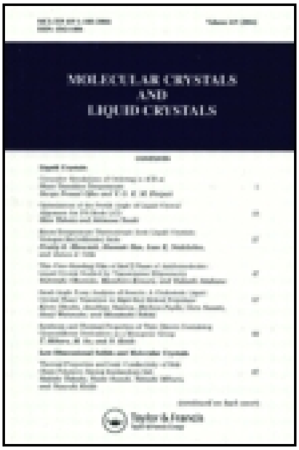

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Droplet Size Effects in Polymer Dispersed Nematic Chiral Liquid Crystal Materials

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Version of record first published: 24 Sep 2006.

To cite this article: Murielle Radian-Guenebaud & Pierre Sixou (1992): Droplet Size Effects in Polymer Dispersed Nematic Chiral Liquid Crystal Materials, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 220:1, 53-62

To link to this article: http://dx.doi.org/10.1080/10587259208033428

Mol. Cryst. Liq. Cryst., 1992, Vol. 220, pp. 53–62
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Printed in the United States of America

Droplet Size Effects in Polymer Dispersed Nematic Chiral Liquid Crystal Materials

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(August 13, 1991; in final form January 23, 1992)

Polymer dispersed liquid crystal films are prepared with a nematic chiral liquid crystal which forms both a cholesteric and a smectic phase.

The influence of the liquid crystal droplet size on the cholesteric-isotropic and smectic-cholesteric transition temperatures has been investigated.

For large liquid crystal inclusions, the wavelength of selective reflection associated with the cholesteric phase and its evolution with temperature depend on the size of the droplet inside which the liquid crystal is confined.

INTRODUCTION

There is a growing interest in a new type of material called "polymer dispersed liquid crystals" (PDLC). These materials are obtained from a heterogeneous mixture of a resin and a liquid crystal. Films are easily prepared by use of the polymer characteristics and at the same time the electro-optical properties of the pure liquid crystal are preserved. Various methods of preparation are used such as photo or polymerization of the resin or evaporation of a solvent. Due to phase separation generally a heterogeneous material is formed of droplets of liquid crystal encapsulated in a resin matrix. The liquid crystal droplets retain their properties with slight differences due to the confinement of the mesogenic molecules in inclusions of reduced size.

Up to now, studies were made mainly in liquid crystals presenting a nematic phase.[1–4]

The use of cholesterics or chiral nematics provide new aspects. For example what is the texture and what is molecular arrangement for a cholesteric constrained within a reduced volume.[5]

But the interest of a "polymer dispersed nematic chiral liquid crystal" arises not only from the size effect problem but also from potential applications which may develop. The case of cholesteric droplets was approached by Crooker, *et al.*[6] who proposed a display device using a material in which the dielectric anisotropy is negative.

The aim of the present work is mainly a study of selective reflection of the liquid crystal droplets of various sizes in the cholesteric phase as a function of temperature, as well as the influence of droplet size on the transition temperature. Depending on the method of preparation chosen, the distribution in droplet size obtained is more or less narrow. In this work, we consider inclusions of various different sizes. When the droplets are relatively large (up to 60 μm) and relatively isolated in the sample, they can be studied separately.

MATERIALS AND PREPARATION

The mixture considered is composed of the TM 29.8–38.0 chiral nematic of B.D.H and of an epoxy resin R2 of type diglycidylether of A bisphenol and of its D2 hardener, a mixture of polypropylene with polyamine cycloaliphatic commercialized under the name of RD2 by TCN.

TM29.8–38.0 features a cholesteric phase between 29°C and 46°C. The selective reflection wavelength relating to this phase varies from red to blue when the temperature is increased (cf. Figure 2). Below 29°C the compound shows a smectic phase.

Prepared at room temperature, the samples contain 31% of TM29.8–38.0, 46% of R2 and 23% of D2. Before reticulation in the resin, the mixture is transparent and isotropic. During polymerization a phase separation occurs and 48 hours later, a solid, opaque and heterogeneous material can be observed in which smectic liquid crystal bubbles from a smectic phase have appeared (photo 1). A wide distribution in droplets size occurs, the largest bubbles being a few tens of microns.

