

ORIGINAL ARTICLE

A new approach for the kinetic modeling of free radical bulk polymerization of styrene

Oskar Bera, Radmila Radičević, Dragoslav Stoiljković, Mirjana Jovičić and Jelena Pavličević

The kinetics of styrene-free radical bulk polymerization was studied by differential scanning calorimetry (DSC). The data obtained from DSC thermograms were used to model and predict the autoacceleration during styrene polymerization and to understand how it is influenced by temperature. The experimental data were well described by the estimated kinetic model. The model included two processes (the first-order reaction and autoacceleration), because they occur simultaneously as two parallel reactions rather than being strictly separated. It was found that the autoacceleration activation energy is approximately four times lower than the energy of the first-order reaction. In addition, the first-order reaction followed by the autoacceleration of the styrene-free radical bulk polymerization occurs simultaneously only between 41.7 and 110.5 °C.

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INTRODUCTION

It is well known that the free radical bulk polymerization of vinyl monomers (derivates of acrylic and methacrylic acids, vinyl acetate, styrene, ethylene and so on) is characterized by the autoacceleration phenomenon.^{1–3} The free radical polymerization of these monomers can be explained by classical theory up to definite conversion. After that conversion, autoacceleration of polymerization occurs. The onset of autoacceleration is the moment when the polymerization rate departs from the value anticipated by the classical theory of free radical polymerization.^{3–7} The onset and the intensity of autoacceleration are determined by the type of monomer, initiator concentration, temperature and other reaction conditions.

Ebdon and Hunt³ used differential scanning calorimetry (DSC) to follow the course of free radical bulk polymerization of styrene and concluded that autoacceleration is less pronounced at 90 °C than at 80 °C and is absent at 100 °C and above. Autoacceleration appeared at about 2% conversion of styrene polymerized at 20 °C for 252 days in the presence of 2,2'-azobisisobutyronitrile.⁸ To explain this autoacceleration, an equation was applied to the kinetic data obtained under the condition of predominant transfer to the monomer. It was concluded that polymer molecules may move by repetition and the mobility of segments decreases with decrease of free volume.⁸ Comparisons of the results obtained for styrene-free radical bulk polymerization with model predictions have quantified the dependence of the gel effect strength on the predominance of chain transfer events.⁹ Cioffi *et al.*¹⁰ performed a rheokinetic study of the bulk-free radical polymerization of styrene with a helical barrel rheometer. The rheokinetic measurements show that autoacceleration in the free radical polymerization of styrene can be reduced when the polymer-

ization is performed at a high screw rotational velocity. Simulation of styrene-free radical polymerization in batch reactors has been performed;¹¹ the model predicts the monomer conversion, number and mass average molecular masses as a function of time. A comprehensive kinetic model was developed for the combined chemical and thermal-free radical polymerization of styrene to predict the styrene polymerization rate and molecular weight distribution of the polystyrene.¹² To determine the steady-state and dynamic behavior of a continuous process, a mathematical model for the free radical polymerization of styrene was developed.¹³

Many theories have been developed to explain the polymerization autoacceleration of styrene and other vinyl monomers.^{4,14–22} According to the origin and reason of the autoacceleration onset, they can be classified as follows: theory of gel effects, theory of entanglement, free volume theory, theory of impenetrable macromolecular coils, theory of polymerization of organized monomer systems and theory of microheterogeneous polymerization. These theories have been reviewed elsewhere.²³

However, the existing theories have not been completely verified experimentally. Their main shortcoming is that they mainly take the onset of acceleration as a characteristic point in polymerization rate vs time curve. We have shown that there are some additional characteristic points in the case of methyl-, ethyl-, butyl- and dodecyl methacrylate polymerization:^{4,5,24} the maximum polymerization rate and the two inflection points before and after that maximum.

The aim of this work was to confirm the existence of these characteristic points and find a suitable mathematical model of the kinetics of styrene-free radical bulk polymerization. The data obtained from DSC thermograms were used to model and predict the

autoacceleration during styrene polymerization and understand how it is influenced by temperature.

