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ACYLATION OF THE ANHYDRITE-CONTAINING COPOLYMERS WITH VINYL CARBINOL FOR PREPARATION OF PHOTOSENSITIVE MATERIALS

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***Abstract**. By copolymerization of cycloalkyl-substituted methylenedioxolanes with maleic anhydride the copolymers, which were subjected to acylation reactions with vinyl carbinol were obtained. It was revealed that as a result of the reaction, the copolymers with various degrees of etherification were obtainedIt found that the obtained etherified copolymers exhibited various UV sensitivity depending on the degree of etherification. It revealed that the availability of highly absorbing fragments such as allyl and carbonyl groups in macromolecules of the etherified copolymers provides these polymers, along with high light-sensitivity, with film-forming properties and good adhesion to quartz substrate.*

***Keywords**: methylenedioxolane, copolymerization, maleic anhydride, etherification, photosensitivity.*

Introduction

It is known that the polymers containing functionally active groups in macromolecules are subjected to some changes under the action of various sources of irradiation. This circumstance allows using them in microelectronics as a light-sensitive basis for photo- and electron-resists. Depending on the mechanism of photochemical processes occurring in the light-sensitive layer, the photoresists are divided into negative and positive ones. In the negative photoresists, under the action of radiation, the processes leading to a loss of solubility of the polymer film take place. In the positive photoresists, the processes proceed during irradiation, as a result of which the exposed areas are destroyed [1].

The basis of practically any photo- and electron-resist are high-molecular compounds possessing own sensitivity to the used radiation.

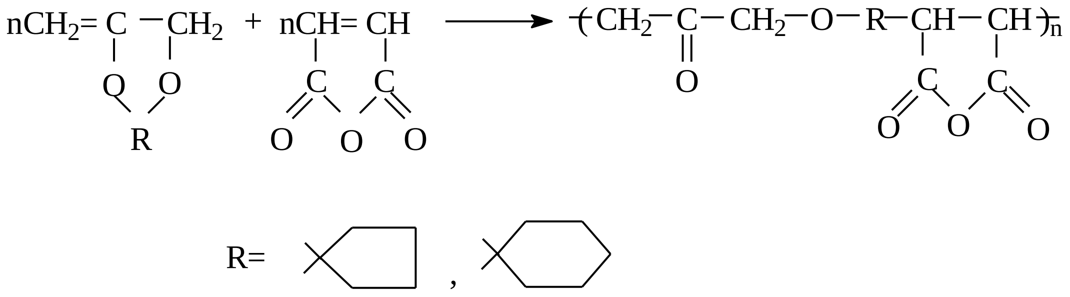
It is known that for making of photo- and electron-resists of negative-type, the polymers containing chemically active groups, including vinyl, epoxide, allyl, etc., are mainly used [2].

One of the main most widely used methods of preparation of the negative photosensitive polymers is the modification of the properties of the known polymers by introduction of highly absorbing groupings into the macromolecule [3]. The main advantage of this method is the possibility of preparation of materials with various photosensitivity on the basis of the same high-molecular compound**.**

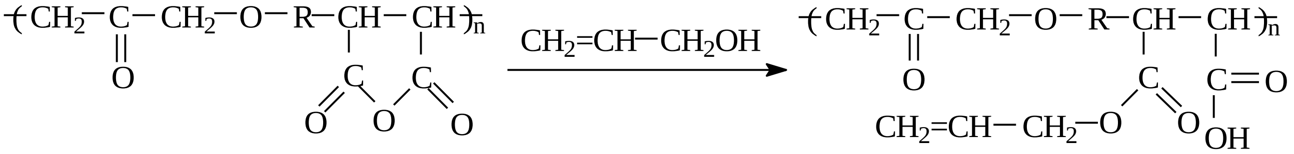
In this work, with the aim of preparation of the polymers used as negative photoresists, we have carried out the etherification reaction of copolymers previously synthesized by us on the basis of cycloalkyl substituted methylenedioxolanes and maleic anhydride (MA).

