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Twisted smectic A phases in side chain liquid crystal polymers

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The syntheses of two side chain liquid crystal polymers, a polyacrylate and a polymethacrylate, are reported. In each of the polymers the liquid-crystalline side group carries an asymmetric carbon atom, thereby making some of the liquid crystal phases formed by the polymers optically active and chiral. For the chiral polyacrylate smectic A and chiral ferroelectric smectic C phases are observed, however for the chiral polymethacrylate a cholesteric phase is detected above the smectic A phase. It is found that the smectic A to cholesteric phase transition is mediated by the formation of an intermediary twisted smectic A phase. This intermediary phase is a liquid-crystalline analogue of the Abrikosov flux phase found in Type II superconductors.

1. Introduction

Renn and Lubensky showed theoretically [1] that when an optically active liquid crystal undergoes a transition from the smectic to the cholesteric (chiral nematic) state, the phase change can be mediated by the formation of an intermediary twist grain boundary phase. On heating, the layered structure of the smectic A phase breaks down to give the helical orientational arrangement of the molecules in the cholesteric phase. Under certain circumstances, for example where the layer ordering is weak and/or the chirality is strong, the transition can take place via an intermediary phase where the layer structure is retained, but with a helical ordering of the molecules imposed in the same plane as the layers. These two structural features are, however, incompatible with each other. This problem is resolved by the formation of a periodic array of defects which allow for the generation of a helical structure Thus, the structure of the intermediary frustrated twisted smectic A phase is one where the molecules are arranged randomly in layers with their long axes perpendicular to the layer planes. A helix is formed in the plane of the layers by the small rotation, in the same direction, of small blocks of the smectic phase. The rotation between blocks is allowed by the formation of screw dislocations. As the overall structure is helical the distribution of the defects is periodic, thereby forming a lattice (see figure 1). The screw dislocations form grain boundaries and hence this intermediary phase is called a twist grain boundary phase [1]. The physics of the incorporation of screw dislocations into the structure of the smectic A phase is similar to that for the penetration of a magnetic field into the superconducting phase of a Type II superconductor in order to produce an Abrikosov flux phase [2]. Thus, the twisted grain boundary phase has also been called the liquid-crystalline analogue of the Abrikosov flux phase [3].

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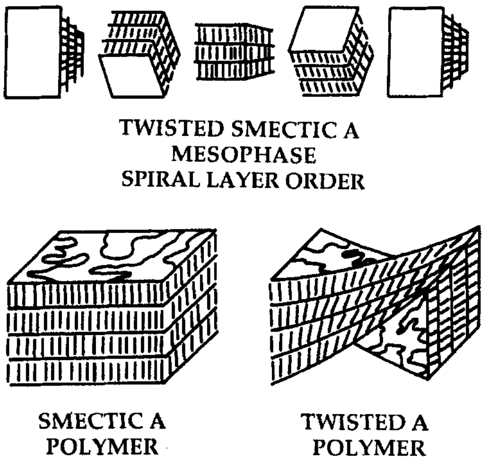
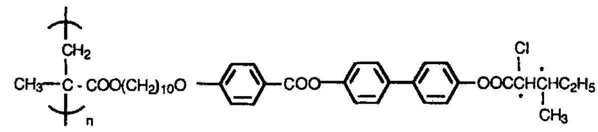


Figure 1. Schematic representation of the structure of the twisted smectic A phase in low molar mass and polymeric liquid crystals.

Experimental verification of the existence of this novel phase came through the investigation of chirality in liquid crystal systems. Both low molar mass and polymer liquid crystals have been found to exhibit this phase [4, 5], as shown in figure 1. In low molar mass systems we have found twisted smectic A phases at both the transition from the isotropic liquid to the smectic A phase and at the cholesteric to the smectic A phase change. For the materials that form the twisted smectic A phase at the transition to and from the amorphous liquid, the helical pitch was found to be between 0·38 and 0·65 μm and the block size 185 Å [8]. However, as yet the presence of a lattice of defects has not been established.

In this article we turn our attention to the polymeric variant of the twisted smectic A phase (see figure 1). We have prepared two side chain polymer liquid crystals that have the following structures,

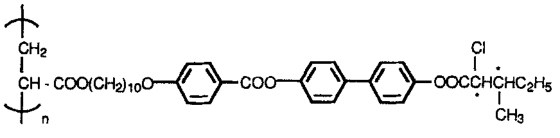
Polymer I



(6a)

poly[(2*S*, 3*S*)-4′-(2-chloro-3-methylpentanoyloxy)-4-biphenylyl 4-(10-methacryloxydecyloxy)benzoate]

Polymer II



(6b)

poly[(2*S*, 3*S*)-4′-(2-chloro-3-methylpentanoyloxy)-4-biphenylyl 4-(10-acryloxydecyloxy)benzoate]

