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SYNTHESIS OF BINARY COPOLYMERS OF ISOHEXYLACRYLATE

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Abstract

The aim of this work is to study the copolymerization of isohexyl acrylate with styrene. To achieve this goal, at the first stage, the process of obtaining isohexyl acrylate by the esterification reaction of hexene isomers with acrylic acid in the presence of an acid catalyst and then the copolymerization of isohexyl acrylate with styrene in the presence of a radical initiator in an organic solvent environment was studied.

Keywords: *isohexyl acrylate, styrene, initiator, copolymerization*

Introduction

The synthesis of polyfunctional polymers attracts many researchers, and this interest is steadily growing. This is due to the wide range of useful properties of these polymers, which have proven themselves to be promising flocculants, sorbents, carriers of physiologically active agents, separating membranes (Solovskiy M. V., Korchagin A. M., Tarabukina Ye.B., 2005 p. 188–191). Advances in this area of high-molecular compounds are determined, first of all, by the development of effective methods for synthesizing polyfunctional polymers based on available raw materials. One of the promising methods for obtaining polymers with a set of specified properties is radical copolymerization. The study of such reactions is not only of practical value, but is also important from a theoretical point of view, since it allows for an assessment of the comparative reactive activity of functional monomers and for finding approaches to elucidating the features of radical processes occurring with the participation of various functional groups during the formation of a polymer chain. Most often, monomers of the vinyl and acrylic series containing carbonyl and amino groups in the structure were used to obtain such polymers (Batig S. M., Melnichenko V. I., 2014, p. 140–143).

The paper presents the results of the initiated radical copolymerization of methyl methacrylate with methacrylic acid in solvents with different polarities: acetone, toluene and methanol (Fleischmann S., Percec V., 2010, p. 484–488). It is shown that in the presence of acetone and methanol the activation energy increases, while in toluene it decreases.

However, there is no information about copolymerization of isohexyl acrylate in the literature. In connection with the above, the search, development of new approaches and effective methods for the synthesis of new copolymers based on unsaturated ester – isohexyl acrylate with vinyl monomers is an urgent task.

Methodology

Acrylic acid, 2-methyl-1-pentene, DMF, ethyl alcohol was distilled before use, drying was carried out according to standard methods. The initiator – benzoyl peroxide (BP) – was recrystallized from a solution in absolute ethyl alcohol, dried in a vacuum desiccator to constant weight.

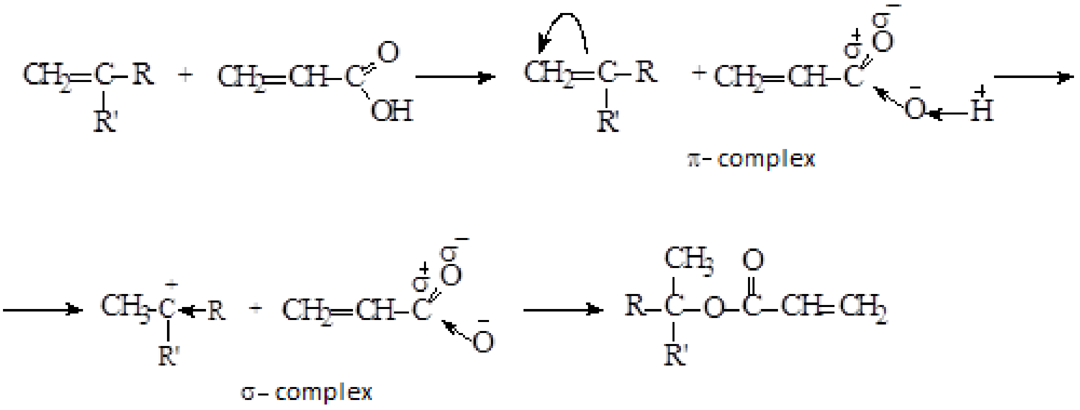
The studies were carried out using the gravimetric method (Avakumova N. I., Budarina L. A., Divgun S. M., 1990, P. 304). This method is based on the isolation of the polymer from the reaction medium by precipitating it in a solvent in which the monomer dissolves, but the copolymer does not dissolve. The copolymer is isolated as a precipitate, which is washed with a precipitant, then dried to a constant mass and weighed on an analytical balance.

