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Liquid crystal/liquid-crystalline network composite systems

Structure formation and electro-optic properties

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The supermolecular structure and the electro-optic properties of a composite system consisting of a dense liquid-crystalline network and a low molar mass liquid crystal embedded in the network have been characterized. The composite systems were obtained by a photopolymerization of mixtures of a rigid mesogenic spacerless diacrylate and a low molar mass liquid crystal. They are characterized by a homogeneous distribution of the low molar mass liquid crystal in the network. The network has a cocontinuous periodic spinodal-type structure having a characteristic length scale of the order of 10 nm, if the low molar mass liquid crystal is removed or replaced by other solvents. The electro-optic switching properties are characterized by the fact that the active switching time and the width of the Frederiks transition are shifted to larger values as compared to those of the pure liquid-crystalline state. The decay times, on the other hand, are strongly reduced in the network.

1. Introduction

Liquid crystal/polymer network composite systems are of great interest both from a theoretical and an application point of view [1–6]. With respect to theory, de Gennes [1] has pointed out that the formation of cross-links in such systems promotes an effective attraction between the reacting monomers in this case and that this effect tends to induce a segregation between the network and the solvent. This segregation is expected to happen not on a macroscopic but rather on a microscopic scale as controlled by the competition between curing and phase separation. De Gennes has further pointed out, that particularly interesting features might result, if the network is formed inside a pre-existing organized structure, as for instance in a liquid-crystalline state. On the other hand, as far as applications are concerned, polymer/liquid crystal composites have been studied in recent years for the purpose of using them as large area flexible display devices [2–5]. They consist of an amorphous, isotropic thermoplastic or duromeric matrix in which low molar mass liquid crystals are embedded as the dispersed phase. Externally applied electric fields cause a transition in the distribution of the optic axes of the liquid crystal and thus a switching from a configuration where the refractive indices of matrix and dispersed phase do not match to one where they do. The result is a strong variation of the scattering and absorption properties of the composite films. A characteristic feature of these systems is that the

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orientational distribution in the off-state and the reorientational forces governing the relaxation in the off-state are controlled by the shape of the particles and dispersed phase-matrix surface interactions. These are rather weak and often not well-defined.

This disadvantage does not exist for a very interesting and promising extension of this concept which was recently proposed [6]. The basic idea was to use a macroscopically oriented dense liquid-crystalline network, actually a liquid-crystalline duromer, as the matrix material. Such a composite system was obtained by starting from a mixture of low molecular weight liquid crystal and thermotropic diacrylate monomers containing flexible spacer groups. The network formation was achieved by photopolymerization in the presence of a photoinitiator [7–9]. The intrinsic orientation of the network controls in this case the orientation of the dispersed liquid crystals in the off-state and provides a very effective restoring force in the absence of the external electric field. A feature which was not studied for such networks was the structure formation induced by curing, i.e. the spatial distribution of the low molar mass liquid crystal in the anisotropic network after photopolymerization.

As part of our studies on networks formed by rigid mesogenic spacerless diacrylates and their mixtures with similarly constructed monoacrylates [10] we also became interested in the structure formation in mixtures with low molar mass liquid crystals with such diacrylates and with the corresponding electrooptic properties. This paper reports the results of our investigations of such structural and electro-optic properties.

2. Experimental

2.1. *Materials*

4-Acryloyloxyphenyl-4′-acryloyloxybenzoate **1** was prepared according to the procedure described by van Lyen and Strzelecki [11], as reported previously [10]. The low molar mass liquid crystal component **2** (ZLI 1132, Merck) used for these studies was a mixture with positive dielectric anisotropy used for display purposes. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone **3** (Ciby–Geigy, Basle, Switzerland) was used without further purification. The mixtures were prepared by dissolving the components in dichloromethane and the solvent was subsequently evaporated under vacuum.

2.2. *Experimental techniques*

UV irradiation was carried out with an Osram Ultra-Vitalux 300 W sunlamp. The samples were heated to a polymerization temperature with a heating rate of $20\,\mathrm{K\,min^{-1}}$. The time between heating and UV irradiation was kept as short as possible in order to prevent thermally initiated polymerization.

