Thermal behaviour of switchable nematic emulsions

Jessica Lanzo[a]; Fiore P. Nicoletta[a]; Giovanni De Filpo[a]; Giuseppe Chidichimo[a]

[a] Universita degli Studi della Calabria,

PLEASE SCROLL DOWN FOR ARTICLE

Thermal behaviour of switchable nematic emulsions

JESSICA LANZO, FIORE P. NICOLETTA†, GIOVANNI DE FILPO
and GIUSEPPE CHIDICHIMO*

Dipartimento di Chimica, Università degli Studi della Calabria, 87036 Rende (CS),
Italy

We have investigated the electro-optical performance of switchable nematic emulsions as a function of temperature. The electro-optical properties of nematic emulsions are highly dependent on temperature because several parameters such as droplet size, number density, viscosity, surface free energy, elastic constant, refractive indices, dielectric anisotropy, and liquid crystal/monomer solubility are affected by temperature. In particular, both ON state transmittances and decay times show a decreasing behaviour with increasing temperature. On the contrary, the OFF state transmittances increase, and the rise times do not change in an appreciable way.

1. Introduction

Nematic emulsions are droplets of nematic materials floating in an isotropic fluid matrix [1]. They are important for theoretical investigations of both emulsions and liquid crystals from points of view such as non-classical interactions and structures, defects and stability [2, 3]. Droplet radii can range from hundreds of nano-meters to some tens of micrometers, but they are generally metastable. Their values are determined by the com-petition between elastic and surface energies in droplets. Such competition can generally induce either a normal or tangential alignment of the liquid crystal molecules inside the droplets, giving rise to stable director align-ments or configurations (star and bipolar, respectively) [4–6]. More complicated structures may be observed in particular conditions [7–9]. If an electric field is applied, bipolar droplets rotate and align themselves in the direction of the field.

More recently, we have investigated the electro-optical properties of nematic emulsions formed by droplets of liquid crystal in a fluid organic monomer matrix [10, 11]. Films are prepared by cooling the initial iso-tropic mixture at a controlled rate in order to give a droplet average diameter in the range of a few microns. It has been observed that such emulsions are stable, both as thin films and bulk samples, over several months because of the high value of the monomer viscosity (which prevents the droplets from merging) and the presence of some hydroxylic groups in the monomer structure. OFF state transmittances lower than 1% can be obtained from films prepared with this technique. If the monomer matrix refractive index is matched with the ordinary refractive index of the nematic droplet and a very low electric field (≈ 0.2 V μm^{-1}) is applied, such nematic emulsions can be switched into an ON state with an optical transmittance larger than 85% as the director in these bipolar droplets becomes aligned in the field direction. Such properties have indeed led to such nematic emulsions being proposed for devices alter-native to polymer dispersed liquid crystals (PDLCs), in which droplets are embedded in a solid polymer matrix. In addition to being used as optical shutters, nematic emulsions are also attractive for displays, smart windows, and various other applications. In practical applications, such devices are subjected to variable ambient temper-atures. It is thus important to determine the temperature dependence of the electro-optical parameters such as ON and OFF transmission, threshold field, the slope of transmission versus applied field, and response times which determine the device performance. It is expected that such electro-optical properties would strongly depend on temperature because several parameters such as optical anisotropy, droplet size, number density, dielectric aniso-tropy, liquid crystal rotational viscosity, surface free energy, and liquid crystal/monomer solubility can be affected by temperature.

This paper deals with the electro-optical properties of nematic emulsion films as a function of work temper-ature in order to verify their stability as switchable devices in different thermal situations. Experimental results can be explained by taking into account the droplet radius variation in the model for nematic droplets in a rigid binder [12].

