VLADISLAV M. JAŠO
DRAGOSLAV M. STOILJKOVIĆ
RADMILA Ž. RADIČEVIĆ

Faculty of Technology, University of Novi Sad, Novi Sad, Serbia

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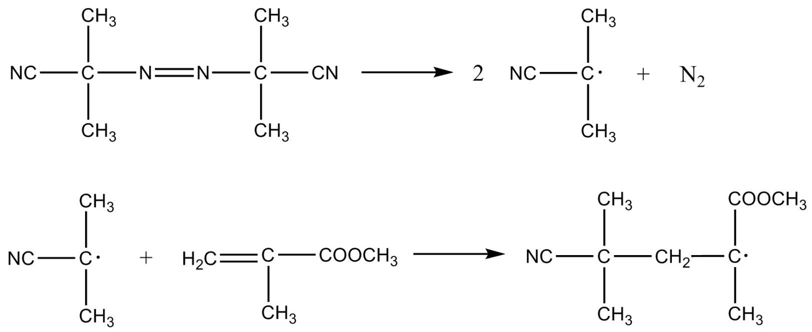
EFFECT OF TEMPERATURE ON INITIAL STAGE OF METHYL METHACRYLATE FREE RADICAL BULK POLYMERIZATION

The classic theory of free radical polymerization is based on two assumptions. The first is that the concentration of the initiator is slightly changed and could be taken as a constant value. The second assumption is that the rate of initiation is equal to the rate of termination. The equation for the polymerization rate based on these assumptions cannot successfully describe the initial stage of free radical polymerization. In order to solve this problem, three mathematical models were developed and used to verify the mentioned assumptions. The models were fitted to experimental data and qualities of their fits were compared. Experimental data of isothermal bulk polymerization of methyl methacrylate were obtained by differential scanning calorimetry at 60, 70, 80 and 90 °C with initiator concentration (AIBN) of 0.5 mass%. The best fit was shown by the model that assumes constant concentration of initiator during the initial stage but takes into account that the rate of initiation is not equal to the rate of termination at the beginning.

Free radical polymerization has become one of the most thoroughly investigated reactions for polymer synthesis. The reason for this is the fact that the majority of polymers produced worldwide today are synthesized by radical polymerization [1]. Free radical polymerization is a chain reaction, composed of three main steps (Schemes 1–3): initiation (formation of primary radicals), propagation (growth of macroradicals by monomer addition) and termination (end of growth by disappearance of two macroradicals).



Scheme 1. Initiation.

Each of these steps could be kinetically described by one differential equation:

$$r_{\mathrm{i}} = -\left(\frac{\mathrm{d}I}{\mathrm{d}t}\right) = k_{\mathrm{d}} I \qquad (1)$$

$$r_{\mathrm{p}} = -\left(\frac{\mathrm{d}M}{\mathrm{d}t}\right) = k_{\mathrm{p}} R M \qquad (2)$$

$$r_{\mathrm{t}} = -\left(\frac{\mathrm{d}R}{\mathrm{d}t}\right) = k_{\mathrm{t}} R^2 \qquad (3)$$

where r_{i}, r_{p} and r_{t} are the rate of initiator decomposition, rate of chain propagation and rate of radical termination, respectively, t is time, I is initiator concentration, R is free radical concentration, M is monomer concentration and k_{d}, k_{p}, k_{t} are rate constants of initiator decomposition, propagation and termination, respectively. In order to solve this system of differential equations, the classic theory of radical polymerization proposes two assumptions. The first is that the concentration of initiator slightly changes during the initial stage and it could be taken as constant and equal to its initial value (assumption 1: $I(t) = I_0 = \mathrm{const.}$). The second assumption is that radical concentration reaches its stationary state almost instantly, *i.e.* the rate of initiation (r_{i}) is equal to the rate of termination (r_{t}) (assumption 2: $r_{\mathrm{i}} = r_{\mathrm{t}}$). According to these two assumptions free radical concentration can be expressed as:

$$R = \left(\frac{k_{\mathrm{d}} I_0}{k_{\mathrm{t}}}\right)^{0.5} \qquad (4)$$

Corresponding author: V.M. Jašo, Faculty of Technology, Bulevar cara Lazara 1, 21000 Novi Sad, Serbia
E-mail: vladislavjaso@yahoo.com

