Moments of the Size Distribution in Radical Polymerization

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For a number of polymerization models, we have developed equations that enable one to follow in time the moments of the polymer size distribution and the conversion. The exact and approximate solutions for the leading moments of the size distribution are presented for polymerization with initiation, propagation, and termination by combination. Approximate solutions for polymerizations with the additions of termination by disproportionation, chain transfer to monomer, and chain transfer to solvent show how these reactions decrease the average polymer size. From a simple model that exhibits autoacceleration a concomitant increase in the average polymer size also occurs.

Although the general kinetic equations of radical polymerization carry complete knowledge of the polymer size distribution as well as the rate of polymerization, they are tractable for relatively few polymerizations (*1* to *5*). Usually in a size distribution study of polymerization, the equations are simplified by the assumption of a stationary state (*6*).

To make a large number of polymerizations amenable to analysis without such a limiting assumption, we focus our attention on the moments of the size distribution rather than on the size distribution itself. As a working matter, we are often content with knowing just the leading moments. This presupposes, of course, that we are describing a unimodal distribution. Although experimental evidence on this point is lacking, we expect on physical grounds that most polymerizations yield unimodal distributions.

In developing equations in the moments we choose for analytical convenience to work with the continuous instead of the exact discrete kinetic equations, that is, we take the polymer size (chain length) to be a continuous rather than a discrete variable. Zeman and Amundson (*2*, *3*) have previously used the continuous approach, but here we develop the equations in the framework given by Hulburt and Katz (*7*) in their study of particulate systems. Consequently, we can write the continuous kinetic equations directly from the pertinent chemical reactions.

Among the reactions which may occur in polymerization, we consider the following:

1. Initiation, where initiator I decomposes into the primary radical R_0

$$I \xrightarrow{\alpha} 2R_0$$

2. Propagation, where monomer M reacts with radical R_i containing i monomer units, to form a radical with $i + 1$ units

$$R_i + M \xrightarrow{\beta} R_{i+1} \quad i = 0, 1, 2, \ldots$$

3. Chain transfer to monomer, where monomer M reacts with R_i to form terminated polymer P_i and radical R_1

$$R_i + M \xrightarrow{\epsilon} P_i + R_1 \quad i = 0, 1, 2, \ldots$$

4. Chain transfer to solvent, where radical R_i reacts with solvent S to form polymer P_i and solvent radical S' which may react further

$$R_i + S \xrightarrow{\eta} S' + P_i$$

$$S' + M \xrightarrow{\zeta} R_i$$

$$S' + R_i \xrightarrow{\xi} P_i$$

$$i = 0, 1, 2, \ldots$$

5. Termination, where two radicals react by combination

$$R_i + R_j \xrightarrow{\gamma} P_{i+j}$$

or by disproportionation

$$R_i + R_j \xrightarrow{\theta} P_i + P_j \quad i, j = 0, 1, 2, \ldots$$

The rate coefficients are shown to be independent of the size indices i, j. Although our moment methods will not directly handle any very general size dependence, certain simple forms of dependence are tractable. We show in the appendix how the moment equations can be developed when the propagation and termination coefficients associated with the primary radicals R_0 differ from the coefficients associated with the higher R_i. The rate coefficients may however depend on such overall factors as the extent of polymerization; in fact we shall study autoacceleration by introducing a dependence of the termination coefficient on monomer concentration.

We shall describe a continuous model of a basic polymerization process, which includes initiation, propagation, and termination. After developing the moment equations for the size distribution, we examine the exact and a few approximate solutions for the leading moments. Then we consider polymerization processes with additional reaction steps. Although the exact solutions of the moment equations of the more complicated situations often require machine computation, we do get approximate solutions analytically.

We assume that each polymerization process given here occurs in an isothermal, well-stirred batch reactor. Although all our equations will be set down for such a batch reactor, the method can easily be extended to the study of continuous inflow-outflow systems. It may be noted

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finally that we deal here only with first-order partial differential equations in radical concentration, ignoring any dispersion in growth rates. Moment methods might well be applied to the second-order partial differential equations that take this dispersion into account (3), but we would in any case expect these dispersion effects to be small in a homogeneous, well-stirred reactor.

A BASIC MODEL

Our basic polymerization model consists of initiation, propagation, and termination by combination:

$$I \xrightarrow{\alpha} 2R_0$$

$$R_i + M \xrightarrow{\beta} R_{i+1} \qquad i = 0, 1, 2, \ldots$$

$$R_i + R_j \xrightarrow{\gamma} P_{i+j} \quad i, j = 0, 1, 2, \ldots$$

The decomposition of initiator I we take as irreversible. (In practice, peroxides, which produce carbon dioxide, as well as the primary radical R_0, are commonly used as initiators.) For analytical convenience we allow the combination of two primary radicals to form the fictional polymer P_0. This fiction is of little consequence when the concentration ratio of primary radicals to all radicals is small, as it usually is.

Noting that the average polymer size is usually large, we treat the polymer size as a continuous variable x, rather than as a discrete index i. To obtain the continuous form of the discrete kinetic equations, we may either take the discrete equations to the continuous limit or, following Hulburt and Katz (7), write the continuous equations directly. In the latter approach one simply sets down the number-density balances for the radicals and terminated polymers.

