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Preliminary communication

Observation of the internal network structure of a polymer-stabilized liquid crystal via transmission electron microscopy

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The internal structure of the network component of a polymer-stabilized liquid crystal has been observed for the first time. These are systems in which a small amount of a monomer is dissolved within a LC host and then polymerized *in situ* to produce a network. Studies performed on a system prepared using the diacrylate monomer RM60 and the nematic mixture BL087 are presented. The concentration of the monomer was 1 wt %. After formation of the network through photopolymerization of the monomer between Melinex layers within a glass cell, the LC host was removed by dissolving it in heptane. Subsequent observation of the internal network structure by transmission electron microscopy was made possible by bromine staining of the network, followed by embedding and ultramicrotomy. A collection of solid, near-circular objects was observed, of mean diameter 0.13 μm. These objects were found to be highly permeable to bromine vapour, suggesting an open, but homogeneous structure.

Polymer-stabilized liquid crystals (PSLCs), materials originally described as anisotropic gels [1], are composite systems formed by dissolving a small amount of a monomer (typically, less than 5 wt % of the system) in a LC host, and then photopolymerizing the monomer *in situ* within the LC phase. The monomer must have more than one reactive group (e.g. a diacrylate) in order to produce a crosslinked network, as opposed to discrete polymer chains. The state of the system during polymerization dictates the resulting network structure. For example, a network formed in the nematic phase within a cell enforcing uniaxial alignment is typically in the form of fibrils, which tend to be well-aligned along the LC director [2]. If the sample is in the cholesteric phase during polymerization, the resulting network is helical [2, 3].

A common practice in the study of PSLCs has been to remove the host by dissolving it in an organic solvent [2]. The network component can then be imaged using scanning electron microscopy (SEM). Such investigations have shown that the network morphology is dependent on the polymerization conditions. For example, increasing the irradiation time has been found to result in the formation of larger, more extended structures [4]. However, while numerous studies have been reported regarding the network surfaces, the nature of the internal structure has not been addressed in the literature to date. This is an important point since it is unclear whether the structures observed are solid or hollow. For example, if the network fibrils are solid, it would mean that they are composed entirely of network, and therefore, that LC host molecules are excluded from a growing fibril. However, if they are hollow, it would mean that the growing network is able to trap host molecules within, and the fibrils would contain less actual network than would appear. In this publication, we report the first observation of the internal network structure of a PSLC. This was achieved using transmission electron microscopy (TEM) of stained sections.

To produce a PSLC, a mixture was prepared comprising the nematic mixture BL087 (a cyanobiphenyl- and terphenyl-based mixture of high birefringence), the terphenyl-based LC diacrylate RM60 (both supplied by Merck R&D UK) and the photoinitiator Irgacure 651 (Ciba Geigy). The monomer concentration was 1.00 wt %, while the initiator concentration was 0.20 wt %. The homogeneous mixture was introduced into a glass sandwich cell with Melinex layers (DuPont) of 100 μm thickness on

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the two internal surfaces. The Melinex layers had been rubbed to promote uniaxial alignment of the molecules, and were separated by 12.5 μm Kapton spacers. In order to photopolymerize the monomer, the sample was irradiated for three minutes using a mercury lamp (Blak-Ray B100 AP, UVP Inc.) emitting strongly over a wavelength region centred around 366 nm. The sample was held at a constant temperature of 39°C during polymerization, a temperature deep within the nematic range of the mixture. Following the polymerization process, the host was removed by immersing the sample in heptane for four days, during which time the host dissolved. The network, which suffered relatively little disruption as a result of this [5], was left behind on the Melinex substrates. The Melinex 'sandwich' was removed from the glass cell and the substrates separated, allowing the network to be stained with bromine vapour for one hour. Since network regions were bonded to one or other of the Melinex substrates, separation did not cause any disruption of the network. The sandwich was then reassembled, and prepared for TEM observation.

Since TEM relies on the passage of electrons through a sample to produce an image, samples must be extremely thin (~100 nm or less). Therefore, the networks formed had to be sliced into ultra-thin sections. In order to do this, a method was developed involving embedding of the network in an epoxy resin, followed by ultramicrotomy. A detailed description of the sample preparation technique will be given in a forthcoming publication [6].

