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Bilayer-by-bilayer antiferroelectric ordering in freely suspended films of an achiral polymer-monomer liquid crystal mixture

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Thin freely suspended films of a mixture of an achiral side-chain liquid crystal polymer and its monomer have been studied with depolarized reflected light microscopy. We observe that regions with an odd number of bilayers exhibit a net spontaneous polarization in the tilt plane of the molecules, while regions with an even number of bilayers have no net polarization. These odd-even effects are direct evidence that the tilted smectic bilayers are anticlinic at the polymer backbone and synclinic at bilayer interface and confirm that the phase is bilayer-by-bilayer antiferroelectric.

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The design of novel polar phases of nonchiral liquid crystalline materials and the developement of techniques for the effective study of polar ordering is of current interest in the field of molecular fluids. Up until recently, only the tilted smectic mesophases of chiral molecules had been shown to exhibit ferroelectricity [1] and antiferroelectricity [2]. But the observation of polar phases in polyphilic liquid crystals [3], bowl-like discotic metallomesogens [4], and antiferroelectric phases in smectic phases of bent-core mesogens [5,6] has renewed interest in finding polar order in nonchiral fluid phases. In all of these cases the mesogens pack more effectively when ordered in a polar way.

Several theoretical routes for obtaining polar order in nonchiral fluids have been discussed for a long time [7]. One interesting possibility for producing new polar phases is the anticlinic ordering of two smectic-*C* layers into a coupled bilayer structure with C_{2v} symmetry [8]. Recently, Soto Bustamante *et al.* reported strong evidence for the antiferroelectric version of such a phase (a double hysteris loop in the polarization versus electric field) in achiral *rod-shaped* mesogens (mixtures of a side-chain polymer and its monomer) [9]. In their experiments, a double hysteris loop in the polarization versus electric field was observed. Subsequent x-ray experiments indicated that the mesogens formed a bilayered structure, with one bilayer having a thickness of 54 Å [9,10]. This evidence led them to propose a supermolecular structure for this phase, where the mesogens of long axis **n** form bilayers, where **n** is tilted with respect to the layer normal **z** in such a way that the relative azimuthal orientation of the mesogens in adjacent smectic layers ($\Delta\varphi=|\varphi_{i+1}-\varphi_i|$) alternates between synclinic ($\Delta\varphi=0$) and anticlinic ($\Delta\varphi=\pi$) ordering [see Fig. 1(a)]. The combination of C_{2v} symmetry at the anticlinic interfaces and C_{2h} symmetry at the synclinic interfaces of such a system allows for antiferroelectricity. Two possible bilayered antiferroelectric structures for this phase are shown in Fig. 1 [9]. The first structure [Fig. 1(b)] has anticlinic mesogen interfaces and is synclinic at the polymer backbone, while in the second structure [Fig. 1(c)] the relative clinicity at the interfaces is reversed. Here we report freely suspended film experiments that prove the alternation of synclinic and anticlinic layer interfaces to produce a bilayered antiferroelectric and suggest that the correct structure for this phase is that of Fig. 1(c).

Freely suspended films of both the pure M6R8 monomer as well as films of the 90% M6R8 and 10% PM6R8 polymer (see Fig. 2) were drawn and studied with depolarized