Here, we express the radical and polymer size distributions as functions $r(x, t)$ and $p(x, t)$, where

$$\int_a^b r(x, t)\,dx \quad ; \quad \int_a^b p(x, t)\,dx$$

are the concentrations of radicals and terminated polymers that have between a and b monomers at time t.

The equations in $r(x, t)$ and $p(x, t)$, together with the equations of initiator concentration $I(t)$ and monomer concentration $M(t)$, appear as

$$\frac{dI(t)}{dt} = -\alpha I(t) \qquad ; \quad I|_{t=0} = i_o$$

$$\frac{dM(t)}{dt} = -\beta M(t) \int r(y, t)\,dy \qquad ; \quad M|_{t=0} = m_o$$

$$\frac{\partial r(x, t)}{\partial t} + \beta M(t) \frac{\partial r(x, t)}{\partial x}$$

$$= 2\alpha I(t)\,\delta(x) - \gamma r(x, t) \int r(y, t)\,dy\,; \qquad r|_{t=0} = 0$$

$$\frac{\partial p(x, t)}{\partial t} = \frac{\gamma}{2} \int r(x - y, t)\, r(y, t)\,dy \qquad ; \quad p|_{t=0} = 0$$

where the integrals are taken over all allowable polymer sizes. Consequently

$$\int r(y, t)\,dy$$

is just the total concentration of radicals.

These equations for radical and polymer size distributions can be easily understood by analogy to the Liouville equation for growing particles. First, analogous to the propagation rate is the growth rate (for a single particle)

$$\frac{dx}{dt} = \beta M(t)$$

which gives rise to the convective term

$$\beta M(t) \frac{\partial r}{\partial x}(x, t)$$

Second, the initiation step is analogous to the point source

$$2\alpha I(t)\,\delta(x)$$

where the delta function indicates that all the primary radicals are formed at size zero.

Finally, we treat the termination step as an agglomeration process, with the rate of disappearance of radicals of size x

$$\gamma r(x, t) \int r(y, t)\,dy$$

appearing in the equation for $r(x, t)$; the corresponding rate of formation of terminated polymer of size x appears as

$$\frac{\gamma}{2} \int r(x - y, t)\, r(y, t)\,dy$$

in the equation for $p(x, t)$.

Introducing the moments for the radical and polymer size distributions in the form

$$\lambda_k(t) = \int x^k\, r(x, t)\,dx; \quad \mu_k(t) = \int x^k\, p(x, t)\,dx \qquad (k = 0, 1, 2 \ldots)$$

we find from the kinetic equations above:

$$\frac{dI}{dt} = -\alpha I \qquad ; \quad I|_{t=0} = i_o$$

$$\frac{d\lambda_0}{dt} = 2\alpha I - \gamma\lambda_0^2 \qquad ; \quad \lambda_0|_{t=0} = 0$$

$$\frac{dM}{dt} = -\beta M \lambda_0 \qquad ; \quad M|_{t=0} = m_o$$

$$\frac{d\lambda_k}{dt} = \beta M k \lambda_{k-1} - \gamma\lambda_0\lambda_k \;;\; \lambda_k|_{t=0} = 0 \qquad (k = 1, 2, \ldots)$$

$$\frac{d\mu_k}{dt} = \frac{\gamma}{2} \sum_{j=0}^{k} \binom{k}{j} \lambda_j \lambda_{k-j} \;;\; \mu_k|_{t=0} = 0 \quad (k = 0, 1, 2, \ldots)$$

The leading moments μ_0 and μ_1 denote, respectively, the concentration of terminated polymer and the total amount of monomer (per reactor volume) associated with the terminated polymer; the moments λ_0 and λ_1 have a corresponding meaning for the radicals (growing polymer). Related to the moments of the distributions are the number-average degree of polymerization $\overline{X}_n$ (average polymer size) and weight-average degree of polymerization $\overline{X}_w$:

$$\overline{X}_n = \frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0} \quad ; \quad \overline{X}_w = \frac{\mu_2 + \lambda_2}{\mu_1 + \lambda_1}$$

These first-order differential equations in the moments can be solved consecutively to give the k^{th} moment of the polymer size distribution μ_k. The solution to the initiator equation is simply

$$I = i_o\, e^{-\alpha t} = i_o \left(\frac{\phi}{a}\right)^2$$

where

$$\phi = a\, e^{-\alpha/2t}; \quad a = \left(\frac{8\gamma i_o}{\alpha}\right)^{1/2}$$

which we use in obtaining λ_0. Noting that the λ_0 equation is of the Riccati type, we can transform it into a Bessel's equation to get

$$\lambda_0 = \frac{4i_o}{a^2}\phi \left\{ \frac{K_1(\phi) - \dfrac{K_1(a)}{I_1(a)} I_1(\phi)}{K_0(\phi) + \dfrac{K_1(a)}{I_1(a)} I_0(\phi)} \right\}$$

