ISSN 0036-0244, Russian Journal of Physical Chemistry A, 2015, Vol. 89, No. 12, pp. 2183–2189. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © M.Zh. Burkeev, A.Zh. Sarsenbekova, E.M. Tazhbaev, I.V. Figurinene, 2015, published in Zhurnal Fizicheskoi Khimii, 2015, Vol. 89, No. 12, pp. 1851–1857.

CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

Thermal Destruction of Copolymers of Polypropylene Glycol Maleate with Acrylic Acid

M. Zh. Burkeev[a], **A. Zh. Sarsenbekova**[a], **E. M. Tazhbaev**[a], **and I. V. Figurinene**[b]
[a] *Faculty of Chemistry, Buketov Karaganda State University, Karaganda, 100028 Kazakhstan*
[b] *Karaganda State Medical University, 100008 Kazakhstan*
e-mail: chem_akmaral@mail.ru

Received January 26, 2015

Abstract—The results from thermogravimetric and kinetic studies of copolymers of polypropylene glycol maleate with acrylic acid at different molar ratios are presented. The results from conventional thermogravimetric studies are used to determine kinetic characteristics of the process of thermal decomposition, i.e., activation energy and pre-exponential factors. These parameters are determined in three ways: the Achar, Freeman–Carroll, and Sharp–Wentworth methods. Activation energies calculated using all the three methods confirm the dependence of the destruction process on the ratio of components in a synthesized copolymer. It is shown that the obtained values of the activation energies and thermodynamic characteristics allow us to predict a copolymer's composition.

Keywords: dynamic thermogravimetry, thermal destruction, copolymer of polypropylene glycol with acrylic acid, activation energy.

DOI: 10.1134/S0036024415120067

INTRODUCTION

In searching for materials with specific properties unsaturated polyester resins continue to be of interest. Solutions of unsaturated polyesters in monomers are solidified at both room and relatively low temperatures with virtually no formation of side products; this played a large role in developing the manufacture of these products.

Due to the low molecular weight of unsaturated polyesters, their solutions generally have low viscosity, allowing us to process them without using high pressure and often without complex technological equipment.

Interaction between unsaturated polyester resins and vinyl monomers was first referred to as the copolymerization reaction by Benig in [1], and this term is now generally accepted.

The ability of unsaturated polyesters to copolymerize with vinylacetate, styrene, and methyl methacrylate was revealed in [2]. The range of comonomers was subsequently extended to allyl ethers [3] and esters [4], vinyl formates [5], and so on. The discovery of unsaturated polyesters' ability to copolymerize with different monomers resulting in the formation of valuable products led to the rapid development of their manufacture and extension of their fields of application.

The authors of [6] described polyester resins containing methyl acrylate. Samples of panels made of glass-fiber plastics based on these resins underwent tests under conditions of accelerated aging in fadeometers and weatherometers. It was found that partially or completely replacing styrene with methyl acrylate improves the stability of a material's coloring and the resistance of its surface layer to fiber erosion, and helps preserve its luster.

A search of the literature and patents reveals there are virtually no data on the solidification of unsubstituted polyester resins with ionogenic comonomers. At the same time, the copolymerization of polyesters with such monomers allows us to obtain spatially cross-linked polymers with a charged network [7].

The aim of this work was to study the thermal destruction of copolymers of polypropylene glycol maleate with acrylic acid in an inert gas medium and in air.

EXPERIMENTAL

Polypropylene glycol maleate was obtained via polycondensation of maleic anhydride with polypropylene glycol according to the standard technique [8]; the reaction was controlled through acid number determination. Reagents of analytical grade were used.

The values of molecular weight of polypropylene glycol maleate determined from the acid number and via optical scattering [9] were very similar and are approximately equal to 2000.0.

Copolymers of polypropylene glycol maleate (p-PGM) with acrylic acid (AA) in molar ratios 9.1 : 90.9 and 87.0 : 13.0 were obtained through copolymerization in dioxane solution at the monomer mixture : solvent mass ratio of 1 : 1 with benzoyl peroxide as an initiator at 333 K.

The synthesized copolymers were washed with dioxane and dried to a constant weight in a vacuum oven at 313 K.

