ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2019, Vol. 93, No. 7, pp. 1252–1257. © Pleiades Publishing, Ltd., 2019.
Russian Text © A.Zh. Sarsenbekova, G.K. Kudaibergen, M.Zh. Burkeev, G.K. Burkeeva, 2019, published in Zhurnal Fizicheskoi Khimii, 2019, Vol. 93, No. 7, pp. 1009–1014.

CHEMICAL KINETICS AND CATALYSIS

Comparative Analysis of the Thermal Decomposition Kinetics of Polyethylene Glycol Fumarate–Acrylic Acid Copolymers

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Received August 10, 2018; revised September 11, 2018; accepted November 11, 2018

Abstract—The thermal decomposition of copolymers based on polyethylene glycol fumarate with acrylic acid in oxygen and nitrogen were studied. The activation energies at different degrees of conversion were evaluated by the Friedman and Flynn–Ozawa–Wall kinetic methods. It was found, using the nonparameteric kinetic methods, that the reaction rate depends on the temperature and degree of conversion in air and inert media.

Keywords: thermal decomposition, kinetics, copolymers

DOI: 10.1134/S0036024419060281

At present, the efforts of researchers are devoted to seeking new compounds for the synthesis of polymers with valuable properties. From this viewpoint, unsaturated polyesters based on fumaric acid are of interest for theoretical and practical research as they have found use in the preparation of biodegradable polymers with wide applications. As is known, the decomposition of these compounds results in the formation of fumaric acid—a natural substance involved in the tricarboxylic acid cycle (Krebs cycle)—and 1,2-diol commonly used as a diluent in pharmaceuticals. In addition to other advantages such as a simple and effective method of synthesis, unsaturated polyesters contain unsaturated double bonds; this can be used for cross-linking with various ionogenic monomers and hence opens the way toward synthesis of materials with a given set of properties. These materials should retain their properties when exposed to high temperatures, corrosive media, moisture, and other destructive factors. The dynamic thermogravimetry methods allow us to determine the activation energy of thermal decomposition, which is used to characterize the mechanisms of thermal destruction and stability of polymers [1–4].

The thermal stability of substances is generally studied in two ways: studies of the temperature dependence of mass loss [5–8] and kinetic analysis [9, 10].

It is reasonable to ask which method would be suitable for determining the kinetic parameters of the destruction of polymers and composite materials.

Earlier, we showed the possibility of using the nonisothermal calculation methods for determining the thermodynamic parameters of polypropylene glycol maleate–acrylic acid copolymers [11]. In continuation of these studies, here we studied the kinetics of the thermal decomposition of copolymers based on polyethylene glycol fumarate with acrylic acid in oxygen and nitrogen at different heating rates.

EXPERIMENTAL

The objects of investigation were the copolymers of polyethylene glycol fumarate (p-EGF) with acrylic acid (AA) with molar compositions of 7.9 : 92.1 and 89.1 : 10.9 synthesized previously [12]. The thermal analysis was performed by differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) using a Setaram DTA/DSC differential scanning calorimeter. The thermograms were recorded under the following conditions: Al_2O_3 crucible, nitrogen or air atmosphere, temperature range 30–800°C, heating rate of 5–20 K/min, 12–16 mg samples. All the calculations were performed using the Mathcad program.

RESULTS AND DISCUSSION

The thermoanalytical characteristics of the decomposition of the p-EGF–AK copolymers are represented by the TG/DTG curves (Fig. 1). Note that the total mass loss at five heating rates was 74.9–81.6% (Fig. 1a). The changes in the relative mass at different heating rates show themselves at temperatures in the range 200–500°C for all the dependences. A change in the heating rate of the samples did not affect the behavior of the TG and DTG curves (Figs. 1a and 1b), and no new peaks were detected. An increase in the

