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Dynamic mechanical and ^{13}C n.m.r. investigations of molecular motions involved in the β relaxation of epoxy networks based on DGEBA and aliphatic amines

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As shown by a precise analysis of the dynamic mechanical data in terms of activation energies and entropies, the extent of the β transition strongly depends on the role played by the crosslinks. In a densely crosslinked network, localized motions at the spatial scale of an epoxy-amine repeat unit occur at low temperatures, whereas cooperative modes implying more than six units are responsible for the high temperature part of the relaxation. In the quasi-linear systems, only modes with a low spatial extent exist. Measurements of the strength of the $^{13}C-^{1}H$ dipolar couplings, together with other n.m.r. techniques, have shown that the motions of the hydroxypropylether units take part in the β transition. The DGEBA ring flips also take part in the β transition. The comparison of dynamic mechanical and ^{13}C n.m.r. results tends to indicate that the sensitivity of the n.m.r. experiments allows it to probe the cooperative motions, which induce a reorientation of quite a large amount of $^{13}C-^{1}H$ bonds, rather than the isolated ones, whose effect on the $^{13}C-^{1}H$ dipolar coupling is rather weak. In addition, it is shown that the β transition is broader and more intense in networks prepared in the presence of secondary diamines than in systems with the same crosslink density obtained by using primary monoamines. This result is interpreted in terms of motions that have a higher intramolecular cooperativity than the cooperativity developed in networks incorporating pending hexamethylene units, and a lower spatial extent than the one observed in the densely crosslinked network. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: epoxy resins; dynamic mechanical relaxation; solid-state ^{13}C n.m.r.)

INTRODUCTION

During the past decades, numerous studies have been devoted to the relaxations of epoxy–amine systems in the glassy state. At low temperatures, the γ relaxation has been assigned to motions of the flexible central parts of sufficiently long aliphatic sequences[1], contained either in the diepoxide moiety[2] or in the amine unit[3]. At higher temperatures, the early work of Dammont and Kwei[1] has shown the existence of a large β transition around −60°C. Since the β transition is known to occur whatever the chemical nature of the epoxide or curing agent,[4,5] it has been associated with motions of the $O-CH_2-CHOH-CH_2$ hydroxypropylether units that are present in all these systems[6,7].

However, epoxy networks are known to exhibit a complex chemical structure resulting from the classical addition of epoxy groups onto amine functions. They include unreacted epoxide and amine functions, and hence dangling chains, as well as chemical units due to side reactions. Although the mechanical behaviour is strongly dependent on the details of the chemical structure, in most reported investigations, epoxy networks were not fully characterized. In this respect, the epoxy systems considered in this work, that have well defined chemical structures, are of major interest. The conditions of their synthesis and cure were chosen in such a way that the epoxy–amine reaction was as complete as possible[8] and that no side reaction could be detected at the sensitivity of ^{13}C n.m.r. and *FT*i.r. measurements[9]. Therefore, as a first approximation, the materials under study can be considered as 'model' epoxy networks.

In agreement with previous experiments performed as a function of the stoichiometric ratio[2,10] or curing temperature[3], dynamic mechanical measurements carried out on these 'model' epoxy networks have shown that an increase in the crosslink density induces dramatic effects in the shape of the β transition[11,12]. Moreover, results obtained using the Starkweather analysis[13] have indicated the cooperative character of the local motions involved in the β transition of densely crosslinked networks.

More information on the nature of the local motions was obtained using high-resolution solid-state ^{13}C n.m.r.. On one hand, phenyl ring flips were detected by Garroway *et al.*[14]. However, there was no spontaneous agreement between the mechanical and flip correlation times. The disparity in the results obtained from the two techniques was removed by assuming that the phenylene rings reorient by rotational diffusion with small jump angles. On the other hand, the existence of motions of the hydroxypropylether sequences in the region of the β transition was pointed out[15]. Phenyl

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ring flips and motions of the methylene units of the hydroxypropylether sequences were also observed by ^{2}H n.m.r. experiments on selectively deuterated samples, reported in a very recent paper[16]. They were shown to lie in the envelope of the mechanical β process, with the flips occurring on the lower temperature side of the envelope and the methylene motions occurring in a higher temperature range. However, as indicated by the authors[16], these two motions cannot account for all the relaxations contributing to the β peak.

Although dynamic mechanical analysis, and ^{13}C and ^{2}H n.m.r. are powerful techniques for investigating the local dynamics of glassy polymers, this short overview of reported data leads to the conclusion that the β relaxation of epoxy–amine systems involves a complex mechanism that is not yet fully understood. The respective roles of the aromatic and aliphatic units are not well defined. The nature and extent of the cooperativity have not been characterized. The aim of this work is to address these questions by considering several 'model' networks based on diglycidylether of bisphenol A (DGEBA) and either neat hexamethylene diamine (HMDA), or mixtures of HMDA with various amounts of hexylamine (HA) or dimethylhexamethylenediamine (DMHMDA). The different types of networks thus obtained are represented schematically in *Figure 1*. Since all the systems contain the DGEBA and hexamethylene moieties, they have very much the same chain flexibility at the scale of the repeat unit. The crosslink density is determined by the relative amount of diamine with respect to monoamine. In addition, it is worth noticing that the two latter series of systems have very different architectures. Networks prepared in the presence of HA primary monoamine exhibit pending hexamethylene units, whereas the role of the DMHMDA secondary diamines is to extend the mesh of the networks

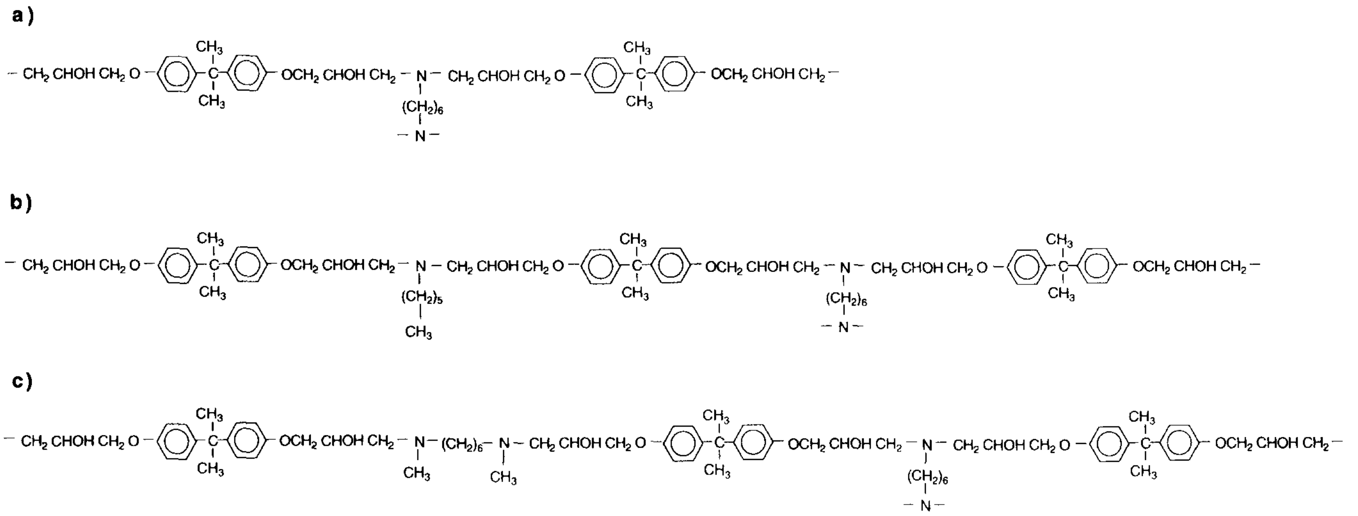


Figure 1 Schematic representation of the different types of networks: (a) DGEBA/HMDA; (b) DGEBA/HA; (c) DGEBA/DMHMDA

