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Poly(propylene fumarate phthalate) and acrylic acid radical copolymerization constants and parameters

Poly(propylene fumarate phthalate) and acrylic acid radical copolymerization in dioxane solution at various molecular ratios of original monomeric mixture was studied in this work for the first time. An unsaturated polyester resin was obtained using the polycondensation reaction. The composition of the obtained poly(propylene fumarate phthalate) was determined according to elemental analysis. The studied copolymers are promising for further study due to their swelling ability, antioxidant activity, and biodegradable ability. Copolymerization reaction kinetics has been studied. The composition of the copolymers was determined using chromate-mass spectrometry. Radical copolymerization constants and parameters have been calculated by Mayo-Lewis integral method. Based on the copolymerization constants the Q-e parameters was calculated according to the Alfrey-Price equation. It was proved that non-solvable polymers of a net-shaped structure are formed in the whole range of the researched comonomer ratios during the radical copolymerization of p-PFF with AA. Based on the results presented in the article, we can say that all copolymer compounds based on poly(propylene fumarate phthalate) and acrylic acid demonstrate the ability to control physical and chemical properties. This in turn will allow to create new materials with a pre-defined behavior program. It was found that the unsaturated polyester resin is characterized by a lower reactivity in case of acrylic acid and poly(propylene fumarate phthalate) copolymerization.

Keywords: poly(propylene fumarate phthalate), acrylic acid, biodegradable, polycondensation, radical copolymerization, kinetics, copolymerization.

Introduction

Over the past few decades fumaric acid-based polyesters comprising Krebs cycle [1, 2] are of much interest in biomedicine due to great biocompatibility and biodegradability [3, 4]. Moreover, polyester resins are relatively cheap products, which in some cases makes materials based on them competitive comparing to other sorts of plastics [5–8].

Poly(propylene fumarate phthalate) is the most researched material among the. It is a perfect option for cross-linking with various monomers, such as acrylic and methacrylic acid.

Cross-linked poly(propylene fumarate phthalate) can satisfy a number of medical requirements, such as biocompatibility, osteoconductivity, sterilisability and manageability [9–14]. It can be polymerized in situ [15] forming solid composite with mechanical properties identical to those of spongeous bone.

In this regard, the poly(propylene fumarate phthalate) (p-PFP) and acrylic acid (AA) copolymerization constants and parameters determination, as well as the development of new methods for vinyl monomers radical polymerization control and polymer characteristics improvement are one of research priorities for high-molecular compounds chemistry development.

External factors sensitive copolymers were previously synthesized by reaction of polyglycolefumarates radical copolymerization with various unsaturated carboxylic acids and dimethylaminoethyl metacrylate [16–21]. Due to this fact, further research in this area appeared to be advantageous.

Reactions of poly(propylene fumarate phthalate)(p-PFP) and acrylic acid (AA) radical copolymerization were studied in this work for the first time.

Experimental

Initial p-PFP was received by fumaric acid, phthalic anhydride and propylene glycol polycondensation at temperatures 423–453 К [22, 23]. The reaction was monitored by determining the acid number and the amount of water emission. The synthesized polyester is a light yellow fusible resinous substance that can dissolve in chloroform and dioxane. Received resin was obtained from original monomers by multiple acetone washing. Received substance content was defined by elemental analysis data.

P-PFP molecular weight was determined by light scattering method at NACH 2100 AN nephelometer and by gel-permeation chromatography, which is 2272 and 2394 atomic mass units.

P-PFP and AA radical copolymerization was performed in solution of dioxane at different original copolymer molecular ratios with benzoyl peroxide (BP) as initiating agent at 333 K. Synthesized polymers were washed by dioxane and dried in vacuum multiple times in order to refine them from remaining unreacted monomers until reaching constant weight.

Contents of received copolymers were defined with potentiometric titration and by a highly efficient chromatograph LC-20 Prominence, Shimadzu (Japan) [24, 25]. In order to find amount of copolymers unreacted double bonds (degree of unsaturation) bromide-bromate method was used [26].

