

ХИМИЧЕСКИЕ НАУКИ

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NEGATIVE PHOTORESISTS ON THE BASIS OF COPOLYMERS OF 2-CHLOROMETHYL-1-(P-VINYL PHENYL)CYCLOPROPANE WITH GLYCIDYL METHACRYLATE

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Abstract. The radical copolymerization of 2-chloromethyl-1-(p-vinyl phenyl)cyclopropane with glycidyl methacrylate is carried out. The composition and structure of the obtained copolymer are established. The constant values of relative activity of monomers are determined and Q-e parameters on Alfrey-Price are calculated. The photosensitivity of new cyclopropane and epoxy-containing photosensitive copolymers is studied. The photochemical structuring is investigated and it is established that the synthesized polymer has a photosensitivity (56 cm²/J) and can be used for creation of photosensitive material.

Keywords: copolymerization; radical polymerization; structuring; cyclopropane; photosensitivity

1. Introduction

The synthesis and application of the technical polymers with photosensitive groups attract great attention in recent decades due to their wide spectrum of their applications in new fields such as advanced microelectronics [1, p. 136], photolithography [2], holographic [3], photo-cured coatings [4, p. 615], etc.

The choice of photoresist and also the conditions of its application are determined by the intended purpose. In this regard, there is a tendency to produce the photoresists of narrow purpose, but this requires the creation of a wide assortment of photosensitive materials. Now, the negative photoresists do not sufficiently satisfy all technological requirements of integrated scheme production. Therefore, there is a relentless interest of the specialists in preparation of new types of negative photoresists meeting certain requirements. Due to, there is a great interest of the researchers in preparation of new types of the photosensitive polymers for microelectronics [5-8]. We have also tried to solve this problem by means of the synthesis and polymerization of functionally substituted cyclopropyl styrene [9-11].

The polymers containing reactive fragments in basic or in the position of the suspension chain, in UV-irradiation are subjected to structuring processes forming negative photoresists with high sensitivity [12]. 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 or in macrochain [13, 14].

This paper has been devoted to the investigation of regularity of the copolymerization of 2-chloromethyl-1-(p-vinyl phenyl)cyclopropane (CMCP) with glycidyl methacrylate (GMA) and to the study of composition and properties of the obtained

copolymers with the aim of creation of new photosensitive copolymers.

CMCP is the new reactive monomer, formula and data of synthesis and homopolymerization of which are presented in work [15]. The choice of this monomer for investigation of the copolymerization with GMA has been stipulated by availability of strongly absorbing light energy of groups (carbonyl, cyclopropane, epoxy and chlorine atom) in the molecule the synthesized copolymer, which in decisive degree influences on such important photolithographic parameters of the resist, as photosensitivity, elasticity, adhesion, etc., which is confirmed by experimental material accumulated to the present time, [16, 17]. It has been shown that for the copolymerization of the studied systems it is important to choose the optimal conditions, under which the polymerization would occur only on vinyl group, and the reactive fragments would remain unchanged in the side chain.

2. Experimental

The synthesis of CMCP was carried out on methodology described in work [15].

The copolymerization of the synthesized CMCP with GMA was carried out in ampoules in benzene solution in the presence of 0.5% (from total monomer mass) dinitrilazoisobutyric acid (AIBN) at 70°C. The total concentration of the initial monomers was constant and was 0.2 mol/l, and the ratio of the initial monomers changed in the concentrations shown in Table 1. The forming copolymer was purified by twofold precipitation from benzene solution to methanol and dried in vacuum (15-20 mm merc.c.) at 30°C to constant mass. After the specified time (10-20 min) the copolymers of various composition of the comonomers have been isolated by addition of the reaction mixture into an excess of methanol. The conversion of the copolymer samples, for which there have been calculated the copolymerization constants, was 10-12%. The elemental analysis: Found, %: C

75.45; H 6.72; Cl 10.68. C₁₉H₂₃O₃Cl. Calculated, %: C 75.33; H 6.87; Cl 10.61.

The copolymers, being white powder, are highly soluble in aromatic and chlorinated hydrocarbons. A yield of the copolymer reaches 92%.

The characteristic viscosity was determined in benzene in Ubbelohde viscometer ($[\eta] = 0.75-0.78$ dl/g).