Oriented samples of the monomer mixtures within the liquid-crystalline state were prepared using a technique which is well known from display technology [12, 13]. It consisted of placing the monomers on a glass slide which was coated with a thin polyimide layer. This layer was rubbed along a given direction. A homogeneous texture was achieved for the monomers by heating the samples into the temperature range in which a liquid-crystalline state exists. In addition we used a magnetic field of 1 T to obtain homogeneously aligned samples [12, 13]. The induced orientational order was characterized for the original monomer mixture, the cured network as well as for intermediate stages by birefringence measurements.

The phase diagrams of the mixtures were determined by polarizing microscopy. The distribution of the low molar mass component was characterized by means of a Kratky small angle X-ray camera equipped with 50 μm slit-like collimators and a position sensitive counter. The results were desmeared by the standard deconvolution procedure.

The experiments were performed on the original composite networks, on networks where the low molar mass component ZLI was removed either by a solvent or by heating the network to elevated temperatures, which resulted in the evaporation of the liquid crystal. The removal of ZLI component was quantitative as apparent from the weight loss. In addition we report small angle X-ray scattering results for networks, which were filled with paraffin after the low molar mass component ZLI had been removed by these methods.

3. Results and discussion

3.1. *The phase behaviour of the monomer mixtures*

Figure 1 shows the phase diagram of the mixtures of the diacrylate with the low molar mass ZLI. The nematic–isotropic transition temperature varies almost linearly with the composition, a feature which is characteristic for mixtures of low molar mass liquid crystals [13]. The mixture becomes heterogeneous at lower temperatures, where it contains both crystalline and liquid-crystalline regions. The photopolymerization was carried out at temperatures well within the homogeneous nematic phase.

3.2. *The structure of the network*

The structure of the composite network obtained by photopolymerization within the nematic state was analysed by means of small angle X-ray scattering. The expectation for a network containing the low molar mass liquid crystal homogeneously distributed is a scattering curve which is predominantly constant in the small angle regime, the absolute value of the scattered intensity being controlled by the

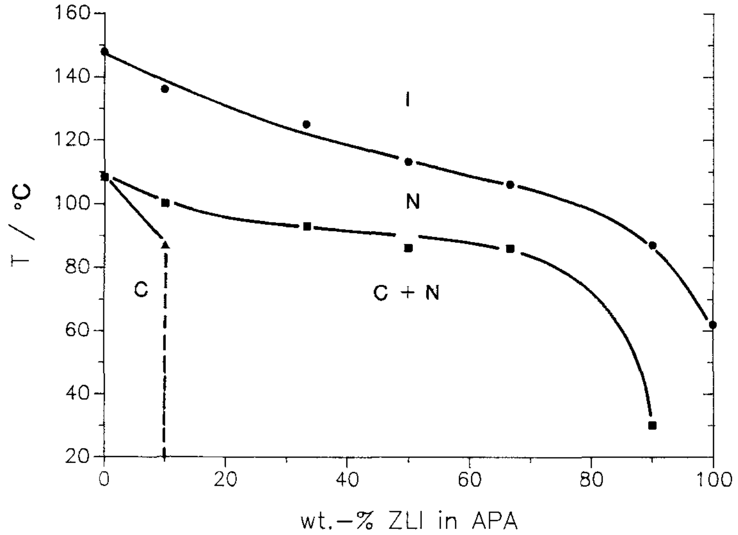

Figure 1. The phase diagram for the mixture of the rigid spacerless diacrylate and the low molar mass liquid crystal ZLI.

