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A New Derivation of Average Molecular Weights of Nonlinear Polymers

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ABSTRACT: A new method for calculating average molecular weights is presented for nonlinear polymers. In contrast to the previous methods of Flory and Stockmayer which first calculate the distribution of all species and then use the distributions to calculate average properties, the new method calculates these properties directly. In contrast to the method of Gordon, probability generating functions are not required. Starting with elementary probability and utilizing the recursive nature of network polymers, property relations can be developed more simply. We illustrate the method for calculations of $\overline{M}_w$, $\overline{M}_z$, and the gel point for a wide variety of polyfunctional polymerizations.

Flory[2] and Stockmayer[3] laid out the basic relations between extent of reaction and resulting structure in nonlinear polymerizations. Starting with the assumptions of equal reactivity of functional groups and no intramolecular reactions, they used combinatorial arguments to derive expressions for the size distribution of the finite molecules as a function of reaction extent. For cases of practical importance these distribution functions become quite complex (e.g., Stockmayer[4]).

At present, experimentally we can only measure average molecular weights of nonlinear polymers. It is possible, though algebraically very tedious, to calculate these averages from the distribution functions. General treatment of nonidealities such as intramolecular reactions or ring formation using distribution functions appears to be prohibitive.

Gordon[5] showed that the molecular weight averages could be calculated directly using the theory of stochastic branching processes.[6] He and coworkers have used this theory extensively on nonlinear polymer problems.[7–10] Gordon's technique involves abstract mathematics and requires deriving probability generating functions. The method is quite general but rather difficult to use.

Our interest in developing mathematical models for network polymer processing motivated us to seek simpler relations which could readily be incorporated into a larger, complex process model. Below we describe a new, simpler method for deriving average properties of nonlinear polymers.

We retain Flory's three simplifying assumptions, namely:
(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.
(Some departures from these assumptions, such as unequal reactivity and substitution effects and some aspects of intramolecular loops, can also be treated with our method.[11])

Our method uses the recursive nature of the branching process and an elementary law of conditional expectation. Let A be an event and $\bar{A}$ its complement. Let Y be a ran-

dom variable, $E(Y)$ its expectation (or average value), and $E(Y|A)$ its conditional expectation given the event A has occurred. Then the *law of total probability for expectations* is

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

This law is discussed in most texts on probability theory.[12]

Stepwise Polymerizations

$\overline{M}_w$ **for Homopolymers.** Let us first illustrate the method with some simple examples. Consider the simplest case, the one treated by Flory,[2] the reaction between similar f functional molecules. An example is the etherification of pentaerythritol:

$$\text{HO—CH}_2\text{—}\overset{\displaystyle \overset{\text{OH}}{\underset{\displaystyle |}{\overset{\displaystyle |}{\text{CH}_2}}}}{\underset{\displaystyle \underset{\text{OH}}{\underset{\displaystyle |}{\overset{\displaystyle |}{\text{CH}_2}}}}{\text{C}}}\text{—CH}_2\text{—OH} \longrightarrow \text{branched polyether} + \text{H}_2\text{O} \qquad (2a)$$
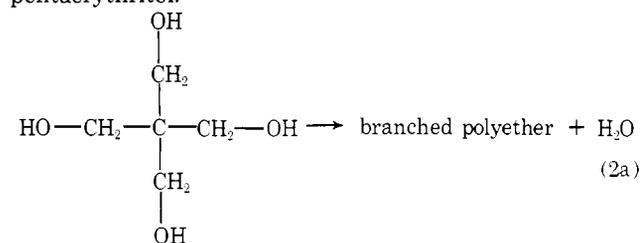
First we will only consider stepwise or condensation polymerizations, ignoring the effects of any condensation products for the moment. A later section treats chainwise or addition polymerizations. We can schematically represent the polymerization of A_f moles of monomer bearing f groups by

(2b)
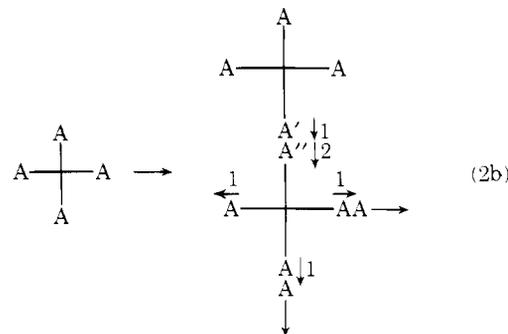
Let the system react until some fraction p of the A's have reacted, where

$$p = (A - A_t)/A \qquad (3)$$

Here and throughout this paper A (or A_f) represents the initial moles of A type groups and A_t equals the moles after some reaction time.

Pick an A group at random, labeled as A' above. What is the weight, $W_{A'}^{out}$, attached to A' looking *out* from its parent molecule, in the direction $\xrightarrow{1}$?

Since A' is chosen at random, $W_{A'}^{out}$ is a random variable. $W_{A'}^{out}$ equals 0 if A' has not reacted. If A' has reacted (with A'', say) then $W_{A'}^{out}$ equals $W_{A''}^{in}$, the weight attached to A'' looking along $\xrightarrow{2}$, *into* A'''s parent molecule.

$$W_{A'}^{out} = \begin{cases} 0 & \text{if A' does not react} \\ W_{A''}^{in} & \text{if A' does react (with A'')} \end{cases} \qquad (4)$$

By equation 1,

$$E(W_A^{out}) = E(W_A^{out}|A \text{ reacts})P(A \text{ reacts}) +$$
$$E(W_A^{out}|A \text{ does not react})P(A \text{ does not react}) =$$
$$E(W_A^{in})p + 0(1 - p) = pE(W_A^{in}) \qquad (5)$$

$E(W_A^{in})$, the expected weight on any A looking into its parent molecule, will be the molecular weight of A_f plus the sum of the expected weights on each of the remaining $f - 1$ arms which is just $E(W_A^{out})$ for each arm. Thus

$$E(W_A^{in}) = M_{A_f} + (f - 1)E(W_A^{out}) \qquad (6)$$

and the repetitive nature of this simple branched molecule leads us back to the starting situation.

