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# Photochemical Modification of Polyethylene Surface with Aryl Azides

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**Abstract**—It has been shown that the formation of a covalently grafted modifying layer takes place during the photolysis of polycrystalline layers of 2-azidoanthraquinone and 4-azidobenzoyl azide on the surface of poly-ethylene. Its thickness is determined by the amount of the azide applied, and phenyl isocyanate groups formed by the photolysis of 4-azidobenzoyl azide are prone to further functionalization of the modified surface with primary amines.

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Photodissociation of aryl azides yields singlet and triplet nitrenes, as well as 1,2-didehydroazepines [1–8]. The reactivity of these short-lived intermediates is determined by the molecular structure, and their basic

reactions are insertion into multiple or C–H and N–H bonds for nitrenes [9, 10] and addition to nucleophilic groups for 1,2-didehydroazepines [11–14].



Scheme. Main photochemical reactions of aryl azides.

The ability of the intermediates to form covalent bonds with substrate molecules found practical application in works related to investigation into the structure and behavior of complex biomolecules [15–17] and in photolithography for creating covalently crosslinked polymer layers [18, 19].

The efficiency of the formation of the covalent "crosslinks" is often not high and is determined not only by the activity of intermediates, but also by the nature of the substrate. In the presence of air oxygen, nitrenes are oxidized to nitro and nitroso compounds, a process that reduces the efficiency of the insertion reaction [20, 21].

One of the challenges in the formation of the covalent crosslinks" is the surface modification of polyethylene (PE). A low reactivity of the methylene groups of the polymer and the uniformity of the surface properties make it an interesting object for photochemical modification with aryl azides. In this study, 2-azidoanthraquinone (2AA), 4-azidobenzoic acid (4ABK) and 4-azidobenzoyl azide (4ABA) were used as photosensitive agents for modifying the PE surface.



## **EXPERIMENTAL**

Electronic absorption (UV/Vis) spectra of polymer layers in the range of 200–800 nm were recorded versus the irradiated but not modified films on an Analytik Jena Specord 40 spectrophotometer. The IR spectra were recorded in the range of 4000–400 cm<sup>-1</sup> on a Shimadzu IRPrestige-21 Fourier-transform spectrophotometer. To increase sensitivity in recording the IR spectra, the films were folded 64 times and compressed into tablets with a hydraulic press (200 MPa).

Corresponding amines (0.015 mol) were dissolved in a mixture of 15 mL of water and 17 mL of HCl conc. and then diazotized with NaNO<sub>2</sub> (1.08 g, 0.015 mol in 10 mL of water) at  $0-5^{\circ}$ C. On cooling and after 30-min agitation of the solution with a magnetic stirrer, the diazonium salts were azidized with sodium azide (1.3 g, 0.02 mol in 10 mL of water).

4-Azidobenzoic acid (white needle-like crystals) was reprecipitated from acetone with water and recrystallized from a boiling mixture of petroleum ether and benzene in a volume ratio of 5 : 2. IR (KBr disks, cm<sup>-1</sup>): 2130.07, 2106.68, 2053.01 ( $v_{as}$  N<sub>3</sub>); 1680.67 (v C=O); 1287.44 ( $v_{s}$  N<sub>3</sub>).

2-Azidoanthraquinone (yellow crystals) was recrystallized from boiling benzene. IR (KBr disks, cm<sup>-1</sup>): 2116.41, 2031.54 ( $v_{as}$  N<sub>3</sub>); 1678.08 (v C=O); 1302.44 ( $v_s$  N<sub>3</sub>).

4-Aminobenzoic acid hydrazide was prepared by heating 2.5 g (0.015 mol) of ethyl 4-aminobenzoate with 15 mL of hydrazine monohydrate for 6 h on a water bath under reflux. Then the crystalline solid formed by cooling was thoroughly filtered off and washed with a little quantity of ice-cold isopropanol. The separated hydrazide was used without further purification for the synthesis of 4-azidobenzoyl azide. IR (KBr disks, cm<sup>-1</sup>): 3424, 3343 (v NH); 1627 (v C=O).

