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Constants and parameters of radical copolymerization of polyethylene glycol maleate with acrylamide at high conversion degree

Radical copolymerization of polyethylene glycol maleate with acrylamide was performed for the first time. Molar mass of polyethylene glycol maleate was determined using light scattering and gel permeation chromatography. The composition of the copolymers was found using gas chromatography. The kinetics of copolymerization reaction studied and copolymerization constants were calculated. Kinetic curves show that with increasing molar fraction of acrylamide in the solution the reaction rate and swelling capacity of the copolymers increase.

Key words: unsaturated polyesters, copolymerization, kinetic data.

Introduction

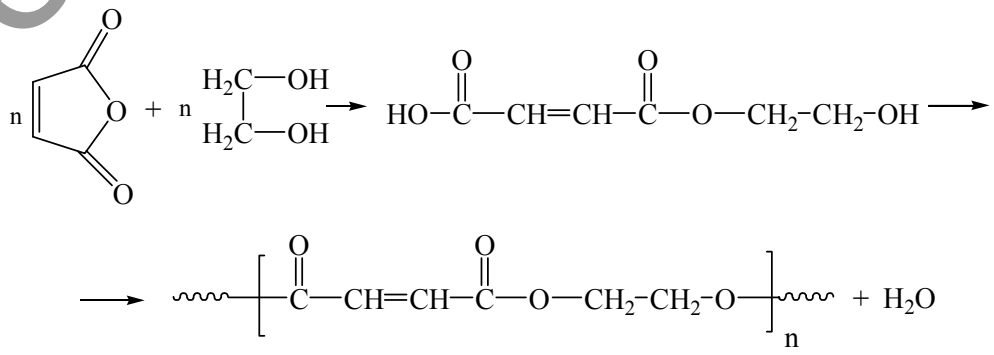
Extensive development of fundamental investigations in the field of radical copolymerization which allows to control the properties, structure and molecular mass of the polymers, and process rate opens new opportunities and new ways of obtaining the polymers with given properties. Considerable interest attracts the products on the basis of unsaturated polyester resins hardened with vinyl monomers which have specific physicochemical and physicomechanical properties [1–3]. The ability of copolymerization of polyester resins with vinyl monomers, in particular with styrene found only a quarter-century ago [4]. Owing to the characteristics described the manufacture of home decoration materials and the goods for constructional purposes made on the basis of the copolymers of polyesters with styrene is extensively developing at present time. However the literature search and patent analysis show the lack of data on the synthesis and investigation of physicochemical properties of hydrogels of polyethylene glycol maleate with other comonomers. Selection of optimal recipes of synthesizing the copolymers on the basis of polyethylene glycol maleate will allow to go for comprehensive studies of the properties of hydrogels and searching the fields of their practical application.

There are data on copolymerization of unsaturated polyester resins with acrylates in literature [5–7], however there is no information on similar reactions of unsaturated carboxylic acids with acrylamides.

In this regard the reactions of radical copolymerization of polyethylene glycol maleate with acrylamide in the solution were investigated in this work.

Experimental part

Polyethylene glycol maleate (p-EGM) was obtained by the reaction of polycondensation of maleic anhydride with ethylene glycol at 393–403 K [8].



The process was controlled by determining acidic number and by the volume of water eliminated. Yield = 98.6 %, T = 375 K. Product was identified due to IR-specters, where present lines of absorption (–C=C–) in regions 1675–1765 cm^{-1}, fluctuation with ethereal bond C–O–C– at 1162 cm^{-1}, fluctuation (C–O) group is 1170 cm^{-1}.

Molar mass of p-EGM determined using light scattering method on nephelometer 2100 AN (NACH) and using gel permeation chromatography on Agilent 1260 Infinity which was equal to 2350 a.m.u. As a solvent tetrahydrophuran was used.

Radical copolymerization of p-EGM with acrylamide (AA) was carried out in solution at the ratio of monomers with the solvent 1:1.5 (on mass) at various initial molar ratios of the comonomers in the presence of dinitrile of azo-bis-isobutyric acid (AIBN) as an initiator at a temperature of 333 K.

Synthesized polymers were washed with dioxane for purifying from unreacted monomer residues.

The composition of the copolymers obtained was determined potentiometrically [9] and according to the residual amount of the monomers gas chromatography was used [10].

