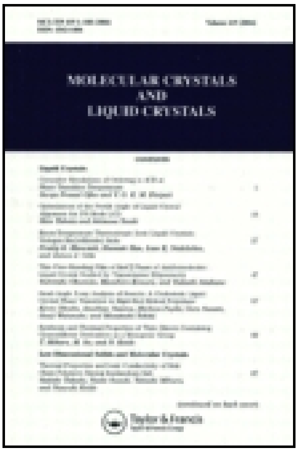

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Structure and Optical Properties of Liquid Crystal Dispersed Polymers

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STRUCTURE AND OPTICAL PROPERTIES OF LIQUID CRYSTAL DISPERSED POLYMERS

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Abstract

Liquid crystal polymer composite systems can be divided into two main subgroups. The first consists of the polymer dispersed liquid crystals (PDLC), where the liquid crystal is dispersed in the *continuous polymer* matrix. The second contains the liquid crystal dispersed polymer (LCDP) systems (sometimes called as liquid crystal/gel dispersions), where only a small amount of polymer is dispersed in a *continuous liquid crystal* matrix. Neutron scattering and optical studies on various LCDP systems were made to investigate the structure of polymers dispersed in nematic and smectic liquid crystals. The results indicate that small (< 100 Å size) fuzzes on the surface of the polymer fibers may play the essential role in the alignment of the liquid crystal molecules. These fuzzes can be realigned by the combination of external fields and heat treatments yielding a fading memory effect. This implies various application possibilities. Among them we describe a novel, electrically driven optical storage effect.

I. INTRODUCTION

Although it was already mentioned by de Gennes[1] in 1979, that liquid crystal-polymer composite systems may have interesting properties, they have attracted significant interest only after their unique electro-optic properties were realized[2,3]. One subgroup of the composite systems is the so called polymer dispersed liquid crystal (PDLC)[2-5] that contain about the same amount of polymer and liquid crystal and forms liquid crystal droplets dispersed in the continuous polymer matrix. These systems can be switched between opaque and transparent states by relatively large voltages. At the OFF state the light is scattered by the misaligned liquid crystal droplets in the micron size range. In the ON state the liquid crystal droplets are uniform, and the light is not scattered provided that the refractive index of the polymer matches that of the liquid crystal. Since the liquid crystal is anisotropic with an angle dependence usually different from that of the polymer matrix, it is difficult to make a haze free transparent state with these materials.

Today there is a great deal of interest in the other type of liquid crystal-polymer composites, the liquid crystal dispersed polymers (LCDP). Here only a small percentage of reactive monomer is dissolved and polymerized *in situ*, in a non-reactive continuous liquid crystal matrix[6-17]. In these composites the polymer makes some kind of network structure which aligns the liquid crystal molecules. The alignment can be altered by external fields, so these systems can also be used for light shutters[9]. Here the matching of the refractive indexes is not important due to the small polymer concentration. Such mixtures offer therefore haze free displays. The alignment of the liquid crystals in these composites was widely studied by polarizing microscopy[7], dielectric[7], diamagnetic[15], NMR[17] and electro-optical technics[7,12,15] which gave, however, only indirect information about the structure of the polymer. X-ray[7,14] and scanning electron-micrographs[13] showed the structure of the polymer skeleton, but only after extraction of the liquid crystal, which may be different from the in situ case. Depending on the compatibility between the polymer and the liquid crystal the composites can greatly differ from each other. Mesogenic polymers are easily dissolved in the liquid crystals[14], while only 1 wt% of a non-mesogenic polymer may phase separate, yielding a paste-like consistency[15].

