

ORIGINAL ARTICLE

Kinetic modeling of bulk free-radical polymerization of methyl methacrylate

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The free-radical bulk polymerization of many monomers is characterized by a sudden rise in the rate of polymerization, a phenomenon called autoacceleration. Many mathematical models have been developed to describe this phenomenon. In this paper, the development of a new kinetic model is described. The model very successfully describes experimental data obtained by differential scanning calorimetry of the bulk free-radical polymerization of methyl methacrylate. The proposed model is composed of two contributions to the conversion of the monomer, one originating from polymerization according to the classical theory of radical polymerization and the other originating from polymerization during the autoacceleration. The rate constant of the autoacceleration (second contribution) is about eightfold higher than the rate constant of the first-order reaction (first contribution).

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INTRODUCTION

Free-radical bulk polymerization is a versatile process because it can be carried out on many monomers and at a wide range of temperatures.¹ It is well-known that the free-radical bulk polymerization of vinyl monomers (derivatives of acrylic and methacrylic acids, vinyl acetate, styrene, ethylene, and so on) is characterized by the autoacceleration phenomenon. The free-radical polymerization of these monomers can be explained by the classical theory up to a certain monomer conversion. After this critical monomer conversion, the autoacceleration of the polymerization appears. The onset of the autoacceleration is defined as the moment when the polymerization rate departs from the value expected according to the classical theory of free-radical polymerization.^{2–4} The onset and the intensity of the autoacceleration are determined by the type of monomer, type and concentration of initiator, temperature and other reaction conditions. This phenomenon is particularly apparent in the bulk polymerization of methyl methacrylate (MMA) and is highly undesirable in industrial applications, as it may lead to the thermal runaway of the process, thus causing depolymerization and the plugging of equipment.^{5–7}

A number of theoretical explanations and kinetic models were developed in order to explain the phenomenon of autoacceleration. The first models^{8–10} considered only the decrease of the chain termination rate constant as a result of an increased viscosity of the reaction system. Later efforts^{11,12} focused on investigating changes of both the chain propagation and chain termination rate constants due to changes in the viscosity. Later still, theories^{13,14} attempted to explain the occurrence of autoacceleration in the rate

of polymerization as a result of entanglement of growing macromolecular chains. O'Driscoll introduced the gel effect index as a measure of the severity of the kinetic effect.¹⁵ The model developed by Chiu *et al.*⁷ used the conversion, temperature and weight-average molecular weight to determine the relative influence of the reaction and the diffusion on the rate of polymerization. Free volume theories^{16,17} considered the decrease in volume on disposal for the movement of growing macromolecules. Kargin and Kabanov¹⁸ and Korolev *et al.*¹⁹ suggested that the autoacceleration phenomenon could be explained by the supramolecular organization of the liquid MMA. Roschupkin *et al.*²⁰ found that poly(methyl methacrylate) (PMMA) grains are formed during the polymerization of MMA and suggested that the autoacceleration is a consequence of the growth of the grain surface.

A model written in terms of the moment generating function and in terms of the moments of molecular weight distribution, and completed with relations that quantify the gel and glass effects was successful in describing MMA bulk polymerization.²¹ A mathematical model was developed for the batch MMA polymerization reactor system by Rafizadeh²² The model includes the complete process, therefore, using the heaters and water valve signals, which make it possible to calculate the process states. Hence, this model is suitable to determine an optimal temperature trajectory during the course of the polymerization and control strategy. More recently, a simple semi-empirical model relating the degree of conversion and the polymerization rate to the time and temperature was developed.¹ The model parameters were calculated from isothermal differential scanning calorimetry (DSC) experiments and then successfully

applied to predict monomer conversion in non-isothermal experiments. Sangwai *et al.*²³ used an empirical model that involves only monomer conversion and temperature, and accounts for the gel and the glass effect to describe the polymerization of MMA in a rheometer-reactor assembly in isothermal and non-isothermal conditions. During the last decade, successful results were achieved through the use of the pulsed laser polymerization technique to determine the values of k_p and k_t for free-radical polymerization.²⁴ Barner-Kowollik *et al.*²⁵ have presented an extensive review of the experimental methods used to study the dependence of k_t on the conversion and chain length. Buback *et al.*²⁶ have used this technique to obtain the chain length dependence of k_t for MMA polymerization.

