Network formation in colloid–liquid crystal mixtures studied by confocal microscopy

J Cleaver and W C K Poon

School of Physics and the Collaborative Optical Spectroscopy, Micromanipulation and Imaging
Centre (COSMIC), JCMB, The University of Edinburgh, Kings Buildings, Mayfield Road,
Edinburgh EH9 3JZ, UK

Abstract
We studied the formation of particle networks in colloid + liquid crystal
mixtures cooled below the isotropic–nematic transition temperature by time-
resolved laser scanning confocal microscopy. Our observations confirm a recent
suggestion that alkane impurities play a crucial role in slowing down the speed
of the isotropic–nematic interface. This enables the growing nematic droplets
to 'push' particles into increasingly concentrated regions, ultimately resulting
in a cellular network solid. We also found that faster cooling rates resulted in
increasingly hierarchical cellular structures.

1. Introduction

In the majority of colloidal suspensions in practical applications as well as academic study, the
dispersing liquid is isotropic. Increasingly, however, attention is turning to colloids dispersed
in *anisotropic* media, principally liquid crystals (LCs). The origins of many of the interesting
new phenomena discovered in colloid–liquid crystal (CLC) mixtures is the distortion of the
director field by the particles. Depending on the anchoring strength, the elastic properties of
the LC and the particle radius, different defect structures such as 'hedgehogs' or 'saturn rings'
can be induced around single particles; the interaction of the defect fields of two particles can
lead to new types of colloidal interaction. These and other effects, studied using CLC mixtures
with a very low volume fraction, ϕ, of colloids, are the subject of many of the articles in this
special issue, and has been reviewed recently [1]. Here, we consider instead the case of denser
mixtures with particle weight fractions $\phi_w \gtrsim 0.1$,

The energetic cost of director-field distortion by particles means that the attempt to
disperse more than a few per cent of particles in LCs usually results in complete phase
separation into particle-rich and particle-poor regions once the mixture is cooled below the
isotropic–nematic (IN) transition temperature, T_{IN} (for a Landau-type theory of this transition,
see [2].) We discovered a few years ago [3], however, that mixtures of sterically stabilized
polymethylmethacrylate (PMMA) particles and 4-*n*-pentyl-4-cyanobiphenyl (5CB) did *not*

phase separate on the macroscopic scale; instead, a metastable particle network was formed, which lasted for many years. Macroscopically, the sample turned from a flowing liquid into a soft wax below T_{IN}. Its optical properties could be switched electrically [4, 5]. The particle network has been imaged by microscopy before (phase contrast [3] and reflection confocal [2]). In this paper, we present a *time-resolved* optical microscopy study of the network formation process. Our results give insight into the mechanism of metastable network formation; in particular, they confirm a recent suggestion that impurities in the liquid crystal play a crucial role in controlling interface-driven particle dynamics [6].

2. Experimental details

The particles used consisted of PMMA cores loaded with the fluorescent dye NBD [7] and sterically stabilized by chemically grafted poly-12-hydroxystearic acid 'hairs' [8]. The particle size was determined by static light scattering; we used particles with diameter σ between 0.6 and 1.2 μm. The liquid crystal, 5CB, was used as purchased from Merck, and had $T_{IN} = 35.3\,°C$. The particles were initially dispersed in hexane or heptane, dried in a vacuum oven ($\approx 10^{-2}$ mbar) at 45 °C for up to 72 h, and then added to 5CB in the isotropic phase to make up mixtures with weight fraction $\phi_w = 0.05$–0.15 of particles. The mixture was sonicated and homogenized extensively by shaking and/or tumbling at 45 °C to disperse the particles in the isotropic LC. Samples were placed between a microscope slide and a cover slip held apart by ~0.1 mm spacers for observation in a Nikon TE300 inverted microscope equipped with a Biorad Radiance 2000 laser scanning confocal head. In the nematic phase, the birefringent LC domains scattered light strongly, so that confocal microscopy was necessary for imaging the internal structure. The highest resolution images, capable of resolving single particles, were obtained using a $100\times$ oil-immersion objective (numerical aperture = 1.4); the excitation wavelength was 488 nm. Observation between cross polarizers and in-transmitted light was also possible in the same microscope. Confocal microscopy of a freshly prepared CLC mixture at 45 °C showed well-dispersed single particles, or occasionally doublets or triples, undergoing Brownian motion, figure 1(a).

