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Robust liquid crystal droplets

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The preparation and properties of cyanobiphenyl liquid crystal droplets encapsulated by the polymerizable lecithin 1,2-bis(10,12-tricosadiynoyl)-*sn*-glyero-3-phosphocholine (DC$_{8,9}$PC) are described. Under a wide variety of preparation conditions the droplets obtain a diameter of approximately 10 µm. These droplets are stable for periods of over one year at room temperature. Furthermore, they are stable upon temperature cycling between the nematic and isotropic phases and between the smectic A to nematic to isotropic phase transitions.

1. Introduction

The studies of thermotropic liquid crystals and of emulsions have been active areas of research for the past several decades. The reason for such interest is two-fold. First, there are great financial rewards to be made in the manufacture and sale of devices and products utilizing these basic sciences, and the associated technological problems are interesting and challenging. Second, there are many basic scientific issues involving these materials which need to be addressed. This development has largely been as two parallel fields with relatively little cross-fertilization. Notable early exceptions are the works by Lavrentovich [1] and Terentjev [2]. However, there has been increased interest in this area in recent years [3–6].

Several developments have led to a cross-fertilization between these two fields. In particular, the invention of polymer dispersed liquid crystals (PDLCs) and their use as displays [7, 8] has prompted a search for a better fundamental understanding of liquid crystals in confined geometries [9–11]. Such geometries are characterized by small aggregates or droplets, which may or may not be spherical, an orientationally ordered inner structure to the droplet, and surface–bulk energy interactions of comparable magnitude. Thus, the behaviour of these aggregates is very different from that encountered in more traditional colloids or bulk liquid crystals. The possibilities for technological uses of liquid crystalline emulsions have been discussed by Terentjev [2], and others can be imagined. A further possibility arising from this work is the formulation of controlled size liquid crystalline spheres.

The growth of this field has also been motivated by basic scientific concerns. These include the fact that such droplets are, in the absence of a permanent membrane, stabilized by topological defects, and under the same conditions cease to be emulsions above the nematic–isotropic phase transition temperature. The orientational order within the droplet is controlled by (i) the orientational elastic properties of the liquid crystal and (ii) the surface tension at the interface between the liquid crystal and the bulk isotropic liquid. Also, in a very simple way these dispersions may help us to understand some of the properties of biological systems [12]. The droplets in these dispersions are of size comparable to biological cells, and have a well defined interior and exterior. However, there is no energy flux, nor could growth and division of these aggregates occur. There is still much work to be done in this last area.

Recently, Terentjev [2] has studied liquid crystal macroemulsions. He found that such macroemulsions, made of the liquid crystal methoxybenzylidene-butilaniline (MBBA) and the surfactant cetyltrimethylammonium bromide (CTAB) in glycerine–water, were stable in the nematic phase. However, touching droplets coalesced within a few seconds after the temperature of the sample exceeded the nematic–isotropic phase transition temperature of the droplets. He demonstrated theoretically that this was due to the nematic curvature elastic energy and that such structures are topologically stabilized by defects within the nematic droplets.

Our work now extends these experiments in several directions. First, the liquid crystal MBBA, which is very weakly polar, was used in the experiments by Terentjev: the present experiments were performed using the

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much more strongly polar 4-cyano-4′-*n*-alkylbiphenyls. Secondly, more robust droplets, that retain their fundamental shape and do not coalesce upon taking the temperature above the nematic clearing point, were developed by using as the surfactant the polymerizable lecithin 1,2-bis(10,12-tricosadiynoy1)-*sn*-glyero-3-phosphocholine ($DC_{8,9}PC$). We find that the resulting droplets are thermally and temporally stable and have a fairly narrow size distribution. Observation under a polarizing microscope indicates that for a variety of cyanobiphenyls and different phases (isotropic, nematic, smectic, and crystalline) the droplets have a fairly narrow distribution of diameters with a most probable size near 10 μm. There were however, some much larger spheres that were generally several times larger than the mean droplet size.

