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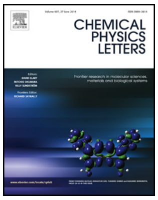

Morphology of polymer networks formed in the chiral and non-chiral phases of an antiferroelectric liquid crystal

Upindranath Singh [a,*], Mathew Spink [b], Frederic Davis [b], Geoffrey Mitchell [c]

[a] *Physics Department, University of the West Indies, P.O. Box 64, Bridgetown, Barbados*
[b] *Centre for Advanced Microscopy (CFAM), University of Reading, Reading RG6 6AD, UK*
[c] *Centro Empresarial da Marinha Grande Rua de Portugal-Zona Industrial, 2430-028 Marinha Grande, Portugal*

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ABSTRACT

We introduced photo-polymer networks into the various liquid crystalline phases of the antiferroelectric liquid crystal AS612 and studied the effects of these networks by measuring the temperature dependence of the Bragg wavelengths selectively reflected. After polymerization, the decrease in Bragg wavelengths with respect to the original values is consistent with a shorter helical pitch due to polymer network shrinkage. Also, by removing the liquid crystalline material, we are able to image the residual polymer network using scanning electron microscopy and polarized light microscopy. The polymer strands are a few microns thick and the networks show both chiral and non-chiral features.

1. Introduction

Owing to their compact size, low voltage demands and low power consumption, liquid crystal displays (LCDs) are expected to dominate the portable market [1]. However, such devices lack ruggedness as the liquid crystalline material can be easily deformed by weak external forces. Polymer networks, which basically stabilize a desired liquid crystal director configuration protect electro-optic devices from mechanical shock [2]. Polymer-stabilized liquid crystals (PSLCs) are blends in which a small amount (∼3–5 wt. %) of cross-linked polymer is dispersed within a liquid crystal medium [3–8]. Usually, a photo-initiator and a monomer are required to introduce cross-linking within a liquid-crystal-polymer blend [9]. However, some polymers contain photo-reactive components that are sensitive to ultraviolet radiation and do not require a photo-initiator. Poly(vinyl cinnamate) for example, undergoes a random cross-linking photo-addition reaction when exposed to ultraviolet radiation. The advantage of using one procedure over the other has not been investigated.

Of the materials presently used in displays, only ferroelectrics and antiferroelectrics offer potential for switching times in the sub-microsecond range [10]. However, antiferroelectric liquid crystals (AFLCs) show larger switching angles of the optical axis than ferroelectric liquid crystals FLCs, which is essential in achieving higher contrast ratios [11]. In AFLCs-based devices, the surface-stabilized Sm-C^*_A phase serves as the dark state, while the field-induced SmC* phase forms the bright state [12]. Recent developments in AFLCs-type displays involve the use of high tilt materials to achieve a completely dark state [13]. Such materials termed orthoconic antiferroelectric liquid crystals (OAFLCs) are characterized by saturation tilt angles of ∼45°.

In addition to enhancing mechanical integrity, low-density polymer networks improve the alignment of AFLCs and reduce the switching times [11,14,15]. However, network stabilization is antagonistic toward liquid crystalline order and a delicate balance must be maintained in order to optimize the performance of polymer stabilized devices. A previous study revealed that for polymer concentrations of 3%, the phase stability of the Sm-C* phase of AS661 was not significantly affected, but, the blends retain enough order to Bragg reflect visible light [16]. Motivated by these results, we studied samples of AS612 (see Fig. 1a) that were doped with 3% of the photo-polymer and then cross-linked at temperatures corresponding to the various liquid crystalline phases of AS612. A photo-polymer network aligns itself roughly parallel to the local director orientation of the mesophase and hence, serves as a template of the liquid crystalline order [17,18]. After cross-linking, the liquid crystal can be dissolved and the residual network can be studied as a representation of liquid crystalline order without having to resort to temperature control. The aim of this study is to prepare and image these networks and gather direct evidence of how liquid crystalline order influence network topology and vice versa.

2. Experimental

The antiferroelectric crystal AS612 was purchased from Kingston Chemicals and used as obtained. The blend was prepared

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* Corresponding author. Tel.: +1 246 417 4376.
E-mail address: upindranath.singh@cavehill.uwi.edu (U. Singh).

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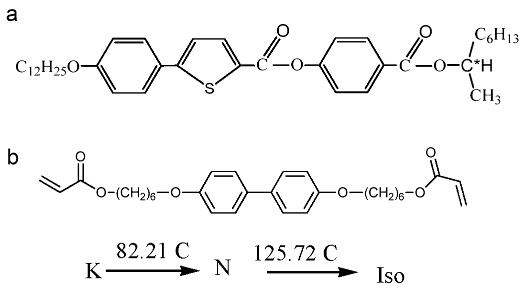

Fig. 1. (a) Chemical structure of AS 612. (b) Chemical structure and phase transitions of BAB6.