We can now solve for the monomer concentration or the fraction of unreacted monomer

$$m = \left\{ \frac{K_0(\phi) + \dfrac{K_1(a)}{I_1(a)} I_0(\phi)}{K_0(a) + \dfrac{K_1(a)}{I_1(a)} I_0(a)} \right\}^{-b}$$

where

$$m = \frac{M}{M_0} \quad ; \quad b = \beta/\gamma$$

Also, we can get the zeroth moment of the polymer size distribution, that is, the concentration of terminated polymers of all sizes

$$\mu_0 = i_o - I - \frac{\lambda_0}{2}$$

which is just a material balance for the radicals. Knowing λ_0 and M, we find that

$$\lambda_1 = \frac{m_o b}{1-b}\{m - m^{1/b}\}$$

$$\mu_1 = \frac{m_o}{1-b}\{1-m\} - \frac{m_o b}{1-b}\{1 - m^{1/b}\}$$

which is consistent with the monomer balance

$$\mu_1 + \lambda_1 = m_o\,(1-m)$$

We continue in this fashion to get the second moments:

$$\lambda_2 = \frac{(a\,b\,m_o)^2\, m^{1/b}}{2i_o\,(1-b)} \int_\phi^a (m^{2-1/b} - m)\, \frac{d\phi_1}{\phi_1}$$

$$\mu_2 = \frac{(a\,b\,m_o)^2}{2i_o} \left\{ \frac{1}{1-b} \int_\phi^a (m^2 - m^{1+1/b})\, \frac{d\phi_1}{\phi_1} + \frac{1}{2(1-b)^2} \int_\phi^a (m - m^{1/b})\, \frac{d\phi_1}{\phi_1} \right\} - \lambda_2$$

Although higher moments can also be found, their solutions are in the form of more complicated quadratures.

APPROXIMATE SOLUTIONS TO THE BASIC MODEL

Since the exact solutions of the moment equations are unwieldy, we shall consider several approximations. First, we note that in most practical situations, the rate coefficients satisfy the inequalities

$$\alpha/i_o << \beta << \gamma$$

Alternatively, we can say that

$$a >> 1; \quad b << 1$$

where a and ab are commonly of the orders of 10^5 and 1, respectively. Under these conditions, the asymptotic form for the concentration of radicals as a function of the pseudo time ϕ becomes

$$\lambda_0 = \frac{4i_o}{a^2}\phi$$

where

$$\phi_L < \phi < \phi_U$$

The bounds are defined (within an arbitrary error) by the asymptotic relations:

Lower bound

$$I_0(\phi_L) \sim I_1(\phi_L) \sim \frac{e^{\phi_L}}{\sqrt{2\pi\phi_L}}$$

$$K_0(\phi_L) \sim K_1(\phi_L) \sim \sqrt{\frac{\pi}{2\phi_L}}\, e^{-\phi_L}$$

Upper bound

$$\tanh\,(a - \phi_U) \sim 1$$

We may take the values of ϕ_L and ϕ_U to be 10 and $a - 5$, respectively. These approximations lead to simpler expressions for the moments and the fraction of unreacted monomer. For the latter we find

$$m = e^{-b(a-\phi)} = e^{-ab(1-e^{-\alpha/2\,t})}$$

In Figure 1 m is plotted as a function of $\alpha t/2$ for several values of ab. Considering both growing and terminated polymer together, we get

$$\mu_0 + \lambda_0 = i_o \left[1 - \left(\frac{\phi}{a}\right)^2 \right]$$

$$= i_o \left[1 - \left(\frac{1}{ab}\ln m + 1\right)^2 \right]$$

$$\mu_1 + \lambda_1 = m_o\,(1-m)$$

$$\mu_2 + \lambda_2 = \frac{3(a\,b\,m_o)^2}{4i_o} \int_m^1 \frac{m_1\, dm_1}{\ln m_1 + ab}$$

$$= 3/4\, \frac{(a\,b\,m_o)^2}{i_o}\, e^{-2ab}\, [Ei(2ab) - Ei(2ab + 2\ln m)]$$

where

$$E_i(A) = \int_{-\infty}^{A} \frac{e^z}{z}\, dz$$

is a tabulated function (8). The bounds expressed in frac-

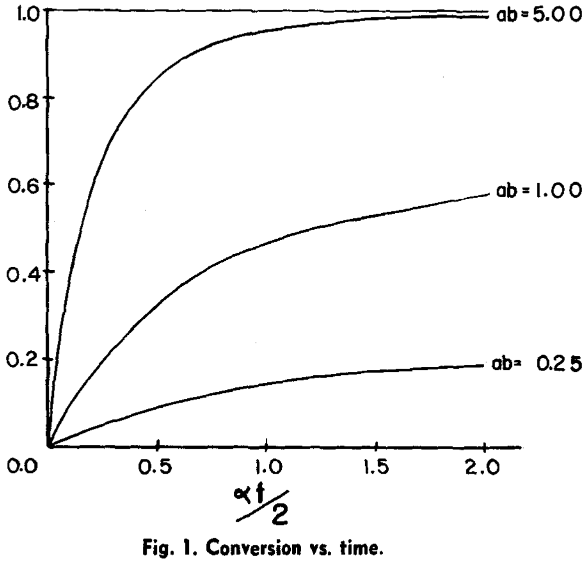

Fig. 1. Conversion vs. time.

tion of monomer are of course

$$e^{-b(a-\phi_L)} < m < e^{-b(a-\phi_U)}$$

From the appropriate moment ratios, we find the number average and weight average degree of polymerization:

$$\overline{X}_n = \frac{m_o}{i_o} \cdot \frac{1-m}{1-\left(\frac{1}{ab}\ln m + 1\right)^2}$$

and

$$\overline{X}_w = \frac{3\,m_o}{4i_o} \cdot (ab)^2 \cdot e^{-2ab} \cdot \frac{Ei(2ab) - Ei(2ab + 2\ln m)}{1-m}$$

The graphs of these functions for several values of ab are shown in Figure 2. For these values of ab the ratio $\overline{X}_w/\overline{X}_n$ is approximately 1.5, a number often found experimentally (9).

