The Cure of Epoxy Novolacs with Aromatic Diamines. II. Statistical Parameters of the Resulting Networks

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SYNOPSIS

The buildup of the network arising from the reaction of an epoxy novolac (derived from a phenol-formaldehyde novolac resin), with 4,4'diaminodiphenylsulfone (DDS), was modeled using a kinetic-statistical procedure that takes into account (i) the complex structure of the starting novolac, (ii) the actual polymerization kinetics including the different reactivity of primary and secondary amine hydrogens, and (iii) the formation of intramolecular cycles. Predictions of gel conversion and sol fraction were in excellent agreement with experimental results. Glass transition temperatures T_g's of networks prepared at different stoichiometries were predicted using Nielsen's equation (J. Macromol. Sci.-Rev. Macromol. Chem., C3, 69, 1969) and the concentration of elastic chains arising from the model. Theoretical predictions explained the presence of a maximum in the experimental T_g for formulations containing a 20% amine excess. Experimental values of T_g as a function of conversion, for stoichiometric samples, were correlated using a model proposed in the literature. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

In the first part of this study,[1] the cure reaction of a commercial epoxy novolac, derived from a phenol-formaldehyde novolac resin, with 4,4'diaminodiphenylsulfone (DDS), was analyzed. It was established that stoichiometric formulations did not reach complete conversion due to the presence of topological limitations. A limiting conversion equal to $x_{max} = 0.8$ could be attained even by prolonged heatings at high temperatures. Gelation took place at $x_{gel} = 0.45 \pm 0.01$, independently of the selected cure temperature.

A unique relationship between the glass transition temperature, T_g, and conversion could be obtained. The maximum T_g for the stoichiometric system was $T_{g_{max}} = 215°C$ for a formulation cured to its limiting conversion. However, samples containing a 20% amine excess showed the maximum value of T_g ($T_g = 230°C$).

The aim of the second part of this paper was to develop a statistical model of the network formation and to compare theoretical predictions with experimental values of x_{gel}, sol fraction (to be reported in this part of the study), and T_g as a function of the stoichiometric ratio and conversion.

EXPERIMENTAL

Figure 1 shows the structure of the commercial epoxidized novolac (EPN 1138, Ciba-Geigy), arising from the experimental determination of the weight per epoxy equivalent, the weight per (epoxy + OH) equivalent, the residual chlorine, the number-average molecular weight, and an analysis of the epoxidation process.[2] The structure is represented in terms of moles of fragments that must be joined at random (bonds labeled with a must be joined to bonds labeled with a'). The average number of 3.6 phenolic rings per chain (as reported by the supplier) has been kept, but only species with three and four phenolic rings have been identified, i.e., the most-probable-distribution was arbitrarily replaced

2.12   (O-a)—CH$_2$—(O-a)—CH$_2$—(O-a)   (M=303)

2.18   (O-a)—CH$_2$—(O-a)—CH$_2$—(O-a)—CH$_2$—(O-a)   (M=408)

┌—CH$_2$—CHOH—CH$_2$—┐
O   O-a   O-a   O
1   (O)—CH$_2$—(O-a)—CH$_2$—(O-a)—CH$_2$—(O)   (M=466)

16.075   a'—CH$_2$—CH—CH$_2$ (epoxide)   (M=57)

0.365   a'—CH$_2$—CHOH—CH$_2$—a'   (M=58)

