Modeling of Diffusion-Controlled Free-Radical Polymerization Reactions

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Synopsis

The present paper introduces a new fundamental approach to the modeling of diffusion-controlled free-radical polymerization reactions. Our analysis follows the original work of Chiu, Carratt, and Soong (CCS), according to which the termination and propagation rate constants are expressed in terms of both a purely reaction-limited term and a diffusion-limited one. The contribution of the latter term to the apparent rate constants is described in terms of the polymer and monomer effective diffusion coefficients and an effective reaction radius. It is shown that all parameters appearing in the original CCS model can be calculated from first principles using available data on the physical and transport properties of a particular monomer–polymer binary system. The generalized free volume theory of Vrentas and Duda and the theory of excess chain end mobility are invoked for the calculation of the effective diffusion coefficients and the reaction radius, respectively. The approach followed in this study is general and needs only the specification of one unknown parameter with a clear physical meaning. All other parameters can be readily calculated from available data. The ability of the new model to predict molecular weight developments and monomer conversion in diffusion-controlled reactions is demonstrated by application of the proposed model equations to the bulk polymerization of MMA.

INTRODUCTION

In free-radical polymerization three diffusion-controlled processes can take place in parallel to the ordinary chemical reactions. These are the cage effect, the gel effect, and the glass effect related to the initiation, termination, and propagation reactions, respectively. These diffusion-controlled processes strongly affect the rate of polymerization and can influence the molecular properties of a polymer.

The cage effect is associated with the probability of a primary radical formed by fragmentation of initiator molecules to diffuse out of its "cage" in order to initiate a polymer chain. The cage effect enhances the primary radical recombination rate, thus reducing the initiator efficiency f. Most investigators[1-5] agree that the initiator efficiency should remain constant until very high conversions. This has been experimentally verified by the work of Brooks.[6] Ito[7] expressed the initiator efficiency in terms of the rate of polymerization, number average degree of polymerization, and initiator concentration. He found that f remained constant for conversions less than 80%. In a later publication, Ito[8] presented a physical explanation of the variable initiator

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efficiency by calculating the diffusion rate of primary radicals out of a solvent cage.

The gel effect is related to the decrease of the termination rate constant caused by a decrease in the mobility of polymer chains due to the increase of the viscosity of the reaction medium. This diffusion-controlled termination process gives rise to autoacceleration of the rate of reaction which very often occurs in free-radical polymerizations. The gel effect can also affect the molecular weight distribution in a free-radical polymerization provided the molecular weight development is not controlled by transfer to monomer or transfer to solvent reactions.

Since it was first reported by Trommsdorff et al.,[9] the gel effect has been the subject of many publications. These have been reviewed by Tulig and Tirrell,[2] O'Driscoll,[10] and Hamielec.[11] The first models developed to describe the dependence of the termination rate constant upon conversion were based on purely empirical relationships.[12,13] Later a number of semiempirical models were developed based on free volume and entaglement concepts of macromolecules.[3-5,14-18] Recently the understanding of the dynamics of polymer chain entaglements has grown considerably through the introduction of the concept of "reptation" after deGennes.[19-23] A number of modeling attempts have been reported on the diffusion-controlled termination reaction based on the reptation theory.[2,7,24-27]

For polymerizations below the glass transition temperature of the polymer T_{gp}, the reaction mixture becomes a glass at monomer conversions less than 100%. At the glassy state, the propagation rate constant and the polymerization rate fall effectively to zero because of the presence of strong diffusion effects which hinder even the movement of individual monomer molecules. Marten and Hamielec[3] applied the free volume theory to model the effect of diffusion on the propagation rate constant. Similar expressions were reported by other investigators[4,28,29] in an attempt to model the diffusion-controlled propagation reaction.

Almost all reported models on diffusion-controlled termination and propagation reactions require the introduction of some critical break points which indicate the onset of the diffusional effects. These points signify the transition of a chemical reaction from a diffusion-free regime to a diffusion-controlled one. Different models are usually defined for the propagation and termination rate constants in each polymerization region as the reaction proceeds from low to intermediate conversion kinetics. Furthermore, most of the reported models contain a number of adjustable parameters, very often, without any real physical meaning.

It is the objective of the present work to introduce a new general approach to the modeling of diffusion-controlled free-radical polymerization reactions. Our analysis follows the original work of Chiu, Carratt, and Soong[1] (CCS) and the generalized free volume theory of Vrentas and Duda.[30-32] It is our intention to show that one can arrive at similar to the CCS models describing the gel and glass effects by following a more fundamental and physical approach. We shall show that all parameters appearing in the new models have a clear physical meaning and can be estimated in terms of available data on the physical and transport properties of the reacting species in a free-radical polymerization.

BACKGROUND THEORY—THE CCS MODEL

It is generally assumed that the termination step between two macroradicals involves a three-stage process. Initially the two macroradicals diffuse toward one another by translation of the center of the macroradicals so that certain segments of the chains are in contact. This process is known as translational diffusion. This is followed by segmental diffusion and rearrangement of radical chain ends so that collision of radical ends is possible. Only after the proper orientation of chain ends, termination reaction can take place.

The development of most gel effect models is based on the above qualitative description of termination reaction as a three-stage process. At low conversion, segmental diffusion is the rate-controlling step in the termination reaction, while, at high conversions, translational diffusion dominates the rate of termination. As pointed out by Chiu et al.,[1] conventional modeling of gel effect suffers from unnecessary model segmentation and introduction of critical break points that mark the transition of polymerization from the segmental diffusion-controlled regime to the translational one. Chiu et al.[1] in their original work adopted a new approach to model free-radical polymerization reactions exhibiting strong diffusion limitations. In the CCS model, diffusion effects are viewed as an integral part of the chain termination and propagation reactions from the beginning of polymerization. Thus, the effect of diffusion on the termination rate constant gradually increases with conversion and becomes dominant around a certain conversion level, which is associated with the onset of the gel effect. This eliminates the need for the use of critical break points, the sudden introduction of diffusional effects, and the associated model segmentation. According to the CCS model, the region around a macroradical is divided into three zones (Fig. 1). r_m denotes the minimum separation distance for an effective biradical collision, and C_m is a hypothetical radical concentration in the region defined by r_m. r_b defines the radius at

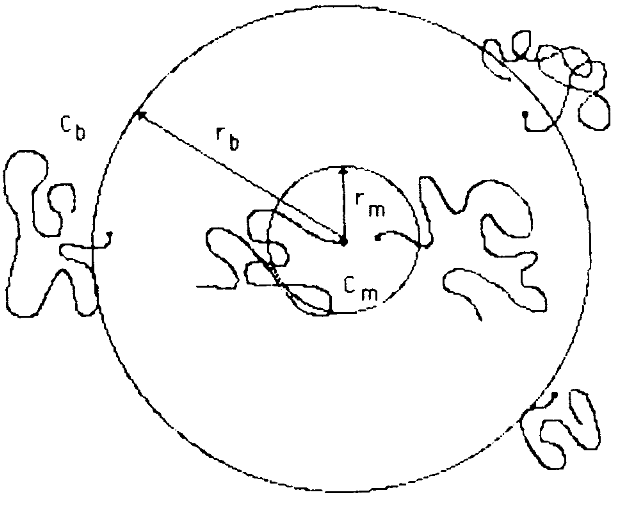

Fig. 1. Schematic representation of the minimum separation distance r_m for an effective biradical collision and the radius r_b at which the concentration of radicals is set equal to C_b.

