

## 아크릴아마이드와 아크릴산을 이용한 Polypropylene Glycol Maleate Phthalate 기반 공중합체 합성

M. Zh. Burkeyev, A. K. Kovaleva<sup>†</sup>, G. K. Burkeyeva, Ye. M. Tazhbayev, and J. Plocek\*

Buketov Karaganda State University

\*Institute of Inorganic Chemistry of the Czech Academy of Sciences

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## Polypropylene Glycol Maleate Phthalate Terpolymerization with Acrylamide and Acrylic Acid

M. Zh. Burkeyev, A. K. Kovaleva<sup>†</sup>, G. K. Burkeyeva, Ye. M. Tazhbayev, and J. Plocek\*

Buketov Karaganda State University, Universitetskaya st., 28, 100026, Kazakhstan

\*Institute of Inorganic Chemistry of the Czech Academy of Sciences, 25068 Rez, Husinec-Rez 1001, Czech Republic

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**Abstract:** The possibility of synthesizing new multifunctional terpolymers based on polypropylene glycol maleate phthalate with acrylamide and acrylic acid was shown. The basic laws of the process of radical terpolymerization in a dioxane medium were studied at various molar ratios of the reactants. The block length, transition probabilities, and Harwood block parameter of the terpolymers synthesized, which reflect information on the location of macroradicals in the chain, were calculated. The radical terpolymerization constants, indicating the possibility of copolymers to form structures with a free distribution of units, were calculated with the help of the Mayo-Lewis equation. The method of scanning electron microscopy was used to study the surface morphology of polymers and to evaluate the surface pore sizes. There were carried out investigations on the effect of pH of the medium and organic solvents on the degree of swelling of the samples studied. Using thermogravimetric analysis, the thermal decomposition of the synthesized terpolymer based on polypropylene glycol maleate phthalate with acrylamide and acrylic acid was studied. The features of mass loss and thermal transformations upon heating were revealed. It was found that the process of thermal degradation intensified in the range of 339-428 °C with the maximum weight loss of the sample ~78.64%.

**Keywords:** terpolymerization, unsaturated polyester, polypropylene glycol maleate phthalate, acrylic acid, acrylamide.

### Introduction

Chemical modification of already known polymers is of particular importance at the present stage of developing new polymeric materials, which allows improving properties and significantly expanding the scope of the latter. Unsaturated polyesters are of particular interest among compounds, which are “convenient” for modification.

Unsaturated polyesters are capable of copolymerizing with many vinyl monomers due to the presence of a reactive double bond; in particular, there is information in the literature on copolymerization with vinyl acetate, styrene, and methyl meth-

acrylate.<sup>1</sup> The field of practical application of such polymers is structural materials,<sup>2</sup> including medical supplies.<sup>3</sup>

High hydrophobicity is a feature of unsaturated polyesters. Thereby attempts to change these properties by modification with hydrophilic monomers to obtain block copolymers have been made.<sup>4</sup>

There is practically no data in the literature on the copolymerization of unsaturated polyesters with hydrophilic monomers before our studies,<sup>5,6</sup> while this opens up wide prospects for the synthesis of “intelligent” polymers. A traditional method for producing these polymers is the radical homopolymerization of unsaturated carboxylic acids in the presence of crosslinking agents.<sup>7</sup> The copolymerization of unsaturated polyesters with hydrophilic monomers allows a significant change in the hydrophilic-hydrophobic balance of macromol-

<sup>†</sup>To whom correspondence should be addressed.  
gulshahar90@mail.ru, ORCID<sup>®</sup>0000-0001-9758-648X  
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ecules by changing the quantitative ratio of the main chain and side branches.<sup>8,9</sup> This approach allowed us to develop methods for the preparation of copolymers of unsaturated polyesters with vinyl monomers of various compositions based on polyglycol maleates, which showed satisfactory moisture-absorbing and nanocatalytic properties.<sup>5,6,10</sup>

It was interesting to synthesize and study the properties of terpolymers based on polypropylene glycol maleate phthalate with acrylamide and acrylic acid in the present work. It was interesting to establish the basic laws and features of the radical ter-(co)polymerization of the above-mentioned monomers, calculate and evaluate their activity constants, as well as the probabilities of formation and microstructure parameters of each of the monomer pairs. Thermal destruction of the terpolymer synthesized was studied in detail using TGA analysis in order to determine the thermostable properties.

## Experimental

The following reagents from Sigma-Aldrich were used in the work, namely propylene glycol, maleic and phthalic anhydrides, acrylamide, acrylic acid, benzoyl peroxide, zinc chloride. All reagents were used without further purification.

