



Kinetics of thermal decomposition of PMMA at different heating rates and in a wide temperature range

O.P. Korobeinichev^{a,*}, A.A. Paletsky^a, M.B. Gonchikzhapov^{a,b}, R.K. Glaznev^{a,b}, I.E. Gerasimov^a, Y.K. Naganovsky^c, I.K. Shundrina^d, A.Yu. Snegirev^e, R. Vinu^f

^a Voevodsky Institute of Chemical Kinetics and Combustion of Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia

^b Novosibirsk State University, Novosibirsk, Russia

^c All-Russian Research Institute for Fire Protection of Ministry of Russian Federation for Civil Defense, Emergencies and Elimination of Consequences of Natural Disasters, Balashikha, Russia

^d N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of Siberian Branch of Russian Academy of Sciences, Novosibirsk, Russia

^e Peter the Great St. Petersburg Polytechnic University, Russia

^f Indian Institute of Technology Madras, Chennai, India

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ABSTRACT

Using the methods of differential mass-spectrometric thermal analysis (DMSTA), thermogravimetric analysis (TGA), microscale combustion calorimetry (MCC), and fast pyrolysis (FP), thermal decomposition of high-molecular-weight polymethylmetacrylate (PMMA) has been investigated in the temperature range of 315–500 °C. Based on these data, the kinetic parameters (the activation energy, the pre-exponential factor) were obtained of a one-step pyrolysis reaction in supposition of a first-order reaction using simple mathematical fitting and an iso-conversion method. Validity of the obtained kinetic parameters was verified by comparing the experimental data on dependence of the decomposition rate on temperature in the broad range of the heating rates with the results of simulating the above dependence, using these kinetic parameters. These parameters, obtained in the broad temperature range, may be further used in numerical simulation of PMMA combustion under fire conditions and for assessing the polymer's flammability.

1. Introduction

Polymethylmetacrylate (PMMA, $(C_5O_2H_8)_n$) refers to the class of thermoplastic polymers. It is widely used due to its excellent thermal stability, good mechanical properties and easy processing [1,2]. PMMA is a combustible polymer with a low oxygen index (LOI = 18), which determines the topicality and significance of studying the kinetics of its thermal degradation, the parameters of which control the conditions of its ignition and combustion. The study of the kinetics of the PMMA pyrolysis is of interest not only in terms of its fire safety but also in terms of destruction of its waste. Numerous publications are dedicated to the study of the kinetics of chemical decomposition of PMMA [1–12]. At the same time, there is a significant scatter of data on the kinetic parameters of PMMA [11], related both to differences in the methods of PMMA synthesis applied and to differences in the methods of obtaining experimental data and their interpretation. PMMA is a convenient object for simulating its thermal decomposition and combustion, as the main product (~95% of all the gases formed) of its thermal

decomposition is a monomer methylmetacrylate (MMA) [1,3,4].

The traditional and widespread method of thermogravimetric analysis (TGA) is the main method of studying the kinetics of the thermal decomposition of polymers. The other methods of investigation include such methods as differential mass-spectrometric thermal analysis (DMSTA) with low [10 K/s] and high (up to 100 K/s) heating rates [13,14], as well as fast pyrolysis with the heating rate amounting to ~20,000 K/s and the decomposition temperature of isothermal conditions [15].

It has been found that the mechanism and the kinetics of polymer pyrolysis in inert medium depend on many factors, such as the molecular mass, tacticity (regularity, or symmetry of the molecular structure), the conditions of the experiment and the degree of branching of the polymeric material. The thermogravimetric experiments held have shown that the mechanisms of decomposition of PMMA synthesized by different methods [4,6] are different. In [4], it was demonstrated by the thermal volatilisation analysis (TVA) technique that PMMA synthesized by the anion method of polymerization decomposes during one stage.

* Corresponding author at: Voevodsky Institute of Chemical Kinetics and Combustion, Institutskaya str. 3, Novosibirsk, 630090, Russia.

E-mail address: korobein@kinetics.nsc.ru (O.P. Korobeinichev).

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PMMA samples polymerized by the free radical method decompose in inert medium during several stages. In [16], 3 stages were found by the TGA method, which have decomposition rate maxima at temperatures 165, 270 and 360 °C (at the heating rate 2 K/min), each of which is related to a certain process: (1) 165 °C – scission of the bond between monomers of the head-to-head type, (2) 270 °C – scissions at the chain-end initiation from vinylidene ends, (3) 350 °C – random scission in the polymer chain. In the case of anionic synthesis of PMMA polymer, its decomposition in nitrogen takes place during one stage at 360 °C only by random scission in the polymer chain.

For PMMA samples with MW = 29,000 g/mol synthesized by free radical polymerization of MMA [5], the following kinetic parameters were determined in nitrogen in assumption of the first-order reaction: $E_a = 168$ kJ/mol, $\lg k_0 = 11.57$ (k_0, s^{-1}).

Thermal decomposition of high-molecular-weight PMMA (MW = 996,000 g/mol) synthesized by free radical polymerization of MMA [6] proceeds in argon during 4 clear stages. When the molecular weight decreases to 350,000 g/mol, stages 2 and 3 disappear, with stage 1 remaining hardly visible and stage 4 clearly visible. For the fourth basic decomposition stage, the following kinetic parameters in the range of changing the decomposition degree were found: $\alpha = 0.1$ – 0.9 : the reaction order is equal to 1.21, $\lg k_0 = 16.06$ (k_0, s^{-1}), $E_a = 200.4$ kJ/mol. Depending on α , the activation energy (kJ/mol) varies from 130 ($\alpha = 0.1$) to ~ 170 ($\alpha = 0.3$ – 0.7), and 200 ($\alpha = 0.9$). The fractional reaction order indicates simultaneous passage of several reaction stages. For PMMA samples (Plexiglas G, Atofina) [7], in supposition of a first-order reaction, the following kinetic parameters were obtained: $\lg k_0 = 12.93$ (k_0, s^{-1}), $E_a = 188$ kJ/mol. According to the authors of [8], who made a review of the kinetics of the processes of thermal decomposition of polymers, including PMMA, which may be important in their use in development of hybrid engines, the high value of the activation energy of PMMA decomposition (Plexiglas G, Rohm and Haas, Inc., MW = 402,000 g/mol, free radical polymerization process) in nitrogen, equal to 233 kJ/mol, characterizes not the reaction of MMA formation but the initial act of decomposition of the PMMA molecule in the condensed phase.

