# Kinetic and Molecular Weight Control for Methyl Methacrylate Semi-Batch Polymerization. I. Modelling

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**ABSTRACT:** There are gel, glass, and cage effects in the methyl methacrylate (MMA) bulk polymerization. These effects will cause the propagation and termination rate constants and initiator efficiency change during the polymerization process, and make the kinetics and molecular weight more complex. A violent increase of conversion will bring a large amount of reaction heat evolved in a short time, and will promote temperature increase if the heat cannot be removed in time. Molecular weight of polymer will raise ten times at the same time. So, the temperature of polymerization system, kinetics of polymerization, and molecular weight and its distribution of polymer cannot be controlled. To control and unify them, the semibatch polymerization method is preferably selected. Furthermore, the kinetic and molecular weight models for MMA semibatch polymerization with the participation of chain transfer agent and new materials addition flow rate are presented. Using the presented models, the effects of temperature, initiator concentration and type, monomer or solvent concentration, and chain transfer agent concentration and type on the kinetics, and molecular weight and its distribution are simulated in this article. Experimental data of kinetics and molecular weight obtained from the published literature are compared with the simulation results to examine the presented models. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 2838–2846, 2006

**Key words:** methyl methacrylate; modeling; kinetics; molecular weight

## INTRODUCTION

Methyl methacrylate (MMA) is often polymerized by a free radical mechanism. The polymerization consists of four elementary reactions: initiation, propagation, termination, and chain transfer. Free radicals are formed by the decomposition of initiators. Once formed, these radicals propagate by reacting with surrounding monomers to form long chains, and the active site is shifted to the end of the chain when a new monomer is added to the chain. The reaction terminates when two radicals react. A new radical is yielded when an active site reacts with a active hydrogen atom from chain transfer agent, monomer, polymer, or solvent.

The kinetics of MMA polymerization are often complex because the growing and dead polymers reduce chain mobility and hamper radical termination. A strong autoacceleration in the rate first occurs along with a concomitant increase in the medium viscosity. A limiting conversion is later reached when even the propagation step is slowed by the high viscosity. Hence, modeling the kinetics of MMA polymerization and the molecular weight of PMMA must take these considerations into account. A detailed understanding of each elementary reaction is needed if accurate predictions are to be achieved.

Molecular weight is an important parameter for polymer. It will decide the final physical properties of polymer, but the molecular weight of PMMA is dependent on the kinetic process. Number– or weight– average molecular weight will increase with the free radical accumulation when the gel effect appears, and decrease when the glass effect happens. So, molecular weight of PMMA is connected with each species in the MMA polymerization process, and with the changes of the reaction rate constants. Not only should the model of molecular weight include the changes of species, but also the changes of the reaction rate constants in the MMA polymerization process, if the molecular weight need to be controlled.

There are many articles[1,2] and reviews[3,4] about the gel, glass, and cage effects in the MMA bulk polymerization, and many articles[1,2,5–7] for the kinetic model of MMA polymerization, and molecular weight and its distribution model of PMMA at various mediums, thermal conditions, and reactors. Most of them are those of bulk or solution polymerization in the batch

reactor or CSTR under isothermal condition. There are no models for a semibatch process, and with the participation of chain transfer agent (CTA). However, the best method to control the kinetics of MMA polymerization, and molecular weight and its distribution of PMMA is achieved in the semibatch reactor with or without the participation of CTA or solvent, and so the models of the kinetics, molecular weight, and its distribution are very interesting. The mechanistic models are the precondition for the control of kinetics, molecular weight, and its distribution.

In the present article, the generalized models for MMA polymerization and molecular weight in the semibatch process are derived. The kinetics, molecular weight, and its distribution are simulated.

## Derivation of kinetic and molecular weight models

To present new models for MMA bulk or solution polymerization in semibatch process with the participation of chain transfer agent, the elementary reaction should be known at first.

### Elementary reactions and rate equations

The elementary reactions and rate equations of methyl methacrylate are listed as following:

Initiation: $I \xrightarrow{k_d} 2R^*$

$$R^* + M \xrightarrow{k_i} M_1^*$$
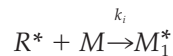
The final expression for the rate of initiation, if the initiator efficiency $f$ is taken into account, is $R_I = fk_d[I]$.
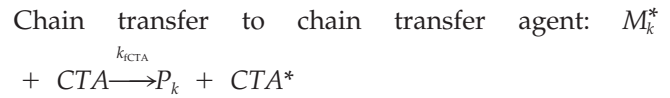
Propagation: $M_k^* + M \xrightarrow{k_p} M_{k+1}^*$
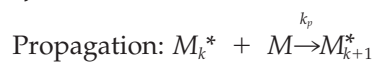
The rate of propagation, which may be regarded as the rate of polymerization, is $R_p = k_p[M][M^*]$.

where $[M^*] = \sum_{k=1}^{\infty}[M_k^*]$, is a summation of all radicals with chain length of 1 to infinity.

Combination termination: $M_k^* + M_j^* \xrightarrow{k_{tC}} P_{k+j}$

Disproportionation termination: $M_k^* + M_j^* \xrightarrow{k_{td}} P_k + P_j$

The rate of termination is $R_t = k_t[M^*]^2$.
where $k_t = k_{tC} + k_{td}$.

Chain transfer to monomer: $M_k^* + M \xrightarrow{k_{fM}} P_k + M_1^*$

Chain transfer to solvent: $M_k^* + S \xrightarrow{k_{fS}} P_k + S^*$

Chain transfer to initiator: $M_k^* + I \xrightarrow{k_{fI}} P_k + I^*$

Chain transfer to polymer: $M_k^* + P_j \xrightarrow{k_{fP}} P_k + M_j^*$

Chain transfer to chain transfer agent: $M_k^*$
$+ CTA \xrightarrow{k_{fCTA}} P_k + CTA^*$

The rate of chain transfer, for example of chain transfer to CTA, is $R_{tr} = k_{fCTA}[M^*][CTA]$. New kinds of radicals are yielded from the chain transfer reactions. It is certain that the activities of $M_1^*$, $M_j^*$, and $I^*$ are equal to that of monomer radicals, but that of $S^*$ is far less than that of monomer radicals. However, not all of the CTA radicals can initiate monomer, the activity of $CTA^*$ is not equal to and less than that of monomer radicals. It will change the differential equation of monomer radicals, which will be offered later.

