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Liquid-crystalline side chain polymers containing a chiral spacer unit exhibiting chiral smectic phases

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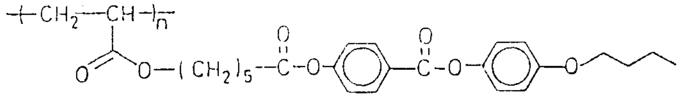
The synthesis and mesomorphic properties of two liquid-crystalline side chain polymers with a chiral centre in the α or β position of the ω-hydroxy acid representing the spacer unit are described. The chiral α branching leads to a dramatic decrease in the transition temperatures and a strong narrowing of the smectic mesophase (compared with the unbranched model compound I). The chiral β branching results in a chiral smectic phase, a pronounced contraction of the S_C phase, and the loss of the higher ordered S_F phase. The S_C^* phase was confirmed by X-ray investigations of oriented samples. Depending on the polymerization conditions samples were obtained which were oriented in melt drawn fibres either with their smectic layers or their mesogenic units in the direction of stress.

1. Introduction

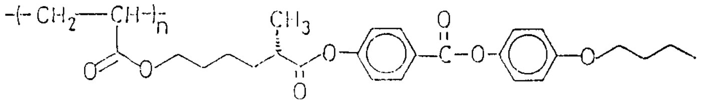
Chiral liquid-crystalline phases, in particular chiral smectic C, have attracted great interest in recent years because of their ferroelectric properties. Although our knowledge in this field has grown strongly in recent years, little has been done in the area of liquid-crystalline *polymers* exhibiting chiral smectic phases [1–4]. Hitherto all known examples contain the chiral centre in the terminal alkyl chain of the mesogenic group. The aim of our work was to introduce chirality into the spacer unit of the side chain polymers at different distances from the mesogenic moiety. To succeed in obtaining a chiral smectic phase we have looked for a side chain polymer exhibiting



I

S_F 45 S_C 145 I

Figure 1.



II

Figure 2.

