Adiabatic Reaction Calorimetry for Data Acquisition of Free-Radical Polymerizations

MICHAEL MOSEBACH, KARL-HEINZ REICHERT

Institut für Technische Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

ABSTRACT: This article deals with the determination of kinetic and thermodynamic data of free-radical polymerization by adiabatic reaction calorimetry. The polymerization of methyl methacrylate in solution, suspension, and emulsion were chosen as systems to be studied. From the measured temperature–time courses of the polymerizations the overall rate constants can be determined with and without gel effect. With knowledge of an appropriate mathematical model describing the kinetics of reaction it was also possible to estimate elementary reaction constants if the molecular weight distribution of the polymer formed was considered as well. The temperature rise and the self-heating rate can be modeled very well for polymerization in solution over the entire range of concentration and, in the case of polymerization in suspension and emulsion, up to a volume fraction of monomer of 20%. The modeling of molecular weight distribution of polymers produced by polymerization in solution and suspension is satisfactory. For emulsion polymerization, however, only the order of magnitude of the average molecular weight could be calculated with the model used. The average particle size of the polymer latex formed could be calculated rather well. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 673–681, 1997

Key words: reaction calorimetry; free-radical polymerization; data acquisition and modeling; adiabatic Dewar calorimeter; modeling of kinetic mass and molecular weight distribution

INTRODUCTION

Adiabatic reaction calorimetry is a very simple method for acquisition of kinetic and caloric data of chemical reactions. The quantity being measured is the temperature of reaction mass, which corresponds directly to the kinetic course of the reaction. Adiabatic calorimetry is also a very sensitive method if the heat capacity of the reactor is low compared with that of the reaction mass. Moreover, it is also possible with this method to study very fast-running chemical reactions.

The disadvantage of the adiabatic calorimetry is that the differential equation of heat and mass balance of the chemical reaction are coupled. The consequence is that for the determination of reliable kinetic and caloric parameters a well-known mathematical model of reaction must be available for the simultaneous evaluation of experiments at various starting temperatures in order to decouple concentration and temperature effects.

Adiabatic reaction calorimetry has been applied to polymerization reaction since 1965.[1–10] The aim of this work is to learn whether adiabatic reaction calorimetry can be used to determine elementary rate constants of free-radical polymerization of different polymerization processes if the molecular weight distribution of the formed polymer is also considered for parameter estimation.

MODEL EQUATIONS

The *heat balance* of the adiabatic reaction calorimeter is given by eq. (1).

$$\frac{dT}{dt} = \frac{V_R c_{M,0} (-\Delta H_R) \dfrac{dX}{dt}}{\varphi \cdot \sum_i m_i c_{p,i}} \qquad (1)$$

where $c_{M,0}$ is the starting monomer concentration; c_p, specific heat capacity; ΔH_R, reaction enthalpy; m, mass; T, temperature of reaction mass; t, reaction time; V_R, reaction volume; X, conversion; and φ, the thermodilution factor of the calorimeter. The thermal dilution factor φ is the ratio of the overall heat capacity of the reactor, including its content, to the heat capacity of the reactor content. In the case of adiabatic suspension polymerization the thermal dilution factor is given by eq. (2), using values for the heat capacity and mass of monomer (M), polymer (P), water (S), and dispersing agent (E).

$$\varphi = \frac{\begin{array}{c} m_M c_{p,M}(1-X) + m_M c_{p,P}X \\ + m_S c_{p,S} + m_E c_{p,E} + W_R \end{array}}{\begin{array}{c} m_M c_{p,M}(1-X) + m_M c_{p,P}X \\ + m_S c_{p,S} + m_E c_{p,E} \end{array}} \qquad (2)$$

The specific heat capacities are a function of the temperature of reaction mass. This was considered by using polynomial functions.

The following assumptions were made. Temperature gradients within the reactor were not assumed. The heat produced by stirring was neglected because the viscosity of the reaction mass is in any case relatively low. The mass of the initiator added to the system and its specific heat capacity were also neglected. Furthermore, φ was expected to be constant during the entire reaction. For modeling the free-radical polymerization under adiabatic conditions, the heat balance must be solved numerically together with the coupled mass balances of the polymerization processes considered.

