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A COMPARATIVE STRUCTURAL STUDY OF THREE PROSPECTIVE LONGITUDINAL FERROELECTRIC SMECTIC LIQUID CRYSTALS

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Abstract A longitudinal ferroelectric smectic phase lacks a reflection or mirror symmetry, which may be achieved with appropriate chemical design of molecules. Using x-ray diffraction, we have examined three candidate systems: a fraternal-twin triester, a mixture of polyphilic compounds, and a cyclic siloxane co-oligomer. These systems have been reported to exhibit properties indicative of longitudinal ferroelectric phases. A comparative structural analysis of these materials is presented.

INTRODUCTION

In conventional ferroelectric smectic phase, *i.e.*, C^* phase, the mirror symmetry is eliminated by chiral molecules[1] and the spontaneous polarization lies in the smectic plane and varies helically through the sample. Petschek and Wiefling[2] first proposed the longitudinal ferroelectric smectic phase in which the spontaneous polarization is uniquely defined in space to be achieved with nonchiral molecules composed with three or more different moieties. The essential idea is to form sublayers within smectic layers in an "$\alpha\beta\gamma\alpha\beta\gamma$" pattern. To realize such an arrangement with free energy minimized, the unlike segments of the molecules should be sufficiently incompatible chemically and/or sterically and the identical segments of adjacent molecules should be segregated with sufficient lateral attraction to form polar layers. To date, three materials, with very different molecular architecture, have been synthesized and promise to be longitudinal ferroelectric. They are fraternal-twin triesters synthesized at Kent[3], polyphilic compounds synthesized at ESPCI[4], and corona poled films of cyclic siloxane co-oligomer prepared at North Carolina[5]. Using x-ray diffraction, we have examined these three materials, and herewith report a comparative structural analysis and the degree of success of the three attempts in developing a longitudinal ferroelectric system.

FRATERNAL-TWIN TRIESTERS

The triester, ([1,1'-biphenyl]-4-carboxylic acid, 4'heptyl-, 7-[4-[[4-[(4-nonylphenoxy) carbonyl] phenoxy] carbonyl] phenoxy] heptyl ester), was synthesized by Keast and

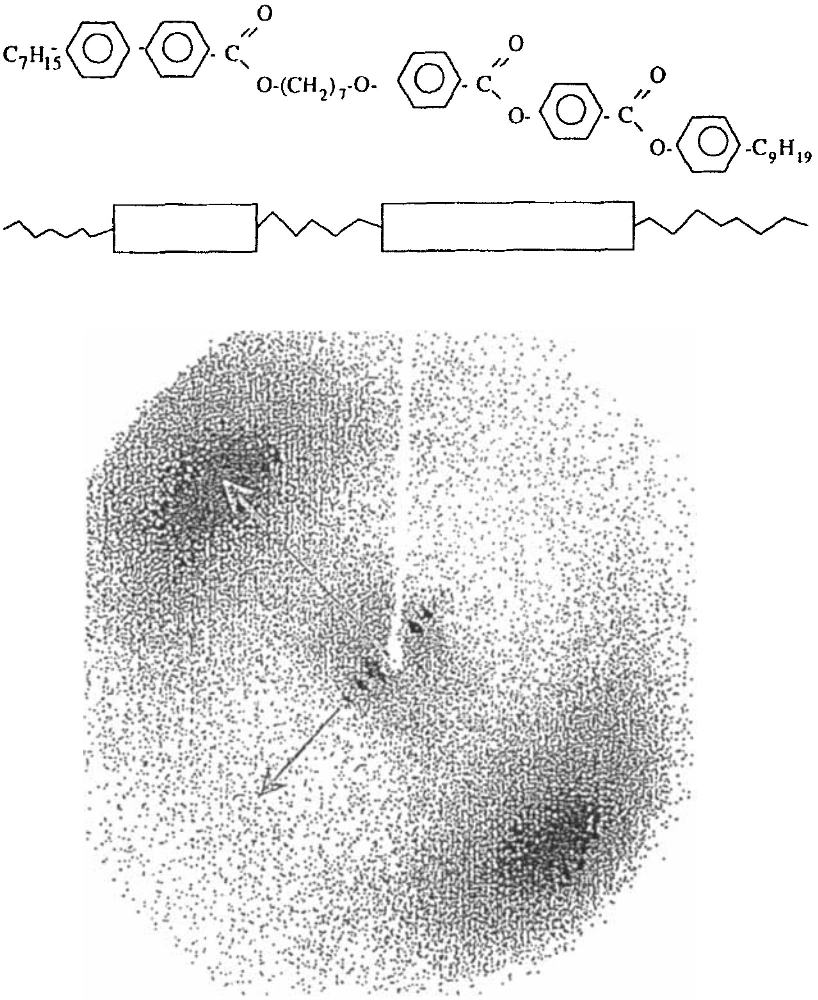

FIGURE 1: Fraternal-twin triester, its schematic representation, and the x-ray diffraction pattern in the smectic A_p phase at 110°C.

