

Experimental and Theoretical Study of the Self-Initiation Reaction of Methyl Acrylate in Free-Radical Polymerization

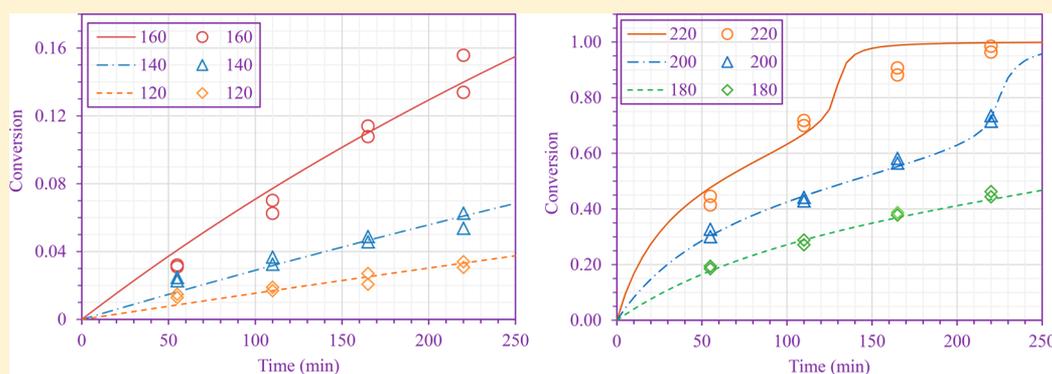
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Supporting Information



ABSTRACT: Extensive experimental results (measurements of the monomer conversion in the absence of any external initiators) indicating the occurrence of the self-initiation reaction of methyl acrylate (MA) at 120–220 °C are presented. To this date, for the MA, experimentally derived values of the rate coefficients of only propagation, termination, transfer to monomer, and transfer to polymer reactions have been reported. As MA and *n*-butyl acrylate (*n*BA) are from the same acrylate family, here, we exploit the family type behavior to obtain the rate coefficients of termination by mid-chain radicals and β -Scission reactions of MA, on the basis of the rate coefficients of the same polymerization reactions of *n*BA. A new, simple, empirical, gel effect model is also presented. Using these rate coefficients and a macroscopic mechanistic polymerization reactor model, the rate coefficients of MA self-initiation and chain-transfer-to-monomer reactions as well as the parameters of the gel effect model are estimated from the MA conversion measurements.

1. INTRODUCTION

Today 25% of all polymer coatings are acrylic.¹ Acrylic polymers provide coatings with excellent gloss, clarity, weatherability, and anticorrosion properties. However, they must be diluted with organic solvents to gain increased coating flow during application.² However, environmental regulations have imposed strict limitations on the level of organic solvent that can be used.³ To decrease the solvent level and simultaneously maintain the brushability and sprayability of the coatings, the polymer industry has lowered the average molecular weights of the polymers.⁴ High-temperature thermal polymerization of acrylate monomers leads to the synthesis of low-molecular-weight polymers, i.e., a weight-average molecular weight, M_w , <10 000. However, at high temperatures, several reactions that are typically ignored at low temperatures strongly affect polymer properties. These include monomer self-initiation, β -scission, inter/intramolecular chain transfers, and backbiting that have been studied extensively in the past decade.^{5–13}

Acrylate polymerizations are typically initiated using conventional thermal initiators, such as potassium persulfate,¹⁴ ammonium persulfate,¹⁵ and azobis(isobutyronitrile).¹⁶ However, it is desirable to curtail or eliminate the use of conventional thermal initiators. First, the initiators are the most expensive component of free-radical polymerization. Second, their residues (unreacted leftovers) in the final product can cause health and weathering problems. Ultraviolet irradiation,¹⁷ ultrasound waves,¹⁸ and high polymerization temperatures¹⁹ have been used to reduce the levels of initiator residue in the final product. Thermal monomer self-initiation can lessen the need for a conventional initiator in free-radical polymerization. This has motivated many studies in the past decade to better understand self-initiation reactions of acrylic monomers.^{20–25}

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Techniques such as macroscopic mechanistic modeling, nuclear magnetic resonance spectroscopy (NMR), and spray ionization-Fourier transform mass spectroscopy (ESI-FTMS), alone are not able to determine the initiation mechanism or initiating species in the spontaneous polymerization conclusively. Macroscopic mechanistic models along with adequate polymer sample measurements allow for estimating rate coefficients on the basis of a postulated reaction mechanism. This approach was used to estimate kinetic parameters of various reactions taking place in thermal free-radical polymerization of vinyl monomers.^{21,25–28} In two studies on spontaneous thermal polymerization of *n*BA in an apparently inert medium,^{21,29} it was assumed that the entire polymerization was initiated by monomer self-initiation, leading to an unrealistically large estimate for the rate coefficient of *n*BA self-initiated reaction.