0.275 {
   OH
a'—CH$_2$—CH—CH$_2$—Cl
   CH$_2$OH
a'—CH
   CH$_2$Cl
}   (M=935)
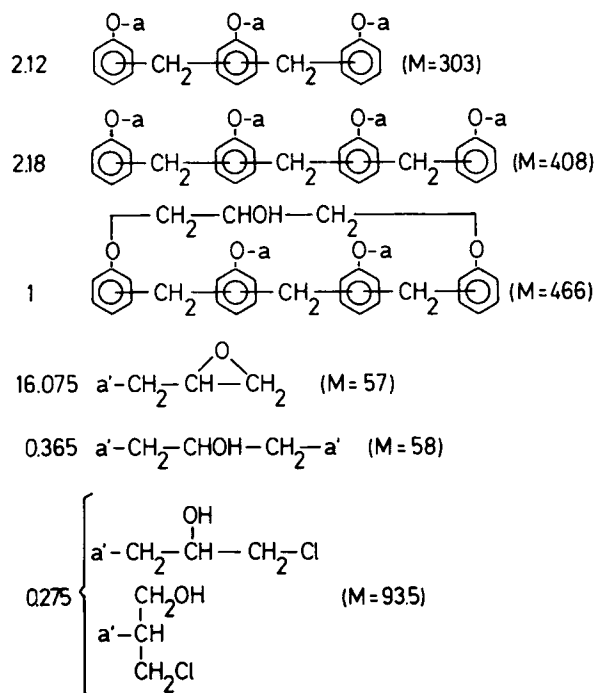
Figure 1 Molecular structure of the commercial epoxidized novolac (EPN 1138, Ciba-Geigy), represented as moles of fragments that must be joined at random (bonds a must be joined with bonds a'). The average number of 3.6 phenolic rings per chain (as reported by the supplier) has been kept, but only species with three and four phenolic rings have been identified.

by a simple distribution consisting on two species. This hypothesis, which has already been used in the literature,[3] is useful for the statistical description of the network buildup.

The epoxidation of four-phenolic-ring novolacs may lead to a fraction of intramolecular cycles through —CH$_2$—CHOH—CH$_2$— bridges. This arises from the fact that terminal rings of novolacs containing four or more phenolic rings in the structure can come within proximity.[4] Therefore, after epoxidation of one terminal OH by epichlorohydrin, there is a finite probability of reacting the other terminal OH to produce an intramolecular bridge.[2] From the structure shown in Figure 1, it is seen that the ratio between inter- and intramolecular —CH$_2$—CHOH—CH$_2$— bridges is 0.365 to 1. Species containing three phenolic rings cannot form intramolecular cycles. The experimental value of the weight per epoxy equivalent of EPN 1138 was 184.2 g equiv^{-1}.

The hardener was 4,4'diaminodiphenylsulfone (DDS, HT 976, Ciba-Geigy). Its structure is shown

in Figure 2. It has an equivalent weight of 62 g equiv^{-1}.

The sol fraction of partially cured samples was determined with a Soxhlet device using acetone as solvent. The mass of sample was close to 1 g and the extraction time to constant weight was about 50–60 h. The conversion of every sample was measured through its T_g and the unique relationship found between this parameter and conversion.[1] Details of the T_g measurement and cure schedules were given in the first part of this study.[1]

KINETIC–STATISTICAL MODEL OF THE NETWORK BUILDUP

The network buildup is described through the fragment approach.[5-7] It consists on the selection of a set of fragments describing the identified nonidealities (substitution effects in the amine hydrogens, formation of intramolecular cycles), the statement and solution of a set of kinetic equations describing the evolution of the different fragments along the polymerization, and the random combination of these fragments at any conversion to generate desired statistical parameters in pre- and postgel stages.

Set of Fragments

The possibility of forming intramolecular cycles must again be taken into account. Thus, when one terminal epoxy group of a particular 4-ring species containing two terminal epoxides reacts with a primary amine group, the secondary amine hydrogen may come within contact with the other terminal epoxide and produce a cycle through an intramolecular reaction. Then, the selected set of fragments must distinguish every possible state of reaction of the terminal phenolic rings in the 4-ring species. Also, and in order to simplify the analysis, it will be assumed that if there is a possibility of producing an intramolecular cycle by a conformational rearrangement of the molecule it will take place at the expense of any other possible competing intermolecular reaction. The set of 25 fragments shown in Figure 3 is necessary to describe the network buildup.
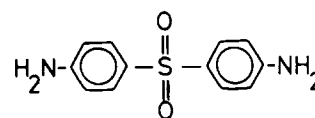
H$_2$N—(O)—S(=O)$_2$—(O)—NH$_2$