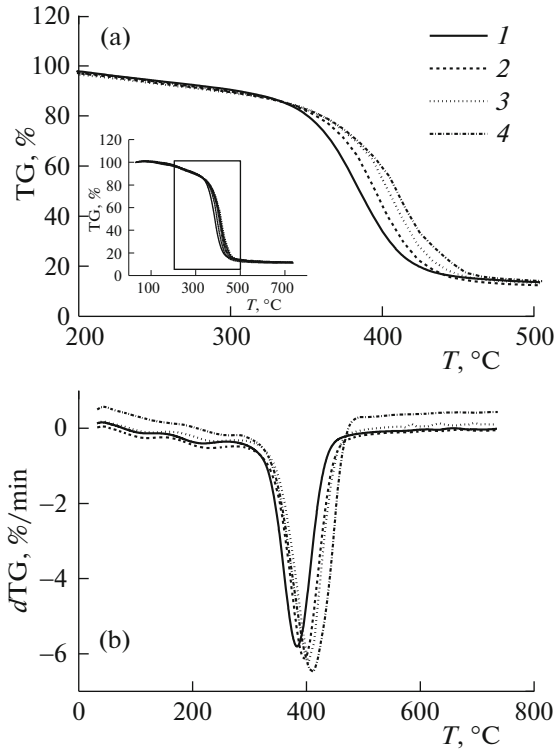

Fig. 1. TG/DTG curves of the p-EGF–AA copolymers at different heating rates: (*1*) 5, (*2*) 10, (*3*) 15, and (*4*) 20 K/min.

heating rate led only to an insignificant change in the temperature of the start of the peaks, the minimum, and the end of the deviation of the curve from the baseline.

The mathematical processing of the thermogravimetric curves presented in Fig. 1 allows us to determine E_a using the Friedman (FR) [13] and Flynn–Ozawa–Wall (FOW) isoconversion methods [14]. To evaluate the complex processes occurring simultaneously with the thermal destruction, the nonparametric kinetic (NPK) method was used [15].

The plot of the kinetic model obtained by the Friedman differential method is shown in Figs. 2a and 2c. For kinetic analysis, a set of points with the same degree of conversion were processed; the plot was a series of several straight lines each characterized by its own activation energy (Figs. 2a and 2c). The output parameters (E, log A) were calculated in a similar way using the Flynn–Ozawa–Wall method (Figs. 2b and 2d). As a result of the thermal decomposition of the p-EGF–AA copolymers, the chain propagates by a heterogeneous reaction on the boundary between the polymer and the gaseous products of thermolysis (CO_2, CO, H_2O, etc.): the particles diffuse to the ash layer accumulating during the combustion of fumarate, which indicates the limiting stage of the process as it requires high activation energy (Figs. 3 and 4). The results of the mathematical processing of the TG curves are presented in Figs. 3 and 4.

For kinetic analysis of the thermal destruction of the samples, the nonparametric kinetic (NPK) method [15, 16] was also used, which is a special approach to the processing of kinetic data. The experimental reaction rates were located in a matrix expressed as the product of two vectors containing $k(T)$ and $f(\alpha)$. This mathematical model is actually a corollary of the equation:

$$r_{i,j} = f(\alpha_i)k(T_j), \quad (1)$$

Here, the reaction model $f(\alpha)$ is the dependence of the degree of conversion, and $k(T)$ is the temperature dependence.

The NPK method uses the singular decomposition (SVD) algorithm for decomposition of a matrix M into two vectors [17]. The matrix M is analyzed in the following way:

$$M_{i,j} = f(\alpha_i)k(T_j). \quad (2)$$

The most important feature of this method is that it can be used to decompose the submatrix with respect to the temperature (v) and conversion function (u) without any assumptions about their functionality:

$$u = \{f(\alpha_1)f(\alpha_2)\dots f(\alpha_i)\}, \quad (3)$$

$$v = \{k(T_1)k(T_2)\dots k(T_j)\}. \quad (4)$$

To determine the kinetic model, we suggest using the Šesták–Berggren equation [18]: $f(\alpha) = \alpha^m(1-\alpha)^n$, where α^m is determined by the physical effect that is due to the presence of the reaction product, and $(1-\alpha)^n$ is due to the chemical effect including the residual reagent $(1-\alpha)$, while the temperature dependence is determined by the Arrhenius equation. The value of the explained variation λ defines the contribution of each of the simultaneous steps for the whole process of thermal decomposition; thus, $\sum\lambda = 100\%$.

