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Dielectric relaxation in polymer dispersed nematic liquid crystal films

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Dielectric absorption studies for polymer dispersed liquid crystal (PDLC) samples of different nematic (4-hexyl-4′-cyanobiphenyl, 6CB) contents (20, 30, and 40 wt %) have been carried out in the frequency range from 10 kHz to 10 MHz. A method for evaluation of the fraction of the molecules which are not affected by the polymer surface anchoring forces in the nematic droplets is proposed.

1. Introduction

Liquid crystals of low molecular mass dispersed in a solid polymer matrix are a new class of composites which can be used in different types of displays, switchable windows and other electro-optic devices [1, 2]. Several methods have been developed for preparing the polymer dispersed liquid crystal (PDLC) films. The most important are the emulsion method [3, 4] and the phase separation method [5, 6]. Despite the differences in the techniques of preparation, the films show many structural similarities. In particular, the average dimensions of the liquid crystal droplets in the polymer matrix are $0.1 \rightarrow 10\,\mu m$, (usually *c.* $1 \rightarrow 3\,\mu m$) independently of the preparation method [1, 7, 8].

Since dispersion of a liquid crystal in a polymer leads to a large surface-to-volume ratio, the electro-optical properties of the PDLC films are essentially determined by interactions between the liquid crystal and the polymer. On the other hand, the PDLC composites are heterogeneous, and the interfacial effects are also of great significance. Due to the structural peculiarities of PDLC films, one can expect an essential difference between the physical properties of these materials and those of pure liquid crystals, especially the dielectric properties measured in alternating electric fields.

Here we present the results of dielectric absorption studies performed on PDLC films consisting of the nematic 4-*n*-hexyl-4′-cyanobiphenyl (6CB) dispersed in polyester resin matrix.

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2. Experimental
2.1. *Material preparation*

Liquid crystal-polymer composites were prepared by the polymerization induced phase separation (PIPS) method [5, 9, 10]. A one phase mixture of appropriate amounts of 6CB (20, 30, and 40 wt %) and the polymer precursor (unsaturated oligoester resin and UV curing agent), placed between ITO coated glass plates (previously coated by a very thin layer of pure oligoester resin to avoid escape of the LC), was exposed to UV radiation to induce the polymerization process. The curing time was 20 min. In the course of the polymerization process, the solubility of the LC decreases until the nematic phase separates in the form of droplets. This does not mean that in the final PDLC film the whole amount of the nematic is dispersed as droplets. Most polymer matrices absorb liquid crystal and the determination of the partition of the LC between the matrix and the droplets is an essential problem. On the other hand, the nematic droplets contain some quantity of polymer precursor, so one can expect shifts of the temperature of phase transitions.

In the films studied, the mean dimension of the droplets was in the range $2 \rightarrow 5\,\mu m$, and the thickness of the films was about $60\,\mu m$. Figure 1 shows a photomicrograph of the PDLC film studied.

2.2. *Apparatus*

Dielectric absorption spectra were recorded with a HP 4194A Impedance/Gain-Phase Analyser in the

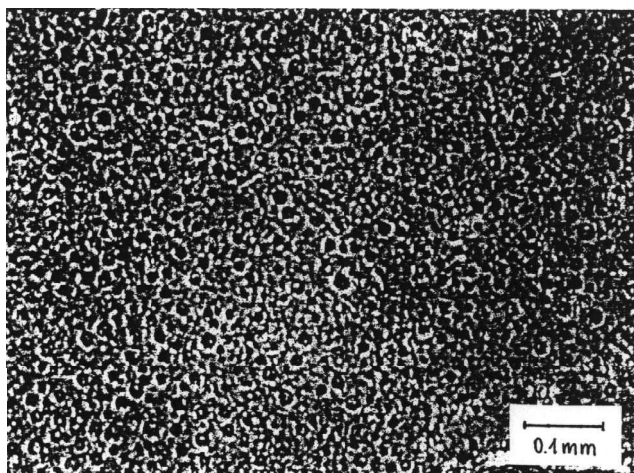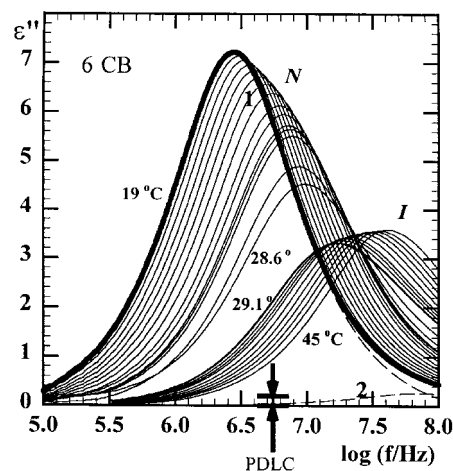Figure 1.   Micrograph of the PDLC film with 30 wt % of 6CB.

