

# Copolymerization Phenylcyclopropylmethacrylates with Glycidyl Methacrylate and Their Properties

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## To cite this article:

Kazim Gafar Guliyev, Aysel Elshad Rzayeva, Afet Mirza Aliyeva. Copolymerization Phenylcyclopropylmethacrylates with Glycidyl Methacrylate and Their Properties. *American Journal of Applied and Industrial Chemistry*. Vol. 6, No. 1, 2022, pp. 7-12.

doi: 10.11648/j.ajaic.20220601.12

Received: October 25, 2021; Accepted: November 12, 2021; Published: February 25, 2022

**Abstract:** New phenylcyclopropyl methacrylates (PhCMA) have been synthesized and studied in detail new monomers radical copolymerization with glycidyl methacrylate (GMA). As a result of laboratory experiments were obtained new cyclopropane and epoxy-containing photosensitive copolymers. PhCMA is a new reactive monomer, its synthesis and homopolymerization have been presented. The choice of this compound to copolymerize it with GMA has been stipulated by the presence of light absorbing carbonyl, cyclopropane and epoxide groups or double bond in the molecule. In the copolymerization of the studied GMAPhCMA system is an important task is choosing the conditions when the polymerization is proceeded only by participation of vinyl group and the reactive fragments would be remained in the side chain without changes. The relative activity of monomers and the parameters of  $Q$  and  $e$  have been determined by Alfrey-Price method. The copolymerization constants of the specified compound (PhCMA) ( $r_1$ ) with glycidyl methacrylate ( $r_2$ ), calculated by the Fineman-Ross method, are:  $r_1=0.57$ ,  $r_2=0.65$  (Cl);  $r_1=0.68$ ,  $r_2=0.55$  ( $\text{NO}_2$ ), respectively; the values of the parameters  $Q$  and  $e$ :  $Q_1=1.19$ ,  $e_1=-0.8$  (Cl);  $Q_1=1.42$ ,  $e_1=-0.9$  ( $\text{NO}_2$ ), respectively. The composition and structure of this copolymer have been established. Photochemical studies of the synthesized copolymer have been carried out. It was found that structuring proceeds due to the opening of the cyclopropane ring and epoxy groups, as well as the carbonyl group. The structure and composition monomers and polymers which were synthesized were studied by IR and NMR spectroscopy. An availability of the synthesized copolymer of the reactive groups of various chemical nature in links of macromolecule arouses interest for investigation of photochemical structuring of this copolymer, i.e. to crosslinking under action of UV-irradiation and such polymers showing as negative type photoresists. These polymers with properties of high light sensitivity, film-forming ability, good solubility before irradiation, resistance to solvents, plasma and etchants after cross-linking and good thermal stability, which are very important for photoresist. Due to availability of strongly absorbing light energy of groups (cyclopropane, glycidyl,  $>\text{C}=\text{O}$  etc.) the synthesized copolymers are photosensitive and under the influence of UV-irradiation are subjected to the photochemical conversions leading to formation of crosslinked structures.

**Keywords:** Microstructure, Monomers, Copolymerization, Phenylcyclopropyl Methacrylates, Photosensitivity

## 1. Introduction

Rapid increasing of information requires new type of materials to record, storage and reproduce data. The polymers and copolymers containing various reactive groups possess valuable properties and possibility of crosslinking under action of radiation which allows to prepare various materials used in microelectronics [1-3]. This is one of the main reasons for interesting of the researchers for the preparation of new types

of the photosensitive polymers [4-8].

Polymerization of functionally substituted cyclopropyl styrene [9-11] is a well-known way of preparing such materials, and polymers made of cyclopropane compounds with functional groups are subjected to UV radiation cross-linking processes to form negative photoresists with high light sensitivity [12, 13]. Copolymerization of the cyclopropanes containing vinyl groups with other reactive monomers results polymers containing cyclopropane groups located in side part of macrochain is also well known [14, 15].

This work has been devoted to synthesis and investigate the copolymerization of phenylcyclopropyl methacrylates (PhCMA) with glycidylmethacrylate (GMA) and study of lithography properties of the copolymers prepared on their basis with the aim of creation of new photosensitive copolymers. The choice of this monomer has been stipulated with large number and chemical nature of double bonds and presence of cyclopropane ring in combination with carbonyl group in the monomer which has influence on such important photolithographic parameters of resists as photosensitivity, adhesion, film-forming exc [16, 17].

