

Synthesis, radical copolymerization of (p-vinylphenyl)cyclopropyl chlorocinnamate with styrene and photosensitivity of the prepared copolymer

K.G. Guliyev*, A.M. Aliyeva, D.R. Nurullayeva, A.M. Guliyev

Institute of Polymer Materials
Azerbaijan National Academy of Sciences
Sumgait, Azerbaijan
ipoma@science.az
*Corresponding author

Abstract

The radical copolymerization of (p-vinylphenyl)cyclopropyl chlorocinnamate with styrene has been studied. The new cyclopropane-containing photosensitive copolymer has been prepared. The composition and structure of the synthesized copolymer have been established, the constant values of relative activity of monomers have been determined and the parameters Q-e have been calculated. The dependence of photosensitivity on composition of copolymer has been revealed.

Keywords- microstructure, monomers, copolymerization, (p-vinylphenyl)cyclopropyl chlorocinnamate, photosensitivity

1 Introduction

It was known that the high-molecular compounds containing functional groups $\text{C}=\text{O}$, $\text{C}=\text{C}$, $\text{C}=\text{O}$, $\text{N}=\text{N}$ in its composition, etc are used in the photolithographic processes as the photoresists [1,2].

The functionally substituted cyclopropanes attract a large attention of the researchers with its specific properties (bactericide activity and photosensitivity) [3-6]. This makes perspective the investigations in the field of synthesis of cyclopropane derivatives with the aim of search of new photoresists with high sensitivity to light action.

The main problem of creation of the light-sensitive polymers and polymer compositions is the preparation of materials possessing sufficiently high degree of light-sensitivity in combination with high resolution ability, stability to aggressive media, good adhesion, thermal stability, etc. In spite of accumulated sufficiently large experimental material on creation of the light-sensitive materials to present time, the search of new more efficient light-sensitive materials remains relevant. The photosensitivity of the polymers is affected by the structure of their chain and presence of various functional groups.

2 Materials and Methods

During investigation it is made an attempt to synthesize the new cyclopropane-containing monomer and polymer on its base, in macromolecule of which there are three-

membered carbon rings, double bonds and chlorine atoms in combination with carbonyl group in the side chain. These groups being photosensitive should give a high photosensitivity and other technological properties to macromolecules, necessary for its use as the light-sensitive base in creation of photoresist materials.

The aim of this work was the systematic investigation of influence of functional substituent on photosensitivity of cyclopropane-containing polymer.

With this aim there has been synthesized the (p-vinylphenyl)cyclopropyl chlorocinnamate (PCCC), its radical copolymerization with styrene has been carried out and the photosensitivity of synthesized copolymer has been investigated. The synthesis of PCCC has been prepared by interaction of 2-hydroxymethyl-1-(p-vinylphenyl)cyclopropane with chloranhydride of chlorocinnamic acid.

The chlorocinnamic acid was obtained by interaction of 2-chlorobenzaldehyde with malonic acid, in solution of absolute alcohol in the presence of pyridine [7]. The composition and structure of the prepared PCCC has been established on the basis of spectral (IR- and PMR-) and elemental analysis. It has been established that the reaction product is the mixture consisting of two individual compounds. As has been revealed, these compounds are geometrical cis- and trans-isomers at ratio cis : trans = 30:70. The purity of the synthesized compounds was controlled by a method of GLC-analysis and in all cases was corresponded > 99,0%. The PCCC

copolymerization with styrene was carried out in various ratios of the initial monomers and in benzene solution at 70°C, in the presence of AIBN.

It has been shown that the copolymerization of the synthesized monomer with styrene proceeds sufficiently smoothly, without touching of cyclopropane ring and leads to the formation of the soluble copolymers to 86% conversion.

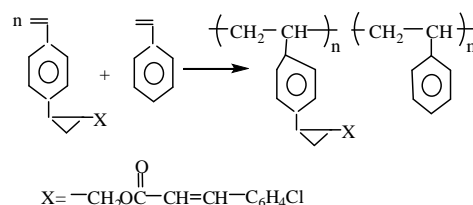
It has been established on data of spectral and chemical analysis that the copolymerization process in the studied conditions proceeds due to opening of vinyl bond with formation of macromolecules with side substituted fragments.

The copolymer after purification and drying was a white powder, soluble in acetone, in aromatic and chlorine-containing hydrocarbons and insoluble in ether and in alcohols.

It has been established in the IR-spectra of copolymers as well as in PCCC that in all samples there are the absorption bands at 675 cm⁻¹ and in the field of 1030-1035 cm⁻¹, referring to vibrations of chlorine atom and cyclopropane ring correspondingly. In the spectrum there are also the absorption bands at 1720 cm⁻¹, corresponding to group C=O, the intensive bands at 1215 and 1170 cm⁻¹, characteristic for 1,4-disubstituted

benzenes and bands at 1110 and 1015 cm⁻¹. These four absorption bands belong to planar deformation vibrations of four hydrogen atoms of benzene ring. In addition, there is a band at 1635 cm⁻¹ in the spectrum, which belongs to >C=C< bond of cinnamic acid.