The existing theories, however, have not been completely verified experimentally. Their main shortcoming is that they take only the onset of acceleration as a characteristic point on the polymerization rate vs time curve. We have shown that there are some additional characteristic points in the case of methyl-², ethyl-³, butyl³ dodecyl-methacrylates²⁷ and the polymerization of styrene:²⁸ the maximum polymerization rate and the two inflection points before and after that maximum.

In the current paper, we have focused on determining the existence of these characteristic points, as well as on testing a mathematical model of the free-radical bulk polymerization developed earlier by our research group and successfully tested on the polymerization of styrene.²⁸ Experimental data were obtained by using DSC to follow the bulk free-radical polymerization of MMA at different temperatures.

MATERIALS AND METHODS

MMA monomer (MMA, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was washed two times with 10% sodium hydroxide solution to remove the inhibitor. Then, the MMA was washed two times with distilled water, dried over anhydrous calcium chloride and vacuum distilled. Initiator 2,2'-azobisisobutyronitrile (AIBN, Merck, Darmstadt, Germany) was recrystallized from methanol before usage. A solution of 0.5 wt.% AIBN in MMA was prepared. Approximately 5–10 mg of the solution was placed in a hermetic aluminum DSC pan and sealed with an aluminum lid. The bulk polymerization of MMA was performed in a Q20 DSC (TA Instruments, New Castle, DE, USA) under isothermal conditions at 60, 70, 80 and 90 °C. Every experiment was repeated three times. The temperature and heat flow scales were calibrated using the melting of high-purity indium. Nitrogen was used as a purge gas with a flow rate of 50 cm³ min⁻¹.

RESULTS AND DISCUSSION

Figure 1 shows the DSC thermograms of MMA free-radical bulk polymerization at different temperatures. Three characteristic moments can clearly be observed in Figure 1: the onset of acceleration (point M), the maximum of the polymerization rate (point S) and the

end of polymerization (point K).^{2,3} Point M was determined as the minimum and point S as the maximum in the DSC thermogram. Point K was determined as the moment when the isothermal DSC curve becomes horizontal.

To find the monomer conversion degree the following formula was applied:

$$X = \frac{\int_0^{\tau} (dH/d\tau) d\tau}{\int_0^{\tau_K} (dH/d\tau) d\tau + H_D} \quad (1)$$

where X is the monomer conversion, $X = (C_{M0} - C_M) / C_{M0}$; C_{M0} and C_M are the initial monomer concentration and concentration after time τ , respectively; dH is the heat evolved by polymerization during an infinitesimal time ($d\tau$); τ_K is the time required to achieve point K; H_D is the heat evolved during polymerization of an unreacted monomer left after point K as determined by dynamic DSC measurement. The conversion of MMA at different temperatures is shown in Figure 2.

The conversion vs time curves of the MMA polymerization exhibit portions that have an 'S' shape, characteristic for autoacceleration. The final conversion of MMA has higher values at the higher temperatures.

The rate of polymerization, $R_{pol} = dX/d\tau$, is equal to the slope of the conversion vs time curve. The acceleration, $dR_{pol}/d\tau = d^2X/d\tau^2$, is equal to the slope of the R_{pol} vs time curves (Figure 3). The polymerization of MMA exhibits the following characteristic points:² the onset of acceleration (M), the maximum acceleration (P) and the

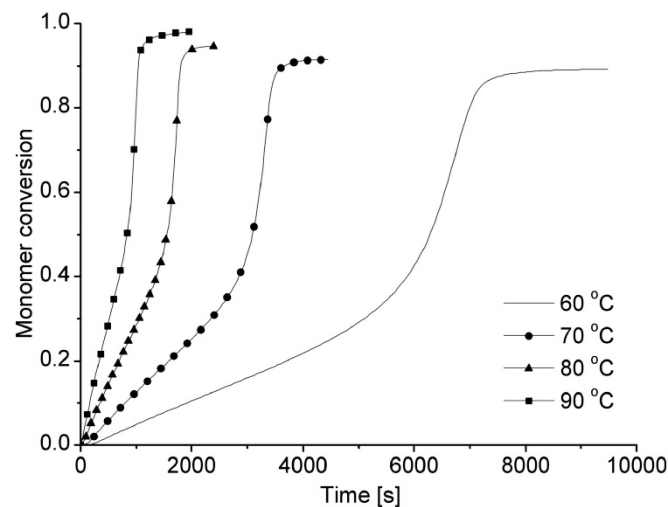


Figure 2 MMA conversion vs time at different temperatures.

