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Bilayer smectic order in a mixture of polyphilic liquid crystals

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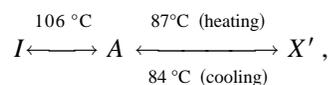
Polyphilic compounds were previously reported [F. G. Tournilhac, L. M. Blinov, J. Simon, and S. V. Yablonski, *Nature* **359**, 621 (1992)] to form a longitudinal ferroelectric liquid crystal phase in the mixture M70 (70% compound I, 30% compound II). The ferroelectric nature was confirmed by measurements of acoustically induced piezoelectric response and hysteretic behavior in the smectic- X' phase. We carefully examined the structure of the smectic- X' phase with high-resolution x-ray diffraction in an aligned sample and discovered bilayer structure, suggesting that molecules actually adopt antiferroelectric arrangement. [S1063-651X(97)06604-X]

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In the conventional chiral ferroelectric smectic- C^* liquid crystalline phase [1], the spontaneous polarization lies in the smectic plane and rotates helically around the smectic layer normal. The search for a longitudinal ferroelectric liquid crystal phase, in which the spontaneous polarization is primarily along the long axis of the rodlike molecules or along any direction but uniquely defined in the three dimensional space, has remained a challenge. As pointed out by Petschek and Wiefling [2], nature does not prohibit the existence of a longitudinal ferroelectric liquid crystalline phase. There have been a few suggestions [2–4] regarding the molecular architecture which will remove inversion symmetry of a smectic phase. Molecules with strong longitudinal dipole moments tend to form antiferroelectric dimers resulting in the bilayer smectic- A_2 phase, partial bilayer smectic- A_d phase, smectic antiphases \bar{A} and \bar{C} , reentrant nematics, and a rich variety of phenomena [5–8] but no longitudinal ferroelectric phase. It is clear that the molecules must be specially designed to overcome the undesirable antiferroelectric coupling. Petschek and Wiefling [2] proposed a fraternal-twin molecular configuration realized by linking two rigid liquid crystal forming moieties with a flexible spacer and similar flexible hydrocarbon end chains. Theoretical calculations [9] indicate that a ferroelectric arrangement of molecules is energetically allowed.

Stimulated by the amphiphilic character of self-assembly in lyotropic systems [10], Tournilhac and colleagues [4,11] postulated that the segregation between unlike chemical moieties, such as hydrocarbon and fluorocarbon chains, could provide sufficient lateral attractive forces to generate homogeneous polar domains and ferroelectric packing of molecules. They synthesized the “polyphilic” compounds to test the idea. The polyphilic molecules consist of perfluoroalkyl and alkyl side chains, and a diphenyl rigid core, as shown in Fig. 1 [3]. Compounds I and II, as labeled, are essentially the same polyphilic molecules except that the ether and ester linkages have been interchanged. The pure polyphilic compound I has a phase sequence of isotropic (I) – smectic- A (A) – smectic- X (X). The X phase was a metastable state which exhibited piezoelectric response and hysteretic behavior [3]. To reduce the intralamellar electrostatic repulsion, a binary mixture of compound I and II in a

70:30 ratio, defined as M70, was prepared. The phase sequence of M70 was



where X' stands for the smectic- X' phase. Previous structural study [12] reported that the X' phase possessed a smectic- C type layer structure. Surprisingly, *no optical biaxiality and schlieren texture*, characteristics of the smectic- C phase, were detected in the X' phase. In order to improve our understanding of the structure and properties of this new phase, we carefully examined the smectic ordering with high-resolution x-ray diffraction in a sample aligned with strong and *in situ* magnetic field. To our surprise, we found the X' phase to have antiferroelectric molecular ordering contrary to the previous report [12]. Based on these facts, we believe that the smectic- X' is actually a smectic- A_d -like phase.

