

Copolymerization of (P-Chlorophenoxy-carbonyl)-Cyclopropyl Styrene with Styrene and Methyl Methacrylate

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ABSTRACT: The radical copolymerization of (p-chlorophenoxy-carbonyl)cyclopropyl styrene with styrene and methyl methacrylate has been studied. New cyclopropane-containing copolymers have been obtained. It has been established that the synthesized copolymers due to peculiarities of their structure and polyfunctionality, namely with content of carbonyl and cyclopropane groups sensitive to UV irradiation in the macromolecule have photosensitivity. The constant values of relative activity of monomers have been determined and Q-e parameters on Alfrey and Price have been calculated. The copolymerization constants of this compound (r_1) with styrene and methyl methacrylate (r_2), calculated on Fineman-Ross method are: $r_1 = 1.1$ and 1.05 , but $r_2 = 0.56$ and 0.48 , respectively; Q and e parameters values: $Q_1 = 3.1$ and 2.4 , $e_1 = -1.4$ and -0.8 , respectively. The photochemical structuring has been investigated and it has been shown that the structuring process proceeds due to of cyclopropane ring opening and carbonyl group. The composition and structure of these copolymers have been established and their some characteristics (heat resistance, hardness, adhesive strength, water absorption) have been investigated. The structuring process has been also studied and it has been established that the synthesized copolymer has relatively high photosensitivity ($50-55 \text{ cm}^2 \cdot \text{J}^{-1}$).

KEYWORDS: microstructure, monomers, copolymerization, (p-chlorophenoxy)cyclopropyl styrene, photosensitivity

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I. INTRODUCTION

One of the first polymer materials investigated as electronoresists were negative photoresists on the basis of polyvinylcinnamate and cyclo-rubber. A review of these works is presented in [1]. Now, the use of synthetic polymers in the field of microelectronics as photo-and electron-resists does not sufficiently meet the requirements of this industry, namely, high photosensitivity, satisfactory resolution, resistance to chemical influences, good adhesion of the photoresist film to the substrate, and good deformation and strength characteristics.

This explains the great interest of researchers to preparation of new types of photosensitive polymers for microelectronics [2-8]. We have solved this problem by polymerization of functionally substituted cyclopropyl styrenes [9-11].

The interest in the preparation of such polymers has been stipulated by the fact that the forming macromolecules contain reactive functional groups of various nature in the form of hangers in the main macrochain. As a result of copolymerization of functional cyclopropane-containing vinyl compounds, being one of the most perspective reactive monomers, the polymers containing cyclopropane groups, regularly located in the side hangers or macrochains have been synthesized [12,13].

This work has been devoted to the investigation of copolymerization of (p-chlorophenoxy-carbonyl)-cyclopropyl styrene (CPhCCS) with styrene and methyl methacrylate (MMA) and study of the structure and properties of copolymer obtained on their basis with the aim of creation of new photosensitive copolymers. The choice of this monomer has been stipulated by the fact that the concentration of double bonds and their chemical nature, and also the availability of cyclopropane ring in combination with carbonyl group in the monomer decisively influence on such important photolithographic parameters of the resist as photosensitivity and resolution, as evidenced by sufficiently large experimental material accumulated to now.

The choice of this compound for investigation of copolymerization with traditional monomers (styrene and MMA) has been stipulated by availability of strongly absorbing the light energy of groups (carbonyl, chlorine and cyclopropane) in molecule of new monomer. For copolymerization of the studied systems, it is

important to choose conditions under which the polymerization would occur only along the vinyl group, and the reactive fragments would remain unchanged in the side chain.

II. EXPERIMENTAL PART

Synthesis of 2-chlorophenoxy carbonyl 1-(p-vinyl phenol) cyclopropane (CPhCCS) (I). 12.85 g (0,1 mol) of p-chlorophenol dissolved in ethylmethyl ketone (EMK, 150 ml) was added into a three-neck flask equipped with mechanical stirrer, thermometer, and drop funnel, the contents were cooled to 0°C. Then 20.65 g (0.1 mol) of 2-chlorocarbonyl-1-(p-vinylphenyl)cyclopropane in 30 ml of EMK was added dropwise for 30 min. at constant stirring and cooling. The reaction mixture was stirred for 30 min and for another 20 min. at room temperature.

The obtained residue was extracted with ether and the ether solution was washed consequently with 0.5% NaOH solution and distilled water to remove the unreacted contents.

The ether layer was dried with anhydrous Na₂SO₄ and then evaporated using a rotary evaporator. The product was recrystallized from ethanol and obtained with yield 25.97 (87%), m.p.=50-52°C.

Elemental analysis (%): C=72.36; H=5.10, Cl=11.90 (calculated); C=72.20; H=5.0; Cl=11.70 (found).

The copolymerization of the synthesized CPhCCS with styrene and MMA was carried out in ampoules in benzene solution in the presence of 0.5% of dinitrilazoisobutyric acid (AIBN) (from total monomer mass) at 70°C. The forming copolymer was purified by twofold reprecipitation from benzene solution and dried in vacuum (15-20 mm merc.c.) at 30°C to constant mass. The copolymers being white powder are well soluble in aromatic and chlorinated hydrocarbons. The characteristic viscosity was determined in benzene in Ubbelohde viscometer. The molecular weight value (MW) (300000-450000) was estimated on characteristic viscosity ($[\eta]=0.95-1$ dl/g).