Polypropylene glycol maleate phthalate (p-PGMP) was obtained by polycondensation of propylene glycol with maleic and phthalic anhydride at a temperature of 423-433 K in a four-necked flask, which was equipped with a reflux condenser, overhead stirrer, thermometer, a Dean-Stark trap and a nitrogen supply tube. Polycondensation was carried out according to the standard method<sup>11</sup> with constant stirring in the presence of a zinc chloride catalyst in a stream of nitrogen in order to avoid gelation processes.

The molecular weight of p-PGMP synthesized was determined by light scattering<sup>12</sup> on a NACH nephelometer 2100 AN and determining the number of end groups by acid (AN) and hydroxyl (HN) numbers. When determining the molecular weight by the nephelometric method, dedusted chloroform was used as a solvent (the error is  $\pm 2\%$ ). The obtained values of the molecular weight of p-PGMP by both methods have good convergence and averaged 2530 amu.

The radical terpolymerization of p-PGMP with acrylamide (AAm) and acrylic acid (AA) was carried out at various initial molar ratios of comonomers. The temperature of the process was 333 K. Dioxane was used as a solvent (weight ratio 1:1), and benzoyl peroxide was the initiator. The resulting copolymers were purified by washing twice with dioxane and dried

under vacuum until a constant weight was established.

The compositions of the terpolymers obtained were determined by the residual amount of monomers by chromatography-mass spectroscopy.<sup>13</sup>

The parameters of the terpolymers microstructures, the average length  $L$  of the block, and the Harwood parameters  $R_x$  were calculated using well-known formulas.<sup>14</sup>

Equilibrium swelling was achieved within 1-2 days. The swelling degree  $\alpha(\%)$  of the terpolymers was measured gravimetrically. The calculation of  $\alpha(\%)$  was carried out as the ratio of the absolute mass of the swollen hydrogel at the point of equilibrium swelling to its initial mass in the dry state:

$$\alpha(\%) = \frac{m_1 - m_0}{m_0} \times 100 \quad (1)$$

where  $m_1$  and  $m_0$  are the masses of the swollen and dry polymer, respectively.

The IR spectra of the samples were recorded in KBr pellets with the help of an FSM 1201 spectrometer.

Electron microscopy was carried out using a TESCAN MIRA 3 scanning electron microscope at an accelerating voltage of 20 kV. The pore sizes of the polymers were determined by processing microphotographs in the ImageJ program.

Thermal degradation was analyzed according to the results of a study on a LabSYS Evo synchronous TGA/DTA/DSC analyzer in the temperature range of 30-1030 °C in an alumina crucible at a heating rate of 10 °C/min in air with a flow rate of 30 mL/min. The analysis was carried out by decomposition of a sample of a copolymer weighing 20 mg.

The pH of the medium was set with buffer solutions of the required value. Control of the medium was carried out using an I-160MI ionomer. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and ethanol in various ratios with water were used as organic solvents.

## Results and Discussion

The formation of spatially cross-linked polymers of insoluble nature occurs during the radical copolymerization of unsaturated polyesters with vinyl monomers.<sup>4,11</sup> The mechanisms of such reactions with hydrophobic monomers have been adequately studied.

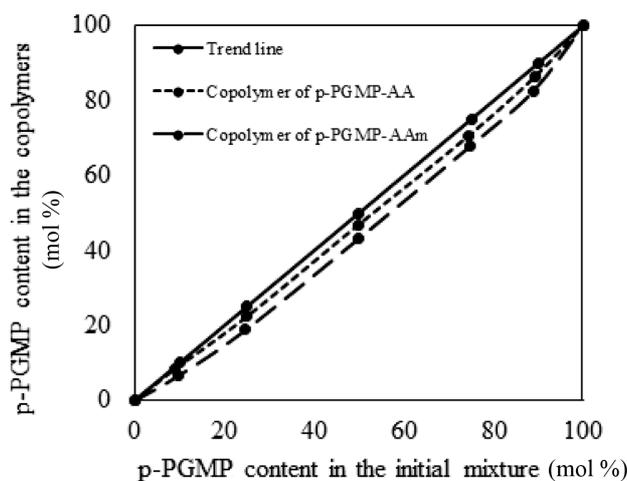
The equations for the composition of the copolymers deduced by Alfrey and Goldfinger allow for quantitative prediction of the behavior of the three-component system of monomers  $M_1$ ,  $M_2$ ,  $M_3$  during copolymerization. Six constants

