



COPOLYMERIZATION OF 2-(4-VINYLPHENYL)CYCLO- PROPYLMETHYL CINNAMATE WITH GLYCIDYL METHACRYLATE

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The radical copolymerization of 2-(4-vinylphenyl)cyclopropylmethyl cinnamate with glycidyl methacrylate has been studied and new cyclopropane- and epoxy-group containing photosensitive copolymers have been prepared. The relative activity of monomers and the parameters of Q and e by Alfrey and Price method have been determined. The copolymerization constants of 2-(4-vinylphenyl)cyclopropylmethyl cinnamate (r_1) and glycidyl methacrylate (r_2) were determined by the Fineman-Ross method and proved to be $r_1 = 1.05$ and $r_2 = 0.4$, respectively; the parameters Q_1 and e_1 were found to be 1.82, -0.79, respectively. The composition and structure of this copolymer have been established. The photochemical investigations of the synthesized copolymer have been carried out. It has been established that during the photochemical transformation a re-structuring takes place due to cyclopropane and epoxide ring opening and reaction of double bond in cinnamate fragment as well.

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group in the monomer which has influence on such important photolithographic parameters of resists as photosensitivity, adhesion.^{16,17}

PhCPC is a new reactive monomer, its synthesis and homopolymerization have been presented recently.¹⁸ The choice of this compound to copolymerize it with GDMA has been stipulated by the presence of light absorbing carbonyl, cyclopropane and epoxide groups or double bond in the molecule. In the copolymerization of the studied GDMA-PhCPC system is an important task is choosing the conditions when the polymerization is proceeded only by participation of vinyl group and the reactive fragments would be remained in the side chain without changes.

INTRODUCTION

Rapid increasing of information requires new type new type of materials to record, storage and reproduce data. The polymers and copolymers containing various reactive groups possess valuable properties and possibility of cross-linking under action of radiation which allows to prepare various materials used in microelectronics.¹⁻³ This is one of the main reasons for interesting of the researchers for the preparation of new types of the photosensitive polymers.⁴⁻⁸

Polymerization of functionally substituted cyclopropyl styrenes⁹⁻¹¹ is a known way to prepare this kind of materials, and the polymers prepared from unsaturated ethers of cinnamic acid undergo cross-linking processes upon UV irradiation with forming negative photoresists with high light sensitivity.^{12,13} Copolymerization of the cyclopropanes containing vinyl groups with other reactive monomers results polymers containing cyclopropane groups located in side part of macrochain is also well known.^{14,15}

This work has been devoted to investigate the copolymerization of 2-(p-vinylphenyl)cyclopropylmethyl cinnamate (PhCPC) with glycidyl methacrylate (GDMA) and study of properties of the copolymers prepared on their basis with the aim of creation of new photosensitive copolymers. The choice of this monomer has been stipulated with large number and chemical nature of double bonds and presence of cyclopropane ring in combination with carbonyl

EXPERIMENTAL

The synthesis of PhCPC was carried out by methodology described in our work.¹⁸ The copolymerization of PhCPC with GDMA was carried out in benzene solution in the presence of 0.5 % azobisisobutyronitrile (AIBN) (from total mass of monomers) at 70 °C. The total concentration of the initial monomers was 1.0 mol·L⁻¹, and a ratio of the initial monomers was changed as it is given in Table 1. The copolymers of various composition have been isolated after 10-20 min by addition excess of MeOH to the reaction mixture. The resulting copolymers were re-precipitated twice from theirs benzene solution with methanol and sulphuric acid and dried in vacuum (15-20 Hgmm) at 30 °C until constant weight.

The copolymers formed were white solids which are well soluble in aromatic and chlorinated hydrocarbons. Elemental analysis for C₂₈H₃₀O₅: Calculated: C, 75.33 %, H, 6.72. Found: C, 75.20, H, 6.35.

The content of constituents in the co-polymers could be determined from their bromine number (relates to the number of double bonds). The characteristic viscosity value was determined in benzene solution with using an Ubbelode viscosimeter which was proved to be $\eta = 0.7\text{--}0.72 \text{ dL}\cdot\text{g}^{-1}$.

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

The photosensitivity of co-polymers was determined at various concentrations (4-13 % solutions) with making a layer on the glass substrate in a dust-free medium with centrifuging at $2500\cdot\text{min}^{-1}$. The photoresists were kept for less than 20 min for increasing of adhesion to the substrate before cutting on contour on contour of the procurement preventing the film detachment.

Thickness of the prepared film-resists was measured by microinterferometer „LINNIKA”, which was proved to be $0.20\text{--}0.25 \mu\text{m}$ after drying for 10 and 20 min at room temperature and $30\text{--}35 \text{ }^{\circ}\text{C}/10 \text{ Hgmm}$, respectively.

