

INFLUENCE OF EXTERNAL FACTORS ON BINARY SYSTEMS DURING RAFT POLYMERIZATION

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Abstract. The article discusses the method of radical copolymerization as an effective way to obtain new polymer compounds with practically valuable properties. Due to the relative simplicity of this method, it makes it possible to produce a large number of polymers for various purposes on an industrial scale. Unsaturated polyesters of various compositions and molecular weights, which can significantly affect the properties of the final products, are considered promising coreagents capable of entering into radical copolymerization reactions with vinyl monomers. The following describes the structure analysis of p-PGFPh copolymers with these acids, where important characteristics such as the presence of ionized units in vinyl monomers are discussed. The significance of these studies for the creation of materials with the necessary properties of sorption and interaction with other substances. Study of the influence of environmental pH on the behavior of copolymers based on polypropylene glycol fumarate phthalate with acrylic and methacrylic acids. The equilibrium degree of swelling of the studied copolymers in aqueous solutions at different temperatures was also determined by the gravimetric method. In general, analysis of the swelling curve when varying the acidity/alkalinity of the external solution indicates that the gels we synthesized are polyelectrolytes; analysis of the curve when exposed to temperature, the resulting copolymers are thermosensitive. Thus, the main idea of the article is the importance of using unsaturated carboxylic acids to create polymer gels with high sorption capacity and emphasizes the importance of analyzing the structure of such materials to understand their properties and application possibilities.

Key words: Unsaturated polyesters, vinyl monomers, influence of environmental. pH, behavior of copolymers

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1. Introduction

The radical copolymerization method is a polymer formation process proceeding in accordance with the conditions of the free radical mechanism, which is based on the sequential addition of molecules of an unsaturated monomer compound to a growing macroradical. By modeling the radical copolymerization process by using various initiators or replacing monomers with close analogues, it becomes possible to obtain new polymer compounds with a complex of practically valuable properties [1-3].

Due to the relative ease of formation of the polymer compound through radical copolymerization, this method makes it possible to obtain on an industrial scale more than half of all manufactured polymers for various purposes [4-7]. At the same time, one of the promising co-reagents capable of entering into radical copolymerization reactions with vinyl monomers to form solidified products is unsaturated polyesters of different composition and different molecular weight, which can have a significant effect on the property of the final products [8-9].

In [10-11] the authors described synthesis and research of copolymers of polypropylene glycol fumarate with vinyl monomers, which have a wide range of applications, in particular, as moisture burners for wastewater treatment. In this paper we have tried to study in more depth the degree of swelling to select optimal parameters for their further use as flocculants.

2. Experimental part

In order to determine the degree of swelling, weighed amounts (~ 0.3 g) of the synthesized copolymers were kept in distilled water for two weeks. The equilibrium degree of swelling of the obtained gels is determined by formula (1) [12]:

$$\alpha = \frac{m - m_0}{m_0} \quad (1)$$

where m – mass of swelling sample, g;
 m_0 – dry mass, g.

The degree of swelling of the copolymers was also determined under the influence of various external factors (pH variation of the medium, temperature). Thus, buffer solutions have a certain stability of the concentration of H⁺ ions. The level of acidity (pH) of such solutions remains practically unchanged when small volumes of strong acids or bases are added to them, as well as when their initial concentration is changed by dilution or, conversely, concentration. Buffer systems include a solution of a weak acid or salt thereof which is a proton donor and an acid-conjugated weak base or salt thereof which is a hydrogen ion acceptor.

Used for the present analysis of the effect of varying the pH values of the medium on the behavior of copolymers of p-PGFPh with AA, the MAA universal buffer mixture was made on the basis of 0.04 M solutions of H_3PO_4 , CH_3COOH and H_3BO_3 . In order to obtain a buffer solution of the required acidity, a certain volume of 0.2n of freshly prepared sodium hydroxide solution was added to 100 mL of the mixture [13].

The study of the effect of medium pH on the behavior of copolymers based on polypropylene glycol fumarate phthalate with acrylic and methacrylic acids was carried out by establishing their equilibrium degree of swelling in solutions with different values of medium acidity by the gravimetric method. For this purpose, samples of the tested copolymers (~ 0.3 g) were taken, which were then kept in buffer solutions (pH from 2 to 9) until a constant weight was achieved. The equilibrium swelling rate of the obtained gels was determined using formula (1) [14].