### Mass balance equations for each species in the MMA polymerization

The quantity of each species in the reaction mixture can be calculated through a differential equation based on the species mass balance. Since it simulates the MMA polymerization in the semibatch reactor, input flow rates of any reactant species or materials are taken into account in all the kinetic, molecular weight, and differential equations. The following is a list of all these equations. In these equations, $F_j^{in}$ is the inlet molar flow rate of species j, and V is the volume of the reaction mixture.

Monomer: $\dfrac{d(V[M])}{dt} = F_M^{in} - (k_p + k_{fM})[M][M^*]V$
$$+ [M]\dfrac{dV}{dt}$$

Initiator: $\dfrac{d(V[I])}{dt} = F_I^{in} - k_d[I]V + [I]\dfrac{dV}{dt}$

Solvent: $\dfrac{d(V[S])}{dt} = F_S^{in} - k_{fS}[S][M^*]V + [S]\dfrac{dV}{dt}$

Polymer: $\dfrac{d(V[P])}{dt} = \{k_t[M^*] + k_{fM}[M] + k_{fS}[S]$
$+ k_{fI}[I] + k_{fP}[P] + k_{fCTA}[CTA]\}[M^*]V + [P]\dfrac{dV}{dt}$

Chain transfer agent: $\dfrac{d(V[CTA])}{dt} = F_{CTA}^{in} - k_{fCTA}[CTA]$
$\times [M^*]V + [CTA]\dfrac{dV}{dt}$

Radical: $\dfrac{d(V[M^*])}{dt} = \{fk_d[I] - k_t[M^*]^2 - k_{fS}[S][M^*]$
$- (1 - f_{tr})k_{fCTA}[CTA]\}[M^*]\}V + [M^*]\dfrac{dV}{dt}$

where $f_{tr}$ is the concentration ratio of the CTA radical with the same activity of monomer radical to the all of CTA radical.

We assume that the volume of the mixture is a summation volume of all reactants and products, and neglect the volume of initiator and CTA. We have

Volume: $V = \dfrac{(M_0 + \int F_M^{in} dt)M_M \rho_M^{-1} + (S_0 + \int F_S^{in} dt)M_S \rho_S^{-1}}{1 - [M]M_M(\rho_M^{-1} - \rho_P^{-1})}$

thus, $\dfrac{dV}{dt} = \dfrac{F_M^{in} M_M \rho_M^{-1} + F_S^{in} M_S \rho_S^{-1}}{1 - [M]M_M(\rho_M^{-1} - \rho_P^{-1})}$
$\dfrac{-VM_M(\rho_M^{-1} - \rho_P^{-1})(k_P + k_{fM})[M][M^*]}{1 - [M]M_M(\rho_M^{-1} - \rho_P^{-1})}$

The conversion at any time can be calculated by the following equation.

Conversion: $x = 100 \times [1 - ([M]V)(\int F_M^{in} dt + M_0)]$

## Molecular weight and its distribution

The concentration changes of the living radicals with chain length from unity to $k$ are

$$\frac{d[M_1^*]}{dt} = fk_d[I] + k_{fM}[M]([M^*] - [M_1^*]) - k_p[M_1^*][M]$$

$$- k_t[M_1^*][M^*] - (k_{fS}[S] + k_{fCTA}[CTA] + k_{fI}[I] + k_{fP}[P])[M_1^*]$$

$$\bullet \quad \bullet \quad \bullet \quad \bullet$$

$$\frac{d[M_k^*]}{dt} = k_p[M]([M_{k-1}^*] - [M_k^*]) - k_t[M_k^*][M^*]$$

$$- (k_{fM}[M] + k_{fS}[S] + k_{fCTA}[CTA] + k_{fI}[1] + k_{fP}[P])[M_k^*]$$

$$+ k_{fP}[M^*][P_k]$$

and those of the dead polymer with chain length $k$ is

$$\frac{d[P_k]}{dt} = k_{td}[M_k^*][M^*] + \frac{1}{2}k_{tc}\sum_{j=1}^{k-1}[M_j^*][M_{k-j}^*] + (k_{fM}[M] + k_{fS}[S]$$

$$+ k_{fCTA}[CTA] + k_{fI}[I] + k_{fP}[P])[M_k^*] - k_{fP}[M^*][P_k]$$

where $[M^*] = \sum_{k=1}^{\infty}[M_k^*]$, and $[P] = \sum_{k=1}^{\infty}[P_k]$

Let $\lambda_n = \sum_{k=1}^{\infty} k^n[M_k^*]$, and $\mu_n = \sum_{k=1}^{\infty}k^n[P_k]$, where n=0,1 or 2.

$$\frac{d\lambda_0}{dt} = fk_d[I] - k_t\lambda_0^2 - (k_{fS}[S] + k_{fCTA}[CTA] + k_{fI}[I])\lambda_0$$

$$\frac{d\lambda_1}{dt} = fk_d[I] - k_t\lambda_0\lambda_1 - (k_{fS}[S] + k_{fCTA}[CTA] + k_{fI}[I])\lambda_1$$

$$+ k_p[M]\lambda_0 + k_{fM}[M](\lambda_0 - \lambda_1) + k_{fP}(\lambda_0\mu_1 - \lambda_1\mu_0)$$

$$\frac{d\lambda_2}{dt} = fk_d[I] - k_t\lambda_0\lambda_2 - (k_{fS}[S] + k_{fCTA}[CTA] + k_{fI}[I])\lambda_2$$

$$+ k_p[M](2\lambda_1 + \lambda_0) + k_{fM}[M](\lambda_0 - \lambda_2) + k_{fP}(\lambda_0\mu_2 - \lambda_2\mu_0)$$

and

$$\frac{d\mu_0}{dt} = \left(k_{td} + \frac{1}{2}k_{tc}\right)\lambda_0^2 + (k_{fM}[M] + k_{fS}[S] + k_{fCTA}[CTA]$$

