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Synthesis and characterization of chiral smectic C liquid crystalline terpolysiloxanes

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A number of tailor-made side chain liquid crystalline terpolysiloxanes, containing chiral cyanohydrin ester, phenyl pyrimidine and fluorinated phenylbenzoate as the side groups, have been synthesized for potential applications as ferroelectric liquid crystal polymers. All the polysiloxanes exhibit the mesomorphic sequence of crystal–chiral smectic C–smectic A–isotropic phases.

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1. Introduction

Liquid crystals (LCs) and liquid crystal polymers (LCPs) containing a chiral smectic C phase are of interest because of their potential applications as spatial light modulators [1–5]. The LCPs tend to have slow dynamic response times because of their high viscosities. With respect to the viscosities of LCPs, polysiloxane-based ferroelectric liquid crystal polymers (FLCPs) possessing low viscosity have shown promising results because of the flexible nature of the polymer backbone [6, 7].

The appearance of a ferroelectric phase in a mixture containing a chiral dopant and a smectic C (S_C) material host, reported by Kuczynskci and Stegemeyer [8], has resulted in a concerted effort to explore low molecular weight FLC mixtures (LMWFM) which use chiral material exhibiting high spontaneous polarization. To prepare a useful ferroelectric liquid crystal (FLC) mixture for electro-optics, it is necessary to use a high spontaneous polarization chiral dopant to reduce the concentration of chiral dopant and thus reduce the viscosity of the resultant mixture. The magnitude of spontaneous polarization of a ferroelectric mixture is governed solely by the chiral dopant. Therefore, if the chiral dopant exhibits a tilted smectic phase, its spontaneous polarization can be known prior to the fabrication of the mixture [9].

The aims of the work reported here were to synthesize and characterize side chain chiral S_C LCPs with the tailoring of a LMWFM onto the backbone of a polysiloxane as the side groups. The design and synthesis included the chiral dopant **1a**, a cyanohydrin mesogenic monomer which exhibits a large spontaneous polarization value [10], the phenyl pyrimidine monomer **7**, which is known to exhibit an S_C phase with wide temperature range [11] and a fluorinated nematogenic side group **16**, which was expected to reduce the transition temperature and has a nematic phase at room temperature. The terpolsiloxanes **I** are composed of mesogenic side groups **1a**, **7b**, **16** and the copolysiloxanes **II** consist of the chiral mesogenic **1b** and the dimethylsiloxane side groups.

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2. Experimental

2.1. *Materials*

All starting materials for the preparation of the LMWLC monomers were obtained from the Aldrich Chemical Company and used as received. The poly(methylhydro)siloxane having 36 repeating units was obtained from the Aldrich Chemical Company and used as received. The poly(methylhydro)siloxanes with 80 repeating units was obtained from Hüls Chemical Company and used as received. The catalyst, chloroplatinic acid hexahydrate, was obtained from Strem Chemicals Company and used as received.

2.2. *Techniques*

The ^{1}H and ^{13}C NMR spectra were recorded on a Varian FT-200 spectrometer (200 MHz) with TMS as the internal standard. The purity of compounds were determined using a Waters HPLC equipped with a C-18 reverse phase column and a 944 diode array detector. The elemental analyses were performed by the Oneida Corporation, New York. The transition temperatures and textures of the polymers were obtained from a Leitz-Laborlux S Polarizing Optical Microscope fitted with a Mettler FP-5 heating stage and a Perkin–Elmer DSC-7.

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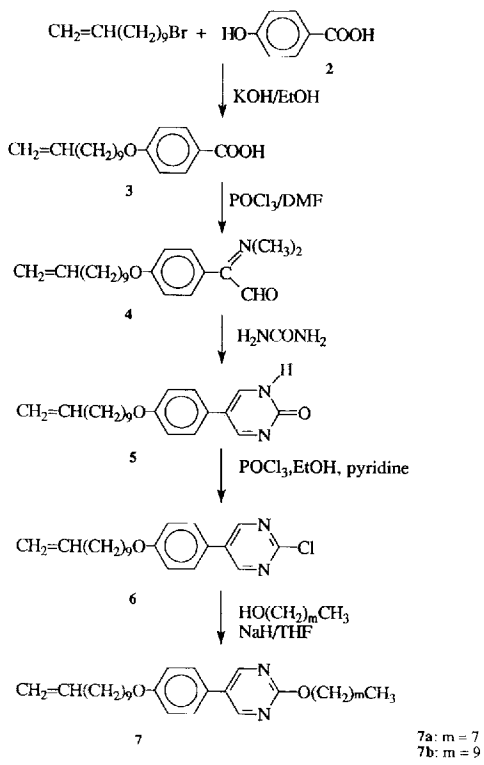
Heating and cooling rates for monomers and polymers were 5°C min^{-1} and 20°C min^{-1}, respectively. Optical rotations were performed on an Optical Activity AA-10 Automatic Polarimeter with a concentration of 30 mg ml^{-1} at 25°C.

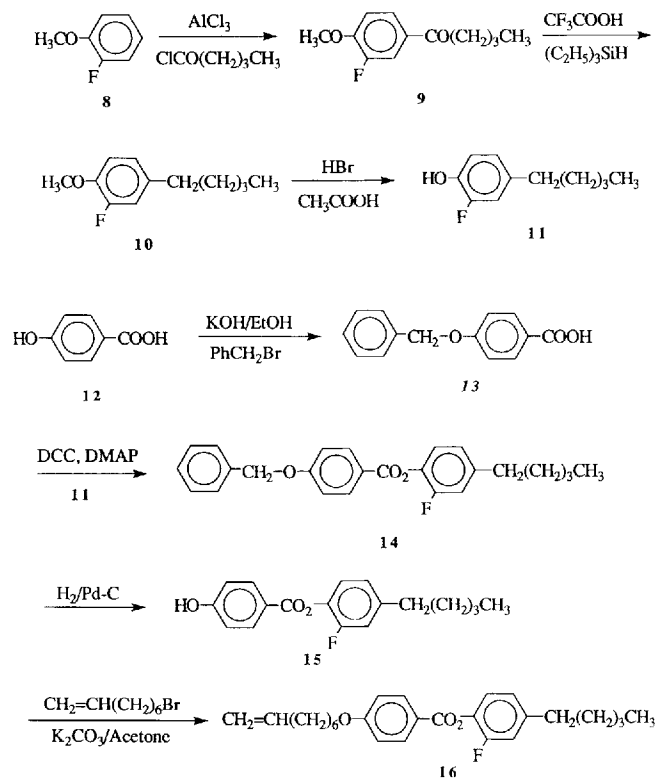
2.3. *Synthesis*

The syntheses of pyrimidine and fluorinated monomers were performed following the synthetic paths outlined in schemes 1 and 2. The synthesis of monomers **7a** and **b** and **16** are described as follows.