Table 1 Characteristics and origins of the chemicals used in this work

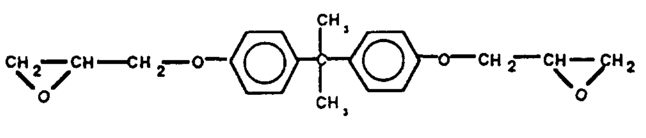
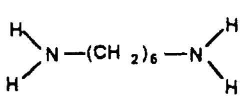
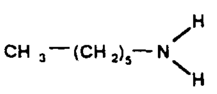
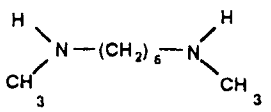
Chemical	Formula	Origin
Diglycidylether of bisphenol A (DGEBA)		Bakelite
Hexamethylene diamine (HMDA)		Aldrich
Hexylamine (HA)		Merck
Dimethyl hexamethylene diamine (DMHMDA)		Aldrich

Table 2 Code names, compositions and glass transition temperatures of the samples

Code name	Mol% of primary diamine	Mol% of primary monoamine	Mol% of secondary diamine	T_g (°C)
DGEBA/HMDA	100	0	0	121
DGEBA/HA60	25	75	0	70
DGEBA/HA95	2.5	97.5	0	56
DGEBA/DMHMDA60	25	0	75	60
DGEBA/DMHMDA95	2.5	0	97.5	32

by inserting flexible units in the chains containing the bisphenol-A residue. The cooperative character of the local dynamics in the region of the β transition will be investigated in the first part of this paper, by analysing the dynamic mechanical behaviour of these systems as a function of the chemical parameters that govern the network architecture (density of crosslinks, pending hexamethylene units, mesh extenders). In the second part, the local motions of the aliphatic and aromatic DGEBA carbons will be studied simultaneously by using different ^{13}C n.m.r. techniques such as measurements of the ^{13}C–^{1}H dipolar couplings, $T_{1\rho}(^{13}\mathrm{C})$ spin-lattice relaxation times in the rotating frame and chemical shift anisotropies. Results thus obtained will then be compared with the conclusions derived from the dynamic mechanical analysis.

EXPERIMENTAL

Materials

Characteristics and origins of the chemicals used in this study are summarized in *Table 1*. The epoxide was RUTAPOX 0162 from Bakelite Co. Its polymerization degree is close to unity. The code names of the different samples, their compositions and glass transition temperatures (measured at the maximum of E'' at 1 Hz) are listed in *Table 2*. The proportions of monoamine and secondary diamine are the same in the DGEBA/HA and DGEBA/DMHMDA systems and, therefore, the comparison of the respective roles of pending groups and chain extenders can be made quantitatively. The two 'quasi-linear' systems (DGEBA/HA95 and DGEBA/DMHMDA95) were preferred to the true linear systems which are brittle materials of rather low degree of polymerization. As indicated in *Table 2*, stoichiometric proportions were systematically maintained between the epoxy and NH groups. In order to have an epoxide–amine reaction as complete as possible, all the samples were cured at 40°C for 12 h, then at $T_g + 30$°C for 24 h. Under these conditions, the diglycidyl ether of bisphenol A does not produce side reactions with amines and the number of unreacted epoxy groups is very low[9].

Mechanical testing

Dynamic mechanical properties of these materials were determined using two different machines:

(i) a servohydraulic testing machine MTS 831.10 operating in tensile mode. A sinusoidal deformation (strain amplitude as small as 0.1%) was superimposed on a static deformation of about 0.1%. The frequency domain covered by the experiments ranged from 0.03 to 80 Hz. Measurements were performed from −90 to 150°C. The sample size was $3 \times 15 \times 40\,\mathrm{mm}^3$.

(ii) a dynamic mechanical analyzer Dupont DMA 983. Experiments covered the frequency range from 0.1 to 2 Hz and temperatures from −150 to 25°C. The applied strain was 0.15% in flexural mode. Samples of about $2 \times 10 \times 40\,\mathrm{mm}^3$ were used.

Viscoelastic experiments performed in the tensile mode yield directly the storage modulus, E', loss modulus, E'', damping, $\tan\delta (= E''/E')$, and the loss compliance $J'' (= E''/[E'^2 + E''^2])$. The flexural data were transformed into E' and E'' by using a routine available on the DMA and a Poisson ratio equal to 0.33 in the glassy state.

N.m.r. experiments

The 75 MHz ^{13}C n.m.r. spectra of the networks were obtained on a Bruker ASX300 spectrometer using the combined techniques of proton dipolar decoupling (d.d.), magic-angle spinning (MAS) and cross-polarization (CP)[17]. ^{13}C and ^{1}H magnetic field strengths of 64 kHz were used for the matched spin-lock cross-polarization transfer. The spinning speed was of the order of 4 kHz.

The $t_{1/2}$ values were obtained at 75 MHz from the variation of the intensities of the different CH or $\mathrm{CH_2}$ lines. The maximum magnetization that can be acquired by cross-polarization, $S_{\max}$, was derived by extrapolating, to zero time, the $T_{1\rho}(^{1}\mathrm{H})$ decrease of the ^{13}C magnetization observed at long contact times. In the rigid lattice, the characteristic times for the coherent and incoherent transfers that participate in the cross-polarization phenomenon are very different. When the ^{13}C–^{1}H dipolar interaction is motionally averaged, the separation between coherent and incoherent transfer may be less clear-cut. To overcome this problem, the time necessary to reach the fourth of the total magnetization, $t_{1/4}$, has been determined and transformed into a $t_{1/2}$ value using the following equation:

$$t_{1/4} = 3/2\, t_{1/2} \qquad (1)$$

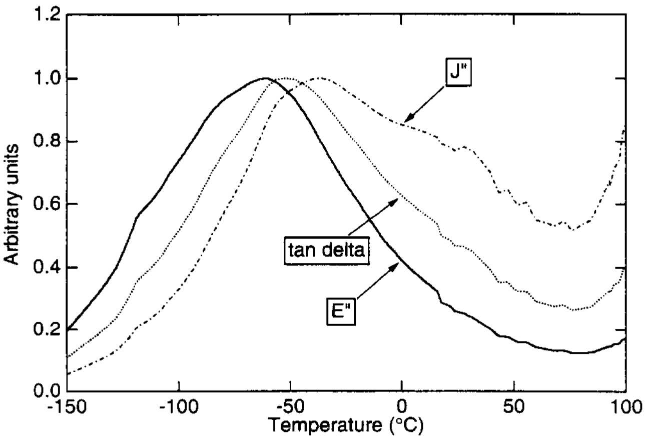


Figure 2 Temperature dependences of E'', $\tan\delta$ and J'' determined at 1 Hz in the DGEBA/HMDA system

Table 3 Characteristics of the transitions of the DGEBA/HMDA, DGEBA/HA60 and DGEBA/HA95 systems

	$T_{\mathrm{beginning}}$ (K)	$E_{\mathrm{a\ beginning}}$ (kJ mol^{-1})	$T_{\max}$ (K)	$E_{\mathrm{a\ max}}$ (kJ mol^{-1})	$T_{\mathrm{end\ of\ peak}}$ (K)	$E_{\mathrm{a\ end\ of\ peak}}$ (kJ mol^{-1})
DGEBA/HMDA	150	36	212	70	277	111
DGEBA/HA60	145	34	199	53	234	80
DGEBA/HA95	140	32	190	50	218	64
	$\Delta H^{\neq}_{\mathrm{beginning}}$ (kJ mol^{-1})	$\Delta S^{\neq}_{\mathrm{beginning}}$ (J mol^{-1} K^{-1})	$\Delta H^{\neq}_{\max}$ (kJ mol^{-1})	$\Delta S^{\neq}_{\max}$ (J mol^{-1} K^{-1})	$\Delta H^{\neq}_{\mathrm{end\ of\ peak}}$ (kJ mol^{-1})	$\Delta S^{\neq}_{\mathrm{end\ of\ peak}}$ (J mol^{-1} K^{-1})
DGEBA/HMDA	35	7	68	95	108	163
DGEBA/HA60	33	3	51	31	78	105
DGEBA/HA95	31	0	48	28	62	58

The accuracy for a $t_{1/2}$ determination is of the order of 0.5 μs.

