these structural units [19, 20]. When the two structural units are non-isomorphic within a certain composition, a continuous dependence of both transition temperatures and enthalpy changes with a triple point at a certain copolymer composition can be observed [19(b–e)].

Presently, we are investigating copolymers based on monomer pairs containing dissimilar mesogens and dissimilar spacer lengths but identical polymerizable groups which correspond to class 3 of the copolymers. In the case of different chemical structure for each mesogen, the components of such polymer blends are generally immiscible and attempts to obtain homogeneous mixtures were not successful [6]. Copolymers from this class are however of interest for the fundamental understanding of phase diagrams obtained by copolymerization.

This paper will describe the synthesis and characterization of two copolymer series based on 11-[(4-cyano-4′-biphenyl)oxy]undecanyl vinyl ether (6-11) and 3-[(4-cyano-4′-biphenyl)oxy]propyl vinyl ether (6-3) with poly{(2*S*, 3*S*)-(+)-2-chloro-3-methylpentyl 4′-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate} (15-8). All copolymers were synthesized with a degree of polymerization of 20 and different compositions. When the mesomorphic phases exhibited by the parent homopolymers with a degree of polymerization of about 20 are determined from the second heating scans, poly(6-11) [16 (a)] exhibits enantiotropic S_A and S_X, poly(6-3) [16 (b)] enantiotropic nematic, and poly(15-8) [20 (c)] enantiotropic S_A, S_C^* and S_X mesophases. Therefore, it is expected that the investigation of these two series of copolymers will provide information about the phase behaviour of the copolymers containing different mesogens and different spacer lengths derived from pairs of homopolymers exhibiting as the high temperature mesophases, S_A and S_A, and respectively, N and S_A. Therefore, this investigation will provide a quantitative understanding of class 3 of the copolymers.

2. Experimental

2.1. *Materials*

All materials were commercially available and were used as received or purified as described previously [16 (a), (b)]. Methyl sulphide (anhydrous, 99 per cent, Aldrich) was refluxed over 9-borabicyclo[3.3.1]nonane (9-BBN, crystalline, 98 per cent, Aldrich) and then distilled under argon. Dichloromethane (99·6 per cent, Aldrich) used as a polymerization solvent was first washed with concentrated sulphuric acid, then with water, dried over anhydrous magnesium sulphate, refluxed over calcium hydride and freshly distilled under argon before use. Trifluoromethane sulphonic acid (triflic acid, 98 per cent, Aldrich) was distilled under argon.

2.2. *Techniques*

^{1}H NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. TMS was used as internal standard. A Perkin–Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic and exothermic peaks, respectively. In all cases, heating and cooling rates were 20°C min^{-1} unless otherwise specified. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. For certain polymer samples, the first heating scans sometimes differ from the second and subsequent heating scans. However, the second and subsequent heating scans are identical. The first heating scans can be reobtained after proper thermal treatment of the polymer sample. A Carl–Zeiss optical polarized microscope (magnification: × 100) equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the thermal transitions and to analyse the anisotropic textures [22, 23]. Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin–Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler and a Nelson analytical 900 series integrator data station. The measurements were made at 40°C using the UV detector. A set of Perkin-Elmer PL gel columns of 10^4 and 500 Å with $CHCl_3$ as solvent (1 ml min^{-1}) and a calibration plot constructed with polystyrene standards was used to determine the molecular weights. Therefore, all molecular weights discussed in this paper are relative to polystyrene. High pressure liquid chromatography (HPLC) experiments were performed with the same instrument.

2.3. *Synthesis of monomers*

11-[(4-Cyano-4′-biphenyl)oxy]undecanyl vinyl ether (6-11) [16 (a)] 3-[(4-cyano-4′-biphenyl)oxy]propyl vinyl ether (6-3) [16 (b)] and (2*S*, 3*S*)-(+)-2-chloro-3-methylpentyl 4′-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8) [20 (c)] were synthesized and purified as described in previous publications. Their purity was higher than 99 per cent (HPLC). Their detailed characterization was described in previous publications.

2.4. *Cationic polymerizations and copolymerizations*

Polymerizations were carried out in glass flasks equipped with teflon stopcocks and rubber septa under argon atmosphere at 0°C for 1 h. All glassware was dried overnight at 130°C. The monomer was further dried under vacuum overnight in the polymeriz-

Table 1. Cationic copolymerization of 6-11 with 15-8 (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0=[6\text{-}11]+[15\text{-}8]=0{\cdot}205-0{\cdot}256M$; $[M]_0/[I]_0=20$; $[(CH_3)_2S]_0/[I]_0=10$; polymerization time, 1 h) and characterization of the resulting copolymers. Data on first line are from first heating and cooling scans. Data on second line are from the second heating scan.

Sample No.	[6-11]/[15-8] (mol/mol)	Polymer yield %	$M_{nx}10^{-3}$	M_w/M_n	D P	Phase transitions (°C) and corresponding enthalpy changes ($kJ\,mru^{-1}$)	
						Heating	Cooling
1	0/10	77	8·6	1·08	18	g 16·7 S_X 55·2 (0·54) S_C^* 93·4 (0·71) S_A 104·7 (4·60) I g 16·1 S_X 53·7 (0·54) S_C^* 92·1 (0·63) S_A 103·7 (4·02) I	I 95·7 (3·89) S_A 86·3 (0·59) S_C^* 45·9 (0·50) S_X 13·6 g
2	1/9	84	10·1	1·22	21	g 25·1 C 45·2 (1·72) S_C^* 89·1 (0·29) S_A 130·8 (5·02) I g 24·4 S_X 42·8 (0·63) S_C^* 88·9 (0·46) S_A 129·9 (0·46) I	I 122·5 (5·15) S_A 79·3 (0·46) S_C^* 32·9 (0·88) S_X 19·8 g
3	2/8	77	8·8	1·10	19	g 33·3 C 49·5 (0·63) C 58·0 (2·80) S_C^* 79·4 (–) S_A 141·7 (5·65) I g 32·5 C 52·9 (2·51) S_C^* 78·2 (–) S_A 140·6 (5·27) I	I 132·7 (5·31) S_A 66·2 (–) S_C^* 44·5 (2·68) C 25·4 g
4	3/7	91	10·2	1·11	22	C 51·3 (0·42) C 63·1 (4·14) S_A 149·5 (5·69) I C 61·7 (3·35) S_A 150·4 (5·15) I	I 141·9 (4·94) S_A 52·7 (3·22) C
5	4/6	89	9·4	1·10	21	C 62·3 (0·54) C 74·2 (4·85) S_A 158·9 (5·65) I C 74·4 (4·56) S_A 158·9 (5·19) I	I 150·6 (5·06) S_A 65·1 (4·23) C

