Polymerization of Methyl Methacrylate at High Temperature with 1-Butanethiol as Chain Transfer Agent

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ABSTRACT: The free-radical polymerization of methyl methacrylate (MMA) at high temperature (120 to 180°C) has been studied in the presence of di-tertiobutyle peroxide as an initiator and 1-butanethiol as a chain transfer agent. No solvent was used, and the polymerization was run to high monomer conversion. Based on the experimental data collected with a dilatometric reactor, the features of the reaction have been pointed out. Working at high temperature with a chain transfer agent proved efficient to reduce the intensity of the gel effect and control the molecular weight obtained. At a temperature up to 170°C, however, the burn-out of the initiator limits the final conversion, and the increase of the polymerization rate during the gel effect has been more difficult to detect and quantify. An empirical expression of the termination rate constant has been adopted to describe the autoacceleration and predict the conversion versus time curves and the average molecular weight of the polymer obtained. The mathematical model includes two adjustable parameters that have been determined as a function of the temperature and the initial concentration of the chain transfer agent. The agreement between the predicted and experimental data on conversion and molecular weight was good, while the polydispersity index was often underestimated. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1589-1599, 1999

Key words: methyl methacrylate; high temperature; 1-butanethiol; radical polymerization; kinetics

INTRODUCTION

The present study is a part of a more extended research program, the aim of which was to design a continuous reactor working at high temperature and perform an optimum process control strategy for the bulk polymerization of methyl methacrylate (MMA). In this scope, a preliminary task was to analyze, in detail, the kinetics of the polymerization reaction for our specific operating conditions. For the radical polymerization of MMA, the classical polymerization kinetics applies at low conversion, but then the viscosity of the reaction mixture increases so that the termination reaction becomes diffusion-controlled. The autoacceleration of the reaction (Trommsdorf effect or gel effect) leads to higher monomer conversion than expected.

The autoacceleration of the reaction is a source of serious problems in industrial polymerization processes where the control of the viscosity and the temperature is critical to obtain the desired molecular weight distribution. In addition, the reaction must be kept under control to avoid thermal runaway of the reactor.

Although a considerable amount of literature has been published on the modelization of the free

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radical polymerization of MMA, only a few articles are concerned with the polymerization at temperatures above 120°C.

Fleury et al. investigated the polymerization of MMA at high temperature $(130-170^{\circ}C)$ in the presence of di-*tert*-butyle peroxide (DTBP) but they did not use any chain transfer agent.^{1,2} They reported that the autoacceleration of the reaction was much less pronounced than at low temperature and they proposed an empirical expression of the termination rate constant k_t .

Corpart³ modeled the polymerization of MMA in the presence of 2,5-dimethyl hexyne (3)-2,5-dit-butyl peroxide (DYBP) and 1-butanethiol (BSH). The author adapted the model of Hamielec modified by Stickler and Panke to her specific working temperature.³ She correlated the adjustable parameters of the model by fitting the experimental data collected. The predictions obtained were satisfactory at a temperature below 130°C, but the increase of the overall termination rate during the autoacceleration of the reaction was always underestimated at a higher temperature. In addition, Corpart and Clouet et al.⁴ pointed out the importance of the initiation of the polymerization by impurities contained in the monomer, even after careful purification.

In this article, we first focus on the experimental study of the free radical polymerization of MMA in the temperature range of 120–180°C in the presence of di-*tert*-butyl-peroxide (DTBP) as initiator and BSH as a chain transfer agent. The modifications on the onset and magnitude of the gel effect are especially investigated. Based on the collected data, a mathematical model of the polymerization is developed.

EXPERIMENTAL

The monomer conversion is followed using a dilatometric polymerization technique. The device consists of a temperature-regulated cylindrical dilatometric reactor, into which slides a piston that is driven by a pressure cylinder. It is working under pressure to reach a high temperature up to 200°C without creating a vapor phase into the reactor. The working pressure is constant and equal to 50 bars. The evolution of the reaction volume is followed with a displacement transducer attached to the piston. The movement of the piston that hermetically seals the reactor is recorded, and the data are converted via a data

acquisition system. The calculation of the conversion is automatically carried out on a computer.

The initial volume of the reactor is around 10 cm^3 , and its inner diameter is small (10 mm) to reduce the radial temperature gradient. A smalllag temperature sensor is placed in the reacting medium to measure its effective temperature. The diameter of the thermocouple is small (1.5 mm) so that the response is fast and allows to follow the temperature at the center of the reactor with a short delay time.