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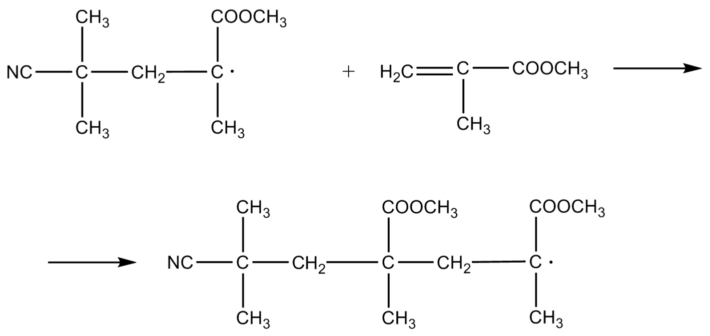
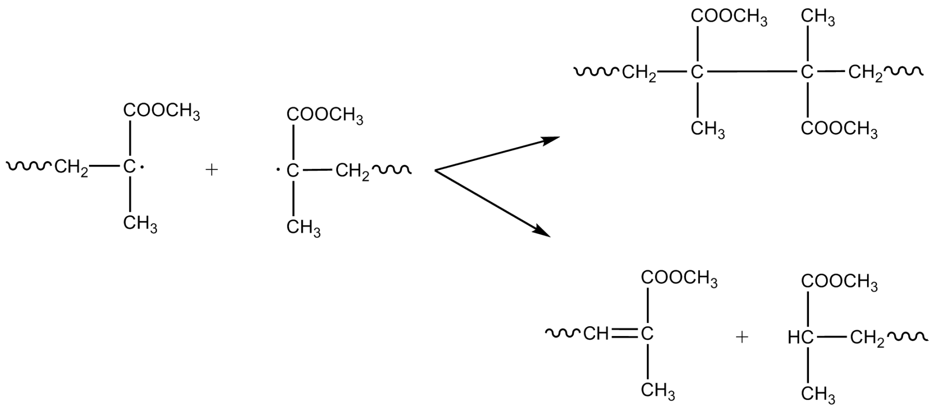


Scheme 2. Propagation.



Scheme 3. Termination.

Rate of polymerization, r_{pol}, can be considered as conversion of monomer to polymer and equals to the rate of propagation. On the basis of these assumptions, classic theory of radical polymerization derives the Eq. (5) for the rate of polymerization:

$$r_{\mathrm{pol}} = -\frac{\mathrm{d}M}{\mathrm{d}t} = k_{\mathrm{p}}\left(\frac{k_{\mathrm{d}}}{k_{\mathrm{t}}}\right)^{0.5} I_0^{0.5} M \qquad (5)$$

It is well known, however, that Eq. (5) cannot successfully describe the initial stage of radical polymerization [1,2].

Differential scanning calorimetry (DSC) is a very convenient method for the studying of polymerization kinetics since it enables very accurate measurements of the heat of polymerization which is proportional to the rate of reaction. The focus of our investigation was to experimentally obtain DSC thermograms of methyl methacrylate polymerization and to find a suitable mathematical model that would successfully describe the initial part of the DSC thermogram.

EXPERIMENTAL

Methyl methacrylate monomer (MMA), from Tokyo Chemical Industries, was washed two times with 10% sodium hydroxide solution to remove the inhibitor, then washed two times with distilled water, dried over anhydrous calcium chloride, and vacuum distilled. Initiator 2,2'-azobisisobutyronitrile (AIBN), from Merck, was recrystallized from methanol before usage. Solution of MMA with 0.5 mass% AIBN was prepared and about 5–10 mg of the solution was placed in hermetic aluminium DSC pan and sealed with aluminium lid. The bulk polymerizations of MMA were carried out in DSC TA Model Q20 instrument under isothermal conditions at 60, 70, 80 and 90 °C. Temperature and heat flow scales were calibrated using the melting point of high-purity indium. Nitrogen was used as purge gas with flow rate of 50 $\mathrm{cm^3\ min^{-1}}$.

RESULTS AND DISCUSSION

In order to develop a mathematical model that would successfully describe the initial part of DSC thermogram, it is necessary to find an equation suitable for fitting experimental DSC data. The potential models need to have heat flow as a dependent variable as the ordinate on the DSC thermogram.

Development of the model is based on heat balance of the reaction system. The heat evolved during reaction, dH, of infinitely small mass of monomer, dm, can be expressed as:

$$\mathrm{d}H = -Q\mathrm{d}m \qquad (6)$$

The value of the heat of polymerisation (Q =560 J/g) was taken from the literature as an average value for the investigated interval of temperature [3].

