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A transmission electron microscopy study of polymer-stabilised liquid crystal structure

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A method has been established for observing the internal structure of the network component of polymer-stabilised liquid crystals. *In situ* photopolymerisation of a mesogenic diacrylate monomer using ultraviolet light leads to a sparse network (∼1 wt%) within a nematic host. Following polymerisation, the host was removed through dissolution in heptane, revealing the network. In order to observe a cross-section through the network, it was embedded in a resin and then sectioned using an ultramicrotome. However, imaging of the network was not possible due to poor contrast. To improve this, several reagents were used for network staining, but only one was successful: bromine. The use of a Melinex-resin composite for sectioning was also found to be advantageous. Imaging of the network using transmission electron microscopy revealed solid "droplets"of width 0.07–0.20 μm, possessing an open, yet homogeneous structure, with no evidence for any large-scale internal structures.

1. Introduction

Polymer-stabilised liquid crystals (PSLCs) or anisotropic gels are materials produced by dissolving a small amount of a monomer within a LC host, and then photopolymerising the monomer *in situ* within the LC phase [1–3]. In order to produce a cross-linked network, the monomer must have more than one reactive group. By polymerising the monomer within an anisotropic medium, the resulting network is itself anisotropic. For example, when formed within a nematic monodomain, the network has been observed as a collection of fibrils which are well-aligned along the LC director [4]. When formed within the cholesteric phase, the twisting of the director is matched by the network, which is helical [4, 5]. Interactions between the network and host allow more varied control over the host molecules than is the case in a bulk LC [6–10], which makes these materials attractive for use in a variety of applications, particularly for new types of displays.

Imaging of network surfaces is possible using scanning electron microscopy (SEM), and has been reported in a series of publications [4, 5, 11–19]. As well as the striking images which have been obtained (e.g. Fig. 1), the popularity of this technique with regard to PSLCs is also due to the ease of sample preparation. This simply involves removing the host through dissolution using an organic solvent, then coating the network with a heavy metal (e.g. gold or palladium). While several studies have taken place regarding the surface morphology, no investigations on the internal structure of the network have been reported. The question of internal structure is an important one, since it is impossible to tell from SEM observations whether the network fibrils which have been observed are solid or hollow, heterogeneous or homogeneous. If the fibrils are solid, it would mean that they are composed entirely of polymerised monomer. If they are hollow, it would mean that they contain some host molecules. This has implications for the polymerisation process, since a high degree of segregation between the host and the growing network during polymerisation would lead to structures composed entirely of network. Low segregation would lead to structures within which appreciable amounts of host could be trapped.

In this paper, internal network structure is revealed using transmission electron microscopy (TEM). In contrast to SEM, sample preparation for TEM is not straightforward. Ultra-thin samples are required (100 nm or less) in order for a significant proportion of the electron beam to pass through, while there are the added problems of being able to obtain a cross-section through the fibrils, and to establish a mechanism for obtaining good contrast in an image. This paper builds on a preliminary communication [20], and will detail the experimental approaches used in enabling an image of internal network structure to be obtained, along with analysis of the resulting images.

2. Experimental

PSLCs were prepared from a mixture of the terphenyl-based LC diacrylate monomer RM60, the host nematic

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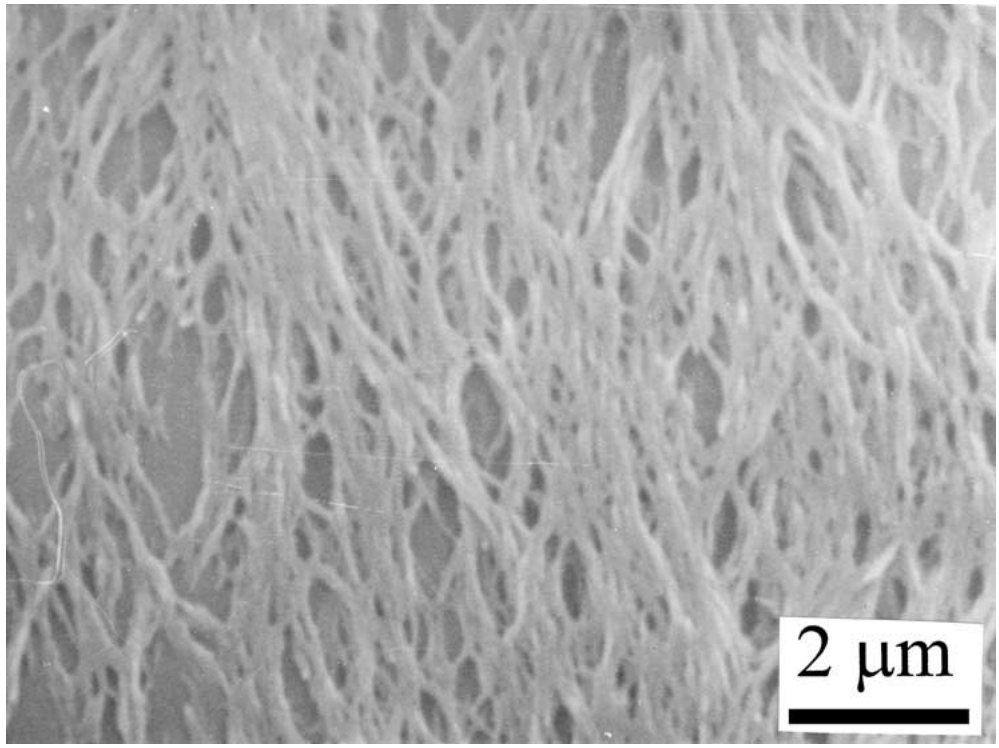

Figure 1 Scanning electron micrograph of a sample after extraction of the LC host, clearly demonstrating the fibrillar nature of the network. It was formed from the monomer RM103, using a five minute irradiation at 39°C in a cell 50 μm thick.

