

Comparison of the Kinetics of Conventional and Microwave Methyl Methacrylate Polymerization

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ABSTRACT: A comparative investigation of the conventional and microwaves kinetics of methyl methacrylate (MMA) polymerization was performed. A method for determining the increase of the reaction rate in the microwave field (β) was presented. It was found that at all of the investigated temperatures and powers the polymerization rates increased in the presence of microwave energy by up to 8.9 times compared with conventional polymerization. Isothermal kinetics of the conventional MMA polymerization was investigated and its parameters were determined using iso-conversion method. It was found that the calculated kinetics parameters changes complexly with degree of MMA conversion (α) and are in the mutual linear functional relationship, which is so called "compensation effect." The complex changes of the kinetics parameters with α are explained with the postulated model for the mechanism of the MMA polymerization. The kinetics of the MMA polymerization

under the microwave field (MWF) with different input power was investigated and its parameters were determined on the basis of the conversion-temperature curves and Arrhenius equation. The values of the kinetics parameters for MMA polymerization in the MWF are dependent on α and are from 1.2 to 12 times lower than that for conventional MMA polymerization. A new method for the determination of activation energy (E_a) of the investigated process in the MWF was described. Decreased E_a value of the polymerization process in the MWF compared with the conventional polymerization is explained with the formation of the nonequilibrium energetic distribution of the reactants due to the rapid transfer of energy in the reaction system. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1775–1782, 2007

Key words: activation energy; kinetics; modeling; processing; radical polymerization

INTRODUCTION

One of the most important unmodified acrylic materials is poly(methyl methacrylate) (PMMA). Although it was discovered and commercialized many years ago, PMMA is one of the most widely used industrial and commercial polymeric materials and still remains an active material for research in new frontiers. PMMA is usually produced using a peroxide or azo initiator. The free-radical polymerization of MMA can be carried out in bulk, solution, suspension, or emulsion. Polymerization temperatures can range from 50 to 170°C, depending on the process being used and the desired properties of the polymer. The polymerization of methyl methacrylate (MMA) under "classical" conditions has been studied in detail.¹

Conventional heating, long known to be inefficient and time-consuming, has been recognized to be creatively limiting as well. Microwave synthesis represents a major break-through in synthetic chemistry

methodology, a dramatic change in the way chemical synthesis is performed and in the way it is perceived in the scientific community.²

Jacob et al. investigated MMA polymerization by microwave radiation at three different power settings, 200, 300, and 500 W. They found that under comparable experimental conditions the rate of polymerization by microwave energy did not show a significant rate enhancement. Actually, the rate of polymerization at 200, 300, and 500 W was found to be almost similar to polymerization at 69, 78, and 88°C, respectively. Polymerization in the presence of microwaves at 500 W showed a limited conversion.³

The current debate on the alternative use of microwaves to conventional heating has focused on the involvement of a specific microwave effect other than the well-accepted dielectric heating. There are reports of various reactions that show similar kinetics in both the presence and absence of microwaves at comparable temperatures,^{4–6} suggesting the simple dielectric heating of materials by microwaves. There are other reports, however, which show a clear reaction rate enhancement in the presence of microwave radiation compared with polymerization at elevated temperatures under comparable reaction conditions,^{7,8} indicating a "specific microwave effect" other than the well-accepted dielectric heating.

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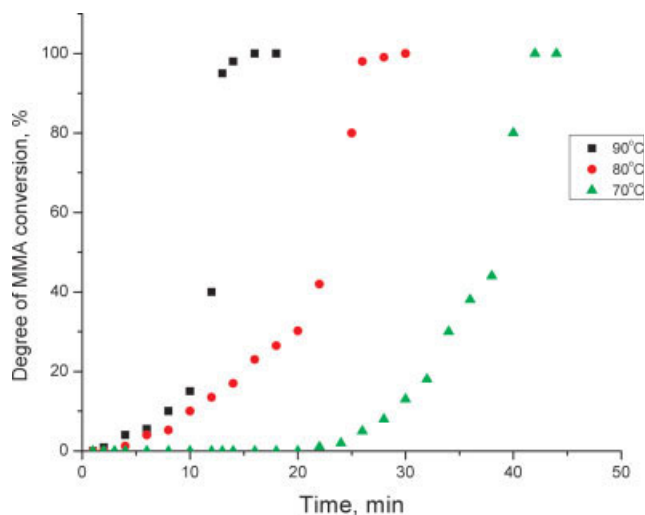


Figure 1 Kinetics curves of MMA polymerization under the conventional conditions. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In this work, the conventional and microwaves kinetics of MMA polymerization was compared and discussed.