If now both sides of Eq. (6) are divided by the initial mass of sample, m_0, and then by infinitesimal time, dt, required for the reaction of dm mass of monomer, the following expression is obtained:

$$\frac{dH}{\mathrm{d}tm_0}=\frac{-Q\mathrm{d}m}{\mathrm{d}tm_0} \tag{7}$$

On the right side of the Eq. (7) the numerator and denominator are divided by the volume of the system and by molar mass of methyl methacrylate. The resulting Eq. (8) has a differential of monomer concentration, dM, in the numerator and initial monomer concentration of monomer, M_0, in the denominator:

$$\frac{dH}{\mathrm{d}tm_0}=\frac{-Q\mathrm{d}M}{\mathrm{d}tM_0} \tag{8}$$

Instead of –dM/dt in Eq. (8), the right side of Eq.(2) was inserted:

$$\frac{dH}{\mathrm{d}tm_0}=\frac{k_\mathrm{p}QR(t)M(t)}{M_0} \tag{9}$$

Here $M(t)$ and $R(t)$ are monomer and free radical concentrations that are time dependent. It is well known that $M(t)/M_0$ is equal to $1–X(t)$ where $X(t)$ is time dependence of monomer conversion. So we have:

$$\frac{dH}{\mathrm{d}tm_0}=k_\mathrm{p}QR(t)(1-X(t)) \tag{10}$$

In Eq. (2) variables can be separated so that the integration could be applied:

$$-\int_{M_0}^{M}\frac{\mathrm{d}M}{M}=\int_0^t k_\mathrm{p}R(t)\mathrm{d}t \tag{11}$$

The integration provides Eq. (12):

$$-\ln(M)+\ln(M_0)=k_\mathrm{p}\int_0^t R(t)\mathrm{d}t \tag{12}$$

Left side of Eq. (12) can be transformed in the following way:

$$\ln(\frac{M_0}{M})=\ln(\frac{M}{M_0})^{-1}=\ln(1-X(t))^{-1}=-\ln(1-X(t)) \tag{13}$$

Now, the final result of Eq. (13) can be put in Eq.(12) on the left side which as a result gives Eq. (14):

$$-\ln(1-X(t))=k_\mathrm{p}\int_0^t R(t)\mathrm{d}t \tag{14}$$

From Eq. (14), $X(t)$ is equal to:

$$X(t)=1-\exp(-k_\mathrm{p}\int_0^t R(t)\mathrm{d}t) \tag{15}$$

Now, if $X(t)$ from Eq. (15) is put in Eq. (10) it becomes:

$$\frac{\mathrm{d}H}{\mathrm{d}tm_0}=k_\mathrm{p}QR(t)\exp(-k_\mathrm{p}\int_0^t R(t)\mathrm{d}t) \tag{16}$$

Equation (16) is the basis for the development of all our mathematical models of free radical polymerization initial stage. This equation requires an analytical form of function $R(t)$ which has to be derived by each model.

Firstly, we have tested Model 0 based on the assumptions 1 and 2 of classic theory. After that, three separate additional models were developed. Each of these three models is based on different assumptions which provide function $R(t)$ and its integral which are required for the final analytical form of the basic Eq. (16).

Model 0

According to the assumptions 1 and 2 of the classic theory of free radical polymerization, free radical concentration is constant, Eq. (4). And integral of free radical concentration is equal to Eq. (17):

$$\int_0^t R(t)\mathrm{d}t=\int_0^t\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}\mathrm{d}t=\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}t \tag{17}$$

After putting Eqs. (17) and (4) in Eq. (16) we have:

$$\frac{\mathrm{d}H}{\mathrm{d}tm_0}=k_\mathrm{p}Q\left(\frac{k_\mathrm{d}I_0}{k_t}\right)^{0.5}\exp[-k_\mathrm{p}\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}t] \tag{18}$$

In Eq. (18), it is necessary to introduce a new constant $K=k_\mathrm{p}(k_\mathrm{d}/k_\mathrm{t})^{0.5}$. After putting K in Eq. (18) we get the final equation of Model 0:

$$\frac{\mathrm{d}H}{\mathrm{d}tm_0}=KQI_0{}^{0.5}\exp[-KI_0{}^{0.5}t] \tag{19}$$

The results of fitting by Model 0 are very poor (Figs. 1–4). The model only fits to the part of the thermogram after the local maximum.

Hence, we decided to reconsider and test the assumptions 1 and 2 of classic theory of radical polymerization.