which the radical concentration is that of the bulk phase, C_b. Following the mathematical analysis of Chiu et al.,[1] the apparent termination rate constant k_t can be expressed as

$$\frac{1}{k_t} = \frac{1}{k_{t0}} + \frac{r_m^2}{3}\frac{C_b}{D_{\text{eff}}} = \frac{1}{k_{t0}} + \Theta_t \frac{\lambda_0}{C} \tag{1}$$

An analogous expression for the propagation rate constant, k_p, can be derived to account for the glass effect:

$$\frac{1}{k_p} = \frac{1}{k_{p0}} + \frac{r_m'^2}{3}\frac{C_b}{D'_{\text{eff}}} = \frac{1}{k_{p0}} + \Theta_p \frac{\lambda_0}{C} \tag{2}$$

k_{t0} and k_{p0} are the true values of the intrinsic termination and propagation rate constants, respectively. D_{eff} and D'_{eff} are the corresponding effective diffusion coefficients for polymer macroradicals and monomer molecules. λ_0 is the zero-moment of the "live" polymer distribution, and it is equal to the total concentration of macroradicals. The term C in eqs. (1) and (2) accounts for the concentration dependence of D_{eff} and D'_{eff}. Chiu et al.[1] invoked the Fujita–Doolittle free volume theory[33] to express C as follows:

$$C = \exp\{\varphi_m/[A(T) + B(T)\varphi_m]\} \tag{3}$$

where $A(T)$ and $B(T)$ are treated as adjustable parameters of temperature. For the free-radical polymerization of methyl methacrylate (MMA), Chiu et al.[1] found that the parameters $A(T)$ and $B(T)$ can be expressed as

$$A(T) = C_1 + C_2(T - T_{gp})^2, \qquad B(T) = \text{const} \tag{4}$$

The parameters Θ_t and Θ_p have dimensions of time and can be viewed as the characteristic diffusion time for macroradicals and monomer, respectively. In the original work of Chiu et al.,[1] the following expressions are reported for the parameters Θ_t and Θ_p in relation to the batch polymerization of MMA:

$$\Theta_t = C_3 I_0^{\alpha} \exp(E/RT), \qquad \Theta_p = C_4 \exp(E'/RT) \tag{5}$$

Substituting the expressions for C, Θ_t, and Θ_p into eqs. (1) and (2), we obtain the following results:

$$k_t^{-1} = k_{t0}^{-1} + \lambda_0 I_0^{\alpha} C_3 \exp(E/RT)/\exp\left\{\varphi_m/\left[C_1 + C_2(T - T_{gp})^2 + B\varphi_m\right]\right\} \tag{6}$$

$$k_p^{-1} = k_{p0}^{-1} + \lambda_0 C_4 \exp(E'/RT)/\exp\left\{\varphi_m/\left[C_1 + C_2(T - T_{gp})^2 + B\varphi_m\right]\right\} \tag{7}$$

We note that eqs. (6) and (7) describing the diffusion effects on the termination and propagation rate constants contain eight adjustable parameters, namely, C_1, C_2, C_3, C_4, α, B, E, and E' that must be estimated from experimental measurements on conversion and molecular weight averages of the polymerization system under study. Furthermore, the physical meaning of all model parameters is not obvious, and their application to other polymerization systems and reactor operating conditions may not be possible. For example, if we assume that initiator is continuously added to a batch reactor, then the functional dependence of Θ_t [eq. (5)] upon the initial initiator concentration I_0 may not hold true.

As stated in the introduction, it is our objective to show that we can estimate the numerical values of all parameters appearing in eqs. (1) and (2) using available data on the physical and transport properties of the reacting monomer, solvent, and polymer species. The approach followed in this work is general and needs only the specification of one unknown parameter, which has a clear physical meaning. We believe that the present study offers a new fundamental approach to the modeling of diffusion-controlled free-radical polymerization reactions.

THE NEW MODEL

In the CCS model described in the previous section, the rate constants k_t and k_p are expressed in terms of both a purely reaction-limited term and a diffusion-limited one [eqs. (1) and (2)]. The terms k_{t0} and k_{p0} represent the true kinetic rate constants for chain termination and chain propagation, respectively, and exhibit the usual Arrhenius temperature dependence. The contribution of mass diffusion processes to the overall rate constants k_t and k_p is described in terms of the effective diffusion coefficients D_{eff} and D'_{eff}, respectively, and the reaction radii r_m and r'_m. In what follows we show that the diffusion coefficients and the reaction radii can be estimated from first principles using available data on the physical and transport properties of a particular monomer–polymer system. The approach adopted for the calculation of D_{eff} and D'_{eff} utilizes the generalized free volume theory of Vrentas and Duda.[30-32] For the calculation of r_m the theory of excess chain end mobility is invoked.[17]

In the early stages of polymerization the termination rate constant is primarily governed by the intrinsic term k_{t0}. As the polymerization proceeds, a transition from the reaction-limited (or segmental-limited) regime to the translational diffusion-controlled regime takes place. This causes a decrease in the termination rate constant k_t. Several investigators have modeled the observed decrease in k_t by considering a dependence of k_t upon the self-diffusion coefficient of polymer. This means that the effective diffusion coefficient D_{eff} in eq. (1) will represent the self-diffusion coefficient of polymer macromolecules. By analogy, D'_{eff} in eq. (2) will represent the self-diffusion coefficient of monomer molecules.

Over the past 20 years, the free volume theory originally developed by Cohen and Turnbull[34,35] and later modified by Fujita[33,36] has been extensively used in the analysis of diffusional behavior of concentrated polymer solutions. Recently, a more general version of the free volume theory was presented by Vrentas and Duda[30,31] and equations for the determination of the self-diffusion coefficients of the polymer and the solvent were developed. According to the Vrentas–Duda's generalized free volume theory, the self-diffusion coefficients of polymer and monomer in a polymer–monomer binary system can be calculated by the following equations:

$$D_{\text{eff}} = N^* D_{p0} \exp(-E_p/RT) \exp\left[-\gamma\left(w_m \hat{V}_m^* + w_p \hat{V}_p^* \xi\right)/\left(\hat{V}_f \xi\right)\right] \tag{8}$$

$$D'_{\text{eff}} = D_{m0} \exp(-E_m/RT) \exp\left[-\gamma\left(w_m \hat{V}_m^* + w_p \hat{V}_p^* \xi\right)/\hat{V}_f\right] \tag{9}$$

where the specific free volume $\hat{V}_f$ of the solution is given by

$$\hat{V}_f = w_m\left[K_{11}\left(K_{21} + T - T_{gm}\right)\right] + w_p\left[K_{12}\left(K_{22} + T - T_{gp}\right)\right] \tag{10}$$

$$w_m = \varphi_m/\left(\varphi_m + \varphi_p \hat{V}_m^0/\hat{V}_p^0\right), \qquad w_p = \left(\varphi_p \hat{V}_m^0/\hat{V}_p^0\right)/\left(\varphi_m + \varphi_p \hat{V}_m^0/\hat{V}_p^0\right) \tag{11}$$

All symbols are defined in the nomenclature.