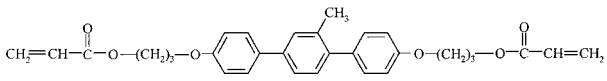

Figure 2 The molecular structure of RM60.

mixture BL087, and the photoinitiator Irgacure 651. RM60 (Fig. 2), which formed 1.00 wt% of the overall system, and BL087 (a cyanobiphenyl and terphenyl-based mixture of high birefringence) were both supplied by Merck R&D UK, while the initiator (present as 0.20 wt%) was supplied by Ciba-Geigy. The three materials were weighed to give the desired proportion of each, and mixed together. RM60 and Irgacure 651, which are both solid at room temperature, dissolved in the BL087 with gentle warming and shaking to give a homogeneous mixture. Samples of this were introduced into glass sandwich cells featuring internal aligning surfaces, and were separated by Kapton spacers of 12.5, 25 or 50 μm. The aligning layers took the form of Melinex films of thickness 100 μm, or of polyimide films spin coated from solution. When these layers are rubbed along a particular direction, a LC material placed in contact with them is subject to interactions which promote a specific alignment of the local director [21]. The LC director throughout the material points along the direction of rubbing, i.e. the individual molecules tend to point along this direction. This is known as a monodomain arrangement. Without rubbing, the director would point in different directions in different regions of the LC, giving a multidomain (see Fig. 3).

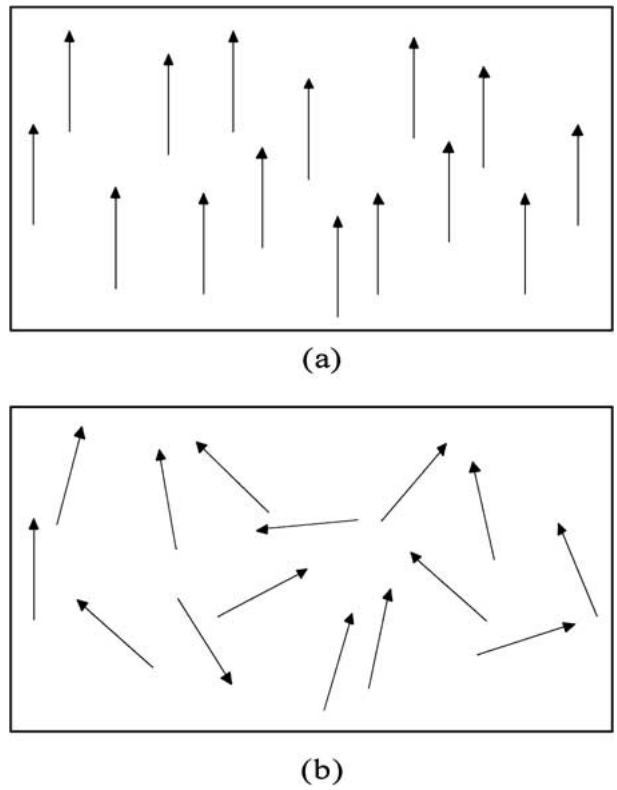

Figure 3 Schematic diagram showing the alignment of the LC director throughout a sample when in contact with (a) a treated and unidirectionally-rubbed surface and (b) an untreated surface. In (a), the director points in a common direction throughout, while in (b), the director points in different directions in different areas of the sample.

To generate a network (see Fig. 4), samples were irradiated using a mercury lamp (Blak-Ray B100 AP, UVP Inc.) emitting at 366 nm, with an intensity of $\sim$25 mW cm^{-2}. This caused the monomer to undergo a cross-linking photopolymerisation reaction [22]. During irradiation, which occured for well-defined time intervals, samples were held at a constant temperature of 39°C, which is deep within the nematic range of the

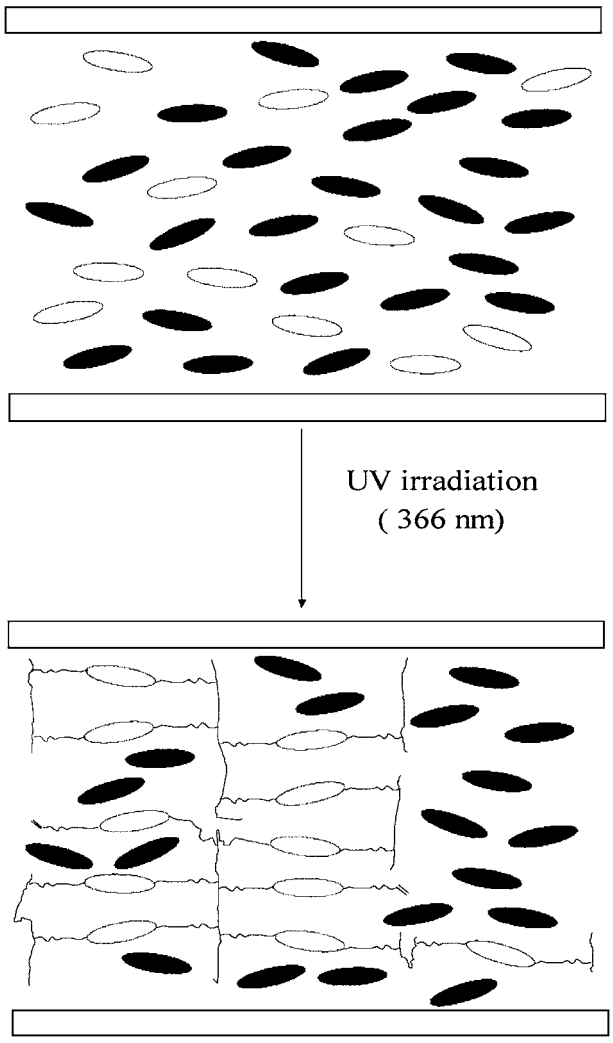

Figure 4 Schematic diagram of a PSLC system before and after irradiation. Initially, the monomer units (white) are dissolved within the LC host (black units). Irradiation causes the monomer to polymerise, giving a network dispersed within the host.

mixture. The amount of monomer which polymerised under a given set of reaction conditions could be calculated using a method involving high performance liquid chromatography [23].

To observe the resultant networks using electron microscopy, they were separated from the LC host within which they were formed by immersing samples within heptane for four days, during which time the host was dissolved. This process was found to cause relatively little disruption to the network [24], which was left behind on the alignment layers in the form of fibrils. These fibrils (e.g. see Fig. 1), which tended to align along the original LC director, appeared to be made up of groups of connected anisotropic droplets. In order to observe the interior of these network structures using TEM, the network was removed from the glass and embedded in an epoxy resin for support during sectioning, which was carried out using an RMC MT-7 ultramicrotome, in conjunction with glass knives. Sections of ∼100 nm thickness were obtained on a reproducible basis.

