Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 18 Oct 2010

To cite this article: Upindranath Singh & Andrew Primak (2004): High Resolution X-Ray diffraction on a polymer-stabilized ferroelectric liquid crystal, Molecular Crystals and Liquid Crystals, 412:1, 29-36

To link to this article: http://dx.doi.org/10.1080/15421400490431084

Mol. Cryst. Liq. Cryst., Vol. 412, pp. 29/[1639]–36/[1646], 2004

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490431084

HIGH RESOLUTION X-RAY DIFFRACTION ON A POLYMER-STABILIZED FERROELECTRIC LIQUID CRYSTAL

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Mesophase ordering behaviour of blends of a ferroelectric liquid crystal (W46) and photo-cross-linked polymeric network has been investigated using high-resolution x-ray diffraction. The SmA-SmC transition in pure W46 appears to be a weak first-order transition which becomes continuous if traces of polymer are added to W46. Irradiation of the blend produces a network which forces the liquid crystal to adopt a configuration which has a reduced layer spacing. Also, the liquid-crystalline phase, which existed, when photo-polymerization was initiated is stabilized at the expense of the adjacent phases.*

Keywords: cross-linking; ferroelectric; photo-polymer; X-ray diffraction

INTRODUCTION

Ferroelectric liquid crystals (FLCs)are anisotropic, chiral fluids, which possess permanent macroscopic dipole moments in the absence of external fields. Ferroelectricity in liquid crystals was discovered by Meyer and coworkers [1] in 1975. The-surface stabilized ferroelectric-light-valve which has spawned a new generation of electro-optic displays and other optical elements was invented by Clark and Largerwall [2] about five years later.

The idea of mixing a polymer and a liquid crystal to form new substances having the mechanical strength of a conventional polymer with the unique optical properties of a liquid crystal is quite attractive. These systems, depending on the miscibility of the components, may be tailored for specific applications over a broad composition and temperature range [3].

The phase behaviour and miscibility of polymer-liquid crystal blends has been found to depend on the chemical structure, mesophase properties, and concentration of the components [4].

Photo-polymerization plays a central role in the fabrication of polymer-liquid crystal blends. Photo-polymerization entails the use of radiation such as ultraviolet or tunable laser light sources to polymerize and cross-link multifunctional photoreactive monomers. This technique has many advantages over thermal curing. These include fast curing times, uniformity, and ease of controlling the reaction. Polymerization temperatures can be low, thus reducing the possibility of chemical degradation of volatile ingredients.

The aim of this study is to explore the possibility of modifying the tilt, polarization, pitch and transition temperature(s) of a FLC by the addition of a tiny fraction of a photopolymer. The magnitudes of these parameters ultimately determine what type of application is possible. Hence, the ability to control these variables will enhance the industrial potential of FCLs.

EXPERIMENT

Blends of the liquid crystal 4-[(S,S)-2,3-Epoxyhexyloxy]pheny1-4-(decyloxy)benzoate(W46) with the monomer 4,4′-bis (6-(acryloyloxy)-hexyloxy)bipheny1 (BAB6) and the photo-iniator Irgacure 651 (in the ratio 98.8/1/0.2) were prepared by polymerization with UV-Visible light of intensity 2 Wcm^{-2} for two minutes. Under these conditions, photo-polymerization is expected to be completed [5].

W46 is available from Aldrich and the monomer/photo-iniator combination from Ciba-Geigy. In order to conserve materials and still retain the desired ratio of materials BAB6 and Irgacure 651 were dissolved in dry dichloromethane and relevant amount was added to W46. The blends were then dried at 60°C.

High-resolution x-ray scattering studies were carried out on an 18 kW Rigaku RU-300 rotating anode generator and a two-circle Huber goniometer, which has an angular resolution of $\pm 0.00025^\circ$ for θ and 2θ motions. The monochromator and analyzer were a pair of Ge (111) crystals. The samples were heated into the isotropic phase ($\sim$105°C) and then cooled at a very slow rate ($\sim$0.5°C/h) in the presence of a 2.5 kG field. Temperatures could be controlled to ± 10 mK.

Direct observations with a polarizing microscope revealed that glass cells (5 μm thick) which were chemically treated with polyimide for homogeneous alignment retained only pockets of alignment as the sample was cooled just a few degrees into the SmC* phase. Consequently, bulk samples were used in our X-ray analysis. The samples were contained in special 1.5 mm X-ray capillaries (available from Charles-Supper).

