

SYNTHESIS AND PROPERTIES OF CYCLOPROPANE-CONTAINING OPTICALLY TRANSPARENT COPOLYMER

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Abstract. By radical copolymerization of (p-2-methoxycarbonyl)cyclopropyl styrene with acrylonitrile the new cyclopropane-containing optically transparent copolymer has been obtained and characterized. The composition and structure of this high-molecular compound have been established and its main operational properties have been investigated. It has been shown that the copolymerization reactions proceed with opening of double bond of the vinyl group of (p-2-methoxycarbonyl)cyclopropyl styrene and acrylonitrile. The copolymerization constants have been determined; Q-e parameters on Alfrey-Price and copolymer microstructure have been calculated. It has been established that the synthesized copolymers are characterized by good light transmission (86 %) and optical index ($n_d^{20} = 1,5830$).

Keywords: p-cyclopropyl styrene, copolymerization, 2(p--methoxycarbonyl)cyclopropyl styrene, acrylonitrile microstructure, optically transparent materials.

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1. Introduction

The high rate of development of promising optically transparent materials and technology requires the creation of optical materials with the best physical and physical-mechanical properties. For the creation of optical materials with complex properties, a suitable choice – the functional monomers on the basis of polycarbonate, polymethyl methacrylate, polyacrylonitrile, polystyrene and their derivatives (Shepurev, 1987; Wang *et al.*, 2003; Davitashvili *et al.*, 1991). The polymer materials for manufacture of the optical materials should contain the functional groups capable of refracting light and having the ability to form a high-quality material with good strength, adhesive and heat-physical properties. The increasing interest to the synthesis of new polyfunctional monomers has been stipulated by the fact that their polymerization and especially, their copolymerization with known industrial monomers leads to the creation of high-molecular compounds with high operational parameters. One of the ideal derivatives of styrene in terms of creation of optically transparent homo- and copolymers are the functionally substituted cyclopropyl styrenes (Guliyev *et al.*, 2010; Mamedli & Dzhamalov, 2019). In use of polymers as optical materials, their ability to refract light plays a significant role. The industrial polystyrene has almost the same transparency as PMMA.

With the aim of synthesis of a novel optically transparent copolymer containing a reactive functional group, in this work the copolymerization of (p-2-methoxycarbonyl)cyclopropyl styrene (MCCPS) with acrylonitrile (AN) and also the properties of the obtained polyfunctional copolymers was studied.

2. Experimental part

The synthesis of MCCPS was carried out on previously described methodology (Guliyev *et al.*, 1999). The MCCPS has been identified by the methods of elemental, chemical, IR- and PMR-spectroscopic analyses. Its purity determined by a method of gas-liquid chromatography was 99,9 %. The preparation of copolymer based on these monomers is realized by radical copolymerization in mass and in benzene solution in the presence of dinitrilazoisobutyric acid. The copolymerization reaction MCCPS with AN was realized in ampoules at 70°C in benzene solution in the presence of 0.2 mol % from total mass of comonomers. The obtained copolymers were purified by two-fold precipitation from benzene solutions with pentane and dried at 30°C in a vacuum (15-20 mm merc.c.). The total concentration of the initial monomers was constant and was 2.0 mol/l, and a molar ratio of the initial monomers was changed in the range shown in Table 1. The copolymers obtained in different compositions of comonomers after a given time (10-20 min) by addition of the reaction mixture of pentane in excess quantities were isolated. The conversion of the copolymer samples, for which the copolymerization constants have been calculated, was 8-10%.

The synthesized copolymer is a white powder, dissolved in chlorinated hydrocarbons, acetone, benzene and dioxane at 20°C. The characteristic viscosity for copolymer MCCPS+AN containing 56.15 mol % of MCCPS links was determined by Ubbelohde viscometer. It was ($[\eta] = 0.95$ dl/g).

The copolymer composition was determined on content of the elemental nitrogen (Toroptseva *et al.*, 1972). Using an equation from (Zilberman, 1979) the parameters of copolymer microstructure have been determined.

The IR spectra of the initial monomers and the synthesized copolymer have been registered on spectrometer "Agilent Cary 630 FTIR" of firm "Agilent Technologies", UV spectra have been registered on spectrometer "Agilent Cary 63" of firm "Agilent Technologies" and the PMR spectra – on spectrometer "Fourier" of firm "Bruker" (FRG) (300.18 MHz) in dioxane solution.

The refractive index was determined by use of a device Anton Paar Abbemat 200.