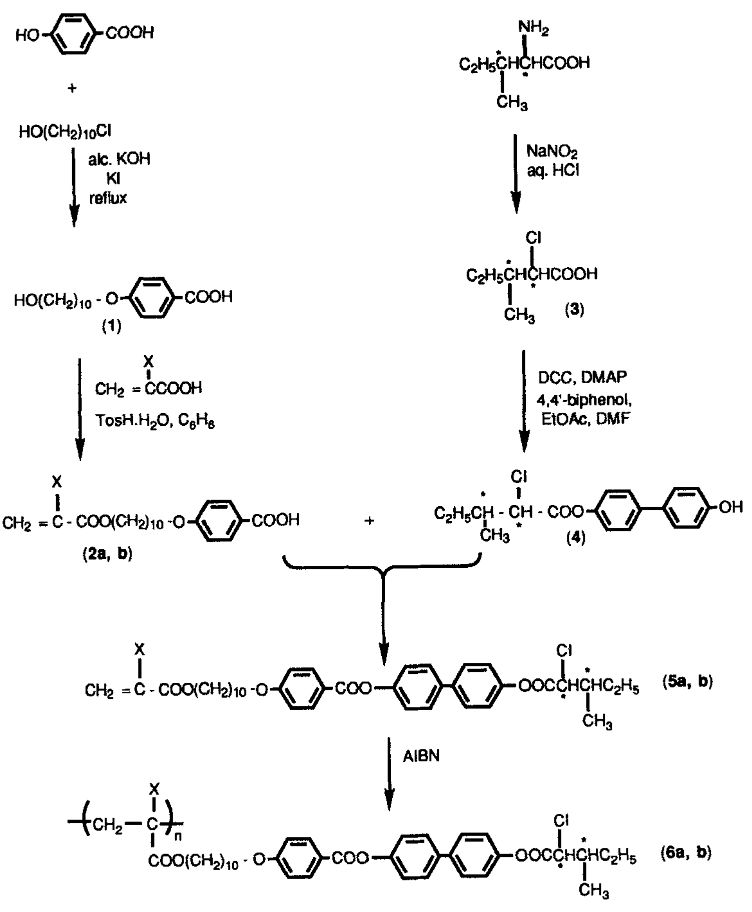
where the terminal aliphatic chain of each mesogenic unit carries two sequential asymmetric atoms. The second of these two materials, compound **6b**, has been prepared previously [9], however as our results are different to those already reported we have included data on this polymer in this article. The polyacrylate was found to exhibit relatively normal liquid crystal phases, however, the polymethacrylate exhibits a twisted S_A phase. The identification and classification of the phases exhibited by these polymers are the topics of discussion in the following sections.

2. Experimental

The materials were synthesized as reported in the following section. Unless noted to the contrary all solvents were redistilled before use. The analyses of the structures of the materials prepared were determined by a combination of NMR spectroscopy (Joel JNM-GX 270 MHz spectrometer), infrared spectroscopy (Perkin–Elmer 783 spectrometer) and mass spectrometry (Finnegan 1020 spectrometer). The results obtained were found to be consistent with the predicted structures of the target materials. Chemical purities of the intermediates and final products were determined by thin layer chromatography and normal and reversed phase HPLC. Reversed phase chromatography was carried out over octadecylsiloxane (5 μm pore size, 25 × 0·46 cm, ODS Microsorb Dynamax 18 column) using both acetonitrile and methanol–water (9 : 1) as the eluants. Normal phase chromatography was carried out over silica-gel (5 μm pore size, 25 × 0·46 cm, Dynamax Scout column) using acetonitrile as the eluant. Detection of the eluting products was achieved using a Spectroflow 757 UV/vis detector ($\lambda = 254$ nm). Optical purities were determined by polarimetry studies. The polydispersity M_w/M_n (γ) and degree of polymerization of the polymers were determined by gel permeation chromatography using a PL-gel column (5 μm, 30 × 0·75 cm, mixed C column) as the stationary phase and THF as the mobile phase. The column was calibrated using polystyrene standards ($Mp = 1000$–430500).

The phase transitions of the intermediates and final polymers were investigated by thermal optical microscopy and differential scanning calorimetry. Thermal microscopic studies were made using a Zeiss Universal polarizing light microscope in conjunction with a Mettler FP 52 microfurnace and FP 5 control unit. Transition temperatures were determined to better than 0·1°C by this technique. Differential scanning calorimetry was used to determine both the temperatures and heats of transition. These studies were carried out using a Perkin–Elmer DSC 7 calorimeter equipped with a thermal analysis data station. The instrumental accuracy was calibrated against an indium standard (measured ΔH 28·63 J g ^{1}, literature value 28·45 J g^{-1}).

The synthesis of the two polymers share a common route starting with 4-hydroxybenzoic acid and *L*-isoleucine. The 4-hydroxybenzoic acid was alkylated with 10-chloro-decan-1-ol to give 4-(ω-hydroxydecyloxy)benzoic acid (**1**). Esterification of this material with acrylic or methacrylic acid yielded 4-(ω-acryloyloxydecyloxy)benzoic acid (**2b**) and 4-(ω-methacryloyloxydecyloxy)benzoic acid (**2a**), respectively. These acids were subsequently esterified with (2*S*,3*S*)-4′-(2-chloro-3-methylpentanoyloxy)-4-hydroxybiphenyl (**4**) which was prepared by the esterification of 4,4′-biphenol with (2*S*,3*S*)-2-chloro-3-methylpentanoic acid (**3**). The resulting acrylates, formed by the combination of compound (**4**) with either (**2a**) or (**2b**), were polymerized in the presence of α,α-azo-isobutyronitrite (AIBN) to yield the final target polymers poly[2*S*,3*S*)-4′-(2-chloro-3-methylpentanoyloxy)-4-biphenylyl (4-(10-methacryloyloxydecyloxy)benzoate] (**6a**) and poly[(2*S*,3*S*)-4′-(2-chloro-3-methylpentanoyloxy)-4-biphenylyl 4-(10-acryloxydecyloxy)benzoate] (**6b**), as shown in the scheme.