There was used gaseous chromatograph Agilent 7890A by mass-selective detector Agilent 5975C to establish copolymer's structure. Obtained copolymers were washed by dioxane (25 ml) by mixing intensively and periodically during 1–1.5 hours. Uterine solution was filtered and entered into gas analyzing column.

Analysis was carried out in the following conditions:

– Length of the column — 21 m;
– Diameter of the column — 0.25 mm;
– Temperature of evaporator — 250 ºC;
– Temperature of thermostat 60–300 ºC;
– Carrier gas — helium;
– Consumption of the carrier gas — 1 ml/min;
– Volume of the probe — 0.2 mkl.

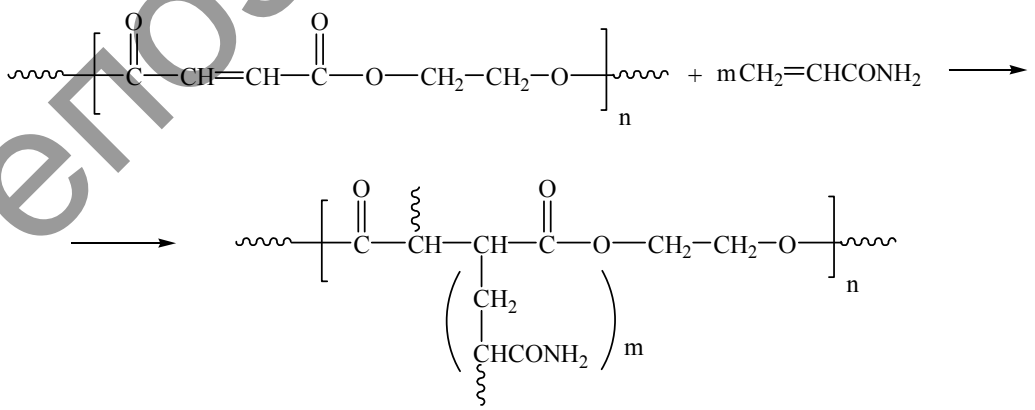
Processing of results is produced automatically by the program GS-MSD Data Analysis.

Equilibrium swelling degree of the polymers was measured gravimetrically. The amount of liquid absorbed was determined on mass of swollen sample. Swelling degree of the gel α was calculated as a relation of the mass of swollen hydrogel at a equilibrium swelling point to its mass at dry state:

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

Results and discussion

The presence of unsaturated double bonds in the molecules of p-EGM allows to use it as a matrix for obtaining network copolymers when polymerizing with highly reactive acrylamide. In this regard the attempt to obtain such polymers by the reaction of p-EGM with AA was made by our group:



Data on copolymerization of p-EGM with AA are given in Table 1.

Table 1

Dependence of composition of the copolymers on the composition of initial mixture when copolymerizing p-EGM (M_1) with AA (M_2), AIBN [I]=8 mol/m^3, T = 333 K

Initial monomer ratios, mol.%		Composition of the copolymers, mol.%		α, %	Yield, %	Maleate groups, %
M_1	M_2	m_1	m_2			
9.99	90.01	8.21	91.79	166.2	48.7	59.8
24.99	75.01	22.13	77.87	154.0	42.4	61.7
50.04	49.96	48.82	51.18	133.1	37.9	63.2
75.06	24.94	73.64	26.36	129.5	31.5	69.4
90.16	9.84	88.33	11.67	104.3	28.7	71.5

Table 1 shows obtained copolymers are enriched with the segments of AA at any ratio of the initial mixture. The yield of the copolymer and swelling degree increases with increasing the concentration of AA in initial mixture which is most probably due to rather high degree of branching and crosslinking. However it is necessary to note that swelling ability of synthesized copolymers is lower in comparison with the ones obtained before at mass ratio [11, 12].

The dependence of the composition of the copolymer on the composition of initial mixture is more clearly demonstrated on composition diagram (Fig. 1).

Using integrated equation of Mayo-Lewis on the basis of the data on composition of the copolymers and initial mixture relative activities of the monomers have been calculated.

From given data (Table 2) it can be said that the meaning of relative activity r_1 in the system p-EGM-AA is lower than 1, which justifies that the macroradical ending with the segment of p-EGM shows higher activity to «other» monomer or radical, whereas the macroradical ending to the chain of the second monomer (AA) reacts much easier with «its» monomer or radical.