The molecular weight, W_{A_f}, of the entire molecule to which a randomly chosen A_f belongs, will just be the weight attached to one of its arms looking in both directions (*in* and *out*)

$$W_{A_f} = W_A^{in} + W_A^{out} \qquad (7)$$

and thus the average molecular weight attached to a random A_f will be

$$\overline{M}_w = E(W_{A_f}) = E(W_A^{in}) + E(W_A^{out}) \qquad (8)$$

This is the weight average molecular weight because picking an A_f or an A group at random corresponds to picking a unit of mass and then finding the expected weight of the molecule of which it is a part. Flory,[2b] p 293, comments on this.

Solving eq 5 and 6 and substituting into eq 8 yields

$$\overline{M}_w = M_{A_f} \frac{1 + p}{1 - p(f - 1)}$$

or

$$\bar{x}_w = \frac{\overline{M}_w(p)}{\overline{M}_w(0)} = \frac{1 + p}{1 - p(f - 1)} \qquad (9)$$

which is in agreement with Flory's result derived by the much longer process involving the size distributions.[2] It should be noted above that solutions to eq 5 and 6 exist only when $1 > p(f - 1)$. If $1 \leq p(f - 1)$, then the weight average molecular weight diverges and the system forms a gel or infinite network. The tetrafunctional polyether network of eq 2 is used to illustrate eq 9 in Figure 1.

If a condensation product is involved, as in eq 2 above, we need to subtract out M_C, the molecular weight of the condensate. In polyetherification $M_C = 18$. The effect of condensation products is shown in Figure 1 and described in more detail in the Appendix.

$\overline{M}_w$ for Copolymers. Most stepwise polymerizations involve two reactive groups, for example urethane formation from pentaerythritol and 1,6-hexanediisocyanate. Consider
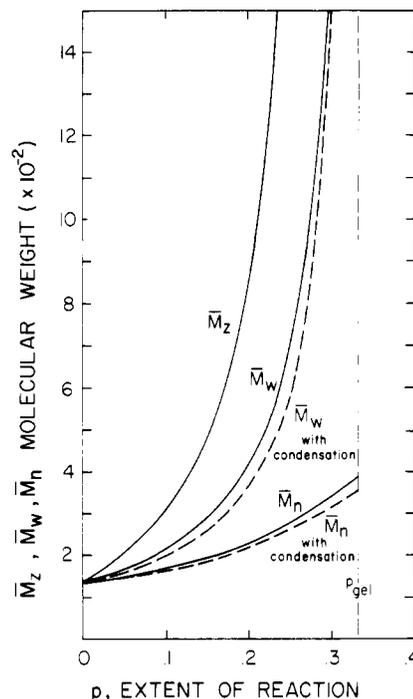

Figure 1. Calculated average molecular weights for the polyether network formation by the stepwise homopolymerization of pentaerythritol (eq 2). The effect of condensation products on $\overline{M}_w$ and $\overline{M}_n$ is shown (see Appendix, eq A7 and A20).

A_f moles of f functional A–type monomer reacting with B_2 moles of bifunctional B type shown schematically:
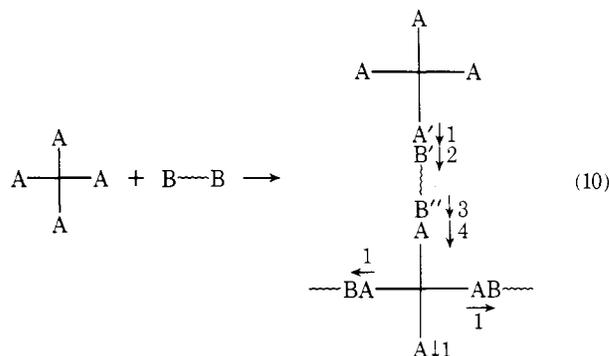
Let the system polymerize until some fraction p_A of the A groups and some fraction p_B of the B's have reacted. If A + B is the only type of reaction then these are not independent and

$$p_A f A_{f0} = p_B 2 B_{20} \qquad (11)$$

or

$$p_A = p \quad \text{and} \quad p_B = \frac{f A_{f0}}{2 B_{20}} p_A = rp \qquad (12)$$

Again let us pick an A at random, A' above, and ask what is the weight $W_{A'}^{out}$ in direction $\xrightarrow{1}$? Here $W_{A'}^{out}$ will equal zero if A' has not reacted. If A' has reacted (with B', say) it equals $W_{B'}^{in}$, the weight attached to B' looking in direction $\xrightarrow{2}$.

$$W_{A'}^{out} = \begin{cases} 0 & \text{if A' does not react} \\ W_{B'}^{in} & \text{if A' does react (with B')} \end{cases} \qquad (13)$$

As in eq 5, the law of total probability for expectations (eq 1) now implies

$$E(W_A^{out}) = pE(W_B^{in}) \qquad (14)$$

In a similar way as before we can write expected weights following the arrows in eq 10 until the recursive nature of

the structure brings us back to eq 14

$$E(W_B{}^{in}) = M_{B_2} + E(W_B{}^{out}) \tag{15}$$

$$E(W_B{}^{out}) = rpE(W_A{}^{in}) \tag{16}$$

$$E(W_A{}^{in}) = M_{A_f} + (f - 1)E(W_A{}^{out}) \tag{17}$$

Let W_{A_f} be the total molecular weight of the molecule to which a randomly chosen A_f belongs. Let W_{B_2} be the weight for a randomly chosen B_2. Then

$$E(W_{A_f}) = E(W_A{}^{in}) + E(W_A{}^{out}) . \tag{18}$$

$$E(W_{B_2}) = E(W_B{}^{in}) + E(W_B{}^{out}) \tag{19}$$

Solving eq 14 through 17 and substituting into eq 18 and 19 gives

$$E(W_{A_f}) = M_{A_f} + fp\left[\frac{M_{B_2} + rpM_{A_f}}{1 - rp^2(f-1)}\right] \tag{20}$$

$$E(W_{B_2}) = M_{B_2} + 2rp\left[\frac{M_{A_f} + p(f-1)M_{B_2}}{1 - rp^2(f-1)}\right] \tag{21}$$

