at low pH, the formation of a nonionic, *o*-quinoidal structure, also called an *o*-hydroxystyrylic salt, absorbing at 435 nm. At high pH, the ultraviolet photogenerated species is a zwitterionic merocyanine, absorbing at 520–560 nm.

We have detected an initially unexpected pressure dependence of the quantum yield of the photoreaction at low pH which would deserve more investigations. Indeed it may have some interesting applications in biologically related experiments. For example, the light detection capabilities of the rod outer segments over an enormous dynamic range of 8 decades is still an unraveled puzzle.[8] In view of our results, it would be worth checking if the elastic coupling between the photoexcitable rhodopsin proteins imbedded in the disk membranes does not affect the quantum yield of the cis–trans photoisomerization of the retinal chromophore.

We have also studied the reversibility of these ultraviolet photoinduced surface pressure changes. At low pH, a spontaneous return of the *o*-hydroxystyrylic salt to the spiropyran form is observed under dark conditions. At high pH, there is no such dark thermal relaxation and the photoexcitation of the monolayer in the visible is required. The photoconversion of the merocyanine molecules to the spiropyran molecules takes place through at least one different merocyanine stereoisomer.

The dynamics of the light-induced changes have been investigated in the time domain from 1 s to 1 h. Although our experiments are still not very detailed, it is worth pointing out that they represent a new approach to flash photolysis. Here the transient photoexcited species are not detected through their optical spectrum changes with a spectrophotometer but rather through their molecular configuration changes with a mechanical force transducer. Such a two-dimensional method may be important when the scarcity of the material to be investigated is a premium parameter. A drawback is, however, that investigation of short-lived species seems precluded because of the slow detector response. Other measuring devices, which would allow faster reaction rates to be followed, typically down into the 10^{-3}-s range, have been described recently in the literature.[15,16]

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Registry No. Methyl methacrylate–1-(β-(methacryloxy)ethyl)-6′-nitro-DIPS copolymer, 85115-81-7.

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Asymmetric Bonding of Identical Units: A General A_gRB_{f-g} Polymer Model

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ABSTRACT: Flory's A_gRB_{f-g} model describes the polymerization of identical structural units, each having g functional groups of type A and $(f - g)$ groups of type B. In this model, the units react subject to three conditions: (a) Functional groups of type A react only with those of type B and vice versa (thereby forming asymmetrical A–B bonds between the units). (b) Intramolecular reactions do not occur (and therefore only branched-chain (noncyclic) polymers are formed). (c) *Flory's principle of equireactivity*, all functional groups are equally reactive, is followed. This paper uses the theory of branching processes to relax the equireactivity condition. Let the probability that a unit has k reacted A's and l reacted B's be p_{kl}. Using $P(a,b) = \sum p_{kl}a^kb^l$, the generating function of $\{p_{kl}\}$, we give the average molecular weights and size distribution of the sol before gelation and derive the gel point. Using the corresponding *conditional* probabilities $\{\tilde{p}_{kl}\}$ for units in the postgelation sol, we give postgelation results as well. We derive the $\{\tilde{p}_{kl}\}$ by the method of extinction probabilities. Our results agree with known results for the equireactive case. Although we refer to chemical bonding between groups, our results apply to asymmetric bonding in general.

Introduction

In 1941, Flory[1] introduced the RA_f (f functional random polycondensation) model of polymerization. In the RA_f model, each structural unit of a polymer has f functional groups of type A. The units react subject to three conditions: (a) Functional groups of the type A react with one

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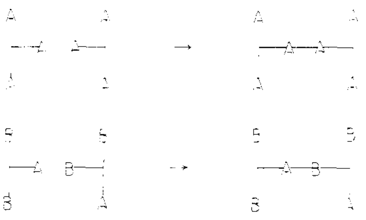

Figure 1. Pairs of units bonding to form dimers. (Above) Units of the RA_3 type; (below) of the A_1RB_2 type.

another to form bonds between the units. (The A–A bonds so formed are *symmetric.*) See Figure 1. (b) Intramolecular reactions do not occur (and therefore only branched-chain (noncyclic) polymers are formed). (c) The units follow *Flory's principle of equireactivity*, which states that all functional groups are equally reactive.