Mass Balance of Solution Polymerization of Methyl Methacrylate

Coupled mass balances are the basis for modeling the kinetics and molecular weight distribution. The kinetic mechanism of free-radical polymerization consists of well-known elementary steps such as initiator decomposition, chain initiation, chain propagation, and chain termination by disproportionation and/or recombination, as well as chain transfer reactions. Azo *initiators* generally decompose according to a first-order reaction (X_I,

initiator conversion; A_d, preexponential factor; E_d, activation energy; R, ideal gas constant).

$$\frac{dX_I}{dt} = A_d e^{-E_d/\mathrm{RT}} (1 - X_I) \qquad (3)$$

Considering the initiator consumption and volume contraction of the reaction mass, the mass balance of *monomer* is given by eq. (4).

$$\frac{dX}{dt} = \sqrt{\frac{2 f k_d}{k_{t,d} + k_{t,c}}} \, k_p \sqrt{c_{I,0}} (1 - X_I)^{0.5} c_0 \frac{(1-X)}{\sqrt{1 + \varepsilon X}} \qquad (4)$$

where ε is the volume contraction constant of the polymerizing system; f, radical efficiency factor; and k, the reaction rate constant of propagation p, disproportion t, d, and recombination reaction t, c. The number average and the weight average of degree of polymerization can be calculated by integrating the moment equations. In the case of methyl methacrylate (MMA), polymerization-only chain transfer reactions to monomer molecules are considered. The *moment equations* of the inactive polymer chains μ_i are given by

$$\frac{d\mu_0}{dt} = k_{\mathrm{tr},M} c_M \lambda_0 + (k_{t,d} + 0.5 k_{t,c}) \lambda_0^2 \qquad (5)$$

$$\frac{d\mu_1}{dt} = k_{\mathrm{tr},M} c_M \lambda_1 + (k_{t,d} + k_{t,c}) \lambda_0 \lambda_1 \qquad (6)$$

$$\frac{d\mu_2}{dt} = k_{\mathrm{tr},M} c_M \lambda_2 + (k_{t,d} + k_{t,c}) \lambda_0 \lambda_2 + k_{t,c} \lambda_1^2 \quad (7)$$

where $k_{\mathrm{tr},M}$ is the rate constant of transfer reaction to monomer. With the quasi-stationary-state hypothesis, the values of the moments of the active polymer chains λ_i can be calculated by eq. (8)–(10).

$$\lambda_0 = \sqrt{\frac{2 f k_d c_I}{k_t}} \qquad (8)$$

$$\lambda_1 = \frac{k_t \lambda_0^2 + k_{\mathrm{tr},M} c_M \lambda_0 + k_p c_M \lambda_0}{k_{\mathrm{tr},M} c_M + k_t \lambda_0} \qquad (9)$$

$$\lambda_2 = \lambda_1 \left(1 + \frac{2 k_p c_M}{k_{\mathrm{tr},M} c_M + k_t \lambda_0} \right) \qquad (10)$$

The differential average degrees of polymerization can be directly calculated from the moments

of the inactive polymer chains $P_n = \mu_1/\mu_0$, $P_w = \mu_2/\mu_1$. The cumulative average degrees of polymerization for the batch reactor can be obtained by integrating the conversion-versus-time correlation.

Mass Balance of Suspension Polymerization of MMA

For suspension polymerization, the mass balance of solution polymerization can be used but gel and glass effect must be taken into account. For that purpose one of the numerous models has to be used which is appropriate for evaluating adiabatic temperature–time courses of the polymerization. The model ought to include physically sensible parameters. The number of parameters should be as small as possible. The dependences of these parameters from reaction conditions (concentration and temperature) should be well known since, in the case of adiabatic calorimetry, temperature and concentration effects do overlap. If the temperature dependence of each parameter is expressed by an Arrhenius equation, the number of parameters to be optimized doubles. For adiabatic polymerization, most gel-effect models published can be excluded because either the number of the model's parameters is too large or the temperature dependence of the parameters is not known. The most important gel-effect models were tested with respect to adiabatic polymerization.[11] In the case of the adiabatic suspension polymerization of MMA, the gel-effect model of Marten, Hamielec, Stickler, and Panke[12-16] works very well. After the set-in of *gel effect,* the rate constant of chain termination is coupled with the free volume of the polymerizing system according to eq. (11).

$$k_t = k_{t,0}\left(\frac{M_{w,\text{cr1}}}{M_w}\right)^n e^{-A(1/V_f - 1/V_{f,\text{cr1}})} + k_p c_{M,0}(1 - X)$$

(11)

where M_w is the cumulative mass average of molar mass distribution and V_f is the free volume of the polymerizing system. This gel-effect model had to be verified in order to account for the glass effect. After the set-in of the glass effect, the radical efficiency factor had to be correlated with the free volume instead of the propagation rate constant. Only then it was possible to describe not only the kinetics but the molecular weight as well. The *glass effect* is observed at a certain free vol-

ume ($V_{f,\text{cr2}}$); from that time on the radical efficiency factor can be calculated using the following equation:

$$f = f_0 e^{-B(1/V_f - 1/V_{f,\text{cr2}})}$$

(12)

The onset of the gel effect is given when the following correlation is fulfilled:

$$K_3 = M_{w,\text{cr1}}^{0,5} e^{A/V_{f,\text{cr1}}}$$

(13)

where K_3 is the model parameter of gel effect and V_{cr1} is the free volume of set-in of the gel effect. The orders of eqs. (11)–(13) have the following values for polymerization of MMA: for ideal kinetics, $n = 0$, $A = 0$, $B = 0$; after setting in of the gel effect, $n = 1.75$, $A = 1.11$, $B = 0$; after setting in of the glass effect, $n = 1.75$, $A = 1.11$, $B = 1$.

