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Build-up of polymer networks by initiated polyreactions

5. Comparison of fragment vs cluster approaches to derive postgel parameters for postetherification in diamine-diepoxide curing

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Summary

The network build-up by polyetherification of a diepoxide released by hydroxyl groups formed in the primary reaction with a diamine was treated by two different methods: i) a rigorous approach in which kinetically generated clusters are statistically combined (cluster approach), and ii) an approximate calculation in which kinetically generated fragments are statistically combined (fragment approach). The cluster approach was used to calculate pregel parameters in part 2 of the series (K.Dušek, Polym.Bull. 13,321,1985) and postgel parameters in part 4. of the series (K.Dušek et al., Polym.Bull. 18,209,1987). A comparison with the fragment approach for the pregel stage was provided in part 3 of the serie (R.J.J.Williams et al., Polym.Bull. 17,515,1987). The same comparison for the postgel stage is now provided. Very close results are found when using both methods for the calculation of the sol fraction and the concentration of elastically active network chains.

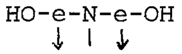
Introduction

The ideal polyetherification of excess epoxy groups in diamine-diepoxide curing is a typical example of an initiated polyreaction. The amino alcohols formed by the addition of epoxide to primary or secondary amine are sources of proton donors for the subsequent polyetherification. In the absence of other initiators (i.e. tertiary amines of high basicity), it may be accepted that polyetherification sets in only after the amino groups have been practically consumed (1,2). The actual mechanism of polyetherification in epoxy-amine systems is, however, more complicated (3).

In the ideal system after the amine hydrogens have been exhausted in the reaction with epoxides (first step), the following fragments are present:

unreacted epoxy (half of a diepoxide molecule),
tertiary amine (arising from half of a diamine molecule),

$$e \rightarrow \qquad \text{(F1)}$$



$$\text{HO-}\underset{\downarrow}{\text{e}}\text{-}\underset{|}{\text{N}}\text{-}\underset{\downarrow}{\text{e}}\text{-OH} \qquad \text{(F2)}$$

The resulting network is build up by randomly joining arrows with arrows, and segments (lines)(issuing from the nitrogen

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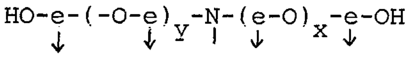
*To whom offprint requests should be sent atom) among themselves. This implicitely assumes that each amino group of the diamine molecule and each epoxy group of the diepoxide have independent reactivity.

The postetherification step may be analyzed by using two methods:

(i) Cluster Approach

The polyetherification reaction leads to the following clusters (superspecies):

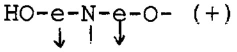


$$HO\text{-}\underset{\downarrow}{e}\text{-}(\text{-}O\text{-}\underset{\downarrow}{e})_y\text{-}\underset{|}{N}\text{-}(\underset{\downarrow}{e}\text{-}O)_x\text{-}\underset{\downarrow}{e}\text{-}OH$$

The time dependence of their concentrations is described by kinetic differential equations which are converted into a differential equation of the generating function for the degree of polymerization distribution (2). The resulting network is built up by randomly joining arrows (pertaining to the clusters or to unreacted epoxy), regenerating the diepoxide structure, and segments, regenerating the diamine structure. This recombination is performed using a statistical algorithm of the theory of branching processes (2).

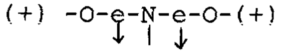
(ii) Fragment Approach

The polyetherification reaction is described using the following fragments that may be identified in clusters. Thus:



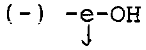
$$HO\text{-}\underset{\downarrow}{e}\text{-}\underset{|}{N}\text{-}\underset{\downarrow}{e}\text{-}O\text{-}\ (+)$$

(F3)



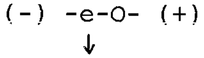
$$(+)\ \text{-}O\text{-}\underset{\downarrow}{e}\text{-}\underset{|}{N}\text{-}\underset{\downarrow}{e}\text{-}O\text{-}(+)$$

(F4)



$$(-)\ \text{-}\underset{\downarrow}{e}\text{-}OH$$

(F5)



$$(-)\ \text{-}\underset{\downarrow}{e}\text{-}O\text{-}\ (+)$$

(F6)

where (+) bonds must be linked to (-) bonds.

