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Terpolymerization of polyethylene glycol maleate with acrylamide and monovinyl ether of monoethanolamine

Radical copolymerization of polyethylene glycol maleate with acrylamide and monovinyl ether of monoethanol amine has been performed for the first time. Radical co- and terpolymerization of the systems polyethylene glycol maleate with acrylamide and monovinyl ether of monoethanol amine has been studied. Molecular weight of polyethylene glycol maleate has been determined using light scattering and gel permeation chromatography. The compositions of the polymers and copolymerization constants of the studied systems have been determined. The composition of the copolymers has been found using gas chromatography. Kinetic curves show that with increasing molar fraction of acrylamide in the solution the reaction rate and swelling capacity of the copolymers increase. It has been shown that the composition of terpolymers determined experimentally differs considerably from the one calculated taking into account obtained constants of copolymerization. Deviations found are due to various intermolecular interactions in these systems. The possibility of controlling the properties of network copolymers of polyethylene glycol maleate by changing external factors has been studied. Swelling capacity of the copolymers investigated was studied using gravimetric method.

Keywords: unsaturated polyesters, copolymerization, terpolymerization, polyethylene glycol maleate, acrylamide, copolymer, terpolymer.

Introduction

At present the use and preparation of polymeric materials makes a big contribution to every-day life of humanity. Wide application of polymers can be seen in many branches of household, architecture, medicine, science and technique.

The most commonly used method of obtaining such synthetic polymers is the reaction of radical terpolymerization. Such processes are necessary and they are very suitable from practical point of view [1]. The usefulness of this reaction is that by addition of the third monomer into the reaction mixture it is possible to obtain the polymer which is modified at a specific «place» and the change of physicochemical properties of copolymer may be achieved. Using different ways of modification of macrochain it is possible to improve the properties and to obtain novel polymeric materials.

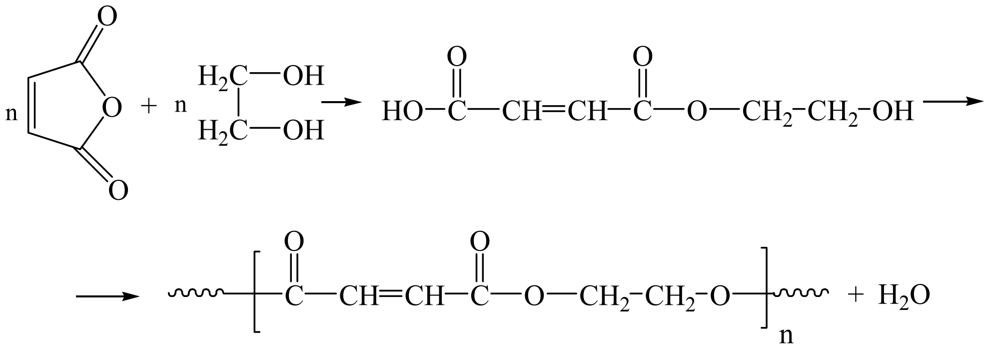
One of the perspective reagents used as a structure forming agent for obtaining polymers is polyethylene glycol maleate. As it is known unsaturated polyester resins are thermosetting polymers which have –CH=CH– active group [2]. One of the important properties of them is their ability to polymerize with vinyl monomers at room temperature or at relatively low temperature without elimination of side products. Hardened products have good physico-mechanical and chemical properties which can be varied by choosing corresponding monomers. The ability of polyether resins to copolymerize with vinyl monomers, for instance, with styrene has been found a little more than quarter century ago. In connection with this radical copolymerization of polyethylene glycol maleate with some vinyl monomers has been thoroughly investigated and the possibility of formation of the polymers of linear and cross-linked structure has been shown. Polymers can posses given complex of properties by using vinyl ethers (VE) as reagents. Introduction of the chains of

VE into the composition of polymers improves their processability, adherence and allows to exclude the use of plasticizers and stabilizers. Among the compounds of this class monovinyl ether of monoethanolamine (MVEMEA) which has hydrophobic fragments and active NH_2-group is of special interest. It is important to note that MVEMEA polymerizes badly by radical mechanism which can be used to control the kinetic chain length.

On the basis of the aforesaid triple system consisting of polyethylene glycol maleate (p-EGM) — acrylamide (AA) — monovinyl ether of monoethanolamine (MVEMEA) has been chosen.

Experimental part

Polyethylene glycol maleate has been obtained by polycondensation reaction of maleic acid and ethyleneglycol at a temperature 393–403 К [3, 4]:



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.

