Photochemical modification of a polymer surface with bifunctional dyes of the phenothiazine series

Darya Yu. Dzhons, Andrei V. Budruev
Lobachevsky State University of Nizhni Novgorod, Gagarin Ave., 23, Nizhnii Novgorod, 603950, Russia.
E-mail: budruev@gmail.com

Abstract

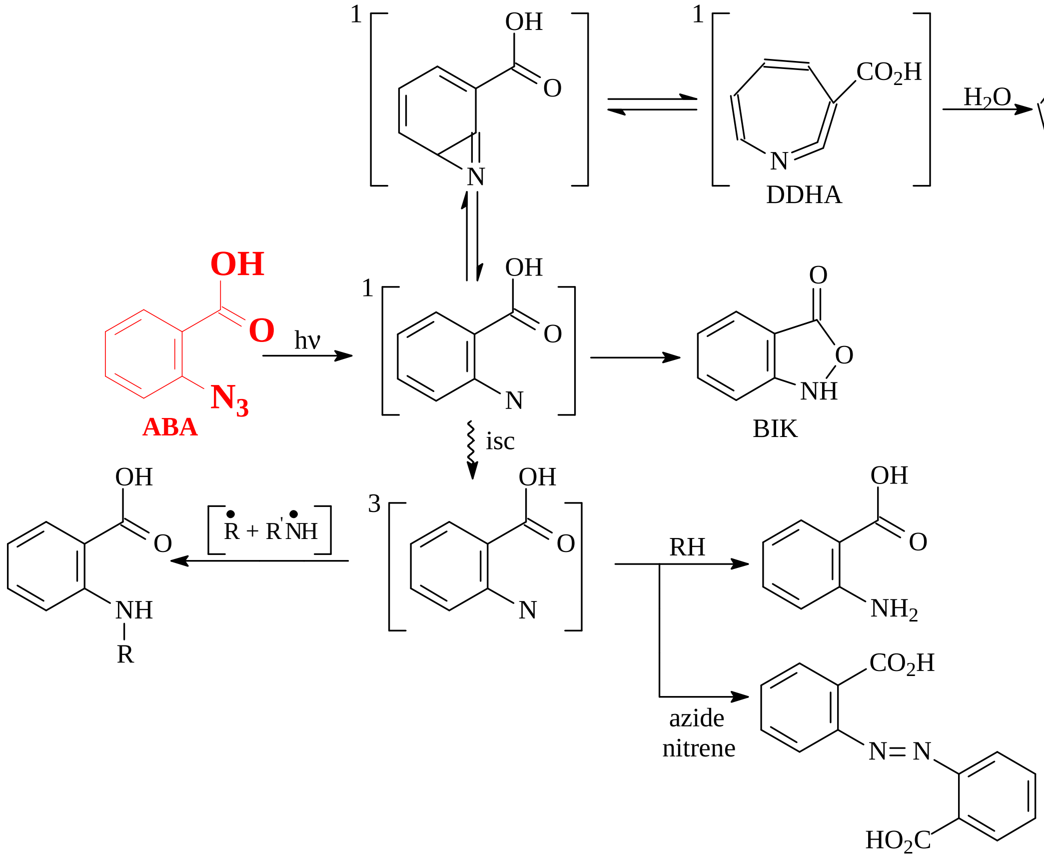
To create a durable bioactive coating we tested the effectiveness of the photochemical surface modification of polyethylene terephthalate (PET) by bifunctional dyes of the phenothiazine series and selected the optimal conditions of the process. For that purpose a series of the bifunctional photosensitizers containing aryl azide group forming covalent bonds with the polymer matrix under UV and generating singlet oxygen under visible light exposure was synthesized.

We have synthesized a series of amides of toluidine blue O (TBO) with 2 – , 3 – , and 4 – positions of benzoic acid substituted by the azide groups. Surface modification was carried out by irradiation of solutions of the synthesized bifunctional dyes when the samples of PET were inserted into acetonitrile by the low pressure mercury-quartz lamp. Based on the comparison of the UV spectra of PET films before and after the photochemical modification we found that the most effective modifier was TBO – 4– azidobenzoic acid with concentration of 3×10^{-3} M, but the least effective modifier was TBO – 2– azidobenzoic acid. Obviously it is caused by the sterically hindered insertion of a nitrene formed in the course of the azidobenzoic acid photolysis into the C = O bond of the polymer matrix.