Some samples were quenched to room temperature and then observed in the microscope. In these cases, we estimate that the average quench rate to be $\dot{T} \approx 1$ K min^{-1}. In other cases, samples were cooled at a fixed rate and observed on a Linkam LTS350 temperature stage. A range of cooling rates, 0.1 K min$^{-1} \lesssim \dot{T} \lesssim 30$ K min^{-1}, could be studied using this set up.

3. Network formation

Micrographs for the 'cellular network' structure of the soft solids formed when mixtures of PMMA particles and thermotropic liquid crystals are cooled have been shown before (for 5CB [3] and MBBA [2]). Here we concentrate on kinetics. The network formation process in a sample with $\phi_w = 0.10$ of $\sigma = 0.780$ μm particles cooled at ~1 K min^{-1} through the IN transition is shown in figure 1 (see also the on-line movie).

After passing through T_{IN}, circular nematic domains began to nucleate (black droplets in figure 1(b), their nematic nature was confirmed by observation between crossed polarizers) and grow, figure 1(c). Particles expelled from these regions accumulated at, and were pushed along by, the IN interface of growing nematic droplets. Soon we observed a texture consisting of nematic domains separated by boundaries consisting of particles. Initially nematic domains could coalesce by the breakage of thin particulate boundaries, figures 1(d)–(f), giving rise to more elongated domains. Soon, however, the particle packing at the boundaries compacted and the gross domain structure became fixed, figures 1(g)–(i), until all motions ceased. The gross features of this sequence of events are essentially generic for all particle sizes, concentrations
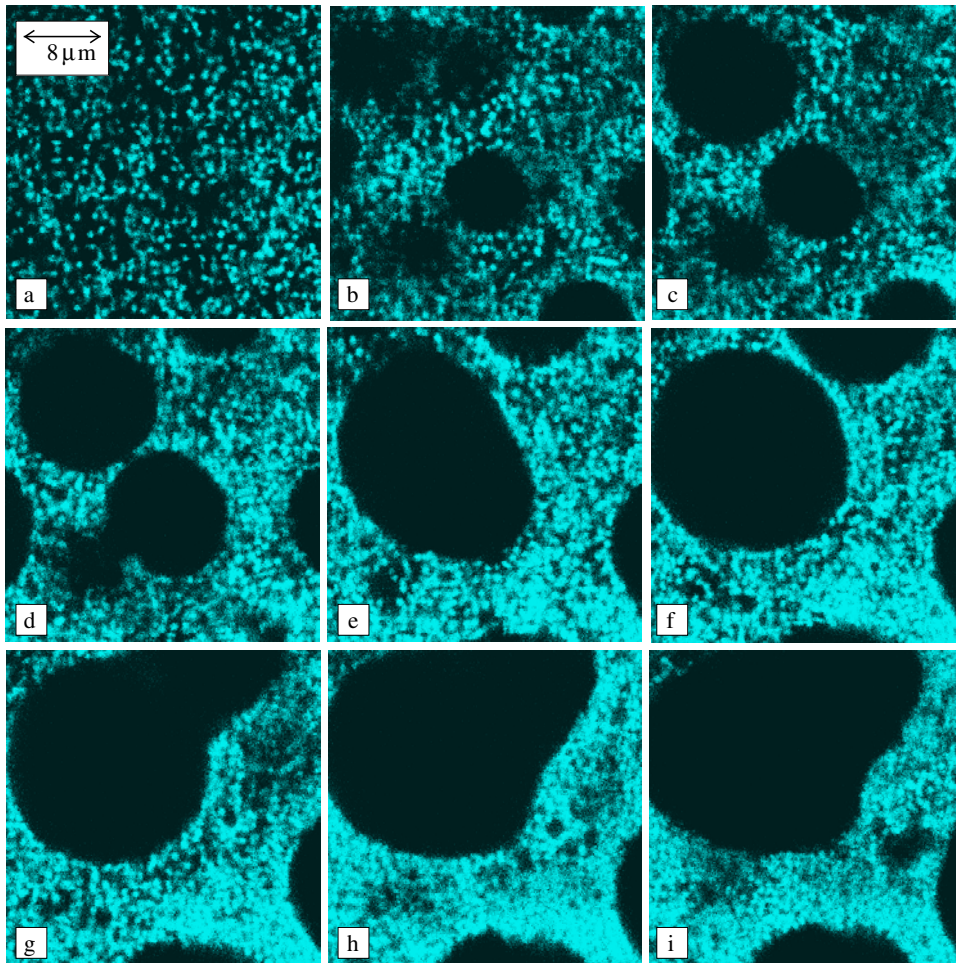
Figure 1. Network formation in a sample of 5CB with $\phi_w = 0.10$ of $\sigma = 0.780$ μm PMMA particles cooled at ~ 1 K min^{-1} through T_{IN}. (a) Just above T_{IN}, (b) $t = 0$ just below T_{IN}, (c) $t = 1.2$ s, (d) 2.4 s, (e) 3.6 s, (f) 7.2 s, (g) 9.6 s, (h) 16.8 s and (i) 33.6 s. (This sequence of images has been shown before in a brief conference report [9].)

