Average Property Relations for Nonlinear Polymerization with Unequal Reactivity

Douglas R. Miller[1] and Christopher W. Macosko*[2]

Department of Statistics, University of Missouri, Columbia, Missouri 65201, and the Department of Chemical Engineering and Materials Science, Minneapolis, Minnesota 55455. *Received July 25, 1977*

ABSTRACT: This paper extends the authors' method of calculating average physical properties of ideal nonlinear, stepwise polymerizations to systems with nonequally reactive functional groups. Two special cases are considered in detail: $A_f + A_2 + B_2$, where the two B units comprising a B_2 monomer react at different rates; and $A_f + A_2 + B_2$, where one or two A units on the A_f monomer may react at different (slower) rates than the remaining A's. Weight average molecular weight, the gel point, weight fraction solubles, and cross-link density are derived. These properties are calculated for several systems with unequal, first-order reaction rates and are compared to the corresponding properties for the analogous ideal systems. It is indicated how to extend this approach to other systems with unequal reactivity.

Recently we described a new method for calculating average physical properties such as average molecular weights, gel point, weight fraction solubles, and cross-link density of nonlinear polymers.[3,4] This method uses elementary probability laws and the recursive nature of network polymer structures to calculate average properties directly. Previous treatments either (i) first calculate the distribution of all species and then use these distributions to calculate average properties[5,6] or (ii) use the rather sophisticated technique of probability generating functions.[7]

In our papers,[3,4] we consider only ideal network polymerizations, that is: (1) all functional groups of the same type are equally reactive, (2) all functional groups react independently of one another, (3) no intramolecular reactions occur in finite species. Although polymerizations can be selected which very nearly obey these assumptions most practical network forming systems do not.

In this paper we treat the effect of deviations from the first assumption, namely functional groups of unequal reactivity, on relations for the weight average molecular weight, gel point, weight fraction solubles, and cross-link density. We shall look at particular examples; it is possible to treat the problem with generality using our technique, however, the necessary notation would tend to obscure the simplicity of the technique. We hope the reader will be able to analyze any systems of interest to him after reading our work. In later papers we plan to deal with departures from the other assumptions.

There appear to be only a few specific treatments of unequal reactivities in the polymer literature.[7–10] There do not appear to be explicit structure property relations available for the chemist or engineer to test experimental results. Note however that unequal reactivity is actually a special case of general first shell substitution treated by Gordon and Scantlebury[9] with branching theory. In later work we shall apply our technique to first shell substitution effects. That analysis, however, requires slightly more sophistication than is used here. Also there is a chemical distinction between unequal reactivity and substitution effects. Thus separate treatments may be more accessible to potential users of our technique. Consequently this paper is devoted to a simpler analysis of only unequal reactivity.

A number of important network systems involve monomers with groups of different reactivity. For example the polyesterification of glycerine involves two primary hydroxyls and a secondary which is about four times less reactive.[11] Urethane networks are frequently formed with 2,4-toluene diisocyanate whose ortho NCO is about seven times more reactive than its para NCO.[8,12] Likewise in the oldest synthetic polymer network reaction, phenol–formaldehyde, the ortho and para hydrogens react at different rates.[13]

A detailed treatment of the following two systems will be presented:

$$A_f + A_2 + B^1\!\!\sim\!\!\sim B^2 \rightarrow \text{network polymer} \qquad (1)$$

where the two B units comprising a B_2 monomer react at different rates; and

$$A_f + A_2 + B_2 \rightarrow \text{network polymer} \qquad (2)$$

where one or two A units on an A_f monomer react at different rates from the remaining A's. An indication of the treatment

$$A_{f1} + A_{f2} + \ldots + A_{fk} + B_{g1} + \ldots + B_{gk} \rightarrow \qquad (3)$$

where some or all of the A's react at different rates, will be presented. Finally the homopolymerization

$$A_f \rightarrow \text{network} \qquad (4)$$

will be discussed for the case of unequal reactivity. All reactions are step-wise polymerizations.

The technique presented here is an extension of our previous method.[3,4,14] It is based on the recursive nature of the nonlinear polymer and the following elementary laws from probability theory: the law of total probability,

$$P(\mathrm{A}) = P(\mathrm{A}|\mathrm{B})P(\mathrm{B}) + P(\mathrm{A}|\overline{\mathrm{B}})P(\overline{\mathrm{B}}) \qquad (5)$$

and the law of total probability for expectation,

$$E(\mathrm{X}) = E(\mathrm{X}|\mathrm{B})P(\mathrm{B}) + E(\mathrm{X}|\overline{\mathrm{B}})P(\overline{\mathrm{B}}) \qquad (6)$$

These results appear in virtually all texts on probability theory. Ross[15] is a good reference.

$\overline{M}_w$, Weight Average Molecular Weight

It is customary to consider average properties as functions of extent of reaction. However, in systems with unequal reactivity the extent of reaction at any time will be a vector.[7] For example, for the system in eq 1 we can define

$$p_A(t) = (A - A_t)/A \qquad (7)$$

and

$$q_i(t) = (B^i - B_t{}^i)/B^i, \quad i = 1,2 \qquad (8)$$

Here as previously[3,4] we use the letter A to represent the initial moles of A-type groups and A_t equals the moles of unreacted A units remaining after some reaction time t and similarly for B^i. It follows that

$$p_\mathrm{B}(t) = (B - B_t)/B = \tfrac{1}{2}(q_1(t) + q_2(t)) \qquad (9)$$

and furthermore that

$$p_\mathrm{B}(t)2B_2 = p_\mathrm{A}(t)(fA_f + 2A_2) \qquad (10)$$

0024-9297/78/2211-0656$01.00/0

Letting r represent the stoichiometric balance

$$r = \frac{fA_f + 2A_2}{2B_2}$$

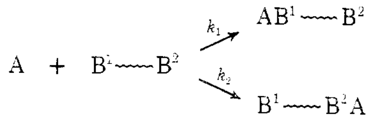
gives

$$p_B(t) = rp_A(t) \tag{11}$$

The extent of reaction of the system in eq 1 at time t is then

$$(p_A(t), q_1(t), q_2(t)) \tag{12}$$

In the remainder of this paper we shall derive various averages in terms of a vector-valued extent of reaction. In general it is not easy to experimentally determine the extent of reaction vector, eq 12. Usually monofunctional A_1 is reacted with $B^1\sim B^2$ and a method must be found to distinguish between the rates of formation of the two species:



$$A + B^1\sim B^2 \begin{cases} \xrightarrow{k_1} AB^1\sim B^2 \\ \xrightarrow{k_2} B^1\sim B^2A \end{cases}$$

It is assumed that these rates are independent of the type of A-bearing molecule, A_1 or A_f. In order to relate k_1 and k_2 to q_1 and q_2, we need some information on the polymerization kinetics. Some of these relations are developed in the Appendix. The property expressions are developed below assuming that the extent of reaction vector is available.

