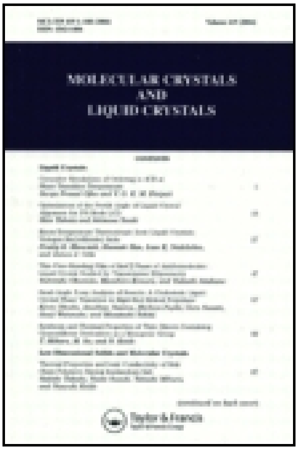

Molecular Crystals and Liquid Crystals

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Self-Supporting Liquid Crystal Composite

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SELF-SUPPORTING LIQUID CRYSTAL COMPOSITE

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Colloid-liquid crystal composites are a novel type of soft condensed matter, formed from dispersions of colloidal particles in liquid crystalline hosts. Here, we investigate the kinetics of network formation in mixtures of the thermotropic liquid crystal 5CB and nearly hard sphere colloids (polymethylmethacrylate particles), occurring as the liquid crystal undergoes a transition from the isotropic to the nematic phase. In the isotropic phase the particles (volume fraction <0.2) are homogeneously distributed. While cooling through the isotropic-nematic phase transition the particles are expelled by the liquid crystal, forming a three dimensional network structure. Using time-resolved laser scanning confocal microscopy (LSCM) we image the dynamics of the network formation at single particle resolution, for the first time. In the isotropic phase the particles perform Brownian motion, whereas in the network they remain frozen in position. We observe a broad distribution of the size of the liquid crystal domains of up to ~ 50 micrometers. Heating shows although the network breaks up clusters of particles remain. DSC measurements show that the particles do not change T_{NI}, suggesting that the particles do not alter the bulk properties of the liquid crystal. These observations provide an important step towards characterising the material properties of this novel composite.

Keywords: fluorescence microscopy; liquid crystal composites; mechanical properties; microstructure; network formation

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*COSMIC: Collaborative Optical Spectroscopy Micromanipulation and Imaging Center.

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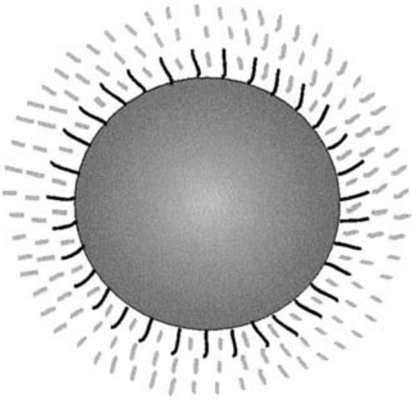

FIGURE 1 Schematic showing LC alignment around colloid particlel in the nematic phase. The LC molecules and stabilizing hairs are of lengths 2 nm and 10 nm respectively. The particle radius ranges from 100–700 nm.

1. INTRODUCTION

It has recently been discovered that a mixture of solid colloidal particles and nematic liquid crystal combines the switching properties of liquid crystals [1,2,3] and the mechanical rigidity of a wax-like soft solid [4,5,6]. Separately the two components have been studied extensively, however the area in which they are combined has entertained very little research.

A poor understanding of these mixtures exists partially because previous attempts have observed macroscopic phase separation between the particles and the liquid crystal. This is not surprising: the ordering of liquid crystal molecules imposed by the boundary condition at particle surfaces (see Figure 1) means necessarily that particles will be associated with defects in a nematic phase. These defects cost energy, and are therefore unfavourable.

The consequence is that a nematic liquid crystal will tend to exclude particles. Therefore, much of the literature on particles in liquid crystal is directed towards the study of single particles (or liquid droplets), and the structure of defects surrounding them [7,8].