Speaking about liquid crystal dispersed polymer systems one has to distinguish between two cases: when the polymerization is carried out in the aligned nematic phase[6-14], and when it is done in the isotropic phase of the liquid crystals[15-17]. Roughly, the behaviour of these systems can be summarized as follows.

a.) If the polymerization occurred in the aligned liquid crystal[6-14], an elongated physical network forms. One domain of the network is schematically shown in Fig. 1. Since the film is aligned, the sample is transparent at the OFF state. (Fig.1/a). By moderate ($1-3V/\mu m$) external fields the director of the liquid crystal can be rotated,* yielding a spatial inhomogeneity of the refractive index. Provided that the mesh size of the network is in the visible light wavelength range, the sample is opaque (Fig. 1/b). Due to large fields ($\sim 10\,V/\mu m$) the liquid crystal transforms to mainly homeotropic (except very thin regions near the polymer) and again becomes optically transparent (Fig. 1/c). In the isotropic phase the sample is generally birefringent.

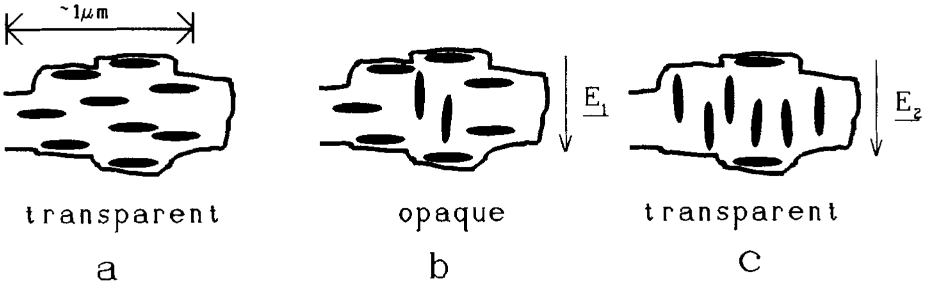

FIGURE 1. Conceptual illustration of one domain of a network structure formed in aligned liquid crystal. a.) if no voltage is applied the sample is planar; b.) under moderate fields $(E_1 \sim 3V/\mu m)$ the director field is perturbed; c.) at large fields $(E_2 \sim 10\,V/\mu m)$ the film is mainly homeotropic.

b.) When the polymerization is carried out in the isotropic phase an isotropic network forms[15-17]. One domain is sketched in Fig. 2. Cooling the sample to the mesophase the polymer imposes a misalignment on the liquid crystal and the sample is opaque in OFF state (Fig. 2/a). Disregarding a very thin region adjacent to the polymer, the liquid crystal can be oriented by large external fields and the sample becomes transparent[15,16] (Fig. 2/b). Such films are generally not birefringent in the isotropic phase.

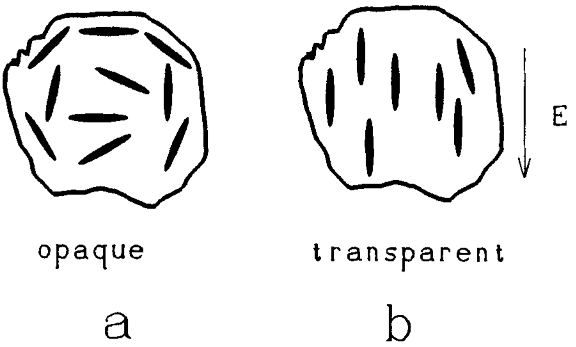

FIGURE 2. Schematic representation of one domain of a network structure formed in the isotropic phase of liquid crystals. a.) no voltage is applied; b.) large voltages are applied on a thin film prepared from bulk material.

By simply putting together the facts that the average mesh size is about 0.5-1 μm (which is clear from optical studies) and that the concentration of the polymer is larger than 1wt%, we get that the domains are separated by polymer fibers of thicknesses larger than about 500 Å, which means a bundle of approximately 10^4 polymer reticulates[15]. It is usually supposed that the shape of the average domain determines the OFF state alignment of the liquid crystal. Our recent neutron scattering studies, however suggest that it is not the case.

In this paper first we review the results of the neutron scattering studies[18,19] and describe a model for explanation. In the second part we present a novel optical storage effect found in an aligned polymer-liquid crystal composite system containing a few percentage of polymer.