M A MOV movie of this figure is available from stacks.iop.org/JPhysCM/16/S1901

(This figure is in colour only in the electronic version)

and cooling rates we have studied. Note also that at all except the slowest cooling rates (see figure 6(a)), the characteristic network size was substantially smaller than the sample thickness, so our results are indicative of bulk behaviour.

4. Impurities and interface velocity

It is clear from the image sequence in figure 1 (cf also the on-line movie) that basic to the process of network formation is the ability of an IN interface to 'sweep along' particles that it passes. West *et al* [10] have recently discussed this process. By considering the balance of hydrodynamic, elastic and surface tension forces on a particle situated at a moving IN interface,
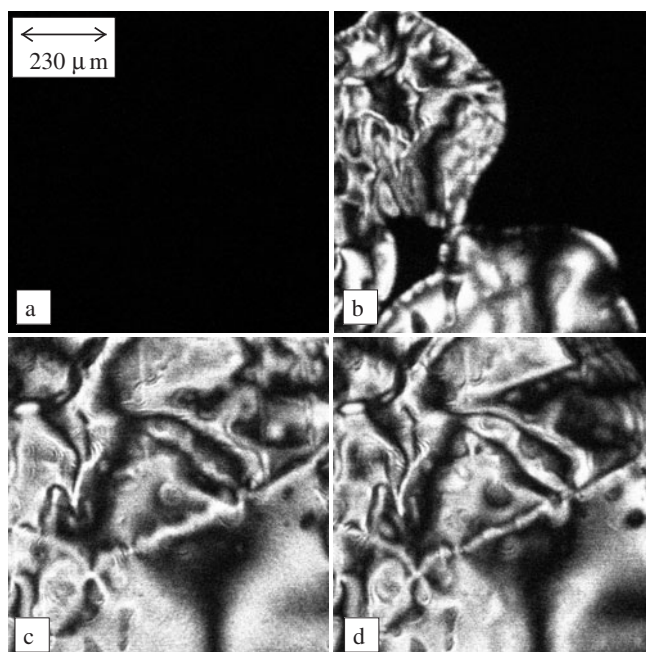
Figure 2. Formation of nematic phase in pure 5CB observed between crossed polarizers. Here, and in all subsequent image sequences, the time t is measured from the moment T_{IN} was reached: $t =$ (a) 0 s, (b) 1 s, (c) 2 s and (d) 3 s. Cooling rate $= 0.1$ K min^{-1}.

they showed that within a broad range of particle sizes ($\sim$10 nm–1 μm), the IN interface must move slower than $v_{crit} \sim W/\sqrt{K\rho}$ for it to sweep particles along. Here W is the anchoring energy of the liquid crystal on the particles, K is a representative Frank elastic constant and ρ the particle density. Using typical parameters, West *et al* found $v_{crit} \sim 1$ mm s^{-1} for their system, a value which was supported by experimental observation. Using typical parameters for 5CB and PMMA particles ($K \sim 10^{-11}$ J m^{-1}, $W \sim 10^{-6}$–10^{-7} J m^{-2} and $\rho \approx 1180$ kg m^{-3}), we expect that $v_{crit} \sim 1$ mm s^{-1}–1 cm s^{-1} for our CLC mixture.

