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Effect of a polymer network on the alignment and the rotational viscosity of a nematic liquid crystal

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Polymer dispersions were made by photoinduced polymerization of 4,4'-bisacryloyl-biphenyl in liquid crystal 4-4'-cyano pentyl biphenyl as nematic solvent. Samples were prepared with 0.5, 1, and 1.5 wt % monomer. The polymerization was done in the isotropic phase. The rotational viscosities of the two lower concentration samples increased only moderately after UV curing (3 mW/cm², 25 min). The 1.5 wt % sample gave under the same condition a nematic with a fairly rigid anisotropic network that did not realign in magnetic field up to 20 kG. We estimate that the mesh size of the network was in the order of 1 μm, significantly smaller than the magnetic coherence length of the solvent that is in the order of 5 μm. The diamagnetic anisotropies of the aligned samples were not affected significantly by the polymer. We studied electro-optical properties on thin films. The films were strongly light scattering but they could be switched to transparent state. We conclude that the polymer forms a network of loosely connected fibrils that interacts strongly with the director field.

I. INTRODUCTION

Recently, new liquid crystal systems with interesting electro-optical properties have been reported that contain a small amount of polymeric material. They were obtained by dissolving reactive monomers in nematic liquid crystals that were polymerized under UV light with the help of a photoinitiator. The polymers can form networks that strongly affect mechanical and optical properties. The systems were first investigated at the Philips Research Laboratories¹⁻³ mainly by Hikmet.^{1,2} He used sandwich cells and performed the polymerization in aligned nematic films.² The samples remained aligned and transparent but they changed to a strongly light scattering texture upon application of an electric field.

Hikmet studied the electro-optic properties of sandwich cells that have a potential for display applications. Similar systems were studied by NMR in bulk samples.⁴ It was confirmed that the orientation of the polymer strongly affects the orientation of the nematic director, even in the presence of a strong magnetic field (4.7 T). The observations indicate that the polymer forms a network that is strongly anisotropic when the polymerization takes place in the nematic state.

The dynamics of the response to fields, the thresholds, and the relaxation processes are controlled by the rotational viscosity of the liquid crystal and the mesh size of the network. It is therefore of interest to explore the dependence of the viscous properties upon network formation and polymer concentration. In this article, we report direct rotational viscosity measurements, measurements of the diamagnetic anisotropy, and microscopic studies of electro-optical properties on samples with various polymer concentrations. The results give information on the properties of the nematic state within the network and how the polymer network depends on the preparation.

II. EXPERIMENTAL ASPECTS

We used 4-4'-cyanopentylbiphenyl (5CB) as the nematic solvent, 4,4'-disacryloylbiphenyl (BAB) as the monomer and benzoinmethyl ether (BME) as a photoinitiator. The same system was used for the NMR research.⁴ Samples were prepared in quantities of 1 g with 0.5, 1.0, and 1.5 wt % monomer. The polymerization was done in the isotropic phase at 50 °C. Typically, the samples were kept in Petri dishes and stirred during the UV illumination but, for comparison, one sample was prepared without stirring. Most of samples were UV cured under a 1.1 kW mercury light exposure system (the flux at the sample is approximately 3 mW/cm²). The composition and the procedures of the curing are summarized in Table I.

The viscosity measurements were done in high-precision NMR sample tubes of 0.5 cm diameter. Some of the samples were UV treated for a second time in the sample tubes without stirring.

The rotational viscosities were measured by suspending the samples in a magnetic field on a thin tungsten wire. The wire, in turn, was connected to a step motor (Oriol 20010). Rotation of the sample at a constant angular velocity ω in a strong uniform magnetic field requires a torque M that is transmitted by the torsion wire. The torque was determined by measuring the twist angle of the torsion wire. See Ref. 5 for further details. For sufficiently high fields and under steady rotation, the director forms a constant angle with the magnetic field while liquid crystals in good approximation rotate with the sample tube. In equilibrium, we then have

$$M = \gamma_1 \omega V = k\alpha. \quad (1)$$

Here α is the angular deviation of the torsion wire and V is the sample volume. Equation (1) is used to measure γ_1 directly.