	X
a	CH_3
b	H

2.1. *Preparation of 4-(ω-hydroxydecyloxy)benzoic acid* (1)

To a solution of 4-hydroxybenzoic acid (15·19 g; 110 mmol), in ethanol (39 ml) a solution of potassium hydroxide (1648 g, 293 mmol) in water (17 ml) was added. The mixture was heated to boiling, then 10-chlorodecanol (23·32 g, 121 mmol) was added dropwise, potassium iodide (spatula-tip) was added and the mixture was heated under reflux for 48 h. Ethanol was distilled off and water added and the reflux continued for 3 h. The mixture was diluted to 800 ml with water, acidified with aqueous HCl (10 per cent *v*/*v*), allowed to stand at 4°C overnight, and the crude product was collected by filtration, and recrystallized from ethanol/water affording (**1**) as a white solid (17·75 g, 55 per cent), mp 196°C; ν(KCl disc) 3450(O-H), 2940(C–H), 1700(C=O), 1250 (C–O), 860(C–H) cm^{-1}; δ_H(270 MHz, $CDCl_3$) 1·15–1·60(16H, m, $(C\underline{H}_2)_8$), 3·55(2H, t, $J = 9{\cdot}3$ Hz, $C\underline{H}_2OH$), 4·00(2H, t, $J = 9{\cdot}3$ Hz, $C\underline{H}_2OAr$), 6·90(2H, m, $Ar\underline{H}$), 7·95(2H, m, $Ar\underline{H}$).

2.2. *Preparation of 4-(ω-methacryloxydecyloxy)benzoic acid* (**2a**)

Compound (**1**) (8·24 g, 28 mmol), methacrylic acid (9·64 g, 112 mmol), 4-toluenesulphonic acid monohydrate (3·36 g, 17 mmol), hydroquinone (1·4 g, 17 mmol), and benzene (200 ml), were heated under reflux for 3 days (Dean–Stark trap). The mixture was diluted with ether (100 ml), washed with water (2 × 75 ml), saturated aqueous sodium chloride (50 ml) and dried over magnesium sulphate. Evaporation and crystallization from isopropanol/hexane afforded (**2a**) as a colourless solid (4·02 g, 40 per cent); ν(KCl disc) 2930(C–H), 2860(C–H), 1710(C=O), 1680(C=O), 1260(C–O), 1170(C–O) cm^{-1}; δ_H(270 MHz, $CDCl_3$) 1·25–1·90(16 H, m, $(C\underline{H}_2)_8$, 1·95(3H, s, $C\underline{H}_3$), 4·05(2H, t, $C\underline{H}_2OAr$, 4·15(2 H, t, $CO_2C\underline{H}_2$), 5·55(1 H, s, $C\underline{H}$=), 6·10(1H, s, $C\underline{H}$=), 7·50(2H, d, $J = 10{\cdot}4$ Hz, $Ar\underline{H}$), 7·55(2H, d, $J = 10{\cdot}4$ Hz, $Ar\underline{H}$).

2.3. *Preparation of 4-(ω-acryloxydecyloxy)benzoic acid* (**2b**)

The preparation of (**2b**), which was the same as for (**2a**) but using acrylic acid instead of methacrylic acid, yielded (**2b**) as a colourless solid (45 per cent); ν(KCl disc) 2930 (C–H), 2860(C–H), 1720(C=O), 1675(C=O), 1250(C–O), 845(C–H) cm^{-1}; δ_H(270 MHz, $CDCl_3$) 1·20–1·90(16 H, m, $(C\underline{H}_2)_8$), 3·95–4·10(2H, t, $C\underline{H}_2OAr$), 4·15(2H, t, $CO_2C\underline{H}_2$), 5·75–5·85(1H, m, $C\underline{H}$=), 605–6·30(1 H, m, $C\underline{H}$=), 6·30–6·45(1H, m, $C\underline{H}$=), 7·50(2 H, d, $J = 9{\cdot}3$ Hz $Ar\underline{H}$), 7·55(2$\underline{H}$, d, $J = 9{\cdot}3$ Hz $Ar\underline{H}$).

2.4. *Preparation of* (−)-*(2S,3S)-2-chloro-3-methylpentanoic acid* (**3**)

To a solution of *L*-isoleucine (30·18 g, 230 mmol) in aqueous HCl (5 M, 300 ml) at 0°C, sodium nitrite (25·39 g, 368 mmol) in water (92 ml) was added over a period of 1 h. The stirred solution was kept below 5°C for 5 h and then left to stand at room temperature. The solution was held under reduced pressure (30 mm Hg) for 3 h in order to remove nitrogen oxides, and then sodium carbonate (23 g) was added in portions with stirring. The reaction mixture was extracted with ether (4 × 100 ml). The combined ether extracts were concentrated to 150 ml and washed with saturated aqueous sodium chloride (10 ml), which was then washed with ether (3 × 50 ml). The ether was removed from the combined fractions by evaporation to give an oil (atmospheric pressure), which was distilled twice (160°C, 20 mm Hg), to yield (**3**) as a colourless oil (14·15 g, 45 per cent; $[\alpha]_D^{21\cdot5} - 3{\cdot}89°$ (*c*7·62, $CHCl_3$); ν(liquid film) 2980(C–H), 2700 (O–H), 1725(C=O), 1290(C–O) cm^{-1}; δ_H(270 MHz, $CDCl_3$) 0·85–1·70 (8H, m, $C\underline{H}_3$ and $C_2\underline{H}_5$), 2·1(1 H, m, $C\underline{H}(CH_3)$), 4·25(1H, d, $J = 13{\cdot}5$ Hz, $C\underline{H}Cl$), 11·2(1 H, s, $COO\underline{H}$).

