Estimating Diffusion-Controlled Reaction Parameters in Photoinitiated Polymerization of Dimethacrylate Macromonomers

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Abstract: The kinetics of photoinitiated polymerization of dimethacrylate macromonomers have been studied to determine the diffusion-controlled reaction parameters using attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). A predicted kinetic rate expression with a diffusion control factor was employed to estimate an effective rate constant and to define the reaction-controlled and diffusion-controlled regimes in the photopolymerization. An effective rate constant, k_e, can be obtained from the predicted kinetic rate expression. At the earlier stages of polymerization, the average values of kinetic rate constants do not vary during the reaction time. As the reaction conversion, α, reaches the critical conversion, α_c, in the predicted kinetic expression, the reaction becomes to be controlled by diffusion due to the restricted mobility of dimethacrylate macromonomers. A drop in value of effective rate constant causes a drastic decrease of reaction rate at the later stages of polymerization. By determining the effective rate constants, the reaction-controlled and diffusion-controlled regimes were properly defined even in the photopolymerization reaction system.

Keywords: photoinitiated polymerization, dimethacrylate macromonomer, diffusion control reaction, kinetics.

Introduction

The photoinitiated polymerization of multifunctional macromonomers leads to highly crosslinked networks and particular behaviors in kinetics. Autoacceleration at the initial stage of reaction and autodeacceleration at the later stage of reaction, limited functional group conversion, delay in volume shrinkage with respect to equilibrium, and unequal functional group reactivity in the photoinitiated polymerization have been reported in some works.[1-7] These polymer systems are widely used in the coatings and biomaterials industries.[8] Because of the high polymerization rate the heterogeneity in the final polymeric material properties is found. In order to modify and control the final polymeric material properties a better understanding of the kinetic behavior of the multifunctional methacrylate systems is required.[2]

Due to the crosslinking nature of these polymers, the kinetics exhibit diffusion limitations even during the initial stages of the reaction. The polymerization rate increases dramatically due to the diffusion controlled termination process in the initial stage of the reaction, which leads to autoacceleration. As the reaction progresses, the propagation reaction also becomes diffusion limited and the polymer-

ization rate decreases in an autodeceleration mode.[1,8-12] The termination process becomes reaction diffusion controlled as termination by segmental movement of the macroradicals eventually becomes suppressed. The classical kinetic model is based on the reaction equations of initiation, propagation and a bimolecular termination.[9,12-16] This mechanistic model assumes that reaction diffusion controlled termination dominates in the reaction. Because of the complex nature of the photoinitiated polymerization, typically in termination process, the mechanistic model can be applied to the crosslinking radical polymerization only at the very early stage of the reaction. In few works, the autocatalytic model has been used to analyze the multifunctional radical polymerization of (meth)acrylate macromonomers. Basically this phenomenological model was widely used to study cure reactions of thermosetting resins. So far, however, the reaction-controlled and diffusion-controlled regimes have not been clearly described in terms of an effective rate constant in the photopolymerization system.

In this paper, the kinetics of the photoinitiated polymerization are to be discussed and the effective rate constants to be determined using a modified mechanistic model with a diffusion factor term. The reaction-controlled and diffusion-controlled regimes will be determined from the present model predictions in the photopolymerization system.

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Experimental

Materials. Poly(ethylene glycol) dimethacrylates (M_w = 330,550,875 g/mol, Aldrich) as macromonomers were used as received. Trimethylolpropane triacrylate (TMPTA, Aldrich) was used to control the functionality and viscosity of the mixture. 1-Hydroxycyclohexyl phenyl ketone (Ciba Geigy, Darocur 184C) as a photoinitiator was dissolved in the mixture of these components under stirring at room temperature and then temperature rose up to the reaction temperature under light cover. The photoinitiator concentration was fixed and the relative amounts of the other products were changed according to experimental conditions. The chemical structures are shown in Figure 1.