There is also interest in how these defects induce anisotropic interactions and recently conditions have been found under which such mixtures remains stable. Poulin *et al.* [9] dispersed micrometer sized surfactant covered water droplets in 5CB. The colloidal droplets formed chains if the LC was in the nematic phase but dispersed when heated into the isotropic phase. Loudet *et al.* [10] dispersed silicone oil in a liquid-crystalline fluid

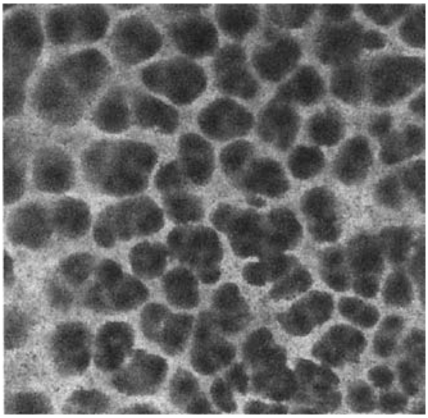

FIGURE 2 LSCM image of network structure with PMMA particles of radius 390 nm and volume fraction 5%.

and the mixture did not separate fully into two phases but self-organised into aligned chains of monodisperse colloidal droplets. In all cases, however, the density of particles is low, often vanishingly small.

In our case, we have succeeded in mixing a significant amount of particles (0.5 to 20 volume percent) with a nematic liquid crystal without macroscopic phase separation. The particles in fact form a three-dimensional network structure in the nematic liquid crystal (see Figure 2), conferring mechanical rigidity [4,6]. Upon crossing the isotropic to nematic phase transition of the LC walls of particles which enclose regions of liquid crystal were formed. With this structure the composite has a surprisingly high storage modulus of up to 10^7Pa, showing the samples ability to be rigid and self-supporting over a wide temperature range. It turns out that the orientation of the liquid crystal molecules in this material can still be electrically switched [11].

In this paper we focus on the kinetics of the phase transition. Using Laser Scanning Confocal Microscopy (LSCM) we image the motion of single particles while the network structure is being formed. A microscope image of this structure is shown in Figure 2, where the liquid crystal appears as black and the PMMA as white dots. We gather detailed information on the kinetics of the transition, examining the particle motion, distribution of LC cell sizes and the wall formation during the process of the transition. We examine the reversibility of the network formation using microscopy and calorimetric measurements, and we discuss why the liquid crystal component of this novel composite appears to have more or less the properties it has in the pure state.

2. METHODOLOGY

Sample Preparation

We focus on mixtures of the model liquid crystal 5CB[†] (4-n-pentyl-4-cyano-biphenyl) and nearly monodisperse PMMA (polymethylmethacrylate) spheres[‡], with a particle radius of between 100 and 700 nm. A layer of poly-12-hydroxystearic acid (PHSA) is grafted onto the particles to sterically stabilize them. See Figure 1. PMMA particles of radius 200 nm, 390 nm and 500 nm are chemically bound with a fluorophore to enable observation by LSCM. The particles are cleaned by dispersing in hexane and then heated to evaporate off the solvent. The particles are dried for ~4 days at ~65°C in a vacuum oven. The particles are then dispersed in isotropic 5CB at approximately 45°C using a heated magnetic stirrer within an oven, and the samples were maintained in this way. At this temperature 5CB is in its isotropic phase (isotropic-nematic transition temperature $T_{IN} \approx 35.3°C$). Composites are made with particle volume fractions of $0.5\% \leq \phi \leq 15\%$. Prior to experimental use the sample is mixed on a whirl mixer, at $T \approx 45°C$, for approximately 30 minutes. Effort is taken to ensure that all samples are loaded into the respective apparatus in the isotropic state.

Microscopy Measurements

A Nikon TE300 inverted microscope is used with a Biorad Radiance 2000 laser scanning confocal microscopy unit [13]. A ×100 oil-immersion objective with numerical aperture 1.4 is used. The confocal microscope is unique in that it allows a 'slice' within the bulk of the material to be imaged. An aperture in front of the objective filters out any out of focus rays from other planes or any scattered light, enabling a larger signal to noise ratio to be obtained. The excitation and emission wavelengths of the fluorophore are 488 nm and 520 nm respectively. With this optical setup and fluorophore the depth of field is 0.52 μm thick. For the 390 nm and 500 nm particles this means that only one layer of particles were imaged at any time. The typical time between successive images is 1.2s. Samples are prepared for observation within an oven ($T \approx 45°C$), by filling a 100 μm capillary with the composite. Samples are prepared with particle volume fractions of $2\% \leq \phi \leq 10\%$. An enclosed heating stage enables the sample to be imaged under controlled temperatures and for the initial network formation to be observed under decreasing temperature. The sample is in contact with the objective oil where the sample temperature would ideally be measured and

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[†] The 5CB was supplied by Merck.

