Structure and Mobility within Anisotropic Networks Obtained by Photopolymerization of Liquid Crystal Molecules

R. A. M. Hikmet,* J. Lub, and P. Maassen vd Brink

Philips Research Laboratories, P.O. Box 80.000, 5600JA Eindhoven, The Netherlands

Received November 18, 1991; Revised Manuscript Received January 23, 1992

ABSTRACT: Liquid crystalline mixtures of mono- and diacrylates were polymerized after macroscopic orientation of the molecules. Refractive indices of the mixtures were investigated both in the LC phase and after polymerization in the macroscopically oriented state. In this way the effect of cross-link density on the optical anisotropy was measured and correlated with order parameter measurements using infrared dichroism. Dielectric measurements were also carried out to investigate the effect of cross-linking on the movement of the side groups around the main chain. Association between the molecules and its consequences on the polymerization kinetics, the network structure, and the dielectric behavior of the molecules was demonstrated.

Introduction

Oriented polymeric structures are of great interest due to their anisotropic properties. One of the important anisotropic properties of oriented polymers is their optical anisotropy. The most common way of orienting a polymer is by deformation.[1] However, this method becomes less applicable in cases where very thin oriented films need to be produced on complicated surface geometries and/or at high speeds. It is for this reason that recently in-situ photopolymerization of liquid crystal (LC) molecules has been suggested.[2-5]

Cross-linking of LC molecules has been known for a long time.[6-10] In early papers, thermally induced polymerization is described.[6-8] In this method an LC system provided with a thermal initiator is heated to a temperature at which the initiator dissociates to start the polymerization. Even though anisotropic structures can be obtained using thermal polymerization, this method has several problems such as the availability of thermal initiators to cover the whole temperature range and early polymerization taking place during heating in an undesired LC phase or in a poorly ordered state. So-called LC elastomers,[9,10] on the other hand, are most commonly obtained by lightly cross-linking side chain polymers. The end product is usually a cross-linked multidomain LC polymer which can subsequently be aligned under tension to produce birefringent films. In-situ photopolymerization of LC molecules, however, combines isothermal vitrification together with the low viscosity of low-mass self-organizing LC molecules. Polymerization can take place at almost any desirable temperature, and any orientation and configuration such as twisted nematic can be induced with ease in electric and magnetic fields and at specially treated interfaces. Orientation of the molecules can also be varied locally, and patterned structures can be made.[11,12] Furthermore, choosing the temperature of polymerization allows the order parameter and the refractive indices of the resultant network to be adjusted.[3] Apart from the uniaxially oriented nematic phase, other phases such as cholesteric[13,14] as well as ferroelectric[15] with properties such as optical activity and molecular orientation can be frozen in. Here we describe the properties as well as the mobility within anisotropic networks obtained by photopolymerization of mixtures containing mono- and diacrylates. The diacrylate concentration was changed to obtain polymers with various cross-link densities. In this way the effect of cross-links on the relaxation behavior of the molecules could be investigated. For this purpose dielectric spectroscopy, IR dichroism, and refractive index measurements were used.

Experimental Section

The structures of the diacrylate (C6M) and the monoacrylate (CB6) are shown in Figure 1. C6M was synthesized according to a previously published procedure.[3] CB6 was synthesized using cyanohydroxybiphenyl kindly supplied by Merck (Poole) using a previously published procedure. Mixtures of the monomers were provided with 2% photoinitiator (2,4,6-trimethylbenzoyl)-diphenylphosphine oxide (Lucirine LR 8728, BASF). Uniform orientation of the monomers was obtained in glass cells provided with uniaxially rubbed polyimide layers. Subsequently, the polymerization was initiated using a high-pressure mercury lamp (10 mW cm^{-2}) to obtain uniaxially oriented polymers. Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer DSC7. The heating rate was 10 °C min^{-1}, and sample quantities in the order of 5 mg were used. Polymerization kinetics was followed by a Perkin-Elmer DSC-2C modified for UV irradiation. Optical measurements were carried out using a polarizing microscope equipped with a rotary compensator. Sample temperatures were regulated using a Mettler FP5 hot stage. An Abbe refractometer which could be heated to 140 °C was used for the refractive index measurements. Dynamic thermal mechanical analysis was performed using a Polymer Laboratories DMTA apparatus. Dielectric measurements were carried out using a Micromet Eumetric System III dielectric analyzer in the parallel plate mode using 120 μm thick samples. Polymers with a homeotropic orientation used in the dielectric measurements were obtained by orienting LC molecules in cells provided with indium tin oxide electrodes under an electric field. Infrared measurements were carried out using a Philips PU9600 swift Fourier transform infrared spectrophotometer provided with a wire grid polarizer and a heating cell. During the measurements uniaxially oriented samples were kept between two potassium bromide plates. X-ray diffraction patterns were recorded by a Statton camera using Ni filtered Cu Kα radiation.