Throughout the course of these experiments, there were two main problems to be overcome. Firstly, a method had to be devised to obtain the network in a suitable form for sectioning. Secondly, a way of obtaining good contrast in the sections was required. The various approaches used in attempting to solve these problems will now be described.

3. Approaches

3.1. Initial methods

Initially, rubbed polyimide alignment layers were used to coat the internal surfaces of the glass cells. Since these layers strongly adhered to the glass, the network was also effectively bound to the glass. To remove it, a selected area was covered with an epoxy adhesive (PermaBond), which was allowed to cure at room temperature. The resulting network-adhesive composite was separated from the glass with a razor blade, and added to an embedding medium (Taab Transmit EM Resin Kit TK10, Taab Laboratories) to produce solid capsules which could be sectioned (Fig. 5).

The embedding mixture was prepared by mixing 2.2 g of an epoxy resin with 3.0 g each of two separate hardeners for 30 minutes. 0.15 cm^3 of accelerator was then added, followed by a further 30 minutes of mixing. Samples of this mixture were added to a network-adhesive composite in embedding capsules, and were cured for 18 hours at 70°C before sectioning. The orientation of the composites within the resin were such that the network fibrils were sectioned end-on, in order to observe a cross-section through them. These were imaged using a Philips CM20 TEM in bright field mode, utilising an accelerating voltage of 200 kV.

3.2. Staining

In order to improve contrast in the microscope compared to the previous approach, various reagents were used in an attempt to introduce electron-dense atoms into the network. In addition to providing bright field contrast, this also enabled the network to be identified unambiguously via energy dispersive spectroscopy (EDS).

Initially, osmium tetroxide (OsO_4, Aldrich Chemical Co.) was used since this is a common stain, and reacts readily with C=C bonds (present in the monomer molecules), forming C−Os bonds [25, 26]. Therefore, reaction between OsO_4 and any pendant double bonds would result in attachment of Os atoms to the network.

Samples were exposed to subliming OsO_4 vapour inside a specially designed sealed container, of the type described by Owen and Vesely [27]. These samples were in the form of microtomed sections, or the dry networks on their glass substrates (which were subsequently embedded and microtomed). The use of the

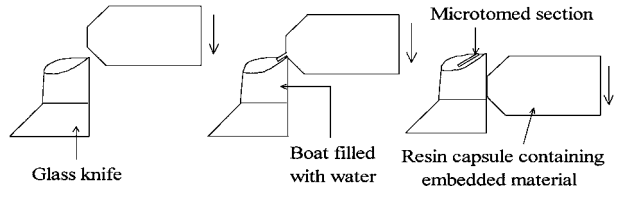

Figure 5 Schematic diagram of the sectioning of a resin block containing embedded material.

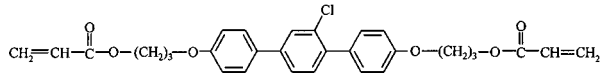

Figure 6 The molecular structure of RM103.

networks was preferred due to the mechanical damage easily inflicted on the sections by repeated handling. Also, exposing the sample before staining meant that only the network could contain osmium, potentially making it easier to observe within the embedding medium. Exposure times of up to 48 hours were attempted. An alternative to vapour staining was the use of a 4 wt% solution of OsO_4 in water: microtomed sections were soaked in solution for 24 hours before being examined in the TEM.

An alternative approach to systems containing alkyl sequences has been described by Kanig [28], and applied with considerable success to many polyethylene systems. Here, chlorosulphonic acid (HSO_3Cl, Aldrich) was used via vapour staining, with samples being exposed for 18 hours in order to introduce sulphur and chlorine into the network. Another approach was to incorporate bromine (Br_2, Aldrich) into the network, by exposing samples to bromine vapour. This had the potential to stain the network through substitution of aromatic hydrogen atoms on the monomer terphenyl units [29]. Exposure times of either 1 hour or 24 hours were used. Samples were exposed to these reagents before any embedding took place so that, as above, the embedding medium could not contain any of the stain. Finally, the monomer RM103 (Merck R&D UK) was used in place of RM60. Since RM103 molecules each contain a chlorine atom (Fig. 6), the necessary electron density is an intrinsic property of the monomer, even before a network is generated.

3.3. The formation of networks on Melinex layers

Aside from the problem of contrast, another difficulty was the inhomogeneity of adhesive regions within sections (see below). In an attempt to overcome this, the network was initially infiltrated using the embedding medium itself, rather than the adhesive.

In an alternative approach to the use of polyimide alignment layers, Melinex layers were used instead. These were more easily obtained than the spin-coated polyimide layers, simply being cut from a 100 μm thick film and then rubbed along a specific direction. The use of Melinex had several advantages, especially the simple removal of network by peeling the Melinex off the glass. The resulting network-Melinex sandwich then had resin introduced between the Melinex layers; this was cured as before (18 hours at 70°C). The resulting composite was held between pre-cured resin blocks inside an embedding capsule, to which more resin was added. Curing produced a solid block, within which the position of the network was well defined (Fig. 7).

3.4. Ultramicrotomy

Sectioning was performed at room temperature using standard procedures. The optimum cutting speed with

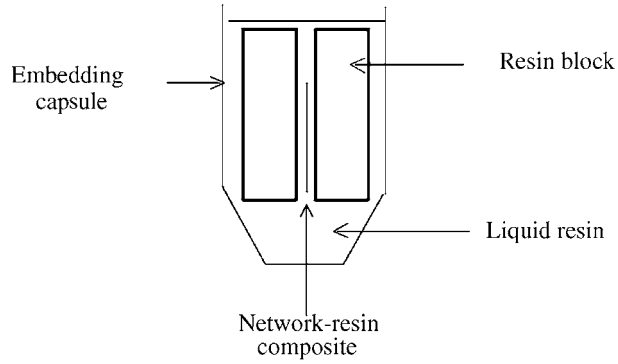

Figure 7 Schematic representation of the method used to hold a network-resin composite flat using two pre-cured resin blocks.

