Internal antiplasticization in copolymer and terpolymer networks based on diepoxides, diamines and monoamines

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Seven epoxy networks based on diglycidyl ether of bisphenol A, isophorone diamine and trimethylcyclohexylamine, and differing in the amine/epoxy molar ratio and/or in the monoamine/diamine molar ratio, were studied by tensile and compressive tests, ultrasonic wave propagation and thermomechanical spectroscopy. It appears that any structural modification leading to a decrease in the glass transition temperatures induces an increase in the elastic modulus in the glassy state, above the β-relaxation. This so-called internal antiplasticization phenomenon cannot be linked to change in volumetric properties, as previously proposed in the literature, but rather to the effect of crosslinks on the local mobility.

(Keywords: epoxy networks; antiplasticization; β-relaxation; crosslink density)

INTRODUCTION

There is now a great deal of published data on elastic and viscoelastic properties of epoxy–amine networks[1–9]. A very interesting feature of these systems is the fact that, in many structural series[4–9], their elastic modulus—determined from a classical tensile, compression or shear test at room temperature—is a decreasing function of their crosslink density, thus behaving in the opposite way to, for instance, their glass transition temperature T_g. It was often observed, but not in all cases[3,9], that the density varied in the same way as the modulus. Various volumetric interpretations based on the hypothesis that the packing in the glassy state is not favoured by crosslinking[7,11] were derived from these observations. The same type of interpretation was also applied to the well known effect of poly(vinyl chloride) (PVC) antiplasticization, in which addition of low-molecular-weight compounds or plasticizers appears to retard the segmental motions of the polymer, although there was a continuous decline of T_g. Increases in modulus and strength at break, accompanying losses in elongation at break, were observed that were the opposite of what was expected for plasticization. The addition of miscible diluents (tricresyl phosphate, N-phenyl-2-naphthylamine and 4,4'-dichlorodiphenylsulphone) to polysulphone[12,13] causes changes associated with antiplasticization. Therefore, antiplasticization was characterized by the simultaneous increase in the stiffness and decrease in the glass transition temperature. Reductions in gas sorption and in permeability coefficients at low diluent concentration were also observed. In poly(phenylene oxide) similar results were

obtained on permeability but no significant stiffening was observed. The authors used a simple free-volume treatment, which gives a satisfactory correlation of the transport and mechanical properties.

However, epoxide–amine networks are more densely packed than the majority of linear polymers and the packing density seems to be related to the cohesion rather than to the network structure[14]. An alternative explanation was proposed on the basis of the observation that the only common feature of all the antiplasticized systems including epoxide networks[15], but also PVC[16,17] and other linear aromatic polymers[18], is a decrease in the intensity of the β-relaxation, i.e. a decrease in the corresponding modulus gap in thermomechanical spectra.

The mechanism by which the cooperative motion is favoured (internal or external plasticization) whereas the local motion is not favoured is not yet understood and seems to be somewhat paradoxical. However, for epoxy networks there are strong arguments in favour of such an interpretation, which is directly linked to molecular dynamics rather than volumetric interpretations.

Our aim in this study is to try to develop these arguments on the basis of experimental data on a structural series based on three monomers: diglycidyl ether of bisphenol A (DGEBA), isophorone diamine (IPD) and trimethylcyclohexylamine (TMCA). In these systems, the monoamine acts as an internal plasticizer by reducing the crosslink density, while all the other structure-dependent properties, for instance cohesion, remain essentially constant.

Previous investigations on these systems have shown that their glass transition temperature can be predicted[19] from the molecular structure and that their volumetric properties are not governed by the steric effects of

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crosslinking, which eventually has an inhibiting effect on packing[20].

EXPERIMENTAL

Materials

The epoxy prepolymer used in this study was almost pure diglycidyl ether of bisphenol A (DGEBA; DER 332 from Dow Chemicals). The curing agent was isophorone diamine (IPD; or 3-aminomethyl-3,5,5-trimethylcyclohexylamine). Three stoichiometric ratios (amine-to-epoxy) were studied (a/e=0.8, 1.0, 1.2). In addition, a chain extender was used in various amounts.

This chain extender, 3,3,5-trimethylcyclohexylamine (TMCA), has a structure similar to IPD but with only one amine function. Both amines were obtained from Veba-Chemie with a purity of at least 99% and were used as received. The chemical structures of the reagents are shown in *Table 1*.