To find the weight average molecular weight, we pick a unit of mass at random and compute the expected weight of the molecule of which it is a part (another application of eq 1)

$$\overline{M}_w = w_{A_f}E(W_{A_f}) + w_{B_2}E(W_{B_2}) \tag{22}$$

where

$$w_{A_f} = \frac{M_{A_f}A_f}{M_{A_f}A_f + M_{B_2}B_2}$$

$$w_{B_2} = 1 - w_{A_f}$$

Substituting into eq 22 yields

$$\overline{M}_w =$$
$$\frac{(2r/f)(1 + rp^2)M_{A_f}{}^2 + (1 + (f-1)rp^2)M_{B_2}{}^2 + 4rpM_{A_f}M_{B_2}}{(2rM_{A_f}/f + M_{B_2})(1 - r(f-1)p^2)} \tag{23}$$

which agrees with Stockmayer.[4] Treatment of this system to include a condensation by-product is discussed in the Appendix. If some of the starting species are oligomers, as is often the case, with a distribution of molecular weight, Ziegel, Fogiel, and Pariser have discussed which average molecular weights should be used in eq 23.[13]

In practice A_f is often mixed with A_2 to control the chain length between branch points and small amounts of A_1 can be present as impurities. It is not hard to write the general system of equations for A_{f_i}'s reacting with B_{g_j}'s. Following Stockmayer's notation[4] this can be represented schematically

$$A_{f_1} + A_{f_2} + \ldots A_{f_k} + B_{g_1} + B_{g_2} + \ldots B_{g_l} \longrightarrow$$

$$\tag{24}$$
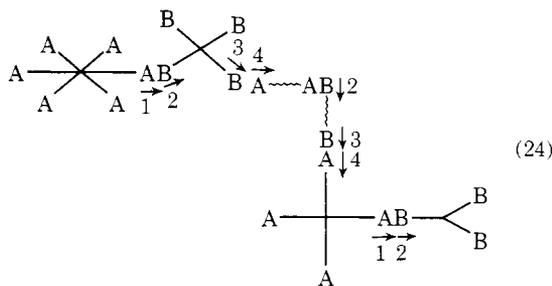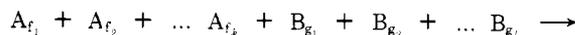
The expected weight along $\xrightarrow{1}$ is the same form as before but now we must consider all the possible B_g's with which the A can react. Thus by a generalization[12] of eq 1

$$E(W_A{}^{out}) =$$
$$E(W_A{}^{out}|\text{A does not react})P(\text{A does not react}) +$$
$$\sum_{j=1}^{l} E(W_A{}^{out}|\text{A reacts with } B_{g_j})P(\text{A reacts with } B_{g_j}) =$$
$$0(1 - p_A) + \sum_{j=1}^{l} E(W_{B_{g_j}}{}^{in})p_A b_{g_j} =$$
$$p_A \sum_{j=1}^{l} b_{g_j}E(W_{B_{g_j}}{}^{in}) \tag{25}$$

where b_{g_j} = mole fraction of all B's on B_{g_j} molecules

$$b_{g_j} = \frac{g_j B_{g_j}}{\Sigma_j g_j B_{g_j}} \tag{26}$$

In direction $\xrightarrow{2}$ there will be a relation for each B_{g_j}. They will all be of the same form as eq 15.

$$E(W_{B_{g_j}}{}^{in}) = M_{B_{g_j}} + (g_j - 1)E(W_B{}^{out}) \tag{27}$$

The expected weights along $\xrightarrow{3}$ and $\xrightarrow{4}$ are derived similarly to 25 and 27.

$$E(W_B{}^{out}) = p_B\Sigma_i a_{f_i}E(W_{A_{f_i}}{}^{in}) \tag{28}$$

$$E(W_{A_{f_i}}{}^{in}) = M_{A_{f_i}} + (f_i - 1)E(W_A{}^{out}) \tag{29}$$

where a_{f_i} = mole fraction of all A's on A_{f_i}

$$a_{f_i} = \frac{f_i A_{f_i}}{\Sigma_i f_i A_{f_i}}$$

and p_B is related to p_A as in eq 11

$$p_B = \frac{\Sigma_i f_i A_{f_i}}{\Sigma_j g_j B_{g_j}} p_A = rp \tag{30}$$

Solving this system of equations we obtain

$$E(W_A{}^{out}) = \frac{p_A M_b + p_A p_B(g_e - 1)M_a}{1 - p_A p_B(g_e - 1)(f_e - 1)} \tag{31}$$

$$E(W_B{}^{out}) = \frac{p_B M_a + p_A p_B(f_e - 1)M_b}{1 - p_A p_B(g_e - 1)(f_e - 1)} \tag{32}$$

where

$$\begin{matrix} f_e = \Sigma_i f_i a_{f_i} \\ g_e = \Sigma_j g_j b_{g_j} \end{matrix} \tag{33}$$

$$\begin{matrix} M_a = \Sigma_i M_{A_{f_i}} a_{f_i} \\ M_b = \Sigma_j M_{B_{g_j}} b_{g_j} \end{matrix} \tag{34}$$

