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A New Derivation of Post Gel Properties of Network Polymers

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ABSTRACT: A simple recursive method is presented which can be used to derive the probability of a finite or dangling chain in a polymer network. Finite chain probabilities are derived for a variety of networks as a function of type and extent of reaction. From these probabilities useful properties such as sol fraction, cross-link density, and the number of elastically effective network chains can be readily developed.

Recently we presented a relatively simple recursive method for calculating molecular weight averages up to the gel point in nonlinear polymerization.[2a] In this paper we show how a similar recursive method can be used beyond the gel point, particularly to write relations for weight fraction solubles, w_s, and cross-link density, X.

We again retain Flory's ideal network assumptions:[2b]

(1) all functional groups of the same type are equally reactive;

(2) all groups react independently of one another;

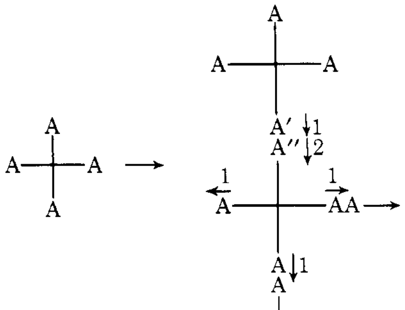
(3) no intramolecular reactions occur in finite species.

We will also use an elementary law of conditional probability.[3] Let A be an event and $\bar{A}$ its complement, B any other event, and $P(B|A)$ the conditional probability of B given that A has occurred. Then *the law of total probability*

$$P(B) = P(B|A)P(A) + P(B|\bar{A})P(\bar{A}) \qquad (1)$$

Probability of a Finite Chain

Stepwise Polymerization of A_f. It is most useful to determine whether a group selected from the polymerization at random is part of a finite chain. Consider first the simple reaction between similar f functional monomers. We can schematically represent the stepwise homopolymerization of A_f by



(2)

Let polymerization procede until some fraction p of the A's have reacted. Pick an A group at random, A' in eq 2. Now we need to know what is the probability that following $\xrightarrow{1}$ (looking *out* from the molecule) leads to a finite or dangling chain rather than to the infinite network, i.e., to the walls of the container. Let F_A^{out} be the event that $\xrightarrow{1}$ is the start of a *finite* chain, then from eq 1 it follows that

$$\begin{aligned} P(F_A^{\text{out}}) &= P(F_A^{\text{out}}|\text{A reacts})P(\text{A reacts}) + \\ &\quad P(F_A^{\text{out}}|\text{A does not react})P(\text{A does not react}) = \\ &\quad P(F_A^{\text{in}})p + 1(1-p) = pP(F_A^{\text{in}}) + 1 - p \end{aligned} \qquad (3)$$

where F_a^{in} is the event that $\xrightarrow{2}$ in eq 2 is the start of a finite chain. For A'' to lead to a finite chain all of the other arms of A_f must be finite. Thus

$$P(F_A^{\text{in}}) = P(F_A^{\text{out}})^{f-1} \qquad (4)$$

and, as with the weight average,[2a] the repetitive nature of this simple branched molecule leads us back to the starting situation. Combining eq 3 and 4 we can solve for $P(F_A^{\text{out}})$

$$pP(F_A^{\text{out}})^{f-1} - P(F_A^{\text{out}}) - p + 1 = 0 \qquad (5)$$

or $P(F_A^{\text{in}})$

$$[pP(F_A^{\text{in}}) + 1 - p]^{f-1} = P(F_A^{\text{in}}) \qquad (6)$$

We desire roots of eq 5 and 6 between 0 and 1. Note that eq 6 can be rewritten as $\phi(x) = x$ where $\phi(x) = (px + 1 - p)^{f-1}$ is the probability generating function[4] of a Binomial random variable with parameters $f - 1$ and p. It can be shown that our situation is exactly that of a branching process with offspring distribution Binomial$(f - 1,p)$ and that our event of a finite chain corresponds to extinction. The probability of extinction is the unique solution of $\phi(x) = x$ in the interval (0,1) if it exists and 1 otherwise.[4] (The analysis in the remainder of this section can be justified in a similar manner.) From eq 4 it follows that eq 5 will have a root in (0,1) if and only if eq 6 does; this will happen when $p > (f - 1)^{-1} = p_{\text{gel}}$. Physically when $P(F_A^{\text{out}}) = 1$ the system has not yet gelled, as we discuss below. Thus for post gel relations the useful root lies between 0 and 1.