Co- and terpolymers of p-EGM have been obtained by radical polymerization in organic phase (the ratio monomer mixture: solvent was 1:3 on mass) in the presence of initiator dinitril of azo-bis-isobutyric acid [AIBN] = 8 mol/m^3 at temperature 333 K at various ratios of monomer.

Synthesized polymers were washed with dioxane for purifying from unreacted monomer residues. The composition of the copolymers obtained was determined potentiometrically and according to the residual amount of the monomers gas chromatography was used [3, 5]. Equilibrium swelling degree of the polymers was measured gravimetrically.

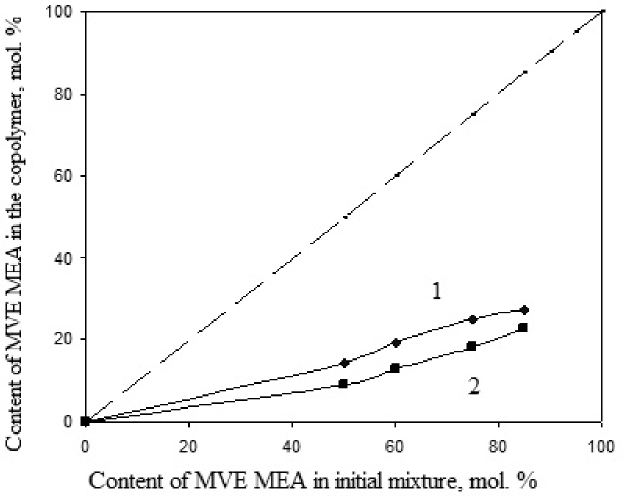
Results and discussion

Since Alfei and Goldfinger's equation is known for triple systems the scientists are using it for theoretical calculations of the compositions of terpolymers. With this aim our task was to calculate theoretical compositions of terpolymers investigated. For that it is necessary to know six constants of binary polymerization: r_{12}, r_{21}, r_{13}, r_{31}, r_{23}, r_{32} for the systems $M_1 – M_2$, $M_1 – M_3$, $M_2 – M_3$.

In connection with this the copolymerization of three binary systems p-EGM–AA, p-EGM–MVEMEA and AA–MVEMEA has been carried out (Table 1).

Experimental results on establishment of dependence of copolymers' composition on composition of the monomer mixture for the systems p-EGM–MVEMEA and AA–MVEMEA are shown in Figure. From Figure it is seen that in both systems the copolymers have less chains of MVEMEA which shows less activity of MVEMEA towards p-EGM and AA in radical copolymerization reaction and that it enables the formation of homopolymers in the condition of radical polymerization. It is necessary to note that the introduction of the chains of vinyl ether to the copolymer's composition is limited.

As it is seen from Table 1 obtained copolymers are enriched with the chains p-EGM and AA. Increase of the content of MVEMEA in initial mixture from 50 to 90 mol. % leads to the increase of its fraction in the copolymers to certain relatively constant amount (from 15 to 31 mol. %).



Copolymers: *1* — p-EGM–MVEMEA; *2* — AA–MVEMEA

Figure. Diagram of copolymer composition from the composition of the initial monomer mixture

Based on literature and obtained data when studying radical co- and terpolymerization of p-EGM–AA, p-EGM–MVEMEA and AA–MVEMEA it can be concluded that with increasing the fraction of MVEMEA in initial mixture soluble copolymers of linear structure are formed and the yield of the copolymers decreases (Table 1).

Table 1

Compositions and properties of the copolymers p-EGM (M_1) – AA (M_2), p-EGM (M_1) – MVEMEA (M_2), AA (M_1) – MVEMEA (M_2). [I] = 8 mol/m^3, T = 333 K, the solvent is dioxane

Initial ratio of the monomers, mol. %		Composition of the copolymer, mol. %		The yield of copolymer, %
M_1	M_2	m_1	m_2	
p-EGM–AA				
15.11	84.89	11.38	88.62	83.2
24.91	75.09	19.74	80.26	86.4
39.81	60.19	34.69	65.31	90.9
49.94	50,06	58.12	41.88	92.5
p-EGM–MVEMEA				
10.10	89.90	69.4	30.6	21.55
14.92	85.08	72.6	27.4	24.32
25.00	75.00	75.0	25.0	25.19
40.11	59.89	76.6	19.3	31.26
49.93	50.07	78.8	14.4	32.77
AA–MVEMEA				
15.19	84.81	77.3	22.7	29.0
25.10	74.90	81.8	18.2	31.1
39.96	60.04	86.9	13.1	34.0
49.86	50.14	91.0	9.0	36.0

Much lower meanings of the yields of the copolymers with increasing the content of VE in the mixture shows antagonistic effect of the latter on polymerization process. It is likely that the macroradical which ends with the chain of MVEMEA is rather stable and it inhibits polymerization process. Therefore MVEMEA in such systems can play the role of the controller of the process rate and molecular mass of copolymer.

