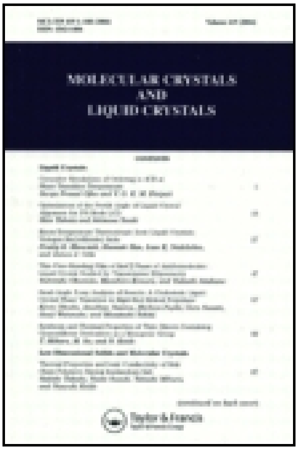

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Photochemical Transformations of p-(methacryloyloxy)-N-phenylimides and their Polymers Under the Action of UV-Light

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Photochemical Transformations of p-(methacryloyloxy)-N-phenylimides and their Polymers Under the Action of UV-Light

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Photochemical behavior under the influence of UV-light of p-(methacryloyloxy)-N-phenylimides and their polymers was investigated. The possibilities of Friese photorearrangement (FPR) as for monomers so for polymers were studied. The velocity of FPR for phenyl methacrylate monomers depends weakly on the structure of imide substituents. But an introduction of substituents, especially of aromatic nature, in maleimide fragments increases the rate of FPR. For polymers with photoactive imide pendant groups both FPR and photocrosslinking reactions are possible. Correlations of velocities for crosslinkings and FPR reactions were found by the data of IR-spectroscopy. Photocrosslinking was found to be more rapidly process than FPR reaction.

Keywords: crosslinking; Friese photorearrangement; IR-spectroscopy; maleimide derivatives; negative photoresist

INTRODUCTION

One of the main tasks of the electronics industry is developing of miniaturized systems, i.e., more components for minimum feature size per chip. Photoresists (negative and positive) that active in UV and blue VIS (365–436 nm) had been developed for microelectronics. But new concepts of minimization the resolution demand the intervention of

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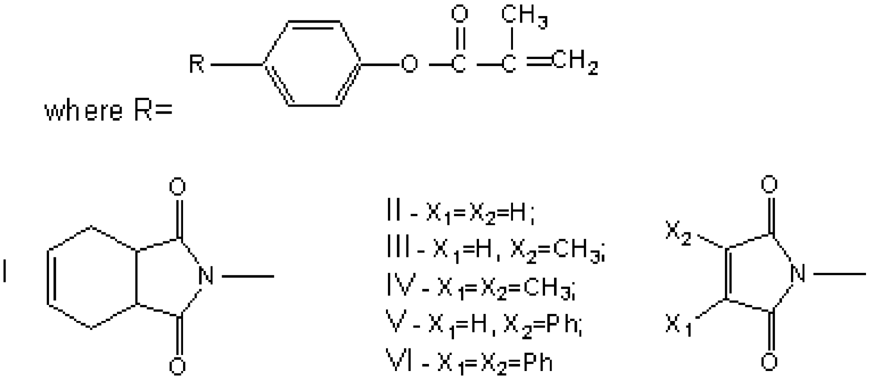
scientists, particularly, chemists, who can develop new materials for formation of photoresist films [1].

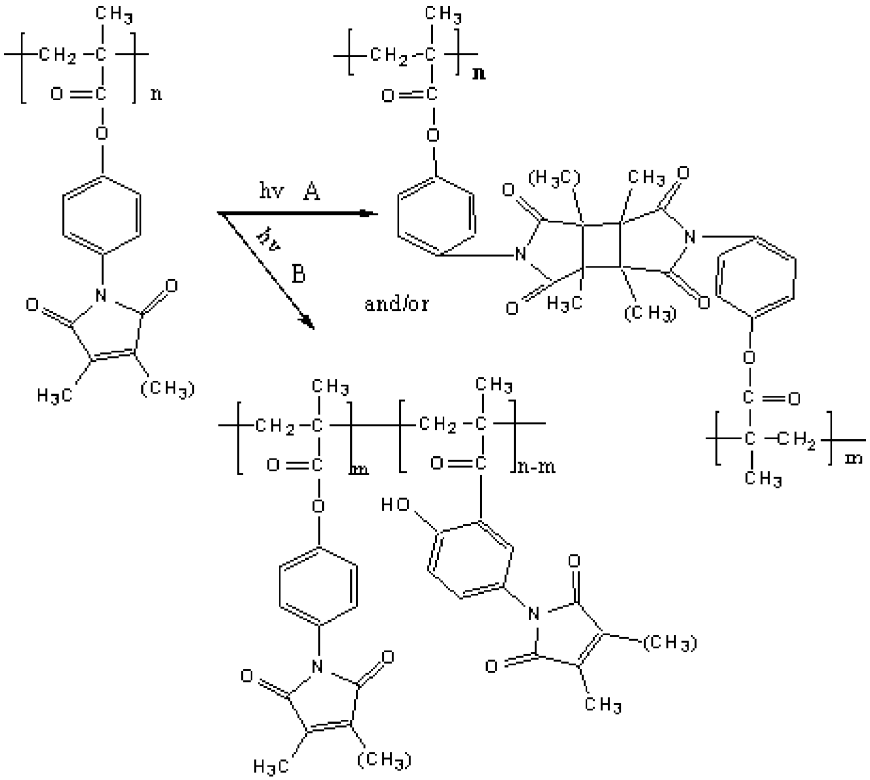
From our point of view, bifunctional monomers with two polymerizable double bonds with different reactivities are perspective materials for negative photoresist creation. In the previous papers we have reported the methods of the synthesis of p-(methacryloyloxy)-N-phenylmaleimide and tetrahydrophthalimide derivatives (Scheme 1), investigations of their polymerizability in conditions of thermo- [2] and photoinitiated [3] radical polymerization.

