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A Model of Complete Classical Treatment of Dispersion Radical Polymerization Kinetics

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ABSTRACT: Kinetic analysis of high-conversion free-radical polymerization is discussed in terms of the complete solution of the classical kinetic scheme, which involves initiation, propagation, termination, and chain-transfer reactions. Expressions for kinetics of formation of each species existing in the polymerization mixture are presented. To demonstrate the applicability of the mathematical model, monomer conversion and the formation of the insoluble polymer component in the dispersion polymerization of styrene and methyl methacrylate (MMA) in 2-propanol have been measured at 70 °C. The values obtained for k_d and $k_p/k_t^{1/2}$, where k_d, k_p, and k_t are dissociation, propagation, and termination rate constants, respectively, are in agreement with those reported in the literature.
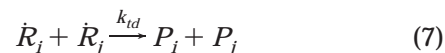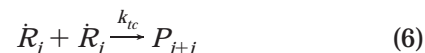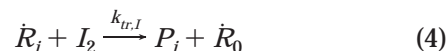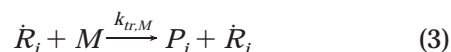
Introduction

Numerous attempts have been made to study and model free radical polymerization up to high conversions. Several mathematical models have been reviewed recently by Tefera et al.,[1] Mita and Horie ,[2] and Achilias and Kiparissides.[3] The application of different models depends on the reaction conditions during the polymerization process. Such effects as cage,[4,5] gel,[6,7] and glass[2,8] effects can take place under certain polymerization conditions. Also, it is generally believed that the bimolecular termination rate constant depends on the size of the free radical, which leads to departures from classical kinetic treatments.[9−11] However, the classical treatment is an excellent approximation in many systems, as illustrated by the work of countless kineticists over the years. The classical treatment of radical polymerization kinetics is based on the assumption that the rate coefficients k_p, k_t, and k_{tr} (for propagation, termination, and chain-transfer, respectively) are independent of the chain-lengths of the participating radicals. One very useful feature of the classical scheme is the possibility of deriving a complete solution of the system of kinetic equations in analytical form,[12] i.e., as analytical functions, up to high conversions.

This article deals with the modeling of dispersion polymerization kinetics based on a complete mathematical treatment of the classical kinetic scheme for free-radical polymerization, which involves initiation, propagation, termination (disproportionation and combination), and chain-transfer reactions. As a result, we present analytical expressions for the kinetics of formation of each of the species existing in the polymerization mixture. Monomer conversion and the formation of the insoluble polymer component in free-radical dispersion polymerization of styrene and methyl methacrylate

(MMA) have been measured to demonstrate the general applicability of this model.

Kinetic Analysis

The mechanism of polymerization considered here consists of chemical initiation by first-order decomposition of an initiator to produce a radical with chain length one, first-order propagation with respect to monomer, and chain-transfer to produce a dead polymer. Second-order termination by disproportionation and combination are taken into account. The reaction scheme can be presented by

$$I_2 \xrightarrow{k_d} 2\dot{R}_0 \tag{1}$$

$$\dot{R}_{i-1} + M \xrightarrow{k_p} \dot{R}_i \tag{2}$$

$$\dot{R}_i + M \xrightarrow{k_{tr,M}} P_i + \dot{R}_i \tag{3}$$

$$\dot{R}_i + I_2 \xrightarrow{k_{tr,I}} P_i + \dot{R}_0 \tag{4}$$

$$\dot{R}_i + \dot{R}_j \xrightarrow{k_{tc}} P_{i+j} \tag{6}$$

$$\dot{R}_i + \dot{R}_j \xrightarrow{k_{td}} P_i + P_j \tag{7}$$

where i and j are chain lengths, I_2 denotes the initiator molecule, $\dot{R}_0$ the initiator radical, M the monomer molecule, $\dot{R}_i$ ($i > 0$) the polymer radical with chain length i, P_i ($i > 0$) the dead polymer molecule, k_d the dissociation rate constant, $k_{tr,M}$ the rate constant of chain-transfer by the monomer, $k_{tr,I}$ the rate constant of chain transfer by the initiator, k_p the propagation rate constant, k_{tc} the rate constant of termination by combination, and k_{td} the rate constant of termination by disproportionation. The rate constant of termination is $k_t = k_{td} + k_{tc}$. We assume that the rate constants are independent of the chain length i. The following rate equations can be derived from the reaction scheme:

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$$\frac{\partial}{\partial t} I(t) = -k_d I(t) \tag{8}$$

$$\frac{\partial}{\partial t} R(0,t) = 2k_d I(t) - k_p R(0,t) M(t) -$$
$$\sum_{j=0}^{\infty} (k_{tc} + k_{td}) R(j,t) R(0,t) +$$
$$\sum_{j=0}^{\infty} [k_{tr,M} M(t) + k_{tr,I} I(t)] R(j,t) \tag{9}$$

$$\frac{\partial}{\partial t} R(i,t) = k_p R(i-1,t) M(t) - k_p R(i,t) M(t) -$$
$$\sum_{j=0}^{\infty} (k_{tc} + k_{td}) R(j,t) R(i,t) -$$
$$[k_{tr,M} M(t) + k_{tr,I} I(t)] R(i,t) \tag{10}$$

$$\frac{\partial}{\partial t} M(t) = -\sum_{j=0}^{\infty} (k_p + k_{tr,M}) R(j,t) M(t) \tag{11}$$

$$\frac{\partial}{\partial t} P(t,i) = \frac{1}{2} \sum_{j=0}^{j=1} k_{tc} R(i-j,t) R(j,t) + \sum_{j=0}^{\infty} k_{td} R(j,t) R(i,t) +$$
$$[k_{tr,M} M(t) + k_{tr,I} I(t)] R(i,t) \tag{12}$$

where $i(t)$, $M(t)$, $R(0,t)$ are the concentrations of initiator, monomer, and initiator radicals as a function of time t; and $R(i,t)$ and $P(i,t)$ $(i > 0)$ are the concentrations of polymer radicals and dead polymer molecules as a function of the chain length i and time t, respectively. It follows from eq 8 that

$$I(t) = I(0) e^{-k_d t} \tag{13}$$

From eqs 9 and 10 we have

$$\frac{\partial}{\partial t} \sum_{i=0}^{\infty} R(i,t) = 2k_d I(t) - \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} (k_{tc} + k_{td}) R(j,t) R(i,t) \tag{14}$$

where $R(\infty,t) = 0$. Denoting

$$S(t) = \sum_{i=0}^{\infty} R(i,t) \tag{15}$$

we obtain from eq 14

$$\frac{\partial}{\partial t} S(t) = 2k_d I(t) - (k_{tc} + k_{td}) S^2(t) \tag{16}$$

where $S(t)$ is the total concentration of all radicals in the system. We consider $R(i,t)$ and $P(i,t)$ as continuous functions of the continuous variable i, and use the steady-state assumption for radicals. Hence the basic eqs 9–12 and 16 may be written as

$$0 = 2k_d I(t) - k_p R(0,t) M(t) - (k_{tc} + k_{td}) R(0,t) S(t) +$$
$$[k_{tr,M} M(t) + k_{tr,I} I(t)] S(t) \tag{17}$$

$$0 = -k_p M(t) \frac{\partial}{\partial i} R(i,t) - (k_{tc} + k_{td}) R(i,t) S(t) -$$
$$[k_{tr,M} M(t) + k_{tr,I} I(t)] R(i,t) \tag{18}$$

$$\frac{\partial}{\partial t} M(t) = -(k_p + k_{tr,M}) M(t) S(t) \tag{19}$$

$$\frac{\partial}{\partial t} P(i,t) = \frac{1}{2} k_{tc} \int_0^i R(i-j,t) R(j,t) \, dj + k_{td} R(i,t) S(t) +$$
$$[k_{tr,M} M(t) + k_{tr,I} I(t)] R(i,t) \tag{20}$$

$$0 = 2k_d I(t) - (k_{tc} + k_{td}) S^2(t) \tag{21}$$

Equation 17 can be simplified by substituting the expression for $2k_d I(t)$ from eq 21 and taking into account that $S(t) \gg R(0,t)$

$$0 = (k_{tc} + k_{td}) S^2(t) - k_p R(0,t) M(t) + (k_{tr,M} M(t) +$$
$$k_{tr,I} I(t)) S(t) \tag{22}$$