If $W_{A_{f_i}}$ is the weight of the molecule to which a random A_{f_i} belongs, similarly for $W_{B_{g_j}}$, then from eq 18, 19, 27, and 29 it follows that

$$E(W_{A_{f_i}}) = M_{A_{f_i}} + f_i E(W_A{}^{out}) \tag{35}$$

$$E(W_{B_{g_j}}) = M_{B_{g_j}} + g_j E(W_B{}^{out}) \tag{36}$$

As before, to find $\overline{M}_w$, we take a unit of mass at random and compute the expected weight of the molecule to which it belongs (again using eq 1):

$$\overline{M}_w = \Sigma_i w_{A_{f_i}}E(W_{A_{f_i}}) + \Sigma_j w_{B_{g_j}}E(W_{B_{g_j}}) \tag{37}$$

where

$$w_{A_{f_i}} = \frac{M_{A_{f_i}}A_{f_i}}{\Sigma_i M_{A_{f_i}}A_{f_i} + \Sigma_j M_{B_{g_j}}B_{g_j}} \tag{38}$$

and $w_{B_{g_j}}$ is defined similarly. Substituting and rearranging we obtain

$$\overline{M}_w = \frac{p_B m_a' + p_A m_b'}{p_B m_a + p_A m_b} +$$
$$\frac{p_A p_B[p_A(f_e - 1)M_b{}^2 + p_B(g_e - 1)M_a{}^2 + 2M_a M_b]}{(p_B m_a + p_A m_b)[1 - p_A p_B(f_e - 1)(g_e - 1)]} \tag{39}$$
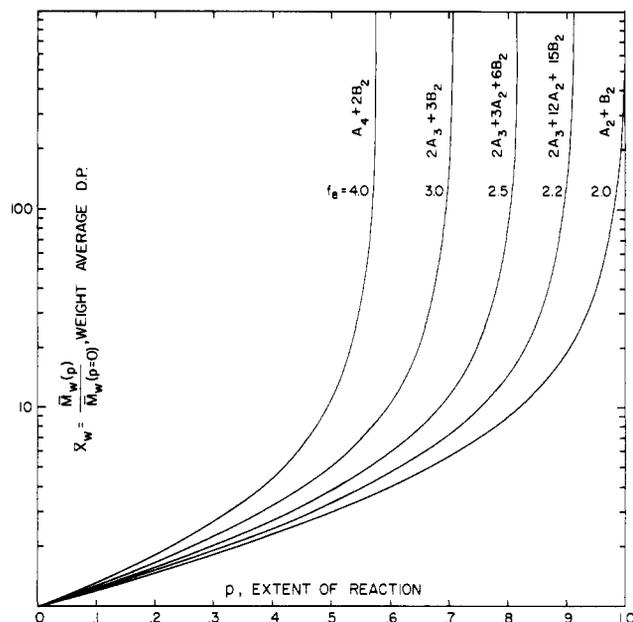
Figure 2. $\overline{M}_w$ vs. extent of reaction for several common stepwise copolymerizations calculated from eq 39, $p_A = p_B = p$.

where

$$m_a = \Sigma_i M_{A_{f_i}} A_{f_i} / \Sigma_i f_i A_{f_i} = \Sigma_i M_{A_{f_i}} a_{f_i} / f_i$$

$$m_a' = \Sigma_i M_{A_{f_i}}{}^2 A_{f_i} / \Sigma_i f_i A_{f_i} = \Sigma_i M_{A_{f_i}}{}^2 a_{f_i} / f_i \qquad (40)$$

and m_b and m_b' are analogous for the B_{g_j}'s.

In eq 39 we have obtained a general relation which covers nearly all nonlinear stepwise polymerization. Equations 9 and 23 are just special cases of eq 39. This result is the same as that which Stockmayer obtained by tortuous combinatorial arguments and manipulation of distribution functions.[3,4] Equation 39 should also be obtainable in principle from Gordon's eq 67 in ref 5.

Figure 2 shows $\overline{M}_w$ plotted vs. p from eq 39 for the most commonly encountered stepwise copolymerizations. The value of p at which $\overline{M}_w$ diverges is called the gel point. This asymptote is indicated on Figure 2. From eq 39 we see that for the general case $\overline{M}_w$ becomes infinite when

$$(p_A p_B)_{gel} = r p_{gel}{}^2 = \frac{1}{(f_e - 1)(g_e - 1)} \qquad (41)$$

Our method can be further extended to problems involving A and B groups on the same molecule. This problem does not appear to have been solved in the literature; however, such systems are rare in practice.

$\overline{M}_z$. Higher molecular weight averages are not readily measured. In principle it is possible to determine these higher averages from ultracentrifuge data. We recall that $\overline{M}_z$ is the ratio of the second moment of the weight distribution to the first (Flory,[2b] p 307) or

$$\overline{M}_z = \frac{E(W^2)}{E(W)} = \frac{E(W^2)}{\overline{M}_w} \qquad (42)$$

We can calculate $E(W^2)$ from the variance of W using our recursive method. Recall from probability theory that, for a random variable X,

$$\text{Var}(X) = E(X^2) - E(X)^2 \qquad (43)$$

Also if X and Y are independent random variables then

$$\text{Var}(X + Y) = \text{Var}(X) + \text{Var}(Y) \qquad (44)$$

Consider the stepwise homopolymerization of A_f's, eq 2. For this simple case

$$W = W_{A_f} = M_{A_f} + \sum_{i=1}^{f} W_{A,i}{}^{out} \qquad (45)$$

where $W_{A,i}{}^{out}$ is the weight attached to the ith branch. Thus by eq 44 and $\text{Var}(W_{A,i}{}^{out}) = \text{Var}(W_A{}^{out})$

$$\text{Var}(W_{A_f}) = f\,\text{Var}(W_A{}^{out}) \qquad (46)$$

which by using eq 43 becomes

$$E(W_{A_f}{}^2) - E(W_{A_f})^2 = f[E((W_A{}^{out})^2) - E(W_A{}^{out})^2] \qquad (47)$$

Similarly,

$$W_A{}^{in} = M_{A_f} + \sum_{i=1}^{f-1} W_{A,i}{}^{out} \qquad (48)$$

and

$$\text{Var}(W_A{}^{in}) = (f - 1)\,\text{Var}(W_A{}^{out}) \qquad (49)$$

which, using eq 43, becomes

$$E((W_A{}^{in})^2) - E(W_A{}^{in})^2 = (f - 1)[E((W_A{}^{out})^2) - E(W_A{}^{out})^2] \qquad (50)$$

