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Fast switching anisotropic networks obtained by in situ photopolymerization of liquid crystal molecules

by R. A. M. HIKMET* and J. A. HIGGINS P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands

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Lightly cross-linked anisotropic networks with uniaxial and $\pi/2$ twisted orientations were produced by photopolymerization of monotropic mixtures containing liquid crystal mono and diacrylates. In this way the polymer backbone was immobilized and became decoupled from the motion of the mesogenic side groups. The networks showed very good reversibility and even after becoming isotropic, upon cooling, the initial orientation was recovered. In the same way, in the presence of electric fields the mesogenic groups could be reoriented in the direction of the electric field, reverting back to the initial orientation on removal of the field at a rate comparable with those observed in the monomeric state. Combining viscoelastic measurements with the dielectric behaviour of the monomeric liquid crystal and the anisotropic network, a comparison between the internal and bulk rotational viscosities was also made.

1. Introduction

Side chain liquid crystal polymers have been gaining academic as well as industrial interest during the last decade. The industrial interest stems mainly from the prospect of their use in displays and data storage [1,2] whereas the influence of the polymer backbone on the dynamics of the mesogenic side groups is of fundamental importance [3-5]. In most applications liquid crystal molecules are macroscopically aligned at specially treated interfaces [6]. Their orientation is locally changed by application of an electric field or heating above the isotropic transition temperature [7]. Upon removal of the external disturbance the molecules revert to their initial state under the influence of surface forces. In the case of low molar mass nematogenic molecules, long range orientation in display cells is assumed spontaneously under the influence of surface forces. In the case of the liquid crystal oligomers, the time required for the induction of a monodomain can run into minutes [8] whereas the induction of long range orientation in high molecular weight liquid-crystalline polymers at treated interfaces is practically impossible. This slow response of side chain liquid crystal polymers is often associated with the increase in the bulk viscosity and the coupled motions of the polymer backbone and the mesogenic side groups. The increase in the viscosity as a result of polymerization is inevitable since polymerization also induces a decrease in the free volume. Therefore, decoupling the motion of the side groups from the polymer backbone has been tried. For this purpose increasing the length of the flexible spacer [8] connecting the rigid unit to the polymer backbone and lateral substitution [9] of the mesogenic unit to the polymer backbone were explored.

Here we describe a new approach in which we try to immobilize the polymer backbone in order to stop its rearrangement during reorientation of the side groups.

* Author for correspondence.

We use the technique of *in situ* photopolymerization where a very lightly cross-linked anisotropic network is formed. Indeed, cross-linking of liquid crystal molecules has already been used in production of liquid-crystalline elastomers (10) where the crosslinks act as load bearing units, so that a multidomain sample can be deformed to produce a uniaxially aligned polymer. Apart from liquid-crystalline elastomers, crosslinking is also used in the production of thermally stable highly cross-linked anisotropic networks by *in situ* photopolymerization of mesogenic diacrylates [11, 12]. In this study lightly cross-linked networks were obtained by photopolymerization of mixtures of mono and diacrylates in the monotropic nematic monodomain state. Response times, rotational viscosity and dielectric behaviour of the anisotropic networks and the monomer have been investigated. The effect of the cross-link density on the response of the system was also studied.

2. Experimental

The structure of the monoacrylate 4-(6-acryloyloxyhexyloxy)-4'-cyanobiphenyl (CB6) and the diacrylate C6M used for cross-linking has been described in previous publications [11, 12]. Mixtures of CB6 containing various amounts of C6M were provided with 1 per cent (w/w) photoinitiator Irgacure 651 (Ciba Geigy) and the polymerization was initiated using a high pressure mercury lamp (10 mW cm^{-2}) after inducing a desired orientation in the monomeric state. Dielectric measurements were carried out using a Hewlett–Packard 4194 A Impedance/Gain-Phase Analyser. An Abbe refractometer, which could be thermostated was used for the refractive index measurements. An optical microscope provided with a stable light source and a photomultiplier was used for the electro-optic measurements. Dynamic mechanical thermo analysis (DMTA) was carried out with Polymer Laboratories DMTA equipment in the shear mode.

3. Results and discussion

3.1. Optical and thermal properties

The properties of CB6 were investigated both in the monomeric state and after copolymerization with C6M. In the monomeric state at room temperature CB6 is crystalline and melts when heated above 73°C to become an isotropic liquid. Upon cooling from the isotropic state it shows a monotropic nematic phase transition (T_{NI}) at around 47°C in the supercooled state. The liquid is highly anisotropic with a birefringence of 0.134 measured at 45°C.