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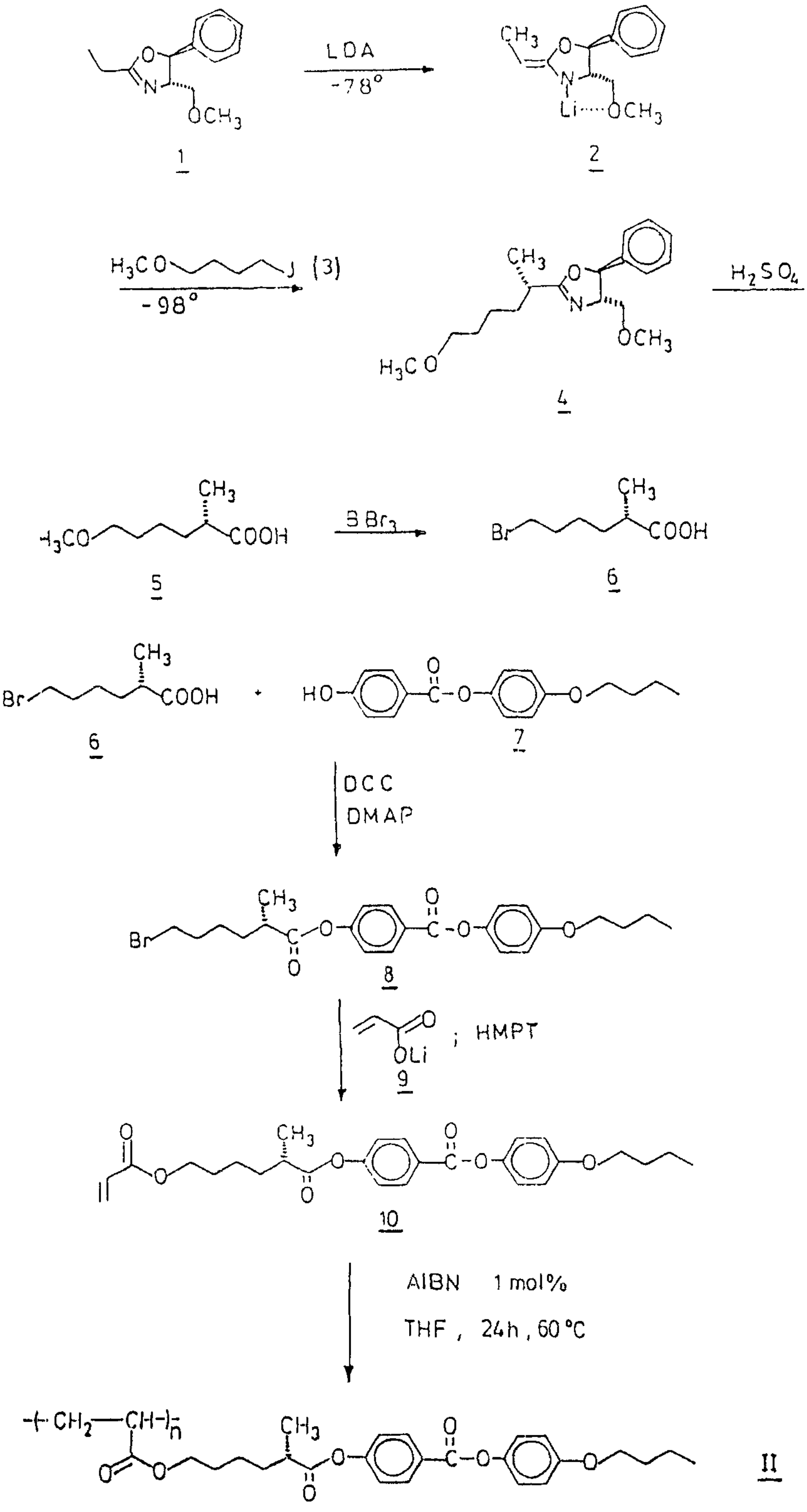
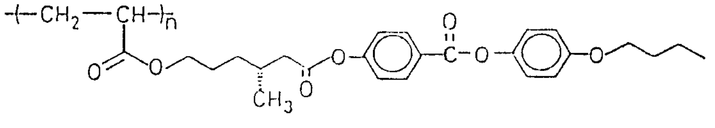


Figure 3. Synthesis of polymer II.



III

Figure 4.

a broad smectic C phase, expecting a contraction of the phase width caused by the disturbance in phase formation due to the chiral branching in the spacer unit. We have selected the known side chain polyacrylate I which has a broad S_C phase, between 45° and 145°C [5]. This paper describes the synthesis and properties of two polymers related to **I** (see figure 1) containing a chiral centre in the α or β position of the ω-hydroxyhexanoic acid, which represents the spacer unit.

2. General part

2.1. *Synthesis of polymer II*

Polymer **II** (see figure 2) was prepared in a twelve-step procedure (see figure 3). Meyer's method for enantioselective synthesis of α-substituted carboxylic acids was used to obtain the chiral building block (ω-substituted(S)-2-methyl-hexanoic acid (**5**)) [6]. The chiral oxazoline **1** was deprotonated by LDA. The lithium chelate complex (**2**) formed, was alkylated by 4-methoxybutyliodide (**3**) to give **4**. Hydrolysis and subsequent BBr_3 cleavage of the ether **5** afforded the chiral bromo acid **6** (40 per cent ee). **6** was combined with the mesogenic unit **7** to give **8**. The monomer **10** was formed from **8** and lithium acrylate **9** in HMPT. The polymerization was performed in THF with AIBN as initiator.

2.2. *Properties of polymer II*

A molecular weight of 9600 ($E = 1.73$) was obtained (G.P.C. calibration with polystyrene as standard). The phase sequence and transition temperatures are T_G 10°C S_X 40°C I.

2.3. *X-ray investigations*

X-ray measurement of a sample contained in a glass capillary (1 mm diameter) resulted in a smectic layer distance of 45.7 Å. The length of the molecule (taken from a space-filling model) is 32 Å. An interdigited double layer or a tilted double layer can be deduced from these data. No oriented samples (by either drawing fibres or applied magnetic fields (1·5 T)) could be obtained.