[‡] The PMMA particles were made by Andy Schofield at The University of Edinburgh [12].

as a result temperature differences between the sample temperature and the measured temperature may exist.

DSC Measurements

A VP-DSC Microcalorimeter (Microcal Inc.) is used to make differential scanning calorimetry measurements [14]. The calorimeter used has two coin shaped cells fixed in place of 0.5 ml each. They are loaded through narrow tubes. Differences in the heat capacity between the reference cell and the sample cell are measured, where the reference cell is filled with water. The cells are cleaned with toluene and then ethanol and allowed to air dry before loading the sample. The sample is loaded into the preheated cell using a syringe that is also heated to approximately 55°C. Generally measurements are made with a cooling rate of 6 K/h and a heating rate of 30 K/h.

3. EXPERIMENTAL RESULTS

3.1. LSCM : Dynamics of the Phase Transition

A sample of PMMA particles of radius 390 nm and concentration 10% is prepared in the isotropic phase, homogenized for several days, loaded into the capillary and placed in the enclosed temperature stage. The temperature of the sample is decreased slowly in order to image the initial network formation. Images from this sequence are shown in Figures 3a–3i and show the progress of the network formation. The particles appear as white dots and the liquid crystal as black.

Figure 3a shows an image of the mixture in the isotropic phase in which individual particles can be resolved. No particle aggregation is observed and the particles exhibit Brownian motion with a diffusion constant of $D \approx 10^{-14} m^2 s^{-1}$. After passing the isotropic to nematic phase transition regions of liquid crystal begin to nucleate, expelling the PMMA particles. As can be seen in Figure 3b these regions are generally spherical. These regions of liquid crystal then begin to grow and locally the particle density increases as can be observed in Figure 3c. The particles form walls and the thin walls break during coalescence. Figure 3d and 3e show these growing regions coalescing and becoming elongated. From the original nucleation to this stage only requires approximately 10 seconds. Upon reaching this stage the kinetics of the phase separation are dominated by a slower process. The walls begin to compactify until motion becomes arrested and particles remain frozen in position. This is observed in images 3e and 3f and occurs over a period of approximately 20 seconds, however these timescales will depend upon the cooling rate. The thickness of the walls is $\sim$10 particle diameters but they are much thicker close to nodes, and there