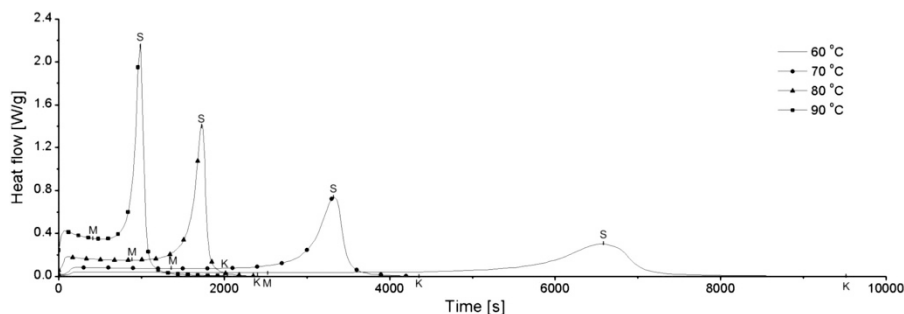


Figure 1 DSC thermograms of MMA free-radical polymerization at different temperatures.

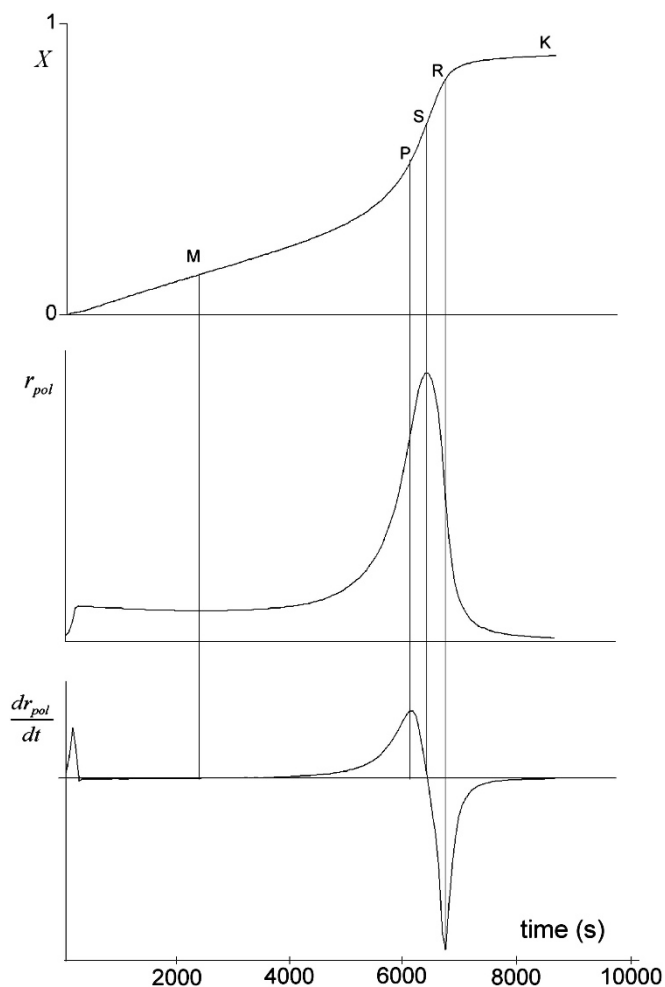


Figure 3 Characteristic points on the conversion (X), rate of polymerization (r_{pol}) and acceleration ($dr_{pol}/d\tau$) vs time (τ) curves obtained by transformation of the DSC curve of MMA polymerization at 60 °C.

maximum polymerization rate (S), preceded by the deceleration stage with minimum (R) and final conversion (K).