2.4. *Synthesis of polymer III*

Polymer **III** (see figure 4) containing a chiral centre in the β position of the spacer was synthesized in a thirteen-step procedure (see figure 5). As starting material *R*-(+)-pulegone (**11**), from natures chiral pool, was used to obtain (*R*)-ω-hydroxy-β-methylhexanoic acid which is needed as the spacer unit.

Addition of HCl to pulegone, subsequent ring fragmentation with base and esterification yielded the unsaturated chiral ester **12** [7]. Ozonolysis and reductive work-up gave the ω-hydroxyester **13** [7], which was protected with DHP and saponified to yield the acid **15**. This was combined with the mesogenic moiety **7** to give **16**, which after deblocking was esterified with acrylic acid to yield the monomer **18**. The polymerization was performed with AIBN in two different solvents, THF and toluene.

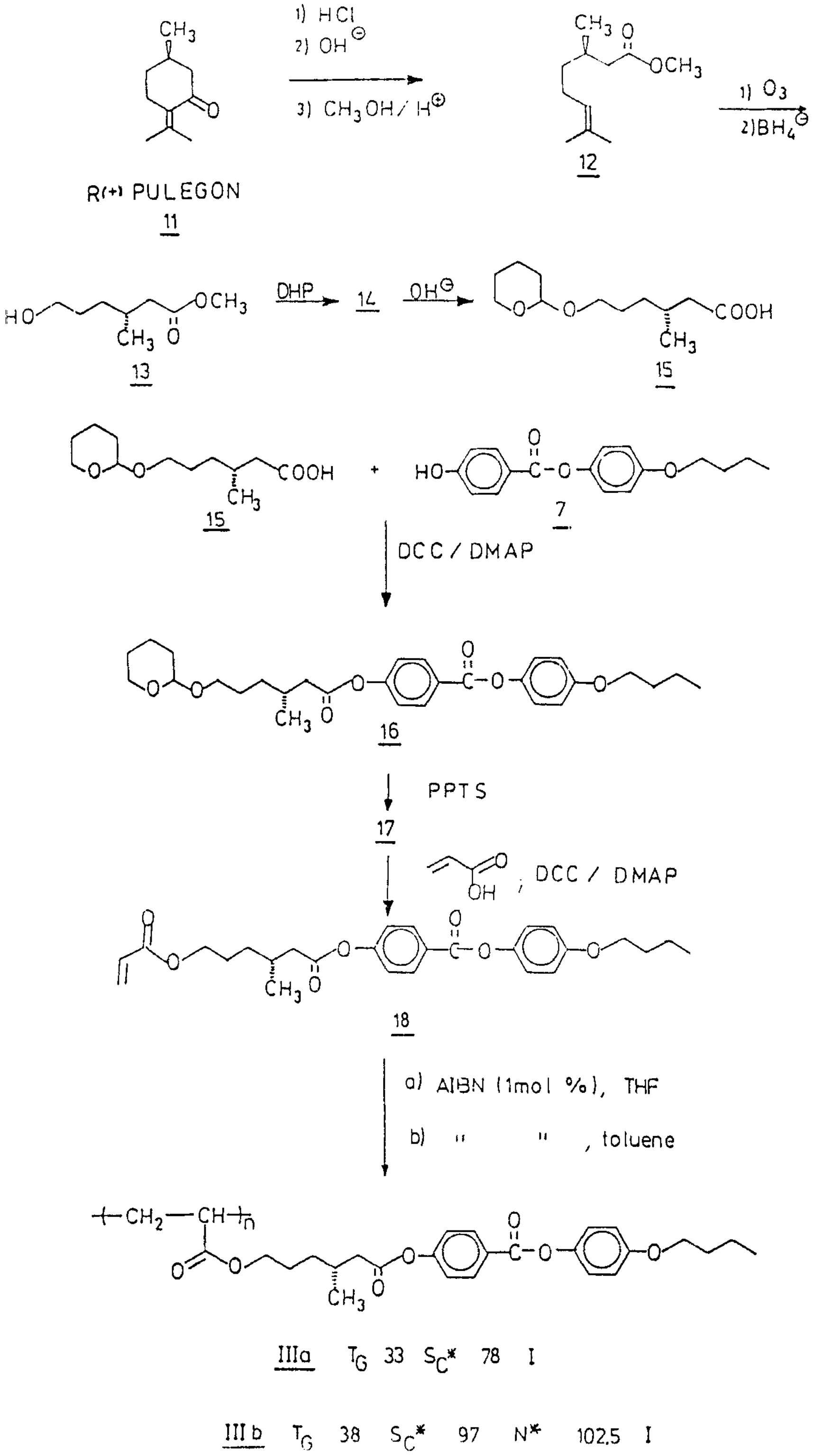
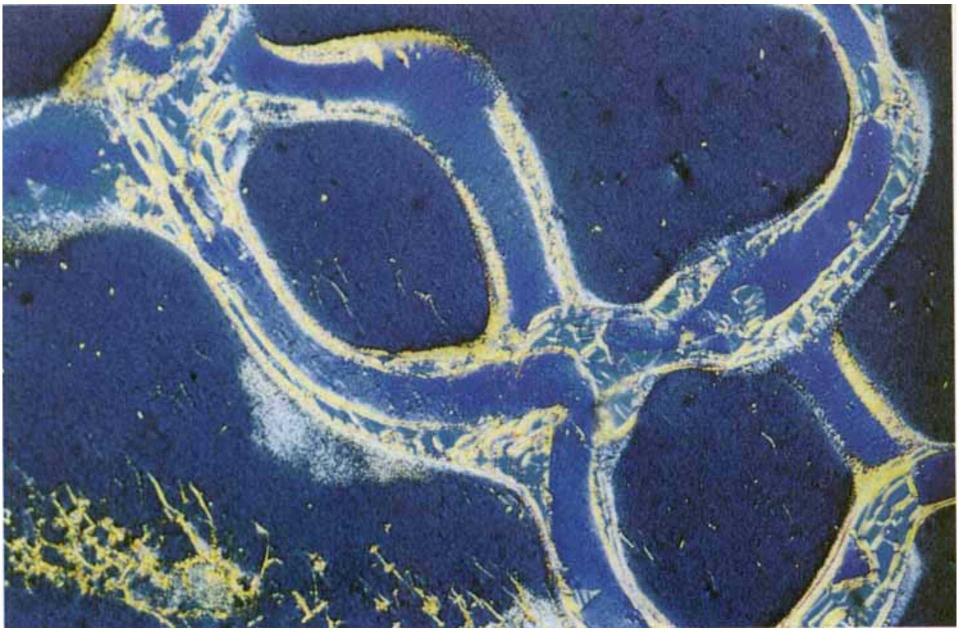
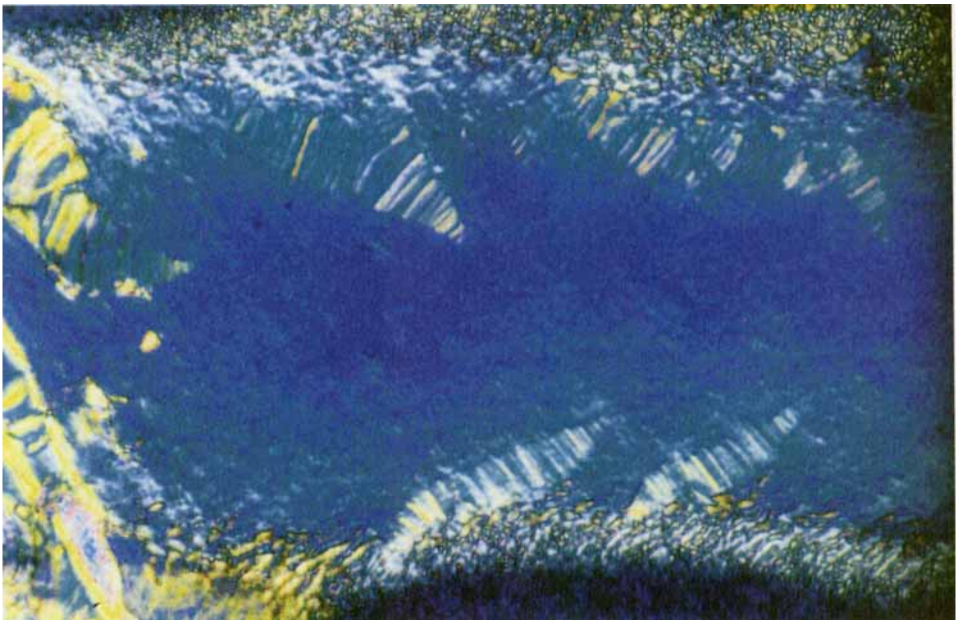