* Author for correspondence.
†e-mail: fiore.nicoletta@unical.it

2. Experimental

E49 and TL202 (Merck Ltd) were used as nematic liquid crystals. The monomer matrix was a mixture of bisphenol A glycerolate diacrylate (Aldrich) and CN945B85 (an aliphatic urethane triacrylate, 85% in hexandiol diacrylate from Cray Valley-Total) in the weight ratio of 39:61. For such a ratio, the saturated liquid crystal monomer matrix has a refractive index almost matched with the ordinary refractive index of the liquid crystal [11]. Samples were prepared by weighing 30 wt% of liquid crystal and 70 wt% of monomer mixture into vials and subsequently stirring them at 100°C. Home-made cells with indium tin oxide conductive substrates were filled by capillarity with a small quantity of the final mixtures heated to a temperature well above the critical solution temperature, i.e. the temperature above which a homogeneous single phase is observed. Sample thickness was set to be about 30 μm by means of glass spheres. Then samples were cooled to room temperature at a rate adequate (≈ 50°C min^{-1}) to give an average droplet radius of about 1.5 μm [10].

The surface free energy of materials, i.e. the work required to bring molecules from the bulk into the surface region, was determined by a ring tensiometer, previously calibrated for temperature and force, interfaced with a computer. The electro-optical properties of such emulsions were measured using the optical line reported in previous work [13]. The intensity of incident light passing through cells containing pure monomer mixture were assumed to be the full scale intensity. The rise time, τ_{rise}, defined as the time required to reach 90% of optical response, was determined by monitoring the drive signal ($\nu = 1$ kHz, $V_{\text{rms}} = 50$ V) and the response of the photodiode using a digital storage oscilloscope. In contrast, the decay time, τ_{decay}, defined as the time required for the nematic emulsion to drop to 10% of the maximum transmittance after the external field is removed, was measured by means of a digital chronometer. The sample temperature was kept constant by a thermostatic apparatus whose stability was better than 0.1°C. Measurements were performed about one hour after each temperature change.

3. Results and discussion

Figure 1 shows some polarizing optical photomicrographs of a TL202 nematic emulsion at different temperatures. The observed patterns are consistent with a bipolar configuration of the droplets.

Droplet average radius increases with temperature as reported in figure 2. No evidence of coalescence and change in the electro-optical properties was observed over ten days at each temperature as the high value of the matrix viscosity prevents the diffusion and merging of droplets during the measuring time.
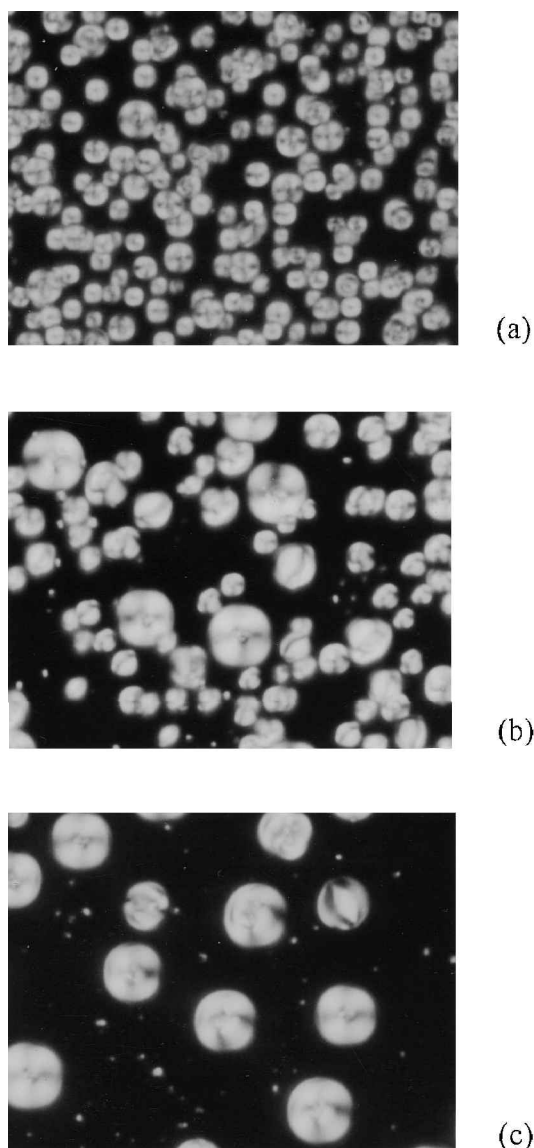

Figure 1. Polarizing optical photomicrographs of a 30 wt% TL202 emulsion at different temperatures: (*a*) 50°C, (*b*) 60°C, (*c*) 64°C. Each photograph area is 60×45 μm^2.

