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of Ce^{+++} and Yb^{+++} , all the other rare earth ions possess levels lower than the phosphorescence level of the dibenzoylmethane complex and yield, because of excitation into these levels by a process already described,¹⁰ compounds which exhibit no visible luminescence or sharp line luminescence characteristic of the rare earth ion. For the former ions, Ce^{+++} and Yb^{+++} , our preparative methods failed to produce the Ce^{+++} compound apparently due to an oxidation to Ce^{++++} ,

¹⁰ S. I. Weissman, *J. Chem. Phys.* **10**, 214 (1942).

while the Yb^{+++} compound, although easily prepared, failed to luminesce. The first excited state of Yb^{+++} involves removal of an electron from the shielded $(4f)^{13}$ configuration to $5d$ or $6s$ or $6p$. The change in the potential energy surfaces of the states of the molecule produced by this mode of excitation may be sufficient to lead to quenching by internal conversion to a high vibrational level of the ground state.¹¹

¹¹ Franck and Livingston, *J. Chem. Phys.* **9**, 184 (1941). E. Teller, *J. Phys. Chem.* **41**, 109 (1937).

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The General Kinetics of Co-Polymerization and an Extension of the Viscosity Method to Determine Velocity Constants

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Completely general kinetic expressions have been developed for the co-polymerization of n monomers, assuming that the reactivities of the radicals depend only on their terminal groups. Allowance has been made for chain transfer and the fact that thermal and photo-chemical initiation may proceed via diradicals. The equations are of the same form as those developed previously for a simple polymerization. The latter appear as a special case in which $n=1$.

It is pointed out that the method previously developed for determining the velocity constants in simple polymerizations can be used without modification in the study of co-polymerizations. In this way 12 of the 14 velocity constants in a binary co-polymerization can be determined absolutely, and a relation between the remaining two obtained.

WE have recently described a method for determining the absolute velocity constants in simple vinyl polymerizations.¹ This method, which has been justified by work in these laboratories,^{1,2} has several advantages; in particular the rate of chain starting need not be measured independently, the velocity constant for the transfer reaction with the monomer can be determined directly, and the measurements can be made at very low conversions. It seemed desirable to see how much information could be obtained by extending this method to co-polymerization. The viscosity method should be particularly convenient, since the low conversions would eliminate inconvenience arising from changes in reactant composition.

As was the case of simple polymerization, a more exact kinetic scheme is required than the one in current use. Not only must chain transfer be included, but also the fact that the initial centers in thermal or photo-polymerizations may be diradicals. The importance of these factors in the polymerization of single monomers was established by Bamford and Dewar.¹

We have found it possible to derive simple expressions for the co-polymerization of n monomers at small conversions, which provide the most complete account of the reaction kinetics at present available. The method is essentially that used by Walling and Briggs³ to derive the co-polymer composition for mixtures of n monomers. However, previous workers have not given general expressions for molecular weights etc., of the co-polymer, possibly because they did not fully realize the similarity between the equations for polymerization and co-polymerization. As already indicated, even the calculations for binary mixtures involved unjustifiable simplifications.

KINETIC SCHEME AND NOTATION

The kinetic scheme is an elaboration of that described in Part I¹ for simple polymerizations. As in the simple case there will in general be two types of radical present; double radicals formed by photo-chemical or thermal initiation, and single radicals formed by catalytic initiation or transfer. We make the usual assumption that the reactivity of a radical is determined solely by its terminal monomer unit. The entities present, and

¹ Bamford and Dewar, *Proc. Roy. Soc. London*, **192**, 309 (1948); This paper is called Part I in the text.

² Bamford and Dewar, (methyl methacrylate) *Proc. Roy. Soc. London*, **197**, 356 (1949); Axford (p-methoxystyrene) *ibid.*, p. 374; Dixon-Lewis (vinyl acetate) *ibid.* **198**, 510 (1949).

³ Walling and Briggs, *J. Am. Chem. Soc.* **67**, 1774 (1945).

the relevant notation are as follows:

M_r monomer r ($r=1, 2, \dots, n$).

X_r any radical center ending in M_r .

D_{2rs} diradical ending in M_r and M_s .

D_{1r} single radical ending in M_r , and formed by the death of one end of a D_2 radical.

