ISSN 1070-4272, Russian Journal of Applied Chemistry, 2018, Vol. 91, No. 2, pp. 304−309. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © K.G. Guliyev, A.I. Sadygova, G.Z. Ponomareva, A.M. Aliyeva, Ts.D. Gulverdashvili, D.B. Tagiyev, 2018, published in Zhurnal Prikladnoi Khimii, 2018, Vol. 91, No. 2, pp. 257−262.

MACROMOLECULAR COMPOUNDS
AND POLYMERIC MATERIALS

Synthesis of 2-Chloromethyl-1-(*p*-vinylphenyl)cyclopropane and Its Copolymerization with Styrene

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Received February 1, 2018

Abstract—A new polyfunctional monomer, 2-chloromethyl-1-(*p*-vinylphenyl)cyclopropane, was synthesized, and its radical copolymerization with styrene was performed. The copolymerization constants were determined, and the Alfrey–Price *Q*–*e* parameters were calculated. The photochemical cross-linking of the synthesized copolymer containing photosensitive groups (cyclopropane ring, chlorinated organic moiety) was studied. The copolymer exhibits relatively high photosensitivity (54 $cm^2 J^{-1}$) and can be used as a photosensitive base of negative photoresists.

DOI: 10.1134/S1070427218020209

The choice of a photoresist and conditions of its use are determined by its purpose. There is a trend toward production of narrow-purpose photoresists, but this approach requires the development of a wide range of photosensitive materials. The presently available negative photoresists do not fully meet all the process requirements in production of integrated microcircuits. Therefore, the development of new types of negative photoresists for definite purposes attracts steady researchers' attention.

Polymers containing various reactive groups in pendant chains exhibit a valuable set of properties and are capable of radiation-induced cross-linking, which allows their use for preparing resists for microelectronics [1–3]. Therefore, there is a great deal of interest in preparation of new types of photosensitive polymers [4–8]. To this end, we have systematically studied the synthesis and polymerization of functionally substituted cyclopropylstyrenes [9–11].

In reactive polymers, reactive functional groups of various kinds are mainly located in pendant chains. In particular, promising reactive polymers containing cyclopropane groups regularly arranged in pendant chains or in the macrochain are prepared from cyclopropane-containing monomers [12, 13].

In this work, we prepared a new monomer, 2-chloromethyl-1-(*p*-vinylphenyl)cyclopropane (CMCPS), examined the relationships of its radical copolymerization with styrene, and studied the properties of the copolymer prepared from this monomer with the aim of developing new photosensitive polymers.

The choice of this monomer is due to the fact that the concentration of double bonds and their chemical nature, and also the presence of the cyclopropane ring in combination with the $–CH_2Cl$ group in the monomer exert a decisive effect on such important photolithographic parameters of the resist as photosensitivity, adhesion, etc. [14, 15].

CMCPS was prepared by the reaction of *p*-divinylbenzene with ethyl diazoacetate in the presence of a catalyst, anhydrous $CuSO_4$. First we prepared ethoxycarbonylcyclopropylstyrene (ECCPS). Then, ECCPS was converted to the corresponding hydroxymethylcyclopropylstyrene in 95% yield by treatment with $LiAlH_4$ in refluxing ether. High selectivity of $LiAlH_4$ used a reducing agent allowed selective reduction of the carbonyl group, leaving the double bond and cyclopropane group intact (see the scheme).

The choice of optimum conditions is important for preparing CMCPS III in high yield. The cyclopropane ring appears to be unstable to electrophilic agents, including HCl and PCl_3, without solvent even at 0°C. Chlorination of alcohol II yields by-products; therefore, the optimum procedure for chlorination of alcohol II was addition of PCl_3 to the alcohol in absolute ether at –40°C. The yield of chloride III was 85%.

The spectra in combination with the GLC data show that reaction product III is a mixture of trans and cis isomers (relative to the three-membered ring) in 65 : 35 ratio. The purity of the synthesized compound was monitored by GLC and in all the cases exceeded 99.2%.

