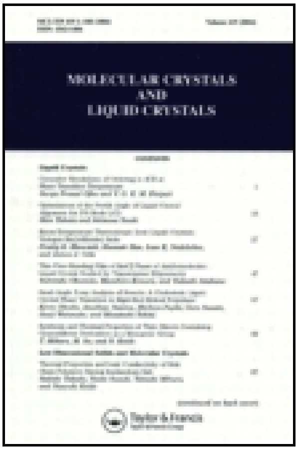

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A TGB-Like, Poorly Birefringent Smectic Phase of Side Chain Polymers

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A TGB-LIKE, POORELY BIREFRINGENT SMECTIC PHASE OF SIDE CHAIN POLYMERS

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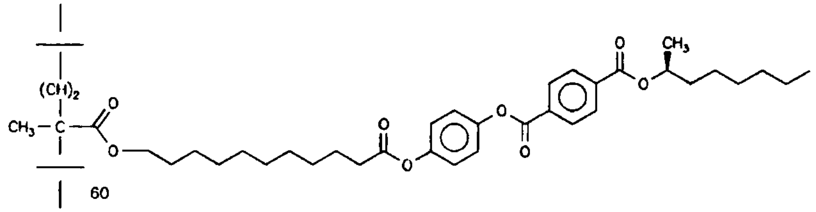
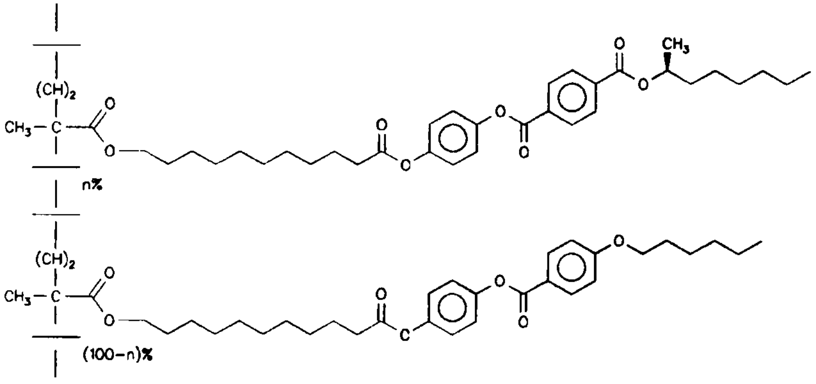
Abstract An almost optically isotropic smectic phase has been observed for some side chain polymers having main chains of different nature (homo- and copolymethacrylates, polysiloxanes) but the same chiral mesogenic side group. Structure and optical properties of the mesophase are investigated.

INTRODUCTION

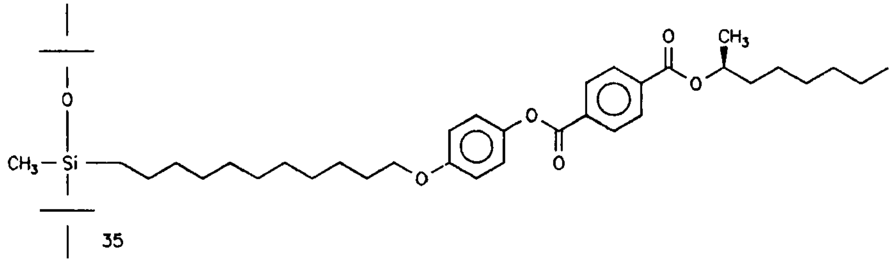
The twist grain boundary smectic phases (TGB-phases) are recently the subject of an increasing interest[1-3]. We have already reported the anomalous phase state of the polymer P8*M:



and relating copolymers C75 and C47:



where n = 75 and 47 correspondingly[4-6]. The polymers show all the DSC, X-ray and NMR properties of a smectic phase but no birefringence. A TGB_A-like amorphous chiral smectic structure has been suggested for the mesophase[6]. Here we report synthesis and characterization of a novel polysiloxane with the same mesogenic side group, P8*S:



which shows quite a similar phase behaviour, and combined optical studies of the mesophase for all the polymers.

EXPERIMENTAL

Synthesis of the polymers

Synthesis and characterization of the methacrylic polymers P8*M, C47 and C75 have been published earlier[4,5].