Results and Discussion

Monomeric Mixtures. The phase diagram for the mixtures of C6M and CB6 is shown in Figure 2. This behavior is typical of mixtures of two nematics.[16] Mixtures in the range 100-70% w/w CB6 show a nematic phase in the supercooled state, and a smectic A phase is also observed in the supercooled state for compositions indicated in Figure 2. The appearance of the smectic phase for the mixtures of nematogens is associated with donor-acceptor interaction, and it is often observed for mixtures consisting of cyano and slightly polar or nonpolar compounds.[16] Refractive indices of pure CB6, C6M, and their mixtures are shown in Figure 3. Here again a typical

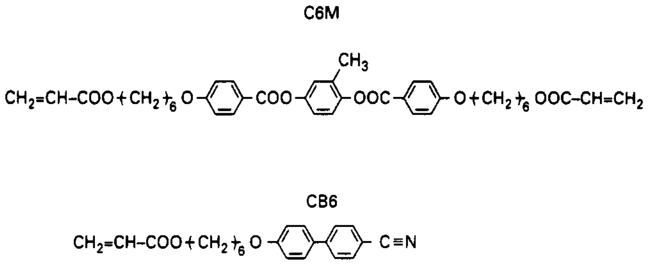

Figure 1. Molecular structure of the monomers.

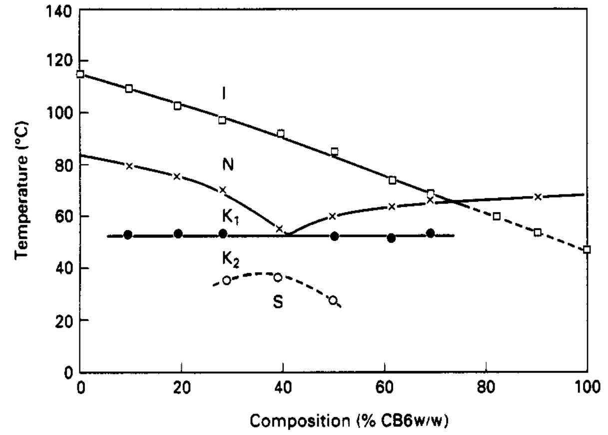

Figure 2. Binary phase diagram of C6M and CB6.

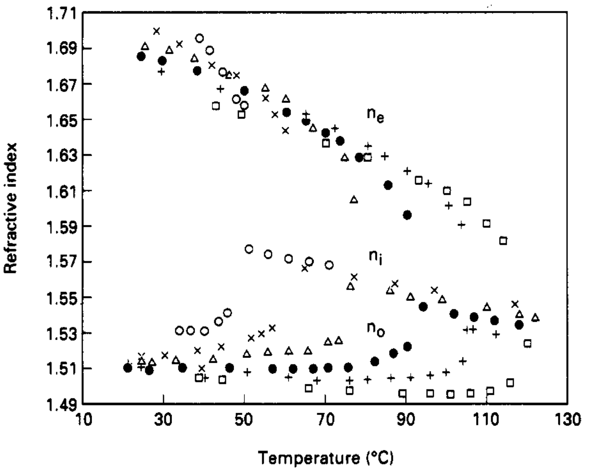

Figure 3. Refractive indices as a function of temperature for monomeric systems. (□) 100% w/w C6M; (+) 80% w/w C6M; (●) 60% w/w C6M; (△) 40% C6M; (×) 20% C6M; (○) 100% CB6.

behavior for nematics is seen, where for a given system with increasing temperature the extraordinary refractive index (n_e) decreases, whereas the ordinary refractive index (n_0) tends to increase with increasing temperature. These changes are associated with the decrease in the order parameter S, which is related to the refractive indices and the clearing temperature T_c as[17]

$$S = \left\{\frac{\bar{\alpha}}{\alpha_{\|} - \alpha_{\perp}}\right\}\frac{n_e^2 - n_0^2}{\bar{n}^2 - 1} \cong \left(1 - x\frac{T}{T_c}\right)^z \qquad (1)$$

where $\alpha_{\|}$ and $\alpha_{\perp}$ are the molecular polarizabilities in the direction parallel and perpendicular to the optical axis of the molecules, respectively, $\bar{\alpha}$ is the mean polarizability, and the mean refractive index $\bar{n} = [(2n_0^2 + n_e^2)/3]^{1/2}$. Haller plots[17] were used to estimate the polarizability term so that S could be estimated. At all compositions the data could be fitted satisfactorily with the parameters $z = 0.22$ and $x = 1$ using eq 1.

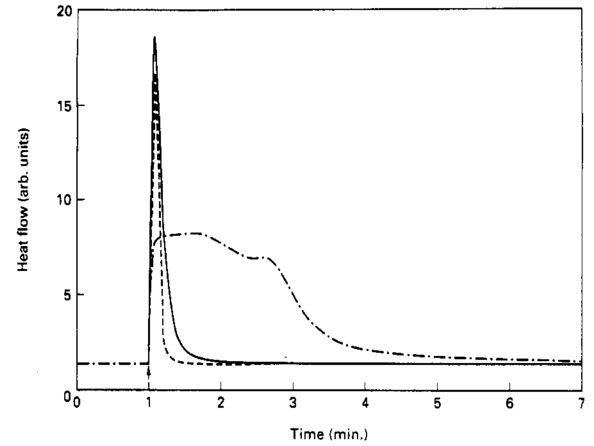

Figure 4. Heat flux of the polymerization reaction as a function of time. (—) 100% w/w CB6; (- - -) 40% w/w CB6; (- · -) phenyl acrylate.