Calculation of D_{eff} and D'_{eff}

For a reacting system the D_{eff} and D'_{eff} coefficients need to be calculated continuously as the polymerization proceeds. The instantaneous values of self-diffusion coefficients for polymer macroradicals and monomer will be given by eqs. (8) and (9), respectively. We note that the expressions contain a number of nonadjustable physical parameters, namely, $\hat{V}_m^0$, $\hat{V}_p^0$, $\hat{V}_m^*$, $\hat{V}_p^*$, T_{gm}, T_{gp}, K_{11}, K_{12}, K_{21}, K_{22}, γ, ξ, N^*, D_{p0}, E_p, D_{m0}, E_m. The values of these parameters can be calculated from available data on the physical and transport properties of the reaction species. The physical meaning and the estimation of the above parameters are discussed next.

Specific Volume $\hat{V}_i^0$

The specific volumes $\hat{V}_m^0$ and $\hat{V}_p^0$ of the pure monomer and polymer can be calculated as a function of temperature using available density data (d_i):

$$\hat{V}_i^0 = 1/d_i \tag{12}$$

Soh and Sundberg[18] have tabulated such values for $\hat{V}_i^0$ for most monomer–polymer systems of interest.

Specific Critical Hole Free Volume $\hat{V}_i^*$

$\hat{V}_i^*$ represents the minimum or critical local hole free-volume required for displacement of a polymer segment. Vrentas and Duda[30-32] have estimated the value of $\hat{V}_i^*$ from the corresponding specific volume of the pure component at 0 K:

$$\hat{V}_i^* = \hat{V}_i^0(0) \tag{13}$$

Howard[37] discusses several methods for calculating the values of $\hat{V}_i^0(0)$ for both polymers and simple liquids. Numerical values of $\hat{V}_i^*$ parameter have been reported by Liu et al.[36] for a number of polymerization systems.

Glass Transition Temperature T_{gi}

Numerical values for the glass transition temperature of monomer, polymer, and solvent have been tabulated by several investigators for a number of free-radical polymerization systems. These values can be found in Refs. 3, 4, 38, and 39.

Free-Volume Parameters (K_{11}, K_{12}, K_{21}, K_{22})

Based on the free volume theory, the free volume of the reacting system can be expressed as

$$V_f = \varphi_m V_{fm} + \varphi_p V_{fp} \tag{14}$$

where

$$V_{fm} = V_{mg} + \alpha_m (T - T_{gm}) \tag{15}$$

$$V_{fp} = V_{pg} + \lambda \alpha_p (T - T_{gp}) \tag{16}$$

Numerical values of the parameters V_{mg}, α_m, T_{gm}, V_{pg}, α_p, T_{gp}, λ for various polymerization systems have been reported by Soh and Sundberg.[4] λ is a constant parameter related to the ratio of thermal expansion coefficients of polymer below and above T_{gp}.[4]

Alternatively, the free volume V_{fi} of the i component can be expressed as the ratio of the specific free volume $\hat{V}_{fi}$ to the critical specific free volume $\hat{V}_i^*$:

$$V_{fi} = \hat{V}_{fi} / \hat{V}_i^* \tag{17}$$

From eqs. (10) and (14)–(17) we obtain the following expressions for the free volume parameters:

$$K_{11} = \alpha_m \hat{V}_m^*, \qquad K_{21} = V_{mg}/\alpha_m \tag{18}$$

$$K_{12} = \lambda \alpha_p \hat{V}_p^*, \qquad K_{22} = V_{pg}/\lambda \alpha_p \tag{19}$$

Overlap Factor γ

The overlap factor γ is introduced because the same free volume is available to more than one molecule. Vrentas and Duda[31,40] have calculated the numerical value of γ for various polymer–solvent systems based on the Williams, Landell, and Ferry equation.[41] The overlap factor γ can be calculated from the first WLF constant $(C_1)_p$ and the free volume of the polymer at the glass transition temperature:

$$\gamma = 2.303 V_{pg} (C_1)_p \tag{20}$$

Values of $(C_1)_p$ parameter have been experimentally measured by several investigators and tabulated by Liu et al.[38]

Factor ξ

The factor ξ is defined as the ratio of the critical molar volume of the monomer jumping unit to the critical molar volume of the polymer and is given by

$$\xi = \bar{V}_m^*/\bar{V}_p^* = \left(\hat{V}_m^* M_m\right)/\left(\hat{V}_p^* M_{jp}\right) \tag{21}$$

where M_m and M_{jp} denote the molecular weight of monomer and polymer jumping unit, respectively. Vrentas and Duda[30,41] have pointed out that the parameter $(\gamma \hat{V}_p^* \xi/K_{12})$ can be approximated by a linear function of the molar volume of the monomer jumping unit at 0 K:

$$\left(\gamma \hat{V}_p^* \xi/K_{12}\right) = \beta \hat{V}_m^* M_m \tag{22}$$

where β is a constant which can be determined experimentally. Numerical values of β for various polymer–monomer binary systems have been reported by Ju et al.[42,43]

Dependence of D_{eff} on Molecular Weight N^*

In general the parameter N^* expresses the dependence of the self-diffusion coefficient upon the molecular weight of polymer. In the literature, various expressions describing the molecular weight dependence of self-diffusion coefficient have been reported. These expressions obey the following general law:

$$D_{\mathrm{eff}} \sim N^* \sim M^{-n} \tag{23}$$

Bueche[44] proposed a value for $n = 3.5$ for the case of large entagled diffusion macromolecules. Marten and Hamielec[3,45] have used a value of $n = 1.75$ when modeling diffusion-controlled reactions in MMA and St polymerizations. The same investigators have assumed that M represents the cumulative weight-average molecular weight. Soh and Sundberg[16,18] used an exponent $n = 3.4$ and for M the instantaneous chain length of the growing polymer macroradicals. In the context of the reptation theory, various investigators[19,23-27] have proposed a value for $n = 2$. In the present work, the variable n is set equal to 2 and M is taken to be equal to the cumulative number-average chain length.

Preexponential Factors D_{p0} and D_{m0} and Activation Energies E_p and E_m

The preexponential terms D_{p0} and D_{m0} and the activation energies E_p and E_m for polymer and monomer, respectively, can be calculated from a limited amount of diffusivity data obtained for a particular system. Duda et al.[40] estimated the numerical values of D_{m0} and E_m for a number of polymer–solvent systems from a limited amount of diffusivity measurements. They have found that the value of E_m lies in the range of 3–25 kcal/g mol.