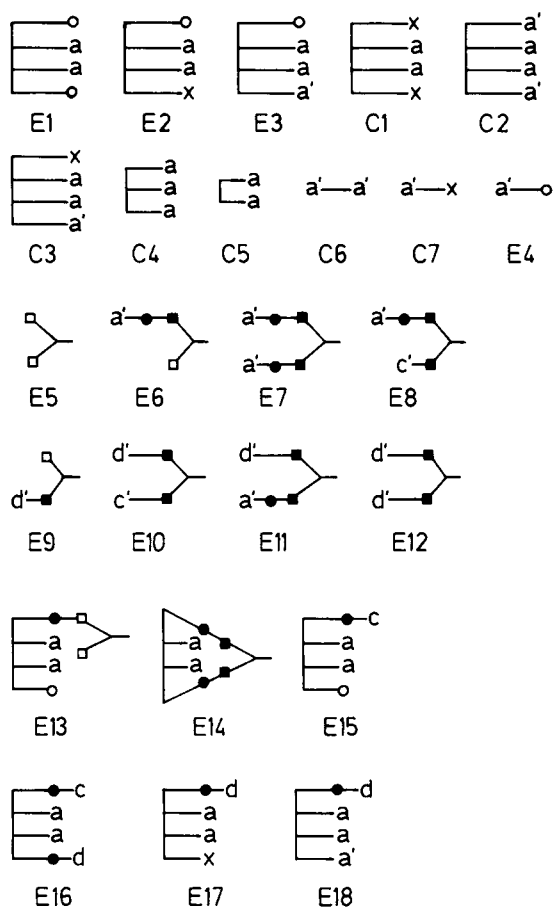**Figure 2** Chemical structure of the hardener.

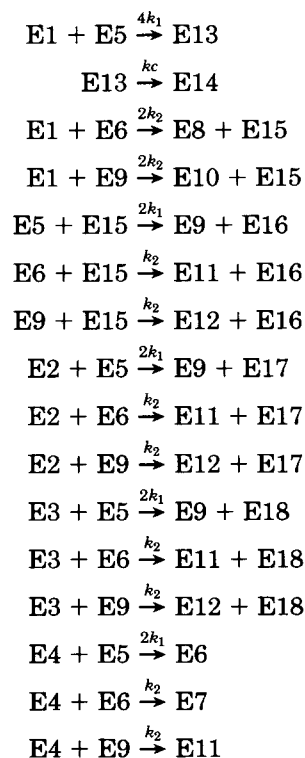Figure 3 Set of 25 fragments necessary to describe the network buildup.

Unreacted epoxides and amine hydrogens are indicated by unfilled circles and squares, respectively. Reacted functionalities are shown by filled circles (epoxides) and squares (amine hydrogens). Fragments present at $t = 0$ are E1–E5 and C1–C7. Although the concentrations of the former vary along the polymerization, those of the latter remain constant. The initial states of reaction of terminal phenolic rings of 4-ring species are indicated. E1 has two terminal epoxides, E2 has one terminal epoxide and one terminal chlorinated group (see Fig. 1), E3 has one terminal epoxide and one terminal intermolecular —CH_2—CHOH—CH_2— bridge, etc. C4 represents the 3-ring novolac species, whereas C5 indicates a 4-ring novolac structure where the two terminal phenolic rings are joined by an intramolecular —CH_2—CHOH—CH_2— bridge (only the bonds of the two interior phenolic rings are shown). Fragment C6 represents the intermolecular —CH_2—CHOH—CH_2— bridge, whereas fragment C7 denotes the chlorinated groups. Bonds a must be ran-

domly joined with bonds a' to generate the network. The initial molar concentration of the different fragments may be calculated from the molar concentrations of the precursors shown in Figure 1 and using probabilities for random combinations. Taking 1 mol of epoxy groups as a reference, the following values result: E1 = 0.12, E2 = 4.11×10^{-3}, E3 = 0.0109, C1 = 3.51×10^{-5}, C2 = 2.47×10^{-4}, C3 = 1.87×10^{-4}, C4 = 0.1319, C5 = 0.0622, C6 = 0.0111, C7 = 0.0127, E4 = 0.7448, and E5 = 0.5 for the stoichiometric system (or the corresponding value for the nonstoichiometric one).

