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The instantaneous distribution of chain compositions and chain lengths in vinyl copolymers is obtained in a simple form valid for long chains. The compositions of chains of a given length are normally distributed about the mean value, with a standard deviation which can be calculated from experimentally observable quantities. The distribution of chain lengths intimately resembles that for simple polymers.

I. INTRODUCTION

RECENTLY several authors[1-3] have independently derived a simple differential equation[4] relating the over-all composition of a long-chain vinyl copolymer to that of its parent monomer solution, and this relation has been found to agree well with experimental data.[2] The distribution of sequences of like monomer units along the chains was also readily obtained.[1,3]

Since the molecular weight of a copolymer is finite, the compositions, as well as the lengths, of the individual molecules cannot all be identical; even in the copolymer formed during a very small time interval, there exists a distribution of chain lengths and compositions. Although one could reasonably expect the fluctuations of composition to be quite small for long molecules, it seems worth while to obtain a quantitative

estimate of their magnitude. A general theory of copolymerization which embraces this problem has been formulated by Simha and Branson,[5] but the equations given by them are unfortunately too complex for convenient use.[6] With the aid of further approximations (but no new assumptions) valid for long chains, the distribution of chain compositions and lengths can be expressed in a simple and tractable form. In this paper, the simplified result is derived, discussed, and illustrated.

II. MEAN COMPOSITION AND CHAIN LENGTH

In describing the mechanistic assumptions and the symbolism to be employed, some repetition of the discussion in previous papers[1-5] inevitably occurs. We consider a binary system with monomer concentrations A and B. The growing free-radical[7] chains present during polymeriza-

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[1] T. Alfrey and G. Goldfinger, J. Chem. Phys. 12, 205 and 322 (1944).
[2] F. R. Mayo and F. M. Lewis, J. Am. Chem. Soc. 66, 1594 (1944).
[3] F. T. Wall, J. Am. Chem. Soc. 66, 2050 (1944).
[4] See Eq. (5).

[5] R. Simha and H. Branson, J. Chem. Phys. 12, 253 (1944).
[6] Some of the equations and all of the numerical examples in the paper of Simha and Branson pertain to a special case which rarely, if ever, is found experimentally.
[7] The expression "free radical" is used advisedly, in conformity with present ideas regarding the most common polymerization mechanism. Actually the equations to be derived are valid for any mechanism in which the concen-
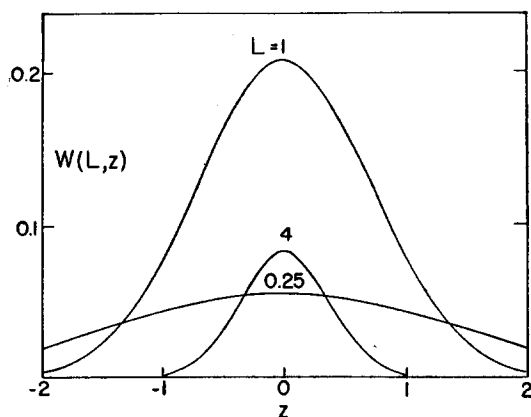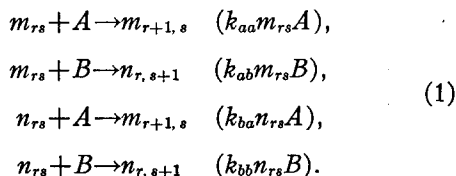
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FIG. 1. Reduced composition distribution according to Eq. (17). Weight fractions are plotted against the reduced composition-deviation at relative lengths of 0.25, 1, and 4.
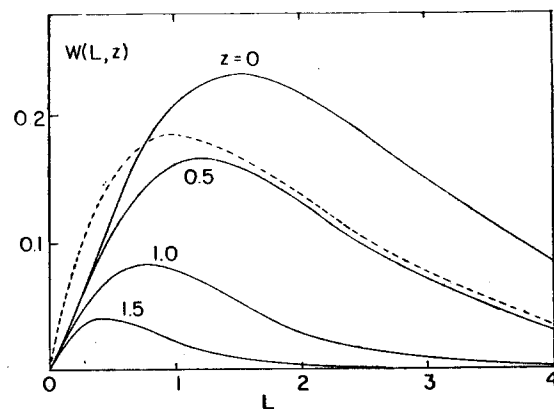

