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Synthesis and Polymerization Of P-(Vinyl Phenyl)-2-Chloromethylcyclo-Propane

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***Abstract*—The synthesis of p-(vinyl phenyl)-2-chloromethylcyclopropane has been realized and its radical polymerization has been carried out. The photosensitivity of the synthesized polymer containing in macromolecule C-Cl groups and cyclopropane ring sensitive to UV-irradiation has been studied. The photochemical structurization has been investigated and it has been established that the synthesized polymer possesses photosensitivity and can be used for creation of photosensitive material.**

***Index Terms*— copolymerization, cyclopropane, photosensitivity.**

I. INTRODUCTION

The analysis of technological properties of photoresists used currently clearly shows that there is no universal photoresist, which would combine the full range of required properties. The choice of photoresist and also the conditions of its application are determined by special purpose. In this connection, there is a tendency to the production of photoresists of narrow special purpose, but this requires the creation of a wide assortment of the light-sensitive materials. Now, the negative photoresists still do not sufficiently satisfy all the technological requirements of production of integrated circuits. This explains the continuing interest of the specialists to the preparation of new types of the negative photo-resists responsible for certain special purposes.

The polymers containing various reactive groups in the side chains possess valuable complex of properties and possibility of cross-linking of such polymers under action of radiation, which allows to prepare the resists used in due to this it is appeared the great interest of the researchers to preparation of new types of the photosensitive polymers for microelectronics [4-8].We have solved this problem by systematic polymerization of functionally substituted cyclopropyl styrenes [9-11].

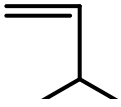
The interest in preparation of the reactive polymers has been primarily stipulated due to the fact that in the formed macromolecules there are reactive functional groups of various nature in the form of pendants to the main macrochain. One of the perspective reactive monomers are the functional cyclopropane-containing compounds containing cyclopropane groups regularly located in the side appendages or macrochain [12, 13].

This work has been devoted to the investigation of synthesis of new monomer – p-(vinyl phenyl)-2-chloromethylcyclopropane (CMCP), investigation of regularities of its radical polymerization and study of properties of polymer prepared on its basis with the aim of creation of new photosensitive polymers.

II. RESULTS AND DISCUSSION

The choice of this monomer has been stipulated with the fact that the concentration of double bonds and their chemical nature and also the presence of a cyclopropane ring in combination with $–CH_2Cl$ group in the monomer in decisive degree influence on such important photolithographic parameters of resist as photosensitivity, adhesion etc about which the accumulated material evidences [14,15].

The synthesis of CMCP has been carried out by interaction of p-divinylbenzene with ethyldiazoacetate in the presence of the catalyst – anhydrous $CuSO_4$. It has been firstly prepared the ethoxycarbonylcyclopropyl styrene (ECCPSt). Then by action of $LiAlH_4$ in the boiling ether ECCPSt has been converted into corresponding oxymethylcyclopropyl styrene with yield 95%. The high selectivity of $LiAlH_4$, used as a reducing reagent allowed to carry out the reduction reaction only on carbonyl group of the initial ether without affecting the double bond and cyclopriopane group. The reaction proceeds on the following scheme:



It has been established that the choice of the optimal conditions plays a great role in preparation of CMCP with

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good yield. It has been revealed the instability of the cyclopropane ring in relation to electrophilic reagents, including HCl and PCl_3, in the absence of solvent even 0°C. During chlorination of alcohol (II) the side products are formed, therefore the optimal chlorination of alcohol (II) was carried out by addition of PCl_3 to alcohol in the absolute ether at -40°C. The yield of chloride (III) was 85%.

It has been established on the basis of the spectral data and GLC-analysis that the reaction product is the mixture of two geometrical trans- and cis-isomers (relatively three-membered cycle); a ratio of these isomers corresponds to trans:cis =35:65. The purity of the synthesized compound was controlled by a method of GLC-analysis and in all cases corresponded to >99.2%.

For study of synthesis and properties of CMCP there can be used the data of its spectral analyses. In the IR-spectrum there are the absorption bands in the fields of 1030-1040, 1640-1645, 1580 and 1600 cm^{-1}, characteristic for three-membered cycle, double carbon-carbon bond of vinyl group and benzene ring, respectively. In the IR-spectrum there is also the absorption band at 635 cm^{-1}, referring to vibrations of chlorine atom (Fig. 1).

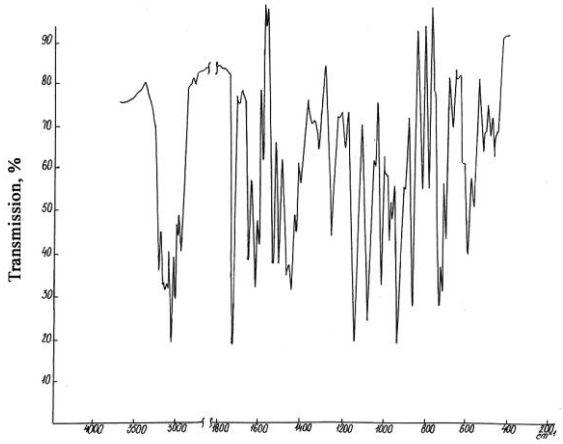

Fig.1. IR-spectrum of monomer of CMCP

In the PMR-spectrum of CMCP there are the signals of protons situated both in double bond (δ = 5.14-6.67 ppm.), and in three-membered cycle (δ = 0.7-1.65 ppm). In addition, in the PMR-spectrum of this compound there are the signals characteristic for protons of the benzene ring (δ = 7.0-7.05 ppm).