Polymerization of mixtures of CB6 containing C6M was carried out in the nematic phase at around 45°C. In all cases a distortion in the average orientation of the molecules was observed as a result of polymerization. However, except for the pure CB6, on heating to above 70°C, a well-oriented monodomain structure could be recovered. This effect is to a large extent associated with polymerization shrinkage and to a lesser extent with a phase transition occurring during polymerization. Here, it is also important to note that as calculated from the heat of polymerization using DSC the conversion of the acrylate groups was almost 100 per cent. Furthermore nothing could be extracted out of the networks using solvents such as chloroform indicating that no uncross-linked polymer molecules were present within the anisotropic networks.

In figure 1 the refractive indices of a polymer containing 0.2 per cent (w/w) C6M are plotted as a function of temperature. In this plot it can be seen that, as also observed for low mass mesogenic molecules as well as liquid-crystalline polymers, the extraordinary

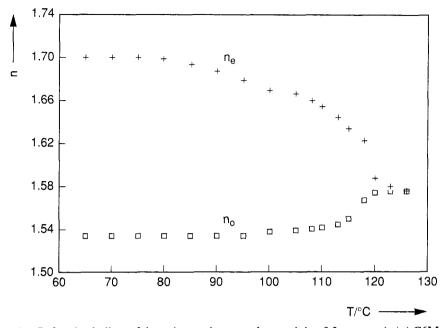


Figure 1. Refractive indices of the anisotropic network containing 0.2 per cent (w/w) C6M as a function of temperature.

 Table 1. Time required to assume long range orientation on cooling from the isotropic to the nematic state.

Material	$\tau_{\rm NI}/{\rm s}$
CB6 (mon) CB6 (pol. 0% C6M) Network (01% C6M) Network (02% C6M) Network (03% C6M) Network (04% C6M) Network (05% C6M)	$ \begin{array}{c} 0.3 \\ \infty \\ 1.5 \\ 2 \\ 3 \\ 5.5 \\ 10 \end{array} $

refractive index (n_e) decreases whereas the ordinary refractive index (n_o) increases with increasing temperature. At around 119°C an abrupt change in the refractive index is observed. Further on in the text this temperature will also be referred to as $T_{\rm NI}$ of the anisotropic network. However, above this abrupt change, unlike lowmass mesogens, the anistropy is not totally lost and it gradually decreases with increasing temperature. When the anisotropic network is cooled to below $T_{\rm NI}$, the long range orientation of the system was recovered. We have tried to estimate the time required for the molecules to assume their initial uniaxial orientation on cooling from the isotropic state. This was done by first heating the cell containing uniaxially oriented mesogenic molecules to above $T_{\rm NI}$ and then cooling the cell to just below the $T_{\rm NI}$ (117°C for the networks and 46°C for the monomer) while measuring the transmission of light through the cell between crossed polarizers as a function of time. The time required ($\tau_{\rm NI}$) for the intensity to change from zero in the isotropic state to a steady state value in the nematic phase was measured for anisotropic networks containing different amounts of C6M as well as for CB6 monomer; the results are shown in table 1. The most important effect to be seen in this table is the fact that within the pure CB6 polymer uniaxial orientation could not be induced at all whereas the anisotropic networks assumed a uniaxial orientation in a matter of seconds. The increase in τ_{NI} upon polymerization can be associated with the increase in the bulk viscosity and the polymer backbone. Indeed using GPC calibrated with a polystyrene standard, the molecular weight distribution of pure CB6 polymer was found to be $\overline{M}_{r} = 200\,000$ and $\overline{M}_{w} = 430\,000\,\mathrm{gmol}^{-1}$ which is considerably higher than the molecular weight of the oligomers [3,4] used in other studies where uniaxial orientation was induced at interfaces. However, the cross-links which play a crucial role in the recovery of the uniaxial orientation tend to cause an increase τ_{NI} as the crosslink density (C6M concentration) increases. This effect may be attributed to the decreased mobility of the main chain with increasing network concentration as the system reverts to the initial state memorized by the cross-links. In coming sections the influence of the cross-links on the bulk, the internal viscosities and the dynamics of the system will be further discussed.