RESULTS AND DISCUSSION

In W46, the nonchiral SmA phase is sandwiched between two chiral phases as shown in the following phase sequence [6] (temperatures are in °C).

$$\text{I} \text{ — } 97 \rightarrow \text{N}^* \text{ — } 81 \rightarrow \text{SmA} \text{ — } 80.5 \rightarrow \text{SmC}^* \text{ — } 64 \rightarrow \text{S}_3 \text{ — } 60 \rightarrow \text{Cr}$$

We used a triple-axis Siemens x-ray diffraction system to verify the existence of the SmA phase. This spectrometer uses a sealed copper target, a graphite monochromator, and an area detector X-1000. A pair of permanent rare earth magnets (∼2 kG) were used to align the samples.

The temperature dependence of the tilt angle ϕ is shown in Figure 1. Two transitions, each accompanied by a discontinuity in ϕ are evident from the data. The transition at 63.20°C corresponds to the crystallization process (multiple peaks observed) while that at 81.74°C corresponds to the SmA-SmC* transition. We controlled the temperature of the oven, which housed the sample holder and not the sample itself. This could have

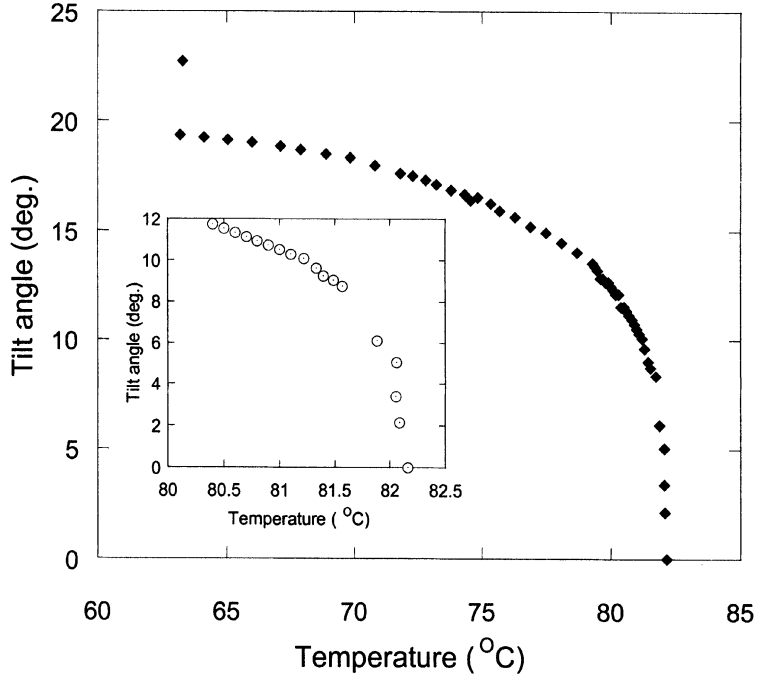

FIGURE 1 Variation of tilt angle with temperature for pure W46. Inset is an expanded view showing the data in the vicinity of the SmA-SmC* transition.

resulted in the 1.2°C shift observed for the SmA-SmC* transition. However, the analysis of the data is not affected by this shift.

The SmA-SmC* transition is accompanied by a discontinuity in ϕ of $\sim 3^\circ$ and a change in slope of the x-ray data. The tilt angle (ϕ) is evaluated from the expression $\phi = \cos^{-1}(d_{C^*}/d_A)$ where d_{C^*} and d_A are the layer spacings in the SmC* and SmA phases respectively. The highest temperature Bragg peak defines zero tilt for both the pure samples and those doped with photopolymer. Bragg peaks could be determined to at least $\pm 0.005^\circ$. Hence, the detection of a 3° discontinuity in ϕ is within the scope of our apparatus.

The SmA-SmC* transition is usually 2nd order but it can be driven to become first-order by large fluctuations in the SmA phase [7]. First-order SmA-SmC* transitions [8,9] are sometimes observed in chiral smectics possessing large spontaneous polarizations. Pretransitional fluctuations accompanying a transition from an isotropic to a chiral phase (isotropic-blue phase) or from a non-chiral to a chiral phase (SmA-SmC*) have been detected over a few degrees [10,11]. Hence, fluctuations in the SmA phase of W46 (range of ~ 0.5 K) are expected to be quite strong.

Tilt angles calculated from measured values of the layer spacings were fitted to the function: $\theta = \theta_0(T_C - T)^\beta$. T_C is the transition temperature to the SmA phase; θ_0 and β are fitting parameters. The fitting parameters derived from the non-weighted linear least square fits shown in Figure 2 are:

$$\text{SmA phase: } \theta_0 = 12.63 \pm 0.52 \text{ and } \beta = 0.55 \pm 0.02.$$

$$\text{SmC}^* \text{ phase: } \theta_0 = 11.99 \pm 0.16 \text{ and } \beta = 0.22 \pm 0.003.$$

The different values of β confirm the change in slope of the x-ray data at the SmA-SmC* transition as shown in Figure 1.

