# Theory of Chain Copolymerization Reactions*

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The kinetics of chain copolymerizations is developed for reactions consisting of three steps: first, an activation of stable monomer; second, a growth of activated polymer radical by means of monomer addition; third, a stabilization of the growing chains by (a) monomer addition, (b) by means of growing polymer [Eq. (1)]. The existence of a steady state in respect to the concentration of growing chains beyond the induction period is assumed. The rate constants of growth and termination will in general depend upon the individual composition and upon the nature of the activated chain end. Equations for the rate of change of mole ratio $z$ of the two monomer species are developed in terms of mean rates of growth and termination obtained by averaging the actual rates over the distribution of growing polymer [(4), (4a), (4')]. The equilibrium conditions lead to a set of difference equations for this distribution [(5), (5')]. It is investigated whether the solution and results derived therefrom are of a form which permits a determination of the dependence of the rate constants for growth and termination upon the composition of the polymer molecule (6). In addition, the influence of the type of active chain end involved on over-all rate and size distribution is considered by introducing four constants for propagation and termination, respectively, according to the four possibilities $A-A$, $A-B$, $B-A$, $B-B$ [(6a), (7), (4b), (4b')], but independent of chain composition. Various special cases according to the relative magnitude of the rates for the two reactants are presented. Experimentally it is difficult to distinguish on the basis of kinetic data between the foregoing mechanism and one in which the rates of growth (and termination) for each of the two kinds of monomer depend solely upon the nature of the monomer molecule added and are independent of the nature of the active chain end [(4c), (4c'), (4c'')]. Relations are derived for the molecular size distribution, the inhomogeneity of the copolymer mixture in regard to composition, the average molecular weight, and the average composition of copolymer as function of the composition of the monomer residue [(8a), (8a'), (9a), (10)]. The importance of these results for soluble and insoluble copolymers and for the theory of gel formation in vinyl-divinyl type polymers is pointed out.

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THE kinetics of chain polymerization reactions has been extensively treated.[1] Starting with the main elementary processes of chain initiation, propagation, and termination, it is possible to derive expressions for the over-all consumption of monomer, for the average chain length of the polymer formed during the various stages of the process and for the distribution of molecular weights. This in turn permits an analysis of the elementary rate constants, and therefore of energies of activation and frequency factors.

If two monomer species copolymerize, additional questions arise, e.g., the composition distribution of polymer, the molecular arrangement of the two types within a chain, particularly if one of the two species acts as cross-linking agent, as in the vinyl-divinyl copolymerization.

The kinetics of copolymer formation has re-

ceived much less attention than that of one-component systems. Norrish and Brookman[2] have considered the over-all rate of the chain process. Jenckel[3] was the first to specify the special types of copolymers obtainable, depending upon the relative values of the rate constants for the two species. However, since he did not introduce the initiation and termination, as pointed out by himself, his method is limited and the results obtained represent rather special cases, as will become evident in the following. Wall[4] has considered this question, however, without treating the process as a chain reaction governed by the above elementary processes. Instead, he starts with the assumption of a first-order over-all rate of disappearance for each of the two kinds of monomer. His equations, therefore, also refer to special cases and are in part identical with those of Jenckel. Recently the present authors approached this problem from the point

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[1] Compare the symposium on "High Polymers" held by the New York Academy of Sciences, Ann. N. Y. Acad. Sci. 44, 263 (1943).

[2] R. G. W. Norrish and E. F. Brookman, Proc. Roy. Soc. A171, 147 (1939).

[3] E. Jenckel, Zeits. f. physik. Chemie A190, 24 (1941).

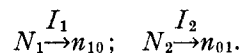[4] F. T. Wall, J. Am. Chem. Soc. 63, 1862 (1941).

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of view of a chain reaction governed by an activation, propagation, and cessation.[5] Expressions for the over-all rate and for the size and composition distribution were given. In the following the previous short account of this work is presented in full and a more complete analysis is undertaken.

The treatment is based upon the steady state method. It is valid if the mean lifetime of the growing polymer is small compared with the half-life of the over-all consumption of monomer. This implies essentially a vanishingly small rate of initiation. In polymerization reactions which lead to the formation of high molecular weight products, this steady state approximation appears satisfactory.[6] The mechanism underlying the mathematical derivations is somewhat simplified by neglecting the possibility of chain transfer[1] between polymer radical and monomer or solvent and by representing the initiation in terms of constant parameters without considering in detail the catalyst action.[1] At the present stage of experimental investigation, considerations of this kind, necessary for a more complete analysis of the data available on simple polymerization processes and on molecular distribution curves, are hardly possible.
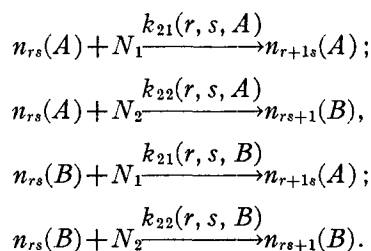
The rates of growth and termination will, in general, depend upon the individual compositions of the chains and upon the nature of their active ends, formed by either of the two monomer species 1 and 2. In the following the rate constants will be designated by symbols $k_{ij}(r, s, A)$ and $k_{ij}(r, s, B)$. $r, s$ indicate the composition of the chain in question, $r$ being the number of type one groups and $s$ of type two groups in the chain. $A$ and $B$ refer to the two kinds of active ends of the growing polymer molecules. $i$ runs from 1 to 3 according to whether the $k$ constant designates initiation, growth, or termination, $j$ assumes the values of one or two, characterizing the type of monomer involved in the kinetic act. In this notation, $k_{21}(r, s, A)$, for instance, signifies the rate of growth of a polymer radical of indicated composition and active end by addition of a monomer of type 1, $k_{22}(r, s, A)$

[5] H. Branson and R. Simha, J. Chem. Phys. **11**, 297 (1943).

[6] R. Ginell and R. Simha, J. Am. Chem. Soc. **65**, 706, 715 (1943).

by addition of type 2. The following reaction schemes are considered:

Initiation:

$$N_1 \xrightarrow{I_1} n_{10}; \quad N_2 \xrightarrow{I_2} n_{01}.$$

Propagation:

$$n_{rs}(A) + N_1 \xrightarrow{k_{21}(r, s, A)} n_{r+1s}(A);$$

$$n_{rs}(A) + N_2 \xrightarrow{k_{22}(r, s, A)} n_{rs+1}(B),$$

$$n_{rs}(B) + N_1 \xrightarrow{k_{21}(r, s, B)} n_{r+1s}(A);$$

$$n_{rs}(B) + N_2 \xrightarrow{k_{22}(r, s, B)} n_{rs+1}(B).$$

Termination:

(a)
$$n_{rs}(A) + N_1 \xrightarrow{k_{31}(r, s, A)} N_{r+1s};$$

$$n_{rs}(A) + N_2 \xrightarrow{k_{32}(r, s, A)} N_{rs+1},$$

$$n_{rs}(B) + N_1 \xrightarrow{k_{31}(r, s, B)} N_{r+1s};$$

$$n_{rs}(B) + N_2 \xrightarrow{k_{32}(r, s, B)} N_{rs+1}.$$

(b)
$$n_{rs}(A) + n_{ik}(A) \xrightarrow{k_3(r, s, i, k, A, A)} N_{r+is+k} \quad (1)$$
$$\text{or } N_{rs} + N_{ik},$$

$$n_{rs}(A) + n_{ik}(B) \xrightarrow{k_3(r, s, i, k, A, B)} N_{r+is+k}$$
$$\text{or } N_{rs} + N_{ik},$$

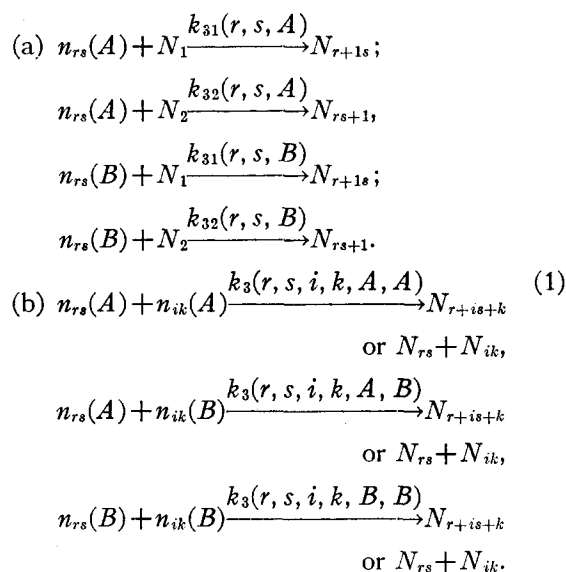$$n_{rs}(B) + n_{ik}(B) \xrightarrow{k_3(r, s, i, k, B, B)} N_{r+is+k}$$
$$\text{or } N_{rs} + N_{ik}.$$

$n_{rs}(A)$ are growing radicals with a reacting end formed by type 1 monomer and similarly for $n_{rs}(B)$. $N_{rs}$ indicates the mole fraction of stable polymer with given composition $r, s$. $I_1$ and $I_2$ indicate the velocities of the initiation act, $I_1 = k_{11}N_1^{n-i-1}N_2^i$; $I_2 = k_{12}N_1^{n-i-1}N_2^i$ for an $n$th-order process. Two possibilities of breaking the growing polymer or monomer are considered, monomer termination and radical-radical termination. The radical mechanism of polymerization makes the latter process the more probable one.[1] However, in order to establish the connection with the special results previously mentioned and with certain results on molecular weight distributions of simple polymer, monomer termination is included. Besides, the mathematical treatment

is closely connected for both cases. It has been suggested[1] that termination occurs by a first-order process when activation proceeds by means of an ionic mechanism. This case can easily be treated on the basis of the following results for the radical distribution.

