Polymer Bulletin 13, 321–328 (1985)

Polymer Bulletin

Build-up of Polymer Networks by Initiated Polyreactions

2. Theoretical Treatment of Polyetherification Released by Polyamine-Polyepoxide Addition

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Dedicated to Dr. B. Sedláček on the occasion of his 60th birthday

Summary

The network build-up by the polyetherification of a diepoxide released by hydroxyl groups formed in the primary reaction with diamine was treated by combination of the kinetic and statistical branching theories. The critical polyetherification conversion at gel point was shown to depend on the initial amine/epoxy molar ratio. Application of a purely statistical approach led to relatively large deviations.

Introduction

The polyetherification (homopolyaddition, homopolymerization) of epoxy groups is a major source of bond formation in many important curing agent-epoxy resin systems. It is released by an initiating species and propagation occurs usually by an ionic mechanism (1,2). Often, the initiating species are proton donors which open the epoxy ring under formation of an OH group which itself serves as a proton donor, i.e. a reactive (living) end of the growing chain.

The polyetherification of excess epoxy groups in diamine-diepoxide curing is an example of such initiated reaction. The amino alcohols formed by the addition of epoxide to primary or secondary amine are sources of proton donors and at the same time basic catalysts for polyetherification. Since their basicity is rather low, polyetherification sets in only after the amino groups have been practically consumed (3). A similar situation arises in the reaction of polycarboxylic acids with polyepoxides catalyzed by tertiary amines in which polyetherification commences after almost all carboxyl groups have reacted (4).

The network build-up in the curing of epoxy resins is of great interest for the understanding and prediction of formation-structure-properties relationships (5). Until now, exclusively the statistical approach has been used for polyetherification accompanying the epoxy-amine curing (6), polyetherification released by diphenols (7,8),or the tert.amine initiated curing of diepoxides with cyclic anhydrides (9). However, in the preceding communication (10) it was shown that the application of the statistical approach to initiated reactions can be the source of a considerable error. The aim of this communication is to explain the branching theory applied to curing of diepoxides with diamines accompanied by polyetherification which is based on a combination of the kinetic and statistical theory and to demonstrate the error arising from the application of a solely statistical approach.

Theory

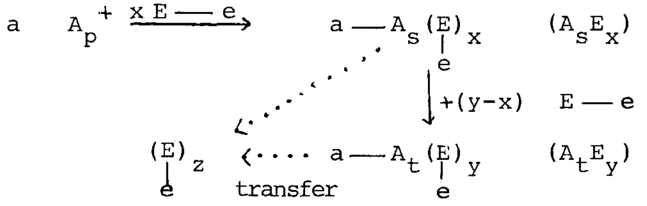
Let us consider the reaction of a diamine having amino groups with independent reactivity but with a substitution effect in each amino group and a diepoxide with an independent reactivity of the epoxy groups. As has been shown in Part I (10), the treatment consists in three steps:

a) The connections between independent groups are cut and the points of cut labelled a or e

$$A_p — A_p \rightarrow 2\ \ a — A_p, \quad E — E \rightarrow 2\ e — E$$

where A_p is the primary amino group and E the epoxy group.

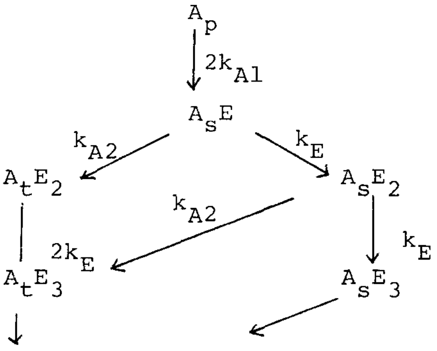
b) The $A_p + E$, $A_s + E$ and $-E + E$ reactions are effectuated and the amine-polyepoxy clusters are generated. Schematically,



(1)

where A_s and A_t are secondary and tertiary amino groups, respectively. The distribution of clusters A_p, A_sE_y is obtained by solving the corresponding set of kinetic differential equations given by the reaction mechanism. For the given reaction conditions, not only the A+E addition and E+E etherification reactions, but also possible termination by chain transfer or deactivation (2) must be taken into account. Then, also clusters of type $(\underset{\stackrel{|}{e}}{E})_z$ are generated by reinitiation and have to be taken into consideration.

For addition and propagation without termination, the reaction scheme can be written down as follows



(2)

where k_{A1}, k_{A2}, k_E are the apparent rate constants the values of which depend on the concentration of catalytically active species and thus on conversion (2).

c) In the last step, the points labelled a and e are combined into pairs a-a and e-e, so that the original bifunctional units are restored. This combination of clusters is effectuated by the statistical (cascade) method. Formation of inactive rings is not considered.

