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Influence of the RAFT Agent on the Reaction Direction of the Copolymerization of Polypropylene Glycol Maleate with Acrylic Acid

This work demonstrates the capability of synthesizing new polymers based on unsaturated polyester and acrylic acid in the presence of a chain-transfer agent in a dioxane solution. The initial unsaturated polyester resin was derived from the polycondensation reaction of alcohol and maleic anhydride. The molecular weight of the polypropylene glycol maleate was determined by gel permeation chromatography. The dependence of the structure, network density and product yield on the concentration of the RAFT agent was proven. It was found that the greater the amount of chain-transfer agent in the monomer mixture, the lower the yield of the crosslinked polymer and the greater the yield of the branched copolymer. The composition of the studied copolymers was determined by FTIR spectroscopy in conjunction with the chemometric method of partial list squares in the R environment. The synthesized objects were characterized by infrared spectroscopy methods and were approximated by Gaussian contours. The study results show that the RAFT agent concentration, as well as the initial ratio of monomers in the copolymer affects the products yield. The surface topography of the studied copolymers was recorded by scanning electron microscopy. The molecular chain structure of the branched copolymers was confirmed by NMR spectroscopy.

Keywords: unsaturated polyester, polypropylene glycol maleate, acrylic acid, RAFT-polymerization.

Introduction

Currently the interest of researchers is directed to the search for new materials for the synthesis of polymers with desired properties and controlled characteristics [1, 2]. From this point of view, unsaturated polyester resins based on polypropylene glycol maleate and acrylic acid are interesting objects for theoretical and practical research, since they have been used in the production of smart systems with a wide range of applications [3, 4].

Due to the presence of a reactive double bond in the composition, unsaturated polyester resins easily enter into a copolymerization reaction with ionic monomers, forming cross-linked copolymers with a random network arrangement. As practice shows, this is because radical polymerization has limitations in terms of the degree of control over the molar mass distribution, copolymer composition, and macromolecular architecture [5].

In this regard, the attention of researchers is attracted by new effective polymers that provide unlimited possibilities for controlling their properties under conditions of reversible chain transfer by the addition–fragmentation mechanism (RAFT) [6]. The RAFT agent influence on the radical polymerization process is due to a change in the course of the reaction of bimolecular chain termination through its interaction with the growing macroradical and transition to a dormant state up to a certain point. There is a possibility of further chain growth under certain conditions, when a radical removal from the latter is possible and, thus, a stepwise growth of a macromolecule is formed, and an impression of a "pseudo-living" radical polymerization is created [7–9]. Such behavior of the polymerizing system is used to obtain polymers with a narrow molecular weight distribution, as well as block copolymers and graft copolymers [10, 11].

Previously, we established the possibility of synthesizing [12] and studying the properties [13] of new RAFT polymers based on polypropylene glycol maleate with acrylic acid. These results showed that the concentration of the chain-transfer agent affected the network density and also led to the formation of a soluble branched polymer. The obtained results demonstrate that work in this direction is promising in terms of obtaining new "smart" systems with desired properties.

However, for the purpose of a comprehensive in-depth study of the obtained materials it seemed interesting to continue research in this direction and follow the reaction course of radical copolymerization of polypropylene glycol maleate with acrylic acid in the RAFT agent presence. It was promising to establish the regularity and feature of RAFT-polymerization, calculate the composition and also study the density of the spatial network of the obtained copolymers.

Experimental

There were used the following reagents in this work: propylene glycol, maleic anhydride, acrylic acid (AA), benzoyl peroxide, zinc chloride, 1,4-dioxane, RAFT-agent (2-Cyano-2-propyl dodecyl trithiocarbonate CPDT) from Sigma-Aldrich.

Polypropylene glycol maleate (p-PGM) was derived from the polycondensation reaction of propylene glycol and maleic anhydride at a temperature of 433–443 K. The polycondensation was carried out according to the standard procedure [14] in the presence of a zinc chloride catalyst in a nitrogen flow to avoid gelatinization. Polycondensation was carried out for 16 hours. The molecular weight of the synthesized p-PGM was determined by gel permeation chromatography (GPC).

