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Liquid Crystalline Epoxide Thermosets. Dynamic Mechanical and Thermal Properties

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ABSTRACT: Dynamic mechanical and thermal properties of a certain liquid crystalline (LC) diepoxide cross-linked with three different aromatic diamines were studied. For one epoxy−amine mixture, the position of the gel point was determined with the aid of frequency-dependent rheological measurements. The value of the critical relaxation exponent was 0.5. The gel point was also determined by solubility experiments. There was a clear agreement between the two methods. The degree of conversion of the epoxy groups at the gel point (55 ± 3%) corresponded well with the value predicted by the statistical theory for network formation in isotropic stoichiometric epoxy−amine mixtures. Mechanical measurements were carried out on macroscopically ordered networks in the direction of orientation. In highly ordered networks prepared from the LC diepoxide and a rigid aromatic diamine, the value of the rubber modulus deviated from the predictions of rubber elasticity theory by a factor of 30 times higher. In networks with the same high level of macroscopic orientation prepared from the LC diepoxide and a relatively more flexible diamine, the deviation from the classical theory was much less (factor of 1.7). In the rubbery region, the value of the Young's elastic modulus decreased as a function of temperature, which seems to be connected to the decrease of the order. This is confirmed by a theory, presented by T. Odijk, concerning the polymer nematic gels under tension (see Appendix). The thermal expansion coefficient of the macroscopically ordered networks was highly anisotropic. It was indeed possible to combine the good mechanical and thermal properties of conventional epoxy polymer networks with the special features that LC polymers offer.

I. Introduction

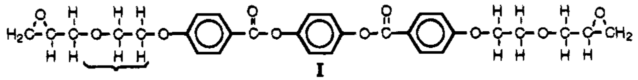
Epoxy networks are widely applied as engineering thermosets because of their good mechanical and thermal properties. Recently, it has been recognized that these properties could be greatly enhanced if liquid crystalline (LC) like structures are incorporated into the epoxy networks.[1]

It is common knowledge that LC main-chain polymers show a high modulus and a very low thermal expansion in the direction of the macroscopic orientation.[2] In the direction transverse to the orientation of the chains, however, the properties are rather poor. These differences can be reduced by the introduction of cross-links between the chains, which improves the dimensional stability of these ordered systems.

Although there have been several attempts,[3−5] it has not yet been possible to produce epoxy networks with both high cross-link density and high macroscopic order. The basic idea has been in nearly all these studies to polymerize and cross-link low molecular weight mesogenic monomers in the mesophase which leads then to the fixation of the LC order.[6] It seems almost trivial to state, but the existence of the macroscopic order is essential when highly anisotropic bulk properties are desired. This point has not always been appreciated in the current literature.[7,8]

Recently, we described the synthesis and LC properties of a series of mesogenic diepoxide compounds.[9] It was shown that highly macroscopically ordered networks can be prepared by photoinitiated chain polymerization of these monomers in the LC phase. The reaction, however, proceeds in quite an uncontrolled manner; the network formation continues in the dark for a long time. This makes control of, for example, mechanical properties, which are directly related to the degree of conversion, very difficult. Alternatively, we showed for the first time that highly cross-linked epoxy networks with a high macroscopic order can also be produced by copolymerization with aromatic diamines.[10] This step growth polymerization proceeds in a much more controllable fashion.[11] Also, the chemical reactions involved are rather specific.

From these investigations it followed that LC diepoxide I was the best monomer for producing ordered networks by copolymerization with aromatic diamines partly because of its broad nematic range:



I

crystal $\xrightarrow{124}$ **nematic** $\xrightarrow{186\ °C}$ **isotropic**

Further studies showed that, owing to the action of the short spacer segment, which decouples the reaction center from the mesogenic part, the orientational order of the diepoxide is less sensitive to the degree of polymerization in comparison with that of the diamine A-1 (see Table 1).[12] In addition, comparison of the reactivity of the epoxy group in compound I with that of compounds where the epoxy groups are connected to the mesogenic group without the short spacer segment (indicated in structure I) revealed that the presence of a spacer also lowers the reactivity of the epoxy groups: upon melting there is sufficient time to orient the reactive LC mixture macroscopically before a substantial amount of reaction takes place.[13] This is probably related to the activating effect of the aromatic group, which diminishes upon insertion of the spacer segment. Also, addition of the spacer lowers the melting point of the diepoxide by almost 62 °C, so that the reaction can be carried out at moderate temperatures. Indeed the

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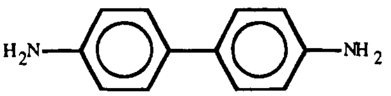
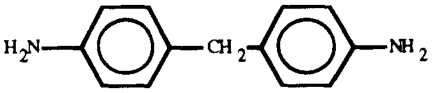
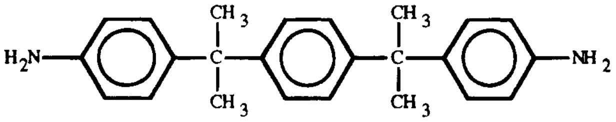
Table 1. Structure and Characteristics of the Various Cross-Linking Agents and Comparison of the Experimental ($E'_{r,exp}$) and Theoretical ($E'_{r,theo}$) Values of the Young's Elastic Rubber Modulus for Different, Fully Cured, Systems

diamine	formula	mp (°C)	code	$E'_{r,exp}$[a] (Pa)	$E'_{r,theo}$[b] (Pa)	$E'_{r,exp}/E'_{r,theo}$
4,4'-diaminobiphenyl		131	A-1	9×10^8	3.0×10^7	30
4,4'-diaminodiphenylmethane		88	A-2	5×10^7	3.0×10^7	1.7
Epikure 1061		162	A-3	1×10^7	2.7×10^7	0.4

[a] These values are determined from the second heating rate at $T = T_g + 50$ °C. [b] These values are calculated using eq 2 with $\varrho = 1.2$ g·cm^{-3} and $T = T_g + 50$ °C.

copolymerization of spacerless epichlorohydrine–bisphenol-based low molecular weight LC diepoxide compounds with aromatic diamines, as was carried out by Barclay et al.,[5] resulted, even under the influence of a very strong magnetic field (13.5 T), in networks with a very low degree of macroscopic orientation. The local level of orientation, on the other hand, was high in view of the fact that the mixture transformed from the nematic phase to the higher order smectic phase during the polymerization. Consequently, the authors rightly concluded that, as result of the high reaction rates, the polydomain structure became fixed before the macroscopic orientation could be fully achieved. This situation is aggravated by the fact that the LC order can also increase the rate of the polymerization.[9,13]

Recently, Mallon and Adams studied the copolymerization of a LC diepoxide containing a spacer segment between the epoxy group and the mesogenic part with aromatic diamines.[8] Although the mesogenic parts were the same, the LC diepoxide synthesized by Mallon and Adams differs from our compound in one essential respect: in contrast to compound I, there is no oxygen atom present in the position β to the epoxy group. In our investigations on photoinitiated polymerization, we demonstrated that replacement of a methylene group by an oxygen atom in the position β to the epoxy group leads to an increase of the reactivity, resulting in densely cross-linked networks which maintain their orientation up to 300 °C.[9] Similar observations were made when the polymerization was carried out with aromatic diamines.[13] Mallon and Adams reported that even after prolonged curing the networks, prepared from the stoichiometric ratio of the LC diepoxide and a certain aromatic diamine, displayed smectic to nematic and even in some cases LC to isotropic transitions. This behavior is characteristic for networks with a low cross-link density. Furthermore, the networks prepared by Mallon and Adams were inhomogeneous since the regions of isotropic, nematic, and smectic phases were all coexisting during the polymerization reaction. As phase separation is a kinetically controlled process, it can be argued that because of the low polymerization rates, the system is prone to become inhomogeneous during the polymerization. Also, it is our experience that the initial mixing process of the two reactive compounds plays an important role in producing well-defined networks. The networks prepared by copolymerization of the diepoxide I with aromatic diamines were all homogeneous and showed no thermal transitions after a short period of curing.[10]

Summarizing, we can state that the LC diepoxide I is a suitable compound for producing ordered networks by copolymerization with aromatic diamines because it has a broad nematic range and the reactivity of the epoxy groups is low enough in order to orient the system macroscopically but also high enough to produce networks with a high cross-link density.