It was confirmed by modeling that none of the model parameters K_3 and $V_{f,\text{cr2}}$ is temperature dependent. In addition to the reaction rate constants, the free volume of the polymerizing system depends on temperature and is responsible for the temperature dependence of the gel effect.

Mass Balance of Emulsion Polymerization of MMA

The kinetic course of emulsion polymerization is generally divided into three stages. During *the particle nucleation stage,* latex particles are generated from micelles by the entering of initiator radicals. The particle balance is given by

$$\frac{dN}{dt} = 2fk_d c_I N_A \frac{A_M}{A_M + yA_L}$$

(14)

where N is the number of particles per liter; N_A, the average number of radicals in the latex particle; y, the probability factor of radical entrance; and A, the surface of micelles M, of latex particle L, and of polymer particle P. The total surface of latex particles can be calculated with knowledge of particle diameter as follows:

$$A_L = \pi d_P^2 N$$

(15)

where d_P is the diameter of the polymer particle.

$$A_M = (c_S - c_{S,\text{CMC}})a_S N_A - A_L$$

(16)

where CMC is the critical micelle concentration and a_S the surface of micelles. The probability factor y has a value of 100 according to Parts and

colleagues.[17] If the micelle concentration is lower than the critical micelle concentration the particle nucleation stage is terminated. During the *particle growth stage* the following reaction rate law is valid:

$$r = k_p \frac{\bar{n}}{N_A} N c_M \quad (17)$$

The monomer concentration in the latex particle is assumed to be constant during the particle growth stage, according to the swelling equilibrium of Morton and associates,[18] and can be calculated from the polymer fraction in the latex particles according to eq. (18). The Flory–Huggins polymer–solvent interaction parameter was calculated by the method of Reimers and coworkers[19] and to the values of Grulke.[20]

$$\frac{2V_1\sigma}{r_P \cdot R \cdot T} = -[\ln(1 - \Phi_P) + \Phi_P + \zeta \cdot \Phi_P^2] \quad (18)$$

where r_P is the particle radius; V_1, the molar volume; ζ, the Flory–Huggins polymer–solvent interaction parameter; Φ_P, the volume fraction of polymer; and σ, the interfacial tension.

The average number of radicals per particle $\bar{n}$ is calculated by the approximation of Ugelstad and Hausen.[21]

$$\bar{n} = 0.5 \times \cfrac{(\alpha/2)^2}{m + \cfrac{(\alpha/2)^2}{m + 1 + \cfrac{(\alpha/2)^2}{m + 2 + \cfrac{(\alpha/2)^2}{m + 3 + \cfrac{(\alpha/2)^2}{m + 4 + \cdots}}}}} \quad (19)$$

with

$$\alpha = \sqrt{\frac{8V_P}{k_t\tau^*}}, \quad m = \frac{k_{\text{des}}A_P}{k_t}, \quad \text{and} \quad \tau^* = \frac{N}{2fk_dc_IN_A}$$

where m and α are parameters of emulsion polymerization; τ^* is the time of radical entrance; and k_{des} is the rate of desorption. In the *monomer finishing stage* all the monomer particles are consumed. The decrease of the reaction rate follows a first-order law. This effect is compensated by the gel effect. An estimation of the number average of the molecular weight distribution was made by the method of Nomura and Fujita.[22]

EXPERIMENTAL

The adiabatic calorimeter (Fig. 1) consists of a 1-L vacuum-jacketed glass Dewar flask (a) with a Teflon lid (b). The reactor contains a Pt-100 thermometer (d), a internal electric heater (e), and a pipe for purging the reactor content with nitrogene (f). On the top of the reactor a reflux condenser (i) was installed in order to prevent the loss of monomer during purging. The reaction mass was stirred by an Intermig stirrer (c) at 400 rpm. The reactor is surrounded by a thermostated air bath (h), which is kept at reactor temperature (g). In this way the heat loss of the adiabatic reaction calorimeter to the surroundings can be
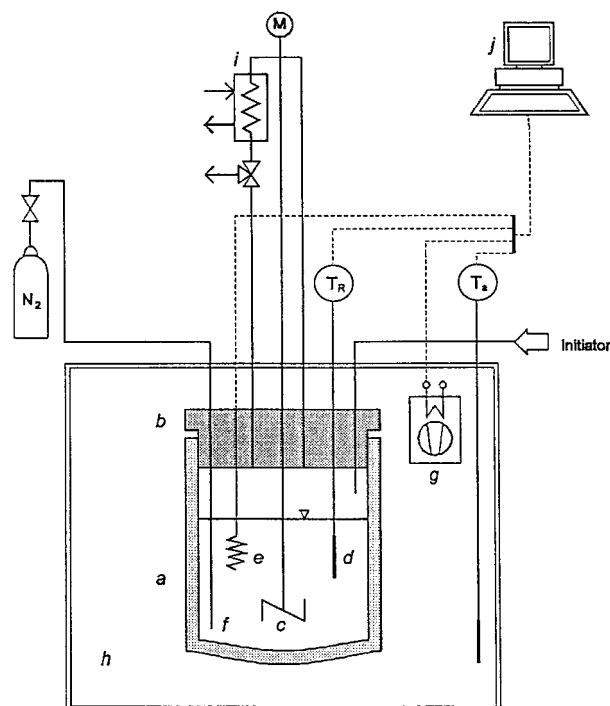

