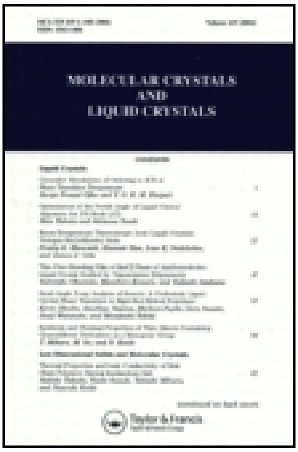

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Temperature dependence of the optical phase shift in a polymer dispersed liquid crystal

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Abstract

We report a study of the temperature dependence of the optical phase shift induced by a polymer dispersed liquid crystal subjected to a low frequency electric field.

In the framework of a recently introduced model we point out the role of two parameters strictly depending on the PDLC configuration: an "effective elastic constant" K_d and a droplet "voltage-constant" V_d.

We show that a suitable temperature dependence of such parameters is able to give a good agreement between experimental data and theoretical values.

1 Introduction

Recently a remarkable scientific interest is grown on composite materials and on polymer dispersed liquid crystals (PDLC): liquid crystal microdroplets embedded in a polymeric matrix. Depending on technical tips, the droplets, randomly dispersed in the polymer, may have a size close to the visible light wavelength, thus producing a strong light scattering.

Droplets have a strong optical anisotropy, depending on liquid crystal's orientation inside them, and therefore, on applied electric field. So it is possible to reduce the refractive index mismatching between droplets and polymeric matrix, thus switching the sample to a transmission state[1]. This well known effect is the basis of many applications which are presently studied for these materials. From a fundamental point of view they are interesting because many physical properties of liquid crystal are strongly influenced by the confinement of the material in a small cavity. Furthermore the interfacial interaction polymer-liquid crystal must play a very important role in every physical phenomenon because of the very high surface to volume ratio in the liquid crystal droplet.

In a previous paper[2] we have reported the study of the optical phase shift induced by a PDLC sample when a low frequency electric field is applied to it. We have shown that a theoretical model based on the description of the sample by means of molecular, droplet and sample order parameters is able to give a good agreement with experimental data.

In this paper we present further experimental measurements, obtained at different temperatures below the nematic-isotropic transition, and we show that the same model is able to describe the phenomenon.

2 Theory

According to currently accepted theoretical models[2,3] droplets reorientation in a PDLC sample, subjected to a low frequency electric field, can be described by means of three order parameters: the usual scalar order parameter

$$S = \left\langle P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{l}}) \right\rangle \tag{1}$$

which takes into account of the thermal fluctuations of molecular axys: the droplet order parameter

$$S_d = \left\langle P_2(\hat{\mathbf{N}}_d \cdot \hat{\mathbf{n}}) \right\rangle_{droplet\ volume} \tag{2}$$

which takes into account of the droplet configuration; and the sample, field-induced, orderder parameter

$$S_f = \left\langle P_2(\hat{\mathbf{E}} \cdot \hat{\mathbf{N}}_d) \right\rangle_{whole\ sample} \tag{3}$$

which takes into account of the droplet reorientation produced by applied electric field. Here $\hat{\mathbf{l}}$ is the molecular symmetry axys, $\hat{\mathbf{n}}$ is the local molecular director, $\hat{\mathbf{N}}_d$ is the droplet director (i.e. the mean value of $\hat{\mathbf{n}}$ inside each droplet) and P_2 is the second order Legendre polynomial.

The order parameter S takes into account of the temperature dependence of the electric, optical and mechanical properties, i.e. dielectric constants, refractive indices, elastic constants, and so on.

As usual we have assumed[4,5] S to be a universal function of the reduced temperature $\tau = TV/T_{NI}V_{NI}$, T_{NI} and V_{NI} being the temperature and volume at nematic-isotropic transition.

$$S = (1 - 0.89\tau)^{0.22} \tag{4}$$

Droplet order parameter S_d allows us to compute ordinary and extraordinary droplet refraction indices[2] ($F(\theta, m)$ is the complete elliptic integral of the first kind)

$$n_{do} = \frac{2}{\pi} n_o \; F\left(\frac{\pi}{2}, \frac{1}{n_e}\sqrt{\frac{2}{3}(n_e^2 - n_o^2)(1 - S_d)}\right) \tag{5}$$

$$n_{de} = \frac{n_o \, n_e}{\sqrt{\frac{2}{3}(n_o^2 - n_e^2)S_d + \frac{1}{3}(n_o^2 + 2n_e^2)}} \tag{6}$$

As we have shown in a previous paper[2] S_d cannot be assumed to be field independent. An empiric expression which takes into account such dependence is

$$S_d(V) = 1 - (1 - S_{d0})\exp(-V/V_d) \tag{7}$$

where V_d (units: Volt) is a parameter which can be seen as a "voltage-constant" and takes into account of the voltage dependence of the alignment of liquid crystal molecules inside each droplet.