Since $P(F_A{}^{\text{out}}) = 1$ will always be a root of eq 5, and not of interest, we can factor it out.

$$p \sum_{i=0}^{f-2} P(F_A{}^{\text{out}})^i - 1 = 0 \tag{7}$$

which can readily be solved

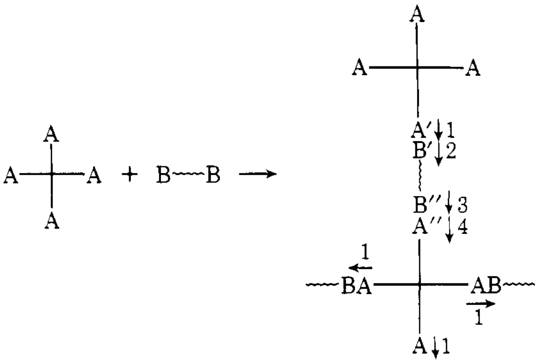
$$\text{for } f = 3 \qquad P(F_A{}^{\text{out}}) = (1 - p)/p \tag{8}$$

$$\text{for } f = 4 \qquad P(F_A{}^{\text{out}}) = (1/p - \tfrac{3}{4})^{1/2} - \tfrac{1}{2} \tag{9}$$

Roots between 0 and 1 for higher f are easy to find numerically because $\psi(x) = px^{f-1} - p + 1$ is convex and strictly increasing. We will use $P(F_A{}^{\text{out}})$ later to calculate w_s and cross-link concentration.

Dobson and Gordon[5] have used probability generating functions to calculate the extinction probability or $P(F_A{}^{\text{in}})$ for the A_f polymerization case and for vulcanization of long chains. Our eq 8 and 9 agree with their eq A1 and A3. Our approach and theirs use the same underlying theory but it appears simpler to extend ours to more complicated cases such as stepwise copolymerization.

Stepwise Copolymerization. As with the molecular weight averages,[2a] calculation of $P(F_A{}^{\text{out}})$ can be generalized to random copolymerization. Consider first the reaction of A_f with B_2 shown schematically below



(10)

Looking out from A_f along $\xrightarrow{1}$ and using eq 1 gives

$$P(F_A{}^{\text{out}}) = p_A P(F_B{}^{\text{in}}) + 1 - p_A \tag{11}$$

where p_A is the fraction of A groups which have reacted and p_B the fraction of B groups, $p_B = rp_A = rp$ (ref 2a, eq 12). The probability of B′ leading to a finite chain in $\xrightarrow{2}$ is just the same as B″ in $\xrightarrow{3}$ thus

$$P(F_B{}^{\text{in}}) = P(F_B{}^{\text{out}}) \tag{12}$$

Following $\xrightarrow{3}$ is similar to following $\xrightarrow{1}$

$$P(F_B{}^{\text{out}}) = p_B P(F_A{}^{\text{in}}) + 1 - p_B = rpP(F_A{}^{\text{in}}) + 1 - rp \tag{13}$$

and finally following $\xrightarrow{4}$ we obtain eq 4 again

$$P(F_A{}^{\text{in}}) = P(F_A{}^{\text{out}})^{f-1} \tag{4}$$

Combining equations yields

$$rp^2 P(F_A{}^{\text{out}})^{f-1} - P(F_A{}^{\text{out}}) - rp^2 + 1 = 0 \tag{14}$$

As above $P(F_A{}^{\text{out}}) = 1$ will always be a root. Again, from the theory of branching processes[4] there may be a root between 0 and 1. If there is, it will be unique and that will be the root of interest, otherwise 1 is the root. The roots of eq 14 are

$$\text{for } f = 3 \qquad P(F_A{}^{\text{out}}) = (1 - rp^2)/rp^2 \tag{15}$$

$$\text{for } f = 4 \qquad P(F_A{}^{\text{out}}) = (1/rp^2 - \tfrac{3}{4})^{1/2} - \tfrac{1}{2} \tag{16}$$

As before, roots for higher f are easy to find numerically.

As with $\bar{M}_w$ it is not hard to extend this approach to the general case of a polymerizing mixture of A_{f_i}'s and B_{g_j}'s (shown schematically in ref 2a, eq 24). The recursion relations are identical with eq 4, 11–13, except that each species must be weighted by its mole fraction of functional groups, a_{f_i} and b_{g_j} (ref 2a, eq 26).

$$P(F_A{}^{\text{out}}) = p_A P(F_B{}^{\text{in}}) + 1 - p_A \tag{17}$$

$$P(F_B{}^{\text{in}}) = \Sigma_j b_{g_j} P(F_B{}^{\text{out}})^{g_j - 1} \tag{18}$$

$$P(F_B{}^{\text{out}}) = p_B P(F_A{}^{\text{in}}) + 1 - p_B \tag{19}$$

$$P(F_A{}^{\text{in}}) = \Sigma_i a_{f_i} P(F_A{}^{\text{out}})^{f_i - 1} \tag{20}$$

Combining equations yields

$$p_A \Sigma_j b_{g_j} [1 - p_B + p_B \Sigma_i a_{f_i} P(F_A{}^{\text{out}})^{f_i - 1}]^{g_j - 1} - P(F_A{}^{\text{out}}) - p_A + 1 = 0 \tag{21}$$

Useful special cases of eq 21 include of course eq 5 and 14, and mixtures with only B_2 present:

$$rp^2 \Sigma_i a_{f_i} P(F_A{}^{\text{out}})^{f_i - 1} - P(F_A{}^{\text{out}}) - rp^2 + 1 = 0 \tag{22}$$

For the system $A_3 + A_2 + A_1 + B_2$ the desired root is

$$P(F_A{}^{\text{out}}) = (1 - (a_3 + a_2)\, rp^2)/a_3 rp^2 \tag{23}$$

and for $A_4 + A_3 + A_2 + A_1 + B_2$

$$P(F_A{}^{\text{out}}) = [a_3{}^2 - a_4(3a_4 + 2a_3 + 4a_2 - 4/rp^2)]^{1/2}/2a_4 - \tfrac{1}{2} \tag{24}$$

provided they are between 0 and 1.

