Polymer Reactors and Molecular Weight Distribution: Part II. Free Radical Polymerization in a Batch Reactor

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The free radical polymerization of styrene in benzene was studied theoretically and experimentally over ranges of monomer and catalyst (AIBN) concentrations and temperature in an isothermal, stirred batch reactor. Molecular weight distributions were measured with a gel permeation chromatograph. Tung's hermite polynomial method was used to correct for imperfect resolution.

The differential rate equations have been solved to predict the conversion of monomer and molecular weight distribution of the polymer as a function of time. These solutions were used to interpret the experimental rate data.

Good agreement between theory and experiment was found for narrow and broad distribution, provided the variation of the termination constant with solvent concentration was accounted for.

The agreement between the experimental and calculated molecular weight distribution suggests the utility of gel pemeation chromatography in the investigation of polymer reaction kinetics.

The kinetic mechanisms of free radical polymerization of vinyl monomers in solution have been well established for small conversions of monomer (*1*). This is not so for large conversions. In many instances the resulting differential equations have not been solved to predict the molecular weight distribution as a function of time. Amundson (*2*) has solved the equations describing several of these mechanisms. However, until now, experimental verification of these mechanisms has not been attempted due to the tedious nature of the available methods for measuring molecular weight distribution. The recent development of the gel permeation chromatograph (*3*), which allows the rapid measurement of molecular weight distribution, has made such a verification possible. The present investigation has exploited the use of the gel permeation chromatograph (GPC) and digital computer to this end.

THEORY

The following steps describe the mechanism of solution polymerization using a free radical catalyst (AIBN) that has been investigated in the present study:

Initiation:

$$\text{Cat} \rightarrow 2R_c^o \quad \text{rate constant } k_d$$
$$R_c^o + M \rightarrow R_1^o \quad \text{rate of formation of } R_1^o \text{ is I}$$

Propagation:

$$R_1^o + M \rightarrow R_2^o$$
$$R_2^o + M \rightarrow R_3^o \quad \text{rate constant } k_p$$
$$R_r^o + M \rightarrow R^o_{r+1}$$

Transfer:

$$R_r^o + S \rightarrow P_r + S^o \quad \text{rate constant } k_{fs}$$
$$R_r^o + M \rightarrow P_r + M^o \quad \text{rate constant } k_f$$

Termination:

$$R_r^o + R_s^o \rightarrow P_{r+s} \quad \text{rate constant } k_{tc}$$
$$R_r^o + R_s^o \rightarrow P_r + P_s \quad \text{rate constant } k_{td}$$

In these equations R_c^o represents one of two identical free radical fragments formed in the decomposition of the catalyst; R_r^o represents a polymer radical comprising r monomer units, S is a solvent, and M is a monomer molecule, while P_r represents a dead polymer molecule containing r monomer units. In the development of the differential rate equations it is assumed that only the above reactions take place. Furthermore, it is assumed that the solvent and monomer radicals formed in the chain transfer

process have the same reactivity as any other radical. This implies that S is neither a retarder nor an inhibitor. Numerous other reactions can and do take place and there is substantial literature on the subject (*1*). The present authors are attempting to show that the above mechanism is adequate for the prediction of molecular weight distribution over a rather wide range of conditions of monomer and catalyst concentrations and temperature.

On the basis of the foregoing set of reactions, the rate of formation of R_1^o is

$$\frac{dR_1^o}{dt} = I - k_pMR_1^o + (k_{fs}S + k_f)R^o - (k_{fs}S + k_fM)R_1^o - (k_{tc} + k_{td})R_1^oR^o \quad (1)$$

where R^o is the total free radical concentration:

$$R^o = \sum_{r=1}^{\infty} R_r^o$$

The rate of formation of R_2^o and longer chains is

$$\frac{dR_r^o}{dt} = k_pMR^o_{r-1} - k_pMR_r^o - (k_{fs}S + k_f\ M)R_r^o - (k_{tc} + k_{td})\ R_r^oR^o \quad (2)$$

The rate of monomer consumption is

$$\frac{-dM}{dt} = I + k_pMR^o + k_f\,MR^o \quad (3)$$

For long chains the first and third terms of Equation (3) become insignificant, giving

