

# Rheo-optical FTIR Spectroscopy of Epoxy Resins

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## SYNOPSIS

This article presents the results of the first application of rheo-optical Fourier transform infrared (FTIR) spectroscopy to monitor orientation phenomena in highly crosslinked epoxy/amine networks during the uniaxial deformation above their glass transition temperature. The resins were prepared from the diglycidyl ether of bisphenol-A (DGEBA) and various polyether di- and triamines in order to influence the structure of the network formed. The molecular orientation is discussed with respect to network density and structure. The orientation behavior is mainly determined by the flexibility of the polyether chain and the homogeneity of the network structure. Additionally, the epoxy resins were subjected to successive loading–unloading cycles. The investigations show that the orientation of epoxy networks in their rubbery state is completely reversible, and that no significant fatigue due to gradual chain rupture occurs until sample failure. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The mechanical properties of polymers are strongly influenced not only by the morphological structure of the material but also by its molecular orientation. The increased need for specific data concerning the mechanical behavior of polymeric materials has led to a great deal of interest in a better understanding of the complex orientation phenomena. Thus the characterization of effects resulting from various orientation processes has become a field of intense investigation in polymer science, with the goal of establishing more detailed relationships between molecular orientation and mechanical properties.

Molecular orientation studies of polymeric systems carried out simultaneously with the mechanical treatment are of particular interest since they provide valuable information on the mechanisms involved in polymer deformation. FTIR dichroism spectroscopy is one of the most powerful tools for monitoring transient structural changes occurring during the deformation process. Moreover, it allows quantitative measurement of the developing orien-

tation imposed by the mechanical treatment. In the past, a wide variety of polymers, including some networks, have been investigated successfully by the means of rheo-optical FTIR spectroscopy.<sup>1–7</sup> However, the rheo-optical characterization of polymer networks was restricted to the deformation of weakly crosslinked networks such as poly(dimethylsiloxane)<sup>1,8</sup> and rubber.<sup>2,4</sup> To the best of our knowledge, until now highly crosslinked networks like epoxy resins have not been investigated by rheo-optical FTIR spectroscopy. The reason may be the difficulties in preparation of thin films suitable for both infrared spectroscopy and mechanical measurements. Because of the high adhesive strength of epoxy resins, the main problem consists of detaching the films from the substrate.

Epoxy resins are one of the most popular classes of thermosets. Their outstanding properties—such as chemical and electrical resistance, high strength, and excellent adhesion—have led to widespread use of these materials in numerous technical applications. On the other hand, their considerable brittleness represents the most important drawback for the use of epoxy resins. Extensive research in the field of modification of epoxies has been carried out in the last decade to improve their ductility without a loss of strength. To pursue an efficient strategy in search of optimum modification procedures, a com-

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prehensive understanding of the molecular mechanisms occurring during elongation, recovery, stress relaxation, fatigue, and fracture of epoxy networks is required. The FTIR-rheo-optical technique allows one to achieve detailed information about these processes on a molecular level and to correlate them with macroscopic properties.

This article presents some results of the first application of rheo-optical FTIR spectroscopy to monitor orientation phenomena during the uniaxial deformation of highly crosslinked epoxy/amine networks at temperatures above their glass transition temperature. Furthermore, the behavior of epoxy resins subjected to several successive loading-unloading cycles was studied. Results from systematic investigation of the molecular orientation behavior of epoxy resins exposed to extension in the glassy state will be reported in a forthcoming article.

## THEORETICAL BACKGROUND

Although the use of rheo-optical FTIR spectroscopy to measure orientation in polymers is discussed in detail elsewhere,<sup>3-6</sup> it is useful to summarize its basic principles and the information available from infrared-dichroism measurements briefly.

The orientation of a polymer chain can be described by an orientation distribution function  $f(\theta, \phi, \psi)$ . In the case of uniaxially oriented samples, the segmental orientation with respect to a preferential orientational axis may be expressed in terms of the second Legendre polynomial  $\langle P_2(\cos \theta) \rangle$  as

$$f = \langle P_2(\cos \theta) \rangle = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (1)$$

where  $\theta$  is the average angle between the chain axis and the stretching direction. This expression corresponds to the well-known Hermans orientation function defined for X-ray diffraction measurements. In the case of uniaxial elongation of a network, the preferential direction coincides with that of the extension.

In infrared spectroscopy, the anisotropy of a polymer sample can be described by the dichroic ratio of a well-assigned vibrational mode

$$R = \frac{A_{\parallel}}{A_{\perp}} \quad (2)$$

where  $A_{\parallel}$  and  $A_{\perp}$  represent the absorbances measured with radiation polarized parallel and perpen-

dicular to the stretching direction, respectively. The second moment of the orientation distribution function  $\langle P_2(\cos \theta) \rangle$  is related to the dichroic ratio by the expression

$$f = \frac{(R - 1)(R_0 + 2)}{(R + 2)(R_0 - 1)} \quad (3)$$

where  $R_0 = 2 \cot^2 \alpha$  is the dichroic ratio for perfect uniaxial order, and  $\alpha$  is the angle between the transition moment vector of the considered vibrational mode and the local chain axis segment of the polymer. The angle  $\alpha$  can usually be obtained from theoretical considerations.<sup>5</sup> Alternatively, if the orientation function value is known by using either another method or a well-defined absorption band attributed to the same phase of the polymer, the orientation of the transition moment vector relative to the chain axis can be determined for any other absorption band. If the exact transition moment angle  $\alpha$  of the absorption band under investigation is unknown, the rheo-optical orientation data can be expressed in terms of the dichroic function  $d$  defined by Samuels<sup>6</sup>:

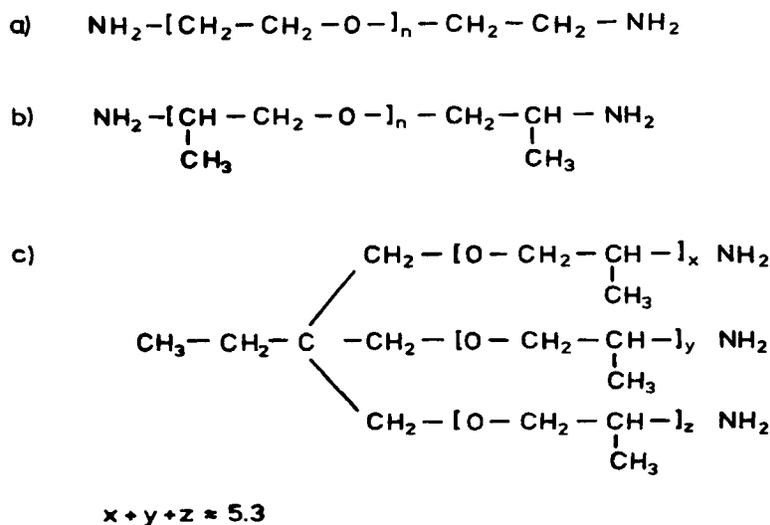
$$d = \frac{(R - 1)}{(R + 2)} \quad (4)$$

which differs from the orientation function  $f$  by a constant factor only. Although this approach is based on relatively simple models, it has been used extensively to study the orientation mechanisms in a wide variety of polymers.