PhCMA is a new reactive monomer, its synthesis and homopolymerization have been presented recently [18]. The choice of this compound to copolymerize it with GMA has been stipulated by the presence of light absorbing carbonyl, cyclopropane and epoxide groups or double bond in the molecule. In the copolymerization of the studied GMAPhCMA system is an important task is choosing the conditions when the polymerization is proceeded only by participation of vinyl group and the reactive fragments would be remained in the side chain without changes.

## 2. Experiment

The synthesized monomer PhCMA was polymerized as a 2 mol/l ethyl-methyl kethone (EMK) solution using benzoyl peroxide (BPO) as a free radical initiator at  $70 \pm 1^\circ\text{C}$ . The specified amounts of PhCMA and BPO were dissolved in benzene, introduced into a polymerization tube, and the mixture was purged with a slow flow of oxygen-free nitrogen for 20 minutes. Then the tube was tightly closed and placed in a thermostated water bath at  $70 \pm 1^\circ\text{C}$ . After the specified time (4 h), the reaction mixture was precipitated in excess methanol or in sulfuric ether to isolate the poly (PhCMA) polymer. The crude polymer was purified by redissolving in chloroform and precipitating in methanol, filtering, then washing with methanol and drying in vacuo at  $45^\circ\text{C}$  for 2 hours. The yield was 88%.

The synthesis of PhCMA was carried out by methodology described in our work [18].

The copolymerization of PhCMA with GMA was carried out in benzene solution in the presence of 0.5% azobisisobutyronitrile (AIBN) (from total mass of monomers) at  $70^\circ\text{C}$ . The total concentration of the initial monomers was 1.0 mol/l, and a ratio of the initial monomers was changed as it is given in table 1. The copolymers of various composition have been isolated after 10-20 min by addition excess of MeOH to the reaction mixture. The resulting copolymers were re-precipitated twice from their benzene solution with methanol and sulphuric acid and dried in vacuum (15-20 Hg.mm) at  $30^\circ\text{C}$  until constant weight. The copolymers formed were white solids which are well soluble in aromatic and chlorinated hydrocarbons. Elemental analysis for  $\text{C}_{21}\text{H}_{25}\text{O}_5\text{Cl}$ : Calculated: C, 64.20%, H, 6.37%, Cl, 9.04%. Found: C, 64.35%, H, 6.41%, Cl, 9.11%; for  $\text{C}_{21}\text{H}_{25}\text{O}_7\text{N}$ : C, 62.53%, H, 6.20%, N, 3.47%. Found: C, 62.60%, H, 6.53%, N, 3.27%.

The composition of the copolymer was determined by the analysis of functional groups (determination by the epoxy number).

The IR-spectra of the copolymers were registered on spectrometer "AgilentCary 630 FTIR", NMR-spectra – on spectrometer "BrukerAFR-300 (80 MHz)" in solution of euterated chloroform.

The photosensitivity of co-polymers was determined at various concentrations (4-13% solutions) with making a layer on the glass substrate in a dust-free medium with centrifuging at  $2500\cdot\text{min}^{-1}$ . The photoresists were kept for less than 20 min for increasing of adhesion to the substrate before cutting on contour on contour of the procurement preventing the film detachment.

Thickness of the prepared film-resists was measured by microinterferometer "LINNIKA", which was proved to be 0.20-0.25 mkm after drying for 10 and 20 min at room temperature and  $30\text{-}35^\circ\text{C}/10\text{ Hgmm}$ , respectively. The exposure of the procurements was carried out on a device with light point source through photomask with a DPT-220 mercury lamp (current intensity was 2.2 A, distance from source of radiation was 15 cm, mobile shutter rate of exonometer was  $-720\text{ mm}\cdot\text{h}^{-1}$ , exposure time was 5-20 s).