The processing of the obtained data allowed to calculate the constants of copolymerization for the pairs of monomers. The meanings of the constants of binary polymerization have been found using integral equation of Mayo-Luis which is used for calculation of polymerization constants at a high polymerization degree [6, 7] (Table 2).

Table 2

Constants and parameters of copolymerization of binary systems

M_1	M_2	r_1	r_2	$r_1 \cdot r_2$	$1/r_1$	$1/r_2$	Q_1	e_1	Q_2	e_2
p-EGM	AA	0.93	1.45	1.34	1.07	0.68	0.05	0.55	0.14	1.15
p-EGM	MVEMEA	3.80	0.12	0.45	0.26	8.33	2.30	0.40	0.51	1.21
AA	MVEMEA	5.90	0.08	0.47	0.17	12.5	1.37	0.59	0.22	0.77

Comparison of copolymerization constants has shown that p-EGM and AA show higher activity in the radical copolymerization reaction in comparison with MVEMEA. The meanings of r_1 for these monomers are considerably higher than 1 and equal to 3.8 and 5.9 correspondingly which justifies high activity of the monomers and macroradicals, which end to the chains p-EGM and AA towards its monomer or radical, whereas the radical which ends to MVEMEA is able to bind mainly to the other monomer. The meanings of r_2 which approximate to 0 in both systems confirm it.

It is necessary to take into account that in spite of no possibility of homopolymerization of MVEMEA, it can bind with considerably low activity to its monomer or radical in copolymerization reaction with p-EGM and AA. It is confirmed by the copolymerization constant r_2 which differs from zero. Relative activity of VE in binary polymerization with both monomers is equally low. In the system p-EGM–AA the meaning of relative activity r_1 is less than 1 (r_1 = 0.93), which shows that the macroradical ending to the chain p-EGM shows high activity to the other monomer or radical, whereas macroradical which ends to the chain of second monomer (AA) reacts considerably easier with its monomer AA (r_2>1). $1/r_1$ is higher than 1 and equal to 1.07, at the same time $1/r_2$ is considerably lower than 1 and equal to 0.68. This shows and confirms the fact that macroradical which ends with p-EGM shows higher activity to the other monomer (AA), whereas the macroradical which ends to the chain with second monomer (AA) also reacts easier with its monomer.

The product of two constants of copolymerization in two studied systems p-EGM–MVEMEA, AA–MVEMEA is lower than 1 which gives opportunity to assume that the interchange of monomer chains in the copolymers does not take place. So the meanings r_{12} = 0.93; r_{21} = 1.45; r_{13} = 3.80; r_{31} = 0.12; r_{23} = 5,90; r_{32} = 0.08 have been found.

Different internal factors influences on reactivity of monomers. Among the key factors there are coupling, spatial hindrances, polarity of the monomer or radical. Alfrei and Price [6] have established the quantitative dependence between structure and reactivity. In spite of the incompleteness of the parameters Q and e introduced by them which describe resonance and polar effect correspondingly, in many cases they describe the process rather sufficiently. On the basis of the copolymerization constants we have calculated the parameters Q and e according to the equation of Alfei and Price. As it is seen from data given in Table 2 both monomers p-EGM and AA have similar meanings of polarity of double bond. The meanings of Q for these monomers differs a little bit but have the same degree, therefore the coupling degree with the substitutes also has close meaning. MVEMEA differs from the first two monomers on the meanings of its activity and polarity. Probably it determines high tendency of the monomers and radicals with the end VE in the polymerization condition to bind other monomers.

Equation made by Walt and Medvedev [8] independently allows to define the probability of formation of the structures (f) on copolymerization constants: M_1–M_1, M_1–M_2 and M_2–M_1, M_2–M_2 (Table 3).

As it is seen from table 4 the probability of formation of the structures M_1–M_1 is higher at any ratio of the monomers in the systems p-EGM–MVEMEA and AA–MVEMEA. In this case for these systems the probability of formation of the structures M_1–M_1 is almost one-degree higher than M_1–M_2 and the probability of formation of the structures M_2–M_2 is extremely low. Probability of the formation of the structures MVEMEA–MVEMEA is rather low.