The equilibrium degree of swelling of the tested copolymers in aqueous solutions at different temperatures (25-45 °C) was also determined by the gravimetric method. To do this, weighed samples of the dry image were placed in distilled water (pH 7), thermostated to a given temperature and kept in water until a constant weight was established. The equilibrium swelling ratio was also calculated using formula (1).

3. Results and discussions

According to previous studies, it was found that polymer gels obtained on the basis of unsaturated carboxylic acids - AA and MAA - have high sorption capacity. It is known from the literature that the original UP itself does not show such hydrophilic properties. At the same time, analyzing the structure of the obtained copolymers based on p-PGFPh with AA and MAA, it should be noted that together with the vinyl monomer units, including the presence of ionized carboxyl groups that are covalently attached to the main chain, there are also unsaturated polyester units - p-PGFPh. The latter circumstance indicates the probability of changing the properties and, accordingly, the behavior of the spatially cross-linked copolymers based on p-PGFPh with AA and MAA obtained by us in comparison with the already known vinyl hydrogels.

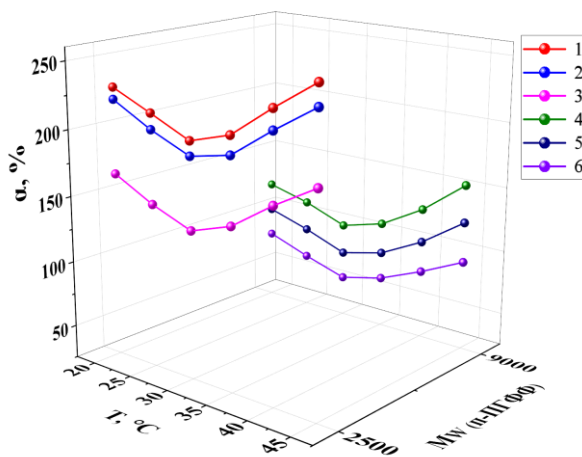
Due to the practical need to study the effect of various factors on the behavior of spatially cross-linked binary systems of p-PGFPh with AA and MAA obtained without and with the RAFT agent, the sensitivity of the above copolymers to the effect of the acidity/basicity of the external environment, temperature changes, as well as the presence of low molecular weight mono-, bi- and polyvalent salts and solvents of organic nature in the external solution, differing in polarity, was established. We selected copolymers of the composition ~ 10:90 mol%, ~ 50:50 mol% and ~ 90:10 mol% as the objects of study of the influence of various factors.

Thus, in order to analyze the effect of variation in ambient temperature, in accordance with the literature, it should be noted that there are three types of heat-

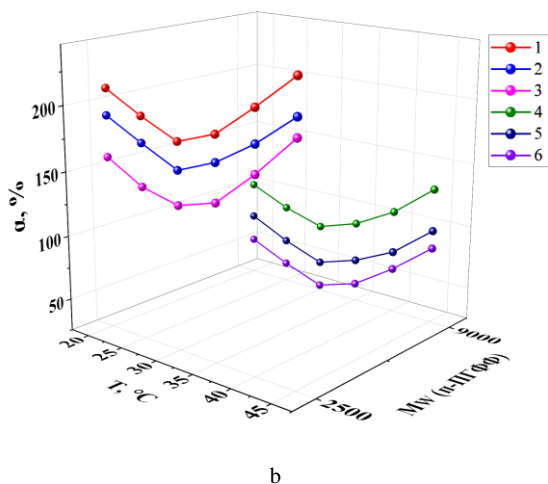
sensitive gels. The first type includes gels that dramatically increase in volume (swell) with increasing temperature. The second type, on the contrary, includes gel samples that collapse as the temperature increases. The third type of polymer gels combines the behavior of the first and second types of gels and is a mixed behavior of the type "swelling - collapse - swelling" or "collapse - swelling - collapse."

The existing difference in the behavior of gels with increasing temperature is due to the difference in the nature of the interactions that determine the course of the volume-phase transition. In this case, the weakening of the influence of hydrogen bonds, which determine the onset of gel collapse, becomes the determining factor: for example, with an increase in temperature, a decrease in their dominant contribution to the behavior of the gel is observed, as a result of which a significant increase in the size of the polymer network is observed, i.e. the polymer swells. In contrast, when hydrophobic interactions dominate, an increase in temperature results in a transition of the gel to a collapsed state. This is explained by an increase in hydrophobic attraction with increasing temperature.

