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Synthesis and Properties of a Photosensitive Copolymer Based on 2-formyl-1-(P-vinylphenyl)cyclopropane and Glycidylmethacrylate

Saida Mamedli

ipoma@science.az

Ministry of Science and Education of the Azerbaijan Republic Institute of Polymer Materials
https://orcid.org/0000-0003-2269-3306

Bakhtiyar Mamedov

Aysel Rzayeva

Vusala Vahabova

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SYNTHESIS AND PROPERTIES OF A PHOTOSENSITIVE COPOLYMER BASED ON 2-FORMYL-1-(p-VINYLPHENYL)CYCLOPROPANE AND GLYCIDYLMETHACRYLATE

S.B. Mamedli[1,2] (http://orcid.org/0000-0003-2269-3306)**, B.A. Mamedov**[1] **(**https://orcid.org/0000-0001-6135-832X), **A.E. Rzayeva**[1] **(**https://orcid.org/0000-0002-2920-9292)**, V.A.Vahabova**[1] **(**https://orcid.org/0000-0002-6278-1047)

[1]*Institute of Polymer Materials of the Ministry of Science and Education of the Republic of Azerbaijan, Sumgait, Azerbaijan Republic*
[2]*Sumgait State University, Sumgait, Azerbaijan Republic*
e-mail:ipoma@science.az

Abstract. The new polyfunctional photosensitive copolymer by the radical copolymerization of 2-formyl-1-(p-vinylphenyl)cyclopropane and glycidylmethcarylate has been synthesized. It has been shown that the copolymerization proceeds only with the opening of the vinyl double bond in the monomers. The copolymerization constants values of these monomers ($r_1 = 1.1$; $r_2 = 0.35$) have been calculated and it has been revealed that in this case, 2-formyl-1-(p-vinylphenyl)cyclopropane is a more active monomer during radical copolymerization. The average molecular weights of the samples synthesized under various copolymerization conditions are varied in the range of $\overline{M}_w$ = 111500-146600 and $\overline{M}_n$ = 61400-90600. The composition, structure and photosensitive properties of the synthesized copolymer samples have been determined. It has been shown that the obtained copolymer has an alternating structure and the availability of highly absorbing ketone, cyclopropane, epoxide and ester groups in the macromolecules gives the copolymer a high photosensitive activity. The copolymer samples are inclined to be undergo photochemical transformations during radiation and the absorption boundary of the electron spectra of the copolymer samples is below 320 nm. For increasing the photosensitivity of the copolymer, a sensitizer was introduced and as a result, by means of a sensitizer, the absorption boundary was shifted to 360 nm. It has been shown that by varying the copolymerization conditions, the photosensitive properties of copolymers can be purposefully adjusted. The dependence of the cross-linking rate of the copolymer of 2-formyl-1-(p-vinylphenyl)cyclopropane and glycidylmethacrylate on exposure time has been studied.

Key words: 2-formyl-1-(p-vinylphenyl)cyclopropane, copolymer of glycidylmethacrylate, photosensititvity, negative photoresist

INTRODUCTION

Photoresists are photosensitive materials capable of change their properties under the influence of UV radiation, as they are photo-structured. They are intended for realization of the photolithographic processes in the manufacture of semiconducting devices and integrated schemes, which are used in various fields of technology [1-5]. In creation of the light-sensitive polymers for photoresists, the main problem is the preparation of materials possessing sufficiently high degree of the light-sensitivity, good adhesion, thermal stability, endurance, good solubility, etc. By inclusion of the photosensitive functional groups of various nature in the composition of

