Liquid Crystalline Epoxide Thermosets: A Deuterium Nuclear Magnetic Resonance Study

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ABSTRACT: The orientational order for a reactive liquid crystalline epoxy–amine mixture was monitored in real time with the aid of deuterium nuclear magnetic resonance (^{2}H-NMR) and birefringence (Δn) measurements. The orientational order increased during the chain extension process, and it became irreversibly fixed as a result of the cross-linking reaction. The order parameter of the amine compound was more sensitive to the degree of the polymerization reaction than that of the epoxide. During the isothermal polymerization, the point where Δn started to level off corresponded well with the point of gelation as determined by solubility experiments. The relative increase of the orientational order according to ^{2}H-NMR agrees with the value extracted from birefringence measurements. X-ray diffraction measurements revealed that the orientation of the network hardly changes upon heating and cooling in the absence of the magnetic field. The reaction was also measured in quasi-real time by gel permeation chromatography (GPC) and so the nature of various species, formed during the reaction, was determined. There was a good agreement between the reaction kinetics as determined by GPC and ^{2}H-NMR experiments. The conversion (α) of the epoxy groups at the gel point agreed well with the value predicted by the statistical theory for network formation in isotropic stoichiometric epoxy–amine mixtures, namely, $\alpha \approx 55\%$. In addition, good agreement was found between the experimentally determined increase in the number-average molecular weight and theoretical predictions.

I. Introduction

Ordered networks can be prepared by polymerization of low molecular weight mesogenic monomers in the liquid crystalline (LC) phase. This concept has been used by many investigators active in the rapidly growing field of ordered networks. As the polymerizing unit a broad range of functional groups have been used like acrylates[1,2] or bismaleimides.[3] The possibility of using epoxy groups has also been recognized.[4] This is because in comparison with other materials, conventional epoxy polymers have proved to be among the best as far as their mechanical and electrical properties are concerned.[5]

In a previous publication we studied the LC properties of a series of mesogenic diepoxide compounds. It was shown that highly macroscopically ordered networks can be prepared by photoinitiated chain polymerization of such materials in the LC phase.[6] One of the aims of our investigation was to monitor the change of physical and material properties during network formation in an orientationally ordered state. Chain polymerization reactions often proceed very fast, which makes the monitoring of the reaction in real time difficult. As an alternative we have investigated the copolymerization reaction of a LC diepoxide monomer with several aromatic diamines.[7] This step-addition polymerization proceeds in a slower and much more controllable fashion. The chemical reactions involved are rather straightforward and usually free of side reactions.[8] These investigations indicated that the diepoxide (**I**) and the diamine (**II**) displayed in the upper section of Figure 1 are very suitable for studying network formation in the LC state; the polymerization reaction proceeds relatively slowly at low temperatures, allowing for various real-time measurements to be carried out. Figure 1 also shows the differential scanning calorimetric (DSC) trace of a stoichiometric mixture of the two compounds. The mixture is a eutectic with the melting point at 115.9 °C, above which a nematic phase is formed. With the aid of dichroism measurements, it was shown for

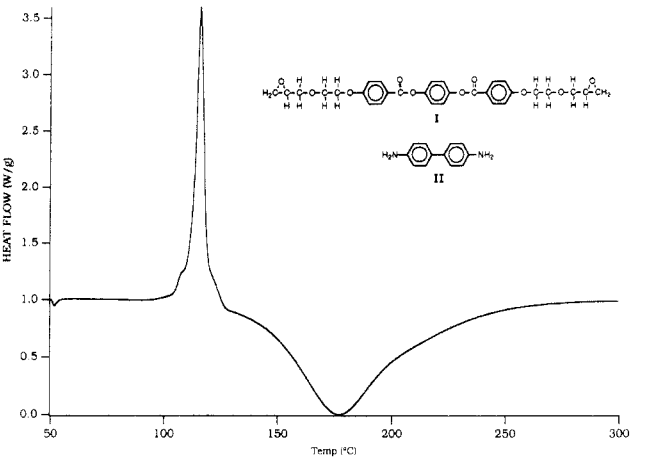

Figure 1. DSC trace of a stoichiometric mixture of compounds **I** and **II**.

the first time that epoxy–amine networks with high macroscopic order can be produced by conducting the polymerization just above the eutectic melting point (i.e., at 120 °C).[7]

It is the purpose of the present paper to establish how the state of ordering for this particular mixture is affected by the polymerization reaction. In this regard two stages can be distinguished. The initial stage of the reaction consists of a chain extension process which results in the so-called sol fraction. Depending on the polymerization conditions somewhere along the reaction path, a smooth transition from the sol to a gel state starts to take place. The possibility of a transition to a glassy state (vitrification) is present. Caruso et al.[9] claimed that chain extension of a certain linear oligomer favored an increase in the stability of the nematic phase, whereas cross-links between the linear chains disfavored it. They based these conclusions on the fact that the nematic to isotropic transition temperature (T_i), measured for the network, was lower than that found for the complete polymer and higher for the oligomer.[9] Here we examine in real time the effect of both processes on the order.

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As a first measure of orientational order, we have measured the birefringence (Δn) during the polymerization. Δn is a measure of long-range orientational order, and it also provides information concerning the macroscopic order. Deuterium nuclear magnetic resonance spectroscopy (^{2}H-NMR), on the other hand, is a powerful technique to monitor the orientational order at a molecular level. ^{2}H-NMR has already proved to be very useful for studying systems like low molecular weight LC compounds,[10] side-chain[11] and main-chain LC polymers,[12] and strained elastomers.[13,14] One of the most important advantages of the ^{2}H-NMR technique is that the observed spectra in the LC state are very well resolved in comparison with proton (^{1}H)-NMR spectra for example. This is because the magnetic moments of deuterons are small, which leads to a small dipolar interaction, and so they can be considered, at least in the first approximation, as isolated nuclei. The main feature which then dominates the ^{2}H-NMR spectra is the electrostatic interaction between the quadrupole moment of the nucleus with the electric field gradient (efg) around it.[15] Nevertheless, in order to study the orientational order of the system, it is also very useful to consider the interactions between the neighboring deuterons (the dipole interactions). The other advantage of ^{2}H-NMR is that by isotopic substitution of the protons the molecular order can be monitored in real time separately for each of the reacting monomers. This will be illustrated in the present paper.

The nature of various species, formed during the polymerization reaction, is determined by gel permeation chromatography (GPC). Also, the system has been characterized by viscosity and X-ray measurements.

II. ^{2}H-NMR: Some Basic Relations

In anisotropic fluid media some anisotropic magnetic and electrostatic interactions are not averaged to zero by the molecular motion. In the case of deuterons the most important are the quadrupolar interaction (ν_q) and the dipole–dipole interaction between neighboring deuterons (D). These can be written as:[16]

$$\nu_q = \frac{3}{4}\frac{e^2qQ}{h}S(\langle 3\cos^2\varphi\rangle - 1)/2 \qquad (1)$$

$$D = dS(\langle 3\cos^2\alpha\rangle - 1)/2, \quad \text{where } d = -\gamma_D{}^2h/2\pi^2r_{DD}{}^3 \qquad (2)$$

In these equations φ and α are respectively the angles that the C–D bond and the radius vector r_{DD} connecting the two deuterons make with the long molecular axis. The angular brackets denote the average over all molecular orientations. The quadrupolar coupling constant e^2qQ/h for deuterons bonded to unsaturated carbons is around 185 kHz.[17] In eq 2 with r_{DD} = 2.487 Å, $h\gamma_D{}^2/2\pi^2$ = 5663 Hz·Å^3 (see ref 18). S denotes the orientational order parameter of the long molecular axis with respect to the director which is identified as the direction of the magnetic field when the magnetic susceptibility is positive. In writing these equations several assumptions have been adopted. (1) The efg tensor is axially symmetric around the C–D bond. (2) The symmetry of the liquid crystal is considered to be unaxial. (3) The LC molecules can be approximated by a rigid cylindrical rod whose symmetry is parallel to the long molecular axis. The important issue is whether the last two assumptions will hold throughout the polymerization reaction. Some evidence in favor of these simplifications will be presented later in this paper. In the following we have also assumed that the effect of the director fluctuations is negligible.