The reaction rate ($\beta d\alpha/dT$) of the decomposition of the p-EGF–AA copolymers obtained experimentally at different heating rates was interpolated as a surface in a 3D space ($\beta d\alpha/dT$, α, T). The surface is organized as a matrix $i \times j$, where the lines correspond to different degrees of conversion from α_1 to α_i, and the columns represent the temperatures from T_1 to T_j (Fig. 5).

The results of the NPK study of the p-EGF–AA copolymers (7.9 : 92.1 and 89.1 : 10.9 mol) are summarized in Table 1. Note that the main process is a chem-

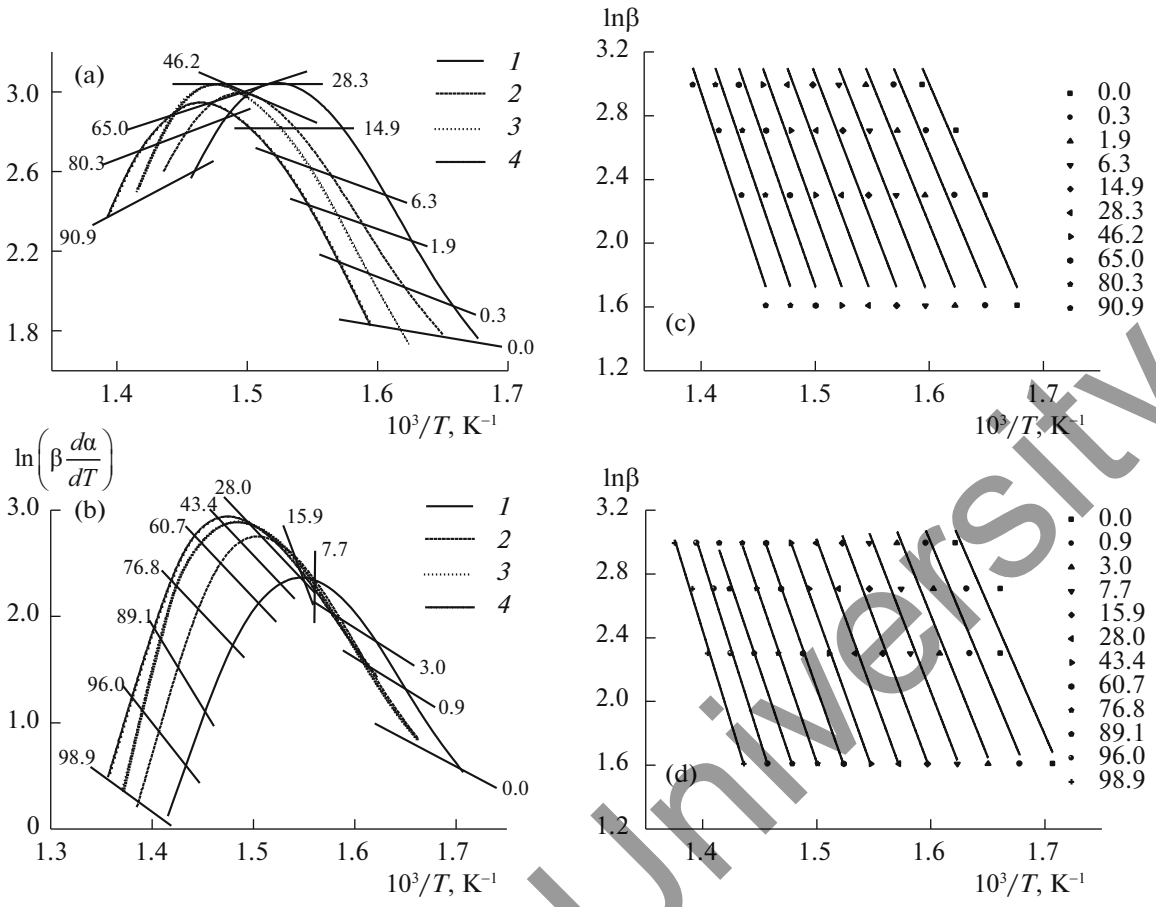

Fig. 2. Graphical data obtained by the (a, b) Friedman and (c, d) Flynn–Ozawa–Wall methods for the p-EGF–AA copolymers at different heating rates: (*1*) 5, (*2*) 10, (*3*) 15, and (*4*) 20 K/min.

ical reaction with a reaction order $n = 0.5$ accompanied by a physical process ($m = 0$). In the thermal decomposition analysis, a process with the activation energies shown in Table 2 was identified. The average value of the activation energy obtained by the NPK method agrees with the values obtained by the isoconversion methods (Table 2).

CONCLUSIONS

Thus, the simultaneous use of the TG/DTG data for kinetic analysis gave a more complete picture of the thermal destruction of the p-EGF–AA copolymers. This made it possible to evaluate the kinetic parameters using three kinetic methods and to compare the activation energies obtained from the experimental

Table 1. Kinetic parameters of the thermal decomposition of p-EGF–AA copolymers calculated by the nonparameteric kinetic method (NPK)

p-EGF–AA	λ, %	$\bar{E}_a$, kJ/mol	$\bar{A}$, s^{-1}	*m*	*n*	$\bar{E}_a$, kJ/mol	$\bar{A}$, s^{-1}
In nitrogen							
7.9 : 92.1	100	153.73	4.30×10^{13}	0	0.5	111.94	6.68×10^{9}
89.1 : 10.9		210.67	5.67×10^{18}			155.72	5.25×10^{9}
In air							
7.9 : 92.1	100	161.97	6.24×10^{14}	0	0.5	117.43	1.52×10^{8}
89.1 : 10.9		194.67	1.07×10^{18}			155.67	3.49×10^{9}