Sample order parameter S_f is obtained[3] minimizing the free energy density due to interacion with the electric field. It can be shown that

$$S_f = \frac{1}{4} + \frac{3}{16}\frac{e_a^2 + 1}{e_a^2} + \frac{3}{32}\frac{(3e_a^2 + 1)(e_a^2 + 1)}{e_a^3} \ln\left|\frac{e_a + 1}{e_a - 1}\right| \tag{8}$$

where

$$e_a(S_f) = E\sqrt{\frac{3\,\epsilon_p\, v_{lc}}{\epsilon_{lc} + 2\epsilon_p - v_{lc}(\epsilon_{lc} - \epsilon_p)}\,\frac{\epsilon_{\parallel} - \epsilon_{\perp}}{K_d}} \tag{9}$$

is the reduced field, v_{lc} is the volume fraction of liquid crystal in the sample, ϵ_p is the dielectric permittivity of the polymer,

$$\epsilon_{lc} = \epsilon_{\perp} + \frac{1}{3}(1 + 2SS_dS_f)(\epsilon_{\|} - \epsilon_{\perp}) \tag{10}$$

is the effective scalar dielectric permittivity of the liquid crystal.

In eq.(9), we have introduced an "effective elastic constant" per unit surface, K_d (units: Newton per square meter), which is related to the effective droplet radius R_{eff} and the droplet ellipticity ζ defined in ref. [3] by $K_d = K\zeta^2/R_{eff}^2$, being K the liquid crystal elastic constant. In the theory these terms were introduced as a droplet shape effect to take into account of the restoring torque which, after the field switch-off, produces relaxation of the droplets to the original orientation. As a matter of fact relaxation can also be induced by surface anchoring effects, therefore we prefere to include all these parameters into just one, K_d, since at this stage we are unable to distinguish between the above mentioned phenomena. From the definition we can see that high values of K_d require an intense external field to rotate droplets.

The sample order parameter S_f allows us to compute optical phase shift induced by PDLC in a probe beam impinging on the sample with a propagation direction different from the one of the low frequency electric field. We are interested in the phase difference $\Delta\phi$ between two ortogonal polarization components: in ref.[2] we have shown how it can be worked out using the expressions (5) and (6) of the droplet's refractive indices; in this paper we are interested in the dependence of $\Delta\phi$ vs. the temperature T as well as vs. the applied voltage V.

3 Temperature dependence

It is hard to find in literature data about the temperature dependence of the liquid crystal parameters required by the theoretical model, but we can make some reasonable assumptions. We have assumed[5], that dielectric permittivity can be expressed as

$$\epsilon_{\|}(S) = C_1 + 2C_2\,S \qquad \epsilon_{\perp}(S) = C_1 - C_2\,S \tag{11}$$

where C_1 and C_2 are constants. A similar assumption, with different values of the constants, can be done for refractive indices $n_o(S)$ and $n_e(S)$, but we have no way to know the temperature dependence of two important parameters: K_d and V_d. So

Table 1: parameters used to obtain curves in fig.1 and 2

Liquid Crystal (E7)
$T_{NI} = 54.5^{o}C$ (experimental value in our PDLC sample)
$\epsilon_{\|} = 7.2\ \epsilon_0$ (at $T = 20^{o}C$)
$\epsilon_{\perp} = 6.0\ \epsilon_0$ (at $T = 20^{o}C$)
$n_e = 1.716$ (at $T = 20^{o}C$)
$n_o = 1.513$ (at $T = 20^{o}C$)

Polymer (EPON 815)
$\epsilon_p = 5\ \epsilon_0$
$n_p = 1.55$

Sample
thickness $= 8\mu m$
$v_{lc} = 0.6$
droplet radius $= 0.2\mu m$
$S_{d0} = 0.7$
$V_d = \infty$ (in fig 1)
$K_d = 4N/m^2$ (in fig 2)

Experimental setup
Incidence angle $= 20deg$
$T = 35.4^{o}C$
Probe beam wavelength $= 632.8nm$

let us examine their effect on the phase difference: in Fig. 1 and Fig. 2 we can see theoretical curves obtained for different values of K_d and V_d respectively. The other parameters are standard values, obtained from literature, and are summarized in Tab. 1.