The reaction scheme is as follows:

$$F1 + F2 \xrightarrow{2k_E} F_3 + F5 \quad (1)$$

$$F2 + F3 \xrightarrow{k_E} F4 + F5 \quad (2)$$

$$F1 + F5 \xrightarrow{k_E} F5 + F6 \quad (3)$$

By solving the set of kinetic differential equations, the concentration of fragments as a function of polymerization conversion may be obtained. The network may be assembled by randomly joining arrows among themselves, segments among themselves and (+) with (-) bonds (3).

Both approaches use a combination of kinetic and statistical calculations. However, the cluster approach is a rigorous method because the true distribution of chain lengths is used. The fragment approach is an approximate method because a random joining of fragments yields a most-probable distribution of degrees of polymerization, although the actual distribution may be different, e.g. a Poisson distribution in case of living polymerization with a fast initiation step (4).

For simple polymerization schemes the kinetic differential equations of the cluster approach may be solved and rigorous statistical parameters obtained. However, as the fragment approach is a convenient tool for polymerizations showing very complex reaction schemes (5,6), including formation of small cycles (7), etc., it is convenient to compare both approaches for a simple case as the present one.

The cluster approach was already used to calculate pregel properties of the present system in Part 2 of the series (2), and postgel parameters in Part 4 of the series (8). A comparison between the cluster and fragment approaches for the pregel stage was provided in Part 3 of the series (9). A very close prediction of the gel point conversion by both methods was shown. The aim of this part of the series is to compare both methods in the postgel stage.

The fragment approach in the postgel stage

The reaction extent of epoxy groups is given by

$$\alpha_E = 1 - F1/F1(0) = 1 - F1^* \qquad (4)$$

At the end of the epoxy-amine reaction (first step), the conversion of epoxy groups is $\alpha_E = 2/r_E$, where r_E is the molar ratio of amino groups (half of the diamine) over epoxy groups (half of the diepoxide). The concentration of different fragments at the end of the first step ($\alpha_E = 2/r_E$) is the following

$$F1^*=1 - 2/r_E;\ F2^*=F2/F1(0)=1/r_E;\ F3^*=F4^*=F5^*=F6^*=0\ (F^*=F/F1(0))$$

Kinetic differential equations arising from the reaction scheme, i.e. eq(1) to (3), can be analytically solved to give

$$F2^* = p^2/r_E \qquad (5)$$

$$F3^* = 2p(1-p)/r_E \qquad (6)$$

$$F4^* = [1 + p(p-2)]/r_E \qquad (7)$$

$$F5^* = 2(1-p)/r_E \qquad (8)$$

$$F6^* = \alpha_E - 2(2 - p)/r_E \qquad (9)$$

where $p = \exp\{-\frac{r_E}{2}(\alpha_E - \frac{2}{r_E})\}$

The reaction extent in the second step (polyetherification) is given by

$$\alpha_{ETH} = (\alpha_E - 2/r_E)/(1 - 2/r_E) \qquad (10)$$

In order to calculate postgel parameters, it is necessary to determine the probability of having finite chains when looking out of a fragment via an arrow (R), a segment (S), an (+) bond (T_P) or an (-) bond (T_N). The total number of arrows is equal to F1(0), the total number of segments is equal to

$F1(0)/r_E$ and the total number of (+) or (-) bonds is given by $(F5 + F6)$. Then, $R = \sum_i$ (probability of joining fragment i by an arrow) (probability that every bond issuing from fragment i is finite) =

$$(F1 + 2F2\ RS + 2F3\ RST_P + 2\ F4\ RST_P^2 + F5\ T_N + F6\ T_PT_N)/F1(0) \tag{11}$$

Similarly,

$$S = (F2\ R^2 + F3\ R^2T_P + F4\ R^2T_P^2)r_E/F1(0) \tag{12}$$

$$T_P = (F5\ R + F6\ RT_P)/(F5 + F6) \tag{13}$$

$$T_N = (F3\ R^2S + 2\ F4\ R^2ST_P + F6\ RT_N)/(F5 + F6) \tag{14}$$

With the aid of eqs(5) to (9), eqs (11) to (14) may be numerically solved to give the extinction probabilities R, S, T_P and T_N as a function of α_{ETH}. Any postgel parameter may be expressed as a function of these extinction probabilities.

