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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

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

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Abstract—2-Formyl-1-(*p*-vinylphenyl)cyclopropane was prepared, and its homopolymerization and copolymerization with styrene were performed. The effect of the substituent on the monomer reactivity and the photosensitivity of the copolymer obtained were examined.

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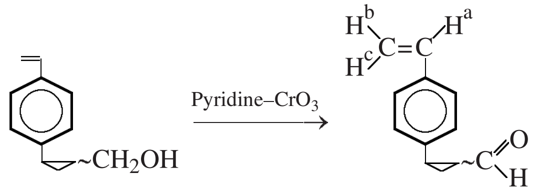
Functional polymers find growing use in microelectronics owing to their high heat resistance, good electrical properties, and high deformation-and-strength characteristics. Such a set of properties makes some functional polymers useful for preparing protective and insulating layers in the production of microelectronic devices and circuits. A topological pattern is usually created in a polymer film by optical photolithography using a multilayer system of resists, or by appropriate modification of the polymer to make it photosensitive [1–5]. The latter alternative has a number of significant advantages, as it considerably simplifies and reduces the process of pattern formation and increases the resolving power of lithography.

The aim of this study was to prepare a new formyl-substituted cyclopropylstyrene monomer, 2-formyl-1-(*p*-vinylphenyl)cyclopropane (FVPC), and to examine its radical polymerization and copolymerization with styrene. We also intended to study systematically the influence exerted on the photosensitivity of cyclopropane-containing polymers by the substituent at the cyclopropane ring in the pendant chain of the macromolecule [6, 7].

2-Formyl-1-(*p*-vinylphenyl)cyclopropane is a new promising monomer for preparing polymers with valuable properties for microelectronics. FVPC was synthesized as follows. First, we prepared 2-ethoxycarbonyl-1-(*p*-vinylphenyl)cyclopropane. Then, this ester was reduced to 2-hydroxymethyl-1-(*p*-vinylphenyl)cyclopropane [8], which was subsequently oxidized to FVPC according to [9]:



The structure of the aldehyde prepared was determined from the IR and ^{1}H NMR spectra. The results of spectroscopic studies and GLC analysis show that FVPC is a mixture of two geometric isomers, *cis* and *trans*, in a 30 : 70 ratio.

The IR spectrum of FVPC shows absorption bands at 1635–1640, 1035–1045, 1500, and 1605 cm^{-1}, characteristic of the vinyl group in cyclopropane and benzene rings. It also contains a band at 3010 cm^{-1} characteristic of the aldehyde C–H bond and a band at 1709 cm^{-1} corresponding to the C=O group.

In the ^{1}H NMR spectrum, the vinyl proton signals are observed at 6.76 (H^a), 5.38 (H^b), and 5.80 ppm (H^c). The aromatic ring protons are manifested at 6.60–7.30 ppm. The aldehyde proton appears as a singlet at 9.1 ppm.

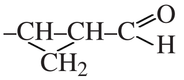
The vinyl proton signals are shifted downfield relative to unsubstituted styrene (H^a, 6.4; H^b, 5.11; H^c, 5.58 ppm). This shift is mainly caused by the mesomeric effect of substituents; specific distribution of the electron density in the cyclopropane ring also has a certain effect. The spectra suggest that all the synthesis steps leave the vinyl group and cyclopropane ring intact.

Copolymerization of FVPC (M_1) with styrene (M_2) in benzene at 333 K ($\Sigma[M]$ = 0.2 M; 0.1% AIBN)

FVPC fraction in starting mixture, mol %	Yield, %	Aldehyde group, %	$[\eta]$, dl g^{-1}	Copolymer composition, mol %	
				m_1	m_2
90	12	15.5	1.19	92.19	7.81
75	8.5	13.67		81.10	18.9
50	10	10.6	1.08	63.97	37.03
25	80	7.06		41.86	58.14
10	7.5	3.79	1.05	22.48	77.52

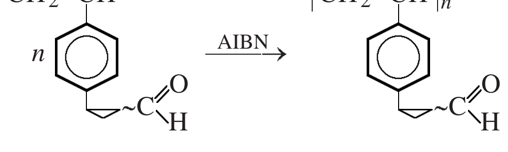
From the monomer synthesized, we prepared new homo- and copolymers. The FVPC polymerization was performed in the bulk and in benzene at 70°C in the presence of azobis(isobutyronitrile) (AIBN). Polymerization in the bulk yields 1–2 wt % of an insoluble fraction. In polymerization in solution, no insoluble fraction is formed. The polymerization occurs without induction period at a constant rate up to 85% conversion. The polymers after precipitation and drying to constant weight are white powders readily soluble in benzene, chloroform, and dimethylformamide.