Analyzing the structure of binary systems of spatially cross-linked copolymers of p-PGFPh with AA and MAA, it should be noted that an increase in temperature will provoke a bulky-phase transition in the "swelling-collapse-swelling" type. Thus, Figures 1 (a, b) show curves reflecting the behavior of the above binary systems with increasing temperature:



a

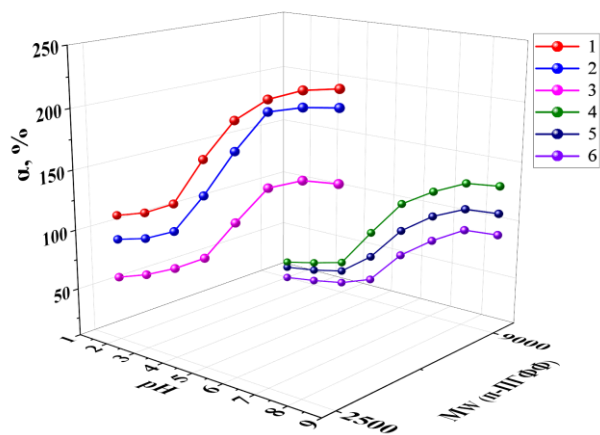


a – p-PGFPh –AA composition: 1 – 6.77:93.23; 2 – 44.17:55.83; 3 – 86.67:13.33 mol.% at M_{w1} (p-PGFPh); 4 – 5.14:94.86; 5 – 43.53:56.47; 6 – 84.24:15.76 mol.% at M_{w2} (p-PGFPh);
 b – p-PGFPh –MAA composition: 1 – 7.53:92.47; 2 – 45.02:54.98; 3 – 86.25:13.75 mol.% at M_{w1} (p-PGFPh); 4 – 5.06:94.94; 5 – 43.13:56.87; 6 – 84.15:15.85 mol.% at M_{w2} (p-PGFPh)

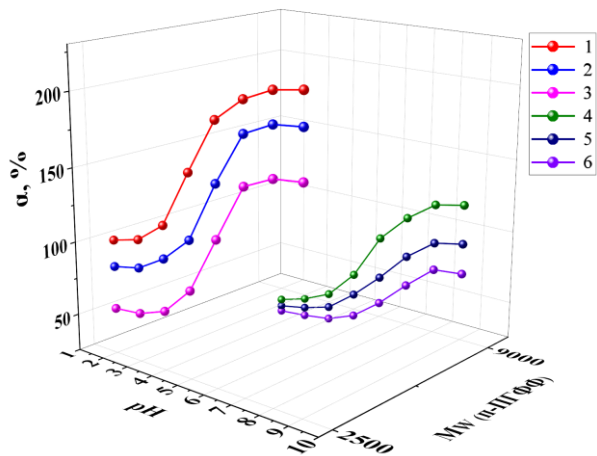
Figure 1 – Degree of swelling of p-PGFPh-VM copolymers versus temperature change.

Thus, based on the above, we can conclude that the copolymers based on p-PGFPH (different molecular weight MW) with AA and MAA of different mole composition synthesized by us are heat-sensitive gels, and by varying the temperature of the external environment, it becomes possible to control their behavior.

Further, the sensitivity of the obtained copolymers of p-PGFPH with AA and MAA was determined by varying the pH of the external solution. The results obtained are shown in Figures 2 (a, b):



a



b

a – p-PGFPh –AA composition: 1 – 6.77:93.23; 2 – 44.17:55.83; 3 – 86.67:13.33 mol.% at M_{w1} (p-PGFPh); 4 – 5.14:94.86; 5 – 43.53:56.47; 6 – 84.24:15.76 mol.% at M_{w2} (p-PGFPh);
 b – p-PGFPh –MAA composition: 1 – 7.53:92.47; 2 – 45.02:54.98; 3 – 86.25:13.75 mol.% at M_{w1} (p-PGFPh); 4 – 5.06:94.94; 5 – 43.13:56.87; 6 – 84.15:15.85 mol.% at M_{w2} (p-PGFPh)

Figure 2 – p-PGFPh-VM copolymers swelling ratio versus medium pH.