Previous purely theoretical studies of the self-initiation reaction of several alkyl acrylates such as *n*BA, MA, and ethyl acrylate, using density functional theory confirmed that alkylacrylate monomer self-initiation has three elementary reaction steps in series:^{22,23}



In the first reaction, two monomer molecules react and form a singlet diradical. In the second step, the singlet diradical undergoes intersystem crossing to form a triplet diradical. Finally, in the third reaction, the triplet diradical reacts with a third monomer molecule to form two monoradicals. Kinetic studies showed that the first step in the series is the fastest reaction, and the second step is the slowest one, which governs the overall rate of the monomer self-initiation.^{22,30} The overall (apparent) reaction, in which three monomers react to form two monoradicals, is



which is second order.

On the basis of the overall self-initiation reaction (eq 4) and other polymerization reactions that are most likely to occur for *n*BA, a macroscopic mechanistic model of *n*BA polymerization in a batch reactor was developed.^{24,25} Using the macroscopic model, the frequency factor and activation energy of the monomer self-initiation reaction were estimated from measurements of *n*BA conversion in free-radical homopolymerization in the absence of any conventional thermal initiators.²⁴ The reaction-rate parameter estimates obtained from conversion measurements were reported to agree well with estimates obtained via our first-principles quantum chemical calculations.^{23,30}

In this study, for the first time the rate coefficient of the overall self-initiation reaction (i.e., eq 4) of MA is estimated using a macroscopic mechanistic MA batch polymerization model and conversion measurements. For MA, experimentally based rate coefficients of propagation and termination by end-chain radicals (ECR) as well as transfer to the monomer and polymer constants are reported. However, no kinetic data are available for termination by mid-chain radicals (MCR), and β -scission reactions of MA. As MA and *n*BA belong to the same acrylate family, here, we exploit the family relationship to obtain the unavailable rate coefficients of MA reactions on the basis of

the rate coefficients of the same reactions of *n*BA. Using the MA reaction-rate coefficients and the macroscopic mechanistic model,²⁴ we then estimate the activation energy and pre-exponential factor of the MA apparent self-initiation reaction and optimum chain-transfer-to-monomer constant from the MA conversions measurements and then compare them to first-principles values.^{22,23}

2. EXPERIMENT

MA was supplied by ACROS Co. 4.8 mL mini-batch reactors made of stainless steel tubes (Swagelok Inc., Huntingdon Valley, PA, USA) were used. Stainless steel Swagelok caps were used to cap both ends of the reactor tubes. The tubes and caps can withstand pressures up to 3300 psig. Inhibitor removal columns DHR-4 were purchased from Scientific Polymer Products of Ontario, New York, to remove the inhibitors that were present in the supplied MA. After the monomer passed through the column, the inhibitor-free MA was collected in a glass flask. The flask was then capped with a septum, and the monomer inside the flask was bubbled with ultrahigh purity nitrogen (>99.999%) using a long needle inserted through the septum for 60 min to remove any possible trace of oxygen. After the nitrogen flow was interrupted by removing the needle from the septum, the septum was covered with aluminum foil, and the aluminum foil was tied with a rubber band to double ensure that oxygen does not penetrate through the septum into the oxygen-free monomer. The flask, the reaction tubes, the caps, and a pipet were then moved to a glovebox (LC Technology Solution, Salisbury, CT, USA), where the concentration of oxygen is lower than 1 ppm. Inside the glovebox, the aluminum foil and rubber septum were then removed, the 2.5–3 mL of the MA was poured into each reaction tube, and the caps were attached and tightened. Next, the capped tubes weighed. A fluidized sand bath was used to maintain each reaction tube at a desired temperature for a specific period of time. After the bath temperature set-point was set to the desired temperature, the bath was allowed to reach steady state after several hours. Next, two tubes at a time were placed inside the sand bath and then removed after a specific period of time. To stop polymerization inside the two tubes, the tubes were placed in a cold water reservoir. Each tube was then dried and weighed again to compare its current weight to its weight right after removing it from the glovebox. In the case of a noticeable weight difference, the sample in the tube was discarded. At last, a cap of each tube was opened and the content of the tube was emptied into an aluminum dish. The contents were then dissolved in toluene and dried in a vacuum oven at 40 °C. The time each tube was kept inside the sand bath minus 1 min was considered as the reaction time. Note that our previous studies had shown that it takes approximately 1 min for 3 mL of MA inside a reaction tube to reach the temperature of the sand bath.²⁴ The conversion of monomer to polymer was calculated using the gravimetric method.²⁴

3. RESULTS AND DISCUSSION

Figure 1 shows the monomer-conversion measurements at six temperatures: 120, 140, 160, 180, 200, and 220 °C. At 120 °C, a maximum conversion of 3.4% was achieved after 220 min and the conversion increased with time approximately linearly. As expected, the conversion also increased with the reaction temperature. For example, at 220 °C the conversion was about 98% after 220 min. The results indicate that the MA thermal