Radical copolymerization of p-PGM with AA (10:90 mol %) was carried out in a dioxane solution (1:1 by mass) in the presence of benzoyl peroxide (PB) as an initiating agent at 333 K. After purging with an inert gas for 30 minutes, the radical copolymerization was carried out for 52 hours. The resulting copolymers were repeatedly washed with dioxane and dried to a constant weight in a vacuum drying oven.

RAFT polymerization of p-PGM-AA was carried out in a dioxane solution with the addition of the RAFT agent. Monomer solutions were poured into ampoules, degassed in a vacuum unit, and then sealed; the ampoules were placed in a thermostat, in which the temperature was maintained with an accuracy of ±0.10C for 52 hours. After a period of time, the ampoules were cooled and opened. The products obtained as a result of the reaction were divided quantitatively: the cross-linked polymers were filtered from the mother liquor and sent to dry in a vacuum oven until a constant weight was established. Branched polymers were precipitated from the mother liquor in alcohol.

The structural parameters of the molecular chain of branched p-PGM-AA-CPDT copolymers and the initial p-PGM oligomer were determined through ^{1}H-NMR spectroscopy in deuterated $CDCl_3$ using a JNM-ECA Jeol 400 NMR spectrometer.

The composition of the derived polymers was determined by HPLC on a Shimadzu (Japan) chromatograph by the amount of unreacted monomers, as well as by IR spectroscopy.

Fourier-transform infrared spectra of the copolymerization products were recorded on an FSM 1201. For complete reliability of the obtained data, the IR spectra of the reaction products were recorded in a KBr tablet, absorption spectra were recorded in the range of 450–4000 cm^{-1}.

The surface topography of the samples was carried out on a MIRA3 scanning electron microscope (TESCAN, Czech Republic).

The swelling behavior of the copolymers was identified gravimetrically by the formula:

$$\alpha(\%) = \frac{m_1 - m_0}{m_0} \times 100,$$

where, m_1 and m_0 are the masses of swollen and dry copolymer, respectively.

Results and Discussion

In our previous studies [12], the use of controlled radical polymerization in the presence of RAFT agents made it possible to obtain polymer matrices with a less rigid structure, capable of sorbing a significantly larger volume of water, as well as to obtain branched copolymers. Thus, in continuation of these works, this article studied the effect of RAFT agent concentrations on the direction of the copolymerization reaction of polypropylene glycol maleate (p-PGM) with acrylic acid (AA) at a molar ratio of 10:90. Table 1 illustrates the calculated data for copolymerization with the addition of a RAFT agent.

According to Table 1, the copolymerization of p-PGM with AA yields two products, branched and cross-linked copolymers. It is established that the higher the concentration of the RAFT agent contained in the monomer mixture, the greater the yield of branched copolymers. It should be noted that the yield of network copolymers is higher than in the case in the ratio of 50:50 [13]. Also, with an increase in the amount of chain transfer agent, the degree of swelling of network copolymers increases, which is associated with a decrease in network density.

Table 1

Radical copolymerization of polypropylene glycol maleate with acrylic acid in a dioxane solution in the presence of a RAFT agent. [M1]:[M2] = 9.9: 90.1 mol %, T = 343 K, [PB] = $8 \cdot 10^{-3}$ mol/l

[RAFT], mM	Cross- linked Copolymer			Branched copolymer	
	Yield, %	$[m_1]:[m_2]$ Mol, %	Swelling, α, %	Yield, %	$[m_1]:[m_2]$ Mol, %
–	97.16	10.74:89.26	109.14	–	–
10.01	93.15	10.43:89.57	133.18	3.46	5.5:94.5
30.03	91.02	10.61:89.39	156.21	5.23	8.33:91.67
50.01	81.81	10.78:89.22	191.13	13.70	7.9:92.1
80.02	74.23	9.80:90.20	204.18	20.59	9.67:90.33

