

Influence of Microwave Heating on the Kinetic of Acrylic Acid Polymerization and Crosslinking

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ABSTRACT: Kinetics of isothermal formation of poly (acrylic acid) (PAA) hydrogels through polymerization of acrylic acid and crosslinking of the PAA formed in a conventionally heated reaction system and in a microwave heated reaction system were investigated. It was found that in the microwave heated system the reaction rate constant of PAA hydrogel formation significantly increased (from 32 to 43 times) when compared with the conventionally heated system. The isothermal kinetics of the PAA hydrogel formation during the microwave process could be described by the so-called first-order chemical reaction kinetics model. In contrast, the so-called second-order chemical reaction rate model could best describe the isothermal kinetics of the PAA hydrogel formation during the conventionally heated process. Also, in the microwave heated system, the reaction kinetics of the

PAA hydrogel formation and its kinetic parameters changed, that is, the activation energy (E_a) decreased by about 19% and the pre-exponential factor ($\ln A$) decreased by 2.2 times. The decrease in activation energy, change in entropy of activation energy, and decrease in the pre-exponential value of PAA hydrogel formation under microwave heating are caused with increased energy of the reactive species when compared with their energy in thermal activation. Increased energy of the reactive species is a consequence of rapid transfer and absorption of the energy of microwave field to the existing reactive species. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 55–63, 2010

Key words: poly(acrylic acid); hydrogel formation; heating; microwave; kinetics; model

INTRODUCTION

Microwave synthesis represents a major breakthrough in synthetic chemistry methodology, an important change in the way chemical synthesis is performed and in the way it is perceived in the scientific community.¹ The use of microwave irradiation as a heating source for polymerizations reactions is rapidly growing branch in polymer science.² Microwave-assisted heating could accelerate the rates of polymerization reactions and improve the properties of the products, which is the reason why microwave-assisted chemical synthesis has attracted wide attention. The enhanced reaction rates have been focused to originate from thermal effects for large number of these reactions. For some reactions, however, it seems that these advantages do not result from higher reaction temperatures, but from the selective excitation of one of the educts involved. The current debate on the use of microwaves as an

alternative to conventional heating has focused on the involvement of a specific microwave effect, other than the well-accepted dielectric heating.^{1,2} There are reports of various reactions that show similar kinetics in both the presence and absence of microwaves at comparable temperatures,^{3–5} suggesting a simple dielectric heating of materials by microwaves. In contrast, however, there are other reports that show a clear reaction rate enhancement in the presence of microwave radiation compared to polymerization at elevated temperatures under comparable reaction conditions^{6,7} indicating a “specific microwave effect” other than the well-accepted dielectric heating.

Superabsorbing materials have been prepared under microwave irradiation by the copolymerization of corn starch, sodium acrylate, and poly(ethylene glycol) diacrylate by Zheng et al.⁸ Xu et al. prepared superabsorbers by the copolymerization of starch, sodium acrylate, and 2-acrylamido-2-methylpropanosulfonic acid and found that the polymerization was faster under microwave irradiation, and that the swelling rate of the material prepared under microwave irradiation was much higher than for the material prepared by conventional heating.⁹ Shi and Liu reported microwave-assisted preparation of poly(*N*-iso-propylacrylamide) (PNIPAAm) hydrogel with improved responsive properties, such as faster swelling and shrinking rates. They found that the

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polymerization/crosslinking reaction of the microwave hydrogel under 75 W microwave irradiation was completed in 40 s, with a yield of 99%, whereas the reaction of thermal hydrogel formation at 62°C needed 5 min to form a bulk hydrogel with approximately the same yield.¹⁰ The results of Zhao et al. showed that the use of microwave irradiation can greatly shorten the reaction time required for PNIPAAm hydrogel synthesis from several hours to several minutes in comparison with water bath heating method and obviously improve the yields of the PNIPAAm gels, which were up to 99% after a short reaction time. The PNIPAAm hydrogels synthesized using microwave irradiation had more porous structure and had much higher swelling ratios at 10.0°C below the LCST, whereas swelling ratio at 60.0°C above the LCST was lower compared with the hydrogels synthesized by water bath method.¹¹

Also, microwave-assisted synthesis of hydrogel-forming polymers based on hydrophobically modified poly(acrylic acid) (PAA) was described. In that work, gel-forming polymer systems based on PAA were prepared via polymer analog reactions under microwave irradiation in a short time frame.¹²

Acrylic acid was grafted onto chitosan under microwave irradiation. The results showed that the microwave irradiation method can increase the reaction rate by eight times over the conventional method and that the grafting degree and grafting efficiency of the resins approached to the ones obtained by the traditional heating method.¹³

Microwave irradiation has also been used in the synthesis of chitosan-*g*-poly(acrylonitrile) without any radical-initiator in a very short time of 1.5 min¹⁴

Prasad et al. reported one-pot route of the synthesizing a very high yield graft copolymer of κ -carrageenan with methyl methacrylate (MMA) in the presence of potassium persulfate as an initiator in aqueous medium. They showed that microwave irradiation under controlled conditions can result in the formation of undegraded copolymer of κ -carrageenan. Optimum microwave irradiation conditions for obtaining maximum yields are described.¹⁵

Conventional and microwave kinetics of MMA polymerization were compared and discussed.¹⁶ The decreased activation energy of the polymerization process under microwave heating with respect to the conventional polymerization was explained by formation of nonequilibrium energy distribution of the reactants due to a rapid transfer of energy in the reaction system.

