

# High-resolution solid-state $^{13}\text{C}$ nuclear magnetic resonance investigation of local motions in model epoxy resins

Françoise Lauprêtre\*, René-Paul Eustache and Lucien Monnerie

*Laboratoire de Physicochimie Structurale et Macromoléculaire associé au CNRS, ESPCI,  
10 rue Vauquelin, 75231 Paris cedex 05, France*

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The local dynamics of some 'model' epoxy networks based on various diepoxides and diamines was investigated in the bulk state using high-resolution solid-state  $^{13}\text{C}$  nuclear magnetic resonance. The strength of the  $^{13}\text{C}$ – $^1\text{H}$  dipolar coupling was determined from the rises of  $^{13}\text{C}$  magnetization in cross-polarization experiments using very short contact times. A restricted motional averaging of the  $^{13}\text{C}$ – $^1\text{H}$  dipolar coupling was observed below the glass transition temperature for the hydroxypropyl ether groups and methylene carbons adjacent to the crosslinks, indicating the existence of local motions of these units in the tens of kilohertz range. The extent and temperature dependence of the motional averaging depend on the chemical structure of the epoxy network considered. Comparison with results derived from dynamic mechanical experiments leads to the conclusion that the motions of the hydroxypropyl ether groups are likely to participate in the phenomena responsible for the  $\beta$  secondary relaxation. Moreover, the relatively high mobility of the central methylene units in the aliphatic sequences of the diglycidyl ether of the butanediol-based network, and of the hexamethylenediamine-based network, can be associated with the  $\gamma$  relaxation of epoxy networks.

(Keywords: epoxy resins; solid-state  $^{13}\text{C}$  n.m.r.; local motions)

## INTRODUCTION

Epoxy networks, built up from diepoxides and diamines, are materials that are largely used as matrices of composite materials. In the last decade, numerous studies have been devoted to the dependence on the chemical structure of the viscoelastic properties<sup>1–12</sup>. However, such studies dealt essentially with commercial networks, the structures of which are not well defined. Indeed, a number of different chemical reactions are known to occur during the curing of epoxy–amine systems. It has been shown that, besides the classical addition of amine functions to epoxy groups, other reactions involving the addition of secondary alcohol functions to the epoxy functions, or homopolymerization of epoxy functions, may occur<sup>13</sup>. In addition, the crosslink density varies as a function of the diamine/epoxy ratio and the curing conditions. Therefore, depending on the exact preparation conditions, epoxy–amine resins may take quite different chemical formulae.

The epoxy resins considered in this work are well characterized materials whose preparation, chemical structure and dynamic mechanical properties have been described elsewhere<sup>11,12,14</sup>. Stoichiometric proportions were systematically maintained between the epoxide and the N–H groups, and a post-curing step was performed to yield an epoxy–amine reaction as complete as possible. Moreover, high-resolution solid-state  $^{13}\text{C}$  n.m.r. and FTi.r. spectroscopy have shown that, at the sensitivity

of the experiments, the considered networks result from the dominant epoxy–amine reactions only. Therefore, as a first approximation, the materials under study can be considered as 'model' epoxy networks.

In order to study the role of chain flexibility on the dynamic mechanical properties of epoxy networks, these 'model' networks were based either on the diglycidyl ether of bisphenol A (DGEBA), whose central aromatic unit is rigid, or on the more flexible aliphatic diglycidyl ether of butanediol (DGEBU). Use of different types of diamines (hexamethylenediamine (HMDA), isophorone diamine (IPD) and 4,4'-diaminodiphenylmethane (DDM)) also facilitated the variation of the chain flexibility. As examples, the chemical structure of the DGEBA/HMDA and DGEBU/DDM systems are schematized in *Figure 1*. All these diamine-based networks are densely crosslinked networks. For comparison purposes, mixtures of 75 mol% hexylamine (HA) and 25 mol% hexamethylenediamine were used to produce loosely crosslinked networks without significant modification of the chain flexibility with respect to the HMDA cured system.

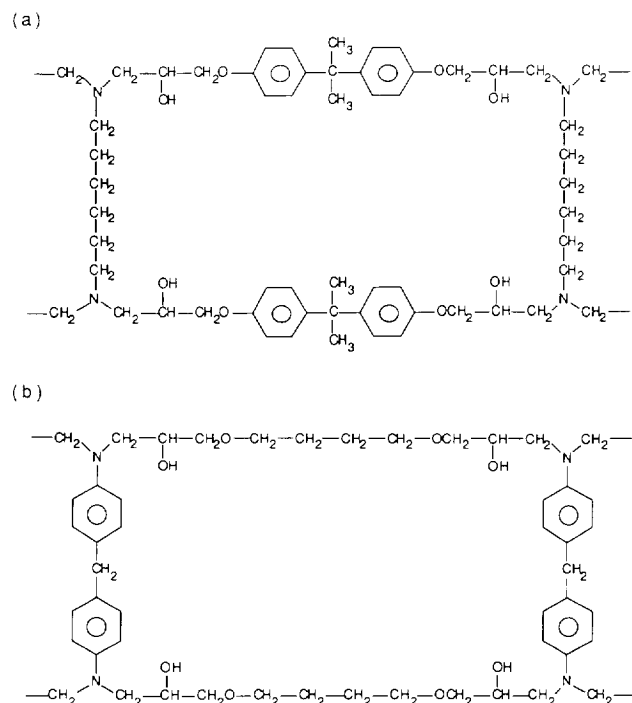
In addition to the glass transition temperature,  $T_g$ , which depends markedly on the chain flexibility and crosslink density, epoxy–amine networks may exhibit  $\gamma$  and  $\beta$  secondary relaxation processes well below the  $T_g$ . It has been shown that the existence of the  $\gamma$  relaxation is restricted to epoxy networks containing long enough aliphatic sequences either in the diepoxide moiety<sup>9</sup>, as, for instance, in DGEBU-based resins, or in the amine unit, as, for example, in hexamethylenediamine-based

\*To whom correspondence should be addressed

systems<sup>5,9</sup>. In contrast, the  $\beta$  relaxation is observed in diepoxide-based networks whatever the chemical nature of the epoxide, DGEBA or DGEBU, or of the curing agent.

