441. *The Kinetics of Catalytic Polymerizations. Part IV.* Molecular-weight Distribution in Polar Polymerizations.*

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Theoretical distribution functions have been calculated from various possible mechanisms for polar polymerizations. The application of molecular-weight distribution data to the determination of kinetic mechanisms is discussed.

The form of the molecular-weight distribution curve of any inhomogeneous polymer is generally dependent upon the mechanism of chain initiation and termination. The comparison of experimental molecular-weight distribution curves with those calculated for various possible reaction schemes may thus be a valuable method for deciding which of several alternative reaction mechanisms is operating. Since, however, it is possible that different reaction schemes may lead to the same calculated distribution curve, the method is more useful for the confirmation of a reaction scheme which has already been established by kinetic analysis. Nevertheless, such a comparison may give information on the mechanism of reactions which cannot be studied by other methods.

No attempt has been made previously to study polar polymerizations in this way although such studies have been made for free-radical polymerizations. Theoretical distribution functions for free-radical polymerizations have been obtained by Gee and Melville (*Trans. Faraday Soc.*, 1944, **40**, 240), who considered first- and second-order initiation and termination occurring spontaneously, by monomer collision, or by disproportionation. Their calculations were restricted to reactions in which k_t/k_p was independent of chain length (k_t and k_p are the specific rates of the termination and propagation reactions, respectively). Herington and Robertson (*Trans. Faraday Soc.*, 1942, **38**, 490), however, have allowed for a possible variation of k_t/k_p with chain length and have also illustrated the effect of the variation of monomer concentration during the reaction on the form of the distribution curve.

Comparisons of theoretical and experimental distribution curves have been made by Schulz (*Z. physikal. Chem.*, *B*, 1939, **43**, 25) and Schulz and Dinglinger (*ibid.*, p. 47) for

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* Part III, preceding paper.

polystyrene prepared by thermal polymerization, and they obtained good agreement. Baxendale, Bywater, and Evans (*Trans. Faraday Soc.*, 1946, **42**, 675) have shown that the kinetic scheme which they established for the polymerization of methyl methacrylate catalysed by hydroxyl radicals in aqueous solution, leads to a theoretical distribution curve in agreement with that obtained experimentally.

Calculation of the Distribution Functions.—Symbols employed. These are: M = concentration of monomer (m); M_0 = initial concentration of monomer, at time $t = 0$; M_1^* = concentration of activated monomer (m_1^*); M_r^* = concentration of active polymer of chain length r (m_r^*), and M_r = concentration of corresponding deactivated polymer (m_r); G = total concentration of active polymer ($= \Sigma M_r^*$); S = concentration of solvent, which will be regarded as constant in dilute solution; and S^* = concentration of " active " solvent occurring in solvent transfer.

The velocity constants used are: k_p, propagation; k_t, spontaneous termination; k_{tm}, monomer termination; k_{ts}, solvent termination; k_{st}, solvent transfer; k_{tr}, monomer transfer; and k_s, solvent initiation following transfer. The following symbols will be used to denote velocity-constant ratios:

$$\lambda = k_t/k_p, \quad \lambda_{ts} = k_{ts}S/k_p, \quad \phi_1 = k_t/k_{ts}S, \quad \phi_3 = k_t/k_{tr}, \quad \phi_{m_1} = k_{tm}/k_{ts}S \quad \phi_{m_3} = k_{tm}/k_{tr}$$

$$\lambda_m = k_{tm}/k_p, \quad \lambda_{st} = k_{st}S/k_p, \quad \phi_2 = k_t/k_{st}S, \quad \phi_4 = k_{ts}/k_{st} \quad \phi_{m_2} = k_{tm}/k_{st}S$$

w_r = weight fraction of polymer molecules of chain length r.