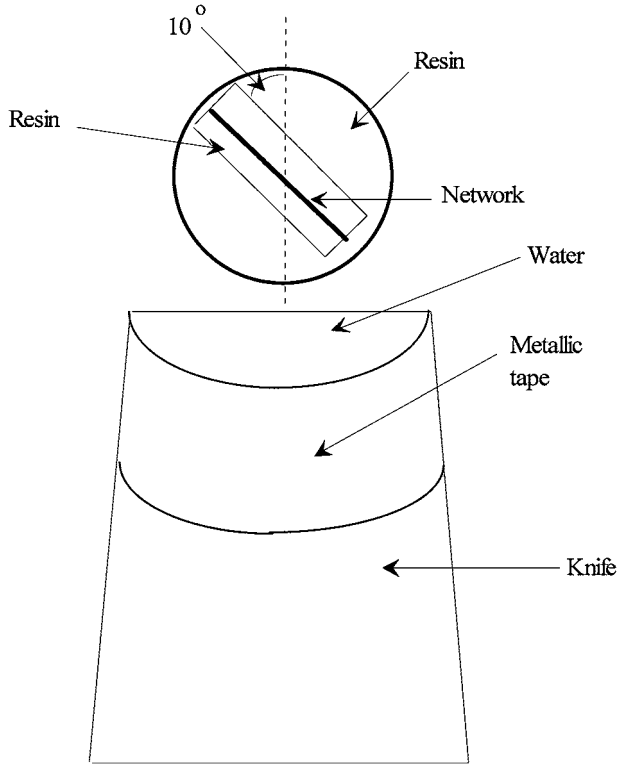

Figure 8 Schematic diagram to show the orientation of the network band during sectioning.

45° glass knives was found to be 0.5 mm s^{-1}; 100 nm was selected as the nominal section thickness. Groups of sections were obtained at various planes through the sample, and were subsequently imaged using TEM. During sectioning, the orientation of the sample relative to the knife was as shown in Fig. 8. The block was aligned so that any potential network band would be at ~10° to the cutting direction. This was to distinguish the specimen from any knife marks or orthogonal compression bands.

4. Results

4.1. Initial methods

As has been mentioned previously, the diacrylate network had to be in a suitable form to allow sectioning and subsequent imaging. This required embedding of the network in a resin to provide support during sectioning, which was carried out using an ultramicrotome.

However, it was not possible to image the network due to poor contrast with the embedding medium, while the thin sections were prone to tearing. In addition, any defects in the glass knives used to cut the sections resulted in knife marks, while compression bands were also observed parallel to the knife edge due to the movement of the knife edge through the sample.

4.2. Staining

Although OsO_4 is normally employed to stain unsaturated polymers, it has also been applied with success to systems where the mechanism involved physical absorption [30]. However, here, observation of sections which had been exposed to subliming OsO_4 did not reveal any potential network areas, while the sections showed a high degree of tearing. This was probably due to the extra handling (via tweezers) involved in removing the sections from their grids and then replacing them after staining. This was done so that there was no possibility of any osmium being deposited on the grids since, then, it could only be associated with the network itself. Elemental analysis of sections using EDS similarly revealed no evidence of osmium. Comparable results were obtained after exposing sections to an aqueous solution of OsO_4. Sections within which the network was exposed to OsO_4 before any embedding took place showed minimisation of section damage, due to the lower degree of handling required. However, no potential network areas were observed and, again, no Os was detected through EDS. The results obtained clearly show that osmium does not stain this system. Although it was expected that OsO_4 would not oxidise the phenyl rings present in the monomer molecules (it does not tend to oxidise aromatic systems [25, 31, 32]), its inability to stain any component of the network is significant. This indicates that the olefinic double bonds which are initially present are mostly used up in the polymerisation process such that very few, if any, remain (or those which are present are inaccessible). Chemical reactions, therefore, do not constitute a viable staining mechanism. Physical absorption, similarly, does not occur, suggesting that either desorption is rapid or, more significantly, that the network particles are sufficiently dense that the relatively large OsO_4 molecules are unable to penetrate them.

In contrast to OsO_4, HSO_3Cl was effective in staining the network: samples exposed to the vapour appeared orange-brown in colour, whereas before, they were white. However, the stained network sample could not be embedded immediately, since it had first to be decontaminated to remove any traces of HSO_3Cl remaining on its surface. Because the acid is so reactive, it could not be washed directly with distilled water, due to the violent reaction which would have occurred. Therefore, the sample was washed in an 80 vol% solution of H_2SO_4 which had been cooled using dry ice. The washing was then repeated using 22 vol% H_2SO_4 (also cooled with dry ice) before final washing with distilled water. Unfortunately, the decontamination process removed the network from the glass: it appeared to have dissolved, probably due to cleavage of the ester bonds by the sulphuric acid. In an attempt to avoid this, a different decontamination procedure was used. A stained sample was washed in a mixture of acetone and water (90:10 by volume) which had been cooled in liquid nitrogen. However, this also dissolved the network, since some H_2SO_4 was still formed. Therefore, it would appear that HSO_3Cl is not a suitable stain for any polymer that contains ester linkages due to the H_2SO_4 that is an inevitable by-product of recovery.

The use of the chlorinated monomer RM103 instead of RM60 provided a simple means of incorporating heavy atoms into the network. After embedding and ultramicrotomy, sections were obtained which included a noticeably darker band running across them, $\sim 1\ \mu$m in width (Fig. 9). This band appeared along the boundary between the resin and adhesive, which is where the embedded network would be. One area in particular displayed some fine structure (Fig. 10), with dimensions of the order of that observed in the SEM ($\sim 0.1\ \mu$m, Fig. 1). However, the features in question appeared rather indistinct, possibly due to some of the adhesive penetrating their outer surfaces, causing them to swell. Although EDS analysis showed that chlorine was present in this band, it was also detected in both the resin and adhesive. Therefore, these materials must also contain chlorinated components, and thus, it is not possible to state categorically that the fine structure shown is actually due to the network on the basis of EDS analysis. Nevertheless, when this evidence is combined with the images obtained, we feel that the dark band in Fig. 9 should indeed be associated with the acrylate network. Examination of Fig. 9 reveals an additional problem with the general methodology adopted to prepare this sample for TEM. While the epoxy embedding resin appears reasonably homogeneous, areas corresponding to the adhesive are not, appearing extremely uneven. This factor alone serves, partially, to obscure the network structure.