6	5/5	88	8·5	1·09	19	C 59·9 (4·56) C 79·1 (4·39) S_A 160·7 (5·82) I C 75·4 (–) S_X 78·6 (4·85)† S_A 160·8 (4·85) I	I 153·0 (4·98) S_A 68·8 (4·90)† S_X 61·2 (–) C
7	6/4	93	9·6	1·17	22	C 58·6 (1·63) C 76·7 (4·02) S_A 163·7 (5·06) I C 69·5 (—) S_x 77·1 (4·31)† S_A 163·9 (4·44) I	I 155·9 (4·48) S_A 67·1 (4·18) S_X 55·8 (2·59) C
8	7/3	89	7·5	1·08	18	C 51·7 (1·21) C 69·4 (3·10)† S_A 160·3 (4·44) I C 68·3 (2·22) S_A 161·0 (5·02) I	I 154·2 (4·77) S_A 55·8 (1·76) C
9	8/2	85	7·4	1·07	18	g 13·2 C 51·5 (4·69) C 62·2 (–) S_A 161·2 (5·02) I g 12·5 C 56·0 (1·21) S_A 161·2 (4·14) I	I 154·6 (0·50) S_A 35·3 (0·50) C 10·1 g
10	9/1	96	7·7	1·12	19	g 14·1 C 51·6 (9·25) C 56·4 (–) S_A 157·7 (4·27) I g 12·0 S_A 158·3 (3·93) I	I 151·9 (3·77) S_A 8·1 g
11	10/0	81	8·2	1·12	19	g 14·5 C 57·1 (14·4) S_A 157·2 (3·77) I g 14·0 S_X 44·2 (3·89) S_A 156·4 (3·64) I	I 149·4 (3·72) S_A 18·9 (2·64) S_X 8·8 g

† Overlapped peak.

Table 2. Cationic copolymerization of 6-3 with 15-8 (polymerization temperature, 0°C; polymerization solvent, methylene chloride; $[M]_0=[6\text{-}3]+[13\text{-}8]=0{\cdot}205-0{\cdot}358M$; $[M_0/[I]_0=20$; $[(CH_3)_2S]_0/[I]_0=10$; polymerization time, 1 h) and characterization of the resulting copolymers. Data on first line are from first heating and cooling scans. Data on second line are from the second heating scan.

Sample No.	[15-8]/[6-3] (mol/mol)	Polymer yield%	$M_{nx}10^{-3}$	M_w/M_n	D P	Phase transitions (°C) and corresponding enthalpy changes (kJ mru^{-1})	
						Heating	Cooling
1	0/10	87	5·9	1·04	21	g 61·3 S_X 68·8 (0·80) N 102·9 (0·50) I g 60·0 N 102·9 (0·42) I	I 97·6 (0·42) N 51·9 g
2	1/9	86	5·4	1·12	18	g 55·1 S_X 60·1 (1·84) Ch 96·8 (0·38) I g 53·0 Ch 96·8 (0·46) I	I 91·8 (0·42) Ch 42·3 g
3	2/8	85	5·6	1·14	18	g 43·2 S_X 51·4 (0·71) Ch 90·6 (4·10) I g 41·3 Ch 90·1 (0·38) I	I 85·4 (0·42) Ch 37·1 g
4	3/7	83	6·2	1·12	18	g 33·9 S_X 39·3 (0·54) S_A 106·3 (2·26) I g 31·5 N 105·6 (1·72) I	I 97·8 (1·67) N 26·5 g
5	4/6	69	6·2	1·15	17	g 29·8 C 48·9 (1·55) S_A 114·4 (2·72) I g 26·3 S_A 114·0 (2·34) I	I 106·3 (2·34) S_A 20·8 g
6	5/5	82	6·4	1·11	17	g 23·4 C 48·6 (1·80) S_A 116·0 (3·85) I g 21·4 S_A 115·3 (3·35) I	I 107·4 (3·35) S_A 15·8 g

7	6/4	84	6·7	1·08	17	g 19·4 C 46·5 (1·88) S_A 117·4 (4·94) I g 18·2 S_A 116·5 (3·98) I	I 108·7 (3·85) S_A 12·4 g
8	7/3	78	7·9	1·11	19	g 16·4 C 43·1 (0·21) S_A 119·2 (4·98) I g 14·8 S_A 118·7 (4·23) I	I 109·9 (4·18) S_A 10·3 g
9	8/2	77	7·8	1·10	18	g 15·0 S_X 23·9 (0·17) S_C^* 64·1 (0·17) S_A 114·5 (4·81) I g 14·1 S_X 37·4 (0·25) S_C^* 64·3 (0·21) S_A 113·0 (4·18) I	I 104·9 (4·23) S_A 59·9 (0·21) S_C^* 9·5 g
10	9/1	77	9·5	1·10	20	g 16·2 S_X 40·7 (0·59) S_C^* 88·2 (0·38) S_A 114·3 (4·85) I g 14·1 S_X 37·4 (0·25) S_C^* 88·1 (0·46) S_A 113·2 (4·14) I	I 105·5 (4·14) S_A 83·8 S_C^* (0·54) 28·3 (0·29) S_X 9·95 g
11	10/0	77	8·6	1·08	18	g 16·7 S_X 55·2 (0·54) S_C^* 93·4 (0·71) S_A 104·7 (4·60) I g 16·1 S_X 53·7 (0·54) S_C^* 92·1 (0·63) S_A 103·7 (4·02) I	I 95·7 (3·89) S_A 86·3 (0·59) S_C^* 45·9 (0·50) S_X 13·6 g

ation flask. Then the flask was filled with argon, cooled to 0°C and the methylene chloride, dimethyl sulphide and triflic acid were added via a syringe. The monomer concentration was about 10 wt% of the solvent volume and the dimethyl sulphide concentration was 10 times larger than that of the initiator. The polymer molecular weight was controlled by the monomer/initiator ($[M]_0/[I]_0$) ratio. After quenching the polymerization with ammoniacal methanol, the reaction mixture was precipitated into methanol. When necessary, the polymers were reprecipitated until their GPC traces showed complete absence of unreacted monomers. Tables 1 and 2 summarize the polymerization results. Although polymer yields are lower than expected due to losses during the purification process, conversions determined by GPC analysis before polymer purification were almost quantitative in all cases.