Once the polymerization starts, fragments E6–E18 are generated. The network structure results by randomly joining bonds a with a', bonds c with c', and bonds d with d'. E5–E12 represent the different states of reaction of an amine group. When fragment E13 is formed, its only possibility is to form an intramolecular cycle (E14). However, E1 may react with a secondary amine (E6 or E9), leading to E15, a fragment that can only lead to E16, i.e., no intramolecular cycle is produced.

Reaction Scheme

The polymerization may be described by the following set of reactions:

$$E1 + E5 \xrightarrow{4k_1} E13$$

$$E13 \xrightarrow{kc} E14$$

$$E1 + E6 \xrightarrow{2k_2} E8 + E15$$

$$E1 + E9 \xrightarrow{2k_2} E10 + E15$$

$$E5 + E15 \xrightarrow{2k_1} E9 + E16$$

$$E6 + E15 \xrightarrow{k_2} E11 + E16$$

$$E9 + E15 \xrightarrow{k_2} E12 + E16$$

$$E2 + E5 \xrightarrow{2k_1} E9 + E17$$

$$E2 + E6 \xrightarrow{k_2} E11 + E17$$

$$E2 + E9 \xrightarrow{k_2} E12 + E17$$

$$E3 + E5 \xrightarrow{2k_1} E9 + E18$$

$$E3 + E6 \xrightarrow{k_2} E11 + E18$$

$$E3 + E9 \xrightarrow{k_2} E12 + E18$$

$$E4 + E5 \xrightarrow{2k_1} E6$$

$$E4 + E6 \xrightarrow{k_2} E7$$

$$E4 + E9 \xrightarrow{k_2} E11$$

Kinetic equations may be written in terms of the previous reaction scheme and taking into account

that epoxy–amine reactions are catalyzed by OH groups (initially present and generated during the polymerization).[1] For example, the equation giving the variation of E1 concentration along reaction is

$$-dE1/dt = E1(OH)[4k_1E5 + 2k_2(E6 + E9)]$$

where $(OH) = E2 + E3 + 2C1 + 2C2 + 2C3 + C5 + C6 + C7 + E6 + 2E7 + E8 + E11 + E13 + 2E14 + E15 + 2E16 + 2E17 + 2E18$ (summation of hydroxyl groups present in every species). Similar equations may be written for the remaining 17 fragments whose concentration varies along the polymerization. The set of kinetic equations was written in terms of a dimensionless time defined as $t^* = k_1e_0^2t$ and dimensionless concentrations defined as $E^* = E/e_0$ (e_0 is the initial concentration of epoxides taken as 1 mol/associated volume). The solution depends on two dimensionless parameters: k_2/k_1 and $kc/(k_1e_0)$. The reactivity ratio of secondary to primary amine hydrogens was taken as $k_2/k_1 = 0.2$, in agreement with previous experimental results.[1] The cyclization ratio was also taken as $kc/(k_1e_0) = 0.2$, i.e., a ratio equal to the corresponding intermolecular reaction of a secondary amine. Anyway, the solution was not very dependent on the election of the cyclization ratio because the only possibility left for E13 is to be converted to E14.

The numerical solution of the set of 18 coupled differential equations was performed with a fourth-order Runge–Kutta algorithm. Results were expressed in terms of the epoxy conversion defined by

$$x = 1 - (2E1 + E2 + E3 + E4 + E13 + E15)/e_0$$

Statistics of Network Formation

The recursive procedure to generate statistical parameters by randomly joining a set of fragments has been previously described.[5] Details for this particular system are available elsewhere.[8] Of interest to our discussion are the following parameters:

- Gel conversion, x_{gel}.
- Sol fraction, Ws.
- Mass fraction of pendat chains, Wp.
- Mass fraction of elastic chains, $We = 1 - Ws - Wp$.
- Concentration of cross-linking points of order 3, X3, and 4, X4, e.g., C2 becomes an X4 when the network is attained, leaving C2 by any one of its four branches.
- Concentration of elastically active network chains, ν (mol g^{-1}) = (3 X3 + 4 X4)/2.

RESULTS AND DISCUSSION

Gel Conversion and Postgel Parameters

Figure 4 shows the mass fractions of sol (Ws), pendant chains (Wp), and elastic chains (We), as a function of conversion, for a stoichiometric formulation. Both the gel conversion and the maximum conversion imposed by topological limitations[1,9] are indicated. A very good agreement between the theoretical simulation and experimental results is evident.