The development was carried out in a jet installation. As a developer dioxane and sopropyl alcohol was used at ratio 1:2 at temperature of  $18\text{-}25^\circ\text{C}$ . The photosensitivity is valued on the basis of the completeness of photochemical polymerization (crosslinking). The photosensitivity – the inverse of the dose of UV-light absorbed means an UV dose necessary for transformation of photoresist to crosslinked (insoluble) state. Where

$$S = \frac{1}{H} = \frac{1}{E \cdot t} \quad (1)$$

$H$  – exposure (or dose of irradiation with UV light),  $\text{J}\cdot\text{cm}^{-2}$

$E$  – intensity,  $\text{Wt}\cdot\text{cm}^{-2}$

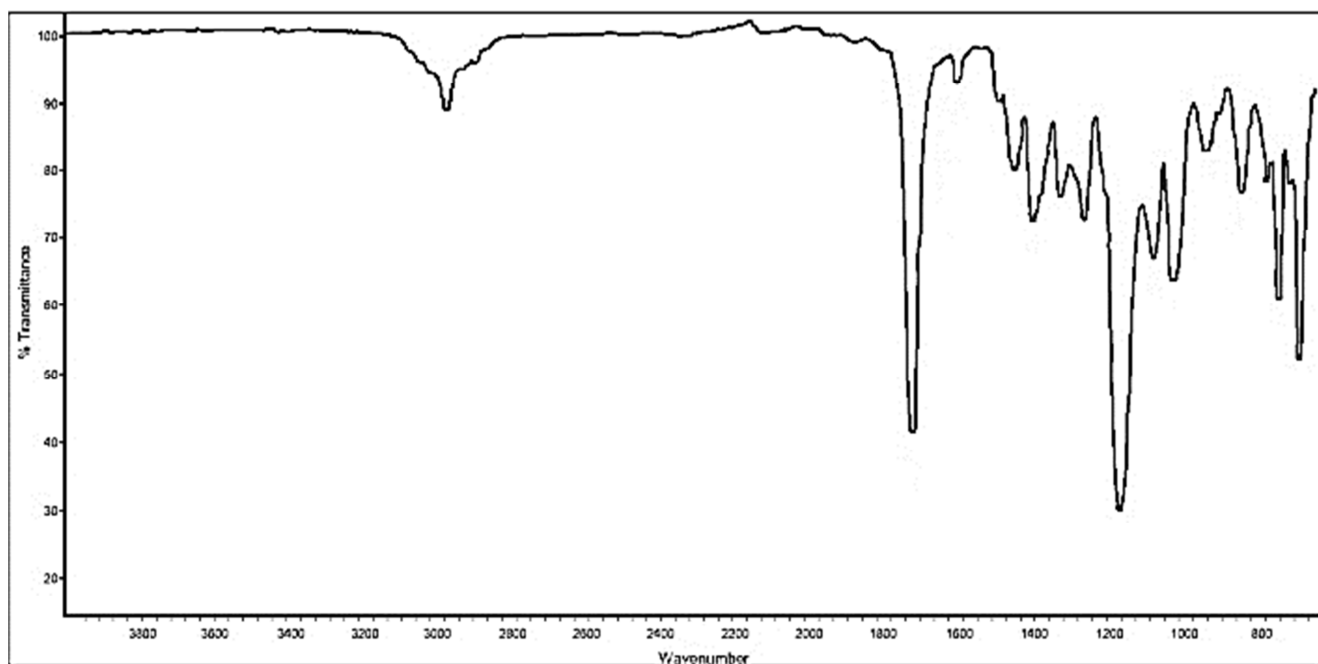
$t$  – irradiation duration, s

## 3. Results and Discussion

During radical co-polymerization of polyfunctional PhCMA with GMA formation of reactive polyfunctional copolymer showed in Formula 1 could be expected. Comparing of the IR-spectra of the copolymers formed with the spectra of the initial monomer (PhCMA) showed that the deformation and valence vibrations of the vinyl group in the initial monomer at  $990$  and  $1640\text{ cm}^{-1}$  are disappeared.

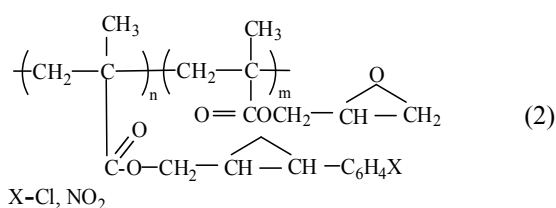
The absorption bands characteristic for benzene and cyclopropane rings ( $1410\text{-}1460$  and  $1500\text{-}1600\text{ cm}^{-1}$ ) and the absorption bands at  $1720$ ,  $1030$  and  $1110\text{ cm}^{-1}$ , referring to the carbonyl vibrations of the cyclopropyl ester fragment are remained unaffected. Availability of the characteristic absorption bands of epoxide groups in structure of the copolymers is confirmed by the absorption band at  $830$ ,  $920$  and  $1260\text{ cm}^{-1}$ .