When considering the properties of ordered networks, there are two topics that are of prime importance. In the first place, of course, the state of order of these systems and possible change of the level of orientation as a function of the degree of polymerization and cross-linking should be investigated. In an earlier study, we monitored the copolymerization reaction in real time with the aid of deuterium nuclear magnetic resonance (^{2}H-NMR) in combination with birefringence measurements.[12] The main conclusion from these investigations was that the orientational order increased during the chain extension process and it became irreversibly fixed as a result of the cross-linking reaction.

The second point of interest, which is also the subject of the present paper, is the elastic behavior of ordered networks. The rigid character of the monomers and the ordered structure are the two main factors which distinguish the networks discussed in this paper from conventional cross-linked polymers. We will examine the mechanical properties of macroscopically oriented networks, from I and different aromatic diamines, in terms of both rigidity and order. Also, rheological measurements (position of the gel point) as a function of reaction time and analyses of the anisotropic thermal expansion coefficient of ordered networks are described and discussed.

II. Experimental Section

The synthesis of the diepoxide compound I has been described previously:[9] epoxy value = 3.48 equiv/kg (theoretical value: 3.63). 4,4'-Diaminobiphenyl (A-1) was supplied by RPL (Leuven, Belgium), 4,4'-diaminodiphenylmethane (A-2) by Aldrich Chemical Co., and Epikure 1061 (A-3) by Shell Resins (USA) (see Table 1). These diamine compounds were used without further purification (purity >98%). All the physical measurements were carried out on stoichiometric mixtures of diepoxide I with the appropriate diamine. The polymerization mixtures were prepared as described earlier.[12] In the text they are referred to according to the codes given to the diamine compounds.

The conversion of epoxy groups (α) up to the gel point was determined by ^{1}H-NMR (Varian VXR 400 S). The reaction mixtures, cured for various times at 120 °C, were dissolved in dimethyl sulfoxide (DMSO). The conversion was calculated from the decrease in the intensity of the epoxy ring protons at 2.77 ppm relative to the intensity of the aromatic part at 8.09 ppm (relative accuracy of 5%). The conversion beyond the gel point was determined by potentiometric titration of

Table 2. Values of Coefficient of Thermal Expansion (CTE) Measured Parallel With (||) and Perpendicular to (⊥) the Direction of the Macroscopic Orientation for Different Systems Measured in the Glassy and Rubbery Regions together with the Values of the Glass Transition Temperatures (T_g)

		CTE[a] (°C^{-1})				
		||		⊥		
code	T_{cure} (°C)	glass[c]	rubber[d]	glass[c]	rubber[d]	T_g[b] (°C)
A-1	120	-2.6×10^{-6}	-1.1×10^{-4}	1.3×10^{-4}	2.8×10^{-4}	118.9
	140	-2.7×10^{-6}	-1.1×10^{-4}	1.2×10^{-4}	2.5×10^{-4}	120.2
	160	-2.9×10^{-6}	-1.2×10^{-4}	1.3×10^{-4}	2.9×10^{-4}	116.0
A-2	120	3.0×10^{-5}	-1.0×10^{-4}	1.1×10^{-4}	3.0×10^{-4}	122.5
	130	2.4×10^{-5}	-1.4×10^{-4}	1.2×10^{-4}	3.3×10^{-4}	121.1
	150	2.5×10^{-5}	-1.6×10^{-4}	1.2×10^{-4}	3.7×10^{-4}	123.0
A-3	140					119.9

[a] Determined from the second heating scan. [b] T_g is taken as the maximum of the tan δ peak. These values are in good agreement with those determined from the thermal expansion measurements. [c] Calculated between 50 and 90 °C. [d] Calculated between 140 and 180 °C.

the remaining epoxy groups; $\alpha = 87 \pm 3\%$ after 1 h at 120 °C (system A-1) and $96 \pm 3\%$ for all systems that have undergone the thermal treatment up to 200 °C.

Rheological measurements were performed with the aid of a Rheometrics RMS-800 dynamic mechanical spectrometer using parallel-plate (8 mm in diameter) geometry. During the frequency-dependent measurements, the strain amplitude was varied inversely with reaction time in order to obtain proper torque signals. The measurements were performed on the reaction mixture A-1, which is a favorable system because it is free of complicating factors occuring during cure like vitrification. The system does not transfer to the glassy state due to the fact that the cure temperature (i.e., $T_{\mathrm{cure}} = 120$ °C) is close to the glass transition temperature of the fully reacted system (see Table 2).

The macroscopically oriented samples were prepared by conducting the polymerization in the NMR probe (Varian VXR 400) at the required temperature (±1 °C) in the presence of a magnetic field (9.4 T). It was shown previously that under such conditions the macroscopic alignment is indeed almost complete.[12]

Mechanical behavior from the glassy state to the rubbery region was studied using a Perkin-Elmer dynamic mechanical analyzer (DMA-7). The storage (E') and loss (E'') Young moduli and the loss tangent (tan $\delta = E''/E'$) were determined on a macroscopically oriented rectangular specimen (20 × 3 × 1.5 mm) in the three-point bending mode. The measurements were carried out in the direction of the macroscopic orientation from 30 to 200 °C at a heating rate of 5 °C/min and a fixed frequency of 1 Hz.

Anisotropic thermal behavior of the macroscopically ordered rectangular samples (4 × 3 × 3 mm) was determined using a Perkin-Elmer DMA-7 which could also be operated in the thermomechanical mode, measuring the linear displacement as a function of temperature. The measurements were carried out between 30 and 200 °C (5 °C/min) under a constant force of 10 mN. The experimental conditions for differential scanning calorimetry (DSC) and birefringence (Δn) measurements have been reported previously.[10]

III. Results and Discussion

A. Rheological Behavior of a Liquid Crystalline Epoxy–Amine Mixture in the Vicinity of the Gel Point. In recent years it has been demonstrated for various chemically[14–19] and physically[20,21] cross-linked isotropic systems that the position of the gel point can be accurately determined by frequency-dependent dynamic mechanical measurements. A brief description of this method is as follows.

At the start of the reaction the system behaves as a viscoelastic liquid; $G'(\omega) \sim \omega^2$ and $G''(\omega) \sim \omega$, where G' and G'' are the storage and loss moduli respectively, and ω is the angular frequency.[22] As the reaction proceeds, small clusters are formed which are often supposed to behave as mechanically self-similar regions; the same properties are found at each length scale. It has been shown by Cates[23] and Muthukumar[24] that the dynamic mechanical properties of these self-similar regions follow a frequency-dependent power law. At high frequencies, probing the small length scales, the system exhibits gel-like behavior whereas at low frequencies liquid-like behavior is observed. The crossover frequency ω^* separates the two regimes. As the reaction proceeds, still larger clusters (self-similar regions) are formed and ω^* tends to zero. Presumably, at the gel point $\omega^* = 0$ and the frequency dependency of G' and G'' is represented by a power law over the entire range of frequenies:

$$G'(\omega) \sim G''(\omega) \sim \omega^n \tag{1}$$

where n is the critical viscoelastic exponent which is expected to be characteristic for the system.