Such experimental behaviour can be explained by assuming that the droplet radius at each temperature is determined by the competition between the Frank elastic energy and the surface energy. In the one elastic constant approximation, the droplet radius, R, should scale as [14]:

$$R \approx \frac{k}{\Sigma_{1c/m}} \qquad (1)$$

where k is a liquid crystal elastic constant and $\Sigma_{1c/m}$ is the interfacial free energy of the liquid crystal in contact with the monomer matrix at the droplet boundaries. It is well known that k shows a linear decreasing behaviour
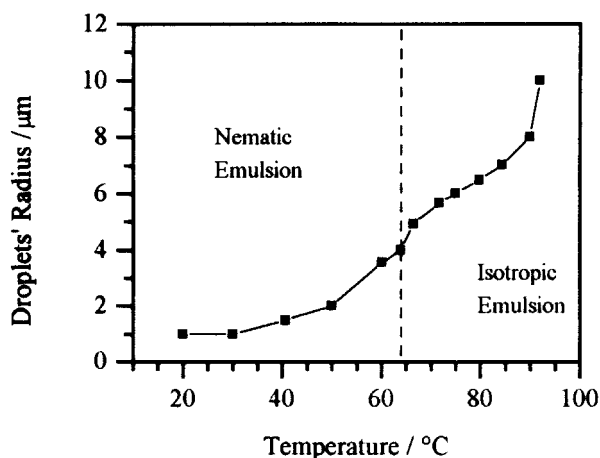
Figure 2. Average radii of droplets as a function of temperature for a 30 wt % TL202 emulsion.

Figure 3. Thermal behaviour of the surface free energy of TL202 liquid crystal, Σ_{1c}, and monomer matrix, Σ_{m}, (*a*). The interfacial free energy of TL202 liquid crystal in contact with the monomer matrix, $\Sigma_{1c/m}$, was obtained by applying the geometrical mean rule with $\rho = 1$ (*b*). The fitting function is: $\Sigma_{1c/m} = \Sigma_0 + \Sigma_1 \exp[-(t - t_0)/\tau]$ with $\Sigma_0 = 0.73 \times 10^{-3}\,\mathrm{N\,m^{-1}}$, $t_0 = 31.79°C$, $\Sigma_1 = 4.09 \times 10^{-3}\,\mathrm{N\,m^{-1}}$, $\tau = 9.53°C$. The interfacial free energy decreases from the initial value $\Sigma_0 + \Sigma_1$ to Σ_0 (for $t \to \infty$).

with temperature [15], while, unfortunately, the interfacial free energy of nematic droplets in a matrix has been determined in only a few special cases (droplets in equilibrium with their own isotropic phases or in matrices with moderate viscosity) [16, 17]. Nevertheless a simple estimation of the interfacial free energy of the liquid crystal at the monomer boundaries as a function of temperature can be obtained from the definition of the work of adhesion, w_{AB}, between two phases, A and B, and the use of the geometrical mean rule. w_{AB}, i.e. the work necessary to separate an interface AB in two liquid–vapour interfaces A and B, is defined as:

$$w_{AB} = \Sigma_A + \Sigma_{A/B} \qquad (2)$$

where Σ_A and Σ_B are the surface free energy of phase A and B, respectively, and $\Sigma_{A/B}$ is the interfacial free energy of phase A in contact with phase B. On the other hand, Girifalco and Good have proposed the geometrical mean rule [18] and obtained the following expression for the work of adhesion:

$$w_{AB} = 2\rho(\Sigma_A \Sigma_B)^{1/2} \qquad (3)$$

where ρ is a function of the molar volumes of the two substances. Empirically, its value ranges from 0.5 to 1.15. The surface free energies of both pure liquid crystal and monomer matrix, Σ_{1c} and Σ_m, respectively, show the decreasing behaviour reported in figure 3 (*a*).