The time and MMA conversions, required to achieve the characteristic points, are given in Table 1. The conversion X_M at the onset of the autoacceleration increases as the polymerization temperature increases, in accordance with published data.²

Kinetic model

Looking at Figure 2, three regions can be observed during the polymerization of MMA. The first is up to point M. The second is the acceleration portion from point M to point S. The third is the deceleration from point S to point K. A potential kinetic model should fit the conversion vs time curves, but it should also exhibit the derivatives ($dX/d\tau$) and ($d^2X/d\tau^2$) that resemble the shape of the corresponding curves derived from the experimental results (Figure 3). A potential model should fulfill the following conditions: conversion starts from zero ($\tau = 0, X = 0$), the first derivative ($dX/d\tau$) has a local minimum (M), then reaches the first inflection point (P) followed by a maximum (S) and second inflection point (R), becoming horizontal (K) at the end.

It is generally accepted that the first part of the conversion vs time curve can be explained by the classical free-radical polymerization. Hence, the polymerization rate R_{pol} in that part can be expressed by

Table 1 Time and MMA conversion, necessary to achieve characteristic points (determined from DSC curves)

T (°C)	Point M		Point P		Point S		Point R		Point K	
	τ_M (s)	X_M	τ_P (s)	X_P	τ_S (s)	X_S	τ_R (s)	X_R	τ_K (s)	X_K
60	2520	0.133	6371	0.530	6732	0.688	7068	0.826	9480	0.892
60	2460	0.142	6262	0.535	6571	0.676	6889	0.815	8880	0.892
60	2340	0.123	6466	0.542	6840	0.714	7085	0.819	8882	0.888
70	1530	0.197	3193	0.556	3360	0.679	3633	0.856	4530	0.924
70	1530	0.193	3217	0.599	3330	0.734	3427	0.843	4440	0.915
70	1440	0.181	3249	0.586	3390	0.734	3498	0.844	4980	0.919
80	876	0.247	1709	0.650	1764	0.773	1805	0.858	3192	0.951
80	852	0.244	1686	0.668	1740	0.801	1769	0.867	2436	0.947
80	816	0.238	1688	0.657	1738	0.776	1778	0.859	2438	0.953
90	542	0.308	963	0.674	992	0.757	1030	0.872	1980	0.978
90	548	0.314	952	0.678	988	0.801	1022	0.877	2010	0.981
90	540	0.306	966	0.695	990	0.786	1017	0.881	2070	0.975

Abbreviations: DSC, differential scanning calorimetry; MMA, methyl methacrylate.

the well-known equation (2a).²⁹ The reaction rate is first order with respect to the monomer and an order of 0.5 with respect to the initiator concentration.

$$R_{pol1} = -\frac{dC_M}{d\tau} = C_{M0} \frac{dX_1}{d\tau} = k_{pol,1} C_M C_I^{0.5} = k_{pol} C_{M0} (1 - X_1) C_I^{0.5} \quad (2a)$$

Here, X_1 is the conversion of a part of the monomers that polymerize according to the classical theory of polymerization and $k_{pol,1}$ is the corresponding polymerization rate constant; C_I is the initiator concentration after time τ . It is usually supposed that there is a negligible change of the initiator concentration during the polymerization, that is, $C_I = C_{I0} = \text{const}$. Hence, the rate of polymerization is described by the equation (2b):

$$\frac{dX_1}{d\tau} = k_1 \cdot (1 - X_1) \quad (2b)$$

where $k_1 = k_{pol,1} C_I^{1/2}$ is the rate constant for the first-order reaction.

All the theories of the autoacceleration in the rate of polymerization assume that the polymer produced during the autoacceleration stage has a catalytic effect on the polymerization. Hence, we propose that, in that stage, the rate of polymerization depends not only on the concentration of the residual monomer M but also on the amount of the created polymer P, that is, equation (3a). This equation can easily be transformed to equation (3b).

$$R_{pol2} = C_{M0} \frac{dX_2}{d\tau} = k_{pol,2} C_M C_P C_I^{0.5} \quad (3a)$$

$$\frac{dX_2}{d\tau} = k_2 \cdot X_2 \cdot (1 - X_2) \quad (3b)$$

where X_2 is the conversion of a portion of the monomers that polymerize according to the autoacceleration and deceleration mechanisms of polymerization and $k_2 = k_{pol,2} C_{M0} C_I^{1/2}$ is the corresponding polymerization rate constant. It should be noted that equation (3b) is a parabola that has a maximum. Hence, it can be used to describe both the acceleration and deceleration portions of the polymerization rate vs time curves.