## EXPERIMENTAL

### Specimen Preparation

All starting materials were commercially available products. The diglycidyl ether of bisphenol-A (DGEBA) was recrystallized from a mixture of acetone and methanol (mp = 42°C). Additionally, some samples were prepared with pure EPON 827 (Shell) used without further purification. However, significant deviations of the results were not found. Various Jeffamines (Texaco) were employed as curing agents. The chemical structures of these polyether di- and triamines are shown in Figure 1. The designation number refers to the approximate molecular weight of each species. All Jeffamines were used as received. The curing kinetics of this epoxy/amine system have been studied extensively by Morgan et al.<sup>9</sup> Their results suggest that the epoxide groups



**Figure 1** Chemical structure of the Jeffamine curing agents. (a) EDR-192; (b) D-400, D-2000; (c) T-403.

reacted primarily with the amine, and that very little side reaction takes place in this system. Therefore, the molar ratio was kept at the stoichiometric ratio throughout this study.

DGEBA was preheated to 75°C for 30 min to melt any microcrystals prior to adding the amine curing agent. After mixing epoxide and amine, the mixture was vacuum degassed. For the preparation of thin epoxy films suited for mid-infrared spectroscopy, the mixture was cast between preheated steel plates covered with release films (Richmond Aircraft Products, Santa Fe Springs, CA; type A 5000). The steel device ensures controllable diversion of the heat of reaction and guarantees isothermal curing. The samples were cured at 95°C for 20 h. To ensure completion of cure, the DGEBA/T-403 system was postcured at 130°C for 1 h, since its ultimate glass transition temperature ( $T_g^\infty = 93^\circ\text{C}$ ) is very close to the curing temperature. No postcuring was necessary for the other compositions.

Besides the single-diamine-cured epoxies, two additional systems containing a mixture of 95 mol % D-400 and 5 mol % D-2000 were prepared. The total epoxide/amine ratio was set at the stoichiometric ratio again. Following a procedure reported by Hunston et al.,<sup>10</sup> two different curing schemes were used to introduce some heterogeneity in the resin structure and possibly influence their mechanical properties. First, prepolymers were prepared. In cure scheme A, the initial mixture consisted of all the D-2000 amine and the corresponding stoichiometric amount of DGEBA. After stirring this mixture at 95°C for 4.5 h, the remainder of the starting materials was added. For scheme B, the total

amount of epoxy resin was precured with the D-2000 at 95°C for 2 h before adding the D-400. Both specimens were then stirred again, degassed, and cured at 95°C for 48 h.

Samples for near-infrared (NIR) spectroscopy, thermomechanical analysis (TMA), and dynamic-mechanical analysis (DMA) were prepared by pouring a part of the epoxy/amine mixture used for film casting into small, preheated steel frames treated with a release agent (Frekote 44-NC; Dexter, Seabrook, NH). The frames covered with Richmond release films were placed between steel plates preheated to the curing temperature as well. Crosslinking proceeded simultaneously with film curing under the same conditions. Until testing, all cured specimens were stored at ambient temperature in a desiccator.

### Sample Characterization

The final conversion of the epoxide and amine functionalities in the cured epoxy networks was verified by near-infrared spectroscopy. The NIR spectra of 2-mm-thick samples were obtained using a Bruker IFS 66 Fourier transform spectrometer equipped with a tungsten source, a silicon-coated calcium fluoride beamsplitter, and an InAs detector operating at 77 K. Thirty-two scans were collected at 2  $\text{cm}^{-1}$  resolution.

For monitoring the epoxide and amine consumption, the bands at 2205 nm and 1530 nm, respectively, were used. The first one is assigned to a combination of the C—H stretching fundamental at 3050  $\text{cm}^{-1}$  with the  $\text{CH}_2$  deformation band at 1460

$\text{cm}^{-1}$ .<sup>11</sup> This band is preferred for quantitative use because it is more sufficiently separated from other bands than the overtones at 1650 and 1159  $\text{nm}$ . The absorption at 1530  $\text{nm}$  represents an  $\text{NH}_2$  overtone.

Neither in the single-diamine-cured samples nor in the epoxies cross-linked with amine mixtures there were found any epoxide or amine functionalities remaining in the cured network. Furthermore, postcuring was not observed during the TMA and DMA temperature scans.

Glass transition temperatures,  $T_g$ , were measured by thermomechanical analysis. A Perkin-Elmer TMA 7 apparatus was employed for experimental data collection. Measurements in the range of  $-80^\circ\text{C}$  to  $150^\circ\text{C}$  were performed on flat, disklike samples (2 mm thick) at a heating rate of  $10 \text{ K min}^{-1}$  in the penetration mode (probe force 2 N). Every sample was scanned twice. The results are given as mean values in Table I.

The average network chain molecular weights ( $M_c$ ) were determined using a Rheometrics Dynamic Analyzer RDA II. Epoxy specimens with dimensions of  $40 \times 10 \times 1 \text{ mm}$  were torqued at oscillating frequencies of 0.1, 1, and 10 Hz. The temperature range was the same as during the TMA measurements.  $M_c$  values were calculated from the rubbery plateau modulus  $G_{\text{eq}}$  at  $T_g + 40^\circ\text{C}$  by using the expression

$$G_{\text{eq}} = A \langle \alpha^2 \rangle \rho R T M_c^{-1} \quad (5)$$

where  $\rho$  is the density, and  $A$  and  $\langle \alpha^2 \rangle$  are assumed to be unity.<sup>12,13</sup> For a highly crosslinked epoxy resin, this expression has been shown to lead to reasonable agreement between theory and experiment.<sup>13</sup> The average molecular weights between crosslinks of the DGEBA/Jeffamine networks are given in Table I.

The thin epoxy films for the rheo-optical investigations were checked visually by a light microscope for possible defects. Their thickness was determined by using a digital length gage with a resolution of  $0.5 \mu\text{m}$ . Its accuracy was checked by comparison with the interference fringes in the infrared spectrum of a polyethylene film. Only specimens with a constant

thickness and without any visible flaws were utilized for rheo-optical characterization.

### Rheo-optical FTIR Spectroscopy

A small electromechanical stretching machine developed by Siesler<sup>14</sup> was used for uniaxial deformation and relaxation measurements. Polymer films can be drawn at variable strain rates and under controlled temperature conditions ( $\pm 0.5 \text{ K}$ ) while the device is mounted in the sample compartment of the FTIR spectrometer for simultaneous spectra recording. The sample cell of the stretching machine is heated by dry air supplied by the spectrometer purge system. For real-time recording of the stress-strain data and controlling parameters such as temperature, elongation rate, etc., the apparatus is equipped with a computer. The stretching device has been described in detail elsewhere.<sup>14</sup> The machine can be moved by micrometer screws to align exactly the central sample area with respect to the infrared beam. The sample position was carefully adjusted at the convergence point of the incident radiation.

The spectroscopic part of the work was performed on a Bruker IFS 66 spectrometer equipped with a MCT detector operating at  $77 \text{ K}$ . Single-beam spectra were run at  $2 \text{ cm}^{-1}$  resolution. For each spectrum, 10 scans were coadded. Spectra were taken successively in 6.5-s intervals. Upon completion of the experiment, absorbance spectra were calculated using two polarizer spectra recorded before the measurement as references.

For orientation measurements, the polarization direction of the incident radiation can be alternately adjusted parallel and perpendicular to the stretching direction by a rotatable gold wire grid SPECAC polarizer mounted in a self-constructed electromechanical rotator. The change of the polarization direction is automatically initiated by the scanner reset signal of the spectrometer after recording of each spectrum.