3. Results and discussion

The copolymerization reaction has been carried out at various molar contents of MCCPS and AN and molar fractions of links m_1 and m_2 have been found. Using these data, the values of the copolymerization constants of MCCPS (M_1) and AN (M_2) have been determined by Feynman-Ross method, and the activity factors ($Q_1=0.509$ $e_1=-0.176$) have been calculated according to Q-e Alfrey-Price scheme. The found values of $r_1=0.60$ and $r_2=0.25$ ($r_1>r_2$) indicate that M_1 is a more active monomer than M_2 at radical copolymerization. In all cases of conversion of the comonomers there are obtained the soluble copolymers, i.e. at copolymerization of M_1 and M_2 the structured process as a result of the chain transfer to a polymer practically do not occur.

The results of elemental and chemical (elemental nitrogen content determinations) analyses of the various fractions of products of joint polymerization of MCCPS with AN after fractionation are practically are almost identical, i.e. at their copolymerization the homopolymers of used monomers are not formed. With the aim of preparation of more precise proof, the turbidimetric titration has been carried out.

The turbidimetric titration has been carried out with use of the solutions of these copolymers in dioxane. As precipitator it was used absolute pentanol. It has been established as a result that the obtained polymer products are true copolymers, but not a mixture of two homopolymers (Fig. 1) (Kantov, 1971).

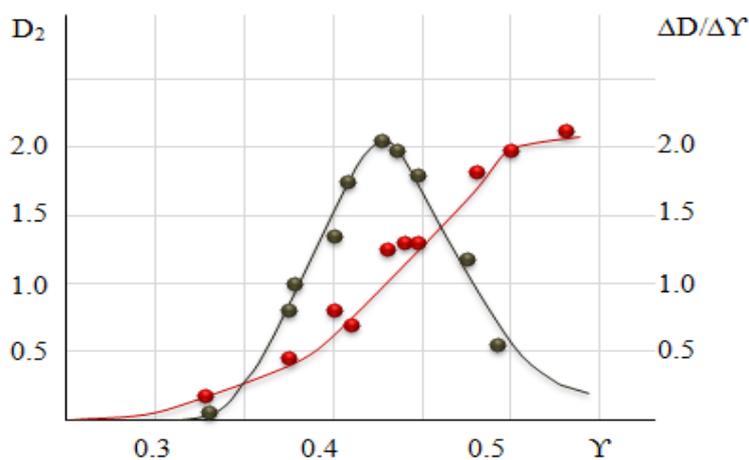
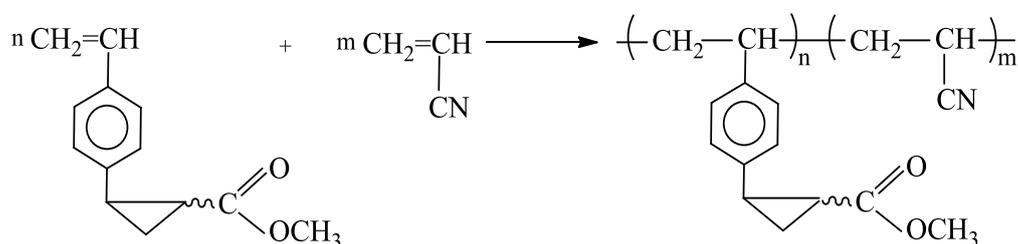


Figure 1. Turbidimetric titration of the copolymer of MCCPS with AN

The MCCS is a polyfunctional compound and its copolymerization with AN is carried out on the following scheme with the formation of a reactive polyfunctional copolymer:



The formation of the copolymer as a result of behavior of the above-mentioned reaction has been confirmed by taken IR spectra of the obtained products (fig. 2).

The absorption bands characteristic for benzene ring (1604 cm^{-1}) and cyclopropane group (1039 cm^{-1}), and also the absorption bands at 1720 and 1110 cm^{-1} , referring to the vibrations of carbonyl group and C–O–C bond, respectively, remain unaffected. In the spectrum of copolymer there are also characteristic absorption frequencies belonging to $\text{C}\equiv\text{N}$ bond ($2260\text{--}2240$). An absence of the absorption band at 1640 cm^{-1} , stipulated by vibrations of the vinyl group confirms that the copolymerization proceeds on double C=C bonds of the comonomers.