In a thick-walled 0.5-L beaker, 2 g (0.015 mol) of dry 4-aminobenzoic acid hydrazide was dissolved in 200 mL of 1.0 N hydrochloric acid. To the solution at  $0-5^{\circ}$ C, a solution of 2.2 g (0.032 mol) of NaNO<sub>2</sub> in 10 mL of water was poured with stirring, and the resulting mixture was stirred for additional 30 min. Then, a solution of 1.3 g (0.02 mol) of NaN<sub>3</sub> in 10 mL of cold water was added. The reaction takes place immediately with the formation of fluffy white crystals, which were reprecipitated from acetone with water and recrystallized from acetone without heating. IR (solution in CCl<sub>4</sub>, cm<sup>-1</sup>): 2176; 2134; 2129; 2092 ( $v_{as}$  ArN<sub>3</sub> and Ar(CO)N<sub>3</sub>); 1698 (v C=O); 1288.5, 1249.05 ( $v_s$  ArN<sub>3</sub>) Ar(CO)N<sub>3</sub>.

A solution of the azide in methylene chloride was applied to have a given mass per unit area on a methylene chloride-degreased and stretched polyethylene film with an area of  $24.6 \text{ cm}^2$ . After evaporation of the solvent, a dense fine-grained layer of the azide was formed on the film.

The stretched films with the deposited azide layers were irradiated with light of a DRK-120 high-pressure mercury lamp at a distance of 14 cm. The irradiated films were washed twice in 20–30 mL of a solvent and dried. Methylene chloride was used to remove 2AA and 4ABA, and 4ABK was removed with acetonitrile as a better solvent for it.

#### **RESULTS AND DISCUSSION**

To reduce the translational diffusion of intermediates, increase the probability of their interaction with the polymer surface, and hinder oxidation with air oxygen, PE was modified by photolyzing dense polycrystalline layers of azides on the polymer surface.

Photolysis of monoazides under these conditions may result in the formation of monolayers of the modifying coating, because the insertion of nitrenes in the aromatic C–H bonds of other azide molecules is unlikely. However, the insertion of nitrenes into carbonyl groups of the azide molecules with the formation of crosslinked three-dimensional layers is possible in the case of 2AA or 4ABK photolysis.

The photolysis of 4ABA (as that of aryl azide or benzoyl (aroyl) azide)) follows a more complex mechanism. Photochemical reactions of the aryl azide moiety of 4ABA are similar to the reactions of other aryl azides. Photolysis of the aroyl azide moiety leads to the formation of both aroyl nitrenes, which can insert into bonds like aryl azides, and isocyanates as a Curtius rearrangement product [6, 22, 23]. Therefore, nitrenes formed by the photolysis of 4ABA are capable of inserting in the multiple bonds of carbonyl and isocyanate groups to form "thick" modifier layers.

Thus, photolysis of 2AA or 4ABK on the PE surface will result in the surface functionalization with the "grafting" of 2-aminoanthraquinone or 4-aminobenzoic acid, respectively, and that of 4ABA will lead to the "grafting" of fragments of substituted 4aminophenyleneizocyanate.



**Fig. 1.** IR spectra of the PE film (1) before and after modification with 4ABA in a quantity of 40  $\mu$ g/cm<sup>2</sup> irradiated for (2) 1, (3) 3, (4) 6, and (5) 12 min.

Since the optical density of the layer is proportional to the amount of a modifier on it, the degree of surface modification and the thickness of the layer formed were estimated by change in the optical density of the modified films relative to irradiated samples without azide deposition.

After washing the irradiated 4ABK-coated films, a layer of photolysis products remained, which had a low adhesion and could be easily mechanically removed from the surface. Since the UV/Vis and IR spectra of the samples after removing the surface layer of the photolysis products did not differ from those of the unmodified layers, the PE modification with 4ABK was not further studied.

In contrast, irradiated and washed films modified with 2AA and 4ABA had a dense, flexible and nonremovable coating. After photolysis, they took a yellowish tint, which was changed by pressing IR spectroscopy disks to a yellow brown color typical of the photolysis products of organic azides.

To study the effect of the photolysis time on the degree of modification of the polymer surface with a constant amount of azide applied on the film, samples with 40  $\mu$ g/cm<sup>2</sup> 4ABA and 50  $\mu$ g/cm<sup>2</sup> 2AA coatings were irradiated.

Comparison of the absorption spectra of the sets of samples has shown that the absorbance of the modified layers increases with the increasing photolysis time. The increase in the optical density may be explained by both a growing proportion of the modified methylene units on the surface layer of PE and an increase in the thickness of the layer of the azide photolysis products on the PE surface.