^{13}C spin-lattice relaxation times in the rotating frame, $T_{1\rho}(^{13}\mathrm{C})$, were measured using the carbon spin-locking sequence described in ref. 18 and recording the ^{13}C magnetization decay as a function of the variable time, Δt, during which the carbons are held in their rotating frame without c.p. contact with the protons. The Δt values used for the $T_{1\rho}(^{13}\mathrm{C})$ determinations ranged from 50 to 500 μs, as proposed by Schaefer *et al.*[18].

The principal values of the chemical shift anisotropy tensor were derived from the relative intensities of the spinning side bands, using Herzfeld and Berger calculations[19].

RESULTS AND DISCUSSION

Dynamic mechanical analysis

The DGEBA/HMDA densely crosslinked network. As indicated in the schematic representation of *Figure 1a*, this system, which is entirely based on the HMDA primary diamine, is the most densely crosslinked system considered in this study. It is known to have a weak γ relaxation around −150°C, due to motions of central methylene groups of the amine moiety, which is not observed under the temperature and frequency conditions of our experiments. Results observed at 1 Hz as a function of temperature for E'', $\tan\delta$ and loss compliance, J'' are shown in *Figure 2*. They show the existence of the broad β transition at low temperatures and of the glass transition phenomenon at temperatures above 100°C. They are in agreement with previous results obtained on densely crosslinked epoxy–amine systems[3,11]. Characteristics of the β transition are listed in *Table 3*. Comparison of the E'', $\tan\delta$ and J'' variations is shown in *Figure 2* where the viscoelastic quantities have been normalized with respect to their maximum value. Although the general shape of the β peak is maintained, the E'', $\tan\delta$ or J'' curves have a temperature shift with respect to each other. Such shifts are inherent to the nature of the viscoelastic quantity considered[20]. In addition, as usually observed in a complex relaxation, the relative importance of the low and high temperature processes depends on the quantity (E'', $\tan\delta$ or J'') which is examined. Low temperature processes occurring in a highly cohesive material are favoured in the E'' representation, whereas high temperature processes are enhanced in the J'' representation, due to the decrease of E' along the transition. The choice of the viscoelastic function that should be used to quantitatively compare different materials is still an open question. However, results obtained by Charlesworth[21] on epoxy–amine networks, as well as data obtained in our laboratory on MMA-based copolymers and semi-aromatic polyamides, indicate that the loss compliance can be considered as the most relevant parameter, at least for additive purposes. Therefore, in the following, the semi-quantitative analysis and the comparison of the viscoelastic data determined for the different systems will be performed in terms of J'', whereas the determination of activation energies associated with the β transition, will be based on loss modulus data.

Figure 3a shows the dependence of the β transition on the test frequency. The plot of the loss modulus vs reciprocal temperature, $1/T$, gives the shifts between the different isochrones. More interestingly, the height of the maximum of the transition increases with the test frequency. This result cannot be interpreted in terms of a single relaxation process, which has no frequency dependence of the height of its maximum. It indicates the existence of several processes having very different activation energies. Indeed, for a high test frequency, the processes that are observed at low temperature and have a relatively low activation energy tend to overlap the higher activation energy processes, so that the observed β peak is narrower and the intensity of its maximum increases with frequency. Therefore, the activation energies determined from the frequency shift of the maximum of the β peak in the densely crosslinked network are apparent activation energies. For qualitative purposes, the activation energies, E_a, have been determined in three different regions of the β transition:

- in the high temperature region corresponding to the last third of the transition (i.e. $E'' < E''_{\max}/3$, $T > T_{\max}$) and in the low temperature region corresponding to the first third of the transition (i.e. $E'' < E''_{\max}/3$, $T < T_{\max}$) by constructing a master curve and assuming an Arrhenius dependence of the shift factors a_{T/T_0}:
$$\ln a_{T/T_0} = E_a/R(1/T - 1/T_0) \qquad (2)$$
- in the middle of the transition by following the frequency dependence of the maximum and assuming that the temperatures T and T_0 at which the maximum of the β peak is observed for test frequencies f and f_0 obey the following relationship:
$$\ln f/f_0 = -E_a/R(1/T - 1/T_0) \qquad (3)$$
The result of the high temperature superposition is shown in *Figure 3b*, where the impossibility of building a master curve over the entire β transition is quite obvious. The three apparent activation energies thus obtained are listed in *Table 3*, together with the activation entropies, $\Delta S\ddagger$, and enthalpies, $\Delta H\ddagger$, derived from the Starkweather analysis[13].
$$\Delta H\ddagger = E_a - RT'$$
$$\text{and } \Delta S\ddagger = E_a - RT'[1 + \ln(kT'/2\pi h)] \qquad (4)$$
where T' is the temperature of the maximum of the β peak observed at 1 Hz.

Low values of the activation entropy can be interpreted in terms of localized motion[22], whereas higher values correspond to cooperative motions[23]. The weak entropy determined at the onset of the β transition indicates that the low-temperature motions are localized, in agreement with results published in a previous paper[11]. As the temperature increases along the β transition, the entropy increases as well and reaches very high values for the high temperature part of the transition. Despite the uncertainty in the determination of activation energies, this enhancement indicates that more and more cooperative motions are taking place with increasing temperature. Therefore, the β relaxation in densely crosslinked networks appears to result from a distribution of motions, ranging from localized modes to increasingly cooperative motions.

Quasi-linear DGEBA/HA95 and loosely crosslinked DGEBA/HA60 systems. As mentioned above, the incorporation of monoamine in the formulation of the reactive mixture leads to the formation of pending hexamethylene units in the network and therefore decreases its crosslink density. The dependences of the loss compliances J'' on temperature are represented in *Figure 4* for the DGEBA/HA60 and DGEBA/HA95 systems. As already noticed in several systems, the width and height of the β transition are decreasing functions of the crosslink density[10–12]. The high temperature part of the transition which corresponds to the more cooperative motions, progressively disappears on decreasing the crosslink density. As shown by the frequency dependence of the β peak plotted in *Figure 5a*, in the quasi-linear DGEBA/HA95 system, there is no significant dependence of the height and width of the transition on the frequency and the master curve can be built over the whole β transition (*Figure 5b*). In the loosely crosslinked DGEBA/HA60 system, the height and width of the transition exhibit a weak dependence with the frequency. These results qualitatively indicate that the distribution of motional modes decreases with decreasing the crosslink density. They are supported by the values of the activation entropies derived from the Starkweather analysis and listed in *Table 3*. The low values calculated at the onset of the transition are independent of the degree of crosslinking and indicate that, for the three systems, comparable localized motions occur at