Cascade generation from clusters: The building blocks for generation of branched and crosslinked structures are represented by unreacted epoxy groups E as well as clusters A_sE_x and A_tE_y which include A_p; their molar concentration is denoted by [ ]. The distribution of A_sE_x and A_tE_y is conveniently expressed by generating functions (gf) $g_1(Z)$ and $g_2(Z)$ defined by

$$\begin{aligned} g_1(Z) &\equiv \sum_x [A_sE_x] Z^x/N = \sum_x (a_s e_x) Z^x , \\ g_2(Z) &\equiv \sum_y [A_tE_y] Z^y/N = \sum_y (a_t l_y) Z^y \end{aligned} \qquad (3)$$

where Z is the variable of gf and $N = [A_p] + \sum_x [A_sE_x] + \sum_y [A_tE_y]$.

Using the theory of branching (cascade) processes, the probability gf for the number of a-a or e-e bonds F_{0C} and F_{0E} issuing from slusters or an E-e unit, respectively, are given by

$$F_{0C}(z) = a_p + g_1(Z_E) + g_2(Z_E)\, z_{CA} \qquad (4)$$

$$F_{0E}(z) = Z_E \qquad (5)$$

where $a_p = [A_p]/N$ and $Z_E = \phi_1 z_{eC} + \phi_2 z_{eE}$ (6)

The variables z_{eC}, z_{eE} are related to e-e bonds extending to an E unit built-in in a cluster and to an unreacted E group, respectively, and z_{CA} to an a-a bond extending (necessarily) from a cluster to an A unit (in a cluster) (the subscript C is in fact superfluous but is retained because of unified notation). The ϕ_1 and ϕ_2 are the probabilities that the e-e bond extends either to E in the cluster or to an unreacted E and are defined by

$$\phi_1 = \frac{[E]_0 - [E_0]}{[E]_0} = \alpha_E \quad , \quad \phi_2 = 1 - \phi_1 \quad , \qquad (7)$$

where $[E]_0$ is the initial and $[E_0]$ is the actual concentration of unreacted epoxy groups and α_E is the conversion of E groups.

Since the z's are related to the probabilities of existence of the bonds that are active in branching, the pgf's for units in generations $g > 0$ are as follows

$$F_{eC}(z) = [\partial F_{0C}/\partial z_{eC} + \partial F_{0C}/\partial z_{eE}]/A_1 = [g_1'(Z_E) + g_2'(Z_E)]/A_1 \qquad (8)$$

$$F_{eE}(z) = \partial F_{0E}/\partial z_{eC} + \partial F_{0E}/\partial z_{eE} = 1 \qquad (9)$$

$$F_{AC}(\mathbf{z}) = \partial F_{0C}/\partial z_{cA} \quad a_p + g_1(Z_E) + g_2(Z_E) \tag{10}$$

with $g'(Z_E) = \partial g(Z_E)/\partial Z_E$ and $A_1 = g_1'(1) + g_2'(1) =$

$$= \sum_x x(a_s e_x) + \sum_y y(a_t e_y) = ([E]_0 - [E_0])/[A]_0 \quad ,$$

where $[A]_0$ is the initial concentration of amine groups. Therefore,

$$A_1 = ([E]_0/[A]_0)\alpha_E = r_E\alpha_E \tag{11}$$

The gel point condition is given by

$$\det A = \det(F_{ij}^{kl} - \partial_{ij}^{kl}) = 0 \tag{12}$$

where $F_{ij}^{kl} = [\partial F_{ij}(\mathbf{z})/\partial z_{kl}]_{\mathbf{z}=\mathbf{1}}$; δ_{ij}^{kl} is equal to 1 for $ij = kl$ and zero otherwise. Because of three F_{ij} (Eqs. (8)-(10)), det A is a 3×3 determinant the solution of which yields

$$1 - \phi_1 A_2/A_1 - \phi_1 A_1 = 1 - \alpha_E(A_2/r_E\alpha_E + r_E\alpha_E) = 0 \tag{13}$$

where

$$A_2 = \sum_x x(x-1)(a_s e_x) + \sum_y y(y-1)(a_t e_y) \tag{14}$$

This approach is applicable to a routine calculation of molecular weight averages and extinction probabilities v_{eC}, v_{eE}, v_{AC} determining the postgel characteristics, such as the sol fraction and concentration of elastically active network chains. However, the limited size of this contribution does not allow us to go into details of this calculation.

In the next section, the postetherification of excess epoxy groups occurring after completion of the epoxy-amine reaction will be treated in more detail.