Photoinitiated polymerization with low intensity of irradiation (3–5 mW/cm^2) permits to synthesize soluble polymers which endowed light sensitive maleimide or tetrahydrophthalimide groups [3]. Such polymers can be used as negative photoresists because double bonds of imide cycle can undergo [2 + 2] cycloaddition with high quantum yields [4,5] (Scheme 2A) and insoluble products are formed.

But such polymers under UV-irradiation are able not only to cross-linking – also Friese photorearrangement (FPR) takes place for them (Scheme 2B). Due to this reaction phenol esters can transform into o- or p-acylphenols and free OH-groups are formed. As a consequence, solubility and chemical resistance of resist films during the pattern process are changed. So, for photoresists development it's very important to value a time, which it is enough for a photocrosslinking, but for which FPR either does not occur or proceeds in such measure, that the resistive properties of crosslinked photoresist films do not change significantly.



SCHEME 1



SCHEME 2

MATERIALS AND INSTRUMENTS

Synthesized monomers (methods of synthesis are presented in [2]) were purified by recrystallization before use.

UV spectra of investigated monomers were recorded with "SPECORD UV VIS" spectrometer (c = 10^{-5} mol/l in ethanol solution). Carring out of FPR reaction for compounds (I–VI) were controlled by UV-spectroscopy also.

Radical polymerizations of the chosen monomers were carried out in quartz dilatometers after degassing by a free-thaw process with argon. Irgacure 1700 was used as a radical photoinitiator. Dimethylformamide (DMF) was purified by distillation under vacuum and was used as a solvent. Samples were irradiated by integral UV-light with 3 mW/cm^2 intensity for 30 minutes at 20°C. After polymerization dilatometers were opened and the polymers were obtained by precipitating into a large excess of methanol. After that these polymers were reprecipitated three times from DMF to methanol. The polymers were dried under vacuum to constant weight.

Films of polymers were prepared in the following way. 10 mas.% solution of chosen polymer in chloroform or 1,2-dichloroethylene was spin coated onto a KBr substrate yielding a dry film thickness of 15–30 μ. Polymer films were irradiated by integral UV-light with 60 mW/cm^2 intensity for 5 – 120 minutes.

Photocrosslinking of investigated polymer films was monitored by changes in infrared spectra. IR-spectra were recorded on a Nexus-470 spectrometer from Nicolet Co.

For UV-irradiation of polymer samples high pressure mercury lamp DRSh-1000 was used.