EXPERIMENT

The samples have a thickness between 10 and 200 μm and most often a thickness of the order of 35 μm was prepared. They are placed between two glass plates and

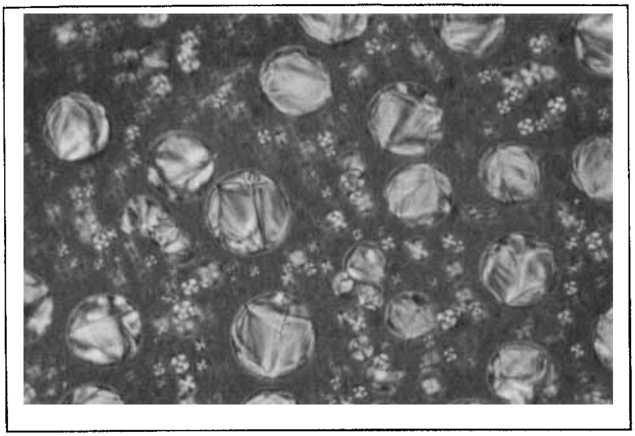

PHOTO 1a Droplets in smectic phase: T = 30°C.

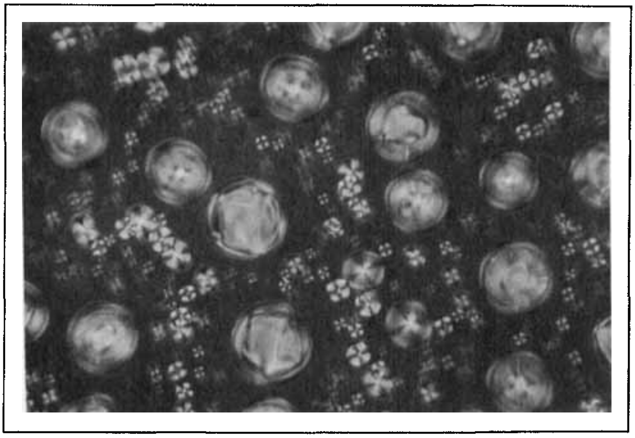

PHOTO 1b Coexistence of small cholesteric bubbles and large smectic bubbles: $T = 33.8°C$.

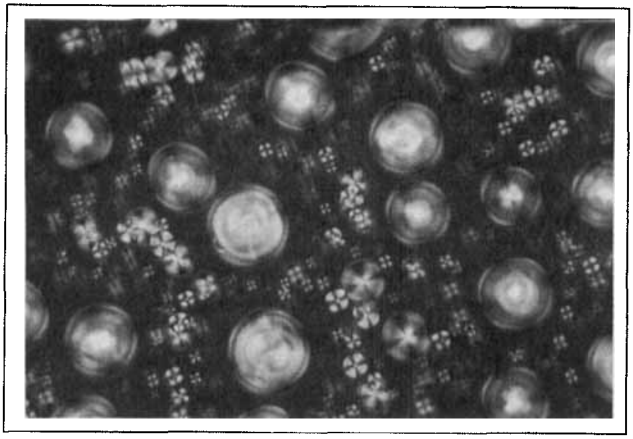

PHOTO 1c Inclusions in the liquid crystal cholesteric phase: $T = 34.5°C$.

are observed by optical microscopy, in reflection, between crossed polarizer and analyser.

The experimental set up allows the direct observation of the sample textures and the detection of wavelengths reflected by the sample. A monochromator and a photomultiplier tube enable us to analyze respectively the wavelength and intensity of the light from the microscope. An automatic control of the monochromator and of the light intensity rapidly determines the selective reflection wavelength in normal incidence. When the films are not too thick (a few microns to a few tens of microns) and when a certain area is properly selected, it is possible to observe one bubble or a few bubbles of equal size.

RESULTS

Transition Temperatures

In comparison to the pure liquid crystal, the isotropic-cholesteric or the cholesteric-smectic transition temperature of the heterogeneous sample are not abrupt but spread out over several degrees. When the liquid crystal is embedded, it is noted that the *Ts* (smectic-cholesteric) and *Tc* (cholesteric-isotropic) transition temperatures depend on droplet size: the larger the droplet diameter, the higher *Ts* and *Tc* (see photos 1a, 1b, 1c). In these photos, the largest droplet size is 30 μm. The transition to the isotropic phase is particularly easy to observe. Within the range of the transition, the smallest inclusions are in the isotropic phase and appear black, the largest ones are in the cholesteric phase and appear birefringent. A slight increase in temperature transforms the smaller birefringent bubbles into black bubbles.