In [3], thermal degradation of a PMMA film (MW = 131,000 g/mol) ~ 83 μm thick (anionic polymerization, MW = 2000, 131,000 g/mol), put on a platinum filament from benzene solution, was studied at a high heating rate (600–1000 K/s) by the method of T-jump/FTIR spectroscopy in the 380–600 °C range in argon at the pressures of 2 and 11 atm. In decomposition of the PMMA film, the amount of yielded benzene at the initial stage was 0.7 of the amount of formed MMA. In addition to MMA (~ 0.9 – 0.97 mol fraction), CO_2 (~ 0.1 – 0.03) was registered, the concentration of which decreased as the molecular mass of PMMA increased. In decomposition of PMMA (MW = 131,000 g/mol) in argon at the pressure of 2 atm, with MMA formed, two different processes were identified, and, in supposition of a first-order reaction, the following kinetic parameters were obtained: $E_a = 296.8$ kJ/mol, $\lg k_0 = 19.1$ (k_0, s^{-1}) in the range of temperatures 380–460 °C, $E_a = 62.7$ kJ/mol, $\lg k_0 = 3.26$ (k_0, s^{-1}) in the 500–600 °C range. The kinetic constants of the first stage obtained in this study were used in [17] in numerical simulation of downward flame spread over PMMA. Satisfactory agreement of the model with the experiment was obtained. Using the method of microscale combustion calorimetry (MCC) [9], thermal decomposition of PMMA powder (MW = 350,000 g/mol) in nitrogen was shown to be described with the n-order reaction ($n = 1.3$, $E_a = 177.6$ kJ/mol, $\lg k_0 = 12.68$ (k_0, s^{-1})). It is reported in [18] that the simulation of PMMA combustion parameters obtained by using the data [9] on PMMA decomposition kinetics better agree with the experiment than the simulation using data [19]. This indicates the importance of measuring the rate constants of PMMA decomposition. The calculations have demonstrated that knowing the pre-exponential factor of the rate constant of PMMA decomposition to the accuracy of 2 is quite sufficient for simulating the flame spread rate and the other parameters of PMMA combustion. Although many studies are devoted

to PMMA pyrolysis kinetics, there are no kinetic data in them that would be obtained under conditions of high temperatures close to those of combustion.

Analysis of the literature data has shown that the kinetic parameters of the reaction of thermal decomposition of PMMA are determined by the characteristics of the material used, depending on the method of its synthesizing; they also depend on the method of obtaining the experimental data and on their processing. These kinetic parameters differ between each other, and their use in the models of PMMA combustion may bring about different results.

2. The objective of the study

The main objective of the work was to study the kinetics of thermal decomposition of PMMA having the molecular weight of 350,000 g/mol (Aldrich, CAS 9011-14-7) using different experimental methods (TGA, DMSTA, MCC and FP) in the broad range of temperature and heating rates, and based on these data, to calculate the kinetic parameters (the activation energy, the pre-exponential factor) using simple mathematical fitting in supposition of a first-order reaction and an iso-conversion method, as well as to validate the obtained kinetic parameters by comparing the experimental data on dependence of the decomposition rate on temperature in the broad range of the heating rates with the results of simulating the above dependence, using these kinetic parameters. These parameters, obtained in the broad temperature range, may be further used in numerical simulation of PMMA combustion under fire conditions and for assessing the polymer's flammability. Until now, the issue of applicability of the kinetic models developed based on low-heating-rate data to predict high-heating rate data remains open to discussion. Another objective of the study was to evaluate the influence of the experimental conditions (the type of the setup, the type of the inert gas) on the kinetic parameters of thermal decomposition of the same PMMA sample.

3. Experimental

3.1. Material

In the study, PMMA with the molecular weight of 350,000 g/mol (Aldrich, CAS 9011-14-7) was investigated as spheres 30–300 μm in diameter or thin plates 0.2 mm thick, obtained by hot pressing at the temperature of 180 °C from PMMA powder (the pressing pressure ~ 1200 atm, the pressing time ~ 180 s). In the experiments, the mass of the sample varied from ~ 0.5 mg (a plate $1.5 \times 1.5 \times 0.2$ mm³ in size) and from 3 to 10 mg (powder).

3.2. The investigation methods

3.2.1. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) of PMMA was conducted using a synchronous TG/DSC analyzer STA 409 PC (Netzsch) (TGA_N) with an aluminum crucible in helium with characteristic consumption of 27 cm³/min (NTP). The mass of the powder sample was 3–4 mg. Heating was conducted at the rates of 10, 20, 30, 40, and 50 K/min.

Thermogravimetric analysis of the PMMA powder in nitrogen flow was conducted at the heating rates 0.4, 1, 1.5 and 2 K/min with simultaneous analysis of the formed gases in a combined installation including a thermal analyzer Du Pont – 9900 with a module of a thermal balance TGA-951 (TGA_p) and an IR-Fourier spectrometer Nicolet iS10(iZ10). The mass of the powder sample was 8–10 mg.

The precision of the MCC and TGA equipment determining the heating rate in the range of temperatures from 250 to 450 °C was $\sim 99.9\%$. This value was determined by calculating the difference between the linear approximation of the set dependence of temperature on time and its measured values.

3.2.2. Microscale combustion calorimetry (MCC)

The kinetic parameters of thermal decomposition of PMMA were measured with an oxygen microcalorimeter (OMC, [20]) in accordance with the standard ASTM D7309-07a [21]. The polymer powder sample weighing 3–5 mg was placed into a ceramic crucible, which was put into a pyrolysis chamber, where it was heated in a nitrogen flow at the rate from 15 to 120 K/min. The formed volatile pyrolysis products were mixed with an additional oxygen flow. The mixture of volatile pyrolysis products, nitrogen and oxygen was delivered to a tubular combustion chamber, where the temperature of 900 °C was maintained and where complete oxidation of the pyrolysis products took place. At the output of the combustion chamber, oxygen concentration was measured, which allowed calculation of oxygen consumption required for complete oxidation of the volatile products. The measured signal was calibrated and synchronized with the change in the crucible temperature in the pyrolysis chamber. This allowed us to determine the dependence of value \dot{q} (interpreted as the heat release rate) during oxidation of volatile pyrolysis products on the sample temperature:

$$\dot{q}(T) = \Delta h_{c,O_2} \left(-\frac{dm_{O_2}}{dt} \right) \frac{1}{m_0},$$

where $\Delta h_{c,O_2} = 13.1$ kJ/g O_2 , m_0 – the initial mass of a sample, m_{O_2} – oxygen concentration.

The degree of transformation (α) in the OMC method was calculated as a fraction of the heat release:

$$\alpha(T) = \left(\int_{T_0}^{\infty} \dot{q}(T) dT \right)^{-1} \int_{T_0}^T \dot{q}(T) dT$$

And the reaction rate was calculated as $W = d\alpha/dt$.

It was shown in [22] that, if decomposition of the material occurs in one stage, and the composition of the volatile pyrolysis products does not depend on the transformation depth, then the results obtained by the MCC and TGA methods are equivalent.