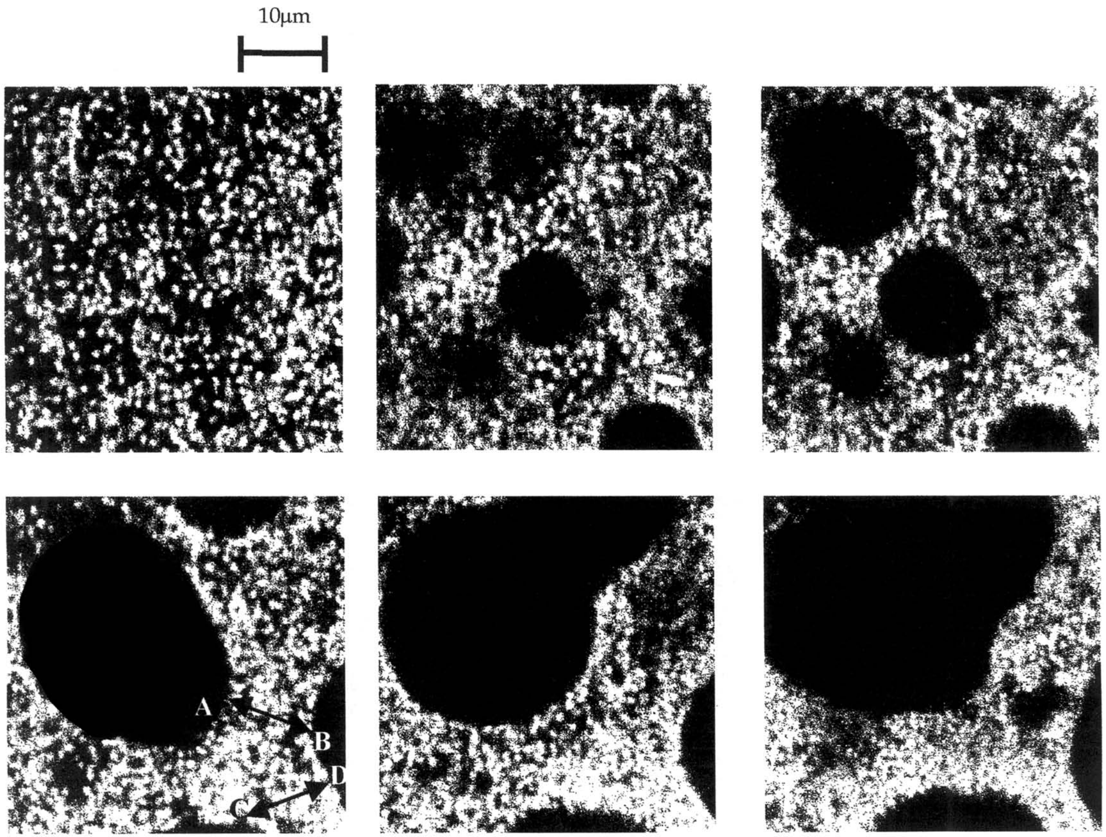

FIGURE 3 (a) PMMA particles of radius 390 nm, $\phi = 10\%$ dispersed in the isotropic phase. A scaling bar is shown at the top of the image and remains constant throughout the image. White dots: colloids. (b) Image of sample just below the transition temperature showing the onset of phase separation, t = 0. (c) Image taken at t = 1.2 seconds, showing the growth of the liquid crystal domains. (d) Image taken at t = 3.6 seconds, showing coalescence of LC domains. AB and CD denote positions where the thickness of the walls is measured. (e) Image taken at t = 9.6 seconds. (f) Image taken at t = 33.6 seconds.

is a broad distribution in the size of the liquid crystal domains. The smallest domains being the regions between the closest packed particles in the walls that are ~1 particle diameter. There are larger LC domains within the walls (see Fig. 3f) and there are the large domains enclosed by the walls that are as big as ~50–100 particle diameters.

To obtain detailed information on the compactification of the walls imaging software is used to measure the thickness of the walls at AB and CD (see Fig. 3d) in successive images. This is carried out from the stage where the original walls are formed until the motion of the network appears frozen. See Figure 4. There is a fluctuation in the thickness of the walls when two nearby domains coalesce. Figure 4 reveals that there is a fast decrease in the thickness within the first 10 seconds, a slower decrease over the next 10 seconds and it is almost constant thereafter.

The network formation appears reversible up to a point. Imaging has shown that upon heating the outermost particles become free until the network is broken up, however successive images taken at a higher magnification reveal that clusters of particles remain.