Similar to the development of eq 5 we can use eq 1 for the random variable $(W_A{}^{out})^2$

$$E((W_A{}^{out})^2) = pE((W_A{}^{in})^2) \qquad (51)$$

Solving eq 5, 6, 50, and 51 simultaneously yields

$$E((W_A{}^{out})^2) = \frac{p[1 - p^2(f - 1)]M_{A_f}{}^2}{[1 - p(f - 1)]^3} \qquad (52)$$

Substituting eq 52, 8, and 9 into 47 gives

$$E(W_{A_f}{}^2) = \frac{M_{A_f}{}^2[(1 + p)^3 - fp^2(3 + p)]}{[1 - p(f - 1)]^3} \qquad (53)$$

Thus for A_f polymerization

$$\overline{M}_z = \frac{E(W_{A_f}{}^2)}{\overline{M}_w} = M_{A_f} \frac{(1 + p)^3 - fp^2(3 + p)}{(1 + p)[1 - p(f - 1)]^2} \qquad (54)$$

which agrees with the result obtained by Gordon (ref 5, eq 30). Equation 54 is illustrated in Figure 1 for the polyether network of eq 2. One can use the same approach that leads to eq 54 to treat the general case of A_{f_i}'s reacting with B_{g_j}'s.

At this point it may be appropriate to discuss how we are using the concept of "randomness" in our models and derivations. Actually there are three different instances where this arises.

(1) Functional units react with each other "at random". By this we mean, for example, that any unreacted A has an equal chance of reacting with any of the unreacted B's. Thus if b_{g_j} is the proportion of B groups residing on B_{g_j} molecules, A will have probability b_{g_j} of reacting with a B_{g_j}.

(2) In computing weight average molecular weight we take a unit of mass "at random", i.e., all units of mass have an equal chance of being chosen. Thus if proportion $w_{A_{f_i}}$ of the mass consists of A_{f_i}'s, we will have probability $w_{A_{f_i}}$ of picking an A_{f_i} when we pick a unit of mass "at random".

(3) Finally we could pick a molecule "at random", i.e., all molecules have an equal chance of selection. If we then look at the expected weight of the randomly selected molecule, we will be computing the number average molecular weight. We have not been able to use this approach to calculate $\overline{M}_n$.

$\overline{M}_n$. However, as Flory and Stockmayer point out, without intramolecular reactions $\overline{M}_n$ can always be calculated from stoichiometry. At extent of reaction p_A, $\overline{M}_n$ is just the total mass, m_t, over the number of molecules present, N. N

is just the number of molecules present initially, N_0, less the number of new bonds formed, N_b.

$$\overline{M}_n = m_t/(N_0 - N_b) \tag{55}$$

Considering the general case shown in eq 24 then

$$m_t = \Sigma_i M_{A_{f_i}} A_{f_i} + \Sigma_j M_{B_{g_j}} B_{g_j} \tag{56}$$

and

$$N_0 = \Sigma_i A_{f_i} + \Sigma_j B_{g_j} \tag{57}$$

while

$$N_b = p_A \Sigma_i f_i A_{f_i} \tag{58}$$

Thus

$$\overline{M}_n = \frac{\Sigma_i M_{A_{f_i}} A_{f_i} + \Sigma_j M_{B_{g_j}} B_{g_j}}{\Sigma_i A_{f_i} + \Sigma_j B_{g_j} - p_A \Sigma_i f_i A_{f_i}} \tag{59}$$

where p_A was defined in eq 3. Note that in the special case of A_{f_i}'s reacting only themselves, two A's are involved in each bond and p_A above is replaced by $p_A/2$.

$\overline{M}_n$ vs. p from eq 59 is illustrated in Figure 1 for the tetrafunctional polyether network of eq 2. The effect of condensate is also shown. Note that $\overline{M}_n$ is finite at p_{gel}.

Cross-Linking of Polymer Chains

Network polymers are often formed by reacting together side groups on long polymer chains or through unsaturation in the chain backbone. Such cross-linking or vulcanization is shown schematically in Figure 3. As Flory[2] points out random cross-linking can be treated with the same equations developed for stepwise reactions. If all the reactive groups are of the same type then we have a polymerization of a mixture of species, A_{f_i}, where f_i may be quite large. If the functionalities are uniformly distributed along the chains then

$$M_{A_{f_i}} = f_i M_c \tag{60}$$

where M_c is the weight between cross-linkable sites and each chain end weight is assumed to be $M_{c/2}$. We also assume that the cross-linking reaction occurs by simple coupling of chains with no weight change.

For the polymerization of a mixture of A_{f_i} eq 39 becomes

$$\overline{M}_w = \frac{m_a'}{m_a} + \frac{p_A M_a^2}{m_a[1 - p_A(f_e - 1)]} \tag{61}$$

Let $p_A = \rho$ be the extent of cross-linking or the fraction of repeat units which are cross-linked. Substituting eq 60 into eq 34 and 40 for M_a, m_a, and m_a' gives

$$\overline{x}_w = \frac{\overline{M}_w}{M_c} = \frac{f_e(1 + \rho)}{1 - \rho(f_e - 1)} \tag{62}$$

Combining eq 33 and 60 shows that

$$f_e = \frac{\Sigma_i f_i^2 A_{f_i}}{\Sigma_i f_i A_{f_i}} = \frac{\Sigma_i M_{A_{f_i}}^2 A_{f_i}}{M_c \Sigma_i M_{A_{f_i}} A_{f_i}} = \overline{x}_{w0} \tag{63}$$

where $\overline{x}_{w0}$ is the weight average degree of polymerization of the initial mixture of long chains.[14] Substituting gives

$$\overline{x}_w = \frac{\overline{x}_{w0}(1 + \rho)}{1 - \rho(\overline{x}_{w0} - 1)} \tag{64}$$

Gordon[5] in attempting to derive this relation started with the A_f relation (our eq 9) rather than the proper one for a mixture of species, A_{f_i}. We see that our result takes the proper limit at $\rho = 0$ and will diverge at

$$\rho = \rho_{gel} = \frac{1}{\overline{x}_{w0} - 1} \tag{65}$$

Figure 3. Schematic representation of cross-linking of polymer chains.

which agrees with Flory's result for the gel point (ref 2b, eq 13).