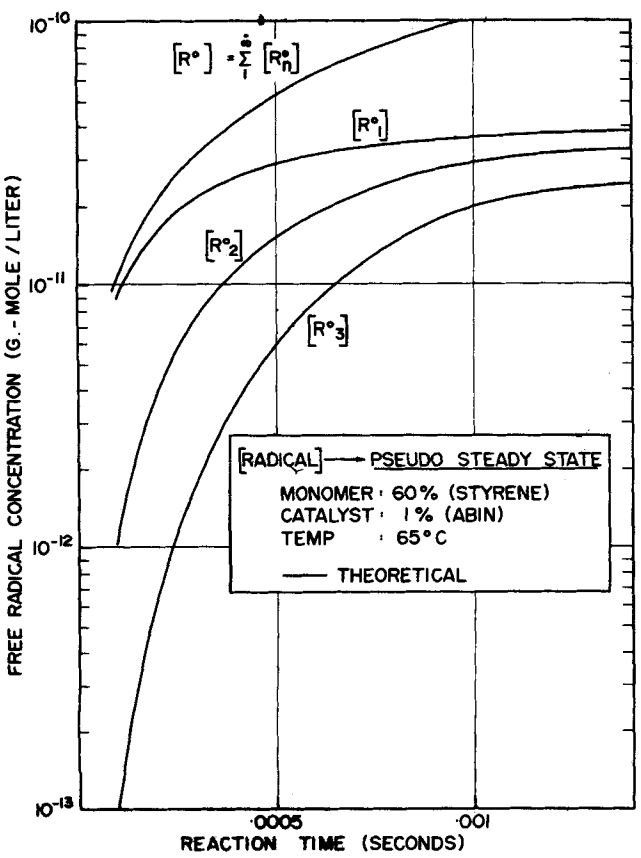

Fig. 1. Solution of Equation (2) showing concentrations of polymer free radicals approaching pseudo-steady state.

$$\frac{dM}{dt} = -k_pMR^o \quad (4)$$

The rate of formation of dead polymer of chain length r is

$$\frac{dP_r}{dt} = (k_{fs}S + k_fM)R_r^o + k_{td}R_r^oR^o + \frac{1}{2}k_{tc}\sum_{n=1}^{r-1} R_n^oR^o_{r-n} \quad (5)$$

Solutions of Equations (1), (2), (4), and (5) would give the monomer consumption and concentrations of free radicals and dead polymer as a function of time. Solution of Equation (2) for styrene polymerization would be extremely time-consuming even with the use of a high-speed digital computer. This difficulty arises because the sum of the positive terms equals the absolute sum of the negative terms to many significant figures on the hight-hand side of Equation (2). When employing a very small step size in time (10^{-4} min.) one introduces errors which can change the sign of dR_r^o/dt and give unstable results. To solve Equation (2) for styrene for more than one hundred species is entirely impractical at the present time. In practice r often becomes as large as 5,000 or more. Liu and Amundson (*2*) have solved Equation (2) for up to one hundred species using a Runge-Kutta method. The rate constants used, however, are considerably different from those for styrene and the aforementioned difficulty is not nearly so severe.

The fact that $dR_r^o/dt = 0$ to many significant figures suggests that a further major assumption can be made, namely, that the free radical concentration reaches a pseudo steady state. As a result, Equation (2) becomes an algebraic equation giving a recurring relationship between R_r^o and R^o_{r-1}. Liu and Amundson (*2*) showed that serious errors can be introduced if the pseudo steady state is not reached quickly. However, most polymerization reactions achieve this state in less than a few seconds. For styrene polymerization this assumption is entirely justifiable (*1*). Typical variations of free radical concentrations with time are shown in Figure 1.

CONVERSION AND MOLECULAR WEIGHT DISTRIBUTION

The pseudo steady state approximation was made and Equations (4) and (5) were solved for 5,000 species. The equation describing the conversion of monomer may be expressed as

$$\frac{dX}{dt} = k_p(1 - X)\left[\frac{2fk_dC_o\exp(-k_dt)}{k_{td} + k_{tc}}\right]^{1/2} \quad (11)$$

and solved analytically to give

$$X = 1. - \exp\left[\left(\frac{2k_p}{k_d}\right)\left(\frac{2fk_dC_o}{k_{td} + k_{tc}}\right)^{1/2}(1 - \exp(-k_dt/2)\right] \quad (12)$$

The total free radical concentration is given by

$$R^o = \left[\frac{2fk_dC_o\exp(-k_dt)}{k_{td} + k_{tc}}\right]^{1/2} \quad (13)$$