Selective Reflection Wavelength

In the case of a planar cholesteric sample, the pitch P is directly linked to the wavelength λ of selective reflection in normal incidence and to the index of refraction by the relation $\lambda = nP$. A typical reflection spectrum for bulk TM29.8–38.0 at a temperature of 37°C is shown in Figure 1. We observe a value λ (498 nm) at the maximum selective reflection. In Figure 2 this value λ is given as a function of the temperature T for the bulk nematic chiral liquid crystal used in this work.

In the case of a polymer dispersed liquid crystal sample prepared with the same liquid crystal, it is difficult to observe only one liquid crystal micro-inclusion due to large density and size distribution and especially for tiny droplets smaller than 1 μm. Therefore sufficiently large droplets have been selected for observation.

Since there is such a large range of different sizes (see photos) in the sample, we use a diaphragm to study only a few droplets and therefore a reduced number of sizes. With the diaphragm the contrast between the reflected wavelengths in normal incidence increases because of a smaller diffusion of the light in the sample. The center of the bubbles is more intense and monochromatic. However the pe-

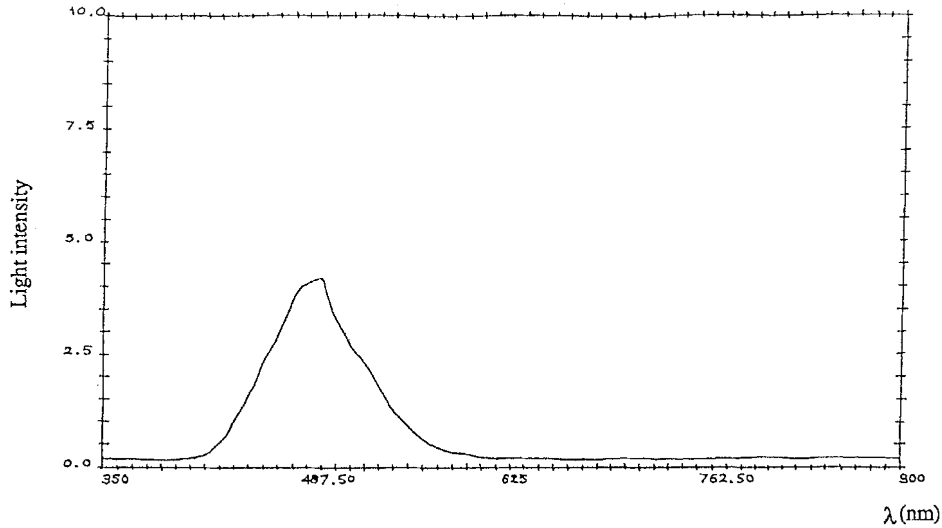

FIGURE 1 Spectrum of reflected wavelength observed for the pure liquid crystal material at T = 37°C.

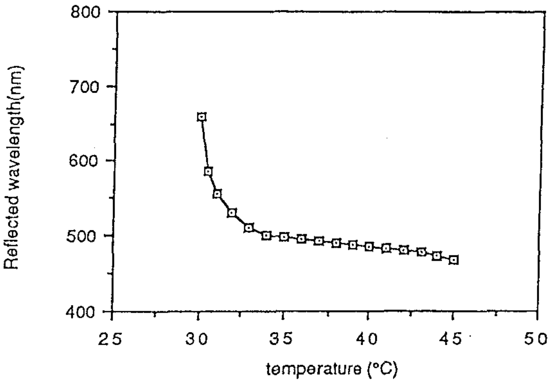

FIGURE 2 Variation of selective reflection wavelength as a function of temperature for pure liquid crystal.