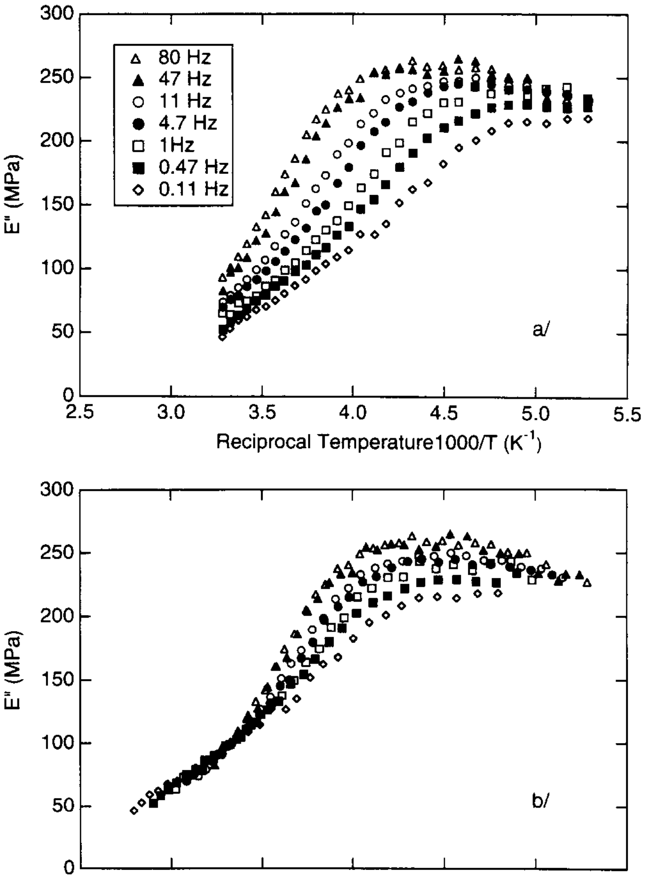


Figure 3 (a) Dependence of E'' as a function of the test frequency in the DGEBA/HMDA system; (b) result of the high temperature superposition

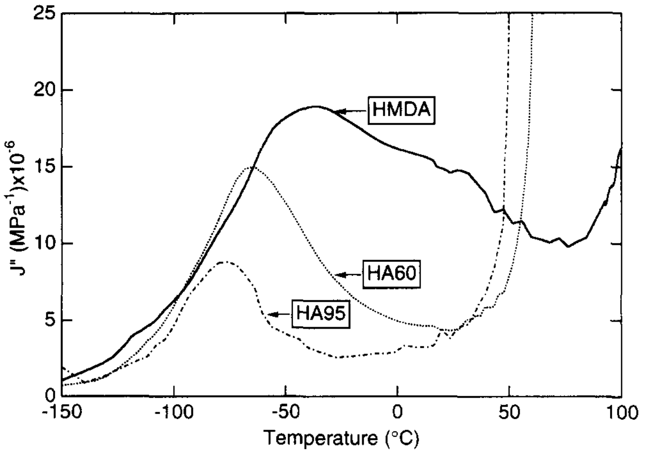


Figure 4 Temperature dependences of the loss compliances J'', determined at 1 Hz, in the DGEBA/HMDA, DGEBA/HA60 and DGEBA/HA95 systems

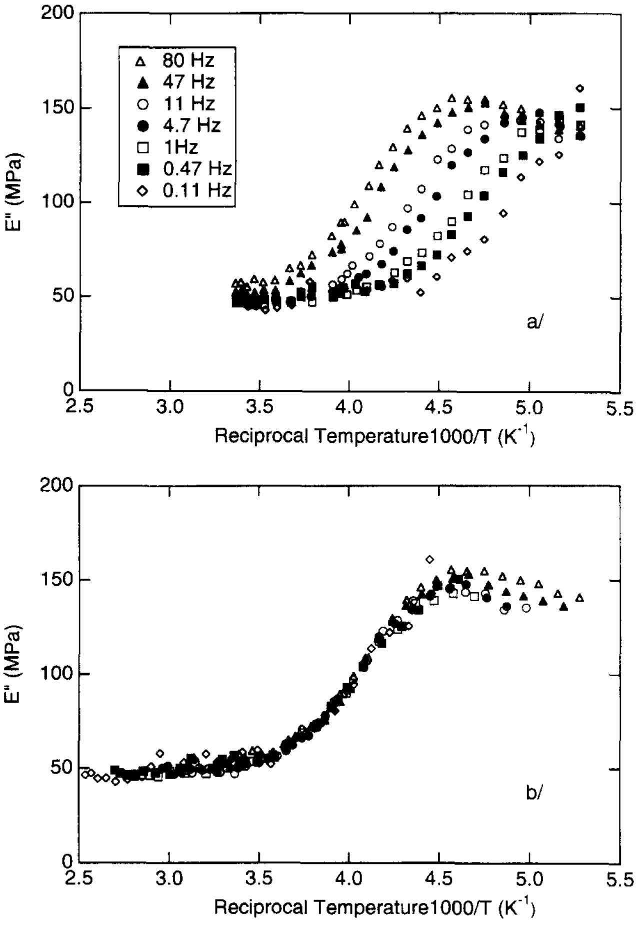


Figure 5 (a) Dependence of E'' as a function of the test frequency in the DGEBA/HA95 system; (b) result of the high temperature superposition

low temperature. In the quasi-linear DGEBA/HA95 system, the activation entropy measured at the upper side of the β peak is 58 J K^{-1}, much smaller than the 163 J K^{-1} activation entropy determined for the densely crosslinked DGEBA/HMDA network. The loosely crosslinked DGEBA/HA60 system has an intermediate behaviour. The same trend is observed for entropies calculated at the maximum of the peak. It emphasized the localized character of the motions involved in the β relaxation of the quasi-linear system.

The above results are a clear indication that the high-temperature part of the β transition in the densely crosslinked network originates from cooperative motions involving the crosslinks. In order to know whether the β transition of the network can be considered as a sum of a simple relaxation due to localized motions (as observed in the quasi-linear system) and a simple relaxation due to cooperative processes of the crosslinks, we have used the quasi-additivity of the compliances, J'', as discussed above. Within this additivity assumption, the relaxation of the DGEBA/HA95 system represents the contribution of the localized modes that are not affected by the presence of the crosslinks. The similarity of the low-temperature parts of the β transition in the three samples corroborates this description.

Figure 6 displays the result of the subtraction of the J'' values, measured at 1 Hz for the quasi-linear sample, from the J'' values determined for the DGEBA/HMDA system, as well as the result of the subtraction of the J'' values of the DGEBA/HA60 system from the J'' values determined for the DGEBA/HMDA system. In this representation, the 'difference' peak between the densely crosslinked and quasi-linear systems is not a simple relaxation; the 'difference' peak between the loosely and densely crosslinked networks is not simple as well. This observation implies that the cooperative part of the relaxation in the densely crosslinked system is made of several processes. This conclusion is supported by the fact that the β transition of the DGEBA/HA60 is not a linear combination of the DGEBA/HA95 and DGEBA/HMDA β transitions. Indeed, the relaxation of the loosely crosslinked network falls to zero at temperatures of the order of 0°C where there are still important mechanical losses in the densely crosslinked materials. This indicates that, rather than adding a single contribution, the increase of the crosslink density permits the development of more and more cooperative processes.

A further insight into the cooperativity of the β processes can be gained by considering the probability of finding N successive crosslinks in the network. In the

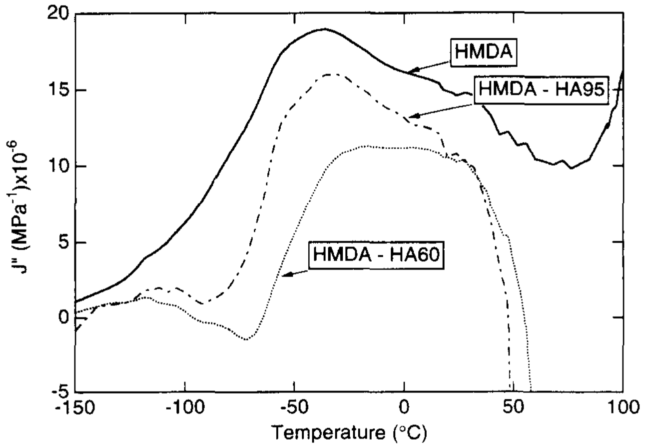


Figure 6 Result of the subtraction of the loss compliances values, J'' (measured at 1 Hz) of the DGEBA/HA95 system, from the J'' values determined for the DGEBA/HMDA system, and result of the subtraction of the J'' values of the DGEBA/HA60 system from the J'' values determined for the DGEBA/HMDA system