The large number of spectra collected during a rheo-optical experiment requires specific evaluation

**Table I** Glass Transition Temperatures and Network Densities of the DGEBA/Jeffamine Networks

Hardener	EDR-192	T-403	D-400	System A	System B
$T_g$ ( $^\circ\text{C}$ ) (TMA)	71	93	50	43	42
$M_c$ (g/mol) (DMA)	420	410	605	680	625

Systems A and B: DGEBA/0.95 D-400 + 0.05 D-2000, cured with schemes A and B, respectively.

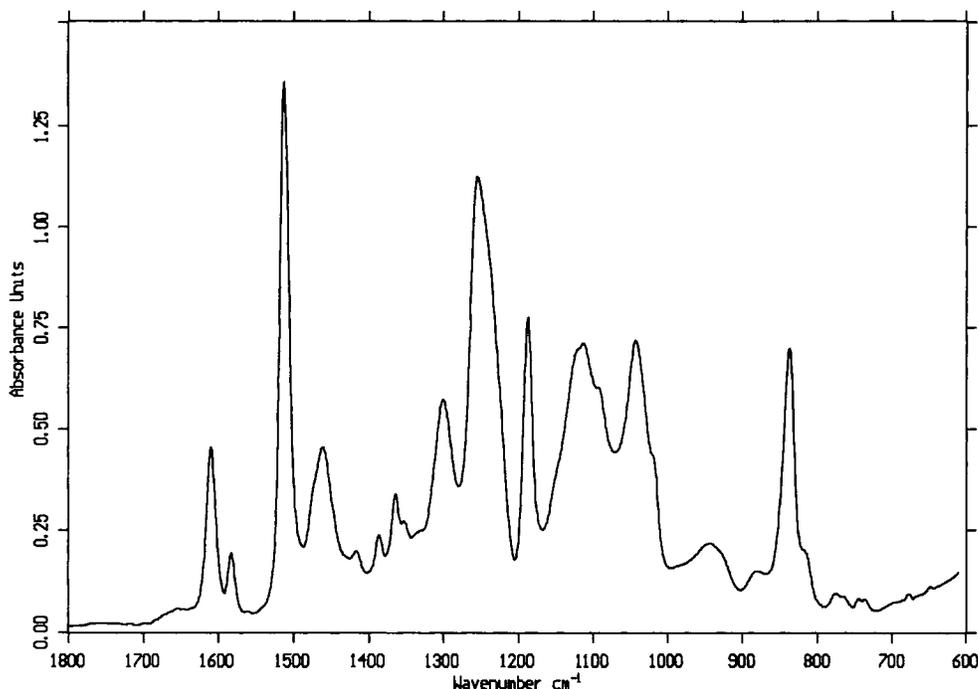


Figure 2 Fingerprint region of the FTIR spectrum of DGEBA/EDR-192.

software for further data processing—carrying out tasks like transformation to absorbance spectra, normalization against a reference band, band separation and integration, calculation of the dichroic ratio and the orientation function as a function of strain or time, and representation of the results. Additional software has been written for treatment and representation of the stress-strain or stress-time data.

One of the most important problems in infrared dichroism measurements arises from the requirement of band absorbances to be sufficiently low to permit the use of the Lambert-Beer law. Therefore, thin epoxy films with a thickness of about 10  $\mu\text{m}$  must be prepared. The epoxy films are extremely brittle. They must be peeled off the release film and handled with great care to avoid any damage of the specimen before mechanical treatment. Film specimens with gauge dimensions 12  $\times$  8 mm cut by use of a scalpel were stretched with a draw and recovery rate of 0.005 mm/s.

For such sheets of epoxy networks with a thickness of about 10  $\mu\text{m}$ , the Lambert-Beer law is obeyed. Only bands with absorptions smaller than 1.0 were evaluated for calculating the orientation function. The absorbance values  $A_{\parallel}$  and  $A_{\perp}$  are based on integral or peak-maximum intensities of well-defined vibrational bands. To take account of the decrease of sample thickness during elongation, the

intensities of all spectra obtained during a rheo-optical experiment were normalized to the intensity of a suitable reference band. The absorption at 1610  $\text{cm}^{-1}$  assigned to the  $\nu$  (C=C) stretching vibration of the *para*-disubstituted benzene ring in the DGEBA molecule was found to represent an appropriate reference band to compensate for decreasing film thickness.

## RESULTS AND DISCUSSION

### Dichroic Behavior of the Investigated Bands

The fingerprint region of the FTIR spectrum of an undeformed DGEBA/EDR-192 film sample taken without polarizer is plotted in Figure 2. As stated earlier, the investigated bands must be well assigned in order to deduce the transition moment direction with respect to the local chain segment. Only a few absorption bands in the infrared spectra of the films used in the present study are suited for orientational measurements.

The transition moments belonging to the  $\text{CH}_2$  stretching vibrations at 2930 and 2872  $\text{cm}^{-1}$  are known to be perpendicular to the polymer chain axis.<sup>5</sup> Due to the almost uncoupled nature of the methyl group, the transition moment directions of the  $\text{CH}_3$  symmetrical bending vibration modes at

1360 and 1386  $\text{cm}^{-1}$  are localized along the C—CH<sub>3</sub> bond<sup>1,2</sup> (i.e.,  $\alpha$  takes a value of 90°). Furthermore, the absorptions at 1460 and 3400  $\text{cm}^{-1}$  exhibit perpendicular dichroism. However, the respective transition moment angles  $\alpha$  are unknown.

The vibrational modes of the *para*-disubstituted benzene ring in the DGEBA molecule, which belongs to the C<sub>2v</sub> symmetry group, have been analyzed in detail by Varsanyi.<sup>15</sup> Kulczycki<sup>16</sup> assigned the absorption bands of bisphenol-A polycarbonate, which is similar in structure to DGEBA, to the various normal modes. Most of these bands are attributed to A<sub>1</sub> or B<sub>2</sub> modes. For A<sub>1</sub> modes, the dipole moment vector is along the C<sub>1</sub>—C<sub>4</sub> axis of the ring. For the B<sub>2</sub> modes, the transition moment is perpendicular to this direction and lies in the plane of the ring. No dichroism was observed for absorptions corresponding to A<sub>1</sub> or B<sub>2</sub> modes. The only relevant B<sub>1</sub> absorption which is influenced by the deformation process is located at 831  $\text{cm}^{-1}$ . It corresponds to an aromatic C—H out-of-plane vibration. This band exhibits an increasing dichroism with proceeding extension of the specimen.

Absorption bands assigned to various vibrations of the backbone of the network chains do not show any variation in dichroic ratio. Apart from the general intensity decrease due to the thickness reduction of the sample, these bands are not influenced by the deformation of the network.

In comparison with other polymers investigated by the means of rheo-optical FTIR spectroscopy, only very small changes of the dichroic ratio could be observed for epoxy networks. The evaluation of the dichroic ratios leads to nearly the same orientation function for all the vibrational modes mentioned earlier. Differences in the orientation behavior of the different structure elements, such as the diphenylpropane unit in the core of bisphenol-A or the aliphatic chains of the amines, could not be observed. Homogeneous deformation of the network as a whole seems to occur. For reasons of convenience, the band due to the  $\nu_s$  CH<sub>2</sub> symmetric stretching vibration at 2872  $\text{cm}^{-1}$  was mostly used for the calculation of the orientation function.