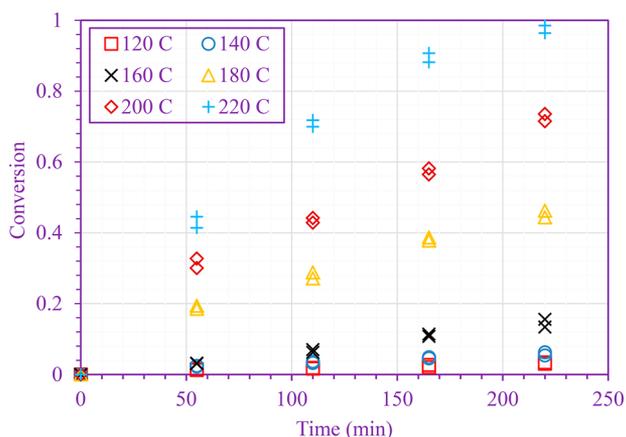


Figure 1. Measured MA conversion at 120, 140, 160, 180, 200, and 220 °C.

self-initiation reaction contributes to polymer chain initiation very significantly at temperatures above 160 °C.

In spontaneous thermal polymerization of alkyl acrylates such as the MA in the absence of any initiators and solvents, many reactions such as chain transfer to monomer,³¹ secondary and tertiary radicals chain propagation, monomer self-initiation,²² backbiting, intermolecular chain transfer to polymer, β -scission, termination by disproportionation, and termination by combination occur.^{9,32,33} A complete list of the reactions that are most-likely to occur in *n*BA polymerization, along with their related kinetic parameter values and rate equations are given in refs 24, 31, and 34. We consider the same set of *n*BA reactions (also given in the Supporting Information) and rate equations (macroscopic mechanistic batch reactor model) for MA, which also belongs to the same alkyl acrylate family.

The available experimentally obtained kinetic parameters of MA free-radical polymerization are given in Table 1. Similar values for the propagation rate coefficient are given elsewhere.^{35–37}

Table 1. Existing Kinetic Parameters of MA-Polymerization Reactions

rate coefficient of propagation by secondary radicals	k_p ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) = $1.41 \times 10^7 \exp\left(\frac{17.3}{RT}\right)$	35
rate coefficient of termination by secondary radicals	$\log k_t$ ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) = $9.48 - 454\left(\frac{1}{T}\right)$	38
transfer to polymer constant	1×10^{-4}	39
transfer to monomer constant	3.60×10^{-6} to 3.25×10^{-5}	40

In high-temperature thermal polymerization of MA, both secondary end-chain radicals and tertiary mid-chain radicals contribute to chain propagation. However, the role of the former is more significant than the latter.⁴¹ In fact, tertiary radicals, which are formed via the intramolecular chain transfer of the secondary radicals, are more stable than their secondary counterparts and the following approximation exists between their rate coefficients:³⁵

$$k_p^{\text{tert}} = k_p/1000 \quad (5)$$

where k_p and k_p^{tert} denote ECR and the MCR propagating rate coefficients, respectively. As for the MA, a k_p^{tert} value has not been reported yet, we will use eq 5 and the MA k_p value³⁵ to calculate k_p^{tert} of MA.

It is worth noting here that most of the reported propagation rate coefficients are based on pulsed-laser polymerization—size-exclusion chromatography (PLP-SEC), which usually gives valid rate coefficients up to a temperature around 30 °C. By the advent of high-frequency PLP-SEC techniques, more trustable rate coefficients up to 80 °C describing just the ECR propagation are obtained. So, simply extrapolating a k_p relation for ECRs to higher temperatures does not yield a reliable propagation rate coefficient, as it does not account for possibly generated MCRs. At high temperatures, as both ECRs and MCRs participate in propagation reactions, both k_p and k_p^{tert} rate coefficients should be included in a high-temperature macroscopic mechanistic polymerization model. Alternatively, an effective propagation rate coefficient, which accounts for the combined propagation reactivities of ECRs and MCRs, can be obtained using³⁵

$$k_p^{\text{eff}} = \frac{k_p}{1 + \frac{k_{\text{bb}}}{k_p^{\text{tert}} c_m}} \quad (6)$$

where k_p is the ECR propagation rate coefficient, k_p^{tert} is the MCR propagation rate coefficient, k_{bb} is the backbiting rate coefficient, and c_m is the monomer concentration. So, given the three propagations rate coefficients, k_p^{eff} can be calculated. Currently, no reliable MA k_{bb} or k_p^{tert} value is available, though k_{bb} of MA can be assumed to be equal to k_{bb} of *n*BA.³⁵ The rationale behind this assumption is that under PLP conditions, the populations of MA and *n*BA MCRs are not very different.³⁵ As far as we know, no reliable expression for MA k_p^{eff} has been reported yet.