## I. THE GENERAL OVER-ALL REACTION

In terms of the above scheme the consumption of monomer is given for monomer termination by:

$$\frac{1}{N_l}\frac{dN_l}{dt} = I_l$$
$$+ \sum_{r,s} \{[k_{2l}(r, s, A) + k_{3l}(r, s, A)]n_{rs}(A)$$
$$+ [k_{2l}(r, s, B) + k_{3l}(r, s, B)]n_{rs}(B)\}, \quad (2)$$

with $l = 1, 2$.

We introduce the mean values of the rates of growth and termination by averaging over the radical distribution.

$$\bar{k}_{ml} \sum_{r,s} [n_{rs}(A) + n_{rs}(B)]$$
$$= \sum_{r,s} [k_{ml}(r, s, A)n_{rs}(A) + k_{ml}(r, s, B)n_{rs}(B)].$$

Equation (2) then becomes:

$$\frac{1}{N_l}\frac{dN_l}{dt} = I_l + (\bar{k}_{2l} + \bar{k}_{3l}) \sum_{r,s} [n_{rs}(A) + n_{rs}(B)]. \quad (2a)$$

Since a steady state is assumed to exist, the rate of production equals the rate of destruction of active chains. This leads at once to an equation for the total concentration of these chains, which assumes the following form:

$$\sum_{r,s} [n_{rs}(A) + n_{rs}(B)] = \frac{I_1 N_1 + I_2 N_2}{\bar{k}_{31} N_1 + \bar{k}_{32} N_2}. \quad (3)$$

Equations (2a) and (3) together determine the over-all rate in terms of the average rates $\bar{k}_{ml}$ and the initiations $I_1$ and $I_2$. The over-all rate is best expressed by introducing the mole ratio of monomer residue:

$$z = N_1/N_2.$$

The above results then lead to

$$\frac{dN_1}{dN_2} = z\frac{R_1 z + R_2}{R_3 z + R_4}$$

and

$$\frac{d \ln z}{dt} = \frac{(R_3 - R_1)z + R_4 - R_2}{\bar{k}_{31}z + \bar{k}_{32}}, \quad (4)$$

with

$$R_1 = I_1(k_{21} + 2k_{31}); \quad R_2 = I_1 k_{32} + I_2(k_{21} + k_{31});$$
$$R_3 = I_2\bar{k}_{31} + I_1(\bar{k}_{22} + \bar{k}_{32}); \quad R_4 = I_2(\bar{k}_{22} + 2\bar{k}_{32}).$$

In the following species two will be assumed to be the more rapidly reacting, such that for $t \to \infty$, $z \to \infty$. It may be noted that (3) cannot be integrated directly, since the average values of the rates depend, in general, upon the instantaneous monomer composition $z$. However, it can be simplified, since the rate of initiation under our assumption is very small and furthermore the velocity of growth much larger than that of termination. Equation (4) then reduces to

$$\frac{d \ln z}{dt} = (\bar{k}_{22} - \bar{k}_{21})\frac{I_1 z + I_2}{\bar{k}_{31}z + \bar{k}_{32}}. \quad (4a)$$

In the case of radical termination one has:

$$-\frac{dN_l}{dt} = I_l + N_l k_{21} \sum_{r,s} [n_{rs}(A) + n_{rs}(B)];$$
$$l = 1, 2. \quad (2')$$

The average value of the termination is defined as follows:

$$\bar{k}_3\{\sum_{r,s,i,j} [n_{rs}(A) + n_{ij}(B)]\}^2$$
$$= \sum_{r,s,i,j} \{k_3(r, s, i, j, A, A)n_{rs}(A)n_{ij}(A)$$
$$+ 2k_3(r, s, i, j, A, B)n_{rs}(A)n_{ij}(B)$$
$$+ k_3(r, s, i, j, B, B)n_{rs}(B)n_{ij}(B)\}.$$

The radical concentration is found from the equation:

$$\bar{k}_3[\sum_{r,s} n_{rs}(A) + n_{rs}(B)]^2 = I_1 N_1 + I_2 N_2.$$

Therefore:

$$\frac{dN_1}{dN_2} = \frac{I_1 + k_{21}N_2^{\frac{1}{2}}\bar{k}_3^{-\frac{1}{2}}(I_1 z + I_2)^{\frac{1}{2}}}{I_2 + \bar{k}_{22}N_2^{\frac{1}{2}}\bar{k}_3^{-\frac{1}{2}}(I_1 z + I_2)^{\frac{1}{2}}},$$
$$\frac{d \ln z}{dt} = I_2 - I_1 + (k_{22} - k_{21})\bar{k}_3^{-\frac{1}{2}}N_2^{\frac{1}{2}}(I_1 z + I_2)^{\frac{1}{2}}. \quad (4')$$

Equations (4) and (4'), containing mean rate constants, are of general validity. The specific dependence of the individual rates upon com-

position and chain end determines the radical distribution and therefore the variation of the average rates with $z$.

## II. DETERMINATION OF RADICAL DISTRIBUTION

Because of the existence of a steady state

$$\frac{dn_{rs}(A)}{dt} = \frac{dn_{rs}(B)}{dt} = 0.$$

Scheme (1) then leads to the following set of difference equations for the concentration of growing polymer of indicated type:

$$\alpha_{rs}(A)n_{rs}(A) = \beta_{r-1s}(A)n_{r-1s}(A)$$
$$+ \beta_{r-1s}(B)n_{r-1s}(B),$$
$$\alpha_{rs}(B)n_{rs}(B) = \gamma_{rs-1}(A)n_{rs-1}(A) \qquad (5)$$
$$+ \gamma_{rs-1}(B)n_{rs-1}(B),$$
$$\alpha_{10}(A)n_{10} = I_1 N_1; \quad \alpha_{01}(B)n_{01} = I_2 N_2.$$

For monomer termination:

$$\alpha_{rs}(L) = [k_{21}(r, s, L) + k_{31}(r, s, L)]N_1$$
$$+ [k_{22}(r, s, L) + k_{32}(r, s, L)]N_2,$$
$$\beta_{rs}(L) = k_{21}(r, s, L)N_1; \quad \gamma_{rs}(L) = k_{22}(r, s, L)N_2,$$

with $L = A$ or $B$. For radical termination:

$$\alpha_{rs}(L) = k_{21}(r, s, L)N_1 + k_{22}(r, s, L)N_2$$
$$+ \sum_{i,j} [k_3(r, s, i, j, L, A)n_{ij}(A)$$
$$+ k_3(r, s, i, j, L, B)n_{ij}(B)]$$
$$= k_{21}(r, s, L)N_1 + k_{22}(r, s, L)N_2$$
$$+ \bar{k}_3(r, s, L, A) \sum_{i,j} n_{ij}(A)$$
$$+ \bar{k}_3(r, s, L, B) \sum_{i,j} n_{ij}(B). \qquad (5')$$

$\bar{k}_3(r, s, L, A)$ and $\bar{k}_3(r, s, L, B)$ with $\bar{k}_3(A, B) = \bar{k}_3(B, A)$ are suitably defined average rates.

The general solution of system (5) leads to complex expressions, depending upon the specific nature of the rates as function of the individual chain composition $r$, $s$. Herington and Robertson[7] have developed equations for simple polymerization processes permitting in principle to deduce the dependence of the growth to termination ratio upon individual molecular size from de-

[7] E. F. G. Herington and A. Robertson, Trans. Faraday Soc. **38**, 490 (1942).

terminations of the instantaneous distribution curve. One may think of a similar procedure here. To investigate this, the complexity of (5) is reduced first by disregarding the dependence of growth and cessation upon the type of active end involved. This will be nearly correct, if no further steric conditions remain to be satisfied once an active end has been formed. The only important contribution of the growing chain to the rate constant then depends upon its size and composition only. In this case one has:

$$n_{rs}(A) + n_{rs}(B) = 2n_{rs}(A) = n_{rs}$$

and (5) reduces to:

$$\alpha_{rs}n_{rs} = \beta_{r-1s}n_{r-1s} + \gamma_{rs-1}n_{rs-1}; \quad r, s \geqq 1. \qquad (5a)$$

This set may be solved by induction, as shown in Appendix I. The solution is:

$$n_{rs} = \frac{\alpha_{0s}}{\beta_{rs}} \prod_{l=0}^{r} \left(\frac{\beta_{ls}}{\alpha_{ls}}\right) n_{0s} + \sum_{j=1}^{r} n_{js-1} \frac{\gamma_{js-1}}{\beta_{rs}} \prod_{l=j}^{r} \frac{\beta_{ls}}{\alpha_{ls}}.$$

For the pure polymers, $n_{r0}$ and $n_{0s}$, we have:

$$\beta_{r-10}n_{r-10} = \alpha_{r0}n_{r0}; \quad \gamma_{0s-1}n_{0s-1} = \alpha_{0s}n_{0s}.$$

Therefore:

$$I_1 N_1 = \beta_{r0}n_{r0} \prod_{l=1}^{r} \frac{\alpha_{l0}}{\beta_{l0}}; \quad I_2 N_2 = \gamma_{0s}n_{0s} \prod_{l=1}^{s} \frac{\alpha_{0l}}{\gamma_{0l}}.$$

Whereupon:

$$n_{rs} = \frac{I_2 N_2}{\alpha_{rs}} \prod_{l=0}^{r-1} \frac{\beta_{ls}}{\alpha_{ls}} \prod_{l=1}^{s-1} \frac{\gamma_{0l}}{\alpha_{0l}} + \frac{1}{\alpha_{rs}} \sum_{j=1}^{r} \gamma_{js-1}n_{js-1} \prod_{l=j}^{r-1} \frac{\beta_{ls}}{\alpha_{ls}}.$$