Provided that we measure the actual temperature of the reacting medium, the degree of conversion may be calculated, even in nonisothermal conditions. Equation (1) is used to express the conversion X, d_m , and d_p are the densities of the monomer and of the polymer, ε is the volume contraction factor, V is the volume of the reactor. They are functions of the temperature T of the reacting mass. m is the total mass of the monomer. The expression of ε is given by eq. (2), as follows:

$$X = \frac{1}{\varepsilon(T)} \left(\frac{d_m(T)}{m} V(T) - 1 \right)$$
(1)

$$\varepsilon = \frac{d_m - d_p}{d_p} \tag{2}$$

The following data are measured in real time: the set temperature of the reactor T_c , the actual temperature of the reacting medium T, and the volume of the reacting medium V. The conversion is calculated as a function of time.

The nonisothermicity of the reaction is illustrated in Figure 1, where the temperature measured at the center of the reactor is shown, together with the degree of conversion. The reactor is filled at room temperature; thus, the first 10 min of the reaction cannot be exploited since the heating rate is very high and the temperature at the center of the reactor is not representative of the temperature of the overall volume of monomer. That is the reason why negative values of the conversion are calculated during the first minutes of the reaction. After this period, the temperature of the reactor is not stabilized vet; however, a "real" temperature is measured. Then, the temperature stabilizes at 135°C, that is, 2°C above the set temperature of the reactor wall because of the exothermicity of the reaction. During the gel effect, the temperature increases because of the acceleration of the reaction. T rises up to 138°C. Finally, when the reaction stops, T



Figure 1 Monomer conversion and temperature of the reaction mixture recorded as a function of time during the bulk polymerization of MMA at 133°C. $I_0 = 1 \times 10^{-3}$ mol L; $A_0 = 8.9 \times 10^{-3}$ mol/L. The exothermicity of the reaction is clearly detected through the measurement of the temperature at the center of the reactor.

decreases until it is equal to the set temperature T_c equal to 133°C.

The polymerization technique and the calculation of the conversion are described in more detail in the literature. 5,6

Monomer and Additives

The requirements on the quality of the monomer and of the additives used were imposed by the industrial context of the present study, whose aim was to design a pilot polymerization unit. The MMA is a commercial monomer stabilized with 15 ppm of 4-methoxy phenol. It is distilled under reduced pressure of an inert gas. After distillation, the concentration in residual inhibitor is less than 0.1 ppm. The initiator is di-*tert*-butyle peroxide (99%), and the chain transfer agent is 1-butanethiol (99%). Both are commercial products used without further purification for reasons linked to the industrial process.

The molecular weight was determined by gel permeation chromatography (GPC) calibrated with PMMA.

RESULTS

The experimental conditions of the polymerization experiments are as follows: set temperature, $120 < T_c < 180$ °C; initial concentration of initiator, $2 \times 10^{-4} < I_0 < 30 \times 10^{-4}$ mol/L; initial



Figure 2 Experimental conversion versus time curves for the bulk polymerization of MMA at 120, 132, 150, 168, and 180°C. $I_0 = 7 \times 10^{-4}$ mol/L; $A_0 = 20.5 \times 10^{-3}$ mol/L.

concentration of chain transfer agent, 1×10^{-3} $< A_0 < 50 \times 10^{-3}$ mol/L; there was no solvent added.

Effect of the Polymerization Temperature

The conversion versus time curves of the polymerization at five different temperatures are shown in Figure 2. At 120 to 150°C, the shape of the curves are very similar to those obtained at low temperature. However, the temperature is above the glass transition of the PMMA; thus, the glass



Figure 3 Experimental conversion versus time curves for the bulk polymerization of MMA at 168°C. $A_0 = 8.9 \times 10^{-3}$ mol/L; $I_0 = 4 \times 10^{-4}$, 10×10^{-4} , and 30×10^{-4} mol/L. The effect of the initial initiator concentration on the final conversion obtained at high temperature is illustrated.



Figure 4 Experimental conversion versus time curves for the bulk polymerization of MMA at different chain transfer agent concentrations: $A_0 = 1 \times 10^{-3}$, 8.9×10^{-3} , 20.5×10^{-3} , and 40×10^{-3} mol/L. $T_c = 150$ °C; $I_0 = 7 \times 10^{-4}$ mol/L. Also shown are the time derivatives of the conversion. Notice how the gel effect is attenuated when the molecular weight decreases and how its onset is shifted to higher conversion.

effect is absent, and the reaction goes to total conversion.