3. Results and discussion

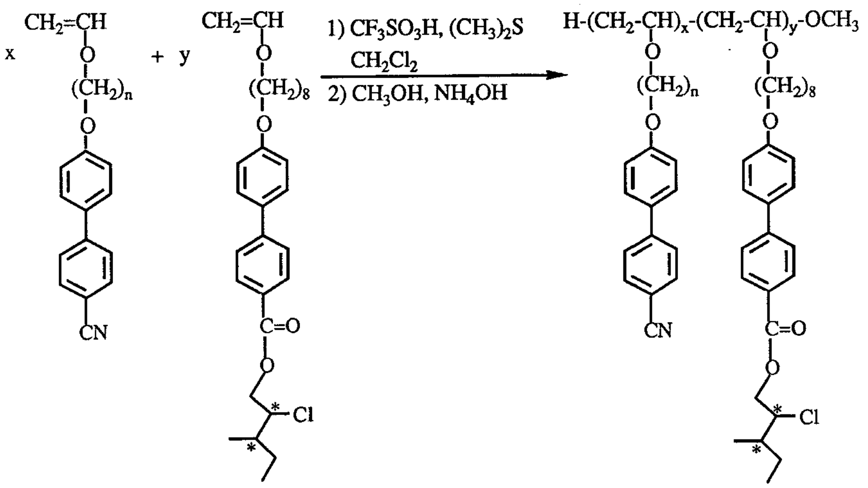
The synthesis, characterization and living polymerization of 11-[(4-cyano-4'-biphenyl)oxy]undecanyl vinyl ether (6-11) [16 a] 3-[(4-cyano-4'-biphenyl)oxy]propyl vinyl ether (6-3) [16(b)] and (2*S*, 3*S*)-(+)-2-chloro-3-methylpentyl 4'-(8-vinyloxyoctyloxy)biphenyl-4-carboxylate (15-8) [20(c)] were described previously. The scheme outlines the synthesis of the copolymers. The initiating system $CF_3SO_3H/S(CH_3)_2$ [24, 25] is known to induce living cationic polymerizations in CH_2Cl_2 at 0°C. The copolymerization results are listed in tables 1 and 2. The yields reported in tables 1 and 2 are lower than quantitative due to polymer losses during the purification process. However, the conversions were quantitative and therefore, the copolymer composition is identical to that of the monomer feed (determined by 200 MHz ^1H NMR spectroscopy). Figure 1 presents a typical 200 MHz ^1H NMR spectrum of the aromatic region of poly[(15-8)-co-(6-3)]5/5 with its proton assignments. The ratio between the integrals of the signal at 6·95 ppm and 8·10 ppm was used to confirm the copolymer compositions. Therefore, these copolymerization systems follow an azeotropic pattern (i.e. $r_1 = r_2 = 1{\cdot}0$).

The GPC traces of all copolymers show a monomodal molecular weight distribution characterized by a polydispersity of about 1·15 (see tables 1 and 2). Attempts were made to synthesize all copolymers with degrees of polymerization of about 20.

We have investigated the following two copolymer systems: poly[(6-11)-co-(15-8)]*X*/*Y* based on a monomer pair whose parent homopolymers exhibit enantiotropic S_A phases as their highest temperature mesophases and poly[(8-15)-co-(6-3)]*X*/*Y* based on a monomer pair whose parent homopolymers exhibit enantiotropic S_A and enantiotropic nematic phases as their highest temperature mesophases.

3.1. *Poly*[(*6-11*)-*co*-(*15-8*)]*X*/*Y*

The synthesis and characterization of poly[(6-11)-co-(15-8)]*X*/*Y* copolymers are summarized in table 1. The first and the second heating, and the first cooling DSC traces of all polymers and copolymers are presented in figures 1 (*a*)–(*c*). As determined from the first DSC heating scans, poly(6-11) [16 (a)] with a degree of polymerization of 19 exhibits an enantiotropic S_A mesophase and a crystalline melting. When the phase behaviour of the same poly(6-11) is determined from the second and subsequent heating DSC scans, it exhibits enantiotropic S_A and S_X (unidentified smectic) mesophases. Regardless of the thermal history of the sample, poly(15-8) [20 (c)] with a



Cationic copolymerization of 6-n with 15-8.