the compound, it can be also improved the chemical, physical and mechanical properties of the synthesized polymer [6-9]. The most common photosensitive monomers proposed for this purpose are compounds having ketone groups in the main and side chains, such as 4-acrylamidophenyl-2',3'-benzostyryl ketone and 4-acrylamidophenyl-4'-N,N'-dimethylstiryl ketone [10], and acrylamide derivatives of piperazine-substituted polyfluorochalcones [11], cyclodextrin derivatives with suspended norbornadiene, azobenzene, cinnamate and anthracene [12], 4-hydroxyphenyl-4'-methoxystyryl ketone [13], as well as polysulfone methylenoxy-4-chalcone and polysulfone methylene cinnamate [14], polystyrene containing an acetyl group (CH_3CO) [15]. Based on bis(4-hydroxy-3-methoxybenzylidene)acetone and epichlorohydrin, the light-sensitive epoxy resin has been synthesized [16] and their photosensitive properties have been studied in works [17-19]. The unsaturated polymers containing ketone groups can undergo cross-linking under the action of UV rays [20-22]. In previous works, we have synthesized the glycidyl photoresists and considered their photosensitive properties [23-25]. The glycidyl esters and its analogues are photofunctional [16, 26-30], and epoxide and ester groups in polymers are also capable of crosslinking under the influence of ultraviolet radiation. Such polymers are considered as negative photoresists. In this paper, we have synthesized a new photosensitive copolymer based on 2-formyl-1-(p-vinylphenyl)cyclopropane (FVCP) and glycidylmethacrylate (GMA).

EXPERIMENTAL PART

Materials and reagents

For the research we used: glycidylmethacrylate (no less 97%, purity, pure for analysis, Sigma-Aldrich, USA), GMA (no less than 97%, purity, analytical grade, Sigma-Aldrich, USA), the catalysts for polymerization of dinitrilisobutyric acid (AIBN) (98.0%, “Aldrich”, USA); benzene solution (“Aldrich”, USA); methanol (Central Drug house (P) ltd., İndia) before use was dried by distillation from magnesium methylate in nitrogen atmosphere; chlorobenzene (99.5 %, “Aldrich”, USA); Mikxler’s ketone (98%, “Aldrich”, USA); hydrochloric acid (Central Drug house (P) ltd., İndia); phenol formalein (Central Drug house (P) ltd., İndia); dioxane chloride (Central Drug house (P) ltd., İndia).

Copolymerization of 2-formyl-1-(p-vinylphenyl)cyclopropane with GMA.

FVCP was synthesized according to the method given [31]. The copolymerization of FVCP with GMA was carried out in ampoules in mass and in a benzene solution in a nitrogen atmosphere at 70 ±0.05ºC in the presence of 0.2% of AIBN (from the mass of monomers) to various depth of conversion. At the end of the reaction, the ampoules were cooled and precipitated with ethanol three times. The copolymer samples were dried to a constant weight. All experiments were duplicated. The quantity of FVCP in the initial mixture of monomers varied from 10 to 90 (10, 25, 50, 75, 90) mol.%.

Compositions of the initial reaction mixture: 1) FVCP – 1.72 g (0.01 mol), GMA – 12.8 g (0.09 mol), AIBN – 2.9 g (0.017 mol); 2) FVCP – 4.3 g (0.025 mol), GMA – 10.6 g (0.075 mol), AIBN – 3 g (0.018 mol); 3) FVCP – 8.6 g (0.05 mol), GMA – 7.1 g (0.05 mol), AIBN – 3.1 g (0.019 mol); 4) FVCP – 12.9 g (0.075 mol), GMA – 3.5 g (0.025 mol), AIBN – 3.3 g (0.02 mol); 5) FVCP – 15.48 g (0.09 mol), GMA – 1.422 g (0.01 mol), AIBN – 3.38 g (0.018 mol). During copolymerization in solution, besides above-mentioned composition, 25 ml of benzene was used.

The copolymer samples are dissolved in chlorobenzene, chlorinated hydrocarbons, chloroform, etc., and their yields reach up to 84%.

In IR-Fourier spectrum of the copolymer, the absorption bands in the field of 1034 cm^{-1} (cyclopropane); 1601, 1529, 1479 cm^{-1} (benzene ring); 2767 cm^{-1} (C-H aldehyde); 2928, 2982 cm^{-1} (CH_2 aliphatic); 1724 cm^{-1} (carbonyl group); 908 cm^{-1} (epoxide group); 1177 cm^{-1} (C-O); 776

cm^{-1} (C-O-C); 1268 cm^{-1} (C-C); 848 cm^{-1} deformation vibrations of C-H in substituted benzene are observed.