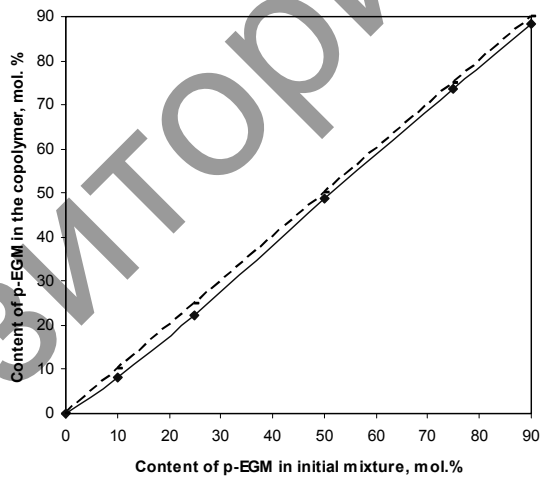


Figure 1. Diagram of dependence of composition of the copolymers of p-EGM-AA on the composition of the initial monomer feed

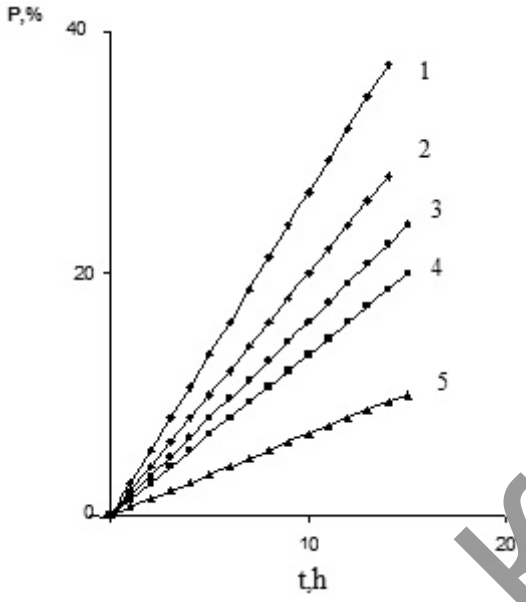
Table 2

Constants and copolymerization parameters

M_1	M_2	r_1	r_2	$r_1 \cdot r_2$	$1/r_1$	$1/r_2$
П-ЭГМ	АА	0.69	1.22	0.84	1.45	0.82

As it is known the meanings of copolymerization constants are the main characteristics when considering the question of relative reactivity of the monomers in dependence on their structure. However more detailed information about relative reactivity of the monomers when copolymerizing can be obtained on the basis of kinetic data.

Figure 2 shows the increase of molar fraction of AA in the solution leads to the increase of total rate of copolymerization which correlates well with data on swelling of final products.



1 — 8.21:91.79 mol.%; *2* — 22.13:77.87 mol.%; *3* — 48.82:51.18 mol.%; *4* — 73.64:26.36 mol.%; *5* — 88.33:11.67 mol.%

Figure 2. Kinetic curve of the dependence of copolymerization of p-EGM-AA

Conclusion

So a brief review of the material given in this article shows that as a result of copolymerization of polyethylene glycol maleate with acrylamide novel polymers of network structure were obtained. The kinetic data show that the copolymerization rate, yield, the degree of swelling of the final products increased with increasing molar content of acrylamide in the initial monomer feed.

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Жоғары айналу дәрежесіндегі полиэтиленгликольмалеинаттың акриламидпен радикалды сополимерленудің константалары мен параметрлері

Алғаш рет полиэтиленгликольмалеинаттың акриламидпен радикалды сополимеризациясы анықталды. Жарық шашырату және гель-сіңіруші хроматография әдісімен полиэтиленгликольмалеинаттың молекулалық массасы зерттелді. Сополимерлердің құрамы газдық хроматография әдісі арқылы белгіленді. Кинетикалық қисық шешуде акриламид мольдік үлесін жоғарылатса, реакцияның жылдамдығының және сополимерлер ісіну қабілетін арттыратынын көруге болады.

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Константы и параметры радикальной сополимеризации полиэтиленгликольмалеината с акриламидом при высоких степенях превращения

Впервые осуществлена радикальная сополимеризация полиэтиленгликольмалеината с акриламидом. Методом светорассеяния и гель-проникающей хроматографии определена молекулярная масса полиэтиленгликольмалеината. С применением газовой хроматографии определен состав сополимеров. Рассчитаны константы и исследована кинетика реакции сополимеризации. Кинетические кривые показывают, что с повышением мольной доли акриламида в растворе увеличиваются скорость реакции и набухающая способность сополимеров.