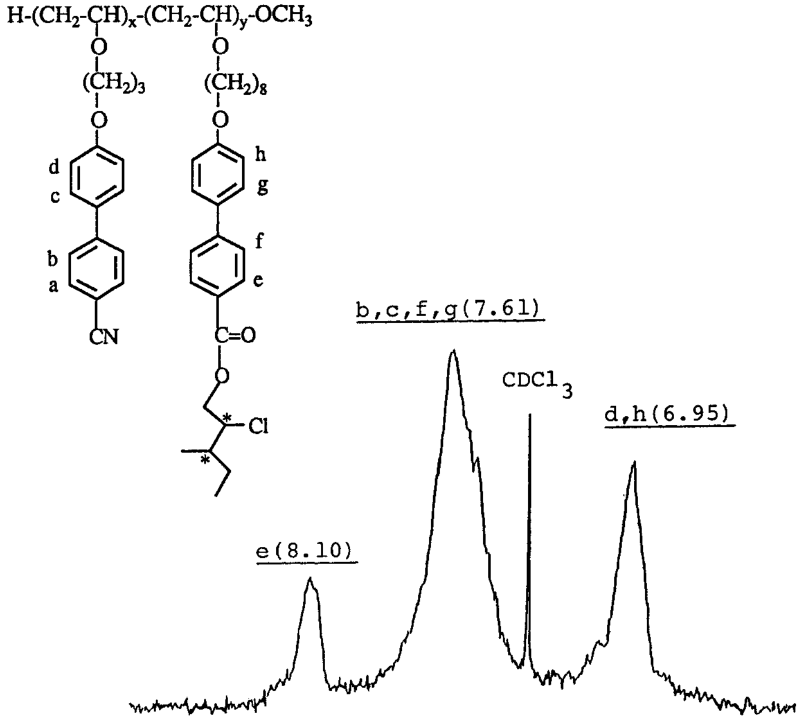
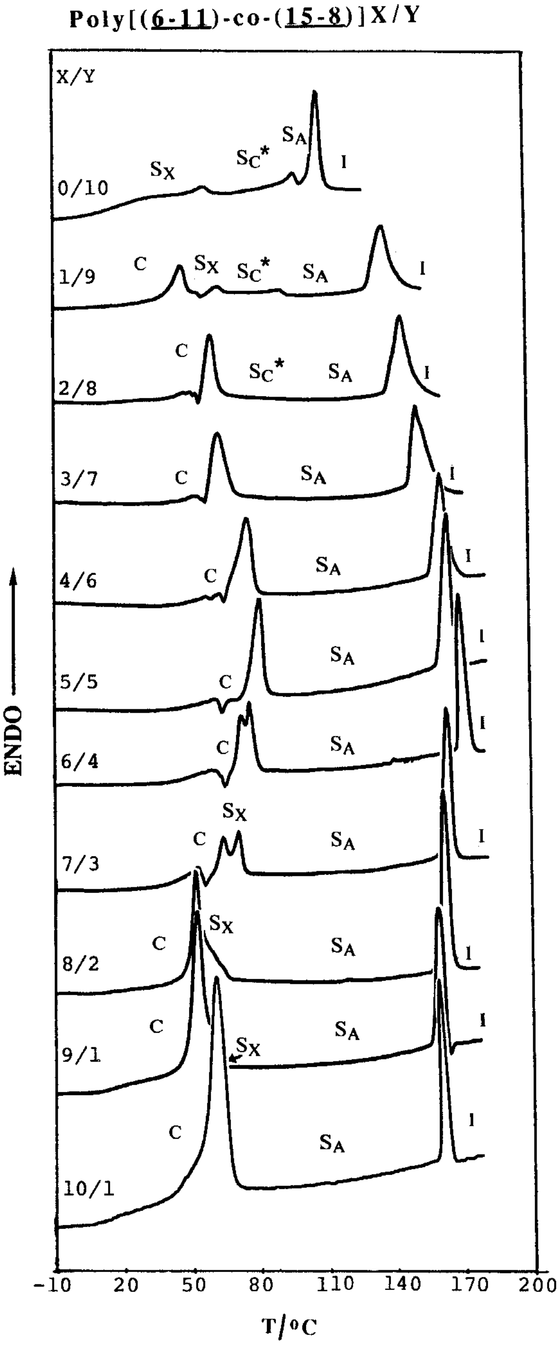
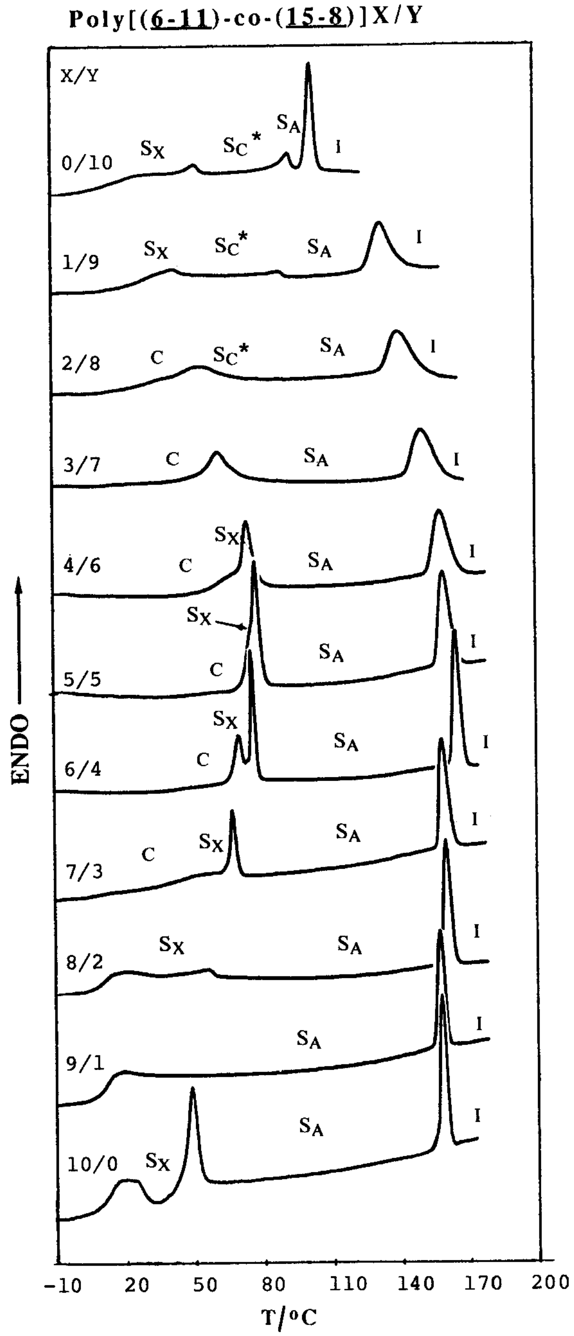


Figure 1. The aromatic region of the 200 MHz ^1H NMR spectrum of poly[(15-8)-co-(6-3)]5/5.


Poly[(6-11)-co-(15-8)]X/Y
X/Y
0/10
1/9
2/8
3/7
4/6
5/5
6/4
7/3
8/2
9/1
10/1
Sx
Sc*
SA
I
C
ENDO
-10
20
50
80
110
140
170
200
T/°C

(a)


Poly[(6-11)-co-(15-8)]X/Y
X/Y
0/10
Sx
Sc*
SA
I
1/9
Sx
Sc*
SA
I
2/8
C
Sc*
SA
I
3/7
C
SA
I
4/6
C
Sx
SA
I
5/5
Sx
C
SA
I
6/4
Sx
C
SA
I
7/3
C
Sx
SA
I
8/2
Sx
SA
I
9/1
SA
I
10/0
Sx
SA
I
ENDO
-10
20
50
80
110
140
170
200
T/°C

(*b*)