FIG. 2. Reduced chain-length distribution according to Eq. (17). Weight fractions are plotted against relative length at reduced composition-deviations of 0, 0.5, 1, and 1.5. The dashed curve is the distribution summed over all compositions, divided by two to facilitate comparison.

tion are called either A-radicals or B-radicals, according to the identity of the monomer unit at the active end. The total concentrations of A- and B-radicals of all lengths and compositions will be written m and n, respectively, while the symbols m_{rs} and n_{rs} denote the concentrations of such radicals composed specifically of r A-units and s B-units. If, as is usually assumed, the reactivity of a radical depends only on the nature of its active end (and not on its length or composition), just four different propagation (growth) reactions must be considered,[8] as set forth in the following scheme:

$$
\begin{aligned}
m_{rs} + A &\rightarrow m_{r+1, s} & (k_{aa}m_{rs}A), \\
m_{rs} + B &\rightarrow n_{r, s+1} & (k_{ab}m_{rs}B), \\
n_{rs} + A &\rightarrow m_{r+1, s} & (k_{ba}n_{rs}A), \\
n_{rs} + B &\rightarrow n_{r, s+1} & (k_{bb}n_{rs}B).
\end{aligned}
\tag{1}
$$

The expressions in parentheses following each equation denote the reaction rates. The bimolecular character of these propagation steps may be regarded as experimentally confirmed,[2] and no other specific kinetic assumptions are required.

The rates of formation of the two kinds of radicals by other than propagation steps will be denoted simply by $i_a A$ and $i_b B$. These rates thus

include not only true initiation processes, but also the possible formation of A- and B-radicals by addition of monomers to other types of radicals produced in chain transfer. Obviously, i_a and i_b are therefore usually not constants, but are functions of monomer, solvent, and catalyst concentrations.[9] Similarly, the rates at which the
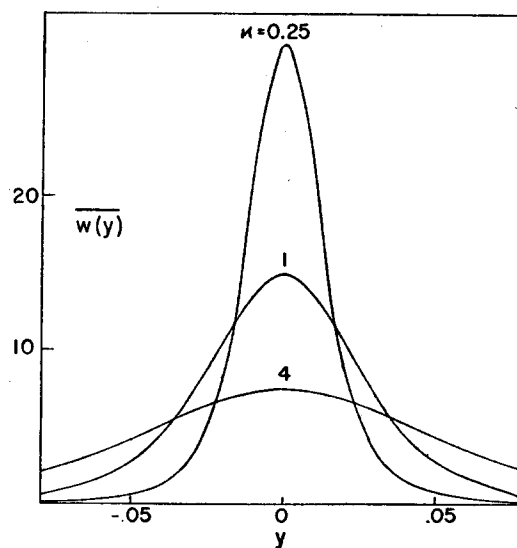
FIG. 3. Over-all distribution of compositions, according to Eq. (14), for copolymers with $\lambda/2p_0q_0 = 400$, showing the effect of the parameter κ.

tration of active growing chains (whether free radicals, ions, or excited molecules) is limited by some termination reaction to such small values that the steady-state assumption is valid.

[8] See the aforementioned articles, references 1–5, or earlier papers by R. G. W. Norrish and E. F. Brookman, Proc. Roy. Soc. (London) A171, 147 (1939) and E. Jenckel, Zeits. f. physik. Chemie A190, 24 (1941).