$$+ k_{fI}[I] + k_{fP}\mu_0) - k_{fP}\lambda_0\mu_0$$

$$\frac{d\mu_1}{dt} = k_t\lambda_0\lambda_1 + (k_{fM}[M] + k_{fS}[S] + k_{fCTA}[CTA] + k_{fI}[I]$$

$$+ k_{fP}\mu_0)\lambda_1 - k_{fP}\lambda_0\mu_1$$

$$\frac{d\mu_2}{dt} = k_t\lambda_0\lambda_2 + k_{tc}\lambda_1^2 + (k_{fM}[M] + k_{fS}[S] + k_{fCTA}[CTA]$$

$$+ k_{fI}[I] + k_{fP}\mu_0)\lambda_2 - k_{fP}\lambda_0\mu_2$$

Let $\alpha_n = V\lambda_n$, and $\beta_n = V\mu_n$, so

$$\frac{d\alpha_n}{dt} = V\frac{d\lambda_n}{dt} + \lambda_n\frac{dV}{dt}$$

$$\frac{d\beta_n}{dt} = V\frac{d\mu_n}{dt} + \mu_n\frac{dV}{dt}$$

The cumulative number–average molecular weight of polymer is

$$\bar{M}_n = 1000 \times \frac{\alpha_1 + \beta_1}{\alpha_0 + \beta_0}M_M$$

The cumulative weight–average molecular weight of polymer is

$$\bar{M}_w = 1000 \times \frac{\alpha_2 + \beta_2}{\alpha_1 + \beta_1}M_M$$

where $M_M$, the MMA molecular weight, is 0.10,013 kg/mol.

The molecular weight distribution of polymer is

$$MWD = \frac{\bar{M}_w}{\bar{M}_n} = \frac{(\alpha_2 + \beta_2)(\alpha_0 + \beta_0)}{(\alpha_1 + \beta_1)^2}$$

## Reaction rate constants and their physical parameters in the equations

$\Psi$

$$\psi = \frac{\gamma\left\{\dfrac{\rho_M\phi_M V_M^*}{\xi_{MP}} + \dfrac{\rho_S\phi_S V_S^*}{\xi_{SP}} + \rho_P\phi_P V_P^*\right\}}{\rho_M\phi_M V_M^* V_{fM} + \rho_S\phi_S V_S^* V_{fS} + \rho_P\phi_P V_P^* V_{fP}}$$

where $\xi_{MP} = V_M^* M_M/(V_P^* M_{jP})$, $\xi_{SP} = V_S^* M_S/(V_P^* M_{jP})$, $\phi_M = M_M[M]\rho_M^{-1}$, $\phi_S = M_S[S]\rho_S^{-1}$, $\phi_P = 1 - \phi_M - \phi_S$ (because the molecular weight of polymer is an average value, the equation of $\phi_P = M_P[P]\rho_P^{-1}$ is wrong and will cause error), $\gamma = 0.763$, $M_M = 0.10013$ (kg/mol), $M_{jP} = 0.150$ (kg/mol),[1] $V_{fP} = 0.0224 + 0.0003 \times (T - 388.15)$,[8] $V_{fM} = 0.025 + 0.00029 \times (T - 147.15)$,[8] $V_M^* = 8.22 \times 10^{-4}$ (m$^3$/kg),[9] $V_P^* = 7.70 \times 10^{-4}$ (m$^3$/kg) $\rho_M = 966.5 - 1.1 \times (T - 273.15)$ (kg/m$^3$),[8] $\rho_P = \rho_M \times [1.1946 + 0.000916 \times (T - 273.15)]$(kg/m$^3$).[8]

For benzene: $M_S = 0.07811$ (kg/mol), $V_S^* = 9.01 \times 10^{-4}$ (m$^3$/kg), $V_{fS} = 0.025 + 0.00039 \times (T - 171.15)$, $\rho_S = 844.18 - 1.07165 \times (T - 273.15)$ (kg/m$^3$).

### $f$ and $k_d$

$$\frac{1}{f} = \frac{1}{f_0}\left(1 + \frac{r_2^3}{3r_1}k_{p0}[M]\frac{\varepsilon_i}{D_{I0}\exp(-\xi_{IP}\psi\gamma_I/\gamma)}\right)$$

where $\xi_{IP} = V_I^* M_I/(V_P^* M_{jP})$, $\gamma_I = 1$,[1] $k_{p0} = 492 \times \exp(-18229/RT)$ (m$^3$/mol/s), $r_1 = [6V_M^*/(\pi N_A)]^{1/3}$ (m), $r_2 = 2.6 \times 10^{-11} \times (\bar{M}_w)_i^{0.574}$ (m), $\varepsilon_i/D_{I0} = 3.7238 \times 10^6$(s/m$^2$) (s/m$^2$),[1] $N_A$ is the Avogadro's number (6.023 $\times$ 10$^{23}$), and $(\bar{M}_w)_i$ is the initial weight–average molecular weight of polymer (100.13).

For AIBN: $f_0 = 0.58$, $k_d = 2.106 \times 10^{15} \exp(-128450/RT)$, $V_I^* = 9.13 \times 10^{-4}$ (m$^3$/kg),[9] $M_I = 0.068$ (kg/mol) (this is the molecular weight of residual initiator group CN(CH$_3$)$_2$C*).

For BPO: $f_0 = 1$, $k_d = 1.69 \times 10^{14} \exp(-125400/RT)$, $V_I^* = 8.25 \times 10^{-4}$ (m$^3$/kg),[8] $M_I = 0.077$ (kg/mol) (this is the molecular weight of residual initiator group *C$_6$H$_5$).