3.2.3. The method of differential mass-spectrometric thermal analysis (DMSTA)

The DMSTA method [13,14] allows the kinetic parameters of the process of decomposition of condensed substances to be determined, with simultaneous identification of the formed gases. The main feature of the DMSTA method consists in the fact that the intensity peaks I_i in the mass spectrum of a sample taken at the output of a reactor are directly proportional to the rates of release of the respective decomposition products W_i :

$$W_i = W_{N_2} \frac{I_i}{I_{N_2}} \frac{1}{K_i}$$

where K_i is the calibration coefficient; I_{N_2} , W_{N_2} are the mass peak intensity and the flow rate of the nitrogen diluent. Simultaneous measurements of the dependence of the sample temperature $T(t)$ and the mass peak intensities $I_i(t)$ of the decomposition products on time allow the decomposition kinetics to be studied. α is the fraction of formation of the i^{th} product at the time t , which was determined as follows:

$$\alpha(t) = \int_0^t I_i(t) dt \cdot \left(\int_0^{\infty} I_i(t) dt \right)^{-1}$$

The mass peak intensity was measured using an automated mass-spectrometric complex with a molecular-beam probe sampling system [14]. The method of probe input in the molecular-beam mode allows probing both stable and labile species (active particles, atoms and radicals, species vapors), as well as excludes the presence of species formed on the probe walls during possible heterogeneous reactions of the decomposition products in the analyzer.

In the study, a time-of-flight mass-spectrometer MSCh-4 was used, with electron impact ionization having the electron energy 70 eV. The time resolution of the system of data acquisition for measuring 6 mass peak intensities of pyrolysis products was 0.02 s. Thermal

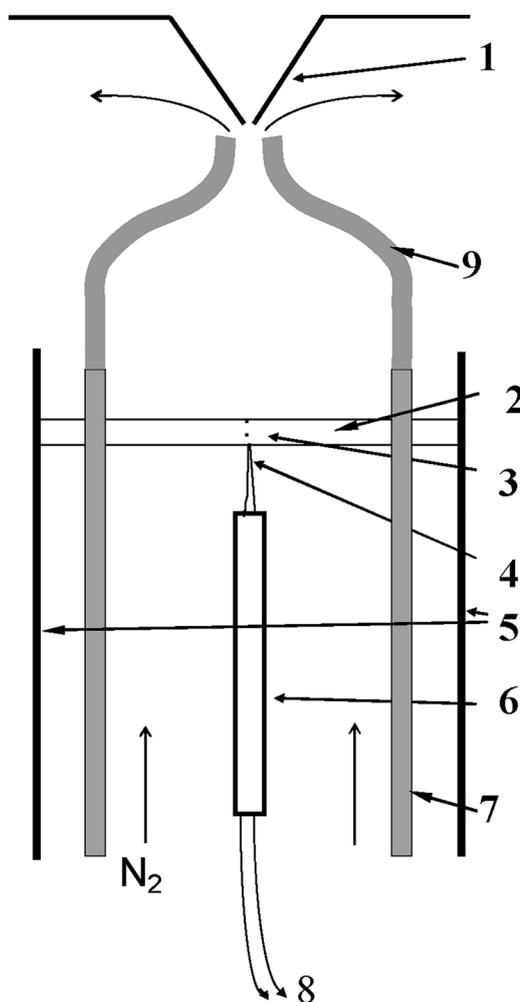


Fig. 1. A flow reactor (FI-R1) for studying thermal decomposition of polymers at the heating rate of 25–150 K/s: 1 – a probe; 2 – a heating plate; 3 – a polymer sample; 4 – a thermocouple junction; 5 – current input leads; 6 – thermocouple output leads; 7 – a quartz tube; 8 – thermocouple output leads to the measuring system, 9 – a quartz funnel.

decomposition of PMMA took place in flow reactors of two types in a nitrogen flow at the pressure of 1 atm. Different designs of the reactors ensured different sample heating rates: 25–150 K/s in the FI-R1 reactor with plates and 2–10 K/s in the two-temperature FI-R2 reactor. Stable consumption of the carrier gas through the reactor was regulated with the gas flow controller and constituted 600 ml/min (NTP) in case of its use with the FI-R1 reactor and 100 ml/min in case of the FI-R2 reactor. In studying the kinetics of the decomposition process, the time of delivery of the probe to the analyzer plays an important role in synchronization of the measured sample temperature and the rate of the decomposition products yield. The time of delivery of the probe from the heater to the analyzer for the FI-R1 and FI-R2 reactors was 0.1 and 3.7 s, respectively. The FI-R1 reactor (Fig. 1) was a quartz tube with the internal diameter of 1 cm, inside which there was a heater consisting of two tightly pressed plates made of transformer steel (thickness ~0.5 mm, width ~2 mm), heated with electric current, between a PMMA sample was pressed. The open end of the tube was covered with a cone-like funnel, ensuring intense mixing of the carrier gas with the formed products flowing to the analyzer. Flow reactors of a similar design have been previously used for investigating thermal decomposition of small quantities of polymers in the form of plates or powders [23,24].

To determine the accuracy of temperature measurement at a high heating rate in the 350–400 °C range, the sample temperature was

measured by using two chromel alumel thermocouples (CA) with the diameter \varnothing 25 μm . One thermocouple was welded to the outer side of the metal plate of the heater at the place of the sample's position (T_{out}), while the other was in contact with the sample and the heater plate (T_{in}). The thermocouples were positioned in one place of the heater but on the opposite sides of one of its plates. The difference between the measured temperatures did not exceed 2 K, as the error of temperature measurement at the temperature of 673 K did not exceed 0.3%. In the thermal decomposition experiments, one thermocouple was usually used, welded to the outer side of the heater plate, where the sample was positioned. To determine consistency of heating the sample, the junctions of two thermocouples were located at the distance of 1.5 mm in the place of the sample's position, as the characteristic sizes of the thin PMMA plates were $1.5 \times 1.5 \times 0.2 \text{ mm}^3$. The difference between the temperatures did not exceed 7 K, i.e., the error of measuring the temperature along the heater plate at the temperature of 673 K did not exceed 1%. The error was random and did not depend on the heating rate. The influence of the thickness of a thin PMMA plate on uniformity of temperature distribution inside the plate at a high heating rate of the sample was evaluated. For this purpose, we evaluated the difference between the surface temperature and the temperature in the middle of the PMMA plate 0.2 mm thick (the internal temperature gradient) placed between two metal plates heated with electric current at the rate of 60 K/s. In the experiment, the temperature of the metal plates was measured with a thermocouple. In evaluation, we used the decision of thermal conductivity equation from [25] Numeric calculation was made of the temperature in the middle of the PMMA plate 0.2 mm thick with the thermal diffusivity being $1.29 \cdot 10^{-7} \text{ m}^2/\text{s}$, positioned between two surfaces, the temperature of which grew at the rate of 60 K/s from 20 °C to 400 °C. The calculation showed that at the temperature higher than 100 °C (1.3 s after the beginning of heating) the difference between the surface temperature and the middle of the PMMA plate was approximately 2.5 K, which is good substantiation for the method of heating chosen for investigating the kinetics of polymer decomposition by the DMSTA method.