If the modification affects only the surface layer of the polymer, it is likely that at long irradiation times when all azide molecules contacting with the surface enter into the reaction, the absorbance of the modified samples will not increase. Consequently, the plot of



**Fig. 2.** The change in the optical density of the samples of the modified PE in the UV and IR spectra, depending on the amount of 4ABA; irradiation time, 15 min: at (*I*) a wavelength of 250 nm, (*2*) a wave number of 2262.5 cm<sup>-1</sup>, and (*3*) a wave number of 2135.7 cm<sup>-1</sup>.

the dependence of the optical density of the films on the irradiation time must flatten out.

The IR spectra of a series of 4ABA-modified samples were found to exhibit an absorption band due to asymmetric stretching vibration of the isocyanate group (2261.56 cm<sup>-1</sup>). After 1-min irradiation of the sample, the absorption band at 2135.37 cm<sup>-1</sup> assigned to asymmetric stretching vibration of the azide group was detected (Fig. 1). This seems to be due to the "grafting" of aroyl azide or aryl azide group of 4ABA without dissociation of another azide group of the molecule.

The study of a set of samples with the amount of the applied 4ABA varying from 10 to  $162 \,\mu\text{g/cm}^2$  and irradiated for 15 min revealed a fivefold increase in the absorbance of the modified films in the UV/Vis range (Fig. 2, curve *I*). The optical density of the asymmetric stretching bands of the isocyanate and azide groups in the IR spectrum also increased with the increasing amount of the modifier (Fig. 2; curves 2, 3).

Similar results were obtained in the study of the effect of the amount of deposited 2AA on the degree of PE modification. A set of samples with a 2AA coating of 9 to 135  $\mu$ g/cm<sup>2</sup> and an irradiation time of 30 min for each sample was examined. By comparing the UV/Vis spectra of these samples, it was found that the optical density of the films increases with an increase in the amount of the azide irradiated on them. Absorption bands with the maximum at ~1679 cm<sup>-1</sup> assigned to the stretching vibration of the carbonyl group appeared in the IR spectra. That is, the modification of the surface with 2AA resulted in the "grafting" of secondary 2-aminoanthraquinone fragments upon the insertion of aryl nitrenes in the CH bonds of the polymer methylene groups.

Since the photolysis of polycrystalline layers of aryl azides may generate sparingly soluble oligoazopolymers covalently not bonded to the polymer surface, dimethylsulfoxide (DMSO) was used as a solvent for washing off the products because of its capability to solubilize such oligomers.

An analysis of the modified films revealed that the replacement of methylene chloride by DMSO does not reduce the optical density of the films (Fig. 3), indicating the chemical "grafting" of the modifier layer.

The last step was the study of the reaction of isocyanate groups of the modified surface with amines in aqueous solutions. Sulfanilic acid, the sulfonate group of which has a characteristic absorption in the infrared range, was used as the amine. An increase in the absorption of the treated samples in this region of the spectrum would be evidence for the interaction of sulfanilic acid with the modified polyethylene.



The isocyanate groups of the modifier will react with the amine group of sulfanilic acid to form substituted diphenylurea. Some of the isocyanate groups can be hydrolyzed with water to form carbamic acid and then a primary amine. However, we have shown previously that the interaction of isocyanates with amines



**Fig. 3.** The change in the absorbance of the modified PE film, depending on the quantity of 4ABA, after the removal of photolysis products with ( $\blacktriangle$ )DMSO and ( $\bullet$ )methylene chloride. Irradiation time, 15 min.

under similar conditions is more likely than their hydrolysis [24].

The modified PE films were incubated in aqueous solutions of sulfanilic acid with concentrations of  $1.9 \times 10^{-2}$  and  $5.6 \times 10^{-2}$  mol L<sup>-1</sup> at 60°C for 30 min and then washed in water and methylene chloride.

By comparing the IR spectra of the obtained samples with the spectra of samples with non-modified layers, an increase in the absorption at  $1255 \text{ cm}^{-1}$  assigned to the stretching vibration of the sulfonate group was detected. An increase in the concentration of sulfanilic acid in the solution resulted in an increase in the optical density of the absorption bands of these groups.

Therefore, photolysis of polycrystalline layers of the series of aryl azides on PE resulted in the formation of bulky, not monomolecular coating covalently linked to the polymer surface.

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