[9] For example, for the simple case of a peroxide-activated polymerization in which chain transfer is negligible, one might expect the following expressions to hold: $i_a A = k_{1a} C A$, $i_b B = k_{1b} C B$, $\tau_a m = k_{3m} m^2 + k_{3x} mn$, $\tau_b n = k_{3x} mn + k_{3n} n^2$, in which C is the peroxide concentration and the various k's are rate constants.

two kinds of radicals are converted into stable polymer (including chain-transfer processes) will be written $\tau_a m$ and $\tau_b n$, where the quantities τ_a and τ_b are certainly not constants.[9]

With these definitions, the total radical concentrations are governed by the equations

$$dm/dt = i_a A - k_{ab} mB + k_{ba} nA - \tau_a m,$$
$$dn/dt = i_b B - k_{ba} nA + k_{ab} mB - \tau_b n. \tag{2}$$

In practical cases, the chains are so long that propagation must be much more rapid than initiation or termination. With the neglect of these latter, the assumption of a steady state[10] $(dm/dt = dn/dt = 0)$ then gives the important approximate equality

$$k_{ab} mB = k_{ba} nA, \tag{3}$$

which, together with the rates of monomer consumption,

$$-dA/dt = k_{aa} mA + k_{ba} nA,$$
$$-dB/dt = k_{bb} nB + k_{ab} nB, \tag{4}$$

leads to the previously mentioned expression[1-3] for the over-all composition of the copolymer which is forming at any chosen time:

$$dA/dB = A(\alpha A + B)/B(A + \beta B) = p_0/q_0, \tag{5}$$

where

$$\alpha = k_{aa}/k_{ab}, \quad \beta = k_{bb}/k_{ba}.$$

For later use, we have here introduced the symbol $p_0 = 1 - q_0$ for the over-all mole fraction of A in the copolymer chains produced during the (infinitesimal) time interval when the monomer concentrations are A and B. The convenience of dealing with symmetrical equations leads us to retain a separate symbol q_0 for the over-all mole fraction of B. The "monomer reactivity ratios"[2] α and β, which with the aid of Eq. (5) may be obtained from experimental studies of copolymer compositions, also play a role in determining the distribution of chain compositions.

The number-average length (polymerization degree) λ of the growing radical chains is simply the total rate of monomer consumption, $-d(A+B)/dt$, divided by the rate either of radical production or of radical termination;[11] thus,

$$\lambda = \frac{-d(A+B)dt}{\tau_a m + \tau_b n} = \frac{\alpha A^2 + 2AB + \beta B^2}{(\tau_a A/k_{ab}) + (\tau_b B/k_{ba})}, \tag{6}$$

with the aid of Eqs. (3) and (4). If all the chains terminate by disproportionation of radicals, the number-average length of the stable polymer chains is also λ; if all the chains combine in pairs when mutually terminating, it is 2λ. In view of the unspecified concentration-dependence of the termination parameters τ_a and τ_b, Eq. (6) is of no direct use as it stands. We shall employ it only to express the chain-length distribution conveniently in terms of the mean chain length.

III. DISTRIBUTION OF COMPOSITIONS AND LENGTHS

When the steady-state condition is applied separately to radicals of each length and composition, the following recursion formulae result:

$$\frac{dm_{rs}}{dt} = k_{aa} A m_{r-1,\,s} + k_{ba} A n_{r-1,\,s} - (k_{aa} A + k_{ab} B + \tau_a) m_{rs} = 0,$$

$$\frac{dn_{rs}}{dt} = k_{bb} B n_{r,\,s-1} + k_{ab} B m_{r,\,s-1} - (k_{bb} B + k_{ba} A + \tau_b) n_{rs} = 0. \tag{7}$$

The species m_{10} and n_{01}, of course, follow different equations, involving $i_a A$ and $i_b B$, respectively. The solution of Eqs. (7) is[5]

$$m_{rs} = \omega_a{}^r \omega_b{}^s \left[\frac{i_a}{k_{aa}} \sum_{j \geq 1} \binom{r-1}{j} \binom{s-1}{j-1} x^j + \frac{i_b}{k_{ab}} \sum_{j \geq 1} \binom{r-1}{j-1} \binom{s-1}{j-1} x^j \right],$$

$$n_{rs} = \omega_a{}^r \omega_b{}^s \left[\frac{i_a}{k_{ba}} \sum_{j \geq 1} \binom{r-1}{j-1} \binom{s-1}{j-1} x^j + \frac{i_b}{k_{bb}} \sum_{j \geq 1} \binom{r-1}{j-1} \binom{s-1}{j} x^j \right], \tag{8}$$

[10] For a brief discussion of the conditions of validity of this assumption, see W. H. Stockmayer, J. Chem. Phys. 12, 143 (1944).