The derivation of Eq. (1) assumes that the sample has rotational symmetry, i.e., all orientations of the director

TABLE I. Sample composition and preparation.

| Sample | Composition | | Curing process |
|--------|-------------|----------|--------------------------------------|
| A | 0.5% BAB | 0.5% BME | 200 W, 5 h, stirred |
| B1 | 0.5% | 0.5% | 1.1 kW, 25 min, stirred |
| B2 | 0.5% | 0.5% | B1+25 min, at 1.1 kW in NMR tube |
| C | 0.5% | 0.5% | the same as B1 |
| D | 0.5% | 0.5% | like B1 without stirring |
| E1 | 1.0% | 0.5% | 1.1 kW, 25 min, stirred |
| E2 | 1.0% | 0.5% | E1+25 min at 1.1 kW in NMR tube |
| F | 1.5% | 0.75% | 1.1 kW, 25 min, stirred ^a |
| G | pure 5CB | | |

^aStirring was stopped when sample became gel (after 15 min).

field are energetically equivalent. This condition does not hold for materials with an anisotropic network. The network couples with the director field and elastic torques have to be considered in addition to the viscous torque. In the limit of high fields, when the magnetic coherence length is much shorter than the effective mesh size of the network, the coupling should be negligible and Eq. (1) may be used again. This implies that the diamagnetic anisotropy of the network itself is relatively small, which is true for the studied samples that contain less than 2% polymer.

In the other limit, when the magnetic coherence length is large compared to the effective mesh size, the viscous torque is negligible. In this limit, it is possible to determine the spontaneous alignment by measuring oscillation frequencies in magnetic fields or by direct torque measurements. The diamagnetic anisotropy is a measure of the degree of alignment of the nematic liquid by the network. It can be compared to the diamagnetic anisotropy of the polymer-free nematic.

For measurements of diamagnetic anisotropies, we used fields in the range of 0.7 to 2.5 kG. For these fields, the coherence length is on the order of 10 μm and viscous damping is small so that oscillation frequencies can be determined accurately.

We complemented the studies of the bulk samples by microscopic studies on films of 20 μm thickness and determined some electro-optical properties, in particular contrast and alignment in electric fields.

III. EXPERIMENTAL RESULTS

A. Transition temperatures

The nematic isotropic transition of 5CB is at 34.9 $^{\circ}\text{C}$. The transition temperature decreases by addition of 0.5% (0.75%) photoinitiator BME by about 1.3 $^{\circ}\text{C}$ (1.7 $^{\circ}\text{C}$), and by addition of 0.5, 1, or 1.5% monomer BAB, it decreases further by approximately 0.4, 0.8, and 1.2 $^{\circ}\text{C}$, respectively. The total change after polymerization was typically less than 1 $^{\circ}\text{C}$.

B. Rotational viscosities

The rotational viscosities of different samples are summarized in Figs. 1 and 2. In Fig. 1 the rotational viscosities are given of pure 5CB and of samples B1 and E1, which

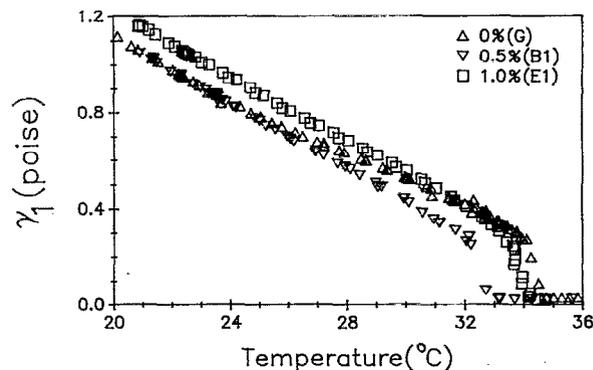


FIG. 1. Rotational viscosities of 5CB and of samples B1 and E1.

contain 0.5% and 1% BAB. Figure 2 shows the viscosities of differently treated samples each containing 0.5% BAB. The results on γ_1 of the pure 5CB agree within 5% with earlier measurements.⁶

For the samples A, B1, C, D, and E1, the rotational viscosity deviates only moderately from pure 5CB, by less than 30%. The results for samples B1 and C, which have the same composition and were treated identically, deviate by about 20%. This shows the limits of the reproducibility. Stirring during exposure had only a negligible effect on the viscosity as comparison between samples D and C shows.

