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Influence of pH and the quality of the solvents of sensitive hydrogels based on polypropyleneglycol of maleate with acrylic and methacrylic acids

In this regard, in this work it was firstly performed the radical copolymerization of polypropyleneglycolmaleate with acrylic and methacrylic acids in various weight ratios at the initial mixture to produce polymers with high sorption properties. It was studied the influence of medium pH, the quality of the solvents on behaveior of hydrogels based on the copolymers of polypropyleneglycolmaleate with acrylic and methacrylic acids. Sensibility of hydrogels to the changes of above mentioned external factors was experimentally established.

Key words: unsaturated polyester resins, copolymers, gels, hydrogels, polypropyleneglycol of acrylic acid, polypropyleneglycol of maleic acid, collapse, copolymerization.

Introduction

At the searching for materials with targeted properties the scientists interested in unsaturated polyester resins which are capable, in comparison with other thermosetting polymers, to solidify at room temperature or at relatively low temperature without disengagement of by-products. At present time the production of decorative materials and products of constructional purposes intensively increases, these materials and products have the above mentioned properties and they are produced on the basis of polyester copolymers with styrene [1].

Unsaturated polyester resins are well combined with various pigments, dyes, plasticizers and dry granular fillers (chalk, talc, sand, kaolin, etc.). Unsaturated resins are cheaper and more functional than ethoxyline resin in practice. They are less viscous and sensitive to the accuracy of dosage of curative agent, easily used and they are fast-curing under normal conditions than others [2]. The study of literature and patents revealed that there is almost no data on synthesis and investigation of unsaturated polyester resins with nonionic comonomers. Selection of optimal formulations of synthesis of polyesters copolymers with unsaturated carboxylic acids make it possible to produce products which are highly absorbent and have three-dimensional cross-linked structure.

Previously we obtained and investigated copolymers based on polyethyleneglycolmaleate with several ionic monomers [3]. This work is devoted to the synthesis of new copolymers based on polypropyleneglycolmaleate with acrylic and methacrylic acids, and to the study the influence of external factors on their behavior.

Experimental

Polypropyleneglycolmaleate was derived from the polycondensation of maleic acid and propyleneglycol using two techniques [4, 5]. Course of a reaction was monitored due on determining of acid index, however, the first of them differs with a lower temperature reaction.

The obtained polymer was reprecipitated in hexane and dried under reduced pressure; the yield of the product was 82 %.

Data on molecular mass of polypropyleneglycolmaleate determined by the acid index and light-scattering method [6] on nephelometer HACH 2100AN have advanced level of reproducible results and was equal to 5630.

Copolymers of polypropyleneglycolmaleate (p-PGM) with acrylic acid (AA) and methacrylic acid (MA) were obtained by the reaction of free radical copolymerization in mass in the presence of initiator — benzoyl peroxide at the temperature 333K at various ratios of initial monomers.

Samples of gels were washed with water and chloroform for 10 days, and then they were transferred into Petri dish and were hold in vacuum oven under reduced pressure up to constant mass at the temperature 313K.

The composition of the obtained copolymers was determined by potentiometry [7]. The equilibrium swelling degree (α) of the copolymers was found by gravimetric method as the mass of water per unit weight of dry gel, according to the formula:

$$\alpha = \frac{m - m_0}{m_0},$$

where m and m_0 — masses of equilibrium swollen and dry gels, correspondingly, g.

The amount of unconverted double bonds of maleate groups of synthesized copolymers was determined by method of using bromate-bromide mixture [8].

pH values were set by binding buffer and it was measured on ionomer 1–160MI using as a measurement electrode combination ESK-10601/7.

Surface morphology of the obtained hydrogels was investigated by scanning electron microscopy on IVS Supra 55VP-3249.

Registration of the IR spectrum of the copolymers was performed on IR Fourier spectrometer FSM 1201.

Results and discussion

The presence of unsaturated double bonds in the molecule of polypropylene glycol maleate, as well as its sufficiently high molecular mass allows suggesting that they will be used as a matrix for producing three-dimensional cross-linked polymers.

As a result it was interesting to study copolymerization of polypropyleneglycolmaleate with acrylic and methacrylic acids with the aim of for synthesizing of copolymers with sufficient hydrophilic balance. Composition and properties of copolymers of polypropyleneglycolmaleate with unsaturated carboxylic acids obtained by free radical copolymerization in mass are presented in the Table 1.

The content of p-PGM in the initial stock increased up to critical concentration of solution.

