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CONSTANTS AND PARAMETERS OF RADICAL COPOLYMERIZATION OF POLY(ETHYLENE GLYCOL FUMARATE) WITH ACRYLIC ACID

Abstract. In the present work, the binary radical copolymerization of poly(ethylene glycol fumarate) with acrylic acid in a dioxane medium was investigated for the first time at various mole ratios of the initial monomer mixture. The kinetics of the copolymerization reaction was studied. Kinetic curves show that with increasing mole fraction of acrylic acid in solution, the reaction rate and sorption capacity of copolymers also increase.

The synthesized copolymers composition was determined by chromatography-mass spectroscopy. The constants and parameters of radical copolymerization were calculated using the integral methods of Mayo-Lewis, Fineman-Ross and Kelen-Tüdos. The Q-e parameters were calculated by the Alfray-Price equation on the basis of copolymerization constants.

A lower reactivity characterization of poly(ethylene glycol fumarate) were found at copolymerization of it with acrylic acid. Direct proportionality of the unsaturation degree of copolymers to the content of poly(ethylene glycol fumarate) in the composition of the initial monomer mixture was shown.

Key words: poly(ethylene glycol fumarate), acrylic acid, radical copolymerization, kinetics, copolymerization.

Unsaturated polyesters are interesting for theoretical and practical studies, since along with the simplicity, the economics of production, and they contain unsaturated double bonds in their composition, which makes it possible to obtain on their basis of spatially cross-linked structures. On the other hand, unsaturated polyesters provide the widest opportunity for directional modification due to polymerization reactions with various ionic monomers and, consequently, open the way to obtaining materials including composite ones with a predetermined valuable complex of properties.

The interaction of polyesters with unsaturated compounds was firstly called the copolymerization reaction by Benig [1], so copolymerization with vinyl acetate, styrene and methyl methacrylate, simple and complex allyl ethers, vinyl formates was investigated. As a result of the studies carried out, the role of unsaturated polyesters macromolecule as a "skeleton" at large formations was shown. From the literature analysis, only comonomers of hydrophobic nature were involved in the copolymerisation with unsaturated polyester resins [1-3], when the matter of hydrophilic monomers lay over until recently, which opens up prospects for new "intelligent" polymers.

The preparation of polymers based on unsaturated polyesters with the required combination of properties is possible only on the knowledge basis of the processes kinetics and mechanism of their radical copolymerization with ionic monomers. It seemed interesting and expedient to fill in the marked gap since the study of the kinetics, constants, and parameters of unsaturated polyesters copolymerization with ionic monomers remains undetermined and actual.

We synthesized earlier copolymers susceptible to changes in external factors by radical copolymerization reaction of polyglycol maleates with a number of unsaturated carboxylic acids, acrylamide [4, 5]. Hence, it seemed interesting to continue the research in this direction.

This paper demonstrates the first studies on the reactions of radical copolymerization of poly(ethylene glycol fumarate) (p-EGF) with acrylic acid (AA).

Experiment

The initial p-EGF was obtained by the polycondensation reaction of fumaric acid and ethylene glycol at a temperature of 403-453 K [6]. The course of the reaction was monitored by determining the acid number and the volume of water released. The synthesized polyester is a light-yellow, resinous, fusible substance, soluble in chloroform and dioxane. The resulting resin was purified from the initial monomers by repeated washing with acetone. The composition of the obtained product was determined from elemental analysis data: m.p. of p-EGF is 80°C.

The molecular weight of the p-EGF was determined by light-scattering methods on the nephelometer 2100 AN by NACH and by the method of determining the end group fraction, which is 2500 amu.

Radical copolymerization of p-EGF with AA was carried out in the dioxane solution at various initial molar ratios of comonomers in the presence of an initiator – benzoyl peroxide (BP) at a temperature of 333 K. The synthesized polymers were repeatedly washed with dioxane and dried under vacuum until constant mass for purifying them from unreacted monomer residues.

The compositions of the obtained copolymers were determined by potentiometric titration and by the residual amount of monomers by chromatography-mass spectroscopy on Agilent 7890A using the Agilent 5975C mass selective detector [7, 8]. A bromate-bromide method was used to quantify unreacted double bonds (the degree of unsaturation) of the copolymers [9].

