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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Photosensitivity of Polymers Based on Epoxy-Substituted Vinylphenylcyclopropanes

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Abstract—The capability of polymers synthesized from new monomers, 2-glycidyloxymethyl- and 2-glycidyloxycarbonyl-1-(*p*-vinylphenyl)cyclopropane, to photochemical cross-linking was evaluated from variation of their solubility after UV irradiation. The dependence of the photosensitivity of the polymers on the structure of substituents was studied.

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The prospects for practical use of functional polymers, in particular, in negative photoresists, cause an interest in their study. The presence of functional groups and also their chemical nature affect appreciably such important photolithographic parameters of a resist as photosensitivity and resolution [1–7].

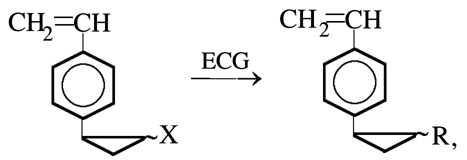
The practice of using some resists in photolithographic processes revealed a number of significant drawbacks, one of which is low photosensitivity. Hence, to improve the photosensitivity and other lithographic characteristics of negative photoresists based on functional polymers, radically new approaches to the synthesis of new monomers and polymers based on these are required.

We studied previously [8] the photochemical characteristics of polymers of functionally 2-substituted cyclopropylstyrenes.

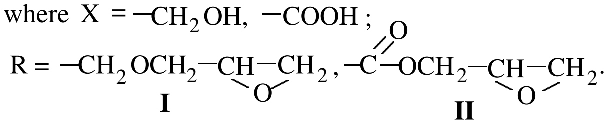
Here we studied how the structure of functional groups affects the photosensitivity of polymers prepared from 2-glycidyloxymethyl- and 2-glycidyloxycarbonyl-1-(*p*-vinylphenyl)cyclopropanes.

The monomer for preparing the polymer was synthesized as follows. First, 2-ethoxycarbonyl-1-(*p*-vinylphenyl)cyclopropane was prepared by the reaction of ethyl diazoacetate with *p*-divinylbenzene in the presence of a catalytic amount of anhydrous $CuSO_4$. Then, 2-ethoxycarbonyl-1-(*p*-vinylphenyl)cyclopropane was saponified to obtain 2-carboxy-1-(*p*-vinylphenyl)cyclopropane and reduced to obtain 2-hydroxymethyl-1-(*p*-vinylphenyl)cyclopropane [9].

To prepare 2-glycidyloxymethyl- and 2-glycidyloxycarbonyl-substituted cyclopropanes, we chose the following pathway:



where X = $-CH_2OH$, $-COOH$;



$$R = -CH_2OCH_2-\underset{O}{CH-CH_2},\ -\overset{O}{\overset{\|}{C}}-OCH_2-\underset{O}{CH-CH_2}.$$

I II

Chromatographic analysis and spectral data showed that the synthesized monomers I and **II** were mixtures of two individual compounds. We found that these compounds were geometric *cis* and *trans* isomers (ratio *cis* : *trans* = 30 : 70). The purity of the monomers synthesized was monitored by gas-liquid chromatography. In all cases it was 99.9%.

In the IR spectra of **I** and **II**, there are absorption bands at 830–850, 990–1000, 1640–1645, 1035–1045, and 1105–1110 cm^{-1}, characteristic of epoxy ring, vinyl group, three-membered carbon ring, and ether bond, respectively. In addition, in monomer **II** there is an absorption band at 1720 cm^{-1} characteristic of the carbonyl group. The absorption bands at 1500 and 1605 cm^{-1} characteristic of the benzene ring are preserved.

The ^1H NMR spectra of **I** and **II** contain signals characteristic of protons of aromatic ring (δ = 6.60–7.30 ppm), cyclopropane ring (0.65–1.66 ppm), and vinyl group (5.10–6.65 ppm). The epoxy ring protons give signals at 2.30–2.60 ppm (CH_2), and 2.96 ppm

(CH). These results suggest that the reactions in all steps proceed smoothly and with quantitative yields of the target products, leaving the vinyl group and three-membered ring intact.

