ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2021, Vol. 95, No. 10, pp. 2009–2013. © Pleiades Publishing, Ltd., 2021.
Russian Text © The Author(s), 2021, published in Zhurnal Fizicheskoi Khimii, 2021, Vol. 95, No. 10, pp. 1496–1500.

# Integral Ways of Calculating the Destruction of Copolymers of Polyethylene Glycol Fumarate with Acrylic Acid

**M. Zh. Burkeev**[a], **A. N. Bolatbay**[a,*], **A. Zh. Sarsenbekova**[a],
**S. Zh. Davrenbekov**[a], **and E. Nasikhatuly**[a]
[a] *Buketov Karaganda University, Karaganda, 100028 Kazakhstan*
**e-mail: abylai_bolatbai@mail.ru, chem_akmaral@mail.ru*

Received March 5, 2021; revised March 5, 2021; accepted March 19, 2021

**Abstract**—The thermal decomposition of polyethylene glycol fumarate–acrylic acid copolymer is investigated at different rates of heating. It is shown that increasing the rate of heating raises the temperature of the onset of decomposition. The kinetic parameters of decomposition are calculated using the integral Kissinger–Akahira–Sunose procedure. It is found that at different degrees of conversion, the activation energies are very close: $E = 205–227$ kJ/mol. The effect the composition of the copolymer has on the results from kinetic calculations is shown. The Coates–Redfern approach is used to determine the pre-exponential factor and the model of thermal decomposition. Calculated thermogravimetric curves are constructed and compared to experimental ones.

**Keywords:** copolymer, polyethylene glycol fumarate, acrylic acid, kinetic parameters, integral ways of calculating

**DOI:** 10.1134/S0036024421100034

Buketov University

## INTRODUCTION

Science's interest in obtaining and producing new materials based on unsaturated polyester resins is growing every year. Unsaturated polyester resins are products of the polycondensation of polyhydric alcohols with unsaturated polybasic acids or anhydrides [1]. In a solution of monomers with additions of a peroxide initiator, they can cure at both room temperature and low temperatures without the release of byproducts. Unsaturated polyesters also provide the greatest possibility of directed modification, due to polymerization with different ionic monomers and thus open the way to obtaining materials with predetermined valuable sets of properties [2].

Copolymers (unsaturated polyester resins with hydrophobic monomers that have a spatially crosslinked structure) are characterized by thermal stability in a wide range of temperatures [3]. Studies have revealed that the composition of unsaturated polyester and the monomers used for crosslinking strongly affect the thermal stability of products of copolymerization. Results from thermogravimetric analysis show that these copolymers are thermally stable up to 250–300°C, after which thermal destruction proceeds in several stages [4, 5]. The thermal decomposition and kinetic parameters of copolymers of polypropylene glycol maleinate with acrylic acid were studied in [6], and the dependence of destruction on the ratio of components was established. The thermal decomposition of copolymers of polyethylene glycol fumarate with acrylic acid was investigated in [7]. Using the Friedman and Flynn–Ozawa–Wall procedures, the activation energies were estimated at various degrees of transformation. Nonparametric kinetics was used to establish the reaction rate's dependence on temperature and degree of conversion.

In this work, we determine the kinetic parameters of the thermal decomposition of a copolymer of polyethylene glycol fumarate with acrylic acid, according to the recommendations (ICTAC) of the Kinetic Committee [8, 9].

## EXPERIMENTAL

Our objects of study were copolymers of polyethylene glycol fumarate (p-EHF) and acrylic acid (AA) synthesized earlier in ratios of 7.95 : 92.05 and 89.05 : 10.95 at a temperature of 293 K [10]. The thermal properties of the copolymers were studied on a LabSYS evo TG/DSC unit (Setaram, France) for simultaneous thermal analysis in the dynamic mode. Samples were brought to temperatures of 30–1000°C with heating rates of 5, 10, 15, and 20 K/min in an atmosphere of nitrogen and air inside an $Al_2O_3$ crucible. The gas flow rate was 30 mL/min. The weight of the samples was 10–12 mg. The experimental data were treated using the Microsoft Excel and Processing programs.