Gel Point. At the gel point $\bar{M}_w$ diverges and the infinite network begins to form. Thus the probability of a finite chain should give us an independent means for determining the gel point. If $P(F_A{}^{\text{out}}) = 1$ then it is impossible to find an A on an infinite chain, that is, the infinite network has not started to form. Thus we wish to characterize the situation for which there is no solution of eq 14 between 0 and 1. Factoring eq 14 yields

$$(P(F_A{}^{\text{out}}) - 1)\left(rp^2 \sum_{i=0}^{f-2} P(F_A{}^{\text{out}})^i - 1\right) = 0 \tag{25}$$

Thus it suffices to determine when

$$g(x) = rp^2 \sum_{i=0}^{f-2} x^i - 1 = 0 \tag{26}$$

has no roots between 0 and 1. Because $g(x)$ is monotonically increasing for x between 0 and 1, and $g(0) = -1$ and $g(1) = rp^2(f - 1) - 1$, eq 26 has no root between 0 and 1 if and only if $rp^2(f - 1) - 1 < 0$. Thus if $rp^2 \leq (f - 1)^{-1}$, $P(F_A{}^{\text{out}}) = 1$ and if $rp^2 > (f - 1)^{-1}$, $P(F_A{}^{\text{out}}) < 1$ and an infinite network has started forming. Thus we define p_{gel} such that

$$rp_{\text{gel}}{}^2 = 1/(f - 1) \tag{27}$$

which agrees with our previous result (ref 2a, eq 41) for the case of $A_f + B_2$ copolymerization.

Cross-Linking of Polymer Chains. As Flory[2b] points out the random cross-linking of long, linear polymer chains with a most probable distribution of chain lengths can be treated with the same equations developed for stepwise reactions. Cross-linking with tetrafunctional units will be identical with a stepwise reaction of A_2 with a small amount of A_4 up to a high conversion, $p = p_0$. The formation of cross-links can be viewed as a series of reactions up to a constant extent, p_0, of A_2 plus increasing amounts of A_4. Thus the same equations apply but with the moles of reacted tetrafunctionals or the fraction of repeat units which are cross-linked, $a_4 = \rho$, as the variable. p_0 can be calculated from the initial degree of polymerization of the chains

$$\bar{x}_{n_0} = 1/(1 - p_0) \qquad (28)$$

To calculate the probability of a finite chain after adding a_4 cross-links we can use eq 21, which for the case $A_4 + A_2$ becomes ($b_2 = p_B = 1$)

$$p_0[a_4P(F_A^{out})^3 + (1 - a_4)P(F_A^{out})] - P(F_A^{out}) - p_0 + 1 = 0$$

or

$$\frac{\bar{x}_{n_0} - 1}{\bar{x}_{n_0}}[\rho P(F_A^{out})^3 + (1 - \rho)P(F_A^{out})] - P(F_A^{out}) + 1/\bar{x}_{n_0} = 0 \qquad (29)$$

Factoring out $P(F_A^{out}) = 1$ the desired root will be

$$P(F_A^{out}) = (1/\rho(\bar{x}_{n_0} - 1) + 1/4)^{1/2} - 1/2 \qquad (30)$$

provided $\rho(\bar{x}_{n_0} - 1) > 1/2$. Note that $\rho_{gel} = 1/2(\bar{x}_{n_0} - 1)$ which agrees with eq 65 of ref 2a since for a most probable distribution $\bar{x}_{w_0} - 1 = 2p_0/(1 - p_0)$.

Chain Addition. In networks formed by ideal stepwise polymerization, a finite or dangling chain on the network results from incomplete reaction. In chainwise polymerizations chains can also be finite due to termination reactions. To treat this, as discussed previously,[2a] we introduce the probability q that an activated or growing chain will add one more unit.