Figure 1 Scheme of the adiabatic reaction calorimeter.

minimized. The reaction volume of all polymerizations was between 800 and 900 mL.

The *solution polymerization* was carried out in toluene. The concentration of MMA was varied between 1 and 4 mol/L and the concentration of the azoinitiator 2,2′-azobis(2,4-dimethylvaleronitril)(ADVN) was varied between 0.01 and 0.05 mol/L. In carrying out adiabatic polymerizations it is important that the starting temperature is high enough for a remarkable initial reaction rate, and at the same time low enough so as not to reach the boiling point of one component at the end of reaction. The optimum starting temperature of the adiabatic solution polymerizations was between 40 and 60°C.

The *suspension polymerization* was run at volume ratios of monomer of 0.1 to 0.2. An aqueous polyacrylic acid solution (25 weight percent M = 190,000 g/mol/Rohm and Haas) was used as dispersing agent with concentrations between 1 and 2 mass % related to the water phase. The concentration of ADVN was varied between 1 and 5 mass % relative to the monomer. The starting temperature of polymerization was between 40 and 70°C.

The *emulsion polymerization* was run at a volume ratio of monomer of 0.15. The polymerizations were carried out at starting temperatures from 40 to 60°C. The water-soluble azoinitiator 2,2′-azobis(2-methylpropionamidin)dihydrochloride was used. The initiator concentration was varied between 0.5 and 2.5 g/L relative to the water phase. As emulsifier, sodium dodecylsulfate was used at concentrations of 5 to 20 g/L.

Before initiation of the reaction, the reactor contents were purged with nitrogen. The thermal dilution factor φ was determined by calibration with an electric heater. The value of φ is 1.1. After heating to starting temperature, the initiator was injected into the reaction mass. At the end of reaction the final conversion was determined gravimetrically.

The final molecular weight distribution of the polymer was determined by gel permeation chromatography (GPC), with poly(methylmethacrylate) as standard.

The particle size distribution of the final latex was determined by dynamic light scattering.

Parameter Estimation

In general, values from literature can be used for the decomposition of initiator because much data has been published in this field. Also, the values of parameters which cannot be determined by adiabatic calorimetry (such as activation energy of termination reactions) must be taken from literature. Kinetic parameters describing the gel effect should also be taken from literature.

In order to obtain first estimates of the unknown kinetic parameters of the model, the temperature increase at the beginning of reaction is measured as function of starting temperature and monomer and initiator concentrations. If the initial rate is plotted versus temperature and concentration in logarithmic diagrams, straight lines are obtained, in general. From the slope of the lines, values of the overall rate constant of reaction and the order of reaction can be calculated.

By integration of specific heat versus temperature function, an estimation of the reaction enthalpy ΔH_R was made.

For determination of parameters of elementary reactions it is necessary to refer to the molecular weight distribution of the formed polymer. With consideration of average molecular weights, propagation and termination rate constant can be obtained. The width of molecular weight distribution reflects the ratio between termination by disproportionation and termination by recombination. The transfer rate constant to monomer molecules can be determined by variation of monomer concentrations.

The estimated values of sensitive parameters can be optimized with an optimization procedure. The differential equations of the heat and mass balances are solved numerically to calculate the temperature rise and the self-heating rate of the reaction. For modeling of the molecular weight distribution, a stochastic simulation method was used.[23]

The decoupling of concentration and temperature effects is done by simultaneous evaluation of all experiments carried out at different starting temperatures and concentrations. Sensitive parameters which influence the temperature increase of reaction mass and the molecular weight distribution of the polymer are the kinetic constants of initiator decomposition and of chain propagation. The rate constant of transfer reaction and the frequency factor of termination reaction are sensitive only with respect to the width of the molecular weight distribution.