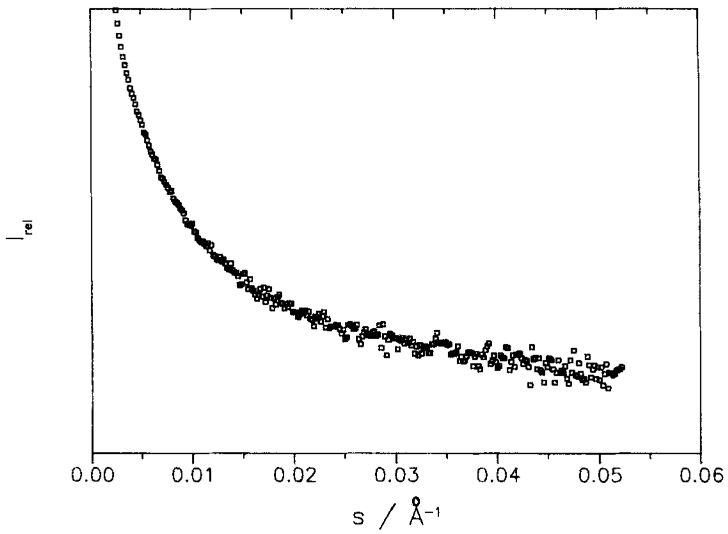

Figure 2. The small angle X-ray scattering curve of the composite network containing the ZLI ($s = 2\sin\Theta/l$, 2Θ: scattering angle, I_{rel}: relative scattering intensity).

magnitude of the concentration and density fluctuations [14, 15]. The actual observation, however, deviates strongly from such an expectation, as is apparent from figure 2. The scattering is large at small angles and decreases continuously with increasing magnitude of the scattering vector. Similar scattering behaviour is also observed for the monomer mixtures and for the partially cured system: the absolute scattering intensity is, however, smaller as compared to the totally cured state. The possible origin of such behaviour will be discussed later. It is sufficient to state here that such behaviour is characteristic of mixtures in the neighbourhood of the critical point or of the spinodal [16].

Next we consider the small angle scattering results obtained for networks from which the low molar mass liquid-crystalline compound has been removed by solvents, i.e. for dry networks. The analysis of the masses of the samples prior to and after the removal of the liquid crystal showed that the liquid-crystalline component ZLI could be removed completely. This has to be taken as a strong indication that some kind of cocontinuous structure exists. Figure 3 displays the small angle X-ray results obtained for such a sample: it shows a distinct scattering maximum. These X-ray results strongly suggest that the rigid network forms a regular periodic structure. Pure particle scattering indicative of a matrix-dispersed phase structure would give rise to a continuously decreasing scattering intensity. Such a structure is at variance with the cocontinuous structure described here. The periodicity, which is obtained from the position of the scattering maximum is of the the order of 10 nm and depends to a certain extent on the original composition of the monomer mixtures. The underlaying periodic structure has to be distorted quite strongly, since we are only able to observe the first order reflection despite the large scattering contrast available. Additional information on this periodic network structure is available from an analysis of the tail of the scattering curves at large values of q [17, 18]. The observation is that the smeared scattering curve decays according to

$$I \sim s^{-3},$$

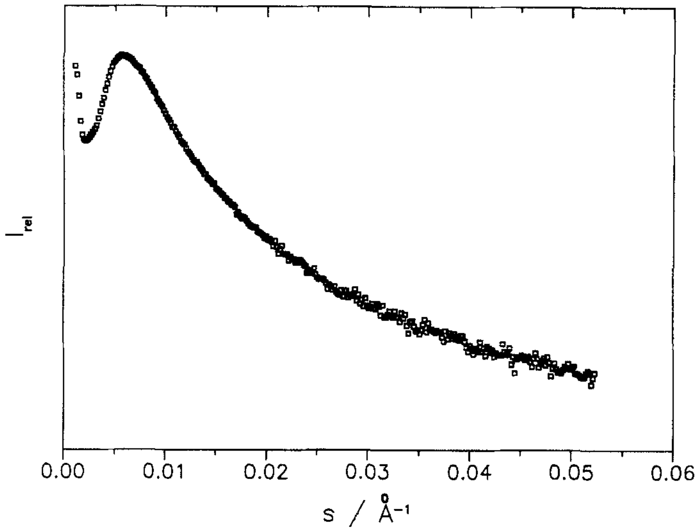

Figure 3. The smeared scattering curve of the network after solvent extraction, i.e. after the removal of component 2.