Sequences of images such as those shown in figure 1 enable us to estimate the interfacial speed in our samples. This was found to increase with cooling rate, $\dot{T}$. Within the range of cooling rates we studied the interfacial speeds were in the range $v_{IN} \approx 1$–10 μm s^{-1}. In other words, $v_{IN} \ll v_{crit}$.

Interestingly, when we imaged the nucleation and growth of nematic domains in pure 5CB, figure 2, we found that the IN interfacial speed was far in excess of what was measurable with our time resolution, so that we can only estimate a lower bound: $v_{IN}^{pure} \gg 100$ μm s^{-1}, which is much greater than the range of v_{IN} we observed in CLC mixtures. In fact, theory predicts [11] that $v_{IN}^{pure} \sim 1$ cm s$^{-1} \gtrsim v_{crit}$. It is therefore marginal whether particle transport by IN interfaces (and therefore network formation) can occur in pure 5CB. The question therefore arises: what is responsible for the slowing down of the IN interface speed in our system?

Inspired initially by calorimetric evidence, we have previously suggested [6] that the slowing down of IN interfacial movement is due to the presence of alkane impurities. The 'hairs' on the surface of our PMMA particles could act as 'traps' for molecules of the alkanes in which the particles were dispersed before drying [12]. These solvent molecules could subsequently be liberated when the particles are dispersed in 5CB. The presence of short-
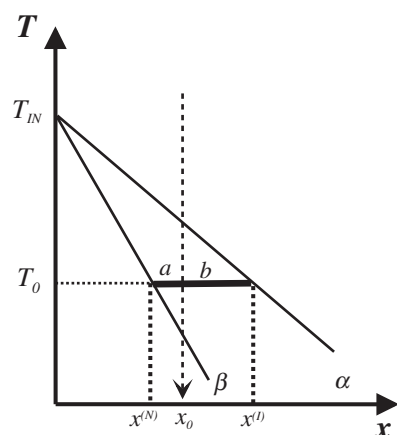
Figure 3. Schematic phase diagram of 5CB with small amounts (mole fraction x) of short-chain alkanes. At $x = 0$, 5CB undergoes an IN transition at $T_{\rm IN}$. A biphasic region opens up, between lines α and β, at finite values of x. The onset of the IN transition temperature now tracks the line α, $T_{\rm IN}(x)$. A 'quench path' at average composition x_0 is shown (dotted arrow). The equilibrium state of a mixture with average composition x_0 at temperature T_0 can be read off the thick horizontal 'tie line' (of total length $a + b$): a fraction $b/(a + b)$ of nematic with composition $x^{(N)}$ coexists with a fraction $a/(a + b)$ of isotropic with composition $x^{(I)}$.

chain alkanes lowers $T_{\rm IN}$ and introduces a biphasic region in the phase diagram in which isotropic (alkane-rich) and nematic (alkane-poor) phases coexist over a temperature range of order 1 K [13], figure 3. The presence of a finite biphasic region in the phase diagram should broaden the width of the peak in differential scanning calorimetry compared to the case of pure 5CB—which was exactly what was observed [6].

Figure 4 shows the early-stage nucleation and growth of nematic domains in a 2% mole fraction hexane-5CB mixture[1]. The interfacial speed measured from this image sequence, $v_{\rm IN} \approx 5 \ \mu{\rm m \ s}^{-1}$, is within the range of speeds we find from samples with particles. Figure 5 shows an image sequence taken from a CLC mixture under identical conditions to that shown in figure 4 for 5CB + hexane—the similarity between the image sequences in figures 4 and 5, and their difference with figure 2, is striking.