The perturbation of the ^{2}H-NMR spectra due to the dipolar interaction could be observed in one case at the start of the reaction where the viscosity was still low, thus resulting in a small line width. However, the spectra were usually dominated by quadrupolar interactions which resulted in the splitting of the signal coming from each type of deuteron into a doublet with a spacing of

$$\Delta = 2\nu_q = \frac{3}{2}\frac{e^2qQ}{h}S(\langle 3\cos^2\varphi\rangle - 1)/2 \qquad (3)$$

III. Experimental Section

The synthesis of epoxide compound **I** has been described previously:[6] epoxy value = 3.48 equiv/kg (theoretical value: 3.63 equiv/kg). The deuterated diepoxide was synthesized by using hydroquinone-d_4 (MSD Isotopes, Montreal, Canada). 4,4′-Diaminobiphenyl (**II**) was supplied by RPL (Leuven, Belgium) and was used without further purification (purity > 98%). The deuterated diamine was supplied by MSD Isotopes (Montreal, Canada).

To prepare the polymerization mixture, a stoichiometric amount of the diepoxide (2 mol) and the diamine (1 mol) was dissolved in dichloromethane. The solvent was then removed under reduced pressure at room temperature (RT). In order to ensure a homogeneous mixing of the two components, after evaporation of the solvent, the mixture was stirred mechanically for ca. 1 min at 120 °C and then quenched to RT. For the ^{2}H-NMR measurements, normally ca. 10% (w/w) of the corresponding monomer was deuterated.

^{2}H-NMR spectra were recorded at 61.4 MHz on a Varian VXR 400 S spectrometer. The spectra were obtained by Fourier transformation of the free induction decay (FID). Typically 200 FIDs were accumulated. The polymerization mixtures were placed in a 5-mm tube. The NMR probe was equilibrated at 120 ± 1 °C before inserting the NMR tube and starting the measurements. The system was homogeneously aligned by the magnetic field (9.4 T) immediately after melting into the LC phase. This was manifested by the sharpness and symmetry of the NMR peaks.[19]

The conversion of epoxy groups up to the gel point was determined by ^{1}H-NMR. The reaction mixtures, cured for various times at 120 °C, were dissolved in dimethyl sulfoxide (DMSO). The spectra were measured with a Varian VXR 400 S. 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 5%). The conversion beyond the gel point (87% after 1 h at 120 °C) was determined by potentiometric titration of the remaining epoxy groups.

Number-average molecular weights (M_n) were determined by GPC with tetrahydrofuran as eluent using a UV detector operating at 279 nm. At this wavelength the extinction coefficients for both diepoxide and diamine were equal. The Ultrastyragel column of 10^3-Å pore size was calibrated with monodisperse polystyrene standards. The experimental conditions for measurements of Δn (relative accuracy 2–3%), wide-angle X-ray diffraction, and melt viscosity have been reported previously.[7]

IV. Results and Discussion

A. ^{2}H-NMR Spectra Measured Continuously during the Polymerization Reaction. The ^{2}H-NMR measurements were conducted in two separate experiments. In the first the orientational order of the epoxide deuterated in the central aromatic ring was monitored during the copolymerization reaction with the nondeuterated amine. In the second experiment the behavior of the deuterated amine was investigated. Both experiments were carried out at 120 °C, inside the NMR probe, under exactly the same conditions. In the following we assume

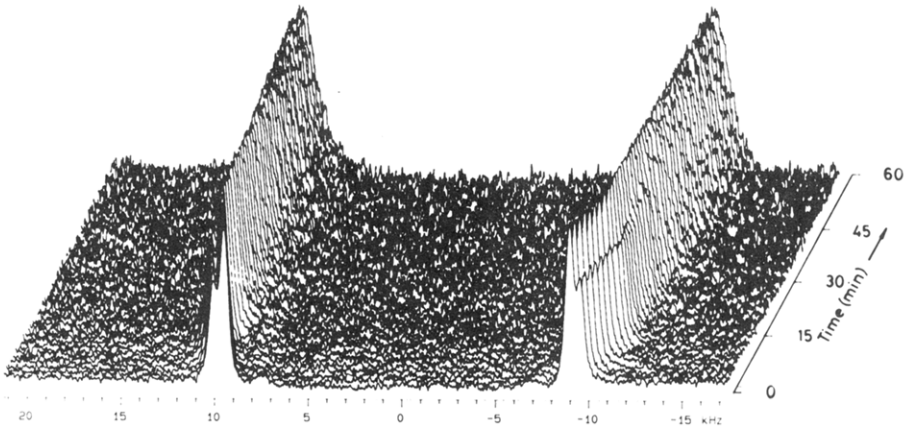

Figure 2. ^{2}H-NMR spectra of the deuterated diepoxide measured as a function of copolymerization reaction time at 120 °C with the protonated diamine.

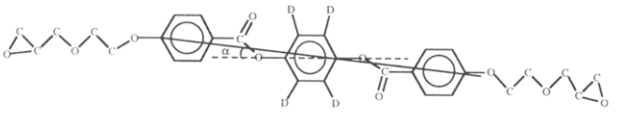

Figure 3. Structural formula of the diepoxide **I** deuterated in the central aromatic ring.

that the quadrupolar splitting (Δ) as a function of the polymerization time is directly proportional to the orientational order of the long molecular axis with respect to the director, an assumption which is proved to be justified later in the text.

Experiment 1. Figure 2 shows the ^{2}H-NMR spectra of the deuterated epoxide measured as a function of time at 120 °C which is the temperature just after the eutectic melting point. The monitoring of the reaction at higher temperatures becomes increasingly difficult because of the rapid reaction rates. Ignoring for the moment the dipolar fine structure, the first spectrum in Figure 2 consists of a sharp doublet, indicating that the four deuterons are equivalent on the NMR time scale because of, for example, 180° rotational jumps of the central ring (see Figure 3). This type of motion seems to be common for phenyl groups; indeed this mechanism has also been suggested to operate in, for example, low molecular weight LC systems[20,21] and side-chain LC polymers.[22,23] The quadrupolar splittings determined directly from the spectra are shown in Figure 4. At the start of the reaction Δ increases linearly with time until the rate is drastically reduced at 13 min. Under the polarization microscope a clear nematic (N) to smectic (S) transition (N → S) was observed around the same reaction time at 120 °C.[7] The transition found in the NMR experiment could then be attributed to the formation of the smectic phase. From Figure 4 it follows that the molecular order in the nematic phase is very sensitive to the degree of polymerization, and although the reaction seems to proceed continuously into the smectic phase (see Figure 5), the dependency in the smectic phase on the chemical conversion is much less pronounced. Evidently the molecular order in the smectic phase has already reached a high value so that it becomes rather insensitive to further reaction.