The molecular origin of the  $\beta$  relaxation in epoxy-amine networks, however, is still an open question. On the one hand, mechanical measurements performed on a series of resins built from different types of amine and epoxy units have led to the conclusion that this secondary transition is due to the motion of the hydroxypropyl ether group<sup>2,4,9</sup>. On the other hand, high-resolution solid-state  $^{13}\text{C}$  n.m.r. experiments<sup>15</sup> have pointed out the existence of phenyl ring motions in a frequency range comparable with that of the  $\beta$  process.

However, until now, no direct evidence of the specific motions of the aliphatic units has been obtained by this technique. The purpose of this paper, therefore, is to exploit the selectivity of the n.m.r. technique to follow the increase in mobility of the different aliphatic units as a function of temperature. Among the numerous n.m.r. parameters that are sensitive to molecular motions—relaxation times, spectrum lineshape, strength of the dipolar coupling and chemical-shift anisotropy—the motional averaging of the  $^1\text{H}$ – $^{13}\text{C}$  dipolar coupling is the most relevant parameter for investigating the local dynamics of the aliphatic units. The results thus obtained are then compared with the characteristics of the  $\beta$  process derived from dynamic mechanical measurements in all the epoxy-amine systems under study.



**Figure 1** Schematic representation of the densely crosslinked DGEBA/HMDA (a) and DGEBU/DDM (b) networks

## EXPERIMENTAL

### Materials

Characteristics and origins of the chemicals used in this study are summarized in *Table 1*. The epoxy-amine networks were prepared as described in ref. 14. The DGEBA/IPD system was kindly supplied by J. F. Gérard from the Institut National des Sciences Appliquées de Lyon. Stoichiometric proportions were systematically maintained between the epoxide and the NH groups. A post-curing step at 30°C above the glass transition temperature was performed to yield an epoxy-amine reaction as complete as possible. Under the above conditions, the diglycidyl ethers of bisphenol A and butanediol do not produce side reactions with amines and the number of unreacted epoxy groups is quite low<sup>14</sup>.

The glass transition temperatures, as determined from d.s.c. traces, are listed in *Table 2* for the different polymers studied.

### N.m.r. experiments

The 75 MHz  $^{13}\text{C}$  n.m.r. spectra of the resins were obtained on a Bruker CXP 300 spectrometer, using the combined techniques of proton dipolar decoupling (d.d.), magic-angle sample spinning (m.a.s.) and cross-polarization (c.p.)<sup>16</sup>.  $^{13}\text{C}$  and  $^1\text{H}$  magnetic field strengths of

**Table 1** Epoxy prepolymers and amines used for the synthesis of epoxy networks

Product	Chemical formula	Origin
4,4'-Diaminodiphenylmethane (DDM)		Fluka
Hexamethylenediamine (HMDA)	$\text{H}_2\text{N}-(\text{CH}_2)_6-\text{NH}_2$	Merck
Hexylamine (HA)	$\text{CH}_3-(\text{CH}_2)_5-\text{NH}_2$	Merck
Isophorone diamine (IPD)		Hüls
Diglycidyl ether of bisphenol A (DGEBA)		Bakelite Rutapox 0162
Diglycidyl ether of butanediol (DGEBU)		CIBA DY026SP

**Table 2** Glass transition temperatures (as measured by d.s.c.) of the epoxy networks

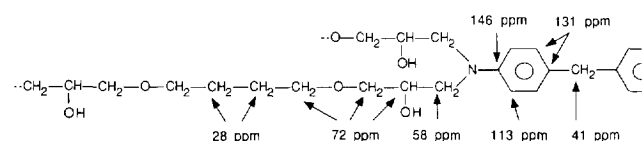
Epoxy network	$T_g$ (°C)
DGEPU/DDM	76
DGEBA/HMDA	118
DGEBA/DDM	184
DGEBA/IPD	164
DGEBA/HMDA/HA	63.5

60 kHz were used for the matched spin-lock cross-polarization transfers. The spinning speed was of the order of 4 kHz. Spin-inversion techniques were used to minimize baseline noise and roll<sup>17</sup>. Flip-back<sup>18</sup> was also used to shorten the delay time between two successive pulse sequences.

The  $t_{1/2}$  values were obtained at 75 MHz from the variation of the intensities,  $S(t)$ , of the  $-\text{O}-\text{CH}_2-\text{CHOH}-$  and  $-\text{CH}_2\text{N}-$  lines as a function of the contact duration,  $t$ . Overlap of the spinning sidebands of the aromatic carbons with these lines was avoided as much as possible. The maximum magnetization that can be acquired by cross-polarization,  $S_{\text{max}}$ , was either approximated as the maximum of the  $S(t)=f(t)$  curve or derived exactly by extrapolating, to zero time, the  $^1\text{H}$   $T_{1\rho}$  decrease of the  $^{13}\text{C}$  magnetization observed at long contact times. Comparison of results obtained by the two methods at both low and high temperatures showed that, for the epoxy-amine resins under study, the approximation of  $S_{\text{max}}$  as the maximum of the  $S(t)=f(t)$  curve leads to a systematic  $t_{1/2}$  underestimation of the order of 10%, but does not induce any change in the relative  $t_{1/2}$  variations as a function of the temperature or material under study. The results described in this paper were obtained using this latter approximation.