Buketov University

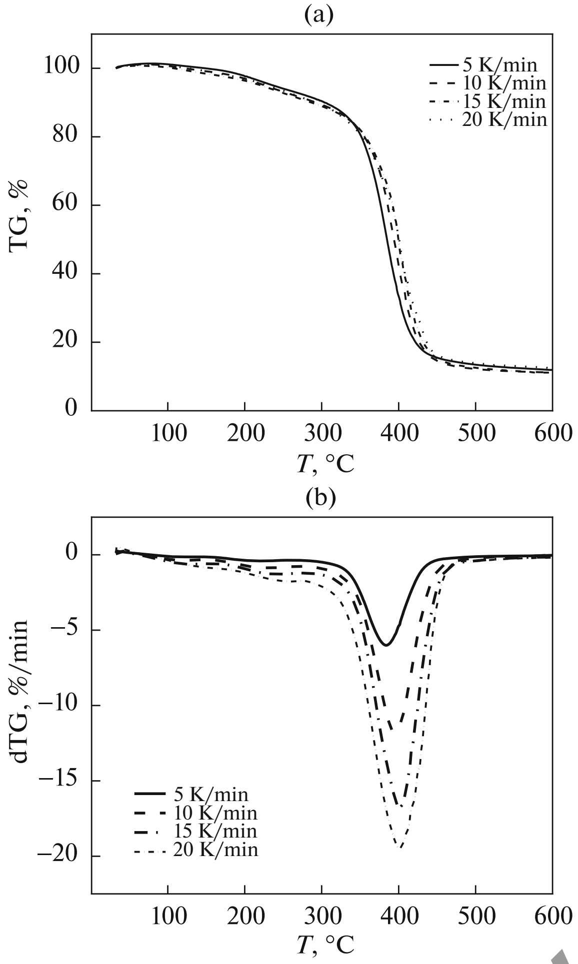

**Fig. 1.** Temperature dependences of (a) weight change and (b) rate of weight change for p-EHF : AA copolymers at a ratio of 7.95 : 92.05 wt % (in nitrogen).

We used integral procedures to determine the activation energy ($E$) and pre-exponential factor ($A$). An approximation of the temperature integral produced an inaccurate value of $E$. The more accurate approximation of Murray and White can be reduced to the familiar so-called Kissinger–Akahira–Sunose equation [11, 12]:

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \text{const} - \frac{E}{RT}. \qquad (1)$$

The Kissinger–Akahira–Sunose equation provides a substantial improvement in the accuracy of the activation energy. Constricting dependency $\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$ on $1/T$, we get a line on which we can determine $E$.

A suitable model can be selected for describing the dependence of the relative change in mass temperature and simultaneously determining the activation energy $E$ and pre-exponent $A$. There are several ways of fitting non-isothermal models. One of the most famous is the Coates–Redfern approach [13], which uses an asymptotic expansion to approximate the integral of the exponential function in the equation

$$g(\alpha) = \int_0^\alpha \frac{1}{(1-\alpha)^n} d\alpha = \begin{cases} -\ln(1-\alpha) \leftarrow n = 1 \\ \dfrac{1-(1-\alpha)^{1-n}}{1-n} \leftarrow n \neq 1, \end{cases}$$

which yields

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT}. \qquad (2)$$

Dependence $\ln(g(\alpha)/T^2)$ on $1/T$ is a line with slope tangent ($-E/R$), which allows us to determine the activation energy.

## RESULTS AND DISCUSSION

One of the most important applied problems in the chemistry of macromolecular compounds is creating heat-resistant polymeric materials. The greatest issue is thus the possibility of determining the activation energy for thermal decomposition, which is used to characterize the mechanisms of thermal destruction and the stability of polymers by dynamic thermogravimetry and other means. In this work, we were able to determine the main kinetic parameters of the decomposition of a copolymer of polyethylene glycol fumarate with acrylic acid (p-EHF : AA) using isoconversion models. Our results demonstrated the practical value of this approach.