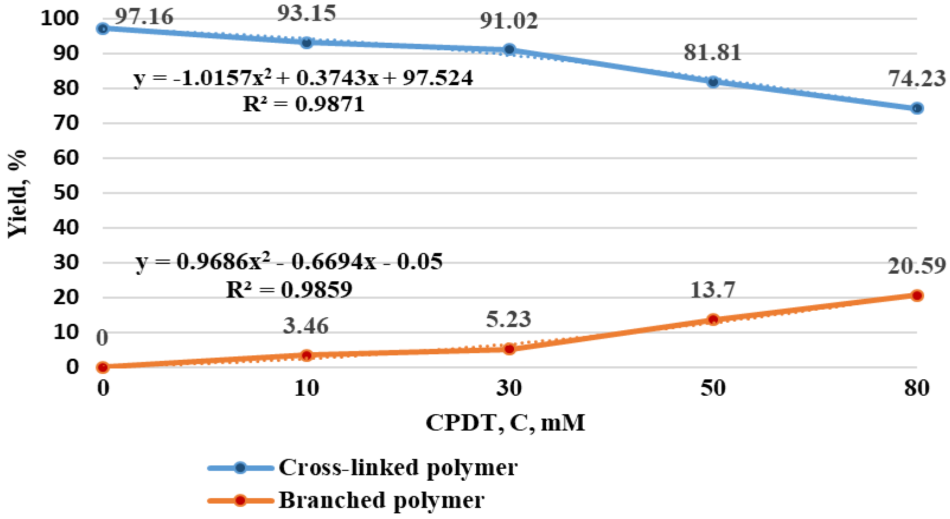


Figure 1. Dependence of the RAFT agent concentration on the polymer yield

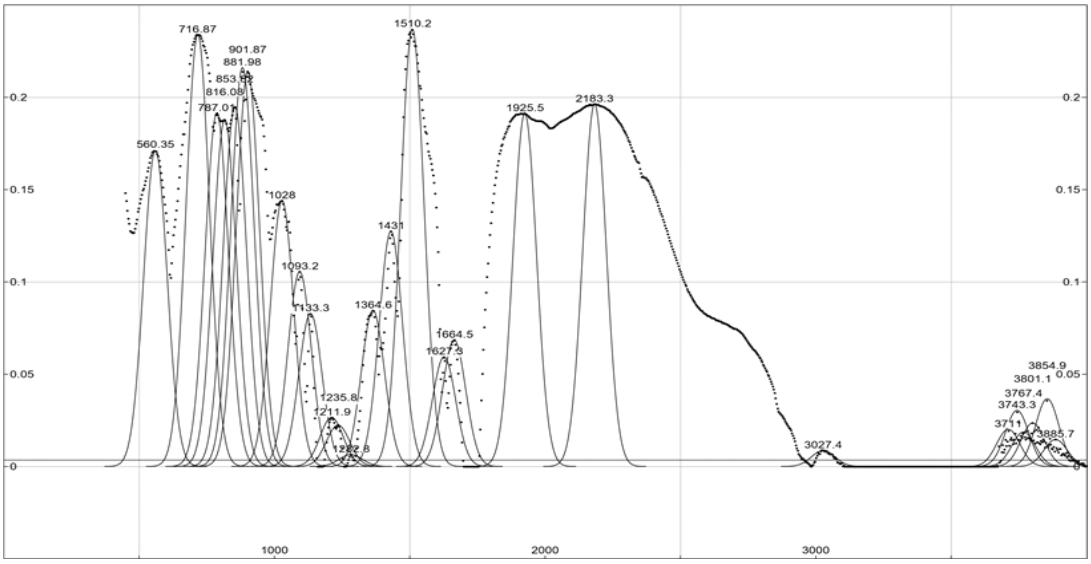
From Figure 1 it can be seen that the dependence of the products yield is polynomial of the second order.