It has been concluded on the basis of the IR-spectroscopy and elemental analysis data that the synthesized polymer has the following structure:



The copolymerization constants of the investigated monomers were found at their conversion no more 10% based on composition of copolymer, determined on data of double bond on bromine number [8]. The values of Q-e scheme of Alfrey and Praice have been also calculated. For estimation of character of links distribution in macromolecular chain there have been calculated the parameters of microstructure LM_1 , LM_2 , R [9]. In Table 1 the results of calculation are presented.

Table1. Copolymerization of PCCC (M_1) with styrene (M_2)

Composition of initial mixture, mol.%		B.n., g	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						LM_1	LM_2	R
10	90	6.1	15.60	84.40						1.12	6.04	28
25	75	13.12	33.52	66.48						1.35	2.68	50
50	50	22.3	57.18	42.82	1.05 ±0.03	0.54 ±0.02	3.1 ±0.01	-1.5 ±0.02	0.56	2.08	1.56	55
75	25	30.62	78.12	21.88						4.24	1.18	37
90	10	35.6	91.10	8.9						10.72	1.06	17

LM_1 and LM_2 – average length of blocks of monomer links; R – coefficient of Harwood blocking

As follows from Table 1, the copolymerization constant values characterize the large activity of PCCC in comparison with styrene. This fact has been apparently connected with availability of conjugation of cyclopropane cycle with substituents in the investigated monomer, which is agreed with data of work [10], as far

as an introduction of cyclopropane with substituent in para position of styrene causes the great changes in the electronic structure of molecule.

The availability of cyclopropane, cinnamate and carbonyl groups, and also chlorine atoms in macromolecules of the synthesized copolymers allowed to create the material

with high light-sensitivity and other improved lithographic properties on the basis of copolymer. Under the action of UV-irradiation a copolymer easily undergoes structuring as a result of which the made polymer films become insoluble. We have studied the photo-structurization rate from copolymer composition (fig.1). It has been revealed that the cross-linking rate grows with increase of cinnamoyl blocks in composition. And only 40-80 second irradiation is enough (transformation 25-35%), for that the polymer films were insoluble. Thus, these polymers interact photochemically in accordance with mechanism similar to cinnamic acid and its derivatives, in which the cyclobutane structures are formed [11]. We have established that the synthesized copolymer firstly enough high photosensitivity, and secondly, the photosensitivity is in the direct dependence on PCCC content (fig.2).

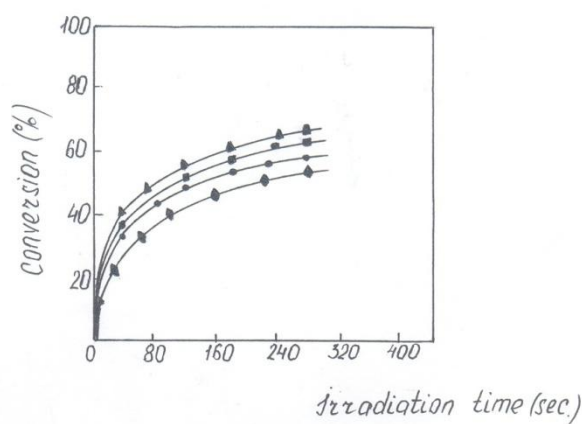


Figure 1. Cross-linking rate of poly(PCCC with styrene as a thin film: (\diamond) 15:85; (\bullet) 34:66; (\blacksquare) 58:42; (\blacktriangle) 78:22.

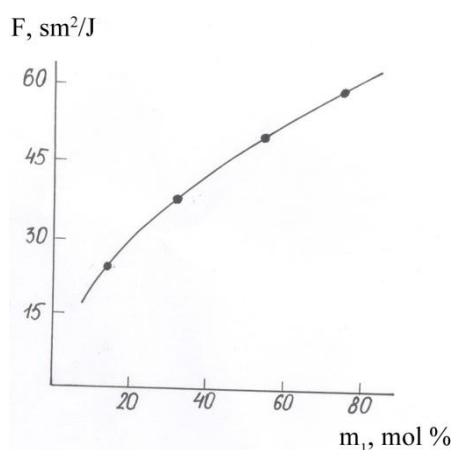


Figure 2. Dependence of photosensitivity (F) of copolymer of PCCC+styrene on copolymer composition.

For clarification of ways and mechanisms of proceeding of photo-reaction, we have studied the IR-spectra of the copolymer films.