Seven different formulations were investigated; their codes and compositions are provided in *Table 2*.

A low-pressure three-component mixing machine (Secmer) was used to fabricate the samples (200 × 300 × 6 mm^3). The cure schedule was 1 h at 140°C followed by 6 h at 190°C, and produced complete cure of the systems.

Techniques

Infra-red measurements. Infra-red measurements were carried out to study hydrogen bonding. The transmission spectra were recorded on a Perkin–Elmer PE1710 *F*Ti.r.

spectrometer. Microtome sections of 25 μm in thickness were used.

Tensile mechanical measurements. Tensile tests were made with an Adamel Lhomargy (DY25) machine, at room temperature with a strain rate of 2.8 s^{-1}, on tensile dogbone specimens (standard NF 51-034). Specimen elongations were monitored using an extensometer (Adhamel Lhomargy EX10).
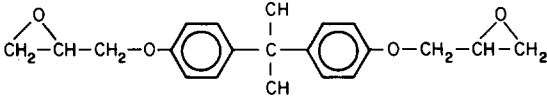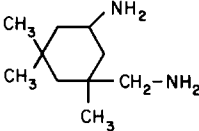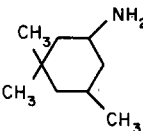
Young's moduli E_T were calculated from the initial part of the stress–strain curves.

Compressive mechanical measurements. Compression tests were made with the same machine as used for the tensile tests, using cylindrical samples (22 mm height, 10 mm diameter) deformed in a compression rig at a strain rate of 7.5 s^{-1}. The yield stress σ_y and the yield strain ε_y were determined.

Ultrasonic measurements. Ultrasonic measurements were made at a frequency of 5 MHz at room temperature using the pulse method[21,22], on milled bars (2.5 × 2.5 × 0.4 cm^3). With this technique, the accuracy and reproducibility depend on the sample surface parallelism; the relative uncertainty of results was less than 2%. The moduli were calculated using the following relations:

$$v_L^2 = \frac{B_u}{\rho}\frac{3(1-v)}{(1+v)}$$

Table 1 Monomer structure and characteristics: M, molecular weight; F, functionality; ρ, density

Code	Formula	M (g mol^{-1})	F	ρ (g cm^{-3})
DER 332		342	2	1.14
IPD		170.3	4	0.920
TMCA		141.3	2	0.844

Table 2 General characteristics: T_g, glass transition temperature; ρ, density; n, crosslink density; [OH], theoretical concentration of hydroxyls; Σ_{OH} molar absorptivity of hydroxyls

Sample	Stoichiometric ratio[a]	IPD/TMCA[b]	T_g (°C)	ρ (g cm^{-3})	n (mol kg^{-1})	[OH] (mol kg^{-1})	Σ_{OH} (kg mol^{-1} cm^{-1})
10.10	1.0	100/0	165	1.164	2.35	4.71	69
10.7	1.0	70/30	132	1.154	1.58	4.53	73
10.5	1.0	50/50	116	1.135	1.10	4.42	75
12.10	1.2	100/0	143	1.161	1.81	4.53	77
12.7	1.2	70/30	113	1.156	1.21	4.33	76
08.10	0.8	100/0	109	1.175	0.98	3.91	69
08.7	0.8	70/30	91	1.161	0.66	3.79	85

[a] Amine to epoxy
[b] Amounts relative to the total number of amine functional groups

$$v_T^2 = \frac{G_u}{\rho}$$

$$E_u = 3B_u(1 - 2v) = 2G_u(1 + v)$$

where v_L and v_T are the longitudinal and transverse wave propagation rates respectively; E_u, B_u and G_u are the Young's, bulk and shear moduli respectively; ρ is the density; and v is Poisson's ratio.

Dynamic mechanical measurements. In order to study the β-relaxation, dynamic mechanical measurements were made in the double cantilever bending mode using a Polymer Laboratories DMTA viscoelasticimeter. Both E', the real part of the complex modulus E^*, and $\tan \delta$, the loss factor, were recorded during a frequency (from 0.033 to 90 Hz)—temperature (from -120 to $50°C$) sweep. The apparent activation energy E_a of the β-relaxation was calculated using an Arrhenius law:

$$\ln v = -\frac{E_a}{RT_m} + K$$

where R is the universal gas constant and T_m the temperature position of the β-peak at the given frequency.