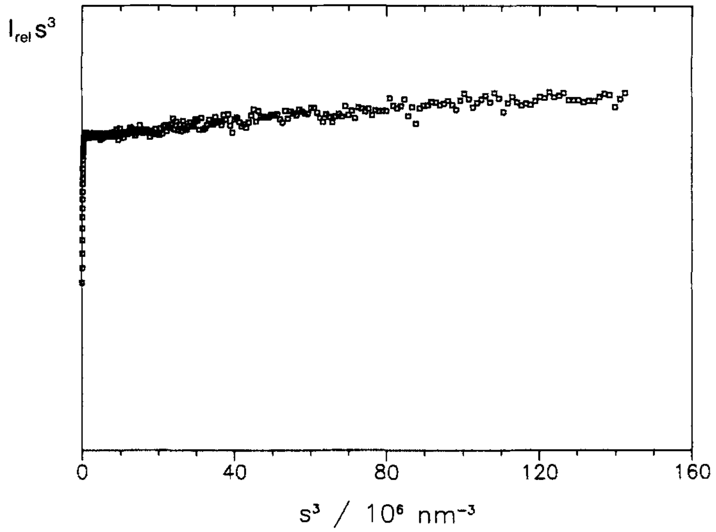

Figure 4. A plot of the inverse of the scattering intensity I^{-1} versus s^3.

which is characteristic of a well-defined two phase structure. This is apparent from a plot of I^{-1} versus s^3 which is shown in figure 4. This result shows that the phase boundaries are, in fact, sharp and no fractal type structure seems to exist [19].

Finally, a feature of interest is the problem of the anisotropy of the supermolecular structure. This problem was tackled by determining the small angle X-ray scattering parallel and perpendicular to the orientation direction of the network after the ZLI had been extracted. The result is that the network structure is isotropic to a very good approximation, scattering maxima are observed in all cases. In order to check whether the liquid crystal extraction procedure has influenced the structure we performed scattering experiments for samples for which the low molar mass liquid-crystalline

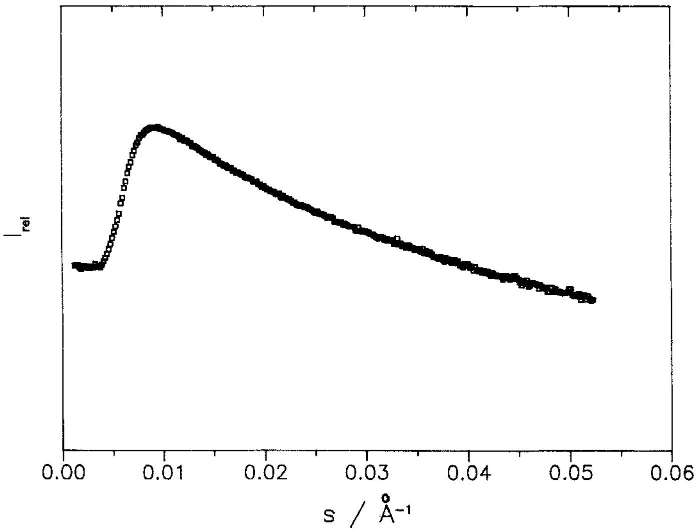

Figure 5. The small angle X-ray scattering curves for the network after high temperature treatment, i.e. removal of the ZLI by evaporation.