The copolymer composition was determined on data of analysis of the functional groups (on epoxide number).

The IR spectra of the copolymers were registered on spectrometer "Agilent Cary 630 FTIR", and PMR spectra – on spectrometer BS-487B Tesla (80 MHz) in solution of deuterated chloroform.

The determination of the copolymerization parameter values presented in Table 1 was carried out on methods described in [18].

For investigation of the photochemical structuring of the copolymer there have been prepared 4-12%-s' solutions of the copolymers, which were applied on a glass substrate with size of 60 × 90 mm. The application was carried out by a method of centrifugation at 2500 rev·min⁻¹. The thickness of the resist layer after its drying for 10 minutes at room temperature and for 20 min. at 25°C/10 mm merc.c was 0.15-0.20 mcm.

The mercury lamp DRT-220 (current force – 2.2 A, distance from radiation source – 15 cm, rate of the

mobile valve of the exposure meter – 720 mm·h⁻¹, exposure time – 5-10 sec.) was used as a source of UV-irradiation. The content of insoluble copolymer was calculated on residue mass as a fact of formation of the cross-linked product.

3. Results and discussion

By a method of delatometry the kinetics of homopolymerization of CMCP has been studied and it has been shown that the reaction order on initiator is 0.5, on monomer – 1, similarly to data of work [19]. This regularity means that the copolymerization process of CMCP with GMA should probably proceed according to the same regularities as radical chain polymerization of the vinyl monomers. The data of the elemental analysis of the synthesized copolymer confirm that the polymers can consist of various combinations of the monomeric links.

CMCP is the new multifunctional monomer, in its radical copolymerization with GMA it would be expected the formation of new reactive polyfunctional copolymer.

The fact of the copolymerization behavior in the investigated systems was confirmed by turbidimetric titration data [20]. The availability of one inflection on the turbidimetric titration curves evidences that in the system it has been obtained the copolymer but not a mixture of two homopolymers (Fig. 1).

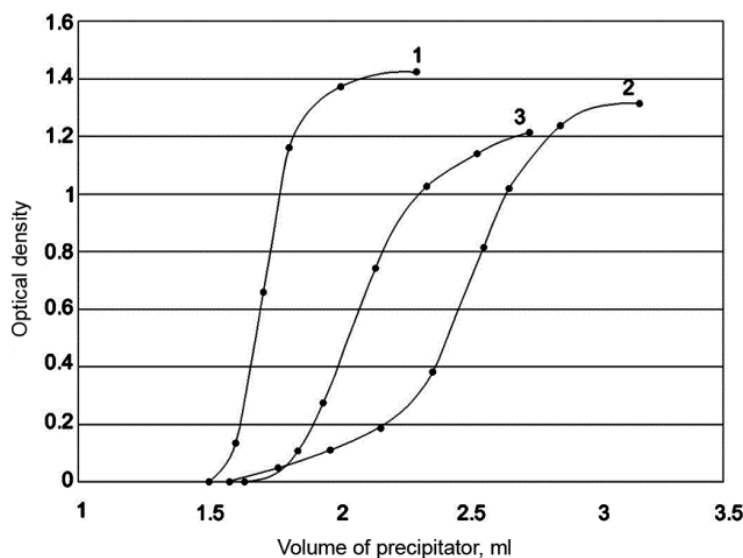


Fig. 1 Curves of turbidimetric titration of the copolymers of CMCP-co-GMA (1 - 21.32 mol% of GMA in the copolymer composition, 2 – 40.65 mol % of GMA in the copolymer composition, 3 – 62.5 mol % of GMA in the copolymer composition)

In carrying out of the copolymerization in any composition of the initial monomer mixture, a content of CMCP and GMA links in the forming copolymers is differed and is from 8.95 to 91.05 mol. Thus, the initial composition is the main factor determining the characteristics of copolymers. It has been revealed that the composition of the forming copolymers depends on composition of the initial monomer mixture.

The parameters of microstructure of the copolymers were determined based on

copolymerization constants [21]. The obtained data are presented in Table 1.

The obtained constant values of relative activity (Table 1) indicate a high reactivity of CMCP in comparison with GMA, which has been probably connected with influence of the substituent in the cyclopropane ring – CH₂Cl on electron density of the double bond of the vinyl group [22]. It has been revealed that the electron acceptor groups in the cyclopropane cycle are included in the general

conjugation system, causing 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 transition state is reduced, leading to an increase in the reactivity of the monomer.