Table 1

Composition and properties of the copolymers of p-PGM (M_1) with AA (M_2) and MAA (M_2) [*I*] = 8 mol/m^3, *T* = 333K

Composition of the initial mixture, mass. %		Composition of the copolymer, mass. %		Yield, %	α, %	Contents of the maleate groups, %
M_1	M_2	m_1	m_2			
AA						
12,8	87,2	10,6	89,4	86,6	1267,4	55,8
15,2	84,8	12,3	87,7	84,2	1187,5	62,9
32,7	67,3	28,7	71,3	82,1	764,1	63,2
41,4	58,6	41,6	58,4	79,4	570,5	63,5
56,1	43,9	50,2	49,8	75,2	400,6	68,9
MAA						
17,6	82,4	10,1	89,9	87,7	1569,3	56,3
25,3	74,7	15,1	84,9	84,3	1243,6	59,8
36,1	63,9	25,2	74,8	82,1	861,7	61,0
51,3	48,7	40,5	59,5	79,3	795,6	62,4
60,6	39,4	49,9	50,1	75,2	698,3	73,1

Comparison of the data of Table 1 shows that the copolymer composition is enriched by AA and MAA units in comparison with the composition of the initial monomer mixture; which is most probably connected with a high reaction rate of linking and cross-linking involving above mentioned substances. When the concentration of p-PGM increases, the viscosity of medium in the initial stock increases too, it leads to the reduction of branching and cross-linking reactions, and it is proved by the values of the free maleate groups.

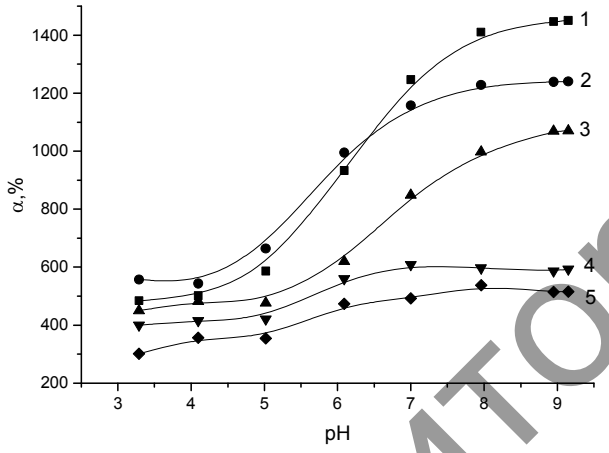
Intensive absorption bands in the range 1670 cm^{-1}, which correspond to the fluctuations of the unreacted double bonds are presented in the IR spectra of copolymers of p-PGM:AA and p-PGM:MAA. There are intense absorption bands in the 1157 cm^{-1}, corresponding to the fluctuations of the ether bonds. The fluctuations of the methyl groups of methyl acid 2926 cm^{-1}, the carboxyl groups providing swelling, are represented in the field of 1723 cm^{-1}.

It should be noted that the degree of swelling of the copolymers with the MAA is slightly higher than with AA.

The swelling capacity of the synthesized copolymers at the change of pH of medium ionic force of solution, and mixtures of organic solvent — water was evaluated to investigate the effect of external factors.

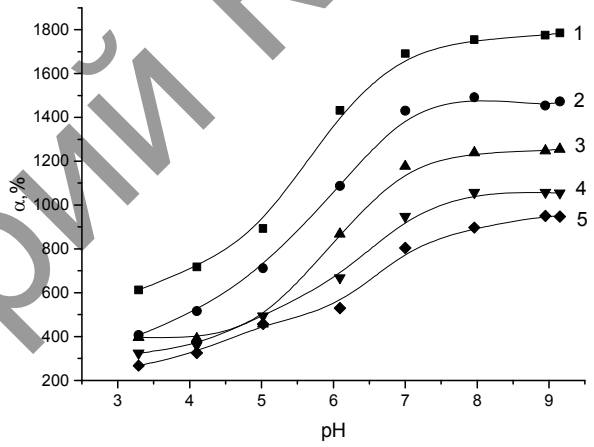
Susceptibility of ionic polymers to changes of pH of medium is one of their most important properties used in practice [9]. It is known from the literature that hydrogels containing residues of weak acid in their composition, usually swell in alkaline medium [10].

Figures 1 and 2 shows the dependence of swelling capacity at the changes of pH of medium for the investigated copolymers, and these features are peculiar to ionic polymers.



1 — 10,6:89,4; *2* — 12,3:87,7; *3* — 28,7:71,3; *4* — 41,6:58,4; *5* — 50,2:49,8

Figure 1. The dependence of the swelling capacity on the copolymers of p-PGM:AA up pH of the medium, mass. %



1 — 10,1:89,9; *2* — 15,1:84,9; *3* — 25,2:74,8; *4* — 40,5:59,5; *5* — 49,9:50,1

Figure 2. The dependence of the swelling capacity of the copolymers of p-PGM:MAA on pH of the medium, mass. %

Copolymers of p-PGM with AA and MAA at low pH values are at the maximally collapsed condition. We see that in all investigated gels in the pH range from 5 to 7, there is the spike of swelling degree in the form of three-dimensional transition which is typical for such systems. It is evident that in this pH range gels are collapsed, and the subsequent shifting of the pH solution to alkalization doesn't significantly influence on the conformation of the polymer macromolecules.