[11] On the steady-state assumption, radicals are made and destroyed at equal rates, so that $i_a A + i_b B = \tau_a m + \tau_b n$.

where

$$\omega_a = k_{aa}A/(k_{aa}A + k_{ab}B + \tau_a), \quad \omega_b = k_{bb}B/(k_{bb}B + k_{ba}A + \tau_b), \quad x = k_{ab}k_{ba}/k_{aa}k_{bb} = 1/\alpha\beta.$$

For the pure radical species m_{r0} and n_{0s} the equations are simpler, but they need not be considered here.

A physical interpretation of Eqs. (8) is not difficult.[5] Each expression falls into two sums, the first describing chains which began with an A-unit and the second those which began with a B-unit. A single term within a sum denotes radicals in which j cross-additions of one kind (A to B in the first equation and B to A in the second) have occurred, and the combinatory factor gives the number of ways (sequences of addition) in which such radicals can be built up. The fractions ω_a and ω_b are propagation probabilities for homogeneous addition (A to A and B to B), while x is a measure of the relative probability of cross-addition.

The procedure followed in simplifying Eqs. (8) is described in some detail in the Appendix. In brief, the sums over j are approximated by integrals and evaluated with the aid of Stirling's formula. The logarithm of m_{rs} can then be expanded as a power series in the composition-deviation y, defined by

$$y = p - p_0 = q_0 - q, \tag{9}$$

where $p = 1 - q = r/(r+s)$ is the composition of an individual chain and $p_0 = 1 - q_0$ is the over-all composition. This procedure leads naturally to a Gaussian distribution[12] of chain compositions about the mean value. To this approximation, the distributions for A- and B-radicals are identical.

The final result is most compactly expressed as a continuous weight distribution, in which equal weights are assigned to the two types of monomer unit. The weight fraction of radicals with lengths (polymerization degrees) between l and $l+dl$ and composition-deviations between y and $y+dy$ is then given by

$$w(l, y)dldy = [\exp(-l/\lambda)ldl/\lambda^2][(l/2\pi p_0 q_0 \kappa)^{\frac{1}{2}}\exp(-ly^2/2p_0 q_0 \kappa)dy], \tag{10}$$

where

$$\kappa = [1 - 4p_0 q_0(1 - \alpha\beta)]^{\frac{1}{2}}$$

$$= \frac{\alpha A^2 + 2\alpha\beta AB + \beta B^2}{\alpha A^2 + 2AB + \beta B^2},$$

and λ is the number-average length of the radicals given in Eq. (6).

If the termination step is entirely one of disproportionation, Eq. (10) also describes the distribution of the stable polymer forming at any instant, for then the concentration N_{rs} of stable chains of the indicated length and composition is determined by the equation

$$dN_{rs}/dt = \tau_a m_{rs} + \tau_b n_{rs}. \tag{11}$$

More generally, if a fraction ρ of the radical chains were terminated by combination, the stable polymer distribution would be

$$w(l, y)dldy = [\exp(-l/\lambda)(1 - \rho + \rho l/2\lambda)ldl/\lambda^2] \times [(l/2\pi p_0 q_0 \kappa)^{\frac{1}{2}}\exp(-ly^2/2p_0 q_0 \kappa)dy], \tag{12}$$

in which λ still denotes the number-average length of the *radicals*. This result is in complete analogy with the size distribution for pure polymers.[13] The radical distribution, of course, is unaffected by the nature of the termination process, being always given by Eq. (10).

It should be emphasized that the distribution equations are as generally applicable as the experimentally confirmed Eq. (5), for no additional assumptions are required for their derivation. Only

[12] For copolymers with a very small percentage of one component ($p_0 \ll q_0$), an equivalent Poisson distribution could be obtained if desired.
[13] E. F. G. Herington and A. Robertson, Trans. Faraday Soc. **38**, 490 (1942).

the uncertainty with respect to the termination process mars their quantitative utility, and this can be seen to affect only the distribution of lengths. It may be concluded that Eqs. (10) and (12) are no less valid than the theoretical distributions heretofore derived for pure polymers. In the paragraphs to follow, we shall for simplicity use Eq. (10) as it stands.