The mass ratio of polyacrylic acid units and polypropylene glycol maleate units in the synthesized objects was determined by FTIR spectroscopy in compatibility with the chemometric method of partial list squares [15] performed in the R environment [16, 17]. Mixtures of p-AA and p-PGM were prepared for the calibration spectrum. A homopolymer mixture with compositions of 1.0, 3.0, 5.0, 7.0, 9.0, and 10.0 % p-AA and p-PGM was ground to 100 % for a long time in a mechanical agate mortar together with potassium chloride. To achieve the ultimate accuracy of the IR spectra in three repeated samples, abrasion was carried out for 30 minutes.

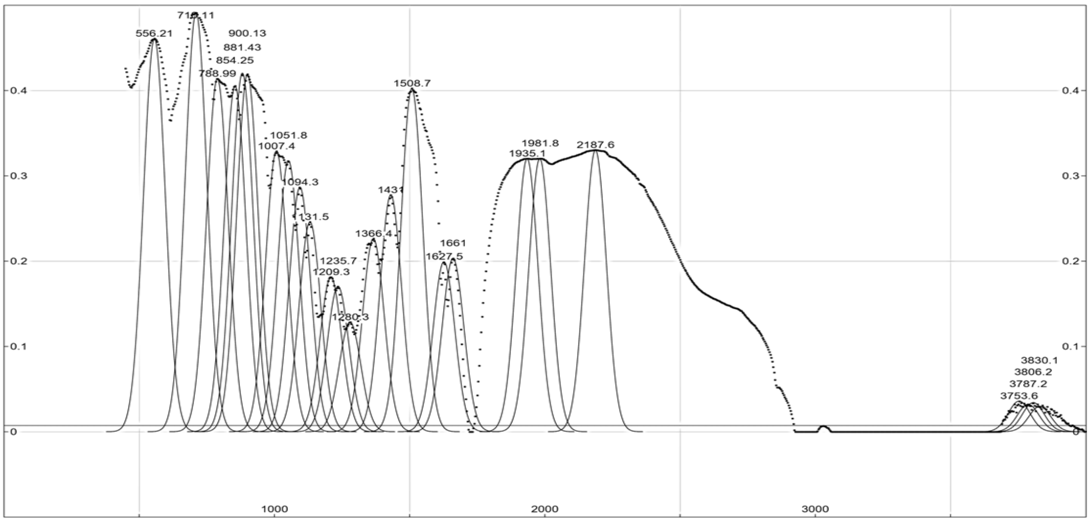
The sample preparation of the synthesized copolymers was carried out in a similar way. Three tablets were prepared from a carefully homogenized mixture. The infrared spectra of tablets containing 4.0 mg of polymers in 300.0 mg of KBr were recorded in the range of 450...4000 cm^{-1}. The data from the spectra were entered into the R environment for the next mathematical processing. Model training with cross-validation was performed on averaged samples. To calculate the mass fraction of polyacrylic acid units in polymers (Table 1) for three parallel samples, the Student's coefficient was taken into account with a confidence level p=0.95. The obtained mass values were converted to molar ratios.

Figure 2 shows the IR spectra of p-PGM-AA and p-PGM-AA-CPDT copolymers.

The IR spectra of the copolymers show (Fig. 2 *a*) absorption bands in the region of 787 cm^{-1} attributed to CH_2- bonds and bands in the region of 1133 cm^{-1}indicating the presence of –C–O–C– ester bonds. The spectrum exhibits a pronounced peak in the region of 1282 cm^{-1}, which is responsible for the –C=C–moiety of the polyester group. Further, the presence of signals at 1627 cm^{-1} and 3027 cm^{-1} indicates C=O bonds of the –COOH group and symmetrically located –CH bonds in CH_2, respectively. It is worth noting the signal in the region of 3711 cm^{-1} indicating the presence of –OH groups.