The same substitutions can be made into eq 59 to give the number average degree of polymerization

$$\overline{x}_n = \overline{x}_{n0}/(1 - \rho\overline{x}_{n0}) \tag{66}$$

Equation 64 and 66 are useful, simple results which are applicable to cross-linking of chains of arbitrary initial molecular weight distribution provided they obey eq 60.

Chain Addition

Up to this point we have considered networks formed by stepwise polymerizations. With a few modifications the approach described above can readily be applied to networks formed by chain addition. Chainwise polymerizations involve an initiation step followed typically by hundreds of addition or propagation steps ending with termination. Thus at any time the reaction mixture will consist of unreacted monomer and rather long polymer with essentially no species of intermediate size.

To treat chainwise systems we need to define q, the probability that an initiated or growing chain will add one more unit. In kinetic terms

$$q = \frac{R_p}{R_p + R_{tr} + R_{td} + R_{tc}} \tag{67}$$

where R_p is the propagation rate, R_{tr} the rate of termination by transfer, R_{td} the rate of termination by disproportionation, and R_{tc} the rate of termination by combination. Once the reaction conditions and the type and concentration of reactants is fixed, q will be fixed and it will be approximately constant, on the order of 0.99 to 0.999, throughout the reaction.

Consider the reaction of a vinyl with a divinyl such as methyl methacrylate with ethylene dimethacrylate:

$$\tag{68}$$

If the system obeys Flory's simplifying assumptions, then we can represent it schematically as A_2 reacting with A_f:

$$\tag{69}$$

Again we let the A groups react to extent p. To calculate $\overline{M}_w$ we consider the weight attached to a randomly chosen A group looking out, W_A^{out}. It will also be convenient to define W_{A*}^{out}, the weight attached to an A group which has been activated, i.e., is part of a chain. Thus following our previous approach

$$E(W_A^{out}) = pE(W_{A*}^{out}) + (1 - p)0 \tag{70}$$

and

$$E(W_{A*}^{out}) = qE(W_{A*}^{in}) + (1 - q)E(W_T) \tag{71}$$

Here $E(W_T)$ is the expected weight added in the termination step. For termination by transfer a hydrogen atom is typically added; for disproportionation, the average of half of a hydrogen; and for termination by combination, two chains couple. Thus

$$(1 - q)E(W_T) = R_{tr}'M_H + R_{td}'M_H/2 + R_{tc}'E(W_{A*}^{in}) \tag{72}$$

where $R_{tr}' = R_{tr}/(R_p + R_{tr} + R_{td} + R_{tc})$; R_{td}', R_{tc}', similarly. Since $M_H = 1$ and R' terms <0.01, to a good approximation eq 71 becomes

$$E(W_{A*}^{out}) = q'E(W_{A*}^{in}) \tag{73}$$

with $q' = q + R_{tc}'$.

Following the approach that led to eq 25-29 we obtain

$$E(W_{A*}^{in}) = (1 - a_f)E(W_{A_2*}^{in}) + a_f E(W_{A_f*}^{in}) \tag{74}$$

where $E(W_{A_f*}^{in})$ is the weight attached to a randomly chosen A* whose parent molecule is an A_f, and

$$E(W_{A_2*}^{in}) = M_{A_2} + E(W_{A*}^{out}) \tag{75}$$

To determine $E(W_{A_f*}^{in})$ we note that one A–A pair will be activated but the other $f - 2$ are not necessarily. Thus

$$E(W_{A_f*}^{in}) = M_{A_f} + E(W_{A*}^{out}) + (f - 2)E(W_A^{out}) \tag{76}$$

Combining eq 70 with eq 73-76 we obtain

$$E(W_{A*}^{out}) = \frac{q'[(1 - a_f)M_{A_2} + a_f M_{A_f}]}{1 - q'[1 + (f - 2)a_f p]} \tag{77}$$

$\overline{M}_w$ is usually determined only on the polymeric portion of the reacting system; the unreacted monomers are separated out. Thus we consider only the expected weight on A* species rather than all A:

$$\overline{M}_w = w_{A_f}^*E(W_{A_f*}) + (1 - w_{A_f}^*)E(W_{A_2*}) \tag{78}$$

where $w_{A_f}^*$ is the weight fraction of polymeric species, consisting of A_f's

$$w_{A_f}^* = \frac{(1 - (1 - p)^{f/2})M_{A_f}A_f}{(1 - (1 - p)^{f/2})M_{A_f}A_f + pM_{A_2}A_2}$$

Analogues of eq 35 and 36 give

$$E(W_{A_2*}) = M_{A_2} + 2E(W_{A*}^{out})$$

$$E(W_{A_f*}) = M_{A_f} + 2E(W_{A*}^{out}) + p(f - 2)E(W_{A*}^{out})$$

where $E(W_{A_f*})$ is the expected weight attached to an A_f chosen at random from the polymeric portion. Substituting these into eq 78 gives

$$\overline{M}_w = w_{A_f}^*M_{A_f} + (1 - w_{A_f}^*)M_{A_2} +$$
$$[2 + w_{A_f}^*p(f - 2)]E(W_{A*}^{out})(79)$$

The approach used above can readily be generalized as in the stepwise case to a mixture of A_{f_i}'s, where f_i should be even.