The system of eqs 18–22 can be solved, and we obtain expressions for the concentrations of each of the species existing in the polymerization mixture. Denoting

$$\delta(t) = \frac{(k_{tc} + k_{td}) S(t) + k_{tr,M} M(t) + k_{tr,I} I(t)}{k_p M(t)} \tag{23}$$

we can write

$$S(t) = \left(\frac{2k_d I(t)}{k_{tc} + k_{td}}\right)^{1/2} = \left(\frac{2k_d I(0)}{k_{tc} + k_{td}}\right)^{1/2} e^{-1/2 k_d t} \tag{24}$$

$$M(t) = M(0) e^{-2(k_p + k_{tr,M})[S(0) - S(t)]/k_d} \tag{25}$$

$$R(0,t) = \delta(t) S(t) \tag{26}$$

$$R(i,t) = R(0,t) e^{-\delta(t) i} = S(t) \delta(t) e^{-\delta(t) i} \tag{27}$$

$$P(i,t) = \int_0^t \left[\frac{1}{2} k_{tc} i S(t) \delta(t) + k_{td} S(t) + k_{tr,M} M(t) + k_{tr,I} I(t)\right] S(t) \delta(t) e^{-\delta(t) i} \, dt \tag{28}$$

Equations 13 and 23–28 represent the complete analytical solution of the basic kinetic scheme of eqs 8–12, assuming steady-state concentrations for the radicals.

We can simplify the mathematical model of the evolution of the insoluble polymer component if we define the critical chain length[12] i_0. This means that we assume that polymer molecules with chain length $i \geq i_0$ are completely insoluble, but polymer molecules with chain length $i < i_0$ are completely soluble. Using this assumption and eq 28, after rearrangements, we derive the following expression for the total volume $V(i_0, t)$ of insoluble polymer component per unit volume

of the medium ("insoluble polymer volume fraction"):

$$V(i_0, t) = \frac{m_0}{\rho} \int_{i_0}^{\infty} iP(i,t)\,di$$

$$= \frac{m_0}{\rho} \int_0^t \int_{i_0}^{\infty} \left[\frac{1}{2} k_{tc} i^2 S(t) \delta(t) + k_{td} i S(t) + \right.$$

$$\left. k_{tr,M} i M(t) + k_{tr,I} i I(t) \right] S(t) \delta(t) e^{-\delta(t)i} \, di\, dt \quad (29)$$

$$V(i_0, t) = \frac{m_0 k_d I(0)}{\rho \left(1 + \dfrac{k_{td}}{k_{tc}}\right)} \int_0^t e^{-k_d t} \times$$

$$\left\{ i_0^2 + \frac{2k_p \left(1 + \dfrac{k_{td}}{k_{tc}}\right) M(t)}{(k_{tc} + k_{td}) S(t)} \left[i_0 + \frac{1}{\delta(t)} \right] \right\} \delta(t) e^{-\delta(t)i_0} \, dt \quad (30)$$

where m_0 is the molar mass of monomer, and ρ is the density of the polymer. The insoluble polymer volume fraction $V(i_0, t)$ is determined as the volume amount of the insoluble polymer component in a unit volume of the medium.

Equation 25 shows that we can obtain k_d and $(k_p + k_{tr,M})/(k_{tc} + k_{td})^{1/2}$ from the experimental data of $M(t)$. As usual, under typical kinetic parameters for the dispersion free-radical polymerization[13] (for example, in polymerization of styrene or MMA)

$$k_{tr,M} M(t) + k_{tr,I} I(t) \ll k_t S(t) = [2 k_t k_d I(t)]^{1/2} \quad (31)$$

$$k_{tr,M} \ll k_p \quad (32)$$

In that case, we can neglect the effect of chain transfer by monomer and initiator. Similarly, it is also possible to show that we can neglect the effect of inhibition or retardation