To find relations in the gel region we consider the probability of a finite chain starting from a randomly chosen A group. As with our previous treatment of the expected weights[2a] we differentiate between any A and an activated one A*. For A_2 reacting chainwise with A_f this leads to the following recursion equations:

$$P(F_A^{out}) = (1 - p) + pP(F_{A^*}^{out}) \qquad (31)$$

$$P(F_{A^*}^{out}) = (1 - q) + qP(F_{A^*}^{in}) \qquad (32)$$

$$P(F_{A^*}^{in}) = (1 - a_f)P(F_{A^*}^{out}) + a_fP(F_{A^*}^{out})P(E) \qquad (33)$$

where E is the event that none of the $f - 2$ remaining A's on the A_f lead to the infinite network. To compute $P(E)$ we must condition over the number of pairs of A's which are activated: $2k$ of the $f - 2$ A's will be activated with probability

$$\binom{(f-2)/2}{k} p^k(1 - p)^{[(f-2)/2]-k} \qquad (34)$$

where $\binom{x}{y}$ is the usual notation for the number of combinations of x things taken y at a time; $x!/y!(x - y)!$. Consequently, using eq 1

$$P(E) = \sum_{k=0}^{(f-2)/2} P(F_{A^*}^{out})^{2k} \binom{(f-2)/2}{k} p^k(1 - p)^{[(f-2)/2]-k} = (pP(F_{A^*}^{out})^2 + 1 - p)^{(f-2)/2} \qquad (35)$$

Combining eq 32, 33, and 35 gives

$$qa_fP(F_{A^*}^{out})[pP(F_{A^*}^{out})^2 + 1 - p]^{(f-2)/2} - (1 + qa_f - q)P(F_{A^*}^{out}) - q + 1 = 0 \qquad (36)$$

Solving for $f = 4$ and taking the unique root between 0 and 1 we find

$$P(F_{A^*}^{out}) = \left(\frac{1 - q}{qa_4p} + 1/4\right)^{1/2} - 1/2 \qquad (37)$$

For complete reaction of linear chains, A_2 only, with $a_4 = 0$, $\bar{x}_{n_0} = 1/(1 - q)$. Substituting $\bar{x}_{n_0}$ into eq 37 gives, as we might expect, the same result as cross-linking long chains, eq 30.

We now have derived relations for the probability of a finite chain for most of the important types of network polymerization. These relations can readily be used to find the sol fraction and cross-link density.

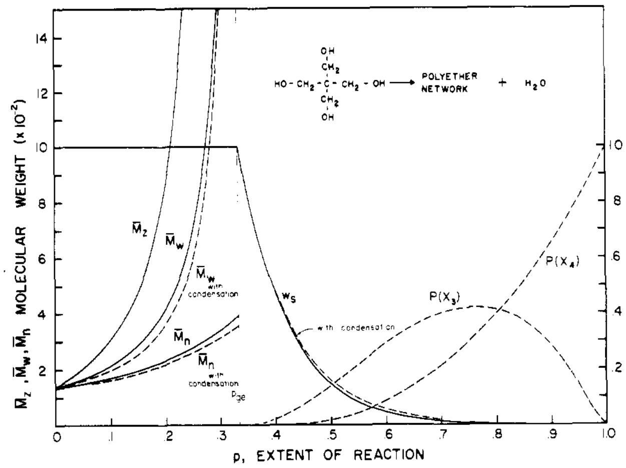


Figure 1. Calculated properties for the polyether network formation by the stepwise polymerization of pentaerythritol. The effect of condensation products on $\bar{M}_w$, $\bar{M}_n$, and w_s is shown.

Weight Fraction Solubles

The amount of soluble material in a network at any given extent of reaction is of practical interest. Up to the gel point all molecules are finite, thus the weight fraction of solubles, w_s, is unity. Beyond the gel point molecules are rapidly incorporated into the network and w_s decreases quickly. For the simple A_f homopolymerization a randomly chosen A_f molecule will be part of the sol if all f of its arms lead out to finite chains. Thus

$$w_s = P(F_A^{out})^f \qquad (38)$$

Using eq 8 for $f = 3$ gives $(1 - p)^3/p^3$ which agrees with Flory (ref 2b, p 376). Substituting in eq 7 gives the same result as Gordon (ref 6, eq 20). Figure 1 shows a plot of w_s vs. p for a tetrafunctional case. Note how rapidly the sol fraction disappears. The effect of condensation products is also shown and discussed in the Appendix.

We can readily generalize eq 38 to a mixture of A_{f_i} and B_{g_j} by weighting each species by its mass fraction in the mixture, $w_{A_{fi}}$

$$w_s = \sum_{i=1}^{k} w_{A_{fi}}P(F_A^{out})^{f_i} + \sum_{j=1}^{l} w_{B_{gj}}P(F_B^{out})^{g_j} \qquad (39)$$

Figure 2 shows eq 39 plotted for an $A_3 + B_2$ copolymerization while Figure 3 illustrates a tetrafunctional. We note that in both of these stepwise cases the finite species have essentially disappeared after 90% reaction.

For cross-linking of long chains eq 39 becomes

$$w_s = P(F_A^{out})^2\{1 - \rho[P(F_A^{out})^2 - 1]\} \qquad (40)$$

$$w_s \cong P(F_A^{out})^2 \qquad (41)$$

This result is illustrated for a typical cross-linking system in Figure 4. The finite species disappear more slowly than in the stepwise examples.