Results and discussion

Our earlier investigations showed that the radical copolymerization of alkyl- and cycloakyl substituted 4-methylene-1,3-dioxolanes with MA basically proceeds with the formation of copolymers of linear structure with anhydride cycles in macromolecules [4]:

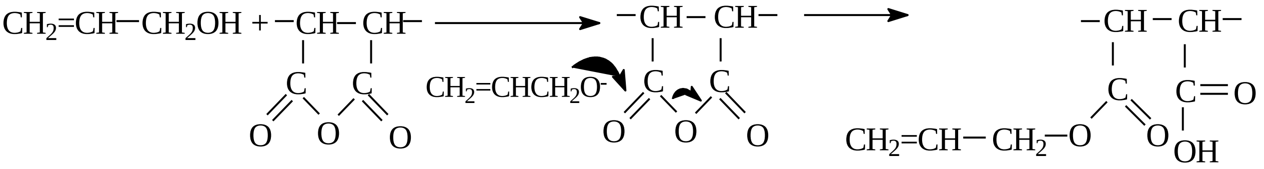


The etherification of the synthesized copolymers with vinyl carbinol was carried out in a solution of dimethylformamide (DMFA) at 70-90°C, for 3 h in the absence of catalyst. The degree of etherification has been determined by a quantity of free carboxyl groups forming as a result of reaction:



The structure of forming modified copolymers was by data of IR spectra. In the IR spectra of acylated copolymers the absorption bands characteristic for double bond (1645, 990, 915, 900 cm^{-1}) were detected. The absorption bands in the fields of 1150-1300 and 1700-1745 cm^{-1} characterized the availability of ether and carbonyl groups in the macromolecular chain of copolymers. The wide absorption band with center at 3000 cm^{-1} can be attributed to out-of-plane deformation vibrations of the associated hydroxyl group of carboxyl [5]. It should be underlined that the used quantity of carbinol is completely consumed for etherification and does not remain in the system in a free form.

The reaction begins by attack of the anhydride group of the copolymer with more nucleophilic oxygen atom:



and is accompanied as a result of protonation with anhydride cycle opening [6-7]. As a result of the acylation reaction, the copolymers with side maleate groups are obtained. The carboxyl groups formed in this case are in a sterically hindered position, and their reaction with the corresponding carbinol proceeds slowly even in excess of carbinol. Consequently, the determination of the quantity of free carbonyl groups can allow to identify the degree of conversion of the anhydride links during the etherification reaction.

Since the degree of conversion of the anhydride groups mainly depends on the conditions of carrying out of the reaction, we first studied the influence of the molar ratio of the copolymer and vinyl carbinol, the temperature and the reaction duration for quantity of carboxyl groups formed as a result of the anhydride cycles opening with vinyl carbinol.

Table 1. Dependence of the quantity of carboxyl groups on the reaction time at various molar ratios of the initial reagents and temperature.

Temperature, °C	Time, min.	Quantity of carboxyl groups at ratios vinyl carbinol:copolymer		
		2:1	4:1	5:1

70	30	0.6	0.9	1.2
	60	1.6	2.1	3.2
	90	2.4	3.6	5.8
	120	3.2	4.8	7.4
	150	3.8	6.4	8.6
	180	4.5	7.6	9.8
80	30	0.8	1.1	1.5
	60	1.8	2.4	2.9
	90	2.8	4.2	6.6
	120	3.7	5.2	8.4
	150	4.8	5.9	9.5
	180	6.3	7.1	10.4
90	30	1.0	1.2	1.8
	60	2.2	2.8	5.9
	90	3.4	4.8	8.5
	120	4.9	6.5	9.8
	150	5.8	7.2	10.9
	180	6.7	8.6	11.6

In Table 1 the data obtained as a result of etherification of the copolymer with vinyl carbinol are presented. As follows from the data in Table 1, the content of free carboxyl groups in use of various molar ratios of vinyl carbinol and copolymer is changed: with an increase of the molar ratio of vinyl carbinol:copolymer, the content of carboxyl groups increased over the same period of time. So, if at the ratio of vinyl carbinol:copolymer, equal to 2:1 in 180 min. (a further increase in the reaction duration leads to a slight growth of the content of carboxyl groups), the content of carboxyl groups is 4.5%, then in a five-fold excess of vinyl carbinol for the same time, the content of carboxyl groups grows to 9.8%. It is simultaneously established that with temperature rise from 70 to 90°C, the conversion rate of the anhydride links in the polymer chain increased, i.e. the quantity of formed free carboxyl groups grows to 11.6%.