RESULTS AND DISCUSSION

General characterization

The glass transition temperatures of the various samples were evaluated by differential scanning calorimetry (Mettler TA3000, heating rate $10 \, K \, min^{-1}$). The values of T_g, density[20], theoretical crosslink density n, theoretical concentration of hydroxyl groups and the molar absorptivity of hydroxyls measured by i.r. are reported in *Table 2*. The density at room temperature was determined by pycnometry.

The theoretical crosslink density was equal to the tertiary amine concentration in the case where no free chain ends remained, i.e. in samples having a stoichiometric ratio of 1.0 and 1.2. In samples having an epoxide excess ($a/e = 0.8$), it was assumed that $n = N_T - N_E$ where N_T was the total number of tertiary amines and N_E the number of tertiary amines linked to a free epoxide group.

For the calculations of the theoretical concentration of hydroxyl groups, two cases were considered: when the stoichiometric ratio was equal to 1.0 and 1.2, the concentration of hydroxyl groups was equal to the concentration of epoxy groups; when the stoichiometric ratio was 0.8, the concentration of hydroxyls was equal to the total concentration of NH groups.

The molar absorptivity was calculated using:

$$\Sigma_{OH} = \frac{A_{3140}}{[OH]\rho e}$$

where e is the thickness of the epoxy film, ρ is the density, $[OH]$ is the concentration of hydroxyl groups and A_{3140} is the absorbance at $3140 \, cm^{-1}$ in the infra-red spectrum.

As expected, the maximum T_g and n were obtained for the sample 10.10 ($a/e = 1.0$, no chain extender). It is also observed that both T_g and n decrease when the chain extender or an excess of epoxy or amine is added to the formulation. Variations of the density depend only on the atomic composition of the system[20]. Infra-red spectra recorded from 3100 to $3700 \, cm^{-1}$ do not show large variation between the various samples.
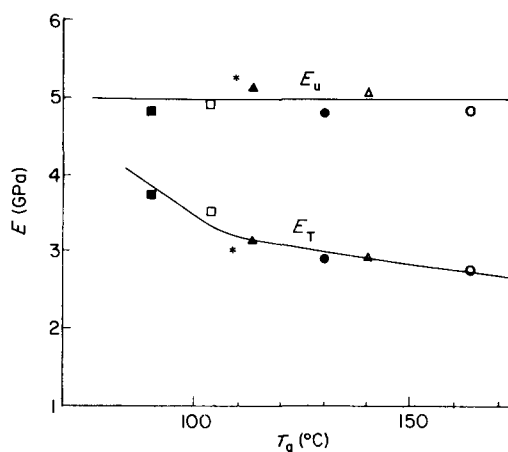
Modulus

As previously found[4–9], the tensile modulus E_T was a minimum for a stoichiometric ratio equal to 1.0 independent of the quantity of the chain extender. For a given stoichiometric ratio, an increase of E_T was observed when TMCA was added in each case. Therefore E_T appeared to be a decreasing function of the glass transition temperature (as can be seen in *Figure 1*) or of the theoretical crosslink density n.

This behaviour is a typical case of antiplasticization by the monoamine TMCA or by an excess of DGEBA or IPD. The influence of volumetric parameters (free-volume fraction, packing degree, etc.) is not suspected.

Variations in E_T as a function of the theoretical concentration of hydroxyls are shown in *Figure 2*. These results are opposite to those observed by Dhaoui *et al.*[23], which were for highly crosslinked epoxy networks ($2 < n < 6 \, mol \, kg^{-1}$); with our networks, E_T decreased as the concentration of hydroxyls increased. As a matter of fact, deconvolution of the infra-red spectra shows that nearly 95% of the hydroxyl groups were active in hydrogen bonding in such DGEBA/IPD/TMCA networks. No correlation was found between E_T and the density ρ.