For the calculation of E_p, eq. (8) is written as follows:

$$D_{\mathrm{eff}} = D'_{p0} \exp\left(-E_{ap}/RT\right) \tag{24}$$

where

$$
\begin{aligned}
E_{ap} &= E_p + E_p' \\
E_p' &= RT^2 \frac{\gamma}{\xi} \\
&\times \left[\frac{\left(\varphi_m \hat{V}_m^* d_m + \varphi_p \hat{V}_p^* d_p \xi\right)\left(\varphi_m \hat{V}_m^* d_m \alpha_m + \varphi_p \hat{V}_p^* d_p \alpha_p\right)}{\left(\varphi_m \hat{V}_m^* d_m V_{fm} + \varphi_p \hat{V}_p^* d_p V_{fp}\right)^2} \right]
\end{aligned}
\tag{25}
$$

The apparent activation energy E_{ap} and the preexponential term D_{p0}' can be estimated from experimental measurements of polymer self-diffusion coefficient at different temperatures. The activation energy term E_p can be subsequently estimated from the known values of E_{ap} and E_p'.

As an example, the numerical value of E_p for the PMMA–MMA system was calculated using the experimental measurements on the polymer self-diffusion coefficient reported by Balloge.[46] For a polymer volume fraction of 0.192, Balloge[46] estimated from dynamic light scattering measurements a numerical value for the apparent activation energy, $E_{ap} = 5.515$ kcal/g mol. From eq. (25), a value of 5.275 kcal/g mol is obtained for the activation term E_p'. Therefore, the numerical value of E_p for the PMMA–MMA binary system will be equal to 0.24 kcal/g mol. This implies that the effect of the exponential term $\exp(-E_p/RT)$ on D_{eff} will be neglibile, which is in full agreement with the recommendation of Vrentas and Duda[30,31] for $E_p \approx 0$.

Calculation of Reaction Radius

For the calculation of the effective reaction radius r_m the theory of excess chain end mobility is invoked.[17] Soh and Sundberg have derived an expression for the termination rate constant by assuming that the chain end of a live macroradical is free to move in a relatively limited spherical region of radius r_m with the node of a chain entanglement at the center. For the calculation of r_m they developed the following equation:

$$r_m = \left\{ \ln\left[1000\tau^3 / \left(N_A [R^\cdot] \pi^{3/2}\right)\right] \right\}^{1/2} / \tau \tag{26}$$

where

$$\tau = \left(3/2 j_c \delta^2\right)^{1/2} \tag{27}$$

δ is the average root-mean-square end-to-end distance per square root of the number of monomer units in a chain and can be measured experimentally. Numerical values for δ have been tabulated by Ferry[41] for various polymers. j_c is the entaglement spacing and is equal to the average number of monomer units in a dangling chain. j_c can be expressed in terms of the critical degree of polymerization for entanglement of pure polymer, x_{c0}, and the volume fraction of polymer, φ_p[17]:

$$j_c = x_{c0} / (2\varphi_p) \tag{28}$$

TABLE I
Kinetic Rate Constants for the MMA Polymerization

$f = 0.58$ for AIBN	
$k_d = 6.32 \times 10^{16}\exp(-30.66/RT)$ (min^{-1}) AIBN	(Tobolsky and Baysal[48])
$k_{p0} = 2.95 \times 10^{7}\exp(-4.35/RT)$ (L/mol min)	(Mahabadi and O'Driscoll[49])
$k_{t0} = 5.88 \times 10^{9}\exp(-0.701/RT)$ (L/mol min)	(Mahabadi and O'Driscoll[49])
$k_{fm}/k_p = 9.48 \times 10^{3}\exp(-13.88/RT)$	(Stickler and Meyerhoff[50])
$k_{tc}/k_{td} = 3.956 \times 10^{-4}\exp(4.09/RT)$	(Bevington et al.[51])

TABLE II
Physical and Transport Properties for the MMA-PMMA System

$d_m = 0.968 - 1.225 \times 10^{-3}T$ (°C) (g/cm^3)	(Tulig and Tirrell[2])
$d_p = d_m(1 + \epsilon)$; $\epsilon = 0.183 + 9.0 \times 10^{-4}T$ (°C) (g/cm^3),	(Soh and Sundberg[18])
$V_{fm} = 0.149 + 2.9 \times 10^{-4}T$ (°C)	(Soh and Sundberg[18])
$V_{fp} = 0.0194 + 3.0 \times 10^{-4}(T - 105)$, $T \geq 105$°C	(Soh and Sundberg[18])
$= 0.0194 + 1.3 \times 10^{-4}(T - 105)$, $T < 105$°C	(Soh and Sundberg[18])
$\hat{V}_m^0(0\ \text{K}) = 0.822$ (cm^3/g)	(Haward[37])
$\hat{V}_p^0\ (0\ \text{K}) = 0.77$ (cm^3/g)	(Liu et al.[38])
$T_{gp} = 115$°C; $T_{gm} = -126$°C	(Soh and Sundberg[17])
$\alpha_p = 3 \times 10^{-4}$°C^{-1}; $\alpha_m = 2.9 \times 10^{-4}$°C^{-1}	(Soh and Sundberg[17])
$\lambda = 0.428$; $V_{pg} = 0.0224$ (cm^3/cm^3)	(Soh and Sundberg[17])
$(C_1)_p = 14.8$	(Liu et al.[38])
$\beta = 12$ (K g mol/cm^3)	(Ju et al.[42,43])
$\gamma = 0.763$ [from eq. (21)]; $\xi = 0.362$ [from eq. (22)]	
$N_A = 6.023 \times 10^{23}$; $\pi = 3.1459$	
$\delta = 6.9$ (Å)	(Ferry[41])
$x_{c0} = 100$	(Soh and Sundberg[18])
$E_p = 0.24$ (kcal/g mol); $D_{p0} = 10$ (cm^2/s)	[eqs. (24)–(25)]
$E_m = 20.844$ (kcal/g mol); $D_{m0} = 223.4$ (cm^2/s)	(Ju et al.[43])
$J_{c0} = 10^{7.66}/x_{n0}^{1.8}$	(this study)

Numerical values for x_{c0} have been reported by Ferry[41] for a number of polymers. It should be noted that application of eq. (28) to very low conversions ($\varphi_p \to 0.0$) will yield unreasonably high values for j_c ($j_c \to \infty$). As a result, eq. (28) has to be properly modified in order to limit the variability of j_c within acceptable limits. A solution to this problem can be obtained by defining an apparent entaglement spacing parameter,

$$j_c^{-1} = j_{c0}^{-1} + 2\varphi_p/x_{c0} \tag{29}$$

where j_{c0} is the critical value of j_c corresponding to zero conversion. Equation (29) can be interpreted as the net result of both a diffusion-free term and a diffusion-limited one. The presence of the second term in eq. (29) will eventually cause a decrease in the effective reaction radius as a result of the restricted chain mobility at high conversions. By analogy to eq. (26), an expression for the effective reaction radius r_m' for propagation can be defined.