(*a*)



(*b*)

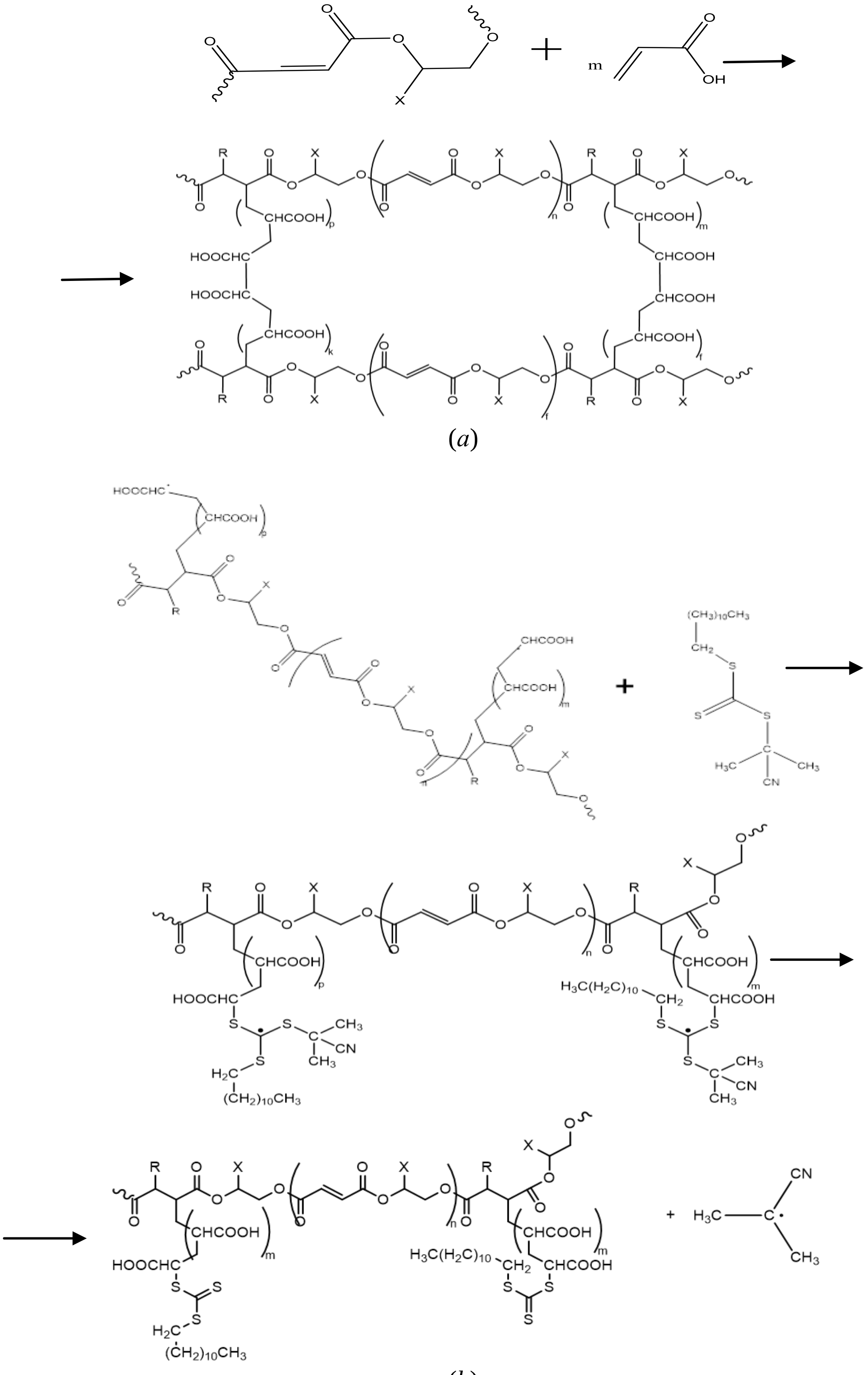
Figure 2. The IR spectra of p-PGM-AA (*a*) and p-PGM-AA-[CPDT] = 80mM (*b*)

Further, the IR spectra of RAFT polymers, namely p-PGM-AA-CPDT (Fig. 2*b*) were obtained. There was a signal in the region of 3753 cm^{-1}, which was characteristic of hydroxyl groups. An absorption band in the region of 3787 cm^{-1} was attributed to the =C–H bonds of the aromatic compound and a weak band in the region of 2187 cm^{-1} was due to C–H groups of the aliphatic compound.