We now consider the dipolar structure which can clearly be observed at least up to the N → S transition. The form of a ^{2}H-NMR spectrum for two equivalent deuterons with quadrupolar and direct dipolar interactions is predicted to consist of a quadrupolar doublet with each line split into three components, with relative intensities of 2, 3, and 1 and with frequencies relative to the center of gravity of $+(3/2)D$, $-(1/2)D$, and $-(3/2)D$.[20] The computer simulation of such a three-component peak has revealed that the observed line shape in Figure 2 can be reproduced to a good approximation by varying just the ratio L/D, where

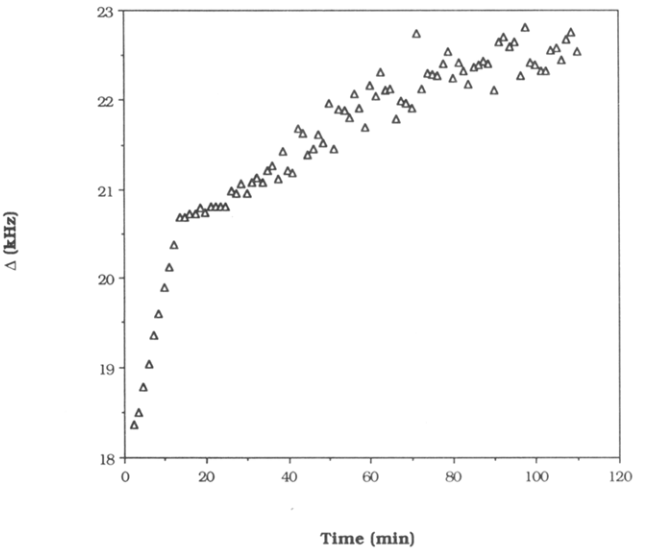

Figure 4. Time dependence of the quadrupolar splittings (Δ) as determined from Figure 2. The increase in scattering of the data points is connected with the extensive line broadening during the polymerization reaction.

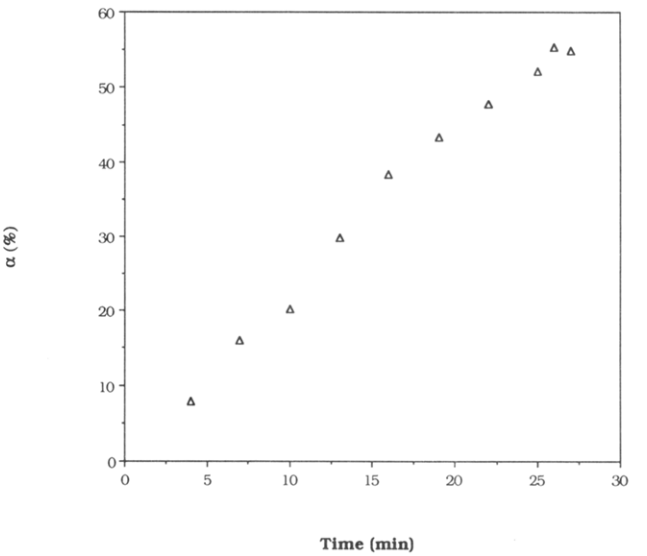

Figure 5. Conversion of the epoxy groups (α) measured up to the gel point as a function of the polymerization time at 120 °C.

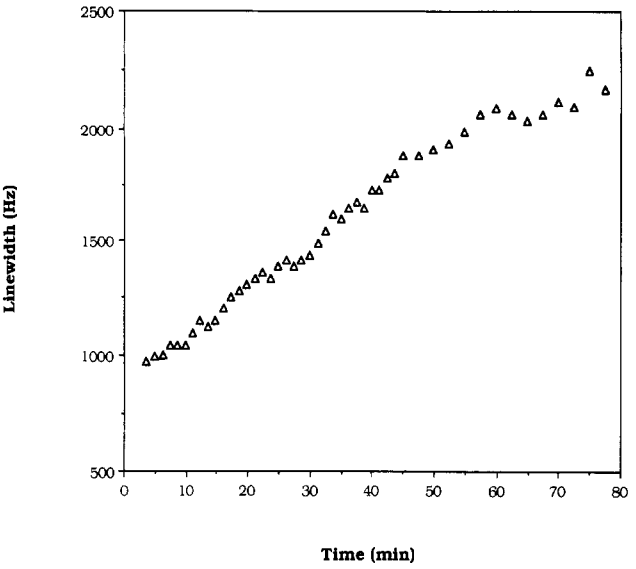

Figure 6. Line width (L) of the ^{2}H-NMR spectra measured directly from Figure 2 as a function of time.

L is the line width. In Figure 6, the line width of a member of the quadrupolar doublet, measured directly from the spectra (Figure 2), is plotted as a function of polymerization time at 120 °C. The line broadening could be the result of various mechanisms, operating either simultaneously or not in these reactive systems.[19] In the first place L broadens due to the increase of the degree of ordering. However, the contribution of this effect seems to be small, because in the nematic phase, where S is rapidly increasing, L is almost constant.

Also the correlation times for different types of motions, like rotation and reorientation of the long molecular axis, are expected to increase as a function of the degree of polymerization, which is reflected in the increase of the viscosity of the system.[12] Figure 7 shows the variation of complex viscosity (η^*) as a function of reaction time at 120 °C. Of course the rheological behavior of liquid crystals is quite complicated and η^* is not sufficient to represent fully the viscosity of the system. In the present case η^* is believed to give a value representative for the degree of conversion. By comparing Figure 6 with Figure 7 it becomes clear that both L and η^* start to increase in the vicinity of the N → S transition until they level off after about 40 min.

It would be interesting to examine how in the present case the ^{2}H-NMR spectra are affected by the process of gelation. Frequency-dependent rheological measurements have shown that the system, at 120 °C, starts to gel at 27 ± 1 min.[24] This corresponds well with the time where the material becomes insoluble in DMSO. Furthermore, the conversion of the epoxy groups at the gel point (55 ± 3%) agrees with the value predicted by a statistical approach for a isotropic epoxy–amine mixture; depending on the relative reactivity of the secondary (K_2) to the primary (K_1) amine hydrogens, the gelation occurs between 50% ($K_2/K_1 \rightarrow 0$) and 61.8% ($K_2/K_1 \rightarrow \infty$).[25] Dynamic mechanical measurements have also shown that at 120 °C the material does not transfer to the glassy state for at least 2 h of reaction time.[7,24] This is because the cure temperature (i.e., 120 °C) is close to the glass transition temperature of the fully cured system (125 °C).[26]

The influences of the cross-linking reaction on the chain mobility and chain conformation are the most important issues when considering the possible effect of the gelation on the observed ^{2}H-NMR spectra. Beltzung et al.[27] demonstrated with the aid of small-angle neutron scattering that the chain dimensions did not change as a result of the cross-linking reaction in a melt of poly(dimethylsiloxane) chains. In the case of ^{2}H-NMR experiments performed on flexible poly(propylene-d_6 oxide) elastomers, some increase of the line width upon the cross-linking reaction was observed, which was attributed to the incomplete averaging of the quadrupolar interactions once the chain mobility is restricted by anchoring the chain ends (by a covalent reaction).[28] In the present case, as can be seen in Figure 6, L is rather insensitive to the process of cross-linking. Apparently the macroscopic phenomenon of gelation is hardly detectable by ^{2}H-NMR which is probing the system on a molecular level.

The line broadening can also be the result of disturbances of the director alignment during the polymerization reaction.[19] In Figure 8 the ^{2}H-NMR spectra at the beginning and the end of the reaction at 120 °C are compared. After 99 min the spectrum asymmetrically broadened, which indicates that this mechanism, operating simultaneously with the previous one, is responsible for the observed line shapes as well.