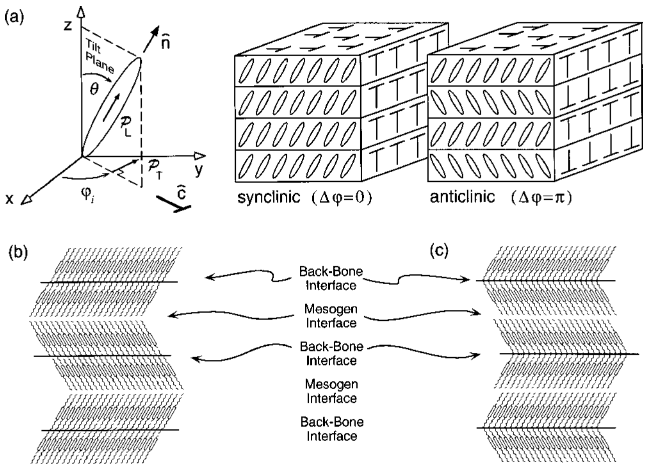

FIG. 1. Film geometry and two possible antiferroelectric bilayer structures. (a) The long axis of the side-chain mesogens defines the director **n** of azimuthal orientation φ_i and its projection on the x-y plane defines the **c**-director (—⊣). $\mathcal{P}_L$ and $\mathcal{P}_T$ denote longitudinal and transverse polarizations, the latter being identically zero in nonchiral materials. Synclinic structures have a relative tilt orientation such that $\Delta\varphi=|\varphi_{i+1}-\varphi_i|=0$, while anticlinic structures have $\Delta\varphi=\pi$. The structures in (b) and (c) consist of a stack of layers alternating between synclinic and anticlinic relative orientations. In (b) the anticlinic interface is at the mesogen interface, while the polymer backbone is synclinic. In (c) the relative tilt sense at the interfaces is reversed.

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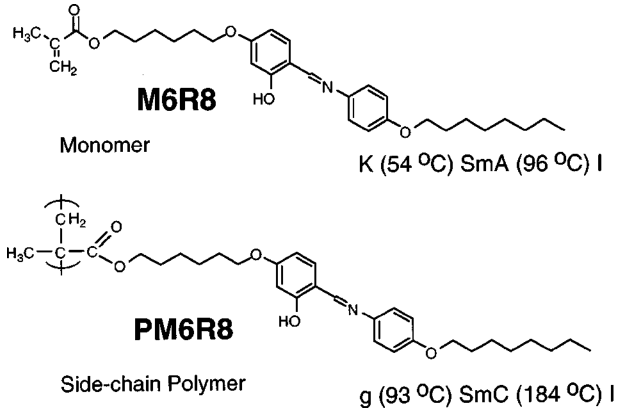

FIG. 2. Chemical structures and phase diagrams for M6R8 and PM6R8.

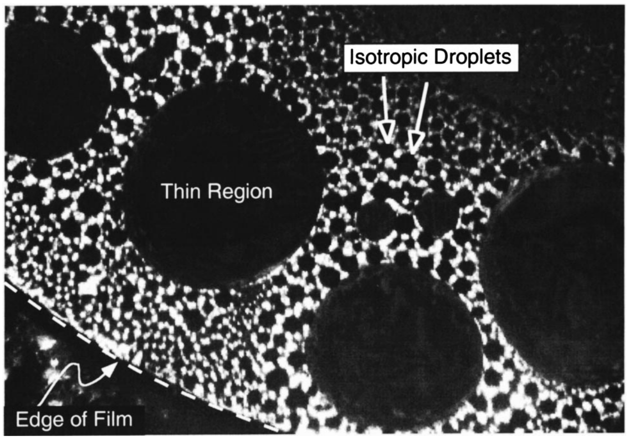

FIG. 3. Isotropic droplets in a freely suspended film. The photomicrograph shows a film heated above its bulk isotropic transition temperature exhibiting round isotropic droplets and thin regions which are slowly expanding. Upon cooling these droplets form thick islands as indicated by their vivid interference colors. This technique of superheating and then cooling is used to obtain thin films. The horizontal dimension of this photomicrograph is −1 mm.

reflected light microscopy. Mixtures of higher concentrations of polymer were made, but we were not successful in drawing films with greater than 10% polymer in the mixture. The films were drawn at temperature $T=98.5\,^{\circ}\mathrm{C}$ over a 3 mm radius hole in a glass cover slip. Titanium electrodes on either side of the hole were used to apply an in-plane electric field E. The projection of the molecular long axis onto the layer plane defines the two dimensional **c**-director field. This field can be visualized with depolarized reflected light microscopy [11].