Photopolymerization of the Mixtures. Polymerization of the mixtures was initiated by a UV source, and the reactions were followed using DSC. A small quantity of material (about 1 mg) was placed in the sample compartment which was flushed with nitrogen. The polymerization was initiated using a 4-W fluorescent lamp (intensity of 0.2 mW cm^{-2} at 350 nm). DSC curves obtained for pure CB6 and a mixture containing 40% C6M are shown in Figure 4. The shapes of both curves are very similar, and they represent typical behavior observed for conventional[18] and LC diacrylates. Immediately after the UV light is switched on, the rate of polymerization increases. This so-called Trommsdorff effect is attributed to the reduced termination of radicals due to the formation of a network at low converions.[18] The polymerization rate then goes through a maximum before falling below the detection limit after about a minute. The decrease is associated with the exhaustion of the reactive groups and/or reduction of mobility within the system.

The behavior observed here for the monoacrylate CB6 is also reported for another LC monoacrylate.[19] It is a rather typical behavior observed for diacrylates which can form networks upon polymerization. A typical behavior for a non-LC monoacrylate is also given in Figure 4, where a DSC curve for phenyl acrylate is shown. It can be seen that the behavior is very different from the behavior observed for CB6 and its mixture. This shows that after an instantaneous increase, the reaction rate reaches almost a constant level before the end of the reaction is attained. The constant polymerization rate is associated with the steady state where termination and initiation occur at the same rate. The fact that CB6 shows a very different behavior from that of conventional monoacrylates can be due to the existence of an LC phase in the monomeric state or its induction during polymerization. To investigate this possibility further, we measured the maximum polymerization rate as a function of temperature. It was found that the speed of polymerization decreases continuously with increasing temperature without an additional effect at 125 °C corresponding to the isotropic transition of (side chain) polymeric CB6, indicating that the LC phase has a minimal effect on the polymerization rate. Another reason for the observed behavior could be dimer formation by the CB6 molecules through specific interactions. Such dimers in turn can form a pseudonetwork where the dimers act as cross-link points. This point will be discussed later when the dielectric and X-ray diffraction measurements are presented.

Optical Properties of the Networks. Anisotropic networks were formed by photopolymerization of the mon-

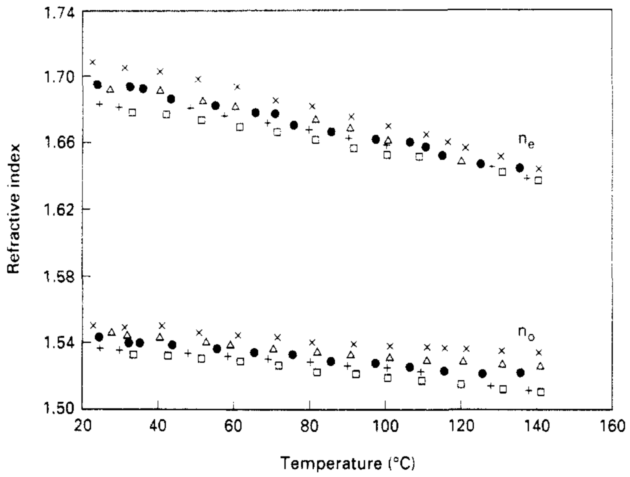

Figure 5. Refractive indices of various polymerized materials. (□) 100% w/w C6M; (+) 80% w/w C6M; (●) 60% w/w C6M; (△) 40% w/w C6M; (×) 20% w/w C6M.

omeric mixtures around 50 °C. The refractive indices of the polymerized networks were measured as a function of temperature, and the results are shown in Figure 5. It can be seen that at a given temperature both n_e and n_0 increase with increasing CB6 concentration. This behavior is associated with the high polarizability of the CB6 molecules rather than the higher order parameter. To estimate the order parameter, we used eq 1 together with the polarizability terms estimated for the monomeric mixtures, and the results are plotted in Figure 6. At a given temperature the order parameter does increase with increasing C6M concentration. This is clearly due to the initial order parameter of the mixtures at the temperature of polymerization since the order parameter of monomeric mixtures with higher C6M concentration was also higher. Furthermore, in Figure 6 it can also be seen that the order parameter of the mixtures with higher CB6 contents decreases faster with increasing temperature. This could be associated with the reduced cross-link density within the system with the increasing concentration of CB6 molecules inducing higher mobility.