PMR spectrum, δ, ppm: 1.3 d (2H CH_2), 2.4 t (1H CH), 7.15 m ($4H_{arom.}$), 1.42 m (H $CH_{cyclopropane}$), 1.54 m (1H $CH_{cyclopropane}$), 1.68 m (1H $CH_{cyclopropane}$), 2.51 m (1H $CH_{cyclopropane}$), 9.5 s (1H $CH_{aldehyde}$), 1.1 s (3H CH_3), 4.0 d (–OCH_2– GMA), 3.1 m (CH– epoxide ring in GMA), 2.4 d (–CH_2– epoxide ring in GMA).

Investigation of photosensitive properties of the copolymer

For investigation of the photochemical structuring of the copolymer samples, their 2÷10% solutions, which applied on a glass substrate (K-8) with size 60×90 mm were prepared. The application was carried out by a method of centrifugation, the layer was dried for 10 minutes. at room temperature for 20 min. at 30-35°C and a pressure of 10 mm merc.c.

DRT-220 mercury lamp (current strength 2,2 A) was used as UV radiation source, the distance from the radiation source – 15 cm, the exponometer shutter rate – 720 mm/h, the exposure time – 5-20 sec. The percentage content of the cross-linked fraction was determined on regarding of the mass of the insoluble copolymer to the initial mass of the copolymer.

The composition of the copolymer has been determined by the content of the epoxide group according to the following procedure, given in [32]. The used method is based on the reaction of epoxide groups of the copolymer dissolved in benzene with hydrochloric acid. The copolymer sample containing about $1.0 \cdot 10^{-3}$ mol of epoxide groups was dissolved in 10 ml of benzene. Then, 10 ml solution of 0.4 mol HCl in dioxane ($2.0 \cdot 10^{-3}$ mol of HCl) was added to the sample solution and stirred for 3 h at room temperature. Then, 3 ml of water was added to this mixture with the aim of precipitation of the copolymer. The copolymer was separated from the solution, and then the remaining sample solution was titrated with 0.1 M NaOH in ethanol using the acid-base indicator – phenolphthalein. In this case, the difference between the quantity of moles of hydrochloric acid added to the analyzed sample and the quantity of moles of NaOH consumed for neutralization of HCl corresponds to the content of epoxide groups in the initial sample.

The copolymerization constants were determined using the Fineman-Ross method [33], and the molecular weight was determined using the Mark-Hoovink formula [34].

Measurements

IR spectra from the surface of the samples were taken on IR-Fourier spectrometer Agilent Cary 630 (Agilent Technologies, USA) in the range from 450 to 4000 cm^{-1}, and PMR spectra – using long exposure time spectrometer Magnet System 300 MHz/54mm Ultra Shield (Bruker Bio Spin AG, Switzerland, working frequency 300.18 MHz) in solution of deuterated chloroform.

The characteristic viscosities of the samples were determined by the viscometric method in an Ostwald viscometer in a chlorobenzene solution at 20°C.

UV irradiation was carried out on DRT-220 installation (current strength 2.2 A) equipped with a mercury lamp, the distance from the radiation source was 15 cm, and the shifted shutter rate of the exposure meter was 720 mm/hour.

The photoresist films were applied to the substrates using GLICHN T-108 centrifuge. The rotation rate – rev/min 300-8000, rotation rate adjustment step – rev/min 100, time setting – min 1-99, accuracy of rotation rate measurement – rev/min 0.5.

UV spectra in the field of 300-800 nm were registered on spectrophotometer UV/VİS, 6850 Yenway, Britaniya.