Neubert based on Petschek and Wiefling's theoretical work[2,6]. The molecule was designed to link two rigid liquid crystal forming moieties: a biphenyl ester (BE) and an oxygen bonded tribenzoate (OTB) with a 7 carbon long flexible spacer terminated by similar flexible hydrocarbon chains at each end, as shown in Fig.1. It was expected that smectic layers would form with separate packing of the polar OTB segment and the weakly polar BE segment, and arranged ferrolectrically[7]. A new smectic phase, denoted as A_p, appeared at 121.6°C below a conventional smectic A (A) phase[6]. This material is readily aligned homeotropically on glass surfaces. The A_p phase exhibits weak in-plane birefringence under homeotropic alignment with a distinct but gradual change in optical texture at the nearly second order A to A_p transition. A bipolar response to low ($\sim 1 \times 10^6$V/m) electric field strengths was observed in the A_p phase[3]. The A_p phase was subjected to a trianglar wave while monitoring the cell current. The polarization reversal peaks, similar to that from chiral smectic-C^* phase, were observed from a misaligned cell with frequencies $\sim$ 200Hz, as shown in Fig. 2, while no response was detected from the homeotropically aligned cell. The switch speed was determined to be faster than 5 ms.

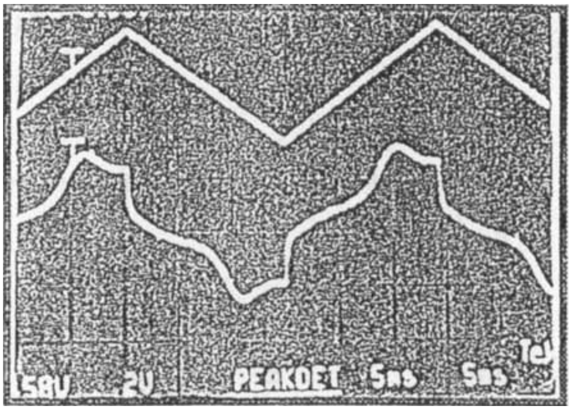

FIGURE 2: Electro-optical response of fraternal-twin triesters: homeotropically aligned cell, no response (curve at the top); misaligned cell, polarization reversal observed (curve at the bottom).

In spite of the absence of a nematic phase, the smectic phases were very well aligned with an *in-situ* $\sim$ 2.5kG magnetic field after slowly cooling from the isotropic phase, suggesting that the molecules possessed large positive diamagnetic anisotropy as expected from these five benzene ring molecules. Fast response and ability to align also indicates a relatively low viscosity, which is unusual for such large molecules. In the x-ray diffraction pattern of the A_p phase, the presence of three multiples of quasi-Bragg peaks were observed at the small angle corresponding to smectic layer spacing in the range 55.3 to 55.7Å, indicates that the smectic layers were better defined than that in the conventional A phase for which the high order peaks were much weaker. This enhanced layering in A_p phase could be due to a stronger lateral interaction between adjacent molecules necessary for forming polar smectic layers. The large angle liquid-like peaks, due to short range in-plane positional order between nearest neighbors, were in a direction perpendicular to the small angle peaks and confirmed