In the chain addition case the expression for w_s is modified because the A's are activated in pairs.

$$w_s = w_{A_2}(pP(F_{A^*}^{out})^2 + 1 - p) + w_{A_f}(pP(F_{A^*}^{out})^2 + 1 - p)^{f/2}$$

However, in the chain addition case we are generally only interested in the soluble portion of the polymeric species. Let w_p equal the weight fraction of the polymeric portion,

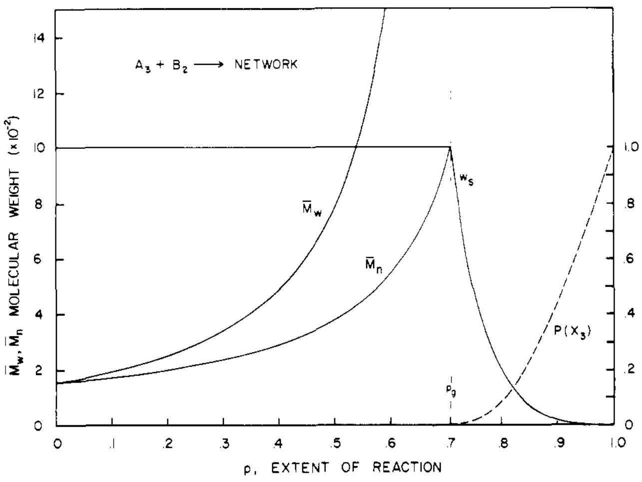


Figure 2. Calculated properties for the urethane network formation by the stepwise polymerization of 2-hydroxymethyl-2-ethyl-1,3-propanediol and 1,6-hexamethylene diisocyanate with $r = 1$.

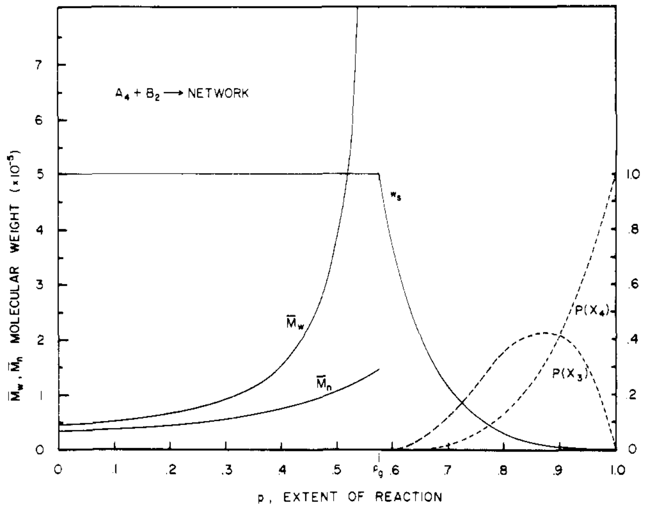


Figure 3. Calculated properties for silicone rubber formation by the hydrosilation reaction of (H $CH_3PhSiO)_4Si$, and vinyl terminated poly(dimethylsiloxane), M_{B_2} = 5000 (monodisperse) with r = 1.

then

$$w_p = pw_{A_2} + (1 - (1 - p)^{f/2})w_{A_f}$$

It follows that the weight fraction solubles in the polymeric portion is

$$w_s^* = (w_s + w_p - 1)/w_p$$

or equivalently

$$w_s^* = \frac{w_{A_2}pP(F_{A^*}^{\text{out}})^2 + w_{A_f}[(pP(F_{A^*}^{\text{out}})^2 + 1 - p)^{f/2} - (1 - p)^{f/2}]}{pw_{A_2} + (1 - (1 - p)^{f/2})w_{A_f}} \qquad (42)$$

This result is illustrated in Figure 5 for the copolymerization of methyl methacrylate and ethylene dimethacrylate. In this case, as with long-chain cross-linking, the second terms in both numerator and denominator above are negligible.

Cross-Link Density

Another important network property is the cross-link density or concentration of effective junction points in the infinite network. An A_{f_i} chosen at random will act as an effective junction point if three or more of its arms lead out to the infinite network, to the container walls. If only one arm is infinite, this A_{f_i} molecule will be just dangling on the network; if two are infinite, A_{f_i} forms part of a chain connecting two effective junction points, but is not an effective junction point.

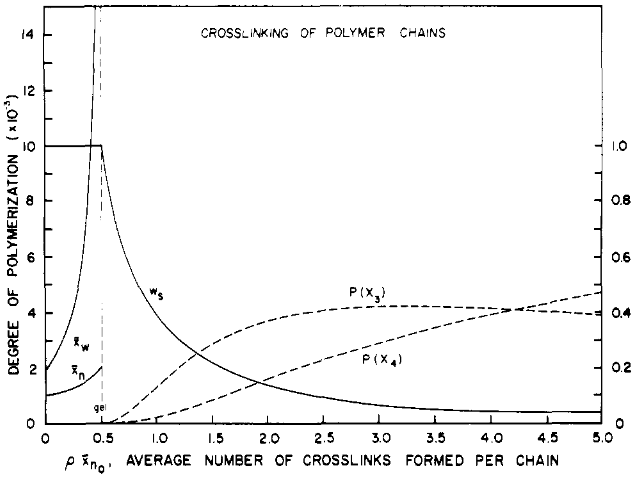


Figure 4. Calculated properties vs. degree of cross-linking for starting chains of $\bar{x}_{n0}$ = 1000 and most probable distribution.