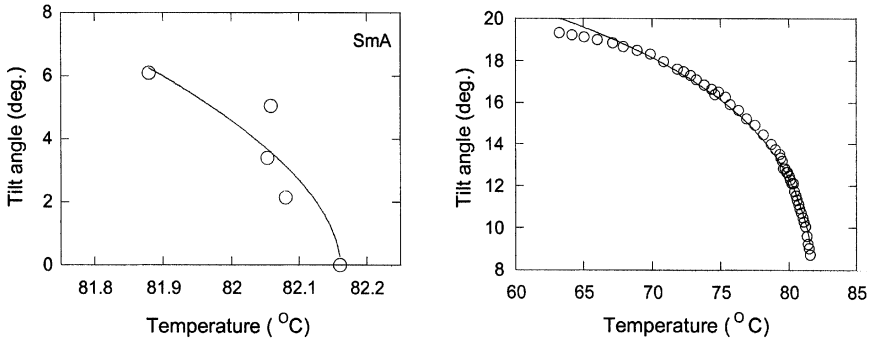

FIGURE 2 Least squares fit of the calculated values of the tilt angles to the function: $\theta = \theta_0 (T_C - T)^\beta$ for pure W46.

The layer spacing in the SmA phase is expected to be constant (hence a $\beta \sim 0$). We observed a 0.6% change in layer spacing of W46 at the SmA-SmC* transition. However, the data of reference 7 shows an increase in the SmA layer spacing from 24.8 to 24.93 Å (0.5% change) in the region T_C-T ~ 0.2°C. The material used in reference [7] has a SmA range of $\sim$0.7°C but close to the SmA-SmC* transition it behaves similarly to W46.

In the neighbourhood of the SmA-SmC* transition we observed a diffraction pattern which consisted of two adjacent peaks. These peaks correspond to wave vectors of both the SmA and SmC* phases which coexist over an interval of about 25 mK. Although temperature gradients of $\sim$25 mK can produce coexisting peaks, it is not likely here since we used a large block, which was well insulated, and we and cooled the sample very slowly. As the sample was cooled into the SmC* phase, the full wave half width of the Bragg peaks increased by about one order of magnitude for $\sim$0.5°C. The Bragg signals then became stronger as the sample was further cooled. We attributed this temporary decrease in signal strength to structural changes within the sample as it adopted the chiral features of the SmC* phase.

X-ray data on W46/polymer blends before they were irradiated revealed that there is no discontinuity in tilt angle in the vicinity of the SmA-SmC* transition (see Fig. 3). Hence, the SmA-SmC* transition in a doped sample of W46 now becomes 2nd order. Detailed x-ray studies on 4-(3-methyl-2-chloropentanoyloxy)4′-heptyloxybiphenyl (C7) show that the first order SmA-SmC* transition is driven towards second order when a second compound is added [7,8]. The tilt angles and temperature range over which

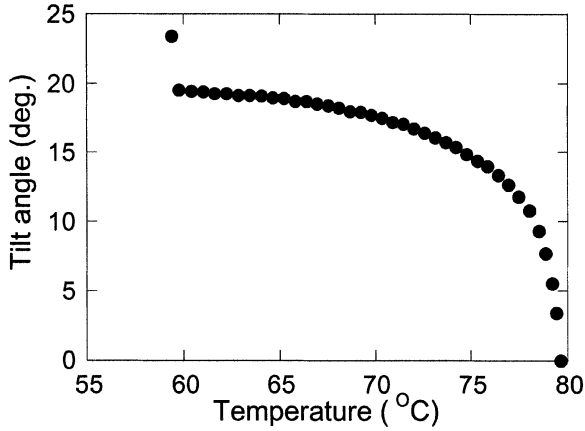

FIGURE 3 Variation of tilt angle with temperature for a doped but non-irradiated sample of W46.

Bragg peaks detected are quite similar to those of the pure material. However, the transition temperature is depressed by $\sim 2^{\circ}$C.

Blends of W46 and the photo-polymer were irradiated with UV radiation at 110°C (isotropic phase) and at 78°C (SmC* phase). The Temperature dependence of the tilt angle of a sample irradiated with UV light while the blend was in the isotropic phase is shown in Figure 4.