2.3.1. *Synthesis of 11-bromo-1-undecene*

The alcohol (50·0 g, 294 mmol), 82·5 ml of toluene, and 7·9 ml of pyrimidine were cooled to −10°C and a solution of 82·5 ml of toluene and PBr_3 (32·4 g 120 mmol) was added dropwise over the period of 2 h at the above temperature. The reaction was allowed to slowly return to room temperature and then refluxed for 2 h at 70–80°C. The inorganic phosphorous acid by-product was filtered. The toluene was evaporated off and the liquid residue was distilled under vacuum at 71–75°C and 2–0·4 mmHg. TLC showed one spot using hexane (R_f = 0·47) as the eluent. 50·23 g were obtained with a 74 per cent yield. FTIR (Neat, cm^{-1}): 3078 (alkene C–H) 2929, 2858 (alkyl C–H). ^{1}H NMR ($CDCl_3$, δppm): 1·49–1·28 (m, 12 H, alkyl), 1·86 (quintet, 2 H, Br–CH_2–CH_2–CH_2–), 2·12–1·99 (m, 2 H, C=C–CH_2–CH_2–), 3·40 (t, 2 H, J = 6·82, Br–CH_2–CH_2–), 4·93 (dd, H, J_1 = 2·2, J_2 = 6·72, HRC=CHH *trans* from R), 5·02 (dd, H, J_1 = 2·08, J_2 = 14·89, HRC=CHH *trans* from H), 5·92–5·61 (m, H, H_2C=CHR).





2.3.2. *4-(11-Undecenoxy)phenlyacetic acid (3)*

4-Hydroxyphenylacetic acid (25·0 g, 108 mmol.) and KOH (13·30 g, 237 mmol) were dissolved in 300 ml of ethanol and stirred for 15 min. 11-Bromo-1-undecene, **2a** (16·37 g, 108 mmol), and 75 ml of water were then added and the mixture was refluxed for 4 d. The ethanol was evaporated, and the mixture poured over water and acidified to approximately pH = 1 with concentrated HCl. The precipitate was filtered and dried in an oven. The precipitate was recrystallized from hexanes; 18·42 g were obtained with a yield of 56·3 per cent. TLC showed one spot using ethyl acetate (R_f = 0·09) as eluent. The reaction was repeated a total of three times with an average yield of 56·3 per cent. m.p. = 186–187°C. FTIR (Nujol, cm^{-1}): 3350–2657 (acid, –OH), 1703 (C=O), 1415 (aromatic stretch), 1220 (C–O–Ph). ^{1}H NMR ($CDCl_3$, δppm): 1·55–1·30 (m, 14 H, alkyl), 1·77 (quintet, 2 H, J = 7·14, Ph–O–CH_2–CH_2–CH_2–), 2·12–1·99 (m, 2 H, C=C–CH_2–CH_2–), 3·52 (s, 2 H, HO(C=O)–CH_2–Ph), 3·95 (t, 2 H, J = 7·98, Ph–O–CH_2–CH_2–), 4·92 (dd, H, J_1 = 2·2, J_2 = 7·98, HRC=CHH *trans* from R), 5·00 (dd, H, J_1 = 2·16, J_2 = 17·26, HRC=CHH *trans* from H),

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5·92–5·61 (m, H, $H_2C{=}CHR$), 6·85 (d, 2 H, $J=8·71$, aromatic Hs *ortho* to –O*R*), 7·17 (d, 2 H, $J=8·67$, aromatic Hs *meta* to –O*R*).

2.3.3. *3-Dimethylamino-2-(4-undecenoxyphenyl)acroleine (4)*

15 ml of phosphorous oxychloride was added to 15 ml of sieve dried DMF. The solution was stirred at 0°C for 1 h. A solution 65 ml of sieve dried DMF and 4-(11-undecenoxy)phenylacetic acid **3** (15 g, 494 mmol) was added dropwise to the above 0°C solution. After the addition, the solution was allowed to return to room temperature and then heated at 50°C for 1 h and then at 70°C for 6 h. The reaction mixture was poured over water and 26 g of K_2CO_3 and a solution of 50 g KOH in 25 ml of water was added. The solution was then heated at 50°C for 2 h. The aqueous solution was extracted with chloroform three times and the organic solution was dried with $MgSO_4$. After filtration, a column was run with a ratio of 1:3 acetonitrile to methylene chloride. 13·87 g were obtained, a yield of 82 per cent. TLC showed one spot using acetonitrile ($R_f=0·56$) as the eluent. The reaction was repeated three times with an average yield of 73 per cent. The product was a liquid. FTIR (Neat, cm^{-1}): 3175 (aromatic/C=C–C–H), 2928 and 2849 (alkyl C–H), 1606 (C=O), 1509 and 1400 (aromatic and C=C stretch), 1210 (PH–O–C). ^1H NMR ($CDCl_3$, δppm): 1·55–1·25 (m. 12 H, alkyl), 1·90–1·70 (m, 2 H, Ph–O–CH_2–CH_2–CH_2–), 2·13–1·95 (m, 2 H, C=C–CH_2–CH_2–), 2·835 (s, 6 H, –N–$(CH_3)_2$), 3·94 (t, 2 H, $J=6·56$, Ph–O–CH_2–CH_2–), 5·00 (dd, H, $J_1=2·2$, $J_2=10·05$, H*R*C=C*H*H *trans* from *R*), 5·00 (dd, H, $J_1=2·16$, $J_2=15·31$, H*R*C=C*H*H *trans* from H), 5·92–5·71 (m, H, $H_2C{=}CHR$), 6·78 (s, H, C=C*H*N$(CH_3)_2$), 6·87 (d, 2 H, $J=8·50$, aromatic Hs *ortho* to =O*R*), 7·08 (d, 2 H, $J=8·67$, aromatic Hs *meta* to –O*R*), 9·08 (s, H, aldehyde H).