Table 1.

Parameters of copolymerization CMCP (M₁) with GMA (M₂).

Composition of the initial mixture, mol.%		E.n.*	Composition of the copolymer, mol.%		r ₁	r ₂	Q ₁	e ₁	r ₁ ·r ₂	Microstructure of the copolymer**		
CMCP M ₁	GMA M ₂		CMCP M ₁	GMA M ₂						L _{M₁}	L _{M₂}	R
10	90	10.45	18.7	81.3	1.08 ±0.03	0.42 ±0.02	1.82 ±0.01	-0.78 ±0.02	0.45	1.12	4.78	33.9
25	75	8.03	37.5	62.5						1.36	2.26	55.24
50	50	5.22	59.35	40.65						2.08	1.42	57.14
75	25	2.74	78.68	21.32						4.24	1.13	37.24
90	10	1.15	91.05	8.95						10.72	1.04	17

*E.n. – content of epoxide groups (%)

**L_{M₁} and L_{M₂} – average length of blocks of monomers links; R – coefficient of Harwood blocking

For determination of activity factors of CMCP the scheme Q-e proposed by Alfrey and Price has been used [18]. The calculated values Q=1.82 and e= -0.78 for CMCP show that an introduction of chloromethylcyclopropane group in styrene in para-position leads to the change of electron-donor properties of the benzene ring.

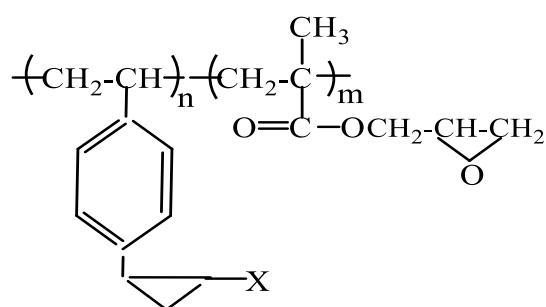
In the spectrum the intensive absorption band at 830 cm⁻¹, and also the absorption bands in the fields of 3068, 1250, 920 cm⁻¹ connected with vibrations of end epoxide cycle have been detected.

In the spectrum there are also the absorption bands in the fields of 1030-1040, 1580 and 1600 cm⁻¹, characteristic for three-membered carbon cycle and benzene ring, respectively. There is an absorption band at 635 cm⁻¹, referring to vibrations of the chlorine atom. It has been revealed that the absorption bands at 990 and 1640 cm⁻¹ presenting in the IR spectrum of the initial monomers and referring to the deformation and valence vibrations of double bond of the vinyl group after copolymerization disappear and the absorption

bands at 1720 and 1110 cm⁻¹, characteristic for vibrations >C=O, and ether bond, respectively, remain unaffected.

In the PMR spectrum of the copolymer the resonance signals are clearly appeared, they can be attributed to the protons of the benzene nucleus (δ=6.70-7.30 ppm) and cyclopropane ring (δ=0.65-1.68 ppm). The protons of epoxide ring are characterized by signals at 2.30-2.60 ppm (-CH₂-) and at 2.96 ppm (-CH-). The signals referring to the protons of the vinyl group (δ=5.10-6.66 ppm) in the polymer sample are completely absent.

Taking into account the above-mentioned one, it has been concluded that the copolymerization of CMCP with GMA proceeds only due to opening of the double bonds of the vinyl groups with conservation of other reactive functional fragments of both monomers. Thus, on the basis of analysis of IR and PMR spectra of the copolymers obtained by copolymerization of CMCP with GMA, the following copolymer structure is assumed



The investigated copolymers have various chemical nature. Due to the availability of reactive groups of various chemical nature in the links of macromolecule, the investigation of photochemical structuring of the synthesized copolymer is of interest.

It has been revealed that under action of UV-irradiation a cross-linking occurs, as a result of

insoluble material showing itself as photoresist of a negative type is formed.

The obtained copolymers have a high photosensitivity (56 cm²/J), good solubility before irradiation, resistance to solvent after crosslinking and good thermal stability, which is very important for photoresist. This copolymer is capable for formation of

the thin films and long-term storage with conservation of good lithographic properties.