From the measured values of the quadrupolar splittings we can determine the order parameter of the long molecular axis (z), provided that the molecular geometry and in particular the angle between the phenyl para axis and z (α) is known. An estimate of this angle can be obtained from the ratio of the dipolar interaction of the two neighboring deuterons and their quadrupolar splitting ($R = D/\Delta$).[16,20] In Figure 9 the values of R in the nematic and the beginning of the smectic phase are plotted as a function of time at 120 °C. D is determined from Figure 4, assuming that the distance between the two maxima on each member of the quadrupolar doublet equals $2D$. The reported values could be an overestimation by as much as 10%.

As can be seen in Figure 9, the values of R are nearly constant, indicating that D and Δ are probing the degree of orientation to the same extent. As stated before, the four deuterons in Figure 3 are equivalent, owing to rapid 180° rotational jumps of the central ring about the para axis. This motion modulates the orientation of the C–D bond relative to z from 60° + α to 60° − α, and so according to eqs 2 and 3, the ratio R can be written as:[16,20]

$$R = \frac{D}{\Delta} = \frac{d(3\cos^2\alpha - 1)}{q\frac{1}{2}[3\cos^2(60° + \alpha) - 1 + 3\cos^2(60° - \alpha) - 1]}$$

$$\text{where } q = \frac{3}{2}\frac{e^2qQ}{h} \quad (4)$$

Solving eq 4, using the data given in Figure 9, an angle of 15° is calculated for the first 15 min of reaction. This is in good agreement with the value of 16° which was obtained from molecular modeling of a LC diacrylate compound with the same mesogenic group.[29] The values of S, shown in Figure 10a, were determined using α = 15°. In order to evaluate the accuracy of these results, it would be worthwhile to compare the calculated values of S just at the start of the reaction with the values reported in the literature for similar mesogenic groups at the same reduced temperature $T^* = T/T_i$. The comparison becomes somewhat difficult because in our case T_i, as a function of the degree of polymerization, is continuously shifted toward higher temperatures.[7,24] Nevertheless, very fast DSC scans have shown that T_i of the unreacted mixture is about 180 °C. Other investigators using various techniques[12,30] for similar systems found a value of around 0.7, at $T^* = 0.87$, which is much smaller than the values reported in the

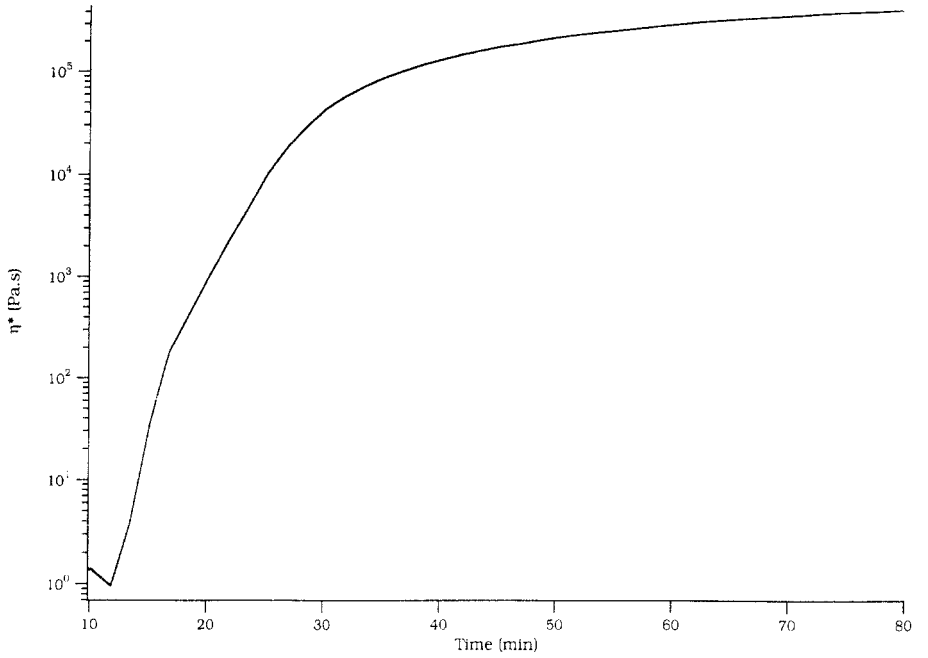

Figure 7. Complex viscosity (η^*) measured at 120 °C as a function of polymerization time (frequency = 15 Hz). The nematic to smectic transition can be recognized as a small deflection from linearity around 17 min.

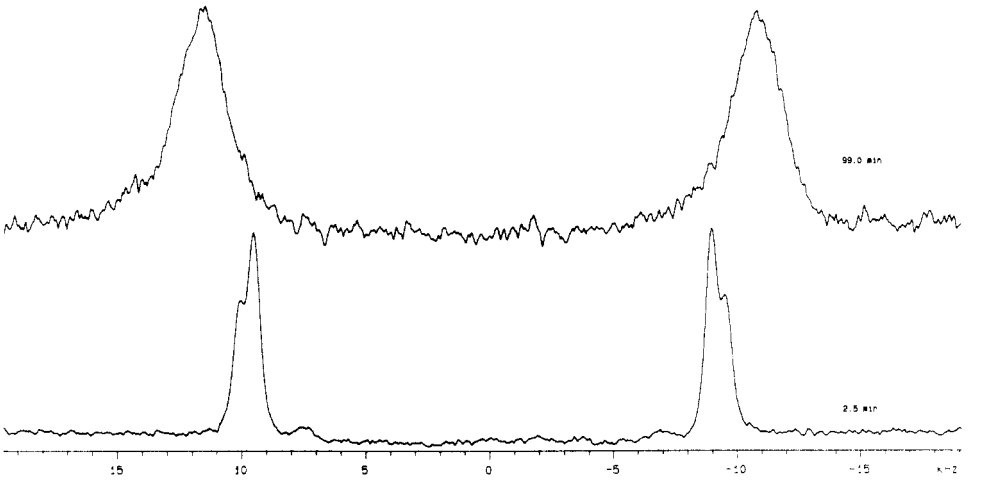

Figure 8. ^{2}H-NMR spectra taken from Figure 2 after 2.5 and 99 min of reaction time.

beginning of Figure 10a. Also the calculated values at the end of reaction are, of course, unrealistically high. By taking into account that the values of D could be overestimated by 10%, an angle of 13° is calculated. With the aid of the same procedure, Luz and co-workers[16,20] determined an angle of 8–12° for a series of two- and three-ring compounds.

The data reported in Figure 10b, using α = 13°, seem to be much more reasonable. However, although it is obvious that the degree of order is high, it remains quite difficult to determine the absolute values of S because of the lack of knowledge of the molecular geometry. The situation is aggravated by the fact that the curve $(3\cos^2\varphi - 1)/2$ is very steep around φ = 60°, which is roughly the angle between the C-D bond and z. This means, according to eq 3, that a small deviation from the actual value in this region will have a large effect on the calculated S.[31]

Experiment 2. Figure 11 displays the measured ^{2}H-NMR spectra of the diamine, deuterated in the aromatic part (see Figure 12), as a function of polymerization time at 120 °C. At the beginning of the reaction two sharp doublets are measured, corresponding to the ^{2}H-NMR spectrum of the unreacted diamine. It is believed that the presence of the amine groups has perturbed the molecular geometry, resulting in two sets of nonequivalent deuterons. Also the value of the quadrupolar constant could be affected by the action of the amine groups.[10] However, the observed difference between the two doublets corresponds to a variation in φ of no more than 1°, indicating that the perturbing effect of the amine groups on the geometry is probably the dominating factor.

