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Constants and parameters of radical copolymerization of poly(propylene glycol)fumarate with acrylic acid

In the present work, the binary radical copolymerization of poly(propylene 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 spectrometry. The constants and parameters of radical copolymerization were calculated using the integral methods of Mayo-Lewis, Fineman-Ross and Kelen-Tüdös. The Q-e parameters were calculated by the Alfrey-Price equation on the basis of copolymerization constants. A lower reactivity characterization of poly(propylene glycol)fumarate was found at copolymerization of it with acrylic acid. The relative activity r_1 in the p-PGF-AA system is less than one. This suggests that the p-PGF ability to copolymerize with other monomers is higher than homopolymerization. Direct proportionality of the unsaturation degree of copolymers to the content of poly(propylene glycol)fumarate in the composition of the initial monomer mixture was shown. Thus, the results of this study show that the synthesized polymers based on PGFP have good characteristics and can be used in various fields of science.

Keywords: unsaturated polyester resins, poly(propylene glycol)fumarate, acrylic acid, copolymerization constants, monomer activity, kinetics, sorption, copolymerization.

Introduction

Unsaturated polyester (UPE) resins are prepared from the polyesterification reaction of diols, unsaturated dibasic acids/acid anhydrides, and saturated dibasic acids/acid anhydrides. UPE resins, the most common thermoset resins for fiber-reinforced thermoset composites account for over 80 % of all of thermoset resins used. 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 [1, 2].

The interaction of polyesters with unsaturated compounds was firstly called the copolymerization reaction by Benig [3], 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 copolymerization with unsaturated polyester resins [3–5], when the matter of hydrophilic monomers lay over until recently, which opens up prospects for new «intelligent» polymers.

Poly(propylene glycol)fumarate (p-PGF), an amorphous unsaturated polyesters resin, has been extensively studied as an injectable biomaterial for bone tissue engineering utilizing particulate leaching to achieve a porous scaffold. p-PGF is biodegraded through hydrolysis of its ester bonds into its original propylene glycol and fumaric acid sub units, both of which are nontoxic. Propylene glycol is used as a food additive in the food industry and it can be metabolized or excreted by the body [6–9].

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 have previously synthesized a number of copolymers based on unsaturated polyester resins with some unsaturated carboxylic acids [10–12]. This paper demonstrates the first studies on the reactions of radical copolymerization of poly(propylene glycol)fumarate (p-PGF) with acrylic acid (AA).

Method

The initial p-PGF was obtained by the polycondensation reaction of fumaric acid and propylene glycol at a temperature of 403–453 K [13]. 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 molecular weight of the p-PGF 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 1488 amu.

Radical copolymerization of p-PGF 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 polymers synthesized were repeatedly washed with dioxane and dried under vacuum until constant mass for purifying them from unreacted monomer residues.

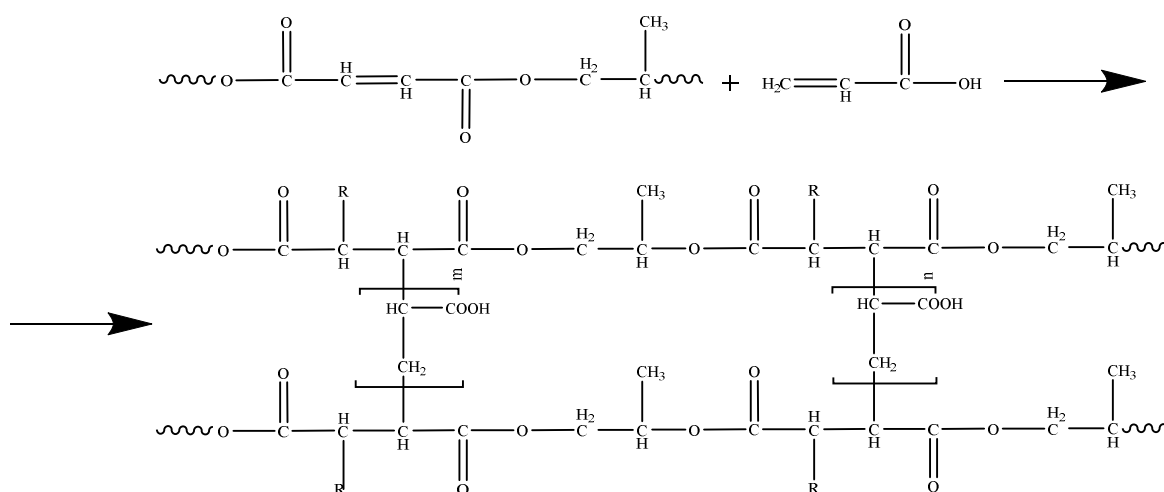
The compositions of the copolymers obtained were determined by potentiometric titration and by the residual amount of monomers by chromatography- mass spectrometry on Agilent 7890A using the Agilent 5975C mass selective detector.