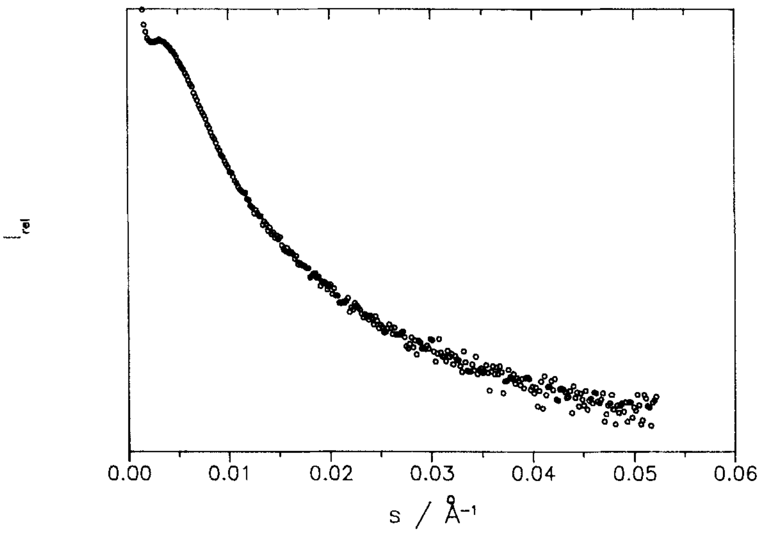

Figure 6. The small angle X-ray scattering curve for the network refilled with paraffin.

component has been removed by evaporation at high temperatures. Figure 5 reveals that a similar scattering behaviour is observed, as that shown in figure 3. Finally we introduced paraffin into the network; again the X-ray data indicate the persistence of the regular periodic structure of the network (see figure 6).

Based on the small angle X-ray results we propose in figure 7 a model for the supermolecular structure of the network void of the low molar mass liquid-crystalline compound ZLI, which is also able to account for the fact that a cocontinuous structure exists, as evident from the extraction studies reported here. The structure which is proposed in figure 7 shows the characteristic features reminiscent of an ideal spinodal

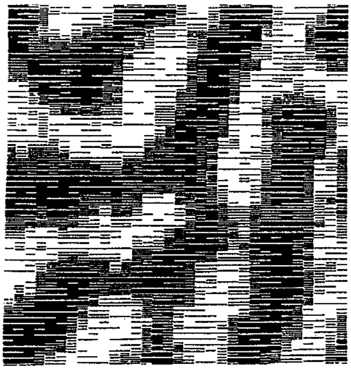

Figure 7. A structural model for the composite network.

structure: a periodic but strongly distorted structure, which thus gives rise to only one scattering maximum, an isotropic periodic structure and one which is cocontinuous.

This structural model was not devised to account for the origin of such a structure. However, it may well be that the structure actually is the result of a phase separation process occurring during network formation. De Gennes [1] has, on the basis of a percolation between correlated objects, calculated the corresponding phase diagrams for systems which contain reacting monomers and solvents and which undergo network formation. A spinodal separation may actually occur in such systems during the progression of curing, since the formation of network points leads to a strong variation of the effective interaction between the various components of the composite system. This concept may at the same time also explain the small angle X-ray results observed for the composite system in the uncured state and the network still containing the low molar mass component ZLI: pretransitional effects occur apparently, i.e. near critical concentration fluctuations related to a tendency towards phase separation. This would mean, in the spirit of the de Gennes treatment, that the ZLI acts as a good solvent for the network component [1] whereas the solvent used for the extraction of the low molar mass component and also the paraffin induce phase separation. It should be mentioned that the findings reported here are not single events but are observed consistently for different compositions and different composites.

Finally we have to address the fact that we observe distances which are extremely small for spinodal structures. The reason is that the phase separation probably happens in the gel state in which phase separation can happen only on a local scale, due to restrictions imposed by the limited mobility of the molecular units incorporated in the growing network. So the conclusion is that the structure of the composite liquid-crystalline network can be controlled by the compatibility of the components of the composite system and by the curing conditions which can be chosen in such a way that phase separation happens prior to or after the sol–gel transition [1].

3.4. *Optical properties of the composite systems*

Information on the persistence of the orientational order of the rigid network at elevated temperatures is available from studies on the temperature dependence of the birefringence of the composite system. Figure 8 shows the birefringence of the composite systems containing various amounts of the low molar mass component ZLI as a function of temperature. The observation is that the birefringence decreases slowly

