

Copolymerization of (p-2-Ethoxycarbonyl) cyclopropyl Styrene with Glycidyl Methacrylate

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Abstract— The radical copolymerization of (p-2-ethoxycarbonyl)cyclopropyl styrene with glycidyl methacrylate has been investigated. The new cyclopropane- and epoxy-containing photosensitive copolymers have been prepared. The constant values of relative activity of the monomers have been determined and the parameters Q - e on Alfrey and Price have been calculated. The copolymerization constants of this compound (r_1) with glycidyl methacrylate (r_2) calculated on Feynman-Ross method are: $r_1 = 1.15$, $r_2 = 0.42$, respectively; values of parameters Q and e : $Q_1 = 1.85$, $e_1 = -0.75$, respectively. The composition and structure have been established and the photochemical investigations of the synthesized copolymer have been carried out. It has been established that structuring proceeds due to opening of cyclopropane ring, epoxide and carbonyl groups.

Keywords— copolymerization, (p-2-ethoxycarbonyl)cyclopropyl styrene, microstructure, monomers, photosensitivity.

I. INTRODUCTION

The rapidly increasing information volume requires the improvement of existence and the creation of new types of its recording, storage and reproduction. The search of non-silver materials for resists is considerably stimulated with exhaustion of the world's silver reserves, which as a result of one cycle of the photographic process is irretrievably lost by half.

The polymers and copolymers containing various reactive and photosensitive groups in the side chains possess valuable complex of properties and possibility of cross-linking under action of radiation, which allows preparing the resists on their basis used in microelectronics [1].

Due to this, a problem of the preparation of new types of photosensitive polymers for microelectronics causes a great interest of researchers [2-7]. Previously the solution of this problem was realized by us by polymerization of functionally substituted cyclopropyl styrenes [8-11].

The interest to preparation of such polymers has been stipulated due to the fact that in the formed macromolecules there are reactive functional groups of various nature in the form of suspensions in the side macrochain. As a result of copolymerization of the functional cyclopropane-containing vinyl compounds being one of the perspective reactive monomers, there have been synthesized the polymers containing cyclopropane groups regularly located in the side appendages to macrochain [12, 13].

This work has been devoted to the investigation of regularities of the copolymerization of (p-2-ethoxycarbonyl)cyclopropyl styrene (ECCPC) with glycidylmethacrylate (GMA) and study of properties of the copolymers prepared on their basis with the aim of creation of new negative photosensitive copolymers. A choice of these monomers has been stipulated by the fact that the concentration of double bonds and their chemical nature and also an availability of cyclopropane ring in combination with carbonyl and epoxide group in monomers in a decisive extent influence on such important photolithographic parameters of the resist as photosensitivity, adhesion, transparency, resolving ability about which a large experimental material accumulated to present time evidences.

ECCPC is the new reactive monomer, the formula and data of the synthesis and homopolymerization of which have been presented in work [11]. For copolymerization of the studied systems it is important to choose the conditions in which the polymerization would be proceeded only on vinyl group, and the reactive fragments would be remained unchanged in the side chain.

II. EXPERIMENTAL

The synthesis of ECCPC was carried out on methodology described in work [11].

The copolymerization of the synthesized ECCPC with GMA was carried out at 70°C in ampoules in the benzene solution in the presence of 0.2% (from total mass of monomers) of dinitrilazoisobutyric acid (AIBN). Total concentration of the initial monomers was constant and was 2.0 mol/l.% and a ratio of the initial monomers changed in the concentrations, shown in Table 1. The forming copolymer was doubly reprecipitated from benzene solution to methanol or sulphur ether and dried in vacuum (15-20 mm merc.c) at 30°C to constant mass. On the expiry of specified time (10-20 min) by addition of reaction mixture to methanol excess there have been isolated the copolymers with different composition of comonomers. The conversion of the samples of copolymers, for which there have been calculated the copolymerization constants, was 10%. The copolymer, being a white powder is well soluble in aromatic and chlorinated hydrocarbons. Elemental analysis $C_{21}H_{26}O_5$. Calculated: C 70.39%, H 7.26. Found: C 70.20, H 7.10. The characteristic viscosity was determined in benzene in Ubbelode viscometer ($[\eta] = 1.08 \text{ dl/g}$).

The composition of copolymer was estimated on content of epoxide groups by chemical method, based on ability of epoxide ring to add HCl quantitatively.