As can be seen (Fig. 1) K_d affects the threshold voltage while has practically no effect on the saturation value. This parameter depends on how deeply boundary effects propagate inside droplet. A low K_d value means that external field can easily rotate droplets, so that there is a low threshold value.

From Fig. 2 we can see thet V_d affects the slope of the curve after the threshold, while treshold itself is only slightly changed. This parameter measures how external field is able to rearrange molecules inside droplets assuming that droplets have already been reoriented. $V_d = \infty$ means that droplets rotate as a whole and external

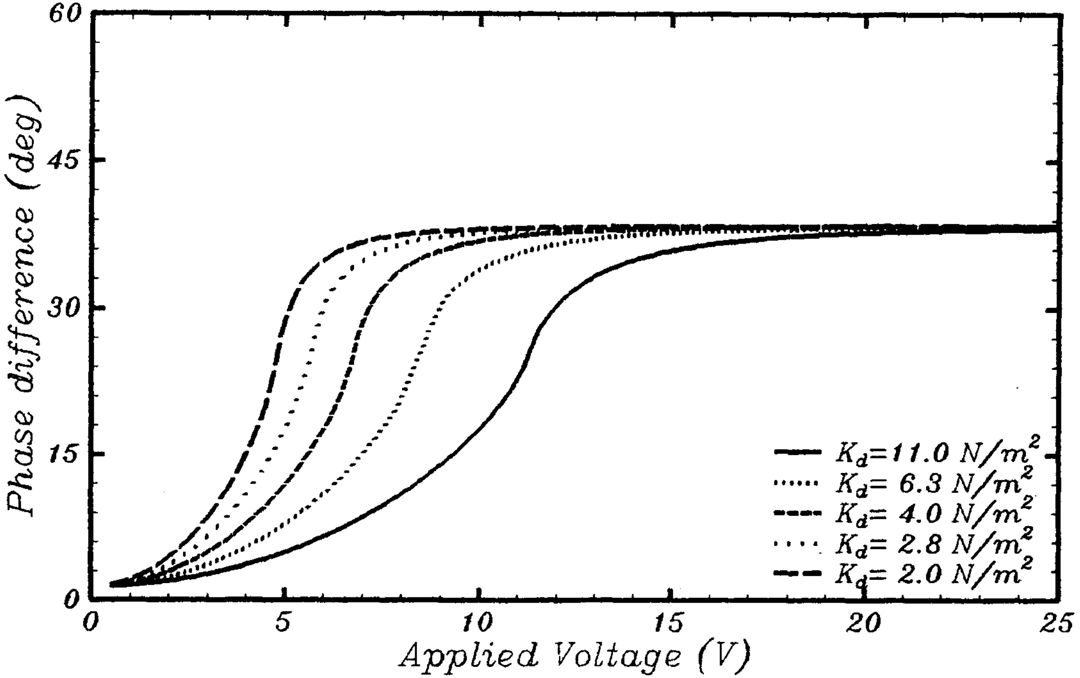

Fig. 1 - Phase difference induced in a PDLC sample (thickness $8\mu m$) by applying external low frequency voltage: theoretical curves obtained for different values of droplet's "effective elastic constant" K_d.