While the use of chlorinated monomer proved a step forward in imaging the acrylate network, the problem of imaging a network made from the original monomer RM60 remained. Therefore, RM60 networks were prepared as before, and exposed to another potential stain, bromine. After exposure to bromine vapour for 24 hours within a sealed jar, the network had clearly been stained, appearing orange. After embedding and sectioning, a dark band just under 2 μm in width was observed between the adhesive and resin areas (Fig. 11). However, it appeared so dark that no fine detail could be observed in the TEM. EDS analysis showed that the band did indeed contain bromine (Fig. 12). Since the TEM contrast suggested that the above specimen contained excessive amounts of bromine, another sample was brominated for just 1 hour. Using this decreased exposure time, a dark band was again observed along the boundary between resin and adhesive, but it appeared lighter than before, with a suggestion of fine texture (Fig. 13). However, the inhomogeneous nature of the adhesive areas again served to obscure the network area, indicating that PermaBond is far from being an ideal embedding support medium for ultramicrotomy. An EDS line scan (11.9 keV – Br K_α emission line) clearly showed that

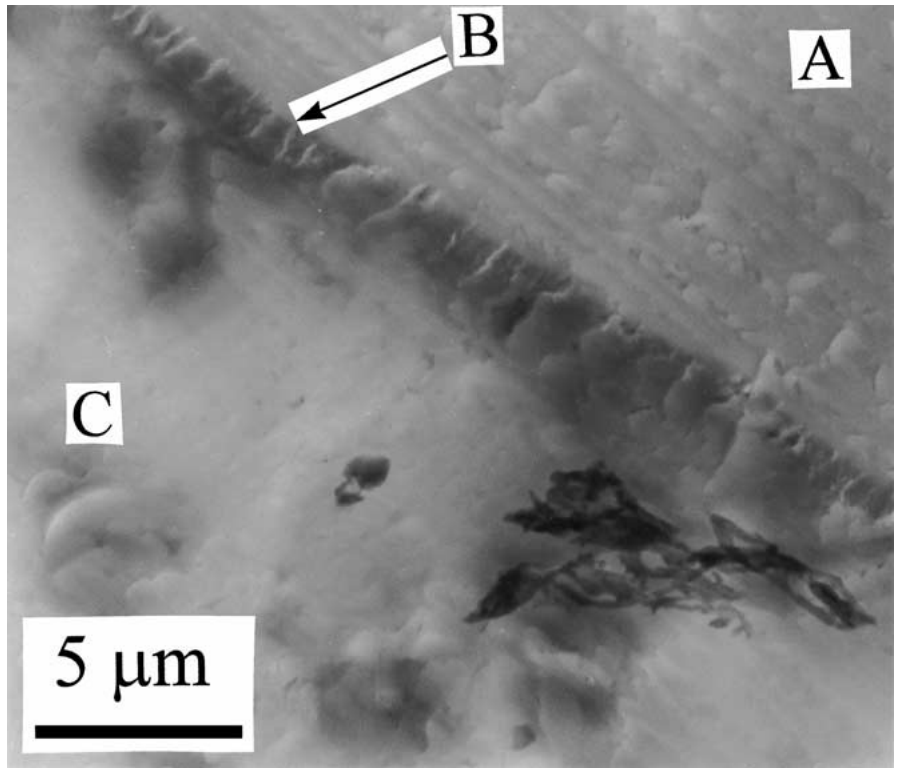

Figure 9 Transmission electron micrograph of a microtomed section believed to contain chlorinated network. Region A is the resin, region B contains the network and region C is the adhesive.

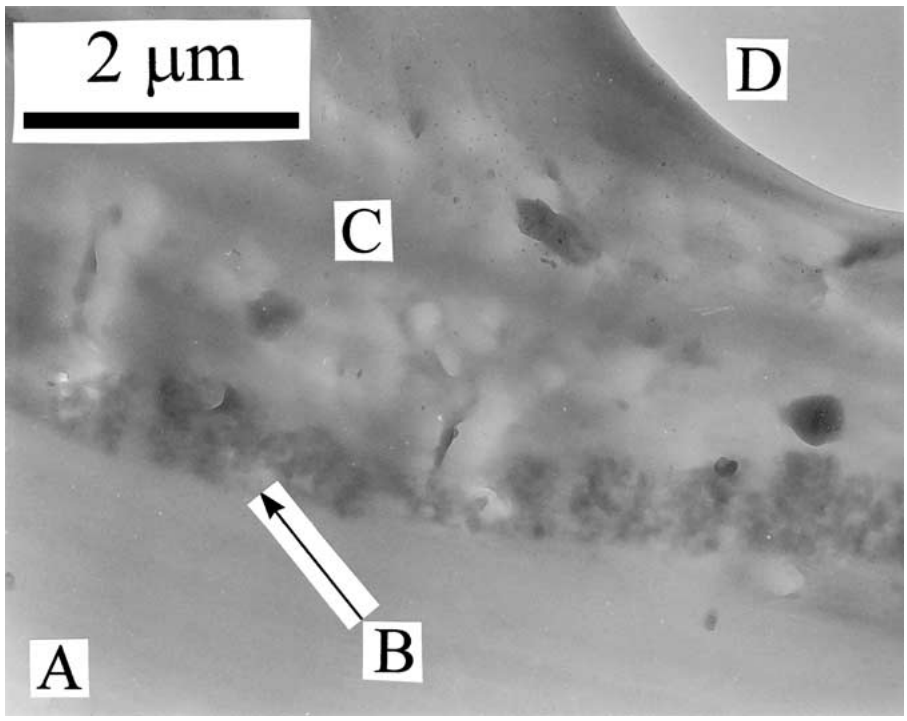

Figure 10 Transmission electron micrograph of a microtomed section containing the chlorinated network. Region A is the resin, region B contains the network, region C is the adhesive and region D is a hole in the adhesive.

this dark feature is associated with a bromine-rich layer (Fig. 14).