$$\dot{R}_i + Z \xrightarrow{k_z} P_i + \dot{Z} \text{ and/or } R_i \dot{Z} \quad (33)$$

if

$$k_Z Z \ll k_t S = [2 k_t k_d I(t)]^{1/2} \quad (34)$$

where Z is the concentration of the inhibitor (or the retarder) and k_Z is the rate constant of inhibition (or retardation). Then

$$\delta(t) \approx \frac{(k_{tc} + k_{td}) S(t)}{k_p M(t)} = \frac{k_t S(t)}{k_p M(t)} \quad (35)$$

and the evolution of the insoluble polymer volume fraction $V(i_0 t)$ is dependent on the following parameters: i_0, k_d, $k_p/k_t^{1/2}$, and k_{td}/k_{tc}.

To show the applicability of this mathematical model, we have considered the dispersion polymerization of styrene and MMA in 2-propanol (iPrOH). By simultaneous parameter estimation from the monomer conversion and insoluble polymer formation data, the model parameters have been determined.

Experiment

Materials. ST (Fluka) and MMA (Fluka) were distilled under reduced nitrogen pressure before use. 2,2′-Azobis(isobutyronitrile) (AIBN) (Fluka) was recrystallized from methanol. All other materials were used
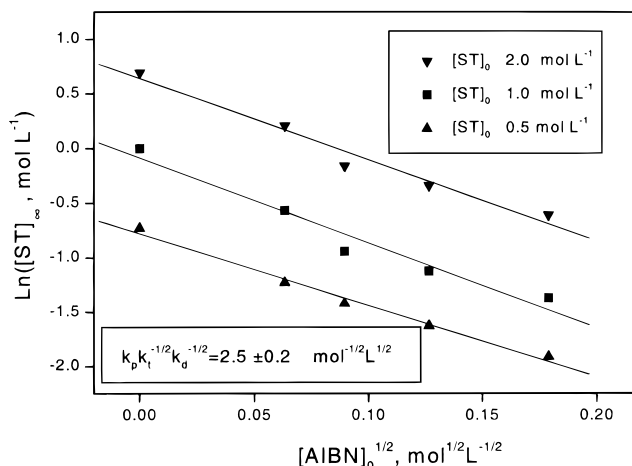
Figure 1. Final concentration of styrene (ST) as a function of the initial concentration of initiator (CAIBN).

without further purification, including iPrOH (Fluka), poly(vinylpyrrolidone) (PVP) (K-30, Fluka), and tetrahydrofuran (THF) (Baker). THF was used as a solvent for UV absorption measurements of polymer.

Polymerization Procedure. AIBN, monomer, and PVP (1%) were dissolved in iPrOH. The mixture was distributed to small (2-mL) polyethylene vials, which then were closed tightly with the screw caps. All vials were put in a water bath at constant temperature (70 °C). The vials were removed from the water bath during the course of the reaction and cooled to room temperature (20 °C); then the insoluble polymer component was separated by centrifugation, washed with iPrOH, and dried under vacuum. The amount of insoluble polymer component was determined with three independent methods: weighing, UV absorption (Perkin-Elmer Lambda 3 UV/Vis), and scanning flow cytometry.[14,15] The monomer concentration in the sample was measured by gas chromatography (Carlo Erba−4200). To measure UV absorption, the insoluble polymer component was dissolved (after washing and drying) in THF.

Scanning Flow Cytometry. Flow cytometry is commonly used for analyzing single particles.[14,16] The scanning flow cytometer[15,17] (SFC) has been used to measure the light-scattering patterns of individual polymer particles in sizes of 0.7 to 8 μm. The parameters of the particles (i.e., size and refractive index) have been obtained from a nonlinear least-squares fitting of the experimental light-scattering patterns of the individual particles on the basis of Mie scattering theory.[18] We measured 1000 particles from every sample and determined the amount of insoluble polymer.