The study was conducted on two x-ray diffractometers with Cu $K\alpha$ radiations. A low resolution Siemens X1000 diffractometer with a sensitive area detector was used to obtain a series of x-ray diffraction patterns as a function of temperature for a general overview and qualitative analysis. The resolution of this diffractometer was $\sim 5 \times 10^{-2} \text{ \AA}^{-1}$. The oven used in this measurement had a thermal stability

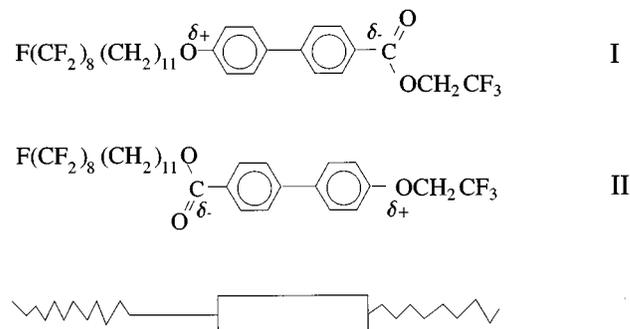


FIG. 1. Molecular formulas of polyphilic compounds (from Ref. [3]) used in mixture M70.

about ± 0.1 K. Quantitative work was done using a high-resolution x-ray diffractometer in a triple-axis nondispersive configuration with two Ge(111) single crystals as monochromator and analyzer and an 18 kW Rigaku rotating anode generator. The resolution in this case was $\sim 4 \times 10^{-4} \text{ \AA}^{-1}$. A specially designed oven was used in the high-resolution study with thermal stability of ± 0.5 mK and an *in situ* magnetic field of 6.5 kG produced by a pair of rare-earth permanent magnets with tapered pole faces to ensure good alignment. The sample was prealigned in an external magnetic field of 25 kG before putting it in the oven for x-ray measurement.

Figure 2 shows the diffraction patterns of M70 obtained with the Siemens diffractometer. The diffraction pattern shown in Fig. 2(a) was taken in the A phase at $T=88^\circ\text{C}$. The direction of alignment was defined by the magnetic field along the q_{\parallel} axis. The two quasi-Bragg peaks at Q_{A1} and its second harmonic Q_{A2} in q_{\parallel} direction yield a smectic layer spacing of 43 \AA , comparable to the molecular length. Two diffuse peaks which appeared at a large angle in the perpendicular q_{\perp} direction yielded an average in-plane intermolecular distance of 5.1 \AA . Figure 2(b) shows the diffraction pattern of the X' phase at 80°C obtained upon slow cooling (~ 0.5 K/h) from the A phase. The peak widths at both small and large angles in the X' phase were considerably larger than those in the A phase because of a wider mosaic, but still remained perpendicular to each other. Splitting of large angle diffuse peaks will be discussed later. Evidently, from Fig. 2(b) one could observe three peaks in the q_{\parallel} direction, labeled as Q_{X2} , Q_{X4} , and Q_{X6} (the latter two being higher harmonics of Q_{X2}), which yielded a smectic layer spacing of 35 \AA . It was found later, in the high-resolution measurement, that there is another peak at a smaller scattering vector which corresponds to bilayer smectic spacing. Figure 2(c) shows the diffraction pattern of the X' phase at the same temperature (80°C) as shown in Fig. 2(b), but obtained with a fast cooling rate (~ 20 K/hr) from the A phase. The diffraction pattern features were essentially the same, but the mosaicity of X' phase was much larger with fast cooling.

The high-resolution longitudinal and ω scans of M70 are shown in Fig. 3. In the A phase ($T=91^\circ\text{C}$), Fig. 3(a), two quasi-Bragg peaks at $Q_{A1}=0.1451 \text{ \AA}^{-1}$ ($\Delta Q_{A1}=0.0009 \text{ \AA}^{-1}$) and $Q_{A2}=0.2901 \text{ \AA}^{-1}$ ($\Delta Q_{A2}=0.0010 \text{ \AA}^{-1}$), indicated good alignment in the A phase with layer spacing of 42.6 \AA . Here ΔQ denotes the value of the full width at half maximum (FWHM) of the peak in the q_{\parallel} direction. The peak intensity of Q_{A1} was comparable to that observed in conventional smectogens, and defined as unity for reference in this paper. The two A peaks had the same mosaicity, as expected, with FWHM width of 7.1° in ω scans (shown in the inset). The intensity of the second peak was measured to be 0.11, which gave a rms thermal fluctuation amplitude of 4.9 \AA for the smectic layers obtained using Debye-Waller factor after Lorentz-polarization correction [13]. Layer spacing in the A phase changed nearly linearly with temperature from 42.1 \AA at 98.6°C to 43.3 \AA at 86.4°C , the increase being due to the reduced molecular flexibility at lower temperatures.