Defining:

$$\frac{\beta_{ij}}{\alpha_{ij}} = \omega_{ij} \quad \text{and} \quad \frac{\gamma_{ij}}{\alpha_{ij}} = \omega'_{ij},$$

the probabilities for growth by means of monomer 1 and 2, respectively, $n_{rs}$ becomes finally:

$$n_{rs} = \frac{I_1 N_1}{\alpha_{rs}} \sum_{i_1=1}^{r} \sum_{i_2=1}^{i_1} \cdots \sum_{i_s=1}^{i_{s-1}} \prod_{l=1}^{i_s-1} \omega_{l0}\omega'_{i_s 0} \prod_{l=i_s}^{i_{s-1}-1} \omega_{l1}\omega'_{i_{s-1}1}$$
$$\times \prod_{l=i_{s-1}}^{i_{s-2}-1} \omega_{l2} \cdots + \frac{I_2 N_2}{\alpha_{rs}} \sum_{i=0}^{s-1} \sum_{i_1=1}^{r} \cdots \sum_{i_i=1}^{i_{i-1}} \prod_{l=1}^{s-i-1} \omega'_{0l}$$
$$\times \prod_{l=0}^{i_i-1} \omega_{ls-i}\omega'_{i_i s-i} \prod_{l=i_i}^{i_{i-1}-1} \omega_{ls-i+1} \cdots \omega'_{i_1 s-1} \prod_{l=i_1}^{r-1} \omega_{ls}. \qquad (6)$$

The term on the right multiplied by $I_1 N_1$ gives the $n_{rs}$ initiated by monomer species 1. The first product gives the probability that the chain

so initiated adds $(j_s-1)$ monomers of species 1 before a species 2 is added, as represented by the factor $\omega'_{j_s0}$. The second product describes the further growth of the polymer by addition of more 1's until there are $(j_{s-1}-1)$ of the first species. At this stage a monomer of the second type is added. The remaining factors express the further growth. Finally, the summations over the $j$'s give the total number of possible intramolecular arrangements consistent with the composition $r, s$ and initiated by the first species. The second term is interpreted similarly.

In the case of radical termination, the same solution is obtained with the $\alpha$'s defined as in (5') after suitable specialization.

We may investigate the specific effect of different growing ends upon the reaction by neglecting the dependence upon chain composition. Equation (5) becomes upon division by $\alpha(A)$ and $\alpha(B)$, respectively:

$$n_{rs}(A) = \omega(A)n_{r-1s}(A) + \omega(B)n_{r-1s}(B),$$
$$n_{rs}(B) = \omega'(A)n_{rs-1}(A) + \omega'(B)n_{rs-1}(B),$$
(5b)

where the $\omega$'s are defined as:

$$\omega(A) = \frac{\beta(A)}{\alpha(A)}; \quad \omega(B) = \frac{\beta(B)}{\alpha(A)};$$

$$\omega'(A) = \frac{\gamma(A)}{\alpha(B)}; \quad \omega'(B) = \frac{\gamma(B)}{\alpha(B)}.$$

They represent probabilities for $-A-A, -B-A, -A-B, -B-B$ addition, respectively. The solutions of (5b) are, as shown in Appendix II:

$$n_{rs}(A) = [\omega(A)]^{r-1}[\omega'(B)]^s$$
$$\times \left\{ \frac{I_1N_1}{\alpha(A)}[F(1-r, -s, 1, x) - F(1-r, 1-s, 1, x)] \right.$$
$$\left. + \frac{I_2N_2}{\alpha(B)}\frac{\omega(A)}{\omega'(A)}F(1-r, 1-s, 1, x) \right\};$$
$$n_{rs}(B) = [\omega(A)]^r[\omega'(B)]^{s-1}$$
(6a)
$$\times \left\{ \frac{I_1N_1}{\alpha(A)}\frac{\omega'(A)}{\omega(A)}F(1-r, 1-s, 1, x) \right.$$
$$+ \frac{I_2N_2}{\alpha(B)}[F(-r, 1-s, 1, x)$$
$$\left. - F(1-r, 1-s, 1, x)] \right\},$$

where the $F$'s are hypergeometric functions with

$$x = \frac{\omega'(A)\omega(B)}{\omega(A)\omega'(B)} = \frac{\gamma(A)}{\beta(A)}\frac{\beta(B)}{\gamma(B)},$$

corresponding to $\dfrac{-A-B \quad -B-A}{-A-A \quad -B-B}$ addition.

The interpretation of (6a) is analogous to that of (6). The first term always gives the total number of active chains of stated composition initiated by the first species. In the case of radical termination (6a) remains valid with the $\alpha$'s defined as in (5'), but independent of $r$ and $s$. For the developments in the next section we need the total number of radicals of specified ends (see Appendix II):

$$\sum_{r, s \geq 1} n_{rs}(A) = \frac{\omega(A)\omega(B)x}{[(1-\omega(A))(1-\omega(B))-x\omega(A)\omega'(B)]}\left[\frac{I_1N_1}{\alpha(A)(1-\omega(A))}+\frac{I_2N_2}{\alpha(B)\omega'(A)}\right],$$

$$\sum_r n_{r0}(A) = \frac{I_1N_1}{\alpha(A)}\frac{1}{1-\omega(A)},$$

$$\sum_{r, s \geq 1} n_{rs}(B) = \frac{\omega(A)\omega'(B)x}{[(1-\omega(A))(1-\omega'(B))-x\omega(A)\omega'(B)]}\left[\frac{I_1N_1}{\alpha(A)\omega(B)}+\frac{I_2N_2}{\alpha(B)(1-\omega'(B))}\right],$$
(7)

$$\sum_s n_{0s}(B) = \frac{I_2N_2}{\alpha(B)}\frac{1}{1-\omega'(B)}.$$

### III. SPECIAL RATE EQUATIONS

From the results obtained for the radical distribution, it is possible to determine the average rates $\bar{k}_{21}, \bar{k}_{22}, \bar{k}_{31}, \bar{k}_{32}$ and introduce them into the general equations (2) and (4'). The mean rates, obtained

by averaging over the rates for $A$ and $B$ ends, respectively, according to the general equation previously given, are:

$$\bar{k} \sum_{r,s} [n_{rs}(A) + n_{rs}(B)] = \sum_{r,s} [k(A)n_{rs}(A) + k(B)n_{rs}(B)],$$

where, as before, the $\bar{k}$'s are independent of $r$, $s$. Substituting for the sums, one has:

$$\bar{k} = \frac{k(A)[I_1 N_1(\alpha(B) - \gamma(B)) + I_2 N_2 \beta(B)] + k(B)[I_1 N_1 \gamma(A) + I_2 N_2(\alpha(A) - \beta(A))]}{I_1 N_1[\alpha(B) + \gamma(A) - \gamma(B)] + I_2 N_2[\alpha(A) + \beta(B) - \beta(A)]}.$$

Therefrom:

$$-\frac{1}{N_l}\frac{dN_l}{dt} = I_l + (\bar{k}_{2l} + \bar{k}_{3l})[\sum_{r,s} n_{rs}(A) + \sum_{r,s} n_{rs}(B)]$$

with $l = 1, 2$. Equation (4a) then yields:

$$\frac{d}{dt}\ln z = (I_1 z + I_2)\frac{c_1 z^2 + c_2 z + c_3}{c_4 z^3 + c_5 z^2 + c_6 z + c_7}, \tag{4b}$$

where

$$c_1 = I_1[k_{22}(A) - k_{21}(A)][k_{21}(B) + k_{31}(B)] \doteq I_1 k_{21}(B)[k_{22}(A) - k_{21}(A)],$$

$$c_2 \doteq I_2 k_{21}(B)[k_{22}(A) - k_{21}(A)] + I_1 k_{22}(A)[k_{22}(B) - k_{21}(B)],$$

$$c_3 \doteq I_2 k_{22}(A)[k_{22}(B) - k_{21}(B)],$$

$$c_4 \doteq I_1 k_{21}(B)k_{31}(A),$$

$$c_5 \doteq I_2 k_{21}(B)k_{31}(A) + I_1[k_{22}(A)k_{31}(B) + k_{21}(B)k_{32}(A)],$$

$$c_6 \doteq I_2[k_{22}(A)k_{31}(B) + k_{21}(B)k_{32}(A)] + I_1 k_{22}(A)k_{32}(B),$$

$$c_7 \doteq I_2 k_{22}(A)k_{32}(B),$$

in which we neglected $k_3$'s with respect to $k_2$'s. It should be noted that for a first-order initiation process $I_1$ and $I_2$ are independent of $N_1$ and $N_2$, the $c$'s are constants, and the right-hand side of (4b) depends solely upon $z$. For higher order initiation, $d \ln z/dt$ depends explicitly upon $z$, the mole ratio, and upon $N_2$, the number of moles of the second species present.