Derivation of the Final Model Equations

Based on the theoretical developments discussed in the previous sections, one can obtain the following final expressions for the apparent rate constants k_t and k_p:

$$k_t^{-1} = k_{t0}^{-1} + \left(r_m^2/3\right)\lambda_0 x_n^2 D_{p0}^{-1}\exp\left(E_p/RT\right) \times\exp\left\{\gamma\left(\varphi_m\hat{V}_m^*d_m + \varphi_p\hat{V}_p^*d_p\xi\right)/\left[\xi\left(\varphi_m\hat{V}_m^*V_{fm}d_m + \varphi_p\hat{V}_p^*V_{fp}d_p\right)\right]\right\} \quad (30)$$

$$k_p^{-1} = k_{p0}^{-1} + \left(r_m'^2/3\right)\lambda_0 D_{m0}^{-1}\exp\left(E_m/RT\right) \times\exp\left\{\gamma\left(\varphi_m\hat{V}_m^*d_m + \varphi_p\hat{V}_p^*d_p\xi\right)/\left[\varphi_m\hat{V}_m^*V_{fm}d_m + \varphi_p\hat{V}_p^*V_{fp}d_p\right)\right]\right\} \quad (31)$$

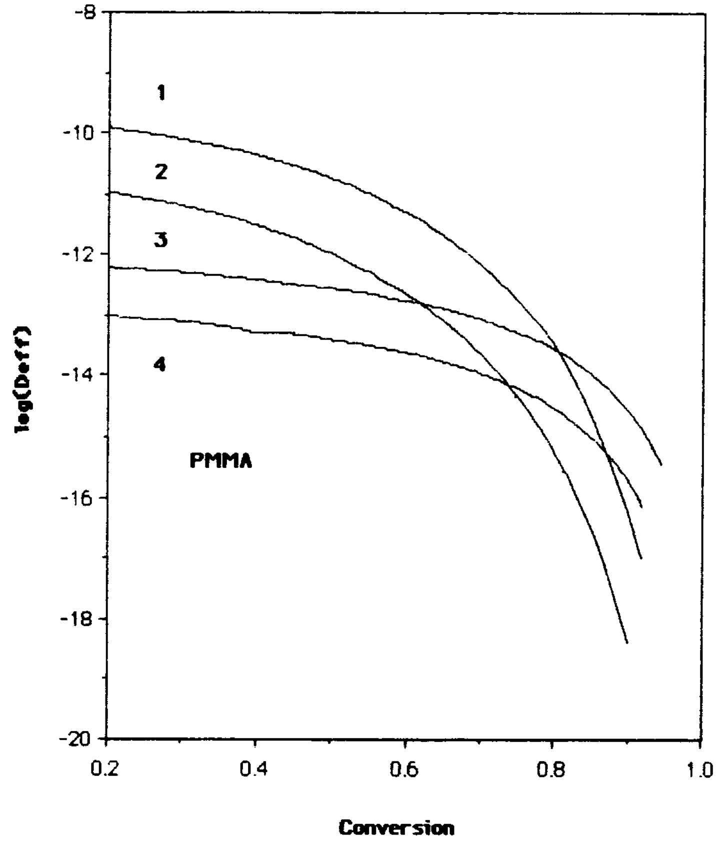

Fig. 2. Change in the polymer, D_{eff} [(1) $T = 90°\text{C}$; (2) $T = 70°\text{C}$], and monomer, D_{eff}' [(3) $T = 90°\text{C}$; (4) $T = 70°\text{C}$], effective diffusion coefficients with conversion for two different temperatures ($I_0 = 0.0258$ g mol/L).

It is instructive to point out that the CCS final expressions for k_t and k_p [eqs. (6) and (7)] are similar to eqs. (30) and (31). However, all parameters appearing in the derived equations have a clear physical meaning, and their numerical values can be obtained from reported data on the physical and transport properties of the reacting species. In addition, the functional dependence of k_t and k_p upon polymerization temperature, monomer, and polymer concentration is naturally introduced through the application of the generalized free volume theory and the concept of excess chain end mobility. By a direct comparison of eqs. (6) and (7) with eqs. (30) and (31), we obtain the following relationships:

$$I_0^\alpha \sim x_n^2 \tag{32}$$

$$E \sim E_p \quad \text{and} \quad E' \sim E_m \tag{33}$$

$$\exp\left[\frac{\varphi_m}{A(T) + B(T)\varphi_m}\right] \sim \exp\left[\frac{\varphi_m}{A'(T) + B'(T)\varphi_m}\right] \tag{34}$$

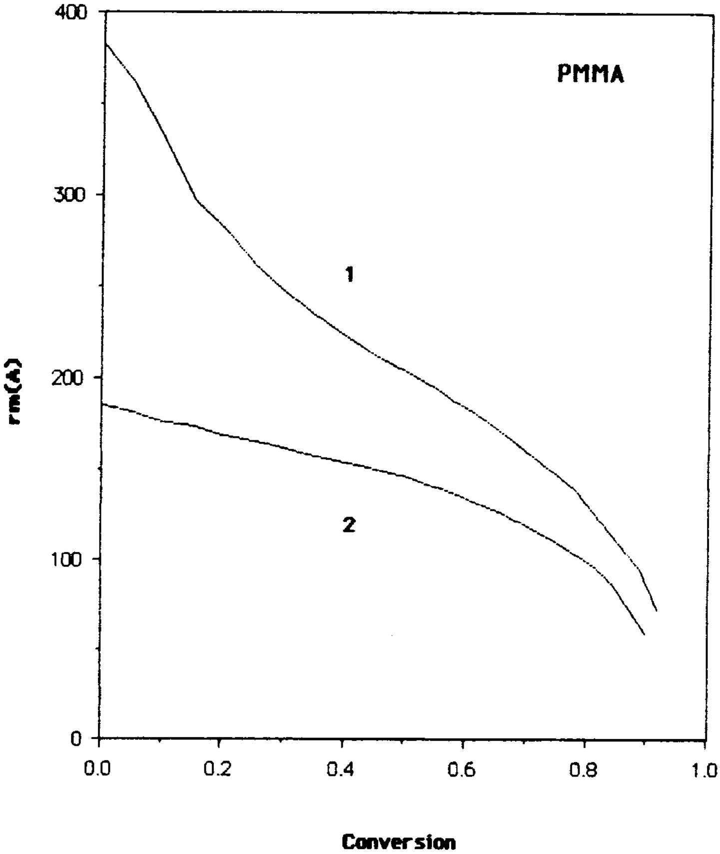

Fig. 3. Change in the effective reaction radius r_m for two different temperatures T (°C) (I_0 = 0.0258 g mol/L): (1) 90; (2) 70.

where

$$A'(T) = \xi \hat{V}_m^0 \hat{V}_p^* V_{fp}^2 / \left[\gamma \hat{V}_m^* \hat{V}_p^0 \left(V_{fm}\xi - V_{fp}\right)\right] \tag{35}$$

$$B'(T) = V_{fp}\xi\left(\hat{V}_m^* V_{fm} - \hat{V}_p^* V_{fp} \hat{V}_m^0 / \hat{V}_p^0\right) / \left[\gamma \hat{V}_m^* \left(\xi V_{fm} - V_{fp}\right)\right] \tag{36}$$