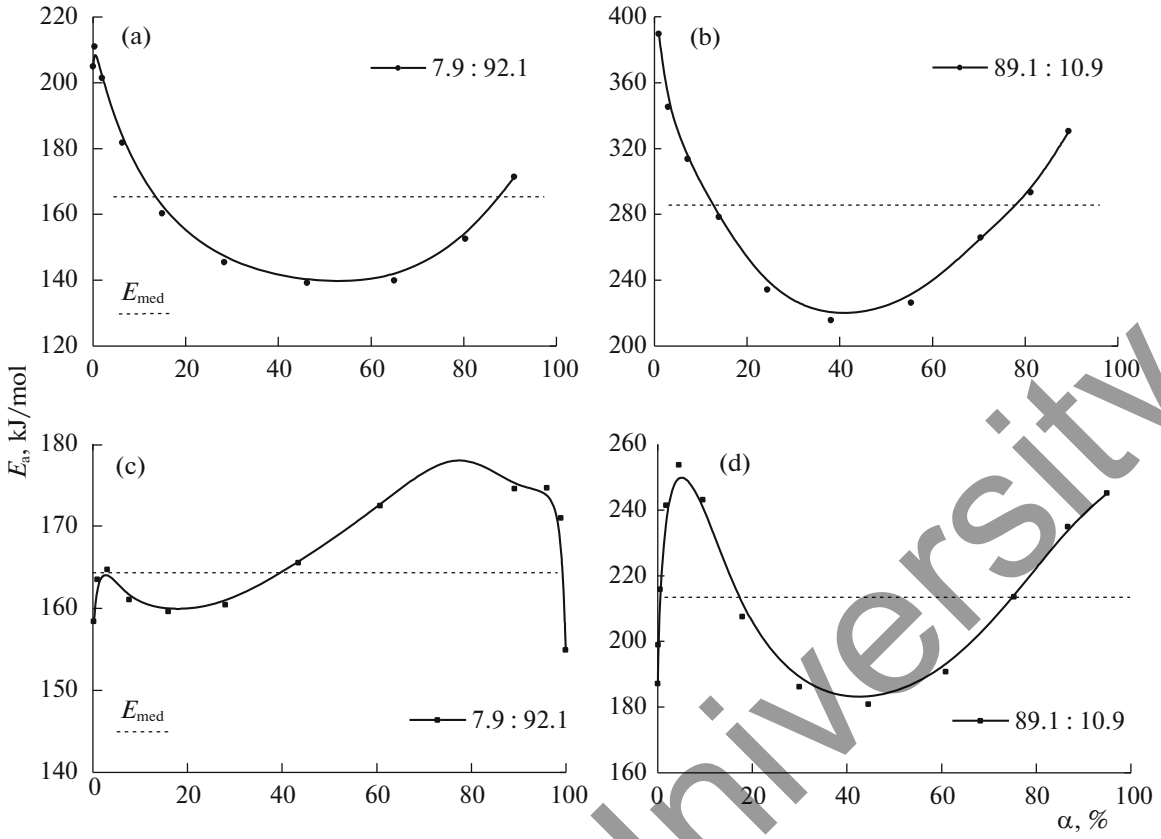

Fig. 3. Dependences of the conversion (α) on the activation energy (E_a) for the p-EGF–AA copolymers in (a, b) nitrogen and (c, d) air calculated by the Friedman method.

