Copolymerization of (p-2-ethoxycarbonyl)cyclopropyl styrene with methacrylic acid

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Abstract. By radical copolymerization the copolymer of p-(2-ethoxycarbonyl)cyclopropyl styrene with methacrylic acid has been synthesized. The copolymerization constants have been determined; Q−e parameters on Alfrey-Price and microstructure of the copolymers have been calculated. It has been revealed that the obtained copolymer has a high optical transparency and sufficiently high photosensitivity, 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.

1. Introduction
One of the modern directions of the development of chemistry and materials science is the creation of materials with a complex of required properties. In the last decade, the investigations on development of new polymeric optically transparent materials, which at the same time have high photosensitive properties has been developing rapidly. This is has been considerably stipulated by the needs of developing optotechnology in a wide various fields: from medicine to telecommunications systems. The optically transparent materials based on organic polymers have a formability providing easiness of details making of a given form. The main requirement for such polymers is the high light transmission in the visible region of the spectrum or in the wavelength range used by optoelectronic devices [1]. The technical and consumer properties of the optically transparent materials determine the quality and quality factor of the made optical details. The purpose of this work was to obtain the optically transparent materials of new generation possessing high physical-mechanical properties.

It was known that the polymethacrylates are widely used for preparation of the optically transparent organic component [2, 4]. The very perspective comonomers in terms of creation of new optically transparent materials are functionally substituted cyclopropyl styrenes. [5]. In spite of intensive investigations of the optical properties of polyconjugated polymers, wide and varied possibilities of their application, there are a number of unsolved problems in this area.

This paper has been devoted to the synthesis and study of properties of new optically transparent material, copolymer – (p-2-ethoxycarbonyl)cyclopropyl styrene [ECCPS] with methacrylic acid [MAA].

2. Experimental
The synthesis of (p-2-ethoxycarbonyl)cyclopropyl styrene was carried out on previously described methodology [6]. The purity of monomer was controlled chromatographically on chromatograph of mark LKhM-8 MD and in all cases it was 99,9 %. The copolymerization of ECCPS and MAA was
carried out in benzene solution in the presence of 0.2 mol % of AIBN from total quantity of the comonomers at 70°C. The forming copolymers were purified by twofold precipitation from benzene solutions by pentane and dried at 30°C in 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 changed in the range shown in Table 1. On the expiry of specified time (10-20 min) by addition of the reaction mixture into an excess of pentane the copolymers with various composition of the comonomers were selected. The conversion of the copolymer samples, for which the copolymerization constants have been calculated, was 8-10%.

The copolymer, which is a white powder, is highly soluble in dioxane and acetone. The characteristic viscosity for copolymer ECCPS+MAA containing 42.86 mol % of ECCPS links was determined in dioxane at 20°C in Ubbelohde viscometer ([η] = 0.98 dl/g).

The copolymer composition was calculated on content of carboxyl groups determined on methodology presented in [7]. The parameters of microstructure of the copolymer have been determined by means of equation from work [8].

The IR spectra of the initial monomers and synthesized copolymer were registered on spectrometer «Agilent Cary 630 FTIR» of firm «Agilent Technologies», and PMR spectra on spectrometer «Fourier» of firm «Bruker» (Germany) (300.18 MHz) in dioxane solution.

The refraction index was determined by means of apparatus Anton Paar Abbemat 200.

3. Results and discussion

The results of elemental and chemical (determination of content of carboxyl groups) analyses of the various fractions of products of joint polymerization of ECCPS with MAA are practically identical, i.e. at their copolymerization the homopolymers of used monomers are not formed. With the aim of preparation of more exact results the turbidimetric titration has been carried out (Figure 1) [9].

![Figure 1. Turbidimetric titration of the copolymer of ECCPS with MAA.](image)

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.

A reaction scheme for preparation of the copolymer ECCPS+MAA can be presented as follows:
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 (figure 2).

Figure 2. IR spectra of the copolymer of ECCPS with MAA.

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 vibrations of carbonyl group and –O– bond, respectively, remain unaffected. In the spectrum of copolymer there are also characteristic absorption frequencies belonging to carboxyl group (3434 cm⁻¹). 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.

The structure of copolymer ECCPS+MAA has been also confirmed by data of PMR spectroscopy. In PMR spectrum of the copolymer the signals characteristic for protons of aromatic nucleus at 6.6-7.30 ppm, carboxyl group (9.0-12.2 ppm) and resonance signals for cyclopropane ring at 0.65-1.66 ppm have been detected.

In PMR spectra of the copolymer obtained at various molar ratios there are not signals at δ = 5.7-6.41 ppm corresponding to double bonds of vinyl group of comonomers the signals of the cyclopropane ring are fixed, which indicates the copolymerization behavior with opening of these double carbon bonds.

Table 1. Copolymerization of ECCPS (M₁) with MAA (M₂).

| Initial mixture comp., mol.% | Copolymers composition, mol.% | r₁, r₂, Q₁, e₁, r₁·r₂ | Microstructure of copolymer | COO H₂, % |
|-----------------------------|-------------------------------|------------------------|-----------------------------|----------|
| M₁  M₂ | m₁  m₂ | Lₘ₁ Lₘ₂ R | Lₘ₁ Lₘ₂ R | Lₘ₁ Lₘ₂ R | Lₘ₁ Lₘ₂ R |
| 90  10  | 75.19  24.81 | 3.25  1.07 | 46.27  6.07 |
| 70  30  | 55.32  44.68 | 1.58  1.27 | 69.88  12.73 |
| 50  50  | 42.86  57.14 | 0.25  0.65 | 0.56  0.69 | 0.1625 | 1.25  1.65 | 68.96  18.14 |
| 30  70  | 30.51  69.49 | 1.10  2.51 | 55.19  24.88 |
| 10  90  | 13.05  86.95 | 1.02  6.85 | 25.38  38.00 |

LM₁ and LM₂ are the average length of blocks of the monomer links, R- Harwood coefficient

To reveal the dependence of composition of the copolymers on composition of the initial mixture of monomers, the copolymerization reaction was carried out at various molar ratios of ECCPS (M₁) and MAA (M₂). The molar fractions of the corresponding links m₁ and m₂ have been found by determination of content of carboxyl groups (Table 1).