Next, let us assume that a stationary state exists, that is

$$\frac{d\lambda_o}{dt} = 0 = 2\alpha I - \gamma\lambda_o^2$$

Strictly speaking, this means that the concentration of radicals λ_o is constant and implies that I is constant also. The deviation of I from its initial value (for usual values of the kinetic parameters) increases as the concentration of monomer decreases according to the expression:

$$I = i_o\left(1 + \frac{1}{ab}\ln m\right)$$

As a result, solutions of the moment equations based on a strict interpretation the stationary state assumption have limited applicability.

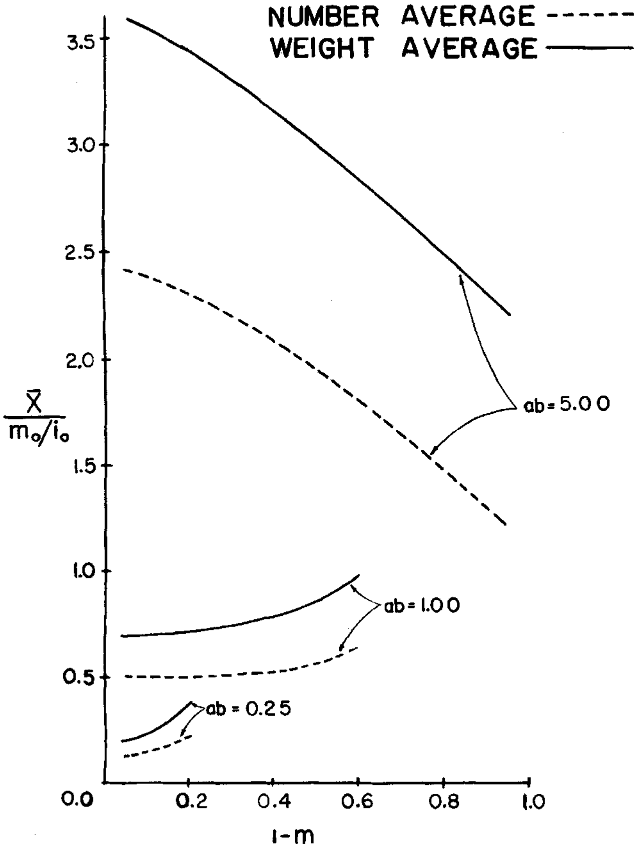

Fig. 2. Degree of polymerization vs. conversion.

If, on the other hand, we take the rate of change of radical concentration just to be suitably small, we can still consider the radical concentration to vary according to

$$\lambda_o = \frac{2\alpha I}{\gamma}$$

This is the same result obtained by the previous approximation.

To facilitate later comparisons with different kinetic models, we shall write the approximate solutions for the zeroth and first moments, assuming that the initiator concentration is constant $I = i_o$. We shall again take the rate coefficients to satisfy the inequalities

$$\alpha/i_o << \beta << \gamma$$

The leading moments are then

$$\mu_0 + \lambda_0 = \left(\frac{\alpha\,\gamma\,i_o}{2\beta^2}\right)^{1/2} \ln m$$

and

$$\mu_1 + \lambda_1 = m_o\,(1-m)$$

where

$$m = e^{-\frac{\alpha\beta}{2\gamma}t}$$

Consequently, the average polymer size is

$$\overline{X}_n = \frac{\mu_1 + \lambda_1}{\mu_0 + \lambda_0} = \left(\frac{2\,\beta^2\,i_o}{\gamma\alpha}\right)^{1/2} \left(\frac{m_o}{i_o}\right) \left\{\frac{1-m}{\ln\frac{1}{m}}\right\}$$

A MODEL FOR AUTOACCELERATION

As the first variation on the basic model, we look at autoacceleration: the rapid increase in polymerization that arises when the polymer concentration becomes great enough to increase the viscosity of the reaction mixture. As the viscosity increases, the movement of the growing polymers becomes more restricted; effectively, the rate coefficient of termination decreases, although not that of propagation.

If we assume that the termination rate coefficient is a function of monomer concentration, we easily obtain the moments of the polymer size distribution. For practical purposes the parameters of the assumed termination function might be found by comparing the polymerization rate from an actual experiment with that from the model.

We shall consider the effect of autoacceleration by using the basic model; consequently, the moment equations differ only in the termination coefficient. Since our comparison with the basic model will be made simply in terms of average polymer size, we shall set down the moment equations only through order 1.