Keywords: Photochemical modification, polymer surface, toluidine blue O, 2-azidobenzoic acid, 3-azidobenzoic acid, 4-azidobenzoic acid, nitrenes, photolysis, singlet oxygen.

Introduction

Photolysis of substituted aryl azides gives a series of high reactive intermediates such as singlet and triplet nitrenes and 1,2-didehidroazepines. The main reaction of the 1,2-didehidroazepines is nucleophilic addition leading to the formation of stable substituted 3H-azepines. Singlet and triplet nitrenes, in turn, inset into multiple C-N and C-C bonds forming the complex fused ring structures (Scheme 1) [1-3]. An ability of intermediates to form covalent bonds with the molecular environment may be used to solve a practical problem such as photochemical modification of polymer surfaces [4], for example, to create a bio-active coating.



Scheme 1. The photolysis of substituted aryl azides, for example 2-azidobenzoic acid.

It is known that some dyes having the phenothiazine structure by absorbtion of visible light becomes excited and reacts with oxygen in its ground triplet state to give a labile intermediate which decomposes with singlet oxygen formation. Further reaction of the active oxygen species with organic substrates leads to its degradation [5, 6]. The above mentioned ability of dyes can be applied to create a coating having a biological activity. For example, when dyes deposited on the surface (polymer products) polymers. However, because of poor adhesion the coatings are short-living and can easily be removed mechanically.

The aim of our work was the synthesis of the bifunctional aryl azide phenothiazine dyes that can be inserted into multiple bonds of the polymer matrix under UV light and which than generate singlet oxygen under visible light, as well as to select the optimum conditions for the photochemical modification of polymer surface.

Experimental Procedure

Synthesis of 2–azidobenzoic acid. 2–azidobenzoic acid was synthesized by diazotizing of hydrochlorous solution of 2–aminobenzoic acid with $NaNO_2$ at 0-5 ^{0}C. Sodium azide was added into the diazonium salt solution and continuously warmed up to room temperature. Warming destabilized the diazonium salt and produced substitution of it by azido group. The synthesized azide was isolated as a crystalline white precipitate. It was filtered out, washed by cold water and dried in darkness at room temperature. The raw azide was recrystallized from heptane – benzene mixture [7]. M.p. = 144 °C. IR (nujol mull, cm^{-1}): 2131.34, 2110.12, 2081.19 (ν_{as} N_3); 1691.57 (ν C=O); 1267.23 (ν_s N_3). UV-Vis in acetonitril (λnm / lg(ε),M^{-1} × cm^{-1}): 221/4.29, 255/3.99, 296/3.43. Synthesis of 3 - and 4-azidobenzoic acid was performed in the similar manner using 3 - and 4-aminobenzoic acid, respectively.

Purification of TBO. 250 mg TBO (chemically pure grade) was dissolved in 250-300 ml H_2O under continuous stirring with a magnetic stirrer, then the solution was filtered, and KOH was added. Then TBO was extracted 3 times by butyl acetate. After that we separated the organic phase with a separating funnel and the solvent was evaporated.

Synthesis of 2– azidobenzoate chloride. 0.65 g (4 mmol) of 2-azidobenzoic acid was mixed with 15 ml of benzene and reflux until complete dissolution of a precipitate, and then 7 ml of thionyl chloride and 2 drops of DMFA was added and boiling was continued for 4 hours. Then all of the solvent was evaporated. Synthesis of 3 - and 4-azidobenzoate chloride was performed similarly.

Synthesis of TBO – 2– azidobenzoic acid. 0.3 g of TBO was dissolved in 10 ml of pipiridine and the solution of 2 - azidobenzoate chloride taken in a 2- fold excess relative to the mass of the TBO in 10 ml of benzene was added dropwise with constant stirring until dissolution. The entire reaction mixture was subjected to magnetic stirring for 4 hours being kept away from light. Then, the solvent was evaporated, and the product was cleaned by preparative column chromatography on silica gel, acetonitrile being the eluent. Synthesis of TBO - 3 - and TBO - 4 -azidobenzoic acid was conducted in the similar way using 3 - and 4-azidobenzoic acid, respectively. The purity of the obtained compounds was determined by HPLC using Shimadzu LC-20A unit with the SPD-M20A detector. The structure of the synthesized dyes was established by analysis of the IR spectra of thin films recorded using the Shimadzu IRPrestige 21 device (Figure 1.).