Regarding the gel conversion, the model predicts a value of $x_{gel} = 0.446$, in excellent agreement with the experimental value,[1] $x_{gel} = 0.45 \pm 0.01$. It is interesting to compare these values with those arising from simplified models. For example, for an ideal polymerization of an A$_f$ with a B$_g$, the gel conversion is given by

$$x_{gel}\,(\text{ideal}) = \left(\frac{1}{(f-1)(g-1)}\right)^{1/2}$$

By replacing $f = 3.6$ (from the structure given by the supplier of the epoxidized novolac) and $g = 4$, we get x_{gel} (ideal) = 0.358.

The kinetic–statistical model was also applied, taking the actual structure of the epoxidized novolac and the substitution effect of the amine hydrogens
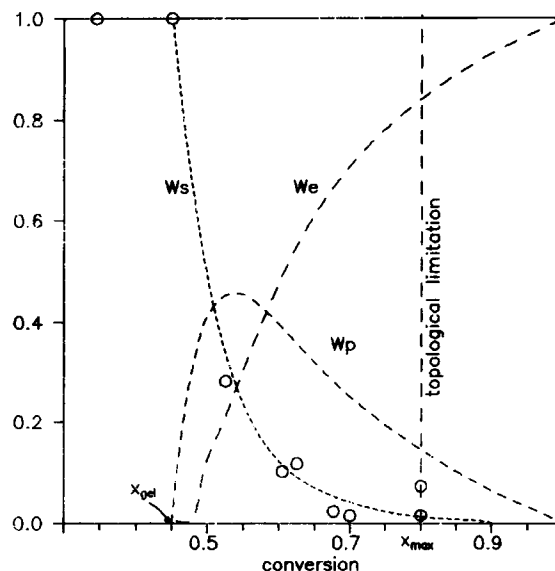

Figure 4 Mass fractions of sol, Ws, pendant chains, Wp, and elastic chains, We, as a function of conversion for a stoichiometric system. The gel conversion, x_{gel} and the limiting conversion (topological restriction) are indicated. Experimental values of sol fractions are also shown.

into account, but without considering the formation of intramolecular cycles during the cure. A value of $x_{gel} = 0.41$ was obtained. Therefore, it was necessary to introduce the possibility of intramolecular cyclization to fit the experimental values.

The topological limitation is introduced in our kinetic model as a step function, i.e., the polymerization is suddenly arrested at $x_{max} = 0.8$ (a more realistic assumption would be to decrease the polymerization rate at lower conversions until it stops completely at x_{max}). At this conversion, a significant number of pendant chains remains in the network (Fig. 4). A 99.8% of unreacted amines are secondary amines, as expected.

The evolution of the dimensionless concentration of the cyclic structure, E14, is shown in Figure 5. A significant increase in its concentration is observed in the postgel stage. However, its presence at low conversion provokes a shift in the gel conversion to higher values and leads to the correct fit between model predictions and experimental results.

T_g vs. Stoichiometric Ratio

It was recently shown[10] that the glass transition temperature (T_g) of nonstoichiometric epoxy–amine networks based on the diglycidylether of bisphenol A (DGEBA) could be reasonably predicted by the following empirical equation reported by Nielsen[11]:
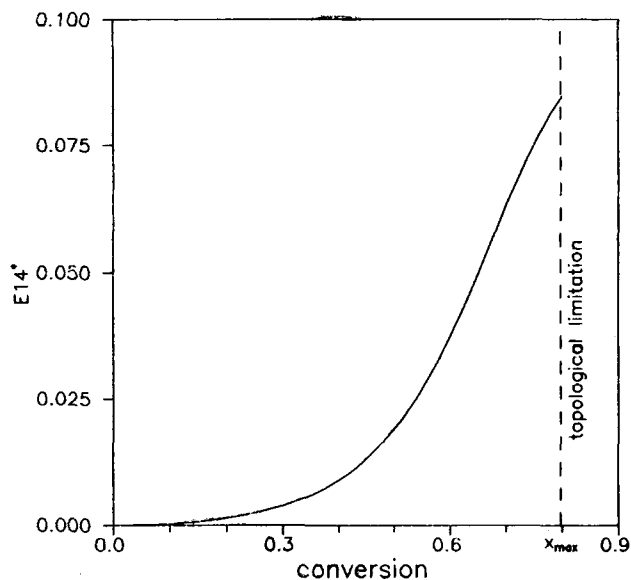
$$T_g(K) = T_{g_0}(K) + 3.9 \times 10^4 \nu$$