The gel effect is present but is much less pronounced compared to the strong autoacceleration observed for lower temperature polymerization. When the temperature increases, its intensity is reduced, and it starts at higher conversion levels.

At 168 and 180°C, the reaction stops before the total conversion is reached. To understand this

trend, one must notice that DTBP decomposes very fast at these temperature (the half-time life of DTBP at 168°C is around 9 min), and this causes the polymerization to stop prematurely due to initiator burn-out. The dead ending of the polymerization occurs earlier when the temperature is higher and, thus, leads to lower final conversion, as can be observed by comparing the curves obtained at 168 and 180°C (Fig. 2). Figure 3 clearly shows how the depletion of the initiator causes the reaction to stop. Only for the initial concentration of 30×10^{-4} mol/L, the DTBP is not exhausted before the reaction reaches total conversion.

The very fast polymerization stage initiated by DTBP is followed by a much slower stage after its exhaustion. Corpart³ and Clouet et al.⁴ have found that thermal initiation was partly responsible for this second stage. In a previous work,^{5,6} we have already found that either a slow decomposition impurity or the 1-butanethiol itself may also initiate the reaction.

Effect of the Molecular Weight

Figure 4 illustrates the effect of the molecular weight on the evolution of the conversion with time at 150°C. Increasing the loading of 1-butanethiol decreases the molecular weight as expected and does not modify the initial polymerization rate. On the other hand, when the molecular weight of the macroradicals and of the polymer lowers, one can notice that the onset of the Trommsdorf effect is shifted to higher conversion, while its amplitude is much less pronounced (Fig. 4).

At a higher temperature (Fig. 5) the burn-out of the initiator makes the interpretation more difficult. However, it appears that the gel effect is absent when the molecular weight is below a critical value. In Figure 5, curves 1 and 2 are the same despite the fact that the molecular weight has been multiplied by 4. For curve 3, the molec-



Figure 5 Conversion versus time curves for the bulk polymerization of MMA at different chain transfer agent concentrations: $A_0 = 1 \times 10^{-3}$, 9.8×10^{-3} , and 40×10^{-3} mol/L. $T_c = 160$ °C; $I_0 = 7 \times 10^{-4}$ mol/L.



Figure 6 Molecular weight of the PMMA as a function of the initial concentration of chain transfer agent. $0 < I_0 < 30 \times 10^{-4}$ mol/L; 132° C $< T_c < 180^{\circ}$ C. The molecular weight is measured at the peak of the GPC chromatogram.

ular weight is multiplied again by a factor 4, and only the presence of the autoacceleration may explain that the final conversion reached is higher (0.8 instead of 0.6).

For curves 1 and 2, the polymerization reaction stops before the autoacceleration starts, so the molecular weight has nearly no effect on the evolution of the conversion with time. On the other hand, when the molecular weight is high, the gel effect starts at a lower degree of conversion, probably 0.3 to 0.4 in the present case, leading to a higher final conversion.

Figure 6 shows the molecular weight measured at the peak of the GPC chromatogram, M_{peak} , as a function of the 1-butanethiol concentration. The polydispersity index *IP* is not represented; its value is always in the range of 1.9 to 2.5.

The results for all the polymerization experiments performed during this study are presented on the same graph to show that the molecular weight obtained in our specific experimental conditions is linked to the initial concentration of 1-butanethiol. The presence of the initiator does not affect the molecular weight much as its concentration is always smaller than the concentration of the 1-butanethiol, and the temperature has only secondary effect on the molecular weight partly because of the weakness of the gel effect.

MODELLING THE POLYMERIZATION AT HIGH TEMPERATURE

Previous work on the polymerization of MMA at high temperature has shown that in the absence

Initiation by the impurity	$Im \ p \xrightarrow{k_{di}} 2R^{\bullet}$
Thermal initiation	$2M \xrightarrow{\mathrm{k}_{\mathrm{th}}} 2R^{ullet}$
Initiation by the chain transfer agent	$A \xrightarrow{\mathrm{k}_{\mathrm{dt}}} R^{ullet}$
Initiation	$\stackrel{\mathrm{k_d}}{I \longrightarrow} 2R^{\bullet}$
	$R^{\bullet} + M \xrightarrow{k_i} P_1^{\bullet}$
Propagation	$P_n^{\bullet} + M \xrightarrow{k_p} P_{n+1}^{\bullet}$
Depropagation	$P_n^{ullet} \xrightarrow{\mathrm{k}_{\mathrm{dp}}} P_{n-1}^{ullet} + M$
Termination by disproportionation	$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{\mathbf{k}_{\mathrm{td}}} P_n + P_m$
Termination by combination	$P_n^{\bullet} + P_m^{\bullet} \xrightarrow{\mathbf{k}_{\mathrm{tc}}} P_{n+m}$
Chain transfer to monomer	$P_n^{\bullet} + M \xrightarrow{k_{trm}} P_n + P_1^{\bullet}$
Chain transfer to the chain transfer agent	$P_n^{\bullet} + A \xrightarrow{\mathbf{k}_{trt}} P_n + A^{\bullet}$