To the best of our knowledge, there are no data on the kinetics of PAA hydrogel formation in a microwave field. The aim of this study was to investigate the kinetics of the overall process of PAA hydrogel formation, which takes place through the polymerization of acrylic acid and crosslinking of the PAA

formed, both in the case of the conventionally and the microwave heated process. Another goal was to establish and explain the effects of microwave heating on the kinetics of the process, in case of a difference between the two heating methods.

MATERIALS AND METHODS

Materials

Materials for hydrogel synthesis: Acrylic acid (99.5%) (AA) was supplied by Merck KGaA, Darmstadt, Germany. The *N,N*-methylene bisacrylamide (p.a) (MBA) was purchased from Aldrich Chemical, Milwaukee, WI. The initiator, 2,2-azobis-[2-(2-imidazoline-2-yl)-propane dihydrochloride (VA044), (99.8%) was supplied by Wako Pure Chemicals Industries, Osaka, Japan.

Synthesis

PAA hydrogel was synthesized following the procedure based on radical polymerization of acrylic acid and crosslinking of the PAA formed, which was done by a procedure based on the general procedure described in our previous papers.^{17,18} It goes as follows: a 20 wt % solution of acrylic acid is prepared and mixed with a solution of MBA (0.1 wt % of the monomer). After stirring these two mixtures well for half an hour to ensure homogeneity of the reaction mixture and nitrogen bubbling through the mixture, the initiator solution (0.06 mol % of the monomer) is added, and the reaction mixture once again rapidly homogenized by stirring. The prepared solution is placed into a glass ampoule of working volume $V = 10$ mL, deoxygenated once again, sealed, and placed in a dry oven or a microwave reactor, for a predetermined time interval (0.5–400 min) at a desired temperature (303, 313, and 323 ± 2 K). After a defined reaction time, reaction is stopped by fast removal ($t = 1$ –2 s) of the ampoules with the reaction mixture from the dry oven or microwave reactor, subsequently exposing them to rapid cooling ($t = 1$ –2 s) in an ice bath. The resulting hydrogel is removed from the ampoules, cut into approximately equal discs, and placed in an excessive amount of distilled water. The water is changed for 7 days for every 2–3 h (or every 12 h during the night), to remove the unreacted monomers and the sol fraction of the polymer. Subsequently, the obtained hydrogel is dried in an air oven in a temperature regime of 353 K for 2 h, 363 K for 3 h, and 378 K until the sample reaches a constant mass.

In the case of microwave-assisted synthesis, the prepared reaction mixture is placed in a focused microwave reactor (Discover, CEM Corporation, Matthews, NC). This reactor is supplied with a

device for maintaining constant temperature by simultaneously varying the input power of the microwave field and cooling the reaction mixture by dry nitrogen. All the reactions are carried out in a microwave field of 2.45 GHz. The temperature of the reaction mixture is controlled by a fiber-optic temperature sensor. The temperature ranged from 303 to 323 K (± 1 K) during 0.5–5 min. This time was sufficient to approximately reach the 100% yield of the PAA hydrogel.

The yield (%) of the obtained product of the cross-linked PAA was determined gravimetrically, by measuring the weight of the washed-out hydrogel, and dried to constant weight (W_t). It was calculated as the ratio of the W_t and the weight of the monomers (monomer and crosslinker) in the reaction mixture (W_o) [eq. (1)]:

$$Y = \frac{W_t}{W_o} \quad (1)$$

The degree of the PAA hydrogel formation (α) is calculated by eq. (1a):

$$\alpha = \frac{Y}{Y_{\max}} \quad (1a)$$

where Y is the yield of the obtained PAA hydrogel at time t and Y_{\max} is the maximum value of the hydrogel yield obtained at a certain temperature.

Determination of the swelling degree

Swelling experiments were performed in distilled water at 25°C in the usual manner, as described in detail.^{17,18} The isothermal swelling degree (SD), defined as the difference between the weight of the swollen hydrogel sample at time (t), (m_t), and the weight of the xerogel sample (m_o), divided by the xerogel weight (m_o), were calculated according to eq. (2) and determined as a function of time:

$$SD[\%] = \frac{m_t - m_o}{m_o} \cdot 100 \quad (2)$$

The equilibrium swelling degree (SD_{eq}) is the SD of the equilibrium swollen hydrogel, that is, the hydrogel sample which attained a constant mass (m_{eq}). At least three swelling measurements were performed for each sample, and the mean values reported.