Figure 5 Evolution of the dimensionless concentration of fragment E14 along the polymerization.
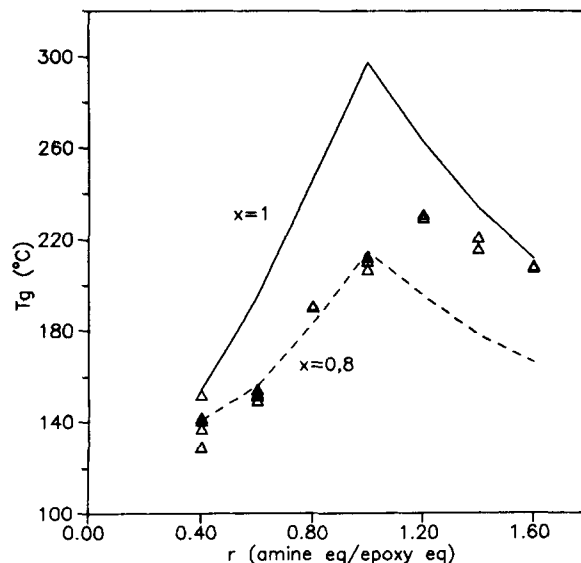
Figure 6 Glass transition temperature as a function of the stoichiometric ratio, r = amine equiv/epoxy equiv. Lines are theoretical predictions using Nielsen's equation and the statistical model, for two different conversion levels: $x = 0.8$ and $x = 1$. Points are experimental values reported in Ref. 1.

where T_{g_0} is the value of the glass transition temperature of the uncross-linked polymer and ν is the concentration of elastic chains expressed in mol/g. The possibility of explaining the dependence of T_g on the stoichiometric ratio, r = amine equivalents/ epoxy equivalents, reported in the first part of the study,[1] will now be analyzed.

To fit T_{g_0}, the value of $T_{g_{max}} = 488$ K ($215°C$), for a stoichiometric formulation ($r = 1$) cured to $x_{max} = 0.8$, will be used. The statistical model predicts a value of $\nu = 1.937 \times 10^{-3}$ mol g^{-1} for this particular condition. Therefore, replacing in Nielsen's equation, we get $T_{g_0} = 412.4$ K. Then, values of T_g for networks prepared at different stoichiometries were predicted from

$$T_g(K) = 412.4 + 3.9 \times 10^4 \nu(x, r)$$

The concentration of elastic chains was calculated by applying the statistical model to formulations with stoichiometric ratios varying from $r = 0.4$ to 1.6. Two different conversion levels were used: $x = 0.8$ and $x = 1$.

A comparison of experimental results with theoretical predictions is shown in Figure 6. Networks prepared with an epoxy excess show T_g values limited by the maximum conversion that can be attained in these conditions. However, networks pre-

pared with an amine excess higher than 20% can be reacted to an almost complete conversion of epoxy groups.[1] Theoretical calculations lead to a correct prediction of the experimental trends (the maximum conversion in the amine-excess region seems to increase continuously with r, reaching $x = 1$ at r close to 1.6. This is in good agreement with calorimetric results[1]). The result of the simultaneous variation of r and x_{max} is the presence of a maximum in T_g (230°C) at $r = 1.2$. It may be noticed that a stoichiometric network would reach a potential value of $T_g = 297.5$°C if it could be reacted to complete conversion.

T_g vs. Conversion

The fitting of the T_g vs. x experimental values reported in the first part of the study,[1] by the equation developed by Pascault and Williams,[12] will be now analyzed.