The sol fraction is given by

$$w_s = w_1R + w_2R^2S + w_3R^2ST_P + w_4R^2ST^2{}_P + w_5RT_N + w_6RT_PT_N \tag{15}$$

where w_i denotes mass fractions.

In order to count the number of elastically active network chains (EANC's), several possibilities may be distinguished (cf. Schemes in Ref. (8)). Here, we will take two possibilities: i) All active branch points are counted. Each active branch point (a branch point from which at least three bonds have infinite continuation) contributes by 3/2 to the number of EANC's, N_{E1}. It can be seen that in fragments F2 and F6, there is one possible active branch point, while in fragments F3 and F4 there are, respectively, two and three possible active branch points. Then,

$$\begin{aligned}N_{E1} = (3/2)\{&F2(1-R)^2(1-S) + F6(1-R)(1-T_P)(1-T_N) + F3((1-S)[(1-R)^2 +\\
&+ R(1-R)(1-T_P)] + (1-T_P)(1-R)[(1-S)+S(1-R)]) +\\
&+ F4((1-S)(1-R)(1-T_P)[(1-R)(1-T_P) + 2R(1-T_P) +\\
&+ 2T_P(1-R) + 2RT_P] + (1-S)[T_P^2(1-R)^2 + R^2(1-T_P)^2] +\\
&+ 2(1-T_P)(1-R)[(1-S) + S(1-R) + S(1-T_P)])\}\end{aligned} \tag{16}$$

ii) Only the bridge in diamine is counted, a situation arising when this bridge is long and flexible compared to diepoxide and ether bridges. In this case,

$$\begin{aligned}N_{e2} = (1/2)(1-S)\{&F2(1-R)^2 + F3[(1-R)^2 + 2R(1-R)(1-T_P)] +\\
&+ F4[(1-R)^2T_P^2 + (1-T_P)^2R^2 + (1-T_P)^2(1-R)^2 +\\
&+ 4RT_P(1-R)(1-T_P) + 2T_P(1-T_P)(1-R)^2 + 2R(1-R)(1-T_P)^2]\}\end{aligned} \tag{17}$$

The concentration of EANC's per unit volume of gel, ν_{ei},

$$\nu_{ei} = \frac{d\ N^*_{ei}}{(M_A/r_E + M_E)(1 - w_s)} \qquad (18)$$

where d is the gel density, $N^*_{ei} = N_{ei}/F1(0)$, and M_A and M_E are, respectively, half of the molar masses of a diamine and a diepoxide. Then, $(M_A/r_E + M_E)$ represents the total mass per initial epoxy equivalent.

Discussion

In order to compare the cluster and fragment approaches, the following numerical values will be taken: $M_A = 200$, $M_E = 175$, $d = 1.15$ g cm^{-3}; the masses of different fragments are: $M_1 = 175$, $M_2 = 176$, $M_6 = 175$. The mass fraction of a particular fragment i is given by

$$w_i = F^*_i\, M_i/(M_A/r_E + M_E) \qquad (19)$$

Values for the cluster approach are taken from equation developed in Part 4 of the series (8).

Table 1 shows the comparison of sol fractions calculated by both approaches for different initial stoichiometric ratios.