### Network Structure and Mechanical Properties

The mechanical behavior of the DGEBA/Jeffamine networks was analyzed in the rubbery state of the resins. The stress-strain curves obtained from tensile tests on film samples show an almost linear behavior instead of the nonlinear dependence typical for most rubbers. Furthermore, the curves for elongation and recovery are identical to each other with-

out any hysteresis effects. Similar results for other epoxy systems in the elastic state were found by LeMay and Kelley<sup>13</sup> and by Truong et al.<sup>17</sup>

The reversibility suggests that the measurements were performed under near-equilibrium conditions. Accordingly, the average molecular weight between crosslinks ( $M_c$ ) can be calculated for each network from the equilibrium tensile modulus by using Eq. (5), in which  $G_{eq}$  must be substituted by  $E/3$ . The elastic modulus and the  $M_c$  values determined from the stress-strain curve at  $T_g^\infty + 40$  K are presented in Table II.

Additionally, the network densities were also determined from dynamic-mechanical measurements.  $M_c$  was calculated from the plateau region of the storage modulus at  $T_g + 40$  K. Results are given in Table I. These  $M_c$  values are generally somewhat lower than those obtained from the tensile moduli. This probably reflects the fact that in a tensile test the correct measurement of the rubbery modulus may be connected with some experimental difficulties. At the high temperatures of measurement, the loads are very low and the specimen may slip on the clamps.<sup>18</sup> In particular, this may apply to the thin films in our experiments. However, despite some differences, the  $M_c$  values calculated from either DMA or the uniaxial tensile experiments are largely consistent.

Theoretical values of  $M_c$  can be estimated from the epoxy and amine concentrations by the expression<sup>13</sup>

$$M_c = \rho N_A / zc \quad (6)$$

where  $\rho$  is the density,  $N_A$  is Avogadro's number,  $z$  is the number of elastically active chains per crosslink, and  $c$  is the number of crosslinks per volume. For epoxy/diamine resins of stoichiometric composition, the theoretical value of  $z$  is 2. The crosslink concentration corresponds to the diamine molecule

**Table II Tensile Properties of DGEBA/Jeffamine Networks at  $T_g + 20$  K**

Hardener	EDR-192	T-403	D-400	System A	System B
$c_b$ (%)	9.2	5.0	5.5	5.8	5.6
$\sigma_b$ (MPa)	2.1	1.2	1.0	0.7	0.7
$E$ (MPa)	24.7	24.8	14.0	12.0	13.1
$M_c$ (g/mol)	415	440	700	795	730

Systems A and B: DGEBA/0.95 D-400 + 0.05 D-2000, cured according to schedules A and B, respectively;  $E$  and  $M_c$  determined at  $T_g + 40$  K. Results are mean values determined from 10 tensile tests for each system.

concentration. Furthermore, the real functionalities of the constituents<sup>19</sup> must be taken into consideration. The calculated molecular weights of the network chains are given in Table III. The experimental values of  $M_c$  are consistent with the theoretical results. In particular, this applies to the network densities obtained from dynamic-mechanical measurements, which are in somewhat closer agreement with the calculated values than those determined from the stress-strain curves.

Elongation and stress at break,  $\epsilon_b$  and  $\sigma_b$ , were determined from the rheo-optical experiments carried out at  $T_g^\infty + 20$  K. The tensile properties of the DGEBA/Jeffamine networks are included in Table II. The ultimate mechanical properties were found to be dependent on the network densities of the epoxies under consideration. Apart from the networks based on EDR-192, which has an oxyethylene instead of an oxypropylene backbone chain, the maximum elongation of the other networks show good correlation with  $M_c$ : The higher the value of  $M_c$ , the greater is the network extensibility. According to the theory of rubber elasticity, the maximum network extensibility is directly related to  $M_c$  by the expression  $\lambda_b \sim M_c^{1/2}$  (with  $\lambda_b = 1 + \epsilon_b$ ).<sup>20</sup> Network densities and ultimate elongations of the networks with oxypropylene skeletons reasonably satisfy this relationship.

The ultimate stress is also expected to depend on  $M_c$ . In the rubbery state, the intermolecular forces are absent, and the samples behave as fluids, with the crosslinks acting as pinning points. Consequently, if the network density decreases, the materials are not able to support high loads and break down at lower stresses. However, the results do not show a strong dependence of  $\sigma_b$  on  $M_c$ .

### Molecular Orientation Behavior of Epoxy Networks in the Rubbery State

#### Conformational Changes as a Molecular Mechanism of Network Deformation

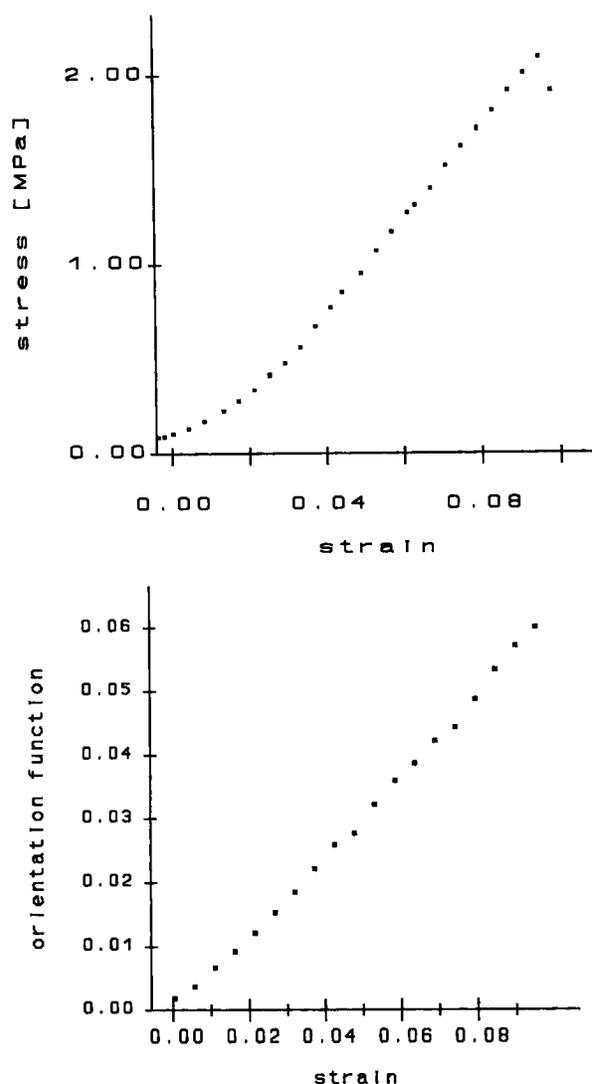
The stress-strain diagram and the orientation function  $f$  calculated from the FTIR spectra taken during the uniaxial deformation of DGEBA/EDR-192 at  $T_g + 20$  K are shown in Figure 3. Analog results were obtained for the other epoxy/Jeffamine systems.

The orientation function, as well as the stress in the stress-strain plot, depends on the strain linearly. Similar results were found for the orientation behavior of polyether chains in the soft segments of polyurethanes<sup>21,22</sup> as well as for other crosslinked

**Table III Comparison of Experimental and Theoretical  $M_c$  Values of DGEBA/Jeffamine Networks**

Hardener	EDR-192	D-400	System B
$M_c$ (g/mol) (tensile test)	415	700	730
$M_c$ (g/mol) (DMA)	420	605	625
$M_c$ (g/mol) (theoretical)	436	552	593

System B: DGEBA/0.95 D-400 + 0.05 D-2000; theoretical  $M_c$  calculated according to Eq. (6).