In the PMR spectrum of the copolymer, the resonance signals at $\delta=6.6\text{--}7.30$ ppm and $\delta=0.65\text{--}1.68$ ppm, characterizing the aromatic nucleus and cyclopropane ring are fixed respectively. In the PMR spectrum of MCCPS the signals characterizing methoxycarbonyl fragments ($\delta=4.0$ ppm and 1.20 ppm) are appeared, and there are also resonance signals of C=N bond at $\delta=$ ppm in the spectra of the copolymer.

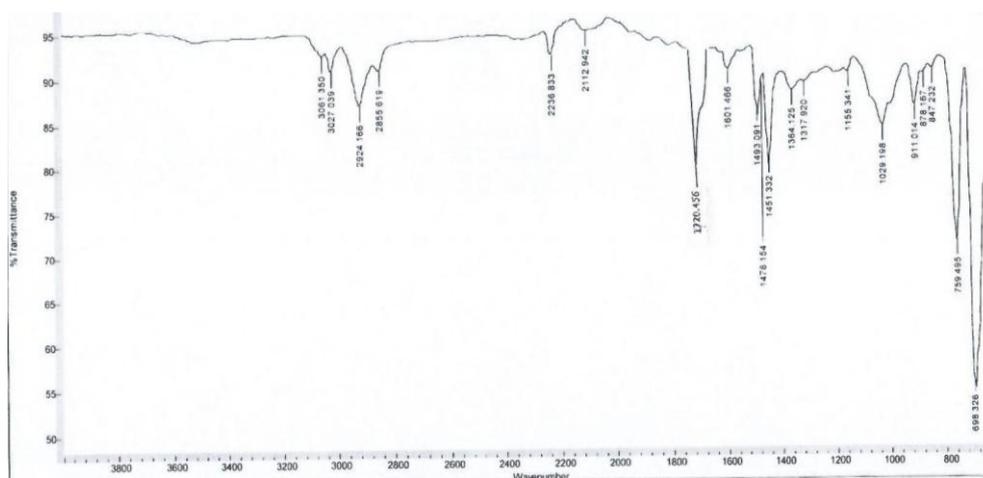


Figure 2. IR spectra of the copolymer of MCCPS with AN

In the PMR spectra of the copolymer obtained at various molar ratios there are not also signals at $\delta = 5.7\text{--}6.41$ ppm corresponding to double bonds of vinyl group of comonomers and the signals of the cyclopropane ring indicating the copolymerization behavior with opening of these double carbon bonds are fixed.

Table 1. Copolymerization of MCCPS (M_1) with AN (M_2)

| Initial mixture composition, mol. % | | Copolymers composition, mol. % | | r_1 | r_2 | Q_1 | e_1 | $r_1 \cdot r_2$ | Microstructure of copolymer | | | N, % |
|-------------------------------------|-------|--------------------------------|-------|-------|-------|-------|--------|-----------------|-----------------------------|-----------|--------|-------|
| M_1 | M_2 | m_1 | m_2 | | | | | | L_{M_1} | L_{M_2} | R | |
| 10 | 90 | 24.7 | 75.3 | 0.60 | 0.25 | 0.509 | -0.176 | 0.15 | 1.06 | 3.25 | 46.331 | 15 |
| 25 | 75 | 40.68 | 59.32 | | | | | | 1.2 | 1.75 | 67.79 | 15.19 |
| 50 | 50 | 56.15 | 43.85 | | | | | | 1.6 | 1.25 | 70.17 | 12.27 |
| 75 | 25 | 70.59 | 29.41 | | | | | | 2.8 | 1.08 | 51.5 | 6.82 |
| 90 | 10 | 86.17 | 13.83 | | | | | | 6.4 | 1.02 | 26.92 | 2.45 |

LM_1 and LM_2 are the average length of blocks of the monomer links, R – Harwood coefficient.

It is seen from Table 1 that MCCPS is a more active monomer at radical copolymerization than AN. The observed relatively high activity of MCCPS during radical copolymerization has been stipulated by the presence of an electron-acceptor ester group in its molecule, which is included in total conjugation system, thus increasing a level of conjugacy of MCCPS molecule. It was known that the mutual polarization of the monomer molecule and the active radical center in the intermediate transition state plays an important role during the polymerization process. In this case, the electron-donor ester group causes the redistribution of the electron density both in the monomer and in the radical center formed from it. As a result, the energy required for the occurrence of a transition state is decreased and both the reactivity of the monomer and the polymerization rates are increased. In comparison with styrene due to the influence of ester groups Q and e values are increased. An increase of polarity is

apparently determined by electron-acceptor character of the ester group and by increase of the polarizability of the double bond of the monomer.