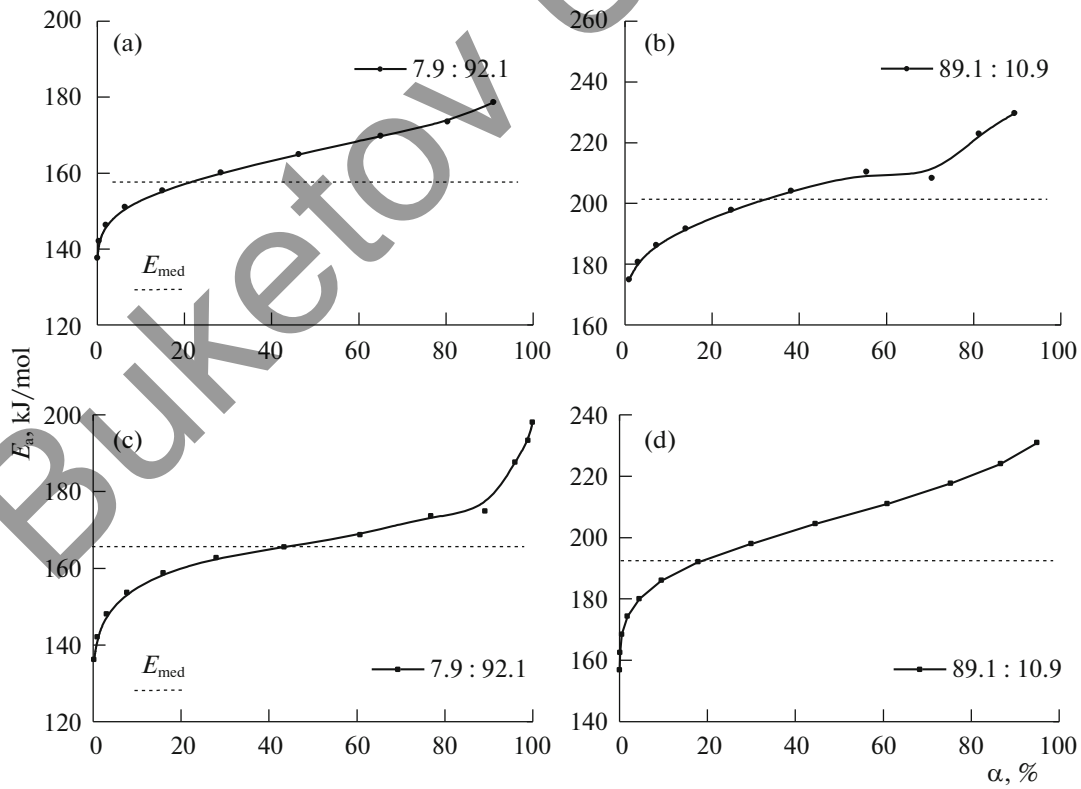

Fig. 4. Dependences of the conversion (α) on the activation energy (E_a) for the p-EGF–AA copolymers in (a, b) nitrogen and (c, d) air calculated by the Flynn–Ozawa–Wall method.