Attenuated Total Reflection Infrared Spectroscopy (ATR-FTIR). Attenuated total reflection infrared spectroscopy (ATR-FTIR) was used to measure reaction conversion versus reaction time. Briefly, the infrared beam enters the ATR crystal from one of the side faces. If the refractive index of the crystal is higher than that of polymeric material and the incident angle of the beam is higher than the critical angle, then the infrared beam totally reflected at the crystal/polymer interface and the beam travels inside the crystal and exits from the other side face which is shown in Figure 2.

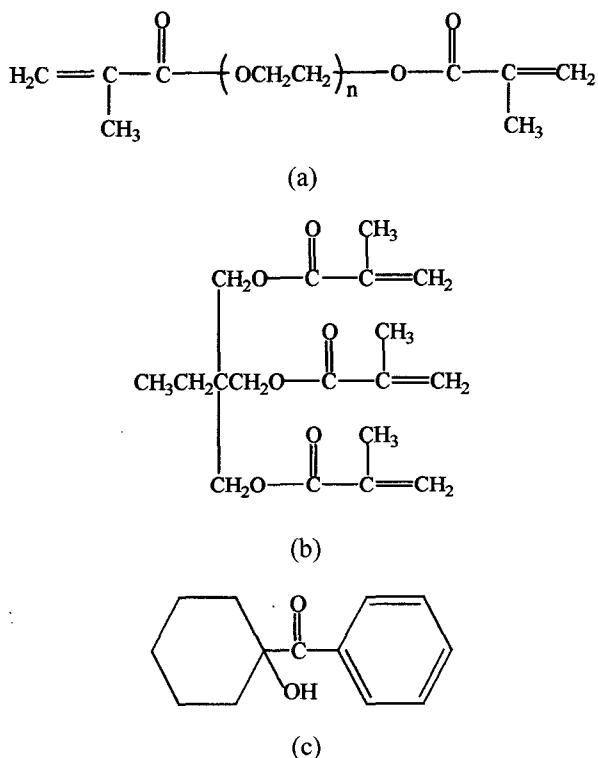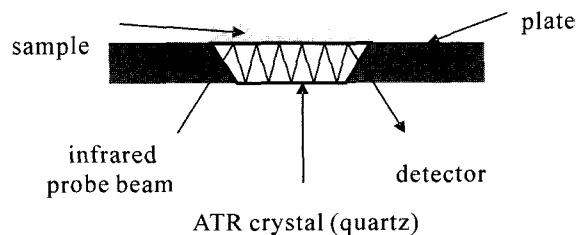As the polymerization reaction starts, the dimethacrylate

Figure 2. Schematic illustration of attenuated total reflection infrared spectroscopy (ATR-FTIR).

double bonds (C=C) are to be consumed and the reaction usually stops because of the complete consumption of the dimethacrylate double bonds. The C=C stretching vibrations of the dimethacrylate functional groups at 1638 cm^{-1} was used to calculate reaction conversions.[17]

Results and Discussion

Reaction Conversion. The kinetics of photoinitiated polymerization were studied to determine polymerization kinetic parameters including reaction conversions. The photopolymerization kinetics were studied using ATR-FTIR. The polymerization temperature maintained at 60°C since photo-initiated polymerization is known to evolve an important thermal effect and kinetic constants are very sensitive to an increase in temperature. The reaction usually stopped because of the complete consumption of the dimethacrylate double bonds. The C=C stretching vibrations of the dimethacrylate functional group at 1638 cm^{-1} was used to calculate reaction conversions. After adjusting the baseline, the conversion of the dimethacrylate functional group can be calculated by measuring at each time of the reaction and determined as follows:[17]

$$\alpha_{c=c(t)} = \frac{A_0 - A_t}{A_0} \times 100 \qquad (1)$$

where $\alpha(t)$ is the conversion of the reactive function at time t, A_0, the initial absorbance and A_t, the absorbance of the function group at time t. A typical decay of the stretching vibration bands of dimethacrylate double bond at 1638 cm^{-1} is shown in Figure 3. It is usually observed that the higher the reaction rate, the higher the free volume, leading to a higher final reaction conversion of the material.