II. NEUTRON SCATTERING STUDIES

We studied various liquid crystal polymer composite systems containing 1.5 - 3 wt% of 4,4'-bis (2-methylpropenyloxy)-biphenyl (BMB)[20] or 4,4'-bisacryloyloxy-biphenyl (BAB)[21] as reactive bifunctional monomers and 0.7 - 1 wt% of benzoin-methyl ether (BME) as a photoinitiator. For liquid crystal solvents 4-4'-cyano pentyl biphenyl (5CB, from Merck), 4-4'-cyano-octylbiphenyl (8CB from E.Merck) and 4'-(2-(S)-methylbutyloxyphenyl)-4-undecyloxybenzoate (MBOPE11-OBA, synthetised in the Budapest liquid crystal group[22]) were used. 5CB has a nematic phase between room temperature and 35 °C. 8CB has a nematic phase between 40.5 °C and 33.7 °C, and a smectic A phase between 33.7 °C 21.5 °C. MBOPE11OBA has S_A^* phase between 66 °C and 46 °C and S_C^* between 46 °C and 37 °C. The polymerizations were induced by UV light. We studied samples polymerized either in the isotropic or, in case of 5CB and 8CB, in the aligned nematic and smectic A phases. All the experimental details concerning the sample preparation and neutron scattering technics are written elsewhere[18,19]. Here we note, that it was possible to measure the scattering from the polymer and the (001) reflection of the smectic layers on the same samples. For this we simply switched from the small to the large angle scattering by changing the sample-multidetector distance and the wavelength of the neutron beam. The measurements were carried out *in situ* without the need of extracting the liquid crystal. It is also important that we did not have to use deuterized liquid crystal molecules, because sufficient contrast was achieved with ordinary molecules too.

A. Structure of the polymer[18]

The paste-like consistencies of the studied samples suggest a phase separation between the polymer and the liquid crystal. For this reason we fitted the scattering intensity by the power law,

$$I(q) \sim \frac{R^{D_s}}{6}\frac{1}{q^{6-D_s}}, \tag{1}$$

which describes three dimensional two-phase systems[23]. Here R is the radius of gyration of the scatterer and D_s is the fractal dimension of the interfaces of the two phases. If the surface is smooth (D_s=2), it gives the Porod scattering formula[24], $I \sim R^2/q^4$. On the other hand, if the surface is maximally rough, D_s approaches 3, and $I \sim R^3/q^3$.

Small angle neutron scattering studies alone are not sufficient to distinguish between the possible shapes of the separated polymer. Using the physically reasonable fiber model[15] the average cross section radius, R_c, can be determined from the slope of $ln(I \cdot q)$ vs q^2. For all the studied samples it was found that $R_c \sim 300\,\mathring{A}$, which is in agreement with the expectations[15]. R_c increases with decreasing temperature. From the slope of $ln(I)$ vs q the fractal dimension, D_s is determined. It is found that $D_s \sim 2.5$. This shows that the polymer-liquid crystal interface is diffuse (perhaps fractal), which indicates very large inner surfaces in the sample. Similar large internal surfaces were concluded from birefringence studies too[27]. We found that there is a correlation between D_s and the average size of the separated polymers: they both increase with decreasing temperatures. In a constant temperature the structure is stable in time (at least for several days). This behavior is typical for gels, where the phase separation process is halted at some intermediate state resulting in micro-phase separated composite systems.

B.) Alignment mechanism

a.) Polymerization in pre-aligned smectic A phase

Samples polymerized in the S_A phase aligned prior to the polymerization preserved more or less their orientation after UV curing. Small angle scattering patterns had elliptical shape with the aspect ratio of about 1.6. The direction of the long axis of the ellipse indicates that the polymer chains are parallel to the liquid crystal molecules, so the network is stretched along the director. The sample showed birefringence in the isotropic phase too. Based on this result one domain is sketched conceptually in Fig.3/a.

b.) Polymerization in the isotropic phase

According to the expectations a random director and polymer orientational distribution was observed when the sample was cooled to the nematic and smectic A phase. A corresponding domain is illustrated in Fig. 3/b. Heating this sample to the isotropic phase and then cooled back in the presence of a magnetic field the liquid crystal became aligned, but the cross section of the network still showed random orientation in the 200-300 Å range. A domain with such properties is presented in Fig. 3/c.