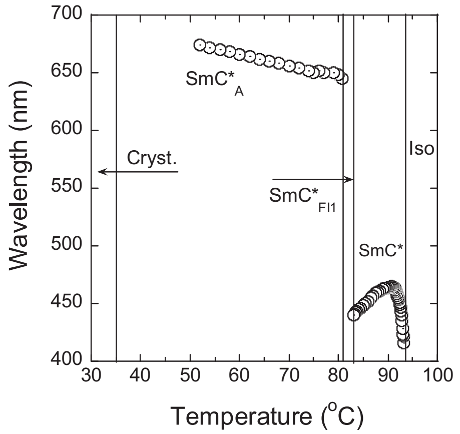

Fig. 2. The Bragg wavelengths selectively from pure AS612 (cooling mode).

by mixing the monomer BAB6, the photoiniatator (Irgacure 651), and AS612. The chemical structure and the associated transitions of BAB6 (from DSC and POM) are shown in Fig. 1b. The ratio of BAB6 to Irgacure 651 was 4:1. To ensure a uniform and accurate composition, the monomer-photoiniatator blend was dissolved in a minimum amount of dry dichloromethane (DCM) and the desired volumes was then added to AS612 to prepare the 3% by weight polymer blend. The solution was then dried in an inert atmosphere at 60 °C. Homeotropically aligned samples were heated into the isotropic phase, cooled slowly into the desired phase of AS612, and then cross-linked. Homeotropic alignment was achieved by using aqueous cetyl-trimethyl-ammonium bromide (CETAB) and polymer networks were introduced by using unpolarized UV radiation (10 mW cm^{-2}), which has a wavelength of 365 nm. The network was recovered by dissolving the liquid crystal component in DCM.

3. Results and discussions

It is useful to report on the phases of pure AS612 before discussing polymer stabilization. The phase sequence (cooling mode) shown below is deduced from combined polarized light microscopy and Bragg scattering studies [19].

$$\mathrm{Iso}\xrightarrow{97.53}\mathrm{SmA}\xrightarrow{93.47}\mathrm{SmC}*\xrightarrow{82.60}\mathrm{SmC}*_{F11}\xrightarrow{80.21}\mathrm{SmC}*A\xrightarrow{36.00}\mathrm{Cry}$$

The Bragg wavelengths selectively reflected by pure AS612 is shown in Fig. 2 and the corresponding polarized light microscopic images are shown in Fig. 3. In general, Bragg reflections in the visible region correspond to half-pitch and full-pitch reflections from the Sm-C* phase and half-pitch reflections in the SmC*$_A$ phase [20]. However, only half-pitch reflections were detected for AS612. The

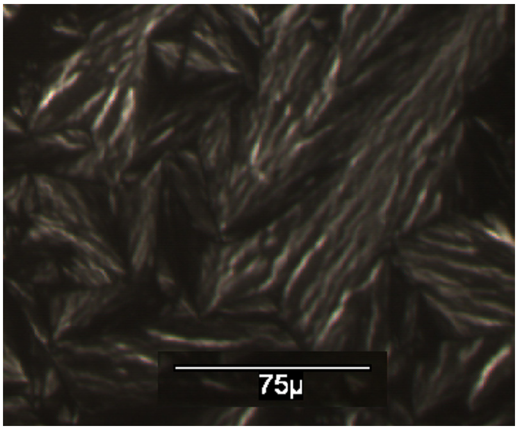

Fig. 4. Polarized optical microscopic image of a 3% polymer blend that was homeotropically aligned prior to cross-linking. The sample was kept in the SmC*$_{FI1}$ phase at 75 °C and irradiated with unpolarized UV light (10 mW cm^{-2} and 365 nm) for 15 min.

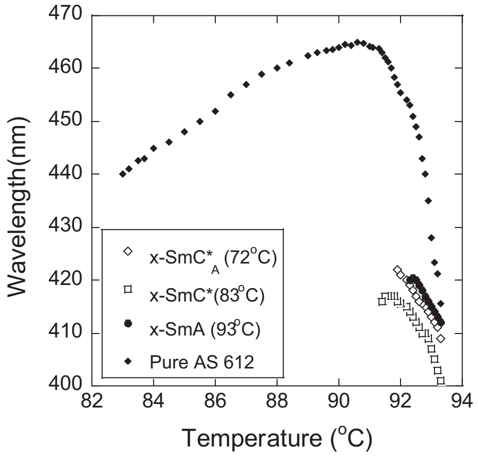

Fig. 5. (a) Temperature dependence of Bragg wavelengths reflected by the SmC* phase for the 3% polymer blends, which were crossed-linked (15 min) at different temperatures: SmA (93 °C), SmC* (83 °C), and SmC*$_A$ (72 °C) phases. For comparison, the pure material is also included.

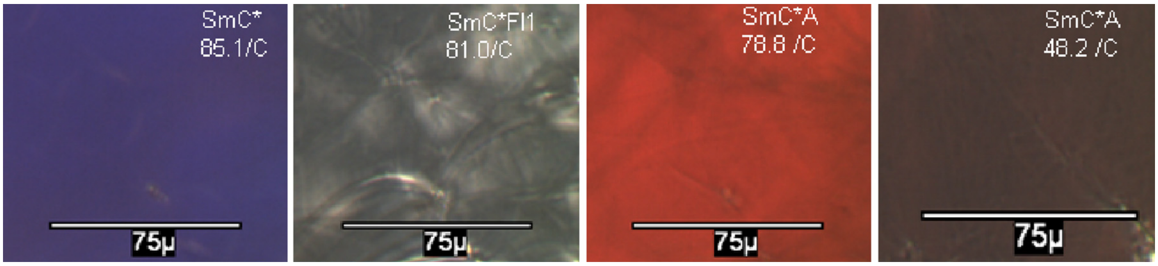

Fig. 3. Bragg wavelengths selectively reflected by the chiral phases of AS612. The wavelengths increase with decreasing temperature. However, the SmC*$_{FI1}$ phase does not reflect visible light.