The IR-spectra of copolymers were registered on spectrometer UR-20, the NMR-spectra – on spectrometer BS-487B Tesla (80 MHz) in the solution of deuterated chloroform.

For determination of photosensitivity of the polymer there have been made some compositions for copolymer at various concentrations (4-13% solutions). Applying a photoresist layer on the substrate was carried out in dust-free medium.

All solutions of the resists were applied on glass substrate by means of centrifuge at 2500 rev/min. After applying of the workpiece the photoresist is sustained for no less 20 min for increasing the adhesion of photoresist to the substrate. Then the photoresist is cut off on contour of the workpiece to prevent any film delamination.

The thickness of the prepared films-resists was measured with microinterferometers „LINNIKA”. The resist layer thickness after its drying for 10 min at room temperature and for 20 min at 30-35°C/10 mm mer.c was from 0.20-0.25 mcm.

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The exposure of the workpieces with applied photoresist was realized on installation with point source of light through a photomask. The mercury lamp DPT-220 (current intensity 2.2A, distance from radiation source – 15 cm, mobile shutter rate of exponometer – 720 mm/h, exposure time 5-20 s) was used as a source of UV-irradiation.

TABLE 1
PARAMETERS OF COPOLYMERIZATION OF ECCPC (M_1) WITH GMA (M_2)

Composition of the initial mixture, mol. %		Epoxide number	Composition of copolymers, mol. %		r_1	r_2	Q_1	e_1	$r_1 \cdot r_2$	Microstructure of the copolymer		
ECCPC M_1	GMA M_2		ECCPC m_1	GMA m_2						L_{M_1}	L_{M_2}	R
90	10	0.98	91.53	8.47	1.15 ± 0.03	0.42 ± 0.02	1.85 ± 0.01	-0.75 ± 0.02	0.483	11.35	1.04	16.14
70	30	2.91	75.73	24.27						3.68	1.18	41.15
50	50	4.78	60.16	39.84						2.15	1.42	56.02
30	70	6.85	42.96	57.04						1.49	1.98	57.63
10	90	9.71	19.09	80.91						1.12	4.78	33.89

L_{M_1} and L_{M_2} – average length of blocks of monomers units; R – coefficient of Harwood blocking

The development was carried out in the jet installation. As the developer it was used the mixture dioxane:isopropyl alcohol – 1:2 at temperature 18-25°C.

A criterion of photosensitivity of the negative photoresists under UV-irradiation is the completeness of passage of the photochemical polymerization reactions (cross-linking) of molecules of base of the photoresist.

After exposure and development, the content of insoluble polymer was calculated on mass of the residue as a fact of formation of the cross-linked product.

Photosensitivity – value, inverse to the dose of UV-light absorbed by the photoresist, in other words, the dose necessary for the photoresist transfer to an insoluble state. It is measured in $\text{cm}^2(\text{Wt}\cdot\text{s})^{-1} = \text{cm}^2 \text{J}^{-1}$:

$$S = \frac{1}{H} = \frac{1}{E \cdot t}$$

H – exposition (or irradiation dose by UV-light), $\text{J}\cdot\text{cm}$

E – intensity, $\text{Wt}(\text{cm}^2)^{-1}$

t – duration of irradiation, s

III. RESULTS AND DISCUSSION

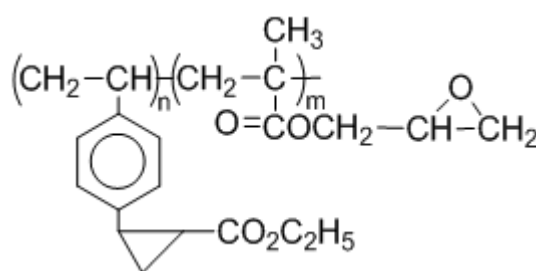
With the aim of establishment of composition and structure of the synthesized copolymer the elemental and spectral (IR- and NMR-spectroscopy) analyses of the synthesized monomer and polymer samples have been carried out.

In view of the fact that ECCPC is the polyfunctional compounds, at its radical copolymerization with GMA it should be expected the formation of new reactive polyfunctional copolymer.

In the IR-spectra of the prepared copolymers on the basis of ECCPC with GMA there are observed the absorption bands, which can be used for structural characteristics of copolymers.