$A_f + A_2 + B^1\sim B^2$. As before,[3] consider A_f mol of f functional A-type monomer and A_2 mol of bifunctional reacting with B_2 mol of B-type monomer which have groups of two different reactivities, B^1 and B^2. This polymerization is shown schematically in Figure 1.

Let this system polymerize to an extent p_A of the A groups, q_1 of the B^1's, and q_2 of the B^2's. Now we pick a B^1 group at random and ask what is the weight $W_{B^1}{}^{out}$ looking *out* of the B_2 molecule, in the direction $\xrightarrow{1}$? If this B^1 group does not react, an event with probability $1 - q_1$, $W_{B^1}{}^{out}$ will equal zero. If this B^1 group reacts with an A_f unit, $W_{B^1}{}^{out}$ will equal $W_{A_f}{}^{in}$, the weight looking in from an A_f unit (along arrow No. 3 in Figure 1); if it reacts with an A_2, $W_{B^1}{}^{out}$ will equal $W_{A_2}{}^{in}$, the weight looking in from an A_2 unit. Letting a_f equal the proportion of A groups belonging to A_f's, these events have probabilities q_1a_f and $q_1(1 - a_f)$, respectively. The expected weight looking out from a B^1 unit can now be obtained using the law of total probability for expectation, eq 6:

$$\begin{aligned} E(W_{B^1}{}^{out}) &= E(W_{B^1}{}^{out}|B^1 \text{ does not react})\,P(B^1 \text{ does not react}) \\ &+ E(W_{B^1}{}^{out}|B^1 \text{ reacts with } A_f)P(B^1 \text{ reacts with } A_f) \\ &+ E(W_{B^1}{}^{out}|B^1 \text{ reacts with } A_2)P(B^1 \text{ reacts with } A_2) \\ &= E(0)(1 - q_1) + E(W_{A_f}{}^{in})\,q_1a_f + E(W_{A_2}{}^{in})q_1(1 - a_f) \\ &= q_1[a_fE(W_{A_f}{}^{in}) + (1 - a_f)E(W_{A_2}{}^{in})] \end{aligned} \tag{13a}$$

The expression for the expected weight attached to a B^2 group in the direction $\xrightarrow{2}$ will be similar, except of course that the B^2 groups have a different reactivity and thus extent of reaction q_2.

$$E(W_{B^2}{}^{out}) = q_2[a_fE(W_{A_f}{}^{in}) + (1 - a_f)E(W_{A_2}{}^{in})] \tag{13b}$$

Following the other arrows in Figure 1 we can write the relations for the expected weight looking into an A group on an A_f molecule $\xrightarrow{3}$ and the weight looking into an A_2 as

$$E(W_{A_f}{}^{in}) = M_{A_f} + (f - 1)E(W_A{}^{out}) \tag{13c}$$

$$E(W_{A_2}{}^{in}) = M_{A_2} + E(W_A{}^{out}) \tag{13d}$$

Since all the A's are equally reactive looking *out* from any A group will be equivalent.

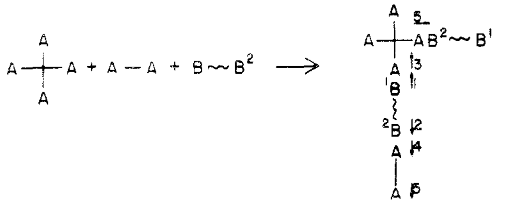


Figure 1. Schematic of network polymerization of $A_f + A_2 + B^1\sim B^2$.

$$E(W_A{}^{out}) = p_A\left[\frac{q_1}{q_1 + q_2}E(W_{B^1}{}^{in}) + \frac{q_2}{q_1 + q_2}E(W_{B^2}{}^{in})\right] \tag{13e}$$

Finally looking into a B^1 group gives

$$E(W_{B^1}{}^{in}) = M_{B_2} + E(W_{B^2}{}^{out}) \tag{13f}$$

While looking into a B^2 gives

$$E(W_{B^2}{}^{in}) = M_{B_2} + E(W_{B^1}{}^{out}) \tag{13g}$$

Note that

$$a_f = fA_f/(fA_f + 2A_2) \tag{14}$$

From eq 9 we get a slight simplification: if $r = A/B$ then $2p_Ar = q_1 + q_2$. This simplifies eq 13e.

Solving the system of eq 13 gives

$$E(W_A{}^{out}) = \left[p_AM_{B_2} + \frac{q_1q_2}{r}([1 - a_f]\,M_{A_2} + a_fM_{A_f})\right] \Big/ \left[1 - \frac{q_1q_2}{r}(1 + (f - 2)\,a_f)\right]$$

$$E(W_{B_i}{}^{out}) = q_i[(1 - a_f)M_{A_2} + a_fM_{A_f} + (1 + (f - 2)a_f)E(W_A{}^{out})] \tag{15}$$

The expected weight attached to a randomly chosen A_2 is $E(W_{A_2}) = M_{A_2} + 2E(W_A{}^{out})$; the expected weight attached to an A_f is $E(W_{A_f}) = M_{A_f} + fE(W_A{}^{out})$; the weight attached to a B_2 is $M_{B_2} + E(W_{B^2}{}^{out}) + E(W_{B^1}{}^{out}) = E(W_{B_2})$. If we pick a unit of mass at random by weight, then we pick an A_2 with probability $M_{A_2}A_2/(M_{A_2}A_2 + M_{A_f}A_f + M_{B_2}B_2)$, and so forth. Thus

$$\overline{M}_w = \frac{M_{A_2}A_2E(W_{A_2}) + M_{A_f}A_fE(W_{A_f}) + M_{B_2}B_2E(W_{B_2})}{M_{A_2}A_2 + M_{A_f}A_f + M_{B_2}B_2} \tag{16}$$

Substituting into eq 16 will yield numerical results. We do not derive a final expression for $\overline{M}_w$ in closed form because it would be algebraically complicated and to evaluate it for different numerical values would probably require breaking it back down into eq 15. We have calculated $\overline{M}_w$ for the system $A_f + A_2 + B^1\sim B^2$ for $r = 1$ as a function of p_A, the extent of reaction of A's. Equation A4 gives the relation between q_i and $\rho = k_1/k_2$. Some of these calculations are plotted in Figure 2. We note that the shape of the $\overline{M}_w$ vs. p curves is not altered greatly with increasing ρ. The curves appear to shift to the right with increasing ρ.