Model 1

Model 1 assumes that initiator concentration decays from the beginning of polymerization according to Eq. (20):

$$I(t)=I_0\exp(-k_\mathrm{d}t) \tag{20}$$

But, Model 1 keeps the assumption 2 of classic theory, *i.e.* the rate of initiation is equal to the rate of termination ($r_\mathrm{i}=r_\mathrm{t}$). So, we have:

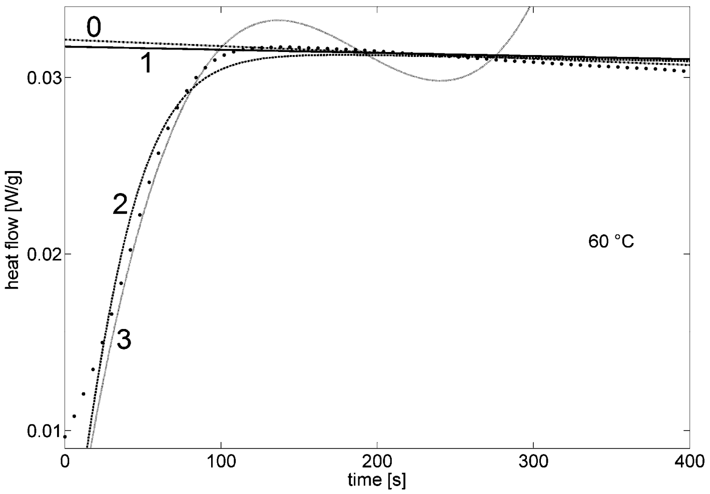


Figure 1. Fitted curves for Models 0, 1, 2 and 3 and experimental data (points) (60 °C).

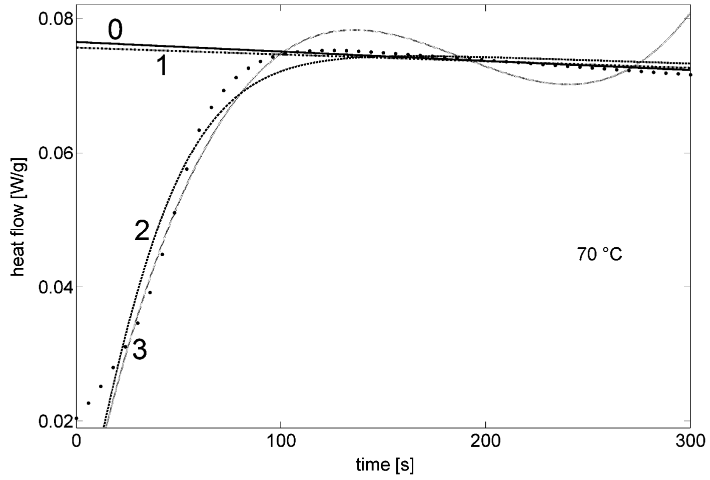


Figure 2. Fitted curves for Models 0, 1, 2 and 3 and experimental data (points) (70 °C).

$$R(t)=\left(\frac{k_\mathrm{d}I(t)}{k_\mathrm{t}}\right)^{0.5} \tag{21}$$

Then, Eq. (20) is inserted into Eq. (21):

$$R(t)=\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}\left[\exp(-k_\mathrm{d}t)\right]^{0.5}= =\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}\exp\left(\frac{-k_\mathrm{d}t}{2}\right) \tag{22}$$

The integral of $R(t)$ is equal to Eq. (23):

$$\int_0^t R(t)dt=\left(\frac{k_\mathrm{d}I_0}{k_t}\right)^{0.5}\int_0^t \exp(\frac{-k_\mathrm{d}t}{2})\mathrm{d}t= =\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}\frac{2}{k_\mathrm{d}}[1-\exp\left(\frac{-k_\mathrm{d}t}{2}\right)] \tag{23}$$

After putting Eqs. (22) and (23) in Eq. (16), we have:

$$\frac{\mathrm{d}H}{\mathrm{d}tm_0}=k_\mathrm{p}Q\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}\exp\left(\frac{-k_\mathrm{d}t}{2}\right)\exp\{-k_\mathrm{p}\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}\frac{2}{k_\mathrm{d}}[1-\exp\left(\frac{-k_\mathrm{d}t}{2}\right)]\} \tag{24}$$

After putting K in Eq. (24), we get the final equation of Model 1:

$$\frac{\mathrm{d}H}{\mathrm{d}tm_0}=KQI_0{}^{0.5}\exp\left(\frac{-k_\mathrm{d}t}{2}\right)\exp\{-KI_0{}^{0.5}\frac{2}{k_\mathrm{d}}[1-\exp\left(\frac{-k_\mathrm{d}t}{2}\right)]\} \tag{25}$$