To investigate the effect of temperature on the order of the CB6 molecules separately, IR dichroism was used. If cylindrical symmetry is assumed for the molecules, the quantity S_0, which is related to the order parameter S, is given as[20]

$$S_0 = \frac{\epsilon_\parallel - \epsilon_\perp}{\epsilon_\parallel + 2\epsilon_\perp} = S(1 - {}^3/_2 \sin^2 \alpha)^{-1} \qquad (2)$$

where $\epsilon_\parallel$ and $\epsilon_\perp$ are absorption coefficients measured with the IR beam polarized parallel and perpendicular to the optical axis of the uniaxially oriented LC, respectively, and α is the angle between the direction of the long axis of the molecule and the direction of the vibrational transition moment. Due to overlapping bands of C6M and CB6, it was only possible to estimate the order parameter of CB6 molecules from the dichroism of the C≡N stretching vibration at 2230 cm^{-1}. S_0, estimated for mixtures containing 30% and 70% w/w C6M molecules polymerized at 60 °C, corresponding to reduced temperatures of 0.97 and 0.90, respectively, is plotted as a function of temperature in Figure 6. It can clearly be seen that at the temperature of polymerization S_0 is slightly higher for the mixture containing 30% CB6. Nevertheless, the difference is much smaller than the difference observed in the monomeric phase and the average order parameter estimated for the networks using the refractive indices. Furthermore, it can also be seen that in the case of the mixture containing 70% C6M (higher degree of cross-links) S_0 increases up to about 80 °C as a function of temperature and decreases at higher temperatures, whereas in the case of the other sample S_0 decreases continuously with increasing temperature. The increase seen in S_0 is probably due to the increased mobility within the system, enabling better packing of the molecules.

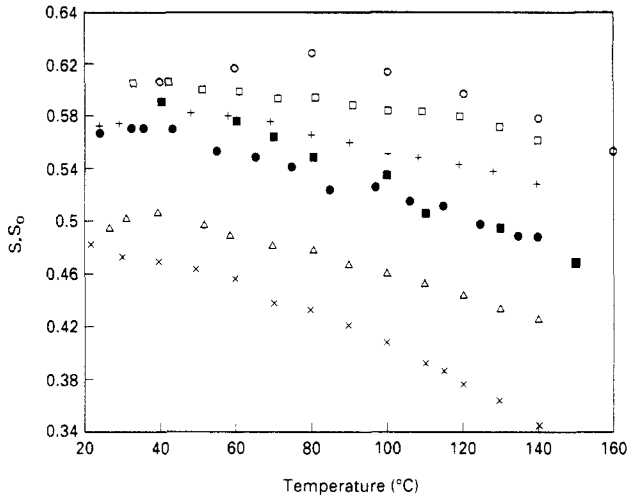

Figure 6. Order parameter (S) estimated from the refractive indices as a function of temperature for various networks. (□) 100% w/w C6M; (+) 80% w/w C6M; (●) 60% w/w C6M; (△) 40% C6M; (×) 20% w/w C6M. Order parameter (S_0) of CB6 molecules built in various networks estimated from IR dichroism. (○) 70% w/w C6M; (■) 30% w/w C6M.

Dielectric Properties. Dielectric relaxation of side chain polymers including CB6 has been described in the literature.[21,22] These materials show complex relaxation associated with the motion of different groups of the molecule. The reorientation motion of the mesogenic group around the main chain corresponding to the relaxation aound the short axis (δ process) is about 100 times slower than the rotation of the mesogenic group around its long axis. Here we investigated the effect of the degree of cross-linking on the δ process by introducing various amounts of C6M. For this purpose polymerization was carried out after homeotropic alignment of the molecules, and the dielectric measurements were carried out in a parallel plate geometry.

First we describe the behavior of 100% CB6 polymer. Using GPC calibrated with a polystyrene standard, the molecular weight distribution of CB6 polymer was found to be $\bar{M}_n$ = 200 000 and $\bar{M}_w$ = 430 000. The polymer showed four transition points. The nematic to isotropic transition (T_c) was determined by microscopy as well as DSC to occur at around 125 °C. The second and third transitions which occur at 104 and 70 °C, respectively, could be detected only by optical microscopy. Following the literature on the same polymer with other molecular weight distributions,[20-24] we shall refer to these transition temperatures as nematic to smectic (T_s) and smectic to reentrant nematic (T_{rn}), respectively. The glass transition temperature (T_g) was determined to be around 40 °C. It is important to point out that all of the transition points observed by us differ from the values reported in the literature. These discrepancies were initially thought to be caused by the molecular weight of the polymers used by different investigators. However, comparison of literature papers showed no correlation between the molecular weight and the transition temperatures.