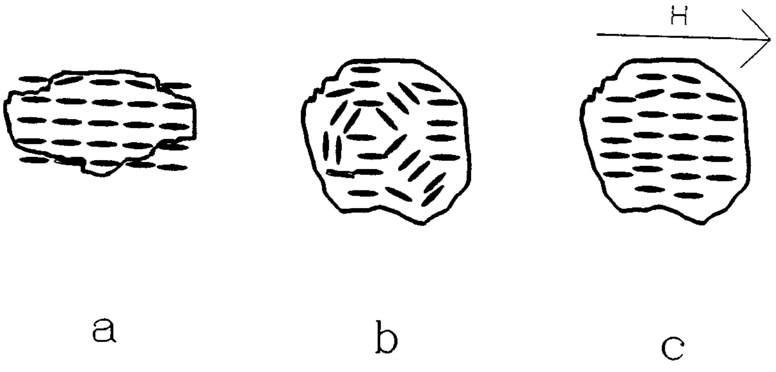

FIGURE 3. Structure of one smectic domain a polymer network based on neutron scattering studies.

a.) After the polymerization is carried out in a pre-aligned smectic A phase.

b.) Cooling the sample to the smectic phase after the polymerization is carried out in the isotropic phase.

c.) Cooling the sample to the smectic phase in the presence of a magnetic field after the polymerization is carried out in the isotropic phase.

After several heating-cooling cycles without magnetic field the sample still remembered the direction of the magnetic field, but the quality of the resulting alignment subsequently decreased, while the polymer structure has not changed in the few hundred Angstrom range. This scenario clearly suggests that the alignment is determined at a less than 100-200 Å scale and not by the overall shape of the network domains. On the basis of the above mentioned experimental results we propose the following model to describe the phase separation process and the mechanism, how the polymer imposes alignment on the liquid crystal.

There are two processes going on when the sample is illuminated by UV light. The first is a cross-linking polymerization, which is a **chemical** process. It is accompanied by a **physical** decomposition of the polymer and the liquid crystal. In a constant temperature the decomposition is halted by the network formation, i.e. by the gelation. This yields the observed *physical network of the polymer.* The extent of the equilibrium segregation depends on the temperature. First only the larger polymers separate out, and the smaller reticulates are still dissolved. As the temperature decreases (especially during the isotropic-nematic phase transition), the liquid crystal medium becomes less good solvent for the polymers and smaller parts separate too. This explains the observed simultaneous increase of R_c and D_s.

When the polymer is dissolved, it is flexible and its shape reflects the symmetry of the system. The polymers that segregated after the phase transition are oriented by the director of the liquid crystal, which is determined by the external field. These oriented reticulates then join to the random network. We think that these fuzzes on the surfaces of the polymer fibers are responsible for the alignment of the liquid crystal molecules. When the sample is heated to the isotropic phase, the oriented parts of the network start to dissolve, but only slowly. Cooling the sample back to the nematic phase, after not a too long stay in the isotropic phase, the polymer network still contains some oriented fuzzes. They remind the liquid crystal molecules to the previous alignment. More intensive heating treatment erases more oriented parts causing the observed fading memory.

According to this model we sketched the structure of the polymer network in different length scales in Fig. 4. The network structure of separated polymer fibers is shown in Fig. 4/a. We suppose that in real the structure is polydisperse, and contains thinner and thicker fibers with different domain sizes. In enlarged (Fig. 4/b) a portion of the liquid crystal polymer interface, formed after cooling the substance in an external magnetic field, is represented. With the largest magnification one polymer reticulate, which is a chemical cross-link of the monomers, is illustrated in Fig. 4/c.