Let α, *the extent of reaction*, be the proportion of A's that have reacted. Let p_k be the proportion of units that have k reacted A's. The equireactivity condition (c) implies that the probability generating function (pgf) of $\{p_k\}$ is

$$P(a) \equiv \sum_{(k)} p_k a^k = \sum_{(k)} \binom{f}{k} (1-\alpha)^{f-k}\alpha^k a^k = (1-\alpha+\alpha a)^f \quad (1)$$

($\equiv$ indicates a definition; $\binom{f}{k}$ is the number of ways of choosing k reacted A's from the f A's on a unit).

When α exceeds a critical value, α_c, an infinite polymer (or *gel*) forms. The principal problems of polymerization theory are to determine the *gel point* α_c and the distribution of the finite polymers (or *sol*) for given α.

The gel point (Flory[1]) and sol distribution (Stockmayer[2]) for the RA_f model are known. Gordon[3] and Good[4] applied the theory of branching processes to relax the equireactivity condition (c) and gave the gel point and sol distribution for arbitrary $P(a)$.

Flory[5] also introduced the A_gRB_{f-g} model of polymerization. This model is like the RA_f model except that (1) each structural unit has g groups of the type A and $(f-g)$ groups of the type B and (2) condition (a) is replaced by (a′): Functional groups of type A react only with those of type B and vice versa (*asymmetric bonds* A–B) (see Figure 1).

In this model, let $\alpha(\beta)$ be the proportion of A's (B's) that have reacted, and let p_{kl} be the proportion of units that have k reacted A's and l reacted B's. Equireactivity implies that the pgf of $\{p_{kl}\}$ is

$$P(a,b) \equiv \sum_{(k,l)} p_{kl}a^k b^l = (1-\alpha+\alpha a)^g(1-\beta+\beta b)^{f-g} \quad (2)$$

(By symmetry of A and B, we assume $g \leq f - g$.) Flory[5] gave the sol distribution for $g = 1$ (a gel never forms in this case). For $g \geq 2$, the gel point (Spouge[6]) and sol distribution (Spouge[7]) are also known.

This paper relaxes the equireactivity condition (c) for asymmetric bonding and uses the theory of branching processes to give the gel point and sol distribution for arbitrary $P(a,b)$. When $P(a,b)$ is given by (2), our results reduce to the known equireactive results. The reader may use those cases as examples of the general theory that follows.

Pregelation

The General Case. As in (2), we define the generating function for the status of a unit (see Figure 2):

$$P(a,b) \equiv \sum_{(k,l)} p_{kl}a^k b^l,\ P(1,1) = 1 \quad (3)$$

The $\{p_{kl}\}$ *are now arbitrary probabilities.* Let the random variable $A_u(B_u)$ be the number of reacted A(B) groups on a random unit. Let $\mathcal{E}$ denote the expectation operator. Then

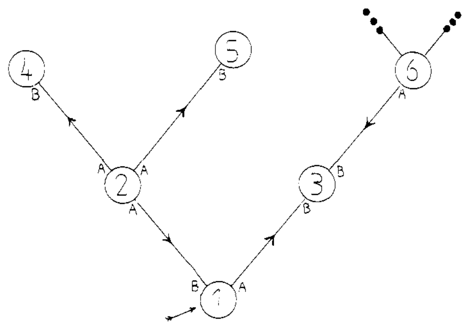

Figure 2. Schematic for a polymer containing a random unit (1). (For convenience, the units (circles) have been numbered.) The A–B bonds have arrows, directed from A to B. The B group of unit 1 "leads to" unit 2; we say also that it leads to the units 2, 4, and 5, which are its "progeny". Because 2,4,5 is a finite set, the B group of unit 1 has "finite progeny".

$$(\partial P/\partial a)_{a=b=1} = \sum_{(k,l)} kp_{kl} \equiv \mathcal{E}(A_u) = \mathcal{E}(B_u) \equiv \sum_{(k,l)} lp_{kl} = (\partial P/\partial b)_{a=b=1} \quad (4)$$

The middle equality follows because every reacted A bonds to exactly one reacted B.