$A_f + A_2 + B_2$. We now consider the system described in eq 2 in which A_f consists of h_1 A^1 units which react at rate k_1, h_2 A^2 units which react at rate k_2, and $f - h_1 - h_2 = h_3$ A^3 units which react at rate k_3. Both A units of the A_2 monomer react at rate k_1. The B's are equally reactive. Analogous to eq 13 we have

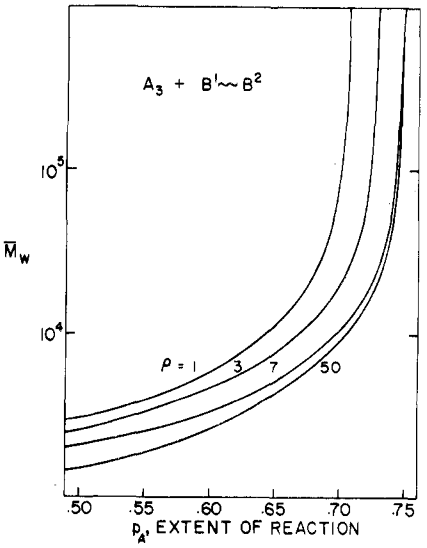


Figure 2. Log $\overline{M}_w$ vs. p_A for polymerization of A_3 with $B^1 \sim B^2$ where B^1 and B^2 differ in reactivity in the ratio $k_1/k_2 = \rho$; $M_{A_3} = 1000$ and $M_{B_2} = 174$.

$$E(W_{A^i}{}^{\text{out}}) = q_i\, E(W_B{}^{\text{in}}) \qquad i = 1, 2, 3$$
$$E(W_B{}^{\text{in}}) = M_{B_2} + E(W_B{}^{\text{out}})$$

$$E(W_B{}^{\text{out}}) = p_B \frac{(a_f/f)\left[\sum_{i=1}^{3} h_i q_i E(W_{A_f}{}^{i\,\text{in}})\right] + (1 - a_f)q_1 E(W_{A_2}{}^{\text{in}})}{(a_f/f)\left[\sum_{i=1}^{3} h_i q_i\right] + (1 - a_f)q_1}$$
$$= \frac{ra_f}{f}\sum_{i=1}^{3} h_i q_i E(W_{A_f}{}^{i\,\text{in}}) + r(1 - a_f)q_1 E(W_{A_2}{}^{\text{in}})$$

$$E(W_{A_f}{}^{i\,\text{in}}) = M_{A_f} + \sum_{j=1}^{3} h_j E(W_{A^j}{}^{\text{out}}) - E(W_{A^i}{}^{\text{out}}) \quad i = 1, 2, 3$$
$$E(W_{A_2}{}^{\text{in}}) = M_{A_2} + E(W_{A_1}{}^{\text{out}}) \qquad (17)$$

where q_1 is the extent of reaction of the A groups which react at rate k_1; q_2 and q_3 are defined similarly. Solving gives

$$E(W_B{}^{\text{out}}) = \frac{\frac{ra_f}{f}\left[M_{A_f}\sum_{1}^{3} h_i q_i + M_{B_2}\left(\left(\sum_{1}^{3} h_i q_i\right)^2 - \sum_{1}^{3} h_i q_i{}^2\right)\right] + r(1 - a_f)q_1(M_{A_2} + q_1 M_{B_2})}{1 - \frac{ra_f}{f}\left[\left(\sum_{1}^{3} h_i q_i\right)^2 - \sum_{1}^{3} h_i q_i{}^2\right] - r(1 - a_f)q_1{}^2} \qquad (18)$$

and

$$E(W_{A^i}{}^{\text{out}}) = q_i(M_{B_2} + E(W_B{}^{\text{out}}))$$
$$E(W_{A_2}) = M_{A_2} + 2E(W_{A^1}{}^{\text{out}})$$
$$E(W_{A_f}) = M_{A_f} + \sum_{i=1}^{3} h_i E(W_{A^i}{}^{\text{out}}) \qquad (19)$$
$$E(W_{B_2}) = M_{B_2} + 2E(W_B{}^{\text{out}})$$

Thus as in eq 16

$$\overline{M}_w = \frac{M_{A_2}A_2 E(W_{A_2}) + M_{A_f}A_f E(W_{A_f}) + M_{B_2}B_2 E(W_{B_2})}{M_{A_2}A_2 + M_{A_f}A_f + M_{B_2}B_2} \qquad (20)$$

For the special case $A_3 + B_2$ with $r = 1$, $h_1 = 2$, $h_2 = 1$ eq 20 becomes

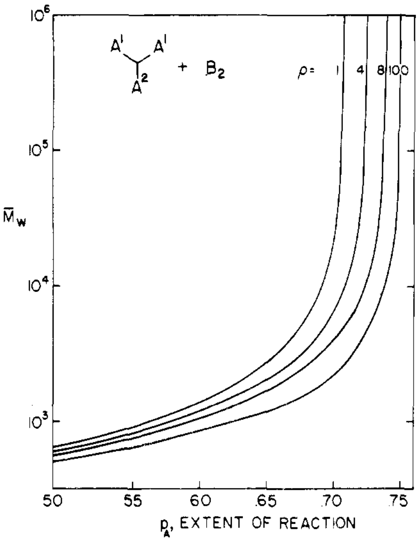
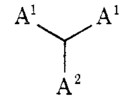


Figure 3. Log $\overline{M}_w$ vs. p_A for polymerization of



with B_2 where A^1 and A^2 differ in reactivity in the ratio $k_1/k_2 = \rho$; $M_{A_3} = 92$ and $M_{B_2} = 168$.

$$\overline{M}_w = \frac{2M_{A_3}{}^2 + 3M_{B_2}{}^2}{2M_{A_3} + 3M_{B_2}} + \frac{18(p_A M_{A_3} + M_{B_2})^2}{(2M_{A_3} + 3M_{B_2})(3 - 2q_1{}^2 - 4q_1 q_2)} \qquad (21)$$

Substituting eq 18 into eq 19 and then substituting eq 19 into eq 20 gives $\overline{M}_w$ in terms of the extent of reaction vector (q_1, q_2, q_3). As discussed in the Appendix this can be determined as a function of p_A, thus it is possible to evaluate eq 20 for different values of p_A. We have done this numerically for the example of eq 21. The results are shown in Figure 3. Qualitatively the results are very similar to $A_3 + B^1 \sim B^2$ shown in Figure 2. The $A_3 + B^1 \sim B^2$ system appears to be more sensitive to small changes in ρ, the reactivity ratio.