The recurring relationships for R_r^o are obtained from Equations (1) and (2) after setting the time derivatives equal to zero. They follow

$$R_1^o = \left[\frac{I}{k_{tc} + k_{td}}\right]^{1/2}$$

$$\left(\frac{k_{fs}S + k_pM + [I(k_{tc} + k_{td})]^{1/2}}{k_pM + k_{fs}S + k_fM + [I(k_{tc} + k_{td})]^{1/2}} \right) \quad (14)$$

$$R_r^o = R^o_{r-1} \left(\frac{k_pM}{k_pM + k_{fs}S + k_fM + [I(k_{tc} + k_{td})]^{1/2}} \right) \quad (15)$$

which holds for $r \geqq 2$. This equation may be written as

$$R_r^o = R^o_{r-1}\zeta \quad (16)$$

where ζ is often referred to as the probability factor. It gives the statistical probability that a certain polymer free radical will propagate rather than enter into a termination reaction of some sort. Equation (14) may also be expressed in terms of ζ:

$$R_1^o = \left[\frac{I}{k_{tc} + k_{td}} \right]^{1/2} (1 - \zeta) \quad (17)$$

Combining (16) and (17) we obtain

$$R_r^o = R_1^o \ \zeta^{(r-1)} = \left[\frac{I}{k_{tc} + k_{td}} \right]^{1/2} (1 - \zeta) \ \zeta^{(r-1)} \quad (18)$$

Equation (18), although here derived from the rate equations rather than statistically, shows immediately why ζ is called the probability of propagation. For example, the probability that a radical will propagate r consecutive times is $\zeta^{(r-1)}$, while the probability of termination is always $(1 - \zeta)$. Thus the probability that an r-mer free radical is formed followed by termination is $\zeta^{(r-1)}(1 - \zeta)$. Equation (5) may now be written as

$$\frac{dPr}{dt} = \left[\frac{2fk_dC_o \exp(-k_dt)}{k_{tc} + k_{td}} \right]^{1/2} (1 - \zeta)\zeta^{(r-1)} \left\{ k_{fs}S + k_f \ M_o(1 - X) + \left[\frac{2fk_dC_o \exp(-k_dt)}{k_{tc} + k_{td}} \right]^{1/2} \left[\frac{(r-1)k_{tc}}{2kpMo(1-X)} (k_{fs}S + k_fM_o(1-X) + [2fk_dC_o \exp(-k_dt)(k_{tc} + k_{td})]^{1/2}) + k_{td} \right] \right\} \quad (19)$$

Solution of Equation (19) for 5,000 species has been obtained with the trapezoidal rule and a 15-min. step size. A plot of P_r vs. r gives the so-called frequency distribution, whereas usually the weight fraction is the more desired quantity. The weight fraction is simply

$$W_r = \frac{rPr}{M_oX} \quad (20)$$

Expressions for the number, weight, and z average chain length are

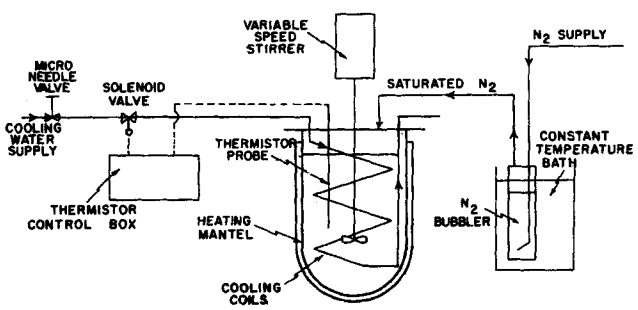

Fig. 2. Isothermal stirred batch reactor.

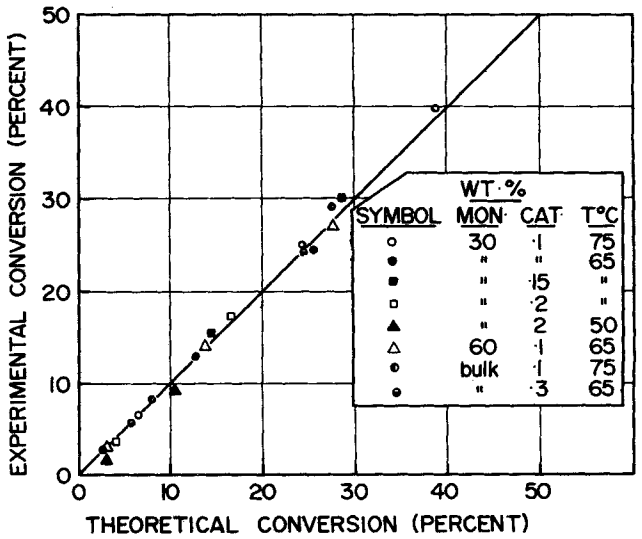

Fig. 3. Experimental conversions of monomer are compared with those predicted by Equation (12).