$r_{12}$  and  $r_{21}$ ,  $r_{13}$  and  $r_{31}$ ,  $r_{23}$  and  $r_{32}$  are needed for the binary systems  $M_1-M_2$  ( $M_2-M_1$ ),  $M_1-M_3$  ( $M_3-M_1$ ),  $M_2-M_3$  ( $M_3-M_2$ ) involved in the triple copolymerization process in order to calculate the theoretical composition of the p-PGMP-AAm-AA ternary system studied. The values of the constants of two pairs of monomers during the reaction under experimental conditions are absent in the literature. To this end, two binary systems p-PGMP-AAm ( $M_1-M_2$ ) and p-PGMP-AA ( $M_1-M_3$ ) were copolymerized under conditions similar to radical terpolymerization. The AAm-AA ( $M_2-M_3$ ) system was studied; therefore, the values of  $r_{23}$  and  $r_{32}$  were taken from the literature.<sup>15</sup>

The radical copolymerization of p-PGMP-AAm and p-PGMP-AA was carried out at various initial molar ratios of comonomers in a solution of dioxane (1:1 by weight). Figure 1 shows the dependence of the composition of the copolymers on the composition of the initial monomer mixture for the binary systems p-PGMP-AAm, p-PGMP-AA.

As can be seen from the Figure 1 the dependence curve lies below the azeotrope line in both p-PGMP-AAm and p-PGMP-AA systems under consideration. This indicates a random distribution of monomer units in the structure of the copolymers. It follows from the graphic data that the copolymers are enriched in vinyl monomer units, namely AA and AAm. A macroradical with p-PGMP end-link is more actively attached to another monomer than to "its own" since p-PGMP is not capable of homopolymerization reactions.

The relative activities of the comonomers of the p-PGMP-AAm, p-PGMP-AA binary systems were calculated based on



**Figure 1.** The dependence of the composition of p-PGMP in the copolymer on the composition of the initial polymer-monomer mixture.

the composition of the copolymers and the initial monomer mixture according to the Mayo-Lewis integral equation.<sup>16</sup> The values of the copolymerization constants for the AA-AAm binary system are given in the literature.<sup>15</sup>

The relative activity  $r_1$  (p-PGMP) is less than one ( $r_1 = 0.7894$  and  $0.9206$ , respectively) in the systems studied (p-PGMP-AAm and p-PGMP-AA). Thus, a macroradical with an end unit of unsaturated polyester is more active towards a "foreign" monomer or radical. On the contrary, a macroradical with an end link of a vinyl comonomer (AA or AAm) reacts much more easily with "its" monomer or radical ( $r_2 = 1.2951$  and  $1.1422$ , respectively). The product of the copolymerization constants ( $r_1 \cdot r_2$ ) is close to one ( $r_1 \cdot r_2 = 1.0224$  and  $1.0513$ , respectively). This fact indicates the possibility of copolymers to form structures with a free distribution of units.<sup>17</sup>

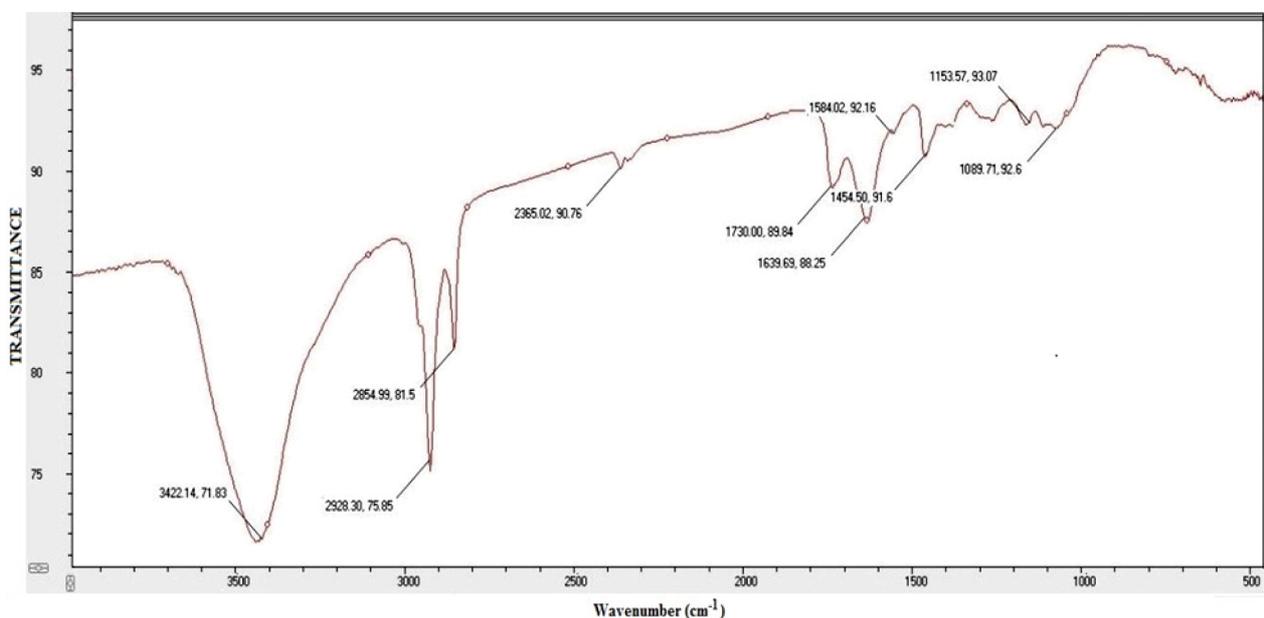
The obtained results of the values of the copolymerization constants for pairs of monomers made it possible to calculate the theoretical composition of p-PGMP-AAm-AA terpolymers. Table 1 presents the calculated and experimental data on the dependence of the composition of terpolymer on the composition of the initial monomer mixture. The experimental composition of terpolymers was determined with the help of the chromato-mass spectroscopic investigation of the mother liquor by determining the residual amounts of unreacted initial mixture.