It should be pointed out that measurement of G' and G'' does not fully describe the rheological behavior of these liquid crystal polymers, which, in general, is quite complex.[25–27] Additional complications may arise from the rigid character of the starting materials and the polydomain structure of the medium. Attempts were made to perform the rheological measurements in the macroscopically ordered state. Although it was possible to induce homeotropic orientation under the influence of surface-active agents, unfortunately the monodomain structure became disturbed as a result of the deformation applied during the measurements. The question is whether, in spite these complexities, the method is still applicable to the present system.

For the investigation of network formation in an ordered state we have used in most of our studies the diamine 4,4′-diaminobiphenyl (A-1; see Table 1) as the cross-linking agent, because as was found earlier[10] it forms a eutectic mixture with the diepoxide I. Figure 1 shows a DSC trace of a stoichiometric mixture of the diepoxide I and diamine A-1. The mixture is a eutectic with a melting point of 115.9 °C, above which a nematic phase is formed.

Figure 2 shows the evolution of G' and G'' at 15 Hz during the isothermal reaction at 120 °C, which is just above the eutectic melting point. At this temperature the reaction can be easily monitored, since it is still relatively slow. As can be seen in Figure 2, both G' and G'' start to increase at around 12 min. This coincides well with the time at which the mixture transforms from the nematic into the higher viscous smectic phase.[10,12] At 27 min the G' and G'' curves cross and then they start to level off. Before this crossover point, viscous properties are dominating ($G'' > G'$) while thereafter the elastic behavior is predominant ($G'' < G'$).

As mentioned above, in order to determine exactly the position of the gel point, frequency-dependent measurements of the moduli are required. Figure 3 shows the result of such measurements where G' and G'' are plotted against the frequency at various reaction times. With our experimental setup, it was not possible to measure the values of G' and G'' instantaneously at different frequencies. The results reported in Figure 3 are obtained by interpolation of the experimental data measured at different times during one frequency cycle. At the gel point (27 ± 1 min), which is defined by a similar power law exponent for G' and G'', the values of the two moduli are equal. This is in agreement with n equaling 0.5 as derived from Figure 3. This is

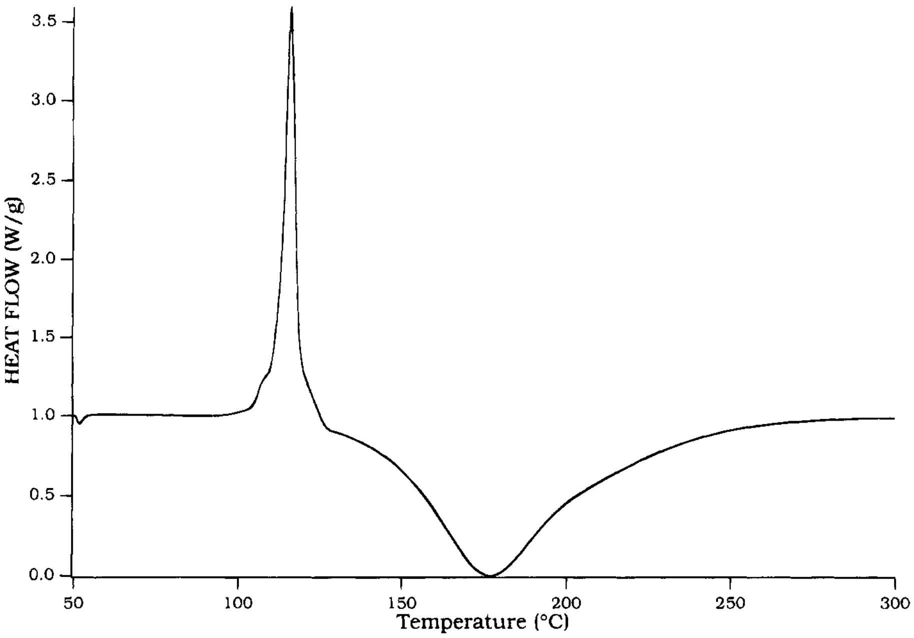


Figure 1. DSC trace of a stoichiometric mixture of diepoxide I and diamine A-1.

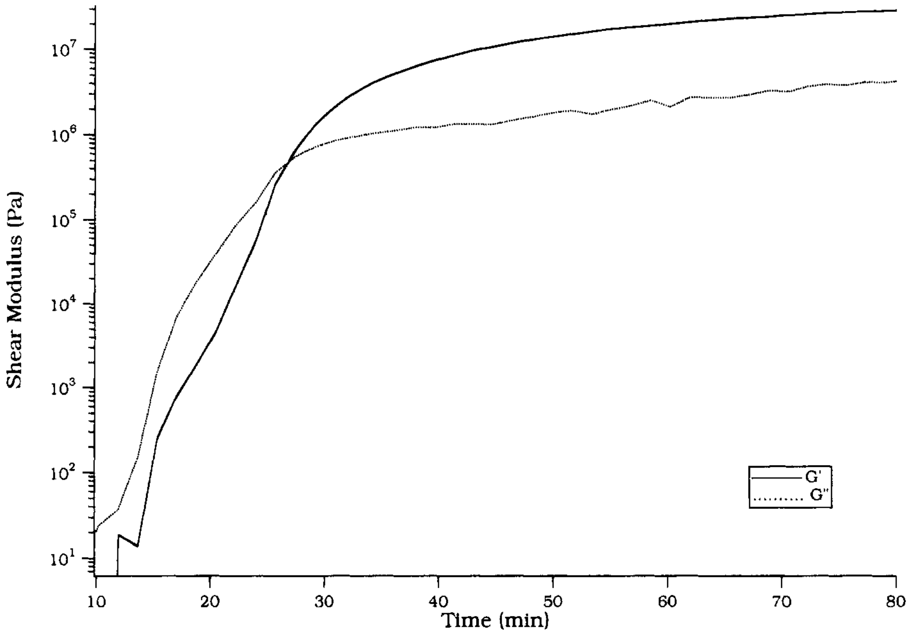


Figure 2. Evolution of the storage (G') and loss (G'') moduli as a function of the reaction time at 120 °C for the mixture A-1 (frequency = 15 Hz).

consistent with the value determined for most of stoichiometrically balanced gels.[28] Somewhat higher values, however, are found for a series of stoichiometric isotropic epoxy–amine mixtures.[29,30] This is not surprising since it is known that the exponent n does not have a universal value, as is suggested by several theories describing the dynamic behavior near the gel point,[29,30] but depends on various parameters such as material structure and stoichiometry.[31]

Solubility experiments during the isothermal reaction at 120 °C have shown that the material becomes partly insoluble in DMSO at 27 ± 1 min. This corresponds well with the gel point, determined by the analyses of G' and G'' above.

We were also interested in examining whether the chemical conversion of the epoxy groups (α) at the gel point corresponds with the theoretical value predicted by a statistical approach for a stoichiometrically balanced isotropic epoxy–amine mixture. Depending on the relative reactivity of the secondary (K_2) to the primary (K_1) amine hydrogen atoms the gelation occurs between 50% ($K_2/K_1 \rightarrow 0$) and 61.8% ($K_2/K_1 \rightarrow \infty$).[32] Figure 4 shows α measured up to the gel point as a function of polymerization time at 120 °C. The good agreement between the experimentally determined ($\alpha = 55 \pm 3\%$) and the theoretical value of α at the gel point indicates that network formation in these ordered epoxy–amine mixtures also seems to proceed in a statistical manner.

