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Substitution Effects in Property Relations for Stepwise Polyfunctional Polymerization

Douglas R. Miller[1]

Department of OR, SEAS, The George Washington University, Washington, D.C. 20052

Christopher W. Macosko*[2]

Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455. *Received September 4, 1979*

ABSTRACT: This paper extends the authors' method of calculating average properties of ideal nonlinear stepwise polymerization to systems with first-shell substitution effects. Two special cases are considered in detail: $A_f + B_2$, where the second and subsequent A groups on the A_f monomer can react at different rates due to the presence of other reacted groups, and $A_f + A_2 + B_2$, where both A_f and A_2 can show substitution effects. Relations for weight-average molecular weight, the gel point, weight-fraction solubles, and cross-link density are derived.

Mathematical modeling and analysis of stepwise network polymerizations enable one to calculate various molecular parameters such as average molecular weight, weight-fraction solubles, or gel point. These models usually have certain simplifying assumptions:[3,4] (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 the finite species. A system satisfying the above assumptions is referred to as an "ideal" system. In previous papers[5–7] we presented a new method for deriving various molecular averages for ideal branched systems. The above ideal assumptions, however, are not appropriate for all systems. We have treated systems with unequally reactive groups,[8] i.e., systems which satisfy assumptions 2 and 3 but not assumption 1. The current paper examines systems exhibiting *substitution effects*, namely, systems which satisfy assumptions 1 and 3 but not assumption 2. In particular, there will be a monomer, an A_f say, whose f reactive sites are equally reactive; however, the f events of reaction at a site are not statistically independent events. More complicated departures from 1 and 2 could involve a combination of substitution effect with nonequal reactivity; our method could analyze such a system; however, we shall not pursue this because we know of no system exhibiting such behavior for which the appropriate kinetic rates are known.

In general, if a substitution effect is present, the probability of a reaction occurring (or the probabilistic intensity) between two unreacted sites on two monomers depends on the configuration of the two molecules to which the monomers belong, respectively. The most extreme case is when the instantaneous probabilistic intensity of reaction depends on entire molecules. The least extreme case of a substitution effect is when the instantaneous probability of a site reacting only depends on the status (reacted or not) of the remaining sites on the monomer and is independent of the configuration of the rest of the molecule of which the monomer is a part. This latter case is usually referred to as a *first-shell substitution effect*. This paper will focus on copolymerizations in which one polyfunctional monomer exhibits a first-shell substitution effect. In this case the only dependencies will be between sites on the same monomers. Higher shell substitution effects give rise to very complicated probabilistic analyses and seem to be an open problem. First-shell substitution effect can also be more complicated for homopolymerizations if the kinetics are other than first order.

Some examples of polymerizations which have substitution effects are phenol–formaldehyde, some polyesterifications, and epoxy–diamine. In reacting with phenol the first formaldehyde group adds to the phenyl ring at 2–3 times the rate of the second.[9] Due to the small size of the formaldehyde linkage, however, higher shell substitution effects and ring formation occur. A similar combination of effects also occurs in melamine–formaldehyde and urea–formaldehyde polymerizations.[9,10] Substitution effects also occur in the cross-linking of adipic acid with a relatively small triol like 2,2-bis(hydroxymethyl)propanol or tetrol like 2,2-bis(hydroxymethyl)-1,3-propanediol (pentaerythritol). For these polymerizations Gordon and Scantlebury[11] report that reaction rate increases about 50% with substitution. A power dependence of the relative rate constant with each substitution fits their results best: $k_n = 1.5^n k_0$. Again, because of the relatively small size of the reactants, significant ring formation occurred.[11] The most common epoxy-curing reaction is the polymerization of a diepoxide with a diamine. The primary hydrogen is about twice as reactive as the secondary hydrogen.[12,13] Thus some chain extension occurs before the branching reaction and delays the gel point.

Previous modeling and analysis of systems with substitution effects has been performed by Gordon and coworkers. Much of our work consists of alternate derivations of results previously obtained by Gordon, who used the theory of stochastic branching processes. Gordon's[14] original pioneering work was not explicitly concerned with substitution effects, but by proper choice of the distribution functions in the branching process, the case of a homopolymerization with a first-shell substitution effect and linear kinetic equations can be solved. This and additional results for homopolymerizations were derived by Gordon and Scantlebury.[15,16] The same authors also treated substitution combined with ring formation in a special inorganic polymerization.[17] More general systems (copolymerizations) with a substitution effect were treated by Gordon and Malcolm.[18] This paper is a significant theoretical extension of Gordon's[14] original work. Gordon and Scantlebury[11] applied results therein to the polyesterifications described above. Dušek extended the results to postgel relations[19] and he and co-workers[20] applied them to the epoxy–diamine system. Durand and Bruneau[21] have given the influence of substitution on gel point for the case of a difunctional copolymerizing with a trifunction. Gordon and Parker[22] discussed higher shell substitution effects. Burchard[23,24] has extended Gordon's probability generating function approach with his path weight generating functions. These permit the calculation of radius of gyration and scattering functions and may be applicable

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to the more complex substitution problems.[25]

Gordon and co-workers use the theory of stochastic branching processes and its method of probability-generating functions. In principle, the use of probability-generating functions allows one to calculate the distribution of molecular weight as well as averages; in practice, however, this calculation may be analytically intractable. (Our approach can only compute averages.) Vectorial, rather than single dimension, generating functions are required for copolymerizations. While conceptually this is not much more difficult, the extra notation can be imposing. Extension from ideal copolymerization systems to systems with a first-shell substitution effect is also not difficult. We encourage the reader to examine Gordon's work and compare it to our approach.[5-8]

As in our previous work, our approach is to deal directly with the polymer structure (rather than use a transform technique such as the probability-generating function). We use the repeating nature of the polymer and two elementary probability laws to establish recursive systems of equations. The solution to these equations is then used in calculating desired parameters. The two probability laws are well-known.[26] They are the *law of total probability*

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

where A and B are events, $\bar{\mathrm{B}}$ is the complement of B, and $P(\mathrm{A}|\mathrm{B})$ is the conditional probability of the event A given that the event B has occurred, and the *law of total probability for expectation*

$$E(\mathrm{X}) = E(\mathrm{X}|\mathrm{B})P(\mathrm{B}) + E(\mathrm{X}|\bar{\mathrm{B}})P(\bar{\mathrm{B}}) \qquad (2)$$

where X is a random variable, $E(\mathrm{X})$ is its expected (or mean) value, and $E(\mathrm{X}|\mathrm{B})$ is its expected value given that the event B has occurred.