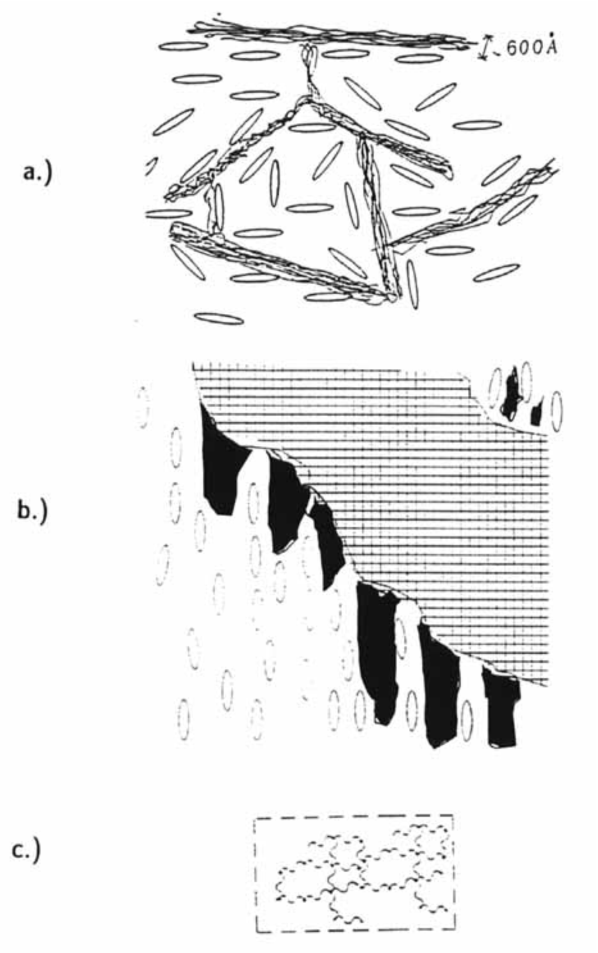

FIGURE 4. Structure of a polymer network in different length scales. Ellipses represent the liquid crystal molecules, the hatched part indicates the stem of the polymer network, and the filled parts are the smaller polymers segregated in the aligned medium. The relative sizes are intended to follow the real situation.

a.) A few domains of the network structure. b.) A portion of the liquid crystal-polymer interface formed after cooling the substance in an external magnetic field. c.) One polymer reticulate, which is a chemical crosslink of bifunctional monomers.

III. ELECTRICALLY CONTROLLED OPTICAL STORAGE EFFECT

Different optical storage effects have already been presented on various liquid crystal composites. For example an interesting erasable storage effect is found by Kreuzer et al.[25] for the so called filled nematics, where silica with 2-3 wt% is dispersed in nematic phase. Recently an optical storage effect was also reported by Hikmet[11] in cholesteric gels containing 28 wt% of mesogenic polymer. In both cases the information was written solely by optical signals. In an aligned nematic gel dispersion film we found a unique optical storage affect, which is controlled by the electric field applied on the sample.

A 40 μm thick sample consisting of 96.5 wt% liquid crystal 5CB, 2 wt% of reactive monomer (BMB), 1 wt% of photoinitiator (BME) and 0.5 wt% of anthraquinon dye (D16) was prepared by means of UV polymerization at T=25°C while the liquid crystal was kept aligned in a magnetic field of H=2 T. Shining the sample with UV for an hour we obtained a planar, optically transparent film. Applying an ac voltage of $U_{\mathrm{eff}} \sim 100\,V$ the film became opaque. Turning the field off it relaxed back (in 1 ms) to the original transparent state (See Fig. 5a). The film was birefringent in the isotropic phase.

Then we illuminated the sample by a He-Ne laser beam (intensities between 3 and 13 mW, diameter $\sim 50\,\mathring{A}$). If an ac voltage was applied simultaneously, the texture had not relaxed back to the transparent state, but remained scattering (Fig. 5/b). Optical micrographs of areas illuminated by a 13 mW He-Ne laser beam for 10 sec and 3 minutes, meanwhile $U=145\,V$ was applied, are seen on Figs. 6/a and 6/b respectively.

Our preliminary results can be summarized as follows.