The kinetic and thermodynamic constants can be optimized by minimizing the sum of square error with the simplex method of Nelder and Mead.[24] This was done with a computer program containing the kinetic mechanism of polymerization in form of differential equations. While calculating the sum of square error, not only was the temperature increase
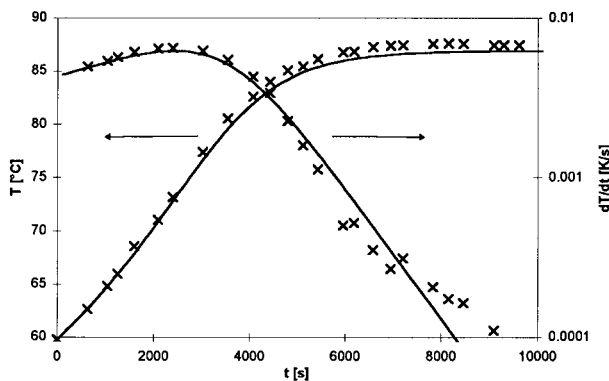
Figure 2 Modeling of temperature rise and self-heating rate of the adiabatic polymerization of MMA in toluene without gel effect ($c_{M,0}$ = 1.5 mol/L; $c_{I,0}$ = 0.05 mol/L): ($\times$) experiment; (——) modeling.

of the reaction mass considered but also the self-heating rate of the reaction mass was taken into account for better results. The deviation in the averages of molecular weight distribution is added accordingly to the sum of square error.

RESULTS

Solution Polymerization

As a result of optimization, the following values of kinetic parameters were obtained for the solution polymerization of MMA in toluene under consideration of temperature courses at various conditions and molecular weight distributions of the final polymer: A_d = 6.73 × 10^{14} s^{-1}, Ref. 25; E_d = 121.26 kJ/mol, Ref. 25; A_p = 2.12 × 10^5 L mol^{-1}
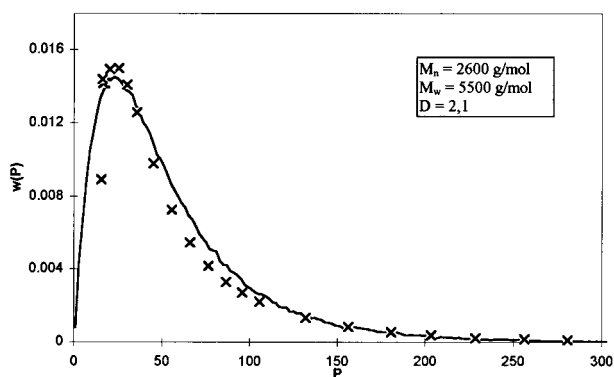

Figure 3 Modeling of molecular mass distribution of the final product of the adiabatic polymerization of MMA in toluene without gel effect ($c_{M,0}$ = 1.5 mol/L; $c_{I,0}$ = 0.05 mol/L; starting temperature T_0 = 60°C): ($\times$) experiment; (——) modeling.
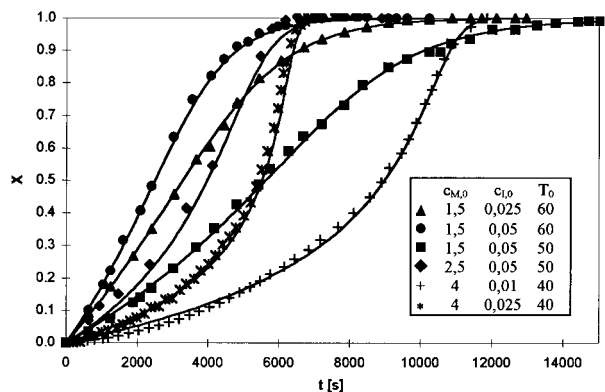

Figure 4 Modeling of conversion of adiabatic polymerizations of MMA in toluene at different concentrations and starting temperatures: ($\times$) experiment; (——) modeling.

s^{-1}, this work; E_p = 19.14 kJ/mol, this work; $A_{t,d}$ = 3.58 × 10^6 L mol^{-1} s^{-1}, this work; $E_{t,d}$ = 0.83 kJ/mol, Ref. 26; $A_{t,c}$ = 3.43 × 10^6 L mol^{-1} s^{-1}, this work; $E_{t,c}$ = 0.83 kJ/mol, Ref. 26; $A_{tr,M}$ = 2.09 × 10^9 L mol^{-1} s^{-1}, this work; $E_{tr,M}$ = 74.35 kJ/mol, this work; ΔH_R = 57.38 kJ/mol, this work.

Figure 2 shows the results of modeling, and Figure 3 shows the molecular weight distribution of the final polymer. A gel effect did not occur in this case. Looking at Figure 2 it can be seen that deviations between experiment and modeling appear much stronger in the case of self-heating rate than in the case of temperature rise. This is due to the numerical derivation process of the temperature data. Therefore, data fitting should best be done with the self-heating rate of the adiabatic polymerization processes and under consideration of the molecular weight distribution of the polymer formed.