An intensive behavior of the photochemical processes in the copolymers is caused by presence of such strongly absorbing groups as glycidyl, cyclopropane, carbonyl and chlorine atoms, etc in them, which increase the sensitivity of the copolymers

to UV-irradiation and are subjected to photochemical conversions leading to cross-linking of the polymer chains. Under action of UV-irradiation, the copolymer on the basis of CMCP and GMA easily undergoes the structuring, as a result of which the polymer films become insoluble and with low defects.

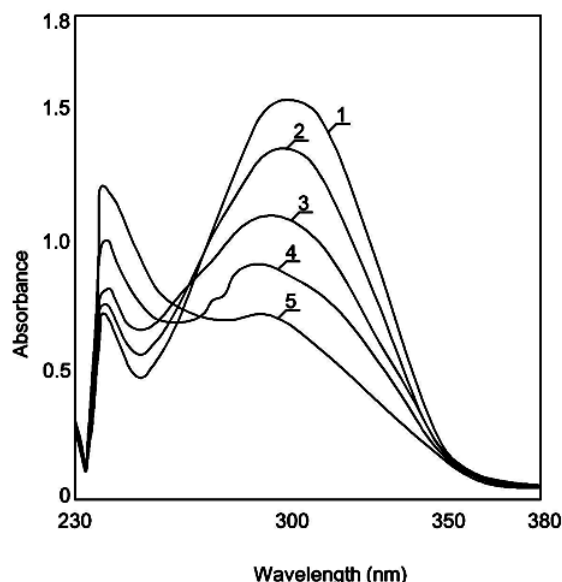


Fig. 2 Change of UV spectrum of absorption of the prepared film from poly(CMCP-co-GMA) at ratio [59.35:40.65]. 1-5 exposure time, respectively, $\tau=5, 10, 15, 20, 25$ sec.

The UV spectra of the copolymers show the absorption bands around 292 and 300 nm, referring to $\pi \rightarrow \pi$ transitions from suspended photoreactive fragments. The influence of irradiation on photosensitive polymers has been investigated by measure of the changes in the UV spectrum. An absorption intensity through various irradiation intervals (Fig. 2) indicates to changes occurring in the UV spectrum of the copolymer samples with composition of the monomer links in macrochain 59.35:40.65.

It has been clearly seen from character of the change of UV spectra of the copolymer that in the first stages of irradiation the change rate in the band maximum 292-300 nm is linear with irradiation time, however, after 30- and 60-sec. the deceleration of process comes and almost complete disappearance within 5 min of irradiation occurs.

It has been revealed that the sensitivity of the samples in the short-wave part of the spectrum strongly depends on layer thickness. In this case, with increase of the layer thickness the three-dimensional structure

forming after irradiation has a view of a loose grid with large cells, which swells strongly when manifested and decreases in drying of the polymer layer, causing folds and wrinkles. It has been shown that the good results have been obtained in working with films by thickness of 0.2-0.3 mcm.

For elucidation of ways and mechanisms of the photoreaction behavior we have studied the IR spectra of the copolymer films. The structuring process of the synthesized cyclopropane-containing copolymers has been studied by IR spectroscopic investigations. As follows from data of Fig.3 in the IR spectrum of the copolymer after irradiation, a decrease in the peak intensities of some absorption bands is observed. Depending on irradiation duration (1-5 min.) an intensity of maxima of the absorption bands characteristic for cyclopropane ring (1030-1035 cm^{-1}), chlorine atoms (635 cm^{-1}), carbonyl group (1720 cm^{-1}) and epoxide ring (830, 1240 cm^{-1}) is changed: with increase of irradiation time these fragments are firstly decreased and then (after ~5 min.) disappear.