The ultimate conversion also increases due to the greater mobility of the small molecules and leads faster reaction diffusion and faster transfer of the radical species through the unreacted functional groups and eventually as a termination mechanism, the radical species encounter a second radical for a termination step. A typical plot of the conversion rate vs. time is shown in Figure 4. The conversion rate drastically increased as time increased, as was also seen in some works on kinetics of dimethacrylate photopolymerization. After a
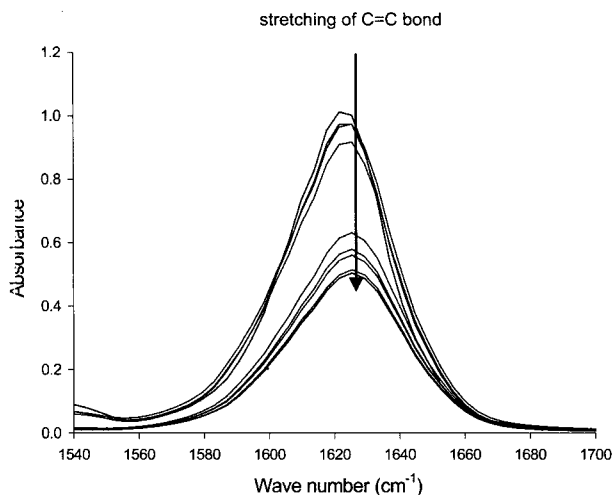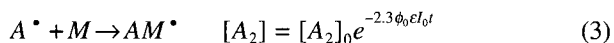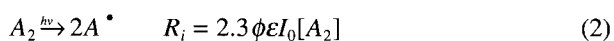

Figure 1. Chemical structures of poly(ethylene glycol) dimethacrylate (a), trimethylolpropane triacrylate (b), and 1-hydroxycyclohexyl phenyl ketone (c).

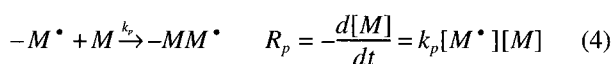**Figure 3.** Typical decay of the stretching vibration bands of d methacrylate double bonds at 1638 cm⁻¹.

d-astic increase in conversion in the early stages of the reaction, a retardation of the reaction conversion occurred gradually as the polymer matrix became vitrified and the reaction rapidly became diffusion controlled. The polymerization rate curves were autocatalytic in nature, with the maximum rate of conversion at the initial stage of reaction, which is similar in behavior with that of other dimethacrylate systems. As the polymerization rate increases, the position of the maximum rate of conversion was shifted to the start of the reaction. As molecular weight of dimethacrylate macromonomer increases, the final values of conversion decrease at the same reaction temperature, which indicates that diffusion control could be described in terms of the mobility and/or molecular weight of macromonomers. Lower molecular weight of dimethacrylate macromonomer leads to lower value of reaction conversion.

Mechanistic Model with Diffusion Control Factor. The model is based on the classical chemical equations of initiation and propagation, and assumes a bimolecular termination:[9]
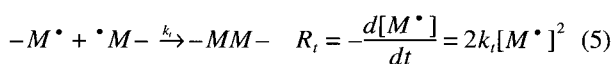
Initiation:

$$A_2 \xrightarrow{h\nu} 2A^{\bullet} \qquad R_i = 2.3\phi\varepsilon I_0[A_2] \qquad (2)$$

$$A^{\bullet} + M \rightarrow AM^{\bullet} \qquad [A_2] = [A_2]_0 e^{-2.3\phi_0\varepsilon I_0 t} \qquad (3)$$

Propagation:

$$-M^{\bullet} + M \xrightarrow{k_p} -MM^{\bullet} \qquad R_p = -\frac{d[M]}{dt} = k_p[M^{\bullet}][M] \qquad (4)$$