To measure the pyrolysis kinetics of PMMA powder at low heating rates, a two-temperature reactor (FI-R2) was produced, which was a quartz tube 15 cm long with two heating elements on the outer surface of the tube. The heating element was a wire wound on the tube surface heated by electric current. In the lower part of the reactor, there was a heating element which heated the carrier gas and the thermocouple embedded inside the tube. A flattened copper-constantan thermocouple junction 0.2 mm in diameter with characteristic area of 3 mm^2 served as a filament onto which the PMMA powder was placed. The upper heating element maintained the temperature of the carrier gas to be 110–120 °C, in order to prevent condensation of MMA vapor formed at thermal decomposition of PMMA in the lower part of the reactor.

Fig. 2 represents the characteristic dependence of mass peak intensity $m/e = 100$ (MMA) and the temperature at degradation of a PMMA thin plates in nitrogen at the heating rate 60 K/s.

3.2.4. Decomposition under isothermal conditions at high heating rates

Mass loss profiles of PMMA under fast heating rate conditions (fast pyrolysis) were obtained in a Pyroprobe® 5150 pyrolyzer (CDS Analytical, USA). The sample quantity taken for recording the mass loss at different temperatures and time periods was $4 \pm 0.2 \text{ mg}$. The sample was taken in a quartz tube and placed inside a resistively heated platinum coil. The sample was instantaneously heated at a rate of 20 K/ms. The temperature was varied from 400 °C to 800 °C at an interval of 50 °C. The sample holding time, or the time for which the platinum coil was heated, was varied in the range of 2 to 70 s. The mass loss was measured using a high-accuracy micro balance (Sartorius Cubis). Each experiment was repeated at least three times. Ultra-high pure argon (99.9992%) was used as a carrier gas at a flow rate of 110 ml min^{-1} .

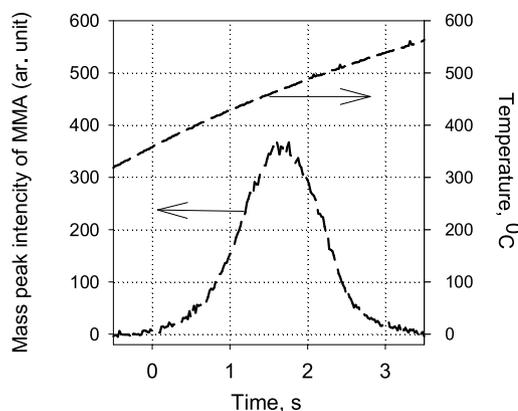


Fig. 2. Characteristic dependence of mass peak intensity $m/e = 100$ (MMA) and the temperature at degradation of a PMMA thin plates in nitrogen. The heating rate is 60 K/s.

4. Methods of processing the experimental data

The review [26] presents 13 models of the decomposition kinetics of solid substances. The majority of kinetic methods used in the area of thermal decomposition consider the reaction rate to be a function of only two variables: the temperature, T and the extent of conversion, α : as follows: $d\alpha/dt = k(T)f(\alpha)$. The dependence of the process rate on temperature is represented by the rate constant, $k(T)$ and the dependence on the extent of conversion by the reaction model, $f(\alpha)$.

Above equation describes the rate of a single-step process $k(T)$ is given by the Arrhenius equation $k(T) = k_0 \exp(-E_a/RT)$, where k_0 , E_a and R are the pre-exponential factor, the apparent activation energy and the universal gas constant, respectively. In the case of the thermal decomposition of PMMA with $MW = 350,000$, the decomposition process is multi-stage [6]. However, due to the necessity of further use of kinetic parameters in combustion models, the kinetic parameters were determined from the experimental data in supposition of a one-stage process, which is reasonable, as the contribution of the main stage to the general process is $\sim 80 \div 85\%$.

The rate constant of the decomposition reaction $k(T)$ was calculated in supposition of the first-order reaction ($n = 1$) by processing dependences α and $d\alpha/dt$ on temperature, obtained by the TGA, MCC, and DMSTA methods i.e., $k(T) = (d\alpha/dt)/(1-\alpha)$. This computation method of determining kinetic parameters will be referred to as Method 1. Averaging of the experimental data $k(T)$ presented in Arrhenius coordinates was conducted by linear approximation (given the minimum mean-square deviation from the experimental values) for the entire array of points obtained at different heating rates by different methods. Processing of linear approximation $\lg k(T) = \lg A - 1/T(0.43E/R)$ in coordinates $\lg k(T)$ and $1/T$ allowed us to find the value $0.43E/R$ and to calculate the value E and $\lg A$ (Method 1, $n = 1$). The kinetic data were also obtained from the TGA data by using an iso-conversion method, described in detail in [9], in which the reaction order n was calculated. This computation method of determining kinetic parameters will be referred to as Method 2. It is described below.

The thermal degradation process was modeled by a single global reaction. The reaction rate was approximated as:

$$\dot{r} = A\phi(\alpha) \exp\left(-\frac{E_a}{RT}\right)$$

where the activation energy E , the pre-exponential factor A , and the conversion function $\phi(\alpha)$ contained information on pyrolysis kinetics.

An iso-conversional method consisted of three major steps:

- 1 Computation of the activation energy as a function of the conversion degree.
- 2 Statement of the conversion function.

3 Computation of the pre-exponential factor.

At the first step the model-free Friedman method was utilized to determine the activation energy without any certain conversion function. The previous equation was represented as follows:

$$\ln \dot{r}_i = -\left(\frac{E_a}{RT}\right)_i + \ln(A\varphi(\alpha))_i,$$

where subscript i corresponds to particular conversion α_i . This equation provides a single point on the $y = \ln(r)$ against $x = 1/T$ plot for a single heating rate. Set of points computed from the set of heating rates are approximated by straight lines $y(x) = a_i x + b_i$ using the least squares procedure, each line corresponding to particular conversion α_i . The obtained a_i and b_i coefficients are used to calculate $E(\alpha_i) = a_i R$ and $\ln(A\varphi(\alpha))_i = b_i$.

At the second step of the iso-conversional method the conversion function $\varphi(\alpha)$ was determined. It was done by plotting

$$\phi(\alpha) = \frac{r(\alpha)}{A} \exp(E/RT(\alpha)),$$

where $r(\alpha)$ and $T(\alpha)$ were measured at different heating rates. Experimental points were approximated by the n -th order reaction model: $f(\alpha) = (1-\alpha)^n$.

At the third step, the pre-exponential factor A was obtained using the values of the reaction rate r_p , temperature T_p and conversion degree α_p corresponding to the maximum reaction rate and equation $A = r_p \exp(E_a/RT_p)/\varphi(\alpha_p)$. The pre-exponential factor obtained from all the heating rates was averaged.