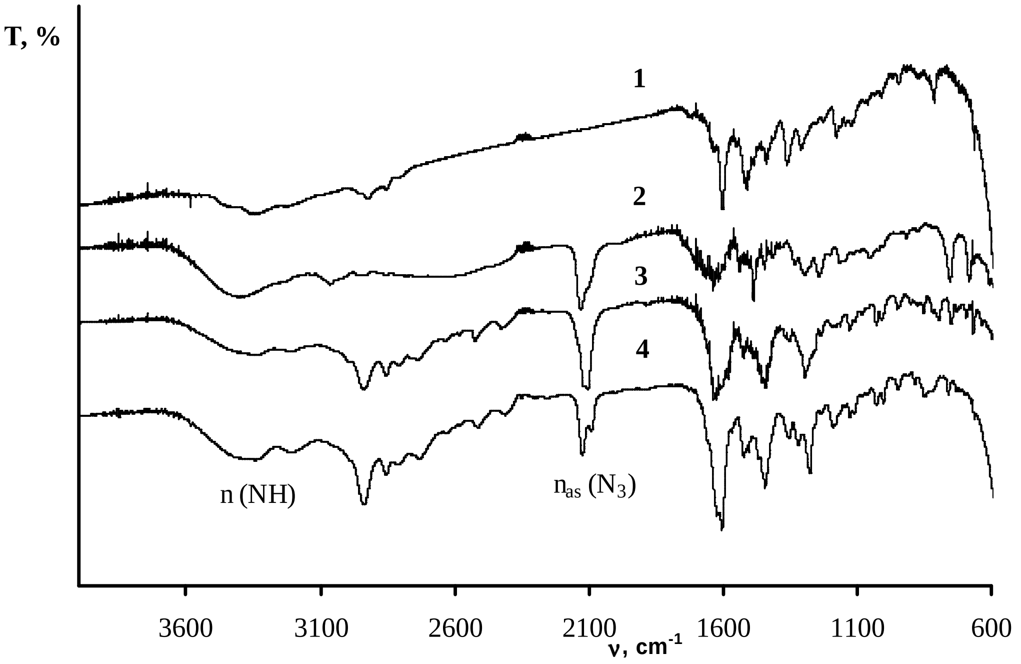


Figure 1. IR spectra of TBO (**1**), TBO – 2– azidobenzoic acid (**2**), TBO – 3– azidobenzoic acid (**3**), and TBO – 4– azidobenzoic acid (**4**) in thin films.

As follows from analysis of UV spectra (in acetonitrile) recorded by the device Analytik Jena Specord 40 phenothiazine group absorbing in the visible region was not destroyed during the synthesis (Figure 2).