Bimolecular termination:

$$-M^{\bullet} + {}^{\bullet}M - \xrightarrow{k_t} -MM- \qquad R_t = -\frac{d[M^{\bullet}]}{dt} = 2k_t[M^{\bullet}]^2 \qquad (5)$$

where R_i, R_p, R_t are respectively the initiation, propagation and termination rates, k_p and k_t are respectively the propagation and termination rate constants, ϕ is the initiation quantum yield, ϕ_0 is the number of radicals produced per absorbed light energetic quanta, ε is the molar extinction coefficient, I_0 is the light intensity, $[A_2]$ and $[M]$ are respectively the photoinitiator and monomer concentrations. At low photoinitiator concentration and assuming a quasi-steady state for $[M^{\bullet}]$, the propagation rate can be expressed by:

$$R_p = \frac{k_p}{k_t^{1/2}}[M]\sqrt{\frac{2.3\phi\varepsilon I_0[A_2]}{2}} \qquad (6)$$

From above analysis, however, we can assume that the average values of kinetic rate constants do not vary during the reaction time, and the change of apparent kinetic rate constants during the reaction time can not be described by this analysis. The dramatic decrease in kinetic rate constants resulting in drastic decrease in polymerization rate is clearly shown in Figure 4. The change in apparent kinetic rate constants should be reflected in the reaction rate expression. In general, termination is controlled by polymer diffusion whereas propagation is controlled by small monomer molecules. At the beginning of the reaction, the diffusion coefficient of the species decreases with the increase in double bond conversion and explains the rapid drop of apparent kinetic constants even keeping the same reactivity of all the double bonds.

A reaction rate equation with a diffusion control factor[18] is a semi-empirical equation based on free-volume considerations, and it has been proposed to explain the retardation of radical/cationic crosslinking reaction in the later stage of the reaction. Due to the gelation of dimethacrylate macromonomer, the later stage of the reaction is virtually subjected to
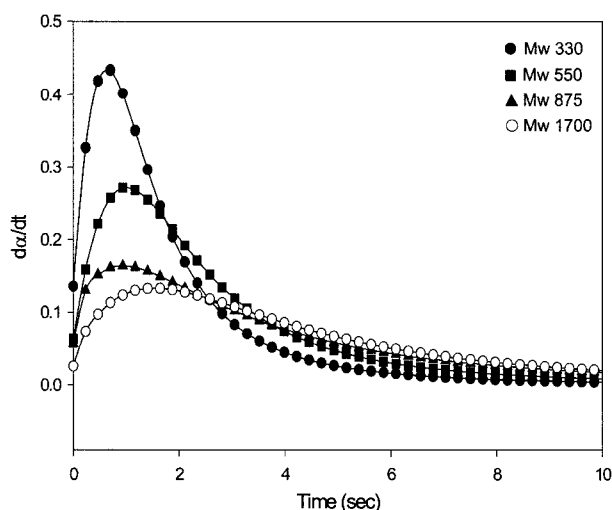

Figure 4. Polymerization rate of dimethacrylate versus reaction time with various molecular weights.

diffusion control. The diffusion-controlled rate constant k_d is as follows:

$$k_d = k_c \exp[-C(\alpha - \alpha_c)] \tag{7}$$

and

$$k_c = \frac{k_p}{k_t^{1/2}} \sqrt{\frac{2.3\phi\varepsilon I_0[A_2]}{2}} \tag{8}$$

where k_c is the rate constant for chemical kinetics, C is a parameter of diffusion control, and α_c is a critical value of reaction conversion. In Eq. (7), as α reaches α_c, the cure reaction becomes controlled by diffusion. The diffusion control factor, $f(\alpha)$ can be expressed as follows :

$$f(\alpha) = \frac{k_e}{k_c} = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \tag{9}$$

where k_e is an overall effective rate constant which is given by the following equation :