The kinetic parameters obtained by both methods were validated by comparing the experimental dependences $d\alpha/dt$ on T for different heating rates with those obtained by simulation using the kinetic parameters found. The dependence $d\alpha/dt$ on T was simulated similarly to [27] and is described below. Model reaction rate was restored for a set of kinetic parameters as a temperature function using the following algorithm. The rate of the thermal degradation n -th order reaction under a constant heating rate is described by equation

$$\frac{d\alpha}{dt} = A e^{-\frac{E_a}{RT}} (1-\alpha)^n,$$

where $\alpha = \frac{m_0 - m}{m_0 - m_\infty}$ – conversion degree, t – time, A – pre-exponential factor, E_a – activation energy, R – universal gas constant.

In case of constant heating rate $\beta = \frac{dT}{dt}$, where T – temperature, this equation can be reformed in the following way:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} (1-\alpha)^n$$

After separation of variables and integration, provided in [28], the equation takes the form

$$\frac{1 - (1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] e^{-\frac{E_a}{RT}} \text{ for } n \neq 1 \text{ and}$$

$$-\ln(1-\alpha) = \frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] e^{-\frac{E_a}{RT}} \text{ for } n = 1.$$

Then, the conversion function $\varphi(\alpha) = (1-\alpha)^n$ was expressed

$$(1-\alpha)^n = \left[1 - (1-n) \frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] e^{-\frac{E_a}{RT}} \right]^{\frac{n}{1-n}} \text{ for } n \neq 1 \text{ and}$$

$$(1-\alpha) = e^{-\frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] e^{-\frac{E_a}{RT}}} \text{ for } n = 1.$$

Thus, the reaction rate as a temperature function for a set of kinetic parameters was restored

Table 1

The mass spectrum of MMA and of the products of thermal decomposition of PMMA.

m/e	41	69	39	100	15
NIST [29]	100	66.1	39.9	33.6	20
MMA	100	61 ± 2	43 ± 2	25.6 ± 0.5	20.9 ± 0.2
PMMA decomposition products	100	59 ± 2	51 ± 5	22 ± 2	–

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} (1-\alpha)^n = \frac{A}{\beta} e^{-\frac{E_a}{RT}} \left[1 - (1-n) \frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] e^{-\frac{E_a}{RT}} \right]^{\frac{n}{1-n}}$$

for $n \neq 1$ and

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{-\frac{E_a}{RT}} (1-\alpha) = \frac{A}{\beta} e^{-\frac{E_a}{RT} - \frac{ART^2}{\beta E_a} \left[1 - \frac{2RT}{E_a} \right] e^{-\frac{E_a}{RT}}} \text{ for } n = 1.$$

5. Results and discussion

5.1. Identification of the forming decomposition products of PMMA

The products of PMMA decomposition were identified by the methods of IR-spectroscopy and mass spectrometry. At the thermal decomposition reaction rate maximum, at the heating rate 5, 10 and 20 K/min, IR-spectra of the PMMA decomposition products were recorded, which with the probability rate ~96% were consistent with the MMA spectrum available in the library of spectra. Thus, MMA is the main product of PMMA decomposition.

Table 1 contains the measured mass peak intensities of the PMMA (powder or plate) decomposition products (m/e 100, 99, 69, 41, 40, 39) in the nitrogen flow at the maximum of the PMMA decomposition rate compared to the mass-spectrum of MMA obtained at the given setup and the mass spectrum from the NIST database [29]. Dependences of peak intensities of different masses are identical, suggesting the one-step character of the process. No difference was recorded between the kinetics and the composition of the products of decomposition of the powder and of the plate during the mass-spectrometric study. The mass spectrum of the PMMA decomposition products is close to the mass spectrum of MMA obtained at the given setup, which also confirms the conclusion that the MMA monomer is the main product of PMMA decomposition. Calculation of the kinetic parameters of thermal decomposition of PMMA in supposition of the first-order reaction by the parent and main MMA peaks (m/e 100 and m/e 41, respectively) provided an identical result. The calculations of the rate constant in the DMSTA method shown below were carried out by the parent MMA peak.

5.2. Thermal decomposition of PMMA in the atmosphere of different inert gases (argon, helium) using different methods

Figs. 3 and 4 demonstrate the DTG data of thermal decomposition of PMMA powder (MW = 350,000 g/mol) and of thin plate at different heating rates: 10, 20, 30, 40, 50 K/min in helium atmosphere. Repeatability of data on the consumption rate of PMMA (DTG) is ± 4%, whereas repeatability of the maximum mass consumption rate temperature on the DTG curves is ± 3 K in all the three experiments. The absence of a small peak preceding the main one in the case of the plate (Fig. 4) observed at decomposition of the powder (Fig. 3) may be related to reduction of the fraction of low-molecular-weight PMMA at hot pressing of the plates.

Fig. 5 demonstrates the characteristic dependences of the reaction rate of thermal decomposition of PMMA in nitrogen at the same heating rate (30 K/min), obtained by the methods of MCC and TGA_N. The scatter of the temperature values corresponding to the maximum value

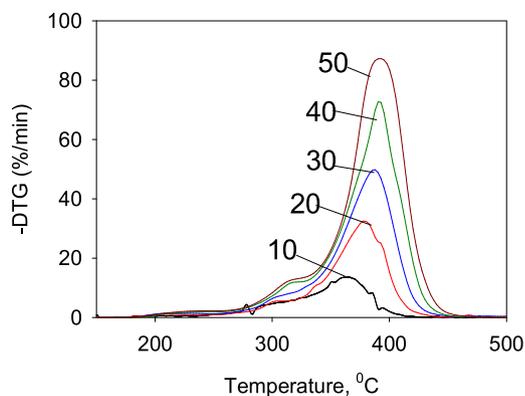


Fig. 3. DTG data on thermal decomposition of PMMA powder (MW = 350,000 g/mol) at different heating rates (indicated in K/min in the figure) in helium.

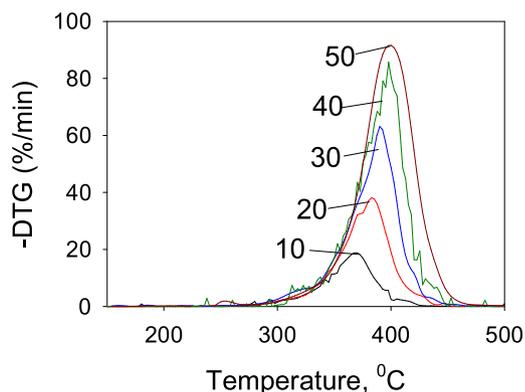


Fig. 4. DTG data on thermal decomposition of PMMA thin plates (MW = 350,000 g/mol) at different heating rates (indicated in K/min in the figure) in helium.