RESULTS AND DISCUSSION

The IR spectra of FVCP-co-GMA copolymer have been analyzed (Fig. 1). A comparison of the spectra of the copolymer samples isolated at various stages of the copolymerization allows to note a considerable broadening of the contour of the carbonyl absorption band for copolymers obtained with a high degree of comonomer conversion. Indeed, in the field of 3100-2900 cm^{-1}, the form and intensity of the bands have been stipulated by the summation of the contributions of C-H absorption in CH_2, CH_3 groups and the characteristic absorption of the aldehyde group, shifted to 2900 cm^{-1} under the influence of resonance interaction with oxygen of the carbonyl group. The characteristic absorption of the cyclopropane ring is observed in the range of 1034 cm^{-1}. The planar symmetrical C-H vibrations of both monomeric links give a series of bands merging into a common contour in the frequency range of 1479, 1451 cm^{-1}. On the C-O and C-O-C vibration contour referred to glycidylmethacrylate, two very narrow bands with frequencies of 1177 and 776 cm^{-1} attract attention. In the field from 1000 to 700 cm^{-1}, there are out-of-plane vibrations of C-H bonds of aliphatic and aromatic groups. The copolymer does not contain the absorption bands of the valence vibrations of the vinyl group, which are present in both monomers at a frequency of 1635-1640 cm^{-1}. As expected, the copolymerization proceeds due to the opening of the vinyl groups of monomers [35, 36].

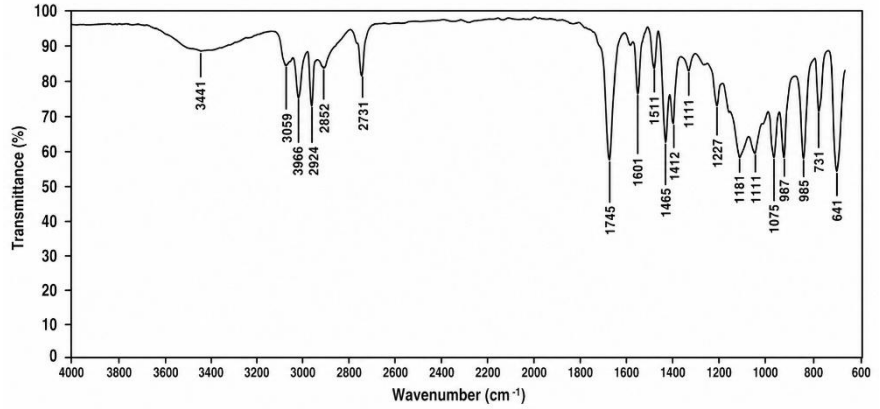


Fig. 1 IR spectrum of the copolymer on the basis of FVCP and GMA. The sample has been synthesized in solution, in equal moles of comonomers at 60°C for 5 h. FVCP – 8.6 g (0.05 mol.), GMA – 7.1 g (0.05 mol), AIBN – 3.1 g (0.019 mol), benzene – 25 ml. Indices of the copolymer sample: $\overline{M}_n$= 90600, $\overline{M}_w$ == 146600, $\overline{M}_w/\overline{M}_n$=1.618

The results of the analysis of the PMR spectra of the copolymers confirm the fact that there are no signals referring to protons of the vinyl group δ = 5.10-6.65 ppm, in the PMR spectra of FVCP-co-GMA copolymers, the resonance signals of the benzene nucleus at δ=7.15 ppm, the benzyl proton at δ=2.4 ppm, the cyclopropane ring at 1.42-2.51 ppm and the epoxide ring at δ=2.4 ppm (–CH_2–) and δ=3.1 ppm (–CH–) are fixed Fig. 2).