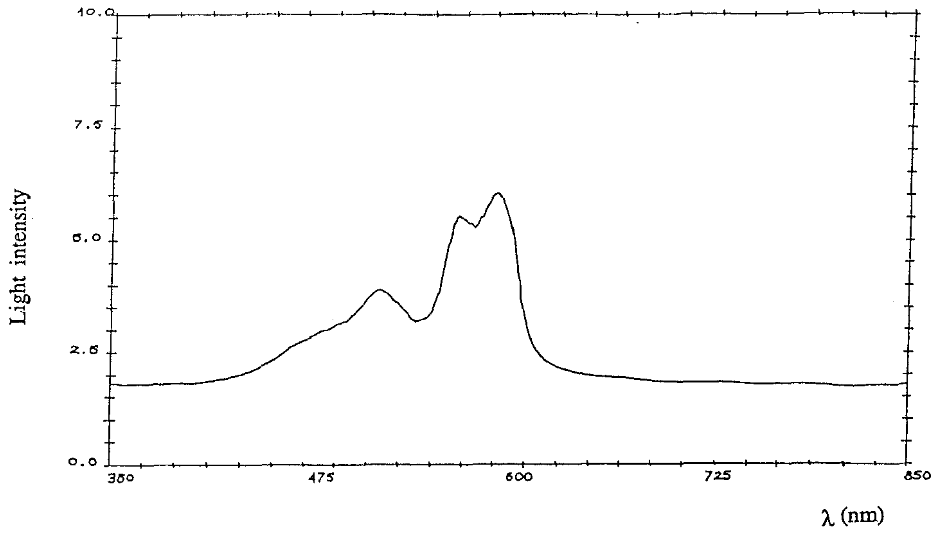

FIGURE 3 Spectrum of reflected wavelength observed when liquid crystal is confined within various size droplets, at T = 37°C.

ripheral zone of the droplets reflects other wavelengths with very weak intensity. According to Fergason (12), the reflection spectrum of a cholesteric material in the planar configuration depends on the angle of incidence according to the Bragg relation. In the present studies the incident light is normal to the sample and the detector selects the monochromatic light reflected in the normal direction corresponding to the center of the droplet. This wavelength is directly related to the pitch inside the droplet for planar orientation in the droplet.

Figure 3 shows three characteristic bubble sizes in reflected wavelengths and in normal incidence, at T = 37°C, showing three principal maxima of selective reflection. We can identify each maximum by direct observation of each bubble. Figure 4 shows the evolution of λ as a function of increasing T for each size; the

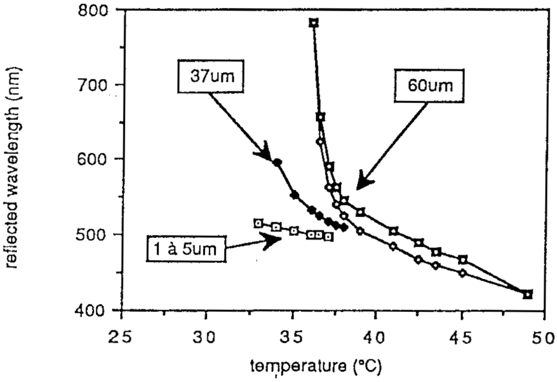

FIGURE 4 Variation of selective reflection wavelengths as a function of temperature when liquid crystal is confined within various size droplets.

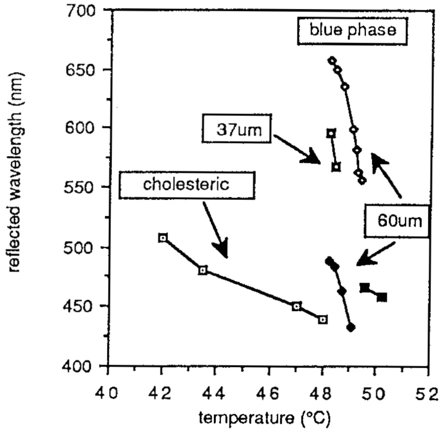

FIGURE 5 Occurrence of blue phase after a decrease in temperature.

selected diameter values are 60 μm, 37 μm and a set of smaller diameters on the order of 1 to 5 μm. A decrease in wavelengths of the selective reflection is observed as a function of diameter value.

In addition, on approaching the isotropic-cholesteric transition or in fact when the temperature decreases, the blue phase first occurs within the largest globules, next within the others by decreasing order in size (Figure 5) (Photo 2). Two selective reflections corresponding to the blue phase are observed and depend on droplet size.