During the last stages of the reaction, $z \to \infty$, the slope of the $\ln z$ curve becomes $I_1/k_{31}(A)[k_{22}(A) - k_{21}(A)]$ which is constant for first-order initiation. The rate of monomer consumption is then given by

$$\lim_{l \to \infty}\frac{1}{N_l}\frac{dN_l}{dt} = -\frac{k_{2l}(A)I_1}{k_{31}(A)}, \quad l = 1, 2.$$

The limiting over-all rate follows the same order as the rate of initiation of the slower species. This result is exactly analogous to the one obtained in simple polymerization reactions where it holds throughout the reaction.[6,7] The rate factor depends only upon the constants characteristic for active ends formed by the slower reacting species. This is not unexpected since this type end is the only one formed during the final stages. Equation (4b) can now be specialized to give copolymer systems equivalent to those defined by Jenckel.[3] Case 1: Each species polymerizes independently; expressed by $k_{22}(A) = k_{21}(B) = 0$, $k_{32}(A) = k_{31}(B) = 0$. The over-all rate is:

$$\frac{d \ln z}{dt} = \frac{I_2 k_{22}(B)}{k_{32}(B)} - \frac{I_1 k_{21}(A)}{k_{31}(A)}.$$

This shows, as one expected, that the result of the copolymerization is the same as that obtained by separate polymerization and subsequent mixing. The first term on the right equals $-(1/N_2)(dN_2/dt)$ and the second $(1/N_1)(dN_1/dt)$. The same type of result was obtained by Wall.[4] Case 2: In the other extreme, each species adds on to active ends formed by the other type; $k_{21}(A) = k_{22}(B) = 0$, $k_{31}(A)$

$=k_{32}(B)=0$. The result is a checker board polymer. One obtains:

$$\frac{d\ln z}{dt} = \frac{(I_1 z + I_2)(z-1)}{k_{32}(A)[k_{22}(A)]^{-1} + k_{31}(B)[k_{21}(B)]^{-1}} \frac{1}{z}.$$

Case 3: $-A-A$, $-B-B$, $-B-A$, and $-A-B$ additions occur with equal probability; $k_{21}=k_{22}$, $k_{31}=k_{32}$ for $A$ and $B$. Equation (4) with constant values for the $R_i$ yields:

$$d\ln z/dt = I_2 - I_1.$$

This is a result of the same type as that holding for case 1; furthermore, if the velocities of initiation are also equal, no change of monomer composition results during the whole process and it remains equal to the composition of polymer formed.

Equation (6a) holds also for radical termination. However, the solution (6a) contains the quantities $\sum n_{rs}(A)$ and $\sum n_{rs}(B)$ explicitly, as can be seen from the definition (5) of the $\alpha$'s. In order to determine the sums, we revert to (7), which represents in this case implicit equations for the desired quantities in terms of rate constants and monomer concentrations. On substituting for the $\omega$'s in (7) a set of simultaneous cubic equations for $\sum n_{rs}(A)$ and $\sum n_{rs}(B)$ results. The linear term is negligible in comparison with the constant and quadratic terms because of the magnitudes of the different rates. The cubic term is also negligible until $N_1$ becomes vanishingly small. The solution obtained with these approximations is:

$$\sum n_{rs}(A) = \beta(B)/\gamma(A) \sum n_{rs}(B)$$

$$= \beta(B)\left\{\frac{I_1 N_1 + I_2 N_2}{\beta(B)[k_3(A,A)\beta(B) + k_3(A,B)\gamma(A)] + \gamma(A)[k_3(A,B)\beta(B) + k_3(B,B)\gamma(A)]}\right\}^{\frac{1}{2}}. \quad (7')$$

This expression may be used to determine the average values of the rates. Introduction of the values into (4') and use of the definitions of the $\beta$'s and $\gamma$'s yields for the over-all rate for radical termination:

$$\frac{d\ln z}{dt} = I_2 - I_1 + \frac{N_2^{\frac{1}{2}}(I_1 z + I_2)^{\frac{1}{2}}\{k_{21}(B)[k_{22}(A) - k_{21}(A)]z + k_{22}(A)[k_{22}(B) - k_{21}(B)]\}}{\{k_3(A,A)k_{21}^2(B)z^2 + 2k_3(A,B)k_{21}(B)k_{22}(A)z + k_3(B,B)k_{22}^2(A)\}^{\frac{1}{2}}}. \quad (4b')$$

If the initiation is first order, (4b') and (4b) show that the distinction between radical and monomer termination lies in the explicit dependence of the over-all rate upon the concentration $N_2$ in the former case.

If the kinetic distinction between the two types of growing ends is dropped as was done in the derivation of (6) for the distribution of active radical, (4b) and (4b') become

$$\frac{d\ln z}{dt} = (I_1 z + I_2)\frac{k_{22} - k_{21}}{k_{31} z + k_{32}} \quad (4c)$$

and

$$\frac{d\ln z}{dt} = (I_2 - I_1) + \left(\frac{I_1 z + I_2}{k_3}\right)^{\frac{1}{2}} N_2^{\frac{1}{2}}(k_{22} - k_{21}), \quad (4c')$$

where all the $k$'s represent true rates, not average rates as in (4a) and (4') which have the same form.

Unless experimental data are very accurate, it will be difficult to distinguish between the type of behavior described by (4b) and that of (4c); for the ratio of a quadratic to a cubic function of $z$ in (4b) is replaced by the ratio of a constant to a linear term in (4c). Analogous reasoning applies to a comparison of (4b') and (4c'). As far as the dependence of growth and termination upon individual chain composition is concerned, the form of (6) seems to preclude our deriving information from

measurements of over-all rate and from size distribution data. We shall, therefore, make (4c) and (4c')
the basis for our further considerations.

Equation (4c) or the full equation (4) with constant coefficients $R_i$ can immediately be integrated.
Equation (4c) and the first equation in (4) yield for a first-order initiation process ($I_1$, $I_2$ constant):

$$k_{32}I_1 \ln \frac{z}{z_0} + (k_{31}I_2 - k_{32}I_1) \ln \frac{I_1 z + I_2}{I_1 z_0 + I_2} = I_1 I_2 (k_{22} - k_{21})t,$$

(4d)

$$\ln \frac{N_2}{N_2(0)} = \frac{R_4}{R_2 - R_4} \ln z/z_0 + \left( \frac{R_4}{R_4 - R_2} - \frac{R_3}{R_3 - R_1} \right) \ln \frac{(R_1 - R_3)z + (R_2 - R_4)}{(R_1 - R_3)z_0 + (R_2 - R_4)} \doteq - \frac{k_{22}}{k_{22} - k_{21}} \ln z/z_0,$$

where $N_2(0)$ and $z_0$ are the initial mole fraction for the second species and mole ratio, respectively.
The approximate equation is valid since rates of growth are large with respect to rates of initiation and
termination, and since $k_{22}/k_{21}$ is of the same order of magnitude as $k_{32}/k_{31}$. This procedure is not
acceptable if the rates are very nearly equal, but this has already been considered as case 3 in this
section.

The rate constants are best determined from the graph of $d \ln z/dt$ *versus* $z$. That is, one would find
experimentally the $\ln z - t$ curve, calculate the slope and plot it *versus* the corresponding values of $z$.
Figure 1[8] is such a curve for selected values of the rate constants and for different ratios of the two
termination rates. Equal velocities of initiation are assumed. Inequality of initiations would not
change the general shape of the curves, except for a possible change of sign of the slope. Differences in
the growth rates merely shift the curves vertically. Jenckel's[3] and Wall's[4] equations yield the hori-
zontal line.

The experimental data of Marvel and co-workers[9] seem to deviate from the horizontal line. It is
difficult to judge from these data whether the deviations follow this theory. For very large values of $z$
the slope is zero since both species are reacting independently. The ratio of the two growth rates can
easily be found from (4d).

Equations (2') for radical termination yield as intermediate integral a relation between $N_1$, $N_2$,
and $t$, which can be written as follows, if the initiations are first order:

$$\ln \frac{N_2}{N_2(0)} = - \frac{k_{22}}{k_{22} - k_{21}} \ln \frac{z}{z_0} + \frac{k_{22}k_{21}}{k_{22} - k_{21}} \left( \frac{I_2}{k_{22}} - \frac{I_1}{k_{21}} \right) t.$$

(4d')

Equation (4c') then gives for the over-all rate:

$$\frac{d \ln z}{dt} = (I_2 - I_1) + [N_2(0)]^{\frac{1}{2}} \frac{(k_{22} - k_{21})}{k_3^{\frac{1}{2}}} \left( \frac{z_0}{z} \right)^{k_{22}/2(k_{22}-k_{21})} (I_1 z + I_2)^{\frac{1}{2}} \exp \left\{ \frac{k_{22}k_{21}}{2(k_{22} - k_{21})} \left( \frac{I_2}{k_{22}} - \frac{I_1}{k_{21}} \right) t \right\}. \quad (4c'')$$

Unless the two rates of propagation are very nearly equal, the coefficient of $t$ in (4d') and (4c'') will be
sufficiently small to make the $t$ factor negligible over a wide interval of the reaction. Under these con-
ditions, (4d') becomes identical with the approximate form of (4d). The slope of the $\ln z - t$ curve
depends also upon the initial monomer concentrations, while monomer termination gives a depend-
ence upon the instantaneous ratio $z$ only (4c). Extrapolation of the slope of the $\ln z - t$ curve to zero
time yields a straight line according to (4c''), if plotted *versus* the square root of the initial mole
fraction $N_2(0)$. Its intercept equals $I_2 - I_1$.

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[8] We are indebted to Mr. Charles P. Powell for his aid in carrying out the numerical computations.
[9] C. S. Marvel, G. D. Jones, T. W. Mastin, and G. L. Schertz, J. Am. Chem. Soc. **64**, 2356 (1942).

## IV. COPOLYMER COMPOSITION AND SIZE DISTRIBUTION

The mole fraction of stable polymer $N_{rs}$ is given by the following equations according to scheme (1), for the stable copolymer formed in a time element $dt$ (hereafter called instantaneous copolymer distribution):

$$\frac{dN_{rs}}{dt} = k_{31}N_1 n_{r-1s} + k_{32}N_2 n_{rs-1};$$

Monomer termination. (8)

$$\frac{dN_{rs}}{dt} = \frac{k_3}{2}\sum_{i,j=0}^{r,s} n_{r-is-j}n_{ij}; \qquad \frac{dN_{rs}}{dt} = k_3 n_{rs}\sum_{i,j} n_{ij};$$

Radical termination. (8')

$n_{rs}$ is derived from (6) for rates independent of $r$ and $s$:

$$n_{rs} = \omega^r(\omega')^s\left[I_1/k_{21}\binom{r+s-1}{s} + \frac{I_2}{k_{22}}\binom{r+s-1}{r}\right], \quad (6a)$$

$$\sum_{i,j} n_{ij} = (I_1 N_1 + I_2 N_2)(\alpha - \beta - \gamma)^{-1},$$

where

$\omega = \omega_{ij}$ and $\omega' = \omega'_{ij}$ are independent of $i$, $j$.