R_r single radical ending in M_r produced by transfer.

$$[M] = \sum_r [M_r], \quad [X] = \sum_r [X_r], \quad [R] = \sum_r [R_r],$$

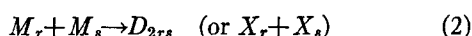
$$[D_2] = \sum_r \sum_s [D_{2rs}], \quad [D_1] = \sum_r [D_{1r}],$$

$$\phi_r = [M_r]/[M], \quad \theta_r = [X_r]/[X].$$

Velocity constants for initiation, propagation, transfer, and termination are denoted as in Part I¹ by k_1, k_2, k_3, k_4 respectively. Two additional suffixes are necessary, however, to specify the reactants. In the propagation and transfer reactions, the second suffix denotes the radical, and the third the monomer. Thus k_{2rs} is the propagation constant for the reaction



The velocity constant for the thermal initiation



would similarly be k_{1rs} , and no distinction would be drawn between k_{1rs} and k_{1sr} . It is convenient, however, to divide this constant into two equal parts k_{1rs}' and k_{1sr}' . Thus for reaction (2) we have

$$\begin{aligned} -d[M_r]/dt &= -d[M_s]/dt = d[D_{2rs}]/dt \\ &= k_{1rs}[M_r][M_s] = k_{1rs}'[M_r][M_s] \\ &\quad + k_{1sr}'[M_s][M_r] = 2k_{1rs}'[M_r][M_s]. \end{aligned} \quad (3)$$

The termination constant k_{4rs} is also split into equal parts k_{4rs}' and k_{4sr}' . Likewise D_{2rs} is divided into equal parts D_{2rs}' and D_{2sr}' .

In deriving the stationary state equations it is convenient to assume that the chains are long, so that the initiation and termination reactions can be neglected. It is also assumed that the degree of polymerization is large, so that transfer is slow compared to propagation and that termination occurs exclusively by disproportionation (see reference 2). The stationary state equations may now be written down. They are

$$- [X_r] \sum_s k_{2rs} [M_s] + [M_r] \sum_s k_{2sr} [X_s] = 0 \quad (r=1, 2, \dots, n). \quad (4)$$

Dividing (4) throughout by $\sum_r [M_r] \sum_s [M_s]$ we obtain

$$-\theta_r \sum_s k_{2rs} \phi_s + \phi_r \sum_s k_{2sr} \theta_s = 0 \quad (s=1, 2, \dots, n). \quad (5)$$

This system of homogeneous linear equations has a non-zero solution, for it is evident that

$$\Delta \equiv \det |k_{2rs} \phi_s - \delta_{rs} \sum_t k_{2rt} \theta_t| = 0 \quad (6)$$

since the sum of the elements of any row is zero. Let D_r be the determinant obtained by striking out the first row and r^{th} column of Δ , and let Δ_r be defined by

$$D_r = (-1)^{n-r+1} \Delta_r, \quad (7)$$

so that Δ_r is always positive. The solution of (5) is

$$\theta_r = \mu \Delta_r = \Delta_r / \sum_s \Delta_s, \quad (8)$$

where μ is a constant. The stationary state equations for $[D_2]$, $[D_1]$, $[R]$ and $[X]$ may now be written down for a thermal polymerization. They are

$$\begin{aligned} d[D_2]/dt &= \sum_r \sum_s k_{1rs}' [M_r] [M_s] \\ &\quad - \sum_r \sum_s \sum_t k_{3rt} [D_{2rs}'] [M_t] \\ &\quad - \sum_r \sum_s \sum_t k_{3st} [D_{2rs}'] [M_t] \\ &\quad - \sum_r \sum_s \sum_t k_{4rt}' [D_{2rs}'] [X_t] \\ &\quad - \sum_r \sum_s \sum_t k_{4st}' [D_{2rs}'] [X_t] = 0, \end{aligned} \quad (9)$$

$$\begin{aligned} d[D_1]/dt &= \sum_r \sum_s \sum_t k_{3rt} [D_{2rs}'] [M_t] \\ &\quad + \sum_r \sum_s \sum_t k_{3st} [D_{2rs}'] [M_t] \\ &\quad + \sum_r \sum_s \sum_t k_{4rt}' [D_{2rs}'] [X_t] \\ &\quad + \sum_r \sum_s \sum_t k_{4st}' [D_{2rs}'] [X_t] \\ &\quad - \sum_r \sum_s k_{3rs} [D_{1r}] [M_s] \\ &\quad - \sum_r \sum_s k_{4rs}' [D_{1r}] [X_s] = 0, \end{aligned} \quad (10)$$

$$\begin{aligned} d[R]/dt &= \sum_r \sum_s \sum_t k_{3rt} [D_{2rs}'] [M_t] \\ &\quad + \sum_r \sum_s \sum_t k_{3st} [D_{2rs}'] [M_t] \\ &\quad + \sum_r \sum_s k_{3rs} [D_{1r}] [M_s] \\ &\quad - \sum_r \sum_s k_{4rs}' [R_r] [X_s] = 0, \end{aligned} \quad (11)$$

$$\begin{aligned} d[X]/dt &= \sum_r \sum_s k_{1rs}' [M_r] [M_s] \\ &\quad - \sum_r \sum_s k_{4rs}' [X_r] [X_s] = 0. \end{aligned} \quad (12)$$