Let X_A, a random variable, denote the number of units that a reacted A group leads to (see Figure 2). Let $(X_A = k)$ be the event that a reacted A group leads to k units and let $p_{Ak} = \mathcal{P}(X_A = k)$ be its probability. Then the pgf of $\{p_{Ak}\}$ is

$$a(u) \equiv \sum_{k=1}^{\infty} p_{Ak}u^k = \sum_{k=1}^{\infty} \mathcal{P}(X_A = k)u^k = \mathcal{E}(u^{X_A}) \quad (5a)$$

(The reason for choosing the letter "a" in (5a) (cf. eq 3) will become apparent.) Similarly

$$b(u) \equiv \sum_{k=1}^{\infty} p_{Bk}u^k = \sum_{k=1}^{\infty} \mathcal{P}(X_B = k)u^k = \mathcal{E}(u^{X_B}) \quad (5b)$$

Let A_{kl} be the event that a reacted A group leads to a unit with k reacted A's and l reacted B's. The probability of A_{kl} is

$$\mathcal{P}(A_{kl}) = \frac{lp_{kl}}{\sum_{(k,l)} lp_{kl}} = \frac{1}{r}lp_{kl} \quad (6a)$$

where r is the common value in eq 4. Proof: We assume explicitly that the reacted A group leads to a random reacted B. Choosing a random reacted B from the system is the same as choosing a random unit (P_{kl}) and then choosing a reacted B on that unit (l) (note the assumption of classical statistics: the B groups, though chemically identical, are distinguishable). The denominator normalizes (6a) into a probability (thereby satisfying the universal consistency relation of Gordon and Malcolm,[8] noted also by Whittle.[9]) Similarly

$$\mathcal{P}(B_{kl}) = \frac{kp_{kl}}{\sum_{(k,l)} kp_{kl}} = \frac{1}{r}kp_{kl} \quad (6b)$$

Let $(X|Y)$ denote the event that X happens, conditional on Y having happened. Conditioning (on the state of the unit that a reacted group leads to) gives a functional equation for $a = a(u)$ and $b = b(u)$. First we note that the distribution of $(X_A|A_{kl})$ is the same as that of $1 + \sum_{i=1}^{k}(X_A)_i + \sum_{j=1}^{l-1}(X_B)_j$, where $\{(X_A)_i\}$ and $\{(X_B)_j\}$ are independent random variables with distributions like those of X_A and X_B. Proof: The total number of units that a reacted A group leads to (X_A), given that it leads to a unit U with k reacted A groups and l reacted B groups (A_{kl}), is 1 (the unit U) plus the number of units that the k reacted A's and $(l - 1)$ reacted B's on U lead to (the remaining B has reacted with the original A group). *This observation is the basis of eqs 7, which are fundamental to this paper.* The use of random variables X_A, A_{kl}, etc., merely provides rigor.

Because the distribution of $(X_A|A_{kl})$ is the same as that of $1 + \sum_{i=1}^{k}(X_A)_i + \sum_{j=1}^{l-1}(X_B)_j$, conditioning on A_{kl} gives

$$a = a(u) = \mathcal{E}(u^{X_A}) = \sum_{(k,l)} \mathcal{E}(u^{X_A}|A_{kl})\mathcal{P}(A_{kl}) = \sum_{(k,l)} u^1\{\mathcal{E}(u^{X_A})\}^k\{\mathcal{E}(u^{X_B})\}^{l-1}\mathcal{P}(A_{kl}) = \frac{u}{r}\sum_{(k,l)} lp_{kl}a^kb^{l-1} = \left(\frac{u}{r}\right)\frac{\partial P}{\partial b} \quad (7a)$$