In Figure 4 the relative conversion $X = \dfrac{T - T_0}{\Delta T_{max}}$

of different polymerization reactions is plotted.

Suspension Polymerization

In the case of suspension polymerizations of MMA with the same initiator as for polymerization in toluene, the following values of constants were obtained by data fitting: A_d = 6.51 × 10^{14} s^{-1}, Ref. 25; E_d = 121.26 kJ/mol, Ref. 25; A_p = 2.08 × 10^5 L mol^{-1} s^{-1}, this work; E_p = 20.16 kJ/mol, this work; $A_{t,d}$ = 3.64 × 10^6 L mol^{-1} s^{-1}, this work; $E_{t,d}$ = 0.83 kJ/mol, Ref. 26; $A_{t,c}$ = 3.42 × 10^6 L mol^{-1} s^{-1}, this work; $E_{t,c}$ = 0.83 kJ/mol, Ref. 26; $A_{tr,M}$ = 4.95 × 10^9 L mol^{-1} s^{-1}, this work; $E_{tr,M}$
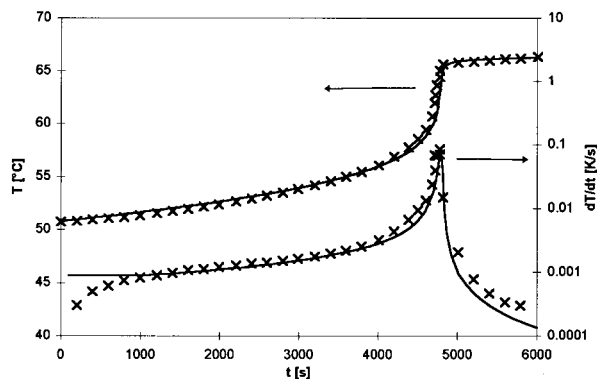
Figure 5 Modeling of temperature increase and self-heating rate of the adiabatic suspension polymerization of MMA ($c_{I,0}$ = 1 mass % with respect to monomer, Φ = 0.15): ($\times$) experiment; (———) modeling.

= 74.23 kJ/mol, this work; ΔH_R = 57.91 kJ/mol, this work.

In this case the gel effect sets in at a conversion of 0.2. The values of the gel-effect parameters used in the model are K_3 = 240,000 and $V_{f,cr2}$ = 0.04.[19]

Figure 5 shows the result of modeling the temperature rise and the self-heating rate. Looking especially at the self-heating rate, some deviations between model and experiment occur in the range of maximum temperature increase. One reason is the exponential structure of the gel-effect functions of the model used. The self-heating rate in the range of maximum reaction rate is overestimated and the set-in of the glass effect is not considered strong enough.

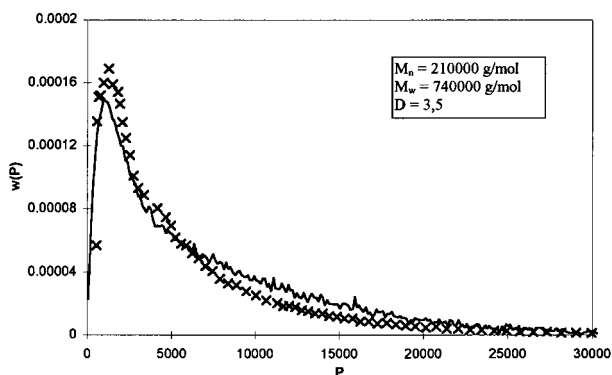In the beginning of the reaction some deviations can also be seen. This may be due to an

Figure 6 Modeling of molecular mass distribution of the final product of the adiabatic suspension polymerization of MMA ($c_{I,0}$ = 1 mass % with respect to monomer, Φ = 0.15, starting temperature T_0 = 50°C): ($\times$) experiment; (———) modeling.
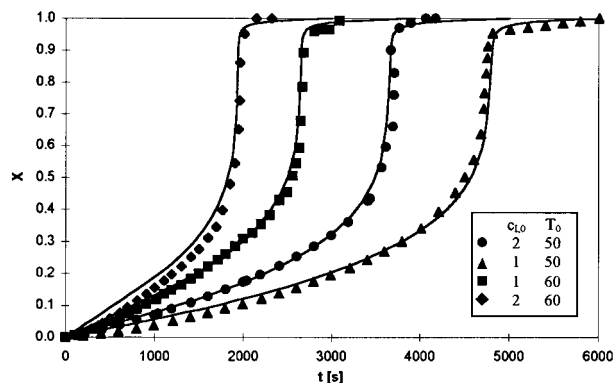

Figure 7 Modeling the conversion of adiabatic suspension polymerizations of MMA (Φ = 0.15 and c_E = 2% with respect to monomer): ($\times$) experiment; (———) modeling.

inhibition caused by the presence of oxygen in the system. Figure 6 shows the result of modeling the molecular weight distribution of the final product with the same kinetic parameters. The deviations are substantial in this case, and may have been caused by transfer reactions which have not been considered in the model.