DISCUSSION

These experimental results demonstrate several phenomena. The first one is the dependence of the critical temperature on the droplet size as predicted in a nematic (7–8). The droplet sizes of the theoretical analysis are smaller than for our ex-

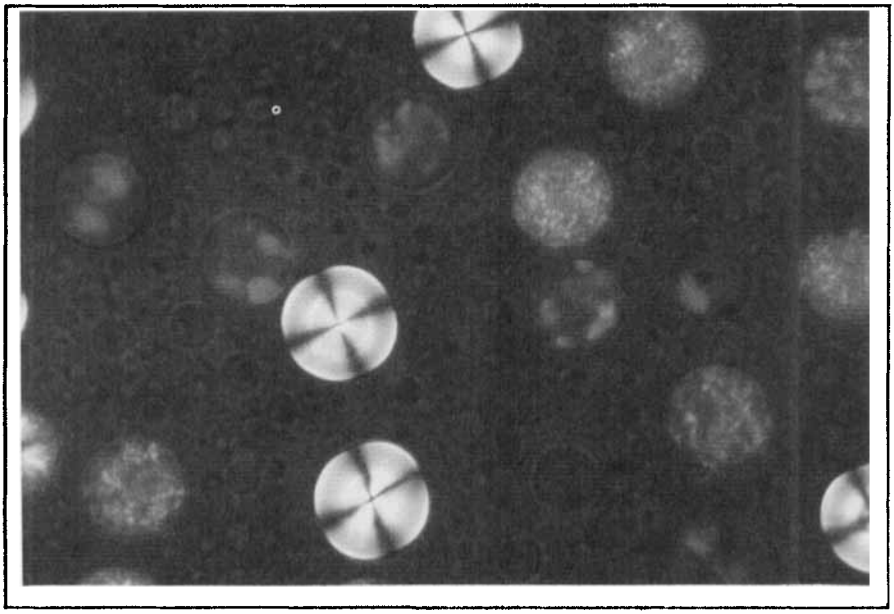

PHOTO 2 Presence of blue phase within inclusions and cholesteric phase within the largest ones: $T = 47.5°C$.

periments: the typical sizes are of the order of 0.1–1 μm in the theory instead of 10 μm inside our samples. We have repeated the calculations following this approach. The equilibrium order parameter is calculated using the Landau-De Gennes formalism. We consider a spherical droplet which has a radius R and a radial configuration of the director. Then we introduce the Landau-De Gennes free energy density (9) including director variations:

$$f = \frac{3}{4} A(T - T_c^*) S^2 - \frac{1}{4} B S^3 + \frac{9}{16} C S^4 + \frac{3}{4} L_1 [\vec{\nabla} S]^2 + \frac{9}{4} L_1 S^2 [\vec{\nabla} \cdot \vec{n}]^2 - G S \delta(r - R)$$

with the approximation that all elastic constants are equal. The last term is an expression of the substrate free energy density (10) where G is the strength of the anchoring. A, B, C, L_1 are the characteristics of the material chosen. Here $A = 8.793 \times 10^3$ J/m^{3}K, $B = 2.448 \times 10^5$ J/m^3, $C = 1.800 \times 10^5$ J/m^3, $L_1 = 6.0 \times 10^{-12}$ J/m, and $G = 2.7 \times 10^{-11}$ J/m.

The order parameter $S(r)$, inside the droplet, has to be a solution of the condition of minimisation $\delta f / \delta S = 0$. We use a Runge-Kutta method and we find one solution which gives a minimum value for the total free energy. In the radial case, we find a transition beginning in the center of the droplet and an extension of the disorder to the surface when the temperature increases from T_c^* to T_c (Figure 6). The interest of this model is the result we obtain when we compare two different sizes of droplets.

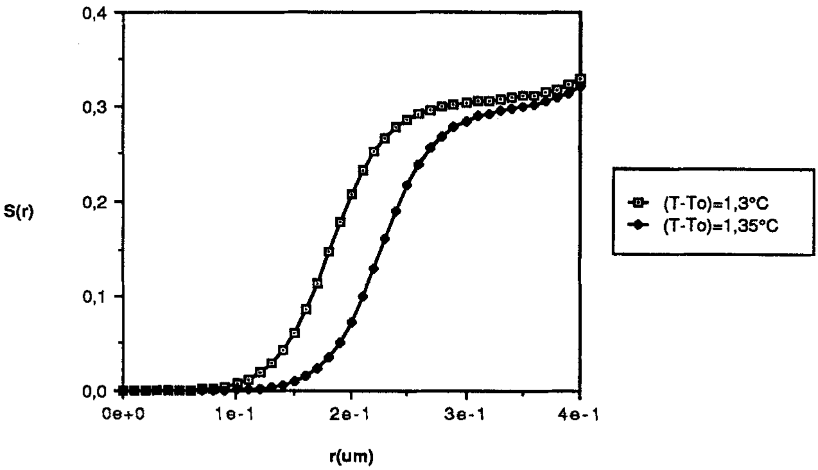

FIGURE 6 Calculated order parameter inside the droplet.