Analysis of the graphs of the degree of swelling of the copolymers versus the change in pH of the medium shows that all samples are sensitive to the acidity/alkalinity of the external environment. Thus, the maximum value of the amplitude of the swelling degree of all tested copolymers is determined at pH values close to a neutral medium, in particular, in the pH range from 5 to 7. The amplitude jump reaches the greatest value in the copolymer p-PGFPh-AA of the composition 6.77: 93.23 at M_{w1} (p-PGFPh). The explanation for this is the

ionized carboxyl groups in the macro chains covalently attached to the main chain. As a result of electrostatic repulsion of similarly charged carboxyl groups, an increase in the size of the polymer network is observed. Moreover, with an increase in the degree of dissociation of these carboxyl groups with a shift towards an increase in the alkalinity of the environment, an increase in their electrostatic repulsion is observed.

In turn, the acidic medium helps to suppress the ionization of carboxyl groups, which leads to the formation of a more compact conformation of the polymer network, i.e. its compression occurs - collapse. Moreover, the enhancement of the collapse effect is strongly influenced not only by a decrease in the number of ionized carboxyl groups, but also by an increase in the importance of additional hydrogen bonds formed during compression between these groups. The shift towards an increase in the pH values of the external solution above pH 7 causes the unfolding of the polymer network, which has adopted a globular conformation in an acidic medium. In this regard, swelling of the polymer gel is observed. Two factors explain this. The first is a more complete dissociation due to the formation of salt molecules in an external solution. The second is the weakening in the alkaline medium of the dominant influence of hydrogen bonds, which, in an acidic medium, on the contrary, contribute to the transition of the gel to the scalloped state. It is worth noting that hydrophobic interactions in this case are so weak that they do not have any significant effect on the mutual attraction of the polymer network links.

In general, the analysis of the swelling curve with variation in the acidity/alkalinity of the external solution indicates that the p-PGFPh gels with AA and MAA we synthesized are typical polyelectrolytes.

4. Conclusion

The acidic environment helps to suppress the ionization of carboxyl groups, leading to the formation of a more compact conformation of the polymer network, i.e. its compression occurs - collapse. In this case, the enhancement of the collapse effect is strongly influenced not only by a decrease in the number of ionized carboxyl groups, but also by an increase in the importance of additional hydrogen bonds formed during the compression process between these groups. A shift towards increasing pH values of the external solution above pH 7 causes the unfolding of the polymer network, which has adopted a globular conformation in an acidic environment. In this regard, swelling of the polymer gel is observed. In conclusion, it can be noted that the copolymers we synthesized based on p-PGPP (of different molecular weights MW) with AA and MAA of different molar compositions are stimulus-sensitive polymers, passing into a swollen or collapsed state under the influence of such external factors as varying temperature conditions, acidity of the external environment. This circumstance indicates the prospects of carrying out targeted synthesis of the above binary systems UP-VM of various molar compositions using the RAFT agent.

Conflicts of Interest: The authors declare no conflict of interest.

Additional information. Dedicated to the memory of Meiram Burkeev, who passed away while pursuing his scientific studies.