Freshly drawn films are initially characterized by large **c**-director fluctuations that rapidly diminish over time so that after approximately 15 min only minimal director fluctuations remain. Films could repeatedly be drawn over a several day period of continuous illumination and heating without adding fresh liquid crystal indicating that the reduction in director fluctuations is not due to heat or light induced polymerization. (An increase in polymer concentration would have inhibited the drawing of films.) Films were stable from $T=101\,^{\circ}\mathrm{C}$ to $T<80\,^{\circ}\mathrm{C}$. At high temperatures there is a tendency for isotropic droplets [12] to form in the film as well as for thinner spots to open up as shown in Fig. 3. If the temperature is subsequently lowered, the isotropic drops result in thick regions in the film as indicated by many layer steps and vivid interference colors. Although films of low molecular weight liquid crystals typically begin to thin within seconds of the appearence of nematic or isotropic dropletes, it was necessary for these films to be kept at elevated temperature for several days to obtain thin films. Laser reflectivity measurements of the layer number, N, in the thin regions indicate that N is quantized in bilayers where a single layer has a thickness of 27 Å.

After preparing a film with several thin regions of different thickness, an electric field is applied at 45° to the slightly decrossed polarizer and analyzer. Figure 4 is a photomicrograph of a film with several $\Delta N=2$ layer steps in the presence of an electric field (20 V/mm) as viewed in depolarized reflected light microscopy. The **c**-director in regions with an even number of bilayers ($N=4$ and $N=8$) does not respond to this field, indicating that these regions are not ferroelectric. In contrast, the **c**-director in regions with an odd number of bilayers ($N=6$ and $N=10$) couples linearly with the electric field and is aligned so that the **c**-director is parallel to **E**, indicating that these regions have longitudinal ferroelectricity, i.e., a net spontaneous polarization in the tilt plane [13]. In the ferroelectric regions 2π reorientations of the **c**-director are trapped in 2π-walls, common features of ferroelectric films in the presence of an electric field. When the sign of **E** is reversed these 2π-walls split, move apart, and then reform as the **c**-director rotates through π. In typical ferroelectric materials the time required to reorient is very short and the **c**-director can follow the field up to several 100 Hz, even with the small fields used here. In the case of these polymer containing films, though, a combination of low polarization and high viscosity make **c**-director reorientations after the reversal of **E** occur very slowly, typically on the order of 10–30 sec.

Freely suspended films of the pure monomer were also studied. In these films $\Delta N=1$ layer steps were common and the films were not ferroelectric. The films were left in the microscope for several days at elevated temperatures, and showed no signs of spontaneous polymerization, although orientation field fracture was observed [14].

To interpret these results, we first consider the structure of the polymer. Since the equilibrium configuration of the side-chain polymer has an equal number of mesogens coming off from each side of the backbone, it is reasonable to assume that the air-liquid crystal interface corresponds to the mesogen interface and not a polymer-backbone interface. This is confirmed by the polarizing microscopy observations of the free surfaces of side-chain polymer films [15]. Figure 4 shows odd and even number of bilayers for the structure of Fig. 1(c). In the case of an even number of bilayers, the C_{2h} symmetry plane in the center of the film requires that the component of the polarization along the **c**-director, $\mathcal{P}(z)_{Lc}$, be antisymmetric about the film's mid-plane. This results in a symmetry requirement that the net longitudinal polarization for the film $\langle P_{Lc}(z)\rangle$ must then be zero, i.e., $\langle P_{Lc}(z)\rangle =1/Na\int_0^{Na}\mathcal{P}_{Lc}(z)\,dz=0$, where a is thickness of one smectic layer. In contrast, in regions with an odd number of bilayers the central plane of the film has C_{2v} symmetry requiring $\mathcal{P}_{Lc}(z)$ to be symmetric about the film's center and