The data in Table 1 show the correspondence of theoretically calculated and experimental compositions of polymers. However, the experimentally found composition of terpolymers is somewhat different from that predicted by the calculation. Thus, the content of p-PGMP units in the terpolymers synthesized was slightly lower than the calculated one. The data in Table 1 indicate an obvious dependence of the swelling degree on the composition of the terpolymers synthesized. An increase in the acrylic acid content in the composition of terpolymers with the same content of p-PGMP in the composition of the initial polymer-monomer mixture (~15 mol%) makes it possible to obtain a sample with a less rigid structure that can sorb more water, and also contributes to an increase in the yield of polymers.

The content of the starting compounds was varied to obtain the required characteristics of polymer gels, namely proper structure, physico-chemical properties, the highest sorption capacity, swelling velocity, etc. For this purpose, terpolymerization with the initial ratio of the polymer-monomer mixture of p-PGMP-AAm-AA 4:23:73 and 4:73:23 mol%, respectively, was additionally carried out (Table 1).

**Table 1.** Terpolymerization of p-PGMP ( $M_1$ ) with AAm ( $M_2$ ) and AA ( $M_3$ ) (Dioxane, 333 K,  $[PB] = 8 \text{ mmol} \times \text{L}^{-1}$ )

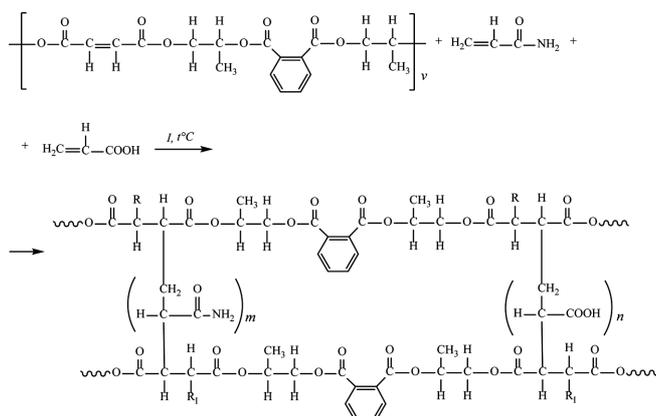
Initial ratio of monomers (mol%)			Experimental composition of the copolymer (mol%)			Calculated composition of the copolymer (mol%)			Yield (%)	Swelling (%)
$M_1$	$M_2$	$M_3$	$m_1$	$m_2$	$m_3$	$m_1$	$m_2$	$m_3$		
4.02	23.73	72.25	3.75	27.24	69.01	4.61	15.98	79.41	93.2	3546.59
3.99	72.56	23.45	3.63	76.28	20.09	5.45	56.56	37.99	92.1	2517.81
14.98	14.98	70.04	8.78	22.98	68.24	16.94	9.84	73.22	91.7	1241.67
14.98	34.97	50.05	9.76	42.39	47.85	17.84	23.59	58.56	90.8	632.83
14.99	49.96	35.05	10.19	57.26	32.55	18.76	35.31	45.93	89.2	399.66
14.97	70.01	15.02	10.41	76.73	12.86	20.45	55.52	24.03	88.5	185.55

**Figure 2.** IR spectrum of p-PGMP–AAm–AA terpolymer of 3.15: 27.84: 69.01 mol% composition.

According to the data in Table 1, the p-PGMP–AAm–AA terpolymer of the 3.15: 27.84: 69.01 mol% composition has the highest swelling degree in comparison with systems of different molar composition considered earlier. So, it should be noted that a decrease in the content of unsaturated polyester in the composition of terpolymer (from ~10 to 4 mol%) causes an increase in the swelling degree in several times. It has been experimentally established that the optimal concentration of p-PGMP for the preparation of p-PGMP–AAm–AA terpolymers with the necessary physico-chemical and operational characteristics is 4 mol%.