(i) The contrast and spot size increases with U and the illumination time (if $U=0$, there is no effect!).

(ii) The scattering of the illuminated spot is stronger than that of other parts at ON state.

(iii) The spot is not visible in the isotropic phase, but reappears cooling back to the nematic phase.

(iv) It does not matter whether the electric field or the laser was turned off first.

(v) The illuminated areas are still birefringent in the isotropic phase.

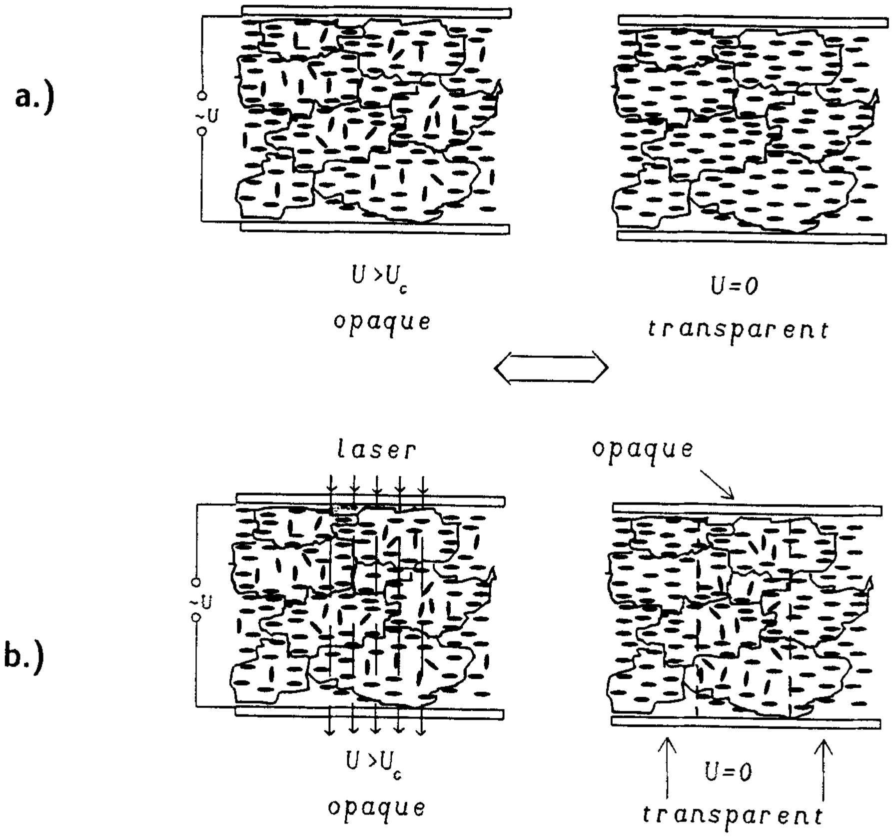

FIGURE 5. Structure of aligned liquid crystal gel dispersion film.
a.) When an electric field ($\sim 3\,V/\mu m$) is applied the film is opaque. After the field is removed it quickly relaxes back to the transparent state.
b.) The sample is shined by a laser light, while an electric field is applied. On removal of the field the film does not relax back to the transparent state.