The paper is arranged as follows: First, derivations for various parameters (such as weight-average molecular weight, gel point, weight-fraction solubles) are presented for $\mathrm{A}_f + \mathrm{B}_2$ with first-shell substitution effects on the A_f only as a function of the extent of the reaction vector. Second, these results are extended to include more complex systems, particularly $\mathrm{A}_f + \mathrm{A}_2 + \mathrm{B}_2$. In the Appendix is shown how the extent of reaction vector is derived from the kinetic differential equations governing the reaction.

Derivation of Molecular Parameters for $\mathrm{A}_f + \mathrm{B}_2$ Copolymerization

In order to calculate various parameters, we shall follow our earlier approach[5,6] of picking part of the polymer randomly and then tracing paths through the molecule, creating systems of equations as we proceed. It is necessary to have extent of reaction probabilities to do this. In the ideal case of an $\mathrm{A}_f + \mathrm{B}_2$ copolymerization the extents of reaction p_A and p_B sufficed, the molecular parameters being derived as functions of p_A and p_B. In the case of nonequally reactive sites on the A_f monomer, it was necessary[8] to calculate the parameters as a function of a vector $(p_1, p_2, ..., p_f)$ where p_i equals the extent of reaction of site i on an A_f monomer.

In the case of an $\mathrm{A}_f + \mathrm{B}_2$ copolymerization with a first-shell substitution effect on the A's and independent reaction for B's, it appears easiest to use the distribution of the number of reacted sites on A_f's as the starting point for the derivation of the parameters of interest. Suppose we start with A_f moles of the A_f monomer and B_2 moles of the B_2 monomer before the reaction begins. Then the stoichiometric imbalance is

$$r = fA_f/2B_2 \qquad (3)$$

If at time t, a fraction p_A of the A's has reacted and a fraction p_B of the B's has reacted, then

$$p_\mathrm{B} = rp_\mathrm{A} \qquad (4)$$

Furthermore, suppose at time t that there are $A_{f,0}$ moles of A_f units with 0 reacted sites, $A_{f,1}$ moles with 1 reacted site, ..., $A_{f,f}$ moles with f reacted sites. Define

$$p_i = A_{f,i}/A_f \qquad (5)$$

as the proportion of A_f units which have exactly i reacted sites at time t. Then, we can calculate by eq 1 the overall extent of reaction of the A groups

$$p_\mathrm{A} = \sum_{i=0}^{f}(i/f)p_i = \sum_{i=1}^{f}(i/f)p_i \qquad (6)$$

We shall derive expressions for various molecular parameters as a function of the extent of reaction vector

$$\mathbf{p} = (p_0, p_1, ..., p_f, p_\mathrm{B}) \qquad (7)$$

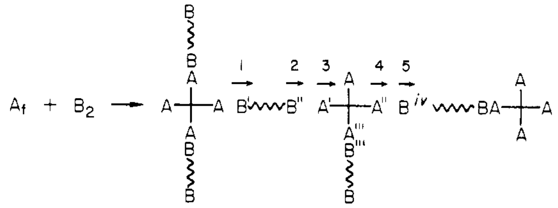
which due to eq 4 really just depends on the first f coordinates. The vector, eq 7, will vary with time t depending on the underlying kinetics. The actual determination of the reaction vector as a function of time t or as a function of p_A can be considered as a separate problem and is treated later in the Appendix. Note that the reaction vector is also the starting point of Gordon and Malcolm's[17] analysis.

In the ideal case, p_i is a binomial probability

$$p_i = \binom{f}{i} p_\mathrm{A}{}^i(1 - p_\mathrm{A})^{f-i} \qquad (8)$$

Thus the derivations presented here reduce to the ideal system, if eq 8 is used.

***M_w* for $\mathrm{A}_f + \mathrm{B}_2$.** To compute the weight-average molecular weight, consider a portion of the resulting polymer



(9)

We assume the mixture has reacted to an extent represented by the vector $(p_\mathrm{A}, p_0, ..., p_f, p_\mathrm{B})$. Referring to eq 9, pick a B unit at random; suppose B′ is chosen. We now ask, what is the expected molecular weight seen looking into the parent B monomer from the chosen B, i.e., along $\xrightarrow{1}$ in eq 9? Define this quantity as $E(W_\mathrm{B}{}^\mathrm{in})$. It will equal the weight of the B_2 unit plus the expected weight looking out from B″, along $\xrightarrow{2}$, which we denote as $E(W_\mathrm{B}{}^\mathrm{out})$

$$E(W_\mathrm{B}{}^\mathrm{in}) = M_{\mathrm{B}_2} + E(W_\mathrm{B}{}^\mathrm{out}) \qquad (10)$$

Now consider the weight seen looking "out" from a B unit: if the B unit does not react, the weight is zero; if the B unit does react, the weight equals the weight seen when looking into the A unit with which it reacts

$$\begin{aligned} W_\mathrm{B}{}^\mathrm{out} &= 0, \text{ with probability } 1 - p_\mathrm{B} \\ &= W_{\mathrm{A},r}{}^\mathrm{in}, \text{ with probability } p_\mathrm{B} \end{aligned}$$