An IR spectral analysis of the structure of the p-PGMP–AAm–AA terpolymer (Figure 2) indicates the presence of the

ester group of PGMP ( $1730 \text{ cm}^{-1}$  C=O vibration). The stretching vibrations of the C–O–C groups of the ester were observed in the regions of 1090 and  $1154 \text{ cm}^{-1}$ . The IR spectrum also contains vibrations that are characteristic for the double bond of the maleate group in the region of  $1570\text{--}1590 \text{ cm}^{-1}$ . Their intensity in accordance with vibrations of the original unsaturated polyester in this area is much lower. This fact is due to the cleavage of the double bond upon copolymerization with a vinyl monomer with the formation of a spatially crosslinked structure. The presence of amide groups (AAm) was detected at  $3422 \text{ cm}^{-1}$  for N–H. C–H stretching vibrations for the  $\text{CH}_3$ – and  $\text{CH}_2$ – groups were determined at  $2955 \text{ cm}^{-1}$ , respectively.



where R is a fragment of the initiator;  
m, n is degree of polymerization

**Figure 3.** Scheme of the formation of p-PGMP with AA and AAm terpolymer.

An analysis of the IR spectra of the p-PGMP–AAm–AA molecular chain showed that both  $-\text{COOH}$  and  $-\text{NH}_2$  groups were present in its structure. This fact confirms the presence of the units of both vinyl monomers in the structure of the terpolymer, which play the role of transverse bridges in the formation of a crosslinked terpolymer.

Thus, the formation mechanism of the terpolymers studied by us can be represented in Figure 3:

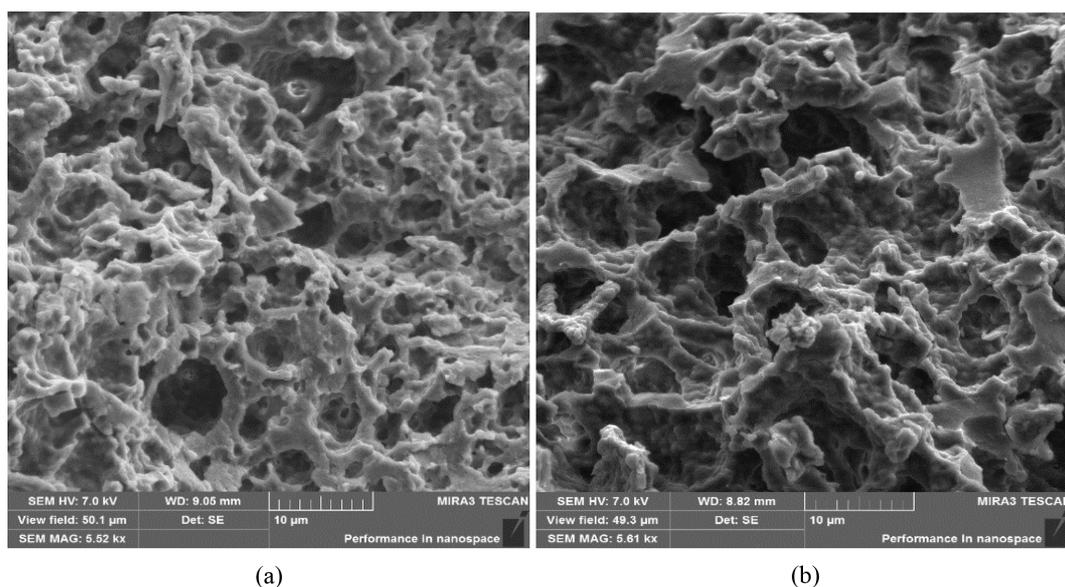
Moreover, as we have shown earlier,<sup>5,6</sup> the length and num-

ber of cross-linking units of AAm and AA depend on the concentration of vinyl monomers.

The surface morphology of the terpolymer was determined using scanning electron microscopy (Figure 4). ImageJ software was used to determine the polymer pore size. It was found from the images obtained that the surface of the test sample had a loose and heterogeneous structure, consisting of globules and pores of various shapes and sizes, with agglomerates of indefinite shape from 12 to 78  $\mu\text{m}$ . The average pore size calculated by ImageJ was 44  $\mu\text{m}$ . The presence of pores in the terpolymer confirmed by SEM results determines the ability of the samples to adsorb liquids.