Bearing in mind the fact that polymerization under the influence of microwave field (MWF) occurred at different conditions than conventional isothermal polymerization, certain procedures for kinetics parameters determinations were developed in this work.

EXPERIMENTAL

Materials and methods

The monomer MMA (p.a.) was obtained from Merck, Darmstadt, Germany, and distilled under vacuum before use. Benzoyl peroxide (BPO) (p.a.) obtained from Merck was used as the polymerization initiator. Toluene (p.a.) and methanol (p.a.) were purchased from Merck.

General polymerization procedure

The polymerization of MMA was undertaken in bulk with 0.05 mass % of BPO, using glass-sealed ampoules with a working volume of 2 cm³. The ampoules filled with the reaction mixture and properly sealed were placed in a thermal or microwave oven. After specified time intervals, the ampoules containing the reaction products were removed from the apparatus and immediately cooled in ice-water to stop the polymerization. The obtained PMMA samples were isolated from the reaction mixture by standard precipitation in methanol. Conventional polymerization was conducted in a 1000-W oven at 70, 80, and 90°C up to 50 min. The microwave polymerization was conducted

in a commercial microwave oven (Samsung model M191DN) modified for chemical application,⁹ with device for temperature measurements, in a MWF of 2.45 GHz frequency with different input powers 510, 540, and 570 W up to 15 min.

Measurements

The degree of MMA conversion (α , %). The degree of MMA conversion was determined by gravimetry.

The intrinsic viscosity ($[\eta]$). The intrinsic viscosity of the PMMA samples was determined using the standard procedure in toluene at $(25 \pm 0.5)^\circ\text{C}$.

Imaginary part of dielectric constant (ϵ''). This was determined by applying the method of oscillatory circuit.

The degree of reaction rate enhancement (β). Neglecting the influence of temperature changes during the polymerization in the MWF, the degree of reaction rate enhancement for MMA polymerization in a MWF compared with conventional polymerization was calculated according to eq. (1):

$$\beta = \frac{t_{T_{i,\alpha}}}{t_{P_{i,\alpha}}} \quad (1)$$

where, $t_{T_{i,\alpha}}$ is the time in which a certain degree of MMA conversion (α) was achieved at a definite temperature (T_i) for conventional polymerization, and $t_{P_{i,\alpha}}$ was the time in which a certain degree of MMA conversion (α) was achieved at a definite power (P_i) in the MWF.

RESULTS AND DISCUSSION

Figure 1 presents the time dependence of the degree of MMA conversion (α) during polymerization at constant temperatures (kinetic curves of MMA polymerization).

As can be seen from the results presented in Figure 1, the kinetic curves of MMA polymerization are similar by shape at all of the investigated temperatures. Three characteristic shapes of changes of the monomer degree of conversion (α) with reaction time can be distinguished. They correspond to particular, well-defined stages of polymerization kinetics: initiation, propagation, and termination. Increase of the polymerization reaction temperature leads to a decrease of the duration of both initiation and propagation reaction stages, i.e., the overall polymerization time.

The presented results agree quite well with the well-known and well-studied behavior in the case of typical free-radical polymerization processes.¹⁰ Increase of the polymerization reaction temperature leads to a significant increase of the overall reaction