Samples F, E2, and B2 had networks of a strong spontaneous anisotropy and showed separation into different phases. Their viscosities could not be measured by the rotating field method. The magnetic fields were not strong enough to obtain a coherence length smaller than the mesh size.

C. Macroscopic structure of the samples

Freshly prepared samples showed no preferred alignment in the NMR tubes. The samples containing 0.5% or 1% BAB became anisotropic on cooling from the isotropic phase in presence of a magnetic field. The axis of anisotropy coincides with the direction of the field at the moment when the sample turned nematic. Once formed, the axis of anisotropy remains fixed. Reheating to the isotropic phase and cooling again, but without the external

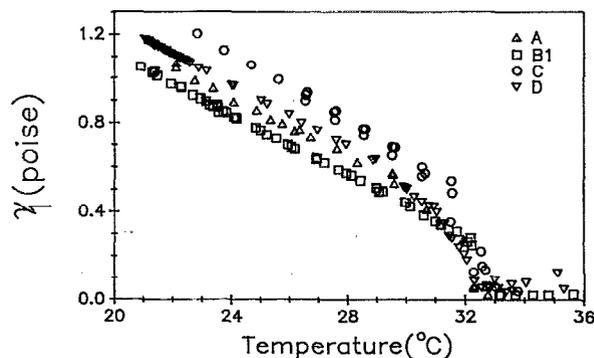


FIG. 2. Rotational viscosities of differently treated samples containing 0.5 wt % BAB.

field, gives a weaker anisotropy with the same axis. After five heating and cooling cycles, the anisotropy had reduced to about one half the original value.

The samples containing 0.5% and 1% BAB remained macroscopically fluid after 25 min of UV exposures, while sample F (1.5% BAB) became gel-like. (It had to be heated to above 100 °C in order to fill the sample tube.) We observed that the sample macroscopically separated after about one week into fractions of gel-like consistency, usually at the bottom or the side walls of the sample tube, and a fluid fraction of lower density. The ratio of the gel-like and fluid parts were approximately 0.1 and 0.9 in case of 0.5% and 1.5% BAB, respectively. The volume of the fluid part could be increased by centrifuging.

We filled cells with materials from the fluid parts and from the gel-like parts and studied their texture microscopically. The fluid fraction aligned homogeneously between polyimide-coated glasses, while the gel-like part gave a strongly light scattering texture. The nematic isotropic transition temperatures of the fluid fraction and of the gel-like fraction were not significantly different and about equal to that of the non-UV-cured materials. Thin films with freshly prepared materials also showed separation. Microscopic studies showed regions that aligned like the pure liquid crystal and regions that consisted of small domains.

D. Diamagnetic anisotropies

Diamagnetic anisotropies were measured by the oscillation method. The derived diamagnetic anisotropies were independent of the field strength in the limit of low fields ($H < 1.5$ kG). For fluid samples, the fields must be low enough so that the time for reorientation of the director field is larger than the oscillation period. For the gel-like sample E2, fields below 1.5 kG also did not change the alignment by the network.

The diamagnetic anisotropies of the different samples are summarized in Fig. 3. The anisotropies differ only slightly for samples containing different amounts of polymers. With increasing concentration, the anisotropy at the transition seems to increase slightly, but the differences decrease with decreasing temperatures. Our results on the pure liquid crystal agree well with earlier measurements.⁷ It is particularly remarkable that the anisotropy of the gel-like E2 is also equal to the anisotropy of the fluid samples. In the gel-like material, the alignment of the nematic director is due to the network and the anisotropy shows that this alignment is essentially as perfect as the field-induced alignment of the liquid samples. It indicates that the major part of the network consists of parallel polymer fibrils or strands.