3.2. Differential Scanning Calorimetry

It has been suggested that impurities can cause the phase transition temperature to shift because of the disorder induced in the director. If the PMMA particles are classed as impurities it might be expected that they cause the transition temperature to decrease. As DSC is a sensitive method

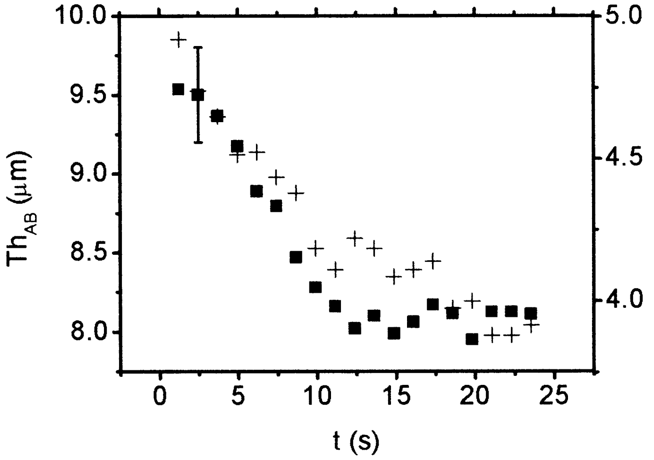

FIGURE 4 The thickness of the walls AB (◆) and CD (+) (see Figure 3f) as the network is formed. R = 390 nm, $\phi = 10\%$.

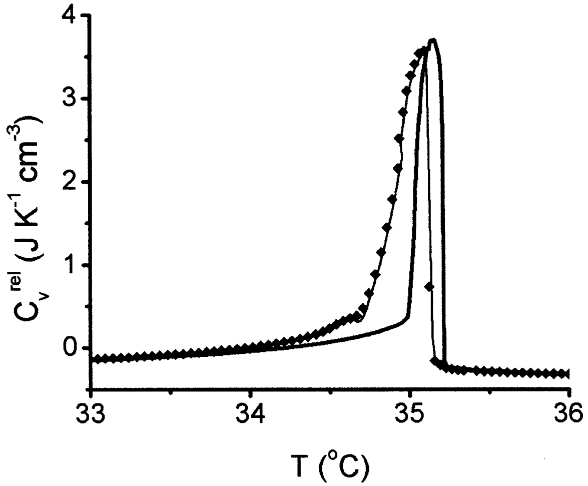

FIGURE 5 1st (▬) and 4th (◆) cooling with particles of radius R = 460 nm and concentration ϕ = 10%. Pure 5CB (▬) Cooling rate = 4.5 K/h from 45°C.

to detect the transition temperature cooling scans of 5CB and composite are run. The thick solid black line in Figure 5 represents the temperature dependence of the specific heat of pure 5CB. The specific heat curve of the pure 5CB remains constant until ~35.2°C, where there is a sharp peak of ~ 0.2° width. The thin solid black line represents the 1st cooling and the ◆ scatter graph shows the 4th cooling of the composite without changing sample material. The specific heat curves of the 1st and 4th cooling are constant until there is a sharp peak at ~35.1°C of width ~0.3°. The similar position and shape of the 1st and 4th cooling curves demonstrates the reproducibility of the phase transition upon successive cooling¶. The position of the composite curves relative to the pure 5CB curve shows a transition temperature difference of only ~0.1°C. Thus concluding that the transition temperature of the liquid crystal is almost unaffected by the presence of the PMMA particles and strongly suggesting that the liquid crystal behaves as it does in the bulk.

4. CONCLUSIONS

We have carried out a series of measurements on the formation of colloidal networks in colloid liquid crystal composites using a combination

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¶These DSC measurements do not support findings published by Petrov and Terentjev [15]. These differences will be discussed in a forthcoming publication of laser-scanning confocal imaging and DSC techniques. We have obtained detailed (single particle resolution) data showing the formation of the network upon cooling from the initial isotropic dispersion. The sequence of images show the mechanism for network formation and suggest that it is a continuous process in which nematic domains grow, expelling particles to form a complex three dimensional network. Calorimetry measurements through the isotropic-nematic transition show that the thermodynamic aspects of the isotropic-nematic transition appear similar to those of the bulk liquid crystal material. This is likely, since imaging reveals the smallest liquid crystal domains in these composites to be typically $\sim$100 nm which is an order of magnitude larger than the correlation length of the liquid crystal molecule $\sim$10nm. This finding is consistent with the observation that the LC switching times in the composites are similar to those of the pure liquid crystal.

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