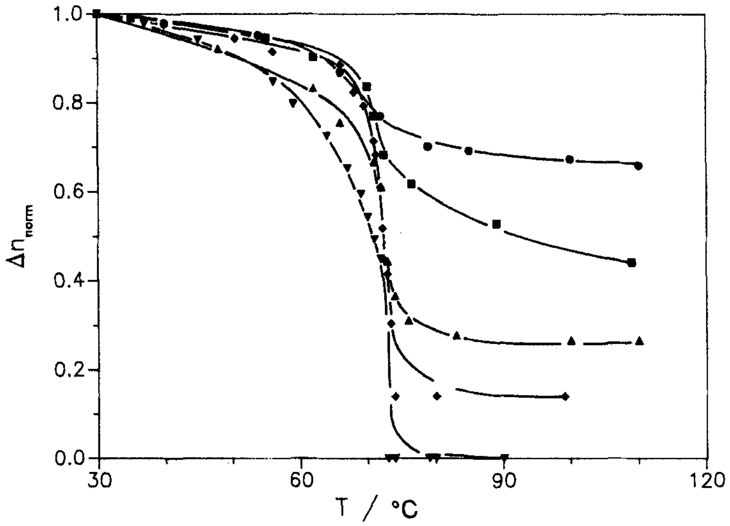

Figure 8. The variation of the birefringence Δn of the network function of temperature ●, APA/ZLI 4:1; ■, APA/ZLI 2:1; ▲, APA/ZLI 1:1; ◆, APA/ZLI 1:2; ▼, pure ZLI.

with increasing temperature up to about 75°C where it suddenly decreases stepwise to a non-zero saturation value. This saturation value is a function of the concentration of the low molar mass liquid crystal in the network. The obvious interpretation is that the sudden decrease of the birefringence is caused by the nematic–isotropic transition of the dispersed phase and that the remaining birefringence is the intrinsic property of the anisotropic network, i.e the orientational order of the network persists in this temperature range. The observed variation of the saturation value with the composition is in agreement with this interpretation.

Additional support comes from DSC studies which reveal that the nematic–isotropic transition happens in the temperature range considered here. It seems that there is no strong effect of the rigid network on the phase transition properties of the ZLI component.

3.5. *Electro-optic properties of the composite systems*

The electro-optic properties were determined using the well-known switching technique described in the literature [12, 13]. The samples were sandwiched between two glass slides carrying thin and optically transparent electrodes. An electric field was applied to the sandwich and the light passing through crossed polarizers was monitored. A reorientation of the directions of the liquid-crystalline domains and thus their optic axes leads to a path difference Γ and thus to modulation of the transmission I/I_0

$$I/I_0 = \sin^2(2\pi\Gamma/\lambda),$$

where $\lambda = 633$ nm, I is the transmitted intensity and I_0 is the primary beam intensity.

We are therefore able to obtain the induced phase shift from the transmission signal. Figure 9 shows a characteristic result for the path difference induced as a function of the applied DC voltage both for pure ZLI and for ZLI dispersed in the anisotropic network. Figure 10 shows the corresponding rising times to half intensity difference. The observation is that a threshold voltage exists below which no phase shift can be

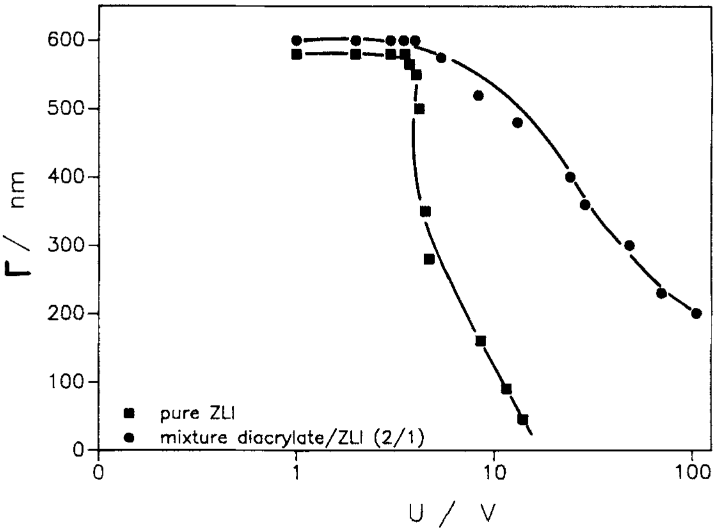

Figure 9. Electro-optic Frederiks transition characteristic of the composite network (U is the switching voltage, Γ is the path difference).