Figure 3(b) shows longitudinal and ω scans in the X' phase at $T=83^\circ\text{C}$, obtained upon slow (~ 0.5 K/h) cooling from the A phase with an *in situ* magnetic field. Five peaks

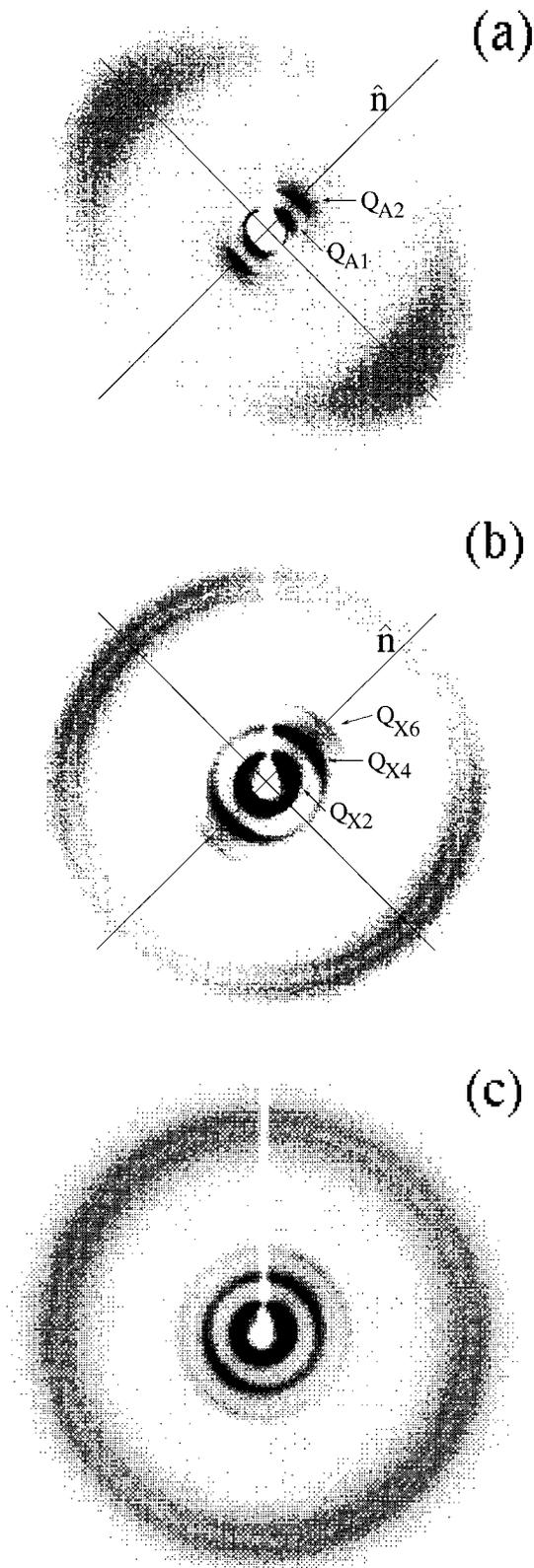


FIG. 2. X-ray diffraction patterns (a) in the smectic-A phase at 88°C , (b) the smectic X' phase at 80°C obtained by slow cooling, and (c) fast cooling from the A phase. \hat{n} is the director of the liquid crystal.