2.5. *Preparation of* (+)-*(2S,3S)-4′-(2-chloro-3-methylpentanoyloxy)-4-hydroxybiphenyl* (**4**)

4,4′-Biphenol (29·79 g, 160 mmol), dicyclohexylcarbodiimide (DCC) (17·33 g, 84 mmol), 4-dimethylaminopyridine (DMAP) (2·44 g, 20 mmol), ethyl acetate (200 ml) and *N*,*N*′-dimethylformamide (25 ml) were stirred at room temperature. Compound (**3**) (12·4 g, 80 mmol) was added dropwise to the mixture. After 24 h oxalic acid (0·50 g, 3·97 mmol) was added and the reactants stirred for 30 min. The mixture was filtered and evaporated to give an oil. Ethyl acetate (200 ml) was added and the solution was washed with aqueous 1 M hydrochloric acid (2 × 50 ml), saturated aqueous sodium bicarbonate (50 ml) and saturated aqueous sodium chloride (50 ml), and dried (magnesium sulphate). Flash chromatography over silica-gel (200–400 mesh) using dichloromethane as the eluant afforded (**4**) as a colourless solid (5·49 g, 22); $[\alpha]_D^{24} + 15{\cdot}0°$ (*c* 4·34, DMF); ν(KCl disc) 3470(O–H), 2980(C–H), 2940(C–H), 1730(C=O), 1500(C–H), 840 (C–H) cm^{-1}; δ_H(270 MHz, CD_2Cl_2), 0·85–1·85(8 H, $C\underline{H}_3$ and $C_2\underline{H}_5$), 2·10–2·40(1 H, m, $C\underline{H}(CH_3)$), 4·45(1 H, d, $J = 9·3$ Hz, $C\underline{H}Cl$), 6·85–7·65(8 H, m, $Ar\underline{H}$).

2.6. *Preparation of (−)-(2S,3S)-4′-(2-chloro-3-methylpentanoyloxy)-4-biphenylyl 4-(10-methacryloyloxydecyloxy)benzoate* (**5a**)

The acid (**2a**) (2·97 g, 8·2 mmol), biphenol (**4**) (2·61g, 8·2 mmol), dicyclohexylcarbodiimide (DCC) (1·95 g, 9·4 mmol), 4-dimethylaminopyridine (DMAP) (0·25 g, 2·05 mmol), and ethyl acetate (50 ml) were stirred at room temperature for 24 h. The mixture was filtered and the filtrate was washed with aqueous 1 M hydrochloric acid (2 × 25 ml), saturated aqueous sodium bicarbonate (2 × 25 ml) and saturated aqueous sodium chloride (25 ml). The solution was dried over magnesium sulphate, filtered and the solvent removed by evaporation to give a semi-solid. Flash chromatography over silica-gel (200–400 mesh) using dichloromethane as eluant afforded (**5a**) as a colourless solid (1·93 g, 35 per cent); ν(KCl disc) 2960(C–H), 2860(C–H), 1715(C=O), 1170 (C–O) cm^{-1}; δ_H(270 MHz, $CDCl_3$) 0·80–2·10(27 H, m, $(C\underline{H}_2)_8$, $C\underline{H}_3$, $C\underline{H}_3$ and $C_2\underline{H}_5$), 2·05–2·30(1 H, m, $C\underline{H}(CH_3)$, 3·90–4·20(4 H, m, $C\underline{H}_2$-OAr and $CO_2C\underline{H}_2$), 4·40(1H, d, $J = 9·31$ Hz, $C\underline{H}Cl$), 5·05(1 H, s, $C\underline{H}$=), 6·10(1 H, s, $C\underline{H}$=), 6·85–8·40(12 *H*, m. $Ar\underline{H}$).

2.7. *Preparation of (+)-(2-S,3S)-4′-(2-chloro-3-methylpentanoyloxy)-4-biphenylyl 4-(10-acryloyloxydecyloxy)benzoate* (**5b**)

Preparation of (**5b**), which is almost the same as for (**5a**) but using the acid (**2b**) instead of the acid (**2a**), yielded (**5b**) as a colourless solid (54 per cent); ν(KCl disc) 2940(C-H), 2860(C-H), 1715(C=O), 1670(C=O), 1230(C-O) cm^{-1}. δ_H (270 MHz, $CDCl_3$) 0·80–2·05(24 H, m, $(C\underline{H}_2)_8$, $C\underline{H}_3$ and $C_2\underline{H}_5$), 2·05–2·35(1 H, m, $C\underline{H}(CH_3)$), 3·95–4·30(4 H, m, $C\underline{H}_2OAr$ and $CO_2C\underline{H}_2$), 4·40(1 H, d, $J = 9·3$ Hz, $C\underline{H}Cl$), 5·82(1 H, m, $C\underline{H}$=), 6·12(1H, m, $C\underline{H}$=), 6·44(1 H, m, $C\underline{H}$=), 6·85–8·20(12 H, m, $Ar\underline{H}$).

2.8. *Preparation of (−)-poly[(2S,3S)-4′-(2-chloro-3-methylpentanoyloxy)-4-biphenyl 4-(10-methacryloyloxydecyloxy)benzoate]* (**6a**)

Compound (**5a**) (1·72 g, 2·6 mmol), AIBN (0·0043 g, 0·026 mmol) and tetrahydrofuran (30 ml) were stirred for 24 h at 60°C under an atmosphere of nitrogen. Evaporation of the solvent afforded an oil from which compound (**6a**) was isolated. Purification was achieved by precipitation from a mixture of tetrahydrofuran–methanol six times, followed by solvation in THF and filtration through a microfilter (5 μm). The solvent was removed by evaporation to afford (**6a**) as a colourless solid. (0·84 g, 49 per cent); $[\alpha]_D^{23}$ −2·1° (*c* 0·011, $CHCl_3$); ν(KCl disc) 2940(C–H), 2860(C–H), 1740(C=O), 1260(C–O), 850(C–H) cm^{-1}; δ_H(270 MHz, $CDCl_3$) 0·70–2·15(27 H, m, $(C\underline{H}_2)_8$, $C\underline{H}_3$, $C\underline{H}_3$ and $C_2\underline{H}_5$), 2·10–2·35(1 H, m, $C\underline{H}(CH_3)$, 3·70–4·15(4H, m, $C\underline{H}_2$–OAr and $CO_2C\underline{H}_2$), 4·30–4·45(1H, m, $C\underline{H}Cl$), 6·75–8·20(12 H, m, $Ar\underline{H}$).