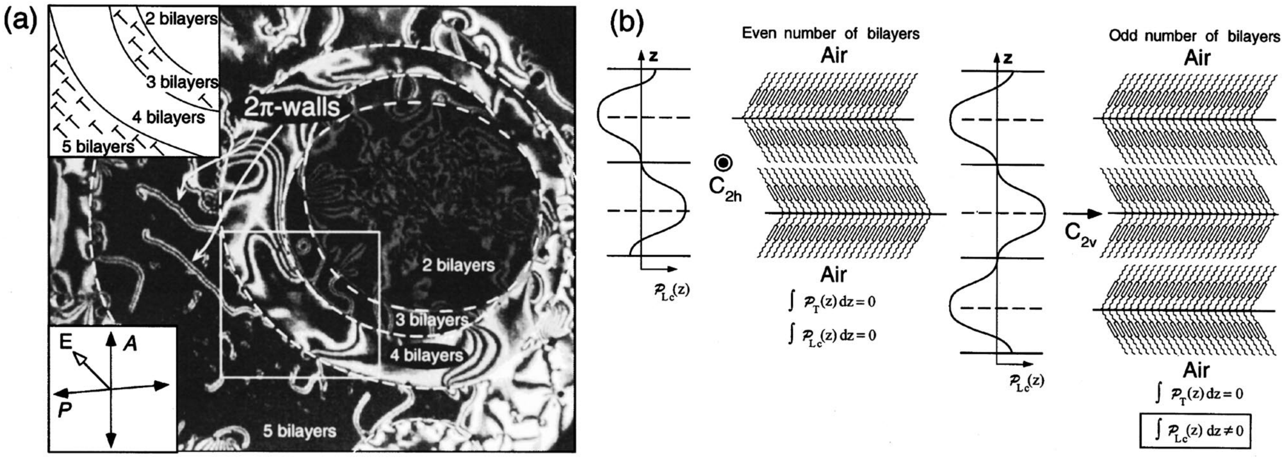

FIG. 4. Odd-even bilayer dependence of the polarization. The photomicrograph in (a) shows a film having several regions of different thickness that are quantized in integer numbers of bilayers. The film is viewed in reflected light through slightly uncrossed polarizer *P* and analyzer *A* with an electric field **E** applied along their bisector. The **c**-director in regions with an *even* number of bilayers [two bilayers $(N=4)$ and four bilayers $(N=8)$] does not couple to the field and these regions are characterized by broad brushes typical of smectic *C* films. In contrast, the **c**-director in regions with an *odd* number of bilayers [three bilayers $(N=6)$ and five bilayers $(N=10)$] is aligned parallel to the field and 2π reorientations of the **c**-director are trapped in 2π-walls, typical features of ferroelectric films in an external field. The inset (top left) shows the alignment of the **c**-director $(\vdash\!-)$ for the region in the white box. The horizontal dimension of the photomicrograph is -1 mm. Sketches numbers of bilayers are shown in (b). In the case of an even number of bilayers, the C_{2h} symmetry plane in the center of the film requires the component of the polarization along the **c**-director, $\mathcal{P}_{Lc}(z)$, to be antisymmetric about the film center. The net longitudinal polarization must then be zero. However, in regions with an odd number of bilayers the central plane of the film has C_{2v} symmetry requiring $\mathcal{P}_{Lc}(z)$ to be symmetric about the film center and allowing for a nonzero net polarization parallel to **c**.

allowing for a nonzero net polarization parallel to **c**, i.e., $\langle P_{Lc}(z)\rangle \neq 0$. The transverse component of the polarization $\mathcal{P}_T(z)$, (parallel to $\mathbf{z}\times\mathbf{n}$) must be identically zero due to the mirror symmetry of the tilt plane. This odd-even dependence of the film's net polarization on bilayer number is consistent with experimental observations, while the symmetry of the structure in Fig. 1(b) requires the opposite odd-even dependence on number of bilayers. These film observations thus provide conclusive evidence for antiferroelectricity in these mixtures and strongly suggest that the anticlinic interface is at the polymer-backbone while the mesogen interface is synclinic.

While the spontaneous formation of a superstructure of alternating synclinic and anticlinic layer orientations provides a route to antiferroelectricity in an achiral polymer liquid crystal mixture, a ferroelectric polymer liquid crystal phase in nonchiral molecules has not yet been observed. A ferroelectric structure, analogous to the antiferroelectric structure reported here, would have bilayers and all anticlinic interfaces as discussed in [9]. A possible strategy for producing such a phase would be to replace half of the tails on the side-chain mesogens of PM6R8 with the methyl-heptyloxycarbonyl tail that is common to most anticlinic materials [2]. The addition of this tail is known to result in anticlinic structures and is likely, in this case, to result in a ferroelectric structure and would be an interesting direction for further investigation.

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