After integration and rearrangement, equations (2b) and (3b) become (4) and (5), respectively:

$$X_1(\tau) = 1 - e^{-k_1\tau} \quad (4)$$

$$X_2(\tau) = \frac{1}{1 + e^{-k_2(\tau - \tau_{2\max})}} \quad (5)$$

where $\tau_{2\max}$ is the time required to achieve the maximum rate of the autoacceleration stage.

Equation (4) and equation (5) are conversions according to classical first-order polymerization and acceleration, respectively. At the end of the polymerization, the achieved final conversion X_K consists of two fractions: a is the monomer fraction polymerized by autoacceleration (that is, equation 5) and $(X_K - a)$ is the monomer fraction polymerized by a first-order reaction (that is, equation 4). Based on these assumptions, the dependence of the conversion on time can be presented by a mathematical model (equation 6). The first addend corresponds to the first-order reaction and the second addend to the autoacceleration reaction. The model takes into account the overlap of these two contributions from the beginning of

the polymerization. This assumption was tested by fitting the model to the experimental data.

$$X(\tau) = (X_K - a) \cdot (1 - e^{-k_1\tau}) + \frac{a}{1 + e^{-k_2(\tau - \tau_{2\max})}} \quad (6)$$

In equation 6, the values for X and τ were obtained from the experimental DSC data, while k_1 , k_2 , a and $\tau_{2\max}$ were calculated using the method of least squares. The values of all calculated parameters are given in Table 2. The proposed mathematical model (equation 6) describes the experimental dependence of the monomer conversion degree on the polymerization time (Figure 4.) The low values of the s.d. and the high correlation coefficients (Table 2) confirm this conclusion. The proposed model includes both addends from the beginning to the end of polymerization. The first addend in equation 6 gives the main contribution to the value of the conversion, in comparison with the negligible contribution of the second addend (Figure 4). The contribution of the second addend becomes important after a certain amount of time after which it increases and becomes dominant in the second portion of the polymerization.

Table 2 The values of the parameters in equation 6 determined for MMA free-radical polymerization at different temperatures (obtained using the method of least squares)

T (°C)	k_1 (s^{-1}) 10^3	k_2 (s^{-1}) $\cdot 10^3$	a	$\tau_{2\max}$ (s)	s.d.	R^a
60	0.344	2.34	0.621	6301	0.027	0.997
60	0.339	2.49	0.600	6202	0.026	0.997
60	0.343	2.45	0.620	6363	0.026	0.997
70	0.661	4.14	0.598	3137	0.028	0.996
70	0.673	5.78	0.588	3136	0.032	0.995
70	0.688	5.23	0.597	3183	0.027	0.997
80	1.27	9.60	0.573	1652	0.028	0.997
80	1.34	10.1	0.574	1619	0.033	0.995
80	1.34	9.84	0.574	1630	0.029	0.996
90	2.26	14.6	0.552	930	0.023	0.998
90	2.30	15.0	0.551	920	0.024	0.998
90	2.34	16.2	0.556	926	0.026	0.997

Abbreviation: MMA, methyl methacrylate.
^aCorrelation coefficient

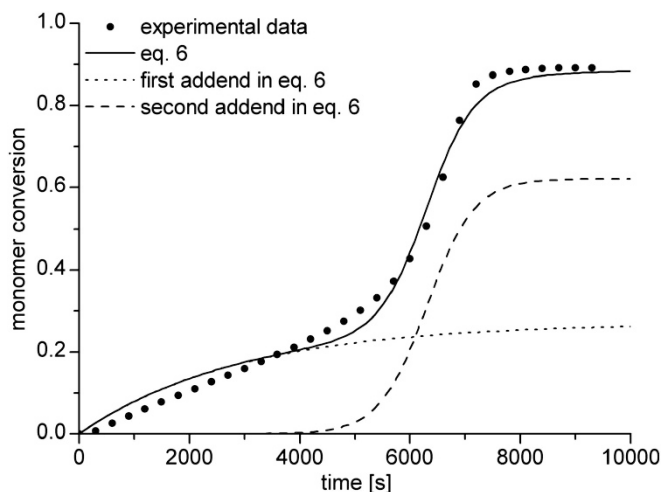


Figure 4 MMA conversion vs time at 60 °C.