Copolymerization was carried out in ground glass test tubes. The required amount of initiator was placed in clean test tubes and the solvent, ester based on 2-ethyl-1-pentene with acrylic acid, styrene in the required proportions were poured in. The mixtures were stirred until the initiator dissolved, then the tubes were purged with nitrogen for 10 minutes, carefully sealed with glass stoppers and placed in a thermostat with a temperature of 60–80 °C. The copolymerization reaction was carried out to low degrees of conversion, which was determined upon reaching a syrupy mass. It was found that the copolymerization rate was different in different ampoules – the reaction rate increased with the increase in the content of the ester in the mixture of comonomers. After the end of the copolymerization, the ampoules were cooled to room temperature and the stoppers were opened, the contents were slowly poured into a glass with a precipitant (acetone, alcohol) while stirring. The copolymer samples were freeze-dried and weighed to constant mass on an analytical balance with an accuracy of ±0.0002. The resulting copolymers are white powdery products that dissolve in benzene, toluene, and dimethylformamide.

The IR spectra of the ester and synthesized copolymers were recorded using a Fourier transform IR spectrophotometer. Infrared Fourier spectrometer "IRTracer-100" (SHIMADZU CORP., Japan, 2017) complete with an attenuated total internal reflection (ATR) attachment MIRacle-10 with a diamond/ZnSe prism (spectral range on the wavenumber scale – 4000÷400 cm^{-1}; resolution – 4 cm^{-1}, sensitivity signal-to-noise ratio – 60,000:1; scanning speed – 20 spectra per second).