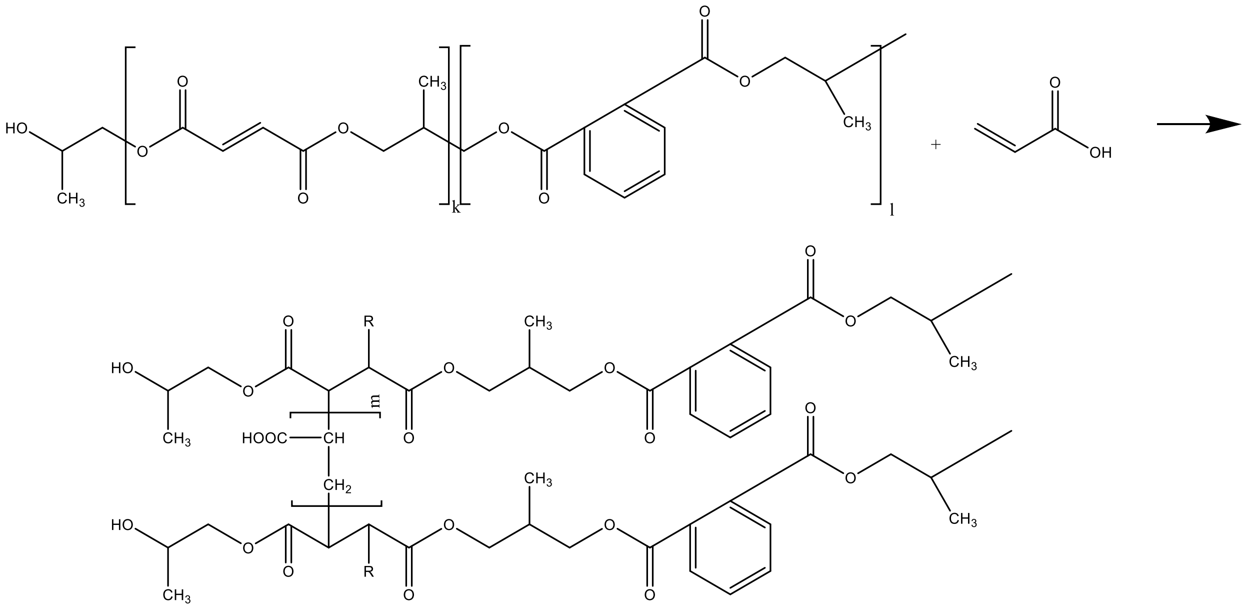
P-PFP and AA radical copolymerization kinetics was investigated by dilatometric method in dioxane. Constants of copolymerization r_1 and r_2 were defined based on contents of copolymers received at deep conversion using Mayo-Lewis integral equation [27].

Results and Discussion

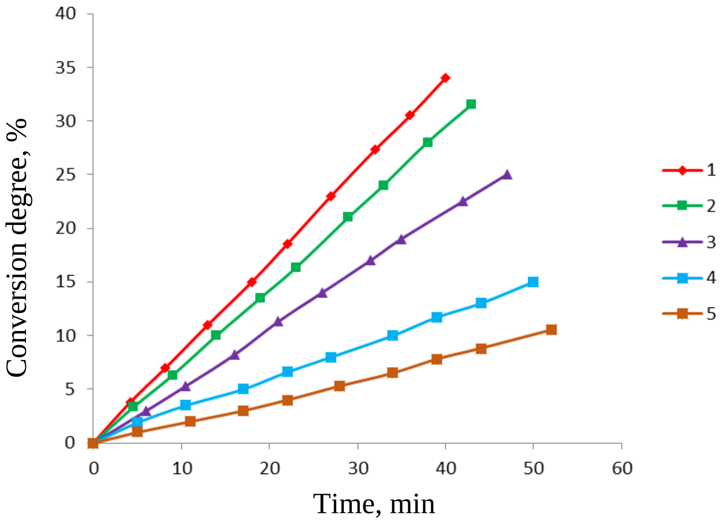
Elaborate development of thorough research in the area of radical copolymerization allows controlling properties of polymers, their structure and molecular mass, and also suggests more methods for producing polymers with the desired properties. As mentioned above, unsaturated polyesters-based products cured with vinyl monomers and having specific physico-chemical and mechanical properties are most desirable. Unsaturated double bonds in p-PFP molecules allow using it as polymeric matrix to receive cross-linked polymers in case of copolymerization with acrylic acid.

P-PFP was received by fumaric acid, phthalic anhydride and propylene glycol polycondensation [22, 23].