$W_{\mathrm{A},r}{}^\mathrm{in}$ is the weight looking in from a randomly chosen *reacted* A unit. Application of eq 2 gives

$$\begin{aligned} E(W_\mathrm{B}{}^\mathrm{out}) &= 0\cdot(1 - p_\mathrm{B}) + E(W_{\mathrm{A},r}{}^\mathrm{in})p_\mathrm{B} \\ &= p_\mathrm{B}E(W_{\mathrm{A},r}{}^\mathrm{in}) \end{aligned} \qquad (11)$$

It is important to note here that any A which has reacted has an equal chance of being "paired" with B″. This is a consequence of limiting the substitution effect to first shell on the A_f's and none on the B_2's. For higher shell effects and for first shell on homopolymerizations with nonlinear kinetic equations this will not be true.

Continuing to trace our way through the molecule in eq 9, we now ask for the expected weight looking in from a randomly chosen reacted A, $E(W_{A,r}{}^{in})$. In order to answer this question, we need the probability distribution of the number of additional A's which have reacted on the A_f to which A′ belongs, eq 9. This is a straightforward application of Bayes' formula[26] (eq 12), where H_i, $i = 1, ..., n$, are mutually exclusive events whose union has probability 1.

$$P(H_i|C) = \frac{P(H_i)P(C|H_i)}{\sum_{j=1}^{n} P(H_j)P(C|H_j)} \tag{12}$$

Equation 12 can be applied to our situation by letting H_i be the event that randomly chosen A_f is an $A_{f,i}$ and letting C be the event that a randomly chosen A on a randomly chosen A_f is reacted; then

$$P(H_i) = p_i \tag{13}$$

and

$$P(C|H_i) = i/f \tag{14}$$

Substituting eq 13 and 14 into eq 12 gives

$$P(\text{A}' \text{ belongs to an } A_{f,i}) = ip_i / \sum_{j=1}^{f} jp_j \tag{15}$$

Now consider $W_{A,r}{}^{in}$: this weight consists of the mass of the A_f plus any weight attached to additional reacted A's on the A_f; there will be $i - 1$ additional reacted A's with the probability given in eq 15. In eq 9, there are 2 additional reacted A's on the A_f in question so

$$W_{A',r}{}^{in} = M_{A_f} + W_{A'',r}{}^{out} + W_{A''',r}{}^{out}$$

From eq 15 this particular configuration has probability $2p_2/\sum_{j=1}^{f} jp_j$. Noting that $W_{A'',r}{}^{out} = W_{B^{iv}}{}^{in}$ and $W_{A''',r}{}^{out} = W_{B'''}{}^{in}$ and taking expectations gives

$$\begin{aligned} E(W_{A,r}{}^{in}|\text{A}' \text{ belongs to } A_{f,3}) = {} & \\ & E(M_{A_f} + W_{B^{iv}}{}^{in} + W_{B'''}{}^{in}|\text{A}' \text{ belongs to } A_{f,3}) \\ & = M_{A_f} + E(W_{B^{iv}}{}^{in}) + E(W_{B'''}{}^{in}) \\ & = M_{A_f} + 2E(W_B{}^{in}) \end{aligned}$$

This is a special case of

$$E(W_{A,r}{}^{in}|\text{A}' \text{ belongs to } A_{f,i}) = M_{A_f} + (i - 1)E(W_B{}^{in}) \tag{16}$$

Substituting eq 15 and 16 into an extended version of eq 2 [$E(X) = \sum_{i=1}^{f} E(X|B_i)P(B_i)$] gives

$$E(W_{A,r}{}^{in}) = M_{A_f} + \left[\frac{\sum_{i=1}^{f} i^2 p_i}{\sum_{i=1}^{f} ip_i} - 1 \right] E(W_B{}^{in}) \tag{17}$$

Here we have derived another elementary probability law, namely, Wald's lemma.[26]

The fraction in eq 17 is the ratio of second to first moments and has special utility

$$\mu = \sum_{i=1}^{f} i^2 p_i / \sum_{i=1}^{f} ip_i \tag{18}$$

μ is a weight-average extent of reaction and may be more experimentally excessible than p_i. It equals the expected number of additional reacted A's on the A_f to which A′ belongs (this is called mean progeny in the theory of branching processes).

We have derived a system of simultaneous equations:

$$E(W_B{}^{in}) = M_{B_2} + E(W_B{}^{out}) \tag{10}$$

$$E(W_B{}^{out}) = p_B E(W_{A,r}{}^{in}) \tag{11}$$

$$E(W_{A,r}{}^{in}) = M_{A_f} + (\mu - 1)E(W_B{}^{in}) \tag{17}$$

Solving the above system gives

$$E(W_B{}^{in}) = \frac{M_{B_2} + p_B M_{A_f}}{1 - p_B(\mu - 1)} \tag{19}$$

and

$$E(W_B{}^{out}) = E(W_B{}^{in}) - M_{B_2} \tag{20}$$

Now we proceed to consider, as with ideal case,[5] by picking an A_f, the weight W_A of the molecule to which it belongs. If 3 sites of the A_f have reacted, as in eq 9, then

$$\begin{aligned} W_A &= M_{A_f} + W_{A',r}{}^{out} + W_{A'',r}{}^{out} + W_{A''',r}{}^{out} \\ &= M_{A_f} + W_{B'}{}^{in} + W_{B''}{}^{in} + W_{B'''}{}^{in} \end{aligned}$$