3.2. Electro-optic measurements

In the previous section the importance of the cross-links (C6M molecules) in the recovery of long range orientation of the system after heating to above the clearing temperature was demonstrated. Here we discuss the response of the anisotropic networks to electric fields beginning with an extreme case where the molecules are oriented in the twisted nematic configuration which is a high energy state induced by the interfaces. Light transmission through cells placed between parallel polarizers (orientation at one of the surfaces being parallel to the polarizers) was measured as a function of voltage. In figures 2(a) and (b) responses of CB6 monomer (at 46° C) and the anisotropic network containing 0.2 per cent C6M (at 100°C) in a 6.2 μ m thick twisted nematic cell to electric fields are compared. The most important effect to be seen in these figures is again the anisotropic network's recovery of its initial state, just like monomeric CB6 after the removal of the electric field. The other effects to be seen in figure 2(a) are the shifting of the intensity-voltage curve to voltages about an order of magnitude higher and induction of hysteresis upon the formation of the anisotropic network. Furthermore, when the response times of the CB6 monomer and the anisotropic network are compared in figure 2(b), it can be seen that in order to obtain a comparable rise time (τ_r) for the network as for the monomer at the applied voltage of $2 V_{rms}$ a much higher voltage was required (40 V_{rms}). The decay times (τ_d) in the absence of an electric field on the other hand, differ to a much lesser extent. These points will be discussed further on in the text.

The threshold voltage (V_c) in a planar cell is given by [13]

$$V_{\rm c} = \pi \sqrt{\left(\frac{K_{\rm 1}}{\varepsilon_0 \Delta \varepsilon}\right)},\tag{1}$$

where K_1 is the splay elastic constant, ε_0 the permittivity of free space and $\Delta \varepsilon$ is the dielectric anisotropy. In figure 2(a) the fact that the intensity-voltage curves shift to higher voltages upon formation of a network indicate an increase in K_1 . From threshold measurements we have tried to estimate K_1 keeping the problems associated with the technique in mind. For this we first estimated $\Delta \varepsilon$ for the CB6 monomer and the

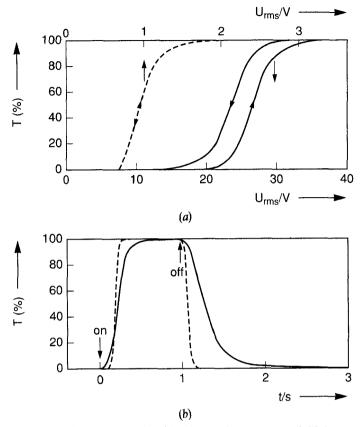


Figure 2. (a) Transmission as a function of voltage. (b) Response of CB6 monomer (broken lines) at 2 V_{rms}, 46°C and the anisotropic network containing 0.2 per cent C6M at 40 V_{rms}, 100°C.

anisotropic network containing 0.2 per cent C6M by measuring ε_{\parallel} and ε_{\perp} at 100 Hz. In figure 3 $\Delta \varepsilon$ for the CB6 monomer and the anisotropic network containing 0.2 per cent C6M is plotted as a function of temperature. In this figure the decrease in $\Delta \varepsilon$ upon formation of the anisotropic network is clear and will be discussed in the section on dielectric relaxation. Using these values of $\Delta \varepsilon$ in equation (1) together with measured values of V_c we have estimated K_1 with the results shown in figure 4. At a given reduced temperature $(T/T_{\rm NI}) K_1$ for the anisotropic network can be a factor of eight higher than that for the monomeric CB6. This is rather different to the behaviour observed for side chain oligomers, the elastic constants of which differ only moderately from those of low mass mesogenic molecules [14]. The other effect to be seen in figure 2(a) is the large difference in the slopes of the curves. As for $V > V_c$ the director deformation is related to K_3/K_1 [15] (K_3 being the bend elastic constant) indicating a large increase in K_3/K_1 upon formation of the network.

The effect of the cross-link density was also investigated by measuring the response of uniaxially oriented networks in 7.3 μ m thick cells to electric fields. In figure 5 a change in the refractive index anistropy is plotted as a function of applied voltage where it can be seen that, with increasing C6M concentration, the curves shift towards higher voltages as the slope of the curves in the linear region become smaller. Here again, increase in K_1 and K_3/K_1 with increasing cross-link density is indicated.

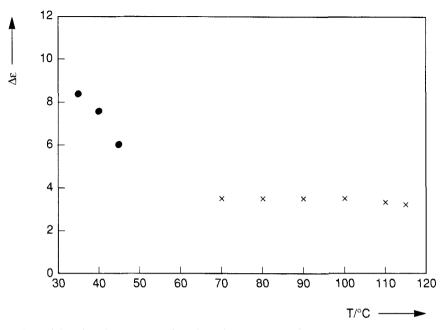


Figure 3. Dielectric anisotropy as a function of temperature. \bullet , CB6 monomer; \times , anisotropic network containing 0.2 per cent (w/w) C6M.

