

PHOTOCHEMICAL PROPERTIES OF CINNAMIC ACID EPOXY ESTERS CONTAINING AN AZOMETHINE GROUPING*

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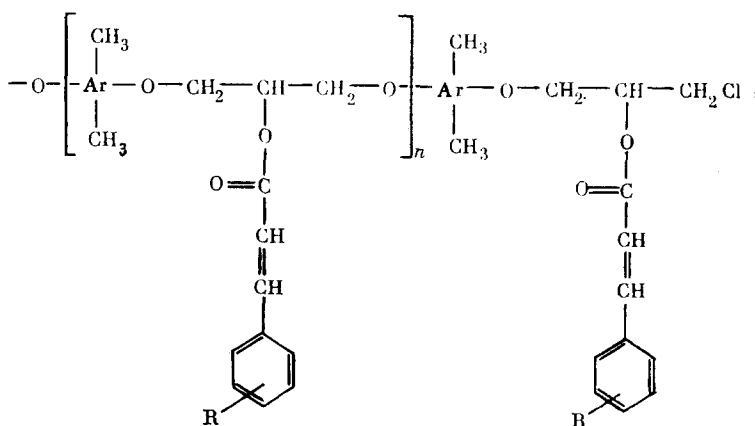
A number of photopolymers based on the polyepoxydiane ester of *p*-aminocinnamic acid and aromatic aldehydes have been synthesized. Their structure is studied by IR and NMR spectroscopy. The effect of stabilizers on the light sensitivity of the photopolymers has been studied. It is shown that they accelerate the crosslinking of the photopolymers and shift the range of light sensitivity to the region of longer waves.

THE rapid development of printing and microelectronics has prompted wider research into the synthesis and physicochemical properties of light sensitive polymers.

These polymers are obtained by modifying macromolecular compounds or polymerizing monomers with light sensitive groups.

Polymers containing cinnamic acid residues are attracting special attention. The best known is the polyvinyl cinnamic acid ester [1-4]. An important place among light sensitive polymers is also taken by the esters of the epoxide resins obtained by condensation of the diene with epichlorhydrin [5].

Esterification of epoxide resins by cinnamic acid chloride leads to the formation of compounds



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where Ar—the residue of 4,4'-dihydroxydiphenylpropane and R = H, CH₃, OCH₃, Cl, Br, I or NO₂.

The introduction into the photopolymer of substituents changes the light sensitivity of the system which depends on their nature and position in the benzene ring. These substituents cause a shift of the working range of light sensitivity of the photopolymers studied towards long waves.

The methods of synthesis and the photochemical properties of the above listed compounds were studied in [6].

The present work is a continuation of these investigations. Its aim is to introduce into the ester of an epoxide resin and cinnamic acid a new phenylazomethine group and study the effect of this group on the photochemical properties of the cinnamic acid epoxy esters.

Obtaining the ester of the epoxide resin epidiene-1 and p-aminocinnamic acid. In a round-bottomed flask was placed 50 ml benzene and 8 g epoxydiane ester of *p*-nitrocinnamic acid and agitated until the photopolymer was completely dissolved. Then 15 g of reduced iron and 5 ml water was added. This mixture was boiled with vigorous agitation for 12 hr. After cooling its iron excess was separated by filtration and the filtrate decanted into cyclohexanone. The sediment formed was filtered off and dried without access of light to constant weight. Thus, 6 g of the photopolymer was obtained in the form of a light cream residue.

Condensation of the ester of p-aminocinnamic acid and the epoxide resin epidiene-1 with benzaldehyde. In a round bottomed flask fitted with a Dean-Stark cap was dissolved 6 g *p*-aminocinnamic acid ester in 50 ml dehydrated benzene. Then 2.2 g (0.02 mole) benzaldehyde added. The reaction mixture was boiled for 4 hr, the water released driven off in the form of an azeotrope with benzene. After cooling the contents of the flask were poured into cyclohexanone. The sediment formed was filtered off and dried in the dark to constant weight. As a result we obtained 6 g of a photopolymer of yellow colour.