Also, from the definition of θ_r ,

$$[D_{2rs}] = \theta_r \theta_s [D_2], \quad [D_{1r}] = \theta_r [D_1], \quad [R_r] = \theta_r [R]. \quad (13)$$

We define $\lambda_1, \lambda_2, \lambda_3, \lambda_4$ by the equations

$$\begin{aligned} \lambda_1 &= \sum_r \sum_s k_{1rs}' \phi_r \phi_s, & \lambda_2 &= \sum_r \sum_s k_{2rs} \theta_r \phi_s, \\ \lambda_3 &= \sum_r \sum_s k_{3rs} \theta_r \phi_s, & \lambda_4 &= \sum_r \sum_s k_{4rs}' \theta_r \theta_s. \end{aligned} \quad (14)$$

Equations (9)–(12) now become

$$\lambda_1[M]^2 - 2\lambda_3[D_2] - 2\lambda_4[D_2][X] = 0, \quad (15)$$

$$2\lambda_3[D_2][M] + 2\lambda_4[D_2][X] - \lambda_3[D_1][M] - \lambda_4[D_1][X] = 0, \quad (16)$$

$$2\lambda_3[D_2][M] + \lambda_3[D_1][M] - \lambda_4[R][X] = 0, \quad (17)$$

$$\lambda_1[M]^2 = \lambda_4[X]^2. \quad (18)$$

From Eqs. (15)–(18) it follows that

$$\left. \begin{aligned} [X] &= (\lambda_1/\lambda_4)^{1/2}[M], \\ [D_2] &= \lambda_1[M]/[4\{\lambda_3 + (\lambda_1\lambda_4)^{1/2}\}], \\ [D_1] &= 2[D_2], \\ [R] &= 4\lambda_3(\lambda_1\lambda_4)^{-1/2}[D_2] = 4\beta[D_2], \\ \beta &= k_3(k_1k_4)^{-1/2}, \\ \bar{P}_1 &= \lambda_2/\{\lambda_3 + (\lambda_1\lambda_4)^{1/2}\}, \\ \bar{P}_2 &= 2\bar{P}_1, \\ d[P_1]/dt &= \lambda_3(\lambda_1/\lambda_4)^{1/2}[M]^2 = \beta\lambda_1[M]^2, \\ d[P_2]/dt &= \frac{1}{2}\lambda_1[M]^2, \\ -d[M]/dt &= \lambda_2(\lambda_1/\lambda_4)^{1/2}[M]^2, \end{aligned} \right\} \quad (19)$$

where \bar{P}_1 , \bar{P}_2 are the mean degrees of polymerization of transfer and initial polymer respectively, and β is the number of times chain transfer occurs in a kinetic chain. These equations are identical in form with those of a simple polymerization,¹ the velocity constants in the latter being replaced by the corresponding λ 's.

In a photo-chemical polymerization, the rate of chain starting is proportional to the light intensity for a given composition, and may then be written in the form

$$\lambda_1[M]^2(1+AI) \equiv \lambda_1\xi^2[M]^2. \quad (20)$$

Equations (19) then hold for photo-polymerizations with λ_1 replaced by $\lambda_1\xi^2$.

We may also assume that the co-polymer obeys the Houwink viscosity law, $[\eta] = K\bar{P}^\alpha$. This is a reasonable assumption since individual polymers appear to obey the law with exponents close to $\frac{2}{3}$. The following results may now be obtained* by applying the method of Part I.¹

$$\left. \begin{aligned} \bar{P} &= [2\lambda_2(\lambda_1\lambda_4)^{-1/2}/(2\beta + \xi)], \\ -d[M]/dt &= \lambda_2\xi[M]^2(\lambda_1/\lambda_4)^{1/2}, \\ \frac{d\eta}{dt} &= K[M]^2 \left\{ \frac{\lambda_1^{1/2}(1-\alpha)\lambda_2^{1+\alpha}}{\lambda_4^{1/2}(1+\alpha)} \right\} \\ &\quad \times \frac{\xi[\beta + (1 + \frac{1}{2}\alpha)\xi]}{(\beta + \xi)^{1+\alpha}}, \end{aligned} \right\} \quad (21)$$

where η is the ideal specific viscosity.⁴ These expres-

* This involves the additional assumption that the molecular weight distribution is similar to that for a single polymer. It can be shown that this is so if Eq. (4) holds.

