

HIGH TEMPERATURE FORMATION OF POLYMER – DISPERSED HYDROGEN BONDED LIQUID CRYSTALS

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High temperature formation of polymer-dispersed liquid crystals using the mixture, photo-pre-polymer NOA65/ 4-(octyloxy)benzoic acid/surfactant, was used. By polarization micro-textural analysis, we have observed, in the pre-polymer/liquid crystal mixture, droplets, which seems to be bifocal. These bifocal droplets indicate a twist of the optical axis as a result of temperature variation, and are fixed by photo-polymerization. A mechanism for the possible chiralization in the bifocal drops is suggested.

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1. Introduction

Polymer-dispersed liquid crystals (PDLCs) [1,2] (Fig. 1), are a relatively new class of materials that hold promise for many applications ranging from projection displays to information carriers. These materials (simply a combined application of polymers and liquid crystals (LC)) are the focus of extensive research in optoelectronics. PDLCs consist of LC droplets that are dispersed in a polymer matrix. The resulting material is a sort of “swiss cheese” polymer with LC droplets filling in the holes. These tiny droplets (a few microns across for practical applications) are responsible for the unique behaviour of the material. By changing the orientation of the LC molecules with an electric field, it is possible to vary the intensity and/or polarization of the transmitted or reflected light through the PDLCs. They have been prepared in several different ways including encapsulation (emulsification) and phase separation. The latter process has become the primary method of manufacture. Each method produces PDLCs with different properties and characteristics. Among the factors influencing the properties of the PDLC material are the size and morphology (shape) of the droplets, the type of polymer and LC used, and the cooling and heating rates during formation. The relationship between the method of formation and these factors is examined below.



Fig. 1. Change of the orientation of LC molecules in an electric field [1].

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2. Materials and methods

Materials: Photopolymerizable mixture Norland Optical Adhesive NOA 65, manufactured by Norland Products, Inc., New Brunswick, N.J., contained 3,3-Bis-hydroxymethyl-4,4,4-trimercapto-butan-1-ol, 2,2-Bis-allyloxymethyl-butan-1-ol and 3-Isocyanato-1-isocyanatomethyl-3,5,5-trimethyl-cyclohexane [10]. Liquid crystal 4-(octyloxy)benzoic acid was synthesized by Laboratoire de Physique des Corps Solides, Universite Paris Sud, Centre d'Orsay, France – Fig. 2.

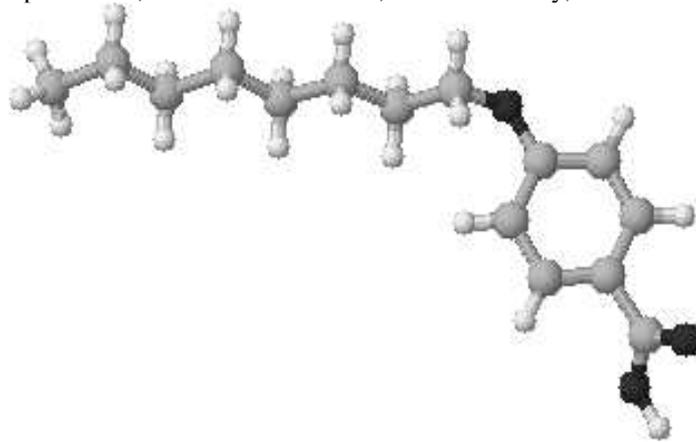
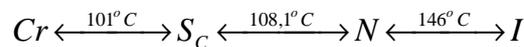


Fig. 2. Liquid crystal 4-(octyloxy)benzoic acid.

The phase transition temperatures of 4-(octyloxy)benzoic acid are:



Sorbitan monooleat, SPAN 80, manufactured by Serva, Feinbiochemica, Heidelberg, was used as a surfactant. The initially mixture consisted of 42% NOA 65, 50% liquid crystal and 8% SPAN 80. All components were mixed in an ultrasonic mixer after shock temperature treatments, down to good homogenization.

Methods: PDLC was obtained by high temperature photo-polymerization induced phase separation (PIPS) [2,3] in a standard liquid crystal cell with 15 μ m spacers. The photo-polymerization parameters were: 100 $^{\circ}$ C and 30 min full cure. After cooling, the PDLC was formed with diameters of the droplets from 5 to 20 μ m.

3. Discussion and concluding remarks

The director \mathbf{n} configuration in a LC in confined volumes is influenced by the presence of surfaces [2]. This influence is significant when the surface dominates over the volume. In a liquid crystal cell (LCC) and more pronouncedly in nematic droplets, the director configurations depend both on the magnitudes of the splay, twist, and bend elastic constants (\mathbf{K}_{11} , \mathbf{K}_{22} and \mathbf{K}_{33}), and on the type and strength of the boundary conditions. On the other hand, the nematic configurations within droplets represent attractive systems whereby topological defects [4,5] and the influence of confining geometry on bulk and surface order transitions can be studied. They are of considerable technological importance in PDLCs as well.