Cross-linked copolymer formation as result of p-PFP oligomeric molecule and AA radical copolymerization in presence of BP as initiating agent can be shown by the following diagram:



Copolymerization constant and parameters values are important characteristics when considering monomers relative reaction ability depending on their structure. However, more comprehensive information on monomers relative reaction ability at copolymerization can be obtained from kinetic data (Fig. 1).



1 — 6.77:93.23; *2* — 20.34:79.66; *3* — 44.17:55.17; *4* — 68.42:31.58; *5* — 86.67:13.33 mol.%

Figure 1. p-PFP:AA copolymerization kinetic graph

P-PFP and AA radical copolymerization kinetics at various initial molecular ratios was studied deeply in order to estimate monomers relative activity (Fig. 1). It was found that the reaction rate and copolymer yield increase with increasing AA content in the initial monomer mixture. However, these parameters decrease with increasing p-PFP in the reaction mixture. This seems to be determined by presence of –COO carboxyl functional group in acrylic acid chain, which can participate in reactions of polymer transfer followed by molecular mass growth due to branching processes. As can be seen in Figure 1, the radical copolymerization kinetics data indicate a constant process acceleration in the case of AA molecular mass increase in initial monomeric mixture.

As mentioned above, cross-linked insoluble polymers are formed throughout the range of studied copolymer ratios in process of p-PFP and AA radical copolymerization.

Experimental data received after studying radical copolymerization processes in p-PFP – AA systems are shown in Table 1. Copolymer yield ranges from 83 % to 62 %.

Table 1

Copolymer content dependence on initial mixture composition **in process of p-PFP (M_1) and AA (M_2) [BP] = 8·10^{-3} mole/m^3, T = 333 K**

Initial monomer ratio, % by mass		Copolymer content, % by mass		Yield, %
M_1	M_2	m_1	m_2	
10.22	89.78	6.77	93.23	83.70
25.00	75.00	20.34	79.66	78.73
50.00	50.00	44.17	55.17	79.33
73.91	26.09	68.42	31.58	71.93
90.00	10.00	86.67	13.33	62.09

As can be seen in Table 1, p-PFP-AA copolymers are enriched with AA components throughout the range of initial mixtures. At that, the proportion of AA components in the copolymer composition increases symbolically with respect to their content in initial monomeric mixture.

Copolymer yield and swelling rating increase as share in original AA mixture rises; this seems to be determined by high degree of branching and cross-linking.

The branching and cross-linking reactions decrease correspondingly with AA molecular concentration reducsing since benzene rings cannot participate in homopolymerization reactions. While the copolymer unsaturation degree increases. Besides, the abovementioned reactions are more complicated when p-PFP concentration rises in initial monomeric mixture, which leads to higher viscosity.

Copolymer content dependence on initial mixture composition can be shown more conveniently on content diagram (Fig. 2).

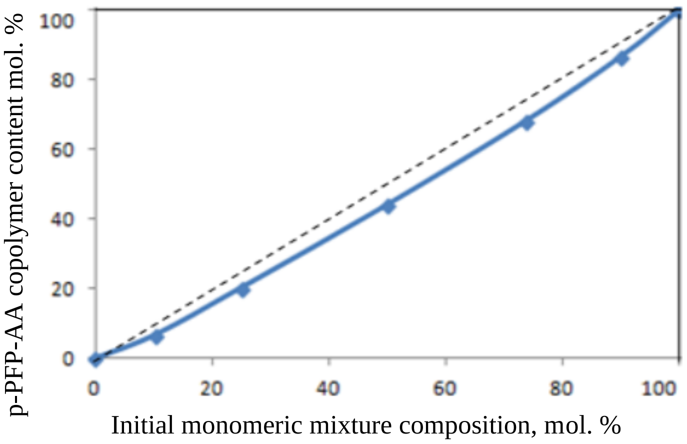


Figure 2. Composition diagram showing p-PFP – AA copolymer content dependence on initial monomeric mixture composition

Copolymer relative activity based on copolymer content and initial monomeric mixture composition has been calculated using Mayo-Lewis integral equation [9], Fineman-Ross and Kelen-Tudos standard methods. Table 2 shows the calculated data that illustrate the higher AA activity in the process of radical copolymerization.