Also, a rate coefficient for the termination reactions of MA tertiary radicals is not available. To address this problem, we use family type behavior relationships;³⁵ that is, there is a relationship between the rate coefficients of the same reaction of two monomers belonging to a family of monomers. This behavior has already been tested for acrylate and methacrylate families. For both families, it has been reported that, in the bulk medium, the propagation rate coefficient increases with the size of the alkyl ester group, while the termination rate coefficient decreases. For example, a direct linear relationship between the propagation rate coefficient and the number of carbons of alkyl ester group of the acrylate family has been reported.⁴² Kockler et al.⁴³ showed that this linearity is valid for alky acrylate monomers containing up to 20 carbon atoms in their alkyl ester group at both 0 and 50 °C. For these two temperatures, they reported that the lines have the slopes of +300 ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) and +550 ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$), respectively.⁴³ In addition, the propagation rate coefficient of the methacrylate family increases by a factor 1.5 at 50 °C going from methyl methacrylate (MMA) to dodecyl methacrylate (DMA).⁴⁴ Some similarities between families have also been reported; the ratio of the propagation rate coefficient of methyl methacrylate to that of butyl methacrylate at 20 °C is 0.87, and the ratio of the propagation rate coefficient of methyl acrylate to that of butyl acrylate at the same temperature is 0.81.³⁵ However, it should be taken into consideration that such family type behaviors are not always applicable to all polymerization conditions. For example, the aforementioned relations between the number of carbon atoms of alkyl ester group and the propagation rate

coefficient are not valid in solution polymerization.³⁵ Moreover, there is no family type behavior for branched alkyl acrylate, whereas there is one for branched alkyl methacrylate.⁴⁵ Therefore, self-initiation rate coefficients of different members of both methacrylate and acrylate families should be calculated independently to check possible existence of any kind of the family type behavior in these monomers.

Given the termination rate coefficients of *n*BA and MA that have already been reported,^{38,46,47} we define the scaling factor:

$$a = \frac{k_{t,MA}}{k_{t,nBA}} = \frac{10^{9.48-454/T}}{10^{8.89-400/T}} \quad (7)$$

where $k_{t,MA}$ and $k_{t,nBA}$ are the ECR termination rate coefficients of the MA and *n*BA, respectively. Considering the family type behavior reported for the acrylate family and that the termination rate coefficient is widely affected by segmental motions of terminating macroradicals,⁴² we assume that the same ratio of the ECR termination rate coefficient of MA to that of *n*BA is also valid for their MCR counterparts. Given the MCR termination rate coefficient of *n*BA and the scaling factor, *a*, we estimate the MCR termination rate coefficient of MA. Similar to Kowollik et al.,³⁵ who reported a constant value of 0.81 for $k_{p,MA}/k_{p,nBA}$, we found (Figure 2) a nearly constant

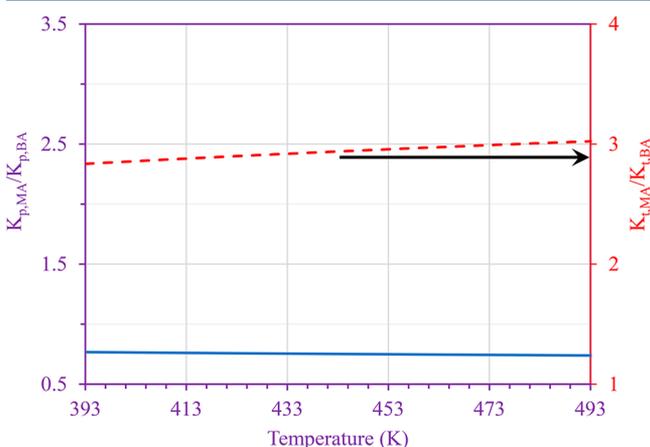


Figure 2. MA to *n*BA termination rate coefficient ratio, and MA to *n*BA propagation rate coefficient ratio.

value of 2.8 for $k_{t,MA}/k_{t,nBA}$ in the temperature range 394–493 (K). Figure 2 also shows that the propagation rate coefficients that we used for MA and *n*BA lead to a constant value of 0.76 for $k_{p,MA}/k_{p,nBA}$, which is in agreement with previously reported values.³⁵ The existence of the family type behaviors reported by the previous studies, the constancy of $k_{p,MA}/k_{p,nBA}$ and the constancy of $k_{t,MA}/k_{t,nBA}$ suggest that the use of the scaling factor, α , for the estimation of the MA-MCR termination rate coefficient is reasonable. The results shown in Figure 2 are also in agreement with previous reports^{35,48} that the termination rate coefficient of acrylates decreases with the length of their alkyl ester, but the propagation rate coefficient of acrylates increases with the length of their alkyl ester group. In fact, a value higher than 1 is expected for α , which is in agreement with the value of 2.8 we obtained. As will be shown, the macroscopic mechanistic model predicts well with this estimate.