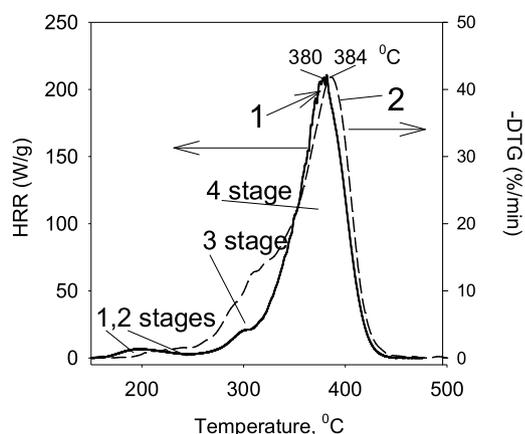


Fig. 5. Dependence of the reaction rate of thermal decomposition of PMMA powder on temperature, obtained at the heating rate of 30 K/min in nitrogen by the methods of MCC (1, HRR) and TGA (2, DTG_N).

of the reaction rate determined by different methods is ± 3 K. For the heating rates from 10 to 50 K/min, the variance of data did not depend on the heating rate and had a random character. Comparison shows that different methods (Fig. 5) satisfactorily describe, like in [6], 4 stages of thermal decomposition of PMMA powder. The temperatures of the maximum reaction rates of the principal fourth stage of the reaction of thermal decomposition of PMMA measured with MCC and TGA differ by 4°, which is within the limits of experimental accuracy (± 3 K) of different methods and setups used.

Analysis of the DTG_N curves of thermal decomposition of PMMA

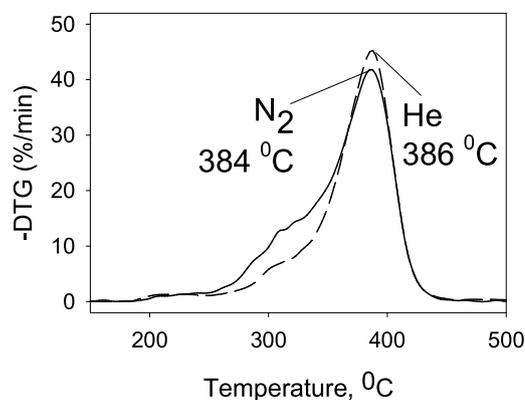


Fig. 6. DTG data on thermal decomposition of PMMA powder at the heating rate of 30 K/min in helium and nitrogen atmosphere.

powder conducted at the same setup (Fig. 6) in different carrier gases (helium and nitrogen) showed that the maximum values of the reaction rates of thermal decomposition for the principal 4th stage of the reaction of PMMA decomposition in nitrogen and in helium within the error margin of (± 3 K) are found at the same temperature at the heating rates of 30 (as indicated in Fig. 6) and 50 K/min. Thus, in the TGA_N method, the carrier gas (nitrogen and helium) influences the 3rd stage of PMMA decomposition, in which a small fraction of the substance, 15% is consumed, but does not have noticeable influence on the main stage, which was used to calculate the kinetic parameters of the thermal decomposition of PMMA.

5.3. Kinetics of thermal decomposition of PMMA

The studies of the kinetics of thermal decomposition of PMMA using different methods were carried out with PMMA powder obtained from the same manufacturer, which essentially increased the relevance of comparing the kinetic parameters obtained by different methods.

The kinetic parameters of thermal decomposition of PMMA powder determined in supposition of a one-stage process and the first-order reaction (Method 1) and shown in Table 2 were calculated by linear approximation of the experimental data obtained by the methods of TGA (Fig. 7), MCC (Fig. 8), DMSTA (Fig. 9) and TGA + DMSTA (Fig. 11), as well as by the TGA method (Fig. 10) for thin PMMA plates for the entire array of the rate constant points obtained at different heating rates. The data for line 1 in Fig. 11 and in Table 2 were calculated by linear approximation of the experimental data obtained by the methods of TGA and DMSTA. The heating rate in K/min is indicated in Figs. 7–10.

In the case of heating a sample in argon at the heating rate of $\sim 20,000$ K/s to the temperature of isothermal decomposition, the time of 30% mass loss at the temperatures 350 °C and 400 °C was 120 s and 60 s, respectively. The value of the rate constant for the reaction of PMMA decomposition at the temperature 350 °C (2.1 s^{-1}) thus obtained agreed to the accuracy of 10% with the values obtained by the

Table 2

Averaged kinetic parameters of thermal decomposition of PMMA as powder and thin plates.

	TGA (Fig. 7)	MCC (Fig. 8)	DMSTA (Fig. 9)	TGA (Fig. 10)	TGA + DMSTA (Fig. 11, line 1)
	powder	powder	powder	thin plates	powder
	He	N ₂	N ₂	He	He + N ₂
T, K	590-700	590-700	630-780	590-700	590-780
lgk ₀ , k ₀ (s ⁻¹)	10.3	10.3	10.9	11.4	12.3
E _a , kJ/mol	150.5	151	152.3	166.1	171.4
R ²	0.96	0.99	0.96	0.99	0.97

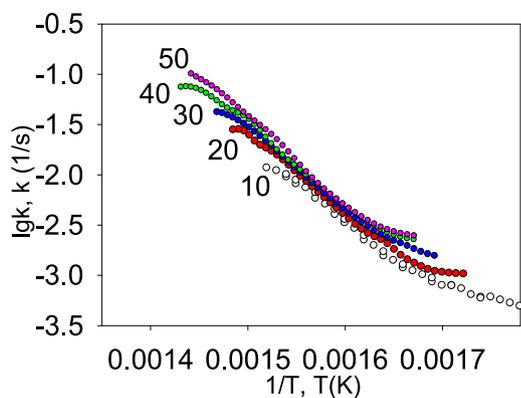


Fig. 7. Arrhenius plots of the rate constants of decomposition of PMMA powder obtained by the TGA method.

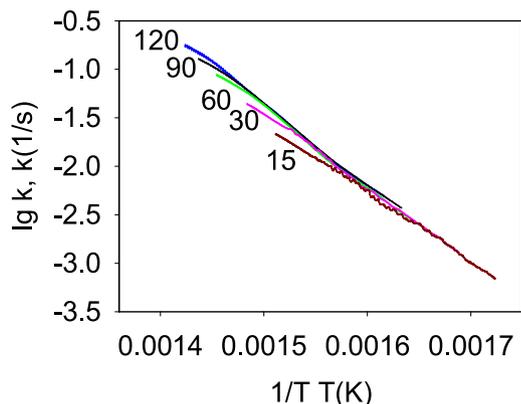


Fig. 8. Arrhenius plots of the rate constants of decomposition of PMMA powder obtained with the MCC method.