The composition of synthesized copolymers was determined from the quantities of unreacted monomers in the dioxane mother liquor solution by means of potentiometry [10] and gas chromatography on an Agilent 180 device.

Equilibrium degree of copolymer swelling α was determined gravimetrically as the mass of water per unit mass of dry gel, according to the formula

$$\alpha = \frac{m - m_0}{m_0} \times 100\%,$$

where m and m_0 are the masses of the swollen (in equilibrium) and dry gels, respectively (g).

The degree of unsaturation for the synthesized copolymers was determined using the bromide–bromate method [11]. The copolymers' IR spectra were recorded on an FSM 1201 IR-Fourier spectrometer.

The copolymers' thermal properties were studied on a Labsys Evolution differential scanning calorimeter (DTA/DSC) under dynamic conditions. Samples were heated in an Al_2O_3 crucible in the temperature range of 30–500°C at a rate of 10 K/min, in both a nitrogen atmosphere and in air.

RESULTS AND DISCUSSION

The presence of unsaturated double bonds in the polypropylene glycol maleate molecule allows us to use them as a matrix for producing spatially cross-linked copolymers, the mechanism of formation of which has been described in many works [12]. This is due to the rather high resistance of polyester resin to aggressive media and its good electrical and mechanical characteristics [13, 14].

In this work, copolymers of polypropylene glycol maleate with acrylic acid were synthesized for the first time, and their thermal stability in an inert medium and in air was estimated.

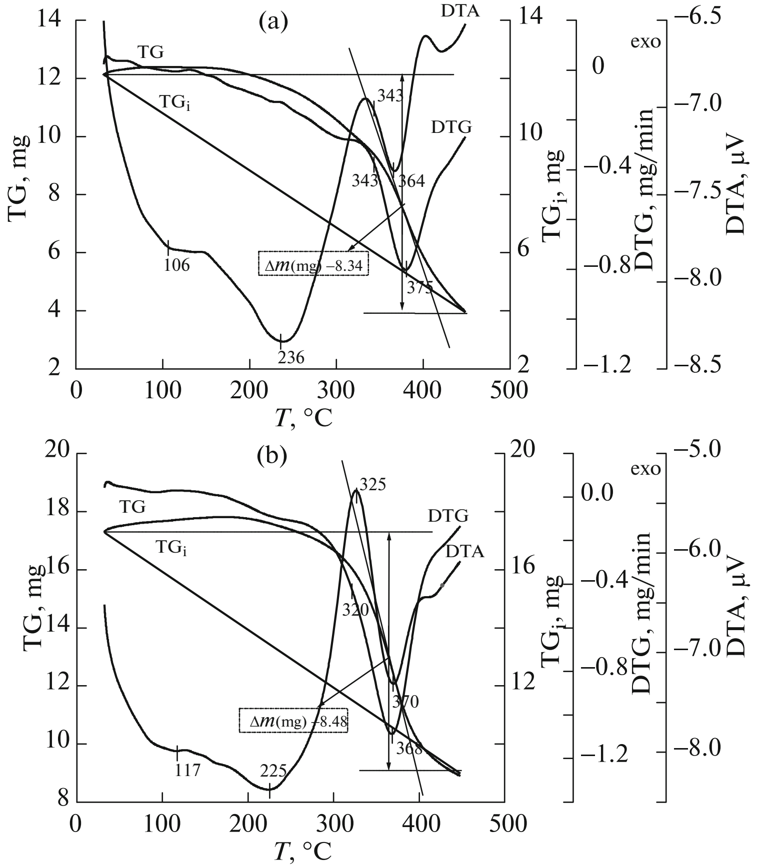

Fig. 1. Temperature dependences of the mass changes (TG curve), mass change rates (DTG curve), and thermal flux (DTA curves) for p-PGM:AA copolymers at initial $M_1 : M_2$ ratios, mol %, of (a) 10.1 : 89.9 and (b) 90.4 : 9.6 (in a nitrogen atmosphere).

The composition and properties of copolymers of polypropylene glycol maleate with acrylic acid obtained through radical copolymerization in solution are shown in Table 1.