Esters of *p*-aminocinnamic acid and the epoxide resin epidiene-1 were synthesized in the same way with other aldehydes: *p*-N,N-dimethylaminobenzaldehyde, cinnamaldehyde, salicylaldehyde and *o*-nitrobenzaldehyde.

METHOD

The NMR spectra were recorded with the BS-487S spectrometer (60 MHz). Tetramethylsilane was used as reference.

The IR spectra were recorded with the Specord UR-71 spectrometer.

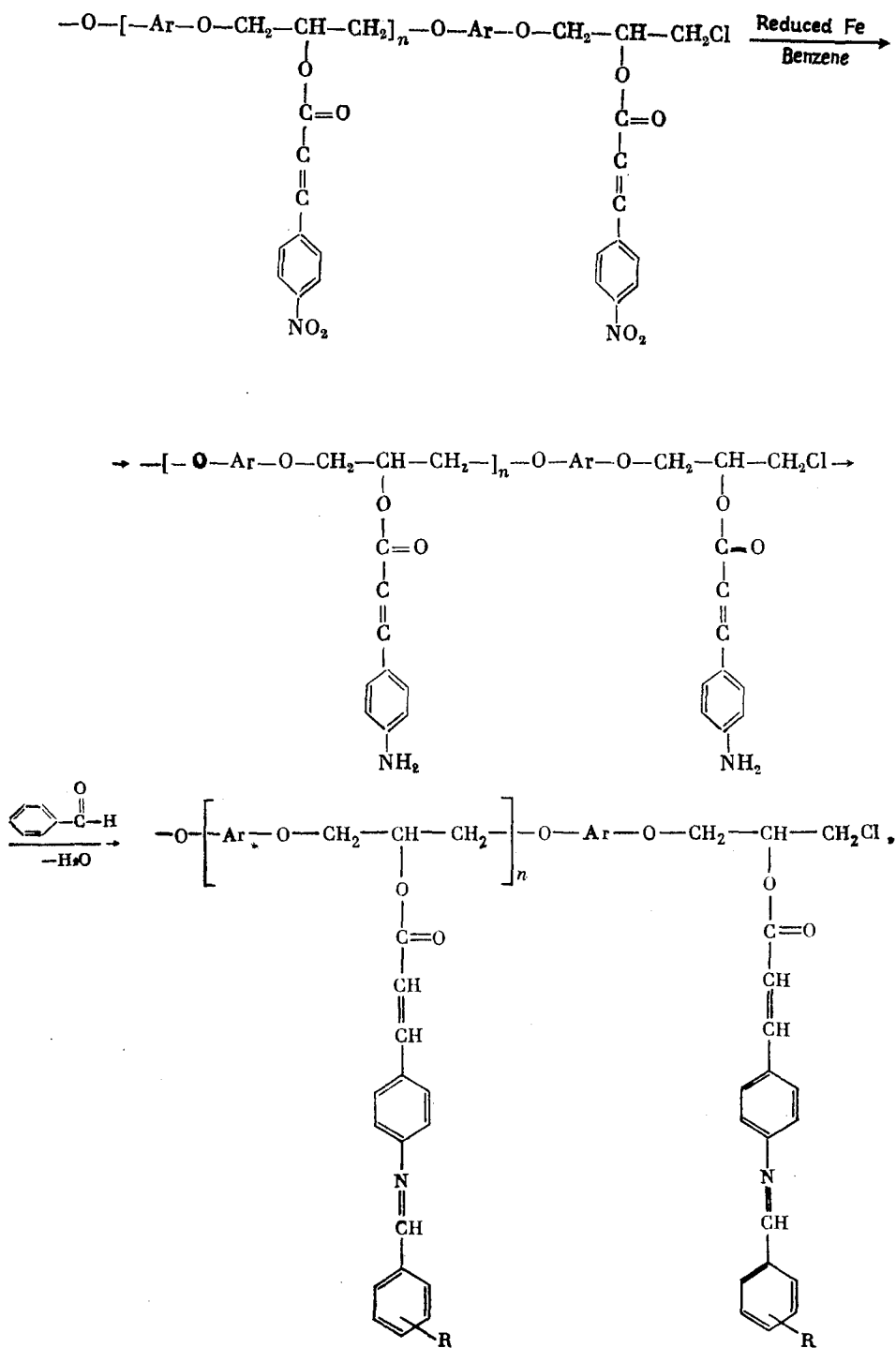
The photopolymers in the form of 2% solutions in chloroform were studied in quartz cuvettes. The surface of the cuvette was irradiated with the Q-250 mercury lamp.