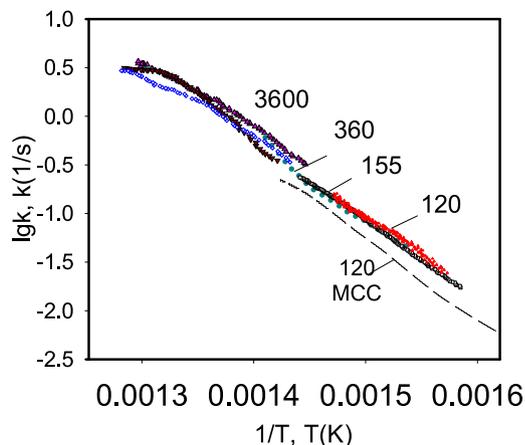


Fig. 9. Arrhenius plots of the rate constants of decomposition of PMMA powder obtained with the DMSTA method. Comparison with the MCC method at 120 K/min.

methods of TGA, DMSTA and MCC, and at 400 °C (47.8 s^{-1}), they proved to be 3 times less (Fig. 11). Shown in Fig. 11 (line 2) are the results of processing the MCC data by Method 2. It can be seen that these data are in good agreement with the TGA + DMSTA data.

Shown in Figs. 7–9 are the values of the rate constant in the conversion range of α varying from 0.05 to 0.95. The maximum relative error of determining the rate constant of the reaction does not exceed 20%, corresponding to $\sim 11\%$ of the accuracy of determining the activation energy. In the case of decomposition of the PMMA thin plates (Fig. 10), processing of the experimental data was carried out in the

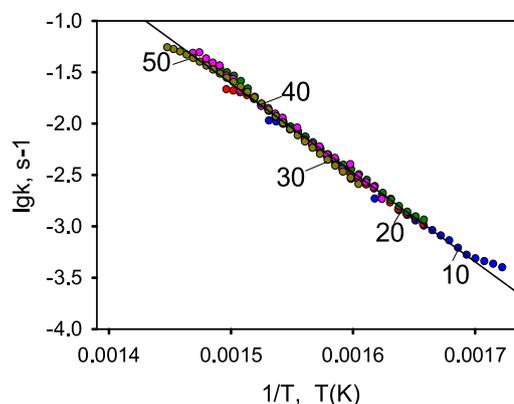


Fig. 10. Arrhenius plots of the rate constants of decomposition of PMMA thin plates.

The TGA method, helium, $n = 1$, the range of the extent of conversion α is 0.05 - 0.8.

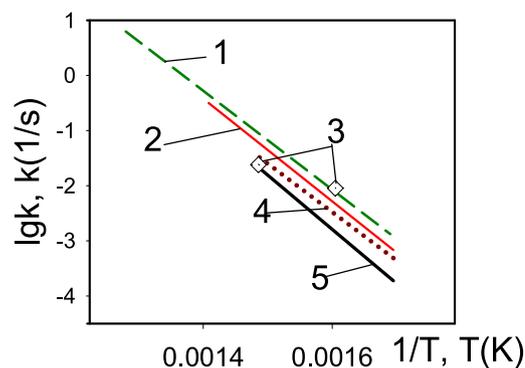


Fig. 11. Arrhenius plots of the rate constants of decomposition of PMMA powder.

1- TGA + DMSTA; 2- MCC ($n = 1$), 3- fast pyrolysis; 4 - Lomakin et al. [5]; 5 - Stoliarov et al. [7].

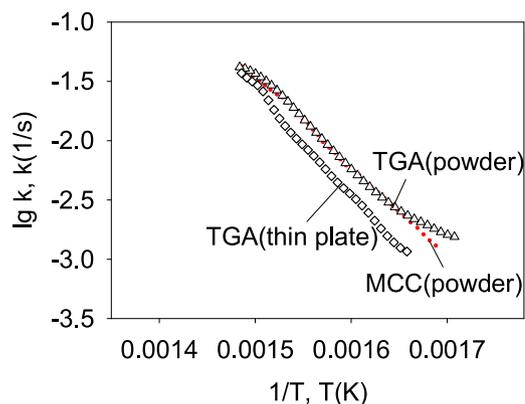


Fig. 12. Comparison of the Arrhenius plots of the rate constants of decomposition of PMMA thin plates and powder obtained by the TGA and MCC at the heating rate of 30 K/min.

range of α 0.05-0.8. The rate constants obtained at the same heating rate (30 K/min) in supposition of $n = 1$ by the TGA and MCC methods agreed well with each other (Fig. 12). The rate constant of PMMA decomposition was two times less for the thin plates (Fig. 12) than for the powder at the temperature lower than ~ 400 °C.

As MMA is the main product of PMMA decomposition, the results obtained by the TGA, MCC and DMSTA methods should be equal. The rate constant obtained by the DMSTA method (Fig. 9) was 1.3–1.6 times greater than that obtained by the MCC method at the same sample

heating rate equal to 120 K/min. The difference of ~ 2 times is considered satisfactory (the permissible error), considering the essential differences between these two methods. Merging of data on the rate constant obtained by the TGA_N and DMSTA methods in a wider temperature range and processed by Method 1 allowed higher reliability of the kinetic parameters of thermal decomposition of PMMA powder (Fig. 11, line 1, Table 2). The obtained values of the pyrolysis rate constant of high-molecular-weight PMMA powder differ from the literature data obtained in supposition of the first-order reaction for other types of PMMA [5,7]. It can be seen that the activation energies of decomposition of PMMA of other types available in the literature are close to that obtained in our study, but the values of the pre-exponential factor differ.

Resulting from merging the data on the rate constants obtained by the TGA method (10 ÷ 50 K/min) and DMSTA (3600 K/min), the kinetic parameters of reaction ($E = 171.4$ kJ/mol and $k_0 = 10^{12.3} \text{ s}^{-1}$) were obtained, averaged for the broad temperature range, including higher temperatures than those in the case of the TGA data, close to the temperatures of PMMA under combustion, which makes their use in simulation of PMMA combustion more reasonable.

Thus, the kinetic parameters of the reaction of thermal decomposition of PMMA powder in the range of temperatures from 315 to 500 °C, obtained on the basis of data of different methods and covering a wide range of the heating rates, in supposition of a one-stage first-order reaction, satisfactorily agree and constitute $E = 171.4$ kJ/mol and $k_0 = 10^{12.3} \text{ s}^{-1}$ within the permissible error limits.

Shown in Fig. 13 is dependence of the activation energy E_a of decomposition of PMMA powder (symbols) on the extent of its conversion obtained in nitrogen by the MCC and TGA_D methods and processed using the iso-conversion method [9] in the range of low heating rates from 15 to 120 K/min and from 0.4 to 2.5 K/min, respectively. The line is the average value over the entire range of α . The kinetic parameters of the reaction of thermal decomposition of PMMA powder in nitrogen in the range of the extent of conversion 0.05–0.95, obtained by the methods TGA_D and MCC [9] and processed with the iso-conversion method are presented in Table 3.