Since $q' \simeq$ constant, the gel point will be the extent of reaction when eq 77 diverges or

$$p_{gel} = \frac{1 - q'}{(f - 2)a_f q'} \tag{80}$$

As with $\overline{M}_w$, $\overline{M}_n$ is based only on the long-chain portion of the reacting system. Thus $\overline{M}_n$ will be the total mass of polymeric material divided by the number of molecules. The number of molecules is half the number of chain ends less the number of cross-links times half the cross-link order minus 1, i.e., A_f's which have reacted more than once. The number of A's in the polymeric portion equals $2pA_2 + f(1 - (1 - p)^{f/2})A_f$ while the number of activated A's is $2pA_2 + fpA_f$. Thus the number of unactivated A's in the polymeric portion is $f(1 - p - (1 - p)^{f/2})A_f$. An activated A is a chain end with probability $1 - q'$ and an unactivated A is a chain end with probability 1. Thus the number of chain ends, N_{ce}^*, in the polymeric portion is

$$N_{ce}^* = (1 - q')(2pA_2 + fpA_f) + f(1 - p - (1 - p)^{f/2})A_f$$

Thus

$$\overline{M}_n = \frac{pM_{A_2}A_2 + (1 - (1 - p)^{f/2})M_{A_f}A_f}{N_{ce}^*/2 - \sum_{m=2}^{f/2}(m - 1)\binom{f/2}{m}p^m(1 - p)^{(f/2)-m}A_f} \tag{81}$$

which for $f = 4$ becomes

$$\overline{M}_n = \frac{2(1 - a_4)M_{A_2} + (2 - p)a_4 M_{A_4}}{2(1 - q') + (4 - 5p)a_4} \tag{82}$$

Conclusions

We have derived useful average properties as a function of reaction extent for the stepwise polymerization of a mixture of A_{f_i} and B_{g_j} monomers without condensation products. Specifically eq 39 gives $\overline{M}_w$, the weight average molecular weight, eq 59 gives $\overline{M}_n$, the number average, and eq 41 gives p_{gel}, the extent of reaction at the gel point. $\overline{M}_z$ is computed for the A_f homopolymerization. Modifications of these equations to treat nonlinear chainwise addition polymerizations and cross-linking are also described. The Appendix discusses the problem of condensation products. From these relations and the nature of the monomer molecules it may also be possible to derive other properties such as thermal and rheological parameters since these are expected to depend on molecular structure.

The advantage of our recursive technique over the combinatorial approach of Flory and Stockmayer should be clear. We derive the molecular weight averages directly rather than the complete size distribution and then the averages. Our derivations are thus much simpler and can be generalized further to include chainwise polymerizations, condensation products and other nonidealities,[11] and post gel properties such as cross-link density.[15]

Gordon also calculates average properties directly using branching theory. His approach appears to be more powerful than ours since it can be used to derive $\overline{M}_{z+1}$ and higher averages and can be extended to compute the molecular weight averages of the sol fraction after gelation.[7,16] However, Gordon's use of abstractions, such as vectorial probability generating functions, makes formulation of specific equations for the molecular weight average difficult. Furthermore, the complexity of the resulting matrix equations seems to be unnecessary for many network polymerizations. We believe our recursive method can be readily understood and applied by the typical polymer chemist.

Appendix. Polymerizations Involving Condensation Products

If a condensation product forms during polymerization, such as water in eq 2, the above analysis must be modified to accommodate this phenomenon.

First consider the homopolymerization of A_f. Suppose that a condensate C of molecular weight M_C is a by-product of an AA bond. We shall compute the weight average molecular weight for extent of reaction p. We proceed as with eq 4 and 5 except we must account for the loss of weight from the condensate.

$$E(W_A^{out}) = p[E(W_A^{in}) - M_C] \tag{A1}$$

Equation 6 remains unchanged:

$$E(W_A^{in}) = M_{A_f} + (f - 1)E(W_A^{out})$$

Solving we get

$$E(W_A^{in}) = \frac{M_{A_f} - p(f - 1)M_C}{1 - p(f - 1)} \tag{A2}$$

Now consider an A_f unit which has n reacted arms and $f - n$ unreacted; denote such a unit as A_f^n. Let $W_{A_f^n}$ equal the weight of the molecule to which a random A_f^n belongs. Then

$$E(W_{A_f^n}) = M_{A_f} - nM_C + nE(W_A^{in}) \tag{A3}$$

Now consider the moles of A_f^n for $n = 0, 1, \ldots, f$ at extent of reaction p. If all A's are equally reactive and there are no substitution effects, then the number of reacted A's on an A_f is a binomial random variable with parameters f and p.

$$A_f^n = \binom{f}{n}p^n(1 - p)^{f-n}A_f \tag{A4}$$

We can assume that each reacting A contributes mass $M_C/2$ to the condensate, thus an A_f^n unit has mass $M_{A_f} - n(M_C/2)$. If we define w_n to be the proportion of mass (condensate removed) consisting of A_f^n units then

$$w_n = \frac{\left(M_{A_f} - n\dfrac{M_C}{2}\right)A_f^n}{\displaystyle\sum_{n=0}^{f}\left(M_{A_f} - \dfrac{nM_C}{2}\right)A_f^n} \tag{A5}$$

If a unit of mass is picked at random, it will be an A_f^n with probability w_n, consequently

$$\bar{M}_w = \sum_{n=0}^{f} E(W_{A_f^n})w_n \tag{A6}$$

Substituting from eq A2–A5 this becomes

$$\bar{M}_w = \frac{1 + p}{1 - p(f - 1)}\left(M_{A_f} - \frac{fM_C}{2}\right) + \frac{(1 - p)fM_C/2}{1 - p(f - 1)}\left[1 - p\frac{(M_{A_f} - M_C)}{M_{A_f} - fM_C/2}\right] \tag{A7}$$

Note that if $M_C = 0$ this agrees with eq 9. Figure 1 shows a comparison of eq A7 and eq 9 for the tetrafunctional polyetherification.