The relevant moment equations are accordingly

$$\frac{dM}{dt} = -\beta\lambda_0 M \qquad ; \; M|_{t=0} = m_o$$

$$\frac{d\lambda_0}{dt} = 2\alpha I - \gamma(M)\lambda_0^2 \qquad ; \; \lambda_0|_{t=0} = 0$$

$$\frac{d\lambda_1}{dt} = \beta M\lambda_0 - \gamma(M)\lambda_1 \qquad ; \; \lambda_1|_{t=0} = 0$$

$$\frac{d\mu_0}{dt} = \frac{\gamma}{2}(M)\,\lambda_0^2 \qquad ; \; \mu_0|_{t=0} = 0$$

$$\frac{d\mu_1}{dt} = \gamma(M)\lambda_0\lambda_1 \qquad ; \; \mu_1|_{t=0} = 0$$

For analytical solution, we assume that

$$I = i_o;\quad \alpha/i_o << \beta << \gamma_0;\quad \gamma(M) = \gamma_0 m^z,\quad z > 0$$

and solve the equations in terms of m. Dividing the first two equations, we get

$$\frac{d\lambda_0}{dm} = -\frac{2\,\alpha\, i_o}{\beta\,\lambda_0\, m} + \frac{\gamma_0\,\lambda_0}{\beta}\, m^{z-1} \quad ; \quad \lambda_0\big|_{m=1} = 0$$

For m somewhat less than 1

$$\lambda_0 = \left(\frac{2\,\alpha\, i_o}{\gamma}\right)^{1/2} m^{-z/2}$$

Working similarly with λ_1, μ_0, and μ_1 we find the average polymer size

$$\overline{X}_n = \frac{z}{2}\left(\frac{2\,\beta^2\, i_o}{\alpha\gamma_0}\right)^{1/2} \frac{m_o}{i_o}\left\{\frac{1-m}{1-m^{z/2}}\right\}$$

With this model we see quantitatively the increase in average polymer size arising from the autoacceleration.

TERMINATION WITH DISPROPORTIONATION

Since disproportionation as well as combination may be important in the termination step, we shall incorporate it in a model with the reactions

$$I \xrightarrow{\alpha} 2R_0$$

$$R_i + M \xrightarrow{\beta} R_{i+1} \qquad (i = 0, 1, 2 \ldots.)$$

$$R_i + R_j \xrightarrow{\gamma} P_{i+j} \qquad (i, j = 0, 1, 2 \ldots.)$$

$$R_i + R_j \xrightarrow{\theta} P_i + P_j \quad (i, j = 0, 1, 2 \ldots.)$$

The kinetic equations of these reactions are

$$\frac{dI}{dt} = -\alpha I \qquad ; \quad I\big|_{t=0} = i_o$$

$$\frac{dM}{dt} = -\beta M \int r(y, t)\,dy \qquad ; \quad M\big|_{t=0} = m_o$$

$$\frac{\partial r(x, t)}{\partial t} + \beta M \frac{\partial r(x, t)}{\partial t} = 2\alpha I\delta(x) - (\gamma + \theta)\, r(x, t) \int r(y, t)\,dy; \quad r\big|_{t=0} = 0$$

$$\frac{\partial p(x, t)}{\partial t} = \frac{\gamma}{2}\int r(x-y, t)\,r(y, t)\,dy + \theta\, r(x, t)\int r(y, t)\,dy \quad ; \quad p\big|_{t=0} = 0$$

Again, for a basis of comparison we assume that $I = i_o$ and $\alpha/i_o << \beta << \gamma$ and consider just the leading moments:

$$\frac{dM}{dt} = -\beta M\lambda_0 \qquad ; \quad M\big|_{t=0} = m_o$$

$$\frac{d\lambda_0}{dt} = 2\alpha i_o - (\gamma + \theta)\lambda_0^2 \qquad ; \quad \lambda_0\big|_{t=0} = 0$$

$$\frac{d\lambda_1}{dt} = \beta M\lambda_0 - (\gamma + \theta)\lambda_0\lambda_1 \qquad ; \quad \lambda_1\big|_{t=0} = 0$$

$$\frac{d\mu_0}{dt} = \left(\frac{\gamma}{2} + \theta\right)\lambda_0^2 \qquad ; \quad \mu_0\big|_{t=0} = 0$$

$$\frac{d\mu_1}{dt} = (\gamma + \theta)\lambda_0\lambda_1 \qquad ; \quad \mu_1\big|_{t=0} = 0$$

The solutions for these equations are very similar to those of previous models. We find that the average polymer size is

$$\overline{X}_n = \left\{\frac{\beta^2\,(\gamma + \theta)\, i_0}{2\alpha\left(\frac{\gamma}{2} + \theta\right)^2}\right\}^{1/2} \frac{m_0}{i_0}\left\{\frac{1-m}{\ln\frac{1}{m}}\right\}$$

which shows the expected decrease of average polymer size with respect to the basic model. The higher order moments could be found numerically, if need be. As with the basic model, we can solve these equations exactly.

CHAIN TRANSFER TO MONOMER

We can represent a polymerization process with chain transfer to monomer by the following reactions:

$$I \xrightarrow{\alpha} 2R_o$$

$$R_i + M \xrightarrow{\beta} R_{i+1} \qquad (i = 0, 1, 2 \ldots.)$$

$$R_i + M \xrightarrow{\epsilon} R_1 + P_i \qquad (i = 0, 1, 2 \ldots.)$$

$$R_i + R_j \xrightarrow{\gamma} P_{i+j} \qquad (i, j = 0, 1, 2 \ldots.)$$

Note that the transfer step is a source of radicals of size one and provides another mechanism for termination. The continuous forms of the equations for this process are

$$\frac{dI}{dt} = -\alpha I \qquad ; \quad I\big|_{t=0} = i_0$$

$$\frac{dM}{dt} = -(\beta + \epsilon)M \int r(y, t)\,dy \qquad ; \quad M\big|_{t=0} = m_0$$