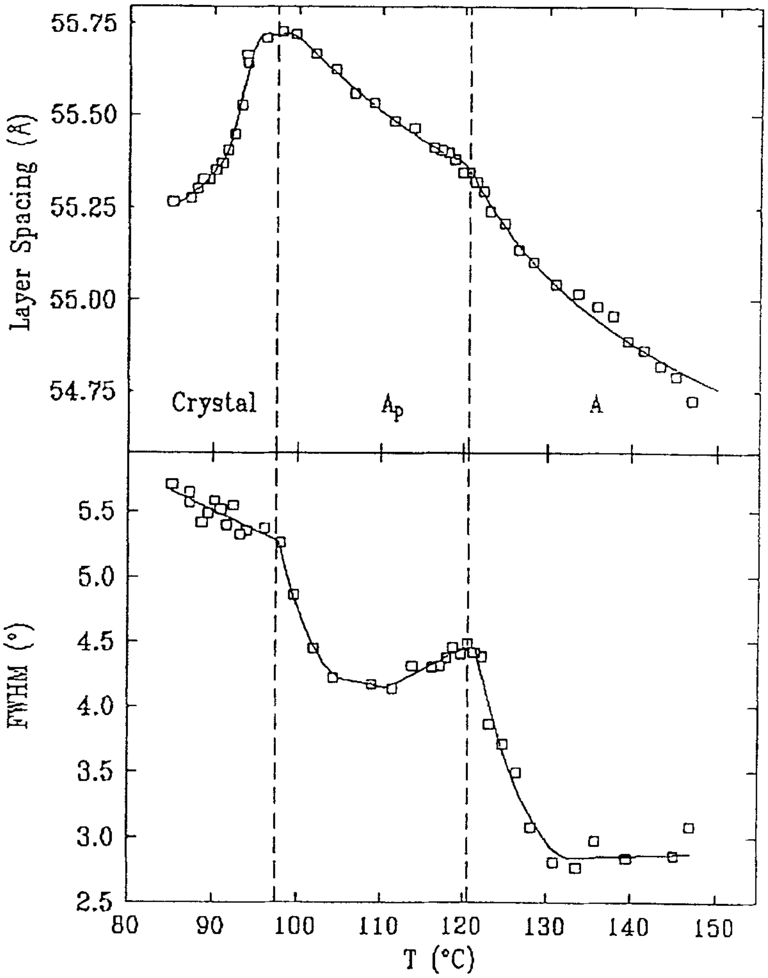

FIGURE 3: Full width of the transverse scans, and smectic layer spacing d as a function of temperature in the smectic A, A_p, and crystalline phases.

the uniaxial nature of the A_p phase. The large angle diffuse peak in the A_p phase was indistinguishable from that in the A phase, confirming the absence of any long range in-plane positional order. The temperature dependence of the smectic layer spacing, d, remained relatively weak in both the A and A_p phases, with a small but noticeable change at the A-A_p transition, as shown in Fig. 3. The value of *d* in both phases was very close to the molecular length, l=56.5Å, estimated with space filling model. The three order of diffraction peaks from smectic layers also indicate a strong deviation from a single sinasoidal density wave of a conventional smectic A phase[8]. These facts suggest the A_p phase to be a good candidate for the longitudinal ferroelectric phase. Obviously, more studies to fully understand the A_p phase are essential.

POLYPHILIC COMPOUNDS

On the basis of the existence of amphiphilic character of self-assembling micelles in lyotropic systems[9], Tournilhac and colleagues independently postulated[9] that the segregation between unlike chemical moieties, such as hydrocarbon and fluorocarbon chains, could generate ferroelectric packing of "polyphilic" molecules. They synthesized such polyphilic compounds to test the idea. The polyphilic molecules consisted of perfluoroalkyl and alkyl side chains, and a diphenyl rigid core, as shown in Fig. 4. Polyphilic Compounds I and II, as labeled, are essentially the same molecule except for an interexchange of the ether and ester linkages.

The ferroelectric properties of polyphilic compounds were determined by measuring their piezoelectric response and the repolarization current. When a ferroelectric material is placed between two conductive electrodes, charge would be induced on the surfaces of the electrodes to compensate the charge accumulated on the boundaries of the material. The polar smectic-X (Sm-X) phase of compound I was found to be metastable as it could be induced only with external poling. To reduce the intralamellar electrostatic repulsion, a binary mixture M70 of compound I and II in a 70:30 weight ratio, was prepared[1]. In this mixture, the smectic-X′ (Sm-X′) phase[4] formed below the conventional Sm-A phase exhibited the same piezoelectric response as the Sm-X phase. The Sm-X′ phase was stable and could be supercooled down to room temperature. The optical texture of the Sm-X' phase was found to be identical before and after applying a piezoelectric voltage, which established the uniaxial nature of the Sm-X′ phase[1].

The polyphilic compounds did not easily align under magnetic field[11]. In previous structural characterization[11], the x-ray diffraction pattern of the Sm-X′ phase from an unoriented sample revealed three peaks at small angle and double broad rings at large angle. In our high resolution experiment with a slower cooling rate (0.5K/hour) and improved alignment, the mosaicity was significantly reduced[12]. The longitudinal scans and rocking curves (ω scans) of M70 at T=83°C in high resolution x-ray measurement are shown in Fig. 4. Five Bragg peaks from the Sm-

X′ phase, as denoted by Q_1, Q_2, Q_4, Q_5, and Q_6, and two peaks from the Sm-A phase, as denoted by q_0 and $2q_0$ are shown. The fundamental smectic layer spacing obtained from the three harmonics, Q_2, Q_4, and Q_6, was 34.3Å. The value of scattering vector