Figure 2.   Dielectric absorption spectra of pure 6CB in the nematic (N) and isotropic (I) phases. The spectrum at 19°C is decomposed into two Debye contributions 1 and 2 (dashed lines). The amplitude of dielectric absorption recorded for 6CB dispersed in polymer is marked at the bottom of the picture.

frequency range $10\,kHz \rightarrow 100\,MHz$ for pure 6CB, and in the range $10\,kHz \rightarrow 10\,MHz$ for the PDLC films. The difference in the measuring frequency range results from the use of capacitors of different design. The PDLC films were examined in a two-electrode plane capacitor, connected to the symmetrical output of the Analyser (via the HP 16047A fixture). A capacitor of this design works properly up to about $10\,MHz$, i.e. when empty, the capacity does not depend on the frequency of the applied electric field. Of course, the frequency limit depends on the required accuracy of the measurements. As we will see, in the case of PDLC films, the experimental requirements are exceptionally high.

Another method of dielectric measurement with a HP 4194A Analyser (mainly for liquids and LC) involves the use of a concentric output (via a HP 4194A impedance probe). The measuring capacitor, placed at the end of the concentric probe, consists of three plane electrodes: one central ('hot') electrode and two grounded electrodes on each side. This type of capacitor works excellently up to $100\,MHz$ or even higher [11].

3.   Results and discussion

Pure 6CB shows the following sequence of phase transitions: crystal, (15°C) nematic, and (29°C) isotropic phase. Figure 2 presents the dielectric absorption spectra of this compound in the isotropic (I) and nematic (N) phases. In the nematic phase, the 6CB molecules were oriented by the biasing d.c. electric field ($\sim 5\,V$) perpendicular to the electrode surfaces, i.e. the permittivity was measured parallel to the long axes of the molecules. In the dielectric absorption spectra of such oriented nematics, one absorption band is strongly predominant [12, 13]. In figure 2 we present the decomposition of the absorption band, recorded at 19°C, into two Debye

elementary contributions:

$$\varepsilon''(\omega) = \sum_{i=1}^{2} A_i \frac{\omega \tau}{1 + \omega^2 \tau_i^2} \qquad (1)$$

where A_i denotes the dielectric strength of a given reorientation process, $\omega = 2\pi f$, f being the frequency of the measuring electric field, and τ_i is the Debye relaxation time. The strongly predominant contribution 1 (figure 2) corresponds to the rotation of dipoles around the molecular short axis, and contribution 2, of very small strength, to the rotation around the molecular long axis [14, 15]. In the isotropic phase or, more generally, in non-oriented phases, both types of molecular rotation give contributions to the total dielectric strength which are not that well differentiated because of the random molecular orientations. Besides, contribution 2 is not usually very sensitive to temperature changes or liquid crystalline phase changes [14, 16].

The dielectric signal of *6CB dispersed in the polymer matrix*, in the frequency range studied, is extremely small. The amplitude of the dielectric absorption recorded for the PDLC films is marked at the bottom of figure 2. Because of the contamination of 6CB in the droplets with the polymer binder, the temperature of the isotropic–nematic phase transition in PDLC films was depressed to a value of about 23°C (from 29°C for pure 6CB), practically independent of the LC contents of the films. For the same reason the crystallization temperature has been considerably shifted down (m.p. $< -10°C$) from the value for pure 6CB (m.p. $= 15°C$). As a consequence of the limited measuring frequency range for the PDLC films ($10\,kHz \rightarrow 10\,MHz$) the studies were carried out

only for the nematic phase. In the isotropic phase of PDLC ($T > 23°C$) only a small part of the dielectric absorption band was observed, making quantitative analysis impossible.

Figure 3 shows the dielectric absorption spectra for the nematic PDLC film with 30 wt % of 6CB at different temperatures. The spectra are presented without the background corresponding to the dielectric absorption of the polymer matrix. In the frequency range studied, the background is practically constant and temperature independent. For all PDLC films studied, the ε'' background value was in the range $0.06 \rightarrow 0.14$.

Two dielectric absorption bands can be easily distinguished in the spectra of polymer dispersed nematic 6CB, especially at the low temperatures. An example of the decomposition of the spectrum recorded at $-10°C$, into two Debye-type absorption bands, is presented in figure 3. The spectroscopic parameters (the strength and relaxation time) can be determined with satisfactory precision only for the band 1, particularly at higher temperatures.

Figure 4 presents, in the form of Arrhenius plots, the temperature dependence of the relaxation time τ_1 obtained for PDLC films and for pure 6CB in the nematic phase. There are no doubts that in both systems band 1 corresponds to the same relaxation process (rotation around the molecular short axis) taking place in the same physical conditions. Two experimental facts confirm this supposition:

(i) the values of the τ_1 for PDLC films (20, 30, and 40 wt %) and pure 6CB are equal (if one takes into account the shift in the nematic to isotropic phase transition temperature),

Figure 4. The Arrhenius plots for the relaxation time τ_1 corresponding to the rotation around the short axis of 6CB in the pure state and dispersed in polymer. The arrows indicate the temperature of the nematic to isotropic phase transitions for 6CB and PDLC films.