Equation (6a) is valid for radical termination if the $\alpha$'s in $\omega$ and $\omega'$ are defined:

$$\alpha = k_{21}N_1 + k_{22}N_2 + k_3 N_2^{\frac{1}{2}}\left(\frac{I_1 z + I_2}{k_3}\right)^{\frac{1}{2}}.$$

Elimination of $t$ in (8) leads by means of relations (4c), (4d), and (6a) to the following expressions valid for first-order initiation and monomer termination:

$$\frac{dN_{rs}}{dz} = \frac{N_2(0)}{z_0(k_{22} - k_{21})}\left(\frac{z_0}{z}\right)^{1 + k_{22}/k_{22} - k_{21}}$$

$$\times \frac{k_{31}z + k_{32}}{I_1 z + I_2}f(r,s)\omega^r(\omega')^{s-1},$$

with

$$f(r,s) = \frac{I_1 k_{22}k_{31}}{k_{21}^2}\binom{r+s-2}{s}$$

$$+ \frac{I_2 k_{32}}{k_{22}}\binom{r+s-2}{s-2}$$

$$+ \left(\frac{I_2 k_{31}}{k_{21}} + \frac{I_1 k_{32}}{k_{21}}\right)\binom{r+s-2}{s-1}. \quad (8a)$$

Unfortunately it is not possible to integrate this expression in closed form and find in this manner the distribution of stable polymer corresponding to a monomer composition $z$. Numerical integration is required after the rate constants have been determined from kinetic data. The distribution of stable polymer first formed may be obtained as:

$$N_{rs}(z \to z_0) = \left[\frac{dN_{rs}}{dz}\right]_{z=z_0}(z - z_0).$$

If the monomer ratio $z_0$ is maintained, this gives the distribution at any instant. The total number of molecules of a certain total chain length $p$ can be determined by means of the equation derived from (8):

$$\frac{d}{dz}\sum_{r+s=p}N_{rs} = N_2\frac{dt}{dz}(\omega + \omega')^{p-2}\left[I_1\frac{k_{22}k_{31}}{k_{21}^2}\frac{\omega^2}{\omega'}\right.$$

$$\left. + \frac{(I_2 k_{31} + I_1 k_{32})}{k_{21}}\omega + \frac{I_2 k_{32}}{k_{22}}\omega'\right].$$

For the total number of polymer molecules we obtain:

$$\frac{d}{dz}\sum_{r+s=2}^{\infty}N_{rs} = N_2(I_1 z + I_2)\frac{dt}{dz},$$

a result which can be written down directly in view of the steady state condition. Integration of the last expression using (4c) and (4d) gives:

$$\sum_{r+s=2}^{\infty}N_{rs} = \frac{k_{31}}{k_{21}}N_1(0)\left[1 - \left(\frac{z_0}{z}\right)^{k_{21}/k_{22} - k_{21}}\right]$$

$$+ \frac{k_{32}}{k_{22}}N_2(0)\left[1 - \left(\frac{z_0}{z}\right)^{k_{21}/k_{22} - k_{21}}\right].$$
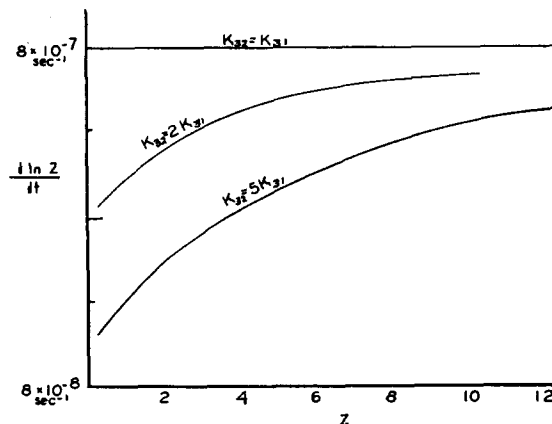


FIG. 1. Slope of $\ln z - t$ curve as a function of $z$, (4c), for various ratios $k_{31}/k_{32}$. $I_1 = I_2 = 10^{-9}$ sec.$^{-1}$; $k_{21} = 2.10^{-3}$ mole$^{-1}$ liter sec.$^{-1}$; $k_{22} = 5k_{21}$; $k_{31} = 10^{-5}$ mole$^{-1}$ liter sec.$^{-1}$.

The number average molecular weight of the polymerized material is given by

$$\bar{M}_n(z) = \frac{M_1[N_1(0) - N_1(z) - n_{10}] + M_2[N_2(0) - N_2(z) - n_{01}]}{\displaystyle\sum_{r+s=2}^{\infty} N_{rs} + \sum_{r,s} n_{rs} - n_{10} - n_{01}}. \tag{9}$$

$M_1$ and $M_2$ denote the molecular weights of the two monomer species. All mole fractions can be expressed as functions of $z$ by means of relations (3), (4d), and (6a). For the final number average molecular weight we find in this manner, if the small amount of monomer radical is neglected:

$$\bar{M}_n(\infty) = \frac{M_1 z_0 + M_2}{\dfrac{k_{31}}{k_{21}} z_0 + \dfrac{k_{32}}{k_{22}}}. \tag{9a}$$

For a one-component polymerization one has in place of (9a) the familiar result:

$$\bar{M}_n(\infty) = M_1 k_{21} / k_{31}.$$

As is to be expected, the result (9a) depends upon the initial monomer composition which appears here as a weight factor in the average formed over the contribution of the two species to the total. One may guess that the weight average molecular weights of copolymer and pure polymer will be similarly related. The quotient of the two terms in (9) equals the weight ratio $w$ of the two species in the polymerized material:

$$w(z) = \frac{M_1}{M_2} z_0 \frac{1 - (z_0/z)^{k_{21}/(k_{22} - k_{21})}}{1 - (z_0/z)^{k_{22}/k_{22} - k_{21}}}. \tag{10}$$

For $z \to \infty$, the polymer composition naturally becomes equal to the initial monomer composition $(M_1/M_2)z_0$. The result (10) can be valid only beyond the induction period, when the concentration of activated chains $n_{rs}$ is stationary and when $n_{10}$ and $n_{01}$, whose initial values cannot be determined by the method used here, are negligible in comparison with the terms retained in the numerator and denominator of (10). On extrapolating, however, the composition curve to zero time, $z = z_0$, (10) reduces to:

$$w(z_0) = \frac{M_1}{M_2} z_0 \frac{k_{21}}{k_{22}}.$$

Hence the intercept of the polymer composition curve gives the ratio of the rates of growth for the two components. Equation (10) may easily be expressed in terms of weight percentage composition of monomer which gives a more accurate graph for large values of $z$. Because of the identity of (4d') and (4d) previously discussed, (10) holds approximately also in the case of radical termination. The instantaneous distribution by weight, $(d/dz)[(M_1 r + M_2 s)N_{rs}]$ according to (8a), is plotted in Figs. 2 and 3 versus the total chain length for constant chain composition $\delta = s/r$ and
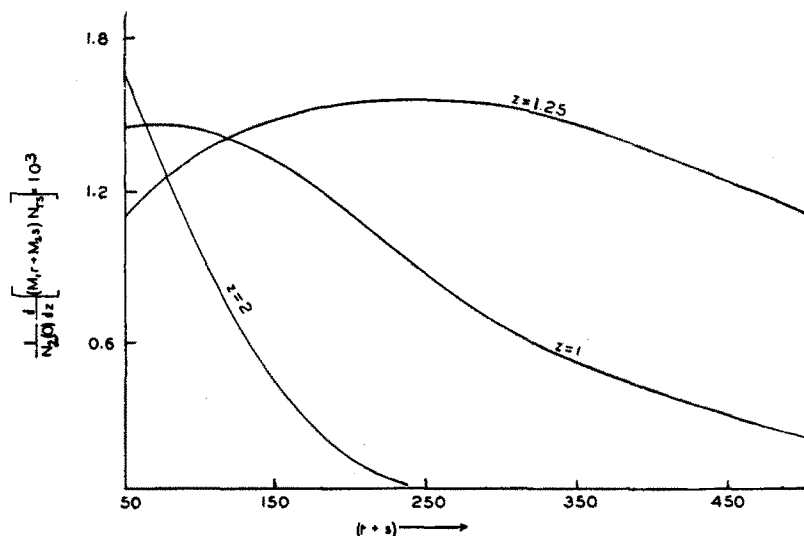


FIG. 2. Instantaneous weight distribution (9) at constant chain composition $\delta = s/r = 4$ as a function of chain length $r+s$, at various stages of the reaction. Rates identical with those in Fig. 1 with $k_{32} = 2k_{31}, z_0 = 0.4$. Vertical scale should be divided by ten for $z = 2$.