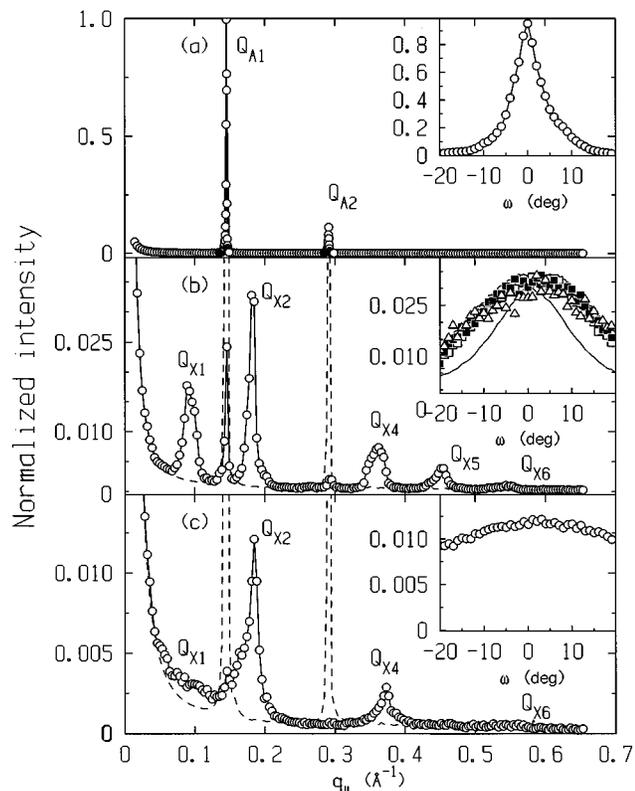


FIG. 3. High-resolution longitudinal and ω scans (insets) in (a) the A phase at 91 °C, (b) the X' phase ($T=83$ °C) obtained by slow cooling, and (c) the X' phase ($T=73$ °C) obtained by fast cooling from the A phase. The symbols in the inset of (b) are filled circles for Q_{X1} , open circles for Q_{X2} , open squares for Q_{X4} , filled squares for Q_{X5} , and triangles for Q_{X6} . The solid curve is for the Q_{A1} peak of the coexisting A phase.

labeled as Q_{X1} , Q_{X2} , Q_{X4} , Q_{X5} , and Q_{X6} , and two peaks from the coexisting A phase at Q_{A1} and Q_{A2} were observed. As the temperature was further decreased, the smectic-A peaks disappeared and the intensities of the peaks from the X' phase increased. The position, intensity, and width of these peaks are listed in Table I. The fundamental smectic layer spacing obtained from the peak at Q_{X1} corresponds to a bilayer structure of spacing 68.4 Å. It appears to be due to the dimerization or (lengthwise) antiferroelectric coupling with overlap of molecules in adjacent layers. In this state, although unlikely, the dipoles belonging to the two molecules can point in the same direction within the smectic plane, and exhibit ferroelectric properties. The absence of a Q_{X3} peak could be explained as a result of destructive interference between the antiferroelectric (bilayer) density wave

TABLE I. List of peak positions, widths, and normalized intensity in the X' phase of M70.

peak	Q (Å ⁻¹)	ΔQ (Å ⁻¹)	I/I_{A1}
Q_{X1}	0.090	0.021	0.019
Q_{X2}	0.183	0.010	0.034
Q_{X4}	0.363	0.025	0.008
Q_{X5}	0.453	0.021	0.004
Q_{X6}	0.547	0.046	0.001

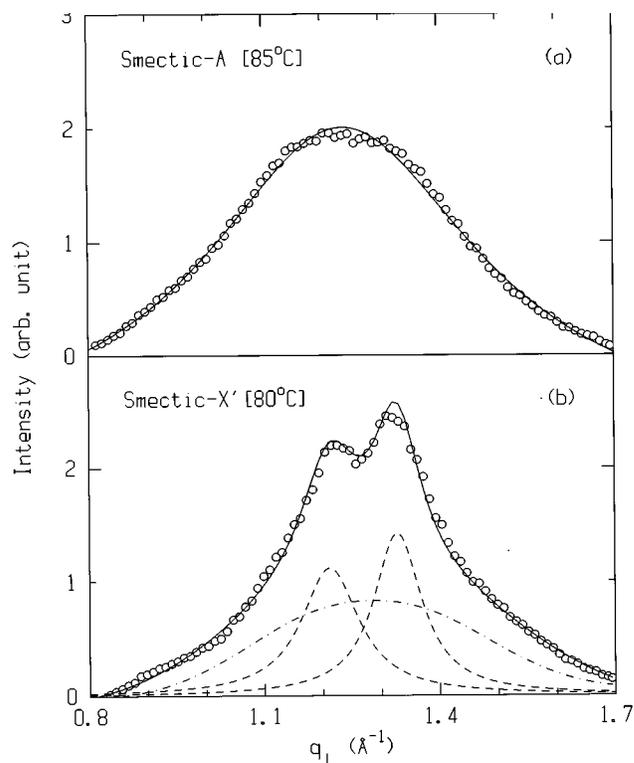


FIG. 4. Diffraction profile of high angle liquidlike peaks in (a) the A phase at 85 °C and (b) the X' at 80 °C with Lorentzian fits.