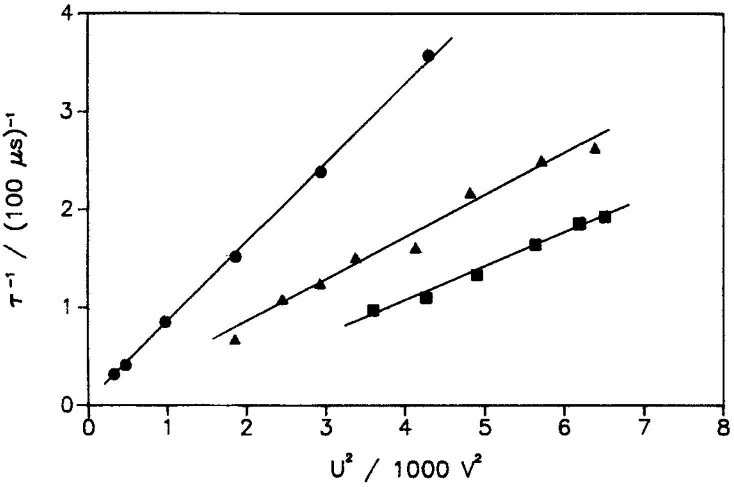

Figure 10. Rise times for pure ZLI and the composite system (U is the switching voltage, τ^{-1} is the inverse switching time). ▲, APA/ZLI 1/2; ■, APA/ZLI 1/1; ●, pure ZLI.

induced. This is in agreement with the results of switching studies reported in the literature. The threshold value U_0 is generally known to be controlled by the corresponding curvature elastic constant K and by the dielectric anisotropy of the liquid-crystalline material via

$$U_0 = \pi(K/\varepsilon_0 \Delta\varepsilon)^{1/2},$$

where $\Delta\varepsilon$ is the dielectric anisotropy. It is apparent that the presence of the network has a strong effect on the quasi-static switching behaviour of the low molar mass component. The Frederiks transition is strongly broadened and the onset voltage is

Orders of magnitude of active switching times (rise times) and passive switching times (decay times) for low molar mass liquid crystals and liquid crystal/liquid-crystalline network composites.

	Liquid crystal display	APA/ZLI-Network
Rise time	10 ms	50–100 ms
Decay time	10 ms	10 μs

shifted slightly to larger values. One consequence is that it is no longer possible to specify a well-defined threshold voltage. Among the possible reasons for the strong effect of the network on the switching characteristics are the strong absorption of the ZLI in the rigid network, affecting its elastic and viscous properties and a heterogeneous distribution of the local field acting on the ZLI rich domains within the network. It seems that the first interpretation is not sufficient to account for the finding, since switching characteristics similar to those reported here have been reported for other composite systems [1–5] containing dispersed phases with mm dimensions. A heterogeneous field distribution, on the other hand, certainly exists in all such composite systems. The effective field acting on the liquid-crystalline region will be controlled in this case to a first approximation by the ratio of the dielectric constant of the network and of the liquid crystal rich phases. Such a weakening of the local field will affect the threshold value.

A second effect of the network is that the switching times of the low molar mass components dispersed in the network are changed (see figure 10). The active switching times t_r become slightly larger as compared to those characteristic of pure ZLI at the same temperature and for about the same reduced voltage U/U_0 (note that this is not a very exact statement because of the large width of the Frederiks transition in the networks). A really unexpected observation is that the decay times are strongly reduced by several orders of magnitude (as apparent from the table) in comparison to those characteristic of the low molar mass system, ZLI. It has been suggested that the strong decrease of the decay time t_d originates from the strongly reduced wavelength of the disturbance induced by the external fields [20, 21]

$$t_d = \eta / K q^2,$$

where η is the viscosity, K is an appropriate elastic constant, and q is a wavenumber for the distortion. This would explain qualitatively the observed decay behaviour. There exists, however, a problem: the switching times in the absence of the field t_d and in the presence of the field t_r should be related to each other by:

$$t_d^{-1} = K/\eta \, (\pi/d)^2,$$

$$t_r^{-1} = t_d^{-1} \, ((U/U_0)^2 - 1),$$

where η is the rotational viscosity, d is the film thickness, and U is the applied voltage. A plot of the inverse rise time as a function of the applied voltage should yield an intercept, corresponding to the negative value of the decay time. As apparent from figure 10 this does not hold at all. So the observed effect cannot be fully explained at the moment; it is however of great technical importance.