RESULTS AND DISCUSSION

A) FPR of Synthesized p-(methacryloyloxy)-N-phenylmaleimides and p-(methacryloyloxy)-N-phenyl-(1,2,3,6)-tetrahydrophthalimide

The Friese photorearrangement (FPR) is very known reaction in photochemistry. It is possible for all compounds, which are aromatic esters, amides or sulfamides. This reaction is particularly used in photostabilization of polymeric materials. Such photostabilization is based on phototransformation of stabilizer, which chemically included in polymer chains. Accordingly to such mechanism the protection of polymers by some ester and secondary amides of acids, which can trans-form under UV-light to oxy- or aminoketone derivatives, takes place. For example, phenyl(meth)acrylates and their polymers is known to enter FPR under UV-irradiation and form o- and p-oxyketone structures [6,7]. By investigations of this phenomenon, similar reactions were found to be possible for compounds of other classes also, for example for N-arylamides of carboxylic acids [8]. Also the reaction of FPR was used for photoactivation of polymeric biocides [9]. Under irradiation of polymers with sulfamide fragments in macrochain “clearing” of NH_2-group takes place and polymer gets antibacterial properties.

As it was spoken before, photoresist technology demands stability of polymer coats in time. That’s why, investigations of FPR for synthesized monomers as phenol esters are so necessary. Kinetic investigations of FPR permit to select such monomers for which photocross-linking, but not FPR plays a main role.

At UV-irradiation of monomer’s solutions in ethanol the formation of new long-wavelength maxima in absorption spectra are observed.

This fact is explained by the formation of new products. Presence in spectrum only one isobestic point is the evidence of only one product formation due to FPR reaction.

As it is visible from presented spectra, during of p-(methacryloyloxy)-N-phenylimides FPR the difference between absorption of irradiated solution D_{max} and initial solution D_0 in the new maximum is increased. More accurate characteristic of FPR velocity is a dependence of differential absorption $\Delta = D_{max} - D_0$ on irradiation time.

In Figure 1 spectra of p-(methacryloyloxy)-N-phenyl-1,2,3,6-tetrahydrophthalimide ethanol solutions before and after UV-irradiation in the new maximum ($\lambda = 370\,\text{nm}$) are presented. As it is visible from the figure, a reaction of FPR has three stages – accelerating, reducing and termination.

In the case of maleimide type monomers the new absorption maxima that can be attributed to products of FPR are observed in region of 320–330 nm (for example, Fig. 2).

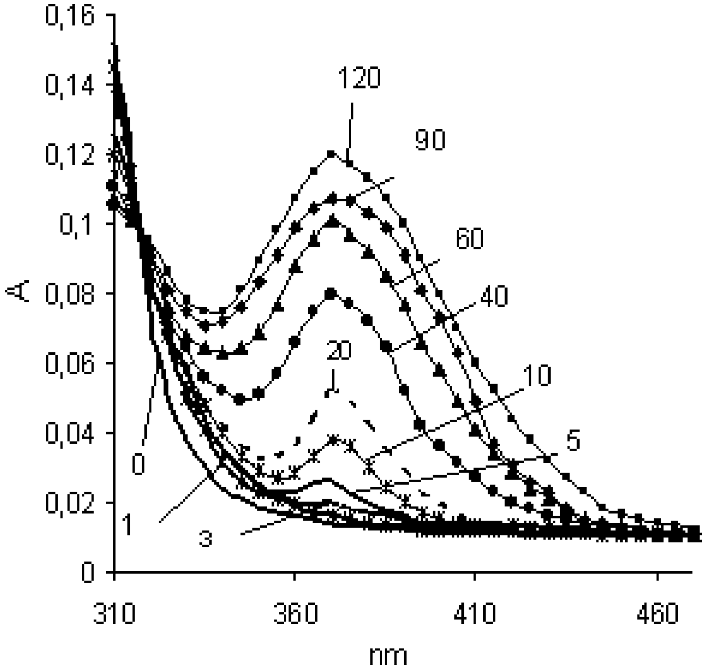


FIGURE 1 Fragments of absorption spectra of ethanol solution of monomer (I) ($c = 1^*10^{-4}$ mol/l, $l = 1\,\text{cm}$) before and after UV-irradiation during 1–120 minutes.