and the simple smectic (monolayer) mass density wave. The dashed curve in Fig. 3(b), a scan in the A phase ($T=84.0$ °C), is shown as reference. ω scans of peaks in the X' phase shown in the inset of Fig. 3(b), have been normalized to the intensity of Q_{X2} peak after background subtraction. These ω scans demonstrate that the mosaicity of five peaks from the X' phase (higher Q peaks have larger uncertainties due to weaker intensities) were essentially the same. Even though ω scans of the X' peaks were significantly broader than the coexisting A peak (solid curve), they were symmetric with respect to the magnetic field. One should also note the fact that small and large angle peaks in the X' phase (shown in Fig. 2) were in orthogonal directions proving an absence of any macroscopic molecular tilt. On this basis, the X' phase may be classified as a smectic- A_d phase.

High-resolution longitudinal and ω scans in the X' phase obtained after rapid cooling (~ 20 K/h) from the A phase at 90.7 °C to the X' phase at 73.5 °C are presented in Fig. 3(c). Three peaks at Q_{X2} , Q_{X4} , and Q_{X6} could be easily identified, whereas the peak at Q_{X1} looked more like diffuse scattering and Q_{X5} disappeared. The peak positions, widths, and intensities were $Q_{X2}=0.186$ Å⁻¹, $\Delta Q_{X2}=0.014$ Å⁻¹, $I_{X2}=0.013$, $Q_{X4}=0.372$ Å⁻¹, $\Delta(Q_{X4})=0.015$ Å⁻¹, $I_{X4}=0.0034$, $Q_{X6}=0.553$ Å⁻¹, $\Delta(Q_{X6})=0.050$ Å⁻¹, and $I_{X6}=0.0005$, respectively. The rms smectic layer thermal fluctuation amplitude in this state was evaluated to be 2.5 Å. The dashed line represents a longitudinal scan in the A phase at 90.7 °C (taken right before rapid cooling) and is plotted as a reference. Evidently, there is additional scattering near the position of Q_{X1} but no well developed peak. The difference in the scans obtained with slow and fast cooling is due to slow equilibration of the system.

Figure 4 shows profiles of the large angle peaks which arise from the in-plane order in the A and X' phases. These profiles were obtained from the low-resolution measurement shown in Fig. 2. Fit to a single Lorentzian in the A phase at 85 °C and three Lorentzians in the X' phase at 80 °C phase after background subtraction are shown in Fig. 4(a) and 4(b), respectively. The solid curves are the best fits to the data. The average intermolecular distance in smectic layers was found to be 5.08 Å in the A phase and 4.91 Å in the X' phase, obtained from the dashed-dotted curve in Fig. 4(b). The two sharper diffuse peaks (dashed curves) at $Q_{\perp 1}=1.21 \text{ \AA}^{-1}$ and $Q_{\perp 2}=1.33 \text{ \AA}^{-1}$ appearing in the X' phase yield a short range (correlation length $\sim 20 \text{ \AA}$) in-plane positional order at 5.18 Å and 4.73 Å, which appeared to correspond to the thicknesses of the perfluoroalkyl and alkyl chains [14] suggesting that the two chemical species were segregating into different sublayers. The increase in the in-plane positional order, even though still short range, may reflect the effect of the enhanced lateral attractive force and the reduced thermal fluctuations at low temperature. This

in-plane order marks the difference between X' and conventional A_d phase.

In summary, we have conducted an x-ray diffraction study of a binary mixture of polyphilic liquid crystals (M70) and found that the smectic- X' phase previously characterized as a polar smectic- C -like phase, actually is a smectic- A_d -like phase possessing antiferroelectric molecular pairing and uniaxial optical properties. Previously reported piezoelectric properties of this phase may be due to phenomena other than ferroelectricity, such as flexoelectric or antiferroelectric effects. It is possible that higher homologs of this series of materials, with larger end chains, will have reduced dipole-dipole interaction, and therefore, be more likely to exhibit the desired ferroelectric phases.

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