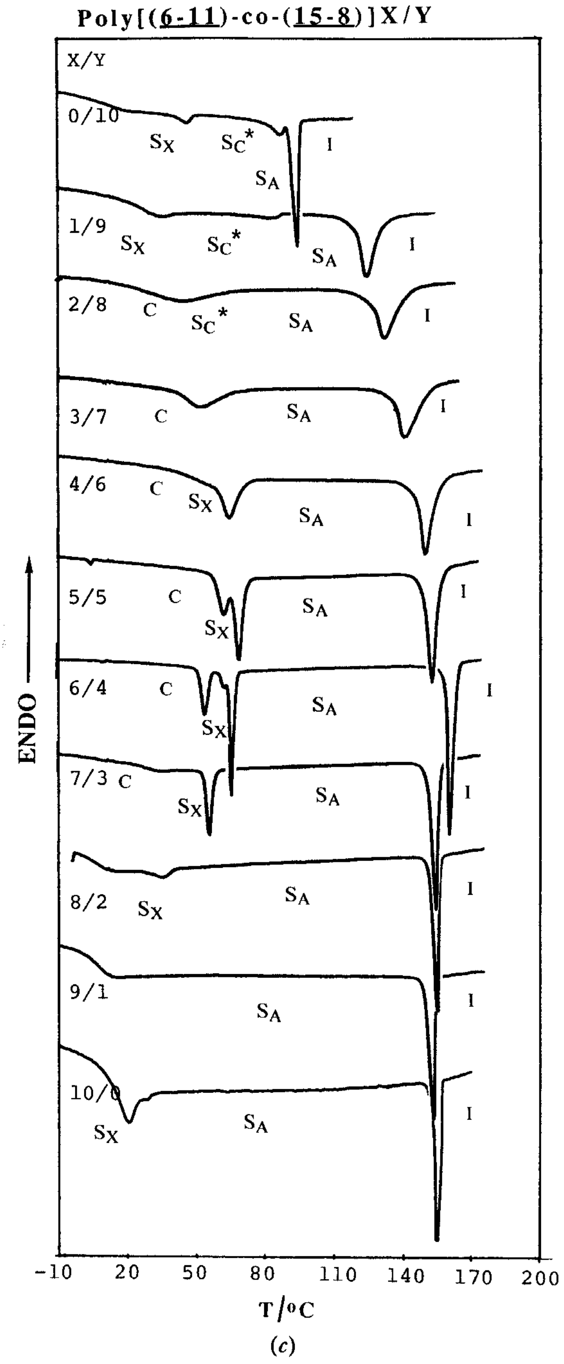


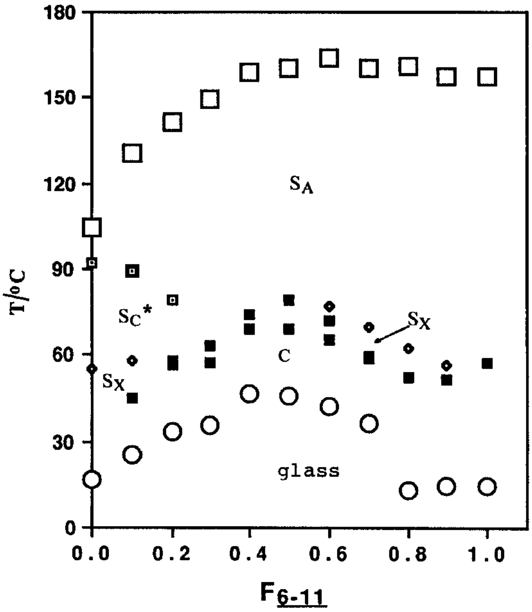
Figure 2. DSC traces displayed during the first heating scan (*a*), second heating scan (*b*), and first cooling scan (*c*) of poly(6-11), poly(15-8) and of poly[(6-11)-co-(15-8)]*X*/*Y*.

degree of polymerization of 18 exhibits enantiotropic S_A, S_C^* and S_X mesophases (see figures 2(*a*)–(*c*)).

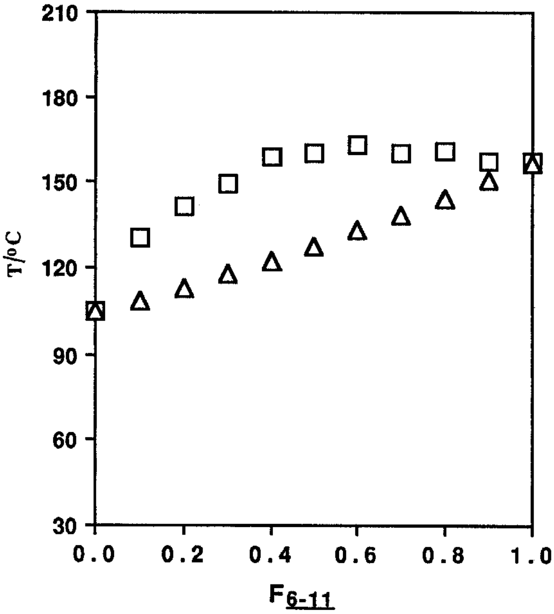
Let us first investigate the phase behaviour of poly[(6-11)-co-(15-8)X/Y as obtained from the first heating DSC scans (see figure 2(*a*)). The nature of the mesophase displayed by various copolymers is presented in this figure. Upon copolymerization, the temperature associated with the S_A–I transition increases and therefore, the S_A mesophase exhibits a continuous dependence of composition with an upward curvature as clearly observed from their DSC traces (see figure 2(*a*)). That is, the structural units of both poly(6-11) and poly(15-8) are isomorphic within the S_A phase over the entire range of copolymer compositions [26]. However, this dependence shows a non-ideal solution like behaviour since there is a significant deviation from what is expected for the same dependence predicted by the Schroeder–van Laar equation for an ideal solution resulting from the structural units of this copolymer (see Figure 3(*b*)) [21]. All poly[(6-11)-co-(15-8)]X/Y copolymers exhibit a crystalline phase, while copolymers with $X/Y=6/4$ to 9/1 exhibit an induced S_X phase. Both the ability to obtain copolymers exhibiting a S_A mesophase with enhanced thermal stability and an induced smectic phase from structural units derived from two homopolymers which both display a S_A phase are interesting results for which we do not have a definitive explanation.

However, the following speculative explanation is suggested. The new S_X mesophase may result because these copolymers contain strong polar cyano and less polar chiral alkyl groups. It is well-known from studies of low molar mass liquid crystals that the mixture of strong polar and less polar mesogens may induce a smectic mesophase and/or enhance the thermal stability of the smectic mesophase [27–32]. We can speculate that polar cyano groups form the antiparallel associations between polar molecules with overlapped aromatic rings, while less polar chiral alkyl groups form a smectic structure with monomolecular layers. Therefore, upon copolymerization, dipolar associations of polar mesogens will rapidly collapse and the layer spacing decreases down to the line corresponding to what would be expected for a monomolecular layer. Consequently, both structural units will form denser packing upon copolymerization. Morphological experiments are required to support this speculative explanation.