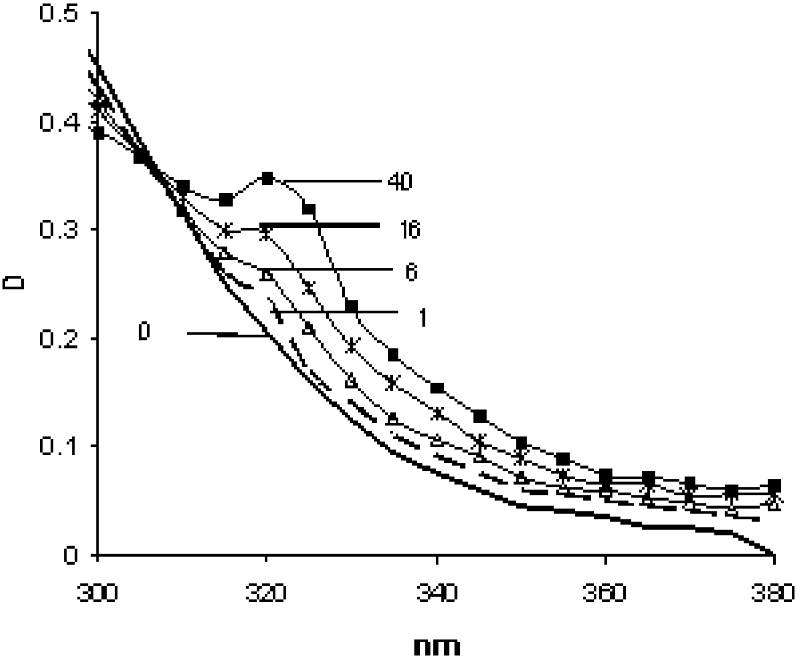


FIGURE 2 Fragments of absorption spectra of ethanol solution of monomer (II) (c = $1^{*}10^{-4}$ mol/l, l = 1 cm) before and after UV-irradiation during 1–40 minutes.

For monomers (I–VI) dependences of differential absorption $\Delta = D_{max} - D_0$ of monomer's ethanol solutions from irradiation time in the new maxima (320 nm for monomers (II–VI) and 370 nm for monomer (I)) were constructed (Fig. 3).

The effective velocities of rearranged product forming ($V_{ef} = (D - D_0)/t$) for monomers (I–VI) were calculated also and their values are presented in Table 1.

As it is visible from the presented dependences and from data of Table 1, the velocity of FPR for phenylmethacrylate monomers are depends a little from the structure of imide substituent – values of V_{ef} for monomers (I) and (II) differ a little: $0.33{*}10^{-4}c^{-1}$ and $0.2{*}10^{-4}c^{-1}$ accordingly. Introduction of substituents, especially of aromatic nature, in maleimide fragment increases the rate of FPR (monomer (VI) rearranges most rapidly, at that time p-(methacryloyloxy)-N-phenylmaleimide (monomer (II)) rearranges most slowly).

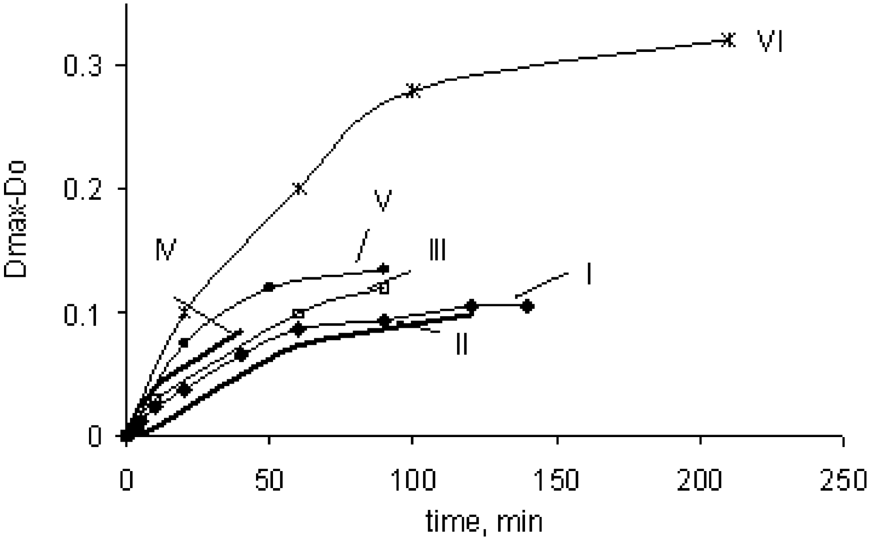


FIGURE 3 Dependences of differential absorption $\Delta = D_{max} - D_0$ of monomer's ethanol solutions from irradiation time at wave-length of new maxima (320 nm for monomers (II–VI) and 370 nm for monomer (I)) ($c = 1*10^{-4}$ mol/l, l, l = 1 cm).