That hexane should slow down the movement of IN interfaces can be understood as follows. In a pure liquid crystal, the whole of the system wants to become nematic at all $T < T_{\rm IN}$. The undercooling itself, $\tau = T_{\rm IN} - T$, rather than the quench rate, $\dot{T} \equiv {\rm d}\tau/{\rm d}t$, controls the speed of the interface between growing nematic droplets and the surrounding (shrinking) isotropic material, $v_{\rm IN} = v_{\rm IN}(\tau)$ [11]. Even a very small degree of undercooling will give $v_{\rm IN} \gg v_{\rm crit}$.

On the other hand, at the cooling rates we can access ($\sim$0.1–30 K min^{-1}), our system with impurities spends macroscopic time ($\lesssim$1 s to $\gtrsim$10 min) in a biphasic region of width of the order of a few kelvin. During this time, we can assume the system to be in quasi-thermodynamic equilibrium at any one instance. At any one temperature within the biphasic region, the state of the system is a fixed amount of nematic droplets coexisting with isotropic phase. The nematic fraction, f, is determined by the 'lever rule', figure 3, and grows linearly with the undercooling, $f \propto \tau$. If the temperature is fixed, ${\rm d}\tau/{\rm d}t = 0$, then f is fixed and the IN interfaces will be stationary[2]. This, we suggest, is the mechanism whereby the existence of a biphasic region

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[1] A $\phi_{\rm w} = 0.13$ mixture prepared with $\sigma = 480$ nm particles should carry enough hexane in the space between their PHSA 'hairs' [12] to release 2% mol fraction of hexane into the 5CB.

[2] This statement, of course, neglects the (slower) processes of droplet coalescence and Ostwald ripening.
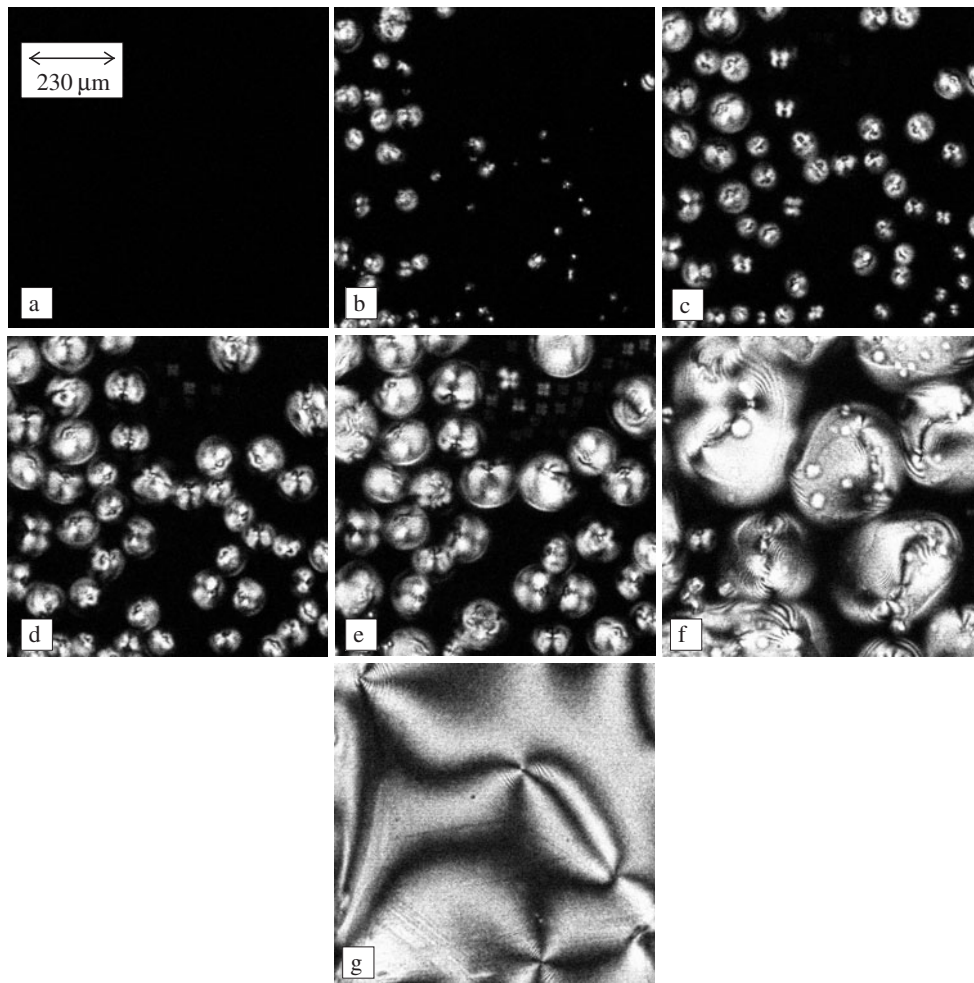
Figure 4. Formation and growth of nematic domains in a 2% mol fraction hexane in 5CB mixture observed between crossed polarizers. Time $t =$ (a) 0 s, (b) 15 s, (c) 30 s, (d) 45 s, (e) 1 min, (f) 2 min and (g) 3 min. Cooling rate $= 0.1$ K min^{-1}.