## RESULTS AND DISCUSSION

As an example, the 75 MHz high-resolution solid-state  $^{13}\text{C}$  n.m.r. spectrum of the DGEPU/DDM system at room temperature is shown in Figure 2. The line assignment, based on the  $^{13}\text{C}$  n.m.r. chemical shifts of the starting materials and compounds obtained from model reactions<sup>14,19,20</sup>, is summarized below:



In the present paper, the lines of interest for the different samples considered are the 72 ppm region, corresponding to the  $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CHOH}-$  carbons resulting from the dominant epoxy-amine addition, and the 58 ppm region, assigned to the  $\text{CH}_2$  groups adjacent to the crosslinks. In the DGEBA/IPD resin, the broad 58 ppm peak due to the two magnetically inequivalent  $\text{CH}_2\text{N}$  carbons splits into two poorly resolved resonances at 55 and 63 ppm at temperatures above 70°C. The behaviour of the central methylene carbons of the DGEPU and HMDA units of the DGEPU/DDM and DGEBA/HMDA samples, respectively, are also considered. These carbons

resonate at 28 ppm in the DGEPU/DDM network. In the DGEBA/HMDA system, however, the more shielded carbons of HMDA and the DGEBA methyl carbons yield overlapping lines at temperatures below 52°C. Above 52°C, nevertheless, two peaks at 28 and 32 ppm appear separately. The 32 ppm line arises from the resonances of the DGEBA methyl carbons and the HMDA methylene carbons in  $\beta$  position with respect to the nitrogen atom, while the 28 ppm line may be assigned to the resonance of the HMDA methylene carbons in  $\gamma$  position with respect to the nitrogen atom, that is, the HMDA central methylene carbons.

### N.m.r. investigation of the local motions of the aliphatic units

As indicated above, the specific motions of the aliphatic units were studied by following the motional averaging of the  $^1\text{H}-^{13}\text{C}$  dipolar coupling as a function of temperature.

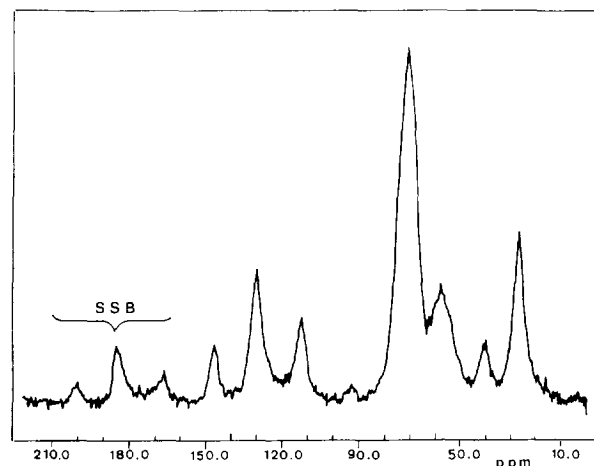
For a powder, the  $^{13}\text{C}-^1\text{H}$  dipolar interaction may be expressed as:

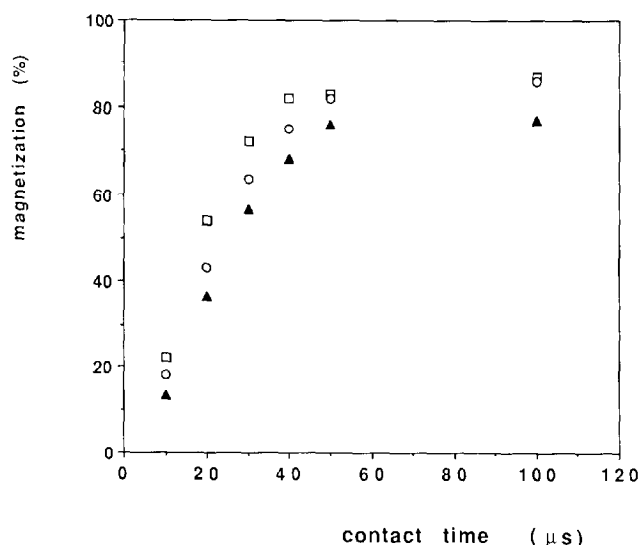
$$\langle b^2 \rangle = \frac{4}{3} (\gamma_C \gamma_H \hbar / r_{\text{CH}})^2 \quad (1)$$

where  $r_{\text{CH}}$  is the carbon-proton distance.

Essentially two techniques<sup>21,22</sup> have been proposed for determining  $\langle b^2 \rangle$ . The first method consists in measuring the intensity of the dipolar sideband patterns, obtained from dipolar rotational spin-echo  $^{13}\text{C}$  n.m.r. and arising from the heteronuclear dipolar interaction, while the homonuclear  $^1\text{H}-^1\text{H}$  dipolar interactions are suppressed by multiple-pulse  $^1\text{H}-^1\text{H}$  (WAHUA) decoupling.