Because the two doublets have the same intensity and considering the molecular symmetry of the compound, the signals correspond either to the four inner deuterons (D_1) or to the four outer ones (D_2). Without specific deuteration, it seems a rather impossible task to give an exact assignment to the signals, but this is not important for further discussion. From Figure 11 it is obvious that the peaks corresponding to the unreacted amines decrease in intensity as a function of time and that somewhat similar double doublets appear with larger quadrupolar splittings. However, the intensities of the two larger doublets are not equal, implying that these signals cannot be attributed to the same species. In fact, a more careful analysis indicates that during the reaction the ^{2}H-NMR spectra consist of a maximum of three double doublets, corresponding to unreacted amine (A), epoxy–amine dimers (D), and higher molecular weight compounds (P). Although some of the

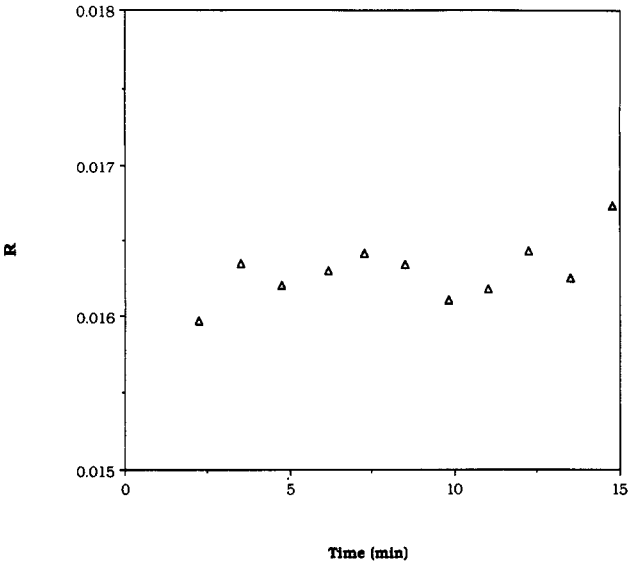

Figure 9. $R = D/\Delta$ as a function of polymerization time at 120 °C where D is the dipolar interaction and Δ is the quadrupolar splitting. The data were extracted from Figures 2 and 4.

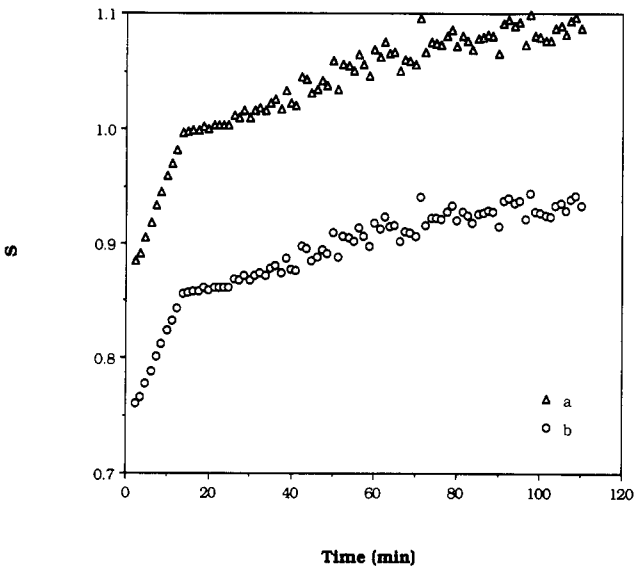

Figure 10. Values of S calculated from the data in Figure 4 taking $\alpha = 15°$ (a) and $\alpha = 13°$ (b).

peaks overlap, the various components can still be recognized in Figure 13, showing the ^{2}H-NMR spectrum measured after 8 min of polymerization time. In this figure the numbers 1 and 2 correspond to the inner and outer doublets, respectively. According to this interpretation, the intensities of the peaks A_1 and P_2 correspond directly to the amount of respectively unreacted amines and higher molecular weight compounds. The difference between the intensities of the P_2 and $P_1 + D_2$ peaks is taken as a measure of the concentration of dimers formed during the polymerization reaction. The relative concentrations of all the compounds are displayed in Figure 14 for the first 15 min of reaction time. The intensity for each compound is normalized relative to its highest value. The concentration of diamine and higher molecular weight species is decreasing and increasing during the polymerization, respectively. The concentration of the dimers increases up to the first 5 min of reaction, and then it starts to decrease until it almost disappears after 15 min. The course of the polymerization, as depicted here, seems to correspond to a step-addition reaction.

With the aid of GPC it is also possible to monitor the reaction in a quasi-real-time manner, determining the relative concentration of various compounds formed (see Figure 15). The peaks assigned with letters A, E, D, and P correspond to the diamine, diepoxide, epoxy–amine dimers, and higher molecular weight species, respectively. The assignments in Figure 15 are made in spite of the slight deviation of the measured molecular weight from the actual values owing to experimental artifacts. Except for the epoxide monomers, a comparison can be made between the relative variation of these peaks and the corresponding ones in ^{2}H-NMR experiment 2. Parts a–c of Figure 16 show that there is good agreement between the relative concentration of various compounds as determined by NMR and GPC experiments. This proves that the interpretation of ^{2}H-NMR spectra in Figure 11 is correct. For the dimers (Figure 16b) the agreement is somewhat less satisfactory, because of the assumptions made concerning the peak intensities in the ^{2}H-NMR and GPC experiments.

As can be seen in Figure 15 the peak corresponding to the higher molecular weight compounds is rather broad. This could be the reason why the components of higher molecular weight cannot be observed separately in Figure 11. The possibility also exists that after a certain degree of polymerization the system becomes, as far as the orientational order is concerned, rather insensitive to further polymerization. Figure 17 also displays the theoretical values of M_n calculated using[25]

$$M_n = \frac{n_A M_A + n_E M_E}{1 - 2n_E \alpha_E} \tag{5}$$

where M_A (M_E) is the molecular weight of the diamine (diepoxide), n_A (n_E) is the molar ratio of the diamine (diepoxide), and α_E is the conversion of the epoxy groups. As M_n is only sensitive to the number of bonds formed, the reasonable agreement between the experimental and theoretical values indicates that only the reaction between the epoxy and amine groups contributes to the polymerization and that consequently no side reactions occur.[5]

In Figure 18 the values of S are plotted as a function of time for unreacted amine, dimer, and higher molecular weight compounds. For the calculation of S in all cases the values of Δ for the larger splittings are taken with $\varphi = 60°$. This gave the best agreement between S of the free amines at the start of the reaction and the corresponding values for the similar two-ring dye molecules in low molecular weight LC mixtures[32,33] at the same T^*. Nevertheless, in this case also the same limitations apply as explained in the previous section. As can be seen in Figure 18 the order increases on going from unreacted amines to epoxy–amine dimers and higher molecular weight compounds. In this regard the nature of the spacer part, connecting the mesogenic groups, could play an important role. A distinct odd–even effect, concerning the orientational order, has already been shown to exist in LC dimers consisting of a flexible core, linking two rigid groups.[34] Similar effects were observed in main-chain LC polymers comprising a rigid mesogenic core and a flexible spacer in a repeating unit.[35] In all these studies relatively simple aliphatic chains were used as the flexible part, whereas in our case the nature of the spacer is quite complex. Also the mesogenic groups connected by the spacer are not similar. Because of these complications, a direct comparison is not possible between the studied LC dimers (polymers) previously and the present system. It seems, however, worthwhile to study systematically the effect of the spacer length on, for example, the relative variation of the orientational order during the polymer-