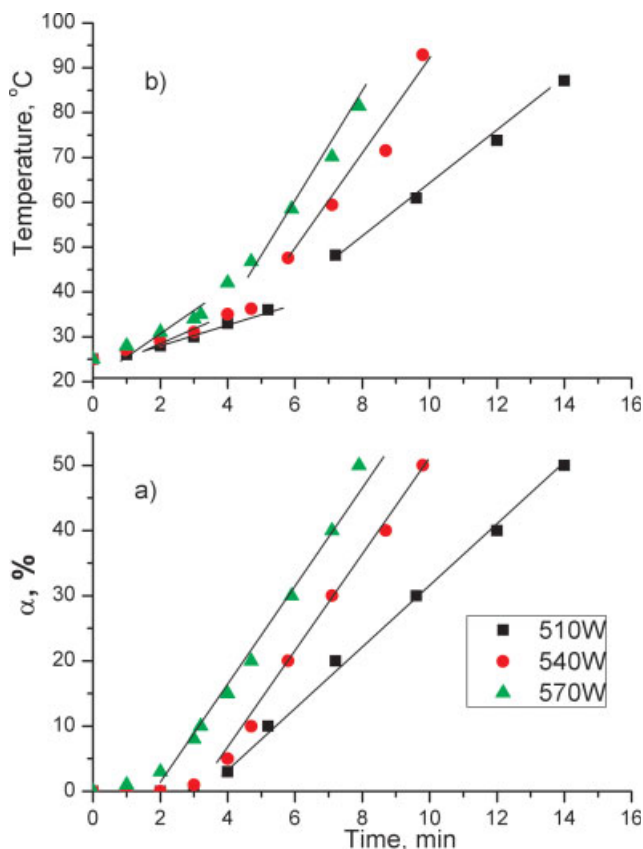


Figure 2 (a) Kinetic curves of MMA polymerization in the MWF. (b) The temperature changes in the reaction system during the MMA polymerization in the MWF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

rate, and a decrease of the initiation reaction stage is particularly pronounced.

The kinetic curves of MMA polymerization in the MWF with different powers are presented in Figure 2(a), while corresponding changes of temperature in that reaction system are shown in Figure 2(b).

The kinetic curves of MMA polymerization in the MWF at all applied MWF powers are similar in shape. From the kinetic curves of MMA polymerization in the presence of microwaves, three characteristic shapes of the monomer degree conversion changes with reaction time can be distinguished, i.e., the so called induction, nonlinear and linear changes. In the induction range, the increase of time did not lead to the formation of any polymerization product ($\alpha < 1\%$), while in the nonlinear and linear range, monomer degree conversion increases nonlinearly and linearly, respectively, with increase in reaction time.

Based on the obtained results, shown in Figures 1 and 2, one can clearly see that the rates of MMA polymerization in the presence of microwaves in all polymerization stages are significantly higher than the corresponding rates of conventional polymerizations.

For example, within the first 10 min of MMA polymerization under conventional conditions, the degree of MMA conversion (α) at 90°C is not higher than 18%, at 80°C it is only 10%, and at 70°C it seems that the reaction has not yet started. In the case of comparable polymerizations in the presence of microwaves for 10 min, $\alpha = 30\%$ at 510 W, and $\alpha = 50\%$ at 540 and 570 W; therefore, it is observable that the duration of the propagation stage is relatively higher when compared with the induction and initiation stages. An increase in microwave power leads to a decrease of the duration of the initiation stages, i.e., their rates are increased.

Changes in the degree of reaction rate enhancement (β) for MMA polymerization in a MWF compared with conventional polymerization, calculated according to eq. (1), for various degrees of MMA conversion (α) are presented in Table I.

As can be seen from the results presented in Table I, at all the used powers of the MWF, the MMA polymerization rates in the MWF were higher than the conventional polymerization rates. The degree of reaction rate enhancement (β) increases with both an increase of power of the MWF and a decrease of the temperature of conventional polymerization. If one compares the values of β obtained at the same power and temperature for different degrees of monomer conversion (α), it could be concluded that an increase in α , in general, leads to a decrease in the degree of reaction rate enhancement (β) for MMA polymerization in a MWF, when compared with conventional polymerization.