The dielectric loss (ϵ'') of CB6 polymer was measured as a function of temperature at various frequencies as shown in Figure 7 where the transition temperatures are

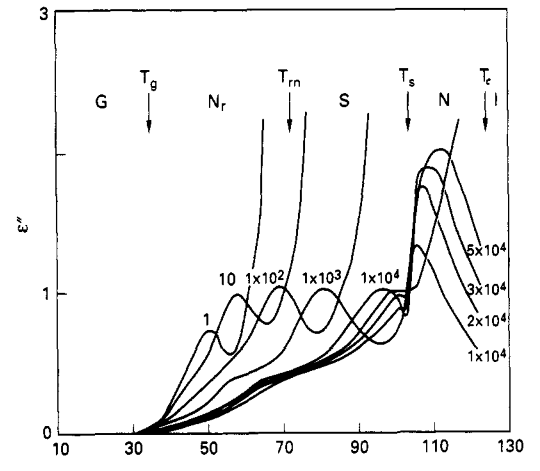

Figure 7. Dielectric loss as a function of temperature measured at various frequencies for CB6 polymer.

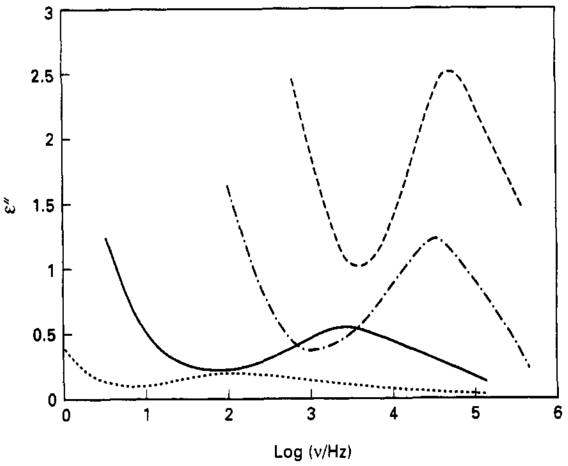

Figure 8. Dielectric loss as a function of frequency for various systems at 110 °C. (- - -) 100% w/w CB6; (- • -) 10% w/w C6M; (—) 50% w/w CM6; (···) 80% w/w C6M.

also given. The relaxation peak corresponding to the motion of the mesogenic group around the short axis appears above the glass transition and shifts to higher temperatures with increasing frequency. At T_{rn} there is no discontinuity, whereas at T_s a sharp change in the dielectric loss peak can be seen. We shall return to this point.

We also investigated the relaxation of CB6 molecules built in a network. In Figure 8 ϵ'' is plotted as a function of frequency for various samples. The peaks seen in this figure are to a large extent associated with the motion of CB6 molecules since C6M molecules do not possess a large dipole component along their long axis and their rotation along the short axis is not possible since they are linked to the network from both ends. In Figure 8 it can be seen that the peak broadens and shifts to lower frequencies with increasing C6M concentration. This broadening indicates that there is a distribution of mean relaxation times associated with the dispersion, and this point will be dealt with further in terms of the Cole–Cole function[25] which uses an empirical factor in the dispersion function and takes the form

$$\epsilon^{x} = \epsilon' + i\epsilon'' = \epsilon_u + \frac{\epsilon_r - \epsilon_u}{1 + (i\omega\tau)^{(1-h)}} \tag{3}$$

where ϵ_r and ϵ_u are the static and the high-frequency permittivities, respectively. In this expression τ represents the mean effective relaxation time of overlapping dispersion processes. The parameter h represents the distribution of the relaxation times and diminishes when a single relaxation time is effective. Figure 9 shows Cole–Cole arcs obtained for networks containing various amounts of C6M. The figure shows depressed semicircles, indicating that distribution of relaxation times is effective. In Table I the parameter h is given for samples containing various amounts of C6M. It can be seen that h increases with increasing C6M concentration. In this table no value for CB6 is given since the polymer showed a very complex relaxation behavior which has already been described in the literature.[22,26] The increase in h indicates that the distribution of mean relaxation times broadens with increasing network concentration. A reason for this behavior is the environment of the CB6 molecules within the network. To investigate this point further, DMTA was used. It was found that with increasing cross-link concentration loss tangent peaks corresponding to the α process became broader and shifted toward higher temperatures as reported before,[5] showing that with increasing cross-link concentration the transition from the glassy to the rubbery state spreads over a wider temperature range. Due to the cross-links above the glass transition temperature the fluctuations within the free volume and the structure of the network remain. For nematics it is known that the relaxation time τ is given by[27]

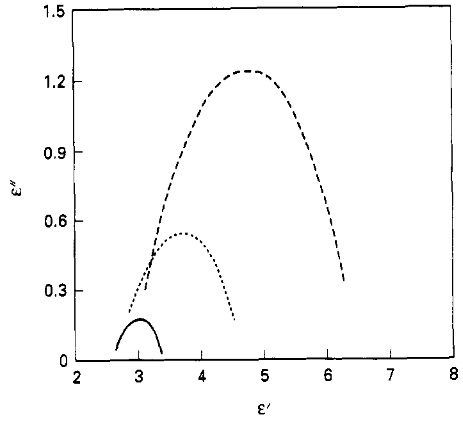

Figure 9. Cole–Cole plot for various networks measured at 100 °C. (- - -) 10% w/w C6M; (···) 50% w/w C6M; (—) 80% w/w C6M.