 Table I
 Kinetic Scheme for the Bulk Polymerization of MMA at High

 Temperature
 Image: Comparison of MMA at High

of initiator, the obtained conversion may be high. It has been impossible to neglect initiation reactions that could go unnoticed at a lower temperature.^{5,6} A mathematical model has been adapted to simulate the polymerization. It included the thermal initiation rate constant k_{th} , and the initiation rate constants by impurities and chain transfer agent, k_{di} and k_{dt} . These rate constants and the concentration of the impurities were specific to the purification and storage conditions of our monomer.

The kinetic scheme of the polymerization is presented in Table I and the balance equations for an isothermal perfectly mixed reactor is presented in Table II. The reaction rate constants are summarized in Table III. The quasi-steady-state approximation is not made, and the contraction in volume is taken into account. The molecular weights were calculated using the method of moments. It is also necessary to point out that as the glass effect is absent, the propagation rate constant is held constant ($k_p = k_{p0}$).

stant is held constant $(k_p = k_{p0})$. So, as the decomposition rate constant of the DTBP, k_d , is known,⁷ we are able to calculate the monomer conversion and the molecular weight during the polymerization stage, in which the classical kinetics applies, that is, before the gel effect. This is illustrated in Figure 7, in which the conversion is successfully predicted before the au-



Figure 7 Predicted conversion versus time curves for the bulk polymerization of MMA. The curves are calculated from classical kinetics without the gel effect. $I_0 = 7 \times 10^{-4}$ mol/L; $A_0 = 20.5 \times 10^{-3}$ mol/L; $T_c = 120$ and 132°C.

Table II Balance Equations for the Bulk Polymerization of MMA

$$\frac{d[I]}{dt} = -\mathbf{k}_{d}[I] - [I]\frac{1}{V}\frac{dV}{dt}$$
(3)
$$\frac{d[Imp]}{dt} = -\mathbf{k}_{di}[Imp] - [Imp]\frac{1}{V}\frac{dV}{dt}$$
(4)

$$\frac{d[M]}{dt} = -\mathbf{k}_{\rm p}[M]\lambda_0 - \mathbf{k}_{\rm trm}[M]\lambda_0 + \mathbf{k}_{\rm dp}\lambda_0 - [M]\frac{1}{V}\frac{dV}{dt}$$
(5)

$$\frac{d[A]}{dt} = -\mathbf{k}_{trt}[A]\lambda_0 - \mathbf{k}_{dt}[A] - [A]\frac{1}{V}\frac{dV}{dt}$$
(6)

$$\frac{d\lambda_0}{dt} = 2f\mathbf{k}_{\rm d}[I] + 2\mathbf{k}_{\rm di}[Imp] + \mathbf{k}_{\rm dt}[A] + \mathbf{k}_{\rm th}[M]^2 - \mathbf{k}_{\rm t}\lambda_0^2 - \lambda_0 \frac{1}{V}\frac{dV}{dt}$$

$$\tag{7}$$

$$\frac{d\lambda_1}{dt} = 2f\mathbf{k}_{\rm d}[I] + 2\mathbf{k}_{\rm di}[Imp] + \mathbf{k}_{\rm dt}[A] + \mathbf{k}_{\rm th}[M]^2 + \mathbf{k}_{\rm p}[M]\lambda_0 - \mathbf{k}_{\rm dp}\lambda_0 + (\mathbf{k}_{\rm trm}[M] + \mathbf{k}_{\rm trt}[A])(\lambda_0 - \lambda_1) - \mathbf{k}_{\rm t}\lambda_0\lambda_1 - \frac{\lambda_1}{V}\frac{dV}{dt}$$
(8)
$$\frac{d\lambda_2}{d\lambda_2} = 22\left[II + 2\mathbf{k}_{\rm d}[I] + \mathbf{k}_{\rm th}[A] + \mathbf{k}_{\rm th}[A]^2 + 4\left[III - \mathbf{k}_{\rm th}(A) + (\mathbf{k}_{\rm trm}[M] - \mathbf{k}_{\rm trt}[A])(\lambda_0 - \lambda_1) - \mathbf{k}_{\rm t}\lambda_0\lambda_1 - \frac{\lambda_1}{V}\frac{dV}{dt} \right]$$
(8)