E. Electro-optical studies on thin films

As mentioned, thin films prepared with the gel-like materials are strongly light scattering. They switch to a transparent state when an electric field is applied. These shutters are similar in appearance to polymer dispersed liquid crystal (PDLC) films. The texture between crossed

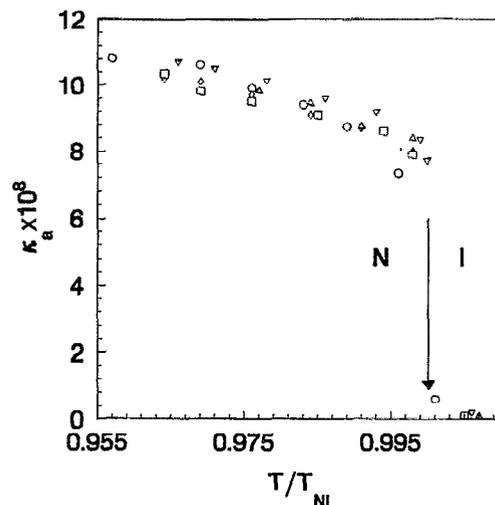


FIG. 3. Temperature dependence of diamagnetic anisotropies. ○: pure 5CB; ◇, □, and △: samples B1, B2, and D (all contain 0.5% BAB); ▽: sample E2 (1% BAB).

polarizers in the off and on states are shown in Fig. 4. The films never become completely black between crossed polarizers even in the isotropic phase.

The voltage dependence of the transmittance is shown in Fig. 5. [Transmittance = $(I_0 - I_s)/I_0$, where I_0 is the transmitted intensity without a cell and I_s the total scattered plus reflected intensity in presence of a cell.] The range between the scattering and the transparent state is very broad. The contrasts are good. With a film prepared from sample F, the contrast ratio is about 500 and about 50 for sample E2. The difference in contrast between the two samples is due to the weaker scattering of the sample E2. The values for typical PDLC films measured by the same technique are 50–100. The relaxation time of sample F at room temperature is 7 ms, whereas it is 15 ms for sample E2.

IV. DISCUSSION

The results show that even a small percentage of polymer can strongly affect the macroscopic properties of the material. The properties depend on the exposure times, the percentage of the monomer, and the phase in which the polymerization takes place. The polymerized mixtures tend

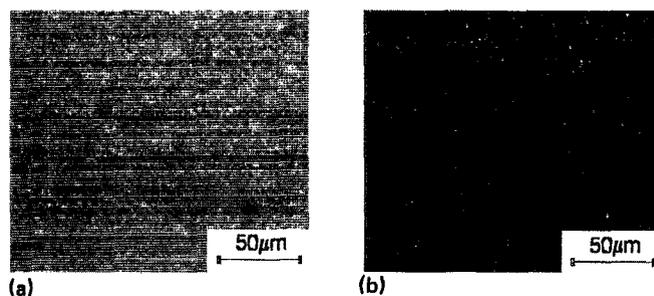


FIG. 4. Microscopic textures of a 20- μ m-thick film of 5CB+1 wt % BAB (a) 0 V; (b) 60 V. (crossed polarized, 500 \times .)