Figure 7 shows the result of modeling the relative conversion of some suspension polymerizations. All adiabatic experiments can be described quite well with one set of parameters.

Emulsion Polymerization

The set of kinetic constants optimized by the simplex process has the following values for all experiments carried out: A_d = 1.06 $\times$ 10^{15} s^{-1}, Ref. 25;
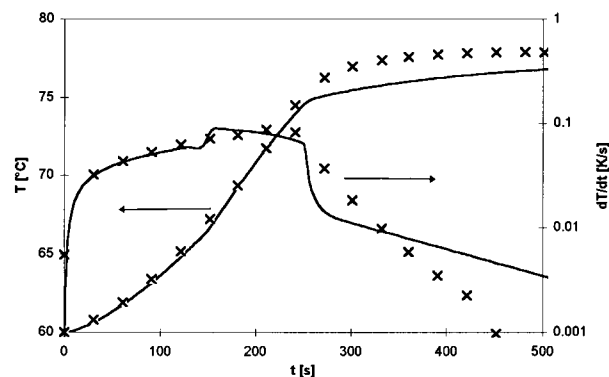

Figure 8 Modeling of reactor temperature and self-heating rate of the adiabatic emulsion polymerization of MMA (Φ = 0.15; $c_{I,0}$ = 1 g/L with respect to water, c_E = 10 g/L with respect to water): ($\times$) experiment; (———) modeling.

E_d = 124.30 kJ/mol, Ref. 25; A_p = 1.92 × 10^5 L mol^{-1} s^{-1}, this work; E_p = 16.91 kJ/mol, this work; $A_{t,d}$ = 3.61 × 10^6 L mol^{-1} s^{-1}, this work; $E_{t,d}$ = 0.83 kJ/mol, Ref. 26; $A_{t,c}$ = 3.43 × 10^6 L mol^{-1} s^{-1}, this work; $E_{t,c}$ = 0.83 kJ/mol, Ref. 26; $A_{tr,M}$ = 2.62 × 10^{11} L mol^{-1} s^{-1}, this work; $E_{tr,M}$ = 74.26 kJ/mol, this work; ΔH_R = 51.63 kJ/mol, this work.

In Figure 8, the courses of reactor temperature and self-heating rate of one emulsion polymerization are plotted. The gel effect at 150 s sets in too abruptly according to the model used. This leads to an unsteady point of the self-heating rate at the end of the particle nucleation stage. As can be seen, the monomer finishing stage can not be modeled satisfactorily with the model used. Reason for this is a poor description of the glass effect during this stage of polymerization.

The relative conversion can be modeled qualitatively with some points of unsteadiness (Fig. 9).

The measured molecular weights are in the range of 2 to 5 × 10^6 g/mol. The molecular mass averages can be calculated with the model used only in the order of magnitude. The measured particle diameters are in the range of 50 to 140 nm and can be calculated rather well.

CONCLUSION

Table I shows that the fitted kinetic parameters of MMA polymerization in solution, suspension, and emulsion, determined by adiabatic reaction calorimetry, correspond well with the values available in literature.[25-27]

In general, it should be remarked that the devi-

Table I Kinetic Constants of MMA Polymerization Taken From Literature for Different Polymerization Processes[25-27]

Constant	Value
A_d	1.14 × 10^{14}–1.12 × 10^{19} s^{-1}
A_p	2.50 × 10^5–4.77 × 10^7 L mol^{-1} s^{-1}
E_p	13.81–31.21 kJ/mol
A_t	9.40 × 10^7–1.40 × 10^9 L mol^{-1} s^{-1}
$A_{tr,M}$	1.93 × 10^{11} L mol^{-1} s^{-1}
$E_{tr,M}$	82.57 kJ/mol

ation of single parameters of different polymerization processes are low except for the pre-exponential factor of transfer reaction that varies from polymerization process to polymerization process. The reason for this is that A_{tr} should be regarded as an overall pre-exponential factor of transfer reactions. In the model used, only transfer reactions to monomer molecules are considered.

The models of solution and suspension polymerization are able to describe very well the kinetics of free-radical polymerization of MMA and the resulting molecular weight distribution under adiabatic conditions.

The model of emulsion polymerization used is suitable only with certain limitations. It can be used to model the general temperature–time course of polymerization and the average particle size of the latex formed. The advantage of the model used is its low number of empirical parameters. It cannot be used to model the self-heating rate of polymerization and the average of molecular weight distribution accurately.