Similar to the MCR termination, no reliable rate coefficient has been reported yet for β -scission reactions of MA. $k_{td}/(k_{td} + k_{tc})$ of MA at 25 °C has been reported to be small.⁴⁶ However, this does not apply to this study, as all of our polymerization

experiments were conducted at temperatures above 100 °C, where β -scission reactions are prevalent. To do this, we take advantage of the family type behavior again by introducing another scaling factor, *b*, which is the ratio of the ECR propagation rate coefficient of MA to *n*BA:⁴⁹

$$b = \frac{k_{p,MA}}{k_{p,nBA}} = 0.638 \exp\left(\frac{72}{T}\right) \quad (8)$$

where $k_{p,MA}$ and $k_{p,nBA}$ are the propagation rate coefficients of MA and *n*BA, respectively. The β -scission rate coefficient of MA will be obtained by multiplying the scaling factor, *b*, by the β -scission rate coefficient of *n*BA. In principle,³⁵ the scaling factor *b* should be less than 1, which agrees with what we obtained here, 0.76.

We also need the transfer-to-monomer rate coefficient of MA. However, a very wide range, 3.60×10^{-6} to 3.25×10^{-5} , has been reported for $C_m = k_{trM}/k_p$.^{40,50} Because of the wide range, we will estimate the chain-transfer-to-monomer rate coefficient in the reported range from our conversion measurements.

The apparent MA termination rate coefficient has been reported to be affected by MA conversion.^{49,51} Matheson et al.⁵² reported that the MA termination rate coefficient is dependent on viscosity even at very early stage of polymerization. Up to 15% monomer conversion, segmental diffusion affects termination rate coefficient and beyond it translational diffusion comes into play.⁵⁰ Also, there have been studies relating the termination rate coefficient of MA to the dead polymer average chain length.^{48,53} These studies together with the failure of own macroscopic model to predict conversion reliably without a gel effect model, motivated us to develop and use a new gel effect model to account for the effect of the viscosity on the termination rates.

The gel and glass effects are important in bulk and low-solvent-concentration polymerization media. They respectively represent declines in the rates of termination and propagation reactions due to diffusion limitations, as the viscosity of the reaction medium rises. Many have proposed different models to describe the effects of reaction-medium viscosity increase on the polymerization rate coefficients.^{54–57} In this study, we ignore the glass effect, as the glass transition temperature of the MA polymer is 10 °C, which is lower than the reaction temperature (120–220 °C).⁵⁸ However, we propose and use a new empirical gel effect model to account for the gel effect in the polymerization. The proposed empirical gel effect model has the following form:

$$\frac{k_{t_a}}{k_t} = \left(1 + \frac{A_1}{T + A_2}(e^{A_3X} - 1)\right) \exp\left(\frac{-A_1}{T + A_2}(e^{A_3X} - 1)\right) \quad (9)$$

$$\frac{k_{t_a}^{tt}}{k_t^{tt}} = \left(1 + \frac{A_1}{T + A_2}(e^{A_3X} - 1)\right) \exp\left(\frac{-A_1}{T + A_2}(e^{A_3X} - 1)\right)$$

where k_{t_a} and $k_{t_a}^{tt}$ are the apparent termination rate coefficients, k_t and k_t^{tt} are the actual termination rate coefficients, superscript tt denotes to tertiary radicals, and the parameters A_1 , A_2 , and A_3 are the model parameters that depend on temperature linearly:

$$A_i = b_i + c_i T \quad i = 1, 2, 3 \quad (10)$$

and $A_1 > 0$, $A_2 + T > 0$, and $A_3 > 0$. Here, b_i and c_i , $i = 1, 2, 3$, are constants. This simple gel effect model accounts for the

Table 2. $k_{i,m}$, C_m , A_1 , A_2 , and A_3 Estimates at the Six Temperatures

	120 °C	140 °C	160 °C	180 °C	200 °C	220 °C
$k_{i,m}$ (L·mol ⁻¹ ·s ⁻¹)	1.59×10^{-14}	6.2×10^{-14}	4.60×10^{-13}	1.73×10^{-11}	7.87×10^{-11}	5.04×10^{-10}
C_m	3.57×10^{-6}	9.85×10^{-6}	1.57×10^{-5}	2.16×10^{-5}	2.79×10^{-5}	3.23×10^{-5}
A_1 (K)	2.37×10^1	2.34×10^1	2.20×10^1	2.00×10^1	1.90×10^1	1.69×10^1
A_2 (K)	-6.76	-4.24	-2.21	-3.40×10^{-1}	1.96	3.98
A_3 (K)	9.11	8.58	8.81	8.39	7.48	7.29

effects of the reaction mixture viscosity, which depends on the reaction temperature, T (K), and the polymer mass fraction (here, the monomer conversion, X), on the apparent termination rate coefficients. This gel effect model has these inherent structural features: $k_t/k_t = 1$ and $k_t^{tt}/k_t^{tt} = 1$ at $X = 0$; as X increases, k_t/k_t and k_t^{tt}/k_t^{tt} decrease monotonically from 1; and as T increases, k_t/k_t and k_t^{tt}/k_t^{tt} increase monotonically, if $c_1b_2 - c_2b_1 - b_1 < 0$. Note that the termination rate coefficient reported in Table 1 is a chain length averaged value.