The modified copolymers obtained as a result of the etherification reaction are well soluble in ketones and esters, but are not dissolved in alcohols, aromatic hydrocarbons and alkanes.

It was known that the polymers, whose macromolecules contain unsaturated or cyclic groups both in the main and in the side chains, easily transform into three-dimensional netlike structures during their thermal treatment or action of radiation or UV irradiation on them [8]. We carried out the photochemical structuring of the modified copolymers. The UV spectra were taken for thin films of the polymers applied on a quartz substrate. The quantitative changes occurring in the investigated polymers during photo-irradiation process were evaluated by the method of UV spectroscopy.

It found that the obtained copolymers are inclined to the photo-cross-linking process during exposition of photo-radiation to them, and it proceeded with the participation of allyl groups. Besides, the changes of the optical density and displacement of the absorption maximum in the field of 205 nm in the UV spectra are observed (Fig.1).

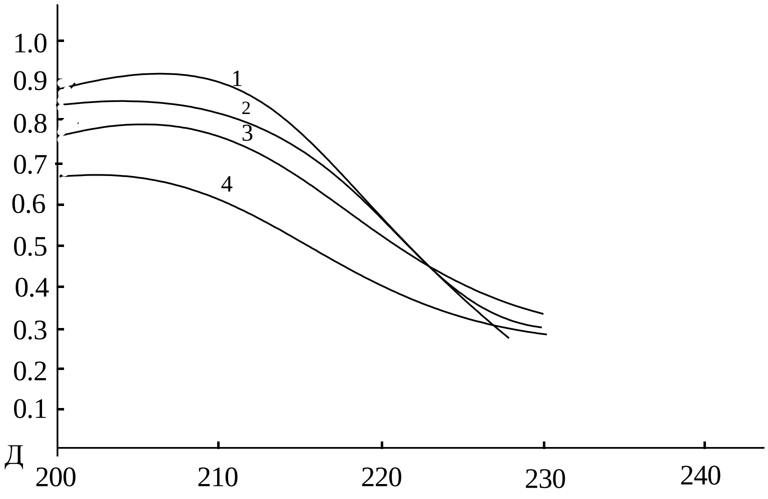


Fig. 1. UV spectra of thin films of copolymer modified with vinyl carbinol on the basis of cyclopentyl substituted methylenedioxolane with MA depending on the irradiation time (1- 0 min., 2- 10 min., 3- 15 min., 4- 20 min.).

For reveal of the participation of highly absorbing functional groups in the cross-linking processes, the thin films were prepared from the copolymers synthesized by us and subjected to the irradiation. Via certain time period of irradiation with UV spectroscopy, the optical density in the field of D_t^{205} was determined which is proportional to the concentration of unreacted side allyl groups. The ratio D_t^{205}/D_0^{205} was calculated from the found values of the optical density and then the relative light sensitivities (LS) were determined on the following formula [9].

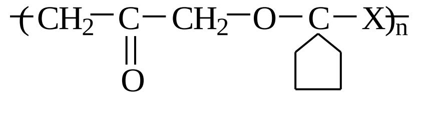
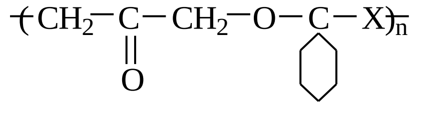
$$\text{LS} = \frac{(A_{\text{в}} - A_{\text{а}})}{A_{\text{в}}} \cdot 100\%$$

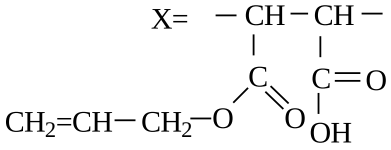
where, $A_{\text{в}}$– intensity of the absorption band before irradiation;
$A_{\text{а}}$– intensity of the absorption band after 20 min. irradiation.

The results of these investigations are shown in Table 2. It can be seen from tabular data that in the irradiation process of the studied polymer films, the intensity of the maximum falls depending on the irradiation time which has been most likely connected with decrease of the quantity of the double carbon-carbon bonds.

It can be assumed that the photo-cross-linking mechanism includes the formation of cyclic structures with the participation of free radicals, as indicated in work [10]. It has been also detected the displacement of the absorption maximum, which has been connected with the break of the double bonds during irradiation, which leads to a redistribution of the electron density throughout the system.

Table 2. Change of the optical density of the obtained polymer films depending on the irradiation time.