and

$$E(W_A|H_3) = M_{A_f} + 3E(W_B{}^{in})$$

In general

$$E(W_A|H_i) = M_{A_f} + iE(W_B{}^{in}) \tag{21}$$

Then, using eq 2

$$E(W_A) = M_{A_f} + \sum_{i=0}^{f} ip_i E(W_B{}^{in})$$

Using eq 6 this becomes

$$E(W_A) = M_{A_f} + fp_A E(W_B{}^{in}) \tag{22}$$

Similarly, the expected weight of a molecule to which a randomly chosen B_2 belongs is

$$E(W_B) = M_{B_2} + 2E(W_B{}^{out}) \tag{23}$$

Finally, pick a unit of mass at random; the expected weight of the molecule to which it belongs will be the weight-average molecular weight

$$\bar{M}_w = w_A E(W_A) + w_B E(W_B) \tag{24}$$

where

$$w_A = M_{A_f} A_f / (M_{A_f} A_f + M_{B_2} B_2)$$

$$w_B = 1 - w_A$$

Substituting eq 19 and 20 into eq 22 and 23, respectively, and then eq 22 and 23 into eq 24 and letting $p_A = p$ and $p_B = rp$ gives

$$\begin{aligned} \bar{M}_w = \{ & (2r/f)[1 + rp(fp - \mu + 1)]M_{A_f}{}^2 + \\ & [1 + rp(\mu - 1)]M_{B_2}{}^2 + 4rpM_{A_f}M_{B_2}\} / \\ & \{[(2r/f)M_{A_f} + M_{B_2}][1 - rp(\mu - 1)]\} \end{aligned} \tag{25}$$

Note that in the ideal case with binomial probabilities, $\mu - 1 = (f - 1)p$ and eq 25 is a special case of eq 23 of ref 5.

The Gel Point for $A_f + B_2$. Note from eq 25 that the weight-average molecular weight diverges when

$$rp_A(\mu - 1) = 1 \tag{26}$$

This corresponds to the gel point. Recalling the definition of μ, eq 18, and using eq 6, eq 26 becomes

$$\sum_{i=1}^{f} i^2 p_{i,\text{gel}} - fp_{A,\text{gel}} = f/r \tag{27}$$

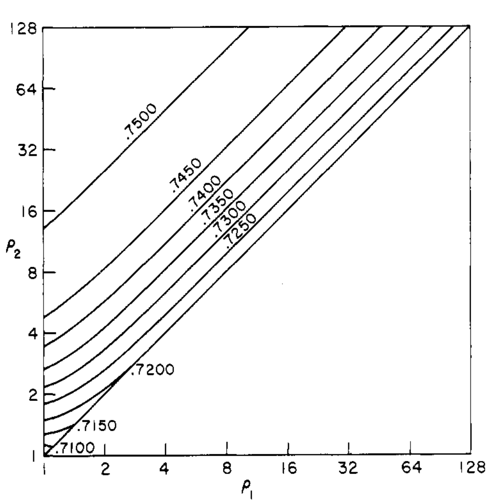


Figure 1. Effect of substitution on gel point for $A_3 + B_2$ copolymerization with first-order kinetics. $\rho_1 = k_1/k_0$ and is the relative decrease in rate after one of the A_3 groups has reacted; $\rho_2 = k_2/k_0$.

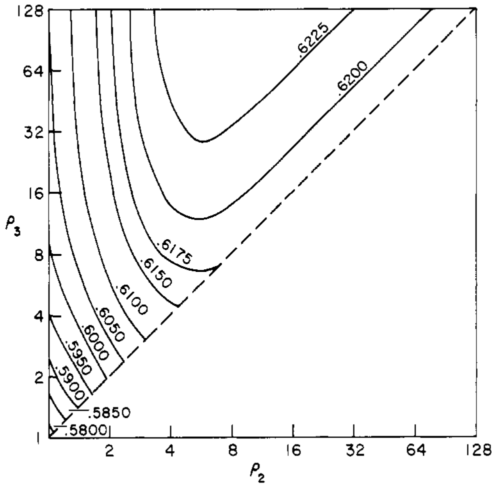


Figure 2. Effect of substitution on gel point for $A_4 + B_2$ copolymerization with first-order kinetics. No substitution effect with reaction of the first group. $\rho_1 = k_1/k_0 = 1$; $\rho_2 = k_2/k_0$; $\rho_3 = k_3/k_0$.

Note that the gel point is specified by only the first 2 moments of p_i. The gel point vector $(p_0, p_1, ..., p_f, p_B)_{gel}$ is the solution of eq 27. It must be found numerically by using the kinetics of the system. Or, vice versa, experimental measures of the gel point can indicate the importance of substitution effects.[11]

The extent of reaction at gelation for ideal systems is $p_{A,gel}$. With substitution it can be interpreted as "the gel point" for these systems. The value $p_{A,gel}$ depends on the relative reaction rates in the substitution reaction. Figures 1 and 2 show contours of $p_{A,gel}$ as a function of reactivity ratio for $A_3 + B_2$ and $A_4 + B_2$, respectively, for *first-order* reactions. These plots are similar to those we have developed for unequal reactivity.[8] In both cases lower reactivity delays the gel point but only up to a maximum level. Gordon and Scantlebury[15] have presented similar plots for homopolymerization.