2.3.4. *2-Dihydro-5-(4-undecenoxyphenyl)pyrimid-2-one (5)*

3-Dimethylamino-2-(4-undecenoxyphenyl)acroleine, **4** (14·20 g, 41 mmol), urea (3·23 g, 52 mmol), and 4·20 ml concentrated HCl were dissolved in 200 ml ethanol. The reaction mixture was refluxed for 2 d. After slow cooling to room temperature, the ethanol was evaporated. The residue was dissolved in chloroform and dried with $MgSO_4$ and decolourized with activated charcoal. After filtration, a column was run with a ratio of 1:3 THF to methylene chloride as the eluent. 5·29 g were obtained with a yield of 38 per cent. TLC showed one spot using 1:3 THF to methylene chloride ($R_f=0·09$) as eluent. The average yield over four reactions was 37·8 per cent. m.p. = 131–133°C. FTIR (Nujol, cm^{-1}): 3302 (N–H) 1670 (C=N) 1630 (C=O) 1387 (aromatic/C=C stretch) 1262 (Ph–O–C). ^1H NMR ($CDCl_3$, δppm): 1·60–1·20 (m, 12 H, alkyl), 1·910–1·650 (m, 2 H, Ph–O–CH_2=CH_2–CH_2–), 2·15–1·99 (m, 2 H C=C–CH_2–CH_2–), 3·98 (t, 2 H, $J=6·56$, Ph–O–CH_2–CH_2–), 4·995 (dd, H, $J_1=2·01$, $J_2=$ 9·08, H*R*C=C*H*H *trans* from *R*), 4·94 (dd, H, $J_1=2·00$, $J_2=15·245$, H*R*C=C*H*H *trans* from H), 5·91–5·51 (m, H, $H_2C{=}CHR$), 6·975 (d, 2 H, $J=8·05$, aromatic Hs *ortho* to –O*R*), 7·35 (d, 2 H, $J=7·78$, aromatic Hs *meta* to –O*R*), 8·50 (s, 2 H, pyrimid-2-one Hs *ortho* to Ph), the N–H was not detected.

2.3.5. *2-Chloro-5-(4-undecenoxyphenyl)pyrimidine (6)*

Phosphorous oxychloride (11·104 g 72 mmol), 1,2-dihydro-5-(4-undecenoxyphenyl) pyrimid-2-one **5** (3·88 g, 11·4 mmol) and 2 ml of *N,N*-dimethylaniline were heated at 110°C for 24 h. The reaction mixture was poured slowly over water and extracted three times with ethyl acetate. The organic layers were dried with $MgSO_4$ and decolourized with activated charcoal. A column was run using flash silica gel with no pressure. 2·95 g were obtained in a 72 per cent yield. TLC showed one spot using methylene chloride ($R_f=0·23$) as the eluent. The average yield for three reactions was 61 per cent. m.p. = 93·5°C. FTIR (Nujol, cm^{-1}): 1543, 1410 and 1390 (aromatic/C=C stretch), 1252 (Ph–O–C). ^1H NMR ($CDCl_3$, δppm): 1·63–1·20 (m, 12 H, Alkyl) 1·91–1·72 (m, 2 H, Ph–O–CH_2–CH_2–CH_2–), 2·15–1·95 (m, 2 H, C=C–CH_2–CH_2–), 3·984 (t, 2 H, $J=6·56$, Ph–O–CH_2–CH_2–), 4·93 (dd, H, $J_1=1·75$, $J_2=9·06$, H*R*C=C*H*H *trans* from *R*), 5·00 (dd, H, $J_1=2·00$, $J_2=16·12$, H*R*C=C*H*H *trans* from H), 5·91–5·71 (m, H, $H_2C{=}CHR$), 7·03 (d, 2 H, $J=$ *8·71, aromatic Hs ortho* to –O*R*), 7·48 (d, 2 H, $J=8·71$, aromatic Hs *meta* or –O*R*) 8·79 (s, 2 H, pyrimidine Hs *ortho* to Ph).

2.3.6. *2-Octanoxy-5-(4-undecenoxyphenyl)-pyrimidine (7a)*

The reagents 1-octanol (225 g, 1·73 mmol) and NaH (54 mg, 2·25 mmol) were stirred for 2 h after removal of the ice bath. 2-Chloro-5-(4-undecenoxyphenyl)pyrimidine **6** (500 mg, 1·4 mmol) was dissolved in the least amount of sodium dried THF and added to the solution. This mixture was stirred at room temperature for 36 h. The solvent was evaporated and the residue was dissolved in diethyl ether. The organic solution was extracted three times with water and dried with $MgSO_4$. A gravity column with flash silica was run with a 1:3 ratio of THF:methylene chloride as the eluent. TLC showed one spot using the same solvent mixture ($R_f=0·91$) as the eluent. HPLC: (>99 per cent). 0·51 g of the product was obtained using the same purification as above. The yield was 75 per cent. FTIR (Nujol, cm^{-1}): 1603 and 1541 (aromatic/C=C), 1252 (Ph–O–C). ^1H NMR ($CDCl_3$, δppm): 0·88 (t, 3 H, $J=6·31$, –CH_2–CH_3),

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1·58–1·15 (m, 22 H, alkyl), 1·91–1·72 (m, 4 H, –O–CH_2–CH_2–CH_2–), 2·11–1·97 (m, 2 H C=C–CH_2–CH_2–), 4·00 (t, 2 H, J = 6·59, Ph–O–CH_2–CH_2–), 4·38 (t, 2 H, J = 6·59, N ring–O–CH_2CH_2–), 4·93 (dd, H, J_1 = 1·92, J_2 = 8·01, H*R*C=C*H*H *trans* from *R*), 5·00 (dd, H, J_1 = 2·00, J_2 = 17·32, H*R*C=C*H*H *trans* from H), 5·91–5·71 (m, H, H_2C=C*HR*), 6·99 (d, 2 H, J = 8·51, aromatic Hs *ortho* to –O*R*), 7·43 (d, 2 H, J = 8·63, aromatic Hs *meta* to –O*R*), 8·66 (s, 2 H, pyrimidine Hs *ortho* to Ph).