Data found on the copolymerization of each pair of monomers M_1/M_2, M_2/M_3, M_1/M_3 separately gives opportunity to predict their behavior at terpolymerization of $M_1/M_2/M_3$. The synthesis where mass ratio of p-EGM was constant (~15 mol. %), and the mass ratios of AA and MVEMEA were changing within the range from ~15 to 75 mol. % has been carried out to check the correspondence of calculated and experimentally found compositions of terpolymers.

In Table 4 the experimental and calculated data showing the dependence of the terpolymer composition on the composition of the initial monomer mixture is shown.

From data shown in Table 4 it is seen that the composition of the copolymer found experimentally differs from calculated ones. The amount of the chains of p-EGM and MVEMEA in the synthesized terpolymer was found to be considerably higher than calculated meaning. At the same time according to the calculations the amount of the chains of AA was supposed to be much higher.

Table 3

Probability of formation of different structures of the copolymers p-EGM (M_1) – AA (M_2), p-EGM (M_1) – MVEMEA (M_2), p-EGM (M_1) – AA (M_2)

Composition of initial mixture, mol.%		f_{M1-M1}	f_{M1-M2} f_{M2-M1}	f_{M2-M2}	L_{M1}	L_{M2}
M_1	M_2					
p-EGM (M_1)– AA (M_2)						
15.11	84.89	0.1129	0.2657	0.6558	1.4249	2.3391
24.91	75.09	0,2137	0.2849	0.7165	1.7501	4.2699
39.81	60.19	0.2899	0.2884	0.8235	2.0052	1.5669
49.94	50.06	0.5431	2.5531	0.8324	1.2127	1.2164
p-EGM (M_1) – MVEMEA (M_2)						
10.10	89.90	0.3158	0.0989	0,0067	2.4258	1.4347
14.92	85.08	0,3693	0.0894	0,0052	3.6860	1.2327
25.00	75.00	0,5493	0.0875	0,0045	4.6178	1.1713
40.11	59.89	0,6248	0.0847	0,0040	18.1788	1.0519
49.93	50.07	0,8933	0.0820			
AA (M_1) – MVEMEA (M_2)						
15.19	84.81	0.7945	0.0940	0.0062	9.0252	1.0676
25.10	74.90	0.8159	0.0800	0.0050	10.1674	1.0584
36.96	60.04	0.8287	0.0760	0.0040	10.6360	1.0523
49.86	50.14	0.8371	0.0730	0.0035	11.0855	1.0481

Table 4

Compositions of terpolymers PEGM (M_1), AA (M_2), MVEMEA (M_3), which were obtained in the dioxane (1:3), [I]=8 mol/m^3 and T=333 K

Composition of the initial mixture, mol. %			Compositions of terpolymers, mol. %						Yield, %
			Calculated			Experimentally found			
M_1	M_2	M_3	m_1	m_2	m_3	m_1	m_2	m_3	
14.89	69.91	15.20	9.3	84.9	5.8	20.5	71.2	8.3	68.6
15.12	49.93	34.95	12.7	77.9	9.4	23.3	64.2	12.5	43.1
15.10	35.03	49.87	16.4	57.3	26.3	25.5	44.1	30.4	27.0
14.92	14.99	70.09	20.0	49.6	30.4	27.2	37.6	35.2	21.1

One of the main factors influencing on properties of the copolymers is its chemical structure which is closely related to the character of interchange and distribution of the sections in polymeric chain. Parameters of microstructures of terpolymers were calculated according to the equation suggested in [9] (Table 5).

Table 5

Parameters of microstructures of terpolymers p-EGM (M_1), AA (M_2), MVEMEA (M_3)

Composition of the reagent mixture, mol. %			The probability of the structure formation					
M_1	M_2	M_3	P_{M1-M2}	P_{M2-M3}	P_{M3-M1}	P_{M1-M3}	P_{M3-M2}	P_{M2-M1}
14.89	69.91	15.20	0.10276	0.05801	0.17190	0.01393	0.80229	0.94593
15.12	49.93	34.95	0.12269	0.16161	0.21352	0.04347	0.71174	0.87899
15.10	35.03	49.87	0.14337	0.27017	0.26087	0.08224	0.60869	0.84395
14.92	14.99	70.09	0.18521	0.48927	0.37037	0.20588	0.37037	0.73530

Composition of the reagent mixture, mol. %			The length of the blocks from one-type chains			
M_1	M_2	M_3	L_{M1}	L_{M2}	L_{M3}	Hardwood parameter of blockiness R_x
14.89	69.91	15.20	1.05279	6.22049	1.02645	47.76
15.12	49.93	34.95	1.07152	1.13983	1.27149	87.18
15.10	35.03	49.87	1.09747	1.16762	1.35294	84.10
14.92	14.99	70.09	1.18881	1.22804	1.58824	76.98

According to the calculations of the probability of formation of the structures M_1–M_2, M_3–M_2 in terpolymers is relatively high. The reason of that can be high reactivity of macroradicals M_2, which joins easily to $M_1^\bullet$ as well as $M_3^\bullet$ and their monomers.