Postetherification in amine-epoxy curing: Build-up from clusters

For usual polyamines and Bisphenol A diglycidyl ether type resins, the basicity of the amino alcohol is so weak that $k_E \ll k_{A1}, k_{A2}$, i.e. etherification occurs only after the primary and secondary amino groups have been exhausted. Then, we have

$$\begin{aligned} A_tE_2 + E_0 &\xrightarrow{k_E} A_tE_3 \\ A_tE_3 + E_0 &\xrightarrow{k_E} A_tE_4 \\ &\vdots \end{aligned} \tag{15}$$

The corresponding set of kinetic differential equations can be transformed into a single differential equation (17) for the number fraction fg, $g(Z_E)$,

$$g(Z_E) = \sum_{x=2}[A_tE_x]Z_E^x/N = \sum_{x=2}(a_t e_x)Z_E^x \tag{16}$$

$$\frac{dg(Z_E)}{2k_E dt} = g(Z_E)(Z_E - 1)[E_0] \tag{17}$$

The decrease in the concentration of unreacted epoxy groups $[E_0]$ is given by

$$\frac{d[E_0]}{2k_E dt} = -\,[E_0][A_t] = -\,[E_0][A]_0 \tag{18}$$

Eqs.(17) and (18) give

$$\frac{dg(Z_E)}{de_0} = -\,g(Z_E)(Z_E - 1)r_E \tag{19}$$

where

$$r_E = [E]_0/[A]_0 \quad \text{and} \quad e_0 = [E_0]/[E]_0 = 1 - \alpha_E \tag{20}$$

α_E is the total conversion of epoxy groups. The conversion of excess epoxy groups into ethers α_{ETH} is given by

$$\alpha_{ETH} = \frac{[E]_0 - 2[A]_0 - [E_0]}{[E]_0 - 2[A]_0} = \frac{r_E\alpha_E - 2}{r_E - 2} \tag{21}$$

The solution of Eq.(19) with boundary conditions $g(Z_E) = Z_E^2$ for $r_E e_0 = r_E - 2$ gives

$$g(Z_E) = Z_E^2 e^{(Z_E - 1)\rho\alpha_{ETH}} \tag{22}$$

with $\rho = r_E - 2$

In the last step, the clusters and unreacted epoxy groups are combined using the cascade method(cf. Eqs.(4)-(5)). The pgf for the number of bonds issuing from clusters and epoxy units in the root can be written as follows

$$F_{0C}(\mathbf{z}) = z_{CA}g(Z_E) = z_{CA}Z_E^2 e^{(Z_E - 1)\rho\alpha_{ETH}} \tag{23}$$

$$F_{0E}(\mathbf{z}) = Z_E \quad , \tag{24}$$

where

$$Z_E = \phi_1 z_{eC} + \phi_2 z_{eE} \quad \text{and} \quad \phi_1 = \alpha_E \;, \; \phi_2 = 1 - \alpha_E .$$

The pgf's for units (clusters and unreacted epoxy units) in generation $g > 0$ are obtained by differentiation (cf.Eqs.(8)-(10))

$$F_{eC}(\mathbf{z}) = \frac{Z_E z_{AC} e^{(Z_E - 1)\rho\alpha_{ETH}}(2 + Z_E\rho\alpha_{ETH})}{2 + \rho\alpha_{ETH}} \tag{25}$$

$$F_{eE}(\mathbf{z}) = 1 \tag{26}$$

$$F_{AC}(\mathbf{z}) = z_E^2 e^{(Z_E - 1)\rho\alpha_{ETH}} \tag{27}$$

The gel point condition is obtained from the determinant A (Eq.(12) or (13)) which gives

$$1 - (2 + \rho\alpha_{ETH})(3 + 2\rho\alpha_{ETH})/r_E = 0 \tag{28}$$

Build-up from units

In this case, structures are built-up from diamine and diepoxide units. The pgf's for the number and type of bonds issuing from units in the root are

$$F_{0A}(\mathbf{z}) = z_{AE}^4 \tag{29}$$

$$F_{0A}(\mathbf{z}) = [\varepsilon_0 + \varepsilon_1(\psi_1 z_{EE} + \psi_2 z_{EA})(\psi_1 z_{EE} + \psi_2)]^2 \tag{30}$$

where ε_0 and ε_1 are fractions of unreacted and reacted epoxy groups, respectively (obviously, $\varepsilon_1 = \alpha_E$, $\varepsilon_2 = 1 - \alpha_E$), ψ_1 and ψ_2 are the probabilities that the bond issuing from a reacted epoxy unit leads to another epoxy group and to an amine group, respectively,

$$\psi_2 = 2[A]_0/([E]_0 - [E_0]) = 2/r_E\alpha_E \ , \ \psi_1 = 1 - \psi_2 \tag{31}$$

The subscripts in variables z_{IJ} mean that the bond extends from unit I to unit J in the next generation. The construction of F_{0E} suggests that the probabilities for an epoxy unit to be bound to an amine group or to an epoxy group are considered independent of the length of the particular epoxy sequence of which the unit is a part.