Embedding and ultramicrotomy were carried out in such a way that the network fibrils were sectioned end-on, so that it would be possible to observe a cross-section through them. Sections were imaged using a Philips CM20 TEM in bright field mode, utilizing an accelerating voltage of 200 kV. The microscope was equipped with an EDS accessory (energy dispersive spectroscopy), which allowed particular elements to be identified within sections from their signature X-ray emissions. The most striking feature observed was a collection of dark, almost circular objects (see figure 1) which was found (via EDS) to contain considerable amounts of bromine. Therefore, these must constitute the stained network. The bromine is probably incorporated into the network by substitution of aromatic hydrogens on the terphenyl units [7]. The image obtained appeared slightly hazy, but the widths of the features observed were measurable, and were in the range 0.07–0.20 μm, with a mean value of 0.13 μm. Since these structures were not quite circular, the width was defined as the mean of the longest and shortest distance across each one. Another sample was then prepared, using identical polymerization conditions, in order to make observations using SEM. This involved removing the host using heptane, and coating the network with a thin layer of gold. Fibrillar structures were observed, and found to be made up of collections of anisotropic droplets (see figure 2). The aggregation of these droplets over the course of a reaction produces fibrils, as has been described in the literature [4]. The widths of the features revealed by SEM were comparable to those observed by TEM, with a range of 0.08–0.22 μm and a mean value of 0.14 μm; this provides evidence that the structures seen using TEM are anisotropic droplets which have collected together to form fibrils which are viewed end-on. This is also consistent with the orientation of the sample

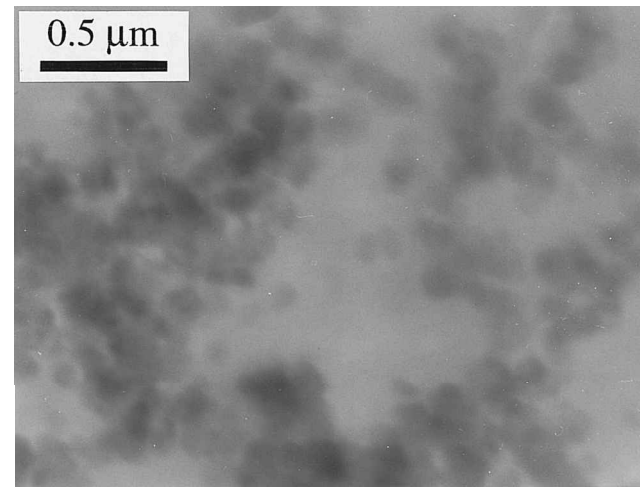

Figure 1. Transmission electron micrograph of a network, formed between Melinex layers, then brominated for 1 h and embedded within resin. The network was produced by UV irradiation of an RM60/BL087 solution for 3 min at 39°C using a sample thickness of 12.5 μm.

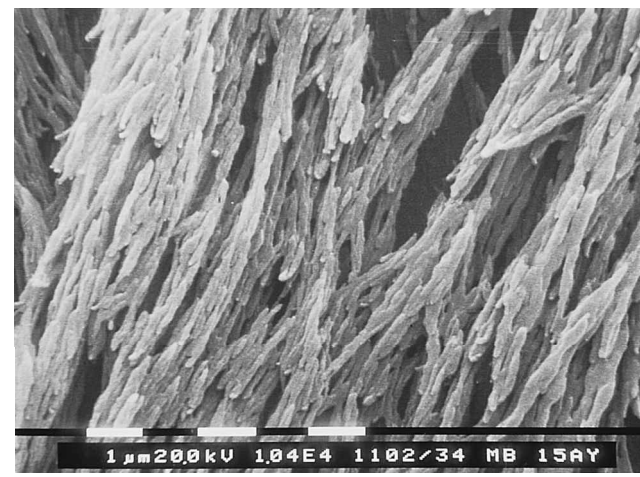

Figure 2. Scanning electron micrograph of a network formed between Melinex layers. The network was produced by UV irradiation of an RM60/BL087 solution for 3 min at 39°C using a sample thickness of 12.5 μm. The host material was extracted using heptane prior to observation.

during sectioning. A comparison of the structural dimensions observed from the two types of electron microscopy is presented in figure 3.