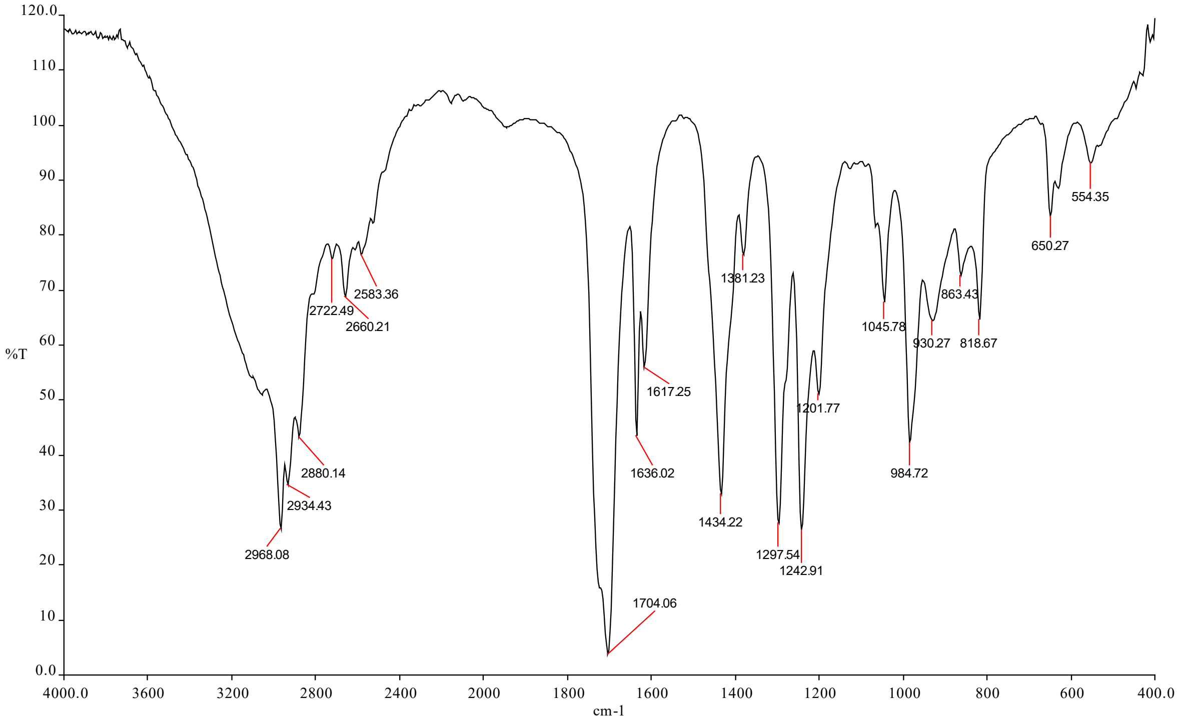
Results and discussions

The synthesis of esters based on olefins with acrylic acid was carried out according to the method described in (Maxmudova F. A., Maksumova O. S., 2012, p. 260–261). 2-methyl-1-pentene, 2-ethyl-1-butene, 2-ethyl-1-pentene were chosen as olefins, and sulfuric acid was used as a catalyst. When carrying out the esterification reaction, hydroquinone was added to the reaction mixture at a rate of 1% of the total volume of the solution. The reaction of the interaction of the indicated olefins with acrylic acid can be described as follows:



where R: –C3H7; R`: –CH3 or –C2H5

Figure 1. *IR spectrum of ester based on 2-methyl-1-pentene with acrylic acid*



The structure of the obtained ether was studied using the IR spectral method (Fig. 1).

In the IR spectrum of the ester based on 2-methyl-1-pentene with acrylic acid, new absorption bands of stretching vibrations of the -C-O-C bond were found in the region of 1297 cm^{-1}, stretching vibrations of the carbonyl group conjugated with a double bond in the region of 1704 cm^{-1}, absorption bands of -CH_3, -CH_2 groups at 2583–2934 cm^{-1}, and a wide spectrum of carboxyl groups in the region of 3600 cm^{-1} are absent. The absorption bands at 1636 cm^{-1} correspond to the stretching vibrations of the –C=C– bond, the ether band C–C(=O)-O and O-C–C- consisting of two interacting antisymmetric vibrations are observed in the region of 1045–1297 cm^{-1} (Fig. 1). The copolymerization reaction of 2-ethyl-1-pentene ester and acrylic acid (M1) with styrene (M2) was carried out in the low conversion region at a temperature of 60–80 °C in the presence of the radical initiator benzoyl peroxide (BP) in an organic solvent medium. Dimethylformamide was used as a solvent. To determine the effect of the composition of the initial monomer mixture on the composition of the resulting copolymers, the reaction was carried out at different molar ratios of the comonomers (Table 1).

Table 1. *Copolymerization of M1 with M2 in DMF solution (PB = 5 · 10^{-3} mol/l, 60 ^{o}C, 3 hours)*

Composition of the initial mixture, mol %		**Yield, %**	**Copolymer composition, mol %**	
M_1	**M_2**		**m_1**	**m_2**
10	90	2.5	11.2	88.8
30	70	3.7	33.6	66.4
50	50	5.0	55.6	44.4
70	30	6.1	78.0	22.0
90	10	8.4	97.8	2.2

The obtained results show that with an increase in the content of M_1 in the composition of the initial mixture, the yield of the copolymer increases and the ratio of comonomer units in the copolymer chain differs significantly.

It should be noted that the copolymerization of the ester with styrene is completely inhibited in the presence of hydroquinone and atmospheric oxygen, which confirms the radical nature of the process mechanism.

The structure of the obtained copolymers was established by IR spectroscopy. The IR spectra of the copolymers were analyzed and compared with the spectra of the initial monomers and their homopolymers obtained under similar conditions. In the IR spectra of the copolymers, absorption bands characteristic of the double bond of monomers in the regions of 1636–1640 cm^{-1} are absent, which confirms the reaction proceeding along the vinyl groups of the initial comonomers. The stretching vibrations of the -C-O and C=O groups are in the region of 1155 cm^{-1} and 1681–1716 cm^{-1}.

The solubility and other properties of copolymers depend both on the ratio of comonomer units in the copolymer chain and on the nature of the second comonomer – styrene. Synthesized copolymers based on M_1 with M_2 at all ratios of monomer units in the macromolecule dissolve well in dimethylformamide, dimethyl sulfoxide, benzene, and toluene.

Thus, an unsaturated ester based on 2-ethyl-1-pentene with acrylic acid was synthesized, and its copolymerization with styrene was carried out in a dimethylformamide medium in the presence of benzoyl peroxide at a temperature of 60 °C.

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