In the IR spectrum, there are absorption bands at 1030–1040, 1640–1645, 1580, and 1600 cm^{-1}, characteristic of the three-membered ring, C=C double bound in the vinyl group, and benzene ring, respectively. The band at 635 cm^{-1} is assigned to C–Cl vibrations (Fig. 1).

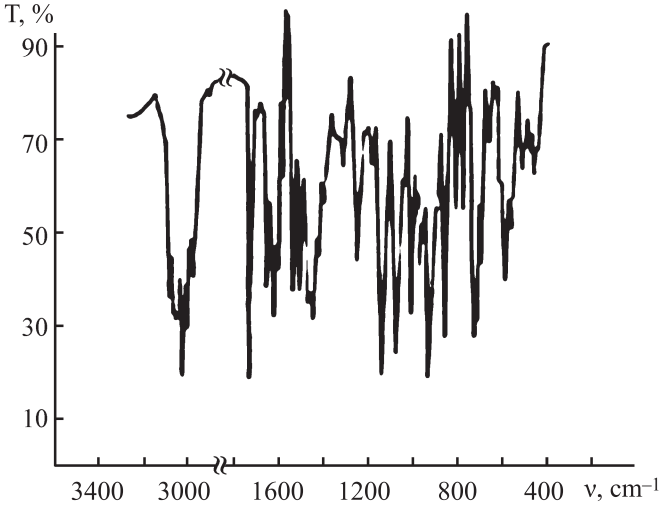


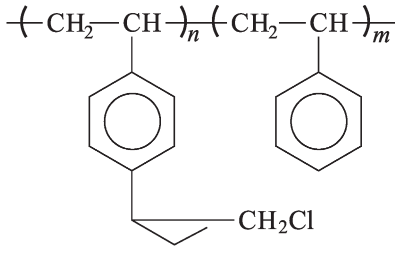
Fig. 1. IR spectrum of CMCPS monomer. (T) Transmittance and (ν) wavenumber.

In the ^{1}H NMR spectrum of CMCPS, there are signals from proton at the double bond (δ = 5.14–6.67 ppm), three-membered ring (δ = 0.7–1.65 ppm), and benzene ring (δ = 7.0–7.05 ppm).

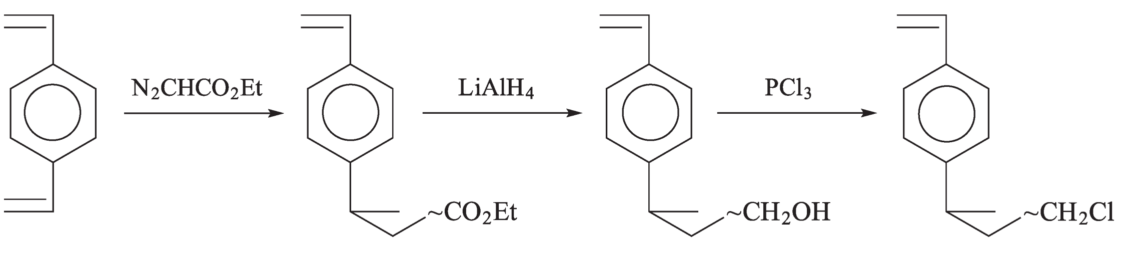
It was important to find optimum conditions for the radical copolymerization of CMCPS with styrene, so as to ensure polymerization exclusively via the vinyl double bond, leaving the reactive fragments in the pendant chain intact. Therefore, the copolymerization was performed in the presence of an initiator, azobis(isobutyronitrile) (AIBN). Radical polymerization of CMCPS was performed in the bulk and in solution.

The chemical structure of the copolymer was confirmed by the IR and ^{1}H NMR data. The absorption bands at 1040 and 3090 cm^{-1}, belonging to the cyclopropane ring in the monomer, are fully preserved in the IR spectrum of the copolymer. On the other hand, the vinyl absorption bands at 990 and 1640–1645 cm^{-1}, present in the IR spectrum of the monomers, disappear. All the copolymer samples contain C–Cl absorption bands at 635–750 cm^{-1}.