In the range of α from 0.3 to 0.95, the MCC [9] and TGA methods provide equal values of the activation energies to the accuracy ± 5 kJ/mol. Such high accuracy in determining the activation energy using different methods proves validity of the initial TGA data and of method 2 of their processing. Essential variance between the activation energies (50 kJ/mol) is observed in the range of α from 0.05 to 0.3, resulting in the variance of ~ 11 kJ/mol for the average value of the activation energy obtained by different methods (Fig. 13, Table 3) in the range of α from 0.05 to 0.95. Depending on α , the maximum deviation of the

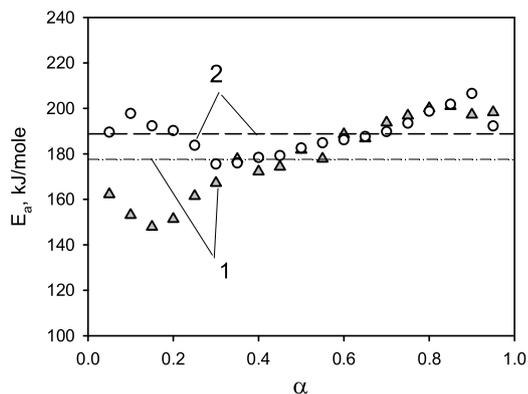


Fig. 13. The activation energy of thermal decomposition of PMMA powder (MW = 350,000) in nitrogen depending on the extent of conversion α , obtained by the MCC method [9] (line 1 and symbols) and the TGA_D method (line 2 and symbols). The symbols are the calculation parameters, the line is the average value over the entire range of the extent of conversion.

Table 3

Kinetic parameters of the reaction of thermal decomposition of PMMA powder in nitrogen in the range of the extent of conversion 0.05–0.95, obtained by the methods TGA_D and MCC [9] and processed with the iso-conversion method.

The line in Fig. 13	Heating rate (K/min), the range of temperatures (K)	Method	n	$\lg k_0$, k_0 (1/s)	E_a , kJ/mol,
1 [9]	15, 30, 60, 90, 120 590–710	MCC	1.3	12.7	177.6 ± 25
2	0.4, 1, 2, 2.5 580–690	TGA	1.52	13.4	188.8 ± 12

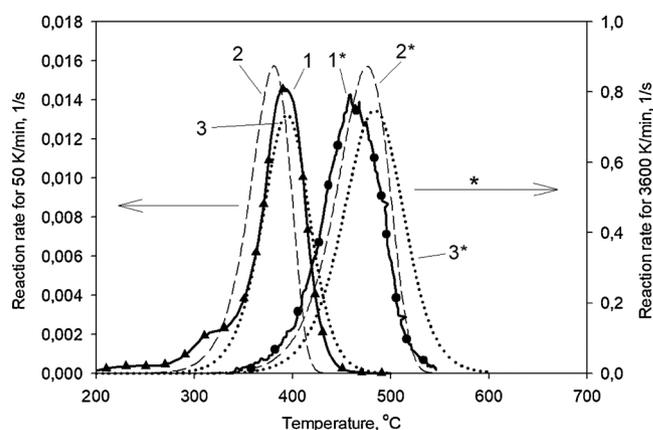


Fig. 14. Comparison of temperature dependences of the rates of the thermal decomposition reaction of PMMA, obtained in the experiment and in simulation using the kinetic parameters determined in this study by two methods (the simple method 1 and the iso-conversion method 2), at essentially differing heating rates of the sample: 50 and 3600 (marked as *) K/min, respectively (1 – experiment; 2 – Method 1: $n = 1$, $E = 171.4$ kJ/mol, $k_0 = 10^{12.3} \text{ s}^{-1}$ 3 – Method 2: $n = 1.52$, $E = 188.8$ kJ/mol, and $k_0 = 10^{13.4} \text{ s}^{-1}$).

activation energy from the average value obtained by the MCC method is ± 25 kJ/mol, and ± 12 kJ/mol in the TGA method.

Fig. 14 demonstrates comparison of temperature dependences of the rates of the thermal decomposition reaction of PMMA, obtained in the experiment and in simulation using the kinetic parameters determined in this study by two methods (the simple method (Method 1, Table 2, column 5) and the iso-conversion method (Method 2, Table 3, line 2), at essentially differing heating rates of the sample: 50 and 3600 K/min. It can be seen from Fig. 14 that the kinetic parameters obtained by Method 2 (Curve 3) better describe the experimental data on the dependence of the reaction rate of thermal decomposition of PMMA on temperature at the low heating rate than at the high heating rate. At the same time, the kinetic parameters obtained by Method 1 (Curve 2) satisfactorily describe the dependence of the PMMA decomposition rate on temperature both at low and high heating rates.

This, simple approximation of the rate constants of the process of PMMA decomposition at extending the temperature range due to increasing the heating rate allows more reliable kinetic data of thermal decomposition of PMMA to be obtained, which may be used in the models of PMMA combustion.

6. Conclusions

- 1 The kinetics of one-step thermal decomposition of PMMA powder (received from one manufacturer) was studied by several differing methods: TGA, MCC, and DMSTA, covering a wide range of the heating rates from fractions of 0.17 K/s to 100 K/s under non-isothermal conditions, and the fast pyrolysis method with the heating rate of $\sim 20,000$ K/s to the temperature of decomposition under isothermal conditions.

- 2 The kinetic parameters of the reaction of thermal decomposition of PMMA powder in the range of temperatures from 315 to 500 °C, obtained on the basis of data of different methods and covering a wide range of the heating rates, in supposition of a one-stage first-order reaction, satisfactorily agree and constitute $E = 171.4$ kJ/mol and $k_0 = 10^{12.3}$ s⁻¹ within the permissible error limits. The obtained kinetic data on thermal decomposition of PMMA may be used in numerical simulation of PMMA combustion under fire conditions and for evaluating its flammability.
- 3 Within the permissible error limits, the type of the inert carrier gas (nitrogen and helium) does not influence the kinetic parameters of the main stage of thermal degradation of PMMA. The rate constant of the reaction of thermal decomposition of a PMMA thin plates made from PMMA powder by the method of hot pressing, in the range of temperatures 315–400 °C ~2 times lower than for the powder itself.
- 4 Processing of the TGA data relating to the reaction of thermal decomposition of PMMA powder in nitrogen with the iso-conversion method provided the following kinetic parameters of thermal decomposition of PMMA powder: $n = 1.52$, $E = 188.8$ kJ/mol, and $k_0 = 10^{13.4}$ s⁻¹
- 5 The obtained kinetic parameters were validated by comparing the experimental data on dependence of the decomposition rate on temperature in the broad range of the heating rates with the results of simulating the above dependence, using these kinetic parameters.

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