The ordinary differential equations of the macroscopic mechanistic model described in ref 24 were integrated using MATLAB and the MA reaction kinetic parameter values to estimate the kinetic parameters of the apparent MA self-initiation reaction and the parameters of the gel effect model from conversion measurements. At each of the six temperatures, $k_{i,m}$, C_m , A_1 , A_2 , and A_3 are estimated from the conversion measurements at the specific temperature (T_j) by minimizing the sum of squared residuals (SSRs_{*j*}):

$$SSR_{s_j} = \sum_{i=1}^{N_j} (X_e(t_i, T_j) - X_m(t_i, T_j, k_{i,m}, C_m, A_1, A_2, A_3))^2 \quad (11)$$

using the `ga` command of MATLAB. Here, $C_m = \frac{k_{tm}}{k_p}$, N_j is the number of conversion measurements available at the temperature T_j , $X_e(t_i, T_j)$ is the measured conversion at time t_i and the temperature T_j , and $X_m(t_i, T_j, k_{i,m}, C_m, A_1, A_2, A_3)$ is the model-predicted conversion at time t_i and the temperature T_j given $k_{i,m}$, C_m , A_1 , A_2 , and A_3 values. The calculated parameter estimates are presented in Table 2. Using the six MA self-initiation rate coefficient estimates and the Arrhenius plot of Figure 3, the activation energy and frequency factor of the MA self-initiation reaction are calculated: $E_{a,i,m} = 176.5 \pm 7.1$ (kJ mol⁻¹) and $\ln z_{i,m} = 21.5 \pm 1.9$ ($z_{i,m}$ in L·mol⁻¹·s⁻¹). The values

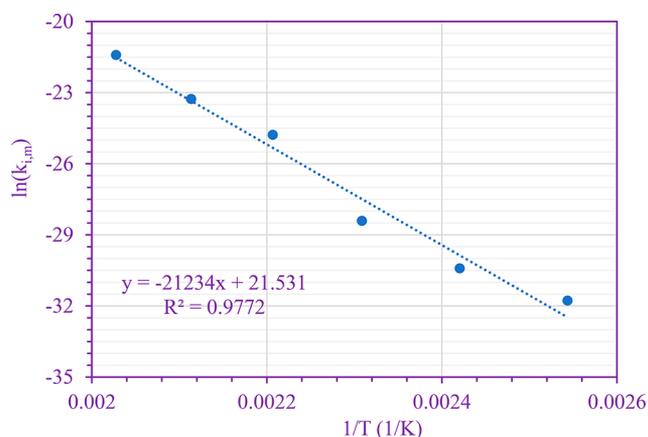


Figure 3. Arrhenius plot of the MA self-initiation rate coefficient.

of $E_{a,i,m}$ and $\ln z_{i,m}$ of the same reaction predicted by quantum chemical calculations are 119.5 (kJ mol⁻¹) and 4.09 ($z_{i,m}$ in L·mol⁻¹·s⁻¹).³⁰ Given the activation energy and the frequency factor of the MA self-initiation reaction, the rate coefficients at the six temperatures are calculated (Table 3). These results show that the estimated and the first-principles predicted MA self-initiation rate coefficient values agree well. The C_m estimates also agree with the fact that transfer reactions are prevalent at higher temperatures. Next, using linear regression, the constant parameters b_i and c_p , $i = 1, \dots, 4$, are estimated from the A_1 , A_2 , A_3 , and C_m estimates at the six temperatures, where $C_m = b_4 + c_4T$. The b_i and c_p , $i = 1, \dots, 4$, estimates are presented in Table 4.

Figure 4 compares the model predictions and the measurements of the MA conversion. As can be seen, the model predicts the MA conversion accurately over wide ranges of time and temperature. Good agreement between model prediction and experimental results are obtained thanks to considering the gel effect model in our simulation process. Figure 5 compares the best predictions with and without the gel effect model; it shows that without the gel effect model, the reactor model predicts very poorly.