Methods used to evaluate the kinetic parameters

Friedman's differential isoconversional method

The kinetic parameters of different degrees of the PAA hydrogel formation ($E_{a,\alpha}$, $\ln A_\alpha$) were deter-

mined using Friedman's differential isoconversional method¹⁹, which is based on the following rate eq. (3):

$$\frac{d\alpha}{dt} = Af(\alpha) \exp\left(-\frac{E}{RT}\right), \quad (3)$$

where T is the temperature, A is the pre-exponential factor, E is the apparent activation energy, $f(\alpha)$ is the reaction model, and R is the gas constant.

The logarithmic form of the rate eq. (3) is eq. (4):

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = \ln A_{\alpha,i} + \ln f(\alpha) - \frac{E_{a,\alpha_i}}{RT_n} \quad (4)$$

where subscript n denotes the ordinal number of the isothermal experiment and subscript α_i denotes the selected degrees of PAA formation in terms of its quantity (α). Because $v_\alpha = \left(\frac{d\alpha}{dt}\right)_{\alpha_i} \approx \frac{1}{t_{\alpha_i T_n}}$, eq. (4) transforms to:

$$\ln\left(\frac{1}{t_{\alpha_i T_n}}\right) = \ln[A_{\alpha,i} + \ln f(\alpha)] - \frac{E_{a,\alpha_i}}{RT_n} \quad (5)$$

where $t_{\alpha_i T_n}$ is the time in which α_i is achieved at T_n .

For $\alpha = \text{const}$, the plot $\ln\left(\frac{1}{t_{\alpha_i T_n}}\right)$ versus $(1/T_n)$ obtained from conversional curve should be a straight line whose slope allowed to evaluate the $E_{a,\alpha}$ and intercept $\ln A_\alpha$.

Characterizations of the synthesized xerogels

The xerogel samples were characterized by the following structural properties: xerogel density (ρ_{Xg}), crosslink density (ρ_c), and the distance between macromolecular chains (d), assuming the homogeneous network structure. The xerogel density was determined by picnometry, using n -hexane as the nonsolvent. The crosslink density and the distance between macromolecular chains (d) were calculated using the following equations proposed by Gudman and Peppas²⁰:

$$\rho_c = \frac{\rho_{\text{Xg}}}{M_c} \quad (6)$$

$$d = 0.154 \cdot v_2^{1/3} [0.19 \cdot M_c]^{1/2} \quad (7)$$

where M_c is the molar mass between the network crosslinks and is a nominal value estimated from the initial composition:

$$M_c = \frac{72}{2X}, \quad (8)$$

where X is the nominal crosslinking ratio (moles of MBA / moles of acrylic acid in the reaction mixture).

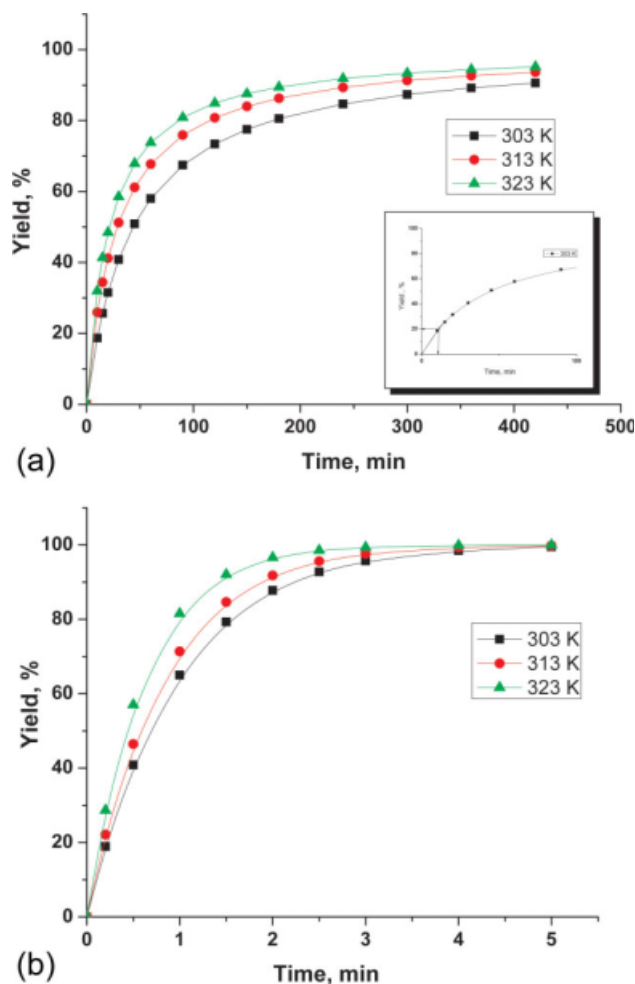


Figure 1 (a) Conversion curves of PAA hydrogel formation under the conventional heating. (b) Conversion curves of PAA hydrogel formation under the microwave heating. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Figure 1 shows the isothermal kinetics of PAA hydrogel formation under the conventional heating (a) and under microwave heating (b) at different temperatures.