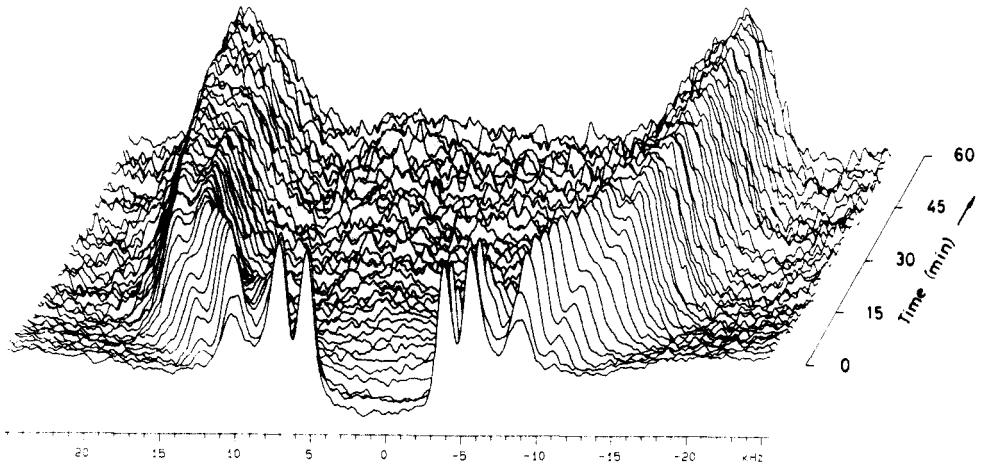

Figure 11. ^{2}H-NMR spectra of the deuterated diamine measured as a function of copolymerization time at 120 °C with the protonated diepoxide. As can be seen, some reaction has occurred during preparation of the polymerization mixture and filling of the NMR tube. One can also recognize some similarities with Figure 2 (i.e., Δ levels off also in this experiment in the vicinity of the N → S transition).

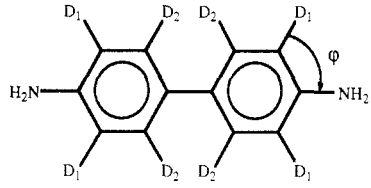

Figure 12. Structural formula of the diamine **II** deuterated in the aromatic part.

ization reaction. The influence of the spacer length was shown to be small on the orientational order of the networks, prepared by photoinitiated polymerization of low molecular weight LC diacrylates.[30]

The slope (P) of the curves in Figure 18 is a measure of the sensitivity of the order of the deuterated amines to the degree of polymerization. In the nematic phase P for the unreacted amine is 0.47 kHz/min, which is somewhat lower than the value for the higher molecular weight compounds (0.57 kHz/min). In both cases these values are about twice as large as the P determined from Figure 4 for the deuterated epoxide also in the nematic phase (0.24 kHz/min). Evidently the epoxide monomer is less sensitive to the polymerization reaction because of the action of the spacer segment, which decouples the mesogenic part from the reaction site. In view of the inaccuracy connected with the absolute values of S, no comments can be given concerning the level of ordering of the amine as compared with that of the epoxide.

B. Birefringence and Wide-Angle X-ray Diffraction Measurements. Figure 19 displays the variation of Δn during the polymerization reaction carried out under various isothermal temperatures. As Δn is directly proportional to S,[36] the ratio of Δn at the start and the end of the reaction at 120 °C should correspond to the relative increases of Δ measured in ^{2}H-NMR experiments 1 and 2. The agreement between the two techniques seems to be quite good; Δn has increased by a factor of 1.65 as compared with an increase of Δ by 1.73. The latter is calculated from ^{2}H-NMR experiments 1 and 2 by taking into account the molar ratio of the two compounds. Consequently the assumption made earlier, that the measured Δ during the polymerization is directly proportional to the orientational order of the long molecular axis, is indeed reasonable.

Optical observations, between crossed polarizers, have revealed that the mixture is transformed into a smectic phase also at cure temperatures up to 150 °C. At higher temperatures the mixture remained nematic during the polymerization reaction. The variation of Δn seems to be influenced only slightly by the N → S transition in contrast with ^{2}H-NMR experiments 1 and 2 where this transition could clearly be observed. Figure 20 shows that there is a very good agreement between the time that the Δn values start to level off at various cure temperatures and the point of gelation determined by solubility experiments in DMSO. This means that in this system the orientational order increases during the chain extension process up to the point where it becomes fixed by the action of the cross-links.

The increase of the orientational order as a function of the degree of polymerization has also been observed in several oligomeric and polymeric systems.[37,38] Clearly this is connected with the increase of the mesogenic potential of the monomers as a result of the chain extension; the nematic to isotropic transition temperature (T_i) increases as a function of the degree of polymerization and so the reduced temperature ($T^* = T/T_i$) decreases and the order increases. However, this does not always have to be the case, as in comparable systems, where the center of the reaction was located in the middle of the LC molecule, the mesogenic potential of the monomers actually decreased.[39] Some theoretical work concerning the influence of gelation on the state of order predicts that cross-linking in the nematic and isotropic phase should respectively raise and lower T_i.[40,41] This seems to be in contradiction with the present results, which demonstrate that the role of the cross-linking process is simply to freeze in the order. The discrepancy in the results is probably caused by the fact that these theories are developed for networks which consist of chains having a Gaussian character. It is more reasonable to approximate the present network as a system consisting of stiff rods.

At 120 °C and at 140 °C Δn reaches the same plateau value, whereas at 160 °C it levels off at a somewhat lower value. This suggests that at cure temperatures up to 140 °C a maximum level of order is achieved. However, this does not necessarily mean that S at these temperatures approaches the limiting value of 1. The possibility exists that the maximum achievable level of orientational order is limited by geometrical constraints. Indeed the order parameter of an added dye guest was only about 0.8 after 1 h of reaction time at 120 °C.[7] However, this value could have been somewhat higher if the dye molecules were chemically attached to the network. In the case of the photoinitiated cross-linking of mesogenic diacrylates, Δn decreased during the polymerization reaction at tempera-

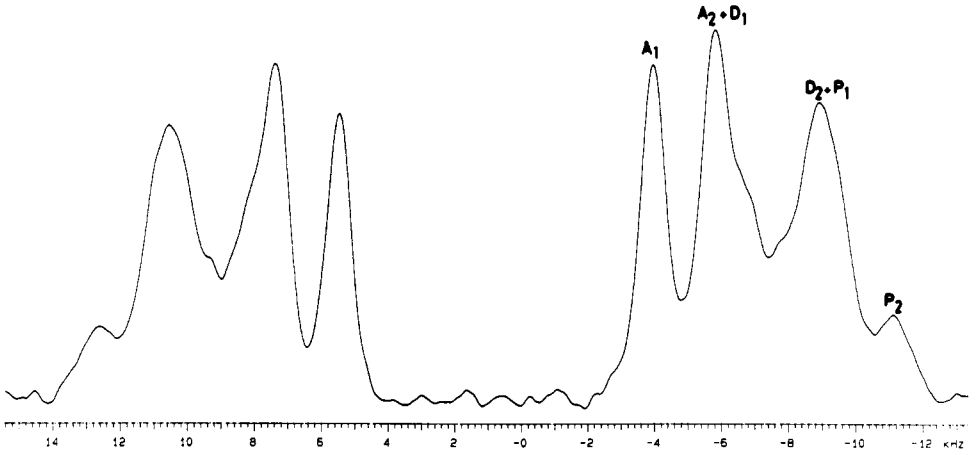

Figure 13. ^{2}H-NMR spectrum taken from Figure 11 after 8 min of polymerization time. In this figure the various peaks can be identified as coming from unreacted amine (A_1, A_2), epoxy–amine dimers (D_1, D_2), and higher molecular weight compounds (P_1, P_2).