The exposure of the procurements was carried out on a device with light point source through photomask with a DPT-220 mercury lamp (current intensity was 2.2 A, distance from source of radiation was 15 cm, mobile shutter rate of exonometer was $-720 \text{ mm}\cdot\text{h}^{-1}$, exposure time was 5-20 s).

The development was carried out in a jet installation. As a developer dioxane and isopropyl alcohol was used at ratio 1:2 at temperature of $18\text{--}25 \text{ }^{\circ}\text{C}$.

The photosensitivity is evaluated on the basis of the completeness of photochemical polymerization (cross-linking). The photosensitivity – the inverse of the dose of UV-light absorbed means an UV dose necessary for transformation of photoresist to crosslinked (insoluble) state.

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

where

H – exposure (or dose of irradiation with UV light), $\text{J}\cdot\text{cm}^2$

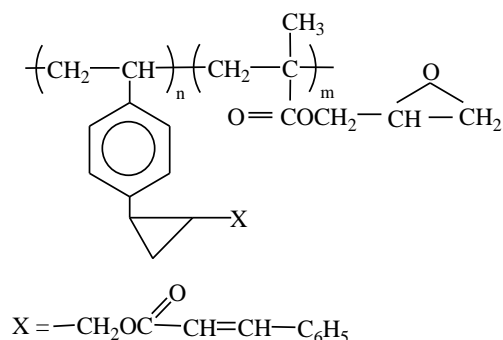
E – intensity, $\text{Wt}\cdot\text{cm}^{-2}$

t – irradiation duration, s

RESULTS AND DISCUSSION

During radical co-polymerization of polyfunctional PhCPC with GDMA formation of reactive polyfunctional co-polymer showed in Formula 1 could be expected.

Comparing of the IR-spectra of the copolymers formed with the spectra of the initial monomer (PhCPC) showed that the deformation and valence vibrations of the vinyl group in the initial monomer at 990 and 1640 cm^{-1} are disappeared.



Formula 1. The structural formula of the expected polyfunctional co-polymer

The absorption bands characteristic for benzene and cyclopropane rings ($1410\text{--}1460$ and $1500\text{--}1600 \text{ cm}^{-1}$) and the absorption bands at 1720 , 1030 and 1110 cm^{-1} , referring to the carbonyl vibrations of the cyclopropyl ester fragment are remained unaffected. The absorption band belong to valence vibration of the vinyl group located in cinnamic acid ester fragment at 1635 cm^{-1} is appeared in the co-polymers spectra.

Availability of the characteristic absorption bands of epoxide groups in structure of the copolymers is confirmed by the absorption band at 830 , 920 and 1260 cm^{-1} , 1388 cm^{-1} referring to the deformation vibrations of $\text{C}-\text{CH}_3$ group in the cinnamate fragment.

In addition, in the range of frequencies $800\text{--}680 \text{ cm}^{-1}$ and at 780 , 750 , 730 and 680 cm^{-1} absorption bands characterizing monosubstituted benzenes in esters of cinnamic acid could be observed. The IR-spectrum of PhCPC copolymer with glycidyl methacrylate is presented in Fig 1a (non-irradiated film).

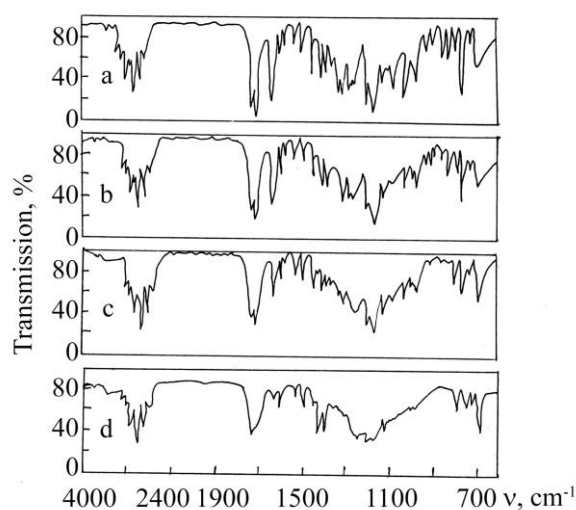


Figure 1. IR-spectra of copolymer film of PhCPC with GDMA: unirradiated (a) and irradiated for 1-st (b), 3-rd (c) and 4-th (d) min., $m_1 : m_2 = 78.7 : 21.3 \text{ mol}\%$.