The kinetics parameters, the energy of activation (E_a), and the preexponential factor ($\ln A$) for conventional thermal polymerization of MMA were determined according to Friedman's isoconversion method.¹¹ Assuming that the reaction rate at the defined degree of conversion (α) and temperature (T_i) was inversely

TABLE I
Changes of Rate Enhancement (β) with Changes of the Monomer Conversion Degree (α) at Different Powers and Temperatures

Temperature (°C)/ power (W)	β				
	10 ^a	20	30	40	50
90/570	2.5	2.38	1.96	1.66	1.54
90/540	1.70	1.93	1.63	1.43	1.24
90/510	1.54	1.55	1.21	1.05	
80/570	3.12	3.02	3.25	3.04	2.80
80/540	2.21	2.46	2.69	2.61	2.27
80/510	1.92	1.97	2.00	1.80	5.04
70/570	8.91	6.60	6.04	5.38	4.08
70/540	6.06	5.37	5.00	4.62	–
70/510	5.48	4.31	3.71	3.19	–

^a 10, 20, 30, 40, and 50 are monomer conversion degrees [α (%)].

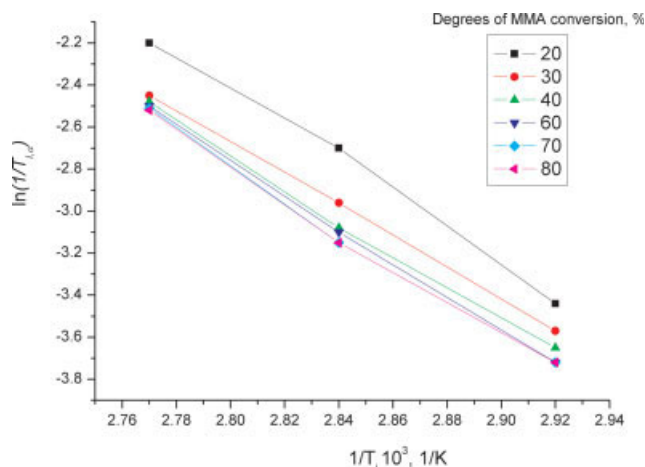


Figure 3 A plot of $\ln(1/t_{i,\alpha})$ versus $(1/T_i)$ for selected degrees of MMA conversion. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

proportional to the reaction time $t_{i,\alpha}$, according to the linear dependence (2):

$$\ln\left(\frac{1}{t_{i,\alpha}}\right) = \ln A_\alpha - \frac{E_{a,\alpha}}{RT_i} \quad (2)$$

the values of the kinetic parameters $E_{a,\alpha}$ and $\ln A_\alpha$ could be determined.

Figure 3 presents dependence of $\ln(1/t_{i,\alpha})$ as a function of $(1/T_i)$ for selected degrees of MMA conversion (α).

For all investigated selected degrees of MMA conversion, the plots of $\ln(1/t_{i,\alpha})$ versus $(1/T_i)$ give straight lines. Bearing this in mind, the eq. (2) is used for calculation of the kinetic parameters of the MMA conventional polymerization. Table II presents the obtained values for the kinetic parameters of MMA conventional polymerization for different degrees of conversion.

Kinetic parameters of conventional thermal polymerization of MMA change complexly with changes of MMA degree of conversion. For degrees of conversion within interval $1\% \leq \alpha \leq 20\%$, values for the kinetic parameters, the preexponential factor and the activation energy, decrease with the increase of the values for the degrees of conversion. Changes of the preexponential factor and the activation energy with the changes of α are in the mutual linear functional relationship, which is so called "compensation effect."¹² This relationship can be described with the following equation:

$$\ln A_\alpha = -3.38 + 0.35E_{a,\alpha} \quad (3)$$

Multipart changes of the kinetic parameters with changes of degrees of conversion and existence of

the compensation effect imply that MMA polymerization under the conventional conditions is a complex and a multistage process. Based on the theoretical consideration^{13–16} about the influence of different models of kinetics schemes on the changes of the kinetics parameters with degrees of conversion, the conventional MMA polymerization could be explained with the existence of the kinetics scheme with two parallel reactions in which the first one is reversible while the second one is irreversible. For small values of degrees of conversion ($\alpha \leq 30\%$) MMA polymerization under the conventional conditions, occurs the reversible stage (initiation) which is due to that characterized with high values of activation energy. The activation energy is, for small degrees of monomer conversion, equal to the sum of the enthalpies of the reversible process, and the activation energy of the irreversible process decreases with the increase of the values of degrees of conversion. Practically, nonchangeability of kinetic parameters with the changes of the degrees of conversion within the interval from 30 to 80% implies that for these degrees of conversion the dominant influence on the kinetics of the process has irreversible process (propagation).