All of the conversion curves, both for the conventional and the microwave heated process of the PAA hydrogel formation, are similar in shape. At all of them, three distinct stages of the changes of the

PAA hydrogel formation in time can be clearly observed: a linear, nonlinear, and a saturation stage. With increasing temperature, both conventionally and by microwaves, the duration of the linear changes in the degree of PAA hydrogel formation decreases, as well as the time required to achieve the saturation stage. As the process of PAA hydrogel formation through simultaneous radical polymerization and crosslinking can reveal the complex nature of the kinetics, the effect of the degree of PAA hydrogel formation on the rate and the kinetics of the process was preliminarily checked. For that purpose, the initial reaction rate (v_{in}) and the reaction rate for the 90% yield were determined. The initial reaction rate was calculated as follows:

$$v_{in} = \frac{Y_L}{t_L} \quad (9)$$

where t_L is the time interval ($t_L - t_0$) within which the degree of PAA hydrogel formation increases linearly with the reaction time, and Y_L is the yield of the PAA hydrogel corresponding to t_L . The values of t_L and Y_L were determined graphically [Fig. 1(a)].

The reaction rate $v_{90\%}$ was calculated from eq. (10):

$$v_{90\%} = \frac{90\%}{t_{90\%}} \quad (10)$$

where $t_{90\%}$ is the reaction time at which 90% yield is achieved, at a defined temperature. The changes of the parameters of the conversion curves (t_L , v_{in} , $t_{90\%}$, and $v_{90\%}$) with temperature for the conventional and the microwave heated process of PAA hydrogel formation are given in Table I.

From the results presented in Table I, it can be seen that the temperature increase leads to an increase in v_{in} and $v_{90\%}$ for both conventional and microwave heated processes. At the same temperature, the values of v_{in} and $v_{90\%}$ are significantly higher for the microwave heated processes. As the v_{in} and $v_{90\%}$ changed exponentially with temperature for both processes, the kinetic parameters for these processes could be determined by applying the Arrhenius equation. The values of the activation

TABLE I
Changes of the Initial Time (t_L), Initial Rate (v_L), $t_{0.9}$, and $v_{0.9}$ with Temperature for PAA Hydrogel Formation by the Conventional and the Microwave Process

T (K)	Conventional process					Microwave process				
	t_L (min)	Y_L (%)	v_{in} (%/min)	$t_{90\%}$ (min)	$v_{90\%}$ (%/min)	t_L (min)	Y_L (%)	v_{in} (%/min)	$t_{90\%}$ (min)	$v_{90\%}$ (%/min)
303	10.04	20.50	1.83	418	0.22	0.21	18.90	90.00	2.20	40.9
313	9.14	24.75	2.52	298	0.30	0.19	20.17	106.15	1.90	47.4
323	7.30	30.00	3.14	240	0.38	0.15	21.29	141.93	1.44	62.5

TABLE II
Kinetic Parameters (Activation Energy, E_a , and Pre-Exponential Factor, $\ln A$) for Poly(acrylic acid) Hydrogel Formation

Rate	Conventional process		Microwave process	
	E_a (kJ/mol)	$\ln Af(\alpha)$ (min^{-1})	E_a (kJ/mol)	$\ln Af(\alpha)$ (min^{-1})
v_{in}	22 ± 1	9.4 ± 0.5	18.5 ± 1	11.8 ± 0.5
$v_{90\%}$	22.6 ± 1	2.96 ± 0.1	17.2 ± 1	6.1 ± 0.1

energies and pre-exponential factors ($E_{a,\text{inv}}$, $\ln A_{\text{inv}}$, $E_{a,90\%}$, and $\ln A_{90\%}$) are given in Table II.

Based on the results presented in Table II, it can be easily concluded that the values of activation energies, both for the conventionally heated and the microwave heated process, are almost independent on the degree of PAA hydrogel formation. Actually, the values of activation energies for the microwave heated process are about 19% lower than those for the conventional process. In contrast, the values of $\ln Af(\alpha)$ both for the conventionally heated and the microwave heated process decreased with increasing α . The values of $\ln Af(\alpha)$ for the microwave heated process are about twice as high as the value for the conventionally heated process.

The established independence of the E_a on the α allows making an assumption that kinetics of PAA hydrogel formation in both processes take place through kinetic mechanisms, which are not complex and can be modeled by a set of kinetic parameters developed for single-step reaction.

To prove that hypothesis, the method of Vyazovkin was applied for examining the complexity of the kinetics of this process. The Vyazovkin method is based on determining the shape of the plot of $E_{a,\alpha}$ versus α .²¹ To apply the method, these plots were established by Friedman's differential isoconversional method¹⁹ for the investigated process under conventional and microwave heating.