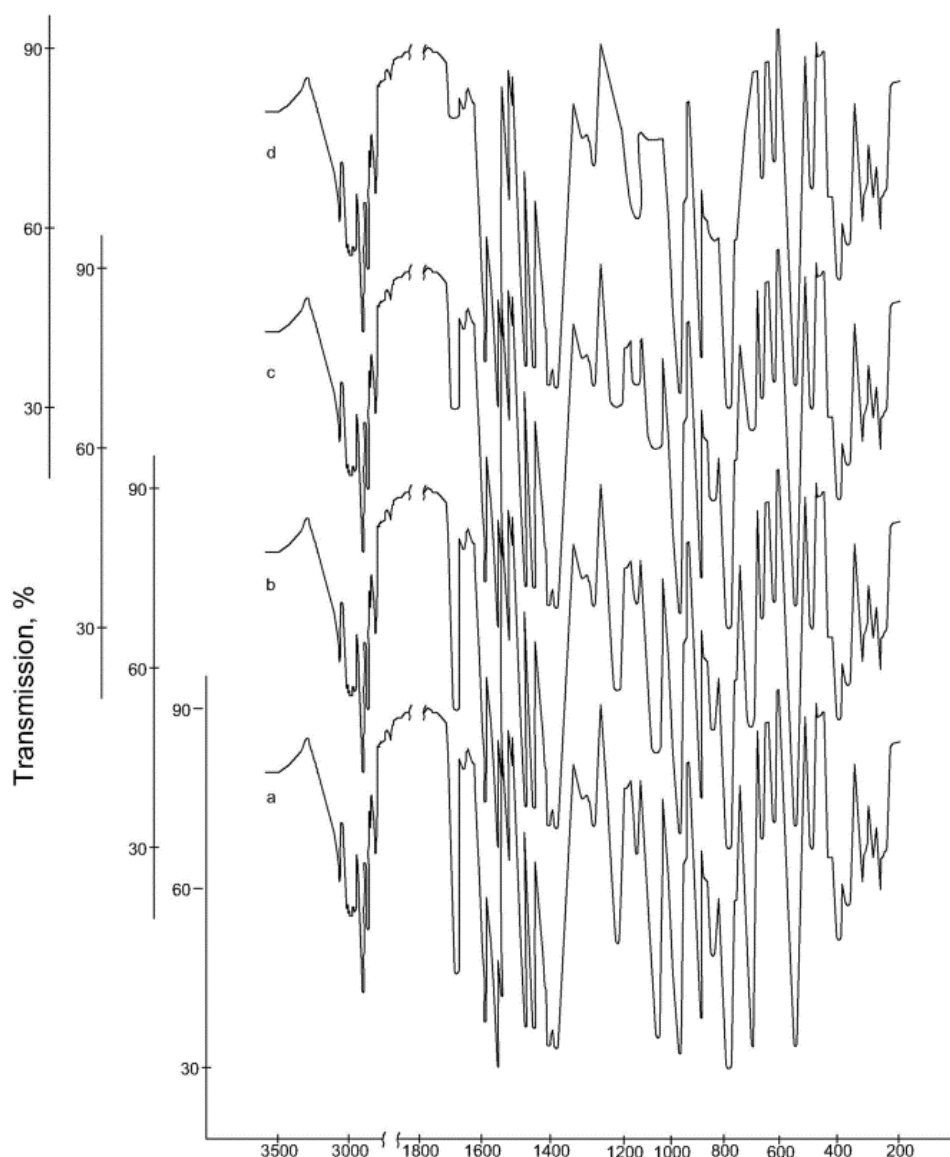


Fig. 3 IR-spectra of the copolymer film of CMCP-co-GMA: unirradiated (a) and irradiated for 1 (b), 3 (c) and 4 (d) sec. $m_1 : m_2 = 78.68 : 21.32$ mol %

Thus, it has been synthesized the new copolymer containing cyclopropane ring, carbonyl groups, chlorine atom and also epoxide groups in macromolecule, which allowed to create the polymer materials with high photosensitivity of negative type on the basis of copolymer.

4. Conclusions

It has been synthesized and characterized the new polyfunctional 2-chloromethyl-1-(p-vinyl phenyl)cyclopropane and it has been carried out its radical copolymerization with glycidyl methacrylate. The composition and structure of the synthesized copolymer have been established.

The copolymerization constants of the copolymerizing monomers ($r_1=1.08$; $r_2=0.42$) have been found and Q-e parameters values of Alfrey-Price scheme ($Q_1=1.82$; $e_1 = -0.78$) have been calculated. It

has been studied the process of structuring of the copolymer and it has been established that the synthesized copolymer has relatively high photosensitivity ($56 \text{ cm}^2/\text{J}$).

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