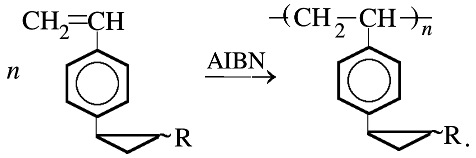
Polymerization of **I** and **II** was performed in the bulk and in benzene solution at 70°C in the presence of azobis(isobutylonitrile) (AIBN).

It was shown that, under the conditions studied, polymerization proceeds via scission of the double bond of the vinyl group to form macromolecules with reactive cyclopropane and epoxy side groups. This fact is confirmed by examination of the structure of the resulting polymers.

A comparison of the IR spectra of the initial monomers and polymers synthesized from them shows that the absorption bands at 990 and 1640 cm^{-1} observed in the spectra of the initial monomers and assigned to the bending and stretching modes of the vinyl bond, respectively, disappear after polymerization. The absorption bands at 1500 and 1605 cm^{-1} and in the range 1035–1045 cm^{-1} characteristic of the benzene ring and cyclopropane group, respectively, are retained during polymerization.

The absorption bands in the spectra of polymers at 1720 and in the ranges 840–850, 1105–1110 cm^{-1}, assigned to vibrations of the C–O, epoxy, and ether groups, are completely retained after the polymerization.

The IR data and elemental analysis suggest that the polymers synthesized have the following structure:



First of all, we should note some features of the structure of the resulting polymers containing two reactive groups, cyclopropane and epoxy, in the side chains of macromolecule. Due to easy rupture of the C–C and C–O bonds under irradiation [10–12], these functional groups impart to the resulting polymers high sensitivity to UV irradiation: under UV irradiation, these polymers easily transform into the insoluble form.

To elucidate the mechanism of photochemical cross-linking, we performed a spectroscopic study. For this purpose, we studied cross-linking of the resulting epoxy and cyclopropane-containing polymers by IR spectroscopy in various stages of UV irradiation. The results of UV irradiation are presented in Table 1.

Table 1. Data on UV irradiation of polymers based on monomers **I** and **II**

Monomer	Amount of polymer, %, after irradiation for indicated time, min				
	1	2	6	10	12
I	17	45	65	88	93
II	23	50	70	91	97

Table 1 shows that the maximal degree of photochemical conversion (the maximal amount of insoluble fractions) is observed with the polymer obtained from monomer **II**. This fact is undoubtedly associated with the structure of the macromolecule: along with cyclopropane and epoxy groups, it contains strongly absorbing carbonyl group, which significantly enhances the uptake of the UV energy.

The spectral analysis of the polymers showed that after UV irradiation the absorption bands characteristic of cyclopropane ring (1030–1040 cm^{-1}) and epoxy fragment (840–850, 917, 1250–1260 cm^{-1}) decrease or disappear. It was shown that the intensities of the absorption bands characteristic of cyclopropane and epoxy fragments decrease to a similar extent during UV irradiation in the initial stages. The clearest results were obtained at irradiation duration of 30 min, when the absorption bands of the above fragments virtually completely disappeared. Since the spectrum of the polymer after irradiation contained no absorption bands corresponding to cyclopropane and epoxy rings, it is evident that these groups participate in the subsequent photochemical reactions and these reactions are apparently resposible for the high capability of the polymer for photochemical cross-linking.

As seen from Table 2, the polymers synthesized have high lithographic characteristics, which allows these polymers to be used as a photosensitive base of photoresists. Thus, our studies demonstrated the possibility of developing a new class of photosensitive materials having high film-forming ability, elasticity, achromatism, and good adhesion characteristics appropriate for formation of photoresist films.