B. Viscoelastic Response and Thermal Behavior of Macroscopically Ordered Networks. Figure 5 shows the dynamic mechanical properties of system A-1 cured isothermally at various temperatures under the influence of the magnetic field. The behavior of ordered networks, especially in the rubbery state, is rather peculiar. First the very high value of the rubber modulus is considered. We will continue to use the term rubber for this state despite its high value of the Young's

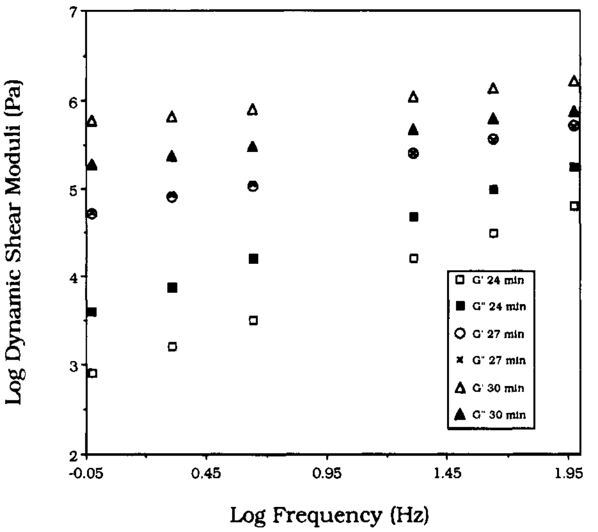


Figure 3. Dynamic mechanical properties of system A-1 as a function of the frequency plotted at different reaction times near the gel point (T_{cure} = 120 °C). The storage (G') and loss (G'') moduli are obtained by interpolation of the experimental data at different times.

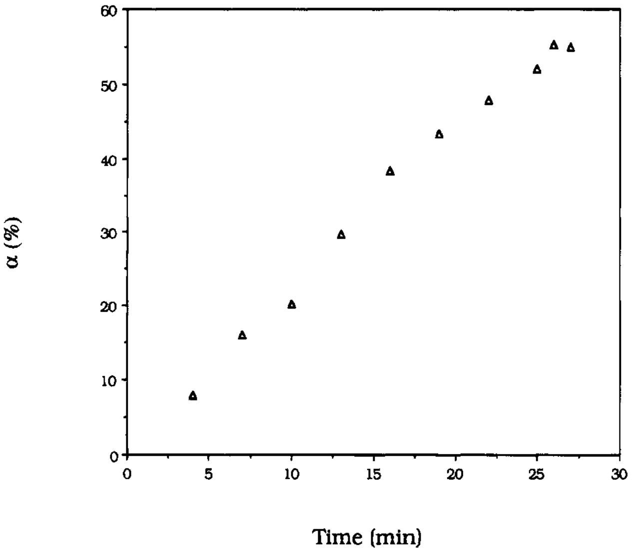


Figure 4. Conversion of the epoxy groups (α) measured up to the gel point as a function of the polymerization time at 120 °C.

elastic modulus. In Table 1 the experimental value of the rubber elastic modulus ($E'_{\mathrm{r,exp}}$) is compared with the theoretical value ($E'_{\mathrm{r,theo}}$) determined with the aid of the simplest form of the classical rubber elasticity equation:[33]

$$E'_{\mathrm{rubber}} = \phi \frac{3\varrho RT}{M_{\mathrm{c}}} \qquad (2)$$

where ϱ is the density of the network at T, R is the gas constant, and ϕ is the front factor which allows for effects of several theoretical approximations. For a phantom network, in which the chains freely penetrate each other, with fully suppressed fluctuations of cross-links displaced affinely with strain, ϕ equals one.[34] M_{c} is the average molecular weight between cross-links which can be calculated by using eq 3.

$$M_{\mathrm{c}} = \frac{m_{\mathrm{a}} + 2m_{\mathrm{e}}}{3} \qquad (3)$$

where m_{a} and m_{e} are the molecular weights of the diamine and diepoxide, respectively.

There are basically two main factors which can be responsible for the large difference between the experimental and theoretical value of the rubber modulus (see Table 1). In the theory of rubber elasticity, it is assumed, in analogy with the behavior of ideal gasses that the retractive stress of a rubber is caused by a reduction of entropy rather than by a change in enthalpy.[34] In this approach the distribution of the end-to-end distances of a single polymer chain is expressed as a Gaussian function. In principle, this can only be expected to hold true for long flexible chains. In the present case the distances between the cross-link junctions are too short and especially too rigid to behave as Gaussian chains. In the literature there are several examples where it has been shown that, in the case of epoxy–amine networks, the deviation from ideal behavior increases with concentration of rigid segments.[35–37] In all these studies, however, the networks have not been examined for their possible LC like structural order.

Several attempts have been made recently to describe the deformation behavior of networks comprising rigid rod segments. On the basis of the nature of the cross-link points, distinction has been made between networks where the rods are rigidly connected at the junction points and networks where the rods are freely jointed.[38] In the first case, assuming the rods cannot freely rotate around the cross-link points, the deformation behavior is purely enthalpic; owing to the rigid character of the chains, no conformational changes occur under stress and deformation of the network can only be accomplished by the bending of the rods.[39] In the second case, because of the flexible nature of the network at the cross-link points, there is still a contribution of entropy to the elastic modulus; the network deforms entropically.[40,41] Due to the presence of the spacer segments, it is believed that our system resembles more the entropic model, although the deformation of the mesogenic groups could also play a role.

In the case of the "entropic networks" produced by rigid rods, it was shown[40,41] in a qualitative manner that surprisingly the elastic behavior for small deformations is the same as for networks comprising flexible chains. At large deformations, however, there is a fast increase of the free energy because of the inextensibility and rigidity of the elements. Similar results were found from some earlier theoretical descriptions of non-Gaussian networks.[42,43] It must be noted that in all these studies the system was assumed to be isotropic and complicating factors such as LC ordering have not been included.

Apart from rigidity of the starting materials, the long-range orientational order is the second factor which distinguishes the present networks from conventional systems. Warner et al.[44,45] have considered the deformation behavior of nematic networks, in continuation of the original work of de Gennes.[46] This theory, however, is derived for networks built up of Gaussian chains and it is basically a modification of the classical theory of rubber elasticity.

In Figure 5 it can be seen that the value of the rubber modulus is independent of T_{cure}. It was shown previously with the aid of ^{2}H-NMR that the networks cured at 120 °C have an order parameter $S \geq 0.9$,[12] where S equals the second-order Legendre polynomial. Furthermore, it was demonstrated that the networks prepared at T_{cure} up to 160 °C have roughly the same Δn value ($\approx$0.15 at 50 °C above T_{g}). Assuming that $\Delta n \propto S$, we conclude that the level of orientation for all the networks