Data concerning Young's modulus E_u, bulk modulus B_u and Poisson's ratio v that were determined by ultrasonic wave propagation are listed in *Table 3*. To a

Figure 1 Young's modulus *versus* T_g: E_u, ultrasonic measurements; E_T, tensile measurements. Symbols used in the figures: (O) 10.10; (●) 10.7; (✳) 10.5; (▼) 10.3; (△) 12.10; (▲) 12.7; (□) 08.10; (■) 08.7
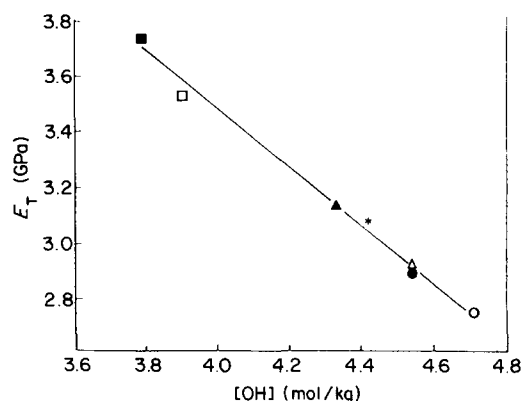
Figure 2 Young's modulus *versus* the theoretical concentration of hydroxyls. See *Figure 1* for symbols

Table 3 Moduli values: E_u, Young's modulus (ultrasonic measurement); B_u, bulk modulus (ultrasonic measurement); E_T, tensile modulus; b, 'timescale' factor; v, Poisson's ratio

Sample	v	E_u (GPa)	B_u (GPa)	E_T (GPa)	b
10.10	0.35	4.85	6.21	2.75	0.433
10.7	0.36	4.79	5.94	2.89	0.397
10.5	0.36	5.26	6.00	3.08	0.414
12.10	0.36	5.08	6.05	2.91	0.427
12.7	0.37	5.15	6.00	3.14	0.390
08.10	0.37	4.91	5.86	3.53	0.281
08.7	0.37	4.82	6.17	3.75	0.222
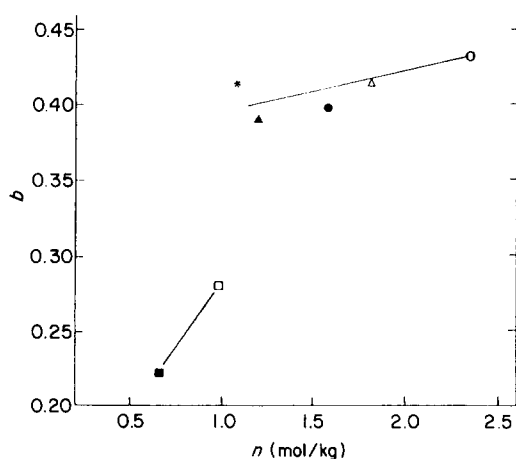
Figure 3 Plot of b factor *versus* the crosslink density n for the various networks. See *Figure 1* for symbols

first approximation, it can be considered that the ultrasonic modulus is constant for all samples studied (*Figure 1*). The average values are $E_u = 5 \pm 0.2$ GPa and $B_u = 6 \pm 0.2$ GPa. Neither T_g nor ρ were found to be related to E_u.

The conditions of the experiments ($T = 20°C$, $v = 5$ MHz) were equivalent to a measurement of the static modulus below the β-relaxation in the glassy state where all motions are frozen. For example, for the sample 10.10 (a/e = 1.0, 100% IPD), it can be calculated (using the activation energy reported in the following section) that the peak of the β-relaxation will be near 165°C. The effects of the shift of timescale between tensile and ultrasonic testing can be represented by a factor b where $b = (E_u - E_T)/E_u$. The b values are also reported in *Table 3*. They represent the change of modulus during the β-relaxation. The factor b is plotted against the theoretical crosslink density n in *Figure 3*. The factor b is obviously an increasing monotonic function of the crosslink density n or of T_g. Two kinds of networks can be observed: 'closed' networks (a/e = 1.0, 1.2) and 'open' networks with dangling end-groups (a/e = 0.8).

Compressive test

Table 4 shows the values of σ_y and ε_y for the seven different systems. The variations of σ_y are very small, between 99 and 115 MPa, and are typical of values obtained for epoxy networks. The addition of the chain extender does not greatly influence σ_y. The main effect is observed when an excess of epoxy prepolymer is used: in both cases (sample 08.10 and 08.7) σ_y increases. These

results are summarized in *Figure 4*, where the variation of σ_y is plotted against the crosslink density n.