$A_{f_1} + A_{f_2} + \ldots A_{f_k} + B_{g_1} + B_{g_2} + \ldots + B_{g_l}$. In this general situation we get the following system of equations, which are quite similar in form to those in ref 3.

$$E(W_{B_{g_j}}{}^{\text{in}}) = M_{B_{g_j}} + (g_j - 1)(E(W_B{}^{\text{out}})) \qquad j = 1, \ldots, l$$

$$E(W_B{}^{\text{out}}) = p_B \frac{\sum_{i=1}^{k}\sum_{j=1}^{f_i} (a_{f_i}/f_i) q_{i,j} E(W_{A_{f_i}}{}^{j\,\text{in}})}{\sum_{i=1}^{k}\sum_{j=1}^{f_i} (a_{f_i}/f_i) q_{i,j}}$$
$$= r\sum_{i=1}^{k}\sum_{j=1}^{f_i} (a_{f_i}/f_i) q_{i,j} E(W_{A_{f_i}}{}^{j\,\text{in}})$$

$$E(W_{A_{f_i}}{}^{j\,\text{in}}) = \mathrm{M}_{A_{f_i}} + \sum_{n=1}^{f_i} E(WA_{f_i}{}^{n\,\text{out}}) - E(W_{A_{f_i}}{}^{j\,\text{out}})$$

$$E(W_{A_{f_i}}{}^{j\,\text{out}}) = q_{i,j} \sum_{n=1}^{l} b_{g_n} E(W_{B_{g_n}}{}^{\text{in}}) \qquad (22)$$

In theory these can be solved and then we can proceed as in the previous case. Of course the main difficulty is an experimental one, to determine the extent of reaction array $q_{i,j}$.

A_f Homopolymerization. Finally we consider weight average molecular weight of the A_f homopolymerization with unequal reactivity. We shall consider the special case of A_3 homopolymerization. The recursive equations are

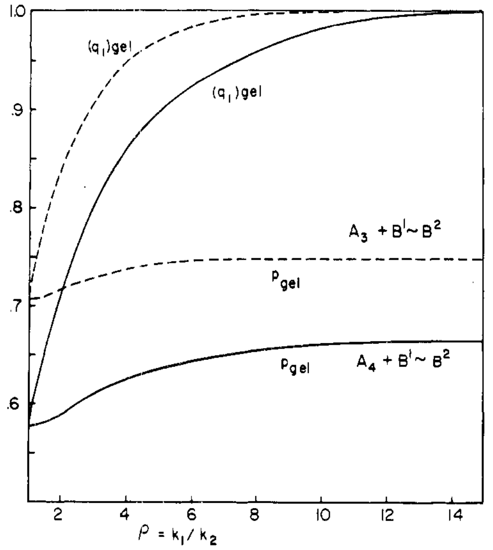


Figure 4. The effect of reactivity ratio on gel point for several $A_f + B^1{\sim}B^2$ systems. Predictions from eq 9, 24, and A4: solid lines for $A_4 + B^1{\sim}B^2$; broken lines for $A_3 + B^1{\sim}B^2$.

$$E(W_{A^1}{}^{out}) = q_{11}E(W_{A^1}{}^{in}) + q_{10}E(W_{A^0}{}^{in})$$
$$E(W_{A^0}{}^{out}) = q_{00}E(W_{A^0}{}^{in}) + q_{01}E(W_{A^1}{}^{in})$$
$$E(W_{A^1}{}^{in}) = M_{A_3} + 2E(W_{A^0}{}^{out})$$
$$E(W_{A^0}{}^{in}) = M_{A_3} + E(W_{A^0}{}^{out}) + E(W_{A^1}{}^{out}) \quad (23)$$

where q_{ij} is defined in the Appendix eq A16. Solving eq 23 gives

$$E(W_{A^1}{}^{out}) = \frac{(q_{11} + q_{10})(1 - q_{00} - 2q_{10}) + (2q_{11} + q_{10})(q_{00} + q_{01})}{(1 - q_{10})(1 - q_{00} - 2q_{01}) - (2q_{11} + q_{10})q_{00}} M_{A_3}$$

$$E(W_{A^0}{}^{out}) = \frac{(1 - q_{10})(q_{00} + q_{01}) + q_{00}(q_{11} + q_{10})}{(1 - q_{10})(1 - q_{00} - 2q_{10}) - q_{00}(2q_{11} + q_{10})} M_{A_3}$$

and

$$\overline{M}_w = M_{A_3} + E(W_{A^1}{}^{out}) + 2E(W_{A^0}{}^{out})$$

$\overline{M}_w$ can be given in terms of the reaction rates and p_A by solving for the extent of reaction vector $(q_{00}, q_{01}, q_{10}, q_{11})$ in terms of p_A.

The Gel Point

Gelation occurs when weight average molecular weight diverges. For the system $A_f + A_2 + B^1{\sim}B^2$ it can be seen that eq 15 diverge when

$$1 - \frac{q_1 q_2}{r}(1 + (f - 2)a_f) = 0$$

This is the definition of gel point for our model. Thus the following system of equations determine the extent of reaction at the gel point:

$$r = q_{1_{gel}} q_{2_{gel}} (1 + (f - 2)a_f) \quad (24)$$

$$1 - q_{1_{gel}} = (1 - q_{2_{gel}})^{\rho} \quad \text{(from first-order kinetics)} \quad (A4)$$

$$2p_{B_{gel}} = 2rp_{A_{gel}} = q_{1_{gel}} + q_{2_{gel}} \quad (9)$$

We solve equations numerically for various systems and p_{gel} and $(q_1)_{gel}$ are plotted as a function of ρ (the ratio of reaction rates) for various systems in Figure 4.