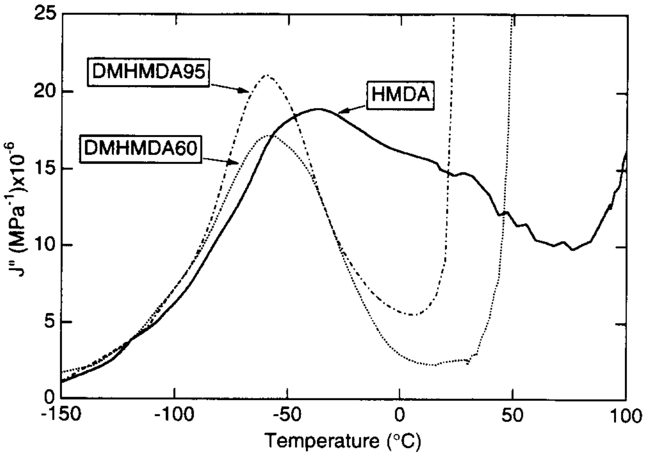


Figure 7 Temperature dependences of the loss compliances, J'', determined at 1 Hz, in the DGEBA/DMHMDA95, DGEBA/DMHMDA60 and DGEBA/HMDA samples

quasi-linear and densely crosslinked systems, the probability of having one crosslink is of the order of 0 and 1, respectively. In the loosely crosslinked DGEBA/HA60 material, the probability of having one crosslink is defined by the hexamethylenediamine content. It is equal to 0.4. Since we are using diamines, the probability of finding a second crosslink point next to the first one is 1. So the probability to find two successive crosslinks in the DGEBA/HA60 sample is 0.4. A third consecutive crosslink has a probability of 0.4 to be next to the arrangement of two crosslinks, in such a way that three consecutive crosslinks have a probability of $0.4^2 = 0.16$. Going further into this process clearly shows that the probability of finding N successive crosslinks drops when N increases and is negligible for $N > 6$ in the DGEBA/HA60 sample. Hence the high-temperature region of the β transition which is observed in the DGEBA/HMDA sample and not in the DGEBA/HA60 sample can be assigned to cooperative motions involving more than six crosslinks. In a forthcoming paper, this result will be compared to the conclusions derived in the presence of additives.

From the semi-quantitative analysis of the viscoelastic data in the three networks considered, it thus appears that:

- the low-temperature region of the β transition mainly results from localized motions that do not involve the crosslinks.
- at higher temperatures, a wide range of cooperative motions can be encountered, involving at least six crosslinks at the end of the β transition of the densely crosslinked DGEBA/HMDA system.

Quasi-linear DGEBA/DMHMDA95 and loosely crosslinked DGEBA/DMHMDA60 systems. The temperature dependences of J'', determined at 1 Hz in the quasi-linear DGEBA/DMHMDA95 and loosely crosslinked DGEBA/DMHMDA60 samples, are plotted in *Figure 7* and compared with data obtained on the densely crosslinked DGEBA/HMDA system. As already mentioned for the networks partly built from hexylamine, the low temperature part of the β transition is independent of the crosslink density, which again indicates that the onset of the transition is due to very localized motions, occurring at the scale of an epoxy–amine repeat unit. As also observed in the monoamine-based systems, the width of the transition is an increasing function of the crosslink density. However, comparison of the DGEBA/DMHMDA95 and DGEBA/HA95 systems, which exhibit the same number of crosslinks, shows that the amplitude of the β peak is higher by a factor of more than two in the DGEBA/DMHMDA95 system than in the DGEBA/HA95 resin.

The frequency dependence of the transition before and after construction of the master curve is plotted in *Figures 8a* and *b*. It shows a strong frequency dependence of the height of the maximum. Results derived from the Starkweather analysis of these transitions are listed in *Table 4*. The activation entropies measured at the low-temperature side of the transition support the localized character of the low-temperature motions. The activation entropy determined at the maximum of the β peak for both the DGEBA/DMHMDA95 and DGEBA/DMHMDA60 systems are higher than those occurring in the monoamine-based systems with equivalent crosslink densities.

All these results can be understood by comparing the chemical architecture of the DMHMDA- and HA-based systems. The DMHMDA secondary diamine plays the role of a mesh extender in the network, whereas the HA primary amine is incorporated in the molecule as a pending chain. The high mechanical losses observed in the secondary diamine-based systems, as well as the frequency dependence of the height of the maximum of

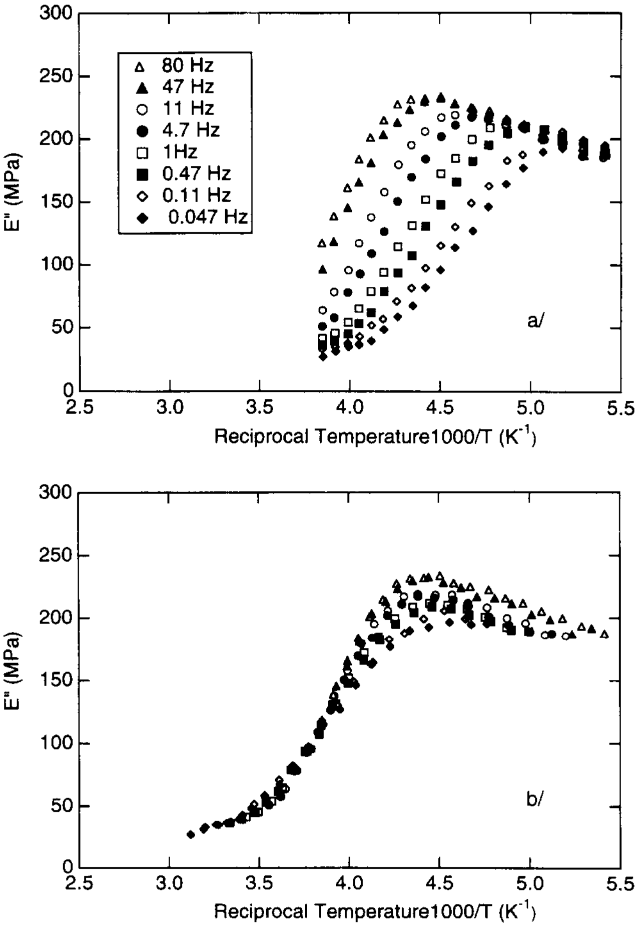


Figure 8 (a) Dependence of E'' as a function of the test frequency in the DGEBA/DMHMDA95 system; (b) result of the high temperature superposition

Table 4 Characteristics of the transitions of the secondary diamine based systems

	$T_{\text{beginning}}$ (K)	$E_{\text{a beginning}}$ (kJ mol^{-1})	$T_{\max}$ (K)	$E_{\text{a max}}$ (kJ mol^{-1})	$T_{\text{end of peak}}$ (K)	$E_{\text{a end of peak}}$ (kJ mol^{-1})
DGEBA/HMDA	150	36	212	70	277	111
DGEBA/DMHMDA60	145	34	205	72	240	85
DGEBA/DMHMDA95	145	35	199	64	235	85
	$\Delta H^{\neq}_{\text{beginning}}$ (kJ mol^{-1})	$\Delta S^{\neq}_{\text{beginning}}$ (J mol^{-1} K^{-1})	$\Delta H^{\neq}_{\text{maximum}}$ (kJ mol^{-1})	$\Delta S^{\neq}_{\text{maximum}}$ (J mol^{-1} K^{-1})	$\Delta H^{\neq}_{\text{end of peak}}$ (kJ mol^{-1})	$\Delta S^{\neq}_{\text{end of peak}}$ (J mol^{-1} K^{-1})
DGEBA/HMDA	35	7	68	95	108	163
DGEBA/DMHMDA60	33	9	70	116	83	118
DGEBA/DMHMDA95	34	3	62	87	83	125

the β peak and the values of the activation entropies, tend to indicate that the presence of the DMHMDA unit located between two epoxy groups allows the development of motions with a larger spatial extent and induces an intramolecular cooperativity along the chain. It differs from the cooperativity induced by the crosslink points, because the chain constraints are much weaker and, therefore, it manifests itself at lower temperatures. As shown by data reported in *Table 4*, the intramolecular cooperativity associated with the chain extender does not seem to be affected significantly by the crosslink density.