⁴ Ideal specific viscosity is defined by $\eta = c[\eta]$, where c is the concentration of the polymer. The determination of η from the observed specific viscosity is discussed in Part I.

sions are naturally identical with those given previously for simple polymerizations,¹ and corresponding equations may be written down for the photo-chemical after- and pre-effects.

For numerical work involving Eqs. (21), it is first necessary to calculate the λ 's from Eq. (14). It is easily seen, however, that Eqs. (21) are unchanged if θ_r is replaced by Δ_r in calculating the λ 's, and for this purpose it is therefore unnecessary to use the full expression in Eq. (8).

To complete the kinetic treatment we give two additional results. The rate of consumption of monomer M_r is given by

$$\begin{aligned} -d[M_r]/dt &= \sum_r k_{2sr}[X_s][M_r] \\ &= \phi_r[M]^2(\lambda_1/\lambda_4)^{1/2} \sum_r k_{2sr}\theta_s, \end{aligned} \quad (22)$$

and the average length of a sequence of M_r units in the polymer, \bar{n}_r , is given by

$$\bar{n}_r = c/(c - k_{2rr}\phi_r), \quad (23)$$

where

$$c = \sum_s \{k_{2rs}\phi_s + k_{3rs}\phi_s + (\lambda_1/\lambda_4)^{1/2}k_{4rs}'\theta_s\}.$$

POLYMERIZATION IN SOLVENTS

The velocity constant for reaction between x_r and solvent S will be denoted by k_{5r} . A quantity λ_5 is defined by

$$\lambda_5 = \sum_r k_{5r}\theta_r. \quad (24)$$

As before, we obtain the equations

$$\begin{aligned} \bar{P}_1 &= \frac{\lambda_2[M]}{\lambda_3[M] + \sqrt{(\lambda_1\lambda_4)[M] + \lambda_5[S]}}, \\ \bar{P}_2 &= 2\bar{P}_1, \\ [R] &= 2[D_1](\lambda_3[M] + \lambda_5[S])/\sqrt{(\lambda_1\lambda_4)[M]}, \\ d[P_1]/d[P_2] &= [R]/2[D_1]. \end{aligned}$$

Hence

$$\bar{P} = 2\lambda_2[M]/\{2\lambda_3[M] + \sqrt{(\lambda_1\lambda_4)[M] + 2\lambda_5[S]}\},$$

i.e.,

$$\frac{1}{\bar{P}} = \frac{1}{\bar{P}_0} + \frac{\lambda_5}{\lambda_2} \frac{[S]}{[M]}. \quad (25)$$

Equation (25) is identical in form with that derived by Mayo⁵ for polymerization of a single monomer in a solvent.

⁵ Mayo, J. Am. Chem. Soc. 65, 2324 (1943).

SPECIAL CASES

(1) $n=1$. Here $\theta=\phi=1$ and $\lambda_r=k_r$ ($r=1, 2, 3, 4$). Equations (21) thus reduce to those given in Part I¹ for a simple polymerization.

(2) $n=2$.

$$\left. \begin{aligned} \Delta_1 &= k_{221}\phi_1, & \Delta_2 &= k_{212}\phi_2, \\ \lambda_1 &= k_{111}\phi_1^2 + k_{112}\phi_1\phi_2 + k_{122}\phi_2^2, \\ \lambda_2 &= k_{211}k_{221}\phi_1^2 + 2k_{212}k_{221}\phi_1\phi_2 + k_{222}k_{212}\phi_2^2, \\ \lambda_3 &= k_{311}k_{221}\phi_1^2 + (k_{312}k_{221} + k_{321}k_{212})\phi_1\phi_2 \\ &\quad + k_{322}k_{212}\phi_2^2, \\ \lambda_4 &= k_{411}k_{221}^2\phi_1^2 + k_{412}k_{221}k_{212}\phi_1\phi_2 + k_{422}k_{212}^2\phi_2^2. \end{aligned} \right\} \quad (26)$$

From Eq. (22)