From the graph we see that a simple urethane network forming system using 2,4-toluene diisocyanate, $\rho \simeq 7$ (ref 12), and a polyester triol will gel at $p = 0.75$ rather than 0.707 as predicted under the ideal assumptions. Conversely an unknown reactivity ratio can be calculated from the experimental gel point. If the reaction order near p_{gel} is other than 1, eq A5 is used. For example for second order $(1 - q_1)/q_1 = (1 - q_2)/\rho q_2$. In general we see that as ρ increases all of the more reactive groups, B^1, have reacted by the gel point. Thus in the limiting case as $\rho \to \infty$, $(q_1)_{gel} = 1.0$, $(q_2)_{gel} = r/(1 + (f - 2)a_f)$ and $p_{gel} = (1 + q_2)_{gel}/(2r)$. Since nearly all real systems have $f \leq 6$, these limits are good approximations at $\rho > 12$.

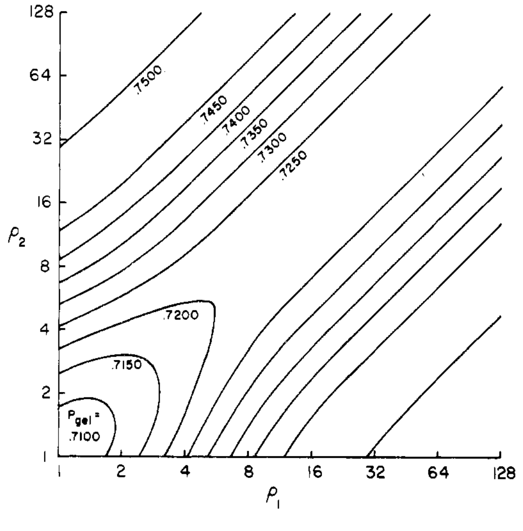
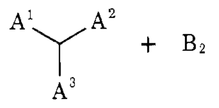


Figure 5. The effect of reactivity ratios on gel point, $(p_A)_{gel}$, for network formation.



For the system $A_f + A_2 + B_2$ of eq 2 it can be seen that eq 18 diverges when

$$1 = \frac{ra_f}{f}\left[\left(\sum_{i=1}^{3} h_i q_i\right)^2 - \sum_{i=1}^{3} h_i q_i{}^2\right] - r(1 - a_f)q_1{}^2 \quad (25)$$

Thus the extent of reaction at the gel point is determined by eq 25 and

$$(1 - q_1)^{1/k_1} = (1 - q_2)^{1/k_2} = (1 - q_3)^{1/k_3} \quad (A9)$$

$$p_A = (a_f/f)\sum_{i=1}^{3} q_i h_i + (1 - a_f)q_1 \quad (A7)$$

These equations can be solved numerically for various systems. We have done this and plotted p_{gel}-contours for $A_3 + B_2$ and $A_4 + B_2$ in Figures 5 and 6, where $\rho_1 = k_1/k_2$, $\rho_2 = k_1/k_3$, and $r = 1$. We also see how complex determination of the gel point becomes if three reactivities are possible for the functional groups. Since it cannot matter if we interchange ρ_1 and ρ_2, the plots are symetric about $\rho_1 = \rho_2$.

It is important to remember that other nonidealities in the polymerization such as substitution effects or loop formation will also increase p_{gel}. In practice it may be difficult to separate these effects.

Average Postgel Properties.

In this section we compute average properties of network polymerization in the postgel region. We compute weight fraction solubles and concentration of effective cross-links for the system of eq 1 and 2.

Consider the system $A_f + A_2 + B^1{\sim}B^2$ with B's unequally reactive. Let $F_A{}^{out}$ be the event that, looking *out* from a random A unit, we see only a finite chain (a dangling chain). As in our earlier work[4] we compute average network parameters

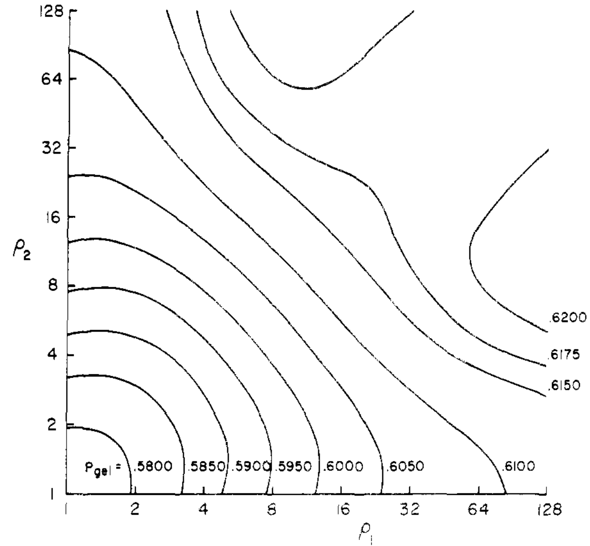
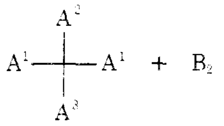


Figure 6. The effect of reactivity ratios on gel point for



$$\mathrm{A^1}\!-\!\underset{\mathrm{A^3}}{\overset{\mathrm{A^2}}{|}}\!-\!\mathrm{A^1} + \mathrm{B_2}$$

from $P(F_A^{out})$. We now compute $P(F_A^{out})$ for the system of eq 1, using eq 5:

$$P(F_A^{out}) = (1-p) + p\left[\frac{q_1}{q_1+q_2}P(F_{B^1}^{in}) + \frac{q_2}{q_1+q_2}P(F_{B^2}^{in})\right]$$

$$P(F_{B^i}^{in}) = P(F_{B^j}^{out}), \quad i \neq j$$

$$P(F_{B^i}^{out}) = 1 - q_i + q_i[(1-a_f)P(F_{A_2}^{in}) + a_f P(F_{A_f}^{in})]$$

$$P(F_{A_i}^{in}) = (P(F_A^{out}))^{i-1}, \quad i = 2, f \tag{26}$$

Solving system 26 gives

$$P(F_A^{out}) = 1 - \frac{q_1q_2}{r} + \frac{q_1q_2}{r}[(1-a_f)P(F_A^{out}) + a_f(P(F_A^{out}))^{f-1}] \tag{27}$$

Thus $P(F_A^{out})$ is a solution of the equation

$$x = 1 - \frac{q_1q_2}{r} + \frac{q_1q_2}{r}[(1-a_f)x + a_f x^{f-1}] \tag{28}$$

We can appeal to the theory of branching processes and learn that there can be at most one root of eq 28 between 0 and 1 in which case that is the desired root otherwise $P(F_A^{out}) = 1$. For the special case $f = 3$,

$$P(F_A^{out}) = \frac{1}{a_3}\left(\frac{r}{q_1q_2} - 1\right)$$

if it is between 0 and 1. As discussed above, given p we can find q_1 and q_2 numerically. Then eq 28 can easily be solved numerically, giving $P(F_A^{out})$ as a function of p, r, a_f, and $\rho = k_1/k_2$.