The pgf's for the number of bonds issuing from units in generation $g > 0$ is again obtained by the differentiation of F_{0A} and F_{0E}; thus

$$F_{EA}(\mathbf{z}) = z_{AE}^3 \tag{32}$$

$$F_{AE}(\mathbf{z}) = (\psi_1 z_{EE} + \psi_2)[\varepsilon_0 + \varepsilon_1(\psi_1 z_{EE} + \psi_2 z_{EA})(\psi_1 z_{EE} + \psi_2)] \tag{33}$$

$$F_{EE}(z) = [\psi_2(1 + z_{EA}) + 2\psi_1 z_{EE}][\varepsilon_0 + \varepsilon_1(\psi_1 z_{EE} + \psi_2 z_{EA})(\psi_1 z_{EE} + \psi_2)] \tag{34}$$

The subscripts XY in F_{XY} mean that pgf describes the distribution of bonds issuing to the next generation from unit type Y rooted by the bond extending from unit Y to unit X in the preceding generation.

Again, the gel point condition is obtained by equating the 3×3 det A of derivatives of F_{EA}, F_{AE} and F_{EE} to zero (cf.Eq.(12)), which yields

$$1 - \psi_1(1 + \varepsilon_1) - 3\psi_1\psi_2(1 + \varepsilon_1)(1 + 2\varepsilon_1) - 3\varepsilon_1\psi_2[1 - \psi_2(1 + \varepsilon_1)] = 0 \tag{35}$$

or the equation

$$r_E^2\alpha_E^3 + 2\alpha_E r_E(3\alpha_E^2 + 8\alpha_E + 2) - 12(1 + \alpha_E)^2 = 0 \qquad (36)$$

which can be transformed into a dependence of α_{ETH} by making use of Eq.(21), i.e. $\alpha_E = [\alpha_{ETH}(r_E - 2) + 2]/r_E$.

Comparison of the two approaches and conclusions

The difference between the build-up from kinetically generated epoxy-amine clusters and the statistical build-up from diepoxide and diamine units is demonstrated by the critical conversion of excess epoxy groups α_{ETH} at the gel point. In order to reach gelation, the chain termination by unreacted epoxy groups due to off-stoichiometry and the alternating type of epoxy-amine addition must be counterbalanced by the formation of epoxy-epoxy bonds. Eqs.(28) and (36) express the dependence of the epoxy/amine ratio r_E on the conversion of excess epoxy groups necessary to reach gelation. Fig. 1 shows that α_{ETH} is expected to be rather low in order to prevent the system from gelation and that r_E must exceed 6 (the possible substitution effect in the amine group is irrelevant).

Comparison of the two approaches shows that the difference between the results obtained using the two approaches is rather significant. This means that any experimental results have to be tested against predictions derived from the cluster model. In reality, the transfer and termination reactions may interfere, which is expected to be reflected particularly in the α_{ETH} vs. r_E dependence at higher r_E. In addition to model experiments, the gelation experiments in real polyfunctional systems can help in elucidating the polyetherification mechanism.

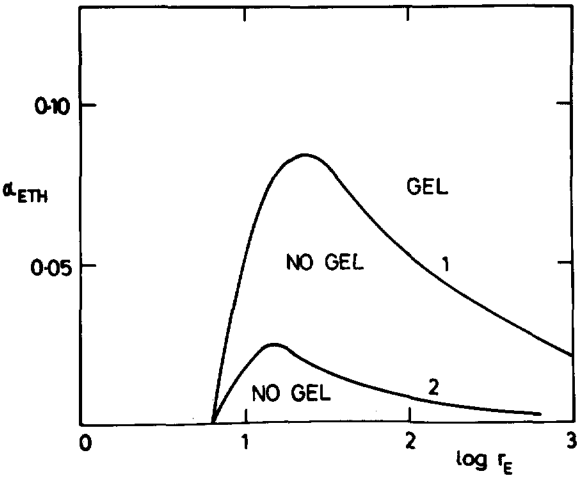


Fig.1. Dependence of the critical conversion of excess epoxy groups α_{ETH} in diepoxide-diamine systems on the initial epoxy/amine ratio, r_E. 1 - build-up from clusters generated kinetically, 2 - statistical build-up from units

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Accepted March 29, 1985