Figure 5. Synthesis of the polymers IIIa and IIIb.



(*a*)



(*b*)

Figure 6. Optical texture of polymer IIIa after annealing for 72 h at 75°C (*a*) magnification × 250; (*b*) magnification × 2000).

2.5. *Properties of polymer III*

Polymerization of **18** in THF (7 h, 62°C, 1 mol per cent AIBN) yielded **IIIa** with an average molecular weight $M_W = 22000$ (G.P.C., polystyrene calibration). D.S.C. measurements reveal a mesophase between 33° and 78°C. Annealed samples show textures exhibiting a blue selective reflection of light in the region of the streaks (see figure 6). Streaks are common in chlorestic textures (oily streaks) but no evidence is given for this phase type in polymer **IIIa**. Streaks are also known to occur in smectics. A proof for the S_C^* structure of the mesophase of **IIIa** is given in the following section.

Polymerization of **18** in toluene (48 h, 60°C) resulted in polymer **IIIb**, having a $M_W > 10^5$. The D.T.A. curve is shown in figure 7; two mesophases are observed.

2.5. *X-ray investigations*

The X-ray patterns obtained from fibres drawn in the broad mesophase of **IIIa** and **IIIb** are displayed in figure 8 (*a*), (*b*):

These X-ray patterns were recorded using a monochromatic ($\mathrm{Cu}K_\alpha = 1{\cdot}541$ Å) point focusing X-ray beam obtained by reflection on a doubly bent pyrolitic graphite. The sample-to-film distance is 95 mm. The experiments were made at room temperature in an evacuated camera.

The pattern of **IIIa** (see figure 8 (*a*)) is that of a S_C^* phase for which the layers tend to be oriented parallel to the direction of stretch, but the mesogenic cores are oriented locally along the helix. Due to the cylindrical symmetry around the helix axis the wide angle diffuse reflection is nearly uniform.

The pattern given by the fibre of polymer **IIIb** (figure 8 (*b*)) is typical of a S_C^* phase with the mesogenic cores oriented along a single direction (the direction of stretch) as inferred from the wide angle diffuse crescent (see figure 9) [8]. The smectic layers are distributed on a cone. The intersection of this cone with the Ewald sphere consists of the two lines on which the small angle reflections are located. The fact that the mesogenic cores are oriented along a single direction means that we have untwisted the helix of the S_C^* structure.

The two polymers (**IIIa** and **IIIb**) do not differ in the symmetry of their phases (both are S_C^*) but rather by their viscoelastic properties. The small angle reflections correspond to Bragg spacings of 45 Å for the layers. The calculated length of the side group is 26 Å (measured on Dreiding stereomodels). The result leads to a tilted double layer structure for the S_C^* phase. The tilt angle of 30° derived from the layer spacing is in fair agreement with that measured from the X-ray pattern of about 25°.

2.6. *Comparision of polymers I–III*

Introducing a chiral branching at the α position in the spacer unit of polymer **I** results in a dramatic shift of the smectic mesophase towards lower temperatures and a narrowing of the mesophase range (see the table). Introducing the chiral branching

Table 1. Mesophases and transition temperatures of polymers I–III.