MATERIALS AND METHODS

Chemicals

- Styrene (Merck, Darmstadt, Germany) was freed of inhibitor before use. It was washed with 10% aqueous NaOH solution, dried over anhydrous CaCl₂, and distilled under nitrogen and reduced pressure.
- Initiator: 2,2'-azobisisobutyronitrile (Merck), was recrystallized from methanol.

Methods

The bulk polymerization of styrene was performed using a DSC apparatus (TA Instruments, New Castle, DE, USA, Model Q20). Approximately 5 mg of the monomer, containing 1 wt% 2,2'-azobisisobutyronitrile, was put into a hermetic aluminum DSC pan and sealed with a hermetic aluminum lid. Nitrogen was used as purge gas with a flow rate of 50 cm³ min⁻¹. Polymerizations were performed under isothermal conditions at five different temperatures (70, 75, 80, 85 and 90 °C). The amount of polymerized monomer (proportional to the heat evolved during reaction) was calculated from the area between the isothermal DSC curve and the baseline, using the method described in the literature.^{20,25,26} The amount of unreacted monomer was determined by prolonging the polymerization in the dynamic thermal range, from the temperature of isothermal polymerization to 220 °C, at a heating rate of 10 °C min⁻¹.^{20,25}

RESULTS AND DISCUSSION

DSC thermograms of styrene-free radical bulk polymerizations at different temperatures are presented in Figure 1. Three characteristic points are clearly observed: the onset of acceleration (point M), the maximum of the polymerization rate (point S) and the end of polymerization (point K).^{4,5} Point M was determined as the minimum and point S as the maximum in the DSC curve. Point K was determined as the moment when the isothermal DSC curve became horizontal.

To find the monomer conversion degree, equation (1) was used:

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

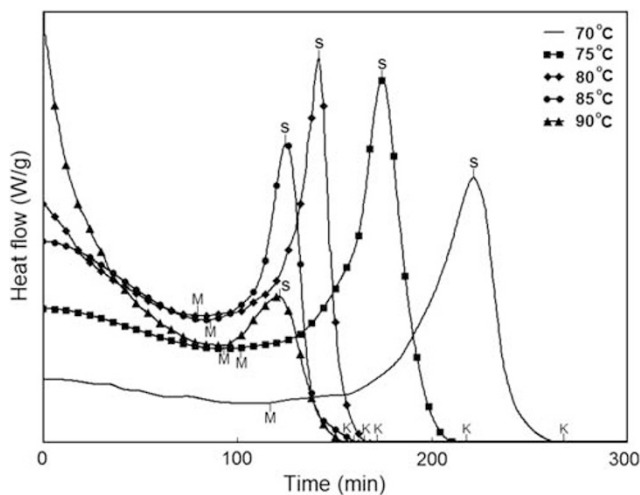


Figure 1 Differential scanning calorimetry (DSC) thermograms of styrene-free radical polymerization at different temperatures (1 wt% 2,2'-azobisisobutyronitrile).

where X is monomer conversion, $X = (C_{M0} - C_M) / C_{M0}$; C_{M0} and C_M are initial monomer concentration and concentration at time τ , respectively; dH is the reaction enthalpy for an infinitesimal polymerization time $d\tau$ (min); τ_K is the time necessary to achieve point K; and H_D is the heat evolved from the polymerization of the unreacted monomer after point K, assigned to the area under the dynamical DSC curve. The dependence of styrene conversion X at different temperatures on the polymerization time is shown in Figure 2.

The conversion vs time curves of styrene polymerization contain a 'S' shape part, which is characteristic of autoacceleration. The rate of polymerization $R_{pol} = dX/d\tau$ is equal to the slope of the conversion vs time curve. Acceleration $dR_{pol}/d\tau = d^2X/d\tau^2$ is equal to the slope of the R_{pol} vs time curves (Figure 3). Styrene polymerization shows the same characteristic points as alkyl methacrylate polymerization:^{4,5} onset of autoacceleration (M), maximum autoacceleration (P) and maximum polymerization rate (S), followed by a deceleration stage with minimum (R) and final conversion (K).