Further there were determined such parameters of the chemical structure of the ternary systems synthesized as the nature of the alternation and distribution of units, block length, transition probabilities ( $P$ ) and Harwood block parameter  $R_x$  for ternary systems (Table 2). The nature of the alternation and distribution of the units was obtained based on an analysis of the copolymerization constants of the binary systems of the starting reagents, namely p-PGMP–AAm, p-PGMP–AA and AA–AAm.

Processing of the data calculated indicates a very high probability of the formation of combinations  $M_1-M_2$ ,  $M_2-M_3$ ,  $M_1-M_3$  and  $M_3-M_2$  in the structure of terpolymers, which is due to the activity of radicals involved in terpolymerization. As the data in Table 2 shows, the structure of cross-linked terpolymers



**Figure 4.** Surface morphology of p-PGMP–AAm–AA terpolymer of the 3.15:27.84:69.01 mol% composition: (a) and (b) are SEM images at various scales.

**Table 2. Microstructure of p-PGMP ( $M_1$ ), AAm ( $M_2$ ) and AA ( $M_3$ ) Terpolymer**

Initial ratio of monomers (mol%)			Values of transition probabilities of terpolymers					
$M_1$	$M_2$	$M_3$	$P_{M_1-M_2}$	$P_{M_2-M_3}$	$P_{M_3-M_1}$	$P_{M_1-M_3}$	$P_{M_3-M_2}$	$P_{M_2-M_1}$
14.98	14.98	70.04	0.1426	0.6511	0.1222	0.7164	0.2252	0.1457
14.98	34.97	50.05	0.3376	0.4286	0.1097	0.5193	0.4717	0.1342
14.99	49.96	35.05	0.4876	0.2834	0.1019	0.3676	0.6259	0.1268
14.97	70.01	15.02	0.6934	0.1130	0.0929	0.1599	0.8006	0.1179
4.02	23.73	72.25	0.9387	0.4008	0.0368	0.6381	0.5799	0.0389
3.99	72.56	23.45	0.9848	0.5498	0.0335	0.7881	0.7839	0.0361
Initial ratio of monomers (mol%)			Terpolymer block length				Harwood block parameter $R_x$	
$M_1$	$M_2$	$M_3$	$L_{M_1}$	$L_{M_2}$	$L_{M_3}$			
14.98	14.98	70.04	1.1642	1.2552	2.8788	67.56		
14.98	34.97	50.05	1.1669	1.7768	1.7195	60.29		
14.99	49.96	35.05	1.1693	2.4377	1.3741	57.59		
14.97	70.01	15.02	1.1719	4.3306	1.1192	40.75		
4.02	23.73	72.25	1.0245	5.274	1.0521	35.31		
3.97	72.56	23.47	1.0281	5.347	1.0223	25.71		

are formed due to covalently linked macromolecules. It should be noted that an increase in the content of the second monomer in the initial mixture leads to an increase in the probability of the formation of this monomer with terminal units of the active macroradicals  $M_1$  and  $M_3$ . An increase in  $M_3$  of the monomer in the initial mixture leads to an increase in the probability of addition of the  $M_1$  radical compared to addition to  $M_2$ . As a result of this, the formation of a combination of  $M_1-M_3$  units is more likely, unlike the  $M_2-M_1$  combination.

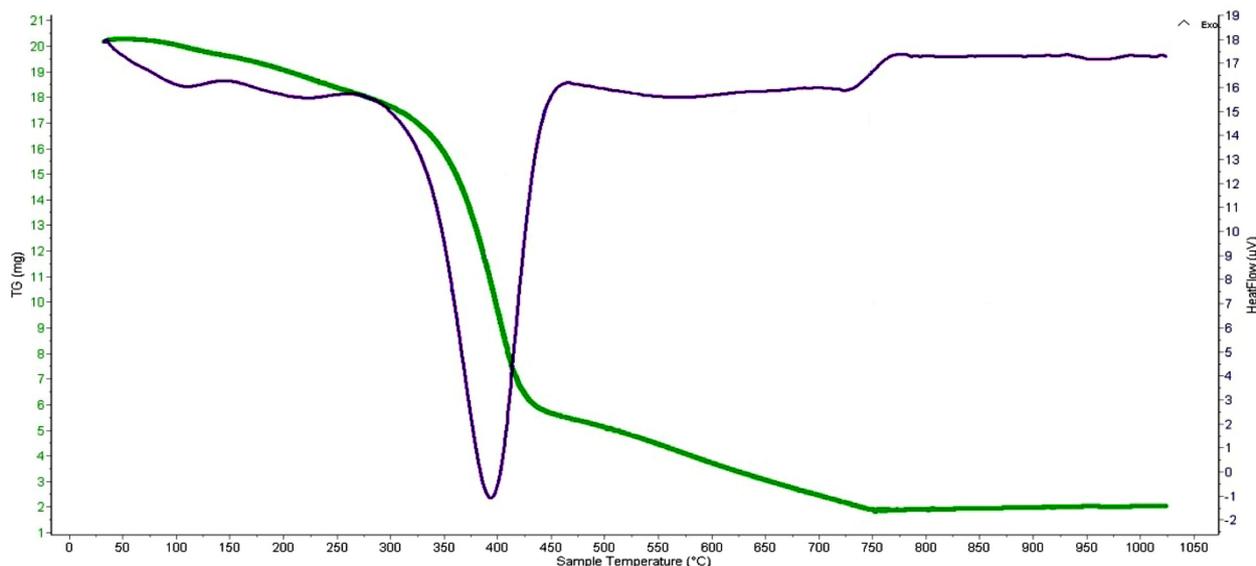
The chemical structure of the polymer is a fundamental factor that determines its important practical characteristics in the processing, operation and disposal of materials and products based on it.<sup>14</sup> Thus, the chemical structure of the polymer determines its resistance to heat, the rate of thermal decomposition, and the nature of the products formed.<sup>18,19</sup> In this regard, with the aim of determining the thermostable properties of the synthesized sample, it seemed interesting to study its thermal degradation.