An analysis of the IR spectra showed that the p-PGM–AA molecular chain contained –COOH and $–CH_2$ groups, which served as transverse bridges in the formation of the cross-linked structure of copolymers. Thus, the mechanism of the copolymerization reaction of p-PGM with AA in the presence of benzoyl peroxide initiator can proceed according to the following scheme shown in Figure 3.

Figure 3(*b*) shows the formation of branched copolymers by reducing bimolecular chain terminations with the help of adding a RAFT agent.

In order to identify branched polymers, their NMR spectra were obtained. In the spectrum, signals of maleic groups and groups characteristic of p-PGM are observed, which are similar to the data of the initial oligomer (Fig. 4). The ^{1}H NMR spectrum of p-PGM-AA-CPDT shows a broad signal in the region of 1.13-1.28 ppm that corresponds to the $-CH_2$ protons of the Hb groups, which are closer to oxygen. Two multiplet signals in the region of 4.01-4.27 and 3.64 ppm point to the protons of simple and ester methine as well as methylene groups of the aliphatic hydrocarbon Hc and Hd. Multiplet signals at 5.02-5.22 and high-intensity multiplet at 6.78-6.82 ppm are assigned to the −CH=CH− proton of the He group.



(*a*)

(*b*)

Figure 3. Schematic structure of p-PGM-AA (a), p-PGM-AA-CPDT (b)

In the ^{13}C NMR spectrum of the copolymer Ca and Cb signals at 16.35 ppm correspond to methyl and methylene carbon atoms. Signals of alkyl groups, Cc and Cd, located next to simple and complex ether groups are in the region of 66.67 and 69.22 ppm. Signals with a chemical shift of 133.83 ppm indicate ethylene carbon atoms, namely Ce. The carbon atoms of −COOH groups and C=O fragments appear at 134.09 ppm.