Assuming strong anchoring at the surfaces, one can derive an instability of the \mathbf{n} configuration in terms of the elastic constants. In order to minimize the total free energy of the system, the liquid crystal confined in the droplets adopts various structures and textures. Two main director configurations, depending on the surface anchoring, have been predicted [5]: a radial one with a point defect at the center for perpendicular orientation of the molecules at the droplet surface and a bipolar one with two surface defects for tangential anchoring. In practice, the director

configuration may often be more complicated than in either of these models, since the configuration adopted in nature is the one that best accommodates differences in the splay, twist and bend elastic energies. The authors [6,7], studying nematic droplets with tangential boundary conditions, found evidence in some materials for the formation of a “twisted bipolar” structure. Williams [8] showed, theoretically, that in strong tangential boundary conditions, the twisted bipolar structure is favoured for $K_{11} \geq K_{22} + 0.431K_{33}$, i.e. when the splay elastic constant is larger and/or the twist and bend elastic constants are small. According to this rule, there is a twist of the director field along the diameter of the droplet. This elastic constant ratio is realized in a liquid crystal system, where the molecular chirality is essential to get bipolar twisted structures in confined geometries. Thus, in a chiral nematic with very low twisting power (where the pitch is much longer than the diameter of the droplet), the bipolar twisted structure could spontaneously appear. In a more simple form, the Williams stability criterion indicates that the internal structures of nematic droplets with low K_{33}/K_{11} ratios are indeed consistent with a twisted bipolar structure.

Nematic droplet formation in an isotropic phase (I), when the nematic-isotropic state coexistence continues over more than 1 °C, as we observed at the isotropic-nematic phase transition of the 4-n-alkoxybenzoic acids used here, gives a new direction for the investigation of confined LC systems. Such nematic droplets provide another example of chiral structures formed from achiral materials due to some characteristics of the materials' intrinsic properties, like nematics organized by dimers. The interest in this phenomenon is now increasing.

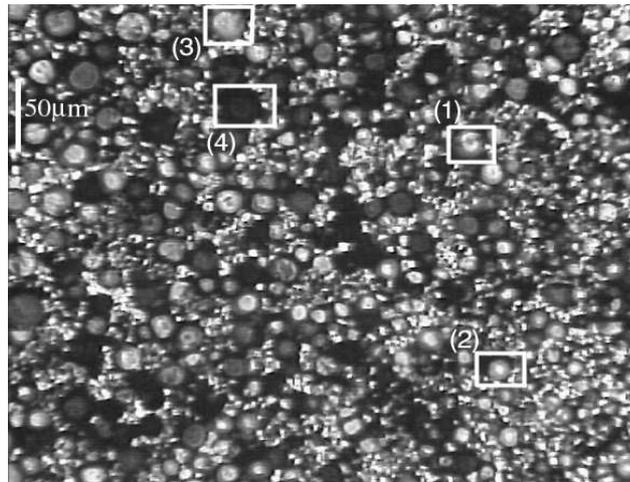


Fig. 3. General view of the PDLC with droplets with radii from 5 to 20 μm , in crossed polarizers. For visualisation, a Carl Zeiss NU2 microscope, with CCD Hitachi VK-C150ED equipment was used. (1) and (2) are chiral centers with axes normal to the substrate. (3) and (4) are chiral centers with axes oblique to the substrate.

Microtextural polarization analysis of the bipolar twisted droplets demonstrated typical extinction crosses in crossed polarizers, when the droplet was sufficiently large to satisfy the Mauguin limit expressed by the relation $d > \lambda \Delta n$, where d is the LC cell thickness, λ the incident light and Δn the birefringence. Following [9], we have found that the extinction crosses of the small droplets (2-5 μm in size), formed in the first stage of growth of the nematic phase in the isotropic one, are rotated at an angle $\approx 45^\circ$ in respect to the crossed polarizer position. This is an optical-polarisation feature indicating that we have observed a spontaneously twisted (chiral) structure.

We indicate in Fig. 3 the texture grown by the above method. The polymer dispersed droplets (with forms near to that of a sphere) in crossed polarizers, reveal a bifocal (twisted bipolar) texture. This texture indicates the chirality imposed by the process of confining of the LC system in the frame of the polymer matrix, and in turn the diminution of the K_{33}/K_{11} ratio. Fig. 3 shows (in crossed polarizers) black and white spherical droplets (already “frozen”). This difference in the birefringence indicates different locations of the built-in chiral axes with respect to the normal of the

cell surface. In the same figure, one of the two poles of the bipolar droplets is seen (for the case when the chiral axis direction is normal to the substrates) as centers – black (1) or white (2) point rings. The difference between the (1) and (2) centers, black or white, is due to the difference of the helix (left or right) direction. The chiral centers (3) and (4) indicate the droplet position (the chiral axis is oblique with respect to the surface normal), where the poles are not seen. Thus, the four types of chiral droplets are distributed in the PDLC system in a disordered way. Small single local monocystals, indicating a transition of chiral N to chiral smectic C, dominate the texture.

A possible mechanism, leading to chiralization in both N and S_C states, could be the lowering of the LC system symmetry to a non centrosymmetric one, due to the imposed (by confinement in drops) deformation. An LC system like 4-(octyloxy)benzoic acid can easily transform into a chiral non-centrosymmetric state, due to the dimer structure of molecules. For the S_C state, however, the symmetry could express itself only by a second order axis, which is typical for the ferroelectric version of the smectic C phase.

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