In the CCS model, α, E, E', $A(T)$, and $B(T)$ are treated as adjustable parameters determined by fitting the model's predictions to experimental measurements on conversion and molecular weights. It is interesting to note that, at low conversions, the identified by Chiu et al.[1] dependence of k_t upon the initial initiator concentration is in agreement with the proposed dependence of D_{eff} upon the number-average chain length in the context of the reptation theory. This can be shown by noticing that the instantaneous number-average chain length $\bar{x}_n$ is proportional to the reciprocal of the square root of the initiator concentration:

$$\bar{x}_n \simeq k_p M / \left(2 f k_d k_t I^{1/2}\right) \sim I^{-1/2} \tag{37}$$

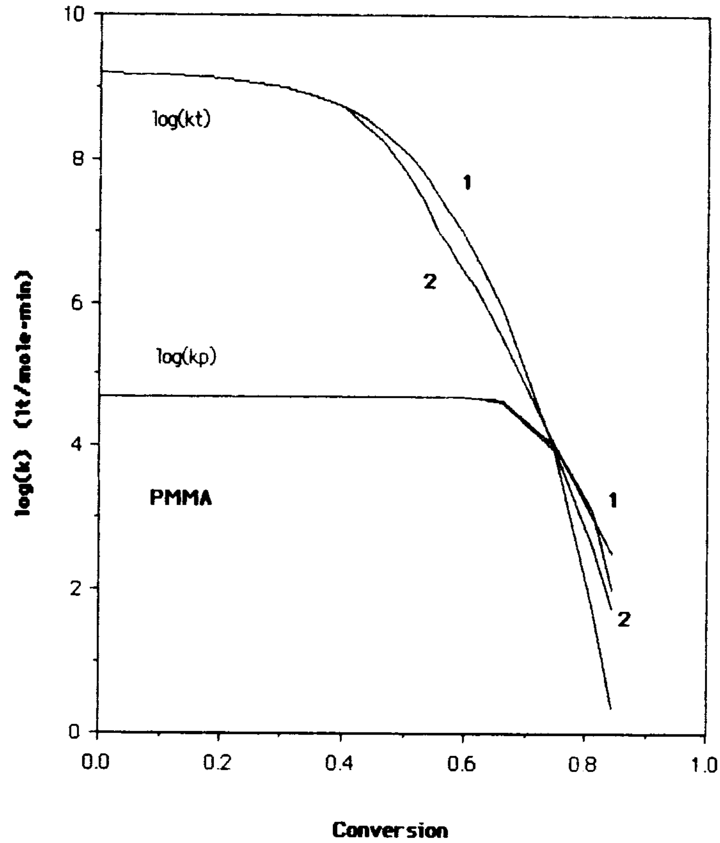

Fig. 4. Dependence of the termination and propagation rate constants upon monomer conversion ($T = 70°\text{C}$, $I_0 = 0.0258$ g mol/L): (1) present model; (2) CCS model.

At low conversions, $\bar{x}_n$ and I will be approximately equal to x_n and I_0. As a result, the relationship 32 will hold true for $\alpha = -1$, which is actually the estimated value of the parameter for the bulk polymerization of MMA.[1]

In order to show that the relationship (34) is valid, we calculate the ratio of polymer diffusion coefficient D_{eff} to the polymer diffusion coefficient at 100% conversion, $D_{\text{eff},0}$:

$$(D_{\text{eff}}/D_{\text{eff},0}) = \frac{x_n^2(\varphi_m = 0)}{x_n^2}\exp\left[\frac{\varphi_m}{A'(T) + B'(T)\varphi_m}\right] \tag{38}$$

The last result shows that the concentration dependence of D_{eff} will be described by an expression similar to eq. (3). Note that the parameter $A(T)$ in eq. (4) depends on the square of the temperature difference $(T - T_{gp})$.[2] In a similar way, the parameter $A'(T)$ in eq. (35) will depend on the square of V_{fp}, which is proportional to the temperature difference $(T - T_{gp})$ as shown by eq. (16).

The ability of the new model to predict molecular weight developments and monomer conversion in diffusion-controlled free-radical polymerizations is subsequently demonstrated by application of the new model equations to the bulk polymerization of MMA.

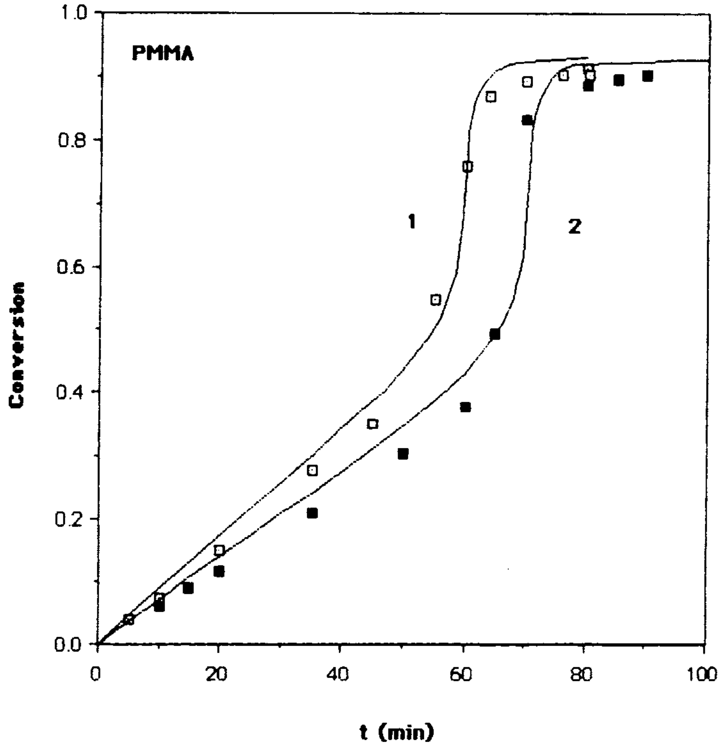

Fig. 5. Effect of the initial initiator concentration on the conversion–time histories in the bulk free-radical polymerization of MMA at T = 70°C. Discrete points represent experimental data,[47] and the solid lines denote the calculated results. I_0 (g mol/L): (1) 0.0258; (2) 0.0155.

APPLICATION TO MMA POLYMERIZATION

The free-radical bulk polymerization of MMA in a batch reactor can be modeled in terms of a set of nonlinear differential equations of the following form:

$$\frac{dX}{dt} = (k_p + k_{fm})(1 - X)\lambda_0 \tag{39}$$

$$\frac{dV}{dt} = -V_0\epsilon\frac{dX}{dt} \tag{40}$$

$$\frac{dI}{dt} = -k_d I - \frac{I}{V}\frac{dV}{dt} \tag{41}$$

$$\frac{d\lambda_0}{dt} = 2fk_d I - k_t\lambda_0^2 - \frac{\lambda_0}{V}\frac{dV}{dt} \tag{42}$$

$$\frac{d\lambda_1}{dt} = 2fk_d I + k_p M\lambda_0 + k_{fm}M(\lambda_0 - \lambda_1)$$

$$-k_t\lambda_0\lambda_1 - \frac{\lambda_1}{V}\frac{dV}{dt} \tag{43}$$

$$\frac{d\lambda_2}{dt} = 2fk_d I + k_p M(2\lambda_1 + \lambda_0)$$

$$+k_{fm}M(\lambda_0 - \lambda_2) - k_t\lambda_0\lambda_2 - \frac{\lambda_2}{V}\frac{dV}{dt} \tag{44}$$