Table I
Cole–Cole Distribution Parameter and Activation Energies Associated with the δ and α Transitions

CB6 concn, % w/w	h	ΔH_δ, kJ mol^{-1}	ΔH_α, kJ mol^{-1}
100		130	
90	0.2	160	420
50	0.3	150	460
10	0.45	140	490

$$\tau \propto \eta G_{\parallel} \propto \exp\left(\frac{\Delta H_N + \Delta H_{visc}}{RT}\right) \tag{4}$$

where $G_{\parallel}$ is the retardation factor imposed by nematic potential ΔH_N and η is the viscosity. η is often also given in the form[28]

$$\eta = \eta_\infty \exp\left(\frac{A}{T - T_0}\right) \tag{5}$$

where T_0 is located below T_g. Therefore, the broadening in the α transition peak with increasing cross-link density is also manifested in the increase of h as suggested by eq 3.

The other effect to be seen in Figure 8 is the decrease in the mean relaxation frequency with increasing C6M

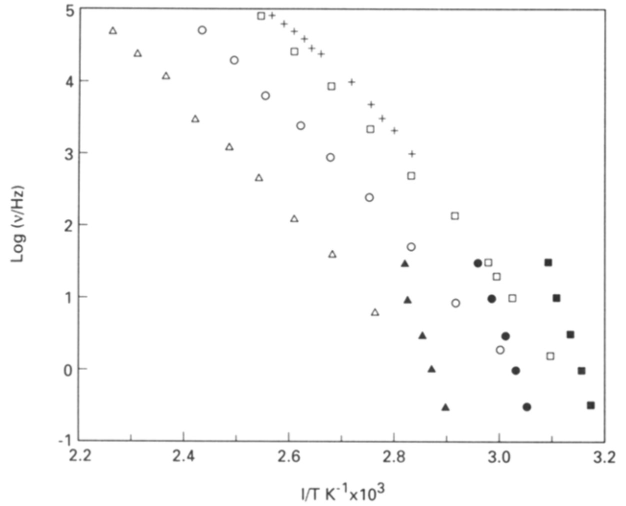

Figure 10. Arrhenius plots for the δ transition (open symbols) from dielectric loss curves and α transition from mechanical loss curves (solid symbols). (+) 100% w/w CB6; (□) 10% w/w C6M; (○) 50% w/w C6M; (△) 80% w/w C6M.

concentration. This effect is also related to the increase in the glass transition temperature. To investigate this effect, we measured the maximum ϵ'' frequency as a function of temperature. Figure 10 shows Arrhenius plots for various samples obtained using the frequency maximum in the ϵ'' together with the values obtained from mechanical loss modulus measurements. Activation energies estimated for the α and δ processes are shown in Table I. It can be seen that the activation energy associated with the α process is much higher than the values obtained for the δ process. Furthermore, if the ΔH_δ values for the cross-linked materials are considered, it can be seen that they tend to decrease with cross-link density, and in all cases they are higher than the value found for 100% CB6 polymer in the nematic phase. This behavior can be caused by the increase in ΔH_{vis} in eq 5 due to the cross-links (C6M), imposing an extra constraint on the movement of the CB6 molecules, or by the increased association of the CB6 molecules. Another possibility is the increase in the nematic potential. In the treatment of Martin et al.[29] the change in the order parameter was directly related to $G_\parallel$. Since the order parameter of CB6 molecules decreases more gradually with increasing cross-link density, one can argue that with increasing cross-link density the nematic potential also increases. However, in Table I it can be seen that even though ΔH_δ for cross-linked samples is higher than the value for the CB6 polymer, in the case of cross-linked samples with increasing cross-link density ΔH_δ decreases. This indicates that even though the cross-links might play a part in the increase in ΔH_{visc} and ΔH_{N}, a change in the degree of association between the CB6 molecules also needs to be invoked to explain the full picture. To investigate this possibility further, we plotted ϵ_{r} and ϵ_{u} as a function of CB6 concentration at 110 °C as shown in Figure 11. It can be seen that with increasing C6M concentration a sharp decrease followed by a more gradual decrease is obtained. With increasing C6M concentration both ϵ_{r} and ϵ_{u} decrease gradually as expected. However, the initial sharp decrease indicates an increased association between the CB6 molecules. In LC systems containing cyanobiphenyl derivatives molecular association is well documented.[30,31] In the present case this association probably becomes even stronger under the influence of the cross-links. However, the initial decrease in ΔH_δ indicates a decreased association with further increase in the cross-link density.

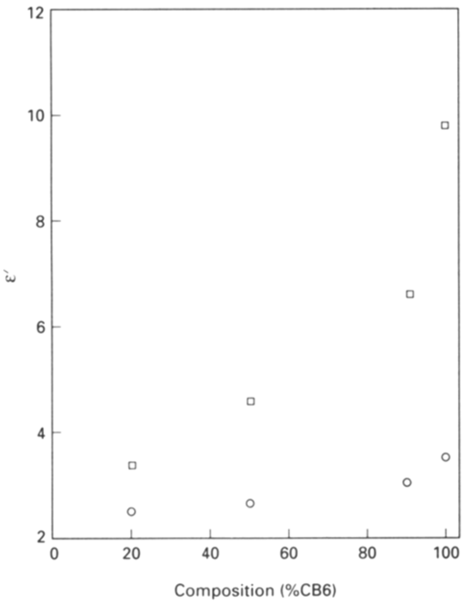

Figure 11. Static (□) and high-frequency (○) permittivities for various systems as a function of CB6 fraction.