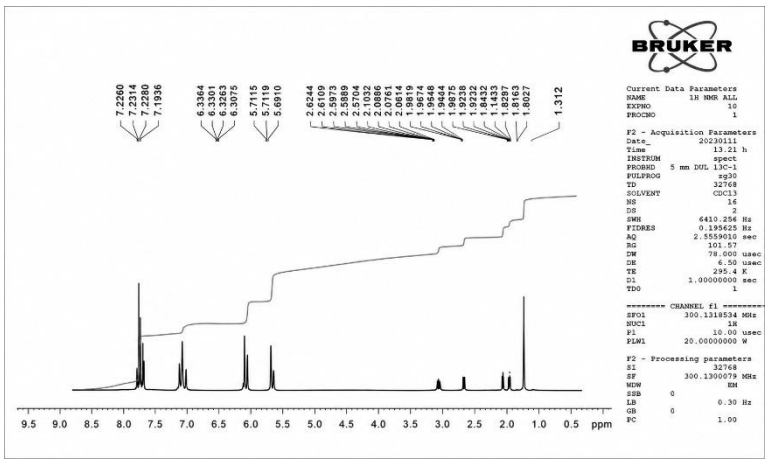
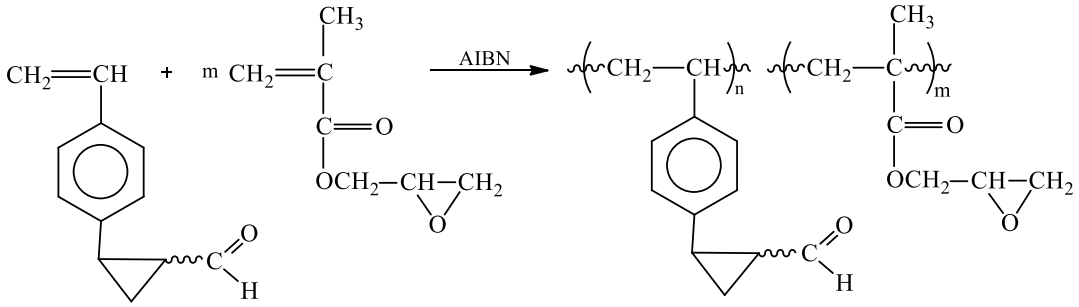


Fig. 2 PMR spectrum of the copolymer on the basis of FVCP and GMA. The sample has been synthesized in solution, in equal moles of comonomers at 60°C for 5 h. FVCP – 8.6 g (0.05 mol), GMA – 7.1 g (0.05 mol), AIBN – 3.1 g (0.019 mol), benzene – 25 ml. Indices of the copolymer sample: $\overline{M}_n$= 90600, $\overline{M}_w$ = 146600, $\overline{M}_w$ /$\overline{M}_n$=1.618

The following chemical structure of the photosensitive copolymer is proposed:



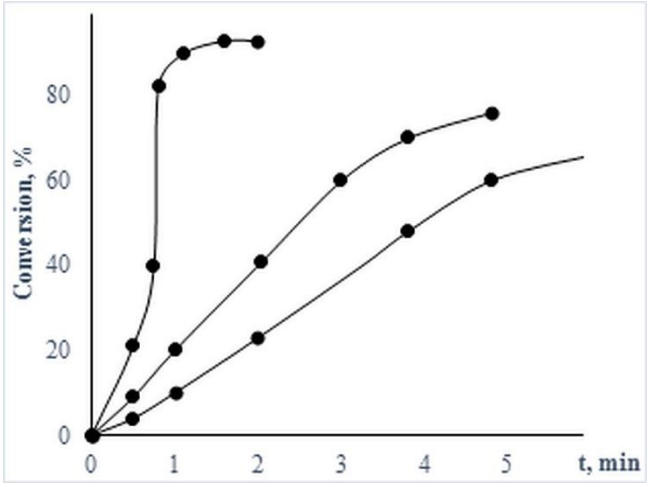


Fig. 3 Dependence of the conversion on the duration of the copolymerization reaction for a mixture of FVCP+GMA monomers. From top to bottom:1) polymerization of MMA; 2) 5.2 mol% of FVCP in chloroform solution; 3) 10 mol % of FVCP in chloroform solution

FVCP and GMA copolymerization was carried out to various conversion depths. The graphical dependence of the conversion depth on the reaction duration in a benzene solution for a monomer mixture of FVCP+GMA containing 5,2 and 10 mol% of FVCP is shown in Fig. 3. It can be seen from the graphics that the presence of FVCP in the reaction mixture noticeably decreases GMA conversion rate. The yield of the polymer product during homopolymerization of GMA is more than 5.5 times higher than during copolymerization of FVCP+GMA monomers (5.2 mol%) during the carrying out of the reaction for one hour under the same conditions (Fig. 3). The

observed effect is explained by the opposite polarities of the comonomers. The monomers with opposite polarities favor the increase of the cross-chain breaking rate and as a result, the total copolymerization rate is decreased [37, 38].