Reaction mechanisms to be considered. It is desirable to consider only those reaction mechanisms which have been thought to be feasible for polar polymerizations. Normally, only one type of initiation and one type of propagation have been considered, *viz.*:

$$\text{initiation} \qquad m + b \longrightarrow m_1^* \qquad V_i \quad . \; . \; . \; . \; . \; . \quad (1)$$

$$\text{propagation} \qquad m_r^* + m \longrightarrow m_{r+1}^* \qquad V_p = k_pGM \quad . \; . \; . \quad (2)$$

where b represents the catalyst. Several termination mechanisms have been suggested for different systems. Pepper (*Trans. Faraday Soc.*, 1949, **45**, 404) and Eley and Richards (*ibid.*, p. 436) have proposed spontaneous termination:

$$m_r^* \longrightarrow m_r, \text{ or } m_r + b \qquad V_t = k_tG \quad . \; . \; . \; . \; . \; . \; . \quad (3)$$

and the latter authors (*Research*, 1949, **2**, 147) have tentatively suggested the occurrence of monomer transfer:

$$m_r^* + m \longrightarrow m_r + m^* \qquad V_{tr} = k_{tr}GM \quad . \; . \; . \; . \; . \; . \quad (4)$$

Monomer termination,

$$m_r^* + m \longrightarrow m_{r+1}, \text{ or } m_r + m \qquad V_{tm} = k_{tm}GM \quad . \; . \; . \quad (5)$$

solvent termination,

$$m_r^* + s \longrightarrow m_r + s, \text{ or } m_r + s + b \qquad V_{ts} = k_{ts}GS \quad . \; . \; . \quad (6)$$

and solvent transfer,

$$m_r^* + s \longrightarrow m_r + s^* \qquad V_{st} = k_{st}GS \quad . \; . \; . \; . \; . \; . \quad (7)$$

followed by

$$m + s^* \longrightarrow m^* + s \qquad V_s = k_sS^*M$$

have been suggested by the present authors (Parts II and III, *J.*, 1952, 621, preceding paper). The carbonium-ion theory suggested by Plesch and Polanyi (*J.*, 1947, 252) and Plesch, Polanyi, and Skinner (*ibid.*, p. 257) is equivalent for the present purpose to the mode of initiation [equation (1)] with spontaneous termination [equation (3)]. Termination by mutual destruction of polymer chains,

$$m_{r_1}^* + m_{r_2}^* \longrightarrow m_{r_1} + m_{r_2}, \text{ or } m_{r_1+r_2}$$

was tentatively suggested by Pepper (*Nature*, 1946, **158**, 789; *Trans. Faraday Soc.*, 1949, **45**, 397), but this view was later retracted (*ibid.*, p. 404). It now seems unlikely that this termination reaction occurs in polar polymerizations, since charge repulsion would oppose the process, and the relatively short chain lengths usually observed indicate that combination of chains does not occur. This mode of termination will, in consequence, not be considered here, the calculations being confined to monomer, spontaneous, and solvent termination, and to monomer and solvent transfer; the distribution equations obtained are independent of the mechanism of initiation.

It will be assumed that the velocity-constant ratios to be considered are independent of r and that steady state conditions exist. These are not new assumptions since they have already generally been made in kinetic analyses.

Termination by spontaneous deactivation. The kinetic reaction scheme is given by equations (1), (2), and (3). Then, for a stationary state, $\mathrm{d}G/\mathrm{d}t = \mathrm{d}M_1^*/\mathrm{d}t = \mathrm{d}M_r^*/\mathrm{d}t = 0$, $V_\mathrm{i} = V_\mathrm{t}$, and hence $G = V_\mathrm{i}/k_\mathrm{t}M$.

The total rate of monomer consumption is given by the equation

$$-\mathrm{d}M/\mathrm{d}t = V_\mathrm{i} + V_\mathrm{p} = V_\mathrm{i}(1 + M/\lambda) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and the rate of increase of concentration of deactivated polymer chains of length r is given by

$$\mathrm{d}M_r/\mathrm{d}t = k_\mathrm{t}M_r^* \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We have $\mathrm{d}M_1^*/\mathrm{d}t = V_\mathrm{i} - k_\mathrm{p}M_1^*M - k_\mathrm{t}M_1^* = 0$, hence