The curves obtained using thermogravimetric analysis and the rates of decomposition are shown in Figs. 1, 2.

As is shown in Fig. 1a, a sample of a copolymer of polyethylene glycol fumarate with acrylic acid in an inert medium begins to decompose at ~180°C. Slow decomposition of the sample with the release of volatile substances is observed up to ~300°C. The main stage of thermal decomposition of the copolymer lies in the range of ~ 320 to ~ 440°C, after which stabilization of the sample mass is observed. The rate of weight loss (Fig. 1b) as that of heating grows is 5 to 18 mg/min. The graphs clearly show the shifts of the curves toward higher temperatures.

For comparison, the weight loss and rate of weight loss of copolymers in air are shown. Figure 2a shows that the copolymer has three main stages of weight loss. Up to ~200°C, there is slow decomposition of the sample with the release of volatile substances. The main stage of destruction lies in the range 300–420°C. At temperatures of 420 to 800°C, the sample burns out until it decomposes completely. As in an inert

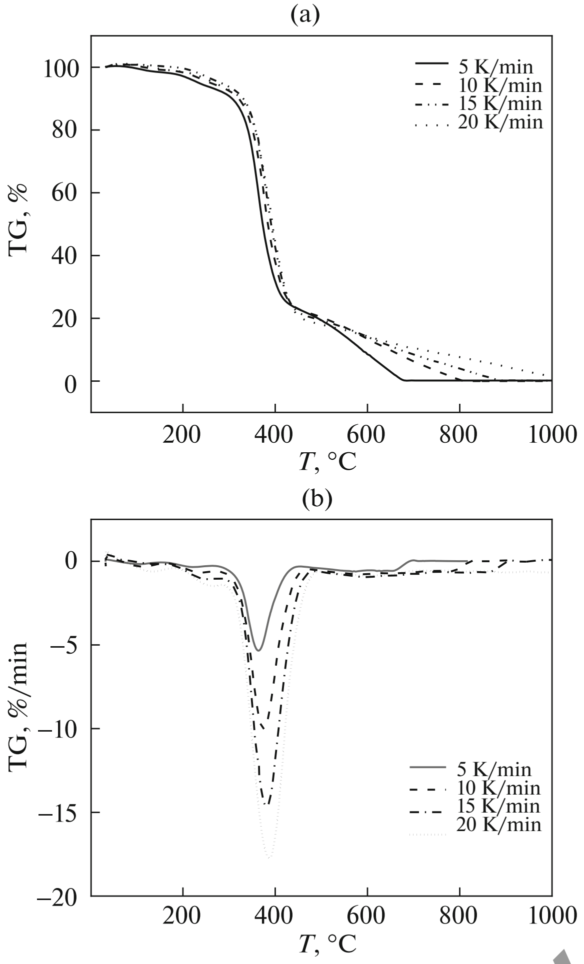

**Fig. 2.** Temperature dependences of (a) weight change and (b) rate of weight change for p-EHF:AA copolymers at a ratio of 7.95 : 92.05 wt % (in air).

medium, the rate of decomposition varies from 5 to 17 mg/min. The main peaks are observed at 400°C.

The thermogravimetric curves at different heating rates were processed using an integral approach. Graphic dependences of the equations of isoconversion method are shown in Fig. 3.

Kinetic parameters were calculated for obtained partial dependences, and the coefficients of correlation given in Table 1 were calculated.

Analysis of the data in Table 1 shows that the activation energy determined with integrals changes slightly and is virtually independent of the experimental system in which thermal destruction was implemented. The preexponential factor is in this case more sensitive to different external parameters and changes by several orders of magnitude. The values of $E$ generally show the same tendency of change, allowing us to consider the ones we obtained to be quite reliable.