The chemical composition of FVCP-co-GMA copolymers has been analyzed by determination of the epoxide groups.

The values of the characteristic viscosity of the copolymer samples have been determined. The values of the characteristic viscosities of the copolymer samples are increased with the growth of the monomer conversion depth during copolymerization process (Fig.4). During FVCP with GMA copolymerization, there is a decrease in the values of the characteristic viscosities of the samples with an increase in FVCP in the initial mixture of monomers to 20 mol%. At 50 mol% FVCP in the copolymer, the sample loses solubility due to the participation of an aldehyde group.

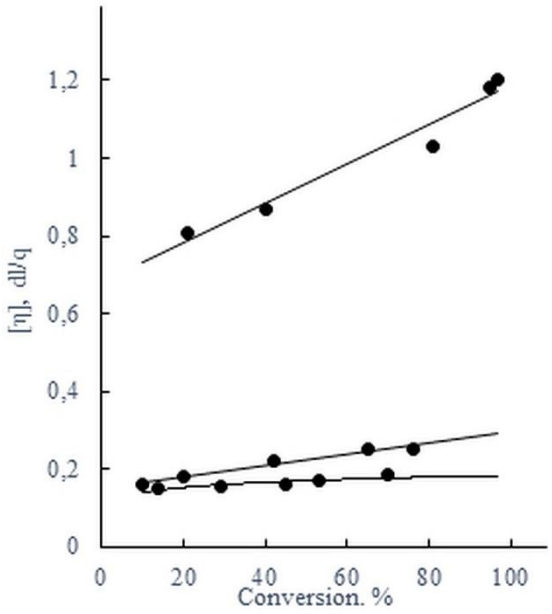


Fig. 4 Change pf the characteristic viscosities of FVCP-co-GMA samples with conversion growth. From top to bottom 1) polymerization of GMA; 2) with the participation of 5.2 mol % of FVCP in chloroform solution; 3) with the participation of 10 mol % of FVCP in chlorobenzene solution.

The content of FVCP links in the macromolecules of copolymers is relatively intensively decreased on growth of the conversion depth. This indicates that in the copolymerization process FVCP is a more active monomer than GMA. Based on data of the chemical composition of copolymers obtained at small conversion depths (5-10%), the copolymerization constants of both monomers have been calculated using the Fineman-Ross method (r_1=1.1; r_2=0.35). $r_1 \cdot r_2$=0.385, i.e. close to zero, which should indicate a considerable inclination of monomers to the alternating copolymerization [39]. According to data [40], with increase of the difference in the polarity or donor-acceptor properties of two monomers, the tendency of their inclination to alternation grows.

Using the viscometric method, the characteristic viscosity of the samples has been determined (Table 1). The average molecular weight of the copolymer samples has been calculated from the Mark-Hoovink equation, which expresses the dependence of the characteristic viscosity ([η]) on the molecular weight (M):

$$[\eta]=kM^{\alpha}$$

The indices of average molecular weight have the following values: $\overline{M}_w$ = 111500-146600 and $\overline{M}_n$ = 61400-90600.