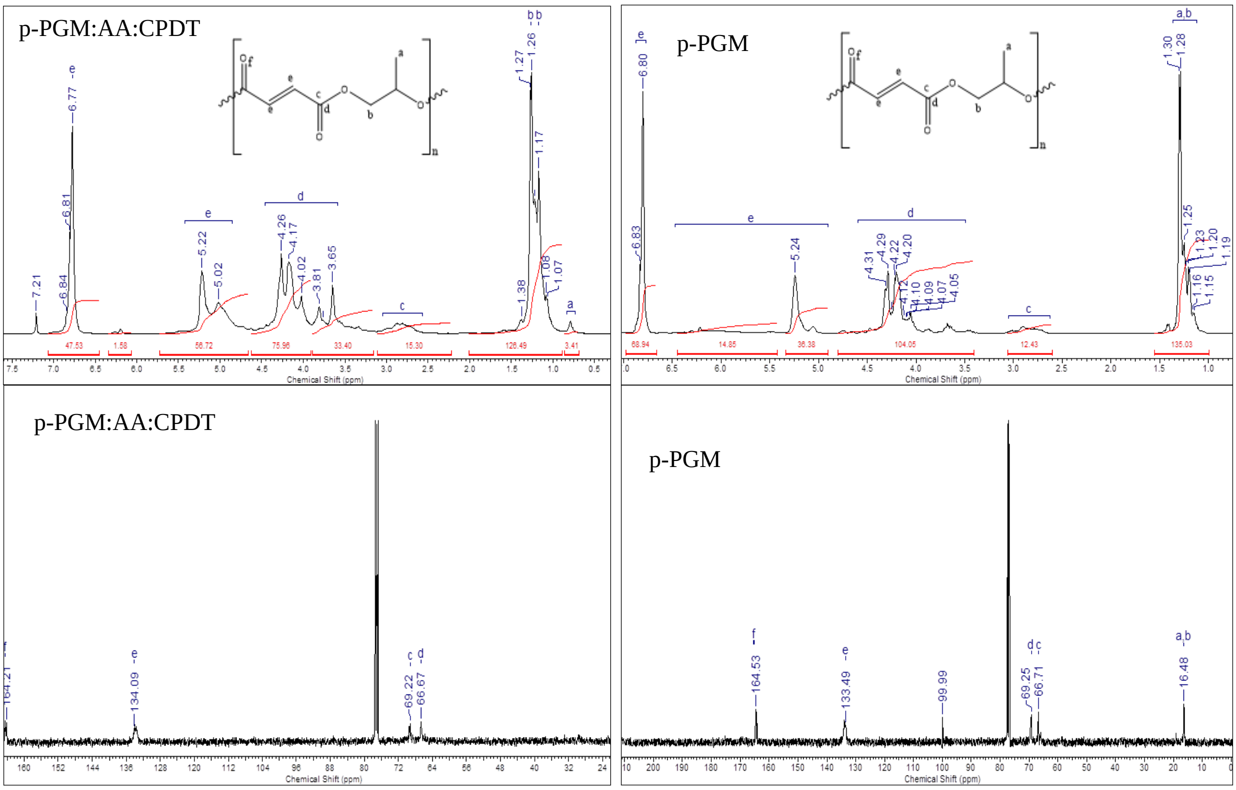
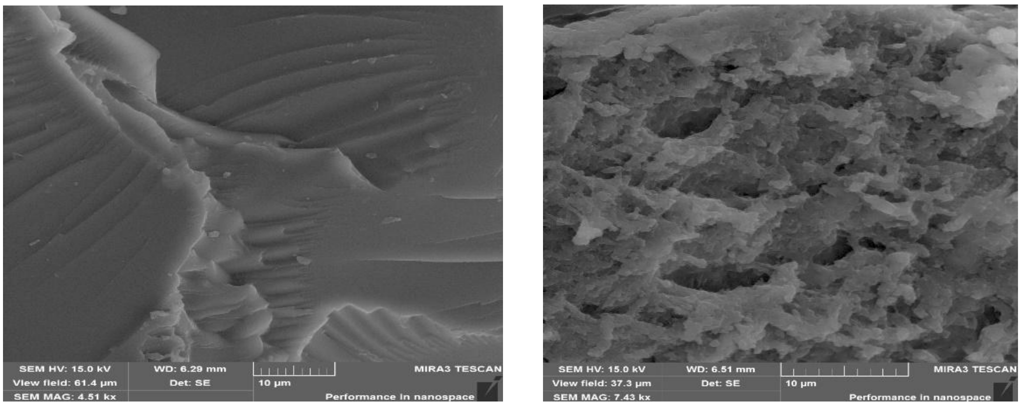


Figure 4. NMR spectra of p-PGM:AA:[CPDT] = 80 mM and p-PGM copolymers

In continuation of the study, the surface topography of the copolymers was determined by SEM.

From Fig. 5(a), under a magnification of 2 nm, it is observed that the surface of the p-PGM-AA cross-linked copolymer particles (a) has brittle cleavages corresponding to solid objects.



(*a*) (*b*)

Figure 5. Surface morphology of p-PGM-AA polymer (*a*);
polymer surface morphology p-PGM-AA-[CPDT] = $80 \cdot 10^{-3}$ mM (*b*)

Micrographs of samples containing the RAFT agent p-PGM-AA-CPDT (b) show that the surface has a layered, loose structure with pores. The surface of RAFT polymers is softer and more airy compared to p-PGM-AA copolymers. The electron microscopy images confirm that an increase in the concentration of the chain transfer agent in the composition of the monomer mixture leads to an increase in pores in the network structure of the crosslinked copolymer.

Conclusions

As a result of the attempt to change the directions of the copolymerization reactions of polypropylene glycol maleate with acrylic acid, it was found that varying the amount of chain transfer agent allowed the reaction to be carried out in two directions, forming cross-linked and branched copolymers. Scanning electron microscopy showed that polymers containing a RAFT agent had a looser, airy surface with the formation of pores. It was established by the gravimetric method that the swelling ability of the obtained hydrogels containing CPDT in the composition of the monomer mixture at a molar ratio of 10:90 PGM and AA made it possible to obtain products with satisfactory sorbing properties.