$$\frac{d\lambda_2}{dt} = 2f\mathbf{k}_{\rm d}[I] + 2\mathbf{k}_{\rm di}[Imp] + \mathbf{k}_{\rm dt}[A] + \mathbf{k}_{\rm th}[M]^2 + (\mathbf{k}_{\rm p}[M] - \mathbf{k}_{\rm dp})(2\lambda_1 + \lambda_0)$$

$$\frac{d\mu_0}{dt} = \left(\mathbf{k}_{\rm td} + \frac{1}{2}\,\mathbf{k}_{\rm tc}\right)\lambda_0^2 + \left(\mathbf{k}_{\rm trm}[M] + \mathbf{k}_{\rm trt}[A]\right)\lambda_0 - \frac{\mu_0}{V}\frac{dV}{dt} \tag{10}$$

$$\frac{d\mu_1}{dt} = \mathbf{k}_t \lambda_0 \lambda_1 + (\mathbf{k}_{trm}[M] + \mathbf{k}_{trt}[A]) \lambda_1 - \frac{\mu_1}{V} \frac{dV}{dt}$$
(11)

$$\frac{d\mu_2}{dt} = \mathbf{k}_t \lambda_0 \lambda_2 + \mathbf{k}_{tc} \lambda_1^2 + (\mathbf{k}_{trm}[M] + \mathbf{k}_{trt}[A]) \lambda_1 - \frac{\mu_2}{V} \frac{dV}{dt}$$
(12)

$$\frac{dX}{dt} = (\mathbf{k}_{\rm p} + \mathbf{k}_{\rm trm})\lambda_0(1+X) - \mathbf{k}_{\rm dp}\frac{M_m}{d_m}(1+\varepsilon X)\lambda_0$$
(13)

$$-\frac{1}{V}\frac{dV}{dt} = -\frac{dX}{dt}\frac{\varepsilon}{(1+\varepsilon X)} = -(\mathbf{k}_{\mathrm{p}} + \mathbf{k}_{\mathrm{trm}})\varepsilon \left(\frac{1-X}{1+\varepsilon X}\right)\lambda_{0} + \mathbf{k}_{\mathrm{dp}}\frac{\varepsilon}{[M]_{0}}\lambda_{0}$$
(14)
$$\overline{M} = -M^{-\lambda_{1} + \mu_{1}}$$
(15)

$$M_n - M_m \frac{\lambda_0 + \mu_0}{\lambda_0 + \mu_0}$$

$$\overline{M_w} = M_m \frac{\lambda_2 + \mu_2}{\lambda_0 + \mu_0}$$
(16)

$$IP = \frac{(\lambda_2 + \mu_2)(\lambda_0 + \mu_0)}{(\lambda_1 + \mu_1)^2}$$
(17)

toacceleration starts and becomes unrealistic after.

To calculate the evolution of the degree of conversion over the entire course of the reaction, we have to take into account the autoacceleration phenomenon, that is, to express the variation of the termination rate constant as a function of the relevant parameters: temperature, conversion, and molecular weight.

We have selected several published models where the evolution of k_t is gradual from the very beginning of the polymerization; that is, it does not present a critical break point.

In the model developed by Chiu et al. 8 (the CCS model), the rate constant for termination $k_{\rm t}$ is

expressed in terms of both a reaction limited term k_{t0} and a diffusion-limited one. k_{t0} is the true kinetic rate constant, and the second term is expressed using three model parameters.⁸ A set of correlations has been proposed by Kumar and Gupta⁹ to improve the agreement between calculation and experiment.

The model of Achilias and Kiparissides¹⁰ follows the approach of CCS but replaces the parameters by available data on physical and transport properties of the monomer and polymer. Only one unknown parameter remains.