Table 1. Composition and properties of copolymers of p-PGM with AA in dioxane solution ($T = 333$ K)

M_1	M_2	m_1	m_2	χ	α	μ
10.1	89.9	9.1	90.9	49.4	623.3	47.9
90.4	9.6	87.0	13.0	34.7	246.3	75.2

M_1 and M_2 are the compositions of the initial mixtures, mol %; m_1 and m_2 are the composition of the polymer, mol %; μ is the content of the maleate groups, %; and χ is the output, %.

As can be seen from Table 1, degree of swelling α falls along with the fraction of acrylic acid in the initial mixture, while the content of maleate groups grows, due probably to the lower number of transverse branches and the increase in the fraction of polypropylene glycol maleate.

It was therefore of interest to compare the energy and thermodynamic characteristics of the synthesized copolymers.

The parameters of thermal destruction were determined by means of dynamic thermogravimetry and processed using the Achar [15], Freeman–Carroll [16], and Sharp–Wentworth methods [17].

Figures 1, 2a, 2b show thermograms of the copolymers of polypropylene glycol maleate with acrylic acid at a constant heating rate of 10 K/min in the temperature range of 30–500°C in nitrogen and air.

Comparing the thermogravimetric curves of the copolymers of p-PGM with AA of compositions of 9.1 : 90.9 and 87.0 : 13.0 mol % (Figs. 1a, 1b), we can see that the first copolymer is characterized by an intense drop in sample mass in the temperature range of ~171–375°C, as is indicated by the shape of the TG curve (the reduction in sample mass on the curve is ~77.27%). This section of the TG curve corresponds to maxima of changes in the rate of mass reduction on the DTG curve at ~303 and ~375°C (Fig. 1a). In this temperature range, the DTA thermogram (Fig. 1a) displays a small exothermal effect at ~236°C and a broad intense peak at ~375°C due to decomposition. Such behavior is also characteristic of a p-PGM:AA composition of 87.0 : 13.0 mol %; as can be seen from the peak on the DTG curve, the maximum rate of sample decomposition is observed at ~370°C. Here,

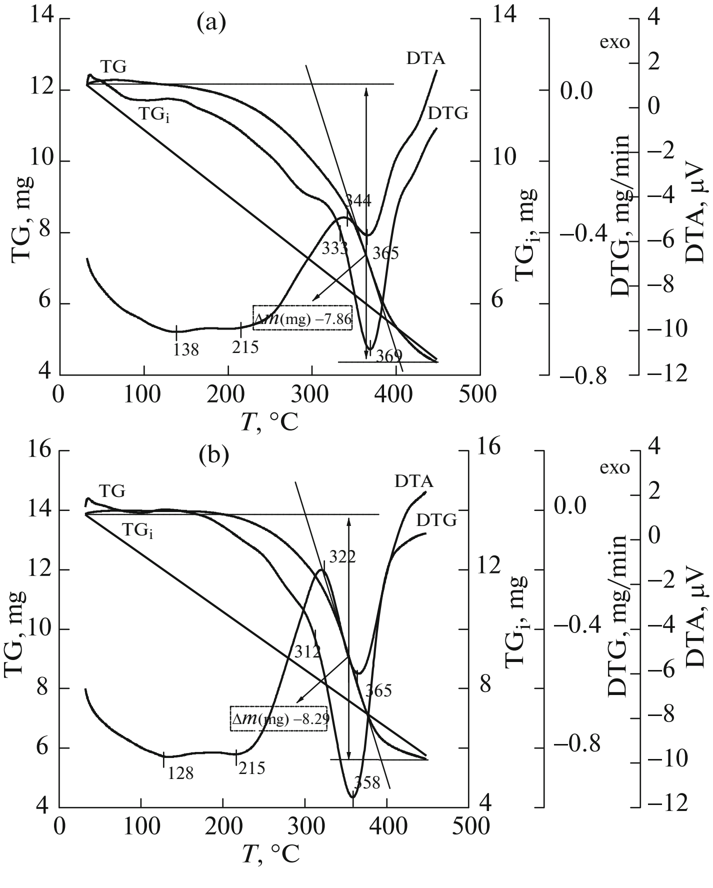

Fig. 2. Temperature dependences of the mass changes (TG curve), mass change rates (DTG curve), and thermal flux (DTA curves) for p-PGM:AA copolymers at initial $M_1 : M_2$ ratios, mol %, of (a) 10.1 : 89.9 and (b) 90.4 : 9.6 (in air).