Table III presents the duration of induction period ($t_{p,i}$), necessary time for the beginning of the linear changes of α with time ($t_{p,i}$), and coefficients a_{p_i} and b_{p_i} of the eq. (2), which describes the linear changes of monomer degree conversion with reaction time

$$\alpha_{p_i} = a_{p_i} + b_{p_i}t \quad (4)$$

According to the obtained results, it may be concluded that with the microwave power increase both induction period duration and the necessary time for the beginning of the linear changes of α with time decrease, while the value of the coefficients of the nonlinear changes b_{p_i} increases.

As can be clearly seen from the results presented in Figure 2(b), MMA polymerization at a defined power of the MWF, on the contrary to the conventional thermal polymerization, was performed under

TABLE II
MMA Conventional Polymerization Kinetics Parameters Dependence on the Conversions Degrees

α (%)	E_α (kJ/mol)	$\ln A_\alpha$
≤ 1	239	80.9
10	71	21.8
20	57	16.6
30	62	18.2
40	65	19
50	66	19.4
60	65	19.7
70	66	19
80	65	19.6

TABLE III
Duration of the Induction Period ($t_{p,in}$), Necessary Time to Begin the Linear Changes ($t_{p,l}$), and Coefficients a_{P_i} and b_{P_i} of the eq. (2)

Power (W)	$t_{p,in}$ (min)	$t_{p,l}$ (min)	a_{P_i}	b_{P_i}
510	3.0	3.8	-12.8	4.46
540	2.0	3.4	-24.9	7.6
570	1.0	1.7	-18.3	8.38

the nonisothermal conditions. To determine the kinetics parameters under that conditions, it is necessary to have knowledge of the changes of temperature in the reaction system [$T_{P_i} = g(t)$] with polymerization time at applied power of the MWF. By means of the expressions (5a)–(5f), changes of temperature in the reaction system during MMA polymerization in the MWF for defined microwave power were analytically described.

$$T_{510} = 25 + 1.44t \quad t \leq 5.0 \quad (5a)$$

$$T_{510} = 18.9 + 4.53t \quad t \geq 5.2 \quad (5b)$$

$$T_{540} = 25 + 2.38t \quad t \leq 3.5 \quad (5c)$$

$$T_{540} = 15 + 6.58t \quad t \geq 4.6 \quad (5d)$$

$$T_{570} = 25 + 3t \quad t \leq 3.0 \quad (5e)$$

$$T_{570} = 18.48 + 7.15t \quad t \geq 4.0 \quad (5f)$$

In that case, for every used MWF power (P) and for every degree of MMA conversion (α) on the basis of the knowledge of polymerization time (t_p), it is possible to determine the polymerization velocity ($v_{P,\alpha} = \frac{\alpha}{t_p}$) at corresponding temperature. By applying

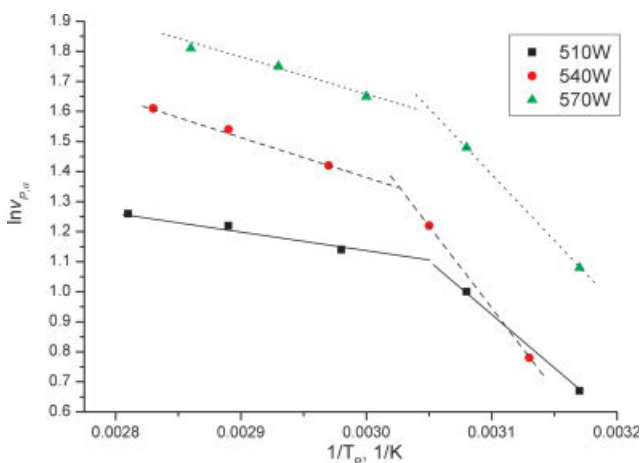


Figure 4 A plot of $\ln v_{P,\alpha}$ versus $\left(\frac{1}{T_p}\right)$ for MMA polymerization in the MWF. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Arrhenius equation: $\ln v_{P,\alpha} = \ln A_{P,\alpha} - \frac{E_{P,\alpha}}{RT_p}$, it is possible to determine the kinetics parameters of that process and to compare them with those that have been obtained under the isothermal conditions. Figure 4 presents the plot of $\ln v_{P,\alpha}$ versus $\left(\frac{1}{T_p}\right)$ for MMA polymerization in the MWF at different powers.