The UV spectra were obtained with the VCY-2P spectrometer of Carl Zeiss (Jena).

The photopolymers were studied by spectrosensitometry with a spectrograph the layout of which is presented in [7].

The basic principles of the investigation concerning photopolymers are outlined in [8].

The epoxy esters were obtained in line with the following scheme:



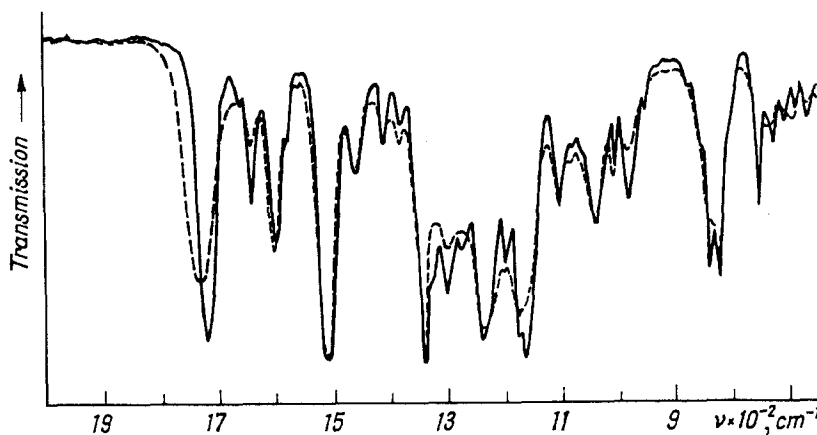
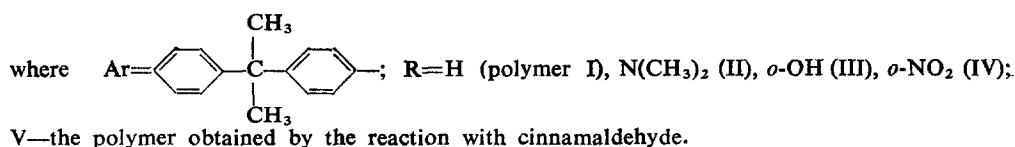


FIG. 1. IR spectrum of polymer IV before irradiation (continuous line) and after irradiation (broken line).

To determine the structure of the photopolymers and also evaluate the conversions occurring in them during irradiation we investigated the IR and NMR spectra of these polymers.

In the IR spectrum of the ester (Fig. 1) after completion of synthesis the absorption bands at 3470 (hydroxyl group) and 915 (epoxide) cm^{-1} are absent. Nor were any free N—H groups found. In all cases absorption was observed at 3000 (methyl groups) and 2900 (methylene) cm^{-1} . In addition, from the IR spectra we established the presence in the polymers of carbonyl, nitrile and ethylene bonds.

Analysis of the NMR spectra reveals the presence of azomethine, ethylene, hydroxyl and $\text{N}(\text{CH}_3)_2$ groups.

The characteristics of the IR and PMR spectra of the polymers formed as a result of the reaction with the aldehydes are presented in Table 1.

Spectral analysis in the range 650–2000 cm^{-1} also showed that after irradiation of the polymers I and II with UV light the bands characteristic of the ethylene group (1640 cm^{-1}) change insignificantly while in the case of the polymers III–V they disappear. The polymers synthesized from the esters of *p*-aminocinnamic acid with the epoxide resin and the corresponding aldehydes have two absorption bands: at $\lambda_{\text{max}} = 220\text{--}230$ and 265–320 nm. The second band splits into two peaks: $\lambda_{\text{max}} = 286\text{--}288$ and 308–312 nm (Fig. 2a).