$$\overline{M}_n = \frac{\sum_{r=1}^{\infty} rP_r}{\sum_{r=1}^{\infty} P_r} \quad (21)$$

$$\overline{M}_w = \frac{\sum_{r=1}^{\infty} r^2P_r}{\sum_{r=1}^{\infty} rP_r} \quad (22)$$

$$\overline{M}_z = \frac{\sum_{r=1}^{\infty} r^3P_r}{\sum_{r=1}^{\infty} r^2P_r} \quad (23)$$

SOURCE AND SELECTION OF RATE CONSTANTS

The selection of rate constants for styrene polymerization has already been discussed in detail in a previous

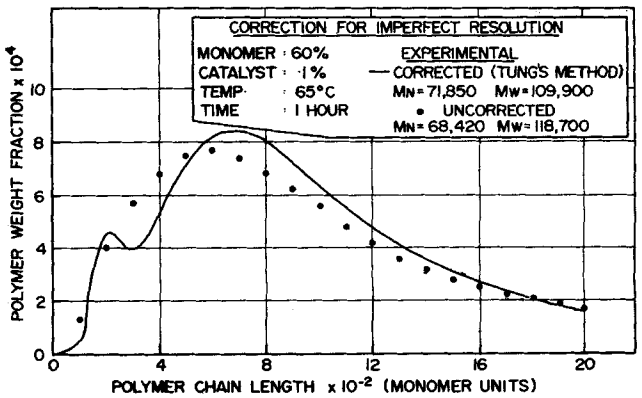

Fig. 4. Experimental molecular weight distributions—*uncorrected* and corrected for imperfect resolution by method of Tung.

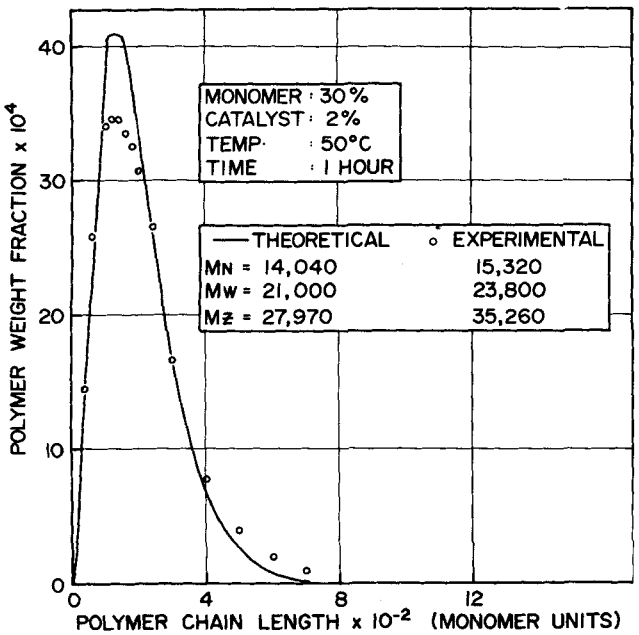

Fig. 5. Experimental molecular weight distribution compared with theoretical for low molecular weight range.

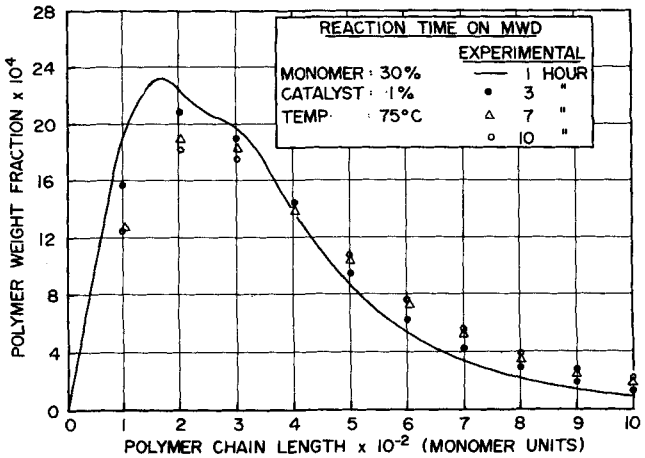

Fig. 7. Experimental molecular weight distributions showing the effect of reaction time for low molecular weight range.

paper of this series (5). The values chosen from the literature and used in this investigation are

$$k_d = 1.58 \times 10^{15} \exp(-15{,}500/T)$$
$$k_p = 1.051 \times 10^{7} \exp(-3{,}557/T)$$
$$k_{tc} = 1.255 \times 10^{9} \exp(-844/T)$$
$$k_f = 2.31 \times 10^{6} \exp(-6{,}377/T)$$
$$k_{fs} = 9.95 \times 10^{10} \exp(-11{,}000/T)$$
$$k_{td} = 0$$

where T is in degrees Kelvin.