Using $P(F_A^{out})$ the weight fraction solubles become (note eq 39, ref 4)

$$w_s = \frac{M_{A_2}A_2(P(F_A^{out}))^2 + M_{A_f}A_f(P(F_A^{out}))^f + M_{B_2}B_2P(F_{B^1}^{out})P(F_{B^2}^{out})}{M_{A_2}A_2 + M_{A_f}A_f + M_{B_2}B_2} \tag{29}$$

where

$$P(F_{B^i}^{out}) = 1 - q_i + q_i((1-a_f)P(F_A^{out}) + a_f(P(F_A^{out}))^{f-1}) \tag{30}$$

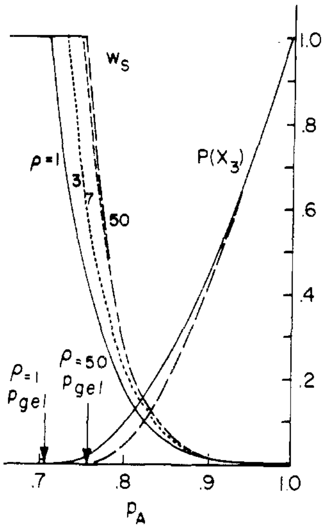


Figure 7. The effect of reactivity ratio on post gel properties, weight fraction solubles, w_s, and fraction of cross-links $P(x_3)$ for the system $A_3 + B^1\!\leadsto\!B^2$ (Figure 2).

The quantity $P(F_A^{out})$ can also be used to calculate the proportion of effective cross-links. An A_f unit is an effective cross-link of degree n (denoted X_n) if exactly n of its arms lead to the infinite network.

$$P(X_n) = \binom{f}{n}(1 - P(F_A^{out}))^n(P(F_A^{out}))^{f-n} \tag{31}$$

As in our earlier work[4] these quantities can be used to predict elastic modulus. The above quantities are plotted in Figure 7 for several different ratios of the rate constants, ρ, for the system $A_3 + B^1\!\leadsto\!B^2$. Note that the effect as with $\overline{M}_w$ is largest around p_{gel}.

Now we consider postgel properties of the system $A_f + A_2 + B_2$, eq 2:

$$P(F_{A^i}^{out}) = 1 - q_i + q_iP(F_B^{in}) \quad i = 1, 2, 3$$

$$P(F_B^{in}) = P(F_B^{out})$$

$$P(F_B^{out}) = 1 - p_B + p_B\frac{(a_f/f)\sum_{i=1}^{3} h_iq_iP(F_{A_f{}^i}^{in}) + (1-a_f)\,q_1P(F_{A_2{}^1}^{in})}{(a_f/f)\sum_{i=1}^{3} h_iq_i + (1-a_f)q_0}$$

$$= 1 - rp_A + r(a_f/f)\sum_{i=1}^{3} h_iq_iP(F_{A_f{}^i}^{in}) + (1-a_f)q_1P(F_{A_2{}^1}^{in})$$

$$P(F_{A_f{}^i\,in}) = \prod_{j=1}^{3} \mathrm{P(F_{A^j}{}^{out})}^{h_j}/P(F_{A^i}^{out})$$

$$P(F_{A_2{}^1}^{in}) = P(F_{A^1}^{out}) \tag{32}$$

Solving eq 32 for the special case $h_1 = f - 1$, $h_2 = 1$, $h_3 = 0$ (only one unequally reactive group on the A_f) $P(F_B^{out})$ satisfies the equation

$$x = 1 - rp_A + r(a_f/f)(1 - q_1 + q_1x)^{f-2}[(f-1)q_1 - fq_1q_2 + q_2 + fq_1q_2x] + (1-a_f)q_1(1 - q_1 + q_1x) \tag{33}$$

The right-hand side of eq 33 is convex increasing and by an argument familiar in the theory of branching processes it will have at most one root between 0 and 1 and it can be found numerically. In fact it is possible to solve eq 32 numerically for $P(F_B^{out})$. Then

$$P(F_{A^i}^{out}) = 1 - q_i + q_iP(F_B^{out})$$

Using this we can compute average properties:

$$w_{\mathrm{s}} = \frac{M_{\mathrm{A}_f}A_f\prod_{i=1}^{3}P(F_{\mathrm{A}_i}{}^{\mathrm{out}})^{h_i} + M_{\mathrm{A}_2}A_2P(F_{\mathrm{A}^1}{}^{\mathrm{out}})^2 + M_{\mathrm{B}_2}B_2P(F_{\mathrm{B}}{}^{\mathrm{out}})^2}{M_{\mathrm{A}_f}A_f + M_{\mathrm{A}_2}A_2 + M_{\mathrm{B}_2}B_2} \tag{34}$$

and

$$P(X_f) = \prod_{i=1}^{3}(1 - P(F_{\mathrm{A}^i}{}^{\mathrm{out}}))^{h_i} \tag{35}$$

for example. A general formula for $P(X_n)$, $n < f$, is complicated, but for specific examples it is easy to apply. As before the q_i's can be determined in terms of p_{A} and consequently these postgel average parameters can be determined as functions of p_{A}. We have computed the special cases of $\mathrm{A}_3 + \mathrm{B}_2$. An example of the latter is polyurethane formation from 1,6-hexane diisocyanate and glycerine. The results for this system are quite similar to those in Figure 7.

Acknowledgment. This work was partially supported by the Army Office of Research (Grant DAAG29-76-G-0110 to the University of Minnesota) and the Office of Naval Research (Contract N0014-76-C-0843 to the University of Missouri).