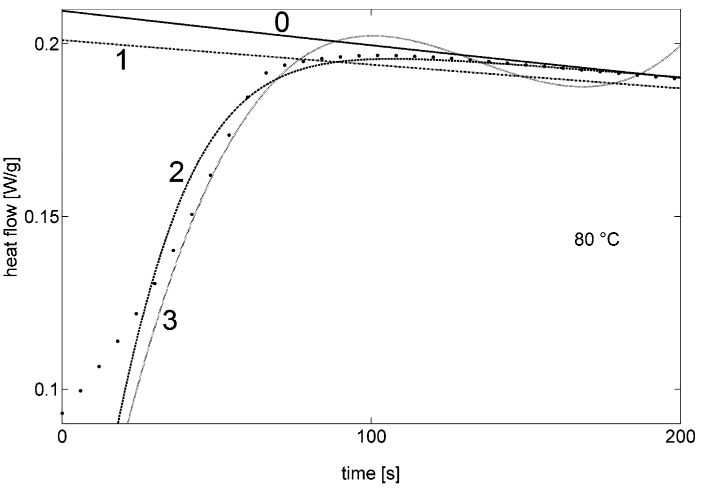


Figure 3. Fitted curves for Models 0, 1, 2 and 3 and experimental data (points) (80 °C).

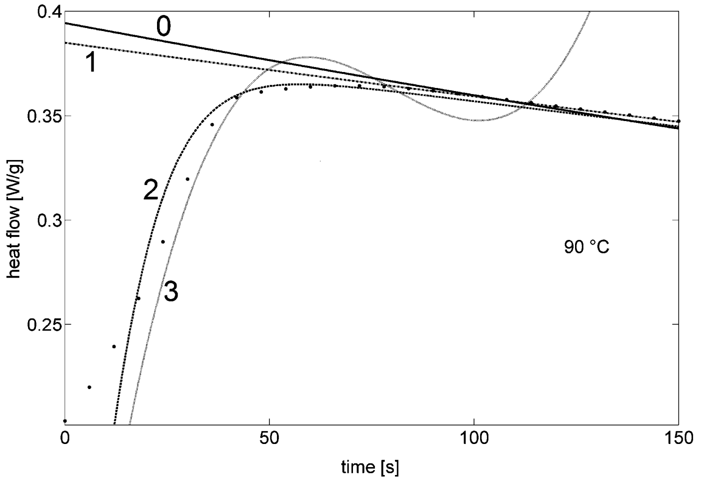


Figure 4. Fitted curves for Models 0, 1, 2 and 3 and experimental data (points) (90 °C).

Model 1 gave slightly better fitting results then Model 0 (Figs. 1–4) but also only fits to the part of the thermogram after the local maximum. This is expected since the model is based on the assumption that steady state is already achieved at the beginning of the reaction. This assumption is true after the local maximum, exactly when good agreement between Model 1 and thermogram starts. Model 1 provides the values for k_d (Table 1) and values for $k_p/k_t^{0.5}$ ratio: 0.022, 0.046, 0.367, 1.768 $dm^{1.5}$ $mol^{-0.5}$ $s^{-0.5}$ at 60, 70, 80 and 90 °C, respectively.

Model 2

In Model 2, the concentration of initiator is held constant during whole period of observation, but the rate of initiation is not equal to the rate of termination. This proposal is also discussed in the literature [2]. Time dependence of free radical concentration has to be derived from the balance of free radicals, Eq. (26), as the difference between the rate of free radical formation and rate of their disappearance:

$$\frac{dR(t)}{dt} = 2k_d I_0 - k_t R(t)^2 \tag{26}$$

The solution for this differential equation is as follows [2]:

$$R(t) = (\frac{k_d I_0}{k_t})^{0.5} \tanh[(4k_t k_d I_0)^{0.5} t] \tag{27}$$

The integral of $R(t)$ is equal to Eq. (28):

$$\int_0^t R(t)dt = \frac{(\frac{k_d}{k_t})^{0.5}}{(k_t k_d)^{0.5}} (0.5\ln\{\exp[4(k_t k_d I_0)^{0.5} t] - 0.5\} - (k_t k_d I_0)^{0.5} t - 0.3465) \tag{28}$$