The IR-spectrum of PhCMA copolymer with GMA is presented in figure 1.



**Figure 1.** IR-spectrum of a polymer film of phenylcyclopropylmethacrylates (PhCMA) copolymer with glycidylmethacrylate (GMA): unirradiated (1) and irradiated during the 10<sup>th</sup> (2), 15<sup>th</sup> (3) and 40<sup>th</sup> (4) seconds.

In the PMR spectrum (figure 2) of copolymer the resonance signals referring to protons of benzene nucleus ( $\delta=7.00-7.50$  ppm) and cyclopropane ring ( $\delta=1.55-2.60$  ppm) are clearly appeared. The protons of epoxide ring are characterized with signals at 2.10-2.20 ppm ( $-\text{CH}_2-$ ) and at 2.40 ppm ( $-\text{CH}-$ ). As  $r_1$  and  $r_2$  is less than 1, in this system there is a tendency to alternation of links. According to the data of spectroscopy the copolymerization of PhCMA with GMA proceeds only due to opening of double bonds of the vinyl groups with maintenance of the other reactive functional fragments of the both monomers. Thus, on the basis of the analysis of IR and PMR-spectra of the copolymers prepared by copolymerization of PhCMA with GMA, the structure of copolymers is assumed as it is given in formula (2).



The copolymerization was carried out at various ratios of the initial monomers. It has been revealed that the composition of forming copolymers depends on the composition of the initial monomer mixture. For estimation of polymerization activity of PhCMA there have been calculated the values of relative activity constants of monomers by Fineman-Ross method [19] and the parameters  $Q-e$  by Alfrey and Price method. The microstructure parameters of the copolymers were calculated by using the copolymerization constants on formulas [20]. The obtained

data are presented in Table 1. The values of the relative activity constants (Table 1) evidence about greater reactivity of PhCMA in comparison with GMA. The conjugation of the ester group causing redistribution of electron density both in the monomer and in the radical formed from it, thus the energy necessary for appearance of transition state is decreased leading to the increase of reactivity of monomer.

The calculated values of parameters  $Q_1$  and  $e_1$  during copolymerization with GMA indicate increased conjugation in monomer (PhCMA) connected with influence of substituent  $-\text{Cl}$ ,  $\text{NO}_2$  stipulating relatively high reactivity of monomer and more low reactivity of the radicals. In calculation of factor  $e_1$  it was chosen the negative mark based on the fact that the electron density of double bond of vinyl group in PhCMA should be less than in GMA, since the influence of substituent of PhCMA leads to redistribute of density of double bond in the vinyl group changing polarity of the radical. This has been connected to the large reactivity of PhCMA in comparison with GMA confirmed by copolymerization constant ( $r_1=0.65$ ,  $r_2=0.57$ , respectively) (Table 1).

An availability of the synthesized copolymer of the reactive groups of various chemical nature in links of macromolecule arouses interest for investigation of photochemical structuring of this copolymer, i.e. to crosslinking under action of UV-irradiation and such polymers showing as negative type photoresists. These polymers with properties of high light sensitivity, film-forming ability, good solubility before irradiation, resistance to solvents, plasma and etchants after crosslinking and good thermal stability, which are very important for photoresist. Due to availability of strongly absorbing light energy of groups (cyclopropane, glycidyl,  $>\text{C}=\text{O}$  etc.)

the synthesized copolymers are photosensitive and under the influence of UV-irradiation are subjected to the

photochemical conversions leading to formation of crosslinked structures.