### $k_t$, $k_{td}$ and $k_{tc}$

$k_{t0} = 98000 \exp(-2934/RT)$(m$^3$/mol/s), $k_{tc0}/k_{td0} = 3.95 \times 10^{-4} \exp(17126/RT)$, $and$ $k_{t0} = k_{tc0} + k_{td0}$.

$$\frac{1}{k_t} = \frac{1}{k_{t0}} + \frac{r_t^2}{3}\frac{[M^*]}{F_{seg}D_p}\left(\frac{\bar{M}_w}{(\bar{M}_w)_e}\right)^2\frac{1}{(\exp - \psi)}$$

$$k_{td} = k_t/[1 + 3.95 \times 10^{-4} \exp(17126/RT)]$$

$$k_{tc} = k_t - k_{td} \times \text{(m}^3\text{/mol/s)}$$

where $r_t = \{\ln[\tau^3/(N_A[M^*]\pi^{3/2})]\}^{1/2}/\tau$(m), $\tau = [3/(2j_c\delta^2)]^{1/2}$(m), $1/j_c = 1/j_{c0} + 2\phi_p/X_{c0}$, $X_{c0} = 100$,[11] $j_{c0} = 10^{7.66}/[(M_n)_c/(1000M_M)]^{1.8}$,[2] $\delta = 6.9 \times 10^{-10}$(m), $F_{seg} = r_e^3[\pi r_c + 6\sqrt{2}\alpha_{seg}r_B]/(16\pi r_B^4)$, $r_e = 1.7 \times 10^{-9}$(m),[12] $\alpha_{seg} = 0.28$[1] for AIBN as an initiator, $r_B = 1.3 \times 10^{-11} \times (\bar{M}_w)_i^{0.574}$ (m), $D_p = k_BT/(6\pi\eta_sR_H)$, $k_B$ is the Boltzmann's constant (1.3806 $\times$ 10$^{-23}$)(J/K), $R_H$

$= 1.3 \times 10^{-11} \times (\bar{M}_w)^{0.574}$ (m), and $\eta_s = \exp(-0.099 + 496/T - 1.5939 \times \ln T)$ (Pa s).

### $k_p$

$$k_{p0} = 492 \exp(-18229/RT) \text{ (m}^3\text{/mol/s)}.$$

$$\frac{1}{k_p} = \frac{1}{k_{p0}} + \frac{r_m^2}{3}\frac{[M^*]}{D_{m0}}\frac{1}{\exp(-\xi_{MP}\psi)}$$

where $r_m$ is the monomer radius ($r_m = r_B$), and $D_{m0} = 8.27 \times 10^{-15}$ (m$^2$/s).[1]

### $k_{fM}$, $k_{fS}$, $k_{fCTA}$, $k_{fI}$, and $k_{fP}$

$k_{fI} = 0$ for AIBN as an initiator,
$k_{fI} = 0.02 \times k_p$ for BPO as an initiator,
$k_{fS} = k_p \times 1.01 \times 10^3 \times \exp(-47700/RT)$ (m$^3$/mol/s) for benzene as a solvent,
$k_{fM} = k_p \times 9.48 \times 10^3 \times \exp(-58077/RT)$ (m$^3$/mol/s),
$k_{fCTA} = 0.15 \times k_p$ (m$^3$/mol/s) and $f_r = 0.85$ for $n$-dodecyl mercaptan as a chain transfer agent,
$k_{fCTA} = 1.26 \times k_p$ (m$^3$/mol/s) and $f_r = 1.0$ for glycol dimercapto acetate as a chain transfer agent,
$k_{fP} = 3.0 \times 10^{-4} \times k_p$ (m$^3$/mol/s)

## Simulation of kinetics and molecular weight

Since there are no experimental data of kinetics and molecular weight obtained from the semibatch process for MMA polymerization, the experimental data in batch reactor are used to compare the results simulated with the presented models, and to examine the reliability of the presented models.

## Changes of the kinetic constants and physical parameters

Because of the diffusion controlled, and cage, glass, and gel effects, the kinetic rate constants will not keep constant values in the polymerization process. The changes of the kinetic rate constants ($k_p$ and $k_t$) and physical parameters (such as $f$ and $r_t$) in the polymerization process are shown in Figures 1–3.

The simulation results show that $k_p$ and $f$ keep constant when conversion is lower than 60 and 80%, respectively, and decrease rapidly after those points for the glass and cage effect. Although the result of x ~ f is different from the simulation of Achilias and Kiparissides,[1] this phenomenon had been proved by the experimental data of Brooks.[13] $k_t$ decreases at the beginning of polymerization, and decreases rapidly when the gel effect appears. The higher the temperature is, the later the gel effect is found, since the polymerization medium viscosity decreases with the
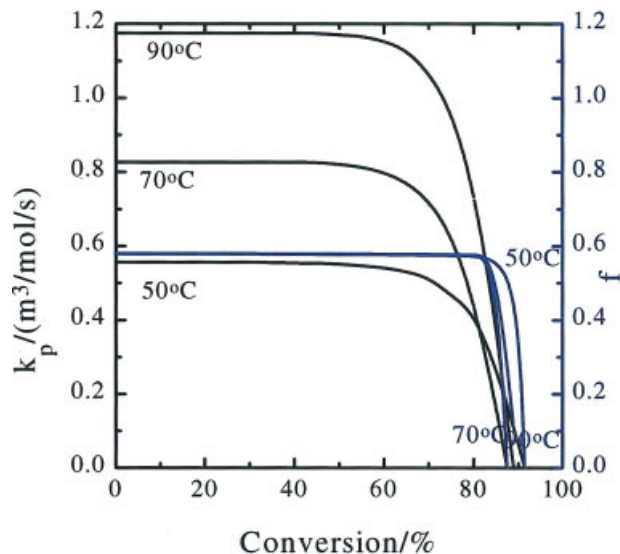
**Figure 1** Propagation rate constant, $k_p$, and initiator efficiency, $f$, for the AIBN-initiated bulk polymerization of MMA at various temperatures ([AIBN] = 0.01548 mol/L). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].

increase of temperature, the termination radius, $r_t$, increases. This result coincides the simulation of Achilias and Kiparissides.[2]