Table 1. Results of model fitting to the experimental data

Temperature of isothermal polymerization, °C	Model No.	Standard deviation, σ, W/g, correlation coefficient, R	Time period of fitting, s	k_d s^{-1}	k_p $dm^3\ mol^{-1}\ s^{-1}$	k_t $dm^3\ mol^{-1}\ s^{-1}$
60	1	$\sigma = 2.2\times10^{-8}$ $R = 0.998$	150–400	2.47×10^{-4}	–	–
	2	$\sigma = 1.8\times10^{-4}$ $R = 0.955$	0–400	1.20×10^{-5a}	0.168	30.60
	3	$\sigma = 2.5\times10^{-4}$ $R = 0.935$	0–300	1.13×10^{-3}	1.63×10^{-3}	5.3×10^{-2}
70	1	$\sigma = 3.9\times10^{-8}$ $R = 0.999$	150–300	3.17×10^{-4}	–	–
	2	$\sigma = 8.9\times10^{-4}$ $R = 0.965$	0–300	5.57×10^{-5a}	0.805	56.70
	3	$\sigma = 7.9\times10^{-3}$ $R = 0.967$	0–250	1.26×10^{-2}	3.76×10^{-3}	5.8×10^{-2}
80	1	$\sigma = 1.1\times10^{-6}$ $R = 0.994$	100–200	3.46×10^{-5}	–	–
	2	$\sigma = 2.7\times10^{-3}$ $R = 0.937$	0–200	1.55×10^{-4a}	1.137	44.55
	3	$\sigma = 1.1\times10^{-3}$ $R = 0.967$	0–150	1.89×10^{-2}	9.52×10^{-3}	8.4×10^{-2}
90	1	$\sigma = 7.1\times10^{-6}$ $R = 0.991$	70–150	5.25×10^{-6}	–	–
	2	$\sigma = 2.3\times10^{-4}$ $R = 0.952$	0–150	4.86×10^{-4a}	1.179	42.66
	3	$\sigma = 3.2\times10^{-3}$ $R = 0.877$	0–120	2.68×10^{-2}	1.88×10^{-2}	0.12

[a] Values from literature [4]

After putting equation (27) and (28) in equation (16) we have:

$$\frac{\mathrm{d}H}{\mathrm{d}tm_0} = k_\mathrm{p}Q\left(\frac{k_\mathrm{d}I_0}{k_\mathrm{t}}\right)^{0.5}\tanh[(4k_\mathrm{t}k_\mathrm{d}I_0)^{0.5}t]\exp\{-k_\mathrm{p}\frac{\left(\frac{k_\mathrm{d}}{k_\mathrm{t}}\right)^{0.5}}{(k_\mathrm{t}k_\mathrm{d})^{0.5}}(0.5\ln\{\exp[4(k_\mathrm{t}k_\mathrm{d}I_0)^{0.5}t]-0.5\}-(k_tk_dI_0)^{0.5}t-0.3465)\} \quad (29)$$

The introduction of new constants, $K_1 = k_\mathrm{p}(k_\mathrm{d}/k_\mathrm{t})^{0.5}$ and $K_2 = (k_\mathrm{d}k_\mathrm{t})^{0.5}$, is required. Result is Eq. (30) which is final equation of Model 2:

$$\frac{\mathrm{d}H}{\mathrm{d}tm_0} = K_1I_0^{0.5}Q\tanh[4K_2I_0^{0.5}t]\exp\{\frac{-K_1}{K_2}(0.5\ln\{\exp[4K_2I_0^{0.5}t]-0.5\}-K_2I_0^{0.5}t-0.3465)\} \quad (30)$$

Model 2 fits even better to experimental results than Model 1 (Table 1). Almost perfect agreement is achieved in the whole initial region from the beginning of polymerization and a few hundred seconds after the local maximum (stationary state) (Figs. 1–4). Better agreement with experimental results then in case of Model 1 is achieved due to the assumption that steady state of free radicals is not reached at the beginning but after a certain period of time. The fits have very good correlation coefficients, R, in case of all temperatures and the relatively low standard deviations, σ. Here, k_p and k_t can be calculated (Table 1) if values for k_d are taken from literature [4].