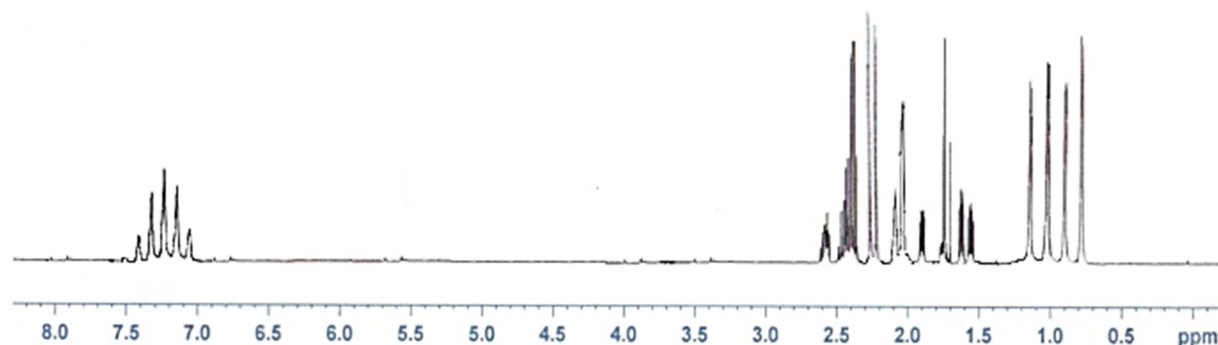


Figure 2. NMR spectrum of a copolymer of *p*-chlorophenylcyclopropylmethacrylate (*p*-ClPhCMA) with glycidylmethacrylate (GMA).

Table 1. Copolymerization of *p*-ClPhCMA ( $M_1$ ) and *p*-NO<sub>2</sub>PhCMA ( $M_1$ ) with GMA ( $M_2$ ).

Composition of the initial mixture, mol. %		Composition of copolymers, mol. %		$r_1$	$r_2$	$Q_1$	$e_1$	$r_1 \cdot r_2$
M <sub>1</sub>	M <sub>2</sub>	m <sub>1</sub>	m <sub>2</sub>					
p-ClPhCMA-co-GMA								
10	90	13.42	86.58	0.57±0.03	0.65±0.02	1.39±0.01	-0.89±0.02	0.3705
25	75	28.73	71.27					
50	50	48.72	51.28					
75	25	68.95	31.05					
90	10	85.10	14.90					
p-NO <sub>2</sub> PhCMA-co-GMA								
10	90	15.26	84.74	0.68±0.03	0.55±0.02	1.42±0.01	-0.90±0.02	0.0374
25	75	31.51	68.49					
50	50	51.93	48.07					
75	25	71.92	28.08					
90	10	87.02	12.98					

The influence of irradiation on photosensitive polymers has been investigated by measurement in UV-spectrum. The photoreactive fragments have been considered with various concentrations 15-150 mg in thin films. The absorption bands in the UV spectrum of polymers at 296 and 300 nm, respectively, are referred to  $\pi \rightarrow \pi$  transitions. The intensities of absorption through various intervals of irradiation were changed in the UV-spectrum of the copolymer with ratio 48.72:51.28 (*p*-ClPhCMA-co-GMA) and 51.93:48.07 (*p*-NO<sub>2</sub>PhCMA-co-GMA) (figure 3).

During irradiation decrease or disappearance of photoactive fragments could be observed. The irradiation led to fast decrease of the absorption intensity at 296 and 300 nm and to disappearance of the bands almost completely after 4 min irradiation. It has been revealed that an increase of concentration of polymers raises a photocrosslinking rate due to large quantity of photosensitive units.

In films of copolymer, a conversion rate of the photosensitive fragments depends on composition of the light-sensitive links in the copolymer chain. The crosslinking rate grows with increase of cyclopropane and epoxy rings in the polymer (figure 4). It could be concluded that after 40-80 sec. irradiation (transformation is 50-70%), the polymer films become insoluble in organic solvents in which they were dissolved at room temperature to do irradiation experiments. Such behaviour is caused by

formation of hard three-dimensional network due to intermolecular photoinduced cycloaddition of hanging units.