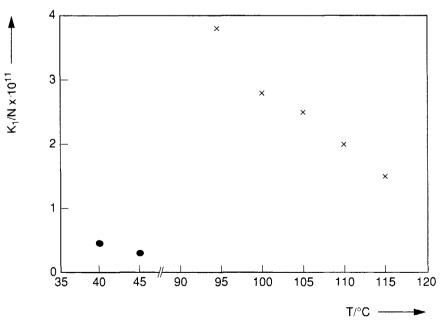


Figure 4. Splay elastic constant as a function of temperature. ●, CB6 monomer; ×, anisotropic network containing 0.2 per cent (w/w) C6M.

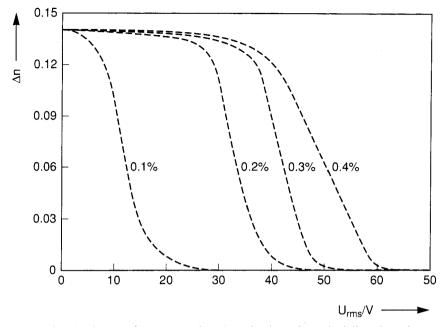


Figure 5. Refractive index difference as a function of voltage for uniaxially oriented networks containing various amounts of C6M.

Response times of the anisotropic networks were also investigated as a function of cross-link density by measuring the time between 5 per cent to 95 per cent transmission; a comparison with the CB6 monomer was also made. In figure 6 τ_r is plotted as a function of voltage for uniaxially oriented anisotropic networks containing various amounts of C6M at various temperatures. It can be seen that, for a given sample at a given voltage, τ_r decreases with increasing temperature. Furthermore, at a given voltage and temperature the rise times increase with increasing C6M concentration. In order to explain these effects it is useful to consider the equation [13]

$$\tau_{\rm r} = \frac{\gamma_{\rm b} d^2}{\Delta \varepsilon \varepsilon_0 V^2 - K \pi^2},\tag{2}$$

where γ_b is the rotational viscosity in the bulk, *d* is the cell thickness, *V* more is the voltage and *K* is an average elastic constant. The effect of increasing temperature on τ_r is associated with the decrease in γ_b and *K*. In the same way, the increase in τ_r with increasing cross-link concentration can be attributed to the increase in γ_b and *K*. However the extent to which each of these parameters changes will become clear later. Figure 7 shows τ_d as a function of temperature for uniaxially oriented networks containing various amounts of cross-links together with CB6 monomer. The relation between the τ_d and the physical parameters of the liquid crystal is given by [13]

$$\tau_{\rm d} = \frac{\gamma_{\rm b} d^2}{\pi^2 K}.\tag{3}$$

As can be seen from this equation the decrease in the decay time with increased crosslink density can be associated with the increase in the elastic constant K and a possible decrease in γ_b . Furthermore the fact that τ_d for samples with high cross-link densities,

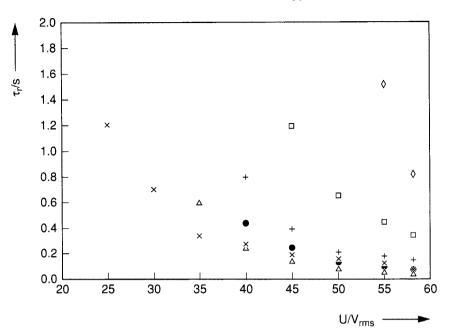


Figure 6. Rise time as a function of voltage for networks containing various amounts of C6M at various temperatures. □, 100°C; +, 107°C; ●, 110°C; △, 115°C; 0·2 per cent (w/w) C6M; ×, 100°C 0·1 per cent (w/w) C6M; ◇, 100°C 0·3 per cent (w/w) C6M.