It is necessary to note that at terpolymerization of p-EGM–AA–MVEMEA at one of the ratios of the monomers (20.5:71.2:8.3 mol. %) the polymer of network structure with high sorption capacity is formed. Comparing to its binary analogue p-EGM–AA [10], terpolymer p-EGM–AA–MVEMEA (20.5:71.2:8.3 mol. %) of lightly crosslinked structure and it is able to absorb much more quantity of water within shorter period of time. It is likely related to less activity of MVEMEA in radical polymerization reaction and as a result of this lightly crosslinked polymers are formed. Consequently, monovinyl ether of monoethanolamine in this case plays the role of the agent which shortens the frequency of polymer network. With this terpolymers p-EGM-AA-MVEMEA with higher content of vinyl ether possess water-soluble, film-forming and complex-forming properties and therefore they acquire critically different physicochemical and mechanical characteristics which can be used in practice.

Conclusion

So obtained data indicates that in triple systems consisting of the monomers which tend to the formation of different types of associates, reactivity of the monomers differs from their reactivity in corresponding binary systems. It is obvious that the nature of the associates formed in the solution by two compounds can change when there is the third compound in the system. Consequently, controlling the amounts of the monomers in the mixture during the synthesis it is possible to control the properties of the polymer.

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Г.К. Буркеева

Полиэтиленгликольмалеинаттың акриламидпен және моноэтаноламиннің моновинилді эфирімен терполимеризациясы

Алғаш рет радикалды со- және терполимерлену әдісімен полиэтиленгликольмалеинаттың акриламидпен және моноэтаноламиннің моновинилді эфирімен тігілген стимулсезімтал полимерлер алынды. Полиэтиленгликольмалеинаттың акриламидпен және моноэтаноламиннің моновинилді эфирімен радикалды со- және термополимеризациясы зерттелді. Жарық шашырату және гель-сіңіруші хроматография әдісімен п-ЭГМ-тың молекулалық массасы анықталды. Полимерлердің құрамы және зерттелген жүйелер үшін сополимеризация константасы, қалдық мономерлер саны арқылы газдық хроматография әдісімен со- және терполимерлердің құрамы белгіленді. Кинетикалық қисықтарда көрсетілгендей, ерітіндідегі акриламидтің мольдік үлесі артқан сайын реакция жылдамдығы мен сополимерлердің ісіну қабілеттігі жоғарылады. Терполимерлердің эксперименталды анықталған құрамы табылған бинарлы сополимеризация константаларынан едәуір ерекшеленетіні көрсетілген. Сыртқы факторлардың өзгеруі арқылы полиэтиленгликольмалеинат сополимерінің торлану қасиетін бақылау мүмкіндігі және гравиметрия әдісімен зерттеліп жатқан сополимерлердің ісіну қабілеті зерттелді.

Кілт сөздер: қанықпаған полиэфир, қанықпаған полиэфир шайыры, сополимерлену, терполимерлену, полиэтиленгликольмалеинат, акриламид, сополимер.

Г.К. Буркеева

Терполимеризация полиэтиленгликольмалеината с акриламидом и моновиниловым эфиром моноэтаноламина

Впервые осуществлена радикальная сополимеризация полиэтиленгликольмалеината с акриламидом и моновиниловым эфиром моноэтаноламина. Исследована радикальная со- и терполимеризация полиэтиленгликольмалеината с акриламидом и моновиниловым эфиром моноэтаноламина. Методом светорассеяния и гель-проникающей хроматографии определена молекулярная масса полиэтиленгликольмалеината. Определены составы полимеров, а также константы сополимеризации для исследованных систем. С применением газовой хроматографии изучен состав сополимеров. Кинетические кривые показывают, что с повышением мольной доли акриламида в растворе увеличиваются скорость реакции и набухающая способность сополимеров. Показано, что экспериментально определенный состав терполимеров значительно отличается от вычисленного с учетом найденных констант бинарной сополимеризации. Исследована возможность управления свойствами сетчатых сополимеров полиэтиленгликольмалеината посредством изменения внешних факторов. Методом гравиметрии изучена набухающая способность исследуемых сополимеров.

Ключевые слова: ненасыщенный полиэфир, ненасыщенная полиэфирная смола, сополимеризация, полиэтиленгликольмалеинат, акриламид, сополимер, терполимер.