Model 3

Model 3 is more complex since it does not take any of the two assumptions from the classic theory. The initiator concentration decays from the beginning of polymerization according to Eq. (20). Time dependence of free radical concentration has to be found from balance of free radicals formation and disappearance, Eq. (31):

$$\frac{\mathrm{d}R(t)}{\mathrm{d}t} = 2k_\mathrm{d}I - k_\mathrm{t}R(t)^2 \quad (31)$$

Initiator concentration can be introduced in Eq. (31) from Eq. (20):

$$\frac{\mathrm{d}R(t)}{\mathrm{d}t}=2k_\mathrm{d}I_0\exp(-k_\mathrm{d}t)-k_\mathrm{t}R(t)^2 \tag{32}$$

Differential equation (32) is more complex then Eq. (26) of Model 2. The analytical solution of the Eq. (32) was not possible to find. That is why we decided to solve it by expanding it into Taylor series [5]:

$$\begin{aligned}R(t)&=R(t_0)+(t-t_0)\frac{\mathrm{d}R(t_0)}{\mathrm{d}t}+\frac{(t-t_0)^2}{2}\frac{\mathrm{d}^2R(t_0)}{\mathrm{d}t^2}+\\&+\frac{(t-t_0)^3}{6}\frac{\mathrm{d}^3R(t_0)}{\mathrm{d}t^3}\end{aligned} \tag{33}$$

Now, we should find differentials of $R(t)$ in the point $t_0 = 0$ and $R(t_0) = 0$:

$$\begin{aligned}R(t)&=R(0)+(t-0)\frac{\mathrm{d}R(0)}{\mathrm{d}t}+\frac{(t-0)^2}{2}\frac{\mathrm{d}^2R(0)}{\mathrm{d}t^2}+\\&+\frac{(t-0)^3}{6}\frac{\mathrm{d}^3R(0)}{\mathrm{d}t^3}\end{aligned} \tag{34}$$

The differential can be found in the following way:

$$\frac{\mathrm{d}R(0)}{\mathrm{d}t}=2k_\mathrm{d}I_0\exp(-k_\mathrm{d}\cdot 0)-k_\mathrm{t}R(0)^2 \tag{35}$$

$$\begin{aligned}\frac{\mathrm{d}^2R(0)}{\mathrm{d}t^2}&=-2k_\mathrm{d}^2I_0\exp(-k_\mathrm{d}\cdot 0)-2k_\mathrm{t}R(0)\frac{\mathrm{d}R(0)}{\mathrm{d}t}=\\&=-2k_\mathrm{d}^2I_0\end{aligned} \tag{36}$$

$$\begin{aligned}\frac{\mathrm{d}^3R(0)}{\mathrm{d}t^3}&=2k_\mathrm{d}^3I_0\exp(-k_\mathrm{d}\cdot 0)-2k_\mathrm{t}\left(\frac{\mathrm{d}R(0)}{\mathrm{d}t}\right)^2-\\&-2k_\mathrm{t}R(0)\frac{\mathrm{d}^2R(0)}{\mathrm{d}t^2}\end{aligned} \tag{37}$$

$$\begin{aligned}\frac{\mathrm{d}^3R(0)}{\mathrm{d}t^3}&=2k_\mathrm{d}^3I_0-2k_\mathrm{t}(2k_\mathrm{d}I_0)^2=\\&=2k_\mathrm{d}^3I_0-8k_\mathrm{t}k_\mathrm{d}^2I_0^2\end{aligned} \tag{38}$$

If the differentials are substituted in Eq. (34), the time dependence of free radical concentration is obtained, Eq. (39):

$$\begin{aligned}R(t)&=0+2k_\mathrm{d}I_0t-\frac{t^2}{2}2k_\mathrm{d}^2I_0+\\&+\frac{t^3}{6}(2k_\mathrm{d}^3I_0-8k_\mathrm{t}k_\mathrm{d}^2I_0^2)\end{aligned} \tag{39}$$

It is equal to:

$$R(t)=2k_\mathrm{d}I_0t-k_\mathrm{d}^2I_0t^2+\frac{t^3}{3}(k_\mathrm{d}^3I_0-4k_\mathrm{t}k_\mathrm{d}^2I_0^2) \tag{40}$$

We should find $\int_0^t R(t)\mathrm{d}t$:

$$\begin{aligned}&\int_0^t(2k_\mathrm{d}I_0t-k_\mathrm{d}^2I_0t^2+\frac{t^3}{3}(k_\mathrm{d}^3I_0-4k_\mathrm{t}k_\mathrm{d}^2I_0^2))\mathrm{d}t=\\&=k_\mathrm{d}I_0t^2-\frac{1}{3}k_\mathrm{d}^2I_0t^3+\frac{1}{12}k_\mathrm{d}^3I_0t^4-\frac{1}{3}k_\mathrm{t}k_\mathrm{d}^2I_0^2t^4\end{aligned} \tag{41}$$