Probability of a Finite Chain in $A_f + B_2$. In order to study behavior of gelled systems we need to compute the probability of a finite chain. Suppose a reacted A unit is chosen at random, for example, A″ in eq 9. Consider $F_{A,r}^{out}$, the event of seeing a finite chain when looking "out" from a randomly chosen A unit. In eq 9, it corresponds to a finite chain in the direction $\xrightarrow{4}$. Since we are assuming the chosen A is reacted, the event $F_{A,r}^{out}$ is equivalent to F_B^{in}, the event of seeing a finite chain when looking "in" from a B, along $\xrightarrow{5}$ in eq 9. Thus

$$P(F_{A,r}^{out}) = P(F_B^{in}) \tag{28}$$

Similarly

$$P(F_B^{in}) = P(F_B^{out}) \tag{29}$$

Now consider F_B^{out}, the event of seeing a finite chain when looking out from a randomly chosen B. If B reacts, an event with probability $p_B = rp$, then $F_B^{out} = F_{A,r}^{in}$, the event of seeing a finite chain when looking in from a reacted A. If B does not react, then the event F_B^{out} occurs. Using eq 1

$$\begin{aligned} P(F_B^{out}) &= P(F_B^{out}|\text{B reacts})p_B + \\ &\qquad P(F_B^{out}|\text{B does not react})(1 - p_B) \\ &= rpP(F_{A,r}^{in}) + 1 - rp \end{aligned} \tag{30}$$

Now consider the event $F_{A,r}^{in}$. In eq 9, this is equivalent to looking along $\xrightarrow{3}$. In this case there are two additional reacted A's on the A_f; thus

$$P(F_{A,r}^{in}|\text{A is on } A_{f,3}) = P(F_{A,r}^{out})^2$$

In general, we have

$$P(F_{A,r}^{in}|\text{A on } A_{f,i}) = P(F_{A,r}^{out})^{i-1} \tag{31}$$

Using eq 1 gives

$$\begin{aligned} P(F_{A,r}^{in}) &= \sum_{i=1}^{f} P(F_{A,r}^{in}|\text{A on } A_{f,i})P(\text{A on } A_{f,i}) \\ &= \sum_{i=1}^{f} ip_iP(F_{A,r}^{out})^{i-1} \Big/ \sum_{i=1}^{f} ip_i \end{aligned} \tag{32}$$

Note that this result is the same as that obtained by Dušek [ref 19, eq 59 and 41, where his $v_1 = P(F_{A,r}^{in})$ and $v_2 = P(F_{A,r}^{out})$]. Combining eq 28, 29, 30, and 32 gives

$$P(F_{A,r}^{out}) = r/f\sum_{i=1}^{f} ip_iP(F_{A,r}^{out})^{i-1} + 1 - rp \tag{33}$$

As before,[6] this equation can be solved analytically for $f = 3$ and $f = 4$. There will either be 1 root or no root between 0 and 1, exclusive. In the former case, that root will be the desired solution of eq 33; in the latter case, the solution of eq 33 is $P(F_{A,r}^{out}) = 1$. If $f = 3$

$$P(F_{A,r}^{out}) = \frac{-b - (b^2 - 4ac)^{1/2}}{2a} \tag{34}$$

where

$$\begin{aligned} a &= rp_3 \\ b &= (2rp_2 - 3)/3 \\ c &= rp_1/3 + 1 - rp \end{aligned} \tag{35}$$

For higher functionalities, eq 33 must be solved numerically.

Weight-Fraction Solubles for $A_f + B_2$. The quantity $P(F_{A,r}^{out})$ can be used to compute weight-fraction solubles, w_s, in a manner similar to before.[6] An A_f unit belongs to the soluble fraction if none of the A's have infinite chains. If a randomly chosen A_f has i reacted A's, then it will belong to the soluble fraction with probability

$$P(A_f \text{ in sol}|A_f \text{ is } A_{f,i}) = P(F_{A,r}^{out})^i \tag{36}$$

Using eq 1 gives

$$P(A_f \text{ in sol}) = \sum_{i=1}^{f} p_iP(F_{A,r}^{out})^i \tag{37}$$

Similarly, a randomly chosen B_2 unit belongs to the soluble fraction with probability

$$P(B_2 \text{ in sol}) = P(F_B^{\text{out}})^2 = P(F_{A,r}^{\text{out}})^2 \tag{38}$$

Combining eq 37 and 38 gives

$$w_s = w_A \sum_{i=0}^{f} p_i P(F_{A,r}^{\text{out}})^i + w_B P(F_{A,r}^{\text{out}})^2 \tag{39}$$

where w_A and w_B are defined in eq 24.

Concentration of Effective Cross-Links. An A_f unit will be an effective cross-link if at least 3 of its A units lead to the infinite network. More specifically, an A_f will be a cross-link of degree k if it has k paths to the infinite network. Let X_k be the event that a randomly chosen A_f is a cross-link of degree k. If A_f has i reacted sites, exactly $i - k$ of these must have finite chains

$$P(X_k|A_f \text{ is } A_{f,i}) = \left(\frac{i}{k}\right) P(F_{A,r}^{\text{out}})^{i-k}[1 - P(F_{A,r}^{\text{out}})]^k \tag{40}$$

Using eq 1 again gives for $k = 3, ..., f$

$$P(X_k) = \sum_{i=k}^{f} p_i \left(\frac{i}{k}\right) P(F_{A,r}^{\text{out}})^{i-k}[1 - P(F_{A,r}^{\text{out}})]^k \tag{41}$$

The concentration of cross-links is

$$[X_k] = P(X_k)A_f$$

Values obtained from the above equation can now be used to compute the effective concentration of cross-links by using eq 51 of ref 6.

More Complicated Systems

Using the principles developed for $A_f + B_2$ here and those presented in ref 5 and 6 for general ideal systems, $A_{f_1} + A_{f_2} + ... + A_{f_i} + B_{g_1} + B_{g_2} + ... + B_{g_m}$, we hope it will be possible for the reader to analyze more complicated systems with several functionalities of both A's and B's, where there is a first-shell substitution effect on one type of monomer, say, A.