FIG. 3. Instantaneous weight distribution (9) at constant chain length $r+s=200$ as a function of chain composition $r/r+s$ at various stages of the reaction. Numerical values of constants identical with those in Fig. 2. Ordinate scale for curve $z=0.51$ should be multiplied by two.
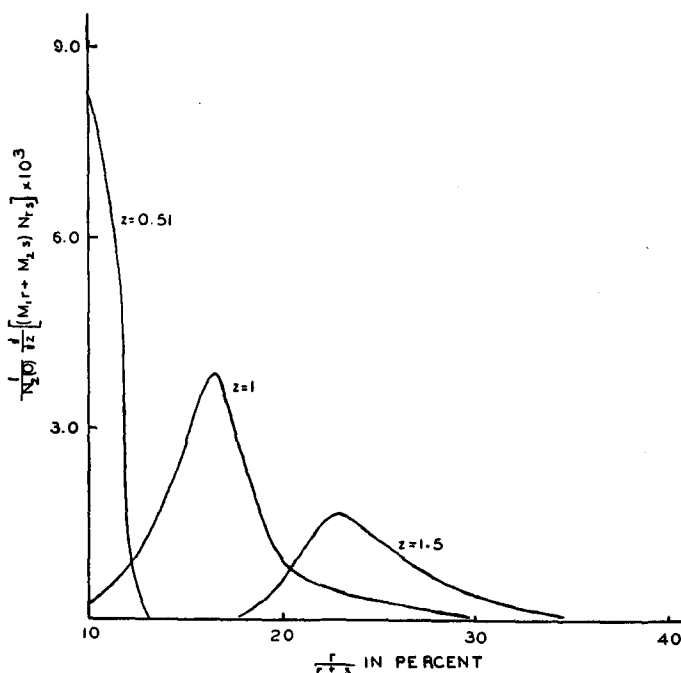
*versus* the composition $r/r+s$ for constant chain length, respectively, at various stages $z$ of the reaction. Some of the values chosen were suggested by Reinhardt's[10] data on the vinyl chloride (species 1) vinylidene chloride (species 2) system. Stirling's formula can be used to replace the factorials for most of the values of $r$ and $s$ shown in the graphs. In the plots at constant $\delta$, (8a) leads to:

$$(M_1 r + M_2 s)\frac{dN_{rs}}{dz} = A(z) r^{\frac{1}{2}} \left\{ \frac{(\delta+1)^{\delta+1}}{\delta^\delta} \right.$$

$$\left. \times \frac{k_{22}^\delta k_{21} z}{[(k_{21}+k_{31})z + (k_{22}+k_{32})]^{\delta+1}} \right\}^r. \quad (9)$$

The maximum of the distribution is at

$$(r+s)_{max} = r_{max}(1+\delta) = \left(\frac{1+\delta}{2}\right)$$

$$\times \left[ \ln \left( \frac{\delta^\delta}{(\delta+1)^{\delta+1}} \frac{[(k_{21}+k_{31})z + k_{22} + k_{32}]^{\delta+1}}{k^\delta_{22} k_{21} z} \right) \right]^{-1}.$$

It may be seen that both for very large and very small values of $z$, the maximum shifts to very small values of $r$. If the composition of the monomer residue is such that (depending essentially upon the growth rates) the mean composi-

[10] R. C. Reinhardt, Ind. Eng. Chem. **35**, 422 (1943).

tion of polymer just formed deviates pronouncedly from the desired one ($\delta$), then the latter will, because of statistical reasons, occur only in very small chains. Accordingly one may expect the maximum in Fig. 2 to be farthest to the right, when the monomer composition $z(max)$ obeys the relation

$$\delta = \frac{k_{22}+k_{32}}{k_{21}+k_{31}} \frac{1}{z\,(max)}. \quad (10)$$

Setting $d(r+s)_{max}/dz$ equal to zero actually leads to this result. The corresponding value of the molecular weight is found from the above equa-
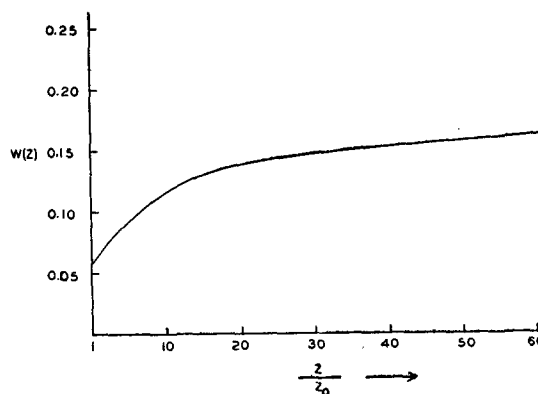


FIG. 4. Weight ratio $w(z)$ of reactants in copolymer as a function of mole ratio $z$ of monomer (10). Numerical values of constants are the same as those in Fig. 2.

tion for $(r+s)_{max}$ after insertion of the value for $z(max)$. Expansion of the logarithm gives the following equation for the largest obtainable molecular weight corresponding to a maximum in the composition distribution curve:

$$\frac{\dfrac{1}{M_1\dfrac{1}{\delta}+M_2}}{\dfrac{2}{}\dfrac{k_{31}}{k_{21}}\dfrac{1}{\delta}+\dfrac{k_{32}}{k_{22}}}. \tag{11}$$

Comparison of this equation with relation (9a) shows that this maximum molecular weight is exactly one-half the final number average molecular weight obtained if the initial monomer ratio $z_0$ equals the desired ratio $1/\delta$ in the chains. If one wishes to maintain throughout the polymerization a given ratio $\delta$ in long chains, the initial composition $z_0$ must be chosen equal to $z(max)$ and $z$ maintained at this value by suitable monomer addition. In Fig. 3 the maximum shifts to larger contents of type one monomer with progressing copolymerization, as is to be expected. The instantaneous distributions of polymer formed by the interaction of two activated chains are given by the following equations, derived from (8') and (6a) in the Appendix III:

$$\frac{dN_{rs}}{dt}=\frac{k_3}{2}\omega^r(\omega')^s\left\{\left(\frac{I_1}{k_{21}}\right)^2\binom{r+s-1}{s+1}(s-1)\right.$$

$$+\frac{I_1I_2}{k_{21}k_{22}}\left[\binom{r+s-1}{s}(s-1)\right.$$

$$+\binom{r+s-1}{r}(r-1)\right]$$

$$\left.+\left(\frac{I_2}{k_{22}}\right)^2\binom{r+s-1}{r+1}(r-1)\right\};$$

$$r,\ s>0,\ \text{Combination};\tag{8a'}$$

$$\frac{dN_{r0}}{dt}=\frac{k_3}{2}(r-1)\omega^r(I_1/k_{21})^2;$$

$$\frac{dN_{0s}}{dt}=\frac{k_3}{2}(s-1)(\omega')^s\left(\frac{I_2}{k_{22}}\right)^2;$$

$$\frac{dN_{rs}}{dt}=k_3^{\frac{1}{2}}N_2^{\frac{1}{2}}(I_1z+I_2)^{\frac{1}{2}}\omega^r(\omega')^s\left[\frac{I_1}{k_{21}}\binom{r+s-1}{s}\right.$$

$$\left.+\frac{I_2}{k_{22}}\binom{r+s-1}{r}\right].\ \text{Disproportionation}.$$

By means of (4c''), (8a') may again be formulated in terms of $z$ through elimination of the time variable. It may be noted from (8a) and (8a') that the distribution by number, $N_{rs}$, will exhibit a maximum in the case of combination, while curves for polymer terminated by means of monomer or by a disproportionation mechanism shows a maximum only if plotted as weight distribution, similarly as in the case of one-component systems.[7] Equation (8a¹) gives at once the distribution $\lim_{z\to z_0} N_{rs}$ of stable polymer formed initially, if $t$ is eliminated by means of $z$ in analogy to the case previously discussed. Plots at constant composition and chain length, respectively, lead to the same conclusions as before. No analytical expression for the maximum chain length obtainable with a desired composition $\delta$ can be found because of the complications arising from the definition of $\omega$ and $\omega'$ in this case. If the factor containing $k_3$ in $\omega$ and $\omega'$ can be neglected, Eq. (10) with omission of $k_{31}$ and $k_{32}$ is again obtained.

Relations for the size and composition distribution developed here or found by similar methods for other polymerization mechanisms should permit at least an estimation of the homogeneity of a copolymer with respect to size and composition at various stages of the reaction, once the kinetics of the process is established and the velocity constants for the elementary steps are known. In the case of insoluble or nearly insoluble cross-linked polymers of the vinyl-divinyl type the only thermodynamic method available at present for an analysis of the product formed is a study of the swelling isotherms.[11] This allows a determination of the average chain length between two cross links. Kinetic investigations enable one to supplement this information with distribution data. Jenckel[3] has carried out fractionations on four soluble copolymer systems, namely, styrene and methacrylic acid ester, methyl methacrylate and vinyl acetate, respectively, and vinyl pyrrolidine-vinyl carbazole. He furthermore attempted to draw conclusions as to the kinetics of the process on this basis. However, in his analysis the inhomogeneity in respect to size was neglected. In general, chain

[11] P. J. Flory and J. Rehner, Jr., J. Chem. Phys. 11, 521 (1943).

composition as well as chain length[12] determine the thermodynamic equilibrium at a given temperature.[13] It is evident for instance, that the shorter chains precipitated from a solution contain more of that component which, as a pure polymer, is less soluble in the same solvent.

Finally, considerations of this type will play a role in the application of Flory's[14] and Stockmayer's[15] theory of gel formation to cross-linked polymers, by determining the relative probabilities with which mono- and divinyl enter the chains, and therefore the average number of cross bonds per chain. The intramolecular distribution of cross bonds can then be calculated in terms of the extent of reaction. The number $P_i$ of groups of monovinyl units containing $i$ members in $N_{rs}$ cross-linked chains of length $(r+s)$ which have been formed in an interval $dz$, is given by:[16]

$$P_i = N_{rs}(r+s)(1-\omega)^2 \omega^i;$$

for $i \ll r+s$, with

$$\omega = \frac{k_{21}z}{k_{21}z + k_{22}}.$$

$k_{22}$ designates the rate of cross-bond formation,

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[12] See, for instance, H. Staudinger and J. Schneiders, Ann. 541, 151 (1939).