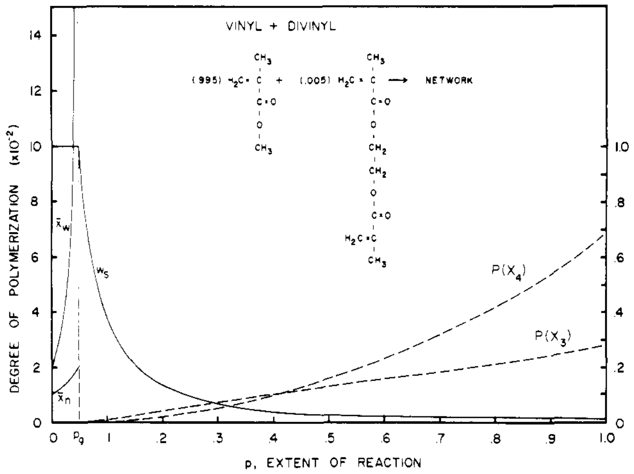


Figure 5. Calculated properties vs. extent of reaction of C=C groups for chain addition polymerization of methyl methacrylate with 0.5 mol % ethylene dimethacrylate, q = 0.999.

Consider A_4. As Scalan[7] has shown the probability that A_4 is an effective cross-link of degree 4 is just

$$P(X_{4,4}) = [1 - P(F_A^{\text{out}})]^4 \qquad (43)$$

A_4 can also be an effective cross-link of degree 3. The probability of X_3 is the probability that exactly three of the four arms are infinite.

$$P(X_{3,4}) = \binom{4}{3} P(F_A^{\text{out}})[1 - P(F_A^{\text{out}})]^3 \qquad (44)$$

In general, the probability that an A_{f_i} monomer will be an effective cross-link of degree m is then

$$P(X_{m,f_i}) = \binom{f_i}{m} P(F_A^{\text{out}})^{f_i - m}[1 - P(F_A^{\text{out}})]^m \qquad (45)$$

Equation 45 is illustrated in Figures 1–3 for several representative stepwise reactions. Note that in the A_4 polymerizations trifunctional cross-links form initially and then give way to tetrafunctionals. At the end of the reaction if there have been no side reactions or small rings formed (by our initial assumptions) then $P(X_{4,4})$ goes to unity. In Figure 4 we see the same trend but $P(X_{4,4})$ will only reach one at complete cross-linking, $\rho = 1.0$.

For networks formed by chain addition, to compute the proportion of cross-links of degree m in the polymeric material we must first pick an $\mathrm{A_f}^*$ at random from the polymeric material (i.e., it has at least a pair of reacted A's). This $\mathrm{A_f}^*$ will have k pairs of A's activated with probability

$$\binom{f/2}{k} p^k(1-p)^{(f/2)-k}/[1-(1-p)^{f/2}]$$

(This is the conditional probability of a Binomial random variable given at least one success.) If there are k reacted pairs then the probability that exactly m A's lead to the infinite network is

$$\binom{2k}{m}(1-P(F_{\mathrm{A}^*}{}^{\mathrm{out}}))^m P(F_{\mathrm{A}^*}{}^{\mathrm{out}})^{2k-m}$$

Using eq 1 gives

$$P(X_{m,f}) = \Sigma_k P(X_m|k \text{ pairs react})\, P(k \text{ pairs react})$$
$$= \Sigma_k \binom{2k}{m}(1-P(F_{\mathrm{A}^*}{}^{\mathrm{out}}))^m P(F_{\mathrm{A}^*}{}^{\mathrm{out}})^{2\mathrm{k}-\mathrm{m}} \times \frac{\binom{f/2}{k} p^k(1-p)^{f/2-k}}{1-(1-p)^{f/2}} \qquad (46)$$

where the summation is over integer values of k between $m/2$ and $f/2$ inclusive.

For vinyl divinyl copolymerization $f = 4$ and eq 46 simplifies to

$$P(X_{3,4}) = 4[1-P(F_{\mathrm{A}^*}{}^{\mathrm{out}})]^3 P(F_{\mathrm{A}^*}{}^{\mathrm{out}})\frac{p}{2-p} \qquad (47)$$

and

$$P(X_{4,4}) = [1-P(F_{\mathrm{A}^*}{}^{\mathrm{out}})]^4 \frac{p}{2-p} \qquad (48)$$

These results are illustrated in Figure 5.