slows down the movement of IN interfaces. Since v_{IN} scales as df/dt, the interfacial speed now tracks the cooling rate $d\tau/dt$ and is a controllable experimental parameter.

5. Cooling rate and hierarchical structure

The structure of the particle network we obtain (see particularly figures 4 and 5 in [2]) is that of an 'open-cell foam' [14]. We have found that the foam structure is dependent on the cooling rate, figure 6. Most obviously, a higher cooling rate gives rise to smaller cells. It also leads to a 'hierarchical' structure—there are 'cells within cells'. The soft solid obtained at high cooling rates is therefore a 'hierarchical cellular material' [15]. The 'hierarchical order' n—the number of levels of 'cells within cells'—increases with cooling rate; the structure in figure 6(b) has $n \gtrsim 4$.
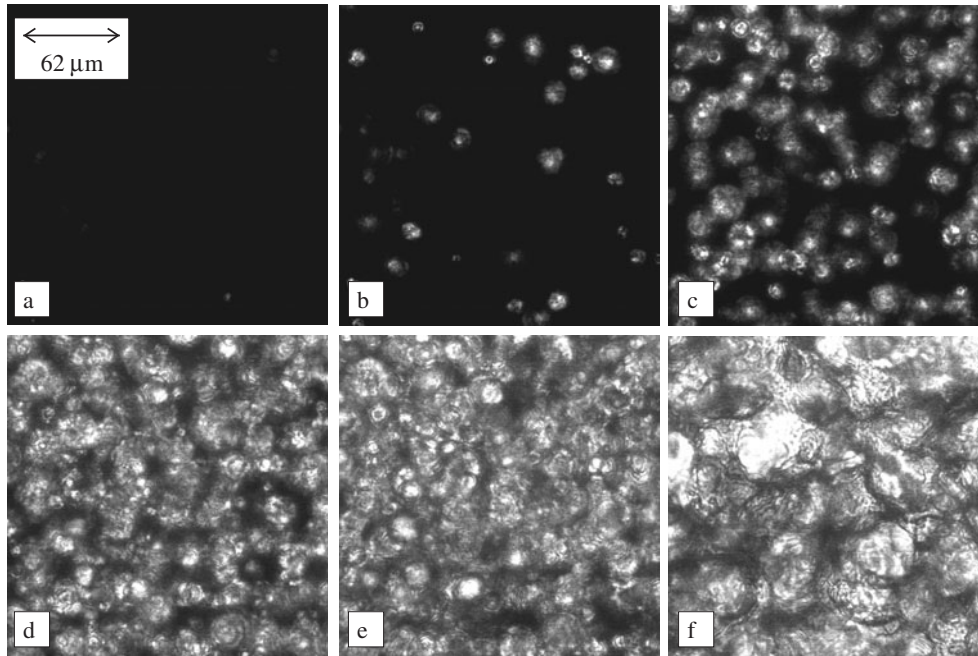
Figure 5. Formation and growth of nematic domains in a CLC mixture taken under identical conditions to the images shown in figure 4. Time $t =$ (a) 0 s, (b) 15 s, (c) 30 s, (d) 45 s, (e) 1 min and (f) 4 min. $\phi_{\mathrm{w}} = 0.05$, $\sigma = 1.06$ μm, and cooling rate $= 0.1$ K s^{-1}.