Results and Discussion

Equation 25 may be linearized into the form

$$\ln(M(\infty)) = \ln(M(0)) - \frac{2k_p(2I(0))^{1/2}}{(k_d k_t)^{1/2}} \quad (36)$$

which can easily be fitted. Here, $M(\infty)$ is the final concentration of the monomer. Using eq 36, we can obtain the parameter $k_p(k_t k_d)^{-1/2}$ from the experimental data of $M(\infty)$. Figure 1 shows the dependence (in linearized form) of the final concentration of styrene on the initial concentration of the initiator, for different initial concentrations of styrene, $[ST]_0$. The final concentration of MMA as function of the initial concentra-
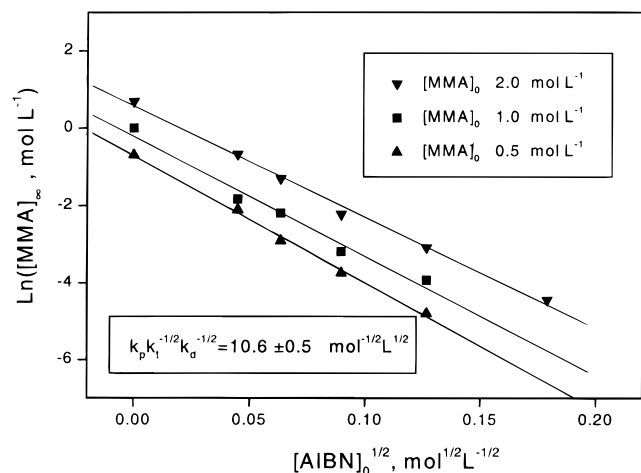
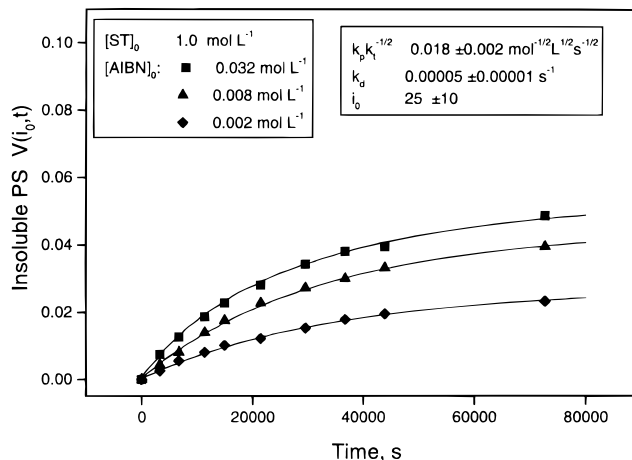**Figure 2.** Final concentration of MMA as a function of the initial concentration of initiator (AIBN).
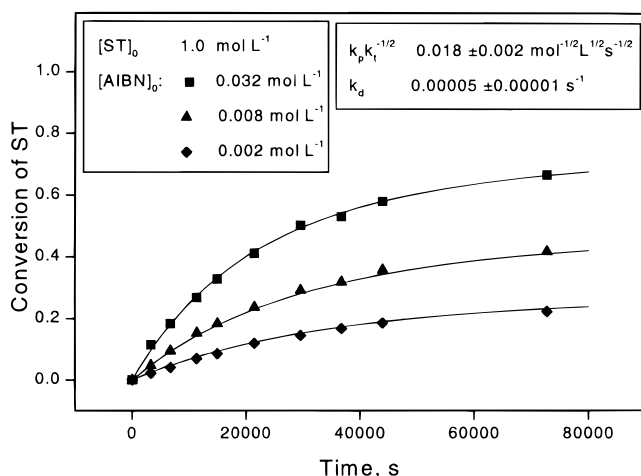
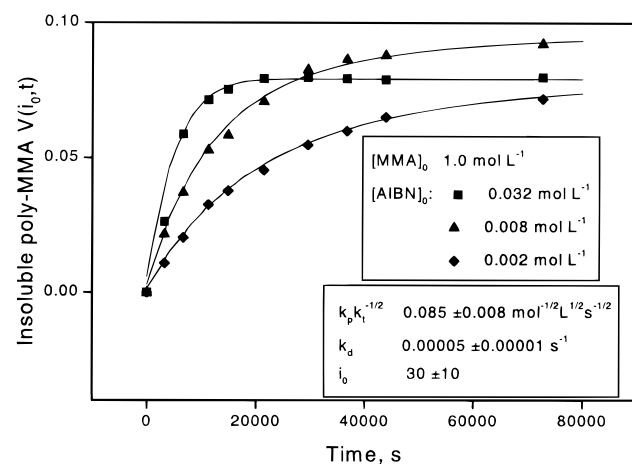**Figure 3.** Conversion versus time profile for styrene.
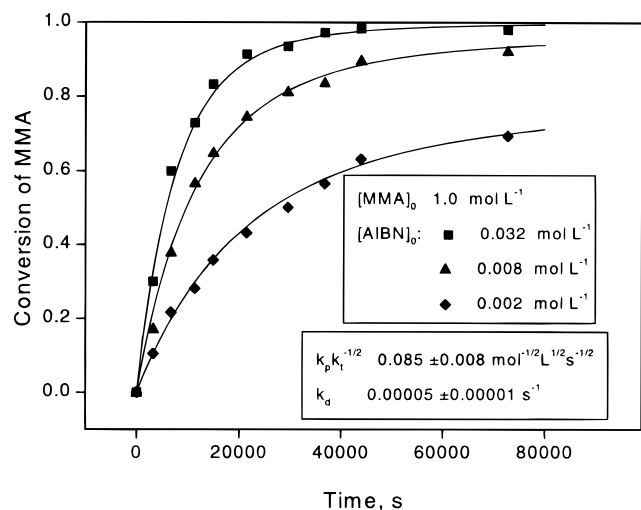
Figure 4. Conversion versus time profile for MMA.