The monomer of the polymer P8*S, i.e. 4-(10-undecenoyloxy)-phenyl 4'-(2-(*S*)-octyloxycarbonyl)-benzoate, has been synthesized in the following way. First, p-10-undecen-1-ylphenol was obtained by reaction of the 10-undecen-1-ol and hydroquinone (in 100% mol excess) with diethyl azodicarboxilate and triphenylphosphine in ether solution at room temperature during 72 h, Mp 66°C. Then the phenol above was reacted with the 4-(2-(*S*)-octyloxycarbonyl)-benzoyl chloride[4] (in 1.2 excess) and triethylamine in toluene solution giving the goal monomer, Mp 39.5°C.

The polymer P8*S has been synthesized from its monomer and poly(methyl hydrogen) siloxane (Merck, Germany) using the standard polyhydrosililation reaction[7] and the chloroplatinic acid as a catalyst. The standard synthetic prescription has been reported earlier[8].

Investigation techniques

The DSC curves of the polymer P8*S were taken with the Perkin-Elmer DSC-2C calorimeter, and the X-ray curves by STOE-2 diffractometer using CuK_α radiation (λ = 1.541 Å) and PSD linear position scanning detector. The size of smectic domains, *r*, was calculated from the width of the main small angle X-ray peak at half maximum level, $\Delta 2\Theta$, as $r = \lambda/\pi\Delta 2\Theta$. The optical transmission was measured by Perkin-Elmer and Cary 17 spectrophotometers; the circular and the linear dichroism were written by IKS-29 spectrometer. The microscopic textures were observed under the Leitz microscope supplied with a Mettler FP-82 heating stage.

RESULTS AND DISCUSSION

All the polymers form below clearing point the same mesophase Sm X, which can be frozen in a glass. Table 1 presents the phase transitions of the polymers, as measured from the DSC curves in heating. The transition temperature in cooling is usually lower, and the difference can achieve 26°C (C75).

TABLE 1 Phase transitions and structural data of the polymers

Polymer	Phase transitions	Interlayer distance, d_1, Å	Domain size, *r*, Å
P8*M	glass 30 Sm X 64 Iso	63.2-64.5	80
C75	glass 40 Sm X 79 Iso	~ 63	80
C47	glass 34 Sm X 92 Iso	~ 63	80
P8*S	glass 24 Sm X 47 Iso	33.1-33.7	230

The Sm X phase for all the polymers show X-ray scattering peaks in small angles typical for smectic phases. The diffraction curves for the methacrylic polymers have been reported earlier[4,5] and show three peaks corresponding to a single lattice with the period d_1 ~ 63 Å, all the peaks being however very wide, so that the calculated domain size include no more than two layers (Table 1). Fig. 1 presents the X-ray curve from the siloxane polymer P8*S. It shows in small angles an intensive peak corresponding to the layer spacing d_1 = 33.4 Å, and two small peaks, one of those being the second order reflex of the same lattice (d_2 = 16.6 Å). The nature of the second small peak, d_i = 19.6 Å, is still unclear. The d_1 value is however somewhat less than the calculated length of the side chain, *l* = 36.5 Å, thus suggesting either tilted structure or overlap of mesogenic side chains from neighbouring layers. In the wide angle range the curve has a broad peak (similar to those for other three polymers[4,5], thus indicating a short order only within smectic layers.

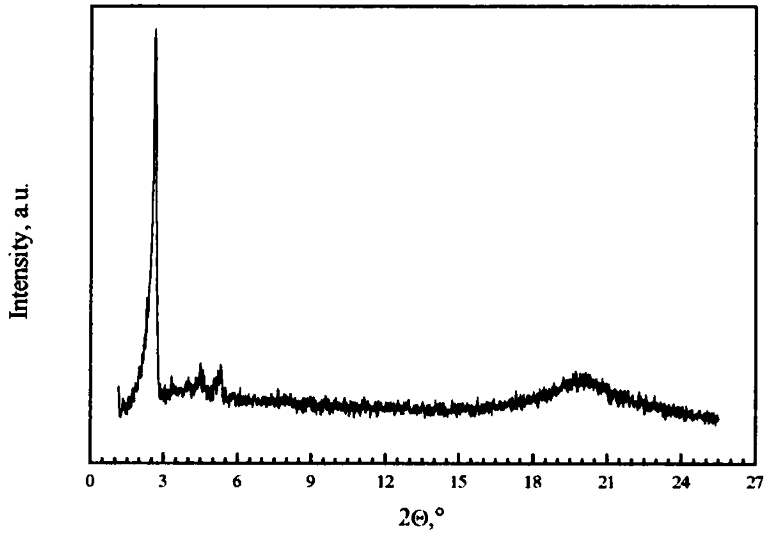


FIGURE 1 X-ray curve for the polymer P8*S (Sm X phase, 21.5°C)