The time and styrene conversions necessary to achieve the characteristic points are given in Table 1. The conversion X_M at the onset of autoacceleration increases with increasing polymerization temperature, in accordance with published data.^{20,27}

Kinetic model

It is necessary to find a kinetic model that fits the conversion vs time curves, and shows the same derivatives ($dX/d\tau$) and ($d^2X/d\tau^2$) as the experimental results (Figure 3).

From Figure 2, it can be seen that the polymerization process consists of three parts: up to point M, autoacceleration from point M to point S and deceleration from point S to point K.

The first part of a conversion vs time curve can be explained by classical free-radical polymerization. Hence, the polymerization rate R_{pol} in that part can be expressed by equation (2). The reaction rate is first order to the monomer and one-half order to the initiator concentration.

$$\begin{aligned} R_{pol} &= \frac{-dC_M}{d\tau} = C_{M0} \cdot \frac{dX_1}{d\tau} = k_{pol,1} \cdot C_M \cdot C_I^{1/2} \\ &= k_{pol,1} \cdot C_{M0} \cdot (1 - X_1) \cdot C_I^{1/2} \end{aligned} \quad (2)$$

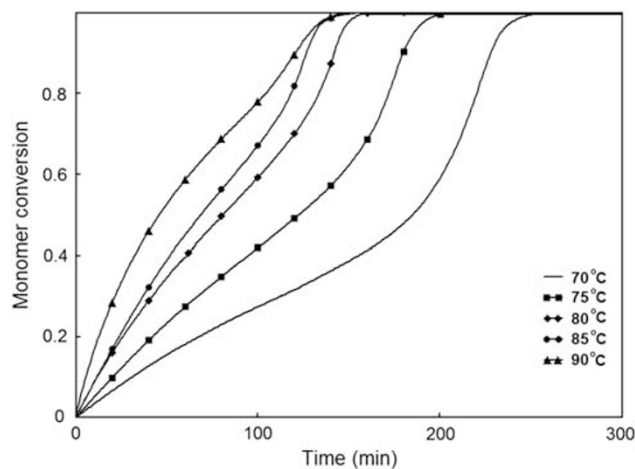


Figure 2 Styrene conversion vs time at different temperatures (1 wt% 2,2'-azobisisobutyronitrile).

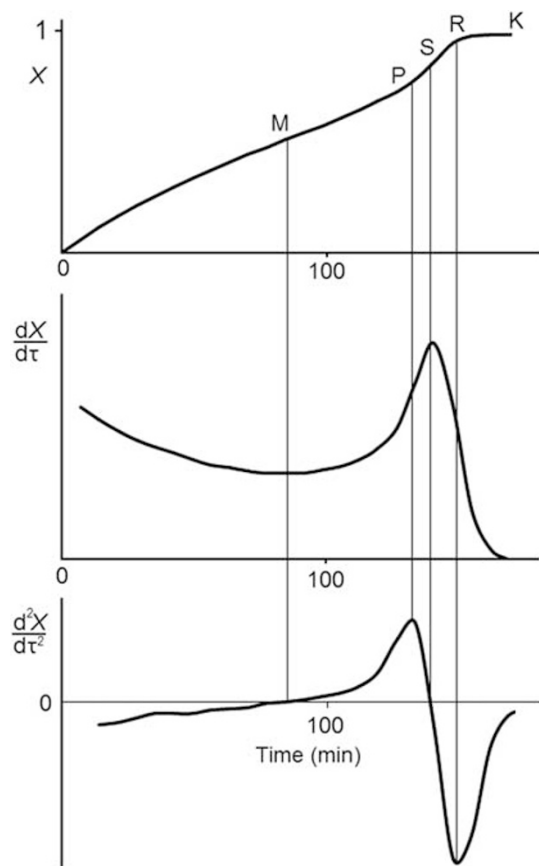


Figure 3 Characteristic points in the conversion (X), rate of polymerization ($dX/d\tau$) and acceleration ($d^2X/d\tau^2$) vs time (τ) curves obtained by transformation of differential scanning calorimetry (DSC) curve of styrene polymerization at 80 °C (1 wt% 2,2'-azobisisobutyronitrile).