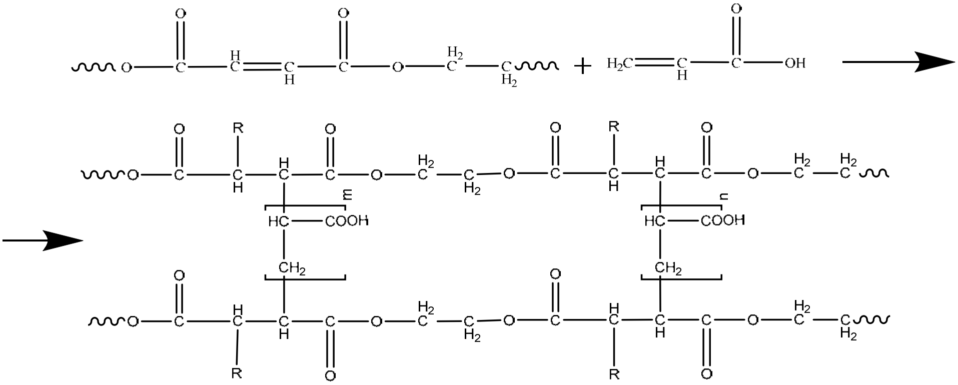
The kinetics of radical copolymerization of p-EGF with AA was studied by dilatometric method in the dioxane solution. The copolymerization constants r_1 and r_2 were determined on the basis of the copolymer compositions obtained at deep conversion ratios using the Mayo-Lewis integral equation [10], as well as the standard methods of Fineman-Ross and Kelen-Tüdos [11, 12].

Results and discussion

The intensive development of fundamental research in the field of radical copolymerization, which allows to regulate the properties, structure and molecular mass of polymers, the speed of the process, opens up new ways of obtaining polymers with given properties. Products based on unsaturated polyesters cured with vinyl monomers having specific physical-chemical and physical-mechanical properties are of considerable interest. The presence of unsaturated double bonds in the p-EGF molecule provides an opportunity to use it as a polymer matrix for the preparation of spatially cross-linked polymers by copolymerization with reactive acrylic acid.

P-EGF is obtained by the polycondensation reaction of fumaric acid and ethylene glycol [6].

As a result of radical copolymerization of the oligomeric molecule of p-EGF with AA in the presence of the initiator - BP the formation of the spatially cross-linked copolymer can be represented by the following scheme:



The values of constants and copolymerization parameters are important characteristics when considering the relative reactivity of the monomers depending on their structure. However, more complete information on the relative reactivity of the monomers during copolymerization can be obtained on the basis of kinetic data (figure 1).

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The kinetics of radical copolymerization of p-EGF with AA at various initial molar ratios was studied in detail to assess the relative activity of the monomers (figure 1). Increase of the reaction rate and yields of the copolymers was found with the growth in the content of AA in the initial monomer mixture, also these parameters decrease with the increase of the p-EGF content in the reaction mixture. This is apparently due to the presence of a functional -COO carboxyl group in the AA chain that capable of participating in elementary polymer transfer

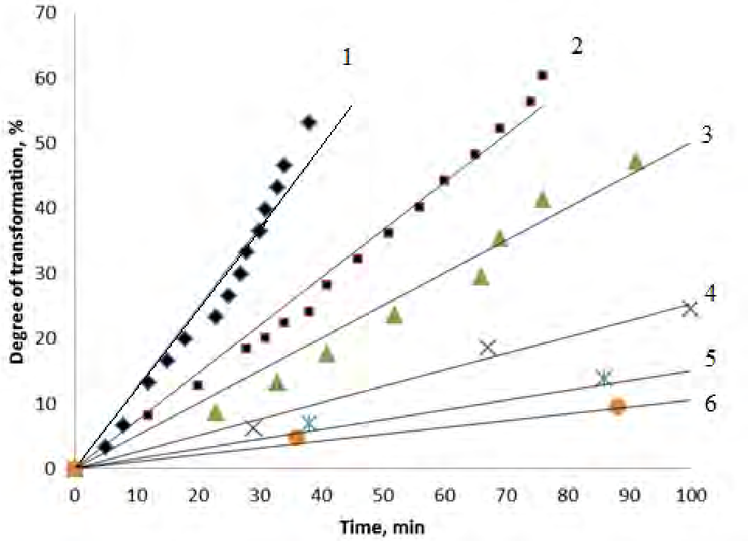

Figure 1 – Kinetic curve of the copolymerization of p-EGF:AA:
1 – 7,95:92,05; 2 – 11,95:88,05; 3 – 21,03:78,97;
4 – 44,05:55,95; 5 – 68,96:31,04; 6 – 89,05:10,95 mol.%

reactions, accompanied by an increase in the molecular weight due to branching processes. Figure 1 shows the kinetic data of radical copolymerization indicating a regular acceleration of the process with increasing molar fraction of AA in the initial monomer mixture.