[13] This can be expressed roughly by an extension of the theory of P. J. Flory, J. Chem. Phys. 10, 51 (1942) and M. L. Huggins, Ann. N. Y. Acad. Sci. 43, 1 (1942). Let the heat of mixing depend solely upon the polymer composition and be independent of the intramolecular arrangement, which is reasonable. Applying G. Scatchard's [Chem. Rev. 8, 321 (1931)] expression for the heat of mixing to the ternary system, the parameter $K$ (in Flory's notation), a ratio between cohesional and thermal energy, assumes the following form:

$$K = 2v_1/RT[A_{12}\kappa + A_{13}(1-\kappa) - A_{23}\kappa(1-\kappa)].$$

$\kappa$ is the chain composition $r/r+s$ in the notation adopted, $v_1$ the molar volume of the solvent. The indices 2 and 3 refer to the two monomer species. The $A$ coefficients depend upon the nature of the respective components only and monomers 2 and 3 are assumed to be approximately equal in size. The relations for the partial molal entropies will in general depend upon the intramolecular arrangement of the two species which determines the internal flexibility of the polymer molecule, unless they are chemically similar enough. Disregarding this factor, the above authors' results give at once a relation between chain length and composition at the critical point of formation of a two-phase system at a given temperature. Furthermore, the slope of the plot of reduced osmotic pressure versus concentration (in weight per volume) for small concentrations is proportional to $(1-K)$ and is therefore a function of the chain composition. Osmotic data on copolymers are very desirable in this connection.

[14] P. J. Flory, J. Am. Chem. Soc. 63, 3096 (1941).

[15] W. H. Stockmayer, J. Chem. Phys. 11, 45 (1943); W. H. Stockmayer and H. Jacobson, ibid. 11, 393 (1943).

[16] F. T. Wall, J. Am. Chem. Soc. 62, 803 (1940); 63, 821 (1941). R. Simha, ibid. 63, 1479 (1941).

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$k_{21}$ that of addition of monovinyl units. If the chain length is not sufficiently large, the effect of the two ends and their mode of formation must be taken into account by the introduction of parameters for initiation and termination and modification of the above formula.[16]

We should like to acknowledge our indebtedness to Dr. R. F. Boyer and Dr. R. C. Reinhardt of The Dow Chemical Company for many helpful discussions.

## APPENDIX

### I. Solution of the Difference Equations (5a)

The result for $n_{r0}$ and $n_{0s}$ is easily found. Direct substitution in (5a) for low values of $r$ and $s$ leads to the following typical equations:

$$\alpha_{12}n_{12} = \beta_{02}n_{02} + \gamma_{11}n_{11};$$

$$\alpha_{32}n_{32} = \frac{\beta_{02}\beta_{12}\beta_{22}n_{02} + \gamma_{11}\beta_{12}\beta_{22}n_{11}}{\alpha_{12}\alpha_{22}} + \frac{\gamma_{21}\beta_{22}}{\alpha_{22}}n_{21} + \gamma_{31}n_{31};$$

or

$$\alpha_{r2}n_{r2} = \alpha_{02}\prod_{l=0}^{r-1}\left(\frac{\beta_{l2}}{\alpha_{l2}}\right)n_{02} + \sum_{j=1}^{r}n_{j1}\gamma_{j1}\prod_{l=j}^{r-1}\frac{\beta_{l2}}{\alpha_{l2}}.$$

The first term on the right expresses that an $n_{r2}$ may be built from an $n_{02}$ by adding on $r$ units of the first kind; the second term that $n_{r2}$ may be built from $n_{11}$, $n_{21}\cdots n_{r1}$ by joining a unit of the second kind and then completing the structure by adding a sufficient number of the first species. This may be generalized to

$$\alpha_{rs}n_{rs} = \alpha_{0s}\prod_{l=0}^{r-1}\left(\frac{\beta_{ls}}{\alpha_{ls}}\right)n_{0s} + \sum_{j=1}^{r}n_{j\ s-1}\gamma_j\ _{s-1}\prod_{l=j}^{r-1}\left(\frac{\beta_{ls}}{\alpha_{ls}}\right)$$

which can be explained as before. It is equivalent to the intermediate result presented in the text. On substituting $n_{0s}$ and $\omega$'s from the text this becomes:

$$\alpha_{rs}n_{rs} = I_2N_2\prod_{l=0}^{r-1}\omega_{ls}\prod_{l=1}^{s-1}\omega'_{0l} + \sum_{j_1=1}^{r}\gamma_{j_1\ s-1}n_{j_1\ s-1}\prod_{l=j_1}^{r-1}\omega_{ls}.$$

This expression can be utilized to establish a recurrence formula between $n_{j_1s-1}$ and $n_{j_2s-2}$ with $1 \le j_2 \le j_1$. $n_{j_2s-2}$ may be expressed in terms of $n_{j_3s-1}$ with $1 \le j_3 \le j_2$. Continued substitution and rearrangement leads to (6).

### II. Solution of Difference Equations (5b)

Equations (5b) gives for the pure radical species:

$$n_{r0} = \frac{I_1N_1}{\beta(A)}[\omega(A)]^r; \quad n_{0s} = \frac{I_2N_2}{\gamma(B)}[\omega'(B)]^s.$$

Examining a $n_{rs}(A)$ for low values of $r$, $s$, for example, $n_{22}(A)$:

$$n_{22}(A) = \frac{I_1N_1}{\alpha(A)}\omega'(A)\omega'(B)\omega(B)$$

$$+ \frac{I_2N_2}{\alpha(B)}[\omega(B)\omega'(A)\omega(B) + \omega'(B)\omega(B)\omega(A)].$$

We see that there will be in all cases two expressions, one

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corresponding to initiation by the first species, the other by the second. The terms in the $\omega$'s again express the manner of growth of the active nuclei. From the meaning of the $\omega$'s we can interpret for this example the first product in the $I_2$ term as growth in the following order: $B-A-B-A-$, and the second: $B-B-A-A$. The $I_1$ term represents: $A-B-B-A$. The total number of terms in the expression for $n_{rs}(A)$ will evidently be equal to the number of ways of arranging the structural units within the chain with specified ends:

$$\underbrace{\frac{(r+s-2)!}{(r-2)!s!}}_{\text{Initiated by } A}+\underbrace{\frac{(r+s-2)!}{(r-1)(s-1)}}_{\text{Initiated by } B.}=\binom{r+s-1}{s}$$

Likewise for $n_{rs}(B)$:

$$\binom{r+s-1}{r}.$$

Let us now characterize a possible intramolecular configuration by $i$, the number of $A-A$, $j$, the number of $B-A$, $k$, the number of $A-B$, and by $l$, the number of $B-B$ linkages. Each configuration gives rise to a term $\omega(A)^i\omega(B)^j\omega'(A)^k\omega'(B)^l$ multiplied by a statistical weight factor. To determine this factor we consider first the $n_{rs}(A)$ initiated by $B$. The conditions to be fulfilled by $i$, $j$, $k$, and $l$ are: $i+j=r$, since an $A$ must follow an $A$ or a $B$; $j=k+i$, since all the groups formed by $B$ except the first are preceded by an $A$ ($A-B$ linkage) and all are succeeded by an $A$ including the first ($B-A$ bond); $j+l=s$, since a $B$ must be followed by an $A$ or by a $B$. Let $m_t$ be the number of groups formed by $t$ structural units of type $A$, whence $\Sigma m_t=j$, $\Sigma tm_t=r$. Let $m_t'$ have the same meaning for type $B$ and $\Sigma m_t'=j$, $\Sigma tm_t'=s$. The weight factor for the specified configuration $i$, $j$, $k$, $l$ is

$$\sum_{m_t'}\frac{(\Sigma m_t')!}{\Pi(m_t')!}\sum_{m_t}\frac{(\Sigma m_t)!}{\Pi(m_t)!}=\sum_{m_t'}\frac{j!}{\Pi(m_t')!}\sum_{m_t}\frac{j!}{\Pi(m_t)!}\quad (A-1),$$

to be summed over all values of $m_t$ and $m_t'$ compatible with the auxiliary conditions. The sum over $m_t'$ gives the independent configurations resulting from a permutation of the $B$ groups, that over $m_t$ of the $A$ groups. The product therefore gives the total number of independent configurations. Using the multinomial theorem to evaluate one of these sums we find:

$$(\Sigma_t x_t{}^tz^t)^j=j!\sum_{m_t}\Pi_t\frac{(x_t{}^tz^t)^{m_t}}{m_t!}=j!\sum_m z^{\Sigma tm_t}\Pi_t\frac{x_t{}^{tm_t}}{m_t!}\quad (\Sigma m_t=j),$$

whence:

$$\sum_{m_t}\frac{j!}{\Pi m_t!}=\lim_{x_t\to1}\{\text{coeff. of } z^r \text{ in } (\Sigma_t x_t{}^tz^t)^j\}$$

$$=\text{coeff. of } z^r \text{ in } \frac{z^j}{(1-z)^j}=\binom{r-1}{j-1}.$$

Replacing $r$ by $s$ gives the sum over $m_t'$. The final weight factor is:

$$\binom{r-1}{j-1}\binom{s-1}{j-1}.$$

For $m_{rs}(A)$ initiated by $A$, the conditions for $i$, $j$, $k$, and $l$ are $\Sigma m_t=j+1$, $\Sigma m_t'=j$, $i+j+1=r$, $j=k$, $j+l=s$. Substituting these values for the sums into $(A-1)$ and using