2.9. *Preparation of (+)-poly[(2S,3S)-4′-(2-chloro-3-methylpentanoyloxy)-4-biphenylyl 4-(10-acryloyloxydecyloxy)benzoate]* (**6b**)

The preparation was similar to that for (**6a**). The polymer was obtained as a colourless solid (48 per cent); ν(KCl disc) 2930(C–H), 2860(C–H), 1735(C=O), 1260 (C–O), 845(C–H) cm^{-1}; δ_H (270 MHz, CD_2Cl_2) 0·90–1·95 (27H, m, $(C\underline{H}_2)_8$, $C\underline{H}$, $C\underline{H}_2$, $C\underline{H}_3$, $C_2\underline{H}_5$), 2·15–2·45(1H, m, $C\underline{H}(CH_3)$, 3·90–4·15(4H, m, $C\underline{H}_2OAr$ and $CO_2C\underline{H}_2$), 4·45(1 H, d, $J = 9·3$ Hz, $C\underline{H}Cl$), 6·90–8·15(12 H, m, $Ar\underline{H}$).

3. Results

3.1. *Transition temperatures*

The transition temperatures and polymerization data for the two polymers are given in the table. The polymerization data for both polymers shows that the degree of polymerization is not particularly large. However the results are roughly comparable for the two and are typical of results normally obtained for side chain liquid crystal polymers. Therefore, in conventional terms these materials could be referred to as oligomers.

The two polymers were examined by thermal optical microscopy and differential scanning calorimetry in order to identify and classify the phase transitions. Thus, the results shown in the table were derived from a combination of the two techniques. The melting behaviour of the polyacrylate, polymer II, appears at first sight to be relatively simple. Initially the polymer undergoes a first order transition at 75·5°C to give a smectic phase, the identity of which is uncertain at this time. On heating to 109°C this phase melts through a second order transition to give a ferroelectric smectic C phase. Subsequent heating produces further phase transitions to the smectic A and isotropic liquid phases as shown in figure 2. The results obtained for the polyacrylate (polymer II) are in fact different to those originally reported by Scherowsky *et al.* [9] for the same polymer. However, later unpublished reports given below by Scherowsky *et al.* [10] seem to be in agreement with the results given in the table for polymer II,

$$S_1\ 80°C\ S_2\ 100°C\ S_c^*\ 140°C\ S_A\ 200°C\ I.$$

The polymethacrylate, polymer I, exhibits very different phase morphology to the analogous acrylate, polymer II. On initial heating the polymer appears to melt from a crystalline solid directly into the ferroelectric S_C^* phase. Subsequent heating cycles result in a glass melting to the S_C^* phase. Heating produces transitions to the smectic. A, twisted smectic A, and cholesteric phases before the isotropic liquid is reached. Thus, two extra phases are observed above the twisted smectic C phase for the methacrylate with respect to the acrylate, whereas the acrylate exhibits two more ordered phases than the methacrylate. Furthermore, the polymethacrylate appears to support helical structures more readily than the acrylate.

3.2. *Phase classification*

Phase identification was achieved primarily by the use of thermal optical microscopic investigations of the defect textures formed when the polymers were cooled from the isotropic liquid, The polyacrylate (polymer II) formed focal conic defects on annealing at a temperature just below the clearing point. The defect texture was typical of that of a smectic A phase. Further cooling produced a transition to the helical S_C^* phase which was characterized by the formation of disclination lines in the focal conic texture. The lines were found to be equally spaced and related to the pitch of

Transition temperatures, degree of polymerization (DP) and polydispersity (γ) for the polymers.

	Transition temperatures	DP	γ
Polymer I polymethacrylate	I 160°C Ch 149°C S_A^* 140°C S_A 73°C S_C^*	15	2·65
Polymer II polyacrylate	I 194°C S_A 152°C S_C^* 109°C S_2 75·5°C S_1	12	1·32

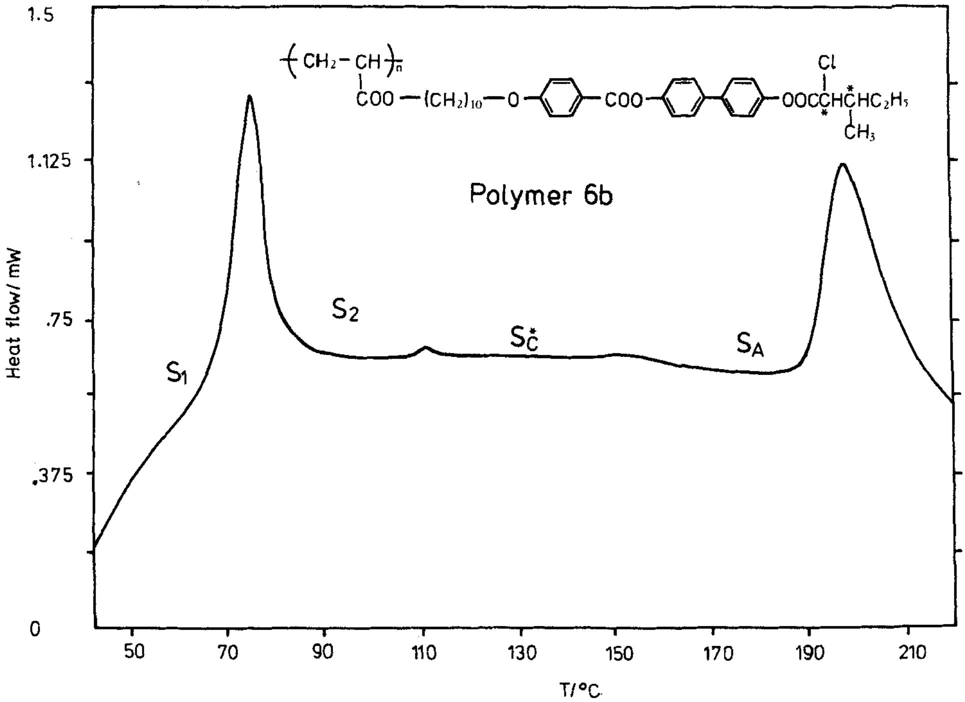


Figure 2. Differential scanning calorimetry heating trace for the polyacrylate polymer (II); the heating rate was 10°C min^{-1}.