Appendix

Consider the following general rate expressions for the disappearance of B^1 and B^2 groups:

$$\begin{aligned} \mathrm{d}B_t{}^1/\mathrm{d}t &= -k_1(B_t{}^1)^{\beta_1}A_t{}^{\alpha} \\ \mathrm{d}B_t{}^2/\mathrm{d}t &= -k_2(B_t{}^2)^{\beta_2}A_t{}^{\alpha} \end{aligned} \tag{A1}$$

and the conservation relation

$$B - B_t = A - A_t$$

where $\beta_1, \beta_2, \alpha \geq 0$.

In general it is impossible to solve eq A1 analytically. However, we only wish to find relations between p_{A}, q_1, q_2, k_1, and k_2. Solving each equation for $A_t{}^{\alpha}$ gives

$$\frac{1}{k_1(B_t{}^1)^{\beta_1}}\frac{\mathrm{d}B_t{}^1}{\mathrm{d}t} = \frac{1}{k_2(B_t{}^2)^{\beta_2}}\frac{\mathrm{d}B_t{}^2}{\mathrm{d}t} \tag{A2}$$

If $\beta_1 = \beta_2 = 1$, integrating (A2) from 0 to $t = s$ gives

$$\frac{\log(1 - q_1(s))}{k_1} = \frac{\log(1 - q_2(s))}{k_2} \tag{A3}$$

which is equivalent to

$$1 - q_1(s) = (1 - q_2(s))^{k_1/k_2} = (1 - q_2(s))^{\rho} \tag{A4}$$

If $\beta_1 \neq 1$ and $\beta_2 \neq 1$, integrating (A2) gives

$$\frac{1 - (1 - q_1(s))^{1-\beta_1}}{(1 - \beta_1)k_1} = \frac{1 - (1 - q_2(s))^{1-\beta_2}}{(1 - \beta_2)k_2} \tag{A5}$$

Note in eq A5 that if both B^1 and B^2 species react completely $q_1 = q_2 = 1$ then eq A5 becomes

$$\frac{1}{(1 - \beta_1)k_1} = \frac{1}{(1 - \beta_2)k_2}$$

Thus the orders and rates of the reactions must satisfy $(1 - \beta_1)k_1 = (1 - \beta_2)k_2$. Thus if $\beta_1 = \beta_2 \neq 1$, then $k_1 = k_2$ and equal reactivity exists. This result strongly suggests that if the reaction is other than first order in species B_i and nonequal reactivity is present then either the rate constants, k_i, or the orders, β_i, must change during the reaction. This of course does happen in actual polymerizations and can be treated if the k_i and/or β_i are available as a function of extent of reaction. To illustrate the approach in this paper we assume $\beta_1 = \beta_2 = 1$ and thus k_1 and k_2 can be independent of extent. We see then from eq A2–A4 that the relationship between q_1, q_2, k_1, and k_2 is independent of the value of α. Equations 9, 11, and A4 determine the extent of reaction vector, eq 12. Throughout this paper we derive average properties as a function of p_{A}. For system (1) with reaction rates k_1 and k_2 and $r = (2A_2 + fA_f)/2B_2$, it is possible to determine the extent of reaction vector in terms of p_{A} by solving eq 9, 11, and A4 numerically. This is done with several examples in the paper.

Now consider system (2). Suppose h_1 A^1 units on each A_f react at rate k_1, h_2 A^2 units react at rate k_2, and the remaining $h_3 = f - h_1 - h_2$ A^3 units on each A_f react at rate k_3. All the A units comprising A_2 monomers react at rate k_1. We shall denote these units as A^1, A^2, and A^3, respectively. Let $p_{\mathrm{B}}(t)$ and $p_{\mathrm{A}}(t)$ be defined as above and

$$q_i(t) = \frac{A^i - A_t{}^i}{A^i} \qquad i = 1, 2, 3 \tag{A6}$$

Then

$$\begin{aligned} p_{\mathrm{A}}(t) &= \frac{q_2(t)h_2A_f + q_3(t)h_3A_f + q_1(t)(2A_2 + h_1A_f)}{fA_f + 2A_2} \\ &= \frac{a_f}{f}\left(\sum_{i=1}^{3} h_iq_i(t)\right) + (1 - a_f)q_1(t) \end{aligned} \tag{A7}$$

where $a_f = fA_f/(fA_f + 2A_2)$ is the proportion of A units on A_f monomers, eq 14, and

$$p_{\mathrm{B}}(t) = \frac{fA_f + 2A_2}{2B_2}p\mathrm{A}(t) = rp_{\mathrm{A}}(t) \tag{A8}$$

Assuming first-order kinetics in A and an arbitrary order in B gives similar results to eq A1–A4, namely

$$(1 - q_1(t))^{1/k_1} = (1 - q_2(t))^{1/k_2} = (1 - q_3(t))^{1/k_3} \tag{A9}$$

Equations A7–A9 can be solved numerically to give the extent of reaction vector

$$(p_{\mathrm{B}}, q_1, q_2, q_3) \tag{A10}$$

as a function of p_{a}, for values $0 \leq p_{\mathrm{A}} \leq \min(1, 1/r)$, for the system in eq 2.

The system described in eq 3 is more general. If the jth A unit on an A_{f_i} monomer reacts at rate $k_{i,j}$ and we assume a first-order reaction in A and arbitrary order in B, and $q_{i,j}$ is the extent of reaction of A's in the jth position on A_{f_i}'s, then

$$(1 - q_{i,j}(t))^{1/k_{i,j}} = (1 - q_{m,n}(t))^{1/k_{m,n}} \tag{A11}$$

$$p_{\mathrm{A}}(t) = \sum_{i=1}^{k} A_{f_{i0}}\sum_{i=1}^{f_i} q_{i,j}\Big/\sum_{i=1}^{k} f_iA_{f_{i0}} \tag{A12}$$

$$p_{\mathrm{B}}(t) = \frac{\sum_{i=1}^{k} f_iA_{f_{i0}}}{\sum_{\mathrm{j}=1}^{1} \mathrm{g_jB}_{g_{j0}}}p_{\mathrm{A}}(t) = rp_{\mathrm{A}}(t) \tag{A13}$$

Using numerical methods it is possible to solve eq A11–A13 for the extent of reaction vector

$$(p_{\mathrm{B}}; q_{i,j}, j = 1, \ldots, f_i, i = 1, \ldots, k) \tag{A14}$$

as a function of p_{A} if the relative reaction rates are known.