As a consequence, the interfacial free energy $\Sigma_{1c/m}$ can be written as a function of the surface free energy of the liquid crystal and monomer in the following way:

$$\Sigma_{1c/m} = \Sigma_{1c} + \Sigma_m - 2\rho(\Sigma_{1c}\Sigma_m)^{1/2}. \qquad (4)$$

The behaviour of $\Sigma_{1c/m}$, as obtained by using equation (4) where we put, for the sake of simplicity, $\rho = 1$ is reported in figure 3 (*b*) with its exponential fit.
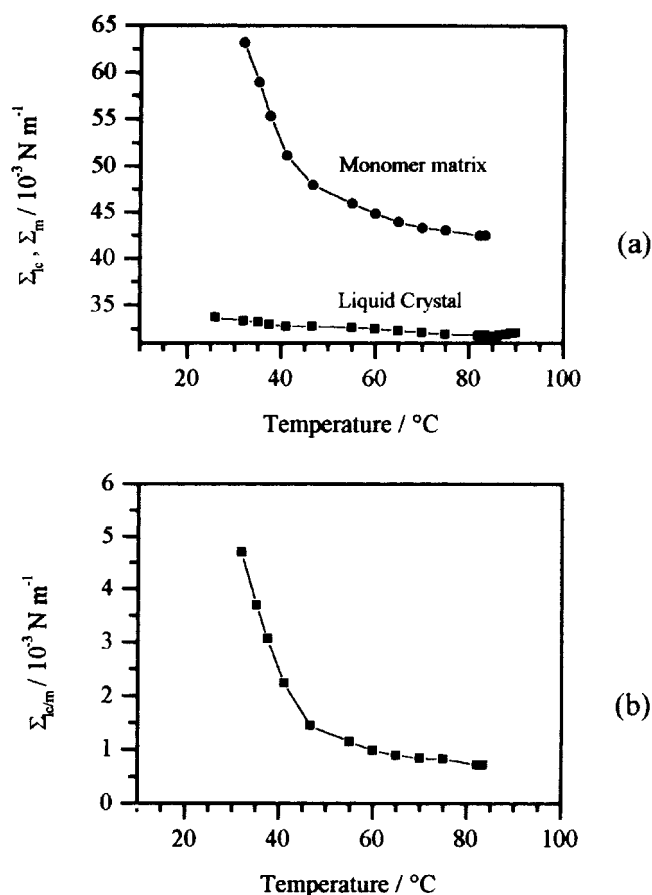
Consequently, it is expected that R should increase as the product of a linear and an exponential function in rather good agreement with the experimental data of figure 2. It should be noted that the calculated interfacial free energy values are larger than those reported by Smith *et al.* [17]. This difference can be attributed, in our opinion, to the particular monomer matrices used in this work.

It is evident from figure 1 that droplet density number decreases with temperature increase. Such an effect can be explained by an increase in the solubility of the liquid crystal in the monomer matrix [11], so determining the disappearance of some droplets.