2. Theory

The basic theory of liquid crystal droplets in emulsions has been discussed previously by Lavrentovich [1], Terentjev [2] and Lubensky *et al.* [4]. This section will review and summarize their results. The equilibrium state of a liquid crystal droplet (ignoring the very small gravitational effects) is the minimum of the free energy functional F, which is decomposed into a volume part and a surface part.

$$\begin{aligned} F &= F_{\text{volume}} + F_{\text{surface}} \\ &= \int_{\text{vol}} F_{\text{volume}}\, \mathrm{d}V + \int_{\text{surface}} F_{\text{surface}}\, \mathrm{d}S \end{aligned} \qquad (1)$$

where F_{volume} is the free energy per unit volume, and F_{surface} is the surface energy per unit area. This later term is modelled as the surface tension which has an isotropic part σ, and an anisotropic part W_{A}. Because we are using lecithin as our surfactant, $\sigma \approx 10^{-3}$–$10^{-4}\ \text{J m}^{-2}$ [2]. The angular dependent part of the surface tension W_{A}, also known as the anchoring energy, is much smaller than σ, obtaining the following typical values: $W_{\text{A}} \approx 10^{-5}$–$10^{-6}\ \text{J m}^{-2}$. Thus,

$$F_{\text{surface}} = F_{\text{S}} \simeq 4\pi(\sigma r^2 + W_{\text{A}} r^2) \approx 4\pi\sigma r^2 \qquad (2)$$

where r is the droplet radius. The important physics is that the surface energy is dominated by the surface tension and is proportional to r^2.

The volume free energy has ‘normal’ thermodynamic components and, more importantly in the present context, a contribution from the curvature elasticity of the enclosed nematic liquid crystal. We will assume that the ‘normal’ contribution is the same in all liquid crystalline phases and much smaller than the contributions due to the curvature elasticity of the liquid crystal. The actual equation which describes the elastic energy contribution to a liquid crystal droplet is rather complex, involving the splay, twist, bend, and saddle-splay elastic coefficients [4]. In order to obtain the basic physics the differences between these coefficients is often ignored and the saddle-splay elastic coefficient is set equal to zero. Thus to a good approximation,

$$F_{\text{volume}} = F_{\text{V}} \approx Kr \qquad (3)$$

where the elastic coefficients have been replaced by a single, typical Frank elastic coefficient K, which has a value of order $K \approx 10^{-11}$ N, and all geometric factors have been set equal to unity. We note in passing that for a nematic droplet containing a radial hedgehog defect (which essentially all of the observed drops contain) the exact expression for the Frank elastic energy of a sphere of radius a is $2\pi K_1 a$, where K_1 is the splay elastic coefficient. Thus, since the geometric factors are essentially the same, we note that for small droplets the bulk elastic energy dominates. For larger droplets, however, the surface energy dominates over the bulk elastic energy.

The shape of the droplet and orientation of the director within a droplet is dictated by two length scales. The positive surface tension of the liquid crystal favours spherical droplets in the absence of distortions caused by the elastic properties of the liquid crystal, through its director, within the droplet. A characteristic length describing this relationship may be formed by taking the ratio of the Frank elastic coefficient to the surface tension. The resulting length may be defined as $r_\sigma = K/\sigma \approx 10^{-7}$–$10^{-8}$ m in the systems under consideration. Thus r_σ ranges from 0.01 to 0.1 μm. Since this is very much smaller than the typical radius of a droplet, roughly 5 μm, one expects the droplets to be spherical–undistorted by the nematic director. This is in fact, experimentally observed. The second length scale determines the length over which one may assume that the director is uniformly aligned. This length scale is given by the ratio of the Frank elastic coefficient to the anchoring energy, that is $r_{\text{w}} = K/W_{\text{A}}$. For the liquid crystals used in this study this may be estimated at 1–10 μm. One expects small droplets, those with radius $a \ll r_{\text{w}}$, to have a more-or-less uniform director orientation at the energy cost of a very small excess surface energy. In contrast, one should expect large drops, $a \gg r_{\text{w}}$, to have the nematic molecules aligned so as to satisfy the local boundary conditions enforced by the surfactant shell. Thus, large drops should contain defects in equilibrium. The droplets studied in this experiment appear to be large, indicating that W_{A} may be larger than the estimates given above.