Table **1** Comparison of sol fractions predicted by the cluster, $w_s(C)$ and fragment, $w_s(F)$, approaches for different excess of epoxy groups as a function of the polyetherification conversion

	$r_E = 4$		$r_E = 6$		$r_E = 12$	
α_{ETH}	$w_s(F)$	$w_s(C)$	$w_s(F)$	$w_s(C)$	$w_s(F)$	$w_s(C)$
10^{-6}	0.3295	0.3295	0.9993	0.9993	1	1
0.05	0.2595	0.2595	0.6205	0.6205	1	1
0.10	0.2109	0.2109	0.4495	0.4495	0.7382	0.7387
0.20	0.1462	0.1462	0.2835	0.2834	0.4470	0.4464
0.30	0.1039	0.1038	0.1964	0.1963	0.3180	0.3174
0.40	0.0731	0.0731	0.1380	0.1380	0.2293	0.2291
0.50	0.0496	0.0496	0.0942	0.0941	0.1586	0.1586
0.60	0.0314	0.0314	0.0599	0.0599	0.1014	0.1014
0.70	0.0176	0.0176	0.0336	0.0336	0.0571	0.0571
0.80	0.0078	0.0078	0.0149	0.0149	0.0254	0.0254
0.90	0.0019	0.0019	0.0037	0.0037	0.0063	0.0063
1	0	0	0	0	0	0

Practically no differences exist between sol fraction predictions given by both approaches for different excess of epoxy groups. The results are very close although there are some significant differences for the highest r_E value. The maximum difference arises in the calculation of ν_{E2} for intermediate α_{ETH} (maximum percent error close to 10% for $\alpha_{ETH} = 0.30$). It is interesting to note that the fragment approach predicts ν_{e1} values slightly higher and ν_{e2} values slightly lower than the true values.

Table 2 Comparison of the concentration of EANC's per unit volume of gel predicted by the cluster, $\nu_{ei}(C)$, and fragment, $\nu_{ei}(F)$, approaches, as a function of the polyetherification conversion for $r_E = 4$

	$R_E = 4$		ν_{ei} 10^3 mol cm^{-3}	
α_{ETH}	$\nu_{e1}(F)$	$\nu_{e1}(C)$	$\nu_{e2}(F)$	$\nu_{e2}(C)$
10^{-6}	0.2578	0.2578	0.0859	0.0859
0.05	0.4239	0.4237	0.1332	0.1332
0.10	0.6109	0.6103	0.1816	0.1819
0.20	1.0309	1.0284	0.2759	0.2772
0.30	1.4964	1.4916	0.3618	0.3642
0.40	1.9971	1.9908	0.4362	0.4394
0.50	2.5293	2.5226	0.4979	0.5014
0.60	3.0930	3.0873	0.5468	0.5499
0.70	3.6912	3.6873	0.5837	0.5859
0.80	4.3290	4.3272	0.6100	0.6112
0.90	5.0128	5.0122	0.6277	0.6281
1	5.7499	5.7499	0.6389	0.6389

It may be concluded that the fragment approach gives postgel parameters very close to those derived by the rigorous method for the postetherification in diamine-diepoxide curing. In general, large differences are not expected between the results obtained by both approaches except of systems with very long primary chains formed by a living polymerization (9). However, it is to be remarked that the real mechanism of postetherification is more complicated than that used here and assuming a simple initiated polyaddition (10).

Table 3 Comparison of the concentration of EANC's per unit volume of gel predicted by the cluster, $\nu_{ei}(C)$, and fragment $\nu_{ei}(F)$, approaches, as a function of the polyetherification conversion for $r_E = 12$

	$r_E = 12$		ν_{ei} 10^3 mol cm^{-3}	
α_{ETH}	$\nu_{e1}(F)$	$\nu_{e1}(C)$	$\nu_{e2}(F)$	$\nu_{e2}(C)$
0.05	0	0	0	0
0.10	0.0554	0.0546	0.0137	0.0145
0.20	0.5389	0.5319	0.1052	0.1159
0.30	1.2113	1.2011	0.1876	0.2086
0.40	1.9548	1.9468	0.2372	0.2600
0.50	2.7528	2.7484	0.2586	0.2757
0.60	3.6188	3.6169	0.2632	0.2726
0.70	4.5740	4.5735	0.2602	0.2640
0.80	5.6432	5.6431	0.2553	0.2563
0.90	6.8600	6.8600	0.2514	0.2516
1	8.2500	8.2500	0.2500	0.2500

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