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1] k_{211}\Delta_1 + k_{221}\Delta_2}{[M_2] k_{212}\Delta_1 + k_{222}\Delta_2} = \frac{k_{221}[M_1] \{ k_{211}[M_1] + k_{212}[M_2] \}}{k_{212}[M_2] \{ k_{221}[M_1] + k_{222}[M_2] \}}, \quad (27)$$

which is a well-known result first obtained by Mayo and Lewis.⁶

(3) $n=3$. In this case only the values of Δ_r will be given. These are sufficient to enable the composition of the co-polymer to be calculated immediately.

$$\begin{aligned} \Delta_1 &= k_{221}k_{231}\phi_1^2 + k_{221}k_{232}\phi_1\phi_2 + k_{231}k_{223}\phi_1\phi_3, \\ \Delta_2 &= k_{232}k_{212}\phi_2^2 + k_{232}k_{213}\phi_2\phi_3 + k_{212}k_{231}\phi_2\phi_1, \\ \Delta_3 &= k_{213}k_{223}\phi_3^2 + k_{213}k_{221}\phi_3\phi_1 + k_{223}k_{212}\phi_3\phi_2, \end{aligned}$$

and

$$\frac{d \log[M_1]}{k_{211}\Delta_1 + k_{221}\Delta_2 + k_{231}\Delta_3} = \frac{d \log[M_2]}{k_{212}\Delta_1 + k_{222}\Delta_2 + k_{232}\Delta_3} = \frac{d \log[M_3]}{k_{213}\Delta_1 + k_{223}\Delta_2 + k_{233}\Delta_3}. \quad (28)$$

This equation is identical with that obtained by Walling and Briggs.³

DISCUSSION

It was pointed out above that there is a formal identity between the equations representing the polymerization of a single monomer, and those for the co-polymerization of n monomers. Since the λ 's will be constant for a constant temperature, and constant composition of reactants, a mixture of n monomers will

behave kinetically as a single monomer with velocity constants $\lambda_1, \lambda_2, \lambda_3, \lambda_4$, provided that measurements are carried out at very small conversions, so that the composition of the reactant mixture is not changed. The methods described previously^{4,7} fulfil this condition, and can therefore be taken over in toto to determine the λ 's in a co-polymerization, and also the quantities K, α which determine the molecular weight-viscosity relation.

With the assumption made previously that the reactivity of a radical depends only on its terminal monomer unit, it is clear that constants of the form k_{rss} ($r=1, 2, 3, 4$) can be identified with velocity constants of the single monomers, and constants of the form k_{rst} ($s \neq t$) with those for co-polymerization of pairs of monomers. To determine absolute velocity constants, including the crossed constants, all that is necessary therefore is to study single monomers, and pairs of monomers. The general equations developed above can then be used to predict the behavior of more complicated mixtures. We therefore consider specially the case of two monomers.

There are in all 14 velocity constants, of which 8 can be determined by measurements on the single monomers. From a study of the co-polymerization of one mixture four further relations—the λ 's—are obtained as indicated above. The study of other compositions gives only one further relation. Thus it is impossible to determine all 14 constants absolutely. Inspection of the equations shows that $k_{112}, k_{212}, k_{221}, k_{412}$ can be evaluated separately, but the quantity $k_{312}k_{221} + k_{321}k_{212}$ cannot be resolved, and hence the crossed transfer constants cannot be isolated.

The following further points of interest emerge:

(1) It is well known that small amounts of an easily polymerizable monomer act as a retarder when added to a monomer which is less reactive (e.g., styrene added to vinyl acetate). This behavior can easily be interpreted in terms of Eqs. (21) and (26). Measurements in these laboratories suggest that the termination constants for radicals of different reactivity do not differ widely; consequently at a given rate of chain starting the stationary concentration of radicals will not be appreciably affected by small additions of one monomer to another. The over-all rate will then be proportional to λ_2 , and it is evident from Eq. (26) that λ_2 will be small when k_{221} and ϕ_2 are both small.

(2) By carrying out solvent polymerization with different monomer ratios it would be possible to study the variation of K and α with the composition of the co-polymer. This could provide some basis for the theoretical treatment of the viscosity of polymer solutions.

(3) A knowledge of the variation of A (Eq. (20)) with composition would provide information as to the nature of the primary photo-chemical process.

(4) It would not be necessary to know the constants for the individual monomers in studying the co-polymerization of a pair provided that the co-polymerization were carried out for at least four different compositions.

Investigations along these lines are now in progress.

⁶ Mayo and Lewis, J. Am. Chem. Soc. 66, 1594 (1944).

⁷ Bamford and Dewar, Proc. Roy. Soc. London 192, 329 (1948).