Figure 7 exhibits the order parameter as a function of temperature for $R = 0.1$ μm and $R = 0.4$ μm. In the smallest droplet, the disorder appears even though the biggest droplets are already ordered. The theoretical results show that the same temperature the order parameter inside the droplet strongly depends on the diameter as in our experiments.

The second phenomenon we observe is the dependence of the pitch of the cholesteric material on the droplet size, at a given temperature (Figure 4). Some possible explanations can be proposed.

1) The order within the bubbles depends on their diameter. The bubble of small diameter is weakly ordered or isotropic when the bubble of larger diameter is anisotropic. The modification of order parameter within an inclusion for a given radius should influence the selective reflection. However a model describing the cholesteric droplet structure has not yet been considered. Yet we cannot exclude a reflected wavelength light dependent on the size.

2) If surface conditions are the same for all bubble sizes, a slight variation of the pitch with droplet size is necessary to fulfill the boundary conditions as observed with a planar cholesteric in an applied electric field (11).

3) The more or less important curvature of surface for different droplet diameter can influence the internal texture of the droplet and consequently the transition characteristics.

4) The microdroplet shape depends on conditions of film preparation. Different thermal dilatation coefficients for the two materials can add a stress and modify the transition phenomena.

5) A cholesteric with planar orientation shows a selective reflection with a reflected wavelength which varies with viewing angle, the largest wavelengths being seen for normal incidence at the surface. We can suppose that the largest bubbles which have dimensions on the order of the film thickness are no longer spherical but are rather like disks lying parallel to surface. Then the selective reflection is shifted to the larger wavelengths.

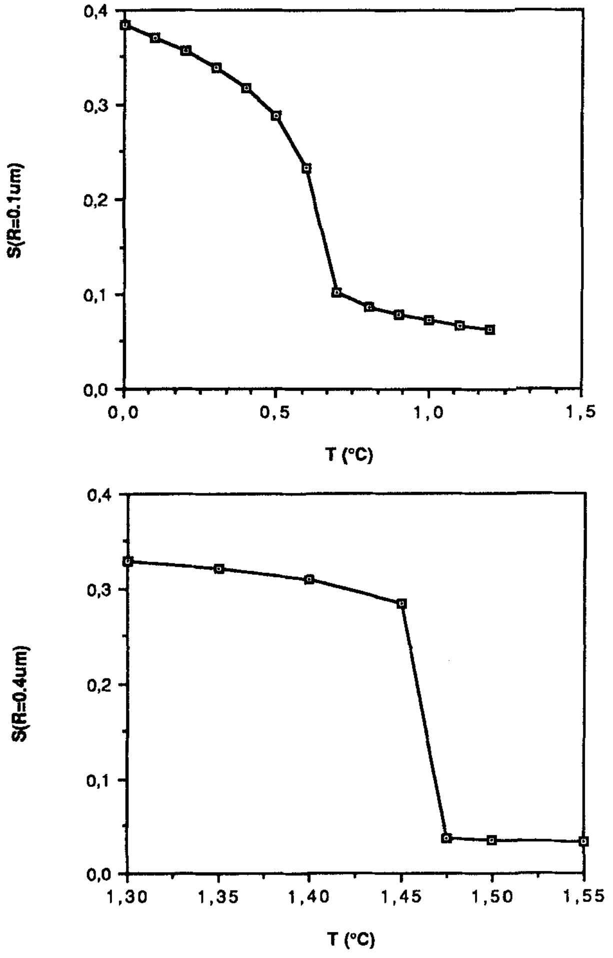

FIGURE 7 Variation of average order parameter S with temperature T for various size bubbles: a) $r = 0.1$ μm, b) $R = 0.4$ μm.

Although these four physical mechanisms can happen simultaneously, the fourth one is to be excluded for bubbles whose dimensions are smaller than film thickness. Retaining only small bubbles, one observes a modification of transition temperatures or occurrence of blue phase and a modification of the selective reflection wavelengths with inclusion size. Therefore other mechanisms must occur.

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