With this purpose, the plots of $\ln v_{\alpha,T_i} = f(1/T)$ for different degrees of PAA hydrogel formation during the conventional and the microwave process were determined and presented in Figure 2(a,b).

As can be seen from the results presented in Figure 2(a,b), there was a linear relationship between the $\ln v_{\alpha,T_i}$ and the inverse temperature ($1/T_n$) for all the degrees of PAA hydrogel formation, for either of the processes. From the slopes and intercepts of these straight lines, the values of the kinetics parameters ($E_{a,\alpha}$ and $\ln A_{\alpha}$) for each value of the degree of PAA hydrogel formation (α) were obtained. The plots of $E_{a,\alpha}$ versus α are shown in Figure 3.

The results presented in Figure 3 enable us to say with great certainty that the E_a of PAA hydrogel formation is independent on the degree of formation both in the conventional and microwave heated

process. That confirms that the investigated processes occurred through the kinetic mechanisms, which are independent on the degree of PAA hydrogel formation for either process.

With that in mind, to establish the kinetic model for PAA hydrogel formation during the microwave and conventionally heated process, a "model-fitting" method was applied.²² The appropriate kinetic model was determined by comparing (graphically and analytically) the experimentally obtained function $\alpha_e = f(t_N)$ with the theoretical functions $\alpha = f(t_N)$ for different solid-state reaction models. The normalized time (t_N) was determined using eq. (11):

$$t_N = \frac{t}{t_{0.9}} \quad (11)$$

where $t_{0.9}$ is the reaction time at $\alpha = 0.9$. The set of kinetic reaction models used to determine the model

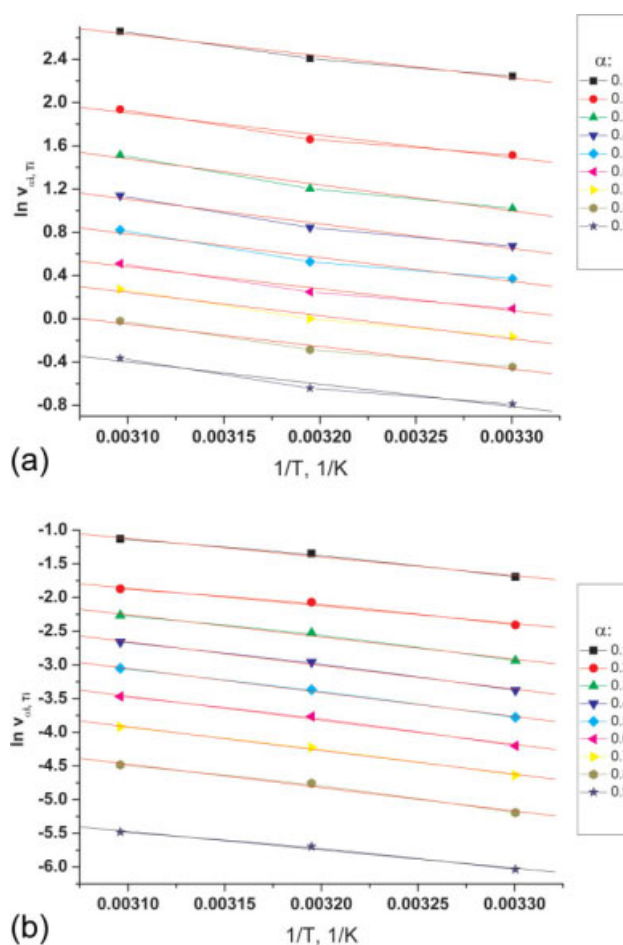


Figure 2 (a) The dependences of $\ln v_{\alpha,T_i}$ on inverse temperature ($1/T$) for different degrees of PAA hydrogel formation (α) for conventionally heated process. (b) The dependences of $\ln v_{\alpha,T_i}$ on inverse temperature ($1/T$) for different degrees of PAA hydrogel formation (α) for microwave heated process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

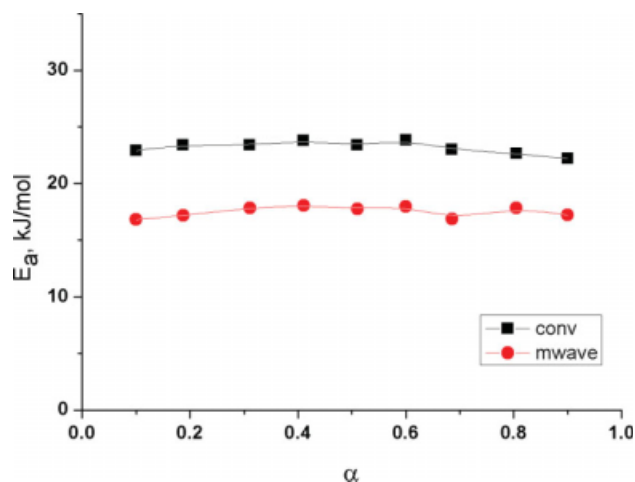


Figure 3 The dependences of E_a versus degree of (α) for conventional (■) and microwave (●) process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