Table 2. Kinetic and thermodynamic parameters of thermal destruction of copolymers p-PGM:AK

p-PGM:AA ratio	A		Sh–W		F–C		$-\Delta S^{\#}$, J/(mol K)	$\Delta G^{\#}$, kJ/mol
	E, kJ/mol	A, min^{-1}	E, kJ/mol	A, min^{-1}	E, kJ/mol	n		
in a nitrogen atmosphere								
10 : 90	22.09	3.81	27.77	8.13	25.85	0.29	174.15	136.89
90 : 10	40.68	20.73	53.53	86.29	47.31	0.53	87.94	105.91
in air								
10 : 90	23.26	4.44	29.04	9.65	26.62	0.32	168.90	134.76
90 : 10	46.87	41.23	55.03	113.08	48.95	0.64	80.31	102.54

A, Achar; Sh–W, Sharp–Wentworth; F–C, Freeman–Carroll; A, pre-exponential factor.

the total reduction in mass for the second copolymer upon heating was ~78.50% (Fig. 1b). The destruction of both samples was virtually complete at ~500°C. The DTA and DTG data agreed well with one another. The reduction in mass at low temperatures (~117°C) in p-PGM:AA copolymers was due to the removal of water, as is also confirmed by the DTA data (Figs. 1a, 1b).

To complete our work, thermogravimetric studies of copolymers of p-PGM with AA were performed in air (Figs. 2a, 2b). According to the TG curve, the samples' mass falls in the temperature range of ~161 to ~365°C. As can be seen on the DTG curve (Fig. 2a), the thermal destruction of p-PGM:AA copolymer with the composition 9.1 : 90.9 mol % occurred at ~344–365°C: here, the total reduction in sample mass

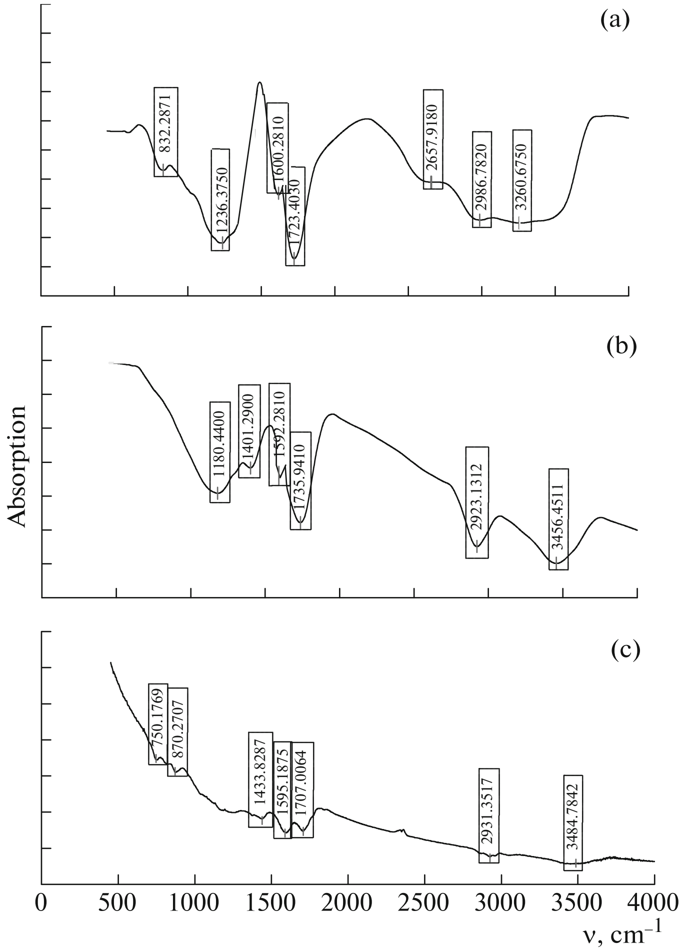

Fig. 3. IR spectra of p-PGM:AA copolymer (9.1 : 90.9 mol %) (a) before and after heating in (b) nitrogen and (c) air.