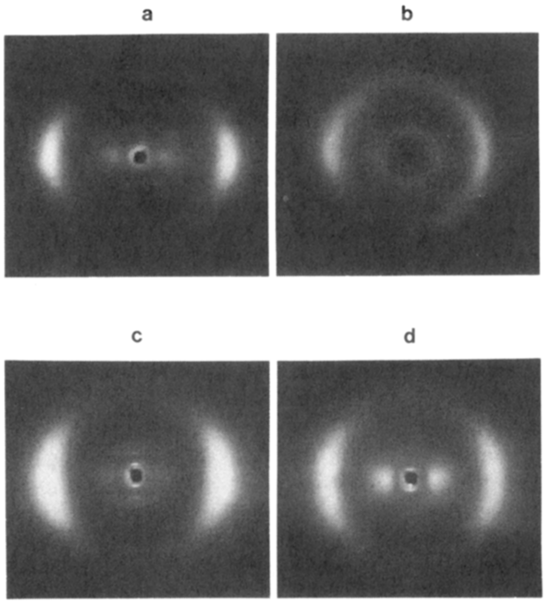

Figure 12. X-ray diffraction patterns of various polymerized samples. (a) 100% w/w CB6 at 23 °C; (b) 100% w/w CB6 at 90 °C; (c) 50% w/w C6M; (d) 80% w/w C6M at 23 °C.

From the literature it is well-known that cyanobiphenyls show smectic phases where bilayers are formed by overlapping molecules. We also investigated the structure within various systems by X-ray diffraction. In Figure 12 X-ray diffraction patterns obtained for networks containing various amounts of C6M molecules obtained at room temperature are shown together with the patterns obtained for the CB6 polymer in the nematic and smectic phases. In the case of the CB6 polymer, only equatorial arcs were observed; in contrast, the cross-linked samples, in addition to broad equatorial reflections, also showed sharp meridional peaks. The absence of sharp meridional peaks is a sign of the nematic phase where only a degree of orientational order exists. In the case of the smectic phase with a degree of translational order sharp off-equatorial peaks due to layer structures as a result of correlation between the centers of gravity of the LC molecules are also observed. Here it is appropriate to point out that for the CB6 polymer no sharp meridional peaks were observed below the transition point at 104 °C referred to as a smectic phase in the literature. Even though the transition was visible in optical microscopy and in dielectric measurements, the absence of structural change as observed by X-ray diffraction brings the nature of this transition into question. Here it is important to point out that a randomly copolymerized structure, especially at high concentrations of C6M, was not expected to show peaks corresponding to CB6 bilayers. The presence of these sharp small angle peaks raises the question of homogeneity of the mixtures in the liquid state and their miscibility on molecular scale.

The meridional peaks obtained for the cross-linked samples indicate density fluctuations due to the layered structure within the systems. Peaks which were not present in the monomeric state appeared upon polymerization. The thickness of the layers (d) was estimated from the meridional peaks to be 34 Å. This spacing is not expected to be caused by C6M molecules since they have a length of 42 Å. This value is also about 1.5 times higher than the length of a fully extended CB6 molecule (22 Å), indicating that the layers are mainly a result of overlapping CB6 molecules with partial association.[32] In Figure 12c the existence of several orders indicates that the layers are fairly uniform in size. The correlation length L was determined to be 2000 Å from $L = d/\Delta\theta$, where $\Delta\theta$ is the angular width of the diffraction peak.[33] With increasing C6M concentration the peaks become less intense but they are clearly present. These results indicate that even high concentrations of C6M networks have a blocky copolymeric structure which gives rise to the meridional peaks. However, the fact that the intensity and the number of orders of the peaks decrease with increasing C6M concentration indicates changes in the structure of the layers and the distribution of the CB6 molecules forming the layers. This change is probably also reflected in the association of the CB6 molecules, causing the observed behavior in the activation energies.

Conclusions. It was shown that mixtures of an LC diacrylate and a monoacrylate can be used in the production of anisotropic networks with varying cross-link densities by in-situ photopolymerization. The polymerization kinetics was followed using DSC, and it was found that diacrylate, monoacrylate, and their mixtures behaved in a similar manner. This unexpected behavior of the monoacrylate was explained in terms of pseudo-cross-links formed by associated molecules.

Optical anisotropy was measured both in the monomeric state and after polymerization. The change in the anisotropy with temperature was found to depend largely on the cross-link density within the system, a higher density of cross-links giving better temperature stability. Average order parameters of the networks were determined from the refractive indices, and it was found that the order parameter decreased for samples polymerized at the same temperature with increasing monoacrylate concentration. This behavior was associated with the order parameter of the mixtures in the monomeric state which also decreased with increasing monoacrylate concentration at a given temperature. When the order parameters of the monofunctional side groups as determined by IR were compared at the temperature of polymerization, a small difference in the order parameter for systems with a large difference in the cross-link density could be observed.