Typical optical transmittances of 30 wt % TL202 nematic emulsions are reported as a function of temperature in figure 4.
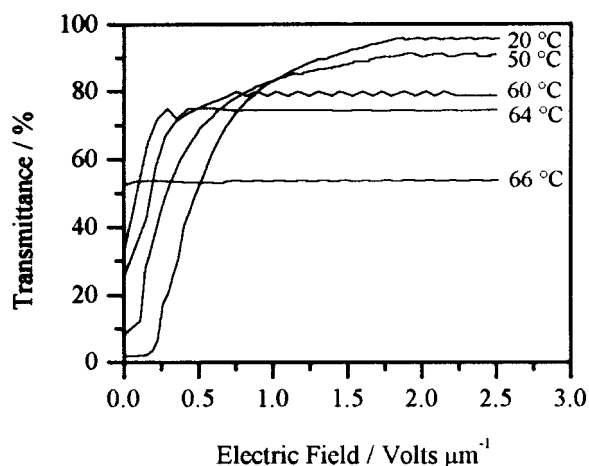
Figure 4. Transmittance dependence on the applied electric field for a 30 wt % TL202 emulsion at different temperatures.

The ON state transmittance is higher than 70% over the entire temperature range, while the OFF state transmittance increases. A similar behaviour is also shown by the E49 emulsions. Both the ON and the OFF state transmittances change in a steeper way for temperatures larger than 50°C. They meet at the TL202 clearing temperature, which is shifted down by dissolution of monomer molecules into the droplets (figure 5).

The thermal behaviour of the ON and OFF state transmittances is similar to that shown by PDLCs [19]. However, the temperature dependent electro-optical properties of nematic emulsions are affected by the changes in droplet density and size, in addition to the refractive index variation [19] and thermal expansion of the matrix [20], which are characteristic of conventional PDLCs. In fact, it is known that the light transmitted through a nematic dispersion can be

expressed by the following relation [21, 22]:

$$Tr = \exp(-\beta\sigma d) \qquad (5)$$

Where β is the number density, d is the sample thickness, and σ is the scattering cross section. According to the anomalous diffraction approximation, which holds in the limit $2\pi R/\lambda \gg 1$ (λ is the wavelength of light), the scattering cross section is expressed by:

$$\sigma = 2\sigma_0 \left(\frac{2\pi R}{\lambda}\right)^2 \left(\frac{n_{\text{droplet}}}{n_{\text{matrix}}} - 1\right)^2 \qquad (6)$$

where $\sigma_0 = \pi R^2$ is the droplet geometrical cross section, n_{matrix} and n_{droplet} are, respectively, the refractive indices of the monomer matrix and the liquid crystal droplets at T. n_{droplet} for pure liquid crystal droplets is equal to the ordinary liquid crystal refractive index, n_{o}, in the ON state, and to the average refractive index of the liquid crystal in the OFF state, i.e. $n_{\text{droplet}} = (n_{\text{e}} + 2n_{\text{o}})/3$, where n_{e} is the extraordinary refractive index of liquid crystal. Obviously, both matrix and droplet refractive indices are affected by the thermal variation of the mutual solubilities. In addition, n_{droplet} is influenced by changes in the liquid crystal order parameter with temperature, which is the major factor characterizing the behaviour of PDLCs as a function of temperature. After some rearrangements equation (5) can be written as:

$$Tr = \exp\left[-const\,\Phi R \left(\frac{n_{\text{droplet}} - n_{\text{matrix}}}{n_{\text{matrix}}}\right)^2\right] \qquad (7)$$

where $\Phi = 4\beta\pi R^3/3$ is the liquid crystal volume fraction which is separated in the droplets. Equation (7) shows that the optical transmittance is affected by the thermal variation of Φ, R, n_{droplet}, and n_{matrix}.

It is also evident from figure 4 that both the threshold and saturation electric fields (i.e. the field at which the transmittance begins to increase from its OFF state and that at which the maximum transmittance is achieved, respectively) decrease with increasing temperature. They scale as [12]:

$$\mathbf{E} \approx \frac{1}{R}\left(\frac{k}{\Delta\varepsilon}\right)^{1/2} \qquad (8)$$

where we have assumed, for simplicity, that the electric properties of both matrix and droplets have the same temperature dependence. As a consequence, both the threshold and saturation fields change with temperature because the ratios $(k/\Delta\varepsilon)^{1/2}$ (as in conventional PDLCs) and $1/R$ decrease.