4.3. The formation of networks on Melinex layers

Since none of the approaches previously described provided entirely satisfactory images of the network, a totally different method was used, in which the network was formed in such a way that it never came into contact with the glass. This involved using rubbed Melinex layers instead of polyimide. Following dissolution of the LC host, the resulting network-Melinex sandwich could be easily separated from the glass, then split and exposed to bromine vapour for 1 hour. After re-assembling the sandwich and cutting it into

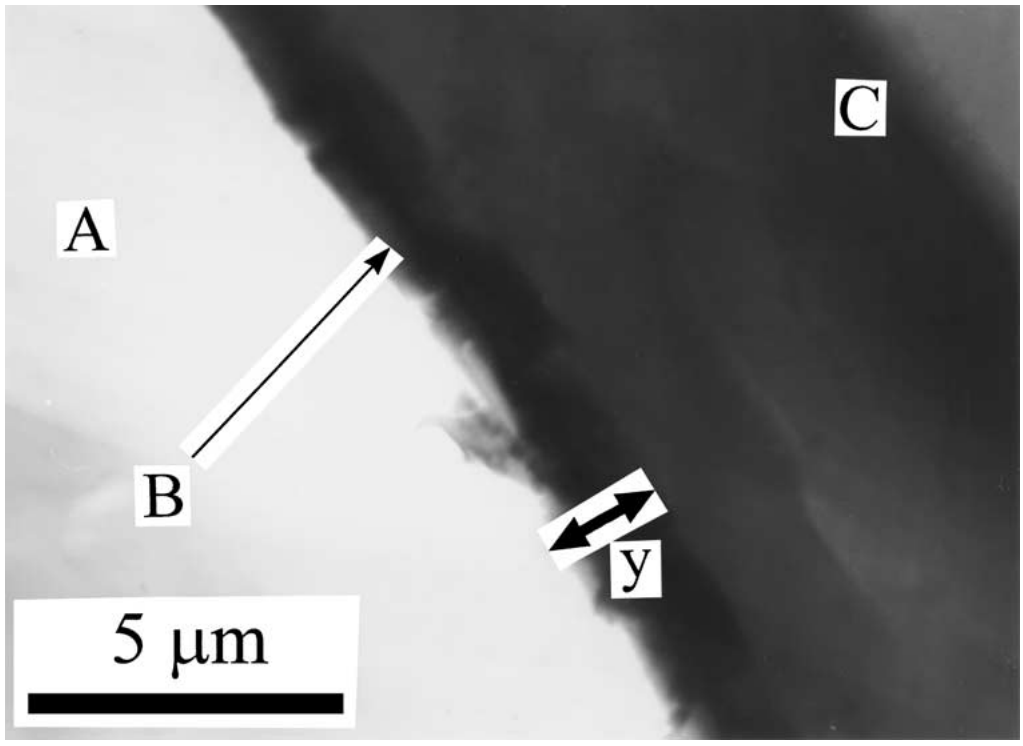

Figure 11 Transmission electron micrograph of a microtomed section containing the brominated network. Region A is the resin, region B contains the network and region C is the adhesive.

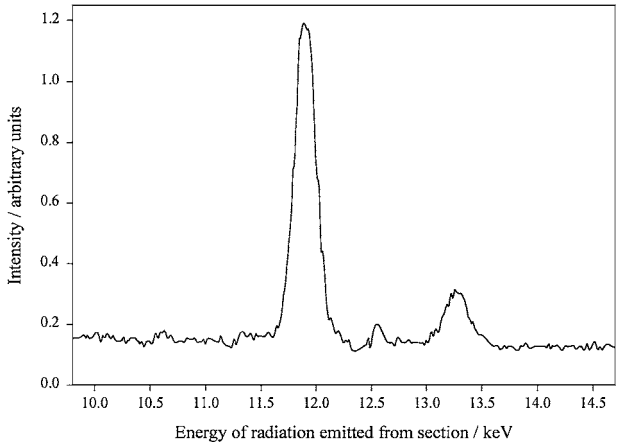

Figure 12 EDS spectrum obtained from analysis of the area described as region B in Fig. 9. Both peaks are characteristic of bromine.

strips, embedding and ultramicrotomy produced sections within which the potential position of the network was well-defined. Imaging via TEM clearly revealed the Melinex layers, and material in between them. This material appeared lighter than the Melinex, but darker features were also present within it (Fig. 15), which took the form of a collection of near-circular objects. These were found to contain considerable amounts of bromine, and therefore must be stained network. 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. The width was defined as the mean of the longest and shortest distance across each one, since they were not exactly circular, but slightly oval-shaped. The values obtained compared well with those determined from observations on a similar sample (Fig. 16) using SEM. This provides further evidence that the structures seen using TEM are anisotropic droplets which have collected together to form fibrils, viewed end-on. This is also consistent with the orientation of the sample during sectioning. A comparison of the structural dimensions observed from the two types of electron microscopy is presented in Fig. 17.

5. Discussion

After several unsuccessful attempts, a method was established for observation of the internal network structure of a polymer-stabilised liquid crystal. This involved the use of Melinex substrates, onto which the network was held, and bromine to stain the network. Subsequent embedding of samples using an epoxy resin produced solid blocks, within which the network was supported, and its position well-defined during sectioning. This method enabled imaging of a cross-section through the network fibrils, which could be identified through their near-circular appearance and dark nature in the microscope, due to staining with bromine. Further evidence was provided by EDS detection of bromine in these dark areas and the strong similarity in structural dimensions with the network material observed via SEM.