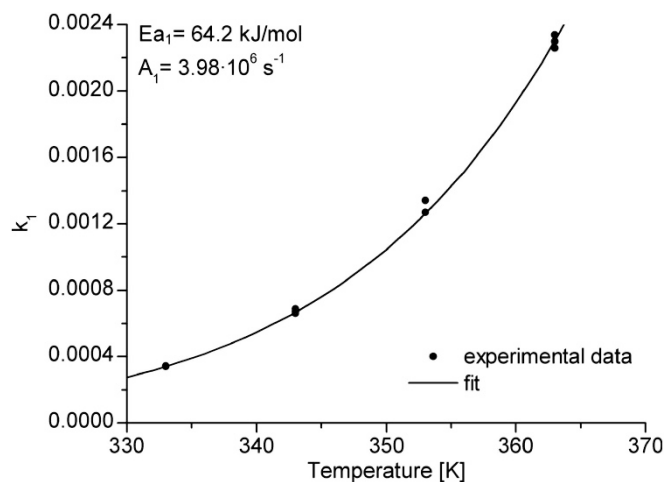


Figure 5 The dependence of k_1 on temperature for MMA polymerization.

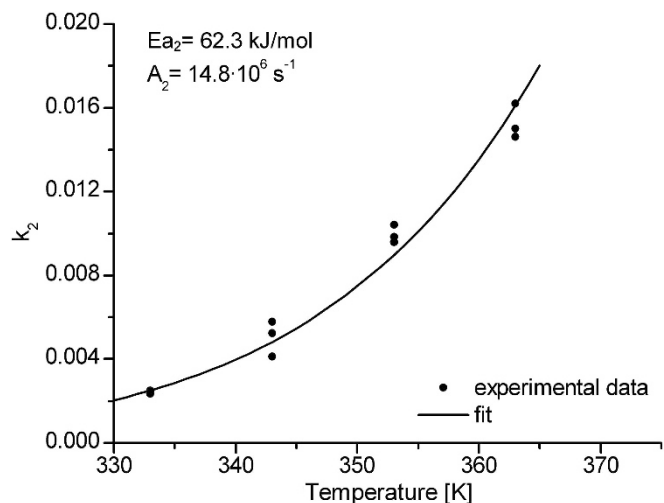


Figure 6 The dependence of k_2 on temperature for MMA polymerization.