3. Experimental

Several techniques were utilized to make the emulsions. They all yield essentially the same droplet size and size distribution. Thus, the following ‘recipe’ is not critical and the amounts of the various constituents may be varied as necessary. The standard procedure was to mix, in a vycor glass crucible, approximately 3.5 g of deionized water, and 1.5 g of glycerine. These were then mixed by adding a standard magnetic stirring bar and stirring for a few moments. Approximately 0.2 g of the $DC_{8,9}PC$, obtained from Avanti Polar Lipids, Alabaster, A1., USA, was added to this fluid mixture and the stirring continued. Lastly 0.05–0.2 g of the desired liquid crystal, all obtained from E. Merck Ltd, UK, was added to the licithin–glycerine–water mixture. The crucible was covered by a quartz plate. The crucible and plate were placed on a heated magnetic stirrer which was under a Fisher Scientific FB-UVLS-150 UV lamp which contains two 15 W UV lamps, operating at 365 and 254 nm. The sample was vigorously stirred and heated (if necessary) so that it was in the appropriate bulk liquid crystalline phase as it polymerized under the UV lamp. This stirring and polymerization continued for 12 to 48 h. From time to time a small amount of the sample was removed and examined under the polarizing microscope. Generally the polymerization was complete by approximately 24 h, but longer times were generally allowed to insure this process had gone to completion. If the sample dried out, more deionized water was added to the crucible.

The resulting samples were yellow to red in appearance and could be easily concentrated in a few hours by centrifugation at accelerations of about 500–600 g. The droplets were stable, as observations before and after centrifugation (and redilution) yielded similar size distributions. The centrifuged samples contained two or three distinct layers. When too much liquid crystal was used it collected as the top layer in the centrifuge tube. Examination of these components indicated that it was a fairly pure bulk liquid crystal. The middle layer, when there was excess liquid crystal, or the top layer when there were only two layers in the tube, consisted of polymerized droplets. The bottom layer was a clear liquid that had very few liquid crystal droplets and appeared to be water and glycerine. This conjecture was verified by heating the samples in the centrifuge and by adding more water. Both reduce the viscosity of the liquid and result in faster separations. Microscopic observation verified that there were very few liquid crystal droplets in the clear fluid. The samples are stable for at least one year at room temperature and are also stable upon heating into the isotropic phase and returning to the nematic phase. The droplets are also stable when a sample is allowed to go into the crystalline phase. Some larger droplets of liquid crystal that could easily coalesce in the nematic phase were on occasion seen in the microscope.

The droplets, both before and after concentration, were characterized by observation of the samples under a polarizing microscope. The phase transition temperatures of the droplets and of bulk samples of the liquid crystals were determined using a heating stage on the polarizing microscope. The pictures were taken using a Javelin CCD camera, and transferred by tape to a computer where the individual frames were captured and printed for further analysis and examination.

4. Results

The important results of this study may be briefly summarized. First, essentially spherical liquid crystalline droplets with a polymer coating, of diameter $\approx 10\,\mu m$ and smaller, that are structurally stable upon crystallization and heating into the isotropic phase, have been prepared using several different cyanobiphenyl liquid crystals. Second, for a given liquid crystal the most apparent droplet size, determined by polarizing microscopy, does not depend on the phase in which the sample is polymerized. Third, the nematic-to-isotropic phase transition temperature is lower in all emulsions studied than it is in the bulk. However, the difference between these two temperatures depends on the liquid crystal and the phase in which it is polymerized. Fourth, these droplets which have a polymerized lecithin coating almost always contain radial hedgehog defects which mean that the droplets are large in the sense that $r > r_w = K/W_A$. Even the smallest easily discernible droplets appeared to satisfy this criterion. Each of these results will be discussed in greater detail in the following paragraphs.

The droplets made in this study are thermodynamically stable. This was easily verified by heating a sample of such droplets into the isotropic phase and then cooling back to the nematic phase. Figure 1 is a photomicrograph of a K15 (5CB) sample in the nematic phase; figure 2 shows the same sample in the isotropic phase. Note that the same droplets are visible in both the nematic (under crossed polarizers) and the isotropic phase (under slightly uncrossed polarizers) and that no aggregation has occurred. The size of the droplets and a visual idea of their size distribution may also be obtained from this figure. Similar behaviour was observed upon letting this sample cool below 24°C, the bulk crystal-to-nematic phase transition temperature, and then allowing the sample to return to the nematic phase. Figure 3 shows a similar figure for K24 (8CB). This material also exhibits a smectic A phase. These droplets are robust upon cooling in to the smectic A phase, and do not disintegrate on heating into the isotropic phase. The size of the droplets and their apparent distribution is very similar to that observed in 5CB. Similar results, as detailed in the table were obtained for other liquid crystals.