The electro-optical response of the nematic emulsions was determined by measuring the rise and decay times. Nematic emulsions always show very short rise times (less than 10 ms at all temperatures) as they are strongly influenced by the external driving electric field rather
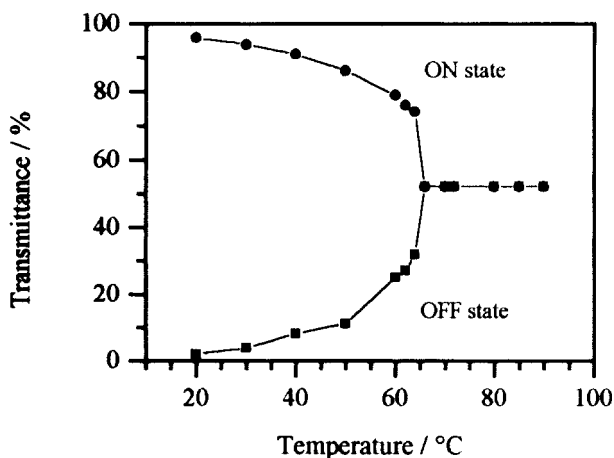

Figure 5. OFF and ON state transmittance dependence on the temperature for a 30 wt % TL202 emulsion.
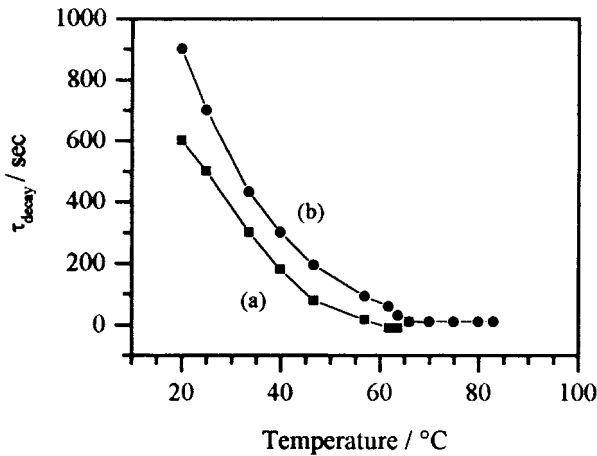
Figure 6. Decay time dependence on temperature for 30 wt % emulsions: (*a*) TL202, (*b*) E49.

than temperature, see equation (9). On the contrary, the decay time shows a steep decrease with increasing temperatures as shown in figure 6.

Decay time values range from some minutes to a few hundreds of milliseconds at a temperature of about 65°C. It is known that the response times of nematic dispersions are dependent on a number of factors such as droplet size, elastic constant, rotational viscosity, and the anchoring strength at the droplet wall. In particular, the decay and rise times for a nematic dispersion have the following form [12, 23]:

$$\tau_{\text{rise}} \approx \frac{\gamma}{\Delta\varepsilon(\mathbf{E}_{\text{appl}}^2 - \mathbf{E}_{\text{th}}^2)} \tag{9}$$

$$\tau_{\text{decay}} \approx \frac{\gamma}{\Delta\varepsilon\mathbf{E}_{\text{th}}^2} \tag{10}$$

where $\mathbf{E}_{\text{appl}}$ and $\mathbf{E}_{\text{th}}$ are the applied and threshold fields, γ is a rotational viscosity coefficient, and $\Delta\varepsilon$ is the dielectric anisotropy of the liquid crystal. Using equation (8) the decay time can be rewritten in the following way:

$$\tau_{\text{decay}} \approx \frac{\gamma}{k}R^2. \tag{11}$$

Thus the decrease of τ_{decay} can be associated with the competition between the exponential decrease of γ/k (as in conventional PDLCs [24]) and the increase of R^2 with temperature. From the experimental data of figure 6 it is possible to state that the former contribution is the main cause of the observed trend.