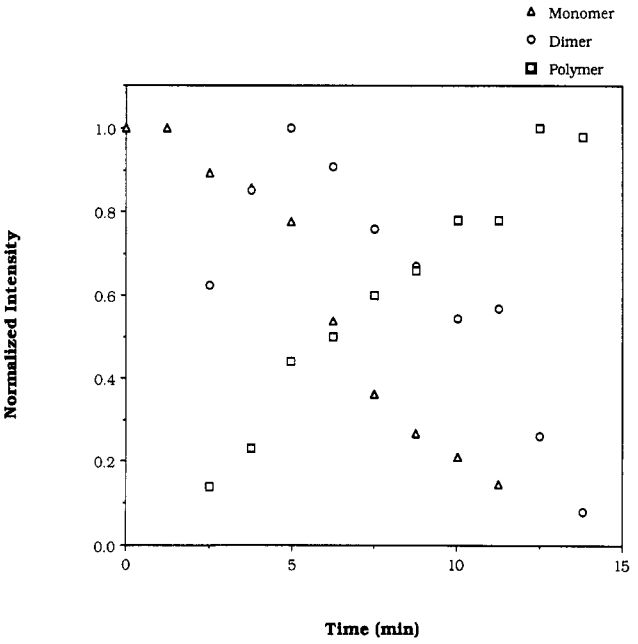

Figure 14. Variation of the relative concentration of various compounds during the polymerization reaction. The data were extracted from Figure 11.

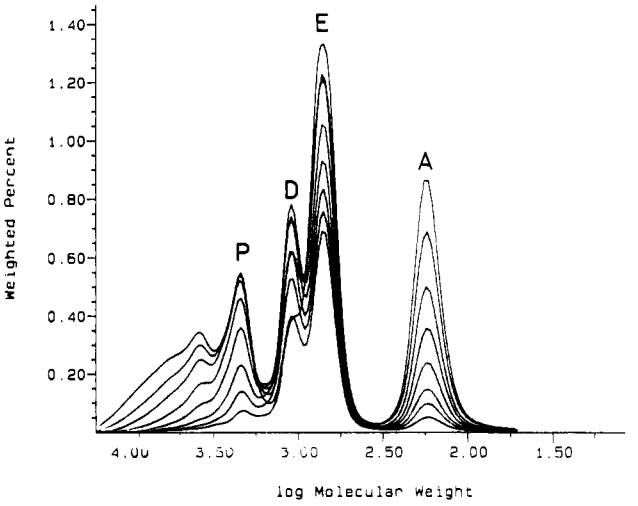

Figure 15. Composition of the polymerization mixture during the first 16 min of reaction time at 120 °C (measured with an interval of 2 min). The peaks marked with the letters A, E, D, and P correspond to the amine monomers, epoxy monomers, epoxy–amine dimers, and higher molecular weight compounds, respectively.

tures just above the melting point and increased at higher cure temperatures.[2] From these observations it is concluded that some of the order is lost when the monomer is polymerized at the highest initial state of order. Comparison with the present system it difficult because acrylates polymerize in a different manner. For example, it is known that gelation for these systems already occurs at a very low degree of conversion.[30]

Figure 21a shows the X-ray diffraction pattern (measured at RT) of the ^{2}H-NMR sample obtained by the reaction at 120 °C. The X-ray and microscopic studies of the same (nonoriented) material pointed to the existence of a S_A structure.[7] As can be seen in Figure 21a the wide-angle crescents are located in a direction perpendicular to the magnetic field, indicating that the mesogenic groups are oriented in the direction of the field as assumed in the analysis of the NMR data. Also some weak reflections, the origin of which is a point of discussion, can be observed on the equator. Figure 21b displays the X-ray pattern of the same material as in Figure 21a, with the exception that the network has undergone a thermal treatment (10 °C/min to 200 °C) in the absence of a magnetic field. The macroscopic order of the material has hardly been altered even though most of the postcuring process took place while the system remained in the rubbery region; the maximum in tan δ occurs at 95 °C after 1 h of reaction at 120 °C, and it shifts by almost 30 °C after the thermal treatment.[7] Similar behavior concerning the state of order was observed with the aid of temperature-dependent Δn measurements.[7] The high stability of the ordered state can be attributed to the action of the cross-links, which have locked in the macroscopic order and prevented it from going to a multidomain structure. It is noteworthy that the variation of Δ in both ^{2}H-NMR experiments was quite reversible after cooling to RT and heating back to 120 °C.

V. Conclusions

The orientational order for both reacting monomers increased during the chain extension step, and it became irreversibly fixed upon cross-linking. The gel point could hardly be detected by ^{2}H-NMR. The Δn measurements, on the other hand, were more responsive to the macroscopic process of gelation; the point where Δn started to level off, during the isothermal polymerization, corresponded well with the point of gelation. Owing to the effect of the spacer segment, the orientational order of the diepoxide was influenced to a lesser extent by the copolymerization

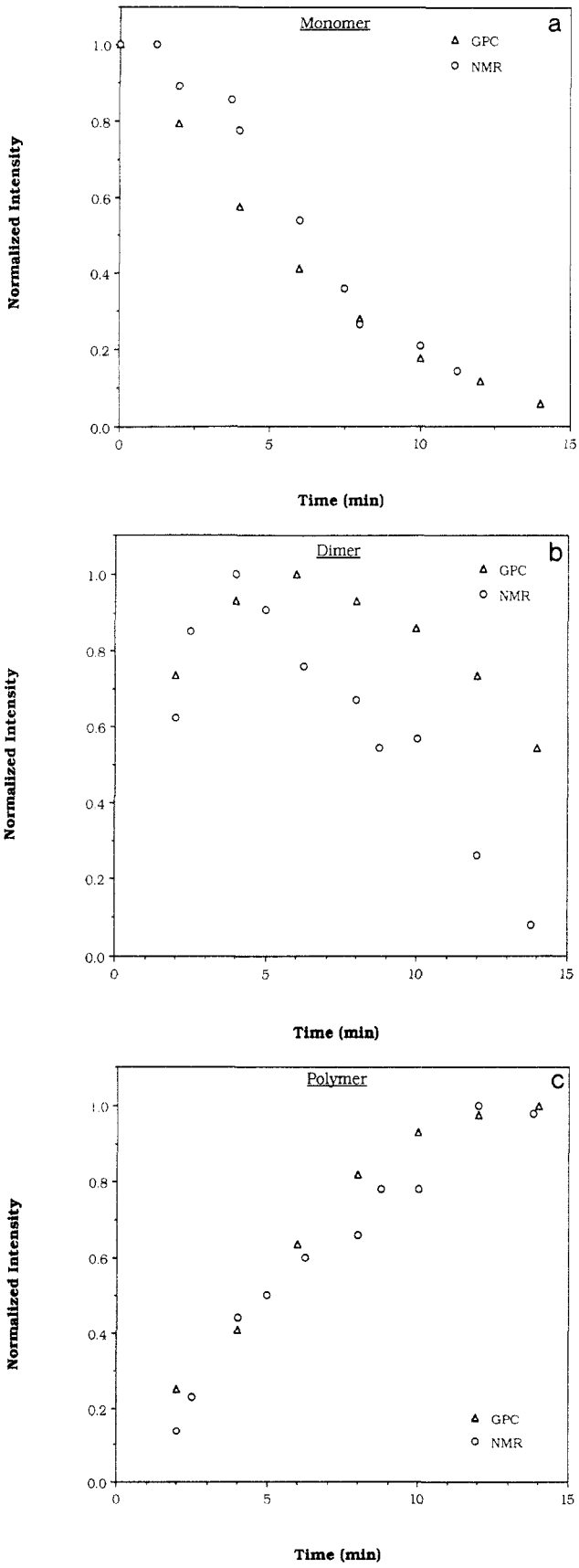

Figure 16. Comparison between the variation of the relative concentration of various compounds as determined by GPC and ^{2}H-NMR: (a) unreacted amine monomers; (b) epoxy–amine dimers; (c) higher molecular weight compounds.