of the investigated reaction was taken from the work of Vyazovkin and Wight.¹⁷

It was found that isothermal curves of the changes of the degree of PAA hydrogel formation with t_N were different for the conventional and the microwave heating processes, which implied different kinetic models and mechanisms of the reaction. Based on the results obtained, it can be stated with great certainty that isothermal kinetics of PAA hydrogel formation during the microwave process can be described by the so-called kinetic model of the first-order chemical reaction. It can also be stated with great certainty that the so-called kinetic model of the second-order chemical reaction rate would be the best model to describe isothermal kinetics of PAA hydrogel formation during the conventionally heated process. That means that the following expressions are valid, respectively:

$$-\ln(1 - \alpha) = k_{M1} \cdot t \quad (12)$$

$$\left(\frac{1}{1 - \alpha} - 1\right) = k_{M2} \cdot t \quad (13)$$

where k_{M1} and k_{M2} are the respective model constants.

Figure 4 presents plots of $\left[\frac{1}{1 - \alpha} - 1\right]$ versus time for the PAA hydrogel formation during the conventionally heated process at the investigated temperatures.

If we defined a range of degree of PAA hydrogel formation within which experimental results are equal to the predicted theoretical model as “periods of applicability” (P), the results presented in Figure 4 show that for a very wide range of such “periods of applicability” ($P \geq 90\%$), at all of the investigated temperatures, the dependence $\left[\frac{1}{1 - \alpha} - 1\right]$ on time giving straight lines for all the investigated temperatures.

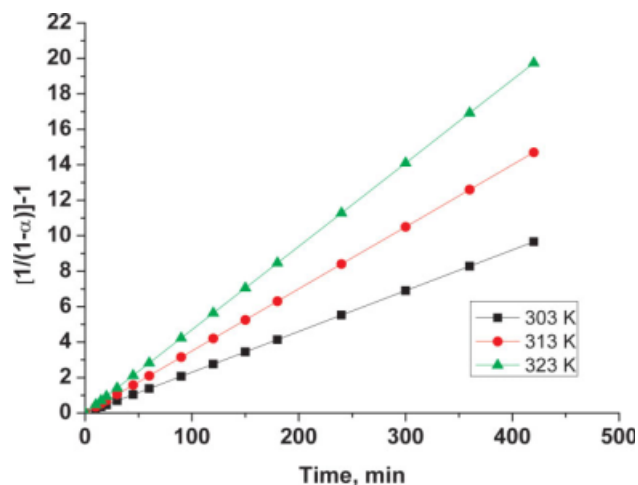


Figure 4 Dependences of $\left[\frac{1}{1 - \alpha} - 1\right]$ on time for PAA hydrogel formation during conventionally heated process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Isothermal plots of $[-\ln(1 - \alpha)]$ versus reaction time in the microwave heated process at different temperatures are shown in Figure 5. These plots for the microwave heated process gave straight lines for almost the whole range of the investigated process, at all the investigated temperatures.

The values of the rate constants (k_{M1} and k_{M2}) were determined from the slopes of the lines obtained according to eqs. (12) and (13), as presented in Figures 4 and 5, respectively. Table III presents the model's rate constants (k_m) and kinetic parameters of PAA hydrogel formation for both processes.

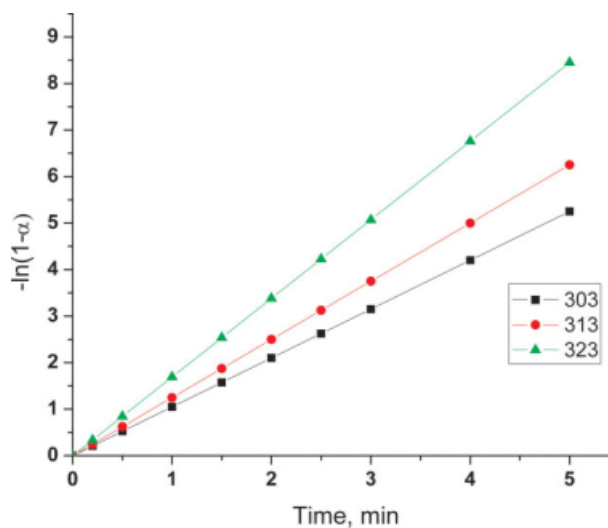


Figure 5 The isothermal dependences of $[-\ln(1 - \alpha)]$ versus reaction time for PAA hydrogel formation in microwave heated process. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
The Model's Rate Constants (k_{M1} and k_{M2}) and Kinetic Parameters for PAA Hydrogel Formation for the Conventional and the Microwave Process