The main source of error in experimental studies is the precision of the GPC which was used for measurement of molecular weight distributions.

If good mathematical models of the kinetics of free-radical polymerizations are available, adiabatic reaction calorimetry is an effective method for fast and precise determination of kinetic constants, especially if the molecular weight distribution and particle size distribution of the formed polymer are considered as well.
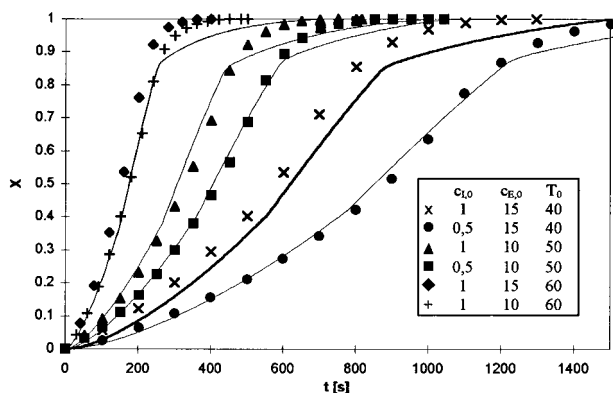

Figure 9 Modeling of conversion of adiabatic emulsion polymerizations of MMA at different concentrations and starting temperatures (Φ = 0.15): (×) experiment; (——) modeling.

REFERENCES

1. P. Wittmer, *Macromol. Chem.,* **89,** 27 (1965).
2. S. D. Lipshitz and C. W. Macosko, *J. Appl. Polym. Sci.,* **21,** 2029 (1977).
3. A. Ya. Malkin, V. G. Frolov, S. L. Ivanova, A. N.

Ivanova, and Z. S. Andrianova, *Poly. Sci. U.S.S.R.,* **21,** 691 (1979).

4. R. E. Camargo, V. M. Gonzalez, C. W. Macosko, and M. Tirrel, *2nd. Int. Conf. Reac. Proc. Polym.,* 774, Pittsburg, 1982.

5. A. Ya. Malkin, V. P. Beghishev, and S. A. Bolgov, *Polymer,* **23,** 385 (1982).

6. A. Ya. Malkin, S. L. Ivanova, V. G. Frolov, A. N. Ivanova, and Z. S. Andrianova, *Polymer,* **23,** 576 (1982).

7. M. Chen and K.-H. Reichert, *Polym. React. Eng.,* **1,** 145 (1992–93).

8. M. Chen and K.-H. Reichert, *Chem.-Ing.-Tech.,* **65,** 78 (1993).

9. M. Mosebach and K.-H. Reichert, *Chem.-Ing.-Tech.,* **66,** 1058 (1994).

10. M. Mosebach, K.-H. Reichert, *Chem.-Ing.-Tech.,* **67,** 1655 (1995).

11. M. Mosebach, diploma thesis, TU Berlin (1993).

12. F. L. Marten and A. E. Hamielec, *J. Appl. Polym. Sci.,* **27,** 489 (1982).

13. F. L. Marten and A. E. Hamielec, *Amer. Chem. Soc. Symp. Ser.,* **104,** 43 (1979).

14. M. Stickler, *Makromol. Chem.,* **184,** 2563 (1983).

15. D. Panke, *Makromol. Chem. Rapid Commun.,* **7,** 171 (1986).

16. M. Stickler, D. Panke, and A. E. Hamielec, *J. Polym. Sci.,* **22,** 2243 (1984).

17. A. G. Parts, D. E. Moore, and J. G. Watterson, *Macromol. Chem.,* **89,** 156 (1965).

18. M. Morton, S. Kaizerman, and M. W. Altier, *J. Colloid Sci.,* **9,** 300 (1954).

19. J. L. Reimers, A. H. P. Skelland, and F. J. Schork, *Polym. React. Eng.,* **3,** 235 (1995).

20. E. A. Grulke, in *Polymer Handbook,* J. Brandrup and E. H. Immergut, Eds., Wiley Interscience, New York, 1989, p. VII 519.

21. J. Ugelstad and F. K. Hausen, *Rubber Chem. Technol.,* **49,** 536 (1976).

22. M. Nomura and K. Fujita, *Polym. React. Eng.,* **2,** 317 (1994).

23. K. Platkowski, Ph.D. dissertation Technische Universität Berlin, 1996.

24. A. J. Nelder and R. Mead, *Computer J.,* **7,** 308 (1965).

25. Wako Chemicals GmbH, Neuss, Germany, technical information papers V50 and V65 (1993).

26. J. Brandrup and E. Immergut, *Polymer Handbook,* Wiley, New York, 1989.

27. G. Weickert, *Polymerisationsreaktoren,* Springer-verlag, Berlin, 1995.