The presence of peaks in the shortwave region may be explained by the transition of the electrons in the benzene ring. The replacement of the phenyl ring leads to shift of the main band in the UV spectrum. After UV irradiation of the polymer (Fig. 2a) a heavy fall in the intensity of the first main band is observed with no change in its posi-

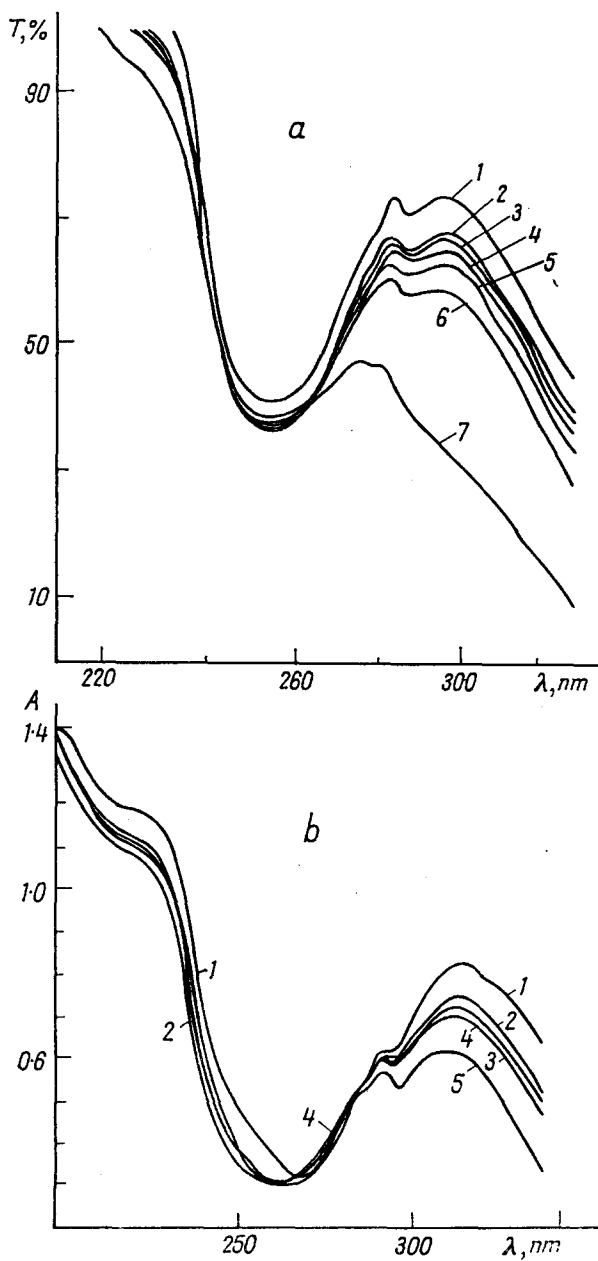


FIG. 2a, b

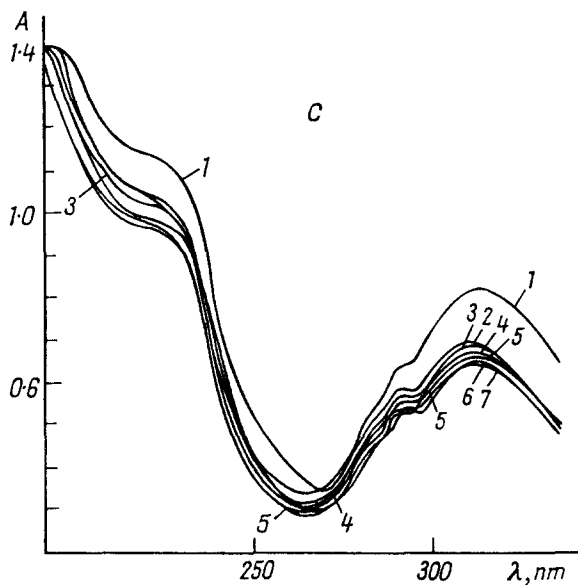


FIG. 2. UV spectra of polymer I: *a*—radiation time in min, 1—0; 2—2; 3—4; 4—8; 5—16; 6—32 7—64; *b*—time of heating at 443 K in hr, 1—0; 2—2.5; 3—5.0; 4—7.5; 5—18.0; *c*—time of heating at 443 K in hr: 1—0; 2—3 and at 298 K in days: 3—1; 4—7; 5—21; 6—30; 7—37.