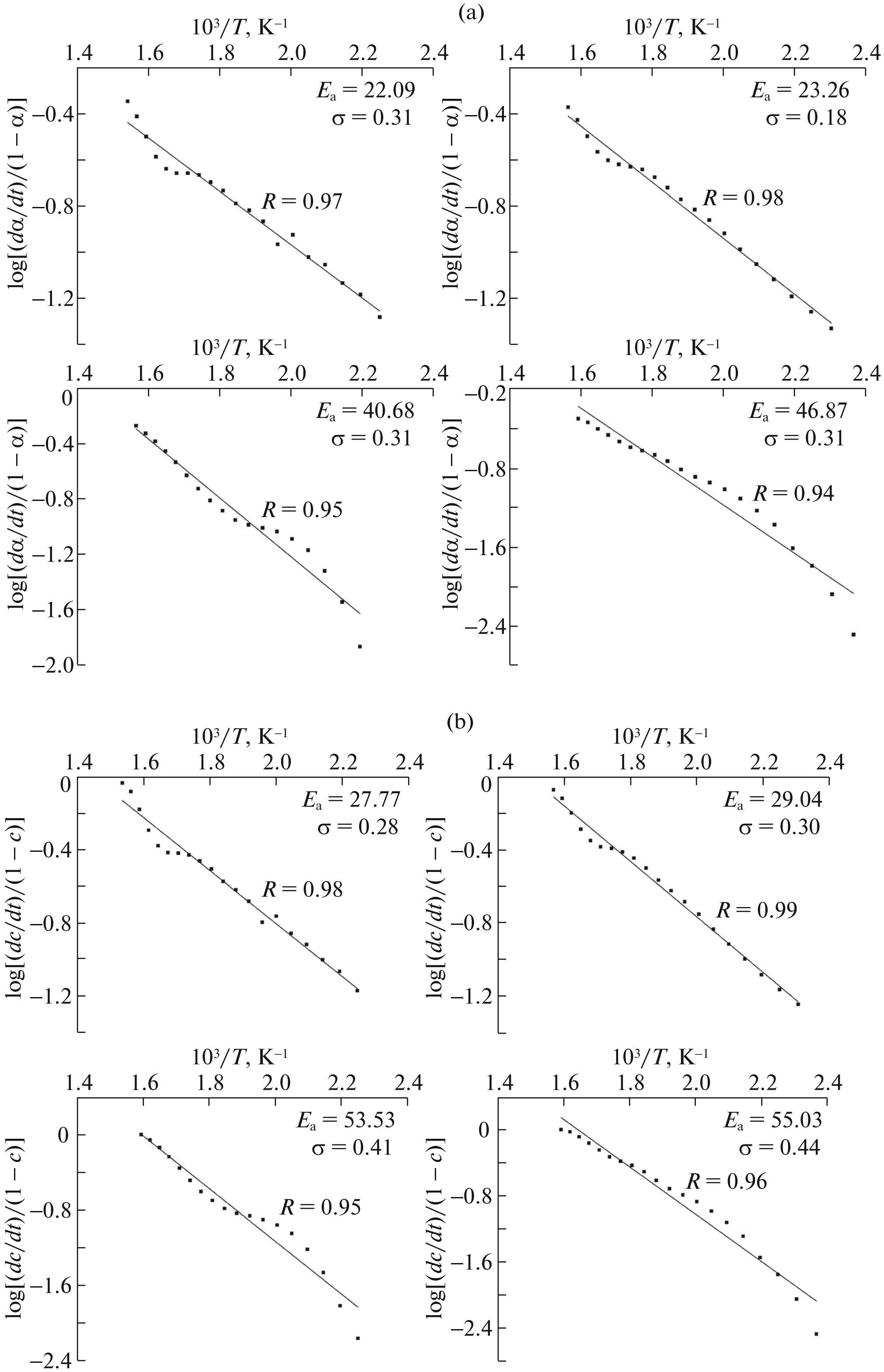

Fig. 4. Linearization of the thermogravimetry data for the p-PGM:AA copolymers studied using the (a) Achar; (b) Sharp–Wentworth, and (c) Freeman–Carroll methods (R is the correlation coefficient; σ is the relative error of the experimental dots [19]).