$$\frac{d\mu_0}{dt} = \left(k_{td} + \tfrac{1}{2}k_{tc}\right)\lambda_0^2 + k_{fm}M\lambda_0 - \frac{\mu_0}{V}\frac{dV}{dt} \tag{45}$$

$$\frac{d\mu_1}{dt} = k_t\lambda_0\lambda_1 + k_{fm}M\lambda_1 - \frac{\mu_1}{V}\frac{dV}{dt} \tag{46}$$

$$\frac{d\mu_2}{dt} = k_t\lambda_0\lambda_2 + k_{tc}\lambda_1^2 + k_{fm}M\lambda_2 - \frac{\mu_2}{V}\frac{dV}{dt} \tag{47}$$

with

$$M = M_0(1 - X)/(1 + \epsilon X) \tag{48}$$

M denotes the monomer concentration and I is the initiator concentration. λ_0, λ_1, λ_2 and μ_0, μ_1, μ_2 are the zeroth, first, and second moment of the "live" and "dead" polymer molecular weight distributions, respectively. ϵ is the fractional volume change at 100% conversion. All other symbols are defined in the nomenclature. Derivation of the above equations can be found in the literature.[1,2,39] If we assume that the quasi-steady-state approximation (QSSA) for live radicals is valid, then we can replace the left-hand side derivatives in eqs. (42)–(44) with zero. The number-average M_n and weight-average M_w molecular weights can be calculated in terms of the leading moments of the polymer MWD:

$$M_n = (M_m)\mu_1/\mu_0; \qquad M_w = (M_m)\mu_2/\mu_1 \tag{49}$$

Tables I and II summarize the numerical values of the kinetic and physical parameters appearing in the new model in relation to the free-radical polymerization of MMA. It should be pointed out that the numerical values of all parameters appearing in eqs. (30) and (31) have been obtained or/and calculated in terms of reported data on the physical and transport properties of MMA–PMMA binary system. The only unknown parameter in the model is the critical value of the entaglement spacing, j_{c0}. It was found that j_{c0} followed a similar to eq. (23) scaling law with respect to the initial value of the number-average chain length, x_{n0}

$$j_{c0} \sim x_{n0}^{1,8}, \qquad 500 \le x_{n0} \le 2200 \tag{50}$$

The last result shows that the initial effective reaction radius r_{m0} will vary with temperature and initial initiator concentration since x_{n0} is a function of these variables.

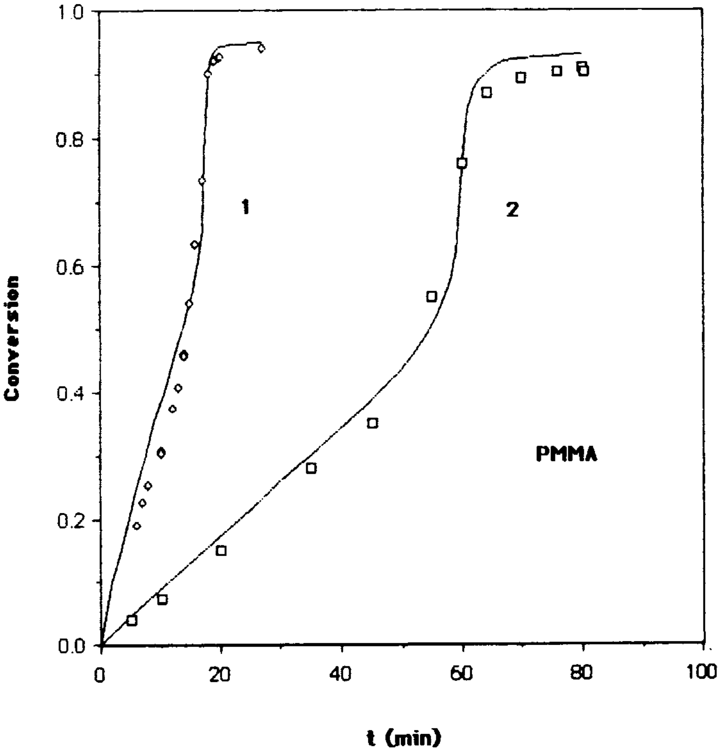

Fig. 6. Effect of the polymerization temperature on the conversion–time histories in the bulk free-radical polymerization of MMA with I_0 = 0.0258 g mol/L. Discrete points represent experimental data,[47] and the solid lines denote the calculated results. T (°C): (1) 90; (2) 70.

In Figure 2, the variation of the polymer and monomer effective diffusion coefficients with respect to monomer conversion is plotted. It can be seen that D_{eff} shows a sharp decrease at a conversion point in the range of 0.5–0.6. On the other hand, D'_{eff} presents a noticeable change only at very high conversions. The variation of the effective reaction radius with conversion is plotted in Figure 3 for two different temperatures. Note that r_m varies continuously with conversion and only at conversions very close to the glass point shows a steep decrease. It is apparent that the effective reaction radius decreases with temperature as a result of the restricted mobility of macromolecules. It should be pointed out that in the numerical calculations, the effective reaction radius r'_m for propagation was approximated by the effective reaction radius r_m for termination.

In Figure 4, the apparent values of k_t and k_p are plotted against the monomer conversion. The solid lines represent the predictions of the present model [eqs. (30) and (31)] while the broken lines are referred to the CCS results [eqs. (6) and (7)]. It is obvious that both models predict similar behaviors for k_t and k_p with respect to conversion.

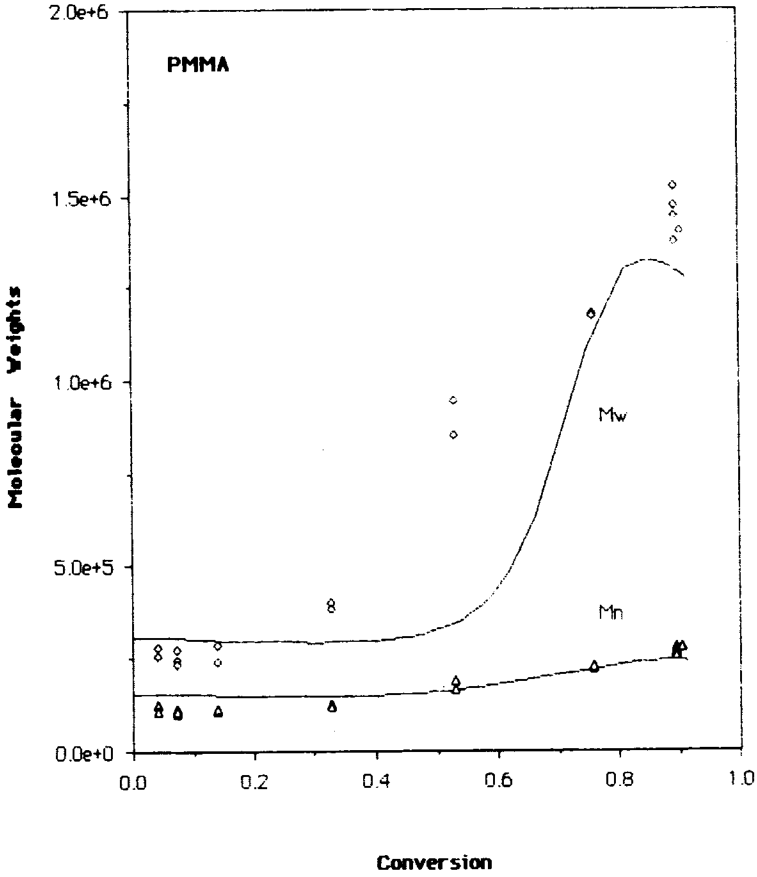

Fig. 7. Comparison of calculated and experimental[47] average molecular weights ($T = 70°\mathrm{C}$, $I_0 = 0.0258$ g mol/L).