The strength of the  $^{13}\text{C}-^1\text{H}$  dipolar coupling can be deduced by a second method from the rises of  $^{13}\text{C}$  magnetization in cross-polarization experiments<sup>21</sup>. When  $^1\text{H}-^1\text{H}$  homonuclear dipolar interactions are much stronger than  $^{13}\text{C}-^1\text{H}$  heteronuclear dipolar interactions, the increase in magnetization, as a function of the contact time, is mainly exponential and its rate,  $T_{\text{CH}}(\text{SL})^{-1}$ , can be calculated exactly<sup>23</sup>. In contrast, when carbons are strongly coupled to protons, the rises of polarization can no longer be described by an exponential law. At the very beginning of the contact, there occurs a coherent energy transfer between the carbon of interest and the strongly coupled protons. This oscillatory transfer is

**Figure 2** The 75 MHz high-resolution solid-state  $^{13}\text{C}$  n.m.r. spectrum of the DGEPU/DDM system at room temperature



**Figure 3** Increases of  $^{13}\text{C}$  magnetization as a function of the contact time for the different aliphatic carbons of the DGEBA/DDM system: (○)  $-\text{CH}_2\text{OCH}_2\text{CHOH}-$  groups; (□)  $-\text{CH}_2\text{N}-$  carbons; (▲) DGEBA central methylene units

damped by the coupling with the more remote protons. For very short contact times, the carbon and its  $n$  strongly coupled protons can be considered as an isolated  $\text{CH}_n$  system. At the end of a very short contact time,  $t$ , the magnetization  $M(t)$  can be described by an oscillatory function whose expression is deduced from results obtained for a C-H group<sup>24</sup> and extended to  $\text{CH}_2$  groups by using the calculation for the magnetization in liquid  $\text{AX}_n$  systems<sup>25</sup>:

$$M(t)/M(\infty) = \sin^2[(n\langle b^2 \rangle)^{1/2}t/4] \quad (2)$$

Therefore,  $\langle b^2 \rangle$  can be estimated in a very simple way by measuring the contact time  $t_{1/2}$  necessary to obtain half the maximum polarization,  $M(\infty)$ :

$$(\langle b^2 \rangle)^{1/2} = \pi/n^{1/2}t_{1/2} \quad (3)$$

For  $r_{\text{CH}} = 1.09 \text{ \AA}$ ,  $t_{1/2} = 24 \mu\text{s}$  for a rigid CH group and  $t_{1/2} = 17 \mu\text{s}$  for a rigid  $\text{CH}_2$  group. For the carbons of the  $-\text{CH}_2\text{OCH}_2\text{CHOH}-$  sequence of the DGEBA/DDM system, the calculated rigid-lattice  $t_{1/2}$  is  $22 \mu\text{s}$ . Experimental  $t_{1/2}$  values longer than these rigid-lattice values are evidence of a reduction in the  $^{13}\text{C}$ - $^1\text{H}$  dipolar coupling by motional processes whose frequencies are higher than a few tens of kilohertz<sup>21</sup>.

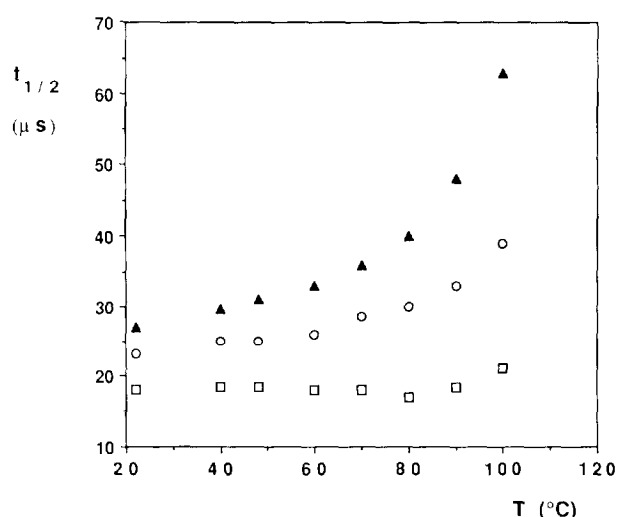
#### Local motions of the hydroxypropyl ether groups

As an example, the increases in the  $^{13}\text{C}$  magnetization with very short contact times in the cross-polarization experiments are shown in Figure 3 for the protonated carbons of interest ( $-\text{CH}_2\text{OCH}_2\text{CHOH}-$  groups,  $-\text{CH}_2\text{N}-$  carbons, DGEBA central methylene units) in the DGEBA/DDM system at room temperature. As a result of the coherent energy transfer described by equation (2), the  $^{13}\text{C}$  magnetization increases very rapidly during the first  $50 \mu\text{s}$  of the contact. At longer contact times, it approaches its maximum value at a much lower rate. Such a two-step behaviour of the protonated carbons was observed for all the systems considered below their glass transition temperature.

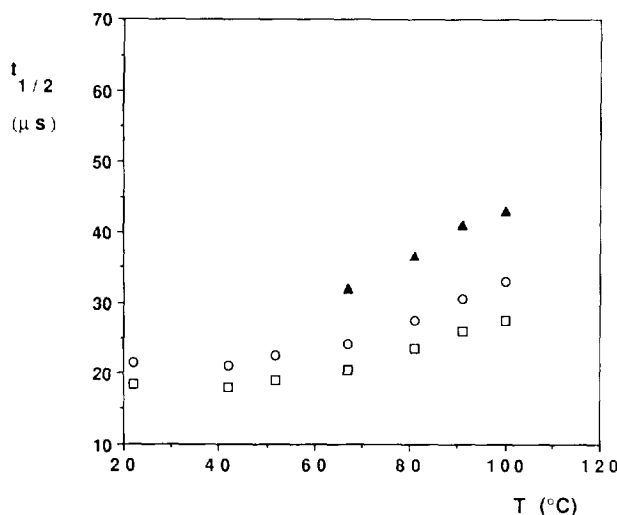
The  $t_{1/2}$  temperature dependence, determined for the