The ^{1}H MNMR spectrum of the copolymer contains well-defined signals from protons of the benzene (δ = 6.60–7.30 ppm) and cyclopropane (δ = 0.65–1.66 ppm) rings. Signals assignable to vinyl protons are absent. The spectroscopic and analytical data obtained allow a conclusion that the copolymerization of CMCPS with styrene occurs via double bond of vinyl groups of the polymer, with the chloromethylcyclopropyl moiety remaining intact:



Scheme.



Copolymerization of CMCPS (M_1) with styrene (M_2)

Initial mixture composition, mol %		Copolymer composition, mol %		r_1	r_2	Q_1	e_1
M_1	M_2	m_1	m_2				
10	90	16.67	83.33	1.03 ± 0.03	0.5 ± 0.02	3.2	–1.5
25	75	34.65	65.35				
50	50	57.45	42.55				
75	25	77.78	22.22				
90	10	90.68	9.32				

The formation of such structure is also confirmed by the ^{1}H NMR data.

Radical copolymerization was performed at different molar ratios of CMCPS and styrene. The mole fractions of the units, m_1 and m_2, were found from the chlorine content of the copolymers.

To calculate the copolymerization constants of the monomers, we determined the dependence of the copolymer composition on the composition of the initial monomer mixture (see table).

The relative activity constants of the monomers, r_1 and r_2, were calculated by the Fineman–Ross method, and the specific activity factor of CMCPS monomer, Q_1, and the radical polarity, e_1, were calculated using the Alfrey–Price *Q*–*e* scheme (see table). For styrene, $Q_2 = 1.0$ and $e_2 = –0.8$.

The copolymerization constants r_1 and r_2 of the system show that CMCPS is more active than styrene ($r_1 > r_2$). This is apparently associated with the effect exerted by the chlorine atom at the cyclopropane ring on the vinyl group through the three-membered ring and with an increase in the degree of conjugation in the monomer molecule. This fact is confirmed by the UV spectra of the monomers [14].

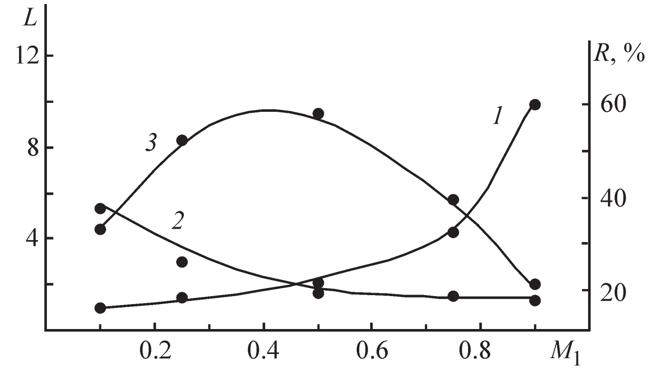


Fig. 2. Copolymer microstructure: length *L* of (*1*) CMCPS and (*2*) styrene blocks and (*3*) block structure parameter *R*. (M_1) Mole fraction of CMCPS.

From the copolymerization constants, we calculated the probabilities of formation of different unit sequences in the copolymer macromolecule.

The difference in the copolymerization constants of CMCPS and styrene leads to variation of the monomer ratio in the reaction mixture in the course of copolymerization, which is responsible for the compositional heterogeneity of the copolymer with different chain microstructure.

To study the copolymer structure in more detail, we calculated the block length *L* and the block structure parameter (Fig. 2).

The block length L_{M1} increases with increasing mole fraction of CMCPS in the copolymer. With an increase in the block length L_{M1} from 1.1 to 10 units, the block structure parameter decreases from 30.2 to 17.6%. The maximal block structure parameter ($R = 56.65\%$) is reached at equimolar ratio of the starting monomers.

Thus, the copolymer structure can be controlled by choosing appropriate compositions of the monomer mixtures, which is one of the ways of modifying the copolymer properties.

The synthesized polyfunctional copolymer containing cyclopropane and C–Cl groups, which are very sensitive to UV radiation, is a valuable object for photochemical studies and can serve as a base for developing photosensitive materials.

Owing to the presence of reactive groups of different chemical nature in the units of the synthesized copolymer, it is interesting to study its photochemical cross-linking under UV irradiation. The development of photoresists requires polymers with high levels of photosensitivity, film-forming ability, solubility before irradiation, resistance to solvents, and heat resistance.