2.3.7. *2-Decanoxy-5-(4-undecenoxyphenyl)pyrimidine (7b)*

The reaction was carried out using the procedure described for the preparation of compound **7a**: 1-decanol (2·20 g, 13·9 mmol), NaH (0·500 g of 80 per cent, 16·7 mmol) and 0,012 mol of 2-chloro-5-(4-undeceyl)pyrimidine **6**. A gravity column with flash silica was run with a 1 : 3 ratio of THF : methylene chloride as the eluent. TLC showed one spot using the same solvent mixture (R_f = 0·91) as eluent. HPLC: (>99 per cent). 4·45 g were obtained in a 74 per cent yield. FTIR (Nujol, cm^{-1}): 1608 and 1548 (aromatic/C=C), 1254 (C–O–Ph). ^{1}H NMR ($CDCl_3$, δppm): 0·88 (t, 3 H, J = 6·27, –CH_2–CH_3), 1·58–1·05 (m, 26 H, alkyl), 1·91–1·72 (m, 4 H, –O–CH_2–CH_2–CH_2–), 2·11–1·97 (m, 2 H, C=C–CH_2–CH_2–), 4·03 (t, 2 H, J = 6·45, Ph–O–CH_2–CH_2–) 4·38 (t, 2 H, J = 6·65, N ring–O–CH_2–CH_2–) 4·94 (dd, H, J_1 = 1·90, J_2 = 7·94, H*R*C=C*H*H *trans* from *R*), 5·00 (dd, H, J_1 = 2·00, J_2 = 17·32, H*R*C=C*H*H *trans* from H), 5·910–5·710 (m, H, H_2C=C*HR*), 6·99 (d, 2 H, J = 8·50, aromatic Hs *ortho* to –O*R*), 7·43 (d, 2 H, J = 8·39, aromatic Hs *meta* to –O*R*), 8·66 (s, 2 H, pyrimidine Hs *ortho* to Ph). ^{13}C NMR ($CDCl_3$, δppm) peak assignments are to c = alkyl carbon, C = aromatic carbon, C = alkene carbon: 164·5 (C–O*R* alpha to both N), 159·3 (C–O*R* of Ph), 156·8 (2CH, each alpha to 1N), 139·2 (CH*R*), 127·9 and 126·7 (2C linking the rings), 127·6 (2C alpha to ring linkage in Ph), 115·3 (2C alpha to C–O*R* in Ph), 114·14 (CH_2), 68·14 and 67·88 (2c,c–O–ring), 33·8, 31·9, 29·6, 29·5, 29·4, 29·3, 29·2, 29·1, 28·9, 26·0, 22·7, 14·3 (alkyl). Elemental analysis: calculated: C = 77·45, H = 10·06, N = 5·83; experimental: C = 76·82, H = 9·95, N = 5·73 per cent.

2.3.8. *1-(4-Methoxy-2-fluorophenyl)pentanone (9)*

This intermediate was prepared by adding pentanoic chloride dropwise (19·12 g, 0·159 mol) to a ice–salt bath cooled solution (−5°C) of 2-fluoroanisole **8** (20·00 g, 0·159 mol) and aluminium chloride (23·74 g, 175 mmol) in 100 ml of sieve dried methylene chloride. The reaction was kept under anhydrous conditons and stirred for 3 h at room temperature. The mixture was then poured over water and extracted with methylene chloride. The organic layer was washed with 5 per cent aqueous NaOH, water, and dried over sodium sulphate. The methylene chloride was filtered and then evaporated off to leave solid residue. The product was isolated by column chromatography using a 70 : 30 volume ratio of methylene chloride : hexanes as the eluent. The product was recrystallized from hexanes and 20·05 g were obtained with a 60 per cent yield. TLC showed one spot using methylene chloride and hexane (70 : 30; R_f = 0·30) as the eluent. The reaction was performed two further times with an average yield of 70 per cent. m.p. = 56–57°C. FTIR (Nujol, cm^{-1}): 1689 (C–O), 1617 (aromatic ring stretch), 1220 (CH_3–O–Ph). ^{1}H NMR ($CDCl_3$, δppm): 0·96 (t, 3 H, J = 7·41, CH_3–CH_2–), 1·41 (sextet, 2 H, J = 7·57, CH_3–CH_2–CH_2–), 1·71 (quintet, 2 H, J = 7·59, –CH_2–CH_2–CH_2–), 2·90 (t, 2 H, J = 7·31, (C=O)–CH_2–CH_2–), 3·92 (s, 3 H, CH_3–O–Ph), 6·99 (t, H, J = 8·42, *ortho* to methoxy), 7·77–7·67 (m, 2 H, *meta* to methoxy).

2.3.9. *2-Fluoro-4-pentylanisole (10)*

The preceding aromatic ketone **9** was reduced to an alkyl chain via a triethyl silane in a stongly acidic medium. The reaction was carried out as follows. The aromatic ketone **9** (10·00 g, 47 mmol) was mixed with 40 ml of trifluoro acetic acid with stirring. The triethyl silane (21·84 g, 188 mmol) was added dropwise over a 25 min period. The reaction was under anhydrous conditions and was exothermic. The mixture was stirred at room temperature for 3 d. The reaction mixture was poured over ice and extracted twice with diethyl ether. This organic layer was then extracted twice with 5 per cent aqueous $NaHCO_3$. The ether solution was dried with anhydrous sodium sulphate. After filtration, the solvents were evaporated and a liquid residue was obtained. The crude product, purified with a column chromatography using hexanes as the eluent, weighed 8·59 g and gave a 92·10 per cent yield. This reaction performed a total of three times with an average yield of 83·40 per cent. The reaction yields decreased with a jump from a 10 g scale to a 20 g scale. Two reactions on the 10 g scale gave yields of an average 92 per cent. The 20 g scale reaction gave a yield of 66 per cent. The final product was a liquid and the TLC showed one spot using methylene chloride and hexane (70 : 30; R_f = 0·74) as the eluent. FTIR (Neat, cm^{-1}): 3000 (aromatic C–H), 2854 (alkyl C–H), 1630 (aromatic stretch), 1597 (aromatic stretch), 1220 (CH_3–O–Ph). ^{1}H NMR ($CDCl_3$, δppm): 0·89 (t, 3 H, J = 6·64, CH_3–CH_2–), 1·30–1·26 (m, 4 H, CH_3–CH_2–CH_2), 1·57 (pentet, 2 H, J = 7·06, Ph–CH_2–CH_2–), 2·52 (t, 2 H, J = 7·66, Ph–CH_2–), 3·86 (s, 3 H, CH_3–O–Ph), 6·93–6·83 (m, 3 H, aromatic Hs).