Table 1 Time and styrene conversion, necessary to achieve characteristic points (determined from differential scanning calorimetry curves)

T (°C)	τ_M (min)	X_M	τ_P (min)	X_P	τ_S (min)	X_S	τ_R (min)	X_R
70	112	0.30	211	0.69	220	0.81	229	0.91
75	91	0.39	167	0.75	174	0.84	181	0.91
80	82	0.51	132	0.78	142	0.90	147	0.96
85	84	0.58	119	0.81	125	0.88	132	0.96
90	92	0.74	108	0.82	121	0.90	134	0.97

Abbreviation: T, temperature.

Here, X_1 is the conversion of the part of the monomer that polymerizes according to the classical theory of polymerization; $k_{\text{pol},1}$ is the corresponding polymerization rate constant; and C_1 is the initiator concentration at time τ .

It is usually supposed that there is a negligible change in initiator concentration during polymerization, that is, $C_1=C_{10}$ =constant. Hence, the rate of polymerization is described by equation (3)

$$\frac{dX_1}{d\tau} = k_1 \cdot (1 - X_1) \quad (3)$$

where $k_1=k_{\text{pol},1} C_1^{1/2}$ is the rate constant for the first-order reaction.

Table 2 Values of parameters in equation (8) determined for styrene-free radical polymerization at different temperatures (obtained using method of least squares)

T (°C)	$k_1 \times 10^2$ (min ⁻¹)	$k_2 \times 10^2$ (min ⁻¹)	a	$\tau_{2 \text{ max}}$ (min)	s.d. ^a	R ² ^b
70	1.193	6.114	0.599	203.9	0.029	0.992
75	1.440	6.826	0.491	156.9	0.031	0.991
80	1.954	7.274	0.428	120.7	0.029	0.992
85	2.204	7.014	0.433	104.9	0.029	0.992
90	2.534	7.982	0.265	104.5	0.014	0.998

Abbreviation: T, temperature.

^aStandard deviation (s.d.) of the residuals.

^bCoefficient of determination.

All theories of rate polymerization autoacceleration assume that the polymer produced during the autoacceleration stage has a catalytical effect on polymerization. Hence, we propose that in that stage, the rate of polymerization depends on both the concentration of residual monomer M and the amount of created polymer P, that is, equation (4). This equation can be easily transformed to equation (5).

$$R_{\text{pol}} = C_{M0} \cdot \frac{dX_2}{d\tau} = k_{\text{pol},2} \cdot C_M \cdot C_P \cdot C_I^{1/2} \quad (4)$$

$$\frac{dX_2}{d\tau} = k_2 \cdot X_2 \cdot (1 - X_2) \quad (5)$$

where X_2 is conversion of a part of monomer that polymerizes according to the autoacceleration and deceleration mechanisms of polymerization, and $k_2=k_{\text{pol},2} C_{M0} C_I^{1/2}$ is the corresponding polymerization rate constant.

It should be noted that equation (5) is a parabola that has a maximum polymerization rate. Hence, it can be used to describe both the autoacceleration and the deceleration parts of the polymerization rate vs time curves.