$$M_1^* = V_\mathrm{i}/(k_\mathrm{p}M + k_\mathrm{t}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Also, $\mathrm{d}M_r^*/\mathrm{d}t = k_\mathrm{p}M_{r-1}^*M - k_\mathrm{p}M_r^*M - k_\mathrm{t}M_r^* = 0$, hence

$$M_r^*/M_{r-1}^* = 1/(1 + \lambda/M) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Since M_r^*/M_{r-1}^* is independent of r,

$$M_r^* = M_1^*(M_r^*/M_{r-1}^*) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Therefore, from equations (8) to (12), we obtain

$$-\mathrm{d}M_r/\mathrm{d}M = \lambda^2/M^2(1 + \lambda/M)^{r+1}$$

and hence $M_r = [\lambda/r(1 + \lambda/M)^r]_M^{M_0}$ where M_0 and M are the concentrations of monomer initially ($t = 0$) and at time t, respectively. The weight fraction of polymer molecules of chain length r is then given by

$$w_r = rM_r/(M_0 - M) = [\lambda/M(1 + \lambda/M)^r]_M^{M_0} \quad . \quad . \quad . \quad (13)$$

Termination by spontaneous and solvent deactivation. The kinetic scheme is given by equations (1), (2), (3), and (6), and by an analogous derivation we obtain

$$w_r = [\lambda(1 + 1/\phi_1)/M(1 + \lambda/M + \lambda/\phi_1M)^r]_M^{M_0} \quad . \quad . \quad . \quad . \quad (14)$$

Termination by spontaneous deactivation with solvent transfer. The kinetic scheme is given by equations (1), (2), (3), and (7). In the same way, but by employing the additional stationary-state criterion that $\mathrm{d}S^*/\mathrm{d}t = 0$, we obtain

$$w_r = [\lambda(1 + 1/\phi_2)/M(1 + \lambda/M + \lambda/\phi_2M)^r]_M^{M_0} \quad . \quad . \quad . \quad . \quad (15)$$

which is identical with (14) if ϕ_2 is substituted for ϕ_1. This substitution is always possible with equations which involve solvent deactivation and solvent transfer processes, and is, in effect, a substitution of k_st for k_ts. This is in order, since the only difference between solvent deactivation and solvent transfer is that the latter is followed by a solvent initiation process which does not affect the form of the distribution equations. A similar substitution may also be made between λ_ts and λ_st, and ϕ_{m_1} and ϕ_{m_2}.

Termination by spontaneous and solvent deactivation with solvent transfer. The kinetic scheme is given by equations (1), (2), (3), (6), and (7), and we obtain

$$w_r = [\lambda(1 + 1/\phi_1 + 1/\phi_2)/M(1 + \lambda/M + \lambda/\phi_1M + \lambda/\phi_2M)^r]_M^{M_0} \quad . \quad . \quad (16)$$

The distribution function for solvent termination only is identical with equation (13) if λ is replaced by λ_{ts}, *viz.*:

$$w_r = [\lambda_{\mathrm{ts}}/M(1 + \lambda_{\mathrm{ts}}/M)^r]M_M^{M_0} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

In a similar way the function for solvent termination and solvent transfer is identical with equation (15) with λ_{ts} replacing λ, and ϕ_4 replacing ϕ_2.

Termination by monomer deactivation. The kinetic scheme is given by equations (1), (2), and (5). The stationary-state criterion is $\mathrm{d}G/\mathrm{d}t = 0$, therefore $V_{\mathrm{i}} = V_{\mathrm{t}}$, and hence $G = V_{\mathrm{i}}/k_{\mathrm{t}}M$. We therefore obtain

$$-\mathrm{d}M/\mathrm{d}t = V_{\mathrm{i}} + V_{\mathrm{p}} = V_{\mathrm{i}}(1 + 1/\lambda_{\mathrm{m}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

$$\mathrm{d}M_r/\mathrm{d}t = k_{\mathrm{tm}}M_r{}^*M \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

$$\mathrm{d}M_1{}^*/\mathrm{d}t = V_{\mathrm{i}} - k_{\mathrm{p}}M_1{}^*M - k_{\mathrm{tm}}M_1{}^*M = 0$$

i.e.,

$$M_1{}^* = V_{\mathrm{i}}/(k_{\mathrm{p}}M + k_{\mathrm{tm}}M) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

$$\mathrm{d}M_r{}^*/\mathrm{d}t = k_{\mathrm{p}}M_{r-1}{}^*M - k_{\mathrm{p}}M_r{}^*M - k_{\mathrm{tm}}M_r{}^*M = 0$$

i.e.,

$$M_r{}^*/M_{r-1}{}^* = 1/(1 + \lambda_{\mathrm{m}}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