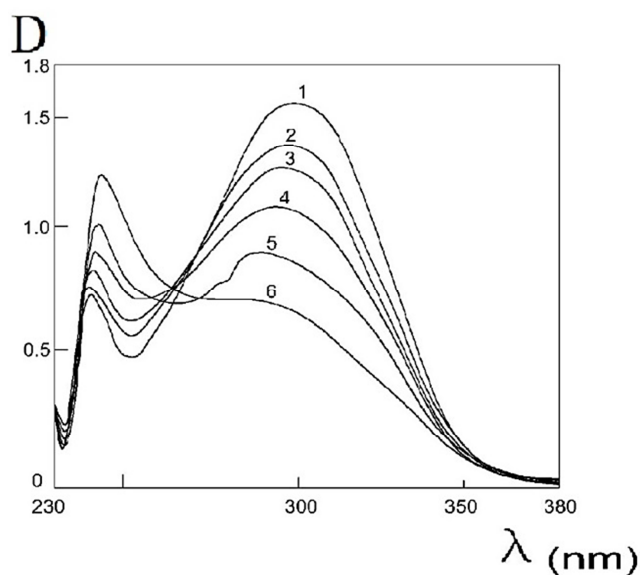
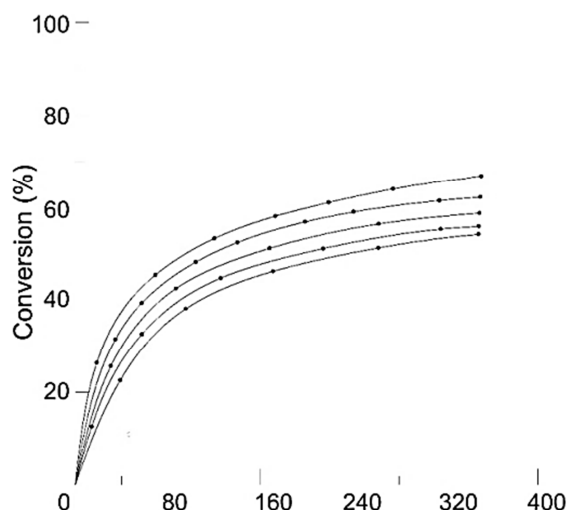


Figure 3. Change in the UV-spectrum upon irradiation of poly *p*-chlorophenyl-cyclopropylmethacrylate (*p*-ClPhCMA) with glycidylmethacrylate (GMA), (from top to bottom, after the irradiation time  $t=0$ ; 50, 100, 150, 300 and 600 s).



**Figure 4.** Disappearance rate associated with cyclopropane and epoxy rings of poly phenylcyclopropylmethacrylates (PhCMA) with glycidylmethacrylate (GMA), as thin film: ( $m_1$  and  $m_2$ ).

The three-dimensional structure during irradiation has a form of a loose net with large cells, which swells strongly during development and is compressed drying of the polymer layer, causing folds and wrinkles. The good results have been prepared in work with films of thickness 0.2-0.3  $\mu\text{m}$ .

The process of 3D-structure evolution during irradiation of the prepared cyclopropane-ring containing copolymers has been followed by IR spectroscopy as well (figure 1). The intensity of the absorption bands characteristic for cyclopropane ring ( $1030\text{--}1035\text{ cm}^{-1}$ ), double bonds ( $1635\text{ cm}^{-1}$ ), carbonyl group ( $1720\text{--}1725\text{ cm}^{-1}$ ), and epoxide ring ( $830, 920, 1260\text{ cm}^{-1}$ ) were decreased with increasing of irradiation time and were completely disappeared  $\sim 4$  min irradiation due to 3D-structure evolution with opening of double bonds and cyclopropane rings.

The absorption band at  $1720\text{ cm}^{-1}$ , characteristic for carbonyl group in ester fragments being in conjugation with double bond is shifted to  $1740\text{ cm}^{-1}$  during irradiation which can be attributed to the opening reaction of double bond and as a consequence the disappearance of conjugation. A new copolymer has been synthesized and its composition, structure and properties have been established.

The availability of cyclopropane ring, glycidyl, carbonyl groups in macromolecules of the prepared copolymer allowed to create a material with high photosensitivity. These copolymers have high photochemical crosslinking ability to create solid elastic layers with good adhesion to substrates and to prepare polymer films with low microdeficiency.

## 4. Conclusions

1. It has been synthesized and characterized the new polyfunctional phenylcyclopropyl methacrylates (PhCMA) and it has been carried out its radical copolymerization with glycidyl methacrylate.
2. The composition and structure of the synthesized copolymers have been established. The copolymerization constants of the copolymerizing

monomers ( $r_1=0.57, r_2=0.65$  (Cl);  $r_1=0.68, r_2=0.55$  ( $\text{NO}_2$ )) have been found and Q-e parameters values of Alfrey-Price scheme ( $Q_1=1.19, e_1=-0.8$  (Cl);  $Q_1=1.42, e_1=-0.9$  ( $\text{NO}_2$ )) have been calculated.

3. It has been studied the process of structuring of the copolymers and it has been established that the synthesized copolymers has relatively high photosensitivity and these copolymers have high photochemical crosslinking ability to create solid elastic layers with good adhesion to substrates and to prepare polymer films with low microdeficiency.

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