$$\frac{\partial r(x, t)}{\partial t} + \beta M \frac{\partial r(x, t)}{\partial x} = 2\alpha I\delta(x) + \epsilon M\delta(x-1)\int r(y, t)\,dy - \epsilon M r(x, t) - \gamma r(x, t)\int r(y, t)\,dy \quad ; \quad r\big|_{t=0} = 0$$

$$\frac{\partial p(x, t)}{\partial t} = \frac{\gamma}{2}\int r(x-y, t)\,r(y, t)\,dy + \epsilon M r(x, t) \qquad ; \quad p\big|_{t=0} = 0$$

from which we get equations in the moments

$$\frac{dM}{dt} = -(\beta + \epsilon)M\lambda_0 \qquad ; \quad M\big|_{t=0} = m_0$$

$$\frac{d\lambda_0}{dt} = 2\alpha I - \gamma\lambda_0^2 \qquad ; \quad \lambda_0\big|_{t=0} = 0$$

$$\frac{d\lambda_k}{dt} = \beta Mk\lambda_{k-1} - \epsilon M(\lambda_k - \lambda_0) - \gamma\lambda_0\lambda_k; \quad \lambda_k\big|_{t=0} = 0$$

$$\frac{d\mu_k}{dt} = \frac{\gamma}{2}\sum_{j=0}^{k}\binom{k}{j}\lambda_j\lambda_{k-j} + \epsilon M\lambda_k \qquad ; \quad \mu_k\big|_{t=0} = 0$$

Proceeding as before with the assumptions $I = i_0$; $\alpha/i_0 << \beta << \gamma$; $\epsilon < \beta$ we find that

$$\overline{X}_n = \frac{\left\{ \dfrac{2(\beta + \epsilon)^2 i_0}{\alpha\gamma} \right\}^{1/2} \dfrac{m_0}{i_0}(1 - m)}{\left(\dfrac{2\,\epsilon^2 i_0}{\alpha\gamma} \right)^{1/2} \dfrac{m_0}{i_0}(1 - m) + \ln\left(\dfrac{1}{m} \right)}$$

As ϵ gets larger, the average polymer size shows the expected decrease. Again, the moment equations may be solved exactly in a consecutive manner.

CHAIN TRANSFER TO SOLVENT

Considering the additional reactions associated with chain transfer to solvent, we write the kinetic scheme

$$I \xrightarrow{\alpha} 2R_0$$

$$R_i + M \xrightarrow{\beta} R_{i+1}$$

$$R_i + S \xrightarrow{\eta} S' + P_i$$

$$S' + M \xrightarrow{\zeta} R_1$$

$$S' + R_i \xrightarrow{\xi} P_i$$

$$R_i + R_j \xrightarrow{\gamma} P_{i+j} \qquad (i, j = 0, 1, 2 \ldots.)$$

Here again, as in previous cases, we allow the formation of the nonexistent polymer of zero size.

We may also consider these reactions in terms of inhibition or retardation. For example, an inhibitor S may react with a radical R_i to form a stable inhibitor S' and a terminated polymer P_i. In this case we take both ζ and ξ to be zero. In retardation, the rate coefficient ζ is much smaller than ξ. The rate equations for this general model are

$$\frac{dI}{dt} = -\alpha I$$

$$\frac{dM}{dt} = -\beta M \int r dx - \zeta M S'$$

$$\frac{dS}{dt} = -\eta S \int r dx$$

$$\frac{dS'}{dt} = \eta S \int r dx - \zeta M S' - \xi S' \int r dx$$

$$\frac{\partial r}{\partial t} + \beta M \frac{\partial r}{\partial x} = 2\alpha I \delta(x) - \eta S r + \zeta S' M \delta(x - 1)$$
$$- \xi S' r - \gamma r \int r dx \qquad ; \; r|_{t=0} = 0$$

$$\frac{\partial p}{\partial t} = \eta S r + \xi S' r$$
$$+ \frac{\gamma}{2} \int r(x - y) r(y) dy \qquad ; \; p|_{t=0} = 0$$

from which we get equations in the moments

$$\frac{dM}{dt} = -\beta M \lambda_0 - \zeta M S' \qquad ; \; M|_{t=0} = m_0$$

$$\frac{dS}{dt} = -\eta S \lambda_0 \qquad ; \; S|_{t=0} = S_0$$

$$\frac{dS'}{dt} = \eta S \lambda_0 - \zeta M S' - \xi S' \lambda_0 \qquad ; \; S'|_{t=0} = 0$$

$$\frac{d\lambda_k}{dt} = 2\alpha I \delta_{k0} + \beta M k \lambda_{k-1}$$
$$- [\eta S + \xi S'] \lambda_k + \zeta M S' - \gamma \lambda_0 \lambda_k \; ; \; \lambda_k|_{t=0} = 0$$

$$\frac{d\mu_k}{dt} = \eta S \lambda_k + \xi S' \lambda_k + \frac{\gamma}{2} \sum_{j=0}^{k} \binom{k}{j} \lambda_j \lambda_{k-j}$$
$$; \; \mu_k|_{t=0} = 0$$
$$(k = 0, 1, 2 \ldots.)$$

Unlike the previous cases examined, the exact solution of these equations cannot be carried out in a consecutive manner. Instead, the equations of M, S, and λ_0 must be solved simultaneously; once these solutions are obtained, the higher order moments can be found successively.