In both the TEM and SEM observations, no structures were present with widths less than 0.07 μm, suggesting that there is a critical width for the droplets. Below this value, the growing material remains dissolved within the LC host, or is removed from within sample cells during solvent dissolution. Another possibility is that individual features of less than 0.07 μm across are present, but are not resolved by the TEM. This is feasible since the final image is a superposition of all features present throughout the thickness of a section

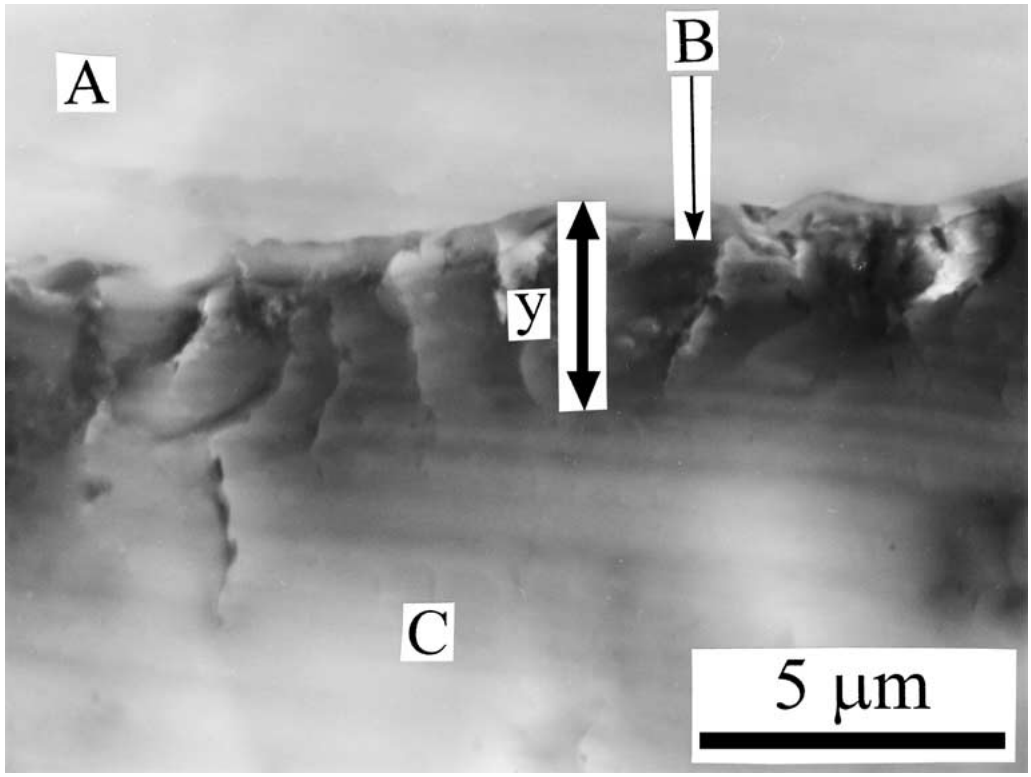

Figure 13 Transmission electron micrograph of a microtomed section containing a sample of the network. Region A is the resin, region B contains the network and region C is the adhesive. "y" refers to the y-coordinate in Fig. 12.

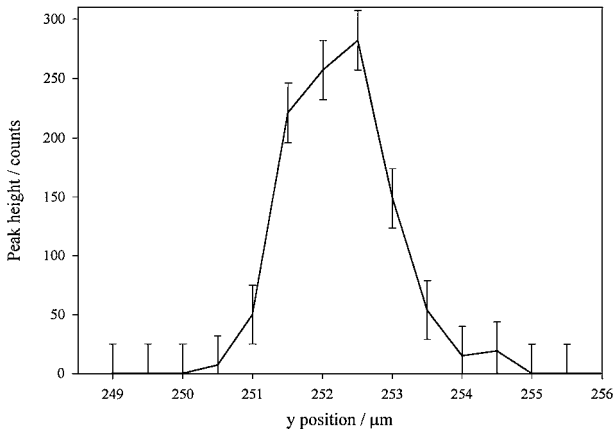

Figure 14 Variation in height of the $Br_{K\alpha}$ peak at 11.9 keV in the EDS spectrum across the suspected network region in Fig. 11.

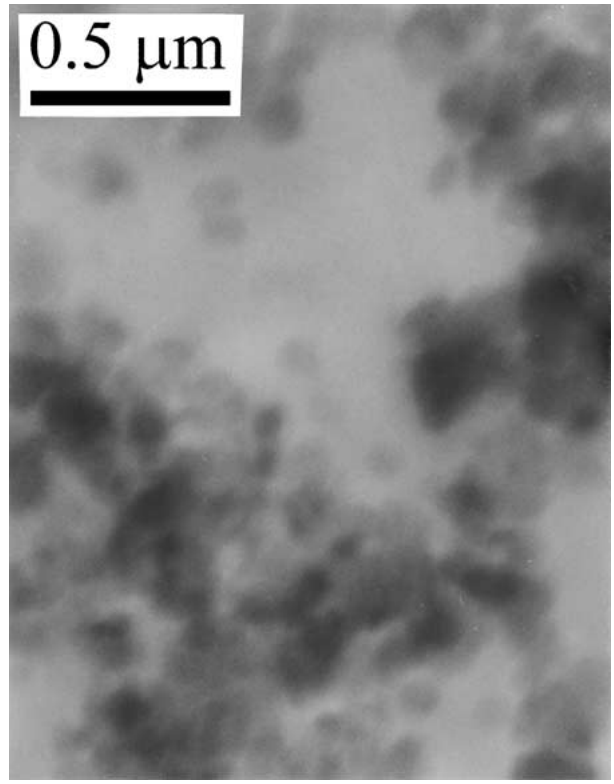

Figure 15 Transmission electron micrograph of a network, formed between Melinex layers 12.5 μm apart by irradiating for 3 minutes at 39°C. Prior to observation, the host was extracted using heptane; the network was then brominated and embedded within resin before being sectioned.

(∼0.10 μm). However, the SEM observations do not suffer from this limiting factor and since, once again, no features were observed of less that 0.07 μm using this technique, it is unlikely that the problem of resolution is responsible for the inability to see material of less than the stated width (the question of network development will be further investigated in a forthcoming paper [33]).