Therefore, from equations (12) and (18) to (21),

$$-\mathrm{d}M_r/\mathrm{d}M = \lambda_{\mathrm{m}}{}^2/(1 + \lambda_{\mathrm{m}})^{r+1}$$

and hence

$$M_r = \lambda_{\mathrm{m}}{}^2(M_0 - M)/(1 + \lambda_{\mathrm{m}})^{r+1}$$

and

$$w_r = r\lambda_{\mathrm{m}}{}^2/(1 + \lambda_{\mathrm{m}})^{r+1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

This equation and equation (13) are similar to those derived by Gee and Melville (*loc. cit.*) for photochemical initiation.

Termination by monomer deactivation with monomer transfer. The kinetic scheme is given by equations (1), (2), (4), and (5), and by an analogous derivation the following expression is derived

$$w_r = r\lambda_{\mathrm{m}}{}^2(1 + 1/\phi_{\mathrm{m}_3})/(1 + \lambda_{\mathrm{m}})(1 + \lambda_{\mathrm{m}} + \lambda_{\mathrm{m}}/\phi_{\mathrm{m}_3})^r \quad . \quad . \quad . \quad . \quad (23)$$

Termination by monomer deactivation and solvent deactivation. The kinetic scheme is given by equations (1), (2), (5), and (6), and we obtain in the same way

$$-\mathrm{d}M_r/\mathrm{d}M = \lambda_{\mathrm{m}}{}^2(\phi_{\mathrm{m}_1}{}^2 + 2\phi_{\mathrm{m}_1}/M + 1/M^2)/\phi_{\mathrm{m}_1}{}^2(1 + \lambda_{\mathrm{m}} + \lambda_{\mathrm{m}}/\phi_{\mathrm{m}_1}M)^{r+1} \qquad (24)$$

The integration of this equation leads to mathematical difficulties, but if we assume that solvent deactivation occurs to a much greater extent than monomer deactivation, ϕ_{m_1} is very small and in dilute solution

$$1/M^2 \gg (\phi_{\mathrm{m}_1}{}^2 + 2\phi_{\mathrm{m}_1}/M)$$

Equation (24) then reduces to

$$-\mathrm{d}M_r/\mathrm{d}M = \lambda_{\mathrm{m}}{}^2/\phi_{\mathrm{m}_1}{}^2M^2(1 + \lambda_{\mathrm{m}} + \lambda_{\mathrm{m}}/\phi_{\mathrm{m}_1}M)^{r+1}$$

which on integration gives

$$w_r = [\lambda_{\mathrm{m}}/\phi_{\mathrm{m}_1}M(1 + \lambda_{\mathrm{m}} + \lambda_{\mathrm{m}}/\phi_{\mathrm{m}_1}M)^r]_M^{M_0} \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Termination by monomer deactivation with solvent transfer. The kinetic scheme is given by equations (1), (2), (5), and (7); by following identical steps to those for the derivation of equation (25) but by employing the additional stationary-state criterion that $\mathrm{d}S^*/\mathrm{d}t = 0$, we obtain

$$w_r = [\lambda_{\mathrm{m}}/\phi_{\mathrm{m}_2}M(1 + \lambda_{\mathrm{m}} + \lambda/\phi_{\mathrm{m}_2}M)^r]_M^{M_0} \quad . \quad . \quad . \quad . \quad . \quad (26)$$

which could also be obtained by substituting ϕ_{m_2} for ϕ_{m_1} in equation (25), as pointed out above.