Similarly

$$b = b(u) = \left(\frac{u}{r}\right)\frac{\partial P}{\partial a} \quad (7b)$$

These functional equations express the recursive nature of the tree model (cf. Figure 2). Let X_u, a random variable, be the size of the polymer containing a random unit. Define $\mathbf{w}_k \equiv \mathcal{P}(X_u = k)$. Call a polymer of k-units a k-mer. The probability that a random unit is in a k-mer equals the proportion of units in k-mers, i.e., the weight fraction of k-mers. Hence $\mathbf{w}_k$ is the weight fraction of k-mers. Call the event that a random unit has k reacted A's and l reacted B's U_{kl}. Conditioning the pgf of $\{\mathbf{w}_k\}$ on U_{kl} gives

$$\sum_{k=1}^{\infty} \mathbf{w}_k u^k = \sum_{k=1}^{\infty} \mathcal{P}(X_u = k)u^k = \mathcal{E}(u^{X_u}) = \sum_{(k,l)} \mathcal{E}(u^{X_u}|U_{kl})\mathcal{P}(U_{kl}) = \sum_{(k,l)} p_{kl}u\{\mathcal{E}(u^{X_A})\}^k\{\mathcal{E}(u^{X_B})\}^l = uP(a,b) \quad (8)$$

Proof: Given a unit has k reacted A's and l reacted B's (the event U_{kl}), the size of the polymer containing the unit (X_u) is 1 (the unit itself) plus the number of units that the k reacted A's and l reacted B's lead to. Equation 8 is derived like eq 7a; eq 3 and 5 complete the proof. Therefore

$$\mathbf{w}_k = \mathcal{C}(u^k)\{uP(a,b)\} \quad (9)$$

where *the operator* $\mathcal{C}(u^k)\{\cdot\}$ *indicates extraction of the coefficient of* u^k.

The mole fraction of k-mers, $\mathbf{x}_k$, is the proportion of k-mers among the polymers. Note that $\mathbf{w}_k$ is proportional to $k\mathbf{x}_k$, $\sum_{(k)}\mathbf{x}_k = 1$. Since integration by u divides the coefficient of u^{k-1} by k (see eq 9), $\mathbf{x}_k$ is proportional to $\mathcal{C}(u^k)\{\int_0^u P(a,b)\,\mathrm{d}u\}$

Define

$$Z = \int_0^u P(a,b)\,\mathrm{d}u \quad (10)$$

For any power series $F(u)$, define

$$\dot{F} \equiv u\frac{\mathrm{d}F}{\mathrm{d}u} \quad (11)$$

(this operator multiplies the coefficient of u^k by k).

Therefore

$$\dot{Z} = \sum_{(k)} \mathbf{w}_k u^k \quad (12)$$

$\dot{Z}$, a, and b are probability generating functions when expanded in powers of u. Hence

$$\dot{Z}]_{u=1} = a]_{u=1} = b]_{u=1} = 1 \quad (13)$$

where $]_{u=1}$ *denotes evaluation at* $u = 1$.

We now calculate the average molecular weights for the system.

Molecular Weights. If the molecular weight of a unit is scaled to 1, then the mole-average molecular weight for the system is (Flory[5])

$$\mathbf{M}_1 \equiv \frac{\sum k\mathbf{x}_k}{\sum \mathbf{x}_k} = \frac{\dot{Z}}{Z}\Big]_{u=1} = \frac{1}{Z}\Big]_{u=1} \quad (14)$$

The weight-average molecular weight is

$$\mathbf{M}_2 \equiv \frac{\sum k\mathbf{w}_k}{\sum \mathbf{w}_k} = \frac{\ddot{Z}}{\dot{Z}}\Big]_{u=1} = \ddot{Z}]_{u=1} \quad (15)$$

where $\ddot{Z} = Z$ with the operator 11 applied twice.