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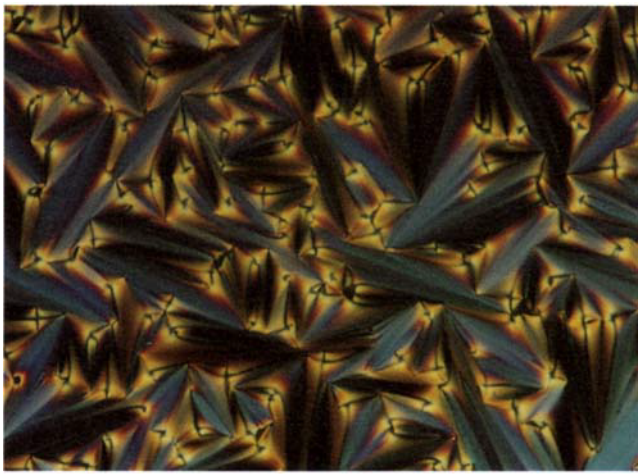

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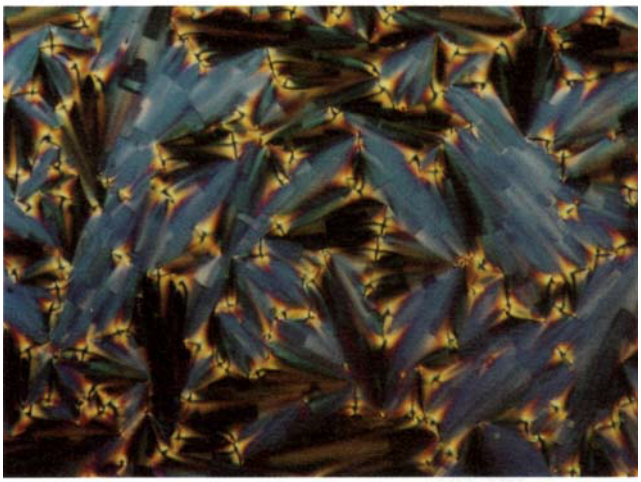

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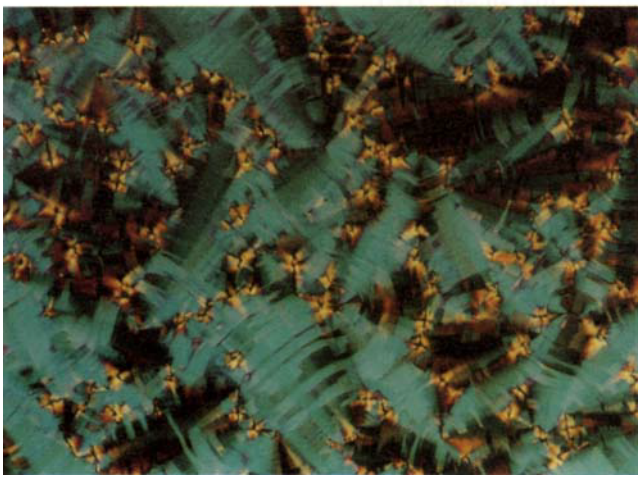
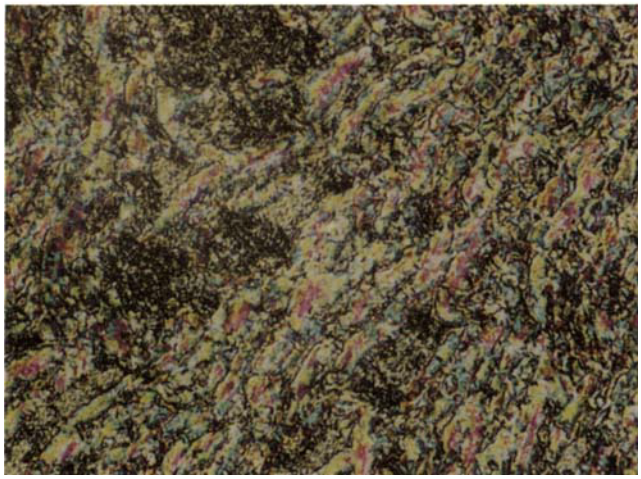


(*c*)

Figure 1. Photomicrograph of monomer **7b**; (*a*) the focal-conic fan texture of the S_A phase; (*b*) the broken fan texture of the S_C phase; (*c*) the S_B phase with transtraion bars on the fan texture.

(*a*)



(*b*)

Figure 2. Photomicrograph of polymer **Ib**; (*a*) the focal-conic texture of the S_A phase and (*b*) the broken fan texture of the S_C phase.

2.3.10. *2-Fluoro-4-pentylphenol (**11**)*

150 ml of 45 wt % hydrobromic acid, 300 ml of glacial acetic acid, and the alkylaryl ether **10** (23·40 g, 119 mmol) were refluxed for 3 d. The reaction mixture was poured over water and extracted twice with diethyl ether. The ether solution was washed with water until the wash water was approximately pH = 7. The organic solution was dried with anhydrous $MgSO_4$. TLC showed only one spot and the product was not purified further. The liquid product gave a 90 per cent yield. The reaction was repeated three times with an average yield of 89 per cent. TLC showed one spot using methylene chloride ($R_f = 0{\cdot}56$) as the eluent. FTIR (Neat, cm^{-1}): 3600 (HO–Ph), 3410 (HO–Ph), 3010 (aromatic C–H), 2938 (alkyl C–H), 2863 (alkyl C–H), 1615 (aromatic stretch),

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1522 (aromatic stretch). ^{1}H NMR ($CDCl_3$, δppm): 0·89 (t, 3 H, J=5·74, CH_3–CH_2–), 1·38–1·21 (m, 4 H, CH_3–CH_2–CH_2–), 1·60–1·50 (m, 2 H, Ph–CH_2–CH_2–CH_2–), 2·52 (t, 2 H, J=7·69, Ph–CH_2–CH_2–), 6·85 (d, H, J=4·03, HO–Ph), 6·94–6·80 (m, 3 H, aromatic Hs).