The second important result is that the apparent size of the droplets does not depend on the liquid crystal phase present during the stirring and polymerization

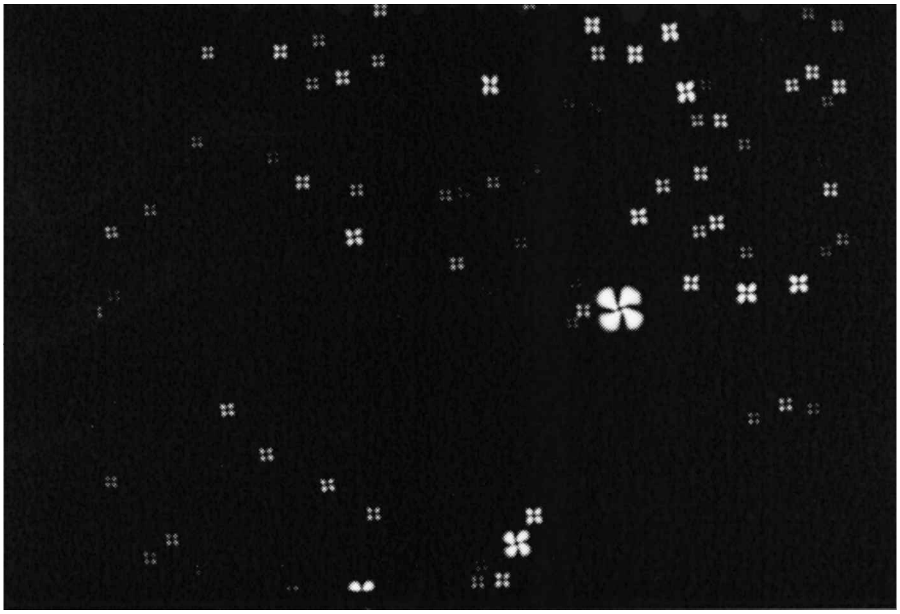

Figure 1. Photomicrograph of K15 (5CB) droplets in which the liquid crystal is in the nematic phase.

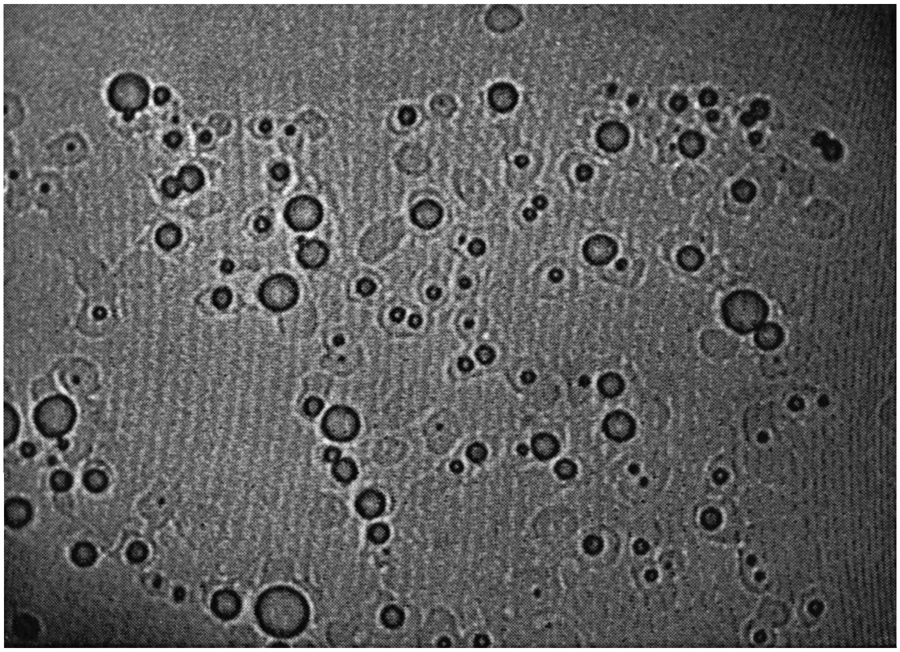

Figure 2. Photomicrograph of K15 (5CB) droplets in which the liquid crystal is in the isotropic phase.