From the curves showing dependence: $\ln v_{P,\alpha} = f\left(\frac{1}{T_p}\right)$, for all applied MWF powers, it is easy to observe two well-defined linear parts that are connected with the particular range of the conversions degrees, which are so called “range of linearity.” Table IV presents the “range of linearity” and corresponding values of the kinetic parameters of MMA polymerization at different powers of the applied MWF.

Kinetic parameters of MMA polymerization at MWF within the previously defined ranges of α are independent on α . For all MWF powers investigated in this work, the values of the kinetics parameters in the range of $\alpha \leq 20\%$ are 3–5 times higher than their values in the range of $\alpha = 20\text{--}50\%$. Depending on the applied MWF power, the kinetics parameters values in the range $\alpha \leq 20\%$ are 1.2–3.8 times lower than the corresponding values under the conventional polymerization procedure. In the range of monomer conversion degree $20\% \leq \alpha \leq 50\%$, the values of kinetics parameters for MMA polymerization depending on the applied MWF power are 5.4–12 times lower than the corresponding values for the same polymerization process but under conventional conditions. The changes of $\ln A$ with activation energy at applied MWF power are linear and can be described with following expressions:

$$\ln A_{510} = 1.09 + 0.36E_{a,510} \quad (6a)$$

$$\ln A_{540} = 1.35 + 0.36E_{a,540} \quad (6b)$$

$$\ln A_{570} = -4.36 + E_{a,570} \quad (6c)$$

With purpose to objectively determine the influence of MWF on the kinetic parameters of MMA polymerization and to explain the influence of the so called “thermal effects” and specific, nonthermal effects on the MMA polymerization, it is necessary to underline that the MWF polymerization investigated in

TABLE IV
“Range of Linearity” and Corresponding Values of the Kinetics Parameters of MMA Polymerization at Different Powers (P) of MWF

P	Range of linearity	$E_{a,\alpha}$ (kJ/mol)	$\ln A_{\alpha}$
510	0–20	30.45	12.29
	20–50	5.9	3.26
540	0–20	45.71	17.99
	20–50	11.34	5.48
570	0–20	15.17	36.92
	20–50	5.09	9.49

TABLE V
Calculated Values of $S_{a,\alpha}^*$ and the Really Established Values of S and MWF T_i for the Proposed Models for Different Powers of the Applied MWF

Degree of MMA conversion (%)	$S_{a,\alpha}^*$ ($\text{J s}^{-1} \text{cm}^{-3}$)	S ($\text{J s}^{-1} \text{cm}^{-3}$)	T_i ($^{\circ}\text{C}$)
At $P = 510$ W			
10	0.222	0.062	36
20	0.25	0.063	48.2
30	0.31	0.062	60.9
At $P = 540$ W			
10	0.25	0.063	36.2
20	0.31	0.062	47.6
30	0.41	0.062	59.4
At $P = 570$ W			
10	0.31	0.063	35
20	0.40	0.063	46.8
30	0.52	0.063	58.5

this work is a nonisothermal process, while the conventional process was an isothermal process.

Bearing this in mind, as well as the established complexity of the investigated process, a question may be posed whether the kinetic parameters determined using Arrhenius equation were valid or not. To overcome this problem, a new method for determination of the activation energy of the process that occurs under the influence of MWF is suggested in the following text. The essence of the suggested process can be explained as follows. Assume that the following parameters are known: reaction time (t), number of mols of the reacting monomer (n), volume of the reacting system (V_s), degree of monomer conversion (α), and activation energy of the investigated process for particular degree of monomer conversion (E_α). In that case, energy (Q) necessary to realize the particular conversion in the reaction system is equal to:

$$Q = \alpha n E_\alpha \quad (7)$$

Because reaction occurs in the MWF, the energy must be equal to the product of the MWF power absorbed per unit volume of the reacting system (S_a), reaction time, and volume of the reacting system, which means that the following must be valid:

$$\alpha n E_\alpha = S_{a,\alpha} t V_s \quad (8)$$

i.e.,

$$E_\alpha = \frac{S_{a,\alpha} t V_s}{\alpha n} \quad (9)$$

Equation (9) is (a) independent on the way of the reaction system activation (whether system is isothermal or nonisothermal); (b) makes possible to calculate, if the E_α value is known, the absorbed power

of the MWF per unit the reaction system ($S_{a,\alpha}^*$) as well as the increase of the temperature in the reaction system (ΔT_α) according to following equations:

$$S_{a,\alpha}^* = \frac{\alpha n E_{a,\alpha}}{t V_s} \quad (10)$$

$$\Delta T_\alpha = \frac{S_{a,\alpha}^* t V_s}{m c_p} \quad (11)$$

where m is the reaction mass of the reacting system, c_p is the specific heat capacity of the reaction system; and (c) makes possible to determine activation energy of the investigated process for particular degree of monomer conversion (E_α), if $S_{a,\alpha}$ is known.

Table V presents the calculated values of $S_{a,\alpha}^*$ and ΔT_α based on the experimental data for α , n , t_α , and on the assumption that the values of activation energies for particular degrees of monomer conversion are the same for both the conventional and microwave processes.

The calculated values for $S_{a,\alpha}^*$ and ΔT_α are drastically higher than the really established values of $S_{a,\alpha}$ and ΔT_α , during MMA polymerization in the MWF. According to this, E_a for MMA polymerization in the MWF is different and significantly lower than E_a under the conventional polymerization conditions. The power of the MWF per unit volume which is absorbed by reaction system under the influence of the MWF due to the dielectric losses is given in the following equation^{17,18}:

$$S_{a,\alpha} = 55.63 \times 10^{-12} f U^2 \epsilon_r'' \quad (12)$$

where f is the frequency (Hz), U is the local field intensity (V/m), and ϵ_r'' is the imaginary part of dielectric constant.

Activation energy of the investigated process for a particular degree of monomer conversion (E_α) for MMA polymerization in the MWF can be calculated on the basis of the experimentally determined values for n , α , and $t_{P,\alpha}$ and the calculated values for $S_{a,\alpha}$ using eq. (12). Table VI presents the calculated values

TABLE VI
Activation Energy E_α for MMA Polymerization in the MWF for Different Powers of the Applied MWF and Different α , and the Corresponding Times

Degree of MMA conversion (%)	E_α (kJ/mol)			t_i (min)		
	510 ^a	540	570	510	540	570
10	20.3	18.4	12.5	5.11	4.59	3.68
20	14.1	11.3	9.2	7.32	5.91	4.57
30	12.5	9.2	7.7	9.6	7.22	5.76
40	11.7	8.5	6.9	11.8	8.54	6.96
50	11.5	7.6	3.1	14.1	8.66	8.15

^a 510, 540, and 570 are different powers (in watt) of the applied MWF.

TABLE VII
Changes of $[\eta]$ with Degree of MMA Conversion (α)

α (%)	$[\eta]$ (g/dL)			
	Conventional polymerization at 90°C	Microwave polymerization		
		510 ^a	540	570
10	0.38	–	0.31	0.32
20	0.39	0.31	0.32	–
30	0.40	0.32	0.33	0.35
40	0.42	0.35	0.36	0.37
50	0.44	0.38	0.38	0.38

^a 510, 540, and 570 are different powers (in watt) of the applied MWF.

for E_a for different powers of the applied MWF and different α .

According to the obtained results, increase of the applied power of the MWF at all investigated degrees of MMA conversion (α) causes decrease of activation energy. Activation energy for all of the investigated powers of the MWF continually decreases with increase of the MMA conversion degree. Calculated values of activation energy according to suggested method are smaller than the values obtained from conversion-temperature curves.

The presented results (significantly lower values of the kinetic parameters, different shapes of E_a changes with α) imply that the mechanism and, therefore, kinetics of MMA polymerization under the MWF are quite different than the mechanism and kinetics of conventional polymerization conditions. Most probably, the changes in mechanism and kinetics of the investigated polymerization process are not consequence of the so called "thermal effects" which are connected with the local overheat due to the dipolar and charge space polarization, but are consequence of the rapid transfer of energy in the reaction system (time about 10^{-9} s), which leads to the nonequilibrium energetic distribution of the reactants. Reactants' energy significantly increases due to the nonequilibrium distribution, which causes the changes in the reaction way, and so E_a and $\ln A$ are decreased and the reaction significantly speeds up. Increase of the power of the applied MWF under the some value additionally favors these processes and due to this E_a and $\ln A$ decrease with MWF power increase.