Therefore, according to the submitted data it becomes apparent that hydrogels based on copolymers of p-PGM with AA and MAA behave as typical polyelectrolytes containing ionized acidic groups covalent-bonded to the backbone chain.

In continuation of the research works it was studied the influence of the mixed aqueous organic solvent on the swelling of the polymer network based on copolymers of polypropyleneglycolmaleate with acrylic and methacrylic acids. As model systems were chosen following mixtures of solvents: water – ethanol, water – DMF, water – DMSO content of solvent in the mixture was varied from 0 to 1 volume percent (%).

Figures 3 and 4 reveal the curves of swellings of copolymers p-PGM with AA and MAA, which were placed into the water-organic solvent mixture of different compositions.

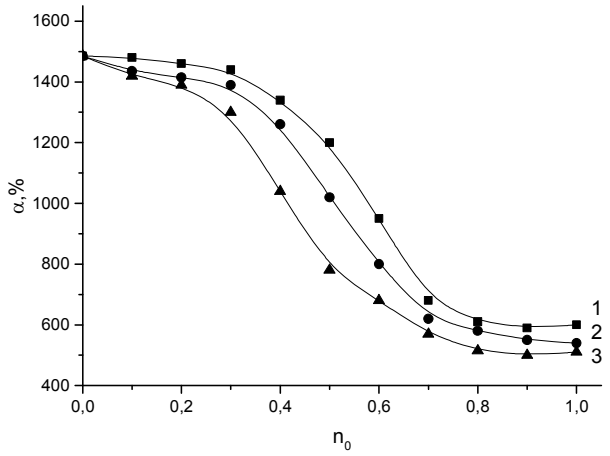


Figure 3. The influence of DMSO – water solvent (1), a water – DMF (2), water – ethanol (3) on swelling of the copolymer based on p-PGM with AA, 10,6:89,4 mass. %

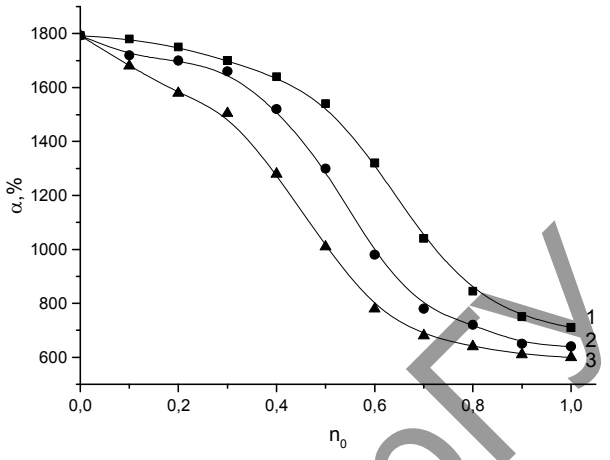


Figure 4. The influence of DMSO – water solvent (1), a water – DMF (2), water – ethanol (3) on swelling of the copolymer based on p-PGM with MAA, 10,1:89,9 mass. %

Data presented in Figures 3, 4 reveal that the more the parameter values determining the polarity of the solvents, the better polymers swell in them. As it is seen from Figure 4, the gel in the range from 0,3 to 0,7 volume percent in water- DMSO gradually shrinks due to the fact that the degree of dissociation of carboxyl groups providing electrostatic repulsion of sub chains from each other reduces, after that the collapse occurs. When we add DMF and ethanol into the system, the volumetrically-phase transition occurs at lower values of added solvent due to the lower dielectric permittivity of the medium of DMF and ethanol.

Conclusions

Thus, the experimental data have shown the perspectiveness of the use of polypropyleneglycolmaleate for three dimensional cross-linked polymers which are susceptible to changes of external conditions.

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Полипропиленгликольмалеинат пен акрил және метакрил қышқылдары негізіндегі сезгіш гидрогельдердің қасиеттеріне pH ортаның және еріткіш сапасының әсері

Мақалада радикалды сополимеризация полипропиленгликольмалеинат пен акрил және метакрил қышқылы негізінде бастапқы заттардың әр түрлі қатынастардағы ерітіндіде алынған. Полипропиленгликольмалеинат пен акрил және метакрил қышқылдарының сополимерлері негізіндегі гидрогельдердің қасиеттеріне pH ортасының әсері, еріткіштің сапасы зерттелді. Гидрогельдердің жоғарыда көрсетілген сыртқы факторлардың өзгерісіне тәжірибелі түрде сезімталдылығы анықталды.

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Влияние pH среды и качества растворителя на поведение чувствительных гидрогелей на основе полипропиленгликольмалеината с акриловой и метакриловой кислотами

В статье впервые осуществлена радикальная сополимеризация полипропиленгликольмалеината с акриловой и метакриловой кислотами в растворе при различных соотношениях исходной смеси. Изучены влияние pH среды, качества растворителя на поведение гидрогелей на основе сополимеров полипропиленгликольмалеината с акриловой и метакриловой кислотами. Экспериментально установлена чувствительность гидрогелей к изменению указанных выше внешних факторов.

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