To find the chain-length distribution irrespective of composition, Eq. (10) must be integrated over y. The limits of integration may be taken as infinite because the distribution of compositions is narrow, and in fact the equation is already normalized to these limits. The result is therefore simply

$$\langle w(l) \rangle dl = \exp(-l/\lambda)ldl/\lambda^2, \tag{13}$$

which is exactly the equation for pure polymers terminating entirely by disproportionation.[13]

The over-all distribution of compositions irrespective of chain length is found in similar fashion by integrating over l, the result being

$$\langle w(y) \rangle dy = \frac{3dz}{4(1+z^2)^{5/2}}, \tag{14}$$

with

$$z^2 = \lambda y^2/2p_0 q_0 \kappa.$$

It is interesting to express the parameter κ, which controls the spread of chain compositions, in somewhat different terms. For sufficiently long chains, the number-average lengths of sequences of like monomer units are given[1, 3] by

$$\bar{l}_A = 1+(\alpha A/B), \quad \bar{l}_B = 1+(\beta B/A). \tag{15}$$

Employing these relations together with Eq. (5), one obtains

$$\kappa = p_0(\bar{l}_B-1)+q_0(\bar{l}_A-1), \tag{16}$$

identifying κ as a certain kind of average sequence length. Thus longer sequences correspond to a broader distribution of compositions, as would be expected.

For the special case $\alpha\beta=1$, which corresponds to an earlier theory of Wall,[14] and which also was given great prominence in the work of Simha and Branson,[5] Eq. (10) shows that $\kappa=1$. In fact, for this case the distribution of compositions could have been written down directly, for if $\alpha\beta=1$ the probability of chain growth depends solely on the nature and concentration of the monomers, and not at all on the type of active end possessed by the growing chain.

The distribution may be more compactly expressed in terms of the relative length, $L=l/\lambda$, and the reduced composition-deviation, $z=(\lambda/2p_0q_0\kappa)^{\frac{1}{2}}y$, which has already been introduced in Eq. (14). With these substitutions, Eq. (10) becomes

$$w(l, y)dldy = W(L, z)dLdz = \pi^{-\frac{1}{2}}L^{\frac{3}{2}} \exp[-L(1+z^2)]dLdz. \tag{17}$$

The shape of the $W(L, z)$ surface thus defined can be visualized from Figs. 1 and 2, in which $W(L, z)$ is plotted against z for several values of L, and against L for several values of z. It is seen that greater deviations of composition occur in the shorter chains, and conversely that chains with the average composition are the longest.

The magnitude of the effect produced by a change in κ may be judged from Fig. 3, in which the over-all distribution of chain compositions, given by Eq. (14), is plotted for several systems with an arbitrarily chosen value of $\lambda/2p_0q_0=400$. The abscissa scale is seen to be proportional to the quantity $(2p_0q_0\kappa/\lambda)^{\frac{1}{2}}$, which is a convenient measure of the breadth of the distribution, for integration of Eq. (14) shows that 88.4 percent by weight of the copolymer falls in the range $|y| < (2p_0q_0\kappa/\lambda)^{\frac{1}{2}}$.

It must be emphasized that the practical utility of Eq. (10) and its corollaries is severely limited, in that only the distribution for the copolymer forming at any instant is described. Since the

[14] F. T. Wall, J. Am. Chem. Soc. 63, 1862 (1941).

parameters p_0, q_0, κ, and λ will in general change as the reaction proceeds,[15] these equations may safely be used only for copolymers of very low conversion. For higher conversions, the instantaneous spread of compositions will often be quite insignificant in comparison with the steady change of the mean composition, governed by Eq. (5), as the reaction progresses. In principle, the complete distribution for a high-conversion copolymer could be found by integration from Eqs. (5) and (10) and a detailed knowledge of the dependence of λ on concentration and conversion. In the absence of the latter information, such an effort would at present necessarily be speculative and scarcely worthwhile.

It should be possible to subject the distribution formulae to experimental test, preferably by fractionating "azeotropic" copolymers of low conversion. These should have rather low average molecular weights, in order to secure a sufficiently broad distribution of compositions.