Similar results were obtained by Yamini *et al.*[24] with epoxy networks based on DGEBA cured with various amounts of triethylenetetramine. They showed that the plastic deformation below T_g is identical to that of amorphous, glassy thermoplastics and can be explained by the yield theories of Argon and Bowden. Interesting results have also been obtained by Caux *et al.*[25]. They showed that σ_y is always higher for a DGEBA/diamine network than for a DGEBA/diamine/monoamine network, in a large temperature range.

The β-relaxation

Plots of tan δ as a function of temperature are shown in *Figure 5* for the system 10.10 (a/e = 1.0, 100% IPD) at various frequencies. At a low frequency (0.033 Hz), the β-peak exhibits a very different shape than that at high frequencies. The β-peak is broad and two maxima can be observed. It is well known that the β-relaxation involves various relaxation mechanisms, but their attribution is still subject to controversy. Undoubtedly, there is relaxation induced by motion of hydroxyether groups[26–28], but motions of diphenylpropane groups[28] and motions of the crosslinks themselves[29] could also be involved.

The magnitude of tan δ depends on two factors: these are the concentration of the relaxing species and the stress sensitivity of the free energy wells characterizing the motions[8]. Unfortunately, we are unable to separate these
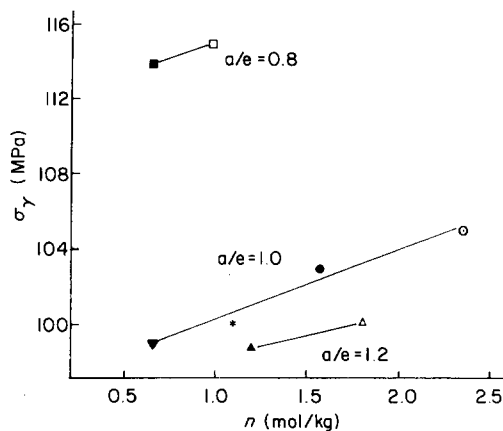
Figure 4 Yield stress σ_y against the crosslink density n. See *Figure 1* for symbols
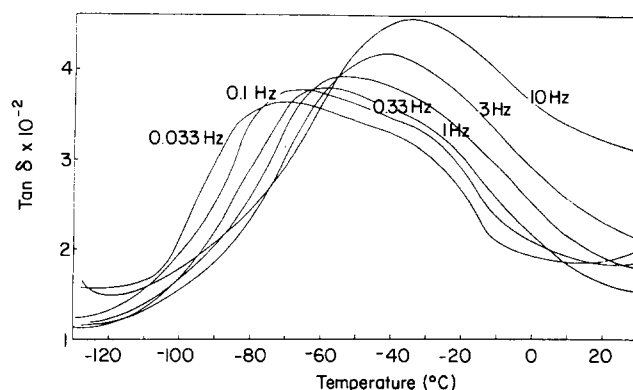
Figure 5 Plot of tan δ *versus* temperature at various frequencies for the network 10.10 (a/e = 1.0, 100% IPD)

factors; thus only an apparent activation energy can be calculated. The results for $E_{a\beta}$ are reported in *Table 5*. Although the variations of $\bar{E}_{a\beta}$ are small, we observed that $E_{a\beta}$ is a decreasing function of the crosslink density (*Figure 6*). This observation is in disagreement with the results of Charlesworth[8] on terpolymer epoxy networks and of Arridge *et al.*[30] on non-stoichiometric systems. Nevertheless, the studies of Garton *et al.*[15] on fortifiers

Table 4 Yield stress σ_y and yield strain ε_y for the different networks

Sample	σ_y (MPa)	ε_y (%)
10.10	105	8.4
10.7	103	7.5
10.5	100	7.4
12.10	100	7.5
12.7	99	7.2
08.10	115	6.2
08.7	114	5.3

Figure 6 Apparent activation energy $E_{a\beta}$ of the β-relaxation *versus* the crosslink density n. See *Figure 1* for symbols