Table. Summary of liquid crystal transition temperatures: I = isotropic, N = nematic.

Liquid crystal	T_{NI}(bulk)/°C	T_{NI}(droplets)/°C	Phase polymerized	Mean diameter (μm)
K15	35.32	32.3	N	5
K18	29.11	27.65	N	6
K18	29.11	25.3	I	6
K24	40.55	37.35	N	7
K24	$T_{NA} \approx 33.6$	$T_{NA} \approx 30.5$	N	7
E7[a]	—	—	N	6–7

[a] E7 is a mixture of various liquid crystals and has a very wide nematic temperature range.

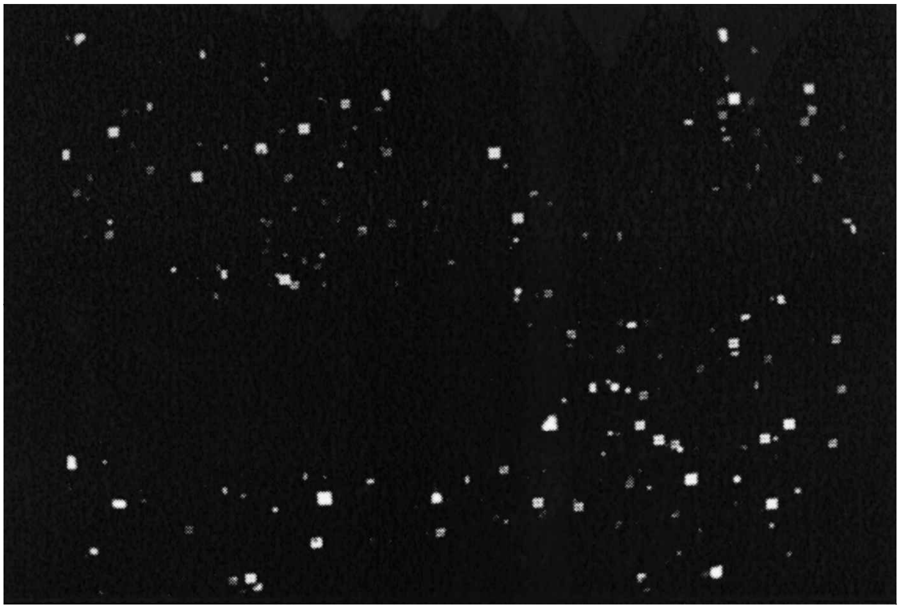

Figure 3. Photomicrograph of K24 (8CB) droplets in the nematic phase.

process. This was demonstrated by preparing emulsions composed of K18 (6CB) at two different temperatures. The first was prepared at room temperature (approximately 22°C). At this temperature the sample, both bulk and in the form of droplets, is in the nematic phase. A second sample was prepared similarly and maintained at a temperature of 47 ± 2°C. The bulk isotropic-to-nematic phase transition of the same material as was used in the droplets was 29.11°C, corresponding to the liquid crystal being well into the isotropic phase. The mean size of the droplets is very similar in both preparation. Figure 4 is a photomicrograph of the sample prepared in the isotropic phase. This also indicates that the size of the droplets is dominated by entropic and surface tension effects, not liquid crystal elasticity. One of the more interesting observations obtained from these experiments is that the difference beween the temperature of the isotropic-to-nematic phase transition in the bulk and in the emulsions depends on both the liquid crystal utilized in the droplets and the phase of the liquid crystal during polymerization. In all cases the transition temperature of the liquid crystal in the droplets was lower than that obtained in the bulk. This is indicative of the disordering effect of the hedgehog defect. However, in