The data presented in Table 2 indicate that the activation energy is high for copolymers with lower polyester resin contents. Thermal destruction in air reduces the thermal stability of the copolymers. Its effective activation energy is therefore relatively low. The obtained kinetic characteristics of the destruction of copolymer p-EGF:AA can therefore be used to identify it, since they are strictly individual for each compound.

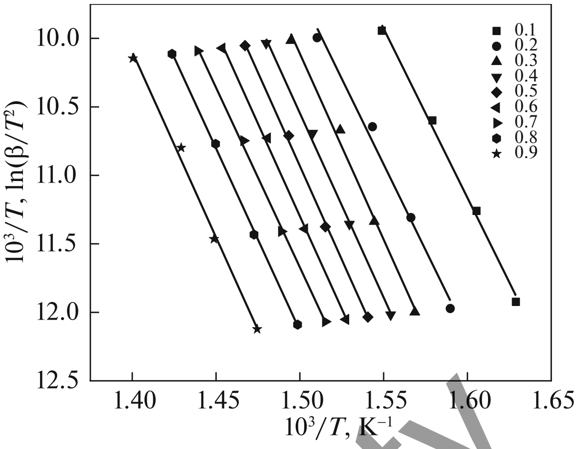

**Fig. 3.** Graphic dependences of the Kissinger–Akahira–Sunose equations for the p-EHF:AA copolymer at a ratio of 7.95 : 92.05 wt % and different rates of heating.

The Coates–Redfern approach was used to determine the model of the reaction associated with the main stage of decomposition. According to Eq. (2), the activation energy for different functions $g(\alpha)$ can be calculated at a constant rate of heating by fitting linear dependence ln $(g(\alpha)/T^2)$ on $1/T$. The slope of the corresponding dependences allows us to determine the activation energy for each possible model (Fig. 4). The Coates–Redfern approach thus allows us to determine

**Table 1.** Kinetic parameters calculated using the Kissinger–Akahira–Sunose approach at different degrees of conversion

| $\alpha$ | $E$, kJ/mol | $A$, min$^{-1}$ | $R^2$ |
|---|---|---|---|
| 0.1 | 205.23 | $2.02 \times 10^{12}$ | 0.9964 |
| 0.2 | 208.02 | $1.26 \times 10^{12}$ | 0.9909 |
| 0.3 | 225.79 | $1.99 \times 10^{13}$ | 0.9943 |
| 0.4 | 223.88 | $9.17 \times 10^{12}$ | 0.9978 |
| 0.5 | 227.04 | $1.10 \times 10^{13}$ | 0.9988 |
| 0.6 | 224.93 | $5.21 \times 10^{12}$ | 0.9984 |
| 0.7 | 218.06 | $1.04 \times 10^{12}$ | 0.9986 |
| 0.8 | 221.13 | $1.41 \times 10^{12}$ | 0.9993 |
| 0.9 | 225.21 | $1.23 \times 10^{12}$ | 0.9946 |

Buketov University

Buketov University

the total kinetic triplet ($E$, $A$, and $g(\alpha)$). The parameters obtained from the slopes and intersection of the lines are presented in Table 3.

**Table 2.** Activation energies for p-EHF copolymers : AA ($m_1 : m_2$) in an atmosphere of nitrogen and air

| $m_1 : m_2$, wt % | $E$, kJ/mol |
|---|---|
| In a nitrogen atmosphere | |
| 7.95 : 92.05 | 219.92 |
| 89.05 : 10.95 | 201.87 |
| In air | |
| 7.95 : 92.05 | 148.47 |
| 89.05 : 10.95 | 149.54 |