2.3.11. *4-Benzyloxybenzoic acid (13)*

Hydroxy benzoic acid **12** (15·12 g, 110 mmol) and KOH (13·49 g, 241 mmol) were dissolved in 450 ml of ethanol. Benzyl bromide (18·73 g, 110 mmol) and 75 ml of water were then added to the flask and the mixture was refluxed for 2 d. The ethanol was evaporated off and the reaction mixture was poured over water. The water solution was acidified (approximately pH = 1) with concentrated HCl. The resulting precipitate was filtered and recrystallized from 2-propanol. TLC showed one spot using ethyl acetate (R_f=0·16) as the eluent. The average yield for two batches of reactions was 75 per cent; m.p. = 69°C. FTIR (Nujol, cm^{-1}): 2664–2558 (weak –(C=O)–*OH*), 1698 (C=O), 1617 (aromatic stretch), 1268 (C–O–Ph). ^{1}H NMR ($CDCl_3$, δppm): 5·13 (s, 2 H, Ph–CH_2–O–), 7·00 (d, 2 H, J=9·95, aromatic 2 H *meta* to –(C=O)–OH), 7·49–7·32 (m, 5 H, aromatic Hs of the mono-substituted ring), 7·96 (d, 2 H, J=8·91, aromatic 2 H *ortho* to the –(C=O)–OH).

2.3.12. *(2′-Fluoro-4′-pentylbenzyl)-4-benzyloxybenzoate (14)*

4-Benzyloxybenzoic acid **13** (1·75 g, 0·00765 mol), 2-fluoro-4-pentylphenol **11** (1·50 g, 7·65 mmol) and the catalyst DMAP (0·04 g, 0·33 mmol) were dissolved in sieve dried THF (50 ml). DCC (1·90 g, 9·18 mmol) was then added and the reaction mixture was refluxed for 2 d. The reaction was kept under anhydrous conditions. The THF was evaporated off and, after mixing with dichloromethane, the solid DCHU was filtered off. The organic solution was washed with 5 per cent aqueous HCl, 5 per cent KOH, and water. The organic solution was dried with $MgSO_4$ and filtered. The crude product was purified with column chromatography using an 1 : 1 volume ratio of hexanes and dichloromethane as the eluent. The TLC showed on spot (R_f=0·36) and 1·38 g were obtained with a yield of 44 per cent. The reaction was repeated on an 11 g scale of the acid and a 39 per cent yield resulted; m.p. = 83°C. FTIR (Nujol, cm^{-1}): 1749 (C=O), 1630 (aromatic stretch), 1387 (aromatic stretch), 1268 (C–O–Ph). ^{1}H NMR ($CDCl_3$), δppm): 0·92 (t, 3 H, J=6·56, CH_3–CH_2–), 1·43–1·28 (m, 4 H, –CH_2–CH_2–CH_2–CH_3), 1·75–1·50 (m, 2 H, Ph–CH_2–CH_2–CH_2–), 2·62 (t, 2 H, J=7·65, Ph–CH_2–CH_2–), 5·17 (s, 2 H, Ph–CH_2–O–), 7·18–6·93 (m, 3 H, PhF aromatic Hs), 7·02 (d, 2 H, J=9·01, *ortho* to –(C=O)O–), 7·50–7·32 (m, 5 H, Ph–CH_2–O– aromatic Hs), 8·17, (d, 2 H, J=8·87, *meta* to –(C=O)O–).

2.3.13. *(2′-Fluoro-4′-pentylbenzyl)-4-hydroxybenzoate (15)*

The aryl ether was prepared by hydrodebenzylation. The Parr pressure apparatus was used at 40°C. (2′-Fluoro-4′-pentylbenzyl)-4-benzyloxybenzoate **14** (8·00 g, 0·0198 mol) was dissolved in 60 ml of ethyl acetate. 0·5 g of 10 per cent Pd on carbon was added. The reaction was monitored by TLC. The reaction took 3 d until only one TLC spot (methylene chloride, R_f= 0·21) was detected of the newly formed phenol. The reaction mixture was filtered through Celite 521 which resulted in 6·16 g of product with a 99·18 per cent yield. m.p. = 133–134°C. FTIR (Nujol, cm^{-1}): 3394 (–OH), 1708 (C=O), 1606 (aromatic stretch), 1376 (aromatic stretch). ^{1}H NMR ($CDCl_3$, δppm): 0·90 (t, 3 H, J=6·64, CH_3–CH_2–), 1·50–1·21 (m, 4 H, CH_3–CH_2–CH_2–CH_2–), 1·65 (quintet, 2 H, J=6·70, Ph–CH_2–CH_2–CH_2–), 2·60 (t, 2 H, J=7·34, Ph–CH_2–CH_2–), 6·92 (s, H, *H*O–Ph–), 7·25–6·81 (m, 3 H, PhF aromatic Hs), 6·88 (d, 2 H, J= 9·01, *ortho* to HO–), 8·10 (d, 2 H, J=8·80, *meta* to HO–).

2.3.14. *(4-undecenyl)-(2′-fluoro-4′-pentylbenzyl) benzoate (16)*

This reaction is a simple S_N2 alkylation. The fluorinated phenol **15** (6·06 g, 19 mmol), 8-bromo-1-octene (3·64 g, 19 mmol), and oven dried K_2CO_3 (5·25 g, 38 mmol) were mixed with sieve dried acetone (200 ml) and refluxed for 3 d. The acetone was evaporated and the reaction mixture was mixed with water. The water mixture was extracted three times with dichloromethane and dried with magnesium sulphate. After filtration, a chromatographic column was run with a 2 : 1 volume hexanes to CH_2CH_2 mixture as the eluent. TLC yielded one spot using 1 : 1 hexane to methylene chloride (R_f= 0·46) as the eluent. HPLC: (>99 per cent). 6·02 g were obtained and gave a 74·5 per cent yield. m.p. = −5°C. FTIR (Neat, cm^{-1}): 3080 (aromatic/C=C–C–H), 2948 (alkyl C–HO), 2860 (alkyl C–H), 1765 (C=O), 1506 (aromatic/C=C stretch), 1261 (C–O–Ph). ^{1}H NMR ($CDCl_3$, δppm): 0·9110 (t, 3 H, J=6·41, CH_3–CH_2–), 1·584–1·265 (m, 10 H, alkyl Hs), 1·70–1·63 (m, 2 H, PhF–CH_2–CH_2–) 1·87–1·76 (m, 2 H, –Ph–O–CH_2–CH_2–), 2·10–2·03 (m, 2 H, C=C–CH_2–), 2·61 (t, 2 H, J= 7·69, PhF–CH_2–CH_2–), 4·05 (t, 2 H, J=6·47, Ph–O–CH_2–CH_2–), 4·951 (d, H, J=7·61, H*H*C=CH*R* *trans* to alkyl), 5·01 (d, H, J=15·71, H*H*C=CH*R* *cis* to alkyl), 5·90–5·73 (m, H, H_2C=C*H*R), 6·97 (d, 2 H, J= 9·04, aromatic Hs *ortho* to the –O*R*), 7·26–7·09 (m, 3 H, PhF aromatic Hs), 8·15 (d, 2 H, J=8·99, aromatic Hs *ortho* to –(C=O)O–). ^{13}C NMR ($CDCl_3$, δppm): Peak assignments are to c = alkyl carbon, C = aromatic carbon, *C* = alkene carbon: 164·4 and 163·3 (c=O–C–O–*R*), 156·5 (C–F) 142·5 and 142·3 (C*H*R and C–*R*), 138·9, 136·2, and 132·5 (2C alpha to C–ester,