Structural link	D_t^{205}/D_0^{205}			Relative light sensitivity for 20 min, %
	10 min	15 min	20 min	
	0.91	0.84	0.75	16.8
	0.92	0.86	0.80	16.2



The availability of allyl and carbonyl groups in the structure of the synthesized polymers provides these materials, along with high light-sensitivity, also film-forming properties, good adhesion to glass, and in some cases comparatively higher thermal stability.

Experimental part

The IR spectra were taken on device Specord M80, the registration of absorption spectra in the field of 350-200 nm realized on spectrophotometer “Specord UV-WIS”. For irradiation of the polymer films, a lamp PRK-20 was used as an irradiation source.

The copolymers were obtained through the method described in [4] under conditions of radical initiation. The etherification reaction of copolymers with vinyl carbinol was carried out in the solution. The calculated quantity of vinyl carbinol from dropping funnel was added to 0,006 mol of the copolymer in 100 ml of methyl ethyl ketone at temperature of 70°C and in certain time period after the beginning of the reaction, the samples were taken for determination of the quantity of formed etherified copolymer. After precipitation of the copolymer from the solution with petroleum ether, it was repeatedly washed, dried to a constant weight and analyzed for determination of the quantity of carboxyl groups according to the procedure described in [11].

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ANHİDRİD TƏRKİBLİ BİRGƏ POLİMERLƏRİN VİNİLKARBİNOLLA ASİLLƏŞMƏSİ İLƏ FOTOHƏSSAS MATERİALLARIN ALINMASI

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Xülasə: *Tsikloalkil əvəzli metilendioksolanların malein anhidridi ilə birgə polimerləşməsi ilə alınmış birgə polimerlər vinilkarbinolla asilləşmə reaksiyasına cəlb edilmişdir. Müəyyən edilmişdir ki, reaksiya nəticəsində müxtəlif efirləşmə dərəcələrinə malik birgə polimerlər alınır. Müxtəlif parametrlərin, o cümlədən ilkin reagentlərin nisbətlərinin, temperaturun və prosesin aparılma müddətinin efirləşmə dərəcəsinə və çıxıma təsiri öyrənilmişdir. Efirləşmiş birgə polimerlərin alınmasının optimal şəraiti müəyyən edilmişdir. Alınmış efirləşmiş birgə polimerlər efirləşmə dərəcələrindən asılı olaraq UB-şüalanmaya qarşı müxtəlif aktivliklər göstərirlər. Müəyyən edilmişdir ki, efirləşmiş birgə polimerlərin makromolekullarında yüksək işıqudma qabiliyyətinə malik fraqmentlərin, o cümlədən allil və karbonil qruplarının olması, həmin polimerlərə yüksək işığahəsaslıqla bərabər, həm də plyonka əmələgətirmə və kvars səthə qarşı yaxşı adgeziya xassələri verir.*

Açar sözlər: *metilendioksolan, birgə polimerləşmə, malein anhidridi, efirləşmə, fotohəssaslıq*

АЦИЛИРОВАНИЕ АНГИДРИДСОДЕРЖАЩИХ СОПОЛИМЕРОВ ВИНИЛКАРБИНОЛОМ ДЛЯ ПОЛУЧЕНИЯ ФОТОЧУВСТВИТЕЛЬНЫХ МАТЕРИАЛОВ

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Аннотация: *Сополимеризацией циклоалкилзамещенных метилендиоксоланов с малеиновым ангидридом получены сополимеры, которые были подвергнуты реакции ацилирования винил карбинолом. В результате реакции получены сополимеры с различной степенью этерификации. Изучено влияние различных параметров, таких как соотношение исходных реагентов, температура и продолжительность процесса на выход и степень этерификации для определения оптимальных условий получения этерифицированных сополимеров. Установлено, что полученные этерифицированные сополимеры в зависимости от степени этерификации* *проявляют различную чувствительность к УФ-облучению. Выявлено, что наличие в макромолекулах этерифицированных сополимеров сильнопоглощаюших фрагментов типа аллильных и карбонильных групп придает этим полимерам, наряду с высокой светочувствительностью, также пленкообразующие свойства и хорошую адгезию к кварцевой подложке.*

***Ключевые слова**: метилендиоксолан, сополимеризация, малеиновый ангидрид, этерификация, фоточувствительность.*