### Effects of temperature on kinetics and molecular weight

Using the presented models, we calculate the kinetics of MMA bulk polymerization and molecular weight of PMMA at three temperatures, and compare with the
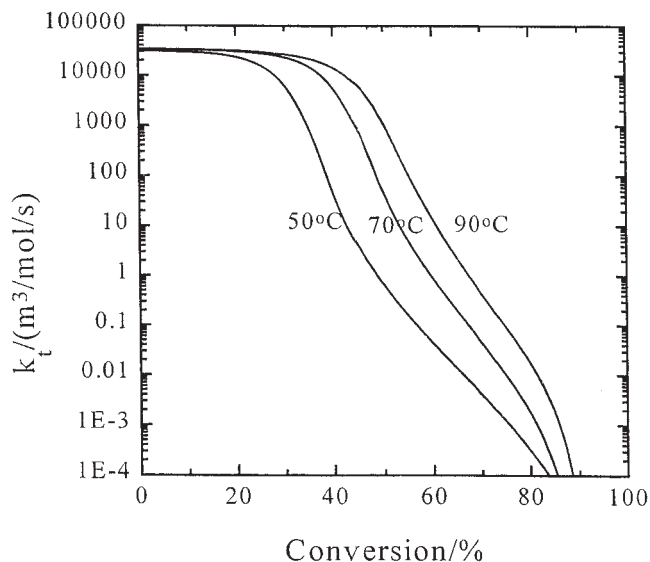


**Figure 2** Termination rate constant, $k_t$, for the AIBN-initiated bulk polymerization of MMA at various temperatures ([AIBN] = 0.01548 mol/L).
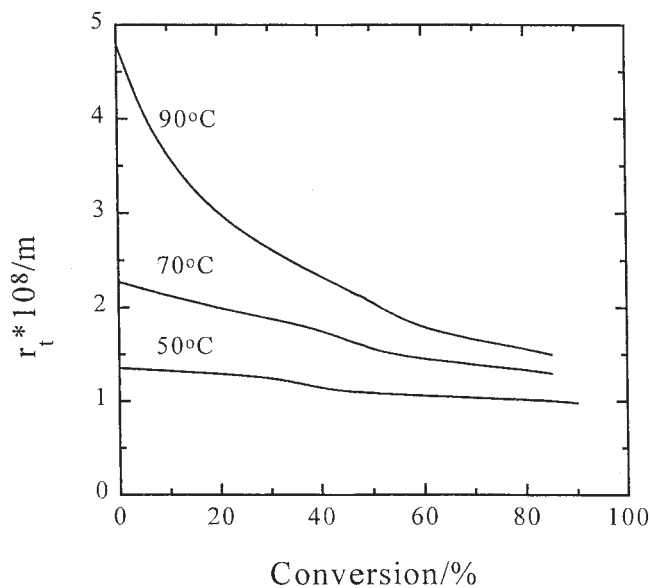


**Figure 3** Termination radius, $r_t$, for the AIBN-initiated bulk polymerization of MMA at various temperatures ([AIBN] = 0.01548 mol/L).

experimental data of Zhu et al.[14] The results are shown in Figures 4–6. The agreement between model predictions and experimental data in all case is very good. With the enhancement of reaction temperature, the reaction rate increases, and the molecular weight decreases.

### Effects of initiator concentration and type on kinetics and molecular weight

The model predictions of conversion at 70°C under various concentration of AIBN, and under different
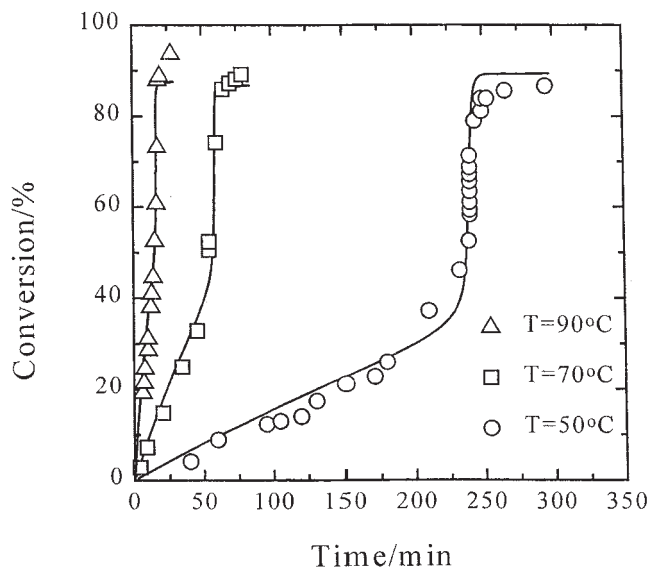