In the above three examples it is only necessary to know the relative rates of reaction. If it is desired to know the state of the system as a function of time rather than as a function of p_{A} then it is necessary to know the absolute rates of reaction. Furthermore, whereas the state of the system as functions of p_{A} is independent of β in eq A1, the state as a function of time will depend on β.

In the most general case it is possible to have unequal reactivity on both reactants, unequal A and B groups, or the homopolymerization of unequally reactive A's. These cases can become more complicated. We illustrate this with homopolymerization of A_3 in which one of the A units reacts more slowly; denote this unit as A′. In this case AA bonds form at a rate proportional to A × A, AA′ bond proportional to A × A′, and A′A′ bonds proportional to A′ × A′. Thus the kinetics can be described by

$$dA_t/dt = -2r_{00}A_t^2 - r_{01}A_tA'_t \qquad (A15)$$
$$dA'_t/dt = -r_{01}A_tA'_t - 2r_{11}A'^2_t$$
$$dAA_t/dt = +r_{00}A_t^2$$
$$dAA'/dt = +r_{01}A_tA'_t$$
$$dA'A'_t/dt = r_{11}A'^2_t$$

These equations must be solved numerically for the five quantities A_t, A'_t, AA_t, AA'_t, and $A'A'_t$. Note that $A_t + 2AA_t + AA'_t = A_0$ and $A'_t + AA'_t + 2A'A'_t = A'_0$. Let $q_{00}(t)$ equal the proportion of A units which have reacted with other A units and $q_{01}(t)$ equal the proportion of A units which have reacted with A′ units; define $q_{11}(t)$ and $q_{10}(t)$ analogously. Then

$$q_{00}(t) = 2AA_t/A_0$$
$$q_{01}(t) = AA'_t/A_0$$
$$q_{11}(t) = 2A'A'_t/A'_0 \qquad (A16)$$
$$q_{10}(t) = AA'_t/A'_0$$

$$A_t = \frac{2AA_t + 2AA' + 2A'A'}{A_0 + A'_0}$$

It is possible to numerically calculate the extent of reaction vector

$$(q_{00}, q_{01}, q_{11}, q_{10}) \qquad (A17)$$

as a function of p_A. These values can be used in eq 23.

References and Notes

(1) University of Missouri, Columbia.
(2) University of Minnesota.
(3) C. W. Macosko and D. R. Miller, *Macromolecules*, **9**, 199 (1976).
(4) D. R. Miller and C. W. Macosko, *Macromolecules*, **9**, 206 (1976).
(5) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, Chapter 9; *J. Am. Chem. Soc.*, **63**, 3083, 3097 (1941).
(6) W. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943); **12**, 125 (1944).
(7) M. Gordon, *Proc. R. Soc. London, Ser. A*, **268**, 240 (1962).
(8) R. A. Martin, K. L. Hoy, and R. H. Peterson, *Ind. Eng. Chem., Prod. Res. Dev.*, **6**, 218 (1967).
(9) M. Gordon and G. Scantlebury, *Trans. Faraday Soc.*, **60**, 604 (1964); *J. Chem. Soc.*, 1 (1967).
(10) F. J. Martinelli, *J. Polym. Sci.*, to be published.
(11) R. W. Lenz, "Organic Chemistry of Synthetic High Polymers," Wiley, New York, N.Y., 1967, p 96.
(12) A. R. C. Cumming and P. Wright, "Solid Polyurethane Elastomers", Maclaren, London, 1969, p 27.
(13) R. W. Lenz, ref 12, p 131.
(14) D. R. Miller and C. W. Macosko, "Proceedings of the Seventh International Congress on Rheology", J. Kubat and K. Klasson, Ed., Gothenberg, 1976, p 568.
(15) S. M. Ross, "Introduction to Probability Models", Academic Press, New York, N.Y., 1972, Chapter 3.

Polymerization of Tetrahydrofuran by Proton Acids

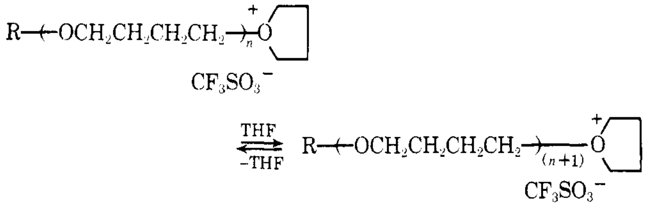
G. Pruckmayr* [1] **and T. K. Wu**[2]

Chemicals, Dyes and Pigments Department and Plastic Products and Resins Department,
E. I. du Pont de Nemours & Company, Inc., Experimental Station,
Wilmington, Delaware 19898.

Received March 31, 1978

ABSTRACT: The mechanism for the polymerization of tetrahydrofuran with strong proton acid initiators has been investigated. Nonhydrolyzable acids such as trifluoromethanesulfonic acid lead to very high molecular weight polymer by a combination of chain coupling–ring opening steps. Hydrolyzable proton acids, such as the halosulfonic acids, lead to polymeric species of lower molecular weight through mono- and dialkyl sulfate formation. Sulfate formation is normally irreversible and slower than chain propagation, causing molecular weights to go through a maximum. Such polymerizations are not "living", but "slowly dying", the rate of termination depending on the polymerization conditions.

The equilibrium polymerization of tetrahydrofuran (THF) with alkyl esters of trifluoromethanesulfonic acid (triflic acid) or fluorosulfonic acid as initiators has recently been investigated in great detail.[3-6] These systems are generally considered to be "living" polymerizations, although chain transfer and cyclization reactions do occur.[7]



Much less has been reported on polymerization of THF with free proton acid initiators.[8] The mechanism of polymerization with proton acids is less straightforward than with initiation by alkyl esters, and some contradictory papers have been published over the years.[9-11]

Chlorosulfonic acid and fluorosulfonic acid were among the earliest examples of catalysts for the cationic ring opening polymerization of THF.[12] Meerwein reported the formation of alkyl sulfate esters during polymerization with chlorosulfonic acid initiation and discussed the necessity for hydrolysis of such esters in order to obtain hydroxy terminated polymer.[13]

The present paper investigates in more detail the alkyl sulfate ester formation during polymerization of THF and

0024-9297/78/2211-0662$01.00/0