At the end of the β peak, the entropies are smaller in the DGEBA/DMHMDA95 and DGEBA/DMHMDA60 systems than in the DGEBA/HMDA network, indicating that cooperativity is likely to have a larger spatial extent when it proceeds from the crosslink points. It thus appears that the secondary diamines lead to an enhancement of the mobility and a development of an intramolecular cooperativity which is more limited than the one observed in the densely crosslinked networks.

N.m.r. investigation of local motions

The DGEBA/HMDA densely crosslinked network. Local motions of the aliphatic units. *Figure 9* shows the 75 MHz high resolution solid-state ^{13}C n.m.r. spectrum of the DGEBA-HMDA network obtained at 80°C with a contact time of 1 ms. The line assignment derived from the ^{13}C n.m.r. chemical shifts of the starting materials and model compounds[9,24,25] may be summarized as follows: the methylene carbons of the central part of the diamine resonate around 30 ppm, close to the resonance of the DGEBA methyl carbons. These two lines are partially resolved above 70°C, yielding two peaks at 28 ppm (DGEBA methyl carbons and HMDA methylene carbon in the γ position with respect to the nitrogen atom) and 32 ppm (HMDA methylene carbon in β position with respect to the nitrogen atom). Two lines arise from the hydroxypropylether sequence: one from the CH_2 directly bonded to the nitrogen at 58 ppm, the other from the $CHOH-CH_2-O$ unit at 70 ppm. The spectrum displays four lines for the

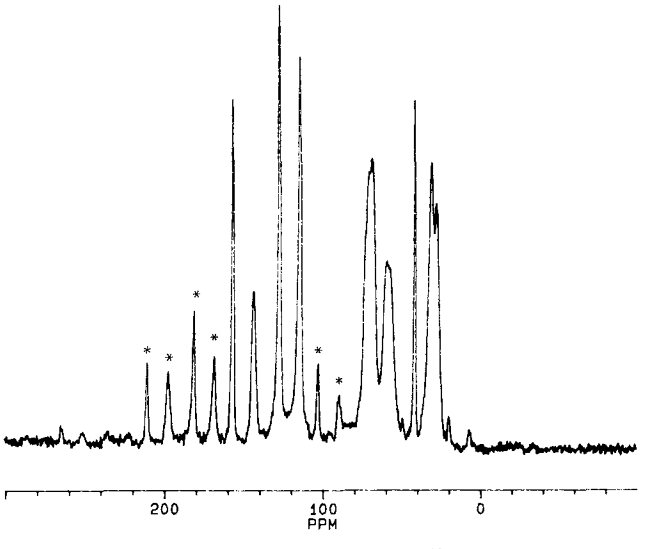


Figure 9 75 MHz high resolution solid-state ^{13}C n.m.r. spectrum of the DGEBA–HMDA network obtained at 80°C with a contact time of 1 ms. Spinning sidebands are indicated by (*)

aromatic part of the DGEBA, at 115 and 130 ppm for the protonated carbons, and 145 and 159 ppm for the unprotonated ones. In the DGEBA/HA60 system, two more lines arise from the hexylamine carbons at 14 and 22 ppm.

In the rigid lattice, protonated aliphatic carbons have a strong dipolar coupling, b^2. In the presence of local motions, the motional averaging of the $^{13}C-^{1}H$ dipolar coupling can be investigated by using $t_{1/2}$ measurements that are based on the rises of the ^{13}C magnetization in cross-polarization experiments with very short contact times[26]. For carbons that are strongly coupled to protons, the rises of polarization are not described by an exponential law. At short contact times, there occurs a coherent energy transfer between the carbon and the directly bonded protons, whereas at longer times, this oscillatory transfer is damped by the coupling with the more remote protons, and an incoherent transfer involving spin diffusion then takes place.

As a result of the coherent energy transfer which is dominant at short contact times, the contact time necessary to obtain half the maximum of the magnetization, $t_{1/2}$, can be expressed as a function of $\langle b^2 \rangle$ and n, the number of directly bonded protons:

$$t_{1/2} = \pi / (n \langle b^2 \rangle)^{1/2} \tag{5}$$

For $r_{CH} = 1.09$ Å and a rigid lattice, $t_{1/2} = 24\,\mu s$ for a CH group and $t_{1/2} = 17\,\mu s$ for a CH_2 group. A reduction in the $^{13}C-^{1}H$ dipolar coupling by motional processes whose frequency is equal or higher than a few tens of kHz corresponds to an increase in the $t_{1/2}$ value[26]. In the following, the ratio $(t_{1/2})_0/t_{1/2} = (\langle b^2 \rangle_0 / \langle b^2 \rangle)^{1/2}$, where $(t_{1/2})_0$ and $\langle b^2 \rangle_0$ refer to room temperature values, will also be considered.

The temperature dependence of the $(t_{1/2})_0/t_{1/2}$ ratio, measured for the $CHOH-CH_2O$ and CH_2-N carbons of the hydroxypropylether sequence in the DGEBA–HMDA sample, are shown in *Figure 10*. The agreement between previous data reported elsewhere[27] and measurements performed in this work is good. The $t_{1/2}$ values obtained for the $CHOH-CH_2-O$ and CH_2-N carbons are constant between room temperature and 60°C. They are equal to 22.5 and 19.5 μs, respectively, which are the rigid-lattice values for these groups. This result indicates that the hydroxypropylether sequence does not undergo any local motions at a frequency equal to or higher than 10^5 Hz in this temperature range. Above 60°C, the $(t_{1/2})_0/t_{1/2}$ ratios are decreasing functions of the temperature for both the $CHOH-CH_2-O$ and CH_2-N carbons. At 100°C, the value of the dipolar coupling is equal to 40% of its room temperature value, indicating the existence of motional processes of the whole hydroxypropylether sequence in the tens of kHz region. As discussed in a previous paper[15], all these results can be interpreted either in terms of rather slow motions with a constant amplitude as a function of temperature or in terms of rapid motions with increasing amplitude.

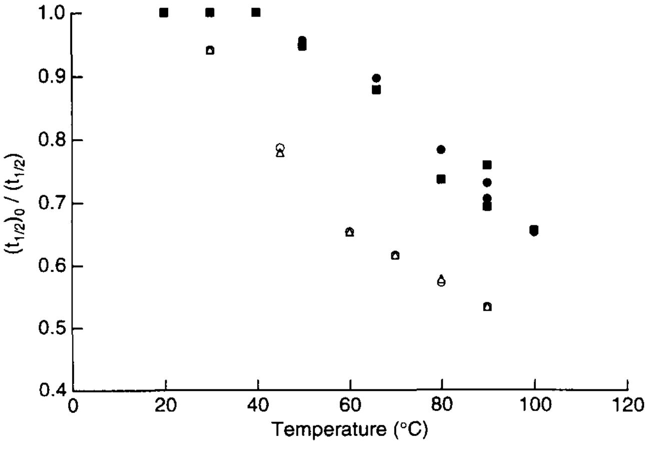


Figure 10 Temperature dependence of the $(t_{1/2})_0/t_{1/2}$ ratio, measured for the $CHOH-CH_2-O$ (●) and CH_2-N carbons (■) of the hydroxypropylether sequence and for the protonated aromatic carbons of the diamine (○, △) in the DGEBA–HMDA sample. Data on aliphatic carbons were partly taken from ref. 15

In addition, the temperature dependence of the ^{13}C spin-lattice relaxation in the rotating frame has been measured for the $CHOH-CH_2-O$ and CH_2-N groups. Results shown in *Figure 11* indicate a parallel increase on temperature of the $T_{1\rho}(^{13}C)$'s of both groups, with a minimum value in the neighbourhood of room temperature. Since the above $t_{1/2}$ measurements have pointed out the existence of motional processes in the tens of kHz region, the $T_{1\rho}(^{13}C)$ relaxation can be considered as originating mainly from spin-lattice processes. The $T_{1\rho}(^{13}C)$ spin-lattice relaxation undergoes a minimum at the frequency of the RF field, ω_{1C}, i.e. 64 kHz. Therefore, data reported in *Figure 11* can be interpreted in terms of motions with frequencies higher than 64 kHz above room temperature, in good qualitative agreement with conclusions derived from the $t_{1/2}$ measurements.