The composition of copolymers was determined according to the data of elemental analysis of the chlorine atom.

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

For investigation of the photochemical structuring of the copolymer there have been made 2-10% copolymer solutions, which were applied on 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 min. at room temperature and for 20 min. at 25°C/10 mm merc.c. was 0.15-0.20 mcm.

A mercury lamp DRT-220 (current strength – 2.2 A, distance from radiation source – 15 cm, rate of the mobile shutter of the exonometer –720 mm·h⁻¹, exposure time – 5-10 seconds) was used as a source of UV irradiation. The content of the insoluble copolymer was calculated on the residue mass.

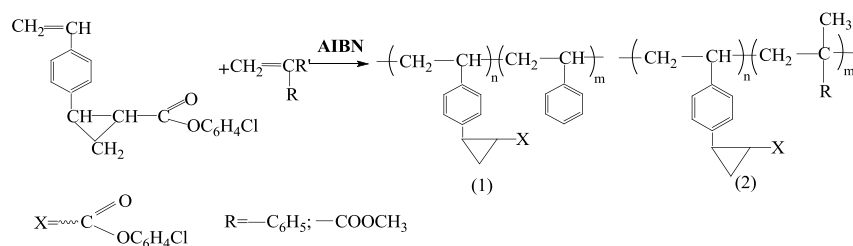
III. RESULTS AND DISCUSSION

With the aim of establishment of the structure of the synthesized copolymers the spectral analyses (IR and PMR spectroscopy) of the synthesized monomer and polymer samples have been carried out.

Due to the fact that CPhCCS is a polyfunctional compound, during its radical copolymerization with styrene and MMA, it should be expected the formation of new reactive polyfunctional copolymers.

It has been established by comparison of IR spectra of copolymers with spectra of the initial monomer that the absorption band in the IR spectrum of the initial monomer at 990 and 1640-1645 cm⁻¹, referring to deformation and valence vibration of double bond of the vinyl group after copolymerization disappear. The absorption bands characteristic for benzene ring and cyclopropane groups are kept after copolymerization. The absorption bands at 1030-1035 cm⁻¹, referring to vibrations of cyclopropane ring at 1720 and 1110 cm⁻¹ of ether bond remain unaffected, respectively.

In the PMR spectra of copolymer the resonance signals referring to protons of benzene nucleus ($\delta = 6.60-7.30$ ppm) and cyclopropane ring ($\delta = 0.65-1.66$ ppm.) are clearly appeared, and the signals referring to protons of the vinyl group ($\delta = 5.10-6.65$ ppm.) are absent. According to the data of spectroscopy the copolymerization of CPhCCS with styrene and MMA proceeds only due to opening of double bonds of the vinyl groups with conservation of remaining reactive functional fragments of p-chlorophenoxy carbonyl)cyclopropyl styrene. Thus, on the basis of analysis of IR spectra of copolymers obtained by copolymerization of CPhCCS with styrene and MMA, the following structure of copolymers is assumed:



The copolymerization was carried out at various ratios of the initial monomer. In any initial ratio of the monomers a copolymer enriched with links of CPhCCS is always formed (**Table I**).

The initial composition is a main factor determining the 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 polymerization activity of XPhKTC there have been calculated the constant values of relative activity of monomers on compositions of the initial monomer mixture on Fineman-Ross method [14] Q-e parameters – on Alfrey and Price. The parameters of microstructure of copolymers were determined on the basis of copolymerization constants [15]. The obtained data are presented in **Table I**.

The constant values of relative activity (**Table I**) indicate to greater reactivity of CPhCCS in comparison with styrene and MMA, which has been connected with influence of substituent at p-chlorophenoxy-carbonyl)cyclopropyl styrene of cyclopropane ring on electron density of double bond of the vinyl group [16]. The ester group is included in the general conjugation system, causing electron density redistribution both in the monomer and in the radical center formed from it. As a result, the energy necessary for appearance of the transition state is decreased, leading to an increase of the reactivity of the monomer.

The calculated values of Q_1 and e_1 parameters during copolymerization with both styrene and MMA indicate to an increased conjugation in the monomer (CPhCCS) connected with the influence of a substituent of p-chlorophenoxy-carbonyl)cyclopropyl styrene stipulating high reactivity of the monomer and lower reactivity of radicals. In calculation of e_1 factor it was chosen the negative sign on the basis that the electron density of double bond of the vinyl group at CPhCCS should be less than at styrene and MMA, because the influence of substituent at CPhCCS leads to redistribution of electron cloud density of the double bond of the vinyl group, changing the radical polarity. The greater reactivity of CPhCCS in comparison with styrene and MMA confirmed by the copolymerization constants ($r_1 = 1.1$ and 1.05 , but $r_2 = 0.56$ and 0.48 , respectively) has been also connected with it. The data of microstructure of copolymers have been obtained on the basis of calculated copolymerization constants (**Table I**). A length of blocks L_{M1} in increased with increase of fraction of PhCCPS in the composition of copolymer. It is seen from Table that R and L_{M1} are maximum (57.42 and 42.63; 2.1 and 54.64 units, respectively) at ratio of the initial monomers 50:50, 75:25. It follows that the selection of certain compositions of the monomer mixtures one can use the directed formation of the microstructure of copolymers, which is one of the most perspective ways of modification of their properties.