After integrating and rearranging, equations (3) and (5) become equations (6) and (7):

$$X_1(\tau) = 1 - e^{-k_1\tau} \quad (6)$$

$$X_2(\tau) = \frac{1}{1 + e^{-k_2(\tau - \tau_{2 \text{ max}})}} \quad (7)$$

where $\tau_{2 \text{ max}}$ is the time necessary to achieve the maximum rate of autoacceleration stage equations (6) and (7) are conversions according to classical first-order polymerization and acceleration, respectively. At the end of polymerization, the achieved final conversion X_K consists of two fractions: a is the monomer fraction polymerized by autoacceleration (that is, equation (7)) and $(X_K - a)$ is the monomer fraction polymerized by the first-order reaction (that is, equation (6)). X_K was very close to 1 in all of our experiments. On the basis of these assumptions, the dependence of the conversion on time can be presented by a mathematical model (equation (8)). The first addend corresponds to the first-order reaction and the second to autoacceleration. The model includes these two processes because they are not strictly separated, occurring simultaneously as two parallel reactions.

$$X(\tau) = (1 - a) \cdot (1 - e^{-k_1\tau}) + \frac{a}{1 + e^{-k_2(\tau - \tau_{2 \text{ max}})}} \quad (8)$$

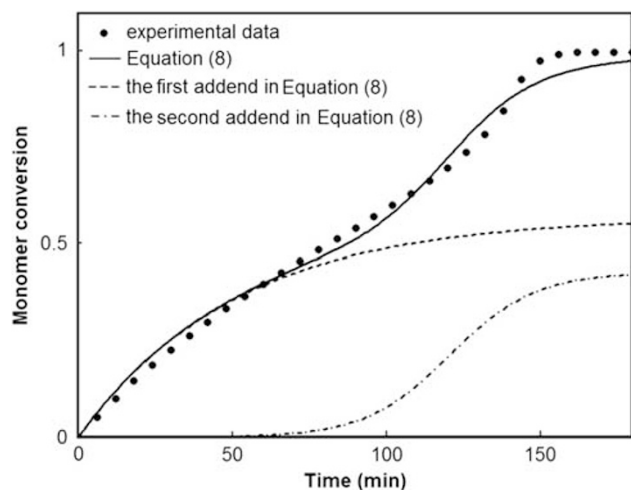


Figure 4 Styrene conversion vs time at 80 °C (1wt% 2,2'-azobisisobutyronitrile).

In equation (8), values for X and τ were obtained from experimental DSC data, whereas k_1 , k_2 , a and τ_{2max} were calculated using the least-squares method. The values of all calculated parameters are given in Table 2. The dependence of the degree of monomer conversion on polymerization time is well described by the estimated mathematical model given in equation (8) (Figure 4). The low values for standard deviation of the residuals and the high determination coefficients (Table 2) confirm this conclusion.

Although the model includes both addends from the beginning to the end of polymerization, the first addend dominates in the first part of conversion vs time curves (Figure 4). The contribution of the second addend, that is, polymerization acceleration, to the conversion is negligible in the first part, appears after some time, increases and becomes dominant in the second part of the polymerization.

Conversion (X), rate of polymerization ($dX/d\tau$) and acceleration ($d^2X/d\tau^2$) vs time (τ) curves obtained by our mathematical model (Figure 5) have the same trends as the experimentally obtained curves (Figure 3).

After the determination of rate constants (k_1 and k_2) at different temperatures, it is possible to calculate apparent activation energies using the Arrhenius equation. The dependences of the natural logarithm of the two reaction rate constants on the reciprocal temperature are presented in Figures 6 and 7. Apparent activation energies for the first-order reaction (E_{a1}) and autoacceleration (E_{a2}) are 40.1 and 11.6 kJ mol⁻¹, respectively. The autoacceleration activation energy is approximately four times lower than the energy of the first-order reaction.

The value of parameter a (Table 2) is very important because it is a monomer fraction reacted by autoacceleration. This value can take values between 0 and 1 ($0 \leq a \leq 1$). If $a=0$, all of the monomer will react by first-order reaction only. On the other hand, if $a=1$, polymerization is described by autoacceleration only. Parameter a is linearly dependent on the reaction temperature, and by extrapolating the fitted line, it is possible to obtain characteristic temperatures at which $a=0$ and $a=1$ (Figure 8).