**Table 3.** Kinetic parameters obtained with the Coates–Redfern procedure at a heating rate of 10 K/min

| Reaction model | $g(\alpha)$ | $E$, kJ/mol | $R^2$ | ln $A$ |
|---|---|---|---|---|
| P4 | $\alpha^{1/4}$ | 19.92 | 0.7028 | 11.07 |
| P3 | $\alpha^{1/3}$ | 30.25 | 0.7846 | 9.74 |
| P2 | $\alpha^{1/2}$ | 50.93 | 0.8391 | 7.09 |
| P2/3 | $\alpha^{3/2}$ | 174.96 | 0.8863 | 8.81 |
| D1 | $\alpha^2$ | 300.58 | 0.8908 | 16.75 |
| F1 | $-\ln(1-\alpha)$ | 163.78 | 0.9982 | 13.20 |
| A4 | $[-\ln(1-\alpha)]^{1/4}$ | 32.63 | 0.9790 | 7.98 |
| A3 | $[-\ln(1-\alpha)]^{1/3}$ | 47.20 | 0.9829 | 5.62 |
| A2 | $[-\ln(1-\alpha)]^{1/2}$ | 76.34 | 0.9859 | 0.92 |
| D3 | $[1-(1-\alpha)]^{1/3}]^2$ | 226.98 | 0.9949 | 39.67 |
| R3 | $1-(1-\alpha)^{1/3}$ | 144.75 | 0.9612 | 6.94 |
| R2 | $1-(1-\alpha)^{1/2}$ | 136.04 | 0.9426 | 5.19 |
| D2 | $(1-\alpha)\ln(1-\alpha)+\alpha$ | 265.15 | 0.9242 | 21.72 |

The best model was chosen according to its agreement with the activation energy calculated earlier. The best fit was for the D3 model (three-dimensional diffusion).

To confirm the correctness of our data, we compared the experimental TGA curves to ones calculated using the equation [14]

$$\frac{m}{m_0} = \exp\left[-\frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{R\theta}\right)d\theta\right], \qquad (3)$$

where $m$ and $m_0$ are the current and initial sample weights, $T$ is temperature (K), $E$ is the activation energy, $R$ is the gas constant, and $A$ is a pre-exponential factor.

Average values of the activation energy, obtained using the Kissinger–Akahira–Sunose approach at different degrees of expansion, were used to calculate the current mass of each polymer sample (Table 1).

As is seen from Fig. 5, the values of the current sample mass, calculated using formula (3), converge satisfactory with the experimental data. This is typical for other values of heating rates as well.

## CONCLUSIONS

The thermal stability of copolymers of polyethylene glycol fumarate with acrylic acid was determined. The kinetic parameters of thermal destruction were determined using the Kissinger–Akahira–Sunose isoconversion approach. It was found that the activation energies rise along with the composition of the copolymer of unsaturated polyester resin. When heated in air, the copolymer was vigorously oxidized by the action of atmospheric oxygen. If the material was heated without air (e.g., in a nitrogen atmosphere), the copolymer broke down into low–molecular weight products. The Coates–Redfern approach

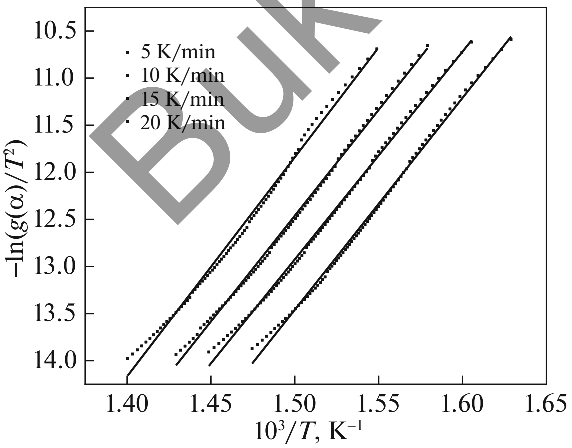

**Fig. 4.** Graphic dependences of the Coates–Redfern equation (reaction model D3) for p-EHF:AA copolymer at different rates of heating.