Because of their simplicity of form and interpretation, these distribution equations should be of at least qualitative assistance to a better understanding of the relationship between structure and properties of copolymers.

APPENDIX

Since the symmetry of Eqs. (8) is obvious, it will be sufficient to consider the expression for $m_{rs}{'}$ which can be rewritten in the form

$$m_{rs} = (\omega_a{}^p \omega_b{}^q)^l [(i_a/k_{aa})(S_0/q - S_1/pq) + (i_b/k_{ab})(S_1/pq)], \tag{A1}$$

where

$$l = r + s, \quad p = r/l, \quad q = s/l = 1 - p;$$

and

$$S_n = \sum_j (j/l)^n T_j,$$

with

$$T_j = (j/l)x^j \binom{lp}{j}\binom{lq}{j}.$$

For reasons of symmetry, it is convenient to retain both p and q as symbols.

For large l, Stirling's formula may be used to evaluate the combinatory factors. Putting $j = lw$, we have

$$T_j = wx^{lw}\binom{lp}{lw}\binom{lq}{lw}, \tag{A2}$$

and hence

$$\ln T_j \cong -\ln(2\pi l) - \tfrac{1}{2}\ln[(p-w)(q-w)/pq]$$
$$+ l[w\ln x - 2w\ln w - (p-w)\ln(p-w) - (q-w)\ln(q-w)]. \tag{A3}$$

By differentiating this expression, we obtain

$$\partial \ln T_j/\partial w = \tfrac{1}{2}\left(\frac{1}{p-w} + \frac{1}{q-w}\right) + l\ln\left[\frac{x(p-w)(q-w)}{w^2}\right], \tag{A4}$$

from which it is seen that T_j passes through a maximum at a certain value of w. For large l, only the last term in Eq. (A4) need be retained. Setting $w_{max} = u$, we therefore have

$$u^2 = x(p-u)(q-u), \tag{A5}$$

or

$$u = \{1 - [1 - 4pq(1 - 1/x)]^{\frac{1}{2}}\}/2(1 - 1/x), \tag{A6}$$

where the negative root is necessary because $u(= w_{max} = j_{max}/l)$ may not exceed unity.

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[15] In the special case of an "azeotropic" copolymerization, reference 3, p_0 and κ remain constant, but λ may still change.

We may pause to recall that j is the number of cross-additions of one kind (actually, A to B) in the chain. Hence $u(=j_{max}/l)$ is the most probable fraction of such bonds in a chain of length l and composition p. For chains with the mean composition p_0, the use of Eq. (5) of the text, together with the relation $x=1/\alpha\beta$, gives, from Eq. (A6), the result

$$u_0=AB/(\alpha A^2+2AB+\beta B^2), \tag{A7}$$

which is readily shown[3] to be the fraction of $A-$ to $-B$ additions taken over all the chains.

The value of a general term T_j may now be found in relation to the maximum term T_m by setting $w=u+v$ and expanding in powers of v. With the aid of Eq. (A5) to effect cancellation, we find

$$(1/l) \ln (T_j/T_m) = -\mu^2 v^2+O(v^3, 1/l), \tag{A8}$$

with $\mu^2=(1/u)+(1-2u)/2(p-u)(q-u)$.

The Euler-Maclaurin sum formula shows that, for large l, the sums defining S_0 and S_1 may be replaced by integrals with little error. Furthermore, the limits of integration may be extended to infinity, because the maximum in T_j is sharp; in fact, as is usual in such problems, the use of infinite limits is consistent with the previous approximations. We therefore may write

$$S_0=\sum_j T_j \cong \int T_j dj=lT_m\int_{-\infty}^{+\infty} \exp (-l\mu^2v^2)dv=(\pi l)^{\frac{1}{2}}T_m/\mu. \tag{A9}$$

Since the maximum term in S_1 occurs at practically the identical value of j, we also have

$$S_1=\sum_j wT_j \cong lT_m\int_{-\infty}^{+\infty} (u+v) \exp (-l\mu^2v^2)dv=uS_0. \tag{A10}$$