**Figure 3** (a) Stress-strain curve of DGEBA/EDR-192 at  $T_g + 20$  K. (b) Orientation function  $f$  as a function of strain for DGEBA/EDR-192 at  $T_g + 20$  K (calculated from the  $\nu_s$  CH<sub>2</sub> symmetric stretching vibration at 2872 cm<sup>-1</sup>).

and uncrosslinked polymers during elongation above their glass transition temperatures.<sup>2,23</sup>

Flexible crosslinked polymers in the rubbery state are relatively easy to deform. They can be stretched by distortion of the complete network structure. The molecular changes accompanying this process can, in fact, be complicated. For example, a chain can increase its end-to-end distance by simply changing the sequences of its conformational states without changing their number. This could occur with little if any change in the spectra investigated. On the other hand, during the extension process the individual network chains become more and more stretched, changing from a coiled to an elongated state. Additionally, the uncoiled chain segments become increasingly oriented—as far as permitted by the geometric constraints. However, highly crosslinked epoxies with short network chains, such as those investigated in this study, are not expected to behave like ideal elastomers. In particular, restrictions caused by the non-Gaussian character and the finite extensibility of the short chains must be taken into consideration.

Nevertheless, uncoiling and orientation of the network chains take place to a certain extent during the elongation of the network. This is reflected in the continuous increase of the orientation function. Above the glass transition temperature, the molecular orientation is completely reversible. Investigations of epoxy resins subjected to successive loading-unloading cycles in their rubbery state have shown that the orientation function totally disappears upon unloading. Results from cyclic deformation experiments are reported in detail later in this article.

Evidently, the storage of elastic strain energy in networks at  $T > T_g$  is based largely on the conformational changes of the network chains, even though the assumption that the networks consist of randomly coiled Gaussian chains may not be justified. Changes in the conformational distribution of polymers are usually easy to detect by infrared spectroscopy. Accordingly, the rise and drop of appropriate bands attributed to specific conformations of the network chains is expected during the deformation process. However, intensity changes originating from stress-induced conformational transitions were not found. Regardless of the larger extensions which usually can be achieved, this fact also applies to the deformation of epoxy networks in the glassy state.<sup>24</sup> The deformation process at  $T < T_g$  includes certain conformational changes, too. This result stands in contrast to the successful observation of conformational changes occurring dur-

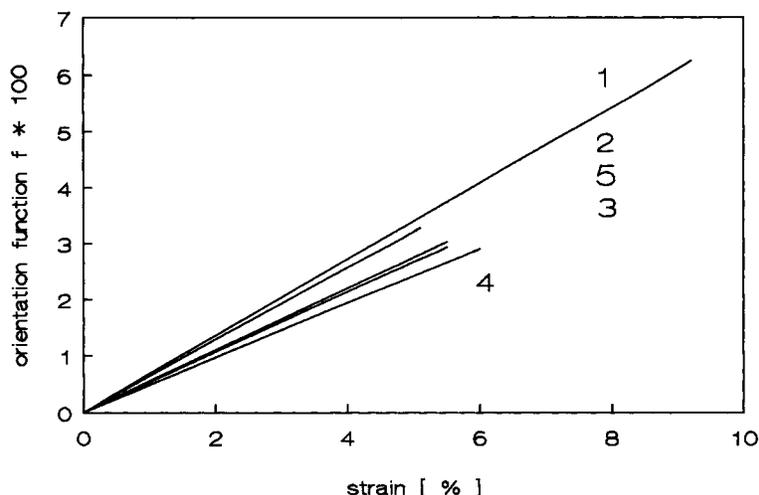
ing the deformation process of a wide variety of polymers,<sup>3,4,14,25</sup> including networks like natural rubber<sup>2</sup> or poly(dimethylsiloxane).<sup>1,8</sup>

Two factors should be responsible for the lack of intensity changes due to conformational transitions. First, there is a molecular reason. The DGEBA molecule and, in particular, the diphenylpropane unit contained in it is an extremely rigid structure which largely resists any deformation. This means that deformation is predominantly localized in the more flexible polyether chains of the Jeffamines. The bisphenol-A unit turns together with the surrounding "matrix" only gradually into the stretching direction. Second, the FTIR spectrum of the epoxy resins is dominated by the bands assigned to the stiff DGEBA molecule because of the strong absorbances of the diphenylpropane unit. The only observable vibrational mode in the fingerprint region attributed to the Jeffamine curing agents is the  $\nu$  C—O—C absorption around  $1105\text{ cm}^{-1}$ , which is the most intense band in the spectra of the pure amine monomers. This band is superimposed by the absorption due to the secondary hydroxyl groups formed in the reaction of epoxide and amine functionalities. In the infrared spectrum of polyethers, a great number of vibrational bands is known to be sensitive to specific conformations. Unfortunately, the  $\nu$  C—O—C absorption is completely independent of changing conformation.<sup>26,27</sup> Nevertheless, though the direct evidence for changes in the conformational distribution during the elongation of epoxy/amine networks failed, conformational changes of the network chains are the base for the storage of mechanical energy transferred to the rubbery sample during deformation. The cyclic deformation experiments clearly support this fact.

### **Orientation Function of DGEBA/ Jeffamine Networks**

In Figure 4 the orientation functions of all investigated epoxy networks cured with Jeffamines are plotted schematically as a function of strain. All networks were elongated at a temperature 20 K higher than their respective glass transition temperature. The curves are average results based on 10 rheo-optical experiments for each system.

The orientation function  $f$  of the various epoxies depends clearly on their network densities listed in Table I. The slope of  $f$  is directly related to the reciprocal value of  $M_c$ : In networks with low molecular weight between the crosslinks, the network chains become more rapidly uncoiled and extended than in networks consisting of longer chains.



**Figure 4** Schematic representation of the orientation function versus strain for various DGEBA/Jeffamine networks elongated at  $T_g + 20$  K. 1: EDR-192; 2: T-403; 3: D-400; 4: D-400 + D-2000/cured according to schedule A or B.

Apart from the  $M_c$  value, the deformability of polymer networks depends strongly on (1) the extensibility of the chain segments forming the meshes, (2) the flexibility of their internal angles, and (3) the ability of the meshes to undergo cooperative deformation with the interconnected neighboring rings. In highly crosslinked systems, the extensibility of the network segments is determined by the specific rotational isomeric configurations of the segments and the perturbation of these configurations from their minimum energy state by geometric constraints. The deformability of the internal angles of the chains is substantially determined by the flexibility of the backbone of the chain segments incorporated into the network. Finally, the cooperative deformation behavior is controlled by the regularity of the network topography. Segmental extensibility and network topography will also significantly affect the ultimate elastomeric network properties.

Though the network densities of the systems on the base of T-403 and EDR-192 are almost identical, the molecular structures of both amines, and consequently of the networks, differ appreciably. The trifunctional T-403 is a star-shaped molecule consisting of amine terminated oxypropylene chains with usually one or two monomer units per arm. The topography of the epoxy networks formed was analyzed by Morgan et al.<sup>9</sup> Networks with a pronounced irregular structure are built up from DGEBA and T-403, which are far from ideal compared to most amine-cured DGEBA epoxies. The networks consist of rings with a wide variety of ge-

ometries, which may develop overstressed segments even at low extensions.

By contrast, EDR-192 is based on an oxyethylene backbone. Because of the easier rotation along the C—O—C bonds, the oxyethylene is much more flexible than the oxypropylene chain, in which the rotation around C—O—C is sterically hindered by the adjacent methyl side groups. Detailed quantum chemical calculations on this subject were performed by Lange.<sup>28</sup> Furthermore, since EDR-192 consists of nearly pure tetraethyleneglycoldiamine (98%), a regular network built up from interconnected rings of similar size and shape is formed.