However, upon copolymerization, the chiral smectic C and S_X phases of poly(15-8) are suppressed up to copolymer compositions of $X/Y=1/9$ and $X/Y=2/8$, respectively. Figure 3(*a*) plots the phase transitions from the first heating DSC scan as a function of copolymer composition. As we can observe from figure 3(*a*), the S_A phase shows a continuous dependence of composition with an upward curvature. In the second DSC heating scan (see figure 2(*b*)), the S_A mesophase exhibits again a continuous dependence with an upward curvature. However, copolymers with $X/Y=2/8$ to $X/Y=7/3$ exhibit an induced crystalline phase, while copolymers with $X/Y=4/6$ to $X/Y=8/2$ an induced enantiotropic S_X phase. Nevertheless, the transition temperatures associated with S_X and S_C^* phases of poly(15-8), and with the S_X phase of poly(6-11) decrease upon copolymerization. The cooling DSC traces of these copolymers are similar to those of the second DSC heating scans (see figures 2(*b*) and (*c*)). The data collected from the second heating DSC scans and the first cooling scans are plotted in figures 3(*c*) and (*d*). Figure 3(*e*) plots the dependence of the enthalpy change associated with the S_A–I transition from first and second heating DSC scans and the I–S_A transition from first cooling scans as a function of copolymer composition. This plot also shows the continuous character of the dependence of the enthalpy change associated with this


180
150
120
90
60
30
0
T/°C
S_A
S_C*
S_X
S_X
C
glass
0.0
0.2
0.4
0.6
0.8
1.0
F6-11

(a)


210
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T/°C
0.0
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0.4
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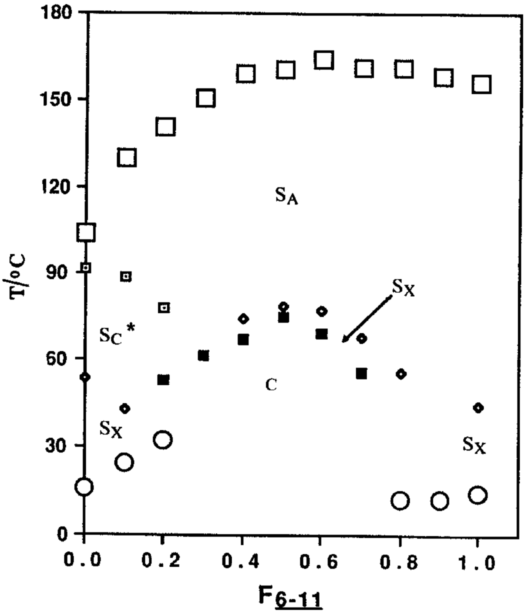
1.0
F6-11

(b)


180
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S_X
S_C*
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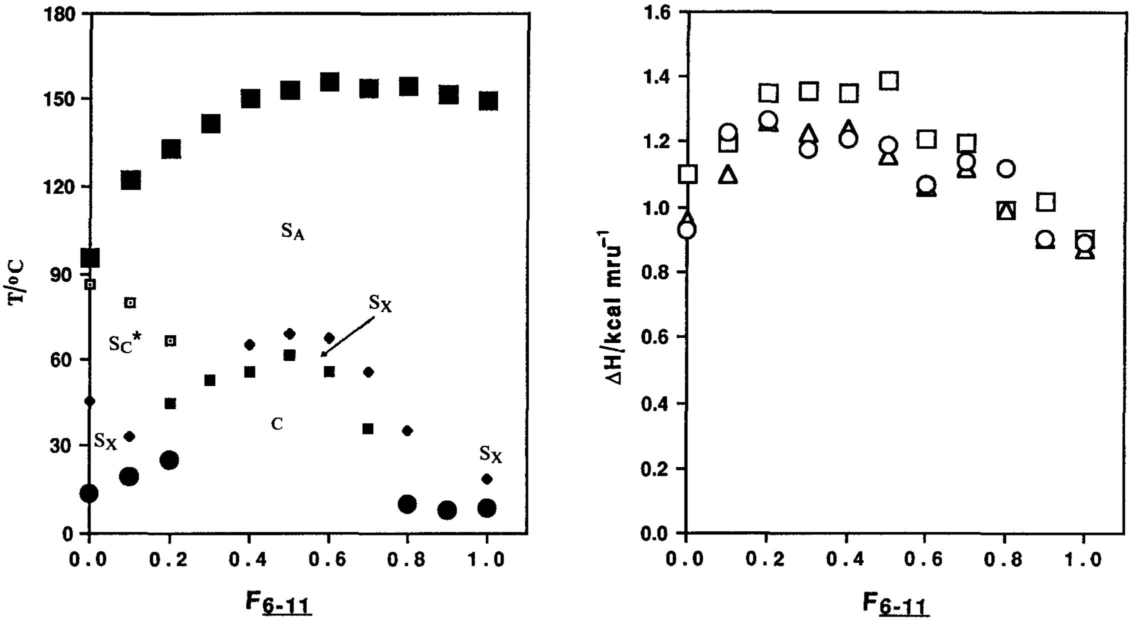
1.0
F6-11

(c)



(*d*) (*e*)

Figure 3. The dependence of phase transition temperatures on the composition of poly[(6-11)-co-(15-8)]X/Y copolymers: (*a*) data from first heating scan: ○, T_g; ■, T_C; ◇, $T_{S_XS_{A(S_C^*)}}$; ⊡, $T_{S_C^*S_A}$; □, T_{S_AI}; (*b*) the dependence of S_A–N and S_A–I transition temperatures on composition of poly[(6-11)-co-(6-5)]X/Y: (Δ) data calculated by Schroeder–van Laar equation; (□) experimental data from the first heating scan; (*c*) data from second heating scan: ○, T_g; ■, T_C; ◇, $T_{S_XS_A}(S_C^*)$; ⊡, $T_{S_C^*S_A}$; □, T_{S_A}I; (*d*) data from first cooling scan: ●, T_g; ■, T_C; ◆, $T_{S_{A(S_C^*)}}S_X$; ⊡, $T_{S_AS_C^*}$; □, T_{iS_A}; (*e*) the dependence of the enthalpy changes associated with the mesomorphic–isotropic–mesomorphic phase transitions on the composition of [poly(6-11)-co-(15-8)]X/Y: □, ΔH_{S_AI} (data from first heating scan); △-ΔH_{S_AI} (data from second heating scan); ○, ΔH_{IS_A} (data from first cooling scan).

phase transition versus copolymer composition. Finally, figure 4 presents some representative textures characteristic for the S_A and S_X phases exhibited by poly[(6-11)-co-(15-8)]6/4.