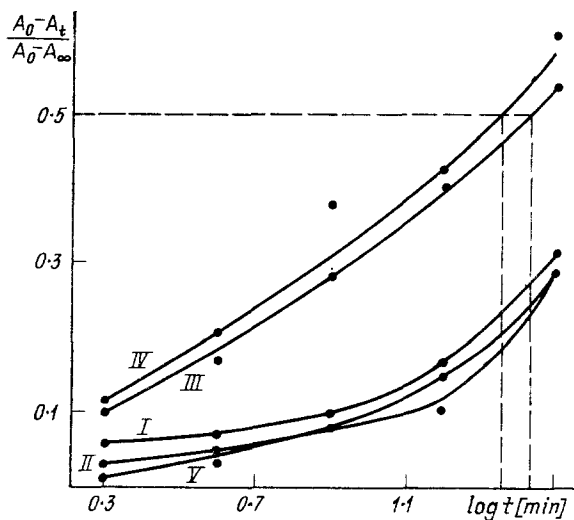


FIG. 3. Influence of exposure time on level of crosslinking of polymers I—IV, $\lambda_{max}=286$ (I, V), 287 (II) and 288 (III, IV) nm.

TABLE 1. SOME CHARACTERISTICS OF THE IR AND NMR SPECTRA OF SYNTHESIZED PHOTOPOLYMERS

Polymer	ν , cm^{-1}			δ_{H} , p.p.m.			
	C=O	C=C	NO ₂	C=N	C=C	OH	N(CH ₃) ₂
I	1715	1635	—	10.0	6.6	—	—
II	1720	1645	—	9.8	6.5	—	3.0
III	1715	1640	—	9.9	6.5	11.0	—
IV	1720	1640	1345	10.5	6.5	—	—
V	1715	1640	—	9.8	6.5	—	—

tion. On exposure of the photopolymers to raised temperature (Fig. 2*b*) the intensity of the first main band also diminishes. As in the case of UV irradiation the absorption peak does not shift.

Comparing the UV spectra presented in Fig. 2*a* with the spectra in Fig. 2*b* one may conclude that heating the photopolymers causes thermal crosslinking. The presence of this process is also confirmed by the results in Fig. 2*c* indicating that in the photopolymers studied crosslinking is irreversible (the polymers become insoluble).

The overall light sensitivity of the photopolymers was studied by the technique in [8]. As criterion of light sensitivity we chose the radiation time $\tau_{\frac{1}{2}}$ for which is valid the relation (Fig. 3)

$$\frac{A_0 - A_t}{A_0 - A_\infty} = \frac{1}{2},$$

where A_0 , A_t and A_∞ are the absorption of the layer before irradiation, after it during time t and after a very prolonged (tending to infinity) radiation time, respectively.

The results of the evaluation of the light sensitivity of the photopolymers for different radiation times for two wavelengths are presented in Table 2.

The results obtained on determination of the total light sensitivity of the photopolymers are presented below.

Polymer	III	IV
$\tau_{\frac{1}{2}}$ (min) at		
λ_{max} 288 nm	27	22
λ_{max} 308 nm	—	17
λ_{max} 310 nm	20	—

The spectrosensitometric investigations showed (Fig. 4*a*) that the most light sensitive are the polymers II, III and IV (range of light sensitivity 260–500 nm). Polymers I and V are less light sensitive (range 260–370 nm).