Due to the higher flexibility of the oxyethylene backbone and the more regular network structure of the epoxies based on EDR-192, the orientation function of these networks increases, in spite of the nearly coinciding values of  $M_c$ , more rapidly than that of DGEBA/T-403. Additionally, the more homogeneous distribution of stress in the regular network enables this system to withstand higher ultimate stress and leads to approximately double elongation-to-break values as compared with the other networks.

The  $M_c$  value of the network based on D-400 is more than 50% larger than that of the other two. In particular, the aliphatic chain segments coming from the diamine molecules are longer. Therefore, they become more slowly uncoiled and oriented when the extension of the sample increases. Additionally, the uncoiling is impaired by the hindered rotation around the skeletal bonds of the oxypropylene backbone in the D-400 molecule. Moreover, the ac-

tual functionality of D-400 is somewhat lower than the theoretical value [3.75 (ref. 19) instead of 4]. Although this was taken into consideration with respect to the calculation of the stoichiometric epoxide-amine ratio, the network should contain some imperfection (such as dangling ends, which decrease the crosslink density). Network density and structure are reflected by the slope of the orientation function. Accordingly, the orientation function of DGEBA/D-400 increases more slowly during stretching than those of the networks cured with EDR-192 or T-403.

In Figure 4 the orientation functions of the two systems prepared with mixtures of Jeffamines are plotted as well. Their microstructure was determined by the different curing schedules. The most probable network structures suggested by Hunston et al.<sup>10</sup> will be described briefly. In the precure step of system A, the D-2000 amine and the stoichiometric amount of DGEBA were converted carefully so that gelation was avoided. During the prepolymerization, large network segments consisting of DGEBA and D-2000 are formed. After adding the remaining constituents and completing the cure, these segments are incorporated into the final network as units containing most of the D-2000 molecules. From this procedure, a network with a heterogeneous structure is produced.

For system B, the total amount of epoxy resin was precured with the D-2000 before adding the D-400. This means a large excess of epoxide is used during the precure step. As a result, the predominant reaction is the addition of four DGEBA molecules to each of the amine molecules. When the remainder of the sample is added, these D-2000/epoxy supermolecules are built into the network in a more or less random pattern, and a network with a less heterogeneous structure is developed.

The different network structures are reflected in their average molecular weights between crosslinks. Due to the small portion of D-2000 and its regular incorporation into the network, the  $M_c$  value of system B resembles that of the DGEBA/D-400 network (625 g/mol compared with 605 g/mol). However, the more heterogeneous system A has a distinctly looser network structure (680 g/mol). Consequently, the orientation functions of the former two are nearly identical, whereas the slope of the orientation function of system A is somewhat lower. This should be caused by the wide-meshed network segments consisting predominantly of DGEBA and D-2000, in which the chains become less uncoiled and oriented than those in the more homogeneous or the unmodified epoxy/diamine network.

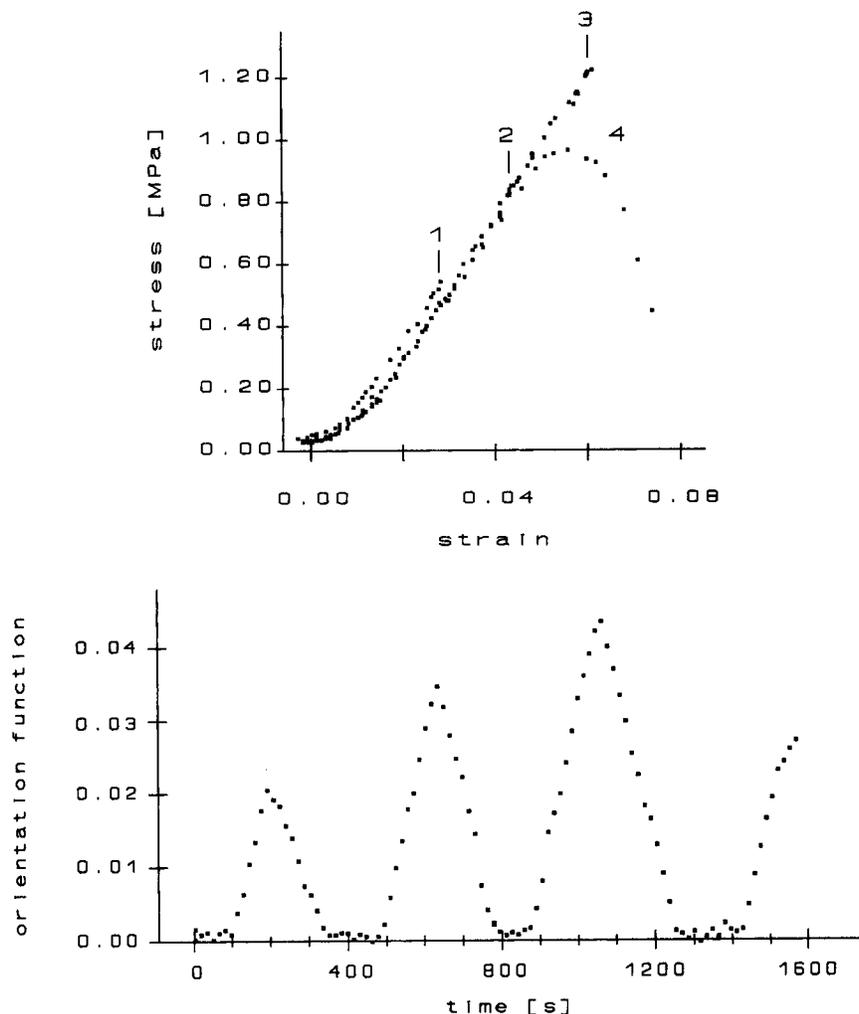
The heterogeneity introduced into the epoxy networks should influence their mechanical properties more markedly in the glassy state. Investigations of the deformation behavior of epoxy resins at  $T < T_g$  will be reported in a future article.<sup>24</sup>

### *Cyclic Deformation of Rubbery Epoxy Networks*

In the preceding section, investigations of the molecular deformation behavior of epoxy networks during a continuous stretching process up to the failure of the sample were reported. Rheo-optical FTIR spectroscopy offers the unique opportunity to obtain detailed information on molecular orientation and relaxation phenomena occurring during deformation cycles, including elongation, recovery, stress relaxation, and fatigue. In particular, the question of reversibility of the orientation during unloading of the sample is essential for a better understanding of the molecular mechanisms involved. Therefore, the epoxy films were subjected to successive loading-unloading cycles at  $T_g + 20$  K, and the developing and disappearing orientation was simultaneously studied by rheo-optical infrared spectroscopy. For example, the stress-strain curve and the orientation function recorded during the cyclic deformation of a DGEBA/EDR-192 network are shown in Figure 5. Analog deformation and relaxation behavior were found for the other systems investigated in this study.

In the course of four loading-unloading cycles, the sample was gradually stretched to higher and higher maximum strain. The stress-strain curves again show linear behavior. The curves for elongation and recovery are identical without any hysteresis effect. The strain completely disappears upon unloading, and no remaining elongation of the samples could be detected. Furthermore, except for the initial cycle, the curves of all subsequent cycles are in agreement as well. Some deviation from the linear behavior can only be observed just before the abrupt failure of the sample. This indicates that successive chain rupture in overstrained network segments obviously did not occur. The minor deviation of the starting cycle could be caused by some irreversible disentanglement or a slight slip of the specimen on the grips.