It is useful to have the concentration of effective network junctions or cross-link density. This will just be the initial concentration of the appropriate A_{f_i} species, $[\mathrm{A}_{f_i}]_0$, times the probability $P(X_{m,f_i})$ summed over $f_i = m$ to the highest functionality f_k:

$$[X_m] = \sum_{f_i=m}^{f_k} [\mathrm{A}_{f_i}]_0 P(X_{m,f_i}) \qquad (49)$$

The total cross-link density $[X]$ will just be the sum of the individual $[X_m]$'s from $m = 3$ to f_k. If we also have B_3 or higher functionality we will have another equation analogous to eq 45 in $P(F_{\mathrm{B}}{}^{\mathrm{out}})$ which will be added to eq 49. Since as p goes to 1, $P(F_{\mathrm{A}}{}^{\mathrm{out}})$ becomes zero, in the limit of complete reaction theoretically $[X_m] = [\mathrm{A}_{f_m}]_0$.

Application to Rubber Elasticity

The above relations can be applied to the equation of rubber elasticity. The shear modulus of an ideal rubber is (ref 2b, p 470)

$$G \equiv \tau/\gamma = \nu RT \qquad (50)$$

where R is the gas constant, T the absolute temperature, and ν the effective concentration of network chains. A network chain will be "effective", act like an entropic spring, if it is long and if its ends are effective cross-links and are spaced such that it can assume a random coil conformation. Frequently a front factor is added to account for deviation from random coil behavior.

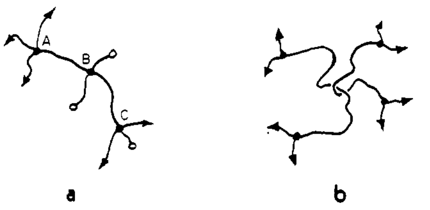


Figure 6. Network defects: (a) finite or dangling chain, —o; (b) a physical cross-link, a trapped entanglement.

There has been considerable debate over how to count effective network chains. Figure 6 illustrates some of the problems. First we will consider network chains resulting from chemical cross-links, ν_c. One defect in these are dangling ends or finite chains. We have accounted for these in the effectiveness m of our cross-links. Thus in Figure 6a branch point A will be an X_4 cross-link, C an X_3, and B an X_2 or just a continuation of the network chain ABC. Thus each X_m cross-link has $m/2$ network chains attached to it. Duiser and Staverman[8] and recently Graessley[9] argue convincingly that under deformation the mobility of the end of a network chain is influenced by m. They find that the network chains should be weighted by $(m - 2)/m$. Thus a chain ending in trifunctional junctions will be ⅓ as effective as one ending in an immobile junction, one with infinite chains to the network. Combining both of these ideas we obtain a relation between effective network chains and the concentration of chemical cross-links.

$$\nu_c = \sum_{m=3}^{f_k} \frac{m-2}{2}[X_m] \qquad (51)$$

Langley and Polmanteer[10] come to this result directly by arguing that one m functional cross-link should be mechanically equivalent to $m - 2$ three functional ones.

Figure 6b illustrates another possible type of mechanically effective cross-link, a trapped entanglement. Langley[10] has recently suggested that entanglements can be quantitatively accounted for by Te, the probability that all four chain ends coming from an entanglement lead into the network, times ϵ, an effective concentration of these pseudo-tetrafunctional junctions. Assuming the same form as eq 51, the concentration of network chains due to entanglements will be

$$\nu_e = \epsilon \mathrm{Te} \qquad (52)$$

with

$$\mathrm{Te} = [1 - P(F_{\mathrm{D}}{}^{\mathrm{in}})]^4 \qquad (53)$$

where the nature of species D depends on the nature of the reactants. For $\mathrm{A_f}$ homopolymerization it is clearly $P(F_{\mathrm{A}}{}^{\mathrm{in}})$. For cross-linking long chains the "$\mathrm{A_2}$" units will be involved in cross-links. Then by eq 20 $P(F_{\mathrm{D}}{}^{\mathrm{in}}) = a_2 P(\mathrm{F_A}{}^{\mathrm{out}})$ or $a_2 P(\mathrm{F_{A^*}}{}^{\mathrm{out}})$ in the chain addition case. For long $\mathrm{B_2}$'s reacting with small $\mathrm{A_f}$'s the $\mathrm{B_2}$'s will be entangled and $P(F_{\mathrm{D}}{}^{\mathrm{in}}) = P(F_{\mathrm{B}}{}^{\mathrm{in}}) = P(F_{\mathrm{B}}{}^{\mathrm{out}})$.

Thus by combining eq 49–52, we obtain

$$\frac{G}{RT} = \nu_c + \nu_e = \sum_{m=3}^{f_k} \frac{m-2}{2} \sum_{f_i=3}^{f_k} [\mathrm{A}_{f_i}]_0 P(X_{m,f_i}) + \mathrm{Te} \qquad (54)$$

For $\mathrm{A_3 + B_2}$

$$\frac{G}{RT} = \tfrac{1}{2}[\mathrm{A_3}]_0[1 - P(F_{\mathrm{A}}{}^{\mathrm{out}})]^3 + \epsilon[1 - P(F_{\mathrm{B}}{}^{\mathrm{out}})]^4$$

or

$$= \tfrac{1}{2}[\mathrm{A_3}]_0\left(\frac{2rp^2-1}{rp^2}\right)^3 + \epsilon\left(\frac{2rp^2-1}{rp^3}\right)^4 \qquad (55)$$