I	S_F	45	S_C	145	I		
II	T_G	10	S	40	I		
IIIa	T_G	33	S_C^*	78	I		
IIIb	T_G	38	S_C^*	97	N*(?)	102·5	I

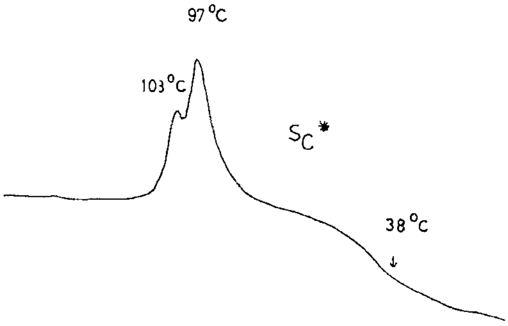


Figure 7. D.T.A. for IIIb, heating rate 10 K min.

at β position of the spacer unit of polymer **I** results in a transformation of the S_C into a chiral S_C^* phases (**IIIa**, **IIIb**), in a decrease of the transition temperatures and a contraction of the S_C phase from a temperature range of 100°C to 45°C (**IIIa**) and 59°C (**IIIb**) respectively. The higher ordered S_F phase of polymer **I** is lost, the chiral smectic C* phase solidifies directly to the glassy state. This, in principle, allows us to freeze in the ferroelectric properties of the S_C^*. Experiments to switch these chiral smectic C polymers in electric fields could not yet be performed successfully.

3. Experimental

The complete experimental part including the synthetic procedure for all compounds and their characterization by ^{1}H N.M.R. (400 MHz), I.R., and M.S. data have been deposited at the British Library, Document Supply Centre, Boston Spa, Wetherby, Yorkshire LS23 7BQ, England. Copies of this supplementary publication comprising 10 pages may be obtained by using the procedure described at the end of this issue and quoting the number sup 16512.

(2S)-2-methyl-6-methoxyhexanoic acid (**5**). $[\alpha]_D^{25} = +6{\cdot}4^\circ$ (c 1·06, $CHCl_3$), ($[\alpha]_D^{25} = +15^\circ$ (c 4·0, $CHCl_3$)$^{(9)}$). b.p.: 85–105°C (0·17 mbar), (b.p.: 108–112°C (0·3–0·6 mm Hg)$^{(9)}$).

(2S)-5-2-methylhexanoic acid (**6**). $[\alpha]_D^{25} = +3{\cdot}4^\circ$ (c 1·07, $CHCl_3$). b.p.: 98–108°C (0·17 mbar).

(2S)-4-(6-bromo-2-methylhexanoyl-oxy)-4′-butoxyphenyl-benzoate (**8**). $[\alpha]_D^{25} \div +6^\circ$ (c 1·5, $CHCl_3$).

(2S)-4-(6-acryloyloxy-2-methylhexanoyl-oxy)-4′-butoxyphenyl-benzoate (***10***). A mixture of **8** (1·5 g, 3·1 mmol), lithium acrylate (0·35 g, 4·5 mmol) and HMPT (9 ml) was stirred at 40°C for 48 h. The reaction mixture was cooled to room temperature and poured into water. The mixture was extracted with ether (3 × 20 ml). The combined ether on silica-gel using ether/petrolether as eluent. Yield 770 mg (52 per cent) of a colourless oil.

$[\alpha]_D^{25} = +4{\cdot}6$ (c 1·6, $CHCl_3$). N.M.R. ($CDCl_3$, 400 MHz): $\delta = 0{\cdot}98$ (t, $J = 7$ Hz; 3 H), 1·33 (d, $J = 7$ Hz; 3 H), 1·45–1·93 (m; 10 H), 2·73 (sext., $J = 7$ Hz; 1 H), 3·97