The effect of solvent on the termination rate has been summarized (5) and the recent results of Henrici-Olive and Olive (6) were used to correct k_{tc} for solvent concentration.

The equation which gives this correction is

$$\phi_p = \frac{M_{\text{bulk}}}{(S)(T_s/T_m) + M} \tag{24}$$

where $T_s/T_m = 1.04$ for styrene in benzene.

The definition of ϕ_p is given by Equation (24a)

$$\frac{1}{(k_{tc})_s^{1/2}} = \frac{\phi_p}{(k_{tc})_{\text{bulk}}^{1/2}} \tag{24a}$$

EXPERIMENTAL PROCEDURE

The reactor consisted of a 1 liter glass vessel fitted with a stainless steel blind flange and a helical stainless steel cooling coil following the wall contour. A variable speed axial stirrer was located centrally, approximately one-third the vessel height above the bottom. The reactor was also equipped with a thermistor temperature probe and an ordinary 0° to 100°C. laboratory thermometer. The temperature was held to within ± 0.1°C. by automatically controlled heating and cooling elements. Figure 2 gives a schematic view of the apparatus.

Techniques of Polymer Analysis

One of the best techniques for analyzing quantitatively the amount of polystyrene in a solution of styrene monomer or some other solvent is a gravimetric one consisting of precipitating the polymer by adding a five- to tenfold excess of methanol (5). Whether very low molecular-weight material such as trimers and tetramers is precipitated is not known. However, in applying this technique to measure conversion in this investigation it was assumed that this error was negligible. Analysis of measured (by GPC) and predicted chain length distributions

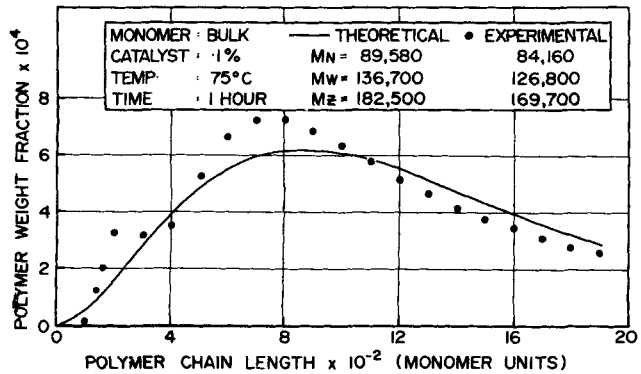

Fig. 6. Experimental molecular weight distribution compared with theoretical for high molecular weight range.

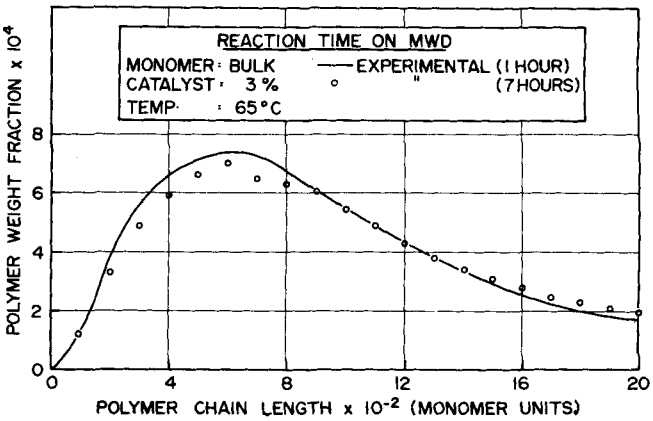

Fig. 8. Experimental molecular weight distributions showing the effect of reaction time for high molecular weight range.

showed that these low molecular weight materials are present in negligible amounts.

Molecular weight distributions of polystyrene were measured with a GPC. Application of the GPC has been described in detail elsewhere (7).

Polymerization Conditions

Solvent. One solvent, benzene, and one monomer, styrene, were investigated.

Monomer Concentration. Concentrations studied included bulk, 60 wt. %, and 30 wt. % monomer.