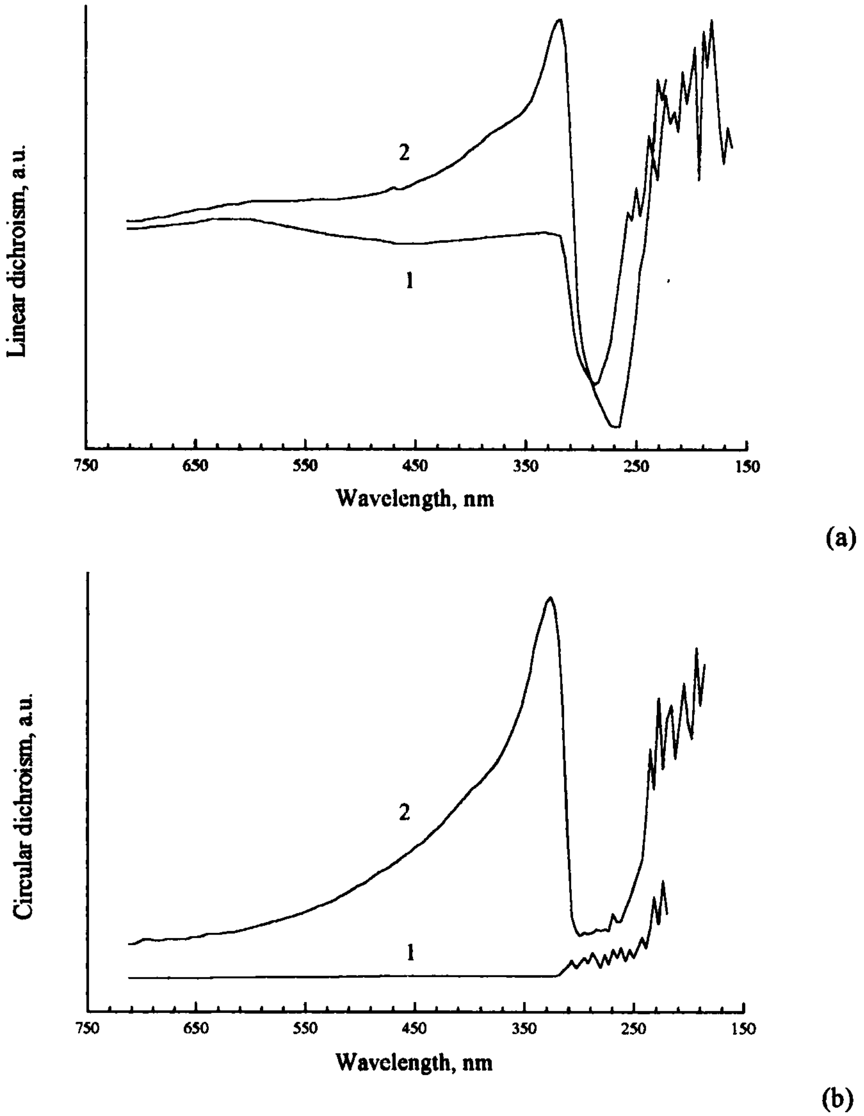


FIGURE 2 Linear dichroism (a) and circular dichroism (b) for the polymer C75 in isotropic phase (1) and Sm X phase (2)

The Sm X phase has however optical properties quite different from other smectic phases. The methacrylic homopolymer P8*M is completely transparent and has no birefringence at all within the visible wavelength range, so that the phase transition to the isotropic phase cannot be seen under the microscope (but can be detected by DSC peak and disappearance of the small angle X-ray peaks). The copolymers C75 and C47 are also transparent and form no specific textures but have a diffuse blue color similar to the cholesteric blue phase III (fog phase). The dichroism measurements for the copolymer C75 show also that it has both linear dichroism (i.e. birefringence) and circular dichroism close to the absorption edge, mostly in the near UV range (Fig. 2).