Figure 5. Insoluble polystyrene volume fraction versus time profile.

Figure 6. Insoluble poly(MMA) volume fraction versus time profile.

Table 1. Kinetic Parameters for Dispersion Polymerization of Styrene

parameter	this paper ($T = 70$ °C)	refs 13, 19−21
k_d	$(5.0 \pm 1.0) \times 10^{-5}$ s^{-1}	$(3-4) \times 10^{-5}$ s^{-1}
$k_p/k_t^{1/2}$	$(1.8 \pm 0.2) \times 10^{-2}$ L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$(3-5) \times 10^{-2}$ L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$
i_0	25 ± 10	$25-350$

tion of initiator is shown in Figure 2, for different initial concentrations of MMA [MMA]$_0$. The good linearity of the experimental data (in Figures 1 and 2) supports the applicability of the model. From kinetic measurements of monomer conversion (Figures 3 and 4), we obtained the parameters $k_p(k_t)^{-1/2}$ and k_d for the polymerization of styrene and MMA (the initial concentration of initiator, [AIBN]$_0$, was varied over a wide range).

Three different methods were used to measure the insoluble polymer component so we could estimate the precision of the measurements. All methods gave the same results for the formation of polymer component within 10% error. Figures 5 and 6 show the kinetics of the insoluble component of polystyrene and poly(MMA), respectively. During the fitting procedure with eq 30, we found it impossible to obtain the parameter k_{td}/k_{tc} from our experimental data for $V(i_0,t)$; the fitting procedure produced a large error for k_{td}/k_{tc}. This means that the effect of the parameter k_{td}/k_{tc} was not so important in our system. We thus obtained only i_0 from the experimental data of $V(i_0,t)$ (assuming $k_{td}/k_{tc} = 0$).

The estimated values k_d and $(k_p/k_t)^{1/2}$ are in agreement with those reported in the literature[1,19,20] (Tables 1 and 2). The value i_0 is close to the range reported by Ober et al.[21]

To clearly outline the limitations of application of this theoretical model, we have analyzed the approximations in more detail. The model is based on the following main assumptions:

Table 2. Kinetic Parameters for Dispersion Polymerization of MMA

parameter	this paper ($T = 70$ °C)	refs 13, 19, 20
k_d	$(5.0 \pm 1.0) \times 10^{-5}$ s^{-1}	$(3-4) \times 10^{-5}$ s^{-1}
$k_p/k_t^{1/2}$	$(8.5 \pm 0.8) \times 10^{-2}$ L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$	$(1.4-2) \times 10^{-1}$ L$^{1/2}$ mol$^{-1/2}$ s$^{-1/2}$
i_0	30 ± 10	-

1. The rate constants are independent of the size of the polymer chain.

2. Polymerization within the precipitated polymer particles is neglected.

3. The width of the molecular-weight distribution of the polymer species is much more than 1 unit of monomer.

4. The viscosity and solubility of the medium are not changing during polymerization.

5. It is possible to define the critical polymer chain length i_0, so that the evolution of the insoluble polymer component can be described.