4. Conclusions

We have presented data on the temperature dependent electro-optical performance of nematic emulsions. We have observed a strong dependence of the electro-optical properties on temperature. A plausible explanation is the change with temperature of both the liquid crystal/monomer solubility and the surface free energy which cause an increase of the average droplet size and a decrease in the number density. The variation of several other parameters such as elastic constant, optical and dielectric anisotropies, rotational viscosities, and anchoring strengths also contribute to the variation of electro-optical performance of nematic emulsions with temperature.

References

[1] MEYER, R. B., 1969, *Phys. Rev. Lett.*, **22,** 918.
[2] JOANNY, J. F., 1997, *Science*, **275,** 1751.
[3] POULIN, P., STARK, H., LUBENSKY, T. C., and WEITZ, D. A., 1997, *Science*, **275,** 1770.
[4] DUBOIS-VIOLETTE, E., and PARODI, O., 1969, *J. Phys. Fr.*, **30,** C4-57.
[5] LE ROY, P., CANDAU, S., and DEBEAUVAIS, F., 1972, *C. R. Acad. Sci.*, **B 274,** 419.
[6] CANDAU, S., LE ROY, P., and DEBEAUVAIS, F., 1973, *Mol. Cryst. liq. Cryst.*, **23,** 283.
[7] MADHUSUDANA, N. V., and SUMATHY, K. R., 1983, *Mol. Cryst. liq. Cryst.*, **92,** 179.
[8] XU, F., KITZEROW, H. S., and CROOKER, P. P., 1992, *Phys. Rev. A*, **46,** 6535.
[9] KRALJ, S., and ZUMER, S., 1992, *Phys. Rev. A*, **45,** 2461.
[10] DE FILPO, G., LANZO, J., NICOLETTA, F. P., and CHIDICHIMO, G., 1998, *J. appl. Phys.*, **84,** 3581.
[11] DE FILPO, G., LANZO, J., NICOLETTA, F. P., and CHIDICHIMO, G., 1999, *J. appl. Phys.*, **85,** 2894.
[12] WU, B. G., ERDMANN, J. H., and DOANE, J. W., 1989, *Liq. Cryst.*, **5,** 1453.
[13] CHIDICHIMO, G., HUANG, Z., CARUSO, C., DE FILPO, G., and NICOLETTA, F. P., 1997, *Mol. Cryst. liq. Cryst.*, **299,** 379.
[14] CASAGRANDE, G., FABRE, P., GUEDEAU, M. A., and VEYSSIE, M., 1987, *Europhys. Lett.*, **3,** 73.
[15] BUNNING, J. D., FABER, T. E., and SHERREL, P. L., 1981, *J. Phys. Fr.*, **42,** 1175; HAKEMI, H., JAGODZINSKI, E. F., and DUPRÈ, D. P., 1983, *J. chem. Phys.*, **78,** 1513.
[16] SMITH, G. W., 1984, *Mol. Cryst. liq. Cryst.*, **102,** 65.
[17] SMITH, G. W., VAZ, N. A., and VANSTEENKISTE, T. H., 1989, *Mol. Cryst. liq. Cryst.*, **174,** 49.
[18] GIRIFALCO, L. A., and GOOD, R. S., 1957, *J. phys. Chem.*, **61,** 904.
[19] MONTGOMERY, G. P. JR, VAZ, N. A., and SMITH, G. W., 1988, *Proc. SPIEE*, **958,** 104.
[20] JIM, Y. W., IM, S. J., SUNG, J. H., NOH, C. H., and SAKONG, D. S., 1995, *Liq. Cryst.*, **19,** 755.
[21] VAN DE HULST, H. C., 1981, *Light Scattering by Small Particles* (New York: Dover).
[22] ZUMER, S., 1988, *Phys. Rev. A*, **37,** 4006.
[23] DRZAIC, P. S., 1995, *Liquid Crystal Dispersion* (Singapore: World Scientific).
[24] PIERANSKI, P., BROCHARD, F., and GUYON, E., 1973, *J. Phys. Fr.*, **34,** 35.