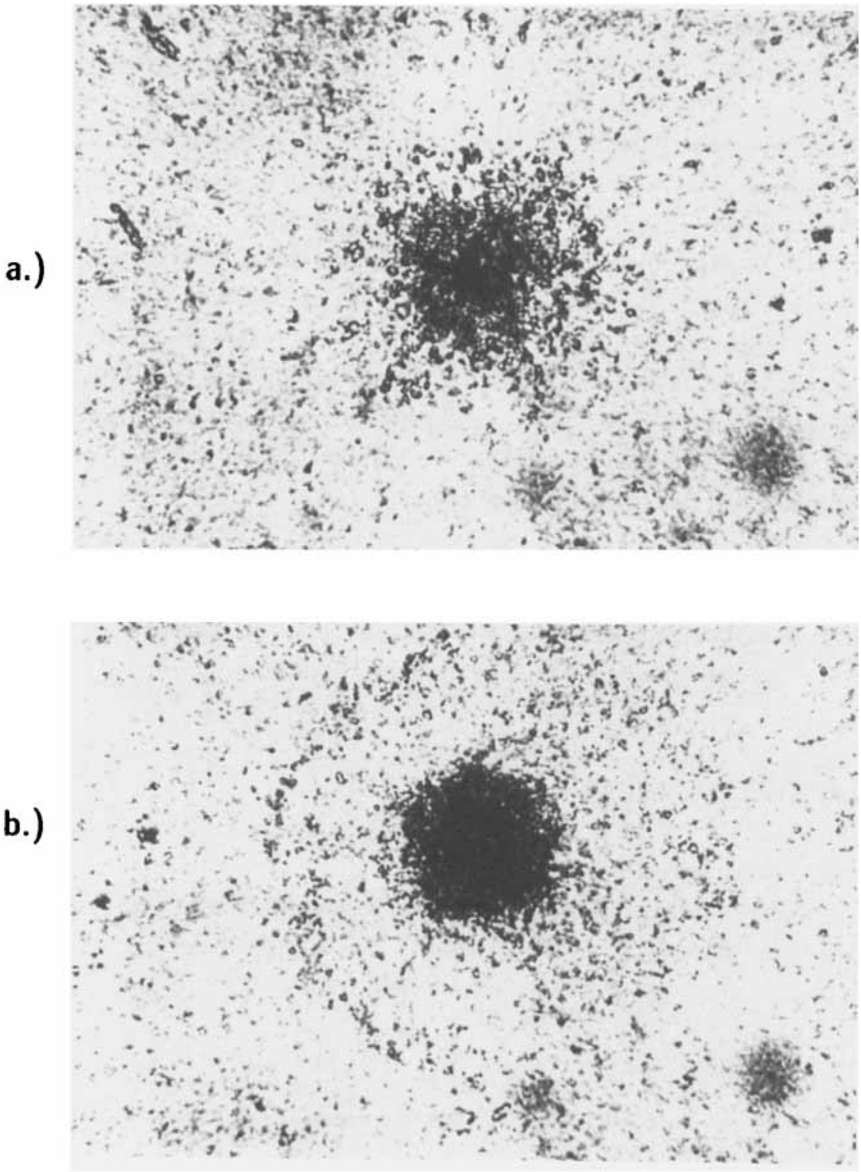

FIGURE 6.: Optical micrograph ($N = 400$) of a $40\,\mu m$ thick aligned liquid crystal-polymer composite film (96.5 % 5CB, 2 % BMB, 1 % BME and 0,5 % dye D16) shined by $13\,mW$ He-Ne laser beam of $50\,\mu m$ diameter for a.) 10 sec, b.) 3 minutes. During the illumination $U = 145\,V$ ac voltage was applied.

At present we do not have a complete explanation for the observed effect. We measured that 75 % of the laser light is absorbed by the dyes, which means that the liquid crystal is considerably heated up. On the basis of calculation given by Jánossy and Kósa[26] we estimate that $13\,mW$ of laser beam heats the illuminated area by about $60\,°C$, so the liquid crystal is well in the isotropic phase. It is reasonable to suppose[15] that the polymer is softer and more deformable at high temperature. It is not clear, however, what kind of an effect of the electric field has in the isotropic phase. There are two possibilities that might play a role. One is that, even in the isotropic phase, there are thin liquid crystal regions at the immediate vicinity of the polymer interfaces. Such kind of bounded liquid crystal layers were indicated by Hikmet for much higher polymer concentrations[7]. An other possibility is that the dielectric anisotropy of the polymer network is not zero. In both cases there would be a torque by the external field deforming the polymer. For a better understanding of this effect more detailed studies are required. Such investigations are in progress.

As a summary, we proposed a model which describes the structure formation of the polymers dispersed in liquid crystals, and explains the observed polymer induced alignment effect. We also presented an electrically controlled optical storage effect in aligned liquid crystal gel dispersions.

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