(ii) the activation energies (the slopes of the $\ln \tau_1 \sim T^{-1}$ dependence) are of the same value ($\Delta E_A = 65\,\text{kJ}\,\text{mol}^{-1}$) both for the PDLCs and pure 6CB.

The main conclusion arising from the results presented is that in the nematic droplets of 6CB dispersed in the polymer, a portion of the molecules behave as in pure 6CB. These 'free' molecules, situated at the centre of droplets, are not affected by the anchoring forces. The important problem requiring an answer is the ratio of the number of 'free' molecules (N_f) to the total number of molecules in droplets (N_t):

$$\xi = \frac{N_f}{N_t} \tag{2}$$

but this can be quite easily resolved here, because the ratio of the dielectric strengths A_1 obtained for the droplets and for pure 6CB gives directly the proportion in question.

Figure 5 presents the dependence of the strengths A_1 on temperature for 6CB in the pure state (A_1^{6CB}) and dispersed in the polymer matrix (A_1^{PDLC}). Because the dielectric strength is proportional to the number of molecular rotators per unit volume, the ξ value can be estimated from the following equation:

$$\xi = \frac{A_1^{PDLC}}{x A_1^{6CB}} \tag{3}$$

where x denotes the fraction of the nematic in the polymer matrix. For the 6CB fractions $x = 0.2, 0.3$, and 0.4, the A_1^{PDLC} values are 0.07, 0.10, and 0.17, respectively (see figure 5). Because the measurements were carried out
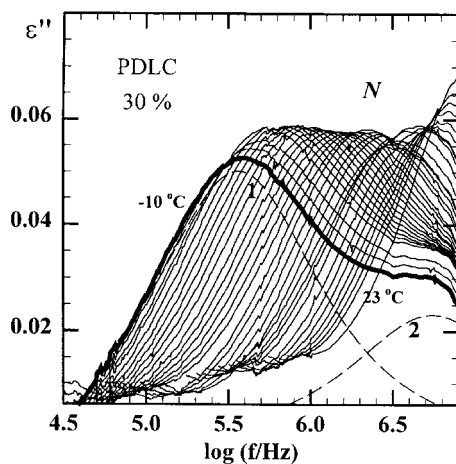

Figure 3. Dielectric absorption spectra for nematic 6CB dispersed in the polyester resin. Dashed lines represent two Debye-type contributions (1 and 2) to the spectrum recorded at $-10°C$.
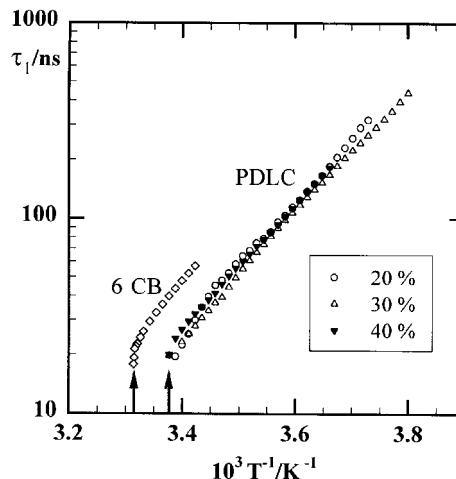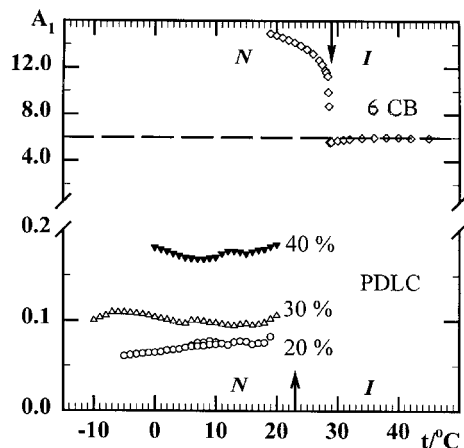
Figure 5. Temperature dependence of the dielectric strength A_1 for 6CB in the pure state and dispersed in the polymer. The dashed line corresponds to the value $A_1^{6CB} \approx 6$, which has been taken as a reference in the estimations of the fraction of 'free' 6CB molecules in the PDLC nematic droplets.

for non-oriented PDLC films, we can suppose that the 'free' 6CB molecules in droplets are randomly oriented. Therefore, as a reference state (for $x = 1$) we chose the isotropic 6CB phase, where the molecules are also randomly oriented. The change in the number of molecules per unit volume caused by the isotropic–nematic phase transition is less than 1% [17] so it is not important for the estimations of the ξ value. As shown in figure 5 the reference value of A_1^{6CB} is equal to about 6.

From the above approximations, the fraction ξ of 'free' 6CB molecules in the nematic droplets, calculated from equation (3) amounts to $7\% \pm 1\%$ independently of the nematic contents in the PDLC films.

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