Integrating (10) by parts gives

$$Z = uP(a,b) - \int_0^u u\left\{\frac{\partial P}{\partial a}\,\mathrm{d}a + \frac{\partial P}{\partial b}\,\mathrm{d}b\right\} = \dot{Z} - rab \quad (16)$$

by eq 7. Evaluating at $u = 1$ gives

$$\mathbf{M}_1 = (1 - r)^{-1} \quad (17)$$

by (13) and (14).

Applying the operator 11 to (16) gives

$$\dot{Z} = \ddot{Z} - r(\dot{a}b + a\dot{b}) \quad (18)$$

Doing the same to (7a) and (7b) gives simultaneous equations for $\dot{a}$ and $\dot{b}$:

$$\begin{bmatrix} r - u\dfrac{\partial^2 P}{\partial a\partial b} & -u\dfrac{\partial^2 P}{\partial b^2} \\ -u\dfrac{\partial^2 P}{\partial a^2} & r - u\dfrac{\partial^2 P}{\partial a\partial b} \end{bmatrix} \begin{bmatrix} \dot{a} \\ \dot{b} \end{bmatrix} = \begin{bmatrix} u\dfrac{\partial P}{\partial a} \\ u\dfrac{\partial P}{\partial b} \end{bmatrix} \quad (19)$$

Evaluate this equation at $u = 1$, then denote the left-hand 2 × 2 matrix by J. Substitution into (18) evaluated at $u = 1$ gives

$$\mathbf{M}_2 = 1 + r[1 \quad 1]J^{-1}\begin{bmatrix} r \\ r \end{bmatrix} \quad (20)$$

(recall eq 15, eq 13, and the value of r: eq 4.) Simplifying (20) gives

$$\mathbf{M}_2 = 1 + \frac{r^2}{\det J}\left\{\frac{\partial^2 P}{\partial a^2} - 2\frac{\partial^2 P}{\partial a\partial b} + \frac{\partial^2 P}{\partial b^2} + 2r\right\} \quad (21)$$

where *all the partial derivatives are evaluated for* $a = b = 1$. Note that the partial derivatives are the moments $\mathcal{E}(A_u^2 - A_u)$, $\mathcal{E}(A_uB_u)$, and $\mathcal{E}(B_u^2 - B_u)$, respectively, of A_u and B_u (see (4)).

$$\det J = \left(r - \frac{\partial^2 P}{\partial a\partial b}\right)^2 - \left(\frac{\partial^2 P}{\partial a^2}\right)\frac{\partial^2 P}{\partial b^2} \quad (22)$$

(Again, partials are evaluated for $a = b = 1$.) Since $\mathbf{M}_2$ diverges when $\det J = 0$, we have the following *gelation criterion*

$$\left(r - \frac{\partial^2 P}{\partial a\partial b}\right)^2 = \left(\frac{\partial^2 P}{\partial a^2}\right)\frac{\partial^2 P}{\partial b^2} \quad (23)$$

We now give the polymer size distribution.

Size Distribution. The weight fraction of k-mers, $\mathbf{w}_k$, is the coefficient of u^{k-1} in $P(a,b)$, expanded in powers of u (see (9)). To extract this coefficient one must replace u in (7a) by y and in (7b) by z. By Good's multivariable generalization of Lagrange's expansion[10] (given in the Appendix), the coefficient of $y^m z^n$ in $P(a,b)$, when $P(a,b)$ is expanded in powers of y and z, is ("ln" denotes log natural to the base e)

$$\mathcal{C}(y^m z^n)\{P(a,b)\} = \mathcal{C}(a^m b^n)\left\{\{P(a,b)\}\left[\left(\frac{1}{r}\right)\frac{\partial P}{\partial b}\right]^m\left[\left(\frac{1}{r}\right)\frac{\partial P}{\partial a}\right]^n \times \left[\left(1 - a\frac{\partial}{\partial a}\ln\frac{\partial P}{\partial b}\right)\left(1 - b\frac{\partial}{\partial b}\ln\frac{\partial P}{\partial a}\right) - ab\left(\frac{\partial}{\partial a}\ln\frac{\partial P}{\partial a}\right)\left(\frac{\partial}{\partial b}\ln\frac{\partial P}{\partial b}\right)\right]\right\} \quad (24)$$

(The expression on the right must be expanded in powers of a and b now.) Setting $y = z = u$ in $P(a,b)$ shows that this expression contributes to the coefficient of u^{m+n} in $P(a,b)$ expanded in powers of u. Hence

$$\mathbf{w}_k = \mathcal{C}(u^{k-1})\{P(a,b)\} = \sum_{m+n=k-1} \mathcal{C}(y^m z^n)\{P(a,b)\} \quad (25)$$

which gives the size distribution.