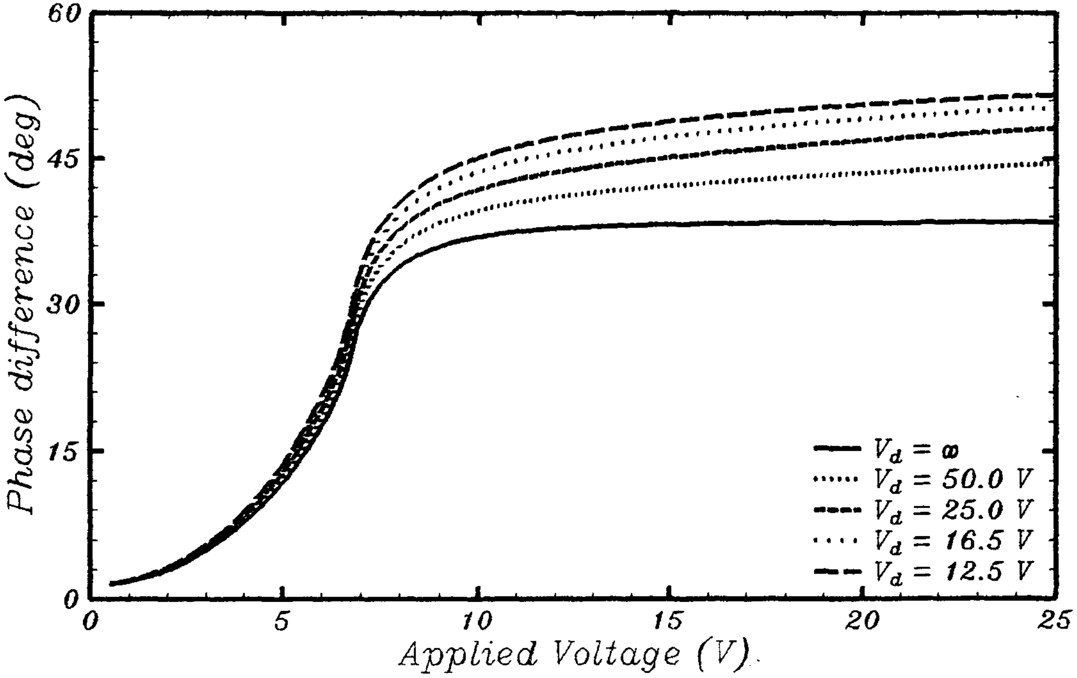

Fig. 2 - Phase difference induced in a PDLC sample (thickness $8\mu m$) by applying external low frequency voltage: theoretical curves obtained for different values of droplet's "voltage constant" V_d.

field is unable to rearrange their internal configuration, so that saturation value is reached just after threshold. On the contrary a low V_d value means that external field has two simultaneous effects: it rotates droplets and rearranges molecules inside droplets, so that droplet optical anysotropy increases after threshold has been reached. The zero field value $S_{d0} = 0.7$, i.e. the droplet order parameter observed without external field, is taken following ref.[3].

4 Discussion of experimental results

The sample (thickness $8\mu m$) was prepared using fluid prepolymer EPON 815 (Shell Chemical Company), MK107 (Wilmington Chemical Corporation), Capcure 3-800 (Diamond Shamack) and B-component by BOSTIK. The liquid crystal was E7 (BDH). Samples were bounded by two conducting glasses. The optical phase shift was measured by a conventional ellipsometric technique using a low power (1mW) He-Ne laser beam as probe and a lock-in detection system to allow a resolution better than 0.5 deg on the phase shift. The sample was placed into a thermostated oven and its temperature was measured using a Pt100 thermoresistence.

Fig. 3 shows experimental data obtained at different temperatures. The theoretical values are obtained assuming K_d and V_d temperature independent ($K_d = 4N/m^2$, $V_d = 20V$). Note that theoretical and experimental behaviour are similar for applied voltage far above threshold (i.e. for $V > 15V$). But theoretical values of threshold slightly increase with temperature while experimental data show that they should decrease as temperature increases (note that experimental data show that curves should intersect each other, i.e. lower threshold corresponds to higher saturation value).

Since in Fig. 1 we have shown that K_d affects the threshold value (while V_d does not), these data suggest that the temperature dependence of the effective droplet elastic constant is very important. On the other hand also the saturation value of the optical phase shift changes with temperature, showing that even V_d has a temperature dependence. Then the experimentally observed lowering of the threshold with temperature means a decreasing value of K_d, while the corresponding higher saturation value means an increasing value of V_d. According to these arguments a satisfactory fit of experimental data is shown in Fig. 4 using different values of K_d and V_d for each temperature. These results allow us to point out that the temperature dependance of the optical phase shift of a PDLC sample is qualitatively