As shown in Figure 8, the first-order reaction followed by autoacceleration takes place only between 41.7 and 110.5 °C. Below 41.7 °C, styrene reacts only by autoacceleration and above 110.5 °C,

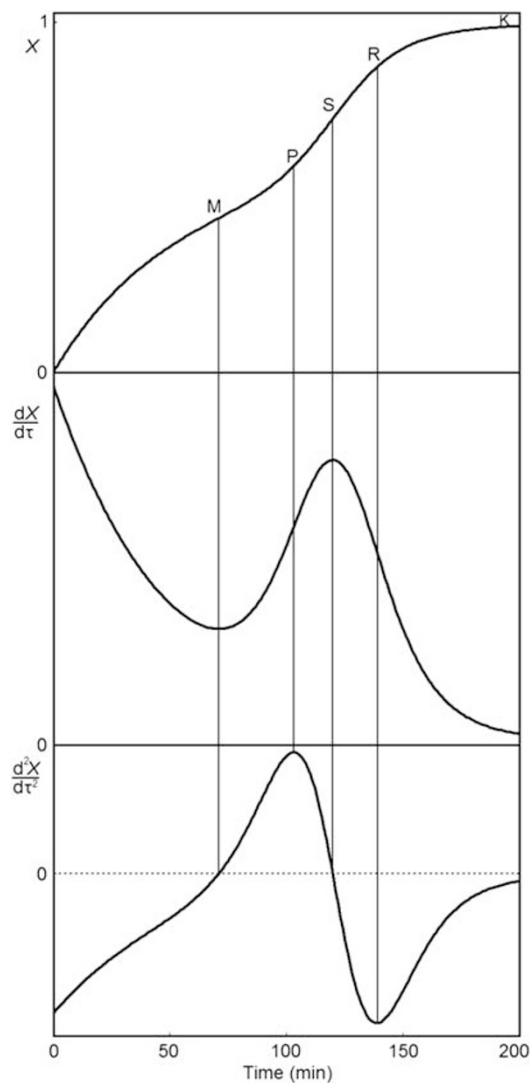


Figure 5 Conversion (X), rate of polymerization ($dX/d\tau$) and acceleration ($d^2X/d\tau^2$) vs time.

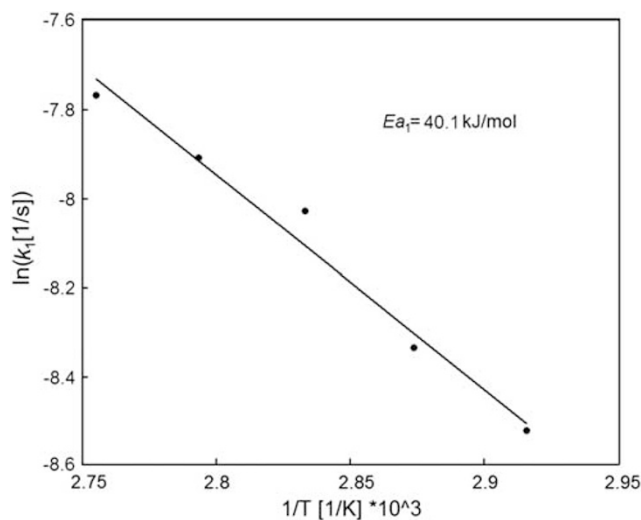


Figure 6 Dependence of $\ln(k_1)$ on reciprocal temperature for styrene polymerization (1 wt% 2,2'-azobisisobutyronitrile).