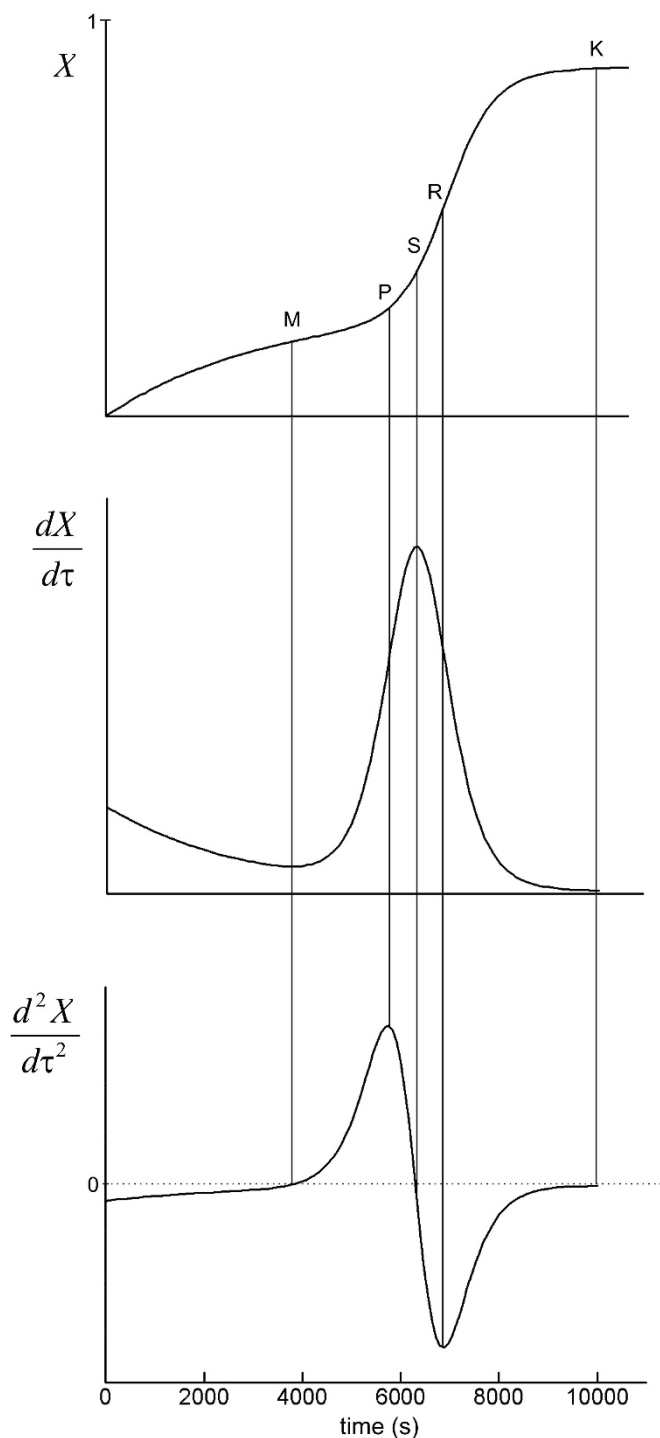


Figure 7 Conversion (X), rate of polymerization ($dX/d\tau$) and acceleration ($d^2X/d\tau^2$) vs time (τ) curves obtained by our mathematical model (equation 6) using parameters from Table 2, describing MMA polymerization at 60 °C.

As shown in Table 2, the values of k_2 are seven to eightfold higher than the values of k_1 . This means that monomers that react by autoacceleration react much faster. The apparent activation energies and pre-exponential factors for the two reaction rate constants were determined according to the Arrhenius law (Figures 5 and 6). The values of the two apparent activation energies are very close but the

pre-exponential factor of autoacceleration is approximately fourfold higher than the first-order reaction.

The conversion (X), rate of polymerization ($dX/d\tau$) and acceleration ($d^2X/d\tau^2$) vs time (τ) curves calculated by our mathematical model (Figure 7) have the same trends as the corresponding curves obtained from the experimental data (Figure 3). The model fulfills all the conditions set during model development and mentioned earlier.

CONCLUSION

The polymerization of MMA exhibits the same characteristic points as the polymerization of other lower alkylmethacrylates^{2,3} and styrene:²⁸ the onset of acceleration (M), the maximum acceleration (P), and the maximum polymerization rate (S), preceded by a deceleration stage with a minimum (R) and a final conversion (K). A kinetic model that has been tested earlier on styrene polymerization²⁸ was adjusted and applied to describe MMA free-radical bulk polymerization. The model is composed of two contributions, one from the first-order reaction and the other from the autoacceleration reaction. Experimental data of MMA conversion dependence on reaction time are well described by the proposed kinetic model. The proposed model provides values for the four parameters. Model parameter a is the monomer fraction polymerized by autoacceleration. Parameter τ_{\max} corresponds to the time required to achieve the maximum rate of polymerization. Parameter k_1 is a compound constant that incorporates three constants: k_i (initiation rate constant), k_p (propagation rate constant) and k_t (termination rate constant), that is, $k_1 = k_p \cdot (k_i \cdot C_1/k_t)^{1/2}$. It is not possible, however, to obtain separate values for these three constants. Parameter k_2 is also a compound constant that describes the polymerization of the monomer fraction by autoacceleration. It can be ascribed to the polymerization of an organized fraction of monomers.^{18,19} This possibility fits into the description of the model discussed previously.^{2,28,30}

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