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Preliminary Communication

Amorphous chiral smectic A phase of side chain copolymers

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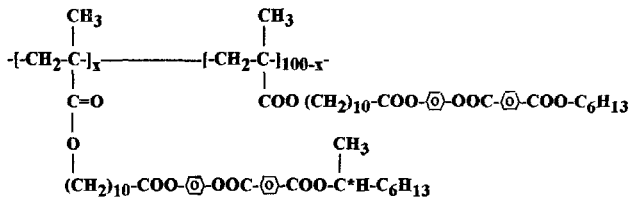
The chiral structure of the anomalous smectic phase recently observed in chiral copolymers has been studied by optical methods. The phase is amorphous, but shows a short range order, as a combination of smectic A and cholesteric structures. This phase is presumed to possess locally the TGB_A structure.

The twist grain boundary (TGB) structures predicted by Renn and Lubensky [1, 2] have been studied intensively in recent times [3–5]. Such phases consist of twisted stacks of smectic A or smectic C(C*) layers separated by walls of disclination. Known TGB phases possess long range order, i.e. monodomain samples of this phase can be produced in a manner similar to cholesterics. In [6–8] an anomalous smectic phase has been reported in chiral liquid crystalline copolymer systems and this possesses only short range positional order. In the present paper, we report results of optical studies of this mesophase (smectic X) and show that this phase reveals an amorphous type of structure with smectic and cholesteric scales of short range ordering. One realistic structure assignment for the smectic X is a TGB_A short range order phase.

We have investigated copolymers with the following structure:



where $x = 37$, 47, 75, 100 per cent.

The syntheses of these materials and their characterization has been described previously [6, 7]. The molecular mass of the homopolymer with $x = 100$ per cent (P8*M) was $M_W = 99\,000$ and the molecular mass dispersion $M_W/M_N = 2{\cdot}7$. The phase diagram for different polymer compositions is shown in Figure 1. For highly chiral copolymers ($x \geq 38$) the smectic X phase, of which the structure was of interest to us, was observed. The typical phase sequence for $x = 75$ is the following: I (73) smectic X (40) glass.

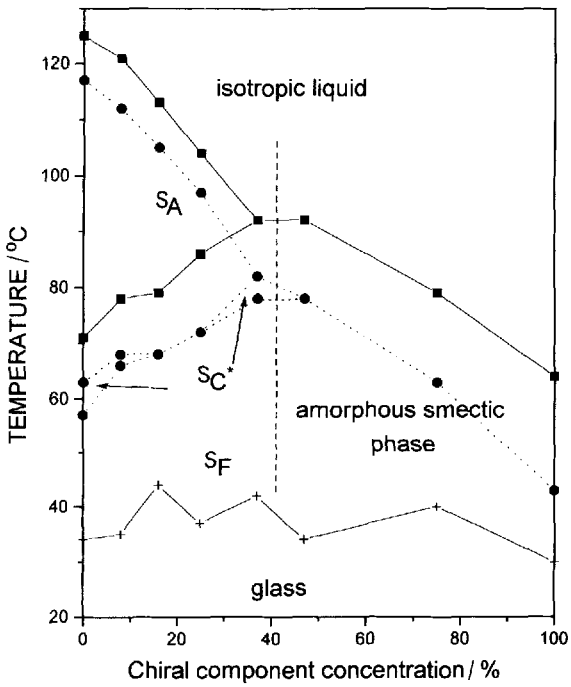


Figure 1. Phase diagram of the copolymer system for different compositions; on cooling (circles), on heating (squares).

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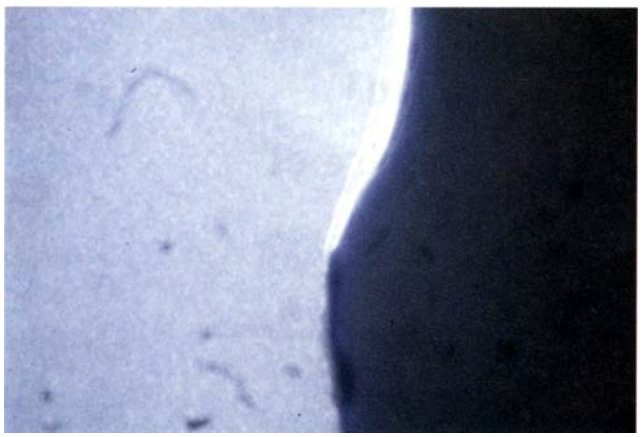

Figure 2. Smectic X phase of polymer C47 at $T = 77°C$ in a cell without spacer.

The typical coexistence region was about 2°C around the isotropic–smectic X transition temperature. Successive phase transitions to S_A and S_F phases have been reported for copolymers with $x \leq 38$. The glass temperature for this polymer system is at $T = 40 \pm 5°C$. The ferroelectric properties of these copolymers have already been studied [8]. We have now measured the optical transmission (Perkin–Elmer spectrophotometer), the circular and linear dichroism (IKS-29 spectrometer) and observed the smectic X textures in the optical microscope (Leitz-Ortholux polarized microscope). X-ray measurements on this system have already been reported [6, 7].