It has been established by comparison of IR-spectra of the copolymers with spectra of the initial monomer (ECCPC) that the absorption bands in the IR-spectrum of the initial monomer at 990 and 1640 cm^{-1} , referring to deformation and valence vibrations of double bond of the vinyl group after copolymerization disappear. The absorption bands characteristic for benzene ring (1410-1460; 1500-1600 cm^{-1}) and cyclopropane group (1030-1035 cm^{-1}) and also absorption bands at 1720, 1030 and 1110 cm^{-1} , referring to vibrations of carbonyl groups and ether bond, respectively, remain unaffected. In the spectrum of the copolymer there are also the characteristic frequencies of absorption belonging to epoxide ring (830-850, 1250-1260 cm^{-1}) preserved after polymerization.

In the NMR-spectrum of copolymer the resonance signals referring to protons of benzene nuclei ($\delta = 6.60$ -7.30 ppm) and cyclopropane ring ($\delta = 0.65$ -1.66 ppm.) are clearly appeared, but the signals referring to protons of vinyl group ($\delta = 5.10$ -6.65 ppm.) – are absent. The protons of epoxide ring are characterized by signals at 2.30-2.60 ppm ($-\text{CH}_2-$) and at 2.96 ppm ($-\text{CH}-$). According to the data of spectroscopy, the copolymerization of ECCPC with GMA proceeds only due opening of double bonds of vinyl groups with preservation of other reactive functional fragments of both monomers. Thus, on the basis of analysis of IR- and NMR-spectra of the copolymers prepared by copolymerization of ECCPC with GMA, the following structure of copolymer is supposed:



The copolymerization was carried out at various ratios of the initial monomers.

The initial composition is the main factor determining characteristics of the polymers. It has been revealed that the composition of forming copolymers depends on composition of the initial monomer mixture.

For estimation of the polymerization activity of ECCPC there have been calculated the constant values of relative activity of monomers on compositions of the initial monomer mixture on Feynman-Ross method [14] and parameters Q-e – on Alfrey and Price. The parameters of microstructure of the copolymers were determined based on copolymerization constant [15]. The obtained data are presented in Table 1.

The constant of values of relative activity (Table 1) evidence about the largest reactivity of ECCPC in comparison with GMA, which has been connected with influence of cyclopropane ring $-\text{CO}_2\text{C}_2\text{H}_5$ on electron density of double bond of the vinyl group [16]. The ester group is included in total system of conjugation causing redistribution of electron density both in monomer and in radical center forming from it. As a result a quantity of the energy necessary for occurrence of transition state is decreased leading to increase of the reactivity of monomer.

The calculated values of parameters of Q_1 and e_1 at copolymerization with GMA indicate to increased conjugation in monomer (ECCPC) connected with influence of substituent of $-\text{CO}_2\text{C}_2\text{H}_5$ fragment stipulating relatively high reactivity of monomer and more low reactivity of radicals. In calculation of factor e_1 it was chosen a negative sign, based on the fact that the electronic density of the double bond of the vinyl group of ECCPC should be less than in GMA, since an influence of substituent of ECCPC leads to the redistribution of density of electron cloud of double bond of the vinyl group changing the polarity of radical. It has been connected with this the large reactivity of ECCPC confirmed by copolymerization constant ($r_1=1.15$, $r_2=0.42$, respectively) in comparison with GMA. On the basis of calculated copolymerization constants the data about microstructure of copolymers have been obtained (Table 1). A length of blocks L_{M_1} is increased with increase of share of ECCPC in the composition of copolymer. It is seen from Table that R and L_{M_1} are maximum (56.02 and 57.63; 2.15 and 1.49 units, respectively) at ratio of the initial monomers 50:50, 30:70. It follows from here that by selection of the determined compositions of the monomer mixtures one can carry out the directed formation of microstructure of copolymers, which is one of the most perspective ways of modification of their properties.

An availability of the synthesized copolymer of reactive groups of various chemical nature in links of macromolecule causes an interest to investigation of the photochemical structuring of this copolymer, i.e. to cross-linking under action of UV-irradiation.

The photochemical investigations of the synthesized copolymers were carried out on methodology [9]. Owing to availability of groups strongly absorbing the light energy (cyclopropane, glycidyl, $> \text{C} = \text{O}$ etc.) the synthesized copolymers are the photosensitive ($55 \text{ cm}^2\text{J}^{-1}$) and under the influence of UV-irradiation are subjected to the photochemical conversions leading to the formation of net structures.