Termination by monomer and solvent deactivation with solvent transfer. The kinetic scheme is given by equations (1), (2), (5), (6), and (7), and by following the procedure used in the derivation of equation (25), we have

$$w_r = [\lambda_{\mathrm{m}}/(\phi_{\mathrm{m}_1} + \phi_{\mathrm{m}_2})M(1 + \lambda_{\mathrm{m}} + \lambda_{\mathrm{m}}/\phi_{\mathrm{m}_1}M + \lambda_{\mathrm{m}}/\phi_{\mathrm{m}_2}M)^r]_M^{M_0} \quad . \quad . \quad (27)$$

Equations (25), (26), and (27) have been derived by assuming that monomer deactivation makes a relatively small contribution to the reaction scheme and that the solvent plays a dominant role. If these conditions do not obtain, distribution curves for these systems may be obtained by a linear combination of the appropriate equations. For example, for monomer deactivation with solvent deactivation, combination of equations (17) and (22) gives

$$w_r = Ar\lambda^2/(1 + \lambda_{\mathrm{m}})^{r+1} + B[\lambda_{\mathrm{ts}}/M(1 + \lambda_{\mathrm{ts}}/M)^r]_M^{M_0} \quad . \quad . \quad . \quad (28)$$

where A and B are coefficients given by $A/B = V_{\mathrm{tm}}/V_{\mathrm{ts}}$, and $A + B = 1$. Similarly, for monomer deactivation with solvent transfer, we have

$$w_r = Ar\lambda_{\mathrm{m}}^2/(1 + \lambda_{\mathrm{m}})^{r+1} + B[\lambda_{\mathrm{st}}/M(1 + \lambda_{\mathrm{st}}/M)^r]_{M_0}^{M_0} \quad . \quad . \quad . \quad (29)$$

by substituting λ_{st} for λ_{ts} in equation (28).

FIG. 1. *Integral distribution curves.*

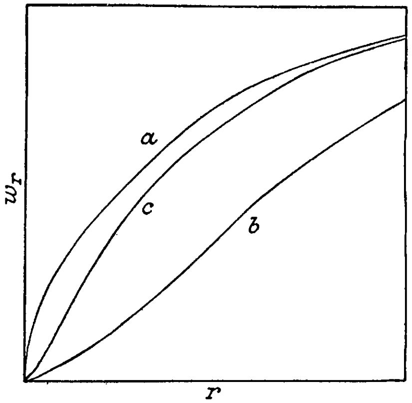
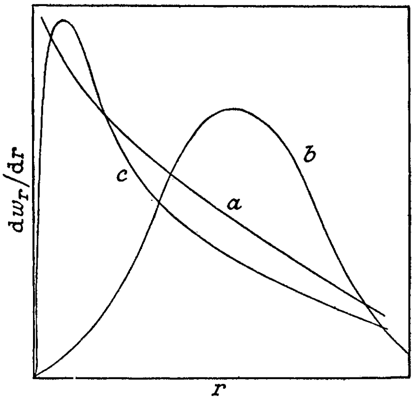


FIG. 2. *Differential distribution curves.*



Distribution functions for reaction schemes involving combinations of termination and transfer reaction other than those given, may be obtained by appropriate substitution in the above equations on the lines indicated.

Application of the Distribution Functions.—The distribution functions for the various reaction schemes considered yield two general types of distribution curve for reactions which have gone to completion ($M = 0$). Mechanisms involving predominantly spontaneous or solvent termination or solvent transfer give integral and differential distribution curves of type (*a*) (Figs. 1 and 2), whereas mechanisms involving predominantly monomer termination or monomer transfer give curves of type (*b*). Where reactions have not gone to completion ($M > 0$) curves of type (*a*) are modified so as to give a new form of curve, (*c*), but curves of type (*b*) remain unchanged. It is therefore possible in general to distinguish between kinetic mechanisms in which monomer termination or transfer predominates, and those in which spontaneous or solvent termination or solvent transfer is the principle mechanism. It is not possible by this method to distinguish between spontaneous and solvent termination, and, if solvent transfer occurs to a considerable extent with monomer termination, the form of the distribution curve will resemble that for spontaneous or solvent termination, rather than that for monomer termination.

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