The structure of the polymer was examined by IR and ^{1}H NMR spectroscopy, and the polymer composition was determined by elemental analysis.

We found that the radical polymerization occurs via vinyl groups with the formation of macromolecules containing  $-\underset{CH_2}{CH-CH}-C\overset{O}{\underset{H}{\lessgtr}}$ pendant fragments. This is confirmed by the fact that the cyclopropane ring and aldehyde group remain intact in the course of polymerization. Comparison of the IR spectra of the starting FVPC and polymer thereof shows that the positions and intensities of the absorption bands of the cyclopropane ring and aldehyde group do not change noticeably, whereas the bands of the vinyl group disappear. The same conclusion follows from the ^{1}H NMR spectra.

The ^{1}H NMR spectrum contains signals from protons of the benzene (δ 6.85–7.25 ppm) and cyclopropane (δ 0.75–1.75 ppm) rings. The aldehyde proton gives a signal at 9.1 ppm. The signals of the vinyl protons fully disappear.

The IR and ^{1}H NMR data suggest the following structure of the polymer:



To reveal specific features in the behavior of FVPC under the conditions of radical polymerization, we also studied its copolymerization with styrene.

The structures of copolymer macromolecules obtained at various conversions and containing units of both monomers in the macrochain were examined by IR spectroscopy. The IR spectra of copolymer samples prepared at various ratios of the starting monomers contain absorption bands of the aldehyde carbonyl group at 1709 cm^{-1} and bands of the cyclopropane ring at 1035–1040 cm^{-1}. Analytical data confirm the occurrence of the copolymerization. We found that the radical copolymerization of the starting monomers follows regular trends characteristic of vinyl monomers. The polymers prepared contain reactive formyl-substituted cyclopropane fragments in the pendant chains.

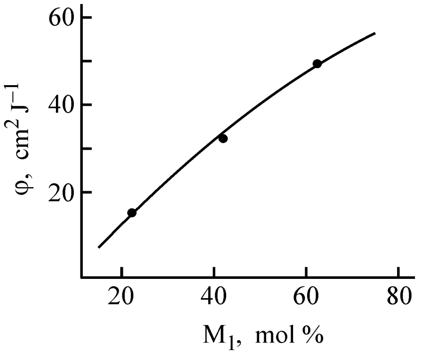
The ratio of styrene and FVPC monomer units in the copolymer macromolecule was determined by elemental analysis and titration of aldehyde groups. The results are listed in the table.

These data show that FVPC is a more active monomer than styrene.

The higher activity of FVPC, compared to styrene, also following from the calculated Fineman–Ross copolymerization constants [10] of FVPC, may be due to conjugation of the cyclopropane ring with an electron-withdrawing formyl substituent, which is consistent with the data of [11, 12]. The copolymerization constants, $r_1 = 1.25 \pm 0.025$ and $r_2 = 0.32 \pm 0.01$, demonstrate the effect of the carbonyl group in the monomer on the electronic structure of the whole molecule. This conclusion is consistent with the UV spectra in which the absorption peaks of FVPC and styrene are observed at essentially different wavelengths: 300 and 240 nm, respectively.

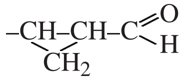
In the monomer, the vinyl group is activated and the protonating radical is stabilized by not only –*J*, but also –*M* effect of the aldehyde group.

Our results and published data suggest that this behavior of FVPC is primarily due to the effect of



Photosensitivity φ of copolymer of FVPC (M$_1$) with styrene vs. copolymer composition.

the cyclopropane ring directly bonded to the carbonyl group and apparently conjugated with the vinylphenyl group. Therefore, the FVPC molecule can be considered a common conjugated system.