T (K)	Conventional process		Microwave process	
	k_{M2} ($\text{min}^{-1} \text{mol}^{-2}$)	Kinetics parameters	k_{M1} (min^{-1})	Kinetics parameters
303	0.023	$E_a = 21 \pm 1 \text{ kJ/mol}$	1.008	$E_a = 17 \pm 1 \text{ kJ/mol}$
313	0.035	$\ln A = 9.4 \text{ min}^{-1}$	1.18	$\ln A = 8.6 \text{ min}^{-1}$
323	0.047		1.59	

From the results presented in Table III, it can be observed that the reaction temperature increase leads to an exponential increase in models rate constants of both processes. It is easy to observe that the models rate constant of the microwave process is significantly higher (33–45 times) at each of the temperatures. Because the rate constants in the models exponentially increase with temperature, it was possible to determine the kinetic parameters: the activation energy (E_a) and pre-exponential factor ($\ln A$) for the models, by using the Arrhenius equation, which is also presented in Table III. The results show that the microwave heated process leads to a decrease in the activation energy as well as in the pre-exponential factor, in comparison with the conventionally heated process.

The previously established values of the rate constants of the process at different temperatures, the validity of Arrhenius equation for the microwave heating conditions, the kinetic models of the reaction, the calculated values of kinetic parameters (E_a , $\ln A$), and their independence on the degree of PAA formation with either of the heating modes allow for a detailed investigation of the effect of microwave heating of the reaction system on the kinetics and mechanism of PAA hydrogel formation. With all that in mind, it was easy to obtain the expression:

$$Z = \frac{k^{\text{mw}}}{k^{\text{con}}} = \frac{A^{\text{mw}} \exp\left(-\frac{E_a^{\text{mw}}}{RT^{\text{mw}}}\right)}{A^{\text{con}} \exp\left(-\frac{E_a^{\text{con}}}{RT^{\text{con}}}\right)}, \quad (14)$$

where T^{mw} and T^{con} are the temperatures of the reaction system under microwave heating and conventional heating, respectively, and E_a^{mw} and A^{mw} are the calculated values of the kinetic parameters under microwave heating. To explain the effect of microwave heating on the kinetic parameters of the process, we can assume the following: (a) under

microwave heating, the values of the reaction temperature and activation energy remained unchanged when compared with their values with the conventionally heated reaction system, that is: $T^{\text{mw}} = T^{\text{con}}$; $E_a^{\text{mw}} = E_a^{\text{con}}$. In that case, using eq. (14), it was easy to calculate the pre-exponential factor under microwave heating at any of the investigated temperatures [eq. (15)]:

$$A^{\text{mw}} = ZA^{\text{con}} \quad (15)$$

(b) the microwave heating of the reaction system did not lead to changes of the values of the reaction temperature and pre-exponential factor compared to their values with the conventional heating, that is: $T^{\text{mw}} = T^{\text{con}}$ and $A^{\text{mw}} = A^{\text{con}}$. Using eq. (15) it was then possible to calculate the value of the activation energy for the process under microwave heating (E_a^{mw}):

$$E_a^{\text{mw}} = E_a^{\text{con}} - RT^{\text{con}} \ln Z \quad (16)$$

(c) under microwave heating, the kinetic parameters remained unchanged, and only local overheating occurred, that is: $E_a^{\text{mw}} = E_a^{\text{con}}$; $A^{\text{mw}} = A^{\text{con}}$; $T^{\text{mw}} \neq T^{\text{con}}$. It was then easy to calculate the local reaction temperature (T^*) and the local overheating (ΔT) using eqs. (17) and (18):

$$T^{\text{mw}} = \frac{T^{\text{con}}}{\left(1 - \frac{\ln Z RT^{\text{con}}}{E_a^{\text{con}}}\right)} \quad (17)$$

$$\Delta T = T^{\text{mw}} - T^{\text{con}} \quad (18)$$

The calculated values of A^{mw} , E_a^{mw} , T^{mw} , and ΔT are given in Table IV.

The calculated values of the pre-exponential factor (A^{mw}) and the values of the activation energy (E_a^{mw}) at all the investigated temperatures are lower than

TABLE IV
The Calculated Values of A^{mw} , E_a^{mw} , T^{mw} , and ΔT

T (K)	k^{mw} ($\text{min}^{-1} \text{mol}^{-2}$)	A^{mw} (min^{-1})	E_a^{mw} (kJ/mol)	T^{mw} (K)	ΔT (K)
303	43.9	8.26	11.7	550	247
313	33.7	7.99	12.0	550	234
323	33.8	8.00	11.8	583	260

TABLE V
Basic Structural Properties and SD_{eq} of the Selected PAA Xerogels Samples

Sample	ρ_{xg} (g/cm ³)	M_c (g/mol)	ρ_c (mol/cm ³)	d (nm)	SD_{eq} (g/g)
PAA-con	1.11	4418.61	0.01629	13.07	22.45
PAA-mw	1.27	2421.52	0.02973	8.375	12.45

the experimentally determined values with both of the heating modes. It follows that microwave heating leads to a change in the values of the kinetic parameters, both the pre-exponential factor and the activation energy, with respect to the same values in the conventionally heated process.