different aliphatic carbons of the DGEBA/DDM system, is shown in Figure 4. At temperatures between 20 and  $60^\circ\text{C}$ , the  $t_{1/2}$  of the  $-\text{CH}_2\text{OCH}_2\text{CHOH}-$  unit is approximately  $23 \mu\text{s}$ , very close to the value calculated for these groups under the assumption of a rigid-lattice behaviour. Therefore, the hydroxypropyl ether groups do not undergo any motion at the sensitivity and frequency of the  $t_{1/2}$  experiment at these temperatures. Above  $60^\circ\text{C}$ , however,  $t_{1/2}$  increases significantly with increasing temperature, demonstrating the occurrence of motions of the  $-\text{CH}_2\text{OCH}_2\text{CHOH}-$  sequences with frequencies of the order of, or higher than, a few tens of kilohertz in this temperature range. At  $100^\circ\text{C}$ ,  $t_{1/2} = 39 \mu\text{s}$ .

The  $t_{1/2}$  values of the  $-\text{OCH}_2\text{CHOH}-$  groups of the DGEBA/HMDA, DGEBA/IPD and DGEBA/DDM networks are shown in Figures 5 and 6. For the three systems considered, the  $t_{1/2}$  values of the  $-\text{OCH}_2\text{CHOH}-$  groups are equal to those calculated using the rigid-lattice assumption up to  $60^\circ\text{C}$ . Therefore, there are no local



**Figure 4** The  $t_{1/2}$  temperature dependence of the different aliphatic carbons of the DGEBA/DDM system: (○)  $-\text{CH}_2\text{OCH}_2\text{CHOH}-$  groups; (□)  $-\text{CH}_2\text{N}-$  carbons; (▲) DGEBA central methylene units



**Figure 5** The  $t_{1/2}$  temperature dependence of the different aliphatic carbons of the DGEBA/HMDA system: (○)  $-\text{CH}_2\text{OCH}_2\text{CHOH}-$  groups; (□)  $-\text{CH}_2\text{N}-$  carbons; (▲) HMDA central methylene units

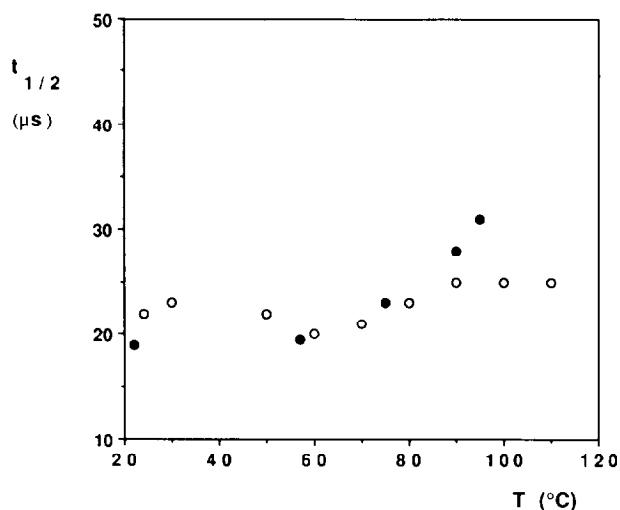


Figure 6 The  $t_{1/2}$  temperature dependence of the  $-O-CH_2-CHOH-$  groups of the DGEBA/IPD (●) and DGEBA/DDM networks (○)

motions of the hydroxypropyl ether sequences at the experimental frequency below this temperature. Then, depending on the system considered, the first increase in  $t_{1/2}$  is observed in the 70 to 90°C temperature range, indicating the existence of local motions in the tens of kilohertz range. At 100°C, the measured  $t_{1/2}$  values are 33, 30 and 25 μs for the DGEBA/HMDA, DGEBA/IPD and DGEBA/DDM samples, respectively. The rather small  $t_{1/2}$  value of the latter sample implies that the motions experienced by the CHOH and CH<sub>2</sub>O groups in the DGEBA/DDM resin are very restricted, even at 100°C.

The partial averaging of the  $^{13}C-^1H$  dipolar interaction evidenced in the above  $t_{1/2}$  experiments can be interpreted either in terms of rather slow motions with a constant amplitude and with an increasing rate as a function of temperature or in terms of rapid motions with an increasing amplitude as a function of temperature. In the following, we will consider a motional model based on fast isolated conformational jumps between *trans*, *gauche* + and *gauche* - positions and assume that the extent of the  $^{13}C-^1H$  dipolar interaction averaging depends on the number of  $-O-CH_2-CHOH-$  bonds in the sample involved in these processes. Using equation (3), one can estimate that the value  $t_{1/2} = 39$  μs, measured at 100°C in the DGEBA/DDM network, indicates that all the  $-CH_2-O-CH_2-CHOH-$  units of the sample undergo conformational jumps. The same calculation performed on the 100°C  $t_{1/2}$  values of the DGEBA/HMDA and DGEBA/IPD systems shows that they correspond to a situation where about 70% and 60%, respectively, of the hydroxypropyl ether groups undergo isolated conformational jumps. In the DGEBA/DDM sample, only about 20% of the CHOH and CH<sub>2</sub>O groups are involved in isolated conformational jumps.