In the PMR-spectrum of copolymer the resonance signals referring to protons of benzene nucleus ($\delta = 6.60\text{--}7.30$ ppm) and cyclopropane ring ($\delta = 0.65\text{--}1.66$ ppm) are clearly appeared, and the signals referring to protons of vinyl group ($\delta = 5.10\text{--}6.65$ ppm) – are absent. The protons of epoxide ring are characterized with signals at 2.30–2.60 ppm ($-\text{CH}_2-$) and at 2.96 ppm ($-\text{CH}-$). The signals of $\text{CH}=\text{CH}$ -groups of cinnamic fragment are $\delta = 6.4\text{--}7.4$ ppm. As r_1 and r_2 is less than 1, in this system there is a tendency to alternation of links.

According to the data of spectroscopy the copolymerization of PhCPC with GDMA proceeds only due to opening of double bonds of the vinyl groups with maintenance of the other reactive functional fragments of the both monomers. Thus, on the basis of the analysis of IR- and PMR-spectra of the copolymers prepared by copolymerization of PhCPC with GDMA, the structure of copolymers is assumed as it is given in Formula 1.

The copolymerization was carried out at various ratios of the initial monomers. It has been revealed that the composition of forming copolymers depends on the composition of the initial monomer mixture.

For estimation of polymerization activity of PhCPC there have been calculated the values of relative activity constants of monomers by Fineman-Ross method¹⁹ and the parameters Q - e by Alfrey and Price method.²⁰ The microstructure parameters of the copolymers were calculated by using the copolymerization constants on formulas.²⁰ The obtained data are presented in Table 1.

The values of the relative activity constants (Table 1) evidence about greater reactivity of PhCPC in comparison with GDMA, which may be the consequence of the influence of cyclopropane ring substituent ($-\text{CH}_2\text{OOC}-\text{CH}=\text{CH}-\text{C}_6\text{H}_5$) on the electron density of double bond in the vinyl group.²¹ The conjugation of the ester group causing redistribution of electron density both in the monomer and in the radical formed from it, thus the energy necessary for appearance of transition state is decreased leading to the increase of reactivity of monomer.

The calculated values of parameters Q_1 and e_1 during copolymerization with GDMA indicate increased conjugation in monomer (PhCPC) connected with influence of substituent – cinnamate fragment – stipulating relatively high reactivity of monomer and more low reactivity of the radicals. In calculation of factor e_1 it was chosen the negative mark based on the fact that the electron density of double bond of vinyl group in PhCPC should be less than in GDMA, since the influence of substituent of PhCPC leads to redistribute of density of double bond in the vinyl group changing polarity of the radical. This has been connected to the large reactivity of PhCPC in comparison with GDMA confirmed by copolymerization constant ($r_1 = 1.07$, $r_2 = 0.42$, respectively).

On the basis of the calculated copolymerization constants there have been obtained the data about microstructure of copolymers (Table 1). A length of blocks L_{M_1} is increased with increase of fraction of PhCPC in the composition of copolymers. It is seen from the Table 1 that R and L_{M_1} are maximal (57 and 37; 2.07 and 4.21 units, respectively) at

ratio of the initial monomers 50:50, 75:25. It follows that by selection of determined compositions of the monomer mixtures one can realize 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 the reactive groups of various chemical nature in links of macromolecule arouses interest for investigation of photochemical structuring of this copolymer, i.e. to cross-linking under action of UV-irradiation and such polymers showing as negative type photoresists. These polymers with properties of high light sensitivity, film-forming ability, good solubility before irradiation, resistance to solvents, plasma and etchants after cross-linking and good thermal stability, which are very important for photoresist.

Due to availability of strongly absorbing light energy of groups (cyclopropane, glycidyl, cinnamate $>\text{C}=\text{O}$ etc.) the synthesized copolymers are photosensitive and under the influence of UV-irradiation are subjected to the photochemical conversions leading to formation of crosslinked structures. The influence of irradiation on photosensitive polymers has been investigated by measurement in UV-spectrum.¹⁰ The photoreactive fragments have been considered with various concentrations 15–150 mg in thin films. The absorption bands in the UV-spectrum of polymers at 296 and 300 nm, respectively, are referred to $\pi \rightarrow \pi^*$ transitions. The intensities of absorption through various intervals of irradiation were changed in the UV-spectrum of the copolymer with ratio 59.19:40.81 (Fig.2).

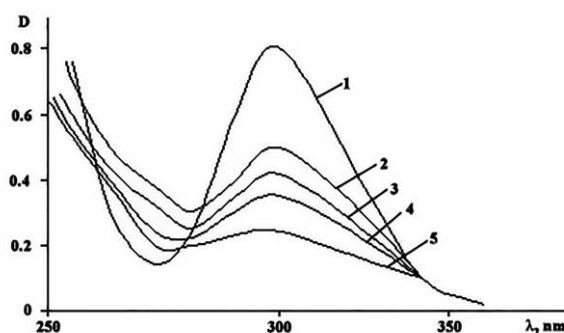


Figure 2. Change of UV-spectrum of absorption of made film from poli (PhCPC-co-GDMA) at ratio [59.19:40.81]. 1-5 light-striking time, respectively, $t=5, 10, 15, 20$ second.