Local temperature and local preheating caused by microwave heating of the reaction system are dramatically higher than those obtained from the experimentally detected temperature changes under microwave heating (± 0.5) and actually possible changes of the temperatures in the reaction system. That fact strongly suggests that under isothermal microwave heating, changes of the E_a and $\ln A$ values really occur.

Based on all said, it may be concluded that in comparison with conventional heating, isothermal microwave heating leads to changes in the kinetic model of PAA formation and to a decrease in both the activation energy and the pre-exponential factor.

The changes established in the kinetic parameters and in the kinetic models for the conventional and microwave heated process can be explained as follows.

Under isothermal microwave heating, a rapid transfer of the microwave field energy occurs ($t \sim 10^{-10}$ s), through thermally nonequibrated absorption of that energy to the existing reactive species (molecules of monomer, initiator, crosslinker, radical-initiator, monomer-initiator radical, macroradicals, etc.)

The absorbed microwave energy leads to an increase in the inherent energy of the reactive species (with respect to thermal activation) and to a change in distribution (relative ratio) of the different values of the inherent energy of the reactive species.

Instead of an equilibrated Maxwell-Boltzman thermal distribution of the energy of the reactive species, a thermally nonequibrated distribution of the inherent energy of the reactive species with a dominant ratio of the reactive species with higher values of inherent energies is formed. Because activation energy for PAA hydrogel formation is inversely proportional to the inherent energy of the reactive species, it makes sense that microwave heating leads to a decrease in activation energy with respect to its value in the conventionally heated process. The increased value of the inherent energy of the molecules of the initiator, the decreased activation energy, and their nonequibrated distribution are

the reasons for the rapid decomposition of the initiator molecules, that is, for a significant increase in the rate of initiation and polymerization.

Also, because of an increase in the polymerization rate and inherent energy of the molecules of the crosslinker, the crosslinking rate significantly increases with microwave heating in comparison to the same with thermal heating.

A pronounced increase in the crosslinking rate is the main reason for the change in the kinetic model of PAA hydrogel formation under microwave heating with respect to thermal heating. Because of the significantly higher crosslinking rate than the polymerization rate, the rate of PAA hydrogel formation depends only on the polymerization rate, that is, on the concentration of the monomers.

The differences recognized in the kinetics of PAA hydrogel formation between the two modes of heating allow for an assumption that the structural properties of the PAA hydrogels formed are also different.

To prove that idea, we determined and compared the basic structural properties and SD_{eq} s of the obtained PAA hydrogel samples synthesized under both heating modes at 50°C and maximum yields. The SD_{eq} s obtained in distilled water at 25°C, basic structural properties of the PAA xerogels synthesized under the conventional and the microwave heating at 50°C, at times of the maximum yield, are given in Table V (denoted PAA-con and PAA-mw, respectively).

Although we are deeply aware of the fact that the obtained xerogels samples are most probably inhomogeneous networks, the basic structural properties were determined assuming the homogeneous network structure. With that in mind, as can be seen from the results, structural properties of PAA xerogel prepared under microwave heating are different from the comparable xerogel prepared under conventional heating at the same temperature (50°C). Xerogel density and crosslink density of the PAA-mw xerogel are higher than that of the PAA-con xerogel, but molar mass between the network crosslinks (M_c) and the distance between macromolecular chains (d) are lower in the PAA-mw xerogel. Consequently, PAA-mw hydrogel has a lower SD.

The properties determined are in agreement with the previously found extremely higher reaction rate of the microwave heated reaction process, which lead to faster formation of shorter polymer chains.

Furthermore, the polymer chains formed also undergo a very fast crosslinking reaction. All this leads to a higher crosslink density structure of the PAA hydrogels.

The increased rate of acrylic acid polymerization and crosslinking under microwave heating leads to a significant decrease in the lengths of the polymer chains formed, and because of that the value of M_c is lower in the microwave heated system than in the conventional process. The formation of short chains and their rapid crosslinking directly leads to an increase in the xerogel density and crosslink density, but to a decrease in the distance between the macromolecular chains and in the SD_{eq} . The established texture differences of the PAA hydrogels between the hydrogels formed under microwave heating and conventional heating confirm the difference in the kinetic models.

CONCLUSIONS

Isothermal microwave heating, when compared with conventional heating, leads to changes in the kinetic model of PAA hydrogel formation, a decrease in the activation energy and the pre-exponential factor. The changes in the kinetic model are a consequence of the more rapid decomposition of the initiator and a nonequilibrated distribution of the reactive species. The decrease in the activation energy and the pre-exponential factor is caused by increased energy of the reactive species.

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