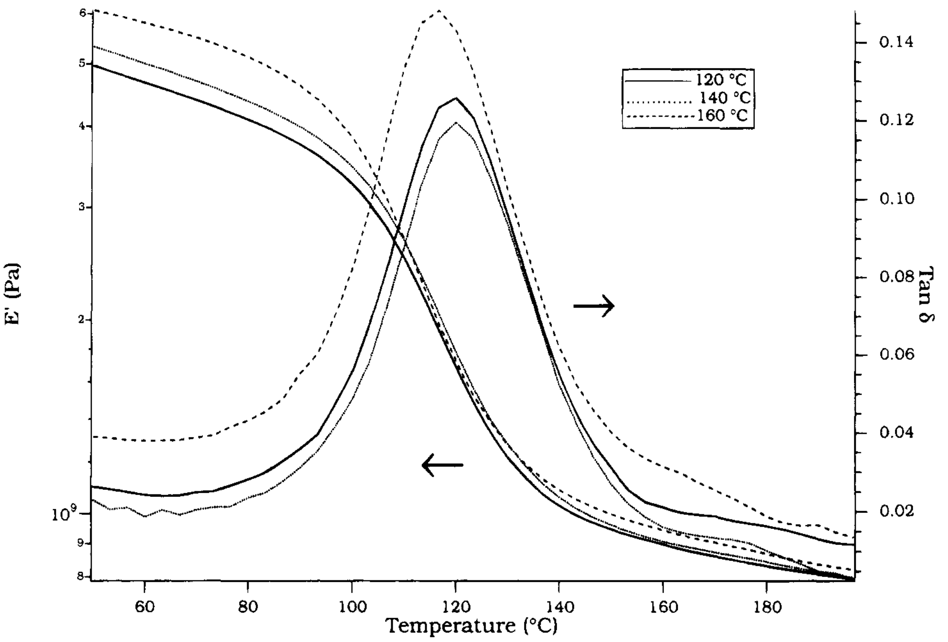


Figure 5. Dynamic mechanical response of the fully cured, macroscopically ordered A-1 system, measured in the direction of the orientation at 1 Hz. The data are shown for different cure temperatures.

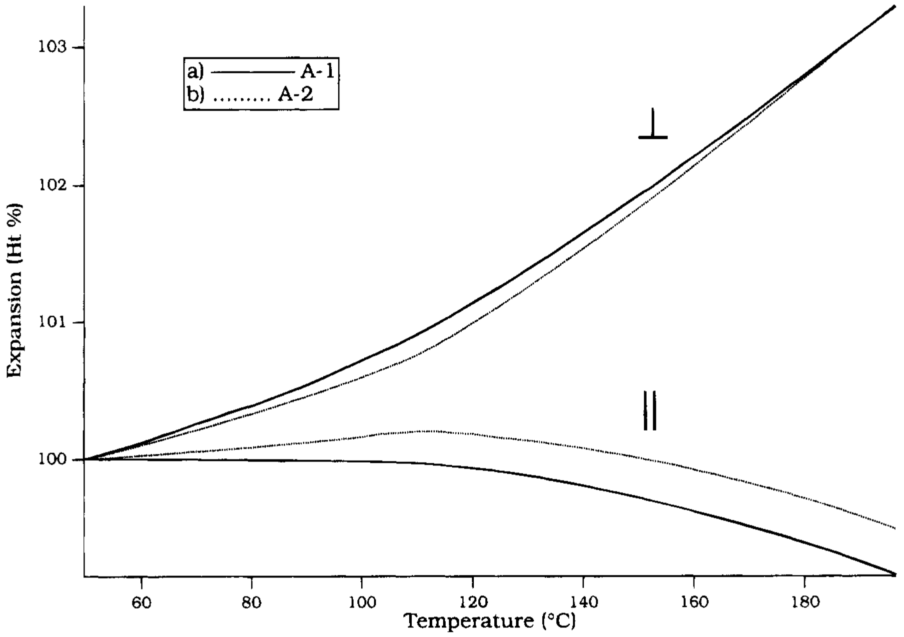


Figure 6. Linear displacement measured parallel with (||) and perpendicular to (⊥) the direction of macroscopic orientation for A-1 (a) and A-2 (b) systems (T_{cure} = 120 °C).

cured isothermally up to 160 °C is equal which is reflected in the same value of the rubber modulus.

In the glassy state, the elastic modulus seems to depend somewhat on T_{cure}. The interpretation of these results in terms of the molecular structure is, however, very difficult, because in the glassy state the mechanical properties are mainly governed by van der Waals interactions and are not directly related to the network topology and chemical structure.[47] The glass transition relaxation for the networks cured at 160 °C occurs somewhat earlier on the temperature scale as compared with those cured at 120 and 140 °C (see Table 2). Furthermore, there seem to be some differences in the amplitude and width of the tan δ peaks. This is an indication of a difference in the homogeneity of macromolecular chain motions associated with the glass transition. These observations could be related to the fact that the networks cured at 120 and 140 °C have a smectic structure (probably smectic A) whereas those cured at 160 °C and above exhibit a nematic structure.[10,12] But, we will show that other factors, like differences in cure kinetics which can ultimately result in different local network structure, could also play an important role.

The insensitivity of the final macroscopic order on T_{cure} is also evident from the anisotropic coefficients of thermal expansion (CTE) of the networks (see Figure 6a). As can be seen in Table 2, the CTE values are highly anisotropic and rather independent of T_{cure}. This anisotropic behavior is characteristic of highly oriented polymers[48] and has also been observed for networks prepared from LC diacrylates.[49,50] However, although several attempts have been reported before,[5,8] this is the first time that such behavior is observed for ordered and highly cross-linked epoxy–amine networks providing a combination of good mechanical and thermal

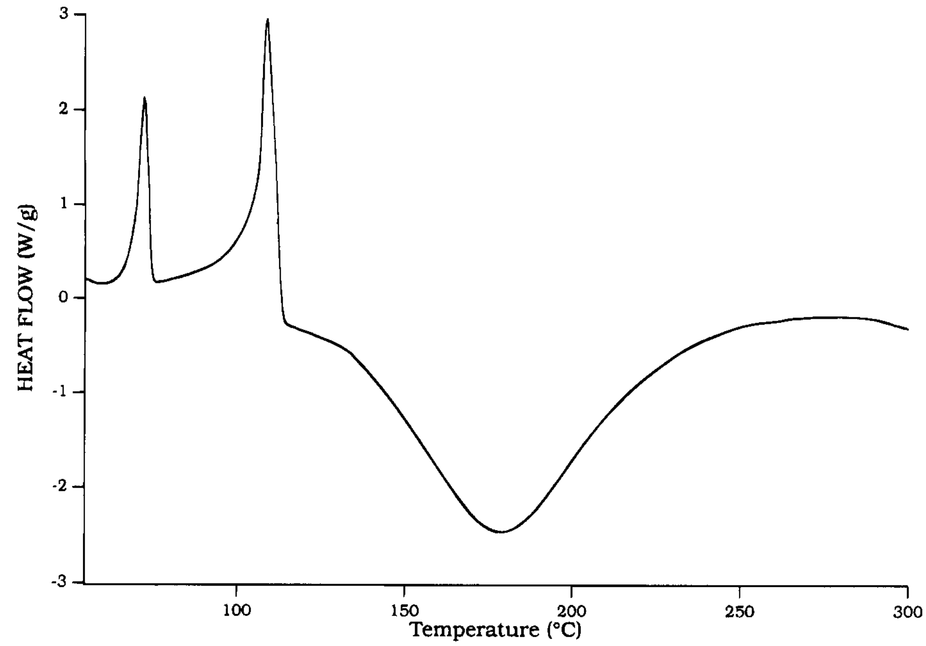


Figure 7. DSC trace of a stoichiometric mixture of diepoxide I and diamine A-2.