At this stage, Eq. (A1) can be rewritten to read

$$m_{rs}=(\omega_a^p\omega_b^q)^l S_0\left[(i_a/k_{aa})\left(\frac{p-u}{pq}\right)+(i_b/k_{ab})(u/pq) \right], \tag{A11}$$

but the dependence of S_0 on l and p, q must be more explicitly stated. By substitution for T_m and μ in Eq. (A9), with the aid of Eqs. (A3), (A5), and (A8), there is obtained

$$\ln S_0= -\tfrac{1}{2} \ln (2\pi l)+\tfrac{1}{2} \ln \frac{pq}{(p-u)(q-u)}-\tfrac{1}{2} \ln \left[\frac{2}{u}+\frac{1-2u}{(p-u)(q-u)}\right]$$
$$+l\left[p \ln \left(\frac{p}{p-u}\right)+q \ln \left(\frac{q}{q-u}\right)\right], \tag{A12}$$

for chains of length l and composition p, q.

We next proceed to expand $\ln S_0$ about its value for chains having a composition p_0, q_0 which equals the over-all composition as given by Eq. (5) of the text. The deviation from this mean composition will be defined as

$$y=p-p_0=q_0-q. \tag{A13}$$

Before attacking Eq. (A12), we require an expansion for u. Eq. (6) leads to

$$u-u_0=y(q_0-p_0)/\kappa+y^2[(q_0-p_0)^2(1-1/x) - \kappa^2]/\kappa^3+O(y^3), \tag{A14}$$

where the important new quantity κ, which persists in the final equations, is defined by

$$\kappa=[1-4p_0q_0(1-1/x)]^{\frac{1}{2}}$$
$$=(\alpha A^2+2\alpha\beta AB+\beta B^2)/(\alpha A^2+2AB+\beta B^2). \tag{A15}$$

Now, upon entering Eq. (A12) with Eqs. (A13) and (A14), there is obtained, after a lengthy but straightforward expansion and collection of terms, the result

$$S_0 = \left(\frac{p_0 q_0}{2\pi l \kappa}\right)^{\frac{1}{2}} \left(\frac{p_0}{p_0 - u_0}\right)^{pl} \left(\frac{q_0}{q_0 - u_0}\right)^{ql} \exp\ (-ly^2/2p_0 q_0 \kappa), \tag{A16}$$

in which terms of $O(y^3)$ in $\ln S_0$ have been neglected.

Before inserting this expression into Eq. (A11), we note the equalities

$$p_0/(p_0 - u_0) = (\alpha A + B)/\alpha A = (k_{aa}A + k_{ab}B)/k_{aa}A,$$

$$q_0/(q_0 - u_0) = (\beta B + A)/\beta B = (k_{bb}B + k_{ba}A)/k_{bb}B, \tag{A17}$$

which may be obtained from Eqs. (5) and (A7). Also, the dependence on composition is so over-whelmingly dictated by the last factor in Eq. (A16) that everywhere else the arbitrary composition p, q may be replaced by the mean composition p_0, q_0 without appreciable error. It can be shown that this maneuver amounts to neglecting a skewness in the distribution which becomes negligible for long chains. With the aid of the definitions of ω_a and ω_b given in Eq. (8) of the text, Eq. (A11) then yields

$$m_{rs} = \frac{A(i_a A + i_b B)}{k_{ab}(\alpha A^2 + 2AB + \beta B^2)} \xi^l (2\pi p_0 q_0 \kappa l)^{-\frac{1}{2}} \exp\ (-ly^2/2p_0 q_0 \kappa) \tag{A18}$$

where

$$\xi = \left(\frac{k_{aa}A + k_{ab}B}{k_{aa}A + k_{ab}B + \tau_a}\right)^{p_0} \left(\frac{k_{bb}B + k_{ba}A}{k_{bb}B + k_{ba}A + \tau_b}\right)^{q_0}.$$

The significance of the two factors in ξ as propagation probabilities, for $A-$ and $B-$ radicals respectively, is clear.