The structures observed via TEM are clearly solid, containing no obvious cavities. They appear dark throughout, suggesting a high degree of permeability to the bromine vapour; this is in sharp contrast to osmium tetroxide, which was completely unable to penetrate the network. The degree of permeability of bromine can be related to the diffusion coefficient for bromine through this diacrylate network, however such data is not found in the literature. A study has been made of bromine interactions with polyacrylonitrile [34], with a diffusion coefficient of $\sim 10^{-12}$ cm^2 s^{-1} obtained. This is two orders of magnitude higher than that necessary for

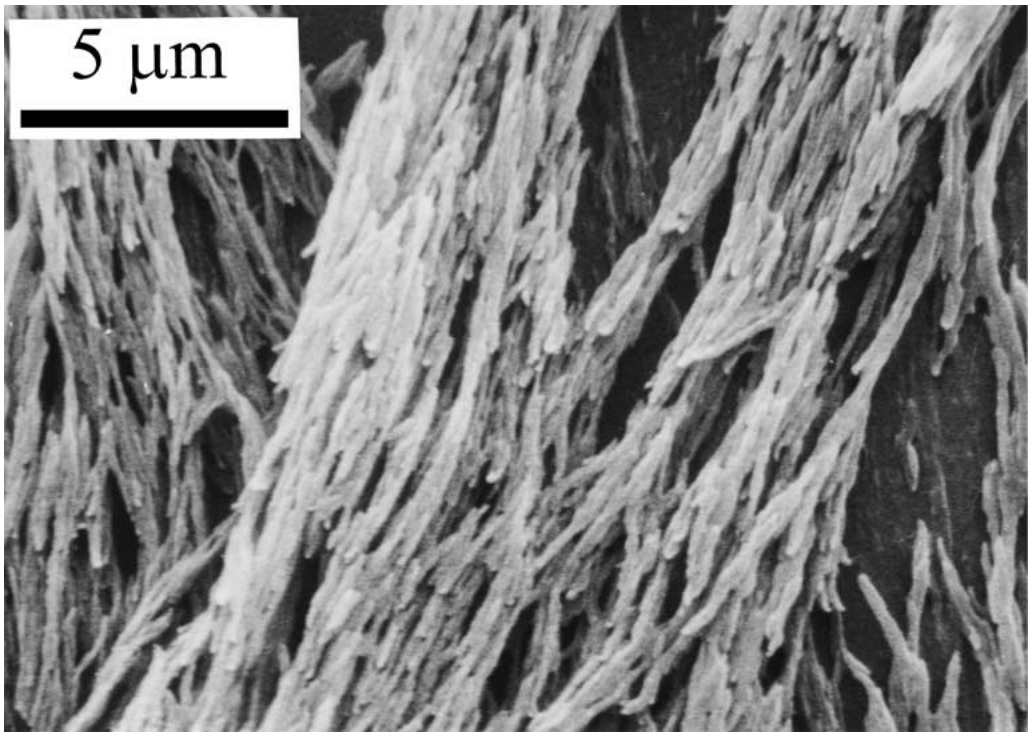

Figure 16 Scanning electron micrograph of a sample which had been formed between Melinex layers 12.5 μm apart by irradiating for 3 minutes at 39°C. The host was extracted using heptane prior to observation.

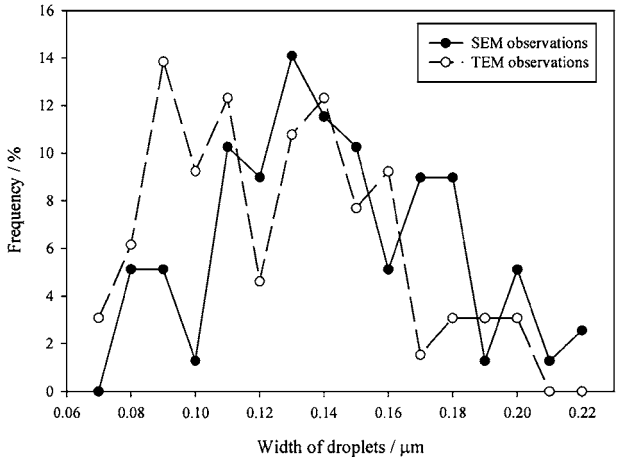

Figure 17 Histogram comparing the widths of structures observed via SEM and TEM for samples prepared between Melinex layers using an irradiation time of 3 minutes, a polymerisation temperature of 39°C and a cell thickness of 12.5 μm.

bromine to pass through the material observed in this publication. However, the high degree of cross-linking and highly-ordered nature of the diacrylate network suggest that a diffusion coefficient of significantly less than 10^{-12} cm^2 s^{-1} is more appropriate in this case. It is possible that it may be low enough that the vapour would not be expected to diffuse through each network droplet in the time allowed. Since the vapour is able to do this (in contrast to that of OsO_4, which consists of larger molecules) it suggests that the droplets have an open, yet homogeneous structure.

The features observed using TEM are generally uniform in shade, with only slight variations. These could be due to substructure, or simply due to thickness variations in the section. However, there is certainly no suggestion of any cavities within the network material. Nevertheless, the possibility of some host being present within cannot be completely ruled out, since it could also be stained by bromine, and therefore appear dark. There is no direct evidence for the idea that the network fibrils are comprised of bundles of "nanofibrils" [35]. However, the extraction of host from between such structures could lead to collapse, with the possible result being the features observed in Fig. 15.

Having devised a method for observing the network, and establishing the appearance and dimensions of its component particles, it is possible to re-evaluate the sections obtained as a result of the unsuccessful methods. Generally, no fine structure could be observed; however, when using the chlorinated monomer (see Fig. 10), material was imaged of similar dimensions and appearance as seen in Fig. 15. This suggests that successful imaging of the network was also obtained in Fig. 10, but this could not be confirmed by EDS, and the inhomogeneous nature of the section meant that the observed material was rather hazy in appearance. Therefore, the use of bromine staining and a Melinex composite was undoubtedly the best method for TEM preparation of these systems.

6. Conclusions

Various methods were used in an attempt to observe the network component of PSLCs. This required embedding of samples and subsequent sectioning using an ultramicrotome. Homogeneous embedding was found to be critical for good sectioning, while poor contrast between the network and resin meant that staining was required.

Osmium tetroxide (OsO_4) was unable to chemically stain the network, suggesting that polymerisation of

the diacrylate monomer units was extremely effective, with little or no unsaturation present in the network. OsO_4 was also ineffective by physical absorption, with its large molecules unable to penetrate the network. An alternative stain, chlorosulphonic acid, was shown to be unsuitable for use with materials containing ester units. Bromine, on the other hand, was able to attach to the network, revealing its suitability for staining open polymeric structures containing aromatic groups.

The use of bromine, along with a Melinex-composite material for embedding, led to successful sectioning and imaging of the network, revealing its component "droplets" as having an open, yet homogeneous solid structure, with a near-circular cross-section. The dimensions of the objects observed suggest a lower limit for droplet formation.

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