$$\frac{1}{k_e} = \frac{1}{k_d} + \frac{1}{k_c} \tag{10}$$

Finally, the predicted kinetic rate expression can be written as

$$R_p = \frac{k_e(1 - \alpha)}{1 + \exp[C(\alpha - \alpha_c)]} \tag{11}$$

Autocatalytic nature of crosslinking reaction, characterized by the maximum polymerization rate at the early stage of the reaction, is clearly shown from the start of the reaction. Model predictions have been made using a conventional mechanistic model as shown in Figure 5. The predictions reveal that as reaction conversion approaches the final conversion, differences between the model predictions without
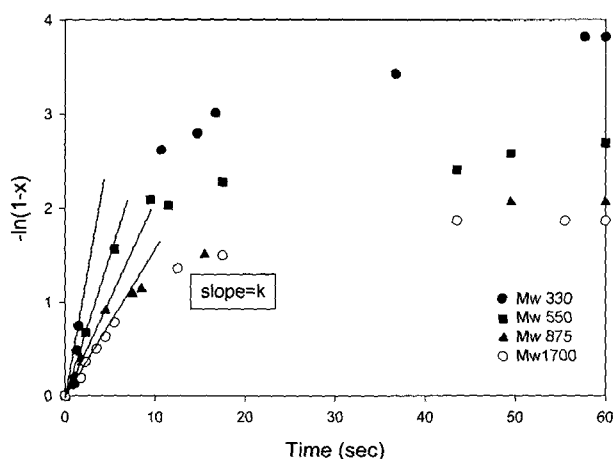
the diffusion control factor and the experimental data become pronounced, indicating that, at the later stage of reaction. Eventually the diffusion control factor in the kinetic rate expression should be considered as shown in Eq. (11). All parameters in Eq. (11) can be simultaneously obtained from Eqs. (6) and (11), i.e., with and without the diffusion control factor, respectively, by applying a nonlinear regression method. The calculated lines compared with the experimental data in Figure 6 and the estimated parameters are listed in Table I. The dashed line, calculated using the conventional mechanistic model, fits the experimental data only in the initial stage of reaction. Whereas, the solid line, calculated using the predicted kinetic rate expression, i.e. the modified mechanistic model, fits the experimental data in the whole range of reaction time. The diffusion control factor can be obtained from the curve fitting of Eq. (11) and the plot of the diffusion control factor versus reaction conversion is shown in Figure 7. At the earlier stages of polymerization, the average values of kinetic rate constants do not vary during the reaction time, and then as the reaction conversion, α, reaches the critical conversion, α_c, in Eq. (11), the reaction becomes controlled by diffusion due to the restricted mobility
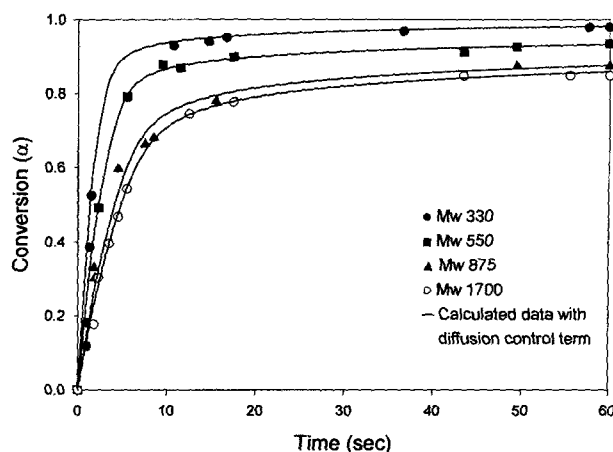

Figure 6. Model predictions using a modified mechanistic rate model with diffusion control factor term.