The orientation function plotted in Figure 5(b) exactly corresponds to the stress-strain curve. It increases and decreases in synchrony with the rise and fall of the strain. Upon unloading the sample, the orientation function totally disappears, and no time lag between the disappearance of the stress and the orientation was found. The molecular orientation of



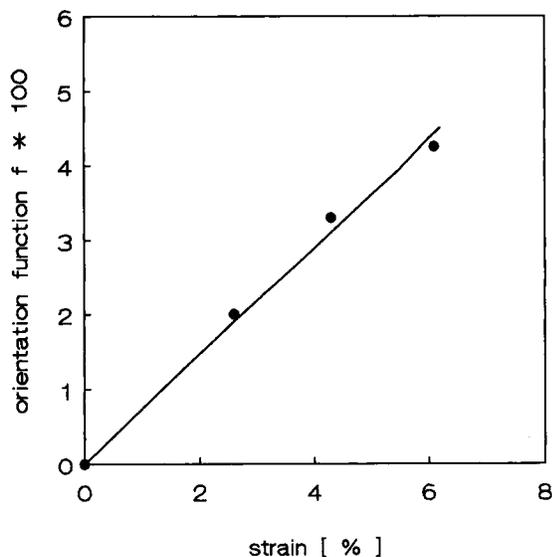
**Figure 5** DGEBA/EDR-192 subjected to successive loading-unloading cycles at  $T_g + 20$  K. (a) Stress-strain curve; (b) Orientation function  $f$  as a function of time (calculated from the  $\nu_s$   $\text{CH}_2$  symmetric stretching vibration at  $2872\text{ cm}^{-1}$ ).

the epoxy networks in their rubbery state is completely reversible.

The orientation function  $f$  is nearly linear with respect to the strain. This is demonstrated in Figure 6, in which the maxima of  $f$  of the first three deformation cycles from Figure 5 are plotted in dependence on the respective maximum strain. Fatigue effects like disentanglement or chain rupture would lead to a lag of  $f$  behind the strain, but  $f_{\text{max}}$  is proportional to the strain, and consequently no significant fatigue occurs in the epoxy network. The orientation function of natural rubber was found to show similar behavior at low extensions. However, with increasing deformation  $f$  becomes more and more influenced by the strain-induced crystallization, leading to a distinct deviation from linearity.<sup>3</sup> The congruence of the stress-strain curves of the

successive loading-unloading cycles, as well as the corresponding behavior of the orientation function belonging to it, are in accordance with the lack of spectroscopic evidence for bond rupture in the network chains, which will be discussed later in this article.

The deformation of epoxy networks above the glass transition temperature is completely reversible. This is due to the molecular mechanism of deformation of polymers in their rubbery state. The distribution of conformational states changes in the course of elongation of the epoxy film samples. Its direct observation failed due to the lack of suitable infrared bands sensitive to such changes. However, the results of the cyclic deformation experiments indirectly confirm the occurrence of conformational changes. In particular, the complete reversibility of



**Figure 6** Maxima of  $f$  versus strain plotted for the first three cycles shown in Figure 5.

the molecular orientation is in agreement with the entropy-driven relaxation of the conformations to their equilibrium distribution when the sample is unloaded.

### Stress Distribution in Stretched Epoxies

If a macroscopic load is applied to a polymer network, the transfer of the stress through the network depends considerably on its topography. In highly crosslinked epoxy networks, the stress transfer is strongly hindered by geometric constraints due to the more or less irregular network structure. Because of the inhomogeneous distribution of the stress in the network overstrained chain segments, backbone bond-angle deformation and other stress-induced defects, such as chain rupture, in the most highly strained regions of the epoxy network may occur. Those effects should be reflected in the infrared spectrum of the sample. Band shifts and other spectroscopic phenomena can be expected as a consequence of the inhomogeneous stress distribution. Vibrational bands may become increasingly asymmetric in their shape, or shoulders on the low-frequency side of absorption bands may appear. New bands in the spectrum could be attributed to new endgroups as a result of chain scission in the strongly overstrained regions of the network, which carry a significantly larger portion of the applied load than the surrounding segments. Furthermore, conformational changes can contribute to those spectral phenomena.

Because all these effects are supposed to be small in magnitude, the infrared spectra series recorded during the uniaxial deformation of epoxy network samples have been inspected carefully. Additional rheo-optical experiments with an improved spectral resolution of  $0.5 \text{ cm}^{-1}$  to detect diminutive shifts have been carried out. The shape of the absorption bands has been analyzed in detail. But neither band shifts, nor a development of shoulders or asymmetries on the low-frequency wing of absorption bands, nor the appearance of new bands in the FTIR spectra could be observed in the course of extending the sample.

A number of conclusions can be deduced from this result. First, the distribution of stress in the rubbery epoxy network obviously seems to be more homogeneous than originally expected. It has been pointed out that network perfection can significantly influence the mechanical properties of a cured epoxy resin. An inhomogeneous network will lead to a nonuniform stress distribution and therefore to the failure of the sample at low extensions. But no indication for such a nonuniformity of the stress transfer was found. Consequently, the structure of the investigated epoxy networks consisting of DGEBA and polyether-based amine curing agents should be rather homogeneous. This corresponds exactly to the previous results from the cyclic deformation experiments. Additionally, the polyether backbones in the Jeffamines, even the oxypropylene chain, are much more flexible than the skeleton of most of the other aliphatic or aromatic curing agents commonly used in epoxy systems. The polyether chains make the network more ductile and permit local stress maxima to relax quickly by distributing the stress in the network more regularly. Due to the remarkable backbone flexibility, the homogenization of the stress is more pronounced in the networks investigated than in other epoxy resins. Moreover, the flexibility of the polyether chains should contribute to the relatively high regularity of the network structure because steric hindrances play a less important role during the network formation process than in other epoxy/amine systems.

Second, new bands or shoulders which could be attributed to new endgroups resulting from chain scission were not observed. This indicates that gradual degradation of the network by successive stress-induced chain rupture in overstrained network segments does not occur upon drawing. This is probably a direct consequence of the reported homogeneous stress distribution in the network because chain scission is expected to be caused by a nonuniformity of the stress due to an irregular net-

work topography. The critical concentration of chain scissions necessary for failure of the sample will obviously be attained in a very short period of time immediately before the breakdown. In various other polymers, significant bond rupture also appears just before the sample tears, as observed by electron paramagnetic spectroscopy.<sup>29</sup> The lack of spectroscopic evidence for chain scission corresponds to the results of the cyclic deformation of DGEBA/Jeffamine networks reported. The stress-strain curves<sup>29</sup> and the orientation functions are completely reversible and show linear behavior over several loading-unloading cycles up to the breaking point. No indication for stress-induced chain scission was found.

However, mainly backbone bonds will become influenced by an inhomogeneous distribution of the applied stress in the network. For the observation of skeletal bonds, and of carbon-carbon bonds in particular, FT-Raman spectroscopy is usually superior to infrared spectroscopy since the  $\nu$  C—C absorption appears with higher intensity in the FT-Raman spectrum. Furthermore, the MCT detector used covers a spectral range, with wave numbers greater than  $600\text{ cm}^{-1}$  only. If absorption bands which are sensitive to specific conformation states can be found in the FT-Raman spectrum, conformational changes occurring in the course of elongation of the sample could be detected directly. However, during the stretching of poly(dimethylsiloxane) (PDMS), only diminutive frequency shifts were found in the spectra.<sup>8</sup> The small spectroscopic effects were caused by rotational isomerization of the PDMS skeletal bonds rather than by bond-angle deformations or even bond stretching. Such structural changes would be expected to be even less important in networks prepared from polymers having skeletal bonds that are less deformable than the atypical Si—O—Si bonds in PDMS.