Thus, from the point of view of properties stability of polymer materials in time under UV-irradiation the p-(methacryloyloxy)-N-phenylimides without aromatic substituents are most suitable for negative photoresist formation, for example p-(methacryloyloxy)-N-phenyl-1,2,3,6-tetrahydrophthalimide (monomer (I)), p-(methacryloyloxy)-N-phenylmaleimide (monomer (II) and p-(methacryloyloxy)-N-phenylcitraconylimide (monomer (III)).

TABLE 1 The Effective Velocities of Rearranged Product Forming V_{ef} of Synthesized p-(methacryloyloxy)-N-phenylimides (I–VI)

Monomer	$V_{ef.}*10^4$, c^{-1}
I	0.33
II	0.20
III	0.42
IV	0.52
V	0.63
VI	0.83

B) The Comparative Analysis of Velocities of FPR and Photocrosslinking of Polymer Based on p-(methacryloyloxy)-N-phenylcitraconylimide

The following step for quantitative characteristic of FPR and photocrosslinking speeds correlation of investigated compounds is studying of both processes velocities by IR-spectroscopy. Experimental researches of imide fragments crosslinking and FPR was carried out for polymethacrylate based on monomer (III) (Fig. 4)—for polymethacrylate with free citraconylimide fragments as pendant groups.

The selection of such polymer material are caused by the next reasons. The first one, for monomer (II) in conditions of thermoinitiated radical polymerization is impossible to synthesize soluble polymer product. The second one, for monomer (III) either in conditions of thermoinitiated or photoinitiated radical polymerization is possible to obtain soluble polymer products with free photoactive double bonds of methylmaleimide (citraconylimide) cycles. At the same time, monomer

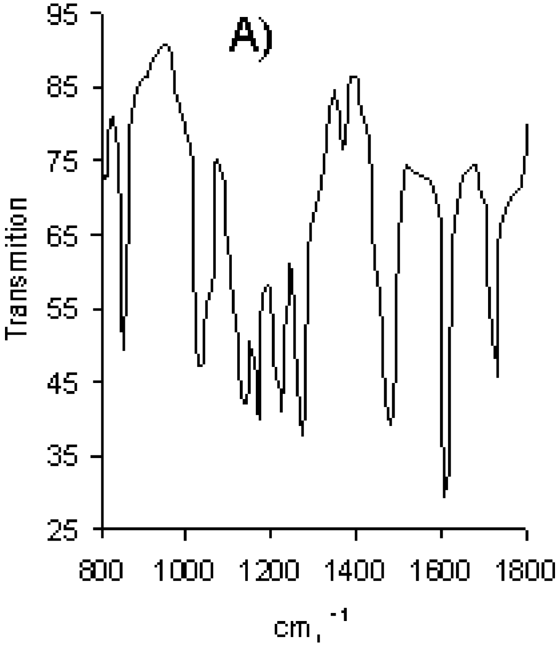


FIGURE 4 IR-spectra of polymer based on p-(methacryloyloxy)-N-phenylci traconylimide before (A) and after irradiation by integral UV-light (intensity of irradiation 60 mW/cm^2) during B) – 5, C) – 10 and D) – 120 minutes.

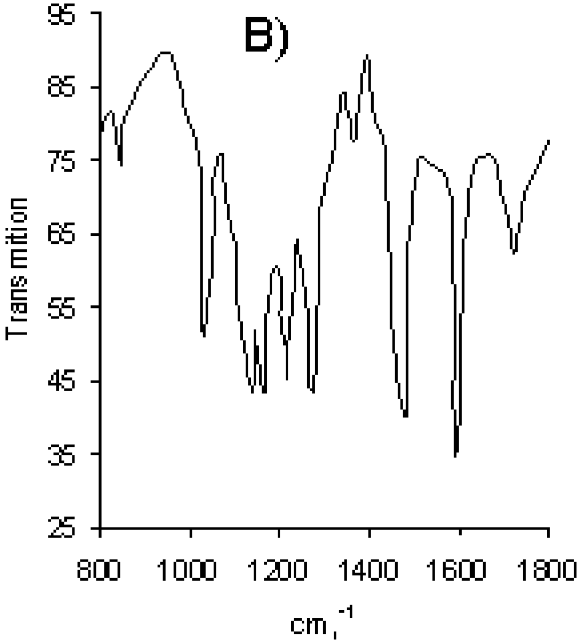


FIGURE 4 (Continued).