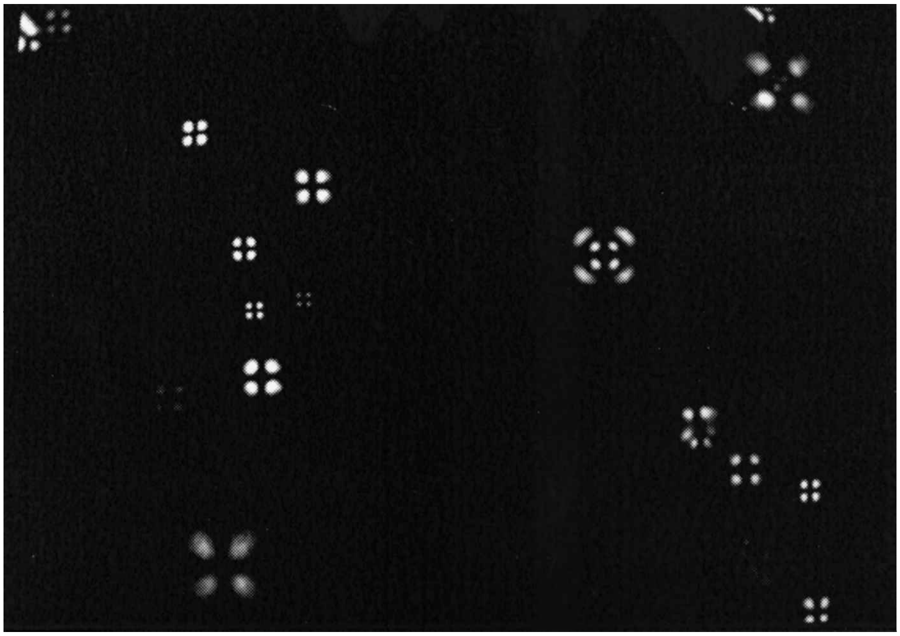

Figure 4. Photomicrograph at maximum magnification of droplets containing K18 at room temperature.

light of the very similar sizes of the droplets there must be a further disordering effect related to the relative length of the alkyl chains in the liquid crystal molecule versus those in the lecithin molecule. Since the cyano group at one end of the molecule is polar there may be a tendency for this part of the molecule to approach the head group of the lecithin. The table summarizes these results; it lists all liquid crystals used in this study, the measured transition temperatures in the bulk and of the droplets, the phase in which the sample was polymerized, and the approximate size of the droplets as determined by photomicrograph measurements.

The final result is that in spite of the variation in transition temperature depression with different liquid crystals in the nematic phase, almost all droplets appear in the photomicrograph as circles with a dark cross parallel to the directions of the two mutually perpendicular polarizers, and a light cross rotated 45° with respect to the dark cross—the polarizing micrograph signature of a radial hedgehog defect. On occasion a non-circular droplet is observed. In these cases it is clear that some droplets have been squeezed; this results in distorted crosses which are not centered on the circle which represents the planar projection of the spherical droplet. This phenomena has also been observed by Terentjev.

5. Conclusions

The droplets studied are different from those often studied in the past, since the surfactant coating on these droplets is polymerized rather than simply self-organized. Thus although their shape is dominated by surface tension just as in the self-organized case, and surface anchoring is still important, they are not just topologically stabilized. This means the droplets contain an equilibrium defect, most typically a radial hedgehog defect, which leads to added stability in the nematic phase; but these droplets are still stable in the isotropic phase where there are no topological defects. As noted by Poulin [3] and others [1] the existence of defects influences both the individual properties of a droplet and their collective behaviour. Thus the existence of thermally robust, essentially uniform, droplets which contain defects, may help further exploration of the cooperative behaviour of such systems.

There are many potential applications of such droplets. One that immediately comes to mind would be the formation of a paint of such droplets and the manufacture of PDLCs by painting them onto the appropriate substrate. A preliminary experiment was performed and there was essentially no visible change in the amount of light transmitted through the sample when viewed under a microscope between crossed polarizers. Further experiments to explore the electro-optic properties of these mixtures are planned.

Other applications include the use of these droplets as a temperature dependent switch, which is cloudy at low temperatures and clear at high temperatures. The possibilities of using other types of polymerizable coatings and attaching various molecules to the coating are extensive. Lastly the placement of such droplets in various other liquid crystalline matrices could lead to interesting technological developments as well as fundamental studies of emulsion droplets in liquid crystals. Since the phase transition temperatures of the droplets are reduced from those of the bulk it may be possible to have equilibrium mixed phase systems.

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