Summarizing the above, it should be noted that the behavior of the synthesized copolymers during swelling directly depends on the amount of the RAFT agent included in the polymers composition. In addition, it can be concluded that the network construction and the products yield depend on the concentration of the RAFT agent, as well as on the comonomers, which prevents randomness in the structure. Thus, this method makes it possible to purposefully obtain copolymers with polyfunctional properties, which makes them promising hydrogels.

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RAFT-агентінің полипропиленгликольмалеинатының акрил қышқылымен сополимерлену реакциясының бағытына әсері

Мақалада қанықпаған полиэфир және акрил қышқылы негізінде диоксан ерітіндісіндегі тізбекті тасымалдаушы агенттің қатысуымен жаңа полимерлерді синтездеу мүмкіндігі көрсетілген. Бастапқы қанықпаған полиэфир шайыры спирт пен малеин ангидридінің поликонденсациялану реакциясынан алынған. Полипропиленгликольмалеинатының молекулалық салмағы гельді-өткізу хроматографиясы арқылы анықталған. Құрылымның, полимердің тығыздығының және өнім шығымының RAFT-агентінің концентрациясына тәуелділігі дәлелденді. Мономер қоспасында тізбекті тасымалдағыштың мөлшері неғұрлым көп болса, соғұрлым тігілген полимердің шығымы төмен, ал тармақталған сополимердің шығымы соғұрлым жоғары болатыны табылған. Зерттелетін сополимерлердің құрамы R ортасында ішінара ең кіші квадраттардың (Жартылай тізім квадраттары немесе жасырын құрылымдарға проекциялау) химометриялық әдісімен бірге FTIR-спектроскопия арқылы анықталған. Синтезделген объектілер инфрақызыл спектроскопиялық әдістермен сипатталды және Гаусс контурларымен жақындатылды. Осы зерттеу нәтижелері сополимердегі мономер буындарының қатынасы өнімдердің шығымына әсер ететінін көрсетеді. Зерттелген сополимерлер бетінің топографиясы сканерлеуші электронды микроскоп арқылы жазылды. Тармақталған сополимерлердің молекулалық тізбек құрылымы ЯМР спектроскопиясымен расталды.

Кілт сөздер: қанықпаған полиэфир, полипропиленгликольмалеинаты, акрил қышқылы, RAFT-полимерлеу.

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Влияние RAFT-агента на направление реакции сополимеризации полипропиленгликольмалеината с акриловой кислотой

В статье показана возможность синтеза новых полимеров на основе ненасыщенного полиэфира и акриловой кислоты в присутствии агента передачи цепи в растворе диоксана. Исходная ненасыщенная полиэфирная смола была получена реакцией поликонденсации спирта и малеинового ангидрида. Молекулярная масса полипропиленгликольмалеината определена с помощью гель-проникающей хроматографии. Доказана зависимость строения, плотности сетки и выхода продуктов от концентрации RAFT-агента. Установлено, что чем больше содержится агента передачи цепи в мономерной смеси, тем меньше выход сшитого полимера и больше выход разветвленного сополимера. Состав исследуемых сополимеров определен посредством FTIR-спектроскопии совместно с хемометрическим методом частичных наименьших квадратов (Partial List Squares or Projection to Latent Structures) в среде R. Синтезированные объекты охарактеризованы методами инфракрасной спектроскопии и были аппроксимированы контурами Гаусса. Результаты данного исследования показывают, что соотношение мономерных звеньев в сополимере влияет на выход продуктов. Топография поверхности исследуемых сополимеров зафиксирована посредством сканирующей электронной микроскопии. Структура молекулярной цепи разветвленных сополимеров подтверждена ЯМР-спектроскопией.

Ключевые слова: ненасыщенный полиэфир, полипропиленгликольмалеинат, акриловая кислота, RAFT-полимеризация.

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