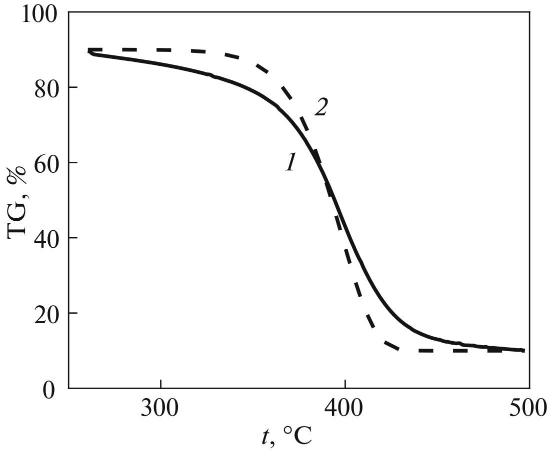

**Fig. 5.** (*1*) Experimental and (*2*) calculated dependences of the relative mass of p-EGF:AA samples on temperature at a heating rate of 10 K/min.

allowed us to calculate the pre-exponential factor and the model of the reaction: $A = 1.69 \times 10^{-17}$ and $f(\alpha) = [(1 - (1 - \alpha))^{1/3}]^2$, respectively.

## REFERENCES

1. H. V. Boenig, *Unsaturated Polyesters: Structure and Properties* (Elsevier, Amsterdam, 1964).
2. C. Benny and T. T. Eby, J. Appl. Polym. Sci. **100**, 457 (2006). https://doi.org/10.1007/s11595-009-4627-2
3. S. V. Vinogradova, V. V. Korshak, V. I. Kul'chitskii, et al., Polymer Sci. U. S. S. R. **10**, 1757 (1968). https://doi.org/10.1016/0032-3950(68)90368-7
4. K. G. Johnson and L. S. Yang, in *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters,* Ed. by J. Scheirs and T. E. Long (Wiley, West Sussex, UK, 2004), p. 697.
5. E. Kicko-Walczak, J. Appl. Polym. Sci. **88**, 2851 (2003). https://doi.org/10.1002/app.11723
6. M. Zh. Burkeev, A. Z. Sarsenbekova, Y. M. Tazhbayev, and I. V. Figurinene, Russ. J. Phys. Chem. A **89**, 2183 (2015). https://doi.org/10.1134/S0036024415120067
7. A. Z. Sarsenbekova, G. K. Kudaibergen, M. Zh. Burkeev, and G. K. Burkeeva, Russ. J. Phys. Chem. A **93**, 1252 (2019). https://doi.org/10.1134/S0044453719060281
8. S. A. Vyazovkin, K. Burnham, J. M. Criadoc, et al., Thermochim. Acta **520**, 1 (2011). https://doi.org/10.1016/j.tca.2011.03.034
9. S. Vyazovkin, K. Chrissafis, M. L. di Lorenzo, et al., Thermochim. Acta **590**, 1 (2014). https://doi.org/10.1016/j.tca.2014.05.036
10. M. Zh. Burkeev, G. K. Kudaibergen, G. K. Burkeeva, T. M. Seilkhanov, E. M. Tazhbaev, J. Hranicek, A. V. Omasheva, and S. Zh. Davrenbekov Russ. J. Appl. Chem. A **91**, 1145 (2018). https://doi.org/10.1134/S1070427218070121
11. H. E. Kissinger, Anal. Chem. **29**, 1702 (1957). https://doi.org/10.1021/ac60131a045
12. T. Akahira and T. Sunose, Sci. Technol. **16**, 22 (1971). https://doi.org/10.17221/115/2016-RAE
13. A. W. Coats and J. P. Redfern, Nature (London, U.K.) **201**, 68 (1964). https://doi.org/10.1038/201068a0
14. A. A. Koptelov, I. A. Koptelov, A. A. Rogozina, and E. S. Yushkov, Russ. J. Appl. Chem. **89**, 1454 (2016). https://doi.org/10.1134/S1070427216090111

Buketov University