Catalyst Concentration. Concentrations of azo-bisisobutyronitrile (AIBN) included 0.1, 0.15, 0.2, 0.3, and 2.0 wt. %.

Temperature. Temperatures included 50°, 65°, and 75°C.

Conversion. The largest conversion of monomer investigated was 42.5%.

One run was carried out at 50°C. with 2 wt. % catalyst to provide rate data which were certain to be free of the influence of thermal polymerization.

RESULTS AND DISCUSSION

Effect of Reaction Variables on Conversion and Molecular Weight Distribution

In a preliminary attempt to interpret the experimental rate data (8) the termination constant k_{tc} was kept constant, while the catalyst efficiency was varied to fit the predicted and measured conversion vs. time data. Catalyst efficiencies varying between 0.48 and 0.82 were found. These catalyst efficiencies did not, however, allow accurate predictions of molecular weight distribution. An alternative interpretation which proved to be the better was to use a constant catalyst efficiency of $f = 0.6$ and to allow k_{tc} to vary with solvent concentration using the correction of Henrici-Olive and Olive [see Equation (24*a*)]. The temperature dependence of the solvent correction factor ϕ_p has already been shown to be negligible (5). In the present study the changes in ϕ_p due to density changes during polymerization were neglected.

Predicted and measured conversions at equal reaction times are plotted in Figure 3. For purposes of clarity only a small percentage of the data measured in this study is shown. The remaining data have been tabulated in a thesis (8). The agreement is satisfactory at low conversions, but there is evidence that experimental conversions are greater than theory would predict at the higher conversions where viscosity might play a role. Unfortunately, there are insufficient data at high conversions to clarify this point. However, a recent work (5) using a CSTR and styrene polymerization with AIBN has indicated a definite increase in conversion due to an increase in viscosity. The mechanism by which high viscosities affect termination is not clear, at least quantitatively. This certainly requires further study before a kinetic model can be developed which is accurate at high conversions. It should be mentioned that corrections to theory for thermal polymerization have been made using values recommended by Boundy and Boyer (10).

Molecular weight distributions have been measured with a GPC and a correction for imperfect resolution after Tung (3). Figure 4 shows the change in the distribution due to this correction. It is not certain whether the secondary peak which has been brought out by the correction is real or is due to mathematical instabilities in Tung's hermite polynomial technique. However, Tung (9) has evaluated this method in some detail and has shown that the corrections to M_N and M_W are justified. We have therefore followed his recommended procedure in correcting all the GPC chromatograms for imperfect resolution.

Refer to Figures 5 and 6 to see that the agreement of experimental with theoretical distributions is satisfactory over quite a range of reaction conditions. Figures 7 and 8 show the effect of polymerization time on molecular weight distribution found experimentally. The effect of time is to broaden the distribution but for the conversions considered, the effect is not too pronounced. Conceivably at higher conversions and viscosities where the termination mechanism may change, a more noticeable difference would be apparent. The theoretical calculations, which do not account for the effect of viscosity, predict an effect of reaction time on distribution which is approximately the same as that found experimentally.

NOTATION

C = catalyst concentration, g.-mole/liter
C_o = initial catalyst concentration, g.-mole/liter
f = catalyst efficiency, fraction of catalyst free radicals that initiate polymer molecules
I = rate of initiation of polymer chains by catalyst free radicals, g.-mole/(liter)(sec.)
k_d = reaction rate constant for catalyst decomposition, sec.$^{-1}$
k_f, k_{fs}, k_p, k_{td}, k_{tc} = reaction rate constants for transfer to monomer, transfer to solvent, propagation, termination by disproportionation, termination by combination, liter/(g.-mole)(sec.)
M = monomer concentration, g.-mole/liter
M_{bulk} = bulk monomer concentration, g.-mole/liter
M_o = monomer free radical
$\overline{M}_n$ = number average molecular weight
$\overline{M}_W$ = weight average molecular weight
$\overline{M}_Z$ = Z average molecular weight
P_r = concentration of dead polymer containing r monomer units, g.-mole/liter
R_1^o, R_r^o = concentration of polymer free radical containing one and r monomer units, respectively, g.-mole/liter
R_c^o = catalyst free radical
S = solvent concentration, g.-mole/liter
S^o = solvent free radical
t = time, sec.
W_r = weight fraction of dead polymer containing r monomer units per molecule
X = conversion of monomer, dimensionless
ϕ_p = correction factor for solvent effect, dimensionless
ζ = probability of propagation, dimensionless
T = temperature, °K.

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