Table 1 Copolymerization of FVCP with GMA in a benzene solution (70ºC, content of AIBN 0.02%). Content of FVCP and GMA content in a benzene solution 30% of total quantity)

Content of FVCP in the initial mixture, mol%	Copolymer yield, %	Characteristic viscosity, dl/g	Content of FVCP links in copolymer samples, mol %
5.2	10.2	0.22	13.9
	20.6	0.25	11.2
	43.3	0.28	8.1
	64.9	0.31	8.3
	75.4	0.32	7.8
	81.7	0.33	7.4
10	13.3	0.22	19.3
	27.2	0.20	15.8
	44.3	0.21	12.8
	54.0	0.23	11.2
	68.9	0.23	9.5
	77.5	0.24	8.9
20	5.8	-	34.5
30	6.5	-	48.5
50	10.5	-	60.2

The investigated FVCP-co-GMA copolymer has a various chemical nature. Aldehyde, cyclopropane, epoxide and ester groups are referred to a number of strongly absorbing groups [41-44]. The compounds containing aldehyde, cyclopropane, epoxide and ester groups are used as photosensitive additives to the polymer systems. They increase the sensitivity of polymers to light and are prone to the photochemical reactions leading to cross-linking of the polymer chains.

Under the action of UV radiation in photosensitive copolymers of this type, the light energy is absorbed by ketone, aldehyde and ester groups, and the cyclopropane and epoxy rings are opened with formation of radicals, which react with the polymer macromolecule forming a polymer radical. The latter one, in turn, interacts with other macroradicals and the cross-links are formed.

It has been established that the form and view of the absorption spectra depends on the ratio of monomer links in the macromolecule of the copolymer and is largely determined by the content of FVCP. FVCP-co-GMA samples have an absorption in the field of 300-120 nm of UV spectra. The character of change of UV spectra of FVCP-co-GMA copolymer is shown in Fig.5. It is clearly seen that at the first stages of irradiation, the change rate of D_0 at the maximum of the band at 258-263 nm is linear with the irradiation time, however, after the 40th and 50th seconds, the process is decelerated. Simultaneously with a decrease of the band at 258-263 nm, an increase in the intensity of the band at 230 nm is observed.

It was known that in the short-wavelength part of the spectrum, the sensitivity of samples strongly depends on the layer thickness [45]. In this case, with increase of the layer thickness, the coincidence of the spectral sensitivity of the sample with the spectral distribution of absorption is decreased. This phenomenon is explained by a decrease in the quantum yield of the photochemical reaction in the short-wavelength part of the spectrum, since most of the absorbed energy goes to photonic and other transitions not causing a photochemical reaction. In addition, in photolithography there are used the glass photo-templates made of glass, absorbing lower 310 nm, which hinders the work with polymer systems possessing spectral sensitivity lower 320 nm. There is a need to shift the absorption boundary of polymers to the field of longer wavelengths, which is achieved by introduction of sensitizers into the polymer system. In this work, the Mikhler ketone (MK) was used as a sensitizer.

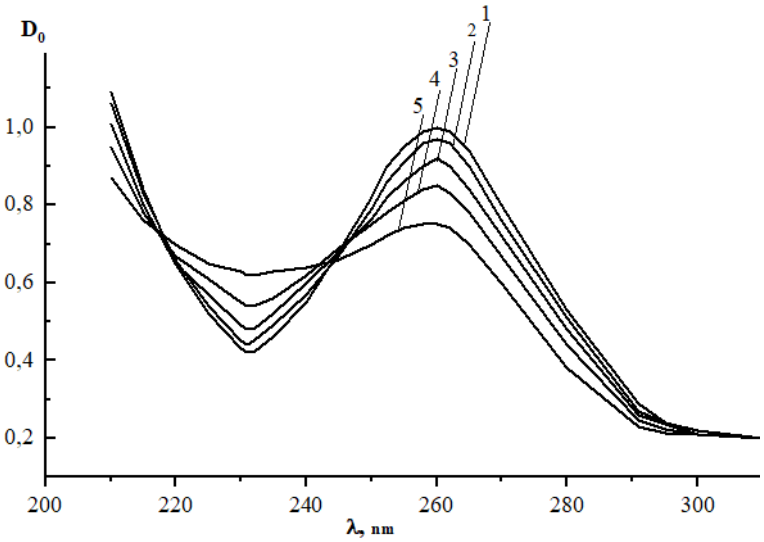


Fig. 5 Change of UV spectra of the copolymer films of FVCP-co-GMA (25% of FVCP) in the irradiation process. From top to bottom 1-5, via irradiation time t =0, 1, 3, 10, 25, 60 sec. D_0-optical density.