The kinetics of radical copolymerization of p-PGF 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 [14], as well as the standard methods of Fineman-Ross and Kelen-Tüdös [15, 16].

Results and discussion

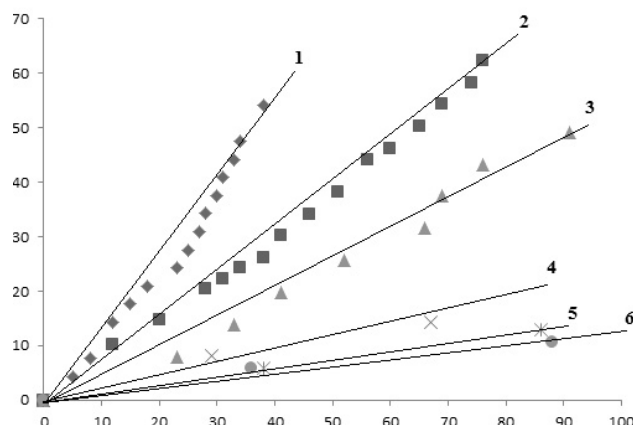
The intensive development of fundamental research in the field of radical copolymerization, which allows regulating the properties, structure and molecular mass of polymers, the velocity of the process, opens up new ways of obtaining polymers with properties given. Products based on unsaturated polyesters cured with vinyl monomers possessing specific physical-chemical and physical-mechanical properties are of considerable interest. The presence of unsaturated double bonds in the p-PGF 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-PGF is obtained by the polycondensation reaction of fumaric acid and propylene glycol. As a result of radical copolymerization of the oligomeric molecule of p-PGF 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 (Fig. 1).

However, more complete information on the relative reactivity of the monomers during copolymerization can be obtained on the basis of kinetic data (Fig. 1).



1 — 9.98:90.02; 2 — 15.04:84.96; 3 — 24.92:75.08; 4 — 50.06:49.94; 5 — 75.25:24.75; 6 — 90.13:9.87 mol.%

Figure 1. Kinetic curve of the copolymerization of p-PGF:AA

The kinetics of radical copolymerization of p-PGF with AA at various initial molar ratios was studied in detail to assess the relative activity of the monomers (Fig. 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-PGF content in the reaction mixture. This is apparently due to the presence of a functional $-\text{COOH}$ carboxyl group in the AA chain that capable of participating in elementary polymer transfer 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-PGF 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-PGF-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-PGF (M_1) with AA (M_2) [BP] = 8 mol/m³, T = 333 K

The initial ratio of monomers, mass. %		Copolymer composition, mass. %		Yield, %
M_1	M_2	m_1	m_2	
9.98	90.02	7.23	92.77	84.23
15.04	84.96	10.85	89.15	82.84
24.92	75.08	20.45	79.55	78.41
50.06	49.94	46.89	53.11	74.98
75.25	24.75	72.36	27.67	69.55
90.13	9.87	89.05	10.95	65.45

Enrichment of the p-PGF-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-PGF 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 (Fig. 2).

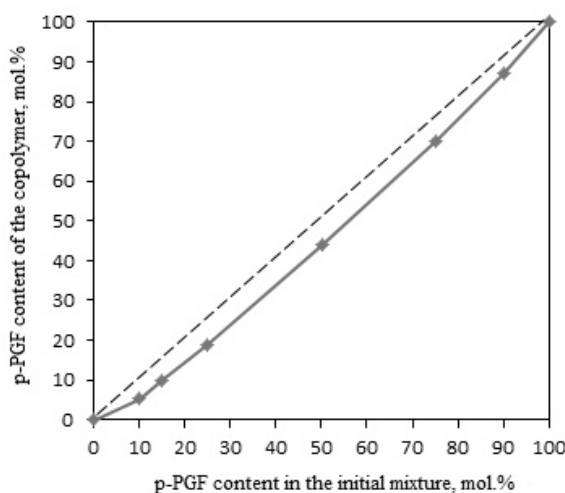


Figure 2. The dependence of the p-PGF-AA copolymers composition on the composition of the initial monomer mixture

The relative activities of the comonomers were calculated using the integral Mayo-Lewis equation [9], the standard Fineman-Ross and Kelen-Tüdös 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 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-PGF-AA system that is less than one. It may indicate more activity of macroradical ending in the p-PGF 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.