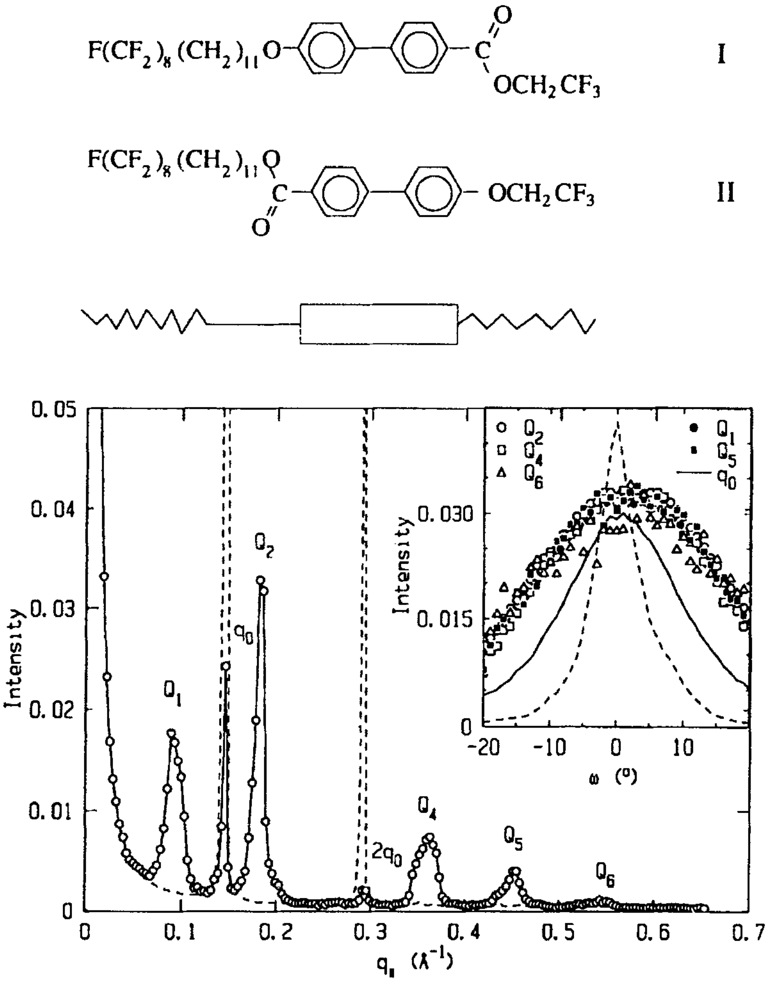

FIGURE 4: Polyphilic compounds I and II, their schematic representation, and x-ray scattering from the mixture M70.

at $Q_1(=Q_2/2)$ and its higher harmonics correspond to a bilayer spacing of 68.4Å. It appears to be due to the dimerization, or (lengthwise) anti-ferroelectric coupling with some overlap, of the molecules in adjecent layers. The dashed curve taken in the Sm-A phase at T=84.0°C is shown for comparison. The normalized ω-scans of the Sm-X′ peaks shown in the inset demonstrate that the mosaicity for the five peaks in the Sm-X′ phase was the same but different from the mosaicity of the Sm-A (solid curve) phase, suggesting evidently a coexistence of Sm-X′ and Sm-A phases at T=83°C. The dashed line in the inset is the ω scan of the first peak in the Sm-A phase measured at 84.0°C, and its intensity has been reduced by 40 in this plot. The fact that small angle peaks from smectic layers and large angle peaks from in-plane positional correlations in the Sm-X′ phase appear in orthogonal directions, indicates the absence of any molecular tilt. In light of the data, it is more reasonable to classify the Sm-X′ phase as a phase very similar to the partial bilayer smectic-A_d phase of frustrated smectics.

CYCLIC SILOXANE CO-OLIGOMER

The co-oligomer is composed of a siloxane ring connected with four side chains to the mesogen cholesteryl-4-allyloxybenzoate and one nonlinear optically (NLO) active chromophore 3-methyl-4-allyloxy-4'-nitrostillbene, as shown in Fig.3.(a). The steric crowding in the siloxance ring imposes constraints on the rotational degrees of freedom of the side chains, and two molecular conformations: cone and cylinder, are frequently observed[5]. A polar arrangement of the co-oligomer could result in longitudinal ferroelectricity.