**Figure 4** Kinetic simulation and comparison with experimental data of MMA polymerization in bulk at 50, 70, and 90°C ([AIBN = 0.0258 mol/L]).
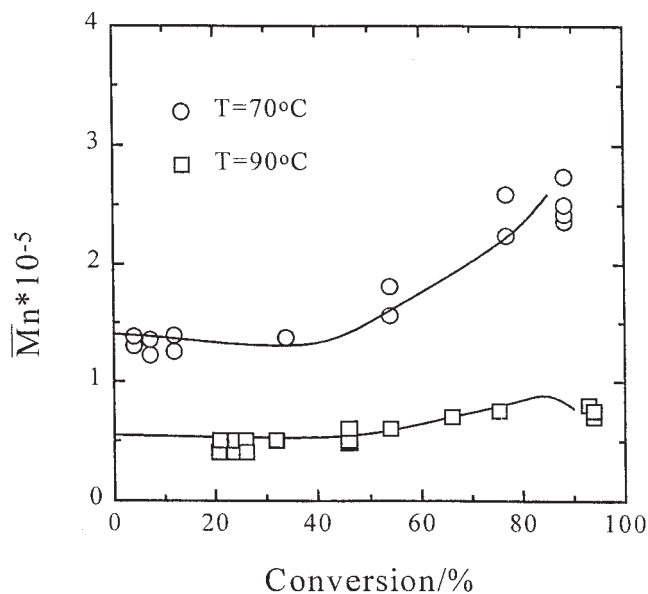
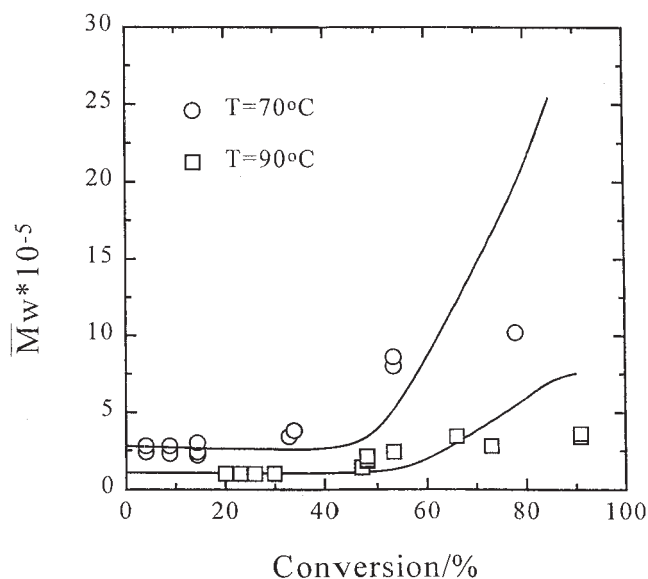**Figure 5** Number–average molecular weight simulation and comparison with experimental data of MMA polymerization in bulk at 70 and 90°C ([AIBN] = 0.0258 mol/L).
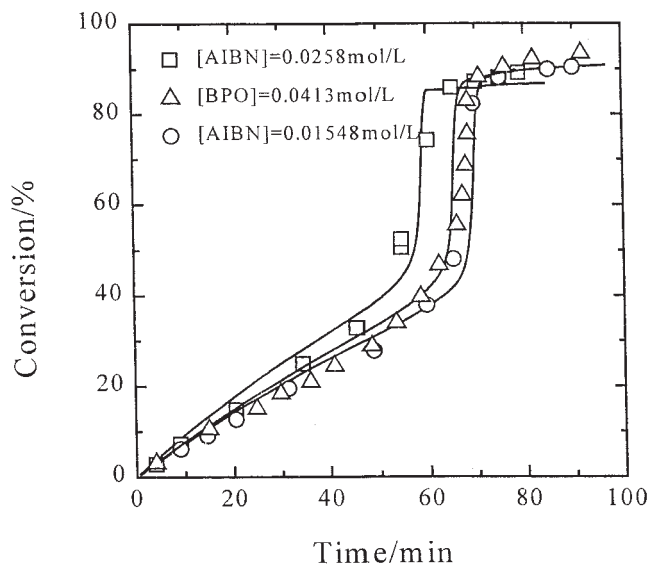
**Figure 7** Kinetic simulation and comparison with experimental data of MMA polymerization in bulk at various initiator concentrations and under different initiators (T = 70°C).

type of initiators (such as AIBN and BPO) are shown in Figure 7. From the kinetic curves, the reaction rate at a higher AIBN concentration is more rapid. However, the reaction rate of BPO concentration (0.0413 mol/L) is situated between those of 0.01,548 and 0.0258 mol/L of AIBN concentration. It means that the activity of AIBN ($k_d \sim 3*10^{-5}$ at 70°C) is higher than that of BPO ($k_d \sim 1*10^{-5}$ at 70°C) at 70°C.

Figures 8 and 9 present the simulation results for number and weight–average molecular weight at various initiator concentrations.

The simulation results are compared with the experimental data of Balke and Hamielec,[15] Zhu et al.,[14] and Schultz and Harborth.[16] The presented models can predict the effects of initiator concentration and type on the conversion and molecular weight.

### Effects of monomer or solvent concentration on kinetics and molecular weight

Using benzene as solvent and BPO as initiator, we simulate the kinetics and molecular weight at 50°C in
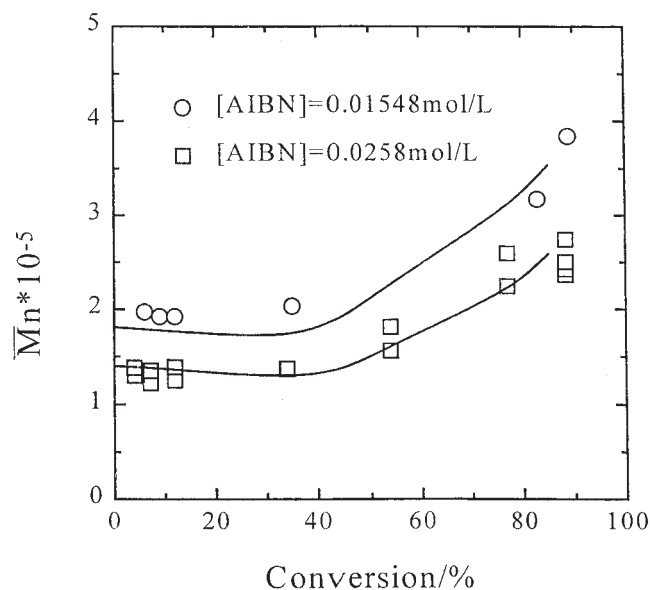
**Figure 6** Weight–average molecular weight simulation and comparison with experimental data of MMA polymerization in bulk at 70 and 90°C ([AIBN] = 0.0258 mol/L).

**Figure 8** Number–average molecular weight simulation and comparison with experimental data of MMA polymerization in bulk at various initiator concentrations (T = 70°C).
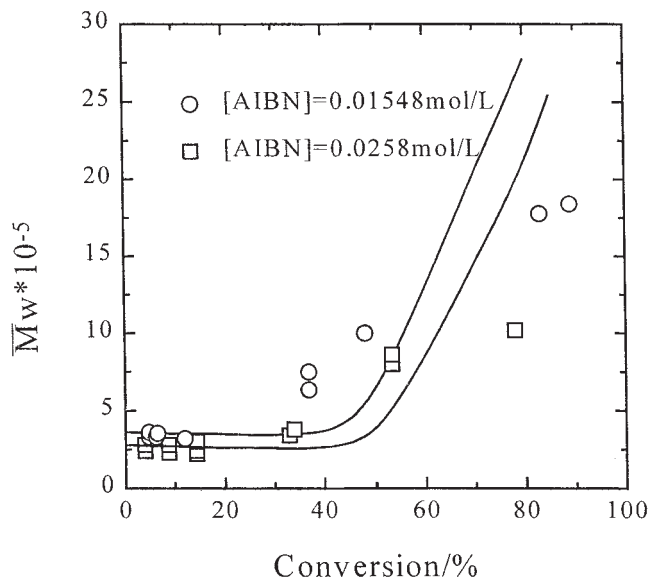
**Figure 9** Weight–average molecular weight simulation and comparison with experimental data of MMA polymerization in bulk at various initiator concentrations ($T = 70°C$).