Figure 5 shows the data of thermogravimetric analysis (TGA) of the p-PGMP-AAm-AA terpolymer of the 3.15:27.84:69.01 mol% composition.

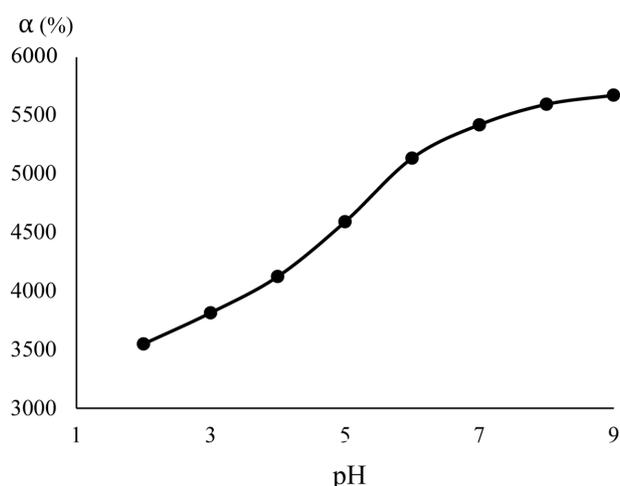
So, the process of destruction of the copolymer on the TG curve can be divided into four sections at a heating rate of 10 °C/min. On the initial section, having autocatalytic mode, insignificant sorption and subsequent desorption of water and

the release of volatile substances were observed in the range of 33-339 °C. Apparently, the chain breaks at this stage. However, for noticeable depolymerization, the lifetime of the resulting radicals is too short. As a result of this, chain breaking is not accompanied by a significant change in mass (~16.67%) of the test sample. The presence of a functional group of a carboxylic acid in the molecule leads in part to addition reactions with both internal and intermolecular formation of anhydride. Formed crosslinking of the polyene compound absorbs visible light well, as a result of which the polymer begins to turn yellow. In the second section, intensification of the process of thermal destruction can be noted in the range of 339-428 °C. This stage is characterized by a significant loss in sample mass (~78.64%), as well as a greater share of the formation of unsaturated bonds in the chain, which is accompanied by a change in the color of the sample to a saturated yellow color. The third stage in the range of 428-757 °C is characterized by a decrease in the intensity of the destruction process and the onset of carbonization. Stabilization of the residual mass of the sample was observed in the final fourth section. Thus, the total weight loss over the entire investigated temperature range from 33 to 1030 °C is 95.78%. High mass loss is also due to the occurrence of thermal degradation in air with the concomitant oxidation of the sample by atmospheric oxygen.

Further, the influence of the pH of the medium and the con-



**Figure 5.** TG and DTG curves of p-PGMP–AAm–AA terpolymer of 3.15: 27.84: 69.01 mol% composition at a heating rate of 10°C/min in air.



**Figure 6.** Effect of pH on the swelling of the p-PGMP–AAm–AA terpolymer of 3.15:27.84:69.01 mol% composition.

centration of organic solvents of various polarity on the swelling degree of the test sample of the p-PGMP–AAm–AA terpolymer of the 3.15:27.84:69.01 mol% composition was studied.

The influence of medium acidity was observed in the pH range from 2 to 9 (Figure 6).