RAFT СОПОЛИМЕРИЗАЦИЯСЫНДАҒЫ БИНАРЛЫ ЖҮЙЕЛЕРГЕ СЫРТҚЫ ФАКТОРЛАРДЫҢ ӘСЕРІ

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Түйіндеме. Мақалада радикалды сополимерлеу әдісі іс жүзінде құнды қасиеттері бар жаңа полимерлі қосылыстарды алудың тиімді әдісі ретінде қарастырылады. Бұл әдіс қанықпаған мономерлі қосылыс молекулаларының өсіп келе жатқан макрорадикалға дәйекті қосылуы жүретін еркін радикалды механизмге негізделген. Бұл әдістің салыстырмалы қарапайымдылығының арқасында ол өнеркәсіптік масштабта әртүрлі мақсаттағы полимерлердің көп мөлшерін өндіруге мүмкіндік береді. Винил мономерлерімен радикалды сополимерлеу реакцияларына түсе алатын перспективалы сореагенттер ретінде әр түрлі құрамдағы және молекулалық массадағы қанықпаған полиэфирлер қарастырылады, олар соңғы өнімдердің қасиеттеріне айтарлықтай әсер етуі мүмкін. Мақалада қанықпаған карбон қышқылдарынан алынған полимерлі гельдерді зерттеу нәтижелері талқыланады. Автор мұндай гельдердің сорбциялық сыйымдылығы жоғары екенін көрсете отырып, алдыңғы зерттеулерге сілтеме жасайды, ал бастапқы материал ұқсас қасиеттерге ие емес. Төменде р-р_{gff} негізіндегі сополимерлердің құрылымын осы қышқылдармен талдау сипатталған, мұнда винил мономерлерінде иондалған байланыстардың болуы сияқты маңызды сипаттамалар талқыланады. Бұл зерттеулердің қажетті сорбция және басқа заттармен әрекеттесу қасиеттері бар материалдарды жасаудағы маңыздылығы. Акрил және метакрил қышқылдары бар полипропиленгликольфумаратфталат негізіндегі сополимерлердің мінез-құлқына ортаның рН әсерін зерттеу. Гравиметриялық әдіспен әртүрлі температурада сулы ерітінділерде зерттелетін сополимерлердің ісінуінің тепе-теңдік дәрежесі де анықталды. Тұтастай алғанда, сыртқы ерітіндінің қышқылдығы/сілтілігінің өзгеруіндегі ісіну қисығын талдау біз синтездеген гельдердің полиэлектролиттер екенін көрсетеді, температураға ұшыраған кезде қисық сызықты талдау нәтижесінде алынған сополимерлер ыстыққа сезімтал. Осылайша, мақаланың негізгі мақсаты жоғары сорбциялық сыйымдылығы бар полимерлі гельдерді жасау үшін қанықпаған карбон қышқылдарын пайдаланудың маңыздылығы болып табылады және олардың қасиеттері мен қолдану мүмкіндіктерін түсіну үшін осындай материалдардың құрылымын талдаудың маңыздылығын көрсетеді.

Түйін сөздер: қанықпаған полиэфирлер, винил мономерлері, қоршаған ортаның әсері. рН

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ВЛИЯНИЕ ВНЕШНИХ ФАКТОРОВ НА БИНАРНЫЕ СИСТЕМЫ ПРИ RAFT СОПОЛИМЕРИЗАЦИИ

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Резюме. В статье рассматривается метод радикальной сополимеризации как эффективный способ получения новых полимерных соединений с практически ценными свойствами. Этот метод основан на свободно-радикальном механизме, в котором происходит последовательное присоединение молекул ненасыщенного мономерного соединения к растущему макрорадикалу. Благодаря относительной простоте этого метода, он позволяет производить большое количество полимеров различного назначения в промышленных масштабах. В качестве перспективных сореагентов, способных вступать в реакции радикальной сополимеризации с виниловыми мономерами, рассматриваются ненасыщенные полиэферы различного состава и молекулярной массы, которые могут значительно влиять на свойства конечных продуктов. В статье обсуждаются результаты исследований полимерных гелей, полученных на основе ненасыщенных карбоновых кислот. Автор ссылается на предыдущие исследования, показывая, что такие гели обладают высокими показателями сорбционной емкости, в то время как исходный материал не обладает подобными свойствами. Далее описывается анализ структуры сополимеров на основе п-ПГФФ с данными кислотами, где обсуждаются важные характеристики, такие как наличие ионизированных звеньев в виниловых мономерях. Значимость этих исследований для создания материалов с необходимыми свойствами сорбции и взаимодействия с другими веществами. Исследование влияния pH среды на поведение сополимеров на основе полипропиленгликольфумаратфталата с акриловой и метакриловой кислотами. Гравиметрическим методом также определялась и равновесная степень набухания исследуемых сополимеров в водных растворах при различных температурах. В целом, анализ кривой набухания при варьировании кислотностью/щелочностью внешнего раствора указывает на то, что синтезированные нами гели являются полиэлектролитами, анализ хода кривой при воздействии температурой полученные сополимеры являются термочувствительными. Таким образом, основная мысль статьи заключается в значимости использования ненасыщенных карбоновых кислот для создания полимерных гелей с высокой сорбционной емкостью и подчеркивает важность анализа структуры таких материалов для понимания их свойств и возможностей применения.

Ключевые слова: Ненасыщенные полиэферы, виниловые мономеры, влияние окружающей среды. pH, поведение сополимеров

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