Substitution of Eqs. (40) and (41) in Eq. (16) gives Eq. (42):

$$\begin{aligned}\frac{\mathrm{d}H}{\mathrm{d}tm_0}&=k_\mathrm{p}Q(2k_\mathrm{d}I_0t-k_\mathrm{d}^2I_0t^2+\frac{t^3}{3}(k_\mathrm{d}^3I_0-\\&-4k_\mathrm{t}k_\mathrm{d}^2I_0^2))\exp(-k_\mathrm{p}(k_\mathrm{d}I_0t^2-\frac{1}{3}k_\mathrm{d}^2I_0t^3+\\&+\frac{1}{12}k_\mathrm{d}^3I_0t^4-\frac{1}{3}k_\mathrm{t}k_\mathrm{d}^2I_0^2t^4))\end{aligned} \tag{42}$$

The introduction of new constants $K_3=k_\mathrm{t}k_\mathrm{d}$ and $K_4=k_\mathrm{p}k_\mathrm{d}$ is necessary. The result is Eq. (43) which is the final equation of Model 3:

$$\begin{aligned}\frac{\mathrm{d}H}{\mathrm{d}tm_0}&=K_4Q(2I_0t-k_\mathrm{d}I_0t^2+\frac{t^3}{3}(k_\mathrm{d}^2I_0-\\&-4K_3I_0^2))\exp(-K_4(I_0t^2-\frac{1}{3}k_\mathrm{d}I_0t^3+\\&+\frac{1}{12}k_\mathrm{d}^2I_0t^4-\frac{1}{3}K_3I_0^2t^4))\end{aligned} \tag{43}$$

Model 3 showed a good agreement with experimental results but not as good as expected (Table 1 and Figs. 1–4). This is probably due to the mathematical approximation made by expansion into a Taylor series. Model 3 provides values for all three rate constants that are not interdependent.

CONCLUSIONS

In this paper, we have shown that Model 0, based on the assumptions of the classic theory does not satisfactorily describe the initial stage of radical polymerization, *i.e.* the beginning of the DSC thermogram of isothermal methyl methacrylate polymerization. We have developed three models in order to describe the initial part of the DSC thermogram and tested them with experimental results. The models developed in this study have shown that the polymerization of methyl methacrylate has a significant initial period during which the radical concentration has to reach its steady state. Model 2 and 3 which take this into account are in much better agreement with experimental results. Model 2 was the most successful considering the correlation coefficients and standard deviations. Model 3, which takes neither of the two assumptions of the classic theory of radical polymerization, was not as successful as Model 2. This is probably due to the mathematical complexity of Model 3 which takes into consideration the decay of initiator concentration.

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IZVOD

UTICAJ TEMPERATURE NA POČETNI STADIJUM RADIKALNE POLIMERIZACIJE METILMETAKRILATA U MASI

Vladislav M. Jašo, Dragoslav M. Stoiljković, Radmila Ž. Radičević

Tehnološki fakultet, Univerzitet u Novom Sadu, Novi Sad, Srbija

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Najveći broj polimera koji se proizvode širom sveta sintetizuje se radikalnom polimerizacijom. Klasična teorija radikalne polimerizacije zasnovana je na dve pretpostavke. Prva pretpostavka ove teorije je da se koncentracija inicijatora može uzeti kao konstantna tokom početnog perioda polimerizacije. Prema drugoj pretpostavci stacionarno stanje u pogledu koncentracije radikala dostiže se već od samog početka reakcije, odnosno brzina reakcije iniciranja i brzina terminacije su izjednačene od samog početka. Jednačina za brzinu polimerizacije, zasnovana na ovim pretpostavkama, ne može sa uspehom da opiše početni period polimerizacije metilmetakrilata. Radi rešavanja ovog problema, razvijena su tri matematička modela pomoću kojih je ispitana opravdanost datih pretpostavki. Modeli su provereni fitovanjem eksperimentalnih podataka dobijenih izotermskom polimerizacijom metilmetakrilata pomoću metode diferencijalne skenirajuće kalorimetrije (DSC) na temperaturama 60, 70, 80, 90 °C uz koncentraciju inicijatora (AIBN) od 0,5 mas%. Najbolje se pokazao model koji polazi od pretpostavke da je koncentracija inicijatora konstantna tokom početnog perioda ali uzima u obzir da je koncentracija radikala u početku nestacionarna i da je za dostizanje stacionarnog stanja potrebno 2–3 min.

Ključne reči: Metilmetakrilat • Radikalna polimerizacija • Početni stupanj • Matematičko modelovanje

Key words: Methyl methacrylate • Free radical polymerization • Initial stage • Mathematical modelling