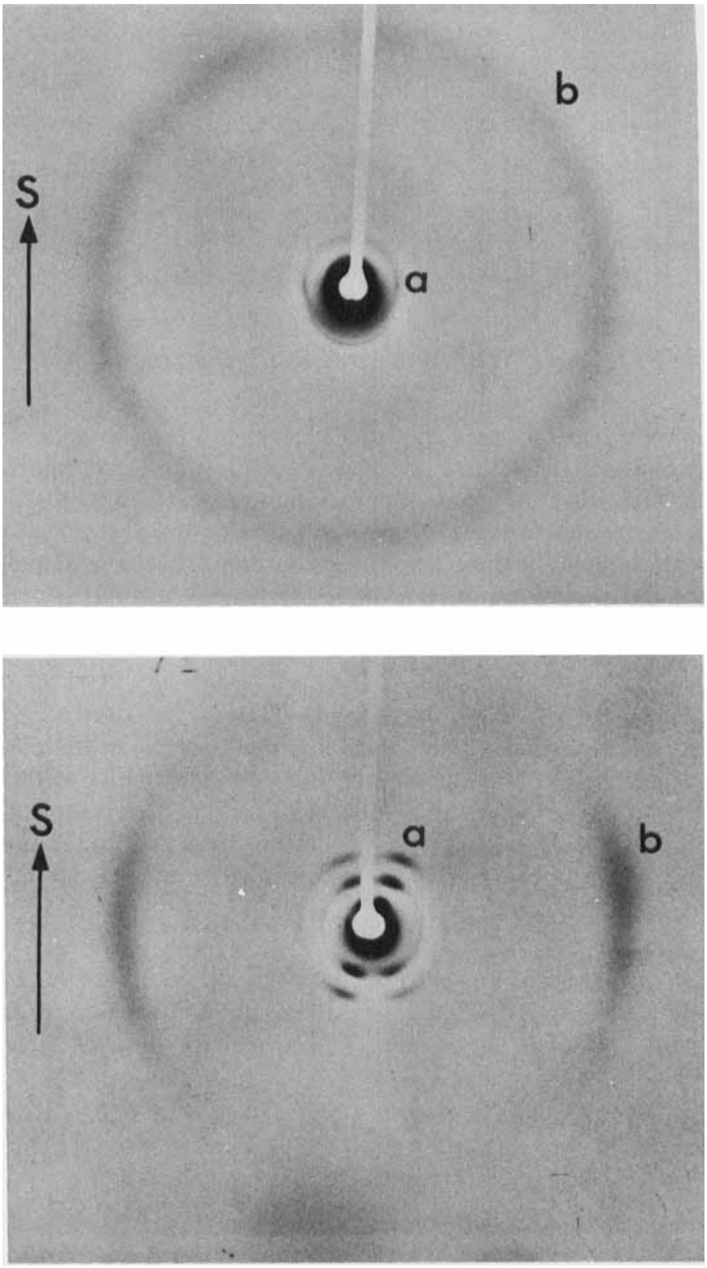


Figure 8 (*a*). X-ray pattern of polymer IIIa. (*b*) X-ray pattern of polymer IIIb $\lambda = 1{\cdot}541$ Å, S is the stretching direction, *a*; Bragg reflections, *b*, wide angle diffuse cresents.

(t, $J = 6{\cdot}5$ Hz; 2 H), 4·20 (t, $J = 6{\cdot}5$ Hz; 2 H), 5·84 (dd, $J = 10$ and 1·5 Hz; 1 H), 6·13 (dd, $J = 17$ and 10 Hz; 1 H), 6·41 (dd, $J = 17$ and 1·5 Hz; 1 H), 6·93, 7·10 (AA′BB′, $J = 9$ Hz; 4 H). 7·21, 8·22 (AABB′, $J = 8{\cdot}5$ Hz; 4 H). MS (90°C): m/e = 468 (1 per cent, M^+), 303 (77 per cent, M–$C_{10}H_{13}O_2$), 166 (8 per cent, M–$C_{17}H_{19}O_5$ + 1), 121 (22 per cent, M–$C_{10}H_{13}O_2$–$C_{10}H_{15}O_3$ + 1), 55 (100 per cent,

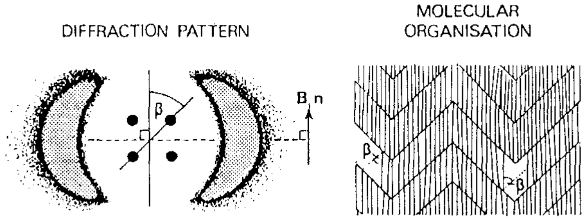


Figure 9. Schematic diffraction pattern and structure for S_C phase.