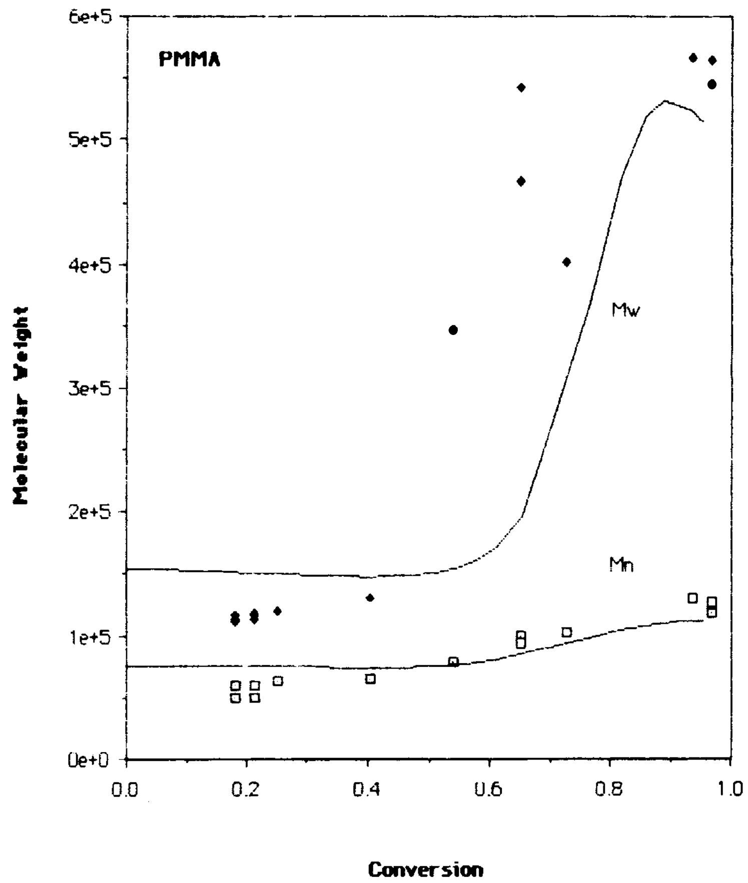

Fig. 8. Comparison of calculated and experimental[47] average molecular weights ($T = 90°C$, $I_0 = 0.01548$ g mol/L).

Finally, in Figures 6–8, predicted model results on conversion, M_n and M_w, are compared to corresponding experimental values reported by Balke and Hamielec.[47] In general, there is an excellent agreement between predicted and experimental conversion values at different polymerization conditions (Figs. 5 and 6).

Similarly, there is a good agreement between experimental and predicted values of M_n and M_w (Figs. 7 and 8). The observed difference between predicted and experimental values of M_w may be due to errors in experimental measurements or/and to a varying initiator efficiency. Actually, the latter is the subject of our present research efforts.

CONCLUSIONS

A new fundamental approach is developed to describe diffusion phenomena in free-radical reactions. It is demonstrated that all parameters appearing in the original model of Chiu, Carratt, and Soong can be readily calculated by using the generalized free volume theory and the theory of excess chain end mobility together with available data on the physical and transport properties of a monomer–polymer binary system.

Simulation results show that the new model equations can satisfactorily predict molecular weight developments and monomer conversion in the free-radical bulk polymerization of MMA. The model introduces actually one adjustable parameter related to the initial effective reaction radius at zero conversion. All parameters appearing in the new model equations have a clear physical meaning, which indicates that the proposed modeling approach will be applicable to other reactive systems. This is substantiated by the successful application of the new model equations to the solution polymerization of MMA. Current research efforts are focused on the extension of the proposed analysis to other diffusion-controlled homo- and copolymerization systems.

APPENDIX: NOMENCLATURE

$(C_i)_p$	first WLF constant of the polymer at the glass transition point
C_m	effective radical concentration in the region defined by r_m
C_b	radical concentration in the bulk phase
D_{eff}, D'_{eff}	effective diffusion coefficients
D_{p0}, D_{m0}	preexponential factors
E, E'	activation energies in the CCS model
E_p, E_m	activation energies
f	efficiency of the initiator
I	concentration of the initiator
j_c	entaglement spacing
k_d	initiator decomposition rate constant
k_{fm}	chain transfer to monomer rate constant
k_p	rate constant for the propagation reaction
k_t	total rate constant for the termination reaction ($k_{tc} + k_{td}$)
k_{tc}	rate constant for termination by combination
k_{td}	rate constant for termination by disproportionation
M	monomer concentration
M_{jp}	molecular weight of the polymer jumping unit
M_m	molecular weight of the monomer
M_n, M_w	number and weight average molecular weights
N_A	Avogardro's number
R	universal gas constant
r_m	minimum separation distance for an effective biradical collision
r_b	defines the region in which the radical concentration is that of the bulk phase
T	temperature
T_{gm}, T_{gp}	glass transition temperature for the monomer and polymer, respectively
t	time
V	volume
V_f	average free volume of the solution
V_{fm}, V_{fp}	free volumes of the monomer and polymer
V_{mg}, V_{pg}	free volumes of the monomer and polymer at the glass transition temperature
$\hat{V}_m^0$, $\hat{V}_p^0$	specific volumes of the monomer and polymer
$\hat{V}_m^*$, $\hat{V}_p^*$	specific critical hole free volumes of the monomer and polymer
w_m, w_p	monomer and polymer weight fractions
X	conversion
x_{c0}	critical degree of polymerization for entaglements of the pure polymer
x_n	cumulative number average chain length
$\bar{x}_n$	instantaneous number average chain length

Greek Letters

α_m, α_p	difference in thermal expansion coefficients between the liquid and the glassy state for monomer and polymer, respectively
γ	overlap factor

δ	average root-mean-square end-to-end distance per square root of the number of monomer units in a chain
ϵ	contraction factor at 100% conversion
Θ_t, Θ_p	adjustable parameters in the CCS model
λ	parameter related to the ratio of the thermal expansion coefficients of polymer below and above T_{gp}
λ_i	moments of the growing radical distribution ($i = 0, 1, 2$)
μ_i	moments of the dead polymer distribution
ξ	ratio of the critical molar volume of the monomer jumping unit to the critical molar volume of the polymer
φ_m, φ_p	volume fractions of the monomer and polymer

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