Figure 6 depicts how k_t/k_t [based on eq 9 and the parameter values given in Table 4] varies with conversion and temperature. It shows the exponential decay of the ratio with the MA conversion and its exponential rise with the reaction temperature. Gel effect models developed by other researchers⁵⁴ for the methyl methacrylate polymerization also show the exponential decay with conversion. The model proposed in ref 54 has one temperature- and initiator-concentration-dependent and two temperature-dependent parameters. As numerical values of these model parameters at two specific initiator concentrations and three specific temperatures have been reported, the applicability of the model is limited to these conditions. The availability of the parameter values of many existing models at a limited number of operating conditions is a drawback of these existing methods. Several models^{54,59} also contain conventional-initiator-concentration-dependent parameters, which make them not applicable to conventional-thermal-initiator-free polymerization systems. Purely empirical gel effect models such as⁶⁰

$$k_{t_a} = k_t \exp(a_1 + a_2X + a_3X^2 + a_4X^3) \quad (12)$$

where a_1, \dots, a_4 are temperature-dependent parameters, have also been developed. This model has several drawbacks. First, $k_{t_a} \neq k_t$ at $X = 0$, unless $a_1 = 0$. Second, this and several other gel effect models^{60,61} can predict $\frac{k_{t_a}}{k_t}$ greater than 1, but this ratio should never exceed 1. However, the gel effect model of eq 9 structurally does not suffer from these drawbacks. It has only three adjustable parameters that are linearly dependent on temperature, and it is applicable at different temperatures and conversions (polymer mass fractions).

Table 3. MA Self-Initiation Rate Coefficient ($\text{L}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$) at the Six Temperatures

	120 °C	140 °C	160 °C	180 °C	200 °C	220 °C
estimated in this work	7.84×10^{-15}	1.07×10^{-13}	1.15×10^{-12}	1.00×10^{-11}	7.25×10^{-11}	4.47×10^{-10}
theoretically predicted ³⁰	7.85×10^{-15}	4.61×10^{-14}	2.30×10^{-13}	9.95×10^{-13}	3.80×10^{-12}	1.30×10^{-11}

Table 4. Estimated Gel Effect Model Parameter Values

i	b_i (K)	c_i
1	$5.22 \times 10^1 \pm 1.49$	$-7.07 \times 10^{-2} \pm 3.30 \times 10^{-3}$
2	$-4.79 \times 10^1 \pm 4.08 \times 10^{-1}$	$1.05 \times 10^{-1} \pm 9.00 \times 10^{-4}$
3	$1.64 \times 10^1 \pm 8.19 \times 10^{-1}$	$-1.83 \times 10^{-2} \pm 1.80 \times 10^{-3}$
4	$3.00 \times 10^{-7} \pm 1.17 \times 10^{-7}$	$1.00 \times 10^{-4} \pm 1.11 \times 10^{-5}$

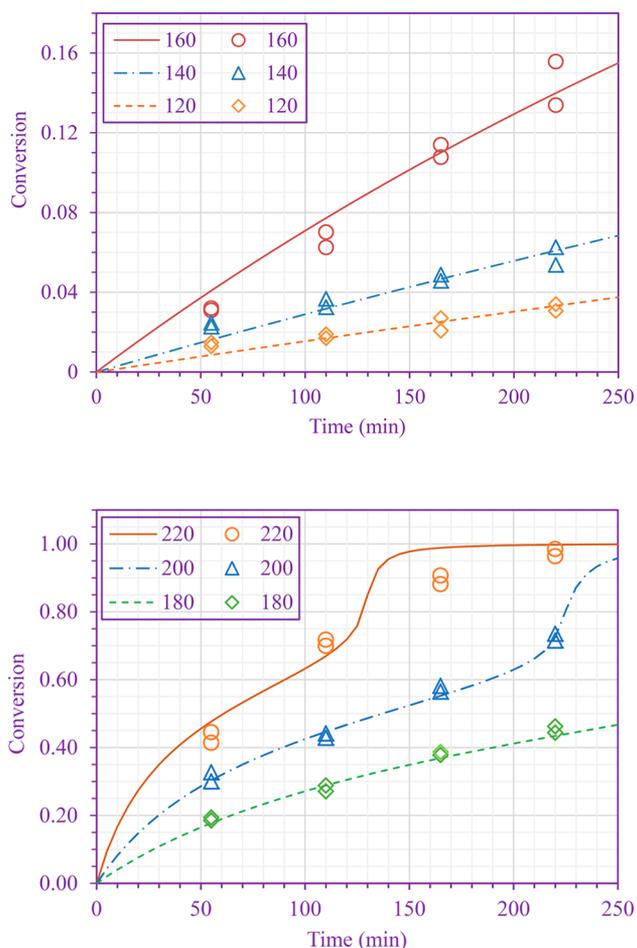


Figure 4. Measurements (shown by symbols) and model prediction (shown by lines) of the MA conversion at the six temperatures.