Local motions of the aromatic units. As shown in previous papers[14,27], at very low temperature, the DGEBA aromatic rings are immobile and the carbons in *ortho* position with respect to the C–O bond are magnetically inequivalent, yielding two resolved lines with a separation of 7 ppm. At room temperature, these lines have merged into a single line, implying that a site exchange between these sites takes place at a rate higher than the frequency derived from the chemical shift difference of the two peaks.

The orientation of the principal axes of the chemical shift tensor is shown in *Figure 12* for an aromatic carbon.

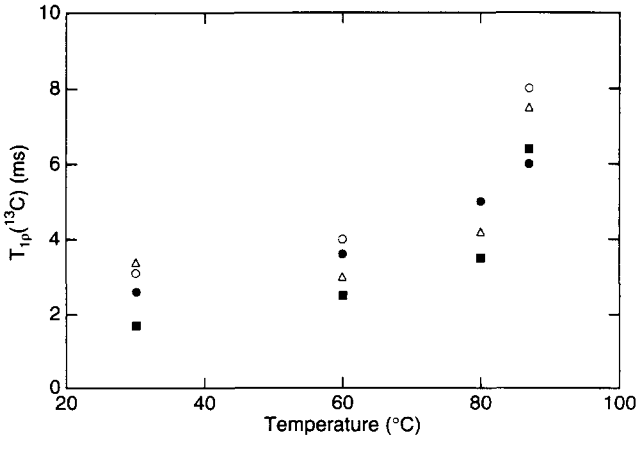


Figure 11 Temperature dependence of the ^{13}C spin-lattice relaxation times in the rotating frame: (△, ○): protonated aromatic carbons; (●) $CHOH-CH_2-O$ carbons; (■) CH_2-N carbons

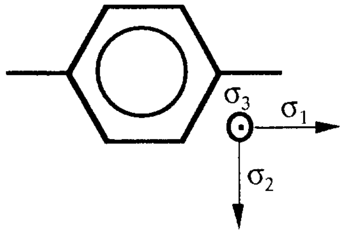


Figure 12 Orientation of the principal axes of the chemical shift tensor for a *para*-substituted aromatic carbon

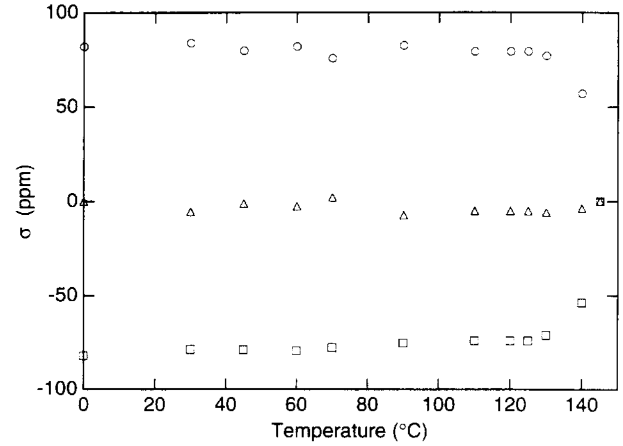


Figure 13 Temperature dependence of the principal values of the chemical shift tensor determined for the unprotonated carbon resonating at 159 ppm: (□) σ_{11}; (△) σ_{22}; (○) σ_{33}

As shown in *Figure 13* for the unprotonated carbon resonating at 159 ppm, the principal values of the chemical shift tensor do not change on increasing temperature until the glass transition temperature. The same behaviour was obtained for the unprotonated carbon resonating at 145 ppm. This result is consistent with the existence of π-flips which do not average the chemical shift anisotropy of the unprotonated carbons.

Results of $t_{1/2}$ measurements performed as a function of temperature for the two protonated aromatic carbons are shown in *Figure 10*. For both carbons, the room temperature $t_{1/2}$ is 26 μs, close to the rigid-lattice value. The agreement with the ring flip frequency derived from the site exchange analysis is good, considering that flips with an approximate frequency of 10^3 Hz do not significantly average the $^{13}C-^{1}H$ dipolar coupling. At higher temperatures, the $(t_{1/2})_0/t_{1/2}$ values indicate a partial averaging of the $^{13}C-^{1}H$ interaction, similar for the two carbons considered and consistent with the π-flips observed in the site exchange analysis. It must be noticed that this motional averaging occurs in the same temperature range as the hydroxypropylether motion.

$T_{1\rho}(^{13}C)$ measurements, performed on the protonated aromatic carbons as a function of temperature, are plotted in *Figure 11*. As already observed in the $t_{1/2}$ measurements, the ring carbons and hydroxypropylether groups show parallel behaviours, consistent with the existence of ring motions of frequency comparable to the RF field ω_{1C} at temperatures of the order of 70°C.

Comparison with results obtained from dynamic mechanical measurements. The $t_{1/2}$ and $T_{1\rho}(^{13}C)$ measurements, which reflect the motional modulation of the $^{13}C-^{1}H$ dipolar coupling, are sensitive to molecular motions with a frequency equal to or higher than a few tens of kHz. Therefore, the low frequency results obtained by dynamic mechanical measurements have to be extrapolated to a frequency of the order of 0.1 MHz, i.e. at least over five decades in frequency. Besides, the measurements of the activation energy are quite inaccurate, especially when different processes overlap. Therefore, a precise determination of the temperature at which a given mechanical relaxation can manifest itself in n.m.r. measurements cannot be made. Moreover, as indicated above, the exact nature of the motions reflected by the averaging of the $^{13}C-^{1}H$ dipolar coupling, either restricted motions of high frequency or large amplitude motions with lower frequency, is not well understood. Under these conditions, only general trends will be discussed in the following.

It has been shown in a previous paper[15] that the rapid reorientation of the methylene units of the central part of the diamine can be related to the γ relaxation of the epoxy networks. This is in good agreement with conclusions derived from dynamic mechanical analysis[2,3]. As a result of the complexity of the β relaxation, the extrapolated temperatures cover quite a broad range: for a frequency of 0.1 MHz, the calculated values are equal to −23°C for the lower temperature processes, 26°C at the maximum of the β peak, and 90°C for the high temperature part of the transition. As a matter of fact, the onset of mobility, as observed from the $t_{1/2}$ and $T_{1\rho}(^{13}C)$ measurements performed on the CHOH–CH_2–O and CH_2–N groups, occurs in the upper part of this range. This result is consistent with previous assignments of the β relaxation to motional processes of the hydroxypropylether sequence[2,6,7,10,11,15]. Moreover, the parallel behaviour of the CHOH–CH_2–O and CH_2–N groups, observed in the n.m.r. experiments tends to show that the crosslink points are involved in the motional processes. This last point, as well as the precise temperature of the n.m.r. onset of mobility, indicate that the sensitivity of the n.m.r. experiments allows it to probe the cooperative motions rather than the isolated ones. This conclusion is also in agreement with results obtained by Shi *et al.* using ^{2}H n.m.r. on selectively deuterated samples[16], which show that the methylene unit motions lie within the central part of the β transition where the cooperative motions have been shown to occur.