These experimental results provide information on the isomorphism of two monomeric structural units derived from two different mesogens and spacer lengths within a smectic A phase. In contrast to binary copolymers based on structural units containing the same mesogen but different spacer lengths which are isomorphic within the same mesogen and behave as an ideal solution derived from the two structural units, structural units based on dissimilar mesogens are isomorphic but behave as a non-ideal solution.

3.2. *Poly*[(15-8)-*co*-(6-3)]X/Y

This copolymer is synthesized from a pair of monomers whose parent homopolymers exhibit different mesophases before isotropization, that is, the highest tempera-

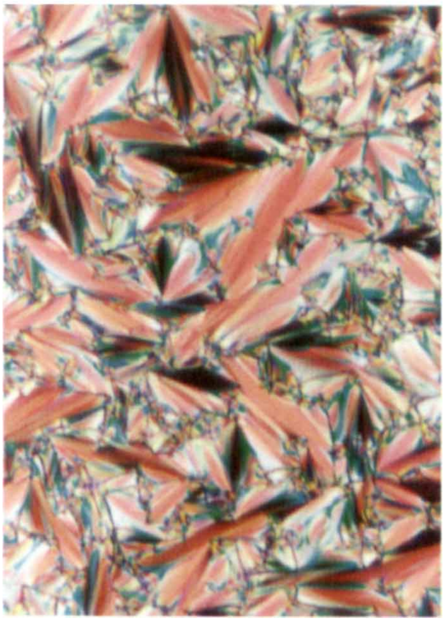


Figure 4 (*a*)

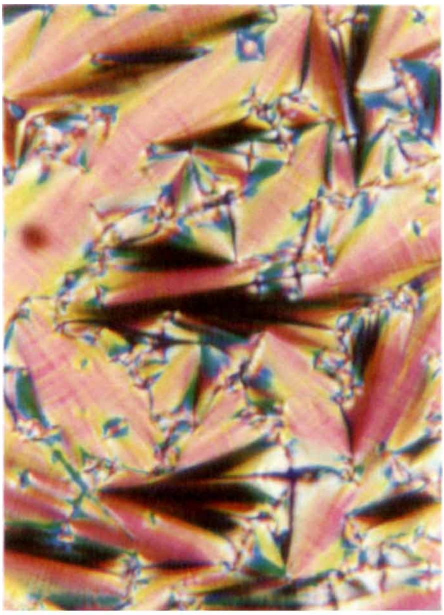


Figure 4 (*b*)

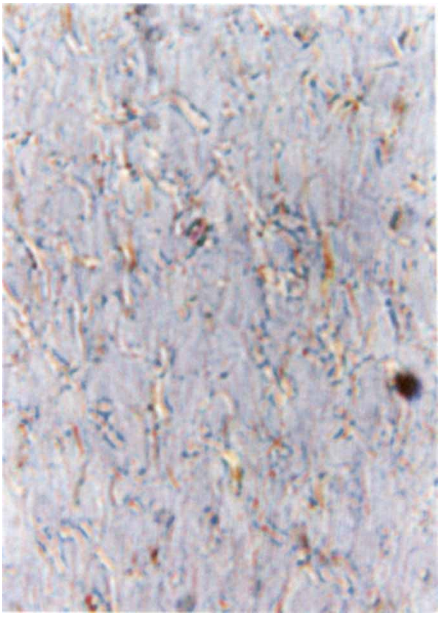


Figure 6.

ture mesophase of poly(15-8) [20(c)] is S_A, while that of poly(6-3) [16(b)] is nematic. In addition, it is expected that this copolymer will generate, at a certain composition, also a cholesteric mesophase since poly(15-8) contains a chiral moiety. The synthesis and characterization of the copolymers poly[(15-8)-co-(6-3)]X/Y are presented in table 2.

Let us first discuss the phase behaviour obtained from the first DSC heating scans (see table 2 and figure 5(*a*)). The S_X phase of poly(6-3) shows a linear dependence up to a value of $X/Y=3/7$. As expected, a cholesteric mesophase was induced in copolymers with $X/Y=1/9$ and 2/8. Copolymers with $X/Y=4/6$ to 6/4 exhibit the S_A and an induced crystalline phase, while copolymers with $X/Y=7/3$ to 10/0 exhibit the S_A, S_C^* and S_X mesophases. The interest in these copolymers has arisen from their propensity to form a cholesteric mesophase. It is well established that copolymerization of a monomer pair based on a monomer containing a chiral group with a monomer whose parent homopolymer exhibits a nematic mesophase generates cholesteric copolymers [33–37].

Figure 5(*a*) plots all the phase transitions from the first heating DSC scans as a function of copolymer composition. As we observe from figure 5(*a*), the nematic and cholesteric mesophases show a linear dependence or composition up to a value of $X/Y=2/8$. This indicates that the structural units of both poly(6-3) and poly(15-8) are isomorphic within the nematic and cholesteric phases over a certain range of copolymer compositions. In addition, the smectic A mesophase also shows a continuous character with an upward curvature over a certain range of copolymer composition which represents a similar behaviour to that of poly[(6-11)-co-(15-8)]X/Y. In the second heating scan (see figure 5(*b*)), the induced crystalline and S_X phases do not appear. This is due to their close proximity to the glass transition temperature of the copolymers. Therefore, these two phases form only when the polymers are precipitated from solution. If the polymer is redissolved and reprecipitated, these phases reappear. However, the S_A, nematic and cholesteric mesophases follow the same trend as the one observed in the first DSC heating scans (see figure 5(*a*)). The cooling DSC scans of these copolymers show the same trend as those of the second heating scan (see table 2). The data collected from the second DSC heating scans and the first cooling scans are plotted in figures 5(*b*) and (*c*). The enthalpy changes associated with the highest temperature mesophase of these copolymers (see table 2) are plotted in figure 5(*d*) as a function of copolymer composition. A representative texture of the cholesteric mesophase is presented in figure 6.