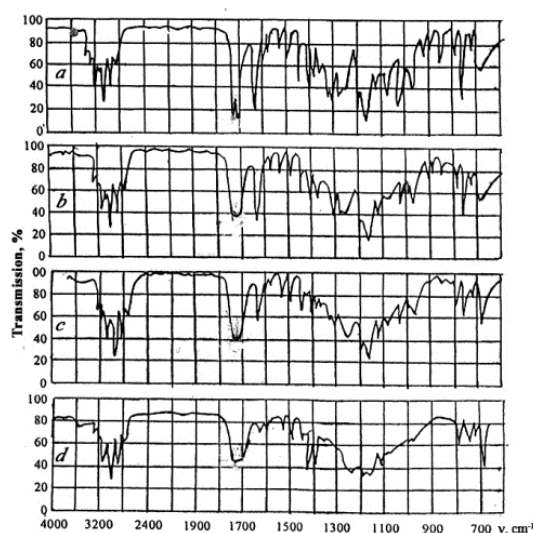


FIGURE 1: IR-SPECTRA OF THE COPOLYMER FILM OF ECCPC WITH GMA : UNIRRADIATED (A) AND IRRADIATED FOR 1-ST (B), 3-RD (C) AND 4-TH (D) MIN. $M_1 : M_2 = 75.73 : 24.27 \text{ MOL}\%$.

The structuring process of the prepared cyclopropane-containing copolymers has been studied by IR-spectroscopic investigations (fig.1). Depending on duration of irradiation, an intensity of maxima of the absorption bands characteristic for cyclopropane ring ($1030\text{-}1035 \text{ cm}^{-1}$), carbonyl group (1720 cm^{-1}) and epoxide ring ($830, 920, 1260 \text{ cm}^{-1}$) is changed; with

increase of irradiation time (more 3 min.) an intensity of maxima of the absorption bands of the indicated fragments are decreased and at irradiation ~ 5 min it practically disappear (fig. 2).

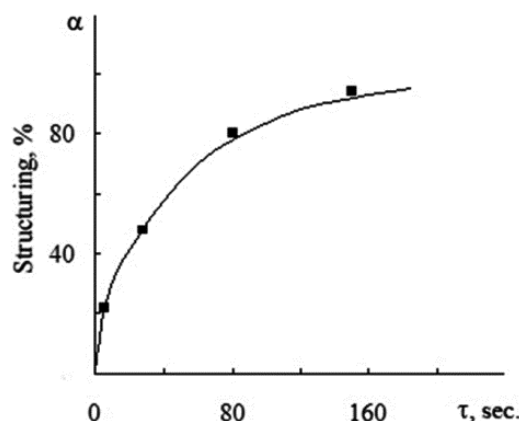


FIGURE 2: DEPENDENCE OF STRUCTURING ON IRRADIATION TIME OF THE COPOLYMER

Structuring proceeds due to opening of cyclopropane ring, carbonyl group and glycidyl fragments.

In the irradiation process on change of values of epoxide number the content of epoxide groups in the copolymer controlled [14].

Thus, an availability of cyclopropane ring, ethoxy carbonyl and glycidyl groups in macromolecules of the prepared copolymer allowed to create the material with high photosensitivity on the basis of copolymer.

As a result of carried out work the new copolymer has been synthesized and its composition, structure and properties have been established. It can be concluded on the basis of the carried out investigations that an availability of cyclopropane ring and glycidyl fragment in the structure of the new synthesized copolymer provides high photosensitivity, creation of a solid elastic layer with good adhesion to substrates and low microdefects of the polymer films for these copolymers.

IV. CONCLUSIONS

1. The radical copolymerization of (p-2-ethoxycarbonyl)cyclopropyl styrene with glycidyl methacrylate has been investigated. The new cyclopropane- and epoxy-containing photosensitive copolymers have been prepared.
2. The constant values of relative activity of the monomers have been determined and the parameters Q-e on Alfrey and Price have been calculated.
3. The composition and structure have been established and the photochemical investigations of the synthesized copolymer have been carried out.
4. It has been established that structuring proceeds due to opening of cyclopropane ring, epoxide and carbonyl groups.

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