Dielectric spectroscopy showed that with increasing cross-link density the mean relaxation frequency corresponding to the δ process shifted to lower frequencies and the distribution of frequencies associated with the process became broader. This effect was associated with the inhomogeneous structure of the network, where the free volume varied locally. The activation energy associated with the motion in the nematic polymer was found to be lower than the values obtained for the cross-linked samples. This increase was correlated with the polymerization-induced blocky bilayer structure with an increased association between the side groups. However, whether the blocky structure was already present in the monomeric state or was formed during polymerization needs to be further investigated.

References and Notes

(1) Ward, I. M. *Mechanical Properties of Solid Polymers*; Wiley-Interscience: New York, 1983.

(2) Broer, D. J.; Finkelmann, H.; Kondo, K. *Makromol. Chem.* **1989**, *189*, 185.

(3) Broer, D. J.; Boven, J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1989**, *190*, 2255.

(4) Broer, D. J.; Hikmet, R. A. M.; Challa, G. *Makromol. Chem.* **1989**, *190*, 3202.

(5) Hikmet, R. A. M.; Broer, D. J. *Polymer* **1991**, *32*, 1627.

(6) Liebert, L.; Strzelcki, L. *C. R. Acad. Sci., Ser. C* **1973**, *276*, 647.

(7) Strzelcki, L.; Liebert, L. *Bull. Soc. Chim. Fr.* **1973**, *2*, 597.

(8) Clough, S. B.; Blumstein, A.; Hsu, E. C. *Macromolecules* **1976**, *9*, 123.

(9) Finkelmann, H.; Kock, H.; Rehage, G. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 317.

(10) Schatzle, J.; Kaufhold, W.; Finkelmann, H. *Makromol. Chem.* **1989**, *190*, 3269.

(11) Hikmet, R. A. M.; Broer, D. J. *Integration of Fundamental Polymer Science and Technology*; Kleintjes, L. A., Lemstra, P., Eds.; Elsevier Applied Science: London, 1989.

(12) Hikmet, R. A. M.; Lub, J.; Broer, D. J. *Adv. Mater. (Weinheim, Fed. Repub. Ger.)* **1991**, *3*, (7/8), 392.

(13) Broer, D. J.; Heynderickx, I. *Macromolecules* **1990**, *23*, 2474.

(14) Hikmet, R. A. M.; Zwerver, B. H. *Mol. Cryst. Liq. Cryst.* **1991**, *200*, 197.

(15) Hikmet, R. A. M. Unpublished results.

(16) Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag Chemie: Weinheim, 1980.

(17) Haller, I.; Huggins, H. A.; Lilienthal, H. R.; McGuire, T. R. *J. Phys. Chem.* **1973**, *77*, 950.

(18) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.

(19) Broer, D. J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1989**, *190*, 19.

(20) Neff, V. D. In *Liquid Crystals and Plastic Crystals*; Gray, G. W., Windsor, P. A., Eds.; Ellis Horwood: Chichester, 1974; Vol. 2, p 231.

(21) Zentel, R.; Strobl, G. R.; Ringsdorff, H. *Macromolecules* **1985**, *18*, 960.

(22) Bormuth, F. J.; Biradar, A. M.; Quotschalla, U.; Hasse, W. *Liq. Cryst.* **1989**, *5*, 1549.

(23) Le Barny, P.; Jean-Claude, D.; Friedrich, C.; Noel, C. *Pol. Bull.* **1986**, *15*, 341.

(24) Kresse, H.; Stettin, H.; Kostromin, S. G.; Shibaev, V. P. *Mol. Cryst. Liq. Cryst.* **1990**, *178*, 1.

(25) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* **1949**, *9*, 341.

(26) Kresse, H.; Stettin, H.; Tennstedt, E.; Kostromin, S. *Mol. Cryst. Liq. Cryst.* **1990**, *191*, 135.

(27) de Jeu, W. H. *Physical Properties of Liquid Crystalline Materials*; Gordon and Breach: London, 1980.

(28) Blender, J. T.; Shlesinger, M. F. *J. Stat. Phys.* **1988**, *53*, 531.

(29) Martin, A. J.; Meier, G.; Saupe, A. *Symp. Faraday Soc.* **1971**, *5*, 119.

(30) Kedziora, P.; Jadzyn, J. *Liq. Cryst.* **1990**, *8*, 445.

(31) Gray, G. W. *J. Phys., Colloq.* **1975**, *36*, C1-337.

(32) Azaroff, L. *Mol. Cryst. Liq. Cryst.* **1987**, *145*, 31.

(33) *Methods of Experimental Physics*; Fava, R. A., Ed.; Academic Press: London, 1980; Vol. 16, p 171.

Registry No. (C6M)(CB6) (copolymer), 139704-61-3.