Table 2

p-PFP – AA binary systems radical copolymerization constants and parameters

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-PFP	AA	0,76	1,21	0,92	1,32	0,83	1,19	1,06	1,15	0,77

As can be seen in Table 2, the relative activity value r_1 in p-PFP-AA system is below one ($r_1<1$). This suggests a higher activity of macroradical ending with p-PFP component towards «outer» monomer or radicals, but macroradical ending with AA second co-monomer component tends to react with «inner» monomer. Copolymerization stabilizer derivatives are close to each other, i.e. copolymer macroradicals can be created by static structures.

Conclusions

Therefore, a brief summary of the studies described in this article shows that new crosslinked polymers can be obtained by poly(propylene fumarate phthalate) and acrylic acid radical copolymerization.

The obtained result demonstrates the ability to control the physicochemical properties of a poly(propylene fumarate phthalate) and acrylic acid based copolymer by changing the content of the polymer composition, which allows you to create new materials with preset properties.

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Полипропиленфумаратфталатты акрил қышқылымен радикалды сополимерлеудің константалары мен параметрлері

Мақалада алғаш рет полипропиленфумаратфталаттың бастапқы мономерлік қоспаның түрлі мольдық қатынасында диоксан ортасында акрил қышқылымен бинарлы радикалды сополимерленуі зерттелген. Поликонденсация реакциясымен қанықпаған полиэфирлі шайыр алынды. Сополимерлену үрдісінің кинетикасы зерттелді. Хромато-масс спектроскопия әдісін қолдану арқылы синтезделген сополимерлердің құрамы нақтыланған. Майо-Льюистің интегралдық әдісімен радикалды сополимерлену константалары мен параметрлері анықталған. Алфрей-Прайс теңдеуі бойынша сополимерлену константасының негізінде Q-e параметрлері есептелген. п-ПФФ пен АҚ радикалды сополимерлеу кезінде сомономерлердің зерттелген ара қатынасының барлық интервалында торлы құрылымның ерімейтін полимерлері түзілетіндігі дәлелденді. Мақалада келтірілген нәтижелер бойынша полипропиленфумарат пен акрил қышқылы негізіндегі сополимерлердің барлық қосылыстары физика-химиялық қасиеттерді басқару мүмкіндігін көрсетеді деп айтуға болады. Бұл өз кезегінде алдын ала берілген бағдарлама тәртібі бойынша жаңа материалдарды жасауға мүмкіндік береді. Акрил қышқылын полипропиленфумаратфталатпен сополимерлеу кезінде қанықпаған полиэфир шайыры аз реакциялық қабілеттілікпен сипатталған.

Кілт сөздер: полипропиленфумаратфталат, акрил қышқылы, биоыдырағыштық, поликонденсация, радикалды сополимерлену, кинетика, сополимерлену.

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Константы и параметры радикальной сополимеризации полипропиленфумаратфталата с акриловой кислотой

В статье впервые исследована бинарная радикальная сополимеризация полипропиленфумаратфталата с акриловой кислотой в растворе диоксана при различных мольных соотношениях исходной мономерной смеси. Реакцией поликонденсации получена ненасыщенная полиэфирная смола. Состав полученного полипропиленфумаратфталата устанавливали по данным элементного анализа. Исследованные сополимеры перспективны для дальнейшего изучения их набухающей способности, антиоксидантной активности, биодеградируемой способности. Исследована кинетика реакции сополимеризации. Состав сополимеров определен с помощью хромато-масс-спектроскопии. Параметры радикальной сополимеризации и константы рассчитаны интегральным методом Майо-Льюиса. Параметры Q-e рассчитаны на основании констант сополимеразации по уравнению Алфрея-Прайса. Было доказано, что нерастворимые полимеры сетчатой структуры во всем интервале исследованных соотношений сомономеров образуются при радикальной сополимеризации п-ПФФ с АК. По приведенным в статье результатам можно заключить, что все соединения сополимеров на основе полипропиленфумаратфталата и акриловой кислоты демонстрируют возможности управления физико-химическими свойствами. Это, в свою очередь, позволит создать новые материалы с заранее заданной программой поведения. Установлено, что при сополимеризации полипропиленфумаратфталата с акриловой кислотой ненасыщенная полиэфирная смола характеризуется меньшей реакционной способностью.

Ключевые слова: полипропиленфумаратфталат, биодеградируемость, акриловая кислота, поликонденсация, радикальная сополимеризация, кинетика, сополимеризация.

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