As shown in Figure 1, in the DGEBA/DDM network, the  $-CH_2-O-CH_2-CHOH-$  groups are located between the DGEBA methylene carbons and the bulky bisphenol A unit. Therefore, the high mobility observed at 100°C for the  $-CH_2-O-CH_2-CHOH-$  sequences of the DGEBA/DDM resin is consistent with the fact that, in this system, the hydroxypropyl ether units benefit from the neighbourhood of the DGEBA flexible methylene

units. On the contrary, the  $-O-CH_2-CHOH-$  groups of the DGEBA/DDM sample, which are in the close vicinity of both the DGEBA and DDM rigid aromatic rings, have a very low mobility at 100°C. The intermediate results obtained for the DGEBA/HMDA and DGEBA/IPD networks originate from the presence of the aliphatic HMDA and IPD diamines, less rigid than the aromatic DDM unit.

#### Local motions of the methylene carbons adjacent to the crosslinks

The temperature dependence of the  $t_{1/2}$  values measured for the CH<sub>2</sub>N carbons of the DGEBA/DDM resin is shown in Figure 4. At room temperature,  $t_{1/2}$  is 18 μs, of the order of the value calculated for a methylene carbon with a rigid-lattice behaviour. Therefore, there is no detectable motion of the CH<sub>2</sub>N groups at room temperature in the tens of kilohertz range of the  $t_{1/2}$  experiment. From room temperature to 90°C, Figure 4 shows that there is no  $t_{1/2}$  variation for the CH<sub>2</sub>N carbon of the DGEBA/DDM network. However, the slight increase in  $t_{1/2}$  to 21 μs at 100°C is the first indication of local motions at a frequency equal to, or higher than, a few tens of kilohertz for the carbons considered. Application of the above motional model shows that about 20% of the CH<sub>2</sub>N units are involved in isolated conformational jumps at this temperature. It must be noted, however, that, in this system, the mobility is much lower for the CH<sub>2</sub>N carbons than for the hydroxypropyl ether groups.

Results obtained from CH<sub>2</sub>N  $t_{1/2}$  measurements in the DGEBA/HMDA, DGEBA/IPD and DGEBA/DDM networks are summarized in Figures 5 and 7. In the DGEBA/IPD system, two slightly different  $t_{1/2}$  values were measured from the 55 and 63 ppm resonances of the two magnetically inequivalent CH<sub>2</sub>N carbons of the IPD unit. Below 70°C, the three samples exhibit a quasi-rigid-lattice behaviour. As shown in Figure 7, the temperature of the first  $t_{1/2}$  increase, as well as the 100°C  $t_{1/2}$  value, depend on the system considered. As for the DGEBA/DDM system, the small  $t_{1/2}$  value determined at 100°C for the DGEBA/DDM sample indicates a strongly restricted mobility of the CH<sub>2</sub>N units at high

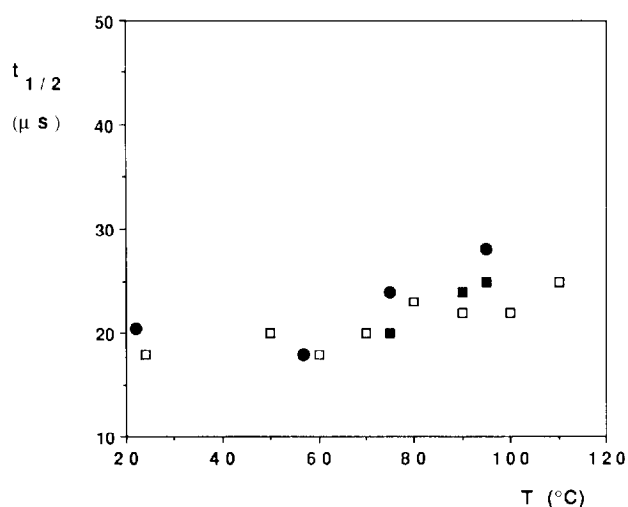


Figure 7 The  $t_{1/2}$  temperature dependence of the  $-CH_2N-$  groups of the DGEBA/IPD (■, ●) and DGEBA/DDM networks (□)

temperature. Higher mobilities are observed in the DGEBA/aliphatic amine (HMDA or IPD) systems. Furthermore, in these samples, in contrast with results obtained on the DGEBU/DDM network, the  $-\text{O}-\text{CH}_2-\text{CHOH}-$  and  $\text{CH}_2\text{N}$  carbons show parallel temperature dependences. At  $100^\circ\text{C}$ , the number of bonds involved in isolated conformational jumps is of the same order of magnitude for both HMDA- and IPD-based systems.

Results reported above show that the extent of the local motions of the  $\text{CH}_2\text{N}$  carbons is largely determined by the nature (aromatic or aliphatic) of the amine unit. In the DGEBA/DDM and DGEBU/DDM samples, the  $\text{CH}_2\text{N}$  group mobility is strongly hindered by the adjacent bulky DDM phenyl rings. On the contrary, aliphatic amines induce much less motional restriction at the crosslink sites and the  $\text{CH}_2\text{N}$  carbons are involved in the same local processes as those undergone by their hydroxypropyl ether neighbours.

#### *Local motions of the DGEBU and HMDA central methylene groups*

As Figure 4 indicates, at a given temperature, the highest  $t_{1/2}$  values are obtained for the central methylene carbons of the DGEBU units in the DGEBU/DDM sample. This result implies that the central part of the aliphatic sequence is the most mobile part of the network. For example, at room temperature, the  $t_{1/2}$  associated with the central  $\text{CH}_2$  carbons of the DGEBU moiety is  $27\ \mu\text{s}$ , which is significantly larger than the  $17\ \mu\text{s}$   $t_{1/2}$  calculated for a rigid  $\text{CH}_2$  group. This  $27\ \mu\text{s}$   $t_{1/2}$  value is an indication of the existence of local motions of these central aliphatic units at room temperature, that is, well below the  $76^\circ\text{C}$  glass transition temperature of the resin. Using the motional model based on isolated conformational jumps, one can estimate that about 80% of the central aliphatic DGEBU units undergo such motions at room temperature.