M–$C_{17}H_{17}O_4$–$C_3H_4O_2$–CO–$2CH_2$). I.R. ($CHCl_3$): 2960, 2940, 2880 (CH_2, CH_3), 1740, 1720 (COOR), 1610, 1505 (C=C).

Poly-(5S)-5-(4-(butoxyphenoxycarbonyl)phenoxycarbonyl]-5-(methylpentylacrylate (***II***). The monomer **10** (720 mg, $1{\cdot}54 \times 10^{-3}$ mol) was polymerized with 2·5 mg AIBN ($1{\cdot}54 \times 10^{-5}$ mol) in 7·7 ml dry THF solution under N_2. The polymerization was carried out at 60°C for 24 h. The polymer was purified by reprecipation from concentrated THF solution into methanol for at least three times. Yield 234 mg (33 per cent). $[\alpha]_D^{25} = +5{\cdot}0°$ (*c* 1·03, $CHCl_3$).

(3R)-4-(6-hydroxy-3-methylhexanoyl-oxy)-4′-butoxyphenyl-benzoate (***17***). m.p.: 55°C.

(3R)-4-(6-acryloyloxy-3-methylhexanoyl-oxy)-4′-butoxyphenyl-benzoate (***18***). 1·99 g (4·8 mmol) **17** and 404 mg (4·8 mmol) acrylic acid were combined using the DCCI method [10]. The acrylate was purified by F.C. on silica-gel with dichloromethane as eluent, giving 1·1 g (48 per cent) of a colourless oil.

$[\alpha]_D^{25} = +6{\cdot}8°$ (c 1·12, $CHCl_3$). N.M.R. ($CDCl_3$, 400 MHz): δ = 1·00 (t, J = 7 Hz; 3 H), 1·11 (d, J = 7 Hz; 3 H), 1·36–1·85 (m; 3 H), 1·52 (sext., J = 7 Hz, 2 H), 1·79 (tt, J = 7 and 6·5 Hz; 2 H), 2·16 (m; 2 H), 2·45 (dd, J = 15 and 8 Hz; 1 H), 2·61 (dd, J = 15 and 6 Hz, 1 H), 3·98 (t, J = 6·5 Hz; 2 H), 4·19 (t, J = 6·5 Hz; 2 H), 5·84 (dd, J = 10 and 1·5 Hz; 1 H), 6·14 (dd, J = 17 and 10 Hz; 1 H), 6·41 (dd, J = 17 and 1·5 Hz; 1 H), 6·94, 7·11 (AA′BB′, J = 9 Hz; 4 H), 7·22, 8·22 (AA′BB′, J = 8 Hz; 4 H). MS (270°C): m/e = 408 (4 per cent, M^+), 303 (20 per cent, M–$C_{10}H_{13}O_2$), 183 (2 per cent, M–$C_{17}H_{17}O_4$), 166 (5 per cent, M–$C_{15}H_{19}O_5$ + 1), 121 (100 per cent, M–$C_{10}H_{13}O_2$–$C_{10}H_{15}O_4$ + 1). I.R.($CHCl_3$): 2970, 2880, 2940 (CH_2, CH_3), 1740, 1725 (COOR), 1605, 1505 (C=C) cm^{-1}.

Poly-(4R)-4-[4-(butoxyphenoxycarbonyl)phenoxycarbonyl]-4-methylpentylacrylate (***III***). (*a*) 900 mg (1·92 mmol) **18** was polymerized with 3·1 mg ($1{\cdot}92 \times 10^{-2}$ mmol) AIBN under N_2 in THF at 60°C for 7 h. The polymer was purified by three reprecipitations from concentrated THF solution into methanol. Yield 235 mg (26 per cent) of **IIIa**. (*b*) 810 mg (1·73 mmol) **18** was polymerized with 2·8 mg ($1{\cdot}73 \times 10^{-2}$ mmol) AIBN under N_2 in toluene at 60° C for 48 h. Purification see previous section. Yield 287 mg (35 per cent) of a white crystalline substance **IIIb**. $[\alpha]_D^{25} = +7{\cdot}4°$ (c 0.72, $CHCl_3$).

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