Figure 6 shows that an increase in the amplitude of the jump in the swelling degree for the test sample is observed in the range of pH values from 4 to 7. In an acidic medium, there is a decrease in the number of ionized carboxyl groups and an

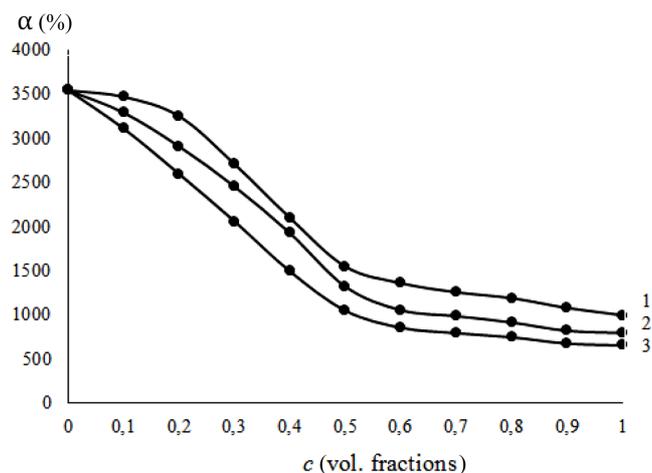
increase in the contribution of additional hydrogen bonds that form between these groups during compression.<sup>20</sup> A shift in pH towards the alkaline medium leads to a weakening of the dominance of hydrogen bonds. Due to this reason the attraction processes are caused by hydrophobic influences, as a result of which the gel swells.

Thus, a study of the influence of pH showed that the synthesized terpolymer based on p-PGMP–AAm–AA exhibited the properties of typical polyelectrolytes.

When studying the effect of an organic solvent on the behavior of the polymer gel synthesized by us, DMSO, DMF, and ethanol were chosen as the organic component. The solvent content in the mixture with water ranged from 0.1 to 1.0 volume fractions. The studies were carried out at  $T = 293$  K. The choice of these solvents is based on the difference in their polarity (Figure 7).

Terpolymer in the different aqueous-organic mixtures behaves the same way according to experimental data. The polymer swells at the initial stage, and then the sample is compressed. The maximum value of the swelling degree is achieved at 0.4–0.5 vol% of organic solvents. When the concentration of the organic solvent overcomes some critical value, the polymer network collapses. In this case, when low-polar solvents are added, collapse occurs as a first-order phase transition.

As a result of the studies it was shown that insoluble polymers with a free distribution of units were obtained by radical



**Figure 7.** Effect of an aqueous-organic mixture of solvents on the swelling degree of p-PGMP-AAm-AA terpolymers (3.15: 27.84: 69.01 mol%): 1 - water-DMSO; 2 - water-DMF; 3 - water-ethanol.

terpolymerization of p-PGMP with AAm and AA. The molecular chain of the terpolymers obtained contains ionic -COOH and -NH<sub>2</sub> groups. Analysis of SEM images of the polymer surface morphology confirmed the presence of pores. The TDA of the copolymer synthesized of the p-PGMP-AAm-AA (3.15: 27.84: 69.01 mol%) composition showed its thermal stability in the temperature range from 33 to 339 °C. Studies of the effect of an external solution pH or the presence of an organic solvent in it showed a high sensitivity of the gel to environmental changes. Thus, the field of application of terpolymers synthesized can be both the production of moisture absorbents and flocculants, and track membranes. This finding allows us to consider the obtained polymer gels as polyelectrolyte polyfunctional polymers.

Thus, the data obtained on the study of the radical terpolymerization of p-PGMP with AAm, AA, a comparative assessment of their reactivity allows us to develop methods for the directed synthesis of new polymer products with desired characteristics (composition, hydrophilic-hydrophobic balance), which can vary widely.

## Conclusions

Polypropylene glycol maleate phthalate, entering into a radical terpolymerization reaction with acrylamide and acrylic acid, forms a network structure terpolymers. Analysis of the copolymerization constants of binary systems involved in the terpolymerization process indicates a lower reactivity of polypropylene glycol maleate phthalate in comparison with the

vinyl monomers considered and its tendency to heteropolymerization reactions. The calculated data on the microstructure of the terpolymer indicate the formation of random polymers formed by covalently linked macromolecules. Scanning electron microscopic analysis of the polypropylene glycol maleate phthalate - acrylamide - acrylic acid terpolymer of the 3.15:27.84:69.01 mol% composition showed the presence of a developed macroporous surface with an average pore size of 44 μm. The result of thermogravimetric analysis exhibited a relatively high stability of the above terpolymer upon reaching 339 °C.

In general, the data obtained on the physico-chemical properties of the terpolymers synthesized indicate the possibility of their use as multifunctional polymer materials, in particular, matrix-type polymer systems, heterogeneous substrates, and stimulus-sensitive moisture-absorbing polymers.

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