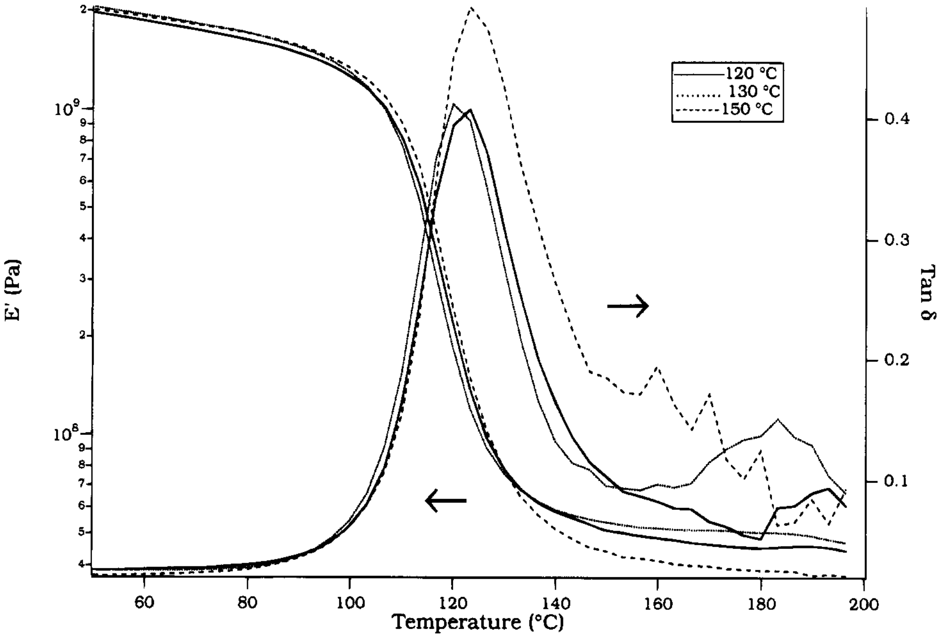


Figure 8. Dynamic mechanical response of the fully cured, macroscopically ordered A-2 system measured in the direction of the orientation at 1 Hz. The data are shown for different cure temperatures.

properties of conventional epoxy networks[51] with the anisotropic behavior connected with the high macroscopic order.

To examine further the effect of both order and rigidity on the mechanical behavior of the networks, we have altered systematically the molecular structure of the cross-linker. First the influence of introducing one flexibilizing unit (methyl group) in the diamine is studied (see 4,4'-diaminodiphenylmethane; A-2 in Table 1).

Figure 7 shows a DSC trace of a stoichiometric mixture of the diepoxide I and diamine A-2. It is evident that, at this ratio, the two compounds do not form a eutectic mixture. Microscopic observations between crossed polarizers revealed that immediately after the second melting point, an isotropic fluid was formed. Obviously, the LC phase has been destabilized by the introduction of the flexibilizing unit. However, as the reaction proceeded, the nematic to isotropic transition shifted to higher temperatures[10,12] and within 1 min the mixture transformed into a nematic phase which became irreversibly fixed upon further polymerization. Similar behavior was observed at higher T_{cure} up to 200 °C, although the time at which the mixture transformed into a LC phase increased somewhat with T_{cure}.

Figure 8 shows the dynamic mechanical properties of the macroscopically oriented A-2 networks cured isothermally at various temperatures under the influence of the magnetic field. Also, in this case the values of the elastic modulus seem to be rather insensitive to T_{cure}. Again, this is in accordance with the observation that the values of Δn (≈ 0.09 at 50 °C above T_g) and CTE do not significantly depend on T_{cure} (see Table 2).

The present data reveal that the systems A-1 and A-2 show roughly the same anisotropic thermal behavior (see Figure 6 and Table 2), which means according to ref 50 that the macroscopic order for both networks is the same. Consequently, the lower values of Δn for system A-2 in comparison with system A-1 is probably not caused by the lower level of orientation, but it is connected with differences in molecular polarizability.[52]

From Table 1 it is obvious that, even though both A-1 and A-2 networks have the same high level of macroscopic orientation, the value of the rubber modulus for system A-2 agrees much better with the theoretical prediction than the value of system A-1. This might suggest that, in the present networks, the rigidity of the segments is playing a more important role in causing a deviation from classical theory than the ordered structure. On the other hand, for system A-1, the value of the Young's elastic modulus, measured on the macroscopically isotropic network is $E' = 3G' = 6 \times 10^7$ Pa assuming the Poisson ratio is 0.5 (see Figure 2). This, in turn, implies that the macroscopic order is the main cause of deviation from the classical behavior. It should be pointed out that the random domain orientation can cause elastic strains and complicate the interpretation of the results.[53] Clearly, on the basis of these investigations it is difficult to decide what the main cause of deviation is from the classical rubbery behavior. Furthermore, one may wonder whether it is justified to make a direct distinction between the effect of both factors, because of the possible coupling of the influence of the rigidity and order on the elastic properties.

As mentioned earlier, for system A-2 at all cure temperatures, there was no change in LC morphology; the nematic structure became fixed as a result of the polymerization reaction. Thus, the differences in the homogeneity of the macromolecular chain motions at the glass transition, as can be seen in Figure 8, cannot be attributed to the modifications in the LC morphology. Some alteration in the network structure is expected to result from the variations in cure kinetics due to the different cure temperatures.

The next interesting point that should be considered is the behavior of the rubber modulus of these ordered networks as a function of temperature. As can be seen in Figures 5 and 8, in all cases the rubber modulus is decreasing as a function of the temperature. Similar behavior was observed for cross-linked LC main-chain polymers.[54,55] The comparison with our system is, however, difficult, mainly because of two reasons: (1) The cross-link densities were, in contrast with our networks, quite low. (2) The mechanical measurements were carried out, in contrast with the present experiments, on nonoriented, macroscopically isotropic systems. As mentioned earlier, this can seriously hamper the interpretation of the results.

For isotropic "enthalpic networks", it was shown experimentally by Aharoni and Edwards[56] that the value of the modulus was independent of temperature. This was later theoretically verified by Jones and Marques.[39] The theoretical predictions concerning the temperature dependence of modulus for isotropic "entropic networks" constituted of rigid rods is not straightforward because of the complex nature of equation of the free energy in ref 40. Assuming that all the terms on the right-hand side of this equation are temperature independent, the modulus should increase with a slope equal to kT. Thus, the temperature behavior of the modulus for the systems discussed here does not agree with the predictions of either of the two models (see Figures 5 and 8). As can be seen in Figure 9, the decrease of the rubber modulus for both A-1 and A-2 networks seems to be connected to the decrease of order as a function of the temperature, assuming again that $\Delta n \propto S$. Also for the networks prepared at higher T_{cure}, we found that a good correlation exists between the relative decrease of the modulus and order as a function of the temperature, provided that the results are only compared in the rubbery region. The temperature dependence of the modulus in the glassy state for highly oriented polymers has recently been discussed elsewhere by Bronnikov et al.[57] The behavior of the rubber elastic modulus for these ordered networks as a function of the temperature is reminiscent of the stress-optical behavior of the Gaussian networks where it is shown that Δn is directly proportional to the applied stress.[42] In the Appendix to this paper a theory is presented by T. Odijk concerning nematic gels under tension, where it is shown that the rubber modulus could indeed decrease as a function of the temperature because of the decrease of order.