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

The photochemical investigations of the synthesized copolymers were carried out on methodology [10]. Owing to the availability of groups strongly absorbing the light energy (cyclopropane, chlorine, carbonyl), the synthesized copolymers are photosensitive and in action by UV irradiation are subjected to photochemical conversions leading to the formation of net structures. The structuring process of the obtained cyclopropane-containing copolymers has been studied with IR spectral investigations. Depending on irradiation duration (3-5min.) the intensity of maxima of the absorption bands characteristic for cyclopropane ring ($1030-1035 \text{ cm}^{-1}$), carbonyl group (1720 cm^{-1}) and chlorine atom ($650-680 \text{ cm}^{-1}$) falls considerably or disappear completely.

Probably, these groups take part in photochemical reactions leading to the structuring of carbonyl group of the copolymers.

Thus, the availability of cyclopropane ring, chlorine atom and carbonyl groups in the macromolecules of the obtained copolymer allowed to create a material with high photosensitivity on the basis of the copolymer.

In Table II the comparative characteristics of properties of the synthesized copolymers, polystyrene and poly-MMA are presented.

It follows from the data shown in Table II that the copolymers containing CPhCCS being photosensitive have higher heat-physical and physical-mechanical properties in comparison with polystyrene and poly-MMA. These qualities allow to use them in making of photosensitive materials with improved lithographic characteristics.

It has been established in investigation of physical-mechanical properties of copolymers (CPhCCS + St and CPhCCS + MMA) that in the temperature range $-20 \div 80^\circ\text{C}$ they retain higher tensile strength and practically

do not decrease elasticity in the field of low temperature.

The synthesized polymers possess also good optical indices ($n_D^{20} = 1.5935-1.6054$). It has been revealed that the obtained polymers retain transparency up to 100°C during their holding for 1-1.5 hours. It has been shown that the light transmission in the visible part of the spectrum is 85-90% and does not depend much on the thickness of the sample up to 6-8 mm, at a relatively high thickness, the optical properties are partially deteriorated, which is typical for all known transparent materials.

As a result of carried out work the new cyclopropane-containing copolymers of negative type has been synthesized. It can be concluded on the basis of carried out investigations that the availability of cyclopropane ring and other fragments in the structure of the synthesized copolymer provides high photosensitivity for this copolymer (50-55 cm²/J). It has been shown that the created photoresists are characterized with high lithographic parameters, good adhesion to substrates and few microdeficiency of the polymer films. The synthesized polymers can be used as photosensitive polymer materials for microelectronics, and also in optics as an optically transparent material.

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Table I. Copolymerization of CPhCCS (M_1) with styrene (M_2) and MMA (M_2).

Composition of the initial mixture, mol. %		Composition of copolymers, mol. %		r_1	r_2	Q_1	e_1	$r_1 \cdot r_2$	Microstructure of copolymer		
M_1	M_2	m_1	m_2						L_{M_1}	L_{M_2}	R
CPhCCS -St											
10	90	15.62	84.38	1.10±0.03	0.56±0.02	3.1±0.01	-1.4±0.02	0.6 1	1.12	6.04	38.74
25	75	33.77	66.23						1.35	2.68	49.38
50	50	57.40	42.60						2.08	1.56	54.64
75	25	78.35	21.65						4.24	1.18	49.40
90	10	98.15	8.85						10.72	1.06	16.72
CPhCCS -MMA											
10	90	19.36	80.64	1.05±0.03	0.48±0.02	2.4±0.01	-0.8±0.02	0.5 0	1.12	4.60	35
25	75	37.90	62.10						1.35	2.20	56
50	50	59.35	40.65						2.05	1.40	58
75	25	78.54	21.46						4.15	1.13	38
90	10	90.91	9.09						10.45	1.04	17

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

**Table II. Some characteristic of the obtained copolymers
(content of CPhCCS in the composition of copolymers – 30 mol.%).**

Index	CPhCCS + St	CPhCCS + MMA	poly-St	poly-MMA	poly- CPhCCS
Refractive coefficient	1.56	1.60	1.59	1.49	1.6
Vicat heat resistance, °C	125	120	103	115	130
Brinell hardness, kg·mm ⁻²	18.0	15.0	14	13	20.5
Specific impact strength, kg·cm·cm ⁻²	18.0	18.8	18	12	21.0
Tensile strength, MPa	34.6	52.0	35.0	60.0	45.0
Adhesion strength, MPa	4.2	5.4	-	-	8.3
Water absorption for 24 h, %	0.08	0.16	0.1	0.3	0.08

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