Figure 7 Effects of the stoichiometric ratio on the β-relaxation at 1 Hz. $\bigcirc$, 10.10; $\triangle$, 12.10; $\square$, 08.10

that act as external antiplasticizers by increasing the stiffness of crosslinked epoxy resins have shown that the activation energy for the low-temperature process is increased by the presence of fortifiers. They conclude that this observation is consistent with the idea of strong interactions between the additives and the network.
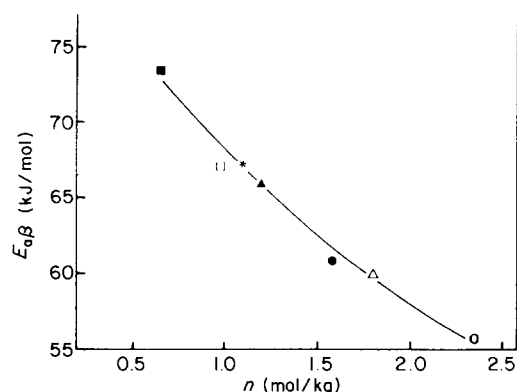
Plots illustrating representative $\tan \delta$ *versus* temperature spectra for networks prepared with a variation of the stoichiometric ratio are shown in *Figure 7*. The incorporation of an excess of epoxy reduces the magnitude of the β-relaxation. This result was expected since, for $a/e = 0.8$, glyceryl constitutional units are present as dangling ends. In fact, some authors[8] have found that hydroxyether groups included in a diepoxide reacted only at one end do not show the same contribution to the β-relaxation as do hydroxyether groups present in difunctionally reacted DGEBA. It has also been demonstrated[25] that the loss peak is not sensitive to glyceryl units that were derived from monofunctional diluents.

When TMCA is added to the formulation, i.e. when the crosslink density decreases, the same trend is also observed: a decrease of the specific loss at the maximum (*Table 5*). This is in agreement with the results obtained by Charlesworth[8] on terpolymer epoxy networks.
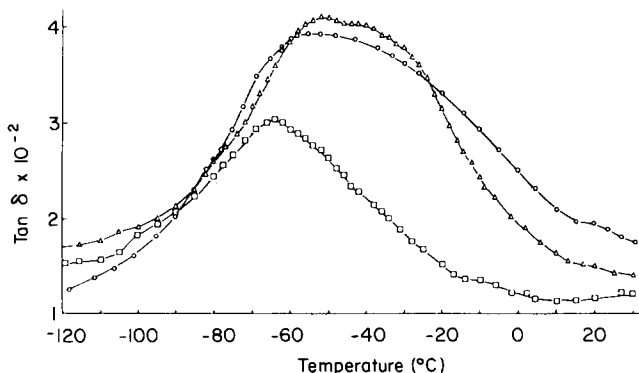
Our results are consistent with the hypothesis that the glyceryl constitutional units linked to the monoamine TMCA are less active than those directly connected to crosslinks. Indeed, a plot of b against the concentration of glyceryl groups directly connected to crosslink points would have the same shape as in *Figure 3*.

CONCLUSIONS

The study of the β-relaxation on various epoxy–amine networks differing in the crosslink density lead to the surprising conclusion that β-motions occur in the most constrained segments, in the immediate vicinity of crosslinks. As a consequence, the Young's modulus at room temperature is higher for the less crosslinked networks. Previous studies[28,29] have shown that β-motions are more or less hindered by hydrogen bonding. On the other hand, it can be assumed that, for reasons of steric hindrance, hydrogen bonding would be locally modified by the presence of crosslinks[30]. However, in the networks under study, no clear correlation between the characteristics of the hydroxyl stretching band and the observed behaviour has been established. Furthermore, it is now obvious that internal antiplasticization occurs in a wide variety of structural series differing strongly in their hydrogen-bonding characteristics. Therefore, it can be supposed that hydrogen bonding does not play an important role in this phenomenon. As observed in *Figure 7*, antiplasticization affects essentially the high-temperature component of the β-relaxation, but more detailed deconvolution studies are needed to elucidate this behaviour.

Table 5 Characteristics of the β-relaxation

Sample	10.10	10.7	10.5	12.10	12.7	08.10	08.7
T_β (°C), 1 Hz	−53	−51	−49	−46	−44	−63	−61
$\tan \delta_{max}$ ($\times 10^{-2}$)	3.95	3.73	3.47	4.12	3.87	3.05	2.70
S_β (arbitrary units)	223.9	210.0	195.2	216.1	200.4	154.5	148.3
$E_{a\beta}$ (kJ mol^{-1})	57	61	68	60	66	68	74

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