EXPERIMENTAL

2-Glycidyloxymethyl-1-(*p*-vinylphenyl)cyclopropane was prepared in a three-necked flask charged with 14.4 g (0.1 mol) of 2-hydroxymethyl-1-(*p*-vinylphen-

Table 2. Characteristics of polymers based on epoxy-substituted vinylphenylcyclopropanes

Copolymer	Concentration of polymer in benzene, %	Content of microdefects, def cm^{-2}	Film thickness, μm	Exposure time, s	Photosensitivity, cm^2 J^{-1}
I	2	0.20	0.15	20	55.8
	5	0.20	0.15	20	56.7
	6	0.20	0.15	20	52.3
	10	0.25	0.20	20	50.5
II	2	0.15	0.15	20	56.4
	5	0.15	0.15	20	58.4
	6	0.20	0.15	20	53.2
	10	0.20	0.15	20	51.7

yl)cyclopropane in 50 ml of dehydrated ethanol, 0.2 g of hydroquinone, and 8 g (0.2 mol) of powdered sodium hydroxide. Then, 14 g (0.15 mol) of epichlorohydrin (ECH) was added with vigorous stirring. The reaction mixture was stirred for 4 h. The NaCl precipitate was filtered off, and ethyl ether was removed. Then the reaction mixture was distilled to isolate the reaction product: bp 150–153°C at 1 mm Hg, yield 18.86 g (82%), n_D^{20} = 1.5220, d_4^{20} = 1.04, $MR_{D\mathrm{calc}}/MR_{D\mathrm{found}}$ = 67.07/67.45.

Found (%): C 78.30, H 7.80.
Calculated (%): C 78.26, H 7.83.

2-Glycidyloxycarbonyl-1-(*p*-vinylphenyl)cyclopropane was prepared in a three-necked flask equipped with a stirrer, a reflux condenser, and a dropping funnel. The flask was charged with 18.8 g (0.1 mol) of 2-carboxy-1-(*p*-vinylphenyl)cyclopropane, 50 ml of anhydrous ether, and 1.2 g of hydroquinone, and 2.3 g (0.1 g-atom) of finely cut sodium metal was added with stirring in a nitrogen atmosphere. After complete dissolution of sodium, 14 g (1.15 mol) of ECH was added dropwise. The mixture was heated to 40°C for 1 h; after reaction completion, NaCl was filtered off, and the ether and unchanged EPC were removed. The residue was distilled in a vacuum; bp 160–162°C at 1 mm Hg, yield 22.21 g (91%), n_D^{20} = 1.5310, d_4^{20} = 1.12, $MR_{D\mathrm{calc}}/MR_{D\mathrm{found}}$ = 67.09/67.36.

Found (%): C 78.30, H 7.80.
Calculated (%): C 78.26, H 7.83.

Polymerization was carried out both in the bulk and in a benzene solution in the presence of 0.2 mol % AIBN at 70°C. The resulting polymers were purified by twofold precipitation from a benzene solution with methanol and dried at 30°C in a vacuum (15–20 mm Hg).

After purification, all the polymers obtained are soluble in aromatic and chlorine-containing hydrocarbons and insoluble in alcohols.

The molecular weight was estimated from the intrinsic viscosity determined in benzene in an Ubbelohde viscometer: [η] = 1.05 (**I**) and 1.1 dl g^{-1} (**II**).

The IR spectra of the polymers were recorded on a UR-20 spectrometer.

To study the photochemical cross-linking of polymers, we prepared 2–10% solutions of polymers, which were applied to a glass support (K-8) 60 × 90 mm in size by centrifugation at 2500 rpm. The thickness of the resulting resist film was measured with an MII-4 Linnik microinterferometer. It was 0.15–0.20 μm.

The layer was dried for 10 min at room temperature and for 20 min at 40–45°C at a pressure of 10 mm Hg.

A DRT-220 mercury lamp (current strength 2.2 A) was used as a UV source, the distance from the radiation source was 15 cm, the velocity of moving the exposure meter gate was 720 mm h^{-1}, and the exposure time was 5–20 s. The content of insoluble polymer was determined from the ratio of the polymer weight to the initial weight of the film.

CONCLUSION

New monomers, 2-glycidyloxymethyl- and 2-glycidyloxycarbonyl-1-(*p*-vinylphenyl)cyclopropane, and polymers based on these were synthesized and characterized. The photosensitivity of the resulting polymers and its dependence on the substituent structure were studied. Participation of cyclopropane and epoxy groups in photochemical cross-linking was established.

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