The  $t_{1/2}$  of the DGEBU central units shows a rather weak temperature dependence in the range from 20 to  $60^\circ\text{C}$  and a much stronger dependence above  $60^\circ\text{C}$ . At  $64^\circ\text{C}$ ,  $t_{1/2} = 34\ \mu\text{s}$ , which implies that all the DGEBU central carbons are involved in isolated conformational jumps. The increase in  $t_{1/2}$  above  $64^\circ\text{C}$  can be interpreted in terms of correlated conformational jumps involving several successive bonds. At  $100^\circ\text{C}$ , the  $63\ \mu\text{s}$   $t_{1/2}$  value corresponds to a situation where all the central  $\text{CH}_2$  groups are involved in correlated jumps.

The  $t_{1/2}$  values of the HMDA central aliphatic carbons, which resonate at 28 ppm, are given in Figure 5 as a function of temperature. Once again, these central methylene carbons possess  $t_{1/2}$  values, at all temperatures, that are much higher than those observed for the  $-\text{O}-\text{CH}_2-\text{CHOH}-$  and  $\text{CH}_2\text{N}$  groups. This indicates that the central part of the aliphatic sequence is much more mobile than the other parts of the network.

#### *Comparison with results from dynamic mechanical experiments*

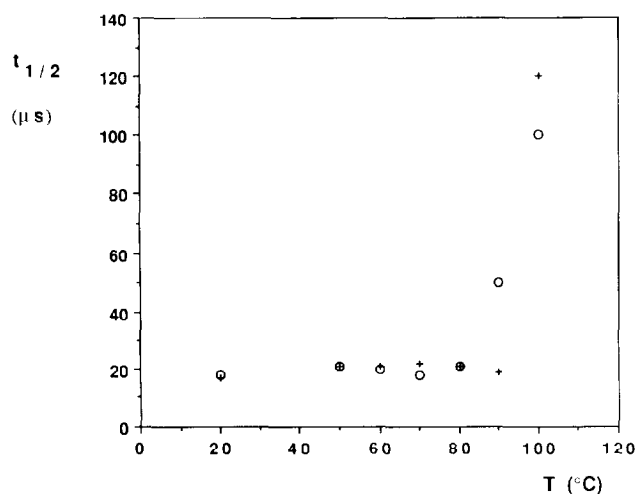
As indicated above, the  $t_{1/2}$  measurement, which reflects the motional modulation of the  $^{13}\text{C}-^1\text{H}$  dipolar coupling, is sensitive to motions with a frequency equal to or higher than a few tens of kilohertz. Therefore, a comparison of the n.m.r. results with the dynamic

mechanical measurements requires the extrapolation of the low-frequency mechanical data to the higher frequency of the n.m.r. experiment. Owing to the inherent inaccuracy introduced by the extrapolation and the fact that all relaxations tend to merge at high frequencies, only general comments will be made in the following.

The  $t_{1/2}$  experiments reported above were performed in the temperature range from 20 to  $100^\circ\text{C}$ , that is, well below the glass transition temperatures, at 1 Hz (Table 2), of all the resins, except the DGEBU/DDM system. Therefore, in all the samples, except DGEBU/DDM, the motional processes observed in the  $t_{1/2}$  experiments must be assigned to sub- $T_g$  processes. The glass transition temperature of the DGEBU/DDM resin at 1 Hz is  $76^\circ\text{C}$ . Taking into account the WLF (Williams-Landel-Ferry) dependence of the frequency of the motions as a function of temperature<sup>26</sup>, the manifestation of the motions responsible for the glass transition phenomenon is expected to occur at about  $102^\circ\text{C}$  for a frequency of 50 kHz. Therefore, the high  $t_{1/2}$  values measured at  $100^\circ\text{C}$  for the central  $\text{CH}_2$  units may result, at least partly, from precursor modes of the glass transition. The line broadening of the aromatic lines at  $90^\circ\text{C}$ , which arises from the motional modulation of the chemical-shift anisotropy, as well as the reduction in the cross-polarization efficiency at  $100^\circ\text{C}$  are other manifestations of the  $T_g$  processes, in the frequency range from  $10^3$  to  $10^5$  Hz, that are observed in the DGEBU/DDM  $^{13}\text{C}$  n.m.r. spectra. In contrast, the motions described for the central methylene groups and the hydroxypropyl ether units below  $100^\circ\text{C}$  are clearly related to sub- $T_g$  processes.

The DGEBU/DDM and DGEBA/HMDA resins show a low-temperature  $\gamma$  transition. In agreement with the conclusions derived from dynamic mechanical analysis<sup>5,9</sup>, the rapid reorientations of the central methylene units of the DGEBU moieties, which are the only processes observed at room temperature by  $t_{1/2}$  experiments, can be associated with the  $\gamma$  relaxation of epoxy networks. A similar conclusion applies to the motions of the HMDA central methylene units.