The small-strain shear modulus, G, of our 'hierarchical foam' is given by [14, 15]

$$\frac{G}{E_0} = k^n \left(\frac{\rho}{\rho_0} \right)^2, \tag{1}$$

where E_0 and ρ_0 are the Young's modulus and density of the densely packed particulate boundaries, and ρ is the average density of the material as a whole, so that $\rho/\rho_0 \approx \phi_{\mathrm{w}}$. The empirical constant k is found to be $\approx 3/8$ (see figure 5.11 in [14]), while n is the hierarchical order [15]. Thus we expect the shear modulus to decrease with cooling rate—a prediction that can be tested by direct rheological measurements[3].

6. Discussion and conclusions

We have studied by time-resolved confocal microscopy sterically stabilized PMMA particles dispersed in the nematogen 5CB. As the mixture is cooled below the IN transition, particles expelled from growing nematic domains are transported and concentrated into boundary regions to form a network. The rate of nematic domain growth was found to be much slower than that in pure 5CB. We provide experimental evidence that this slowing down is due to the

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[3] Interpreting our structures as 'foams' is not without difficulty. First, Anderson and Terentjev [16], found $G \propto \phi_{\mathrm{w}}$ rather than $\propto \phi_{\mathrm{w}}^2$ as predicted by equation (1). However, they did not control the cooling rate, and E_0 may be ϕ_{w}-dependent. Secondly, an order-of-magnitude fit to measured values requires $E_0 \sim 10^7$ Pa. This appears high, although not necessarily inconsistent with the particles being at or close to random-close packing (rcp), figure 1, where G formally diverges [17]. In practice, the mechanical properties of the stabilizing 'hairs' and, ultimately, of bulk PMMA take over. Note that $G_{\mathrm{PMMA}} \sim 10^9$ Pa, so that E_0 can in principle be as high as this. Recent rheological measurements of colloidal glasses of PMMA particles with $\sigma = 0.363$ μm gave $G \sim 10^3$ Pa at $\phi = 0.96\phi_{\mathrm{rcp}}$ [18].

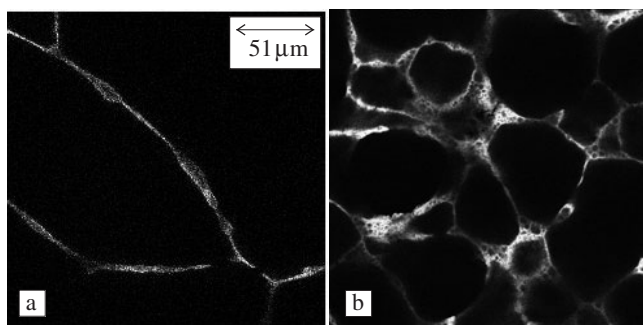**Figure 6.** The network formed in a CLC mixture with $\phi_w = 0.05$ of $\sigma = 0.61$ μm particles at two different cooling rates: (a) 0.2 K min^{-1}, and (b) 30 K min^{-1}. In (b) the 'cell's are smaller and the structure is visibly 'hierarchical'—there are 'cells within cells'.

presence of hexane impurities opening up a biphasic region in the phase diagram. The network structure was found to be cooling-rate dependent. At high cooling rates, a hierarchical cellular structure was formed.

A number of important questions remain. While we have given a qualitative picture of the process of network formation, no quantitative theory of the kinetics yet exists. Moreover, the width of the biphasic region in our samples (as indicated by calorimetry [6]) is somewhat wider than what can be expected from literature phase diagrams of 5CB/alkane mixtures [13]. Vollmer *et al* [6] have suggested that the particles may be responsible (e.g. due to preferential wetting by the alkane).

Finally, it is not understood what holds the particle network together once it is formed. It has been suggested that the force responsible is an isotropic–nematic pressure due to the presence of isotropic LCs in the particulate network. Nuclear magnetic resonance measurements do indeed demonstrate that a significant fraction of the LCs is isotropic after network formation [6], but the origins of this isotropic fraction remains unclear.

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