The polysiloxane P8*S forms a poorely birefringent noncharacteristic texture with a pronounced light scattering. The texture can be however easily oriented by slight shear flow, giving a transparent texture which can be frozen at room temperature. Rotation of the microscope table shows no change of contrast, similar to reported earlier[6] for C47.

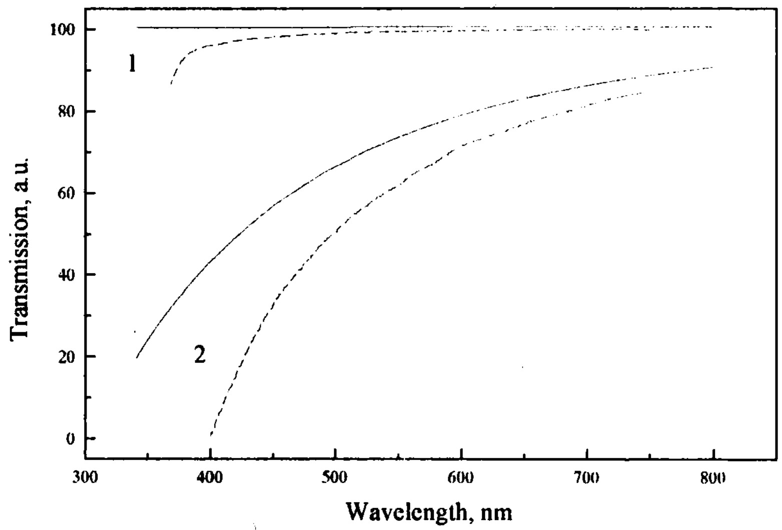


FIGURE 3 Transmission spectra for the polymers C75 (solid line) and P8*S (dashed line) in the isotropic phase (1) and Sm X phase (2)

None of the investigated polymers shows selective light reflection in the visible wavelength range. Nevertheless, transmission spectra of the Sm X phase reveal a decrease to the shorter wavelengths opposite to those of the isotropic phase, thus suggesting a selective reflection area hidden behind the absorption edge (Fig. 3). The selective reflection wavelength could be estimated from the curves of Fig. 3 as $\lambda_{max} \sim 300$ nm for C75 and $\lambda_{max} \sim 350$ nm for P8*S. From those values, the grain dimension of the chiral structure, L, can be estimated similarly to that for BPIII phase[9] as

$$L \approx \lambda_{max}^2/\Delta\lambda n,$$

where line width, $\Delta\lambda$, can be estimated about 300 nm. That gives $L \sim 200$ nm for C75 and $L \sim 280$ nm for P8*S; i.e. one pitch of the helical superstructures includes 12-25 smectic blocks (of r size), which is usual for TGB phases[10].

Let us summarize shortly the properties of the Sm X phase:

- The phase exists in a broad temperature range (up to 60°C) and can be frozen in a glass;
- The heat of the Sm X - Iso phase transition, $\Delta H \sim 7$-9 kJ/mol[4,5], is typical for smectic to isotropic transition and two orders of magnitude higher than for the blue phase - isotropic transition;
- The phase shows poor birefringence only beyond a narrow wavelength range close to the absorption edge;
- The phase has a well developed circular dichroism with a maximum in the near UV range and should have selective reflection in the same range;
- The phase forms highly transparent textures;

- The phase possesses a smectic ordering at short distances (8-23 nm);
- Pyroelectric measurements for P8*M and C47 show absence of ferroelectric properties, i.e. the Sm X phase of those polymers is not tilted[5,11].

Based on the complex of properties above, we suggest that the Sm X phase of the polymers under nvestigation has an amorphous type of TGB ordering. The smectic domains, 10-25 nm in diameter, rotate around a cholesteric axis inside large 200-250 nm domains; and orientations of the chiral axes between neighbouring domains are not correlated.

CONCLUSIONS

A new evidence has been found for the formation of the "isotropic smectic phase" in chiral side chain polymers. The mesogenic phenyl 4'-(2-(*S*)-octyloxycarbonyl)-benzoate moieties separated from the polymer main chain by the spacer of ten methylene groups tend to organize themself in a chiral layered structure with poor birefringence for both methacrylic and siloxane main chains. A TGB-like structure has been suggested for the mesophase.

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