To simplify the solution of this set of equations, we shall assume that S and S' do not change appreciably with time, that $I = i_0$, and that the following inequalities hold:

$$\alpha / i_0 << \beta << \gamma; \quad \zeta < \eta < \beta < \xi; \quad \alpha i_0 \gamma < (\xi S')^2$$

Under these conditions, we find

$$\overline{X}_n = \frac{\left\{ \beta + \dfrac{\xi \zeta S'^2}{\alpha i_0} \right\} M_0 (1 - m)}{\{\eta S + \xi S'\} \ln \dfrac{1}{m}}$$

With the usual values of the parameters, the average polymer size decreases as η and ξ increase. Again, higher moments can readily be found numerically.

CONCLUSION

For a large number of polymerization models, we have developed equations that enable one to follow in time the moments of the polymer size distribution and the conversion. Taking the basic reactions of initiation, propagation, and termination by combination, we find the exact and approximate solutions for the leading moments of the distribution. We show that, depending on the values of an appropriate dimensionless group, the average polymer size may increase, decrease, or remain essentially constant with conversion. In contrast, the ratio of the weight average to number average in each case is 1.5 at low conversion and increases gradually.

With the additional reactions of termination by disproportionation, chain transfer to monomer, and chain transfer to solvent, we find that the average polymer size is decreased. On the other hand we show that an increase in the average polymer size occurs concomitantly with autoacceleration.

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NOTATION

a = dimensionless group
b = dimensionless group
I = concentration of initiation at time
i_0 = initial concentration of initiator

M = concentration of monomer at time
m_0 = initial concentration of monomer
m = fraction of unreacted monomer
P_i = concentration of terminated polymer with i monomer units
$p(x)dx$ = concentration of terminated polymer having between x and $x + dx$ monomer units
R_i = concentration of radical (growing polymer) with i monomer units
$r(x)dx$ = concentration of radicals having between x and $x + dx$ monomer units
S = concentration of solvent
S' = concentration of solvent radical
t = time
x = size of polymer in monomer units
$\bar{X}_n$ = number average degree of polymerization
$\bar{X}_w$ = weight average degree of polymerization
z = arbitrary parameter

Greek Letters

α = rate coefficient of initiation
β = rate coefficient of propagation
γ = rate coefficient of termination by combination
$\delta(x)$ = Dirac delta function
ϵ = rate coefficient of chain transfer to monomer
ζ = rate coefficient of solvent radical-monomer reaction
η = rate coefficient of chain transfer to solvent
θ = rate coefficient of termination by disproportionation
λ_k = k^{th} moment of size distribution of growing polymer
μ_k = k^{th} moment of size distribution of terminated polymer
ξ = rate coefficient of termination by solvent radical
ϕ = pseudo time

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APPENDIX: A MODEL WITH SIZE-DEPENDENT RATE COEFFICIENTS

Since the size dependence of rate coefficients is significant mainly for very short polymers, we select here for study the situation where the rate coefficients have just two values: one for reactions involving the primary radical R_0 and one for those involving only the higher R_i. Assuming initiation, propagation, and termination by combination, we use the kinetic scheme

$$I \underset{\alpha}{\overset{\alpha_0}{\rightleftarrows}} 2R_0$$

$$R_0 + M \xrightarrow{\beta_0} R_1$$

$$R_i + M \xrightarrow{\beta} R_{i+1}$$

$$R_0 + R_i \xrightarrow{\gamma_0} P_i$$

$$R_0 + R_j \xrightarrow{\gamma} P_{i+j} \qquad (i, j = 1, 2, \ldots\ldots)$$

introducing in addition, for illustration, the reversibility of the initiation step.

In writing the rate equations for this model, we treat the primary radical as a species different from the higher radicals R_i and carry its concentration separately as R_0. The distribution $r(x, t)$ accordingly has a different meaning from that assigned to it in the body of this study, referring here only to radicals other than the primary. The distribution $p(x, t)$ for terminated polymer has the same general meaning as before, and the rate equations for the present situation may be written as

$$\frac{dI}{dt} = -\alpha_0 I + \alpha R_0^2 \qquad ; I|_{t=0} = i_0$$

$$\frac{dM}{dt} = -\beta_0 M R_0 - \beta M \int r dx \qquad ; M|_{t=0} = m_0$$

$$\frac{dR_0}{dt} = 2\alpha_0 \mathrm{I} - 2\alpha R_0^2 - \beta_0 M R_0 - \gamma R_0 \int r dx \; ; R_0|_{t=0} = 0$$

$$\frac{\partial r}{\partial t} + \beta M \frac{\partial r}{\partial x} = \beta_0 M R_0 \, \delta(x-1)$$
$$- \gamma r \int r dx - \gamma_0 R_0 r \qquad ; r|_{t=0} = 0$$

$$\frac{\partial p}{\partial t} = \gamma_0 R_0 \int r dx + \frac{\gamma}{2} \int r(x-y)\, r(y)\, dy \qquad ; p|_{t=0} = 0$$