**Figure 11** Number–average molecular weight simulation of MMA polymerization at various benzene volume fraction ($T = 50°C$, [BPO] = 0.0413 mol/L).

various solvent volume fractions for MMA solution polymerization. The results are presented in Figures 10–12. The kinetic curves are in good agreement with the experimental data.[16] So, the models and programs can be used to predict the conversion and molecular weight for MMA solution polymerization.

It is a good idea to add solvent into the MMA polymerization system to weaken the gel effect. In general, the gel effect will start at 40–50% conversion or at the system with about 40–50% monomer concen-
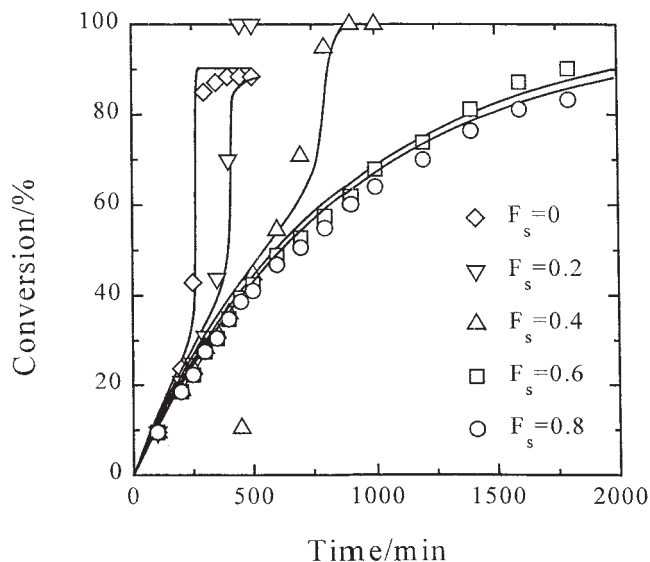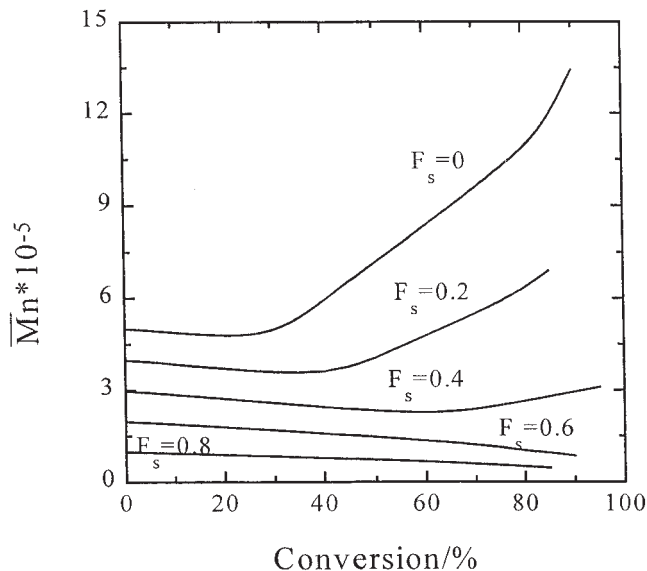
tration. From the solvent volume fraction, $F_S = 0$ (100 wt % monomer), 0.2 (81.22 wt %), 0.4 (61.87 wt %),0.6 (41.87 wt %),and 0.8 (21.28 wt %), we can predict that the conversion of these solution polymerization will be largely changed at 40–50%, 50–60%, 65–80%, over 100%, and over 100% conversion. The prediction results can be proved by the experimental curves (see Fig. 10). The change rule can tell us how the gel effect should be controlled and how many solvent adding rate and mode should be fed.
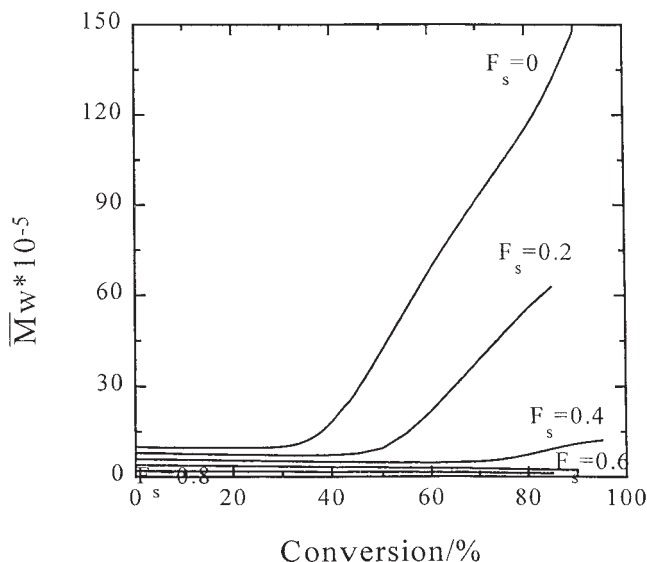


**Figure 10** Kinetic simulation and comparison with experimental data of MMA polymerization at various benzene volume fraction ($T = 50°C$, [BPO] = 0.0413 mol/L).