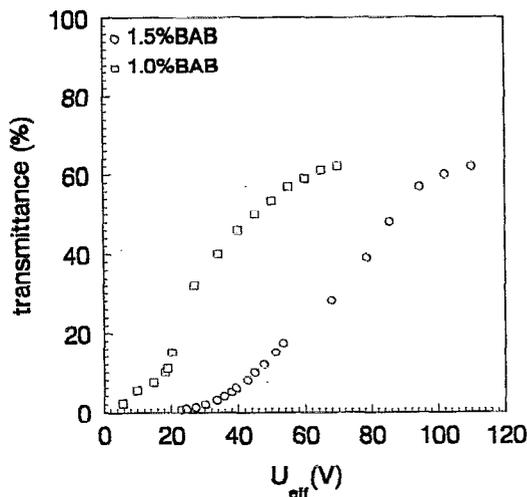


FIG. 5. Transmitted light intensity vs applied voltage. 20 μm films containing 1 and 1.5 wt % BAB. Transmittance of the empty cell is 75%.

to separate into gel-like and liquid parts. The liquid part has properties similar to pure 5CB. The polymer is concentrated in the gel-like part and forms some kind of a network that couples strongly with the nematic director. However, the network is not due to crosslinking by chemical bonds. The observation that some birefringence specks are still present in the isotropic range indicates that the polymer aggregates and separates from the liquid crystal and during this process a network develops. It is remarkable that the network can be made anisotropic so that it perfectly aligns the liquid crystal. This suggests that, in separating, the polymer aggregates to fibrils that arrange fairly parallel. They may be interconnected by single chains or thin strands that do not significantly interfere with the alignment.

At low polymer concentrations, well-aligned anisotropic networks can be obtained by cooling from the isotropic phase in the presence of a magnetic field. Accordingly, the network breaks down to some extent at the higher temperatures, probably by disruption of the connections between the fibrils which then can be aligned by the nematic solvent. As the temperature is lowered, the connections may gradually reform, resulting in a rigid anisotropic network that cannot be changed by electric or magnetic fields.

The mesh size of the network determines the minimum field strength required to compete with the alignment by the network. The coherence length of the fields must be comparable to the mesh size, i.e., the distance between the fibrils. For the two samples of Fig. 5, we estimate critical voltages of about 20 and 40 V for the 1% and the 1.5% BAB samples, respectively. These correspond to mesh sizes on the order of 1 μm [$L(\text{mesh}) \approx (1/E_0) \sqrt{K/\epsilon_0 \epsilon_a}$]. Since the voltage for the 1.5% sample is higher by a factor 2, its mesh size is one-half the size of the 1% sample and the relaxation time should accordingly be smaller by a factor of 1/4, provided that the viscous and curvature elastic properties remain unchanged. The measurements show

that the relaxation time is indeed shorter but only by a factor of 1/2. It seems that the effective viscosity in the higher concentration sample has become larger by a factor of 2. These are, however, very crude estimates. The network probably has a broad distribution of mesh sizes and the effective relaxation times may not be proportional to the inverse square of the average mesh size.

Given the mesh size, we can estimate the radius of the polymer fibril. We assume that the polymer occupies about 1% of the volume and that the strands are parallel and form a regular hexagonal lattice with a lattice constant equal to the mesh size. The radius of the fibril is then

$$r \approx L(\text{mesh})/17.$$

With a mesh size of 1 μm , it follows that $r \approx 600 \text{ \AA}$, or the average strand would consist of a bundle of approximately 10^4 polymer chains. On the other hand, when we assume that the strands consist of single chain of a radius of 3 \AA , the mesh would only be 50 \AA . This estimate shows that the network would be rather dense if it were formed by single polymer chains.

V. CONCLUSION

The proposed structural model of a network formed by loosely connected parallel fibrils that interact strongly with the director field explains qualitatively the relevant electro-optical and mechanical features. Specifically, it is in agreement with the discovery of Hikmet^{1,2} that transparent films can be switched to an opaque state when a field is applied. In these films, the field destroys the uniform alignment induced by a monodomain network. Films that are opaque in the off state require randomly distributed polydomain networks. Although the model can explain our observations, additional work is needed to verify it. It should be noted here that an electromicroscopic study indicates a separation of the polymer as lamellae¹ instead of fibrils. It is, however, not clear how the lamellae can induce a uniform alignment of the nematic solvent. For practical applications, well-defined networks are important and it is of interest to study further the factors that control the network and its structure.

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