In his recent model, $Panke^{11}$ has adopted the formulation of k_t with a chemical contribution and a diffusion contribution depending on the free

Table III Kinetic Rate Constants Used in the Model

Kinetic rate constant for the MMA polymerization

$\begin{split} k_{p} &= k_{p0} = 4.92 \times 10^{5} exp(-2191/T) \\ k_{dp} &= 6.48 \times 10^{11} exp(-9185/T) \\ k_{t0} &= 9.8 \times 10^{7} exp(-353/T) \\ k_{tc}/k_{td} &= 3.956 \times 10^{-4} exp(2065/T) \\ k_{d} &= 2.8 \times 10^{14} exp(-17617/T) \\ f &= 1 \\ k_{th} &= 9.54 \times 10^{-2} exp(-10900/T) \\ k_{di} &= 1.93 \times 10^{10} exp(-12560/T) \\ k_{dt} &= 6.78 \times 10^{7} exp(-15480/T) \end{split}$	$(1 \text{ mol}^{-1} \text{ s}^{-1}) \\ (\text{s}^{-1}) \\ (1 \text{ mol}^{-1} \text{ s}^{-1}) \\ \\ \\ (\text{s}^{-1}) \\ \\ (1 \text{ mol}^{-1} \text{ s}^{-1}) \\ (\text{s}^{-1}) \\ (\text{s}^{-1}) \\ \end{array}$	Chiu et al. ⁸ Chiu et al. ⁸ Chiu et al. ⁸ Chiu et al. ⁸ Brandup and Immergut ⁷ This work Rimlinger and coworkers ^{5,6} Rimlinger and coworkers ^{5,6} Rimlinger and coworkers ^{5,6}
$k_{\rm trm}/k_{\rm p} = 2.024 \exp(-4006/T)$	—	Rimlinger and coworkers ^{5,6}
$ m k_{trt} = 8.93 imes 10^6 m exp(-3567/T)$	$(1 \text{ mol}^{-1} \text{ s}^{-1})$	Rimlinger and coworkers ^{5,6}
Gel effect constitutive equations $\begin{aligned} & \frac{1}{k_{t}} = \frac{1}{k_{t0}} + \frac{1}{k_{t0} \exp[\beta(X_{c} - X)]} \\ & \beta = -17.85 + 0.5756 \ T - 0.002519 \ T^{2} \\ & X_{c} = 4.289 - 0.05799 \ T + 0.00020422 \ T^{2} \end{aligned}$	+ 0.11 Ln(1000 A_0 + 3)	
Other parameters used $\varepsilon = -(0.2256 + 4.81 \times 10^{-4} T + 4.1 \times 10^{-4} M_m = 100.13 \text{ g mol}^{-1}$	$)^{-4} T^2)$	$\mathrm{Stickler}^{12}$

volume of the system. The model has one fixed and four adjustable parameters and takes account of the presence of solvent, chain transfer agent, and prepolymer.

We have made an attempt to apply these models to our experimental data but without success. The calculated values did not fit the experiments: the predicted gel effect was too sharp. This is not surprising as these models are developed for temperature below 100°C and should probably be deeply modified and adapted to describe the features of the reaction at a high temperature.

Finally, we decided to use the empirical correction function for k_t proposed by Fleury^{1,2} and which has proved its efficiency to correctly describe the attenuated gel effect that we observe for above- T_g polymerizations [eq. (18)], as follows:

$$\frac{1}{k_{t}} = \frac{1}{k_{t0}} + \frac{\gamma}{\exp(\alpha - \beta X)}$$
(18)

where α and β are adjustable parameters, and $\gamma = 1$.

We have rewritten the expression of Fleury in order to facilitate the estimation of the two adjustable parameters [eq. (19)], as follows:

$$\frac{1}{k_{t}} = \frac{1}{k_{t0}} + \frac{1}{k_{t0} \exp[\beta(X_{c} - X)]}$$
(19)

Rather than α , we use X_c as a model parameter in order to facilitate the optimization. The relationship between X_c , α , β , and k_{t0} is the following [eq. (20)]:

$$X_c = \frac{\alpha - \ln k_{t0}}{\beta}$$
(20)

The experimental data presented in the first part of this work is used to determine the parameters of the model. The system of nonlinear differential equations in Table II is integrated by a fourth-order Runge-Kutta method. For each polymerization run, we use a Simplex method to determine the parameters X_c and β that gives the best fitting of the experimental degree of conversion. Then, the only remaining task is to link the parameters to the operating variables of the polymerization. It appears that X_c is a function of temperature and molecular weight, while β depends only on the temperature. For the sake of simplicity, we have chosen to express X_c and β as a function of the initial concentration of 1-butanethiol and not directly of the molecular weight. This is possible because the molecular weight is controlled mainly by the chain transfer agent in our specific experimental conditions as we have seen before (Fig. 6). The correlated values of X_c and β are as follows:



Figure 8 The parameter β of the expression of k_t is presented as a function of temperature for different concentrations of chain transfer agent. $1 \times 10^{-3} < A_0 < 50 \times 10^{-3}$ mol/L. The parameter X_c is presented as a function of the initial concentration of chain transfer agent for different temperatures. At a high temperature, the determination of β and X_c is more hazardous because of the low intensity of the gel effect.

$$\beta = -17.85 + 0.5756T - 0.002519T^2 \quad (21)$$

$$X_c = 4.289 - 0.05799T + 0.00020422T^2 + 0.11 \ln(1000A_0 + 3)$$
 (22)

where T is in degrees centigrade and A_0 is in mol/L.