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C–O–(carbonyl), C gamma to C–F), 124·2, 123·4 and 120·9 (2C alpha to C–O*R*, C alpha to C–O–(carbonyl), C gamma to C–F, and C–(carbonyl O) 116·6 and 116·2 (C alpha to C–*R* and C–F), 114·3 (CH_2), 68·3 (Ph–O–c), 35·4 (alkene–c), 31·4 (PhF–c), 33·7, 30·8, 29·0, 28·8, 28·7, 28·2, 25·8, 22·5, 14·1 and 14·0 (alkyl carbons). Elemental analysis: calculated: C = 75·70, H = 8·06; experimental: C = 75·97, H = 8·46 per cent.

2.4. *Synthesis of polysiloxanes*

The preparation of five tailor-made terpolsiloxanes **I** proceeded in a similar way with the yield of polymerizations ranging from 84 to 89 per cent. Only the synthesis procedure for polymer **Ia** is illustrated.

2.4.1. *Polymer **Ia***

Under anhydrous conditions, compounds **1a** (44·3 mg, 0·09 mmol), **7b** (750 mg, 1·56 mmol), **16** (757 mg, 0·18 mmol) and polymethylsiloxane $n = 80$ (93·9 mg, 0·018 mmol) were dissolved in approximately 10 ml of fresh distilled toluene. The solution was purged with nitrogen for 20 min before the addition of two drops of a fresh 5 per cent solution of the chloroplatinic acid hexahydrate catalyst in isopropanol. The flask was again purged with nitrogen before refluxing at 115°C. A nitrogen atmosphere was kept above the solution while it refluxed for 24 h. The extent of reaction was monitored by TLC with dichloromethane as the eluent. The reaction worked by evaporating the toluene and dissolving the polymer in the least amount of dichloromethane and precipitating it with hexanes. The solution was centrifuged and the clear supernatant solution decanted. This procedure was performed three times until the TLC showed only the polymer at the baseline. 0·680 g were obtained in an 84 per cent yield. The polymer was decolourized by stirring the polymer solution with charcoal to give a translucent film.

Data from ^{1}H NMR indicated that the extent of the monomer reaction was almost complete; there was no significant peak at 4·7 ppm due to the Si–H. The purity of the polymers was monitored by TLC with dichloromethane as the eluent. Furthermore, ^{1}H NMR and ^{13}C NMR showed the absence of any alkene hydrogens and carbons . The peaks for alkene carbons in the monomers appeared at 139 and 114 ppm and were not found in the ^{13}C NMR for the polymers. $[\alpha]_D^{25} = -0{\cdot}82°$. ^{1}H NMR ($CDCl_3$, δppm): 0·60–0·49 (m, w, $-CH_2CH_2$–Si), 0·87 (t, $J = 5{\cdot}78$, $-CH_3$, s), 1·61–1·00 (m, vs alkyl), 1·82–1·66 (m, vs, alkyl), 2·50 (m, w, PhF–CH_2–), 3·90 (m, s, Ph–O–CH_2– of pyrimidine and fluorinated monomers), 4·37 t, $J = 6{\cdot}22$, s, Nring–O–CH_2–), 5·50 (d, w, –CH(CN)–$(CH_3)_2$), 6·93 (d, $J = 6{\cdot}96$, s, Ph 2 H *ortho* to –O*R* in pyrimidine, Ar 2 H *ortho* to –O*R* in fluorinated monomer, dopant Ar), 7·36 (d, $J = 7{\cdot}42$, s, Ph 2 H *meta* to –O*R* in pyrimidine, dopant Ar, 3 H of Ph–F in fluorinated monomer), 8·59 (s, s Nring 2 H).

3. Results and discussion

3.1. *Mesomorphic behaviour of the monomers*

The mesomorphic properties of the monomers were determined by polarizing optical microscopy and DSC thermal analysis. The transition temperatures of these monomers are summarized in table 1. The phase transition temperatures were taken from the DSC second heating curves. According to table 1, the decanoxy pyrimidine compound, 2-decanoxy-5-(4-undecenoxypyrimidine **7b**, exhibits an enantiotropic S_A and S_C phases. The difference between the two alkoxy pyrimidines is that the phase sequence of 2-octanoxy-5-(4-undecenoxyphenyl)pyrimidine **7a** does not exhibit a S_C phase. The S_A phase of **7b**, as shown in the photomicrograph see (figure 1(*a*)), has the focal-conic fan texture upon cooling from the isotropic melt. The photomicrograph see (figure 1 (*b*)) shows the broken fan texture of the S_C phase. Figure 1 (*c*) shows the transition bars of the fan texture for the S_C to S_B phase transition. The extension of two methylene groups in the pyrimidine monomer **7a** has little effect upon the appearance of the monotropic S_B phases compared to the pyrimidine monomer **7a**. Although the monomer **7b** had a much narrower S_C phase range, compared to those of pyrimidine LCs with alkoxy/alkyl or dialkyl terminal groups from literature [10], monomer **7b** was selected for the synthesis of side chain terpolysiloxanes because of the appearance of an enantiotropic S_C phase.

The fluorinated phenylbenzoate monomer, 4-[ω-undecenyloxy-(2′-fluoro-4′-pentylphenylene)] benzoate **16**, exhibits the expected nematic phase and low transition temperatures. Crystallization occurs below 0°C because of supercooling. The lateral fluorine substitution suppressed the formation of smectic phases which made this monomer an ideal diluent for lowering the transition temperatures of the terpolysiloxanes.

3.2. *Mesomorphic behaviour of a LMWLC mixture*

In the ferroelectric mixture preparation, we mixed the S_C host **7b**, the chiral S_C chiral dopant **1a**, and the low viscosity nematic liquid crystal **16** in the molar percent-

Table 1. The transition temperatures of monomers **7a**, **7b** and **16**.