the multinomial theorem, we obtain for the weight factor

$$\binom{r-1}{j}\binom{s-1}{j-1}.$$

For $n_{rs}(B)$ initiated by $A$, the analysis is the same as for $n_{rs}(A)$ initiated by $B$ with $\Sigma m_t'=\Sigma m_t=k$, $i+k=r$, $j=k-1$, $k+l=s$, hence the weight factor:

$$\binom{r-1}{k-1}\binom{s-1}{k-1}.$$

$n_{rs}(B)$ initiated by $B$ carries the conditions $\Sigma m_t'=k+1$, $\Sigma m_t=k=j$, $i+k=r$, $k+l+1=s$. The weight factor is:

$$\binom{r-1}{k-1}\binom{s-1}{k}.$$

Introducing the weight factors as coefficients of the $\omega$'s and substituting the values of the exponents in terms of $r$ and $s$, we find:

$$n_{rs}(A)=\frac{I_1N_1}{\alpha(A)}\sum_{j=1}^{s}\binom{r-1}{j}\binom{s-1}{j-1}$$
$$\times[\omega'(A)]^j[\omega'(B)]^{s-j}[\omega(B)]^j[\omega(A)]^{r-j-1}$$
$$+\frac{I_2N_2}{\alpha(B)}\sum_{j=1}^{s}\binom{r-1}{j-1}\binom{s-1}{j-1}$$
$$\times[\omega'(A)]^{j-1}[\omega'(B)]^{s-j}[\omega(B)]^j[\omega(A)]^{r-j};$$

$$n_{rs}(B)=\frac{I_1N_1}{\alpha(A)}\sum_{k=1}^{r}\binom{r-1}{k-1}\binom{s-1}{k-1}$$
$$\times[\omega'(A)]^k[\omega'(B)]^{s-k}[\omega(B)]^{k-1}[\omega(A)]^{r-k}$$
$$+\frac{I_2N_2}{\alpha(B)}\sum_{k=1}^{r}\binom{r-1}{k-1}\binom{s-1}{k}$$
$$\times[\omega'(A)]^k[\omega'(B)]^{s-k-1}[\omega(B)]^k[\omega(A)]^{r-k}.$$

The first expression on the right for $n_{rs}(A)$ may be written as:

$$I=\frac{I_1N_1}{\alpha(A)}[\omega(A)]^{r-1}[\omega'(B)]^s\sum_{j=1}^{s}\binom{r-1}{j}\binom{s-1}{j-1}\left[\frac{\omega'(A)\omega(B)}{\omega(A)\omega'(B)}\right]^j.$$

Now

$$\binom{r-1}{j}\binom{s-1}{j-1}=\binom{r-1}{j}\binom{s}{j}-\binom{r-1}{j}\binom{s-1}{j}.$$

$$\sum_{j=1}^{s}\binom{r-1}{j}\binom{s}{j}x^j=(r-1)sx+\frac{(r-1)(r-2)}{1\cdot2}\frac{s(s-1)}{1\cdot2}x^2+\cdots$$

$$=F(1-r,-s,1,x)-1,$$

where $F(a, b, c, x)$ is the hypergeometric function[17]

$$F(a, b, c, x)=1+\frac{ab}{c}x+\frac{a(a+1)}{1\cdot2}\frac{b(b+1)}{c(c+1)}x^2+\cdots.$$

Likewise:

$$\sum_{j=1}^{s}\binom{r-1}{j}\binom{s-1}{j}x^j=-F(1-r,1-s,1,x)+1$$

and

$$I=\frac{I_1N_1}{\alpha(A)}[\omega(A)]^{r-1}[\omega'(B)]^s$$
$$\times[F(1-r,-s,1,x)-F(1-r,1-s,1,x)].$$

[17] E. T. Whittaker and G. N. Watson, *Modern Analysis* (The Cambridge University Press, 1940).

Application of this procedure to the other summations gives (6a).

In computing the sums over $n_{rs}(A)$ and $n_{rs}(B)$, the sums over the pure polymer species are easily evaluated. In the copolymer $n_{rs}(A)$ we have for the first term, substituting $i = j - 1$:

$$\frac{I_1 N_1}{\alpha(A)} \frac{1}{\omega(A)} \sum_{j=1}^{s} \sum_{r,s \geq 1}^{\infty} [\omega(A)]^r [\omega'(B)]^s \binom{r-1}{j}\binom{s-1}{j-1} x^j$$

$$= x \frac{I_1 N_1}{\alpha(A)\omega(A)} \sum_{i=0}^{\infty} x^i \sum_{s=i+1}^{\infty} [\omega'(B)]^s \binom{s-1}{i}$$

$$\times \sum_{r=i+2}^{\infty} [\omega(A)]^r \binom{r-1}{i+1}$$

$$= x \frac{I_1 N_1}{\alpha(A)\omega(A)} \sum_{i=0}^{\infty} x^i \left[\frac{\omega'(B)}{1-\omega'(B)}\right]^{i+1} \left[\frac{\omega(A)}{1-\omega(A)}\right]^{i+2}$$

$$= \frac{I_1 N_1}{\alpha(A)[1-\omega(A)]} \frac{\omega(A)\omega'(B)x}{[1-\omega(A)][1-\omega'(B)]-x\omega(A)\omega'(B)}.$$

The second term gives

$$\frac{I_2 N_2 x}{\alpha(B)\omega'(A)} \sum_{i} x^i \sum_{r,s \geq 1} [\omega(A)]^r [\omega'(B)]^s \binom{r-1}{i}\binom{s-1}{i}$$

$$= \frac{I_2 N_2}{\alpha(B)\omega'(A)} \frac{x\omega(A)\omega'(B)}{[1-\omega(A)][1-\omega'(A)]-x\omega(A)\omega'(B)}.$$

Combination of these terms gives the sums in (7). $\Sigma n_{rs}(B)$ is determined in the same manner.

## III. Derivation of (8a′)

Introducing the values for $n_{ij}$ and $n_{r-i,s-j}$ from (6a) into (8′) one is led to four sums. The first is:

$$\left(\frac{I_1}{k_{21}}\right)^2 \frac{k_3}{2} \omega^r(\omega')^s \sum_{i,j} \binom{r-i+s-j-1}{s-j}\binom{i+j-1}{j}$$

$$= \left(\frac{I_1}{k_{21}}\right)^2 \frac{k_3}{2} \omega^r(\omega')^s \sum_{\lambda=2}^{r+s-2} S_\lambda = \left(\frac{I_1}{k_{21}}\right)^2 \frac{k_3}{2} \omega^r(\omega')^s S_I,$$

where

$$S_\lambda = \sum_{j=1}^{s-1}\binom{r+s-1-\lambda}{s-j}\binom{\lambda-1}{j}$$

$$= \sum_{j=0}^{s}\binom{r+s-1-\lambda}{s-j}\binom{\lambda-1}{j} - \binom{r+s-\lambda-1}{s} - \binom{\lambda-1}{s}.$$

Now

$$\binom{m+n}{p} = \sum_{j=0}^{p}\binom{m}{p-j}\binom{n}{j}; \quad \binom{m+1}{p+1} = \sum_{j=0}^{m-p}\binom{m-j}{j}.$$

Consequently:

$$S_\lambda = \binom{r+s-2}{s} - \binom{r+s-\lambda-1}{s} - \binom{\lambda-1}{s}$$

and

$$S_I = \binom{r+s-2}{s}(r+s-3) - \sum_{\lambda=2}^{r+s-2}\binom{r+s-\lambda-1}{s}$$

$$- \sum_{\lambda=2}^{r+s-2}\binom{\lambda-1}{s}.$$

The first summation on the right gives with $\delta = \lambda - 2$:

$$\sum_{\delta=0}^{r+s-4}\binom{r+s-3-\delta}{s} = \sum_{\delta=0}^{r-3}\binom{r+s-3-\delta}{s} = \binom{r+s-2}{s+1},$$

since the binomial coefficient is zero when the bottom term exceeds the top. The second summation in $S_I$ may be written with $\delta = r+s-2-\lambda$:

$$\sum_{\lambda=s+1}^{r+s-2}\binom{\lambda-1}{s} = \sum_{\delta=0}^{r-3}\binom{r+s-3-\delta}{s} = \binom{r+s-2}{s+1}.$$

Finally:

$$S_I = \binom{r+s-2}{s}(r+s-1) - 2\binom{r+s-2}{s+1} = \binom{r+s-1}{s+1}(s-1).$$

The second sum is

$$\left(\frac{I_1}{k_{21}}\right)\left(\frac{I_2}{k_{22}}\right)\frac{k_3}{2}\omega^r(\omega')^s \sum_{i,j}\binom{i+j-1}{j}\binom{r+s-i-j-1}{r-i}.$$

Since

$$\binom{r+s-i-j-1}{s-j-1} = \binom{r+s-i-j}{s-j} - \binom{r+s-i-j-1}{s-j},$$

$$S_{II} = \sum_{i,j}\binom{i+j-1}{j}\binom{r+s-i-j}{s-j} - S_I.$$

The first term above on the right may be obtained from $S_I$ by replacing $r$ by $r+1$:

$$S_{II} = (s-1)\binom{r+s-1}{s}.$$

The third and fourth terms are

$$\left(\frac{I_1}{k_{21}}\right)\left(\frac{I_2}{k_{22}}\right)\frac{k_3}{2}\omega^r(\omega')^s \sum_{i,j}\binom{i+j-1}{i}\binom{r+s-i-j-1}{s-j}$$

and

$$\left(\frac{I_2}{k_{22}}\right)^2\frac{k_3}{2}\omega^r(\omega')^s \sum_{i,j}\binom{i+j-1}{i}\binom{r+s-i-j-1}{r-i}.$$

The sums become identical with the second and first upon interchange of $r$ and $s$, $i$ and $j$. Substitution of the values found in this manner gives (8a′).