Under the action of UV radiation, the CMCPS-based copolymer readily undergoes cross-linking. The resulting film is insoluble and has low defectiveness.

The photochemical cross-linking of the copolymer was performed by the procedure described in [10]. Owing to the presence of groups strongly absorbing the light energy (cyclopropane and C–Cl), the synthesized copolymer is photosensitive and undergoes photochemical transformations under UV irradiation to form network structures.

Photochemical experiments were performed at different polymer concentrations, 15–150 mg in thin films.

The photochemical transformation of the copolymer was monitored at different steps of the UV irradiation. The results are shown in Fig. 3.

The photochemical reaction occurring under UV irradiation leads to a decrease in the intensity or to disappearance of the absorption bands at 1040 and 635 cm^{-1}, corresponding to the cyclopropane rings and C–Cl bonds in the pendant chain of the macromolecule.

The cross-linking occurs via opening of the cyclopropane ring with participation of the chlorine atom in photochemical reactions.

Our studies demonstrated the possibility of preparing a new valuable photosensitive copolymer (54 cm^2 J^{-1}). The photosensitivity of the copolymer directly depends on the CMCPS content. As the fraction of chlorinated cyclopropylstyrene is increased from 34.65 to 80 mol %, the copolymer photosensitivity increases from 30 to 54 cm^2 J^{-1}.

Such copolymers with high levels of photosensitivity, film-forming ability, and heat resistance show promise as the photosensitive base for negative photoresists.

The sample photosensitivity strongly depends on the film thickness. At increased film thickness, the three-dimensional structure after the irradiation is a loose network with large cells, which strongly swells in the course of development and shrinks after drying of the polymer layer with the formation of folds. The observed phenomenon is due to a decrease in the spectral sensitivity of the samples with an increase in the film thickness.

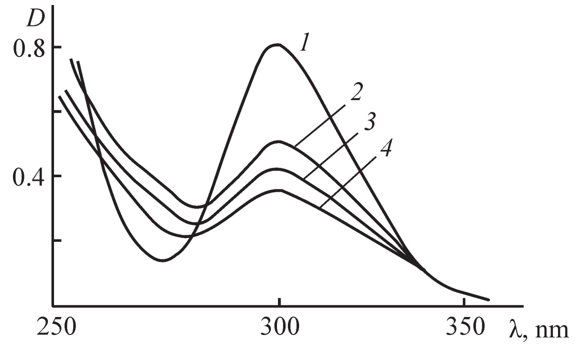


Fig. 3. Evolution of the UV absorption spectra of the CMCPS–styrene copolymer film upon irradiation. (*D*) Optical density and (λ) wavelength. Irradiation time, s: (*1*) 0, (*2*) 5, (*3*) 10, and (*3*) 15.

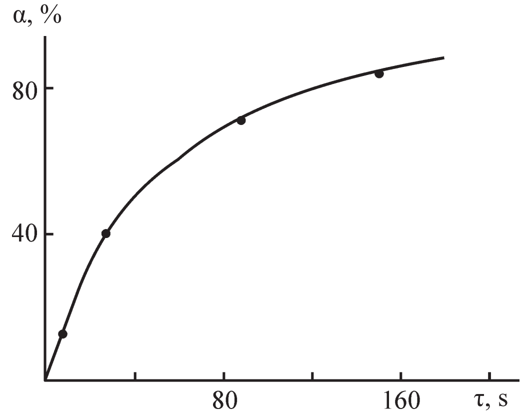


Fig. 4. Influence of the irradiation time τ on the polymer solubility. (α) Content of insoluble fraction.

Good results were obtained in experiments with 0.2–0.3-μm-thick films.

In copolymer films, the rate of conversion of photosensitive fragments depends on the composition of photosensitive layers in the polymer chain (Fig. 4). As can be seen, after irradiation for 40–80 s (50–80% conversion) the polymer films become insoluble in organic solvents in which they were soluble at room temperature before irradiation.