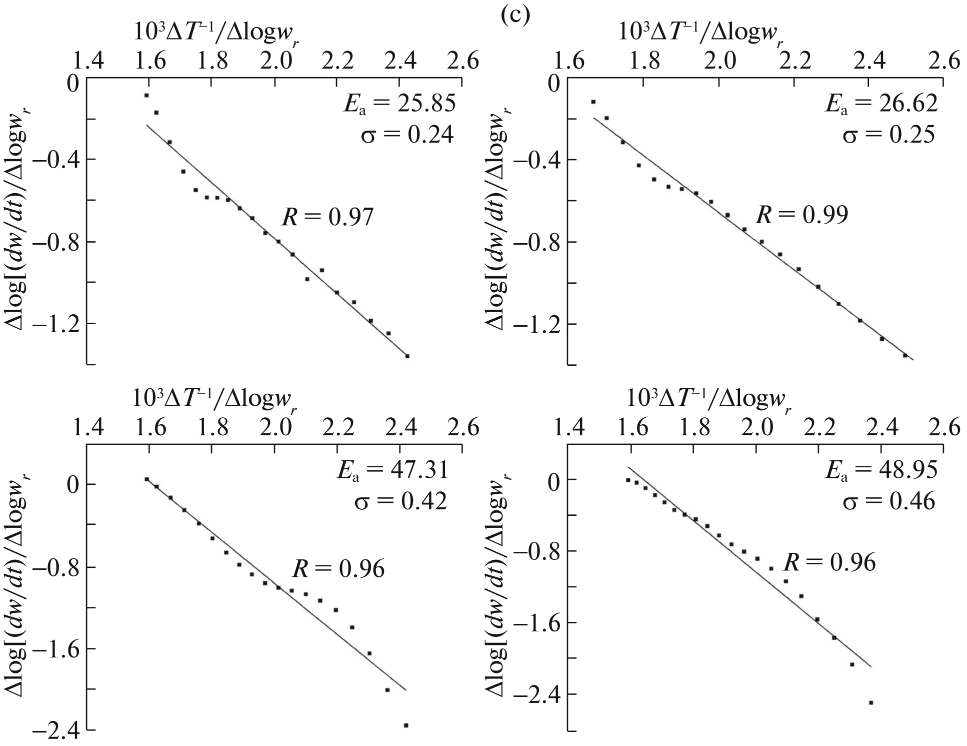

Fig. 4. (Contd.)

was ~72.80% of the initial sample mass. Thermogravimetric (TGA) studies of our p-PGM:AA copolymer with the composition 87.0 : 13.0 mol % were performed in parallel (Fig. 2b). The DTA and TGA data agreed well with one another: the onset of the destruction of the copolymer samples in air was observed at lower temperatures (~358°C) than in the inert medium (500°C), as can be seen both from the changes in the DTA signal (Fig. 2b) and from the reduction in mass.

A comparison of the obtained data for heating in nitrogen (Fig. 1a) and in air (Fig. 2a) shows that p-PGM:AA copolymers are thermally stable. Comparative analysis of the IR spectra of the initial p-PGM:AA copolymer with the composition 9.1 : 90.9 mol % and the sample heated to 500°C in nitrogen and air shows that as the temperature rose, the intensity of bands at 1236 cm^{-1} characterizing the C–O groups gradually fell (Figs. 3a, 3b), indicating the destruction of the ester bonds of polypropylene glycol maleate.

Figure 3 shows the IR spectra of our p-PGM:AA copolymer with the composition 9.1 : 90.9 mol % before and after heating to 500°C in nitrogen and air.

For convenience, the curves are shifted along the vertical axis. The sample spectrum before thermal treatment (Fig. 3a, curve *1*) corresponds to the literature data [18]. On our spectrum, we can see absorption bands around 2986 cm^{-1} corresponding to vibrations of the C–H-bonds of methyl groups and intense absorption bands around 3260 cm^{-1} caused by stretching vibrations of the O–H-bonds of interacting hydroxyl groups. The absorption around 1600 cm^{-1} was caused by the stretching vibrations of C=C bonds; we can also see intense absorption bands around 1236 cm^{-1} corresponding to C–O vibrations and bands at 1723 cm^{-1} corresponding to carboxyl group vibrations.