Figure 2 shows a microscope image of the smectic X phase of an $x = 47$ copolymer (C47) at $T = 77°C$. The phase transition temperature I–smectic X was recorded at 81·5°C. Figure 2 displays a droplet of smectic X phase surrounded by air in a cell without spacer and between crossed polarizers. The smectic X phase has a diffuse blue colour in contrast to the isotropic liquid which shows no difference from the empty cell. Rotation of the microscope table shows no change of contrast. This image is similar to that of the blue phase III (fog phase) of chiral liquid crystals [9]. The difference from BPIII is that the boundary smectic X–air is anisotropic which is possible only when the smectic X phase is anisotropic. In contrast to BPIII, the texture of smectic X can be made anisotropic by shearing, which is not possible for BPIII.

Figure 3 shows the temperature dependence of the circular dichroism in non-oriented samples of the $x = 75$ copolymer. The phase transition isotropic–smectic X takes place at $T \approx 72°C$. Microscopic images of the X phase are similar to those for C47. The circular dichroism of the isotropic liquid was zero, with a peculiarity at $\lambda = 317$ nm, which corresponds to the absorption edge of the material. The smectic X spectra possess a maximum at $\lambda = 330$ nm, which was independent of temperature. The long wavelength wing of each

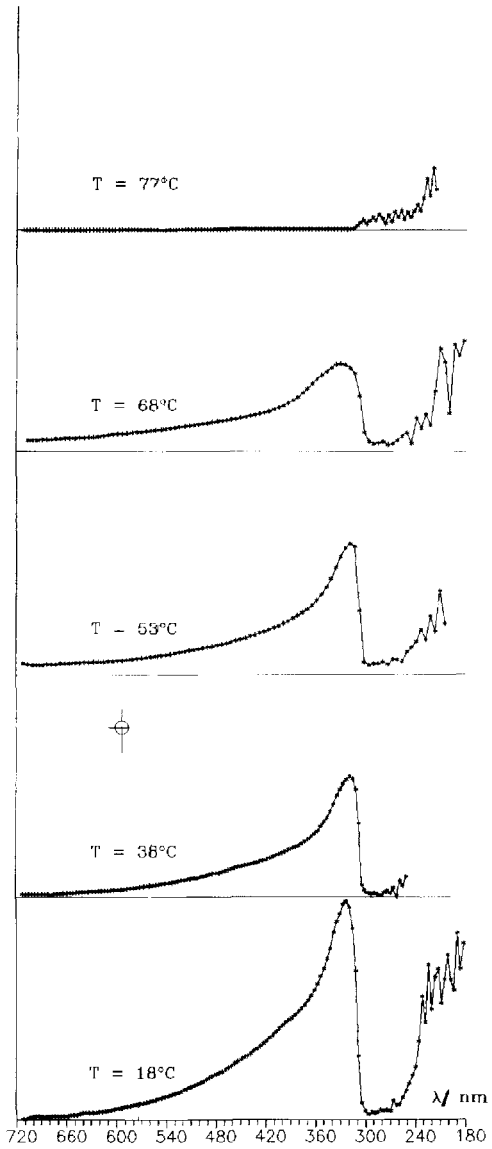

Figure 3. Temperature dependence of the circular dichroism of C75.

spectrum is very broad and decays to zero at $\lambda \approx 600$ nm. The shapes of the spectra demonstrate that this phase possesses a chiral polydomain order with a very small grain size.

Figure 4 shows the temperature dependence of the linear dichroism spectra in non-oriented C75 samples. The linear dichroism in the isotropic liquid reveals a maximum at $\lambda = 600$ nm, which can be explained by an anisotropy of the main chain orientation. This maximum is also present in the smectic X phase. In the later phase, a new maximum at 300 nm occurs. The smectic X linear dichroism spectra show unambiguously that it is an optically anisotropic phase, because in polydomains of isotropic phases, the linear dichroism has to be zero [10].

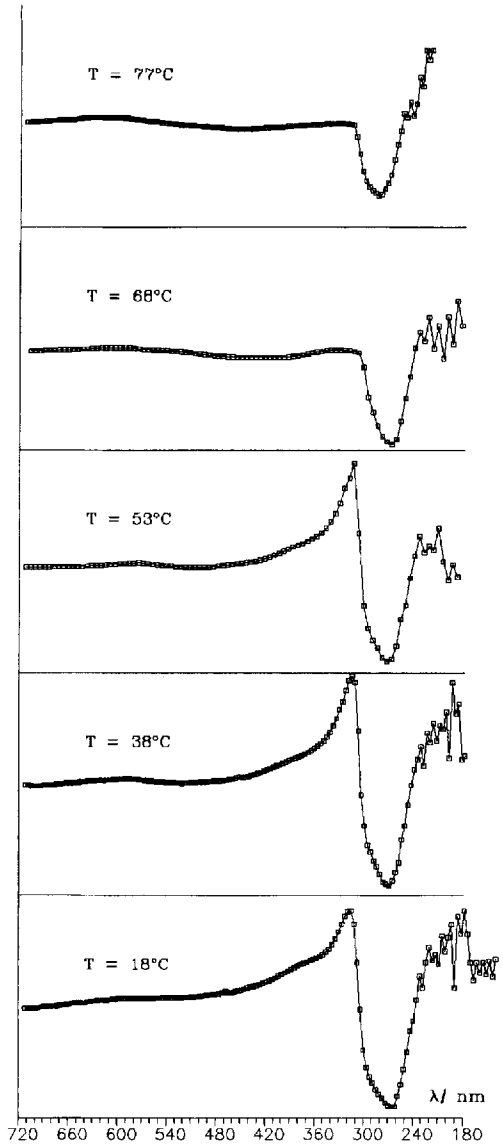

Figure 4. Temperature dependence of the linear dichroism of C75.