The high degree of the light-sensitivity of the photographic material is determined by the coincidence of the absorption spectrum maxima with the radiation bands of the light sources and the transparency of the photo-template for transmission of the active light. Consequently, the photosensitivity is a very complex function, depends on the direction and the rate of the photochemical processes, the spectral sensitivity of polymers and the ratio of the source and absorption spectra.

The photosensitivity is usually expressed as a value inversely proportional to the quantity of the absorbed light energy; i.e., with the decrease of the exposure, the photosensitivity is increased. Mathematically, this is written as follows:

$$S=\frac{I}{H}=\frac{I}{(E\cdot\tau)}$$

where H – exposure, E – illumination, τ – exposure time.

The photoreaction rate has been calculated according to the following regularities:

$$\upsilon=\frac{\rho}{\tau}$$

where υ – photoreaction, ρ – unsaturation, τ – exposure time.

The copolymer solution containing a sensitizer was applied by a method of centrifugation onto an optical quartz substrate at a centrifugation rate of 2500 rev/m. for 40 sec. Drying of the polymer layer was carried out by keeping the film in the air for 10 min, followed by heat treatment at a temperature of 65-70°C for 35 min.

The layer was exposed from the substrate side through a plane-parallel glass plate, which is used to make standard photo-templates. A mercury lamp DRT-220 with a radiation flow of 18 volts was used as the source.

The film development was carried out with a mixture of chlorobenzene-dioxane-methylene chloride (1:1:1) solvents for 10 min, followed by keeping the developed films in air for 10 min. at room temperature and 30 min. at 65-70ºC.

The investigated polymer composition FVCP-co-GMA with the sensitizer KM had the following composition:

1. 45 mol % of FVCP:55 of GMA:5% MK
2. 20 mol % of FVCP :80 of GMA:5% MK
3. 20 mol % of FVCP:80% of GMA:1% MK

The illumination was controlled by a luxmeter and was 30,000 lux. The exposure time ranged from 2 to 800 seconds.

Table 2 Dependence of the crosslinking rate on the exposure time and the shown photosensitivity of the polymer composition FVCP-co-GMA + MK

Samples	Exposure time, sec.	Crosslinking rate υ, weight. %/sec.	Photosensitivity, cm^2/C
1	30-180 180-600	0,165 0,02	2,5
2	30-180 180-600	0,134 0,018	2.0
3	30-180 180-600	0,095 0,008	1,4

The relative photosensitivity values of the polymer samples have been calculated on the basis of obtained experimental data and presented in Table 2. It can be seen from Fig. 5 and Table 2 that the saturation is achieved with increasing exposure time of the samples. After saturation, even a considerable increase in temperature does not lead to any noticeable increase in the cross-linked part of the copolymer. The saturation (*ρ)* for samples (1-3) at film thickness 0.55 ± 1 mcm are 75, 40, 30. The photosensitivity of the investigated samples increases in the range 3, 2, 1. Naturally, the photosensitivity depends on the quantity of the active groups in macromolecules.

The experimental data reflecting the dependence of exposure on the quantity of sensitizer are presented on samples 2 and 3. It is seen that the sample 2 shows the higher photosensitivity.

Since in irradiation with UV light, the cross-linked net structures are formed in negative photoresists and the solubility of the irradiated areas is lost, then as a result of the photochemical conversion of the active reactive groups, the polymer film is cross-linked and loses solubility under the influence of ultraviolet rays. Consequently, the copolymers containing such groups in their macromolecules can be used as a negative photoresist.

As a result of the investigations, the photosensitive copolymer has been obtained. The possibility of using the obtained copolymer as a negative photoresist in microelectronics, photolithography, etc. has been shown.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

AUTHOR CONTRIBUTION

All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by S.B. Mamedli, B.A.Mamedov, A.E. Rzayeva and V.A.Vahabova. The first draft of the manuscript was written by S.B. Mamedli, B.A.Mamedov and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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