CMCP is the new reactive monomer and during its radical polymerization it was important to choose the optimal conditions, under which the polymerization would proceed only on the double bond of vinyl group, and the reactive fragments in the side chain would remain without changes. For this reason the polymerization was carried out in the presence of initiator – dinitrilazoisobutyric acid (AIBN). The radical polymerization of CMCP was carried out in mass and in solution.

The chemical structure of polymer has been confirmed by data of the IR- and PMR-spectroscopy. The absorption bands at 1040, 3090 cm^{-1} stipulated by cyclopropane ring in monomer are completely kept in the IR-spectrum of forming polymer. On the other hand, in the IR-spectrum of the polymer the absorption bands at 990 and 1640-1645 cm^{-1}, characteristic for vinyl group of monomer disappear.

In the polymer sample the bands at 1110 and 635 cm^{-1}, characteristic for –O–C and chlorine atom, respectively, remain unaffected.

In the PMR-spectrum of the polymer the resonance signals referring to protons of the benzene nucleus (δ = 6.60-7.30 ppm) and cyclopropane ring (δ = 0.65-1.66 ppm) are clearly displayed, but the proton signals referring to protons of vinyl group (δ = 5.10-6.65 ppm) are absent in the polymer sample.

The synthesized polyfunctional polymer containing group of chloromethylcyclopropyl very sensitive to UV-irradiation is the valuable object of the photochemical investigations and can serve as a base for creation of the photosensitive materials.

An availability of the reactive groups of various chemical nature in links of macromolecule of the synthesized polymer causes the interest to investigation of the photochemical structurization of this polymer, i.e. cross-linking under action of UV-irradiation. These polymers with such properties as the high light-sensitivity, film-forming ability, good solubility before irradiation, stability to solvents and good thermal stability are very important for photoresist.

Under action of UV-irradiation the polymer on the basis of CMCP easily undergoes structurization, as a result of which the film prepared on its basis becomes insoluble also with small deficiency.

The study of the photochemical structurization of polymer was carried out on method described in work [10]. Due to availability of groups (cyclopropane and C-Cl) strongly absorbing the light energy, the synthesized polymer is the photosensitive and in action of UV-irradiation is subjected to the photochemical conversions leading to formation of network structure.

The photo-reactive fragments have been considered with various concentration of the polymer 15-150 mg in the thin films. The polymers show the absorption bands in the UV-spectrum around 296 and 300 nm.

The influence of irradiation on photosensitive polymer has been investigated by measurement in the UV-spectrum.

The photochemical conversion of the investigated polymer has been studied by means of IR-spectroscopy at the various stages of the UV-irradiation. The results of UV-irradiation are presented in Fig. 2.

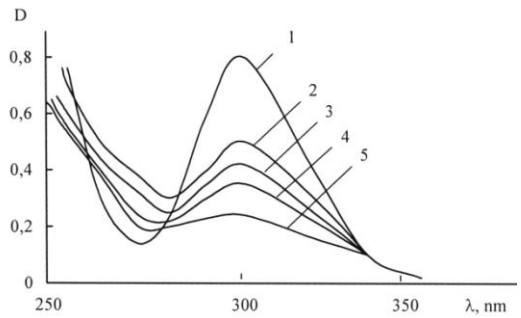

Fig.2. Change of UV-spectrum of absorption of the prepared film from poly-CMCP in irradiation. 0-5 exposure time respectively, t=0, 5, 10, 15, 20 second.

In the photoreaction process during the UV-irradiation it takes place a decrease of intensity or disappearance of the

absorption bands at 1040, 635 $см^{-1}$ corresponding to cyclopropane fragments and chlorine atoms situated in the side chain of macromolecule.

The structurization process was carried out due to opening of cyclopropane ring with participation of chlorine in the photochemical reactions.

The carried out investigations showed the possibility of synthesis of new valuable photosensitive polymer ($54cm^2 \cdot J^{-1}$) with the aim of creation of base of the photosensitive material.

Such polymers with high photosensitivity, film-forming ability and good thermal stability are very important for their application as a light-sensitive base of photoresists of negative type.

It has been revealed that some lithographic properties depend on film thickness. In a case of increase of the film thickness the three-dimensional structure formed under radiation effect has a form of loose mesh with large cells, which is strongly swollen in the manifestation and decreased in drying of the polymer layer, causing the folds and wrinkles.

The good results have been prepared during work with films by thickness of 0.2-0.3 mcm.