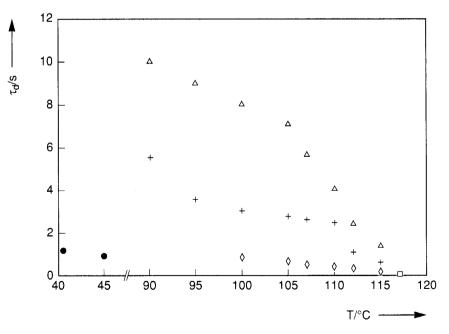


Figure 7. Decay time a function of temperature for: ●, CB6 monomer and anisotropic networks containing various amounts of C6M; △, 0·1 per cent (w/w); +, 0·2 per cent (w/w); ◇, 0·3 per cent (w/w).

especially at high temperatures are very similar to τ_d obtained for CB6 in the monomeric state, indicates that cross-linking increases K while reducing γ_b as the polymer backbone becomes immobilized. This would imply that, with increasing cross-link density, γ_b would tend to become the same as the internal viscosity experienced by the mesogenic side groups. In order to investigate this possibility we have performed dielectric measurements which give information on the internal viscosity and tried to estimate the rotational viscosity in the bulk from the viscoelastic measurements.

3.3. Dielectric spectroscopy

Dielectric spectroscopy was used to compare the relaxation times within the monomeric and the polymeric states. The δ -process which is associated with the rotation of the mesogenic molecules around their short axis (in the case of the side chain liquid crystal around the polymer backbone) has been shown to be related to the internal rotational viscosity [16]. According to the treatment of Martin *et al.* [17] the relaxation time around the short axis τ_{\parallel} in the nematic state is retarded by a factor G_{\parallel} imposed by the nematic potential and is given by

$$\tau_{\parallel} = G_{\parallel} \tau_{\mathbf{i}},\tag{4}$$

where τ_1 is the relaxation time in the absence of the nematic potential and it is found by extrapolation from the isotropic state. In return the relaxation times can be represented in terms of the internal vicosity as

$$\tau_{\parallel} \propto \gamma_{\rm N} \propto G_{\parallel} \gamma_{\rm I}, \tag{5}$$

where γ_N and γ_I are the internal viscosities within the nematic and the isotropic phases, respectively [16].

In order to measure the δ -process both in the monomeric state as well as within the anisotropic networks, the parallel plate geometry was used with the molecules homeotropically aligned. In figure 8, dielectric loss curves are shown as a function of temperature. The curves in figure 8(a) obtained for the monomer show the characteristic behaviour of low mass liquid crystals where a discontinuous change due to the disappearance of the nematic potential is observed. In figure 8(b), however, the behaviour observed for the anisotropic network is quite different and a more gradual change in the dielectric loss curves around the nematic to isotropic transition is shown. In figure 9, Cole–Cole plots [18] comparing the monomer with the anisotropic network in the nematic state are shown. For the CB6 monomer an almost perfect semicircle was obtained showing that a single mean relaxation time is effective within the system. The behaviour observed for the cross-linked network is rather different. In previous work [19] describing the dielectric behaviour of side chain CB6 polymer, the Havriliak-Negami function was used to fit the experimental results. Here we tried to fit the experimental curve to the Cole–Cole function as indicated by the broken line. The deviation manifested as a rapid increase in ε'' at high values ε' (low frequencies) is associated with the increase in conduction due ionic impurities. At low values of ε' (high frequencies) however, the deviation from the Cole-Cole mechanism is more difficult to explain; nevertheless it may be associated with the relaxation of the ester group located close to the main chain. Here it is important also to point out that, upon polymerization, a considerable decrease in the static permittivity is observed. This decrease again may be associated with increased association between the molecules. Indeed in our previous publication [20] the increase in association between the mesogenic molecules with increased density of cross-linking was demonstrated by

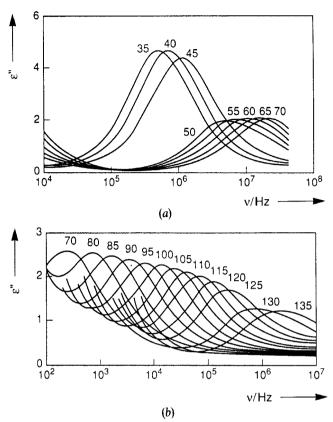


Figure 8. Dielectric loss as a function of frequency at the temperatures indicated for (a) CB6 monomer, (b) anisotropic network containing 0.2 per cent C6M.