Figure 5 shows transmission spectra of the smectic X phase of C75 in a cell without any orientation. All spectra are scaled so that the transmission in the isotropic liquid was 100 per cent. The transmission of smectic X samples decreases monotonically with decreasing wavelength. Such curves are similar to those of polydomain samples of a cholesteric phase with very small grain size [11]. Because no peculiarities of the smectic X spectra are recorded in the region of transmission, the selective reflection wavelength is positioned below the absorption edge. C75 transmission spectra remain unchanged in the interval 50–20%. Shearing has no qualitative influence on the smectic X spectra.

Our optical studies demonstrate that the smectic X phase possesses a chiral order of amorphous type. The grain dimension L of this structure can be estimated similarly to that for BPIII [12–14]. If we take for the line width $\Delta\lambda = 300\,\text{nm}$ and the selective reflection wavelength $\lambda_b = 320\,\text{nm}$, according to the expression [12]

$$L \approx \frac{\lambda_b^2}{\Delta\lambda n} \tag{1}$$

we obtain $L \sim 200\,\text{nm}$. This is approximately 2–3 times smaller than typical values for BPIII in cholesteryl nonanoate [12–14]. Since microscopic observations and linear dichroism measurements show that the smectic X phase is optically anisotropic, we can suggest a cholesteric-like structure inside the grains

Let us summarize other known properties of the smectic X phase: [6–8]:

(i) The transition heat for the isotropic–smectic X transformation is about 7–9 kJ mol^{-1}, which is typical for isotropic–smectic phase transitions and approximately two orders of magnitude larger than those of isotropic–blue phase transitions [7];
(ii) The smectic X temperature interval is about 40–60°C;
(iii) Smectic X possesses smectic ordering inside small regions of diameter about 10 nm [7];
(iv) Smectic X is a chiral phase, but possesses no pyroelectric properties [8]; therefore a short range smectic A order is the most plausible variant of positional order;
(v) This phase cannot be oriented by mechanical and electric fields.

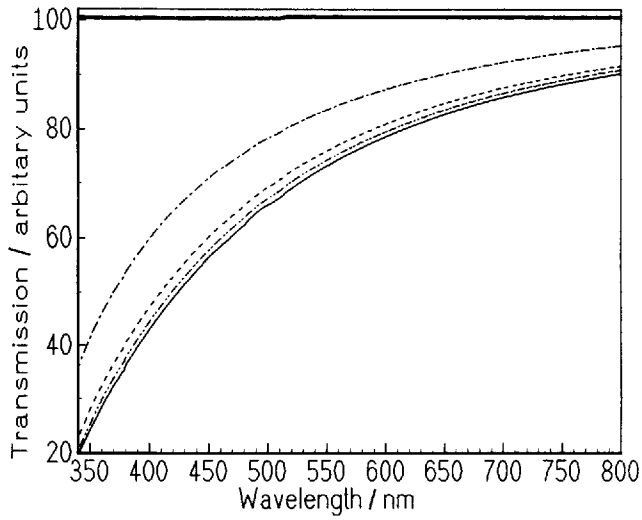

Figure 5. Temperature dependence of transmission spectra of C75: —— (75°C, isotropic liquid), –·–·– (70°C), - - - (65°C), –··–··– (50°C), —— (30°C).

Analysis of these smectic X phase properties shows that this phase has an amorphous structure with smectic and cholesteric scales of short range order. Because of the large transition heat for the transition I–smectic X and the broad temperature interval of the phase, blue phases cannot be considered for structure assignments. Developing the idea of the TGB structure, we suggest that smectic X possesses an amorphous type of TGB_A ordering. The smectic A domains, 10 nm in diameter, rotate around a cholesteric axis inside large 200 nm domains. Orientations of the chiral axes between neighbouring domains are not correlated. It is interesting to note that the ratio of the smectic interlayer distance and the smectic A grain dimensions is about 1·5 [7], which is typical for glasses observed in other liquid crystalline systems [13].

If we look at the properties of the smectic X phase from the polymeric point of view, we can draw an interesting picture of this phase transformation. The phase transition involves the occurrence of local smectic and cholesteric order, whereas the disordered conformation of the main chain present in the isotropic melt remains unchanged. The principle of the smectic X structural organization is similar to that for BPIII which possesses only a chiral short range order after the phase transition from the isotropic liquid [12–15].

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