To raise the light sensitivity of the photopolymers obtained we used the following sensitizers: acenaphthene, 5-nitroacenaphthene, *m*-, *n* and 2,6-dichloro-4-nitroaniline, benzophenone and Michler ketone. The substance 2,6-dichloro-4-nitroaniline greatly improves the total light sensitivity of the polymer (Fig. 4*b*). *Meta*- and *p*-nitroaniline

TABLE 2. LIGHT SENSITIVITY OF THE POLYMERS III AND IV

Radiation time, min	Polymer III ($\lambda=310$ nm)		Polymer IV ($\lambda=308$ nm)	
	A_t	$\frac{A_0 - A_t}{A_0 - A_\infty}$	A_t	$\frac{A_0 - A_t}{A_0 - A_\infty}$
0	0.729	—	0.563	—
2	0.678	0.11	0.509	0.14
4	0.645	0.18	0.480	0.21
8	0.602	0.27	0.412	0.38
16	0.532	0.41	0.375	0.48
32	0.402	0.65	0.287	0.70
∞	0.262	—	0.172	—

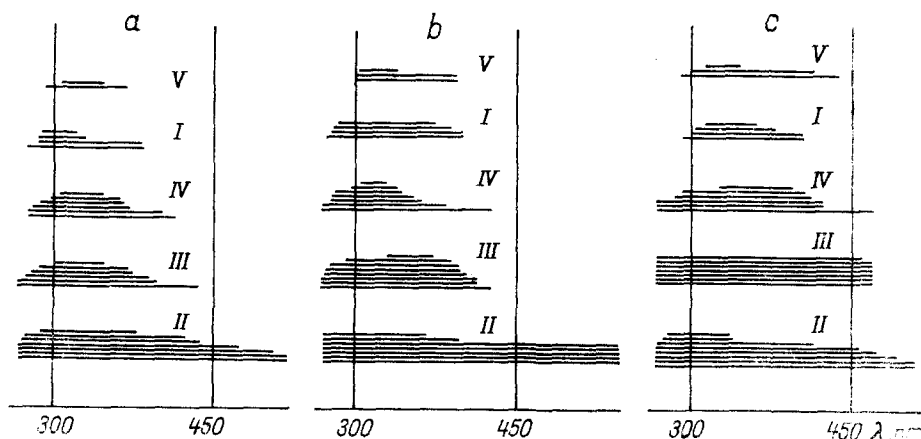


FIG. 4. Spectrosensitograms of the photopolymers obtained by condensation of *p*-aminocinnamic acid esters with benzaldehyde (I) and *p*-N,N'-dimethylaminobenzaldehyde (II) and also with salicylaldehyde (III), *o*-nitrobenzaldehyde (IV) and cinnamaldehyde (V). *a*—Photopolymer without sensitizer; *b*, *c*, in presence of 2,6-dichloro-4-nitroaniline and 5-nitroacenaphthene, respectively.

did not display sensitizing properties while 5-nitroacenaphthene has better sensitizing properties than acenaphthene.

All the sensitizers used accelerate the crosslinking of the photopolymers and shift the range of light sensitivity to longer wavelengths.

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EFFECT OF SODIUM ACETATE ON THE STRUCTURE OF POLYVINYL ALCOHOL*

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The effect of sodium acetate on the degree of crystallinity of PVA has been studied by IR spectroscopy and wide and low angle X-ray structural analysis. It is shown that the introduction of sodium acetate into the PVA samples raises the degree of crystallinity with practically no change in the size of the crystalline regions over a wide filling range. From the results of X-ray structural analysis an assumption is made on the character of the distribution of sodium acetate in the PVA samples as a function of the concentration of filler.

IN the production of PVA a reaction by-products forms—sodium acetate the amount of which in commercial PVA samples may reach several percentages. The presence of sodium acetate in the PVA samples is indicated by the absorption band in the IR spectrum at 1575 cm^{-1} the intensity of which falls on washing with water [1]. The catalytic effect of sodium acetate on the reaction of dehydration of PVA on heating above 100°C has been established [2].

The problem of the influence of sodium acetate on the supramolecular structure of PVA has not been studied although for a sufficient content in the polymer the salt may act as a kind of filler present in molecular or finely disperse form.

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