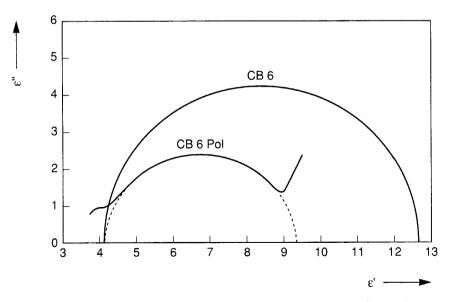


Figure 9. Cole–Cole plots for CB6 (CB6 monomer) and CB6 pol (anisotropic network) containing 0.2 per cent (w/w) C6M. Broken lines indicate a theoretical fit.

combining X-ray diffraction with dielectric measurements. Finally the Cole–Cole function used to fit the experimental curve is a depressed semicircle with a small Cole–Cole parameter h of 0.14. This indicates that, within the network, a narrow distribution of mean relaxation times is effective.

Furthermore taking the frequency corresponding to the maxima in figures 9 (a) and (b) as the mean relaxation frequency, we have produced the Arrhenius plots shown in figure 10. We used the slopes of lines drawn through the data points in order to estimate the activation energies in the nematic $(\Delta H_{\delta}(N))$ and the isotropic $(\Delta H_{\delta}(I))$ states for the anisotropic network and the monomer; the results are shown in table 2. It can be seen that the activation energies obtained for the cross-linked samples are much higher than

Table 2. Activation energies from dielectric and viscosity measurements in nematic and isotropic states for the monomer and the anisotropic network (0.2% C6M).

Material	$\Delta H_{\delta}(N)/kJ mol^{-1}$	$\Delta H_{\delta}(\mathbf{I})/\mathrm{kJ}\mathrm{mol}^{-1}$	$\Delta H_{\rm y}/{\rm kJmol^{-1}}$	$\Delta H_{\eta}/\mathrm{kJ}\mathrm{mol}^{-1}$
CB6 (mon)	96	57		
Network	135	115	130	45

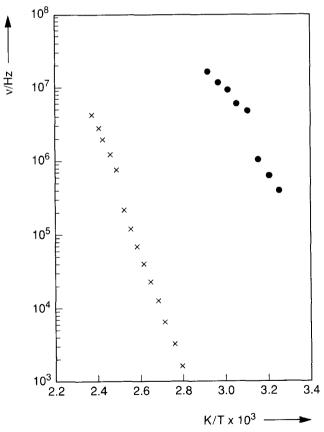


Figure 10. Arrhenius plots for dielectric relaxation of: ●, CB6 monomer; ×, anisotropic network containing 0.2 per cent (w/w) C6M.

the CB6 monomer indicating an increased degree of interaction. This is also in accord with the result shown in figure 9 where a decrease in the high frequency ε' was observed on polymerization. Furthermore, since the relaxation time is associated with the free volume within the system, a change in the density as a function of temperature (expansion coefficient) also effects the activation energy. Indeed in a recent publication [21] anisotropic expansion behaviour before and after the formation of anisotropic networks was demonstrated. The difference in the anisotropic expansion coefficient in lateral directions for the monomer was found to be about a factor of two smaller than that of the anisotropic network. Moreover in our previous study of highly cross-linked networks [20] the δ -relaxation was found to shift towards lower frequencies only when the cross-link density increased considerably. The shift was accompanied by an increase in the α -transition temperature. A significant change in both δ and α transitions could only be observed above 5 per cent C6M indicating that δ -relaxation is indeed associated with the internal viscosity determined by the free volume within the system.

According to equation (5), at a given reduced temperature the ratio of the relaxation times for the CB6 monomer and the anisotropic network should be equal to the ratio of their viscosities. In order to investigate this point further viscosity measurements were carried out.

3.4. Viscosity measurements

The rotational viscosity (γ_b) can be measured by various methods. Here we have measured the viscoelastic coefficient (γ_b/K_1) and from estimated values of K_1 , γ_b was calculated. The procedure used is as follows. A low voltage was applied across a uniaxially planar oriented sample to induce a slight deformation. As a result an decrease of δ_0 in the phase difference between the ordinary and extraordinary rays is induced. Upon removal of the electric field the change in the phase difference as a function of time $(\delta(t))$ changes from $\delta(t) = \delta_0$ at t = 0 to $\delta(t) = 0$ at $t = \infty$ and can be represented as [22]