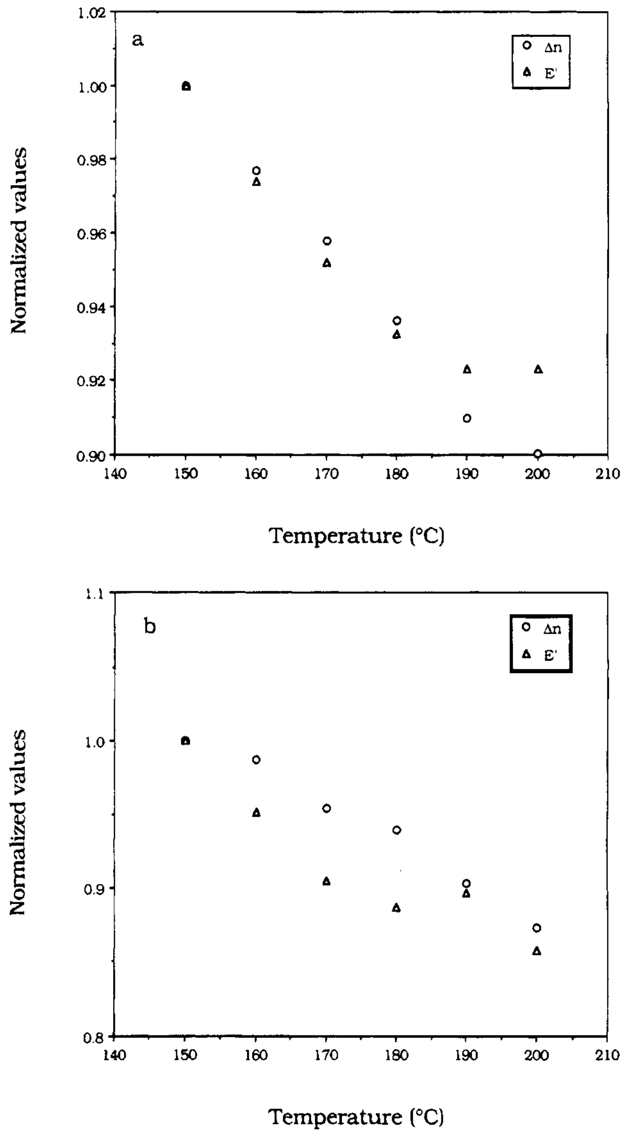


Figure 9. Normalized values of the Young's elastic modulus (E') and birefringence (Δn) measured as a function of the temperature in the rubbery region for macroscopically ordered systems A-1 (a) and A-2 (b). $T_{\text{cure}} = 120$ °C.

In the systems A-1 and A-2, because of the high cross-link density, it was possible to investigate the temperature dependence of the modulus only within a limited range of orientational order. The rubber modulus is expected to reach a plateau value around $S \approx 0$, around the hypothetical LC to isotropic transition. In this regard, it would be interesting to study the temperature dependence of modulus and order in a moderately cross-

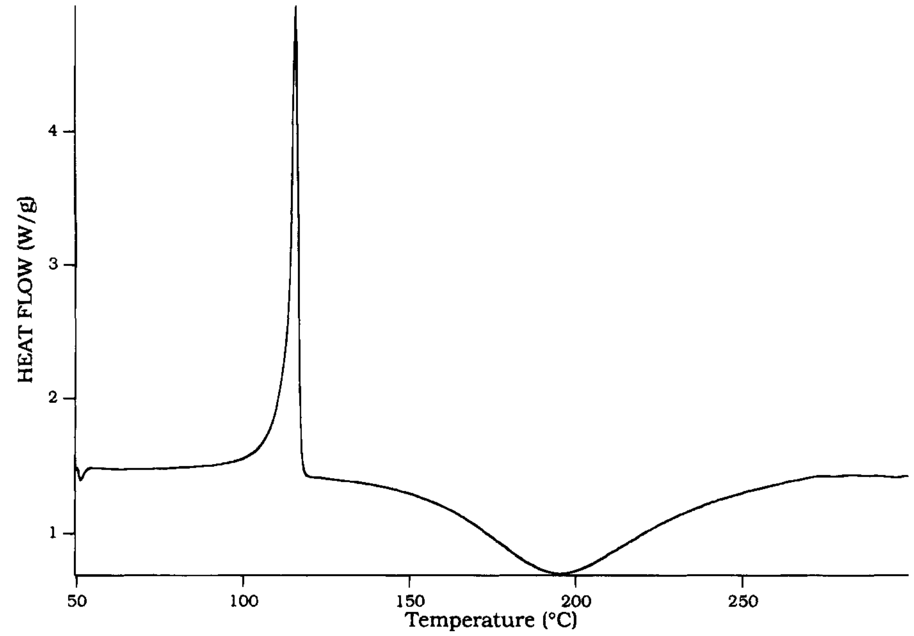


Figure 10. DSC trace of a stoichiometric mixture of diepoxide I and diamine A-3.

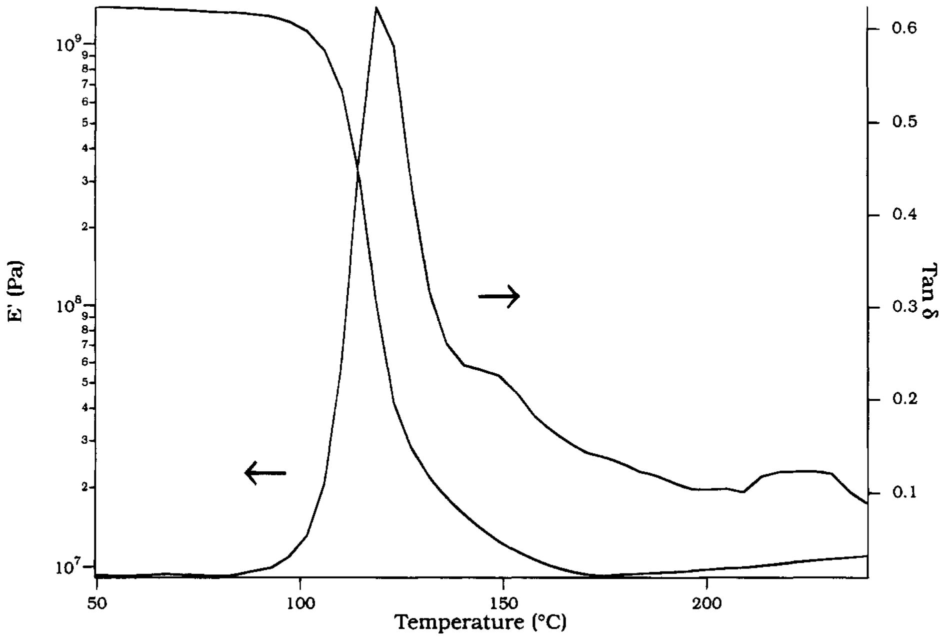


Figure 11. Dynamic mechanical response of the fully cured A-3 system measured at 1 Hz.

linked LC polymer where a nematic to isotropic transition can still be observed.[53,54]

Some attempts were made to study the behavior of the present systems in the isotropic phase. However, in order to prepare isotropic networks the polymerization reaction should be conducted at $T \geq 200$ °C for both the A-1 and A-2 systems. It proved to be difficult to prepare well-characterized samples at these high temperatures. Complications may also arise from the fact that the chemical reactions at such elevated temperatures will probably suffer from side reactions like etherification.[11]

Alternatively, we studied the diamine A-3, which contains two flexibilizing units, as the cross-linking agent (see Table 2). Owing to this flexible nature, the mixture A-3 transformed to an isotropic phase upon melting and remained so during the network formation (see Figure 10). As can be seen in Table 1, there is a good agreement between the theoretical and experimental values of the rubber modulus which gradually increase with temperature (see Figure 11).