As an illustrative example we write down the equations for the copolymerization of $A_f + A_2 + B_2$. These equations parallel very closely those in the previous section. The stoichiometric imbalance becomes

$$r = (fA_f + 2A_2)/2B_2 \tag{42}$$

and the initial proportions of A's on A_f and A_2 are

$$a_f = \frac{fA_f}{(fA_f + 2A_2)}$$

$$a_2 = 1 - a_f \tag{43}$$

The extent of reaction vector, eq 7, must now become a matrix $\boldsymbol{p}_{ij}$ because more than one species with substitution effects is involved

$$\boldsymbol{p} = (p_{f0}, p_{f1}, ..., p_{ff}, p_{20}, p_{21}, p_{22}, p_B) \tag{44}$$

As discussed in the Appendix, obtaining experimental values for this extent of reaction matrix is the key to understanding substitution effects in a particular system. The total extent of reaction of A groups can be calculated from

$$p_A = a_f \sum_{i=0}^{f} (i/f) p_{fi} + a_2 \sum_{i=0}^{2} (i/2) p_{2i} \tag{45}$$

The proportion of *reacted* A's on A_f's is

$$a_{f,r} = \frac{A_f \sum_{i=0}^{f} i p_{fi}}{A_f \sum_{i=0}^{f} i p_{fi} + A_2 \sum_{i=0}^{2} i p_{2i}} \tag{46}$$

and

$$a_{2,r} = 1 - a_{f,r} \tag{47}$$

Following our previous approach, the expected weights attached to each functional group become

$$E(W_{A,r}^{\text{out}}) = E(W_B^{\text{in}}) \tag{48}$$

$$E(W_B^{\text{in}}) = M_{B_2} + E(W_B^{\text{out}}) \tag{49}$$

$$E(W_B^{\text{out}}) = p_B[a_{f,r}E(W_{A_f,r}^{\text{in}}) + a_{2,r}E(W_{A_2,r}^{\text{in}})] \tag{50}$$

$$E(W_{A_f,r}^{\text{in}}) = M_{A_f} + \frac{\sum_{i=1}^{f} i(i-1)p_{fi}}{\sum_{j=1}^{f} j p_{fj}} E(W_{A,r}^{\text{out}}) \tag{51}$$

$$E(W_{A_2,r}^{\text{in}}) = M_{A_2} + \frac{\sum_{i=1}^{2} i(i-1)p_{2i}}{\sum_{j=1}^{f} j p_{2j}} E(W_{A,r}^{\text{out}}) \tag{52}$$

Combining these gives the expected weights on each monomer

$$E(W_{A_2}) = M_{A_2} + \sum_{i=0}^{2} i p_{2i} E(W_{A,r}^{\text{out}}) \tag{53}$$

$$E(W_{A_f}) = M_{A_f} + \sum_{i=0}^{f} i p_{fi} E(W_{A,r}^{\text{out}}) \tag{54}$$

$$E(W_{B_2}) = M_{B_2} + 2E(W_B^{\text{out}}) \tag{55}$$

which combines to give the weight-average molecular weight of the branched copolymer

$$\bar{M}_w = w_{A_2}E(W_{A_2}) + w_{A_f}E(W_{A_f}) + w_{B_2}E(W_{B_2}) \tag{56}$$

where

$$w_{A_2} = \frac{A_2 M_{A_2}}{A_2 M_{A_2} + A_f M_{A_f} + B_2 M_{B_2}}$$

$$w_{A_f} = \frac{A_f M_{A_f}}{A_2 M_{A_2} + A_f M_{A_f} + B_2 M_{B_2}}$$

$$w_{B_2} = 1 - w_{A_2} - w_{A_f} \tag{57}$$

By substituting the various equations into eq 56, it is possible to obtain an explicit relation like eq 25. However, in any actual calculations a simple numerical program will be used which will solve the system of eq 48–56 sequentially.

The probability of a finite chain for the postgel condition can be found again by following the previous approach

$$P(F_{A,r}^{\text{out}}) = P(F_B^{\text{in}}) \tag{58}$$

$$P(F_B^{\text{in}}) = P(F_B^{\text{out}}) \tag{59}$$

$$P(F_B^{\text{out}}) = 1 - p_B + p_B(a_{2,r}P(F_{A_2,r}^{\text{in}})) + a_{f,r}P(F_{A_f,r}^{\text{in}}) \tag{60}$$

$$P(F_{A_f,r}^{\text{in}}) = \sum_{i=0}^{f} i p_{fi} P(F_{A,r}^{\text{out}})^{i-1} \Big/ \sum_{j=0}^{f} j p_{fj} \tag{61}$$

$$P(F_{A_2,r}^{\text{in}}) = \sum_{i=0}^{2} i p_{2i} P(F_{A,r}^{\text{out}})^{i-1} \Big/ \sum_{j=0}^{2} j p_{2j} \tag{62}$$

As with eq 33, these equations can be solved analytically for $f = 3$ and $f = 4$ for the root between 0 and 1.

This result can be used to calculate sol fraction results

$$w_s = w_{A_2}\sum_{i=0}^{2} p_{2i}P(F_{A,r}{}^{out})^i + w_{A_f}\sum_{i=0}^{f} p_{fi}P(F_{A,r}{}^{out})^i + w_{B_2}P(F_B{}^{out})^2 \quad (63)$$

Conclusions

From the above derivations we see that our previous results can be extended in a relatively straightforward manner to include substitution effects. The results are qualitatively similar to those for unequal reactivity. The major new feature in the derivations is keeping track of the state of reaction on molecules with substitution. This is basically just a bookkeeping problem. It prevents writing closed relations as is possible in the ideal case, but the results are easy to apply sequentially and solve with a small computer program for any particular case.

The real problems in dealing with substitution effects are experimental. Testing of these results depends on fairly accurate measurement of the extent of reaction vector as discussed in the Appendix.