$$\delta(t) \cong \delta_0 \exp\left(-2t/\tau_0\right),\tag{6}$$

where τ_0 is given by equation (3) where $K = K_1$. Light transmission through uniaxially oriented samples between crossed polarizers was measured as a function of time, which could later be translated into $\delta(t)$. In figure 11 an example of a $\delta(t)$ curve for CB6 monomer (see figure 11(a)) is compared with a curve obtained for the anisotropic network (see figure 11 (b)) containing 0.2 per cent C6M. In the case of the monomer the experimental points could be fitted to a single exponential decay function given by equation (6). In the case of the anisotropic network however the best fit through the experimental points was obtained when the sum of two exponential decay functions with very different decay constants was used. Using the decay constants and the values of K_1 from figure 4 we have estimated γ_b as a function of temperature and the results are shown in figure 12. It can be seen that at a given temperature within the CB6 monomer a single $\gamma_{\rm b}$, whereas in the anisotropic network two rotational viscosities $\gamma_{\rm b}(1)$ and $\gamma_{\rm b}(2)$ associated with the fast and slow decay rates, respectively, are effective. The values shown for the CB6 monomer in this figure are of the same order as reported for various low mass liquid crystals, whereas for the anisotropic network even the high values of viscosity are a factor of ten lower than the typical values of $\gamma_{\rm h}$ reported for side chain oligomers [4]. At a given reduced temperature, if the ratio of $\gamma_{\rm b}$ for the polymer and the monomer is compared with the ratio of the relaxation times (see figure 10), it can be seen

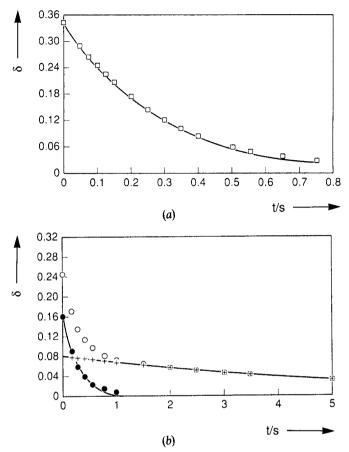


Figure 11. Change in retardation as a function of time. (a) CB6 monomer measured at 45° C (b) Anisotropic network containing 0.2 per cent (w/w) C6M at 100°C. Solid lines indicate theoretical fits.

that for $\gamma_b(1)$ the difference is of the order of a factor of three. Furthermore, the activation energy (ΔH_{γ}) using the values of $\gamma_b(1)$ was also calculated and is compared in table 2 with the activation energy calculated from dielectric measurements where a good correlation is to be seen. Considering also that $\gamma_b(1)$ in figure 12 is several orders of magnitude lower than the values of γ_b reported for side chain oligomers [4] we would like to associate it to a large extent with the internal viscosity of the side groups, whereas $\gamma_b(2)$ is associated to a large extent with the viscosity of the side groups coupled to the polymer backbone.

In order to get information about the bulk viscosity of the anisotropic networks where the polymer backbone is also deformed we have measured the dynamic shear viscosity. Assuming that the loss viscosity η'' is associated with the viscous flow, the Arrhenius plot shown in figure 13 was made. It can be seen that the viscosity is several orders of magnitude higher than the rotational viscosities $\gamma_b(1)$ and (2) shown in figure 12. This large difference also indicates the decreased effect of the main chain on the dynamics of the side groups. This effect is also to be seen in the activation energy ΔH_{η} calculated for η'' given in table 2 and as can be seen, it is much lower than the activation energies calculated from dielectric relaxation and rotational viscosity measurements, again signifying the difference in the origin of the two processes.

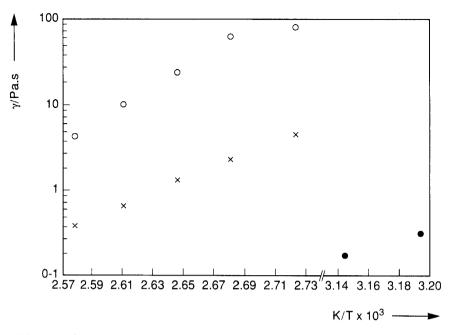


Figure 12. Rotational viscosity estimated for: ●, CB6 monomer; ○, ×, anisotropic network containing 0.2 per cent (w/w) C6M as a function of inverse temperature.

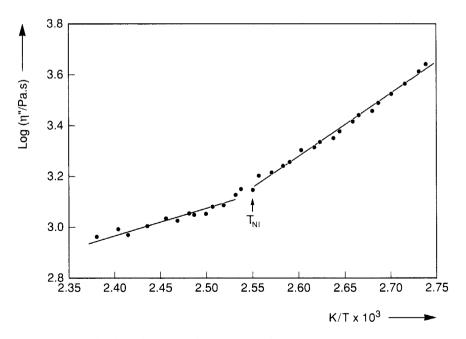


Figure 13. Dynamic shear loss viscosity measured for the anisotropic network containing 0.2 per cent (w/w) C6M.