Postgelation Results

If gelation has occurred, the sol parameters are not determined by the unconditional probabilities p_{kl} but by $\hat{p}_{kl}$, *the probability that a unit has k reacted* A's *and l reacted* B's, *conditional on that unit being in the sol* (see Gordon and Ross-Murphy[11]).

Choose a reacted B group from the system at random. The probability that all the remaining groups on its unit have a finite number of progeny is the *extinction probability* $\hat{a}$. Define $\hat{b}$ analogously. The extinction probabilities satisfy

$$\hat{a} = \frac{\sum_{(k,l)} l p_{kl} \hat{a}^k \hat{b}^{l-1}}{\sum_{(k,l)} l p_{kl}} \quad (26)$$

$$\hat{b} = \frac{\sum_{(k,l)} k p_{kl} \hat{a}^{k-1} \hat{b}^{l}}{\sum_{(k,l)} k p_{kl}} \quad (27)$$

Take, for example, eq 26. The probability $\hat{a}$ is the probability of choosing a unit at random (p_{kl}) and then choosing one of its reacted B's (l) (the denominator normalizes the relative likelihoods of the outcomes to probabilities). $\hat{a}^k \hat{b}^{l-1}$ is the probability that the remaining groups have finite progeny (compare with eq 7a and 7b).

The physically relevant $(\hat{a},\hat{b})$ *are the smallest positive roots of* (26) *and* (27). $(\hat{a},\hat{b}) = (1,1)$ *are always roots of* (26) *and* (27) *and are the smallest positive roots if gelation has not occurred.*

The conditional probabilities $\hat{p}_{kl}$ are

$$\hat{p}_{kl} = p_{kl} \hat{a}^k \hat{b}^l \Big/ \sum_{(k,l)} p_{kl} \hat{a}^k \hat{b}^l \quad (28)$$

since a unit is in the sol when all its reacted groups have finite progeny. (Note that the denominator, $P(\hat{a},\hat{b})$, is the probability that a unit is in the sol; i.e., $P(\hat{a},\hat{b})$ *gives the proportion of units in the sol.*)

Substitution of $\hat{p}_{kl}$ for p_{kl} in the pregelation formulas for sol sizes and average molecular weights yields the corresponding postgelation results.

Independence of A and B

If the status of the A groups on a unit are probabilistically independent of the status of the B groups, then $p_{kl} = s_k t_l$ (eq 3) and

$$P(a,b) = S(a)T(b) \quad S(1) = T(1) = 1 \quad (29)$$

where S and T are the generating functions for $\{s_k\}$ and $\{t_l\}$.

Slight simplifications occur in the gelation criterion (23)

$$r^2(1 - r)^2 = S''(1)T''(1) \quad r = S'(1) = T'(1) \quad (30)$$

and the formula (eq 24) determining $\mathbf{w}_k$

$$\mathcal{C}(y^m z^n)\{P(a,b)\} = r^{-(m+n)}[\mathcal{C}(a^m)\{S^m(S')^n(S - aS')\}\mathcal{C}(b^n)\{T^n(T')^m(T - bT')\} - \mathcal{C}(a^{m-1})\{S^{m+1}(S')^{n-1}S''\}\mathcal{C}(b^{n-1})\{T^{n+1}(T')^{m-1}T''\}] \quad (31)$$

where $S = S(a)$, $S' = S'(a)$, $T = B(b)$, etc.