This is additionally supported with the results obtained for limiting viscosity numbers, $[\eta]$, of the synthesized and isolated PMMA samples obtained by both conventional and microwave processes. Table VII presents the values for $[\eta]$ determined in toluene at 25°C for PMMA samples prepared at different α , for both conventional polymerization at 90°C and different powers of the MWFs.

According to the results presented in Table VII, we can see that at constant powers of the MWF the

limiting viscosity numbers, $[\eta]$, slightly increase as the degree of monomer conversion, α , increases. For the same values of α , as the microwave power increases, the values for $[\eta]$ also insignificantly increase. In other words, the polymerization of MMA under the MWF gives very similar values of $[\eta]$ for all the applied powers and at all degrees of monomer conversion. These values are somewhat different, that is, lower than those obtained for conventional polymerization. The results presented in Table VII revealed that the molecular weight for PMMA obtained from conventional heating method is higher than that from microwave. However, for a same conversion, the lower molecular weight has the higher amount of PMMA, that is, more number (more easy) of monomer radical was created under the microwave system theoretically. This phenomenon is agreeing with the results of activation energy obtained from conventional (higher) and microwave (lower) polymerizations (presented at Tables II and IV, respectively). This again confirms that MMA polymerization process in the MWF is different than the same process which occurs at conventional thermal conditions, i.e., although more rapid, by this process shorter polymer chains have been formed.

CONCLUSIONS

Isothermal kinetics of the conventional MMA polymerization was investigated. Kinetics parameters of this process were determined using isoconversion method. It was found that the calculated kinetics parameters change complexly with α . It was concluded that the changes of the preexponential factor and the activation energy with the changes of α are in the mutual linear functional relationship, which is so called "compensation effect." With the postulated model for the mechanism of the MMA polymerization, complex changes of the kinetics parameters with α are explained. Kinetics of the MMA polymerization under the MWF with different input power was investigated. Kinetics parameters of MMA polymerization in the MWF were determined on the basis of the conversion-temperature curves and Arrhenius equation. Values of the kinetics parameters for MMA polymerization in the MWF are from about 1.2 to 12 times lower than for conventional MMA polymerization. A new method for determination of the E_a of the investigated process in the MWF was described. It was proved that E_a of the process which occurs in the MWF is different than E_a of the same process which occurs at conventional conditions. Decreased E_a value of the polymerization process in the MWF compared with the conventional polymerization is explained with the formation of the nonequilibrium energetic distribution of the reac-

tants due to the rapid transfer of energy in the reaction system.

ϵ_r'' Imaginary part of dielectric constant
 $[\eta]$ Limiting viscosity number

NOMENCLATURE

α	Degree of MMA conversion (%)
β	Degree of reaction rate enhancement
T	Temperature
T_i	Definite temperature
P	Power of the microwave field
P_i	Definite power of the microwave field
E_a	Activation energy
$E_{a,\alpha}$	Activation energy for α
$\ln A$	Preexponential factor
$\ln A_\alpha$	Preexponential factor for α
t_α	Reaction time
$t_{T_i,\alpha}$	Time in which α was achieved at T_i
$t_{P_i,\alpha}^{\mu t}$	Time in which α was achieved at a definite power P_i
$v_{P_i,\alpha}$	Effective reaction rate for particular α at P_i
n	Number of mols of the reacting monomer
V_s	Volume of the reacting system
Q	Energy necessary to realize the particular conversion
$S_{a,\alpha}$	Power of the microwave field absorbed per unit volume of the reacting system for particular α
$S_{a,\alpha}^*$	Calculated values of $S_{a,\alpha}$
ΔT_α	Calculated values of temperature increase
m	Reaction mass of the reacting system
c_p	Specific heat capacity of the reaction system
f	Frequency
U	Local field intensity

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