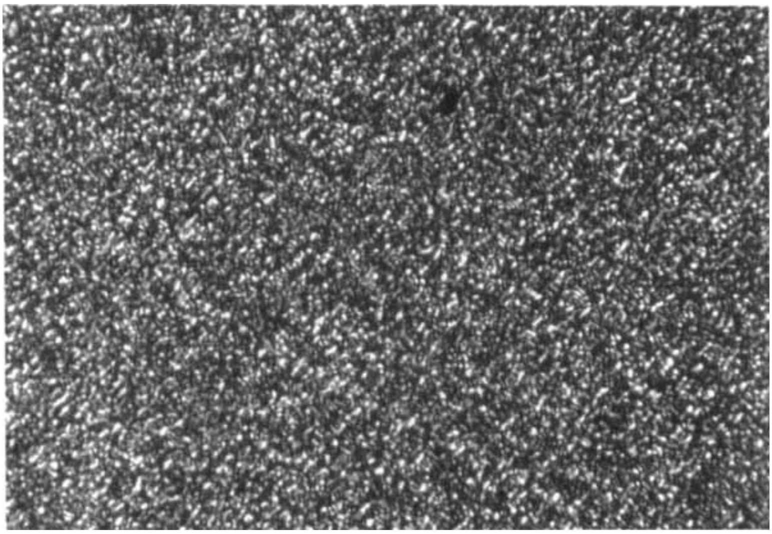


Figure 3. The sanded texture of the cholesteric phase of polymer I (× 100).

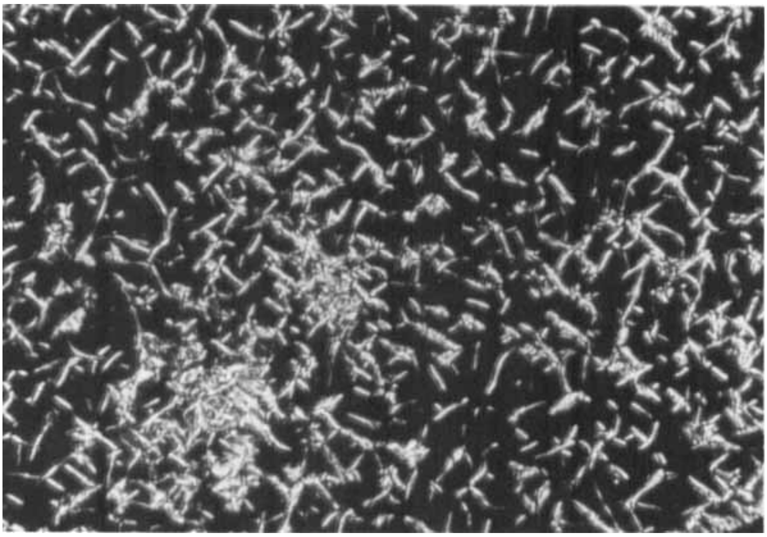


Figure 4. The filament texture of the twisted smectic A phase of polymer I (× 100).

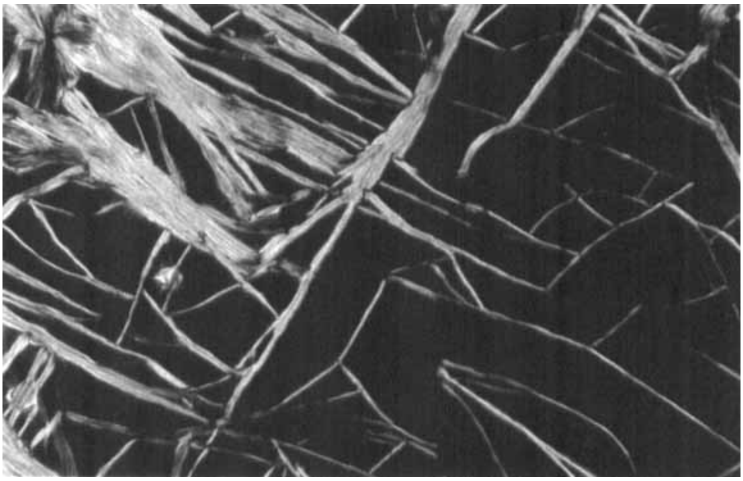


Figure 5. The filament texture of the twisted smectic A phase of (*S*)-2-chloro-4 methylpentyl 4′-(4″-*n*-nonyloxybenzoyloxy)biphenyl-4-carboxylate (× 100).