The reasonable agreement found for system A-3 between the simplest form of the rubber elasticity theory and the experiments is rather surprising, because even though the segments between the cross-link points are more flexible, especially in comparison with system A-1, as mentioned above they are still too short and too rigid to expect a behavior as Gaussian chains. Similar results are found in the literature, where it is shown that, even in the case of some highly cross-linked epoxy–amine networks, the classical theory of rubber elasticity is able to predict reasonably the value of the rubber moduli.[58-60] These findings could be brought in qualitative agreement with the theories of non-Gaussian networks, assuming that the present experiments are carried out in the range of strains (i.e., <0.25%) where the networks exhibit still a behavior similar to the Gaussian networks. The crossover point which separates the Gaussian from the non-Gaussian regime is expected to shift to lower values of strain as the rigidity of the segments

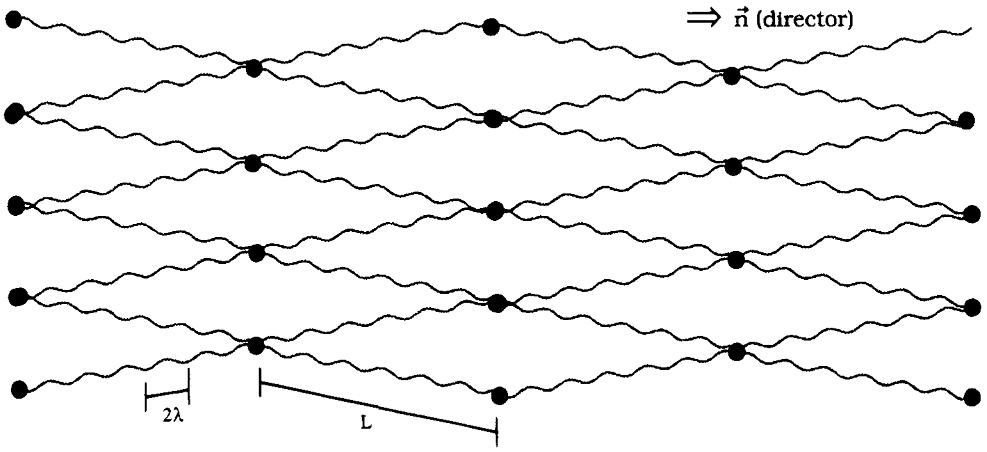


Figure 12. Nematic gel with deflection length $\lambda = P/\alpha$ ($\lambda \ll P$).

increases. Therefore, it might be argued that in the case of the A-1 system the monomers are probably so stiff that even with strain values as low as 0.25% the classical Gaussian theory fails to predict the value of the rubber modulus.

From the above discussion it may become obvious that there is an urgent need for a theory which describes the deformation behavior of rigid rod networks in a quantitative manner. However, in setting up such an theory, one seems to encounter many great mathematical and physical obstacles, partly because the assumptions, like affine deformation, which made the case of the Gaussian networks relatively simple, are no longer valid for non-Gaussian systems.[40,61] The situation is in our systems even more aggravated by the presence of long-range orientational order.

As shown in Figure 11, tan δ shows for system A-3 a maximum at approximately 120 °C, which is comparable with the value found for the systems A-1 and A-2 (see Table 2). Some differences in the T_g's were to be expected in accordance with the rigidity of the monomers.[47,62] However, the comparison of the T_g's becomes difficult, owing to the fact that the LC ordering might also affect the process of glass transition.[63]

IV. Conclusions

The network formation in the LC epoxy−amine mixtures investigated proceeds in a statistical manner in view of the fact that the position of the gel point, on the conversion scale, agrees well with the theoretical predictions, made originally for isotropic systems.

In the case of networks studied here, there are two factors that can cause deviations from the classical rubber-like behavior, namely, the rigid character of the starting materials and the existence of the orientational order. It proved to be difficult to determine which factor is playing a more important role. However, one should be careful with making a direct distinction between the contribution of the two effects. It is more plausible to consider the influence of both rigidity and order as a whole on the elastic properties. The decrease of the rubber modulus as a function of temperature is connected, as theoretically verified (see Appendix), to the decrease of order.

It was shown that the thermal behavior of the macroscopically ordered epoxy−amine networks is highly anisotropic. In some cases, in the direction of the orientation, the coefficient of thermal expansion was almost zero below T_g, and even negative above T_g. These anisotropic properties are a direct consequence of the high macroscopic order of these networks.[12]

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Appendix
Polymer Nematic Gel Under Tension

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In the limit of strong nematic order, the Hamiltonian H for a nematic semiflexible chain of length L under a tension f is given by the sum of a bending energy and a background nematic potential (see eq VIII.19 of ref 64) and a tensile potential (see eq 12 of ref 65)

$$H/k_BT = \frac{1}{2}P\int_0^L\left(\frac{d\vec{\theta}}{ds}\right)^2 ds + \frac{\Gamma_n}{2P}\int_0^L \vec{\theta}^2\, ds + \frac{f}{2k_BT}\int_0^L \vec{\theta}^2\, ds \quad \text{(A1)}$$

Here, k_B is Boltzmann's constant, T is the temperature, P is the persistence length, Γ_n is a nematic coupling constant, and $\vec{\theta} = \vec{\theta}(s) = (\theta_x,\theta_y)$ represents the (small) angles of the tangent vector of the chain at contour point s with respect to the director. The external tension is exerted parallel to the director. The statistical properties of the confined chain are readily analyzed with the help of a Gaussian trial function $\exp[-\frac{1}{2}\alpha\theta^2]$ (see ref 64; α = variational parameter; $\alpha \gg 1$; $\langle\theta^2\rangle = 2/\alpha$). The total free energy is[64]

$$F_{tot}/k_BT = \frac{L\alpha}{4P} + \frac{L\Gamma_n}{\alpha P} + \frac{Lf}{\alpha k_BT} \quad \text{(A2)}$$

valid when $L > \lambda \equiv P/\alpha$, where λ is the deflection length (see Figure 12). The first term is a free energy of confinement. Minimization of eq A2 yields

$$\alpha = \left(\alpha_0^{\,2} + \frac{4fP}{k_BT}\right)^{1/2} \quad \text{(A3)}$$

With $\Gamma_n \equiv \frac{1}{4}\alpha_0^2$ (assumed independent of f at this level of approximation) or

$$\langle\theta^2\rangle = \left(\frac{1}{4}\alpha_0^{\,2} + \frac{fP}{k_BT}\right)^{-1/2} \quad \text{(A4)}$$

As it should, eq A4 reduces to eq VIII.22 of ref 64 as f tends to zero or to eqs 14 and 15 of ref 65 as Γ_n goes to zero.

Finally, the deformational behavior of the chain is derived from the mean extension

$$R \equiv L\langle \cos\theta\rangle \cong L\left[1-\frac{1}{2}\langle\theta^2\rangle\right] = L\left[1-\left(\alpha_0^{\,2}+\frac{4fP}{k_BT}\right)^{-1/2}\right] \quad (A5)$$

$$R(f{=}0) = L(1-\alpha_0^{\,-1}) \quad (A6)$$

Hence, at small tensions we have

$$\delta R \equiv R - R(f{=}0) \cong \frac{2LPf}{\alpha_0^{\,3}k_BT} \quad (A7)$$

or

$$f \cong \frac{\alpha_0^{\,3}k_BT\delta R}{2LP} \quad (A8)$$

which is to be compared to the equivalent expression for a flexible Gaussian chain

$$f = \frac{3k_BT\delta R}{2LP} \quad (A9)$$

We conclude that the front factor in eq 2 is connected with the order parameter

$$S = 1 - 3/\alpha_0 \quad (A10)$$

via

$$\phi \propto \alpha_0^{\,3} \quad (A11)$$

Therefore, on the one hand the modulus increases with temperature because of entropic effects, yet it decreases with increasing T since S and α_0 decrease. Our whole derivation is qualitative in view of the approximations employed.

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