In the polymer films the conversion rate of the photosensitive fragments depends on composition of the photosensitive links in the polymer chain (Fig.3). It is seen from figure that after 40-80 second irradiation (transformation 50-80%), the polymer films are insoluble in the organic solvents, in which they were soluble at room temperature before irradiation.

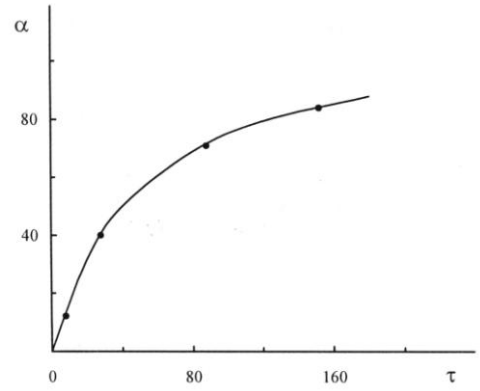

Fig.3. Influence of irradiation time τ(s) on solubility of polymer (α-content of insoluble fraction).

As a result of the carried out work the new polymer has been synthesized and its composition, structure and properties have been established. It can be concluded on the basis of carried out investigations that the availability of cyclopropane ring and $–CH_2Cl$ fragment in the structure of the new synthesized polymer provides for these polymers the high photosensitivity, creation of a solid elastic layer with good adhesion to substrates and low microdefects of the polymer films.

III. EXPERIMENTAL

A. Synthesis of 2-chloromethyl-1-(p-vinyl phenyl)cyclopropane.

0.1 mol of freshly distilled PCl_3 was added on dropwise to solution of 0.1 mol of 2-oxymethyl-1-(p-vinyl phenyl)cyclopropane in 30 ml absolute ether at temperature -35-40°C, was sustained for 1 h at the same temperature and 3 h at 20°C, adding 5 ml of water. The organic part was separated and the aqueous solution was extracted several times with sulfuric ether. The ether extracts were combined, dried by calcined Na_2SO_4, then distilled off the ether on a water bath, and the residue was distilled in vacuum.

The prepared reaction product had the following characteristics: yield – 82%, $n_D^{20} = 1.5720$, $d_4^{20} = 1.180$, MR_D calc./found. 52.266/52.20. The elemental analysis (calc./found.): C 74.8 / 74.2; H 9.0/8.5; Cl 24.65/24.25.

The polymerization of the synthesized monomer was carried out in ampoules in mass and in the benzene solution in the presence of 0.5% dinitrilazoizobutyric acid from total monomers mass at 70°C. The forming polymer was purified by twofold precipitation from benzene solution to methanol and dried in vacuum (15-20 mm merc.c.) at 30°C to constant mass.

The IR-spectra of the polymers were registered on spectrometer "Specord" M-80, PMR-spectra – on spectrometer BS-487B Tesla (80MHz) in the solution of deuterated chloroform.

For determination of photosensitivity of the polymer some compositions for copolymer at various concentrations (4-13% solution) have been prepared. Applying a layer of photoresist on the substrate was produced in dust-free medium.

All solutions of resists were applied on glass substrates by means of centrifuge at 2500 rev/min. After applying of procurement the photoresist is kept for at least 20 min for increase the adhesion of photoresist to substrate. Then it is cut the photoresist on the contour of the procurement, not allowing the film delamination.

Thickness of the prepared film – resists was measured by microinterferometer “LINNIKA”. The resist layer thickness after its drying for 10 min at room temperature and for 20 min. at 30-35° C/10 mm merc.c was 0.20-0.25 mcm.

The exposition of the procurement with applied photoresist was carried out on installation with point source of light through a photomask. As a source of UV-irradiation it was used a mercury lamp DRT-220 (current strength 2,2 A, distance from radiation source – 15 cm, moving shutter rate of exponometer – 720 mm/h , exposition time – 5-20 s).

The development was carried out in the jet installation. As a developer it was used dioxane : isopropyl alcohol – 1 : 2 at temperature 18-25°C

The criterion of the photosensitivity of negative photoresists by UV- irradiation is the fullness of the passage of the photochemical polymerization (crosslinking) reactions of the molecules of base of the photoresist. After exposition and development the content of insoluble polymer was calculated on residue mass as a formation fact of the cross-linked product.

Photosensitivity – value inverse to the dose of UV-light absorbed by photoresist, in other words, the dose required for transfer of the photoresist to insoluble state. It is measured in $cm^2/Wt \cdot s = cm^2/J$:

$$S = 1/H = 1/E \cdot t$$

H – exposition (or irradiation dose by UV-light), J·cm
E – intensity, Wt/cm^2
T – duration of irradiation, s

IV. CONCLUSIONS

1. The new polyfunctional p-(vinyl phenyl)-2-chloromethylcyclopropyl styrene has been synthesized, its radical homopolymerization has been carried out. The composition and structure of the synthesized polymer have been established.
2. The structurization process of polymer has been studied and it has been established that the synthesized polymer possesses relatively high photosensitivity (54 cm^2· J^{-1}).

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