The radical copolymerization of p-EGF with AA forms insoluble polymers of the network structure in the entire range of the studied comonomer ratios.

The experimental data obtained as a result of studying the processes of radical copolymerization in p-EGF-AA systems are presented in table 1. The yield of the copolymers was 83-74%.

Table 1 – Composition dependence of the copolymers on the initial mixture composition in the copolymerization of p-EGF (M_1) with AA (M_2) [BP] = 8 mol/m^3, T=333 K

The initial ratio of monomers, mass %		Copolymer composition, mass %		Yield, %	Degree of unsaturation
M_1	M_2	m_1	m_2		
10,09	89,91	7,95	92,05	83,23	41,3
15,06	84,94	11,95	88,05	78,98	42,5
25,02	74,98	21,03	78,97	76,22	46,8
50,01	49,99	44,05	55,95	75,32	49,6
75,06	24,94	68,96	31,04	75,05	52,1
90,08	9,92	89,05	10,95	73,83	54,4

Enrichment of the p-EGF-AA copolymers with AA units throughout the investigated range of the initial mixtures was seen from Table 1, while the content of the AA units in the copolymer composition increases sympathetically its amount in the initial monomer mixture. The copolymer yield and the swelling degree increase with increasing concentration in the initial AA mixture, which is apparently due to a sufficient degree of branching and cross-linking. Since the fumarate groups are not capable of homopolymerization reactions, the branching and cross-linking reactions diminish with a decrease in the molar AA concentration, respectively, while the unsaturation degree of the copolymer increases. Also, the above reactions are difficult with the increase of the p-EGF concentration in the initial monomer mixture, which in turn leads to the viscosity growth.

The composition diagram demonstrates more clearly the dependence of the copolymer composition on the initial mixture composition (figure 2).

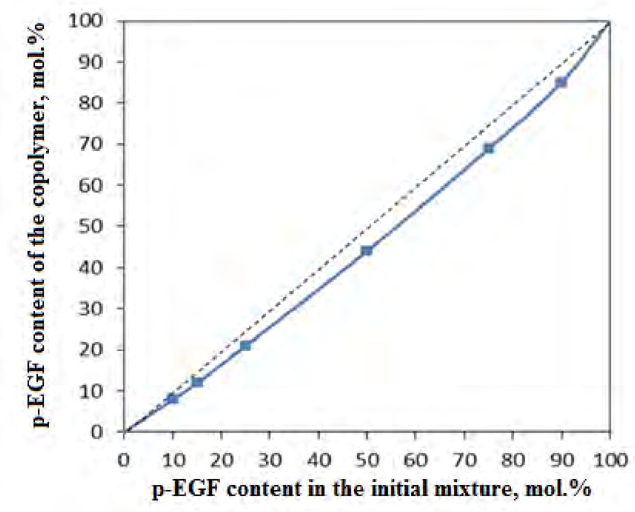

Figure 2 – The dependence of the p-EGF-AA copolymers composition on the composition of the initial monomer mixture

The relative activities of the comonomers were calculated using the integral Mayo-Lewis equation [9], the standard Fineman-Ross and Kelen-Tüdos methods on the basis of the copolymer and the initial monomer mixture compositions data. Table 2 shows the results of calculations. There was an assumption that p-EGF

Table 2 – Constants and parameters of radical copolymerization of p-EGF-AA binary systems

Method	r_1	r_2	$r_1 \cdot r_2$	$1/r_1$	$1/r_2$	e_1	Q_1	e_2	Q_2
Mayo-Lewis	0,84±0,076	1,18±0,050	0,99	1,19	0,85	0,86	0,90	0,77	1,15
Fineman-Ross	0,72±0,006	1,25±0,140	0,90	1,39	0,80	1,09	1,18	0,77	1,15
Kelen-Tüdos	0,83±0,038	1,02±0,094	0,85	1,21	0,98	1,18	1,34	0,77	1,15
Average	0,80±0,04	1,15±0,095	0,91	1,26	0,88	1,04	1,14	0,77	1,15

had a lower reactivity in radical copolymerization compared to AA. The obtained values of the relative activities of the copolymers confirm this assumption. The calculated values of the copolymerization constants indicate a greater AA activity in radical copolymerization. The data from Table 2 demonstrate the relative activity r_1 in the p-EGF-AA system that is less than one. It may indicate more activity of macroradical ending in the p-EGF unit towards the "foreign" monomer or radical, while the macroradical ending in the second comonomer AA ($r_2 > 1$) unit reacts much more easily with its "own" monomer. The product of copolymerization constants ($r_1 \cdot r_2$) close to unity indicates the possibility of copolymers to the formation of statistical structures.