It is also of interest to discuss the role of the DGEBA phenyl groups in the β transition of epoxy networks. The mechanical activity of the ring flips is still an open question. As an example, in polycarbonate, which also contains the bisphenol-A residue, numerous studies tended to show that the π-flips of the phenyl rings are involved in the secondary transition of this polymer, in relation with the chain packing[28–30]. Comparison of data reported in *Figure 10* shows that the ring motions in epoxy networks are detected at a lower temperature than the reorientation of the hydroxypropylether sequences. This observation is in good agreement with the results of the ^{2}H n.m.r. experiments performed by Shi *et al.*[16], which indicate that the phenyl flips correspond to the low temperature side of the β transition of epoxy networks. However, dynamic mechanical experiments carried out on epoxy networks that do not contain any aromatic unit show that the shape of the low temperature side of the β

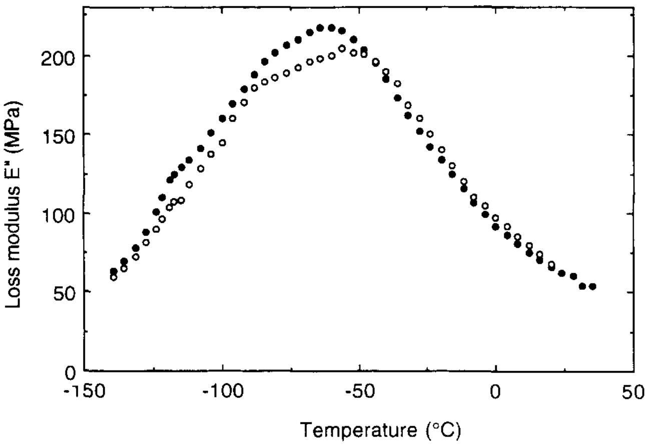


Figure 14 Comparison of the temperature dependences of E'', determined at 1 Hz, for the DGEBA/HMDA (●) and DGERO/HMDA (○) systems

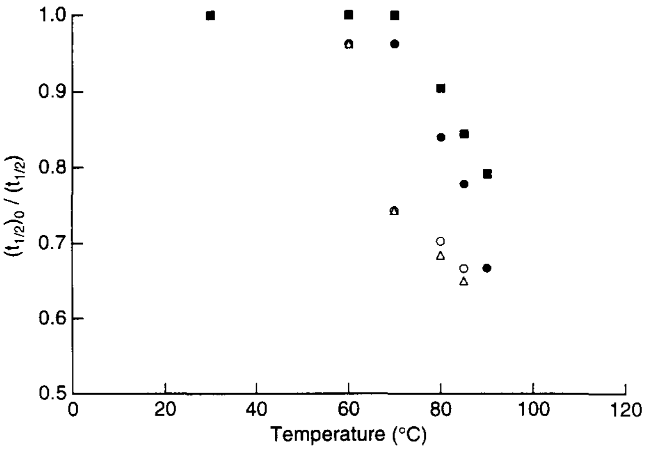


Figure 15 Temperature dependence of the $(t_{1/2})_0/t_{1/2}$ ratio, measured for the CHOH–CH_2–O (●), CH_2–N (■), and protonated aromatic (○, △) carbons in the DGEBA–HA60 sample

transition is identical in the aromatic and aliphatic resins[31]. Besides, as shown in *Figure 14*, the system based on HMDA and diglycidyl ether of resorcinol (DGERO)[32], whose *meta*-substituted rings do not flip, has the same mechanical spectrum as the DGEBA/HMDA system in the low temperature part of the β transition. Therefore, in spite of the good temperature agreement between the two phenomena, the assignment of the low temperature side of the β transition to π-flips of the phenyl rings only is not a reasonable assumption.

It must be noticed that both the n.m.r. experiments reported in the present paper and those performed by Shi *et al.*[16] indicate that, although the flip process is faster than the reorientation of the hydroxypropylether sequences, the motions of the rings and hydroxypropylether sequence share very similar temperature dependence. A likely conclusion to this observation is that the motions of these two parts of the molecule occur in a partly correlated way. This may be due to the fact that, in the DGEBA phenyl rings, as well as in the bisphenol-A units of polycarbonate, the steric hindrance is so high that some ring flips cannot occur without a slight increase of the bond angle between the two rings. Such a process could be associated with the motions of the oxygen atoms next to the phenyl ring and, therefore, with those of the hydroxypropylether sequences. Indeed, it induces a correlation between the ring flips and the reorientation of the hydroxypropylether groups. In such a description, ring flips would be indirectly coupled to the mechanical losses. This result is supported by the weaker intensity of the β transition observed in DGERO/HMDA at the same crosslink density[32].

Loosely crosslinked DGEBA/HA60 system. Local motions of the aliphatic units. At room temperature, the $t_{1/2}$s determined for the CHOH–CH_2–O and CH_2–N units are, respectively, 21 and 19 μs. They are close to the rigid-lattice values. The temperature dependence of the $(t_{1/2})_0/t_{1/2}$ ratios, shown in *Figure 15*, indicates a reduction of the strength of the dipolar coupling, and hence, an onset of mobility, around 70°C for the CHOH–CH_2–O unit and 80°C for the CH_2–N. In contrast with results obtained in the densely crosslinked network, the temperature dependence of the two groups is not strictly parallel, indicating that the methylene carbons directly bonded to the crosslinks are slightly less mobile than the CHOH–CH_2–O units.

Local motions of the aromatic units. The room temperature $t_{1/2}$s determined for the protonated carbons of the phenyl rings are equal to 26 μs and can be considered as rigid-lattice values. The temperature dependence of the $(t_{1/2})_0/t_{1/2}$ ratios is plotted in *Figure 15*. As previously observed for the hydroxypropylether group, the onset of mobility occurs around 70°C, indicating the existence of ring motions, with frequencies equal to or higher than 10^5 Hz, that are likely to be correlated with the reorientations of the hydroxypropylether units.

Comparison with dynamic mechanical results. The extrapolation to 0.1 MHz of the different processes characterized in the mechanical analysis of the β relaxation leads to −28°C for the lower temperature processes, 38°C at the maximum of the β peak and 52°C for the high-temperature cooperative motions. The decrease in the ^{13}C–^{1}H dipolar coupling strength, observed around 70°C in the hydroxypropylether units, roughly corresponds to the most cooperative motions taking part in the β transition of this system. The onset of mobility of the CH_2–N units appears at still higher temperature, which tends to indicate that the nitrogen atoms of the diamine or monoamine moieties are less involved in the β process in the loosely crosslinked network than in the densely crosslinked network. This point is in good agreement with results derived from the dynamic mechanical analysis, that have pointed out a larger cooperativity of the β relaxation in the densely crosslinked network. It is also interesting to note that, although the extrapolated temperatures are lower for the loosely crosslinked material than for the densely crosslinked system, the onset of mobility, as observed by n.m.r., occurs at a higher temperature in the loosely crosslinked network. This observation may be related to the extent of the cooperative motions in the β transition of the two networks. As shown by the dynamic mechanical analysis, the β transition results from a distribution of motional modes, involving an increasing number of units, and hence an increasing activation energy, on increasing temperature. At the high frequency of the n.m.r. experiments, all these processes, either localized or cooperative, tend to merge. Due to the less constrained chain structure, there are less cooperative motions in a loosely crosslinked network than in the densely crosslinked network, which is indeed the result observed in the $t_{1/2}$ experiments. As will be shown in a forthcoming paper, the description also applies to epoxy networks in presence of antiplasticizing additives.

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