Measurements of the widths of the network structures, using both SEM and TEM, revealed that no objects were present of width less than 0.07 μm. This suggests a lower limit for the droplet widths, below which the growing material either remains dissolved within the LC host or is small enough to be removed from a cell during dissolution of the surrounding host. This question of network development in this system will be discussed in a forthcoming paper [8]. In terms of the TEM image, should any features of much less than 0.1 μm diameter have been present, it is unlikely that they would have been resolved. This is because the final image is a superposition of all features throughout the thickness of a particular section; we should not, therefore, expect to resolve to less than that thickness (in this case, ~ 0.1 μm). Due to the difficulty inherent in sectioning the composite material, and the need to obtain good contrast in the image, it was not feasible to obtain sections of less than ~ 0.1 μm thick.

The network material observed in figure 1 is clearly solid, with no obvious cavities within. It appears dark throughout, which implies that it is relatively permeable, since the bromine vapour has stained it uniformly, not just the outer surfaces. The degree of permeability can be related to the diffusion coefficient for bromine through this diacrylate network; however such data are not available in the literature. The closest comparison can be made from a study of the interactions of bromine with polyacrylonitrile [9], in which a diffusion coefficient of $\sim 10^{-12}\,cm^2\,s^{-1}$ was determined. This is two orders of magnitude higher than that required for bromine to pass completely through the structures reported in this publication. However, it would be expected that, due to the highly ordered nature of the network material and the high degree of crosslinking that exists, the diffusion coefficient in this system would be significantly lower than $10^{-12}\,cm^2\,s^{-1}$, perhaps low enough that bromine would not be expected to diffuse completely through a droplet in the time allowed. The fact that it does, suggests that the network possesses an open, yet homogeneous structure.

The objects observed by TEM were generally uniform in shade, although there was some slight variation within, possibly due to thickness variations in the section. Another possibility is that the variations in shade are due to some substructure. Nevertheless, most of the structures do appear reasonably solid, without any evidence of hollow interiors. The idea that the network fibrils are composed of collections of 'nanofibrils' [10] is not supported by these observations, but neither is it disproved: the removal of LC host from between such 'nanofibrils' may lead to collapse, and they could appear as in figure 1. In addition, the possibility of some host being present within the network cannot be completely ruled out.

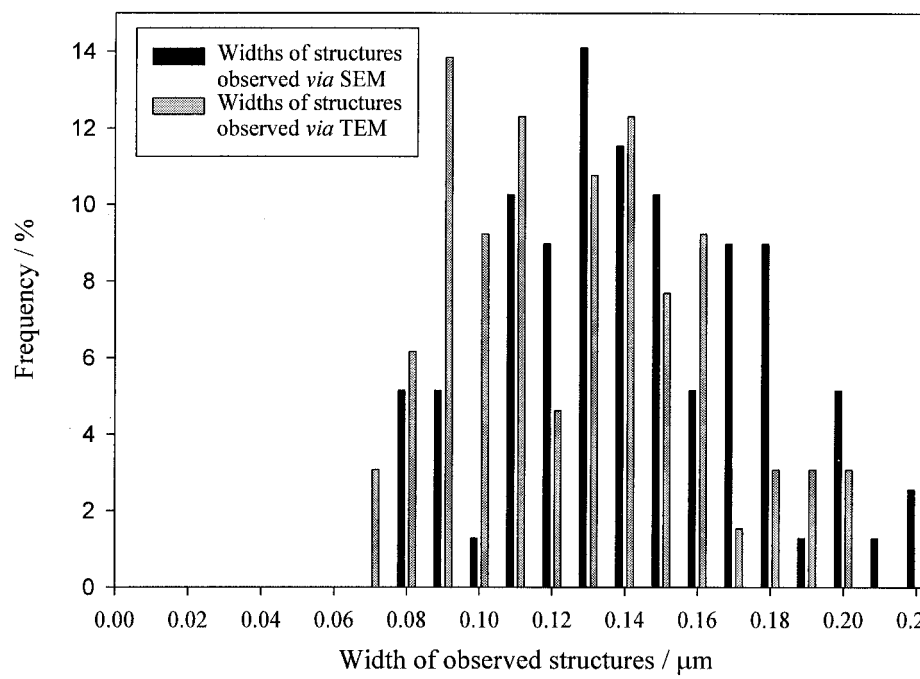

Figure 3. Histogram comparing the widths of structures observed by SEM and TEM for samples prepared between Melinex layers using an irradiation time of 3 min, a polymerization temperature of 39°C and a cell thickness of 12.5 μm. The dark bars refer to the widths of objects observed by SEM, while the lighter bars refer to the widths of objects observed by TEM.

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