Various internal factors as conjugation, steric hindrance, polarity of the monomer and radical, influence on the monomers reactivity. The Q-e parameters were calculated by the Alfray and Price equations based on the values of copolymerization constants [10]. Both p-EGF and AA monomers have different polarities of the double bond (see table 2). The Q values for these monomers are significantly different. The degree of conjugation in the double bond with the substituents is also different due to the less value of Q for p-EGF. This determines the high propensity of monomers and radicals ending in the p-EGF units to attach more "foreign" monomers under the polymerization conditions.

Thus, a brief review of the studies in the paper shows a possibility to obtain new polymers of the spatially cross-linked structure as a result of radical copolymerization of poly(ethylene glycol fumarate) and acrylic acid. The obtained results demonstrate the ability to control the physical-chemical properties of the copolymers based on poly(ethylene glycol fumarate) and acrylic acid, induced by the polymer composition, which allows the creation of new materials with a predefined program of behavior.

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Резюме

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ПОЛИЭТИЛЕНГЛИКОЛЬФУМАРАТТЫҢ АКРИЛ ҚЫШҚЫЛЫМЕН РАДИКАЛДЫҚ СОПОЛИМЕРЛЕНУДІҢ КОНСТАНТАЛАРЫ МЕН ПАРАМЕТРЛЕРІ

Жұмыста алғаш рет диоксан ортасында бастапқы мономер қоспасының әртүрлі мольдік қатынасында полиэтиленгликольфумараттың акрил қышқылымен бинарлы радикалды сополимерленуі зерттелінген. Сополимерлену реакциясының кинетикасы зерттелді. Кинетикалық қисықтар ерітіндідегі акрил қышқылының мольдік мөлешерінің көбейген сайын реакция жылдамдығы мен сорбциялық сыйымдылығы артатыны көрсетілді. Хроматография-масс-спектроскопияны қолдану арқылы синтезделген сополимерлердің құрамы анықталды. Радикалды сополимерленудің константалары мен параметрлері Майо-Льюис, Файнман-Росс және Келен-Тюдоштың интегралды әдісімен есептеледі. Сополимерлену тұрақтыларының негізінде Q-e параметрлері Алфрей-Прайс теңдеуі бойынша есептелінді. Акрил қышқылының полиэтиленгликольфумаратпен сополимерлену кезінде соңғысының төмен реактивтілікпен сипатталатыны анықталды. Сополимерлердің қанықпағандығы бастапқы мономер қоспасы құрамындағы полиэтиленгликольфумараттың мөлшеріме тура пропорцианалды екеніндегі көрсетілді.

Түйін сөздер: полиэтиленгликольфумарат, акрил қышқылы, радикалды сополимерлену, кинетика, сополимерлену.

Резюме

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КОНСТАНТЫ И ПАРАМЕТРЫ РАДИКАЛЬНОЙ СОПОЛИМЕРИЗАЦИИ ПОЛИЭТИЛЕНГЛИКОЛЬФУМАРАТА С АКРИЛОВОЙ КИСЛОТОЙ

Впервые исследована бинарная радикальная сополимеризация полиэтиленгликольфумарата с акриловой кислотой в среде диоксана при различных мольных соотношениях исходной мономерной смеси. Изучена кинетика реакции сополимеризации. Кинетические кривые показывают, что с повышением мольной доли акриловой кислоты в растворе увеличиваются скорость реакции и сорбционная способность сополимеров. С применением хромато-массспектроскопии определен состав синтезированных сополимеров. Интегральным методом Майо-Льюиса, Файнмана-Росса и Келена-Тюдоша рассчитаны константы и параметры радикальной сополимеризации. На основании констант сополимеразации по уравнению Алфрея-Прайса рассчитаны параметры Q-e. Установлено, что при сополимеризации акриловой кислоты с полиэтиленгликольфумаратом последний характеризуется меньшей реакционной способностью. Показано, что степень ненасыщенности сополимеров прямо пропорциональна содержанию полиэтиленгликольфумарата в составе исходной мономерной смеси.

Ключевые слова: полиэтиленгликольфумарат, акриловая кислота, радикальная сополимеризация, кинетика, сополимеризация.