For Flory's equireactive A_gRB_{f-g} *model*

$$S(a) = (1 - \alpha + \alpha a)^g \qquad T(b) = (1 - \beta + \beta b)^{f-g} \quad (32)$$

The gelation condition (30) becomes

$$(1 - r)^2 = (g - 1)(f - g - 1)\alpha\beta \quad r = g\alpha = (f - g)\beta \quad (33)$$

After conversion of notation, this agrees with the gelation condition for the A_gRB_{f-g} model given by Spouge.[6]

Equation 31 becomes

$$\mathcal{C}(y^m z^n)\{P(a,b)\} = (1 - \alpha)^g(1 - \beta)^{f-g}[\alpha\beta(1 - \alpha)^{g-1}(1 - \beta)^{f-g-1}/r]^{m+n} v_{mn} \quad (34)$$

where

$$v_{mn} = \frac{g^n(f - g)^m[g(f - g)(m + n + 1) - gm - (f - g)n]}{[(g - 1)(m + n + 1) + 1][(f - g - 1)(m + n + 1) + 1]} \times \binom{(g - 1)(m + n + 1) + m}{m} \times \binom{(f - g - 1)(m + n + 1) + n}{n} \quad (35)$$

Substitution of (34) and (35) into the eq 25 for the weight fraction w_k agrees with this author's previous result (Spouge,[7] which did not employ branching processes), because the w_k of that paper (*which are not the weight fractions* $\mathbf{w}_k$) satisfy

$$k w_k / k! = \sum_{m+n=k-1} v_{mn} \quad (36)$$

(cf. (34) and (25)). The w_k's satisfy (Spouge[6,7])

$$w_1 = 1, \qquad 2(k - 1)\frac{w_k}{k!} = \sum_{i=1}^{k-1} \frac{w_i}{i!} \frac{w_{k-i}}{(k - i)!}\{2 + (f - 2)k + 2(g - 1)(f - g - 1)i(k - i)\} \quad (37)$$

Equations 35 and 36 give a closed formula for the w_k, but recursion 37 is computationally more efficient.

The extinction probabilities (26) and (27) in the equireactive case satisfy

$$\hat{a} = (1 - \alpha + \alpha\hat{a})^g(1 - \beta + \beta\hat{b})^{f-g-1} \quad (38)$$

$$\hat{b} = (1 - \alpha + \alpha\hat{a})^{g-1}(1 - \beta + \beta\hat{b})^{f-g} \quad (39)$$

These give

$$\hat{a}(1 - \beta + \beta\hat{b}) = \hat{b}(1 - \alpha + \alpha\hat{a}) \quad (40)$$

which eliminates $\hat{b}$ in (38) to give

$$\hat{a} = F(\hat{a}) = (1 - \alpha + \alpha\hat{a})^g\{(1 - \beta)[1 + (\beta\hat{a})/(1 - \alpha + (\alpha - \beta)\hat{a})]\}^{f-g-1} \quad (41)$$

Iteration of $F(\hat{a})$, starting at $\hat{a}_0 = 0$ to avoid the root $\hat{a} = 1$, converges to the smallest positive root of this equation.

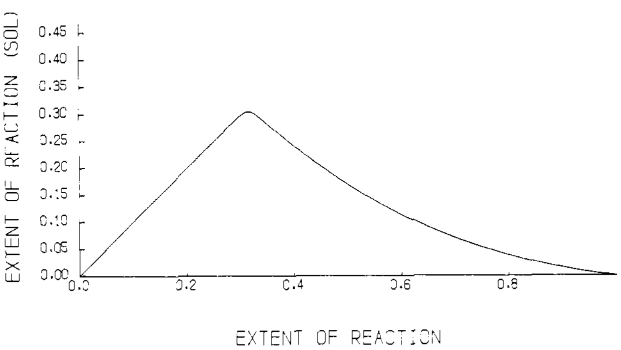

Figure 3. Graph of the extent of reaction in the sol against the overall extent of reaction. They are equal starting from 0 until a gel forms at α_c, when there is a sharp peak (rounded by computer error). The sol extent of reaction then declines monotonously to 0, at which point the gel contains every unit. (The values were computed for the equireactive A_2RB_3 model.)