4. Conclusion

The photopolymerization of a liquid-crystalline acrylate in the presence of a non-reactive liquid crystal, which acts as an anisotropic solvent, leads to the formation of strong nearly critical concentration fluctuations or even to cocontinuous spinodal type structures on a microscopic scale, apparently due to a competition between network formation and segregation. The characteristic scale of the spinodal structure is of the order of 10 nm which suggests for the dry networks a continuous rather regular channel structure with channel diameters of the order of 5 nm. The channels are apparently easily accessible. This suggests that such dry networks may be useful for many applications, among them membranes and absorbing agents. The particular application analysed here for the total composite system was the use as an electro-optic modulator. The advantage relative to the composite systems described in [2–5] is that the liquid crystal rich regions possess sizes much smaller than the wavelength of light which strongly reduces the light scattering. So they can be used like normal low molar mass displays with the advantage of being self-supporting.

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References

[1] deGennes, P. G., *Scaling Concepts in Polymer Science* (Cornell University Press), Chap. V, p. 128.

[2] Crighead, H. G., Cheng, J., and Hackwood, S., 1982, *Appl. Phys. Lett.*, **40**, 22.

[3] Fergason, J. L., 1985, *SID Int. Symp. Dig. Tech.*, **16**, 68.

[4] Drazic, P. D. S., 1986, *J. appl. Phys.*, **60**, 2142.

[5] Doane, J. W., Vaz, N. A., Wu, B. G., and Zumer, S., 1986, *Appl. Phys. Lett.*, **48**, 269.

[6] Hikmet, R. A. M., *Integration of Fundamental Science and Technology*, Vol. 5, edited by P. Lemstra (Elsevier) in the press.

[7] Broer, D. J., 1991, Ph.D. Thesis, University Groningen.

[8] Broer, D. J., Hikmet, R. A. M., and Challa, G., 1989, *Makromolek. Chem.*, **190**, 3201.

[9] Broer, D. J., Boven, J., Mol, G. N., and Challa, G., 1989, *Makromolek. Chem.*, **190**, 2255.

[10] Braun, D., Frick, G., Grell, M., Klimes, M., and Wendorff, J. H., *Makromolek, Chem.* (submitted).

[11] Strezelecki, L., and Liebert, L., 1973, *Bull. Soc. Chim. fr.*, **1973**, 603.

[12] Blinov, L. M., 1983, *Electro-optical and Magneto-optical Properties of Liquid Crystals*, (Wiley).

[13] Kelker, H., and Hatz, R., 1980, *Handbook of Liquid Crystals* (Verlag Chemie, Weinheim), Chap. IV, p. 155.

[14] Stanley, H. E., 1971, *Phase Transitions and Critical Phenomena* (Clarendon Press).

[15] Kopp, W., and Wendorff, J. H., 1982, *Molec. Crystals Liq. Crystals*, **84**, 63.

[16] Hashimoto, T., 1987, *Current Topics in Polymer Sciences*, Vol. 2, edited by R. M. Ottenbrite, L. A. Utracki and S. Inoue (Hanser Publisher).

[17] Guinier, A., 1955, *Small Angle Scattering of X-rays* (Wiley).

[18] Kratky, O., and Glatter, O., 1982, *Small Angle X-ray Scattering* (Academic Press).

[19] Mandelbrot, B. B., 1982, *The Fractal Geometry of Nature* (W. H. Freeman).

[20] Hikmet, R. A. M., 1991, *Liq. Crystals*, **9**, 405.

[21] Hikmet, R. A. M., 1990, *J. appl. Phys.*, **68**, 4406.