The copolymerization constants r₁ and r₂ have been determined on Fayneman-Ross method [10] with mathematical treatment of the experimental data on method of the least squares:

\[
\frac{F}{f} = r_1 \frac{F^2}{f} - r_2 \quad y = \frac{F}{f} (f - 1), \quad x = \frac{F^2}{f} \quad \text{where} \quad F = [M_1]/[M_2], \quad f = [m_1]/[m_2].
\]
A graphical image of determination of the constants \( r_1 \) and \( r_2 \) is presented in Figure 3. The copolymerization constant values \( r_1 \) and \( r_2 \) for ECCPS+MAA system have been shown in Table 1. On the basis of values \( r_1 \) and \( r_2 \), obtained for ECCPS+MAA system, we have determined \( Q \) and \( e \) for ECCPS on Alfrey-Price scheme \[11\] with use of the following dependence:

\[
\frac{lQ_1}{lQ} = \frac{lQ_2}{lQ} + \left( e_1^2 - e_1 \cdot e_2 \right) \cdot 0.45
\]

It is seen from Table 1 that \( r_2>r_1 \), i.e. MAA is the more active monomer than ECCPS at joint radical copolymerization. It should be noted that, in contrast to styrene, the ester group existing in ECCPS is included in general conjugation system, causing a redistribution of the electron density both in the monomer and in the radical center formed from it. As a result, a quantity of energy necessary for transition state is decreased, which leads to an increase of the monomer reactivity. In comparison with styrene due to the influence of ester groups \( Q \) and \( e \) values is 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.

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

The production value of the copolymerization constants shows that both types of forming radicals react faster with "alien" monomer than with own and it is observed a tendency to alternation of the monomer links \( (r_1/r_2<1) \) in the copolymer. One of the reasons of such phenomenon, as is known, is the difference in the polarity of monomers and radicals.

It has been established that (Table 1) a length of blocks \( L_{M_1} \) is increased with growth of molar fraction of ECCPS in the copolymer composition. A parameter of \( R \) blockiness is decreased from 69.88% to 25.38% with increase of block length from 1.58 to 1.02 links. A maximum value of parameter of blockiness \( (R=69.88\%) \) is reached at ratio of the initial monomers 0.7:0.3 (mol frac.).

Due to availability of the photosensitive groups in macromolecules the copolymer is easily structured under action of UV-irradiation and can be used as a resist material of negative type. It has been established by a method of IR spectroscopy that in the structurization process under influence of UV-irradiation there are cyclopropane cycles and also ester and carboxyl fragments existing in the copolymer composition. The results indicate that the material obtained on the basis of ECCPS+MAA is photosensitive \((52 \text{ cm}^2\cdot\text{J}^{-1})\). The links formed from methacrylic acid give the copolymer hardness and stiffness. Functionally substituted cyclopropyl styrene links give it good physical, mechanical and thermal properties. With growth of the content of cyclopropyl styrene fragments, the adhesive strength of the synthesized copolymers is increased \((\text{varies in the range of } 4.2\text{÷}14.8 \text{ MPa})\), and a growth of fraction of MAA fragments leads to an improvement of optical indices. By selection of components and regulation of their correlation one can obtain the copolymers meeting the various requirements of technique.

The physical-mechanical characteristics of the obtained copolymer are presented in Table 2. It is seen that in comparison with polystyrene the synthesized copolymer possesses more high thermal
stability, strength and adhesion. In addition, the copolymer obtained on the basis of ECCPS+MAA shows an optical transparency \(n_d^{20}=1.5870\). In addition, this copolymer has good light transmission (85%). The developed copolymer is a material of optically transparent nature for use in optotechnology, as well as in the making processes of optical lenses for microschemes.

**Table 2.** Physical-mechanical characteristics of the synthesized copolymer.

| Name of indices               | Polystyrene | ECCPS+MAA |
|------------------------------|-------------|-----------|
| Vicat heat resistance, °C    | 103         | 144       |
| Brinell hardness, kg/mm\(^2\) | 14          | 21.5      |
| Specific impact viscosity, kg·cm/cm\(^2\) | 18 | 23 |
| Tensile strength, MPa        | 39.0        | 56.5      |
| Refraction index             | 1.5890      | 1.5870    |

Composition of the copolymer ECCPS:MAA 75.6:24.4.

4. Conclusions
1. The radical copolymerization of (p-2-ethoxycarbonyl)cyclopropyl styrene with methacrylic acid has been carried out. The copolymerization constants \(r_1=0.25, r_2=0.65\) have been determined, Q−e parameters on Alfrey-Price \((Q_1=0.566, e_1=0.697)\) and microstructure of the copolymers have been calculated.

2. It has been revealed that the obtained copolymer has a high optical transparency \(n_d^{20}=1.5870\) and sufficiently high photosensitivity (52 cm²·J⁻¹), 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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