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Appendix. Derivation of Reaction Distribution from Kinetic Differential Equations

In order to use the formulas of the preceding section, the extent of reaction vector (eq 7) (p_0, p_1, ..., p_f, p_B) is needed. This section is devoted to deriving this vector for the special case of an $A_3 + B_2$ system with first-order reaction rates. It is necessary to resort to a computational approach to determine this vector, as opposed to obtaining a single formula. This constitutes a major departure from the solution techniques of previous work in which we were able to obtain analytical results for all simple cases.

For the case of first-order kinetics, the differential equations governing the reaction with first-shell substitution effect are

$$\begin{aligned} dp_0(t)/dt &= -3k_0p_0(t) \\ dp_1(t)/dt &= -2k_1p_1(t) + 3k_0p_0(t) \\ dp_2(t)/dt &= -k_2p_2(t) + 2k_1p_1(t) \\ dp_3(t)/dt &= k_2p_2(t) \end{aligned} \quad (A1)$$

with initial values

$$p_0(0) = 1 \qquad p_1(0) = p_2(0) = p_3(0) = 0$$

Gordon and Scantlebury[11] and Dušek et al.[20] give similar sets of differential equations for other kinetic schemes. Dušek[27] has pointed out recently that proper treatment of the kinetics can lead to complications in application of branching theory.

The system of equations in (A1) can be solved sequentially, starting with the first. Integration gives

$$p_0(t) = e^{-3k_0t} \quad (A2)$$

The second equation of eq A1 becomes

$$dp_1(t)/dt = -2k_1p_1(t) + 3k_0e^{-3k_0t} \quad (A3)$$

Rearranging (A3) and multiplying by the integrating factor e^{2k_1t} gives

$$e^{2k_1t}dp_1(t)/dt + 2k_1e^{2k_1t}p_1(t) = 3k_0e^{-(3k_0-2k_1)t} \quad (A4)$$

which is equivalent to

$$d[e^{2k_1t}p_1(t)]/dt = 3k_0e^{-(3k_0-2k_1)t} \quad (A5)$$

and can be integrated from 0 to t, yielding the solution

$$p_1(t) = \frac{3k_0}{3k_0 - 2k_1}(e^{-2k_1t} - e^{-3k_0t}) \quad (A6)$$

Continuing in the sequential solution of the equations in (A1), the third equation becomes

$$\frac{d}{dt}p_2(t) + k_2p_2(t) = \frac{6k_0k_1}{3k_0 - 2k_1}(e^{-2k_1t} - e^{-3k_0t}) \quad (A7)$$

Multiplying by the integrating factor e^{k_2t} and integrating from 0 to t yields the solution

$$p_2(t) = \frac{6k_0k_1}{3k_0 - 2k_1}\left[\frac{e^{-k_2t} - e^{-2k_1t}}{2k_1 - k_2} - \frac{e^{-k_1t} - e^{-3k_0t}}{3k_0 - k_2}\right] \quad (A8)$$

and finally

$$p_3(t) = 1 - p_0(t) - p_1(t) - p_2(t) \quad (A9)$$

Equations A2, A6, A8, and A9 constitute the solution of (A1) as a function of t. It is easy to see that this solution technique also works for higher functional A_f.

The vector $\mathbf{p} = (p_0(t), p_1(t), p_2(t), p_3(t))$ is a function of time. The overall extent of reaction of all the A sites is

$$p_A(t) = \sum_{i=1}^{3} ip_i(t)/3 \quad (A10)$$

It is often desired to express molecular parameters such as average molecular weight and degree of cross-linking as a function of p_A rather than time, t. This can be done as follows: For a value $p_A{}^*$ find the time t^* such that $p_A(t^*) = p_A{}^*$. This must be done by using an iterative search. However, this will be relatively simple since p_A is a monotonic function of time. Then the vector ($p_0(t^*)$, $p_1(t^*)$, $p_2(t^*)$, $p_3(t^*)$) corresponds to an overall extent of reaction $p_A{}^*$. This vector can then be used as eq 7 in the preceding.

If the kinetics of the system under consideration are known, a system of equations similar to (A1) can be obtained. If it is not a first-order reaction, the equations can be solved sequentially by numerical methods.

References and Notes

(1) The George Washington University.
(2) To whom correspondence should be addressed.
(3) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1953; Chapter 9; *J. Am. Chem. Soc.* **1941**, *63*, 3083, 3097.
(4) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *11*, 45; **1944**, *12*, 125.
(5) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(6) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976**, *9*, 206.
(7) Miller, D. R.; Valles, E. M.; Macosko, C. W. *Polym. Eng. Sci.* **1979**, *19*, 272.
(8) Miller, D. R.; Macosko, C. W. *Macromolecules* **1978**, *11*, 656.
(9) Lenz, R. W. "Organic Chemistry of Synthetic High Polymers"; Wiley: New York, 1967; Chapter 5.
(10) Aldersley, J. W.; Gordon, M. *J. Polym. Sci., Part C* **1969**, *16*, 4567.
(11) Gordon, M.; Scantlebury, G. R. *J. Chem. Soc. Sect. B, Part I* **1967**, 1.
(12) Kakurai, T.; Noguchi, T. *Kogyo Kagaku Zasshi* **1961**, *64*, 398.
(13) Hori, K.; Hiura, H.; Sawada, M.; Mite, I.; Kambe, H. *J. Polym. Sci., Part A-1* **1970**, 1357.
(14) Gordon, M. *Proc. R. Soc. London, Ser. A* **1962**, *268*, 240.
(15) Gordon, M.; Scantlebury, G. *Trans. Faraday Soc.* **1964**, *60*, 604.
(16) Gordon, M.; Scantlebury, G. R. *J. Polym. Sci., Part C* **1968**, *16*, 3933.
(17) Gordon, M.; Scantlebury, G. R. *Proc. R. Soc. London, Ser. A* **1966**, *292*, 380.
(18) Gordon, M.; Malcolm, G. N. *Proc. R. Soc. London, Ser. A* **1966**, *295*, 29.