To obtain the total concentration of radical chains, summation over all compositions and lengths is required, but the approximations previously introduced are obviously consistent with integration over ly, followed by summation over l. Eq. (A18) is therefore more conveniently used in the form

$$m_l(y)dy = \frac{A(i_a A + i_b B)}{k_{ab}(\alpha A^2 + 2AB + \beta B^2)} \xi^l \left(\frac{l}{2\pi p_0 q_0 \kappa}\right)^{\frac{1}{2}} \exp\ (-ly^2/2p_0 q_0 \kappa)dy, \tag{A19}$$

where $m_l(y)dy$ is the concentration of A-radicals with length l and compositions lying between $(p_0 + y)$ and $(p_0 + y + dy)$. From the symmetry of Eqs. (8), a similar equation obviously applied to the B-radicals, $n_l(y)dy$ being given by Eq. (A19) with the factor A/k_{ab} replaced by B/k_{ba}. Thus the steady-state condition of Eq. (3) is seen to hold not only for the total radical concentrations, but also separately for radicals of each length and composition.

The concentration of radicals of length l but of all compositions is found by integration of Eq. (A19) to be

$$m_l = \int_{-\infty}^{+\infty} m_l(y)dy = A(i_a A + i_b B)\xi^l/k_{ab}(\alpha A^2 + 2AB + \beta B^2). \tag{A20}$$

Summation over l then gives the total concentration of A-radicals, yielding

$$m = \sum_{l \geq 1} m_l = [A(i_a A + i_b B)/k_{ab}(\alpha A^2 + 2AB + \beta B^2)][\xi/(1-\xi)]. \tag{A21}$$

For long chains, ξ must be nearly unity, and a sufficient approximation may be found by expanding:

$$\xi = [1 + \tau_a/(k_{aa}A + k_{ab}B)]^{-p_0}[1 + \tau_b/(k_{bb}B + k_{ba}A)]^{-q_0}$$

$$= 1 - [p_0\tau_a/(k_{aa}A + k_{ab}B)] - [q_0\tau_b/(k_{bb}B + k_{ba}A)] + \cdots \qquad (A22)$$

$$= 1 - [(\tau_a A/k_{ab}) + (\tau_b B/k_{ba})]/(\alpha A^2 + 2AB + \beta B^2) + \cdots.$$

Using this relation in Eq. (A21), we obtain

$$m = (A/k_{ab})((i_a A + i_b B)/[(\tau_a A/k_{ab}) + (\tau_b B/k_{ba})]), \qquad (A23)$$

and similarly

$$n = (B/k_{ba})((i_a A + i_b B)/[(\tau_a A/k_{ab}) + (\tau_b B/k_{ba})]). \qquad (A24)$$

These results are seen to be consistent with the steady-state requirement that

$$i_a A + i_b B = \tau_a m + \tau_b n. \qquad (A25)$$

The number-average length of the radicals is at once found to be

$$\lambda = \sum lm_l/\sum m_l = \sum ln_l/\sum n_l = 1/(1-\xi)$$

$$= (\alpha A^2 + 2AB + \beta B^2)/[(\tau_a A/k_{ab}) + (\tau_b B/k_{ba})], \qquad (A26)$$

as previously found more directly in Eq. (6) of the text.

We finally convert Eq. (A19) into a weight distribution. If equal weights are assigned to A- and B-monomers, the weight fraction $w_l(y)dy$ of chains of length l and compositions between $(p_0 + y)$ and $(p_0 + y + dy)$ is given by

$$w_l(y)dy = lm_l(y)dy/\sum lm_l$$

$$= l(1-\xi)^2\xi^{l-1}(l/2\pi p_0 q_0 \kappa)^{\frac{1}{2}} \exp(-ly^2/2p_0 q_0 \kappa)dy. \qquad (A27)$$

Since long chains have been assumed, the distribution of chain lengths can also be conveniently made continuous. With the substitution $\lambda = (1-\xi)^{-1}$ from Eq. (A26), the result is

$$w(l, y)dldy = [\exp(-l/\lambda)ldl/\lambda^2][(l/2\pi p_0 q_0 \kappa)^{\frac{1}{2}} \exp(-ly^2/2p_0 q_0 \kappa)dy], \qquad (A28)$$

which is Eq. (10) of the text.