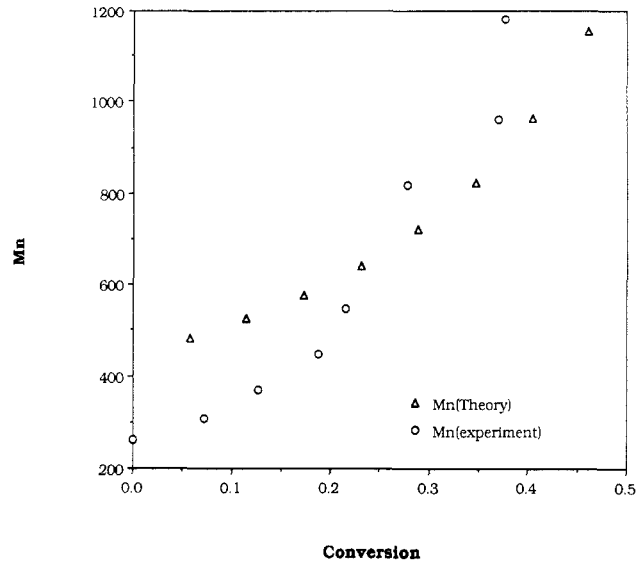

Figure 17. Values of the number-average molecular weights (M_n) in the initial phase of the polymerization as determined by GPC. The agreement between the theoretical and experimental values becomes better as the conversion increases. This is because of greater experimental inaccuracy at the start of the reaction.

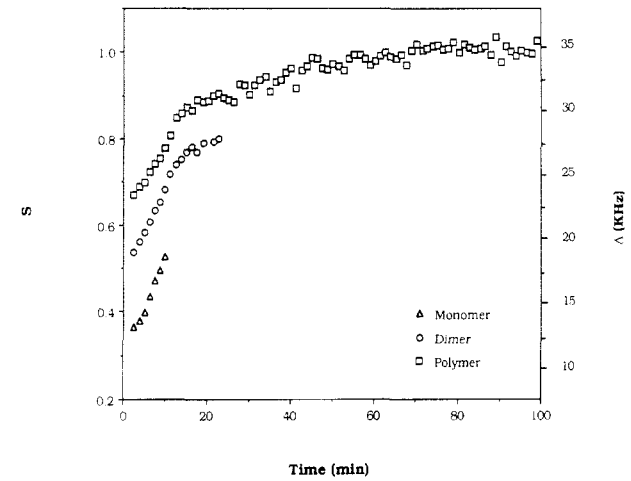

Figure 18. Values of the order parameter S calculated for the deuterated aromatic part of the amine. Also the corresponding values of Δ are displayed.

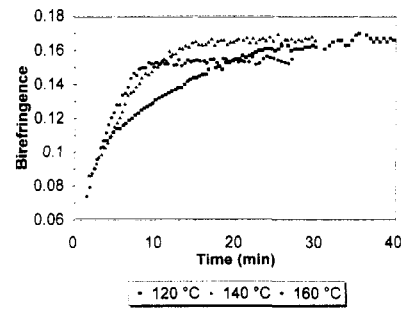

Figure 19. Change of birefringence (Δn) as a function of time at different cure temperatures.

reaction than the orientational order of the diamine. During the isothermal polymerization, at 120 and 140 °C, the maximum level of orientation is achieved. However, this does not necessarily mean that the degree of order of the networks equals 1. The order of the networks hardly changes upon subsequent cooling and heating in the absence of the magnetic field.

The network formation in the ordered state seems to proceed in a statistical manner, as both the position of the gel point on the conversion scale and the increase of the number-average molecular weight agree well with the theoretical predictions.

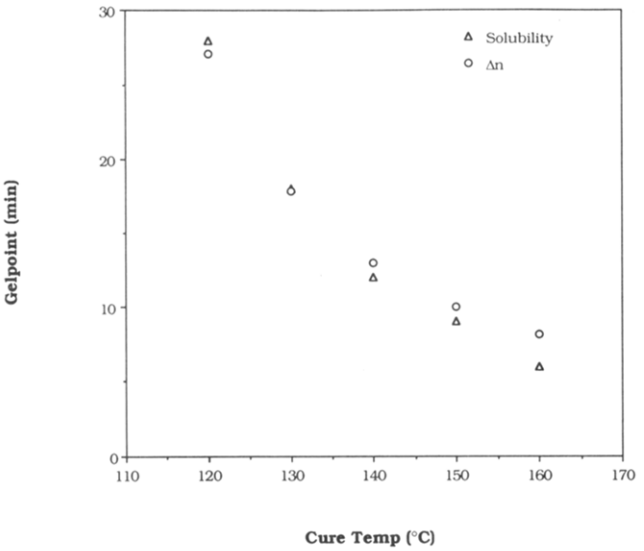

Figure 20. Point of gelation, estimated from the solubility experiments in DMSO and Δn measurements, as a function of cure temperature.

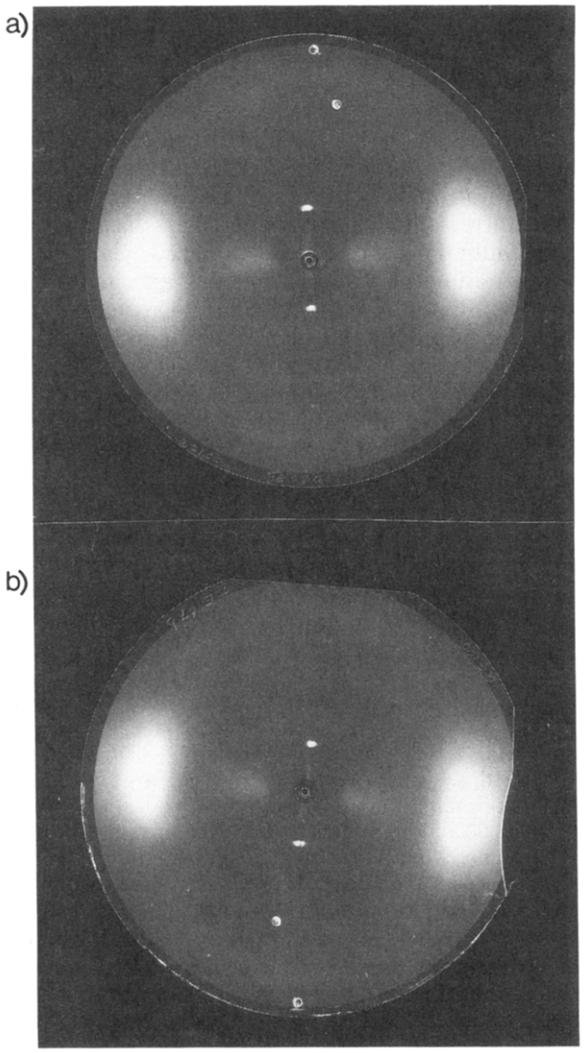

Figure 21. Wide-angle X-ray diffraction pattern taken after 1 h at 120 °C (a) and after the material has undergone an additional postcuring treatment in the absence of the magnetic field (b). Both measurements were carried out at RT.

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