Figure 8 shows X_c and β represented as a function of T and A_0 . The dispersion of the values observed at high temperature is explained by the fact that the Trommsdorf effect tends to disappear and makes the optimization of the parameters questionable. Since the adjustable parameters are known, it is possible to simulate the polymerization over the entire domain of conversion. The experimental and calculated conver-



Figure 9 Model results (——) and experimental data (symbols) for the bulk polymerization of MMA at different chain transfer agent loadings. $T_c = 150$ °C; $I_0 = 7 \times 10^{-4}$ mol/L.

Table IVComparison of Calculated andExperimental Number-Average MolecularWeight and Polydispersity Index

$\frac{A_{\rm 0}}{(10^{-3}~{\rm mol}~{\rm L})}$	$\bar{M}_{n \ \mathrm{exp}} \ (\mathrm{g \ mol}^{-1})$	$IP_{\rm exp}$	$\bar{M}_{n \ \rm calc} \\ ({\rm g \ mol}^{-1})$	$IP_{\rm calc}$
1 8.9	260,000 70,000	2.47 1.93	247,600 76.500	2.05 2.02
$\begin{array}{c} 20.5 \\ 40 \end{array}$	47,000 24,700	$\begin{array}{c} 2.10\\ 2.14\end{array}$	37,400 19,400	$\begin{array}{c} 2.04 \\ 2.06 \end{array}$

 $T_c = 150$ °C; $I_0 = 7 \times 10^{-4}$ mol L⁻¹.

sion-time curves are presented in Figures 9-11. The continuous lines represent the calculation, and the symbols represent the experimental data. The number-average molecular weight and the polydispersity index data are summarized in Tables IV-VI. The ability of the model to describe the polymerization at high temperature is good. The formulation chosen for the overall termination rate constant allows one to follow the very smooth variation of kt associated with a "weak" gel effect. At higher temperature (Figs. 10 and 11), the model is sensitive enough to account for changes of the concentration of 1-butanethiol that produce only small differences in the conversion versus time curves. The number-average molecular weight is correctly predicted with a tendency to be slightly underestimated. The same remark applies to the polydispersity.

CONCLUSION

Interesting experimental data have been collected on the bulk polymerization of MMA at high



Figure 10 Model results (——) and experimental data (symbols) for the bulk polymerization of MMA at different chain transfer agent loadings. $T_c = 160$ °C; $I_0 = 2 \times 10^{-4}$ mol/L.

Table VComparison of Calculated andExperimental Number-Average MolecularWeight and Polydispersity Index

(10^{-3} mol/L)	$\bar{M}_{n \ \mathrm{exp}} \ (\mathrm{g \ mol}^{-1})$	IP_{exp}	$\bar{M}_{n \ \rm calc} \\ ({\rm g \ mol}^{-1})$	$IP_{\rm calc}$
$1\\9.8\\40$	292,800 81,500 22,500	$2.52 \\ 2.05 \\ 2.22$	228,400 70,200 21,000	2.08 2.00 2.00

 $T_c = 160$ °C; $I_0 = 2 \times 10^{-4}$ mol/L.

temperature. It is found that the Trommsdorf effect is attenuated when the polymerization temperature increases or when the molecular weight of the macrospecies decreases. In the same time, the onset of the autoacceleration is shifted to higher conversion levels.

For commercial production systems, one main advantage of running the bulk polymerization of the MMA at high temperature is the reduction of the viscosity of the polymer solution that facilitates the mixing operation and heat removal. On the other hand, the major technical problem is that the reaction vessel must be pressurized. However, several advantages may balance the constraint of operating above the boiling point of the monomer.

One of these is that the polymerization is so fast that it becomes possible to use very small concentrations of initiator. In this case, the molecular weight cannot remain exclusively controlled by the initiator loading as its value would be too high to be of industrial interest. As a consequence, the use of a chain transfer agent is necessary and proves very efficient in the present study.