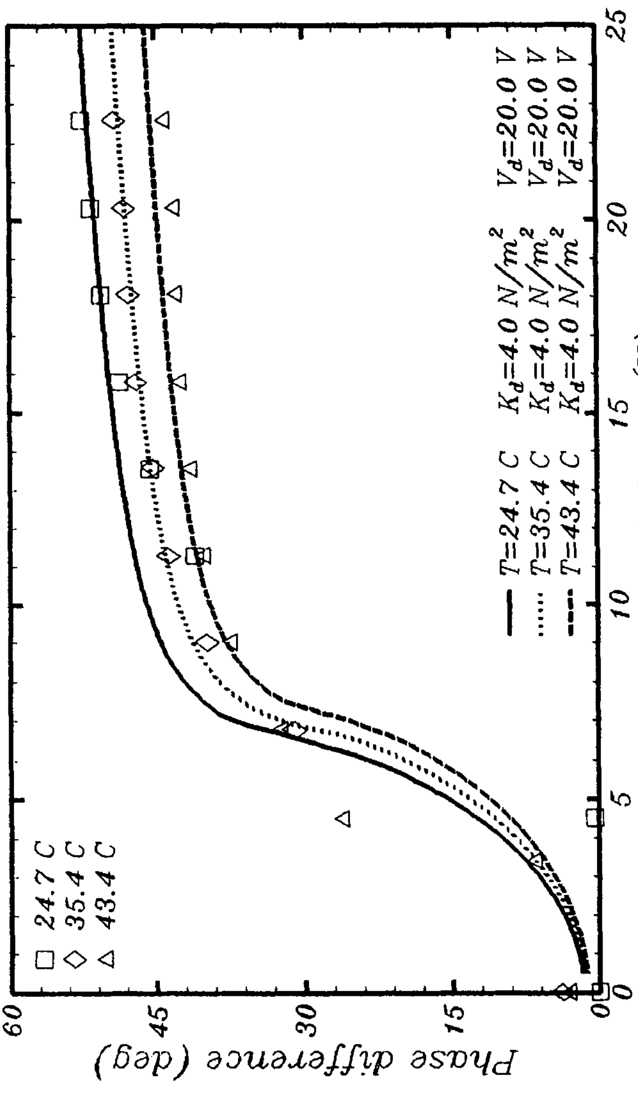

Fig. 3 - Phase difference induced in a PDLC sample by applying external low frequency voltage: experimental values and theoretical curves obtained assuming the same values of K_d and V_d.

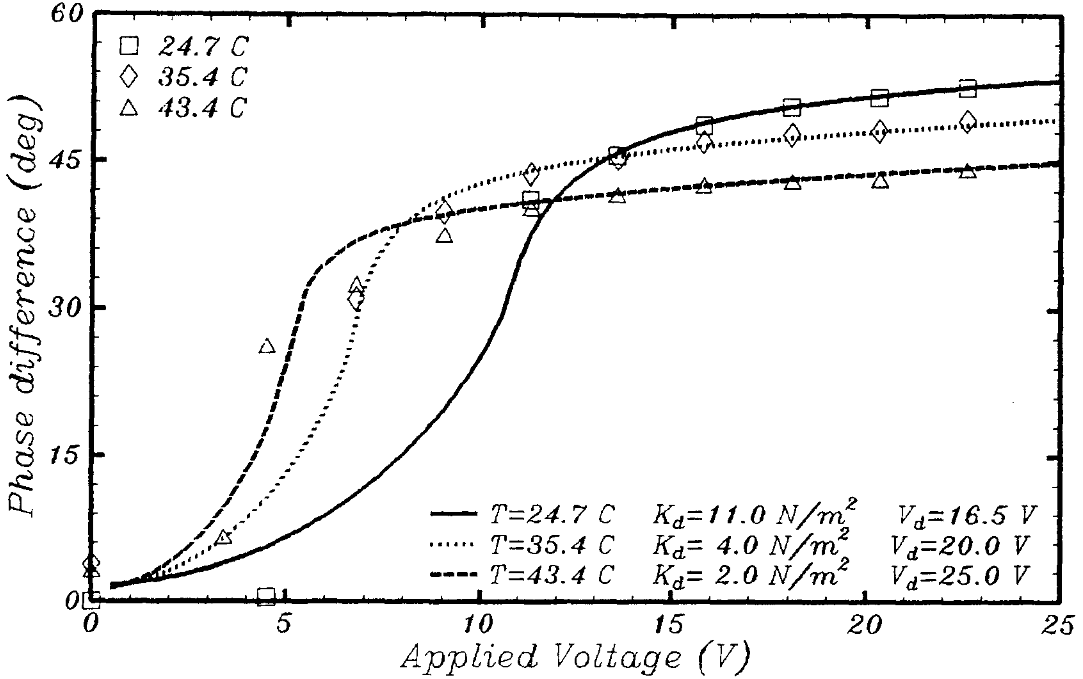

Fig. 4 - Phase difference induced in a PDLC sample by applying external low frequency voltage: experimental values and theoretical curves obtained assuming a different value of K_d and V_d for each temperature.

explained by the model that we have recently introduced using the calculation of the droplet's refractive indices. A more quantitative description needs the knoweledge of the temperature dependence of several material parameters which is not currently available. Anyway our data show the strong dependence on the temperature of the "restoring torque", which needs a deeper study to be completely understood.

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