The presence of strongly absorbing  $-\underset{CH_2}{CH-CH}-C\genfrac{}{}{0pt}{}{=O}{-H}$ groups in polymer macromolecules prepared from FVPC monomer makes these polymers suitable as a photosensitive base for photoresists. The two reactive groups in the pendant chains, cyclopropane and aldehyde, readily cleavable under irradiation, make the polymers highly sensitive to UV irradiation. Under UV irradiation, the polymers fairly readily transform into the insoluble form.

The decrease in the sensitivity of the absorption bands belonging to the cyclopropane and aldehyde groups in the initial steps of UV irradiation is insignificant. Upon longer UV irradiation (30 min), these absorption bands fully disappear. This fact indicates that the cyclopropane and aldehyde groups are involved in photochemical reactions apparently resulting in the photochemical cross-linking of the polymer.

Experiments showed that the presence of a three-membered ring and an aldehyde group, capable of opening and cross-linking under UV irradiation [13, 14], in the pendant chains of the polymers allows preparation of negative photoresists. The photosensitivity of the homopolymer prepared from FVPC is 56 cm^2 J^{-1}. As for the photosensitivity of the copolymers obtained, it depends on the copolymer composition and increases with the mole fraction of FVPC (see figure).

Also, it is possible to prepare from the polymers synthesized thin uniform coatings with low defectiveness and good adhesion to the support.

The polymers synthesized also open up wide prospects for chemical transformations of the aldehyde groups by reactions with, e.g., phenylhydrazine, hydrazine hydrochloride, or aniline with the aim to obtain polymers with required properties.

EXPERIMENTAL

2-Formyl-1-(*p*-vinylphenyl)cyclopropane was prepared by the reaction of 2-hydroxymethyl-1-(*p*-vinylphenyl)cyclopropane with a pyridine–CrO$_3$ complex solution (Sarett reagent) [9]; bp 88–90°C/1 mm Hg, n_D^{20} 1.5810, d_4^{20} 1.082, MR$_D$: calculated 52.15, found 52.98.

Found, %: C 83.52, H 6.35.

Calculated, %: C 83.72, H 6.98.

Homopolymerization of FVPC and its copolymerization with styrene were performed in the bulk and in a benzene solution at 333 K in the presence of AIBN. The molar ratios of the monomers are listed in the table. The reaction was performed in ampules under nitrogen for 3 h, after which the ampules were opened, and the product was precipitated with methanol, washed with methanol, and vacuum-dried at 40°C.

The content of aldehyde groups in the copolymer was determined by titration. A 0.2–0.3-g portion of the copolymer was dissolved in 10–15 ml of dimethylformamide. After the dissolution was complete, a 15-fold excess (by weight) of hydroxylamine hydrochloride in dimethylformamide was added. The mixture was allowed to stand for 2 h at room temperature. Then, 50 ml of distilled water was added. The precipitate was filtered off and washed once more on the filter with 50 ml of distilled water. Then, 0.8 ml of a 1% solution of Bromophenol Blue was added, and the solution was titrated with 0.1 N NaOH until the color became blue-green.

Photochemical cross-linking of the polymers was studied as described in [7].

The molecular weight of the homo- and copolymers was estimated from their intrinsic viscosity determined in benzene in an Ubbelohde viscometer at 20°C; for the homopolymer, $[\eta] = 1.03$ dl g^{-1}, and the values for the copolymer are listed in the table.

The IR spectra of the synthesized monomer and its homo- and copolymers were measured on a UR-20 spectrometer, and the ^{1}H NMR spectra, on a Tesla BS-487B spectrometer (80 MHz) in CCl$_4$. The purity of the compounds was determined by GLC on an LKhM-8MD chromatograph, model 3.

CONCLUSION

A new monomer, 2-formyl-1-(*p*-vinylphenyl)cyclopropane, its homopolymer, and copolymer with styrene were prepared. The compounds show high photosensitivity due to the presence of cyclopropane and aldehyde groups in the macromolecule.

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