Photo-polymerization of the doped sample depresses the SmC*-SmA transition a further 3°C. Also, the temperature interval over which diffraction peaks were detected is $\sim 3.5^{\circ}$C less than in pure W46. Symons, Davis and Mitchell [12] found that cross-linking a liquid crystal polymer has a marked effect on its phase behaviour; cross-linking in a particular range over which the molecules can tilt. Also, there is no discontinuity in the graph of Figure 4. This signals a continuous SmC*-SmA transition.

The temperature dependence of the tilt angles of the sample, which was photo-polymerized at 78°C, is shown in Figure 5. The tilt angles are even more restricted than those of Figure 4. The range now is 11.99°. Also, the lowest temperature Bragg peak is observed in this sample. This means that cross-linking has stabilized the SmC* phase in this sample making it stable at a lower temperature than the doped but non-radiated sample. Once more, the SmA-SmC* transition is continuous.

The network formed is expected to adopt characteristics of the liquid crystalline phase, which existed, while the sample was irradiated. In the

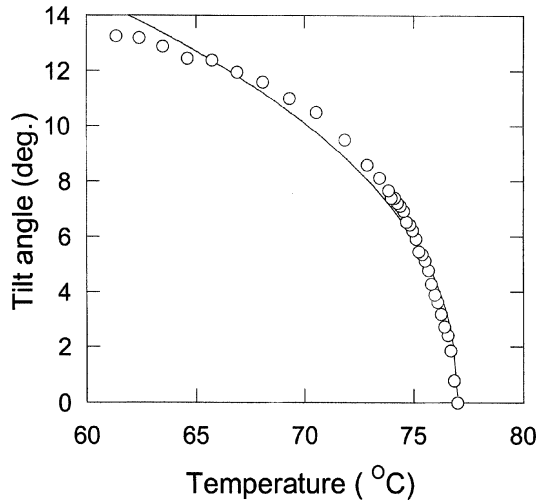

FIGURE 4 Variation of tilt angle with temperature for the photo-polymer/liquid crystal blend. The sample was kept at 110°C while it was irradiated with UV-visible light. $\theta_0 = 4.44 \pm 0.12$ and $\beta = 0.42 \pm 0.012$.

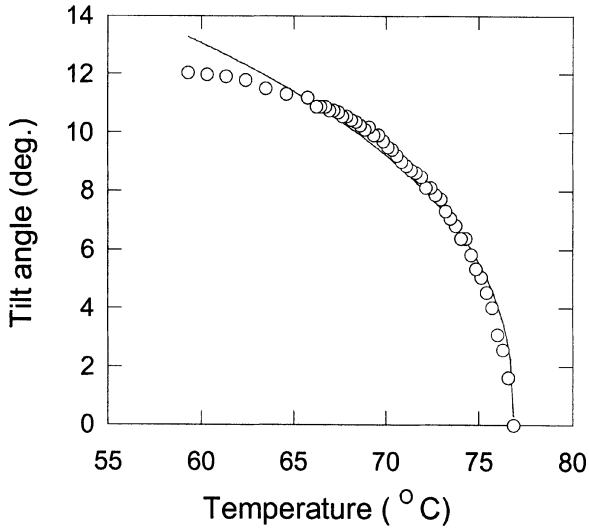

FIGURE 5 Variation of tilt angle with temperature for the photo-polymer/liquid crystal blend. The sample was kept at 78°C while it was irradiated with UV-visible light. $\theta_0 = 4.37 \pm 0.12$ and $\beta = 0.39 \pm 0.012$.

smectic phase, the possibility exists for a tighter network to be formed than for the isotropic phase. Thus, the motion of the molecules would be more restricted when confined by a higher density network. The difference in network density of the two cross-linked samples may be the reason for the 7% difference in value of β deduced from curve fitting. This study raises the question whether it is possible to control tilt angles by varying the network density. Liquid crystalline phase greatly enhances that phase. Thus, polymerization in the isotropic phase is expected to enhance this phase resulting in a lower clearing point and hence, a lower SmC*-SmA transition temperature. The exponent, β, is quite different from those of the pure material and the significance of its value requires further theoretical consideration.

In pure W46, tilt angles varied by 19.35° while in this material the change is 13.26°. Hence, the polymer network formed has reduced the range over which the molecules can tilt. Also, there is no discontinuity in the graph of Figure 4. This signals a continuous SmC*-SmA transition.

CONCLUSION

We have shown that it is possible to modify the tilt (and thus layer spacing) of the molecules when they are in the SmC* phase by confining them within

a network. This network also stabilizes the relevant liquid crystalline phase, which exist at the time of cross-linking. The SmA-SmC* transition in W46 appears to be first order but becomes second order when doped with a photopolymer.

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