The correlation of the motions of the hydroxypropyl ether groups in the  $70-90^\circ\text{C}$  range with some of the  $\beta$  modes is a more difficult problem. Recently, the characteristics of the  $\beta$  relaxation have been carefully examined in several model epoxy networks<sup>11</sup>. The  $\beta$  loss modulus peak is a wide composite peak. For a test frequency of 1 Hz, a maximum is observed at  $-55^\circ\text{C}$  and  $-57^\circ\text{C}$  in the DGEBA/DDM and HMDA/DDM resins, respectively, that is, quite independently of the flexibility of the constitutive amine. The activation energies of the  $\beta$  processes were determined either by considering the temperature dependence of the loss peak maximum as a function of the test frequency, or by using master curves based on the frequency-temperature superposition principle. As a result of the composite character of the  $\beta$  peak, the activation energies are very much dependent on the technique used for the calculation. The  $T_\beta$  temperatures at 0.1 MHz can be derived from the different apparent activation energies<sup>11</sup>. For the DGEBA/DDM and DGEBA/HMDA systems,  $T_\beta$  ranges from 28 to  $65^\circ\text{C}$ , depending on the method of calculation. However, as for the location of the  $\beta$  peak at 1 Hz, the values of the activation energies and the  $T_\beta$  temperatures at 0.1 MHz are very similar for both networks.



**Figure 8** The  $t_{1/2}$  temperature dependence of the  $\text{-O-CH}_2\text{-CHOH-}$  (○) and  $\text{-CH}_2\text{N-}$  (+) groups of the DGEBA/HMDA/HA network

As shown in Figures 4–6, the n.m.r.  $t_{1/2}$  experiments indicate the onset of the  $\text{-O-CH}_2\text{-CHOH-}$  group motions between 70 and 90°C for all the systems considered. This temperature range is somewhat higher than the predictions at 0.1 MHz derived from the dynamic mechanical technique. Moreover, although the first occurrence of a motional process depends on the nature of the constitutive units, this dependence is quite slight since there is only a 30°C difference in temperature between the different resins. Therefore, as also concluded from some previous mechanical investigations<sup>2,4,9</sup>, it is more than likely that the motional processes of the  $\text{-O-CH}_2\text{-CHOH-}$  groups participate in the  $\beta$  relaxation in epoxy networks.

Further correlations can be established between mechanical and n.m.r. data by considering the effects of the network crosslink density on the characteristics of the  $\beta$  transition. Dynamic mechanical experiments performed on the densely crosslinked DGEBA/HMDA sample and the loosely crosslinked DGEBA/HMDA/HA system, based on 25 mol% diamine and 75 mol% monoamine, have shown that the decrease in crosslink density is accompanied by a decrease in amplitude and a narrowing in the high-temperature region of the damping and loss modulus<sup>11</sup>. However, in both systems, the motions responsible for the  $\beta$  process start developing at the same temperature. Moreover, the temperature location of the  $T_\beta$  maximum observed at 1 Hz, as well as its calculated position at 0.1 MHz, are independent of the crosslink density. The  $t_{1/2}$  temperature dependence of the  $\text{-O-CH}_2\text{-CHOH-}$  and  $\text{CH}_2\text{N}$  groups is shown in Figure 8 for the DGEBA/HMDA/HA resin. There is no  $t_{1/2}$  departure from the rigid-lattice behaviour in the 20–80°C range. Comparison with  $t_{1/2}$  data reported in Figure 5 for the DGEBA/HMDA sample leads to the conclusion that the hydroxypropyl ether groups of the loosely crosslinked DGEBA/HMDA/HA network are not more mobile than those of the densely crosslinked DGEBA/HMDA sample. This result is in agreement with mechanical data related to the temperature location of the  $T_\beta$  maximum in both systems. Above 80°C, the  $t_{1/2}$  of the  $\text{-O-CH}_2\text{-CHOH-}$  unit increases significantly. However, it must be noted that the glass transition temperature of the DGEBA/HMDA/HA resin at 1 Hz is

63.5°C (Table 2). Therefore, the high  $t_{1/2}$  values observed at 90 and 100°C for this material are likely to be due to precursors of the glass transition phenomenon at the frequency of the  $t_{1/2}$  experiment.

Another interesting feature in the dynamic mechanical analysis is the interpretation of activation energies in terms of enthalpic and entropic contributions<sup>27</sup>. According to the Starkweather analysis, cooperativity between local motions of neighbouring groups would occur when the entropic contribution is larger than about  $100 \text{ J K}^{-1} \text{ mol}^{-1}$ . Such a condition is roughly fulfilled in the DGEBA/DDM and DGEBA/HMDA resins. Moreover, the entropic contribution is significantly higher for the DDM-based resin than for that based on HMDA. As indicated by the weak  $t_{1/2}$  temperature dependence, this observation suggests that, in the rigid crosslinked DGEBA/DDM system, motions are of small amplitude, but are highly cooperative.

## CONCLUSION

As shown by the measurements of the strength of the  $^{13}\text{C}$ – $^1\text{H}$  dipolar couplings, reported in this paper, the aliphatic units of epoxy resins exhibit several sub- $T_g$  motions in the tens of kilohertz range. Comparison with results obtained from dynamic mechanical experiments indicate that the relatively high mobility of the central methylene units of the aliphatic sequences of the diglycidyl ether of butanediol-based network, and of the hexamethylenediamine-based network, can be associated with the  $\gamma$  relaxation of epoxy networks. Motional processes of the  $\text{-O-CH}_2\text{-CHOH-}$  groups, observed between 70 and 90°C for all the crosslinked systems investigated, probably participate in the  $\beta$  relaxation of epoxy networks. This point is supported by the behaviour of the DGEBA/HMDA/HA resin. The amplitude of the reorientation of the hydroxypropyl ether groups is strongly dependent on their intramolecular environment. As indicated by the Starkweather analysis, in the DGEBA/DDM system, which is the most rigid resin considered, these motions are of small amplitude, but are highly cooperative. At high temperature, very restricted modes of the methylene carbons adjacent to the crosslinks are also detected.

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