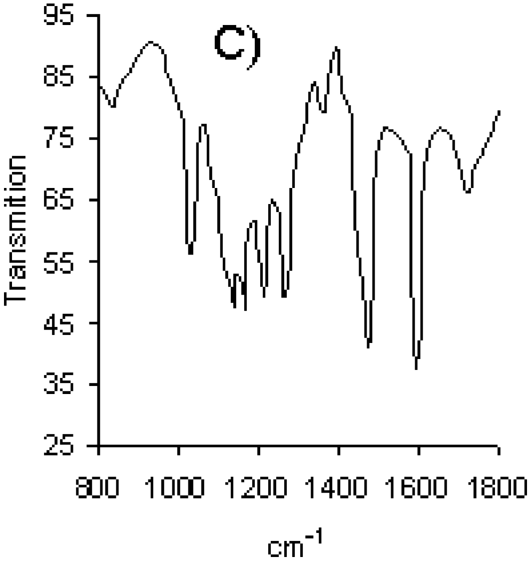


FIGURE 4 (Continued).

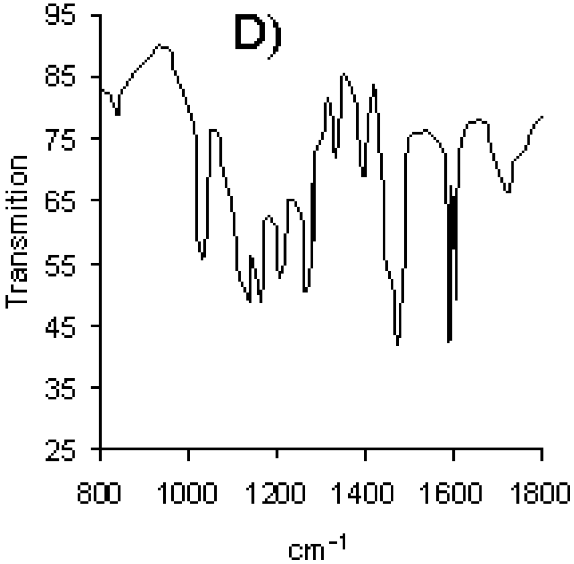


FIGURE 4 (Continued).

(III) has intermediate value of the effective velocity of rearranged product forming V_{ef}.

The first step in the investigation was studying the IR-spectrum of the "initial" polymer film. Their characteristic absorption strips of the functional groups are v (cm^{-1}): 1730 (C=O of imide and ester stretching), 1610 (C=C of aromatic stretching), 1285 and 1050 (C–O bending), 850 (CH=C– of substituted imide fragment). The crosslinking progress of the citraconylimide (methylmaleimide) moieties in the polymer was monitored by determining the decrease in their intensities of absorption bands at 850 cm^{-1} due to the disappearance of the maleimide C=C bonds in the IR spectra. Upon UV exposure for 5 minutes the absorption intensity of citraconylimide (methylmaleimide) moieties at 850 cm^{-1} was significantly decreased owing to [2 + 2] photocycloaddition in comparison with invariable aromatic C=C absorption at 1610 cm^{-1}. Upon UV exposure for 10 minutes decreasing of citraconylimide (methylmaleimide) groups' absorption was very insignificant. So, crosslinking of polymer film occurs upon UV irradiation for 5 minutes. For this time that is necessary and sufficient for the formation of crosslinked polymer (5–10 minutes) there are no new absorption bands in IR-spectra of irradiated polymer which can be interpreted as absorption bands of FPR products. After irradiation during 120 and more minutes appearance of absorption bands of FPR products are observed. The phenol formation are identified by appearance of new absorption bands at 1330 (C–O bond) and 1385 cm^{-1} (OH group). The formation of ketone structures are identified by appearance of new signal at 1680 cm^{-1} (C=O group in o-oksyarylketones). It must be noted that upon UV irradiation of polymer film for a long time (120 minutes) decomposition of crosslinked product had no place.

CONCLUSIONS

It is important in the development of materials for photoresist technologies to pay attention of possibilities of carrying out some parallel photochemical reactions. For polymetacrylate based on p-(methacryloyloxy)-N-phenylcitraconylimide the necessary and sufficient time for negative image formation is 5–10 minutes. For this time FPR does not occur, so physical and chemical properties of irradiated crosslinked material do not change.

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