## CONCLUSION

In this article results of the first application of rheo-optical FTIR spectroscopy to monitor molecular orientation phenomena of highly crosslinked epoxy/amine networks in their rubbery state were presented. Epoxy networks consisting of DGEBA and polyether-based amine curing agents were subjected to uniaxial deformation to achieve detailed information about orientation processes on a molecular level and to correlate them with the macroscopic properties.

The orientation functions  $f$  of the various epoxies investigated mainly depend on their network densities, where  $f$  is directly related to the reciprocal value of  $M_c$ . Additionally, the molecular orientation behavior is strongly influenced by the network structure and the regularity of its topography. The different network densities and the structure of the epoxies cured with amines with an oxypropylene backbone are reflected by the slope of their orientation function. The orientation function of the epoxies containing Jeffamine EDR-192 increases more rapidly than that of the networks based on an oxypropylene skeleton. This is due to the higher flexibility of the oxyethylene chain and the more regular network structure. Furthermore, the more homogeneous distribution of stress in the regular network enables these systems to withstand higher ultimate stresses and leads to nearly double elongation-to-break values.

Additionally, the behavior of epoxy resins subjected to successive loading-unloading cycles was studied. The orientation function increases and decreases in synchrony with the rise and fall of the strain without any hysteresis effect. Upon unloading of the sample, the orientation function disappears. The cyclic deformation experiments have shown that the orientation of epoxy networks above their glass transition temperature is completely reversible, and that no significant fatigue due to gradual degradation of the network by successive stress-induced chain rupture occurs upon drawing until the abrupt failure of the sample. Because chain scission should be a consequence of a nonuniform stress distribution in the network due to its irregular topography, the structure of the epoxy networks investigated seem to be relatively homogeneous.

The molecular mechanism of deformation at  $T > T_g$  is mainly based on conformational changes of the network chains. However, intensity changes originating from stress-induced conformational transitions were not found. Although the direct observation of a changing distribution of conformational states failed due to the lack of suitable conformation-sensitive infrared bands, those transitions were indirectly confirmed by the results of the cyclic deformation experiments. In particular, the complete reversibility of the molecular orientation is in accordance with the entropy-driven relaxation of the conformations to their equilibrium distribution when the sample is unloaded.

In networks with irregular topography, an inhomogeneous distribution of the stress in the network may develop, leading to overstrained chain segments, backbone bond-angle deformation, and other

stress-induced defects, like chain rupture in the most highly strained regions of the network. These effects should be reflected in the infrared spectrum. But no evidence for such a nonuniformity of the stress transfer was found in the FTIR spectra. This result confirms that the structure of the DGEBA/polyether amine epoxy networks investigated should be homogeneous. This is in accordance with the results of the cyclic deformation experiments reported.

In a forthcoming article, results from systematic investigation of the molecular orientation behavior of epoxy resins subjected to simple uniaxial extension or cyclic deformation in the glassy state will be reported.

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## REFERENCES

1. S. Besbes, L. Cermelli, L. Bokobza, L. Monnerie, I. Bahar, B. Erman, and J. Herz, *Macromolecules*, **25**, 1949 (1992).
2. B. Amram, L. Bokobza, J. P. Queslel, and L. Monnerie, *Polymer*, **27**, 877 (1986).
3. H. W. Siesler, in *Advances in Applied Fourier Transform Infrared Spectroscopy*, M. W. Mackenzie, Ed., John Wiley & Sons, Chichester, 1988, p. 189.
4. H. W. Siesler, in *Fourier Transform Infrared Characterization of Polymers*, H. Ishida, Ed., Plenum Press, New York, 1987, p. 123.
5. H. W. Siesler and K. Holland-Moritz, *Infrared and Raman Spectroscopy of Polymers*, Marcel Dekker, New York, Basel, 1980.
6. R. J. Samuels, *Makromol. Chem., Suppl.*, **4**, 241 (1981).
7. B. Jasse and J. L. Koenig, *Polymer*, **22**, 1040 (1981).
8. L. K. Silva, J. E. Mark, and F. J. Boerio, *Makromol. Chem.*, **192**, 499 (1991).
9. R. J. Morgan, F.-M. Kong, and C. M. Walkup, *Polymer*, **25**, 375 (1984).
10. W.-L. Wu, J.-T. Hu, and D. L. Hunston, *Polym. Eng. Sci.*, **30**, 835 (1990).
11. H. Dannenberg, *SPE Transactions*, **3**, 78 (1963).
12. L. R. G. Treloar, *The Physics of Rubber Elasticity*, Clarendon Press, Oxford, 1975.
13. J. D. LeMay and F. N. Kelley, *Adv. Polym. Sci.*, **78**, 115 (1986).
14. H. W. Siesler, *Makromol. Chem., Macromol. Symp.*, **53**, 89 (1992).
15. G. Varsanyi, *Assignments for Vibrational Spectra of 700 Benzene Derivatives*, Academic Press, New York, 1969.
16. A. Kulczycki, *Spectrochim. Acta*, **41A**, 1427 (1985).
17. V.-T. Truong, Y. B. Truong, and B. C. Ennis, *Polym. Comm.*, **32**, 275 (1991).
18. V. B. Gupta, L. T. Drzal, C. Y.-C. Lee, and M. J. Rich, *Polym. Eng. Sci.*, **25**, 812 (1985).
19. K. Dušek, S. Ilavský, S. Štokrová, L. Matějka, and S. Luňak, in *Crosslinked Epoxies*, B. Sedláček and J. Kahovec, Eds., Walter de Gruyter, Berlin, New York, 1987, p. 279.
20. D. H. Kaelble, in *Epoxy Resins. Chemistry and Technology*, C. A. May and Y. Tanaka, Eds., Marcel Dekker, New York, 1973, p. 603.
21. D. Boese, C. D. Eisenbach, E. W. Fischer, H. Hayen, H. Nefzger, G. Planer-Kühne, N. Reynolds, and H. W. Spiess, *Makromol. Chem., Macromol. Symp.*, **50**, 191 (1991).
22. S. Kohjiya, Y. Ikeda, S. Yamashita, M. Shibayama, T. Kotani, and S. Nomura, *Polym. J.*, **23**, 991 (1991).
23. Y. Zhao, B. Jasse, and L. Monnerie, *Makromol. Chem., Macromol. Symp.*, **5**, 87 (1986).
24. T. Scherzer, accepted to *J. Polym. Sci., Polym. Phys. Ed.*
25. I. J. Hutchinson, I. M. Ward, H. A. Willis, and V. Zichy, *Polymer*, **21**, 55 (1980).
26. H. Matsuura and K. Fukuhara, *J. Mol. Struct.*, **126**, 251 (1985).
27. H. Matsuura and K. Fukuhara, *J. Polym. Sci., Polym. Phys. Ed.*, **24**, 1383 (1986).
28. J. Lange, *Das Konformations- und Assoziationsverhalten von Polyoxyethylen und seinen Blockcopolymeren in wäßriger Lösung*, thesis, Technical University Merseburg, 1989.
29. D. K. Roylance, in *Applications of Polymer Spectroscopy*, E. G. Brame, Ed., Academic Press, New York, 1978, p. 206.

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