In the photo-reactions process at UV-irradiation it takes place a decrease of intensity or disappearance of absorption bands at 1635, 1035 cm^{-1} , corresponding to $>\text{C}=\text{C}<$ and cyclopropane fragments being in the side chain of macromolecule. We have established on the basis of data of IR-spectrum of copolymers before and after irradiation that the photo-cross-linking process takes place basically due to opening of double bond and cyclopropane groups. These data confirming proceeding of the photo-cross-linking process are clearly presented in fig 3.

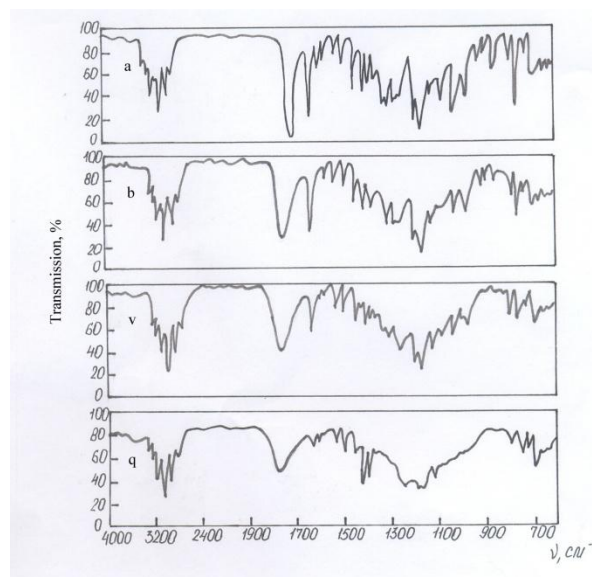


Figure 3. IR-spectra of copolymer film of PCCC (m_1) with styrene (m_2): non-irradiated (a) and irradiated for 1 (b), 3 (c) and 4 (d) min. $m_1:m_2=78.12:21.88$ mol%

2.1 Experimental

The synthesis of (p-vinylphenyl)cyclopropyl chlorocinnamate was carried out in three-neck flask, to which was placed 17.4 g (0.1 mol) 2-hydroxymethyl-1-(p-vinylphenyl)cyclopropane in 30 ml of absolute sulphuric ether, pyridine, 0.1 g hydroquinone and dropwise in cooling in ice bath 40.2 g(0.2 mol) chloranhydride of chlorocinnamic acid was added.

The reaction mixture was stirred for 4 h. The fallen salt was filtered, extracted by sulphuric ether. After drying over MgSO_4 firstly sulphuric ether was distilled off from prepared mixture. The residue was distilled in vacuum (b.p. = 188-190°C/1 mm merc.c.). $n_{D,20}^{20} = 1.55$, $d_{4,20}^{20} = 1.19$,

$MR_{d\text{ calc.}} = 85.90$, $MR_{d\text{ found}} = 85.33$. Yield – 291,11 g (86%). Calculated, %: C 74.5, H 5.61. Found, %: C 74.21, H 5.54.

The copolymerization of the synthesized PCCC with styrene was carried out in ampoules in benzene solution in the presence of 0.5% dinitrileazoisobutyric acid (AIBN) (from total mass of monomers) at 70°C. The total concentration of the initial monomers was constant and was 0.2 mol/l, and a ratio of the initial monomers was changed in the concentrations shown in Table 1. The forming copolymer was purified by two-fold precipitation from benzene solution to methanol and dried in vacuum (15-20 mm merc.c.) at 30°C to constant mass. The copolymer, which is a powder of white color, is well soluble in aromatic and chlorinated hydrocarbons. The characteristic viscosity was determined in benzene and in Ubbelohde viscosimeter. The characteristic viscosity ($[\eta]$) was 0.95 dl/g.

The copolymer composition was determined on data of analysis of the functional groups (determination of double bonds on bromine number).

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

For investigation of photochemical structuring of copolymer there were made 3-12% solutions of copolymers, which were applied on a glass substrate having a size of 60x90 mm. The application was carried out by a method of centrifugation at 2500 rev·min⁻¹. The thickness of resist layer after its drying for 15 min., at room temperature and for 20 min. at 25°C/10 mm merc.c., was 0.2-0.25 mcm.

As a source of UF-irradiation it was used a mercury lamp DPT-220 (current intensity – 2.2 A, distance from radiation source – 15 cm, movable damper rate of exponometer – 720 mm·h⁻¹, exposition time – 10-15 sec.). The content of insoluble copolymer was calculated on residue mass as a fact of formation of cross-linked product.

3 Conclusions

It has been investigated the copolymerization of (p-vinylphenyl)cyclopropyl chlorocinnamate with styrene. The parameters of copolymerized systems have been found. It has been revealed that the (p-vinylphenyl)cyclopropyl chlorocinnamate is more reactive monomer at radical copolymerization than styrene. The composition and structure of the synthesized copolymers have been established.

It has been shown that the synthesized copolymer shows a high photosensitivity, possesses good film-forming ability and adhesion property and can be used as a resist material for microelectronics.

4 References

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