Thus, we have prepared a new copolymer and determined its composition, structure, and properties. The presence of the cyclopropane ring and –CH$_2$Cl group ensures high photosensitivity of the copolymer and formation of a solid elastic layer with high adhesion to supports and low film microdefectiveness.

EXPERIMENTAL

2-Chloromethyl-1-(p-vinylphenyl)cyclopropane. To a solution of 0.1 mol of 2-hydroxymethyl-1-(*p*-vinylphenyl)cyclopropane in 30 mL of absolute ether, 0.1 mol of freshly distilled PCl_3 was added dropwise at a temperature from –35 to –40°C. The mixture was allowed to stand at this temperature for 1 h and then, after adding 5 mL of water, at 20°C for 3 h. The organic layer was separated, and the aqueous layer was extracted several times with diethyl ether. The ether extracts were combined and dried over calcined Na_2SO_4, the ether was distilled off on a water bath, and the residue was distilled in a vacuum.

The product obtained had the following characteristics: yield 82%, n_D^{20} 1.5720, n_D^{20} 1.180, MR_D (calculated/found): 52.266/52.20. Elemental analysis (calculated/found): C 74.8/74.2, H 9.0/8.5, Cl 24.65/24.25.

Copolymerization of the synthesized monomer was performed in ampules in the bulk and in a benzene solution in the presence of 0.5% (relative to the sum of the monomers) azobis(isobutyronitrile) at 70°C. The copolymer formed was purified by double reprecipitation from a benzene solution into methanol and was dried in a vacuum (15–20 mmHg) at 30°C to constant weight.

The copolymer composition was evaluated by the chemical method from the chlorine content.

The IR spectra of the copolymers were recorded with a Specord M-80 spectrometer, and the ^1H NMR spectra, with a BS-487B Tesla spectrometer (80 MHz) from $CDCl_3$ solutions.

The parameters of the copolymer microstructure, namely, the mean length L of a block consisting of like units and the block structure parameter R (Harwood parameter) characterizing the number of blocks of like units per 100 units of the copolymer, were calculated using the equations

$$\bar{l}_2 = 1 + r_2\frac{[M_2]}{[M_1]}, \quad \bar{l}_1 = 1 + r_1\frac{[M_1]}{[M_2]},$$

$$R = \frac{200}{2 + r_1\frac{[M_1]}{[M_2]} + r_2\frac{[M_2]}{[M_1]}}.$$

To determine the photosensitivity of the copolymer, we prepared several copolymer solutions of different concentrations (4–13%). The photoresist layer was applied onto glass supports in a dust-free medium with a centrifuge at 2500 rpm. After application, the photoresist was left for no less than 20 min to enhance its adhesion to the support. Then, the photoresist was cut along the support contour avoiding the film peel-off.

The resist film thickness was measured with a LINNIKA microinterferometer. The resist film thickness after drying for 10 min at room temperature and for 20 min at 30–35°C/10 mm Hg was 0.20–0.25 μm.

The supports with the applied photoresist were exposed on an installation with a point light source through a phototemplate. A DRT-220 mercury lamp was used as a UV radiation source (current 2.2 A, distance from the radiation source 15 cm, velocity of the light meter shutter 720 mm h^{-1}, exposure time 5–20 s).

The development was performed in a jet installation at 18–25°C using a 1 : 2 mixture of dioxane and isopropyl alcohol as a developing solution.

The completeness of the photochemical polymerization (cross-linking) of the photoresist base molecules was used as a criterion of the photosensitivity of negative photoresists under UV irradiation. After the exposure and development, the content of the insoluble polymer was calculated from the weight of the residue (cross-linked product).

CONCLUSIONS

(1) 2-Chloromethyl-1-(*p*-vinylphenyl)cyclopropane was synthesized and characterized, and its radical copolymerization with styrene was performed. The composition and structure of the copolymer were determined.

(2) The copolymerization constants of the monomers were determined ($r_1 = 1.03$, $r_2 = 0.5$), and the parameters of the Alfrey–Price Q–e scheme were calculated ($Q_1 = 3.2$, $e_1 = -1.5$).

(3) Cross-linking of the copolymer was studied. The synthesized copolymer has relatively high photosensitivity (54 cm^2 J^{-1}).

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