We will not discuss here the limitations of the classical kinetic treatment, which is based on the assumption that the rate constants are independent of the polymer chain length. Such treatment is an excellent approximation in many systems. Obviously, this is caused by the "averaging" effect, which occurs during the reactions between polymer species with different chain lengths during polymerization.

In dispersion polymerization, we can neglect reactions within precipitated polymer particles if the insoluble polymer volume fraction is <0.1. The reason for such an estimation is that, in dispersion polymerization, the medium is a good solvent for the monomer and the initiator. In the case of emulsion and suspension polymerization, the solubility of the monomer or the initiator (or both) in the medium is poor. Therefore, we must take into account polymerization within an insoluble polymer.

1. Approximation of the Continuous Functions of Molecular-Weight Distributions. The basis of the present approach is the assumption that continuous functions describe the molecular-weight distributions for the polymer species. The main approximation is as follows:

$$\frac{\partial}{\partial i}R(i,t) = R(i,t) - R(i-1,t) \tag{37}$$

$$\int_0^\infty R(j,t)\,dj = \sum_{j=0}^\infty R(j,t) \tag{38}$$

$$\int_0^i R(i-j,t)\,R(j,t)\,dj = \sum_{j=0}^{j=1} R(i-j,t)\,R(j,t) \tag{39}$$

These substitutions are correct if

$$R(i,t) - R(i-1,t) \ll R(i,t) \tag{40}$$

That means

$$1 \gg \frac{R(i,t) - R(i-1,t)}{R(i,t)} = \frac{(k_{tc} + k_{td})S(t) + k_{tr,M}M(t) + k_{tr,I}I(t)}{k_pM(t)} \tag{41}$$

Thus, our approach (substitutions) is based on the assumption

$$\delta'(t) = \frac{(k_{tc} + k_{td})S(t)}{k_pM(t)} \ll 1 \tag{42}$$

In this case, it is possible to use differential eq 18 instead of eq 10. The inverse parameter

$$\frac{1}{\delta'(t)} = \frac{k_pM(t)}{(k_{tc} + k_{td})S(t)} \tag{43}$$

implies the width of the size distribution of the polymer radical in the system. Therefore, our considerations corresponds to the case in which the width of such a distribution is much larger than 1 unit of monomer. To estimate the value $\delta'(t)$, we substitute eqs 24, 25, and 26 in eq 42:

$$\delta' = \frac{(k_{tc} + k_{td})S(t)}{k_pM(t)} = \frac{(k_{tc} + k_{td})S(0)}{k_pM(0)}e^{2(k_p+k_{tr,M})(k_d)^{-1}[S(0)-S(t)]-1/2k_dt} \tag{44}$$

It follows from eq 44 that

$$\max\{\delta'(t)\} = \frac{k_d(k_{tc} + k_{td})}{2k_p(k_p + k_{tr,M})M(0)}e^{2(k_p+k_{tr,M})(k_d)^{-1}S(0)-1} \tag{45}$$

where

$$S(0) = \left[\frac{2k_dI(0)}{k_{tc} + k_{td}}\right]^{1/2} \tag{46}$$

Equation 45 allows us to estimate the limitations on the approximation of the continuous functions for the molecular weight distributions. For example, for $(k_{tc} + k_{td}) \approx 10^8$ L mol^{-1} s^{-1}, $k_p \approx 500$ L mol^{-1} s^{-1}, $k_d \approx 5 \times 10^{-5}$ s^{-1}, $I(0) \approx 10^{-2}$ mol L^{-1}, and $M(0) \approx 1$ mol L^{-1}, we have:

$$\max\{\delta(t)\} \approx 0.02 \ll 1 \tag{47}$$

2. Change in the Monomer Concentration in the System. Next, we estimate the change of the viscosity of the medium caused by the change in the monomer concentration:

$$\eta_s \approx \nu_1\eta_1 + \nu_2\eta_2 \tag{48}$$

where η_1, η_2, and η_s are the viscosities of solvent, monomer, and their mixture, and ν_1 and ν_2 are the molar fractions of solvent and monomer in the mixture, respectively. This effect is negligible if

$$\frac{\nu_2\eta_2}{\nu_1\eta_1 + \nu_2\eta_2} \ll 1 \tag{49}$$

A similar expression can be applied to estimate the change in the solubility of the medium. The parameter χ_s for the interaction of polymer with molecules in the mixture can be written as

$$\chi_s \approx \nu_1\chi_1 + \nu_2\eta_2 \tag{50}$$

where χ_1 and χ_2 are interaction parameters for the polymer with the solvent and the monomer, and ν_1 and

ν_2 are the molar fractions of solvent and monomer, respectively ($\nu_1 + \nu_2 = 1$). Thus it is possible to neglect this effect if

$$\frac{\nu_2\chi_2}{\nu_1\chi_1 + \nu_2\chi_2} \ll 1 \tag{51}$$

3. Change in the Polymer Concentration of the System. Next we estimate the effect of the dissolved polymer on the viscosity, using the Mark–Houwink equation for intrinsic viscosity (η) of the polymer:

$$[\eta] = K_\eta M_v^a \tag{52}$$

where M_v is the viscosity-average molecular weight of the polymer, and K_η and a are parameters of the Mark–Houwink equation. The maximum value of the concentration c_{max} of the polymer in the system is

$$c_{\max} \approx \frac{M_0}{M_V} M(0) \tag{53}$$

where M_0 is the molecular weight of the monomer, and $M(0)$ is the initial concentration of the monomer. It is possible to show[12] that the change of the viscosity of the medium is not an essential effect if

$$c_{\max}[\eta] = M_0 K_\eta M_V^{a-1} M(0) \ll 1 \tag{54}$$

4. Approximation of the Critical Polymer Chain Length. The Flory–Huggins theory[22,23] has been successfully applied to the quantitative estimation of the effect of precipitation and phase separation in polymer solutions. According to this theory, the solubility of a polymer with chain length i can be represented by the following approximate expressions:

$$\varphi_i \approx e^{-\alpha i} \tag{55}$$

$$\alpha = \frac{m}{i}(\chi - 1) \tag{56}$$

where φ_i is the ratio between the maximum soluble polymer volume and the total volume of the medium, m is the ratio between the polymer mole volume and the solvent mole volume (m is proportional to i), and χ is the thermodynamic parameter for the interaction between a polymer molecule and solvent molecules. We can simplify the mathematical model of the evolution of the insoluble polymer component if we define the critical chain length i_0. Thus, we can assume that polymer molecules with chain length $i \geq i_0$ are completely insoluble, but polymer molecules with chain length $i < i_0$ are completely soluble. Application of this approximation is possible, if $\alpha \gg \delta(t)$, where $\delta(t)$ is the inverse width of the molecular-weight distributions of the polymer species in the system (eq 23).

Conclusions

The complete solution of the classical kinetic scheme, involving initiation, propagation, termination (disproportionation and combination), and chain-transfer reactions, has been carried out. The expressions for the kinetics of formation of each species in the polymerization mixture have been presented as analytical functions. The proposed kinetic analysis is valid only if the gel effect phenomenon is absent. This model also is not applicable to high-conversion polymerization in bulk or in suspension.

Monomer conversion and formation of the insoluble polymer component in free-radical dispersion polymerization of styrene and MMA have been measured to demonstrate the general applicability of this mathematical model.

The critical chain length i_0 of the polymer, the initiation rate constant k_d, and the ratio $k_p/k_t^{1/2}$, where k_p and k_t are propagation and termination rate constants, respectively, have been obtained by using least-squares fitting of the monomer conversion and the insoluble polymer formation experimental data. The values k_d and $k_p/k_t^{1/2}$ are in agreement with those reported in the literature. The value i_0 is close to the range expected for such reactions.[21]

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