(19) Dušek, K. *J. Polym. Sci., Polym. Phys. Ed.* **1974,** *12,* 1089.
(20) Dušek, K.; Ilavsky, M.; Lunak, S. *J. Polym. Sci., Polym. Symp.,* **1975,** *53,* 29.
(21) Durand, D.; Bruneau, C. M. *J. Polym. Sci., Polym. Phys. Ed.* **1979,** *17,* 295.
(22) Gordon, M.; Parker, T. G. *Proc. R. Soc. Edinburgh* **1970,** *69,* 13.
(23) Kajiwara, K.; Burchard, W.; Gordon, M. *Br. Polym. J.* **1970,** *2,* 110.
(24) Burchard, W. *Macromolecules* **1972,** *5,* 604.
(25) Müller, M.; Burchard, W. *Makromol. Chem.* **1978,** *179,* 1821.
(26) Ross, S. M. "Introduction to Probability Models"; Academic Press: New York, 1972; Chapter 3.
(27) Dušek, K. *Makromol. Chem., Suppl.* **1979,** *2,* 35.

Conformations of Polymers Attached to an Interface

P. G. de Gennes

Collège de France, 75231 Paris Cedex 05, France. *Received April 10, 1980*

ABSTRACT: We discuss the conformations and the concentration profiles for long, flexible chains (N monomers per chain) grafted at one end on a solid surface (fraction of surface sites grafted σ). The chains are immersed either in a pure (good) solvent or in a solution of the same polymer (P monomers per mobile chain, volume fraction ϕ). It is assumed that the polymer does *not* adsorb on the wall surface. The zone occupied by the grafted chain may contain a large fraction of mobile P chains: we call this a mixed case (M), as opposed to the unmixed case (UM). Also the chains may be stretched (S) or unstretched (US). The combination of these two criteria gives four possible regimes. Using scaling laws, we locate the domains of existence of these four regimes in terms of the variables σ and ϕ. High σ values may be hard to reach by grafting but could be obtained with block copolymers at an interface between two immiscible solvents.

I. Introduction

Polymers grafted onto solid walls can be useful for many physicochemical applications:[1] wetting, adhesion,[2] chromatography,[3] colloid stabilization,[4] and biocompatibility[5] are typical examples. In the present paper, we discuss theoretically some conformation problems for grafted, flexible polymers immersed in *good* solvents. The situation which we have in mind is described on Figure 1: here, a set of linear chains (with N monomers per chain) is attached to a wall and immersed in a liquid which may be either a pure solvent or, more generally, a solution of the same polymer (with P monomers per chain). We assume that all chains are *uncharged:* this eliminates some important practical situations but is logical in view of the difficulties found in understanding polyelectrolyte conformations in solution. We also assume *no adsorption:* the chains are not attracted to the wall. The opposite case can be treated and has in fact been discussed in some limits[6] but is obscured by the increase in number of relevant parameters.

A global Flory–Huggins theory for the selective properties of a set of grafted chains with respect to solvent mixtures has recently been constructed.[7] Our aim here is somewhat different:

(a) We are mainly concerned with conformational properties and with spatial distributions.

(b) We wish to cover situations where the fraction σ of grafted sites on the solid surface is large (up to unity). Of course, these situations are not easy to achieve on a solid wall. But they may be reached with *monolayers of block copolymers* at an interface between two solvents.

(c) We allow for a liquid phase which contains mobile polymer chains (P chains), but we restrict our attention to P chains which are *chemically identical* with the N chains. This excludes a number of interesting chromatographic effects[7] but preserves some important physical questions: (i) the concentration (or volume fraction ϕ) of the mobile chains can be used to modify the properties of the grafted layer; (ii) the limit of a dense polymer melt ($\phi \rightarrow 1$) which is included here is of interest for certain applications, such as incompatible polymer mixtures doped by block copolymer additives.[8]

Clearly, the statistical problem raised by these rather complex interfaces is very delicate. However, it is possible to delineate the main *qualitative* features by comparatively simple arguments based on scaling laws.[9] We do this here in one limit, namely, when the system is athermal ($\chi = 0$ in the Flory–Huggins[10] notation). Also we restrict our attention to mobile chains which have lengths comparable to (or smaller than) that of the grafted chain ($P \lesssim N$).

There are three successive steps in our discussion. The case of grafted chains plus *pure solvent* is treated in section II. Here, most of the relevant scaling laws have already been constructed by Alexander:[6] we add only a few novel features, such as the concentration profile close to the wall. In section III, we discuss the opposite limit of a grafted wall in contact with a polymer melt. Of particular interest here is the progressive expulsion of the mobile chains from the grafted film when the graft density σ increases. Finally in section IV we deal with semidilute solutions: here we find that the regime of section II is prevalent when $\phi < \sigma^{2/3}$. In the opposite limit ($\phi > \sigma^{2/3}$) there are still two different possibilities, one with penetration of the grafted layer by the P chains and one without penetration.

The main conclusions are summarized in Figure 2, showing the different regimes which we expect for any given ϕ and σ. It should be immediately pointed out that the boundaries between successive regimes are not sharp: they correspond in reality to smooth crossovers.

II. Grafted Chains plus Good Solvent

A. Separate Coils. The limit of low σ is particularly simple (Figure 3): each chain occupies roughly a half-sphere with a radius comparable to the Flory radius for a coil in a good solvent[10]

$$R_F = N^{3/5}a \tag{II.1}$$

where a is a monomer size (a is the mesh size in the lattice model of Figure 1). Here, the different coils do not overlap: thus we must have $\sigma a^{-2}R_F^2 < 1$ or

$$\sigma < N^{-6/5} \tag{II.2}$$

Let us now discuss the *average* profile $\phi(z)$ for a random distribution of grafting points on the wall. We call z the