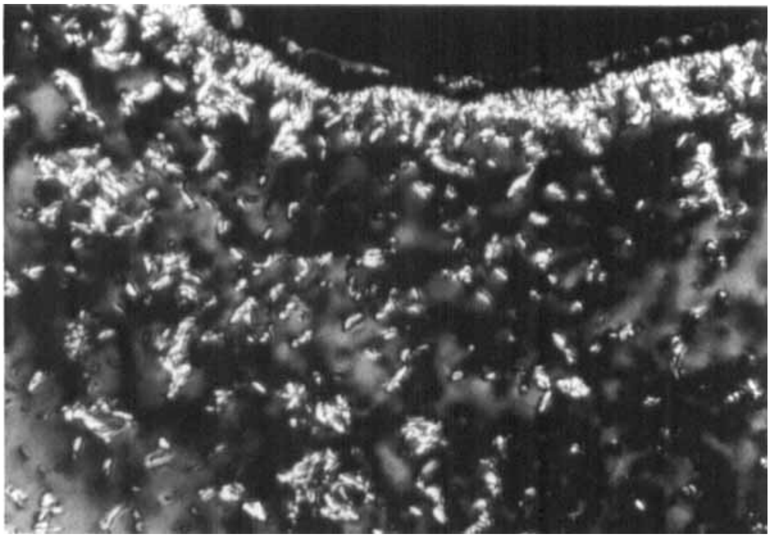


Figure 6. The schlieren texture of the twisted smectic C phase of polymer I (× 100).

the helix of the phase. Measurement of the spacing between the lines by a graticule gave a value of the pitch length between 2 and 4 μm. Subsequent cooling gave a transition to two further smectic phases (S_1 and S_2). The transition temperatures were determined by differential scanning calorimetry, however, the transitions were not discernible by optical microscopy. These observations suggest that the lower temperature phase also has a helical structure which is evident from the presence of pitch bands. This indicates that the lower phases are either twisted smectic I or smectic F, both of which are ferroelectric or that the phases are antiferroelectric or ferrielectric. The major difference between the S_I^* and S_F^* phases and the chiral smectic C phase is that the molecules have short range in-plane hexagonal order and long range bond orientational order, whereas the S_C^* phase has hexagonal order extending only over a few molecules. In the case of the ferri- and anti-ferroelectric phases the tilt orientations of the molecules alternate from layer to layer.

The polymethacrylate forms completely different defect textures to the acrylate on cooling from the isotropic liquid. Initially the material forms a sanded texture which when subjected to shearing produces a Grandejean plane texture. Incident plane polarized light was found to be rotated by this phase indicating that the phase is helical. These observations are consistent with the phase being a cholesteric (chiral nematic) phase. The developing Grandjean plane texture is shown in figure 3. The small domains shown increase in size with the annealing time to give a plane texture which is similar to that obtained in low molar mass cholesteric materials.

On cooling, the Grandjean texture undergoes a transformation at the transition to the smectic state. At the transition the plane texture starts to form a homeotropic texture, however, at the same time filaments appear and spread across the whole of the preparation. The filaments are typical of the twisted smectic A vermis texture. Figure 4 shows the filament texture of the twisted smectic A phase of the polymethacrylate. This texture should be compared with figure 5 which shows the texture of the twisted smectic A phase of a low molar mass liquid crystal. The lengths of the filaments for the polymer are not quite as long as those for the low molar mass material. This may be because the material is a polymer and therefore extended filamentary growth is restricted. Cooling of the filament texture of the S_A^* phase results in a transformation to the homeotropic texture of the smectic A phase which appears optically extinct under crossed polars. Cooling of this phase results in a transition to the chiral smectic C phase which exhibits a schlieren texture, as shown in figure 6. Incident plane polarized light is rotated by this texture indicating that the phase is helical. However, the rotation of plane polarized light is not particularly great thereby suggesting that the pitch could be relatively long in the S_C^* phase.

3.3. *Thermal analysis*

Thermal analysis of the polyacrylate shows a first order transition at the clearing point and a second order phase change for the S_A to S_C^* transition, which is consistent with similar transitions in low molar mass materials. The S_C^* to S_2 transition appears to be second order, however, the enthalpy of the transition was found to be relatively small as shown in figure 2. This would be consistent with a chiral smectic C to antiferroelectric transition. The lowest temperature transition shown (S_1 to S_2) is clearly first order in nature, which is consistent with a greater change in order, for example, at a S_C^* to S_I^* or S_F^* transition.

Thermal analysis of the polymethacrylate, polymer I, gave a less clear thermogram in comparison to the analysis for the acrylate. The peaks tended to be a little more spread out which is probably due to the higher polydispersity for this polymer. However, clear peaks are seen for the isotropic liquid to cholesteric, cholesteric to S_A^* and S_A^* to S_A transitions, as shown in figure 7. Slight decomposition of the polymer was also detected on the heating cycles. Above the clearing point the baseline was found to curve away more sharply as the temperature was increased indicating that the polymer was undergoing thermal decomposition.

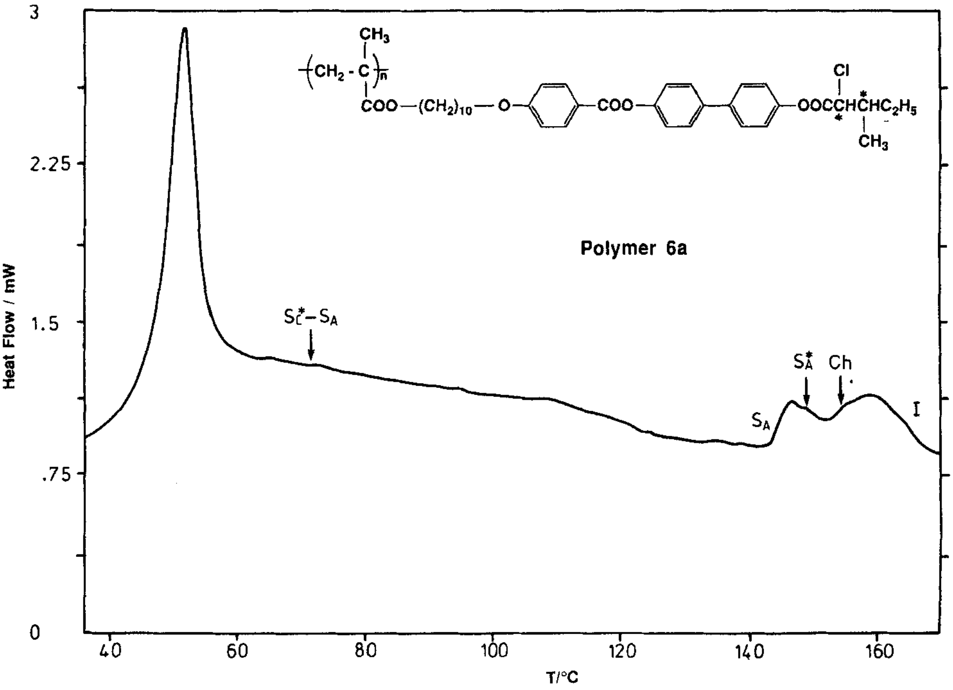


Figure 7. Differential scanning calorimetry heating trace for the polymethacrylate polymer (I); the heating rate was 20°C min^{-1}.