The results obtained for the copolymers poly[(6-11)-co-(15-8)]X/Y show that the copolymerization of a monomer containing a chiral group with a monomer whose parent homopolymer exhibits a nematic mesophase provides a simple technique for the synthesis of copolymers exhibiting an enantiotropic cholesteric mesophase and exhibiting an enantiotropic smectic A phase with enhanced thermal stability.

In conclusion, the results described in this paper have demonstrated that, when two structural units of a copolymer based on dissimilar mesogens are isomorphic within a

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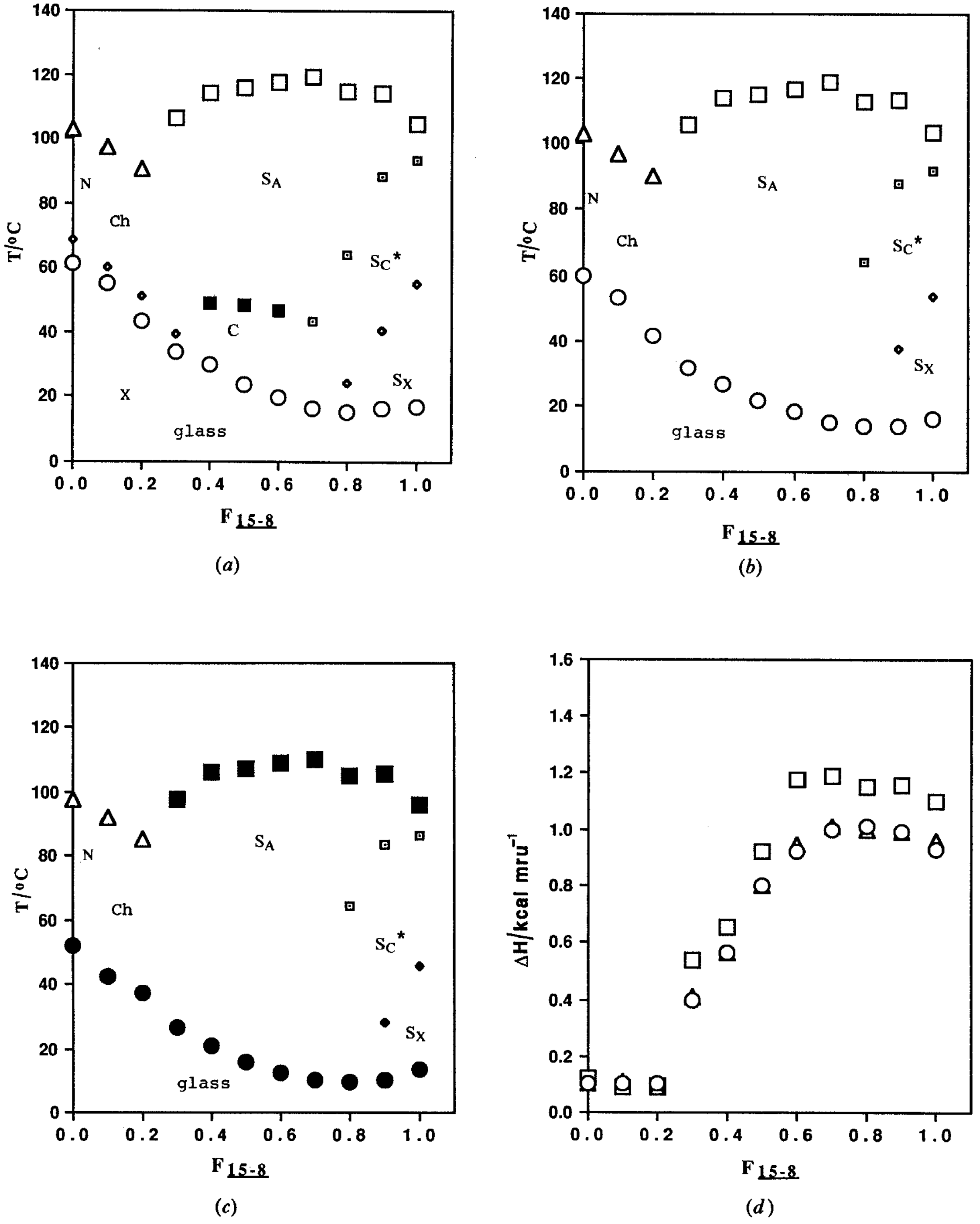
Figure 4. Representative optical polarized micrographs (×66) of (*a*) poly[(6-11)-co-(15-8)]6/4 at 140°C on the cooling scan (S_A phase), (*b*) poly[(6-11)-co-(15-8)]6/4 at 60°C on the cooling scan (S_X phase).

Figure 6. Representative optical polarized micrograph (×66) of: (*a*) poly[(15-8)-co-(6-3)]8/2 at 85°C on the cooling scan (cholesteric phase).



(*a*) (*b*)

(*c*) (*d*)

Figure 5. The dependence of phase transition temperatures on the composition of poly[(15-8)-co-(6-3)]X/Y copolymers: (*a*) data from first heating scan: ○, T_g; ■, T_C; ◇, $T_{XN(Ch)}$; ◇, $T_{S_XS_A}(S_C^*)$; ⊡, $T_{S_C^*S_A}$; □, T_{S_AI}; △, $T_{N(Ch)I}$; (*b*) data from second heating scan: ○, T_g; ◇, $T_{S_XS_A(S_C^*)}$; ⊡, $S^*_{CS_A}$; □, T_{S_AI}; △, $T_{N(Ch)I}$; (*c*) data from first cooling scan; ●, T_g; ◆, $T_{S_A(S_C^*),S_X}$; ⊡, $T_{S_AS_C^*}$; □, T_{IS_A}; △, $T_{IN(Ch)}$; (*d*) The dependence of the enthalpy changes associated with the mesomorphic—isotropic and isotropic—mesomorphic transitions on the composition of poly [(15-8)-co-(6-3)]X/Y: □, ΔH_{S_AI} (data from first heating scan); △, ΔH_{S_AI} (data from second heating scan); ○, ΔH_{IS_A} (data from first cooling scan).

certain mesophase, the transition temperature and enthalpy change associated with this mesophase show a continuous dependence of the the entire range of copolymer composition. However, the dependence of the temperature transitions of this mesophase on copolymer composition behaves as that of a solution derived from these two structural units which exhibits a non-ideal behaviour. In the particular examples described in this part the highest temperature mesophase of these copolymers displays a positive deviation from that predicted by the Schroeder–van Laar equations. In addition, these results have also demonstrated that a new mesophase can be generated by copolymerization.

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