Stockmayer[4] suggested that networks with condensation products could simply be treated by replacing M_{A_f} with $M_{A_f} - fM_C/2$ in the relations derived without condensation. This approach is better than ignoring M_C entirely but it neglects the unreacted ends of the molecules and can only be strictly valid as p approaches 1. The second term in eq A7 can be viewed as accounting for these unreacted ends. Gordon's approach[5] appears to correctly account for condensation.

Now consider the general reaction of A_{f_i}'s with B_{g_j}'s as in eq 26. Equations 25 and 28 must be modified

$$E(W_A^{out}) = p_A\left(\sum_{j=1}^{l} b_{g_j}E(W_{B_{g_j}}^{in}) - M_C\right) \tag{A8}$$

$$E(W_B^{out}) = p_B\left(\sum_{i=1}^{k} a_{f_i}E(W_{A_{f_i}}^{in}) - M_C\right) \tag{A9}$$

Equations 27 and 29 remain unchanged. Solving gives

$$E(W_A^{out}) = \frac{p_A(M_b - M_C) + p_A p_B(g_e - 1)(M_a - M_C)}{1 - p_A p_B(g_e - 1)(f_e - 1)} \tag{A10}$$

$$E(W_B^{out}) = \frac{p_B(M_a - M_C) + p_A p_B(f_e - 1)(M_b - M_C)}{1 - p_A p_B(g_e - 1)(f_e - 1)} \tag{A11}$$

Again let $A_{f_i^n}$ represent an A_{f_i} unit with n reacted arms and $f_i - n$ unreacted. As in the case of A_f's reacting with themselves

$$E(W_{A_{f_i^n}}) = M_{A_{f_i}} - nM_C + n\Sigma_j b_{g_j}E(W_{B_{g_j}}^{in}) \tag{A12}$$

Similarly

$$E(W_{B_{g_j^n}}) = M_{B_{g_j}} - nM_C + n\Sigma_i a_{f_i}E(W_{A_{f_i}}^{in}) \tag{A13}$$

As before

$$A_{f_i}^n = \binom{f_i}{n}p_A^n(1 - p_A)^{f_i-n}A_{f_i} \tag{A14}$$

$$B_{g_j}^n = \binom{g_i}{n}p_B^n(1 - p_B)^{g_j-n}B_{g_j} \tag{A15}$$

Suppose that whenever an AB bond forms, that A contributes M_C^A to the condensate and B contributes M_C^B, $M_C^A + M_C^B = M_C$. Then an $A_{f_i}^n$ weighs $M_{A_{f_i}} - nM_C^A$ and

$$w_{A_{f_i^n}} = (M_{A_{f_i}} - nM_C^A)[A_{f_i}^n]/m_t \tag{A16}$$

$$w_{B_{g_j^n}} = (M_{B_{g_j}} - nM_C^B)[B_{g_j}^n]/m_t \tag{A17}$$

are the proportion of mass (minus condensate) accounted for by $A_{f_i}^n$ and $B_{g_j}^n$ units (for m_t, see eq A19). As before

$$\bar{M}_w = \sum_{i=1}^{k} \sum_{n=0}^{f_i} w_{A_{f_i^n}}E(W_{A_{f_i^n}}) + \sum_{j=1}^{l} \sum_{n=0}^{g_i} w_{B_{g_j^n}}E(W_{B_{g_j^n}}) \tag{A18}$$

It is straightforward, but tedious, to make the substitutions into eq A18. The simplest way to use eq A18 is to program eq 27, 29, and A10–18 on a calculator or small computer then evaluate them for the specific network polycondensation of interest.

We should also note that $\bar{M}_n$ is affected by condensation products through the average weight of a monomer unit. For example with A_f homopolymerization the total mass of the system, m_t, will go from $M_{A_f}A_{f_0}$ at $p = 0$ to $(M_{A_f} - (f/2)M_C)A_{f_0}$ at full conversion. In general eq 56 becomes

$$m_t = \sum_{i=1}^{k} \sum_{n=0}^{f_i} (M_{A_{f_i}} - nM_C^A)A_{f_i}^n + \sum_{j=1}^{l} \sum_{n=0}^{g_i} (M_{B_{g_j}} - nM_C^B)B_{g_j}^n \tag{A19}$$

Thus for A_f only

$$\bar{M}_n = \left(M_{A_f} - \frac{fp}{2}M_C\right)\bigg/(1 - fp/2) \tag{A20}$$

The effect on $\bar{M}_n$ of condensation products, eq A20, is illustrated in Figure 1.

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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*

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

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

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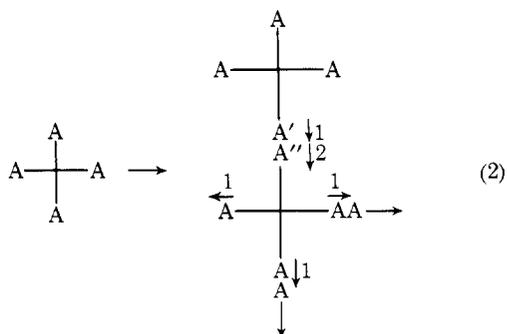
Let polymerization procede until some fraction p of the A's have reacted. Pick an A group at random, A' in eq 2. Now we need to know what is the probability that following $\xrightarrow{1}$ (looking *out* from the molecule) leads to a finite or dangling chain rather than to the infinite network, i.e.,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

$$P(F_A{}^{out}) = P(F_A{}^{out}|A \text{ reacts})P(A \text{ reacts}) +$$
$$P(F_A{}^{out}|A \text{ does not react})P(A \text{ does not react}) =$$
$$P(F_A{}^{in})p + 1(1 - p) = pP(F_A{}^{in}) + 1 - p \tag{3}$$

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

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

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 $P(F_A{}^{out})$

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

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

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

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 $p > (f - 1)^{-1} = p_{gel}$. Physically when $P(F_A{}^{out}) = 1$ the sys-