4. Discussion

The phase classifications of the two polymers are still provisional, however, the polymers are currently being examined by X-ray diffraction in order to characterize fully their structures. Given this limitation, nonetheless, the textures observed by thermal optical microscopy are typical of analogous low molar mass liquid crystals thereby giving us confidence in our classifications. In fact one of the most striking similarities is the filament texture of the S_A^* phase of the polymethacrylate with respect to those observed for low molar mass materials. Similarly, we were concerned that the values for the transition temperatures of the polyacrylate, polymer II, were different to those previously reported. However, recent results by the same workers on the same polymer are reported to be in rough agreement with our observations.

It is interesting that the polyacrylate does not exhibit a twisted smectic A phase whereas the polymethacrylate apparently does. This may be due to the fact that the metacrylate exhibits a helical cholesteric phase, and its presence between the isotropic and the smectic. A phase helps the formation of the defect stabilized S_A^* phase. This phase stabilization is similar to that obtained in low molar mass materials, for example, it is clear from the low molar mass studies that similar chiral chloro-compounds exhibit twisted smectic A phases [7, 11]. These phases are formed when a cholesteric phase is again present between the isotropic liquid and the normal smectic A phase. When the cholesteric phase is not present the S_A^* phase disappears.

We now turn our attention to the polyacrylate polymer II. The two higher temperature phases are able to be classified from their microscopic textures as S_A and S_C^*, but the lower two phases (transitions at 109 and 75·5°C) remain unclassified. However, both phases appear to have helical structures and the large size of the enthalpy of the lower transition at 75·5°C suggests that this phase change may be to a twisted smectic I or F phase. The enthalpy for the transition at 109°C is very small and suggests that there is not a large change in phase structure or order at this transition. Previous polarization studies [12] on this material show that the polarization steadily falls in the twisted smectic C phase after initially rising just below the Curie point. This behaviour is similar to that seen in low molar mass ferri- and anti-ferroelectric smectic C phases [13]. Initially at the Curie point the polarization rises and reaches a maximum as the temperature is reduced. At a transition to the ferri- or anti-ferroelectric phase the polarization starts to fall towards zero because of the opposing alignment of the dipoles that contribute to the polarization. As initial studies [12] on this polymer appear to support this analogy, it is interesting to speculate that these lower temperature

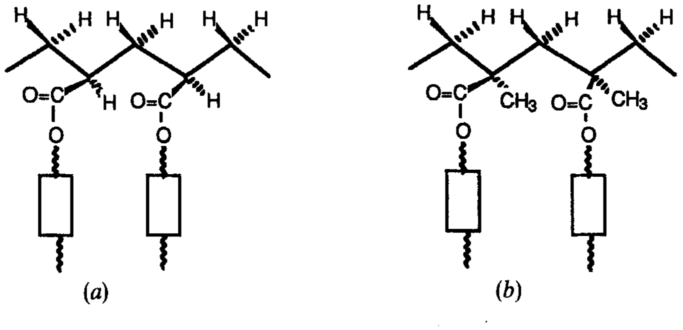


Figure 8. The zig-zag structure of the backbone for (*a*) the polyacrylate and (*b*) the polymethacrylate polymers.

transitions are due to the formation of ferri- and anti-ferrophases. Therfore, detailed electric field and polarization investigations on the polyacrylate have been undertaken, and the results of these studies will be reported at a later date.

If we now examine the overall liquid crystal properties of the polymers, the polyacrylate tends to exhibit more ordered phases than the methacrylate polymer (S_1 and S_2). Conversely, this also supports the argument that the methacrylate polymer exhibits more disordered phases than the acrylate (Ch, A*). This result appears to contradict the belief that the backbone in the methacrylate polymer is stiffer than in the acrylate system and therefore gives more ordered structures. However, it is possible that the methyl substituents in the polymethacrylate backbone sterically hinder the packing of the polymers and mesogenic groups together, as shown schematically in figure 8 for the polyacrylate (*a*) and polymethacrylate (*b*), respectively, for a zig-zag structure of the backbone. In the structure of the actual polymer there will obviously be a variety of diastereoisomers and conformers present in comparison to that shown in figure 8 where only the isotactic structure is depicted.

In relation to the formation of the twisted smectic A phase the degree of polymerization for the polymethacrylate is relatively small; about 15 mesogenic units per oligomer. This means that the polymer backbone length must be between 40 and 60 Å which is much less than the block size obtained for twisted smectic A phases in low molar mass liquid crystals. Thus the degree of polymerization probably has no real effect on the formation of the defect stabilized phase for this polymer. It is possible, that when the polymer length becomes longer than the block size, the twisted smectic A phase will not be formed because the defects will not be stabilized due to interference by the backbones.

5. Conclusion

The results reported appear to show that the polymethacrylate exhibits a twisted smectic A phase. This is only the second example of this phase being observed in polymer systems. The phase appears to be stabilized somewhat by the disordering capacity of the methyl groups, as well as the mesogenic units, being attached to the polymer backbone.

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