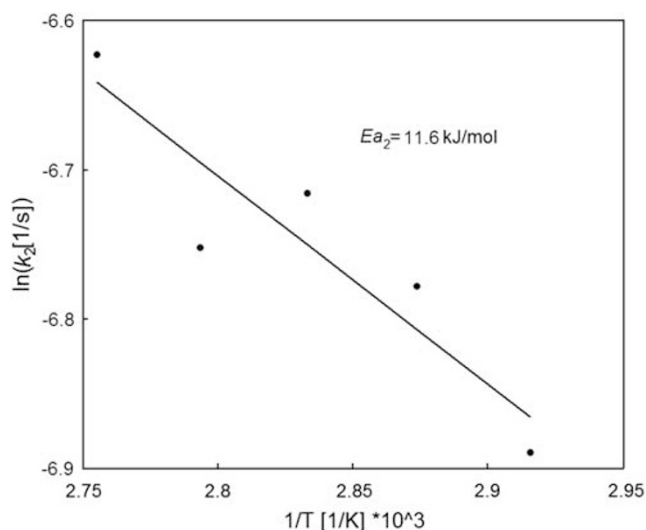


Figure 7 Dependence of $\ln(k_2)$ on reciprocal temperature for styrene polymerization (1 wt% 2,2'-azobisisobutyronitrile).

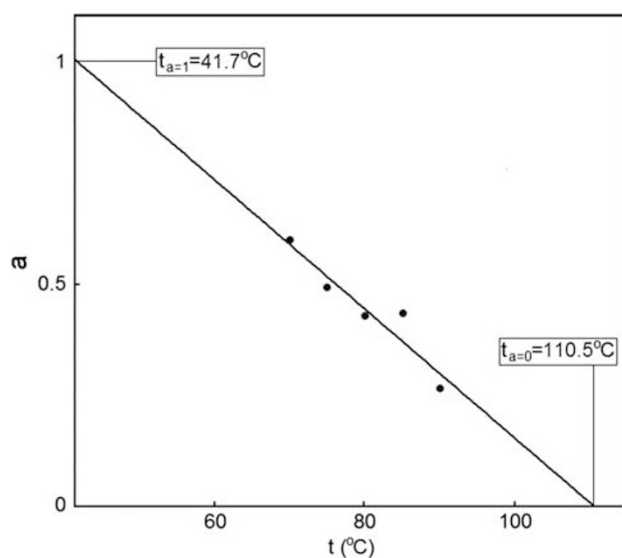


Figure 8 Dependence of parameter 'a' on temperature for styrene polymerization (1 wt% 2,2'-azobisisobutyronitrile).

only by first-order law. The predicted temperatures are very close to the experimental values presented in the literature.^{1,3,8}

Once the boundary temperatures were found, equation (8) could be rewritten more precisely, depending on the temperature range:

$$X(\tau) = \frac{1}{1 + e^{-k_2(\tau - \tau_s)}}, \quad t \leq t_{a=1} (41.7^\circ\text{C}) \quad (9)$$

$$X(\tau) = (1 - a) \cdot (1 - e^{-k_1 \tau}) + \frac{a}{1 + e^{-k_2(\tau - \tau_s)}}, \quad t_{a=1} (41.7^\circ\text{C}) \leq t \leq t_{a=0} (110.5^\circ\text{C}) \quad (10)$$

$$X(\tau) = (1 - e^{-k_1 \tau}), \quad t \geq t_{a=0} (110.5^\circ\text{C}) \quad (11)$$

CONCLUSIONS

The following remarks were made:

- The polymerization of styrene shows the same characteristic points as polymerization of alkyl methacrylates:^{4,5} onset of auto-acceleration (M), maximum autoacceleration (P) and maximum polymerization rate (S), proceeded by deceleration stage with minimum (R) and final conversion (K).
- A new kinetic model of styrene-free radical bulk polymerization was developed. Experimental data of the dependence of styrene conversion on reaction time are well described by the estimated kinetic model.
- Autoacceleration activation energy is approximately four times lower than the energy of the first-order reaction.
- The first-order reaction and autoacceleration of styrene-free radical bulk polymerization occurs simultaneously between 41.7 and 110.5 °C. Below 41.7 °C, styrene reacts only by autoacceleration and above 110.5 °C only by first-order low.

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