For samples of copolymers obtained at various molar ratios of MCCPS (M_1) and AN (M_2), the lengths of blocks of M_1 and M_2 and the parameters of blockiness are calculated (Table 1).

It has been seen that (Table 1) a length of blocks L_{M_1} is increased with growth of molar fraction of MCCPS in the copolymer composition. A parameter of R blockiness is decreased from 70.17% to 26.92% with increase of a length of block from 6.04 to 1.06 links. A maximum value of parameter of blockiness ($R=70.17\%$) is reached at ratio of the initial monomers 0,7:0,3 (mol frac.).

At all depths of the comonomers conversion the soluble copolymers are obtained, i.e. in the copolymerization of MCCPS with AN the structurization processes of the obtained copolymers do not occur.

Due to the presence of reacting cyclopropane, ester and nitrile groups in macromolecules, the copolymers of MCCPS+AN, combining the virtues of both PS and AN can have higher physical-mechanical and heat-physical properties in comparison with polystyrene, and also larger fluidity than AN. Indeed, it follows from data presented in Table 2 that the cyclopropane-containing polymers and copolymers have higher heat-physical and physical-mechanical properties than polystyrene. The synthesized copolymers do not produce dangerous splinters during impacts. These qualities allow them to be used in the manufacture of details of optical devices and contact lenses.

The obtained results indicate that the copolymer of MCCPS+AN along with high physical-mechanical characteristics also has good optical properties. It has been established that MCCPS+AN retains a transparency up to 100°C in its holding for 2 h. The investigation of physical-mechanical properties of MCCPS+AN in the temperature interval from 80° to -20°C showed that at these temperatures it retains a higher tensile strength and an elasticity in the field of low temperatures is not practically decreased.

The transparency (light transmission in the visible part of the spectrum) of MCCPS+AN is 90% and depends little on thickness of the sample up to 6-8 mm. At relatively high thicknesses, a partial deterioration of optical properties occurs, which is typical for all known transparent polymers. The copolymers based on MCCPS+AN on indices in relation to moisture doesn't concede to polystyrene and styrene copolymer with acrylonitrile.

The high-quality optical products made from modified MCCPS+AN can be obtained by pressing, extrusion and casting under pressure.

Thus, it can be concluded analyzing obtained results that the introduction of styrene links $-\text{CH}-\underset{\text{CH}_2}{\text{CH}}-\text{COOCH}_3$ into the aromatic nucleus fragment leads to the

improvement of optical, heat-physical, adhesion, physical-mechanical and other properties of purposeful polymers and allows to obtain high-impact transparent polymer materials with high optical indices.

The obtained copolymer on the basis of monomers of MCCPS+AH shows higher optical transparency ($n_D^{20}=1.5830$) than the copolymer of polystyrene with acrylonitrile (1.568-1.570). Most likely, this has been connected with the availability of a cyclopropane ring and ester fragment in the macromolecule links. This copolymer has good light transmission (86%). The developed copolymer can be used as an optically

transparent material in optotechnology, as well as in the manufacture of optical lens for microschemes.

Table 2. Physical-mechanical characteristics of the synthesized copolymer

| Name of indices | Polymers based on | | |
|--|-------------------|--------|-------|
| | MCCPS+AN | MCCPS | St |
| Density, g/cm ³ | 1.07 | 1.20 | 1.07 |
| Refraction index, n_D^{20} | 1.5830 | 1.5970 | 1.590 |
| Vicat heat resistance, °C | 130 | 138 | 103 |
| Brinell hardness, kg/mm ² | 21.8 | 22.5 | 14 |
| Specific impact viscosity, kg·cm/cm ² | 18.0 | 21.0 | 18 |
| Tensile strength, MPa | 50.0 | 52.0 | 39.0 |
| Adhesion strength, MPa | 4.80 | 8.85 | — |
| Water absorption for 24 h, % | 0.08 | 0.06 | 0.1 |

4. Conclusions

The radical copolymerization of (p-2-methoxycarbonyl)cyclopropyl styrene with acrylonitrile has been carried out. The copolymerization constants ($r_1=0.60$, $r_2=0.25$) have been determined, Q–e parameters on Alfrey-Price ($Q_1=0.509$, $e_1=-0.176$) and microstructure of the copolymers have been calculated. It has been revealed that the obtained copolymer has a high optical transparency ($n_D^{20} = 1.5830$) and sufficiently high light transmission (86%), which opens up the possibility of using it as an optically transparent polymer in optics. The conditions of preparation of optically transparent material with required physical-chemical characteristics have been developed.

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