4. Conclusions

It has been shown that lightly cross-linked anisotropic networks can be obtained by in situ photopolymerization of mixtures of mesogenic mono- and diacrylates. In this way anisotropic networks with uniaxial and twisted nematic orientations could be produced. The macroscopic orientation of the anisotropic networks was found to be highly reversible and even though the network became isotropic at elevated temperatures, the initial orientation was recoverable at a high rate upon cooling. The initial average orientation of the molecules could also be altered by application of an electric field. However, unlike high molecular weight polymers anisotropic networks reverted to the initial orientation. With increasing network concentration the decay time was found to decrease, whereas the threshold voltages and the rise times increased considerably, indicating an increase in the elastic constants. Dielectric measurements showed that the nematic potential for the anisotropic networks disappeared very gradually as opposed to the monomer which showed a discontinuity at the clearing point. Furthermore, compared with the monomer, the activation energies associated with the δ -relaxation for the anisotropic network were found to be much larger. This difference was associated with increased association as well as with a decrease in the expansion coefficient upon polymerization. The rotational viscosity was also estimated in the bulk. For the monomer, a single rotational viscosity was found to be effective, whereas two rotational viscosities with a factor of ten difference could be defined for the anisotropic networks. The low rotational viscosity was associated to a large extent with the motion of the side groups decoupled from the polymer backbone, whereas the polymer backbone contributed to a large extent to the higher rotational viscosity.

Referènces

- [1] SCHMIDT, H. W., 1989, Adv. Mater., 101, 964.
- [2] NAKAMURA, T., UNEO, T., and TANI, C., 1989, Molec. and Crystals liq. Crystals, 169, 167.
- [3] FABRE, P., CASAGRANDE, C., VEYSSIE, M., and FINKELMANN, H., 1984, *Phys. Rev. Lett.*, 53, 993.
- [4] CASQUILHO, J. P., and VOLINO, F., 1990, Molec. Crystals liq. Crystals, 180, 357.
- [5] SHIBAEV, P., and PLATE, N. A., 1984, Advances in Polymer Science, Vols. 60/61 (Springer Verlag).
- [6] COGNARD, J., 1982, Molec. Crystals liq. Crystals, Supplement 1.
- [7] SAGE, I., 1987, Thermotropic Liquid Crystals, edited by G. W. Gray (Wiley).
- [8] FINKELMANN, H., and REHAGE, G., 1984, Advances in Polymer Science, Vols. 60/61 (Springer Verlag).
- [9] GEMMELL, P. A., GRAY, G. W., and LACEY, D., 1985, Molec. Crystals liq. Crystals, 122, 205.
- [10] FINKELMANN, H., KOCK, H., and REHAGE, G., 1981, Makromolek. Chem. rap. Commun., 2, 317; ZENTEL, R., 1989, Adv. Mater, 101, 1437.
- [11] BROER, D. J., BOVEN, J., MOL, G. N., and CHALLA, G., 1989, Makromolek. Chem., 190, 2255.
- [12] BROER, D. J., HIKMET, R. A. M., and CHALLA, G., 1989, Makromolek. Chem., 190, 3202.
- [13] GOODMAN, L. A., 1975, Introduction to Liquid Crystals, edited by E. B. Priestly, P. J. Wojtowicz and P. Sheng (Plenum Press).
- [14] HOPWOOD, A. I., and COLES, H. J., 1985, Molec. Crystals liq. Crystals, 130, 281.
- [15] BAUR, G., 1981, Molec. Crystals liq. Crystals, 63, 45.
- [16] DE JEU, W. H., 1980, Physical Properties of Liquid Crystalline Materials (Gordon & Breach).
- [17] MARTIN, A. J., MAIER, G., and SAUPE, A., 1971, Symp. Faraday Soc., 5, 119.
- [18] HIKMET, R. A. M., and ZWERVER, B. H., 1991, Liq. Crystals, 10, 836.
- [19] BORMUTH, F. J., BIRADAR, A. M., QUOTSCHALLA, U., and HASSE, W., 1989, Liq. Crystals, 5, 1549.
- [20] HIKMET, R. A. M., LUB, J., and MAASEN VD BRINK, P., 1992, Macromolecules, 25, 4194
- [21] HIKMET, R. A. M., ZWERVER, B. H., and BROER, D. J., 1992, Polymer, 33, 89.
- [22] WU, S. T., and WU, C. S., 1990, Liq. Crystals, 8, 171.