Bulk smectic A phase of similar cyclic siloxane co-oligomer was previously studied by x-ray diffraction[1,3,11] and it was determined that the smectic layers are comprised of interdigitated mesogens with an anti-ferroelectric arrangement of chromophores, as shown in Fig.3.(d) and (e). It is obviously not longitudinal ferroelectric in such normal condition.

About 10 μm thick film of co-oligomer with homeotropic alignment was fabricated from the highly-scattering, focal conic Sm-A mesophase by shearing at ~200°C and quenching to room temperature. Two samples were prepared under identical conditions, but one was corona poled with electric field in the Sm-A phase. Strong SHG signals was detected from this sample. Its melt spontaneously assembles into a lamellar supramolecular structure shown in Fig.3.(f) which can be macroscopically aligned and which retains a bistable E-field-induce polar order. The homeotropic alignment of cyclic siloxane co-oligomer on an ITO coated glass substrate was probed with high resolution x-ray reflectivity measurements. The steroidal mesogens and chromophores stratify into lamellae with their major axes normal to lamellae. Additionally, since the siloxane component is chemically very distinct from the hydrocarbon-based steroid and chromophore side chain, the lamellar structure could be further stabilized by nanophase separation of the siloxane moieties from the hydrocarbon mesogens.

The high resolution of x-ray reflectivity experiment makes it possible to deconvolve the two Bragg peaks, as shown in Fig.3.(b) and (c). These two spacings may be due to the coexistence of the distinct regions in the lamellae comprised of incompatible secondary structures. For the unpoled sample, anti-ferroelectric smectic layers of both cone and cylinder conformations form with slightly different layer spacings. In the corona poled sample, a polar arrangement of cone configuration was induced, while the domains of cylinder conformation remained unchanged. We infer that the cyclic siloxane co-oligomer possessed a field-induced metastable but long lived longitudinal ferroelectric phase mixed with anti-ferroelectric domains.

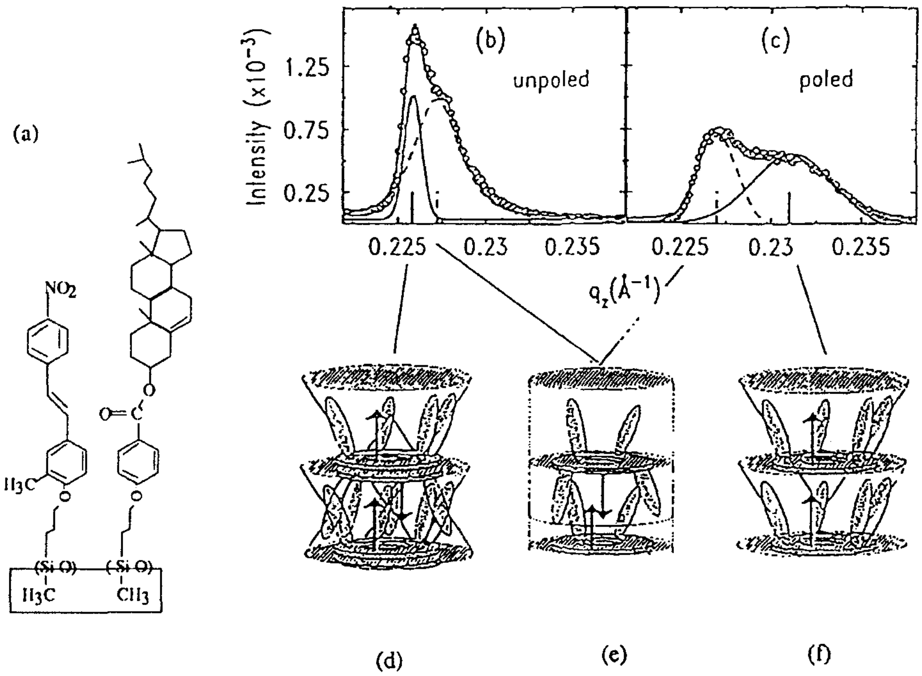

FIGURE 5: Cyclic siloxane co-oligomer, x-ray scattering pattern, and molecular conformations forming ferroelectric and antiferroelectric arrangements.

SUMMARY AND ACKNOWLEDGMENT

Using x-ray diffraction, we have conducted a comparative structural study of three prospective longitudinal ferroelectric liquid crystals. The fraternal-twin triester holds the promise of a longitudinal ferroelectric smectic A phase. The bilayer formed in mixture of polyphilic compounds M70 is indeed anti-ferroelectric. The cyclic siloxane co-oligomers exhibits longitudinal ferroelectric behavior in its smectic phase after corona poling. Further studies of the fraternal-twin triester and siloxane co-oligomer systems are necessary to fully understand the nature of these phases.

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