For cross-linking long chains

$$\frac{G}{RT} = [\mathrm{A}_4]\{1/2P(F_\mathrm{A}^{\mathrm{out}})[1 - P(F_\mathrm{A}^{\mathrm{out}})]^3 + [1 - P(F_\mathrm{A}^{\mathrm{out}})]^4\} + \epsilon[1 - (1 - \rho)P(F_\mathrm{A}^{\mathrm{out}})]^4 \quad (56)$$

where $[\mathrm{A}_4] = \rho(d_0)/2M_\mathrm{c}$, where d_0 is the initial sample density and M_c is the weight between cross-linkable sites.

It is worth noting that the concentration of effective network chains $\nu_\mathrm{c} + \nu_\mathrm{e}$ can also be applied to predict equilibrium swelling of a rubber network (Flory,[2b] p 579).

Conclusions

The probability of a finite or dangling chain on an ideal polymer network has been derived by a simple recursive scheme. In contrast to the method of Dobson and Gordon[5] probability generating function formalism is not required.

The general result, eq 21, and its specific solutions, eq 23, 24, and 30, give the finite chain probability as a function of reactant type and extent of polymerization. They cover most of the important types of network forming polymerizations.

From the finite chain probability useful property relations such as sol fraction, cross-link density, and the number of elastically effective network chains are developed. Because of their simplicity we expect these relations to be further developed and applied to network polymer property measurements.

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Appendix. Effect of Condensation Products on Sol Fraction

Although the relations for probability of a finite chain and cross-link probability remain unchanged, condensation products do affect the weight fraction solubles. We must modify the weight fraction terms in eq 39. The probability that all arms of an $\mathrm{A}_{f_i}{}^n$ (defined in ref 2a, eq A4) lead to finite chains is $P(F_\mathrm{B}^{\mathrm{in}})^n$. Furthermore the proportion of mass in $\mathrm{A}_{f_i}{}^n$'s and $\mathrm{B}_{g_j}{}^n$'s is $w_{\mathrm{A}_{f_i}{}^n}$ and $w_{\mathrm{B}_{g_j}{}^n}$ as defined in ref 2a, eq A16 and A17. Thus with condensation eq 39 becomes

$$w_\mathrm{s} = \sum_{i=1}^{k} \sum_{n=0}^{f_i} w_{\mathrm{A}_{f_i}{}^n} P(F_\mathrm{B}^{\mathrm{in}})^n + \sum_{j=1}^{l} \sum_{n=0}^{g_j} w_{\mathrm{B}_{g_j}{}^n} P(F_\mathrm{A}^{\mathrm{in}})^n \quad (\mathrm{A1})$$

For the special case of A_f homopolymerization

$$w_s = \sum_{n=0}^{f} w_{\mathrm{A}_f{}^n} P(F_\mathrm{A}^{\mathrm{in}})^n \quad (\mathrm{A2})$$

or

$$w_\mathrm{s} = P(F_\mathrm{A}^{\mathrm{out}})^f \left[\frac{2M_{\mathrm{A}_f} - pfM_\mathrm{C}P(F_\mathrm{A}^{\mathrm{out}})^{f-2}}{2M_{\mathrm{A}_f} - pfM_\mathrm{C}}\right] \quad (\mathrm{A3})$$

For the case A_3, $P(F_\mathrm{A}^{\mathrm{out}}) = (1 - p)/p$ if $p > ½$

$$w_\mathrm{s} = \left(\frac{1-p}{p}\right)^3 \left[\frac{2M_{\mathrm{A}_3} - 3(1-p)M_\mathrm{C}}{2M_{\mathrm{A}_3} - 3pM_\mathrm{C}}\right] \quad (\mathrm{A4})$$

Note that for $M_\mathrm{C} = 0$, the correction factor equals 1 and A3 reduces to eq 38.

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Studies on the Mechanism of Alternating Radical Copolymerization. Quantitative Treatment of the Initial Copolymerization Rate

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ABSTRACT: In the previous paper[1] we have proposed the general mechanism involving the participation of both the free monomers and the charge-transfer complex monomer for the alternating radical copolymerization. This paper describes a quantitative treatment of the initial copolymerization rate to estimate the ratio of the contribution of the charge-transfer complex monomer to the free monomers.

A number of studies have been done concerning the mechanism of the alternating radical copolymerization. As for the propagation process of the copolymerization, the following three mechanisms have been proposed: (i) mechanism considering only the cross reactions of the free monomers, (ii) mechanism of homopolymerization of the charge-transfer complex monomer (CT-complex monomer), (iii) mechanism involving the participation of both the free monomers and the CT-complex monomer. Baldwin et al.[2] has explained the results based on the first mechanism. Yamashita et al.[3] has proposed the second mechanism based on the studies of the terpolymerization, suggesting much higher reactivity of the CT-complex monomer as compared with the free monomers.