**Figure 12** Weight–average molecular weight simulation of MMA polymerization at various benzene volume fraction ($T = 50°C$, [BPO] = 0.0413 mol/L).
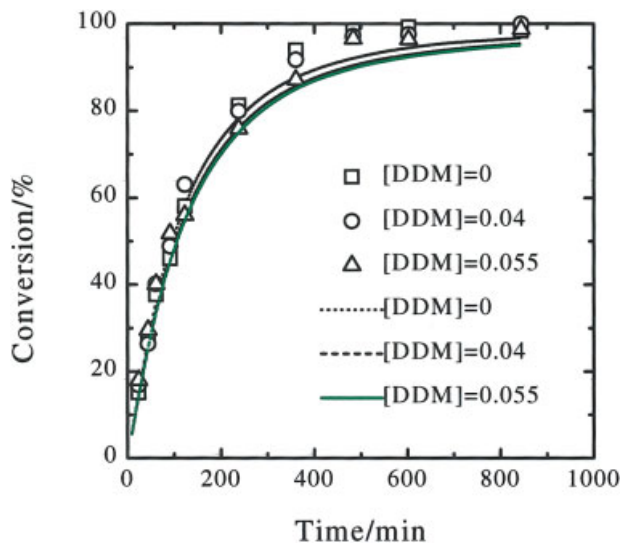
**Figure 13** Kinetic simulation and comparison with experimental data of MMA solution polymerization at various *n*-dodecyl mercaptan concentrations ($T$ = 70°C, [AIBN] = 0.026 mo1/L, [M] = 3 mol/L, benzene). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.].



**Figure 14** Weight–average molecular weight simulation and comparison with experimental data of MMA solution polymerization at various *n*-dodecyl mercaptan concentrations ($T$ = 70°C, [AIBN] = 0.026 mol/L, [M] = 3 mol/L, benzene).

## Effects of chain transfer agent concentration on kinetics and molecular weight

Chain transfer agent can be used to control the kinetics, molecular weight, and its distribution, because the CTA will deactivate some of the macroradicals, keep the radical concentration in a low range ($\sim 10^{-7}$ mol/L), and will transfer to the macroradicals, keeping the molecular weight and distribution constant.

Using *n*-dodecyl mercaptan (DDM) as chain transfer agent and AIBN as initiator, the kinetics and weight–average molecular weight at 70°C in various DDM concentration for MMA solution polymerization are simulated. The results are described in Figures 13 and 14. The kinetic curves and weight–average molecular weight with the participation of CTA are in good agreement with the experimental data.[17] With the participation of CTA, both conversion and molecular weight are reduced, but the molecular weight became more even. These results can serve as a great source of inspiration for the control of kinetics, and molecular weight and its distribution.

Using another CTA, glycol dimercapto acetate (GDMA),[18] for MMA bulk polymerization, get the same results (see Fig. 15).

## CONCLUSIONS

On the basis of the mass balance and diffusion-controlled theory, kinetic, and molecular weight and its distribution, models are presented for MMA polymerization in semibatch process, with the participation of chain transfer agent and new materials addition flow
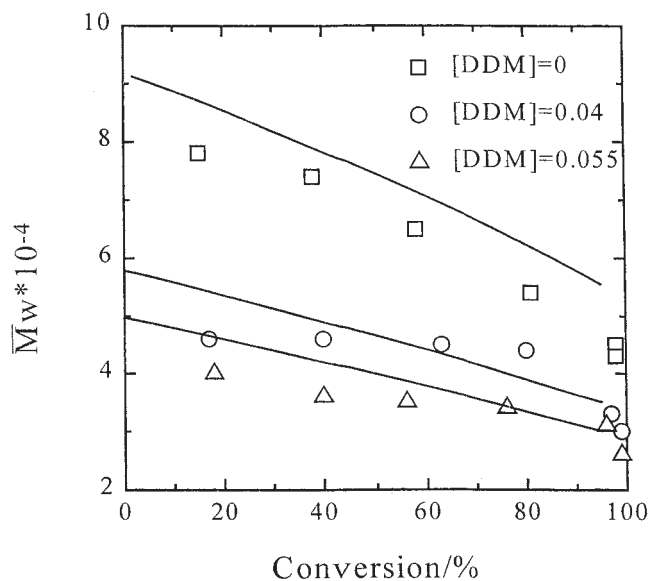
rate. The effects of temperature, initiator concentration and type, monomer or solvent concentration, and chain transfer agent concentration and type on the kinetics, and molecular weight and its distribution are simulated and compared with the experimental data of kinetics and molecular weight obtained from the published literature to examine the presented models. Under the discussion of influence factors, many control methods for kinetics and molecular weight can be
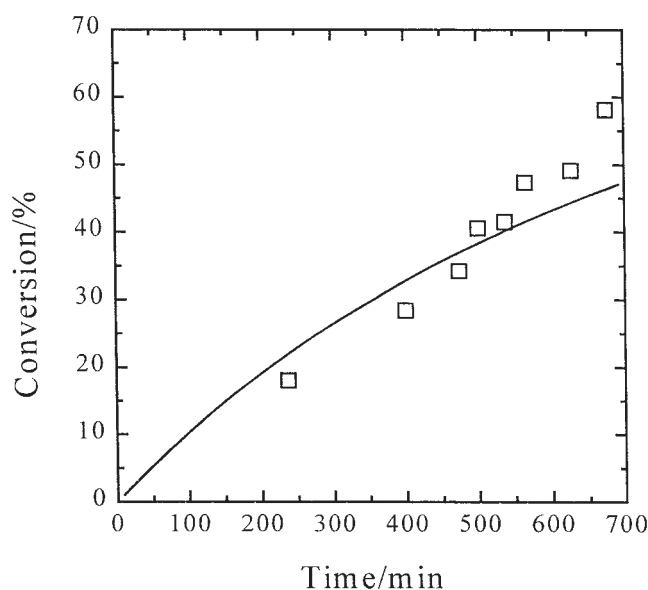


**Figure 15** Kinetic simulation and comparison with experimental data of MMA polymerization with GDMA as CTA ($T$ = 60°C, [AIBN] = 0.00188 mol/L, [GDMA] = 0.0159 mol/L).

obtained. The kinetics and molecular weight can be controlled by the selection of polymerization temperature, and initiator, solvent and CTA concentration, and type after the prediction of the presented models.

From the activity of radical, the new radicals transferred from the chain transfer reaction are divided three sections. The activity of some radicals are equal to that of monomer radical, some are far less, and CTA radical should times a factor to show the contribution to the concentration change of monomer radicals. With this consideration, the kinetic and molecular weight simulation of MMA polymerization with the participation of CTA can be led to.

So, the presented models can be used for bulk or solution polymerization in the batch or semibatch reactor with or without the participation of CTA.

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