During irradiation decrease or disappearance of photoactive fragments could be observed. The irradiation led to fast decrease of the absorption intensity at 296 and 300 nm and to disappearance of the bands almost completely after 6 min irradiation. This behaviour evidently indicates the formation of cyclobutane ring.²² All this process is explained in reference 22.

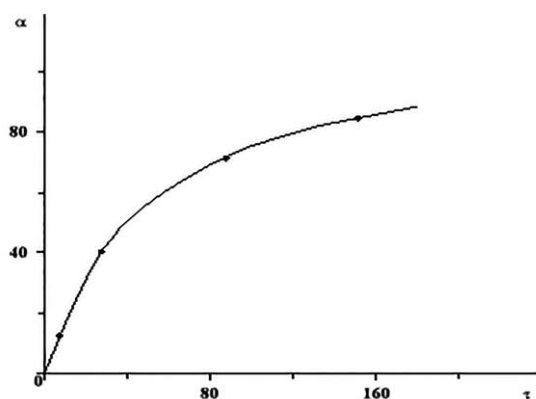
It is also possible that due to irradiation a cyclohexane fragment is formed via cycloaddition of cinnomol unit of the polymer which destroys the conjugation in the electron system of cyclopropane ring. It has been revealed that an increase of concentration of polymers raises a photocross-linking rate due to large quantity of photosensitive units.

Table 1. Parameters of copolymerization of PhCPC (M_1) with GDMA (M_2).

Composition of initial mixture, mol. %		B. N.	Composition of copolymers, mol. %		r_1	r_2	Q_1	e_1	$r_1 \cdot r_2$	Microstructure of copolymer		
PhCPC M_1	GDMA M_2		PhCPC m_1	GDMA m_2						LM_1	LM_2	R
10	90	7.7	18.7	81.3	1.07	0.42	1.82	-0.79	0.44	1.11	4.78	34
25	75	15.0	37.11	62.89	± 0.03	± 0.02	± 0.01	± 0.02		1.35	2.26	55
50	50	23.5	59.19	40.81						2.07	1.42	57
75	25	31.1	78.7	21.3						4.21	1.13	37
90	10	36.0	91.04	8.96						10.63	1.04	17

LM_1 and LM_2 – average length link blocks of monomers; R – Harwood blocking factor

In films of copolymer, a conversion rate of the photosensitive fragments depends on composition of the light-sensitive links in the copolymer chain. The crosslinking rate grows with increase of composition of cinnomol units (Fig.3). It could be concluded that after 40-80 sec. irradiation (transformation is 50-70 %), the polymer films become insoluble in organic solvents in which they were dissolved at room temperature to do irradiation experiments. Such behaviour is caused by formation of hard three-dimensional network due to intermolecular photoinduced cycloaddition of hanging units.

**Figure 3.** Influence of irradiation time τ (s) on solubility of copolymer (α - content of insoluble fraction).

The three-dimensional structure during irradiation has a form of a loose net with large cells, which swells strongly during development and is compressed during drying of the polymer layer, causing folds and wrinkles.

The good results have been prepared in work with films of thickness 0.2-0.3 μm .

The process of 3D-structure evolution during irradiation of the prepared cyclopropane-ring containing copolymers has been followed by IR spectroscopy as well (Fig.1.). The intensity of the absorption bands characteristic for cyclopropane ring ($1030\text{-}1035\text{ cm}^{-1}$), double bonds (1635 cm^{-1}), carbonyl group ($1720\text{-}1725\text{ cm}^{-1}$), and epoxide ring ($830, 920, 1260\text{ cm}^{-1}$) were decreased with increasing of irradiation time and were completely disappeared ~ 8 min irradiation due to 3D-structure evolution with opening

of double bonds and cyclopropane rings. The absorption band at 1720 cm^{-1} , characteristic for carbonyl group in ester fragments being in conjugation with double bond is shifted to 1740 cm^{-1} during irradiation which can be attributed to the opening reaction of double bond and as a consequence the disappearance of conjugation. It is confirmed with following change of the content of double bonds in cinnamate fragment controlled by measurement of bromine number.²³

Conclusions

A new copolymer has been synthesized and its composition, structure and properties have been established. The availability of cyclopropane ring, cinnamate and glycidyl carbonyl groups in macromolecules of the prepared copolymer allowed to create a material with high photosensitivity. These copolymers have high photochemical crosslinking ability to create solid elastic layers with good adhesion to substrates and to prepare polymer films with low microdeficiency.

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