The effective values of the activation energy, preexponential factor, and destruction reaction rate were determined graphically (Fig. 4).

Thermodynamic characteristics (changes in Gibbs energy $\Delta G^{\#}$ and activation entropy $\Delta S^{\#}$) were calculated using the obtained activation energy values (Table 2) [20, 21].

The thermodynamic values of destruction showed that copolymers containing smaller quantities of polypropylene glycol maleate were destroyed as readily in the inert medium as in air.

CONCLUSIONS

We synthesized copolymers of polypropylene glycol maleate with acrylic acid for the first time and determined their kinetic characteristics and thermodynamic parameters. Activation energy values calculated using the methods of Freeman–Carroll, Sharp–Wentworth, and Achar confirm the dependence of the destruction process on the ratio of components in the synthesized polymer. It was been shown that the obtained values of activation energy and thermodynamic characteristics allow us to predict copolymer compositions.

REFERENCES

1. H. V. Boenig, *Unsaturated Polyesters: Structure and Properties* (Elsevier, Amsterdam, 1964; Khimiya, Moscow, 1968).
2. L. N. Sedov and Z. V. Mikhailova, *Unsaturated Polyesters* (Khimiya, Moscow, 1977) [in Russian].
3. E. L. Kropa and T. F. Bradley, Ing. Eng. Chem. **31**, 1512 (1939).
4. G. F. D'Alelio, US Patent No. 2288315 (1942).
5. E. L. Kropa, US Patent No. 2409633 (1946).
6. S. N. Ushakov and S. P. Mitsengendler, Zh. Prikl. Khim. **20**, 1261 (1947).
7. M. Zh. Burkeev, A. K. Magzumova, E. M. Tazhbaev, G. K. Burkeeva, A. K. Kovaleva, T. O. Khamitova, and M. M. Mataev, Russ. J. Appl. Chem. **86**, 63 (2013).
8. A. M. Toroptseva, K. V. Belogorodskaya, and V. M. Bondarenko, *Laboratory Manual on Chemistry and Engineering of Polymers,* Ed. by A. F. Nikolaev (Khimiya, Moscow, 1972) [in Russian].
9. M. Zh. Burkeev, A. J. Sarsenbekova, E. M. Tazhbaev, et al., Bull. Univ. Karaganda, Ser. Chem., No. 2, 15 (2014).
10. D. Harvey, *Modern Analytical Chemistry* (McGraw-Hill, Boston, 2000).
11. E. V. Kuznetsov, S. M. Divgun, L. A. Budarina, et al., *Workshop on the Chemistry and Physics of Polymers* (Khimiya, Moscow, 1977) [in Russian].
12. M. Zh. Burkeev and A. J. Sarsenbekova, et al., in *Proceedings of the 27th International Symposium on Polymer Analysis and Characterization (ISPAC Conference), Les Diablerets, Switzerland, June 16–18, 2014* (2014), p. 122.
13. T. Hanemann and D. V. Szaby, Materials **3**, 3468 (2010).
14. P. K. C. Camargo, K. G. Satyanarayana, and F. Wypych, Mater. Res. **12**, 1 (2009).
15. B. N. Achar, G. W. Brindley, and J. H. Sharp, in *Proceedings of the International Clay Conference, Jerusalem, Israel, June 20–24, 1966* (Israel Program for Scientific Translations, Jerusalem, 1966–1967), p. 67.
16. E. S. Freeman and B. Carroll, J. Phys. Chem. **62**, 394 (1958).
17. J. H. Sharp and S. A. Wentworth, Anal. Chem. **41**, 2060 (1969).
18. L. A. Kazitsyna and N. B. Kupletskaya, *Application of UV-, IR-, NMR-, and Mass-spectroscopy in Organic Chemistry* (Vyssh. Shkola, Moscow, 1971) [in Russian].
19. V. I. Romanovskii, *Basic Problems of Error Theory* (Gostekhizdat, Moscow, 1947) [in Russian].
20. R. W. Hoffmann, *Aufklärung von Reaktionsmechanismen* (Thieme, Stuttgart, 1976; Khimiya, Moscow, 1976).
21. B. V. Romanovskii, *Principles of Chemical Kinetics* (Ekzamen, Moscow, 2006) [in Russian].

Translated by D. Marinin