Monomer	Transition temperature/°C
7a	Cr 71·4 [S_B 62·2] S_A 93·5 I
7b	Cr 65·1 Cr_1 84·5 [S_B 68·8] S_C 89·0 S_A 93·5 I
16	Cr 12·3 Cr_1 21·5 N 28·9 I
LMWFM	Cr 77·1 S_A 87·6 I

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ages of 5, 85, and 10 per cent, respectively. The phase transitions of the liquid crystal mixture, as shown in table 1, exhibited only a smectic A mesophase. Supercooling was observed at the S_A phase to crystal transition. This mixture lacks a S_C phase, depressed by the nematic diluent **16**, because of the use of the short phase range S_C host **7b**.

3.3. *Mesomorphic behaviour of the terpolysiloxanes **Ia-e***

The purpose of preparing side chain terpolysiloxanes was to mimic a low molecular weight ferroelectric mixture [10] by tailoring the monomers **1a**, **7b**, and **16** onto the backbone of a polysiloxane. The mesomorphic behaviour of the terpolysiloxanes, determined by polarizing optical microscopy and DSC are summarized in table 2. The polymer samples for the polarizing optical microscopy studies were annealed in the mesophase from between 3 and 24 h. All the terpolysiloxanes exhibited S_A fan textures and broken-fan textures for the S_C phase on cooling from the isotropic melts (see figure 2(*a*) and 2(*b*). The DSC studies of terpolysiloxanes **1a–e** showed similar mesomorphic behaviour as studied by polarizing optical microscopy. DSC heating and cooling curves of the polymer **1a**, as shown in figure 3, reveal the enantiotropic S_A and S_C^* phases. The nature of the side groups was so dominant in the thermal properties of the polymers **1a–e** that no polymer exhibited glass transition.

Table 2. The transition temperatures of terpolysiloxanes **1a–3**.

Polymer	n	**1** mol %	**7b** mol %	**16** mol %	Transition temperature/°C
Ia	80	5	85	10	Cr 75·1 S_C^* 125·3 S_A 145·0 I
Ib	36	5	85	10	Cr 71·7 S_C^* 118·7 S_A 139·8 I
Ic	36	5	75	20	Cr 66·5 S_C^* 111·1 S_A 134·2 I
Id	36	5	65	30	Cr 62·3 S_C^* 107·0 S_A 128·1 I
Ie	36	5	55	40	Cr 56·1 S_C^* 94·3 S_A 118·3 I

Liquid crystalline polymer **Ia** had higher correlation length, which resulted in higher transition temperatures compared with the phase transitions of polymer **Ib**. This continuity allows for more efficient packing of the side chains and hence, a greater thermal stability. With respect to the compositions of terpolysiloxanes **1a–e**, the side groups were qualitatively identified by NMR spectroscopy. The transition temperatures of terpolysiloxanes **Ib–e** decrease with an increase in the molar concentration of fluorinated side groups. It is noted that the phase sequence remains the same throughout the variation of the side group compositions. This fact indicates that the presence of the nematic side groups **16** did not disrupt the phase sequence of the pyrimidine-host side groups but the thermal stability of the phases. The mesogenic side chains of terpolymers **1a–e** further manifest their liquid crystalline properties by inducing a S_C phase, compared to the LMWLC mixture. Nevertheless, the siloxane polymer backbone stabilizes the smectic layers by acting as a backbone in between the layers.

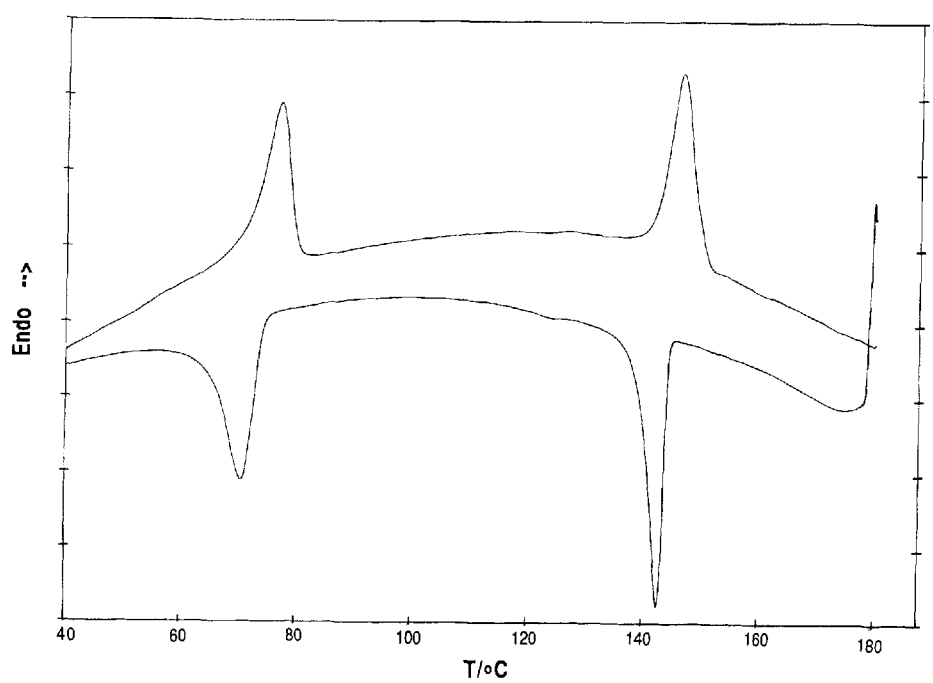

Figure 3. The DSC heating and cooling curves of the polymer **Ia**.

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The Bragg spacings of polymer **Ia** at different temperatures were obtained by a small angle X-ray diffraction (SAXD) study from a polymer film sample. The calculated lengths for the side groups **1a** and **7b** are 36·37 Å and 36·96 Å, respectively. The layer spacing for polymer **Ia** at the S_C^* phase varied from 34·25 to 35·80 Å on cooling from the diffraction experiments which led to a tilted single layer.

4. Conclusions

The synthesized terpolysiloxanes and copolysiloxanes are favourable in the promotion of the S_C^* phase. In contrast to the low molecular weight liquid crystal mixture exhibiting only a S_A phase, the terpolysiloxanes **Ia–e** and copolysiloxanes **IIa–c** possessed the phase sequence of $Cr \rightarrow S_C^* \rightarrow S_A \rightarrow I$, which is necessary for electro-optical materials in ferroelectric display applications. The copolysiloxanes have a low temperature S_C^* phase and a wide mesophase range.

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