In the scope of acquiring a better understanding of the factors that influence the kinetics of the polymerization, it is of particular interest to have an additional degree of freedom in the investigation of the effect of the molecular weight on the gel effect. The use of a chain transfer agent allows to dissociate the obtention (achievement) of the desired molecular weight from the kinetic features of the polymerization reaction, that is, the rate of polymerization, the autoacceleration, and the depletion of the initiator. Of course, this is true only if the initiator concentration is small compared to the chain transfer agent loading. This is the case in this study, and we have been able to clearly observe the influence of the molecular weight on the onset and intensity of the gel effect.



Figure 11 Model results (——) and experimental data (symbols) for the bulk polymerization of MMA at different chain transfer agent loadings. $T_c = 168$ °C; $I_0 = 4 \times 10^{-4}$ mol/L and $I_0 = 10 \times 10^{-4}$ mol/L.

Table VIComparison of Calculated andExperimental Number-Average MolecularWeight and Polydispersity Index

A_0 (10 ⁻³ mol/L)	$\bar{M}_{n \exp} \\ (\mathrm{g \ mol}^{-1})$	${IP}_{\mathrm{exp}}$	$\bar{M}_{n \ \rm calc} \ ({\rm g \ mol}^{-1})$	$IP_{\rm calc}$
$T_c = 168^{\circ}\text{C}; I_0$	$= 4 \times 10^{-1}$	⁴ mol/L		
8.9	69,100	1.92	66,600	2.00
32.1	25,600	2.23	23,800	2.00
$T_c = 168^{\circ}\text{C}; I_0$	= 10 × 10	$^{-4}$ mol 1	L	
8.9	85,500	1.93	60,200	2.00
32.1	30,160	2.03	22,600	2.00

The combination of the following features of the attenuated gel effect and the small amount of initiator compared to chain transfer agent gives access to a wide range of molecular weights without affecting the broadness of the distribution. We obtained number-average have molecular weights ranging from 20×10^3 to 700×10^3 g mol^{-1} .

Finally, we have made a successful attempt to simulate our polymerization experiments. The models of the gel effect available in the literature are not adapted to describe the low intensity of the autoacceleration. The formulation of the termination rate constant used here, despite being empirical, allows one to fit very well the evolution of the conversion with time and predict the molecular weight of the polymer formed. This is particularly interesting if the model is applied to predict the behavior of an industrial reactor.

NOMENCLATURE

A	chain transfer agent
A_0	initial concentration of 1-butanethiol $(mol \ L^{-1})$
d_m, d_p	density of the monomer and of the polymer (kg m^{-3})
I_0	initial initiator concentration (mol L^{-1})
Imp	impurity
IP	polydispersity index
k _d	rate constant for the dissociation of the initiator (s^{-1})
k _{di}	rate constant for the dissociation of the impurity (s^{-1})
k _{dp}	depropagation rate constant (s^{-1})
k _{dt}	apparent rate constant for the initiation by chain transfer agent (s^{-1})
k_p, k_t	rate constant for termination and propagation $(1 \text{ mol}^{-1} \text{ s}^{-1})$
k_{tc}, k_{td}	rate constant for termination by combination and disproportionation (1 $mol^{-1} s^{-1}$)
\mathbf{k}_{th}	rate constant for the thermal initiation $(1 \ mol^{-1} \ s^{-1})$
k _{trm}	rate constant for chain transfer to the monomer $(1 \text{ mol}^{-1} \text{ s}^{-1})$
$\mathbf{k}_{\mathrm{trt}}$	rate constant for chain transfer to the mercaptan $(1 \text{ mol}^{-1} \text{ s}^{-1})$
т	mass of reaction mixture (kg)

M	monomer
M_{m}	molecular

- M_m ar weight of the monomer (kg mol^{-1})
- \bar{M}_n, \bar{M}_w number-average and weight-average molecular weights (kg mol^{-1})
- $M_{\rm peak}$ molecular weight at the peak of the chromatogram (kg mol⁻¹)
- initial number of moles of monomer n_{M0}, n_M and number at time ttime (s)
- Ttemperature of the reaction mixture (\mathbf{K})
- $T_c \\ T_g \\ V$ temperature set-point (K)
 - glass transition temperature (K)
 - volume of the reaction mass (m^3)
- V_m, V_p volume of the monomer and of the polymer (m³)
- Χ monomer conversion
- X_{c} model parameter

α	model parameter (Fleury)
β	model parameter
З	volume contraction factor
`	hthe means and of the meaning and

- kth moment of the growing radicals (k λ_k $= 0, 1, 2) \pmod{L^{-1}}$
- *k*th moment of the dead polymer μ_k chains $(k = 0, 1, 2) \pmod{L^{-1}}$

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