Table I. Kinetic Parameters of the Model Rate Expression

	Molecular Weight			
	M_w 330	M_w 550	M_w 875	M_w 1700
Mechanistic Model				
k	0.62	0.34	0.186	0.15
Mechanistic Model with Diffusion Control Factor				
k_e	0.52	0.3	0.17	0.145
C	35.485	33.761	20.361	19.094
α_c	0.8808	0.8173	0.7127	0.6919

Figure 5. Model predictions using a conventional mechanistic rate model.
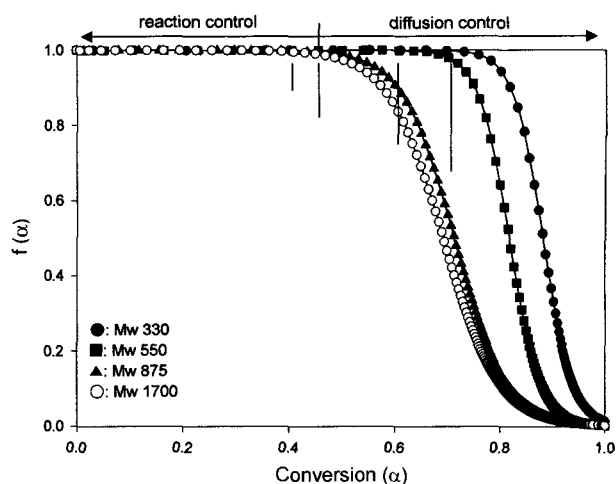
Figure 7. Plot of diffusion control factor versus reaction conversion.
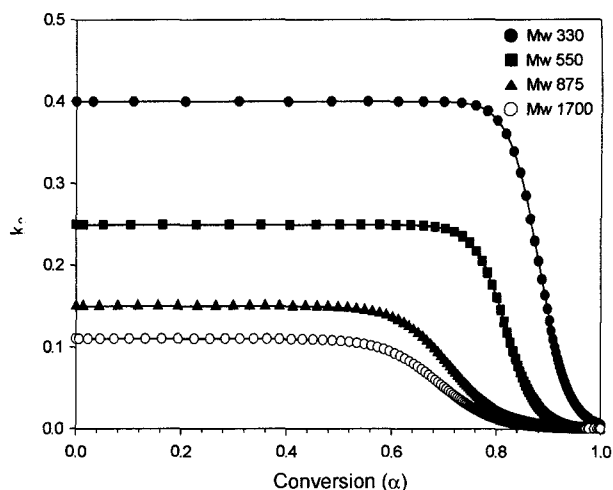

Figure 8. Plot of effective rate constant versus reaction conversion.

of dimethacrylate macromonomer, resulting in the rapid drop of the polymerization rate even keeping the same reactivity of all the double bonds. Furthermore, the critical conversion, α_c, should be placed between the regions of reaction control and diffusion control. The critical conversion value increases with increasing final reaction conversion in the present system.

An effective rate constant, in this study, is a very important term to effectively describe the retardation of photoinitiated polymerization reaction. In the later stage of the reaction, the effective rate constant drastically decreases as reaction conversion increases, as shown in Figure 8. An effective rate constant, k_e, can be obtained from Eqs. (8) and (9). As the onset of the gelation of dimethacrylate macromonomer is

reached, the reaction is evidently subjected to diffusion control and the effective rate constant reveals substantially low value. An incorporation of a diffusion control term into the kinetic rate expression to characterize the kinetics of photoinitiated polymerization of dimethacrylate macromonomers provides a key way to estimate the effective rate constant and to define reaction-controlled and diffusion-controlled regimes in the photoinitiated polymerization system.

Conclusions

A predicted kinetic rate expression having a diffusion control factor was successfully employed to estimate an effective rate constant and to define the reaction-controlled and diffusion-controlled regimes in the photopolymerization of dimethacrylate macromonomers. An effective rate constant, k_e, could be calculated from the predicted kinetic expression using a nonlinear regression method. It was found that the model predictions fit the experimental data during the entire reaction time. The values of effective rate constants do not vary at the earlier stages of polymerization. With the restricted mobility of dimethacrylate macromonomers, the reaction becomes controlled by diffusion. This restricted mobility results in the rapid drop of both the polymerization rate and effective rate constant. By determining the effective rate constants, in this study, the reaction-controlled and diffusion-controlled regimes were properly defined even in the very fast photopolymerization reaction system.

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