The *conditional probability generating function for the sol* is

$$\hat{P}(a,b) \equiv \sum_{(k,l)} \hat{p}_{kl} a^k b^l = \frac{(1-\alpha+\alpha\hat{a}\cdot a)^g (1-\beta+\beta\hat{b}\cdot b)^{f-g}}{(1-\alpha+\alpha\hat{a})^g (1-\beta+\beta\hat{b})^{f-g}} = \left\{\frac{1-\alpha}{1-\alpha+\alpha\hat{a}} + \frac{\alpha\hat{a}}{1-\alpha+\alpha\hat{a}}a\right\}^g \left\{\frac{1-\beta}{1-\beta+\beta\hat{b}} + \frac{\beta\hat{b}}{1-\beta+\beta\hat{b}}b\right\}^{f-g} \quad (42)$$

(See (28) and (2)). Hence *the extents of reaction in the postgelation sol* are

$$\hat{\alpha} = \alpha\hat{a}/(1-\alpha+\alpha\hat{a}) \qquad \hat{\beta} = \beta\hat{b}/(1-\beta+\beta\hat{b})$$

As in Flory's RA_f model (Flory[5]), the postgelation sol at increasing extents of reaction mimics the pregelation sol at decreasing extents of reaction (see Figure 3).

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Appendix

Good's[10] generalization of Lagrange's expansion (stated for 2 variables) is to let $a = yG(a,b)$ and $b = zH(a,b)$, where G and H are analytic in a neighborhood of the origin with $G(0,0) \neq 0$ and $H(0,0) \neq 0$. Then, for any $P(a,b)$ analytic (or even meromorphic) at (0,0)

$$\mathscr{C}(y^m z^n)\{P(a,b)\} = \mathscr{C}(a^m b^n)\{P(a,b)[G(a,b)]^m [H(a,b)]^n \det \mathbf{D}\}$$

where

$$D = \begin{bmatrix} 1 - a\frac{\partial}{\partial a}(\ln G) & -a\frac{\partial}{\partial a}(\ln H) \\ -b\frac{\partial}{\partial b}(\ln G) & 1 - b\frac{\partial}{\partial b}(\ln H) \end{bmatrix}$$

and "ln" denotes log natural to the base e.

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Notes

Molecular Motion of Branched-Chain Polysaccharides Studied by ^{13}C NMR Spin-Lattice Relaxation Rates

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Structural determination of the sequence of polysaccharides by chemical and enzymatic means is a time-consuming and difficult study. However, NMR spectroscopy, particularly ^{13}C NMR, has proved to be an indispensable tool in the structural analysis of polysaccharides.[1] Today NMR spectroscopy is extensively used for structure elucidation as it demonstrates the existence of a regularly repeated unit in the sequence and as it is an essential tool for obtaining direct evidence of the number of sugar residues in the repeating unit. Furthermore, NMR spectroscopy makes it easy to ascertain the anomeric configuration of glycosidic linkages in polysaccharide structures through the one-bond $^{13}C-^{1}H$ coupling constants.[1,2] ^{13}C NMR spectroscopy is thus well suited for structural analysis of polysaccharides because it gives well-defined spectra even in the case of complex and large repeating units. However, an analysis of the ^{13}C chemical shifts and coupling constants does not unambiguously determine the sequence of the monosaccharides that constitute the polysaccharide structure. Additional information on the sequence within the repeating unit can be obtained on the native polysaccharide by use of spin-lattice relaxation studies (R_1 values).

The background for the application of ^{13}C NMR spin-lattice relaxation rates in the study of macromolecular dynamics has recently been discussed in a review by Jardetzky[3] and in a theoretical paper by Bull.[4] Studies on the relaxation behavior of mono- and oligosaccharides have been carried out in order to prove that the relaxation mechanism for this type of compounds is dominated by the intramolecular dipole–dipole relaxation mechanism.[5,6]

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