Based on entropic considerations applied to a model of the thermosetting polymer consisting of a random mixture of a fully reacted network with the initial monomers, the following equation was derived[12]:

$$(T_g - T_{g0})/(T_{g1} - T_{g0}) = \lambda x/[1 - (1 - \lambda)x],$$

where $\lambda = \Delta Cp_1/\Delta Cp_0$; ΔCp represents the change in the specific heat at T_g, the subscript 0 indicates the unreacted system ($x = 0$), and the subscript 1 represents the fully reacted network ($x = 1$).

As it is not possible to obtain complete conversion for the stoichiometric system, the equation must be modified as suggested by Hale et al.[3]:

$$(T_g - T_{g0})/(T_{gM} - T_{g0}) = \lambda' x'[1 - (1 - \lambda')x']$$

where T_{gM} is the glass transition temperature for the network reacted to the maximum possible conversion, x_M, $\lambda' = \Delta Cp_M/\Delta Cp_0$ and $x' = x/x_M$.

Using the experimental values of $T_{g0} = 313$ K (40°C) and $T_{gM} = 488$ K (215°C) and taking λ' as a fitting parameter (the scattering of experimental values of ΔCp did not allow us to obtain a reliable value of λ'), the correlation shown in Figure 7 was obtained. A relatively good fitting results for λ' = 0.15. For a system based on an epoxy cresol novolac cured with a cresol novolac, Hale et al.[3] reported experimental values of λ', at $x_M = 0.78$, varying between 0.1 and 0.35, i.e., a range that includes the λ' used to fit our experimental results (Hale et al.[3] used $\lambda' = 0.30$ for their own results).
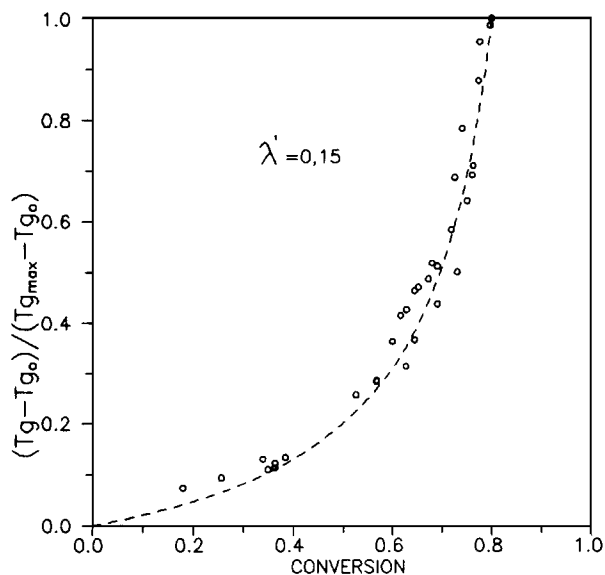

Figure 7 Fitting of the experimental T_g vs. x values by the equation developed by Pascault and Williams[12] and modified by Hale et al.[3]

CONCLUSIONS

The buildup of the network arising from the reaction of an epoxy novolac with an aromatic diamine was modeled using a kinetic–statistical procedure that takes into account (i) the complex structure of the starting epoxy novolac, (ii) the actual polymerization kinetics including the differences in reactivities between primary and secondary amine hydrogens, and (iii) the formation of intramolecular cycles in species containing four phenolic rings.

Predictions of gel conversion and sol fraction were in excellent agreement with experimental results. Glass transition temperatures of networks prepared at different stoichiometries were predicted, replacing the concentration of elastic network chains arising from the model, in the empiric equation proposed by Nielsen.[11] Theoretical predictions supported the observed experimental trends. The maximum conversion seemed to increase continuously from x_{max} = 0.8 in the stoichiometric sample to x_{max} close to 1 for the formulation containing a 60% amine excess, in agreement with previous calorimetric results.[1] The consequence was the appearance of a maximum in the experimental T_g for samples containing a 20% amine excess. In the absence of topological restrictions, a stoichiometric formulation would reach a T_g close to 300°C at full conversion. The dependence of T_g on conversion for a stoichiometric system could be reasonably fitted with the equation developed by Pascault and Williams,[12] assigning a value of 0.15

to the ratio of specific heats. This value lies in the range of experimental results reported by Hale et al.[3] for the cure of an epoxy cresol novolac with a cresol novolac.

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