Table 2

Constants and parameters of radical copolymerization of p-PGF-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	0.75	1.18	0.89	1.33	0.85	0.42	0.74	0.77	1.15
Fineman-Ross	0.82	1.21	0.99	1.22	0.83	0.68	0.89	0.77	1.15
Kelen-Tüdös	0.78	1.28	1.00	1.28	0.78	0.73	0.87	0.77	1.15
Average	0.78	1.22	0.96	1.28	0.82	0.61	0.83	0.77	1.15

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 Alfrey and Price equations based on the values of copolymerization constants. Both p-PGF and AA monomers have different polarities of the double bond (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-PGF. This determines the high propensity of monomers and radicals ending in the p-PGF units to attach more «foreign» monomers under the polymerization conditions.

Conclusions

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(propylene glycol)fumarate and acrylic acid. The results obtained demonstrate the ability to control the physical-chemical properties of the copolymers based on poly(propylene 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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Полипропиленгликольфумараттың акрил қышқылымен радикалдық сополимерленудің константалары мен параметрлері

Мақалада алғаш рет диоксан ортасында бастапқы мономер қоспасының әртүрлі мольдік қатынасында полипропиленгликольфумараттың акрил қышқылымен бинарлы радикалды сополимерленуі зерттелген. Сополимерлену реакциясының кинетикасы анықталды. Кинетикалық қисықтар ерітіндідегі акрил қышқылының мольдік мөлшерінің 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 есептеледі. Акрил қышқылының полипропиленгликольфумаратпен сополимерлену кезінде соңғысының төмен реактивтілікпен сипатталатыны анықталды. п-ПГФ-АҚ жүйесіндегі r_1 салыстырмалы белсенділігі бірден аз. Бұл п-ПГФ басқа мономерлермен сополимерленуге қабілеті, гомополимерленуге қарағанда, жоғары екендігін көрсетеді. Сополимерлердің қанықпағандығы бастапқы мономер қоспасы құрамындағы полиэтиленгликольфумараттың мөлшеріне тура пропорционалды екендігі көрсетілді. Осылайша, зерттеудің нәтижелері п-ПГФ негізіндегі

синтезделген полимерлер жаксы касиеттерге ие және ғылымның әртүрлі салаларында қолданылуы мүмкін.

Кілт сөздер: қанықпаған полиэфирлі шайырлар, полипропиленгликольфумарат, акрил қышқылы, сополимерлену константалары, мономерлер белсенділігі, кинетика, сорбция, сополимерлену.

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Константы и параметры радикальной сополимеризации полипропиленгликольфумарата с акриловой кислотой

В статье впервые исследована бинарная радикальная сополимеризация полипропиленгликольфумарата 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-масс-спектрологии определен состав синтезированных сополимеров. Интегральным методом Майо-Льюиса, Файнмана-Росса и Келена-Тьюдоша рассчитаны константы и параметры радикальной сополимеризации. На основании констант сополимеризации по уравнению Алфрей-Прайса рассчитаны параметры $Q-e$. Установлено, что при сополимеризации акриловой кислоты с полипропиленгликольфумаратом последний характеризуется меньшей реакционной способностью. Относительная активность r_1 в системе п-ПГФ-АК меньше единицы. Это говорит о том, что способность п-ПГФ к сополимеризации с другими мономерами выше, чем к гомополимеризации. Показано, что степень ненасыщенности сополимеров прямо пропорциональна содержанию полипропиленгликольфумарата в составе исходной мономерной смеси. Таким образом, результаты этого исследования показали, что синтезированные полимеры на основе п-ПГФ имеют хорошие характеристики и могут быть использованы в различных областях науки.

Ключевые слова: ненасыщенные полиэфирные смолы, полипропиленгликольфумарат, акриловая кислота, константы сополимеризации, активность мономеров, кинетика, сорбция, сополимеризация.

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