Defining the moments as

$$\sigma_k(t) = \int x^k r(x, t) dx \quad ; \quad \mu_k(t) = \int x^k p(x, t) dx \qquad (k = 0, 1, 2 \ldots)$$

we find from the rate equations

$$\frac{dI}{dt} = -\alpha_0 I - \alpha R^2{}_0$$

$$\frac{dM}{dt} = -\beta_0 M R_0 - \beta M \sigma_0$$

$$\frac{dR_0}{dt} = 2\alpha_0 I - 2\alpha R^2{}_0 - \beta_0 M R_0 - \gamma_0 R_0 \sigma_0$$

$$\frac{d\sigma_0}{dt} = \beta_0 M R_0 - \gamma_0 R_0 \sigma_0 - \gamma \sigma^2{}_0$$

$$\frac{d\sigma_k}{dt} = \beta M k \sigma_{k-1} + \beta M R_0 - \gamma_0 R_0 \sigma_0 - \gamma \sigma_0 \sigma_k$$

$$\frac{du_k}{dt} = \gamma_0 R_0 \sigma_0 + \frac{\gamma}{2} \sum_{j=0}^{k} \binom{k}{j} \sigma_j \sigma_{k-j}$$

The σ_k above do not have quite the same interpretation as the λ_k used in the body of this study to denote the moments of the radical size distribution. The total concentration λ_0 of radicals is here $\sigma_0 + \lambda_0$, but the higher of the radicals size distribution are simply the σ_k.

The solution of these moment equations is now a standard numerical task. The equations in I, M, R_0, and σ_0 must be solved simultaneously. The successively higher σ_k can then be computed one at a time from their respective equations. With R_0 and the σ_k in hand, the μ_k can then be developed by quadratures.

We can, of course, in principle extend this model without difficulty to include rate coefficients dependent on the polymer to any finite size. However, if this dependence had to be carried to any appreciable length of polymer, calculations in this style would become very onerous indeed. In such circumstances it might be preferable to reformulate the whole problem in terms of a continuous dependence of the rate coefficients on size, and to seek approximate solutions to the resulting differential equations in terms of suitable distributional forms.

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Momentum Transfer in Climbing Film Flow in Annular Duct

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The characteristics of upward gas–liquid flow in a vertical annular duct were investigated. The flow regime studied was the climbing film regime in which water flowed as a film up the inner core of the annulus while air flowed in the annular space, the outer wall of the annulus remaining dry. Friction losses, air velocity distributions, and film characteristics were studied, the latter by photographing the climbing film through the transparent outer tube. Friction loss and film thickness were correlated with Lockhart–Martinelli parameters, X, Φ, and R_L. The presence of the climbing film caused the point of maximum velocity of the air profile to move toward the outer tube, indicating that the film created a rough wall condition. The inner portion of the velocity profile was correlated by Nikuradse's rough tube equation, while the outer portion was correlated by a logarithmic equation which previous workers have reported for single-phase flow. Kapitza's theory of wave formation was applied to the climbing film and was found to predict reasonable values for the mean film thickness. However, it failed to predict reliable values for the wavelength of surface waves.

In vertically upward gas-liquid flow in closed ducts, several regimes of flow occur which are a function of the gas and liquid flow rates. These regimes can be observed sequentially as the gas flow rate increases at constant liquid flow rate. At low gas flow rates, the gas flows upward as small bubbles. With increasing gas flow rates, the gas assumes the form of large slugs and ultimately forms a continuous core while the liquid flows as a film up the walls of the duct. This latter regime of flow is the annular flow or climbing film regime. Similar regimes are also observed in a single heated tube in which boiling occurs.

The climbing film regime of two-phase flow has been the subject of many investigations. These studies have been stimulated mainly by the variety of process equipment such as water tube boilers, wetted-wall columns, and coolant channels of nuclear reactors in which such flow occurs. High heat and mass transfer rates occur in climbing film flow. An understanding of the basic transport phenomena taking place in climbing film flow will provide a sounder basis for design of process equipment.

Most previous investigators have used smooth pipes and narrow rectangular ducts to study the various characteristics of climbing film flow. While such ducts operate satisfactorily and provide reliable data, it is not possible to observe the liquid film directly, even though the duct wall is transparent.

In the present study, a long annular duct was employed in which air flowed in the annular space and a water film climbed up the concentric inner core. The outer dry tube was transparent so that the film could be observed directly. It was possible to determine values of momentum flux from velocity profile measurements.

An attempt has been made to investigate both the mechanics of the air flow in the annular duct as well as the mechanics of flow of the climbing film.

THEORETICAL BACKGROUND

Single-Phase Turbulent Flow in Annuli

Friction losses for single-phase flow in smooth annuli have usually been correlated with the hydraulic diameter used as the characteristic length in defining the friction factor and Reynolds number. The correlation is satisfactory for annuli in which $0.2 < \alpha < 0.8$. Prengle and Rothfus (*13*) defined a Reynolds number based upon the equivalent diameter of the outer portion of annular velocity profile.

$$N_{Re2} = \frac{4 r_H U \rho}{\mu} \tag{1}$$

where

$$r_H = 2r_2(1 - \lambda^2)$$

By defining a friction factor

$$f_2 = \frac{2\tau_2 g_c}{\rho U^2} \tag{2}$$

the workers found that

$$1/\sqrt{f_2} = 4.0 \log (N_{Re2} \sqrt{f_2}) - 0.4 \tag{3}$$