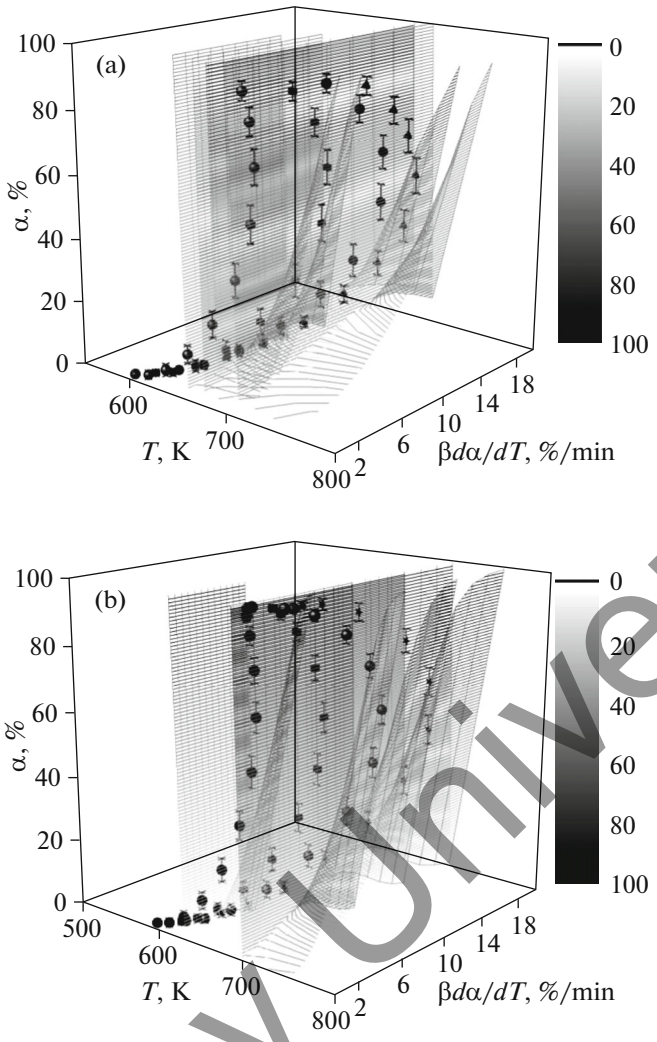

Fig. 5. Surface of the p-EGF–AA copolymers in a three-dimensional space: dependence of the reaction rate $\left(\beta\frac{d\alpha}{dT}\right)$ on the temperature (T) and conversion (α) in (a) nitrogen and (b) air.

TG and DTG data. The kinetic parameters were calculated using the Friedman and Flynn–Ozawa–Wall methods and the nonparametric kinetic (NPK) method. The Friedman and Flynn–Ozawa–Wall methods give the invariant part of the activation energy, but the kinetic description is too formal. The NPK method offers two main advantages: (a) the possibility of separating two or more steps of the complex decomposition reaction and (b) the possibility of discriminating between the degrees of conversion via the corresponding temperature functions from the rate equation.

Table 2. Average values of activation energy obtained by the kinetic methods being compared ($\bar{E}_a$, kJ/mol)

p-EGF–AA	FR	FOW	NPK
In nitrogen			
7.9 : 92.1	165.20	157.75	153.73
89.1 : 10.9	285.93	201.46	210.67
In air			
7.9 : 92.1	164.31	165.82	161.97
89.1 : 10.9	213.47	192.50	194.67

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Translated by L. Smolina