As it is known, k_t/k_i should decrease with the polymer solution viscosity. The viscosity of a polymer solution increases with the polymer mass fraction (here, monomer conversion) but decreases with temperature. Figure 6 indicates that at 120 °C, the ratio decays to zero with conversion earliest, indicating that the termination reactions are suppressed earliest at this temperature among all the temperatures. A semilog version of this figure is given in the Supporting Information. The model of eq 9 with only three adjustable parameters at a specific temperature can account for the gel effect in spontaneous thermal free-radical polymerizations satisfactorily.

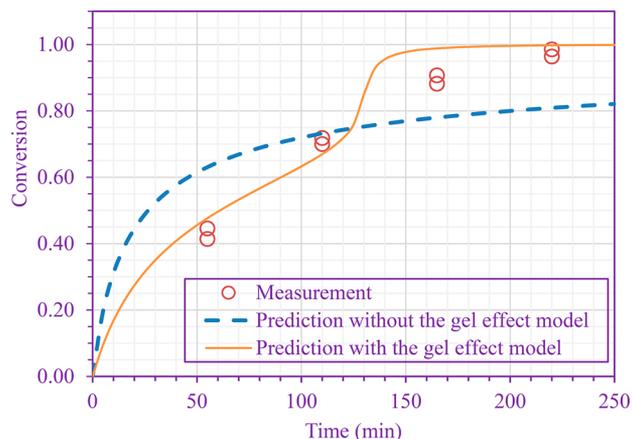
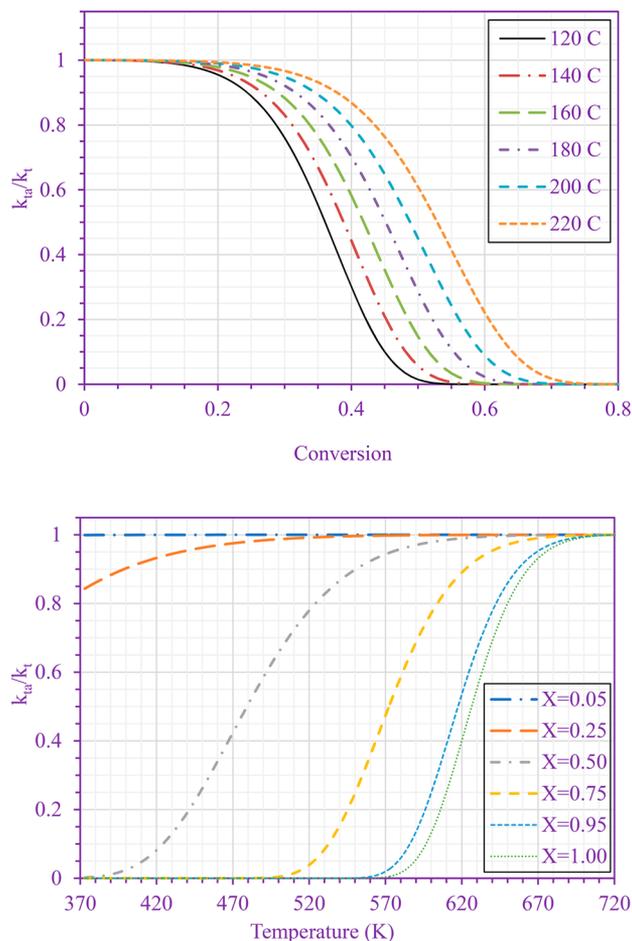


Figure 5. Best predictions made by the reactor model with and without the gel effect model (220 °C).

Figure 6. k_w/k_t calculated using eq 9.

4. CONCLUSIONS

Thermal polymerization of methyl acrylate was carried out at high temperatures in mini-batch reactors, and extensive

experimental results (measurements of the monomer conversion in the absence of any external initiators), indicating the occurrence of monomer self-initiation reactions at temperatures from 120 to 220 °C were presented. As for the MA, experimentally based values of the reaction rate coefficients of only secondary radical propagation, secondary radical termination, transfer to monomer, and transfer to polymer constants had been reported in the literature; we exploited the family type behavior and obtained the rate coefficients of termination by mid-chain radicals (MCR) and β -scission reactions of MA. A new, simple, empirical gel effect model was also presented. The model has three parameters and can accurately capture viscosity effects on the apparent termination reaction rates. The MA self-initiation reaction-rate coefficient values estimated from conversion measurements agree well with first-principles calculated ones. The MA self-initiation-reaction activation energy and pre-exponential factor were found to be $E_{a,im} = 176.5 \pm 7.1$ (kJ mol⁻¹) and $\ln z_{i,m} = 21.5 \pm 1.9$ (L·mol⁻¹·s⁻¹). Also, the macroscopic model predicts the monomer conversion very accurately.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.7b04648.

Semilog version of Figure 6 and a table showing the most-likely reactions in high-temperature polymerization of alkyl acrylates (PDF)

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Notes

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