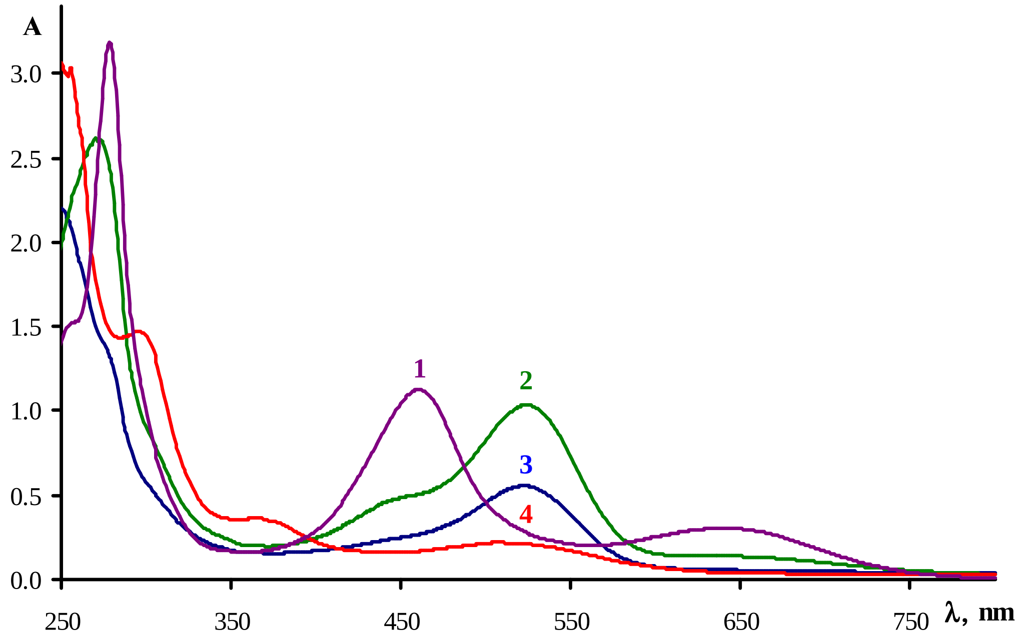
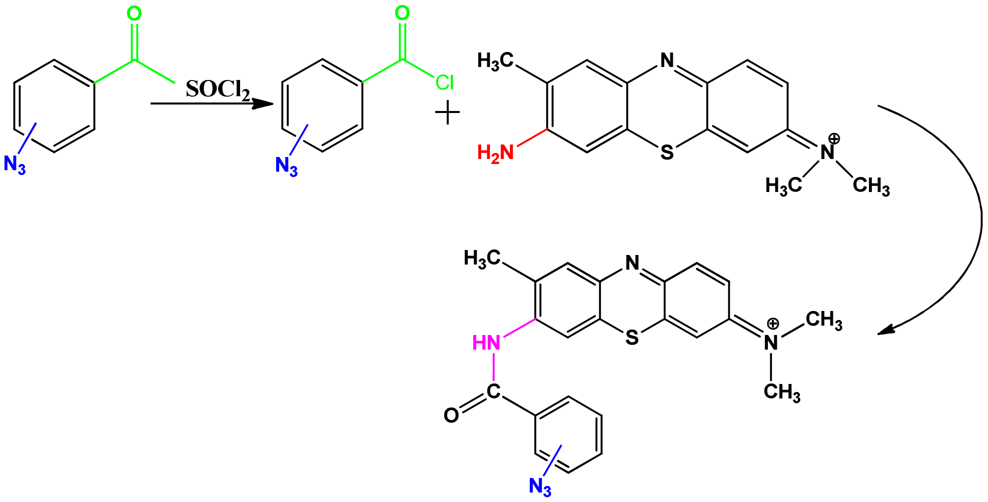


Figure 2. UV spectra of TBO (**1**), TBO – 2– azidobenzoic acid (**2**), TBO – 3– azidobenzoic acid (**3**) and TBO–4– azidobenzoic acid (**4**) in acetonitrile.

The photochemical modification of PET. The PET sample was cleaned with ethanol beforehand and then placed in a quartz reactor with a solution of TBO - 2-azidobenzoic acid in acetonitrile. The sample was irradiated by a low pressure UV lamp with an emission maximum at 254 nm. Surface modification of PET by TBO - 3-azidobenzoic acid and TBO - 4-azidobenzoic acid was carried out in the similar manner.

Results and their discussion

To achieve our goal we had synthesized series of amides of toluidine blue (TBO) with the 2 -, 3 - and 4 - substituted azidobenzoic acids via the corresponding acid chlorides (Scheme 2).



Scheme 2. Formation of a difunctional dye

Surface modification was carried out by UV irradiation of PET samples in the synthesized bifunctional dyes solutions in acetonitrile under the low pressure mercury-quartz lamp having the emission maximum at 254 nm. Thus, when irradiated the phenylthiazine group absorbing in the visible region of the spectrum was not destroyed, and the group containing the azide moiety undergoes photodissociation followed by formation of singlet nitrene and its insertion into the C=O bond of PET.

Comparing the UV spectra of the films of PET before and after photochemical modification (Figure 3-5) it was found that the most effective modifier was TBO - 4-azidobenzoic acid system at a concentration of 3×10^{-3} M (Figure 5). The least effective was the TBO - 2-azidobenzoic acid (Figure 3). It is obviously connected with steric difficulties for insertion of the nitrenes formed after photolysis azidobenzoic acids into the C=O connection of the polymer matrix.

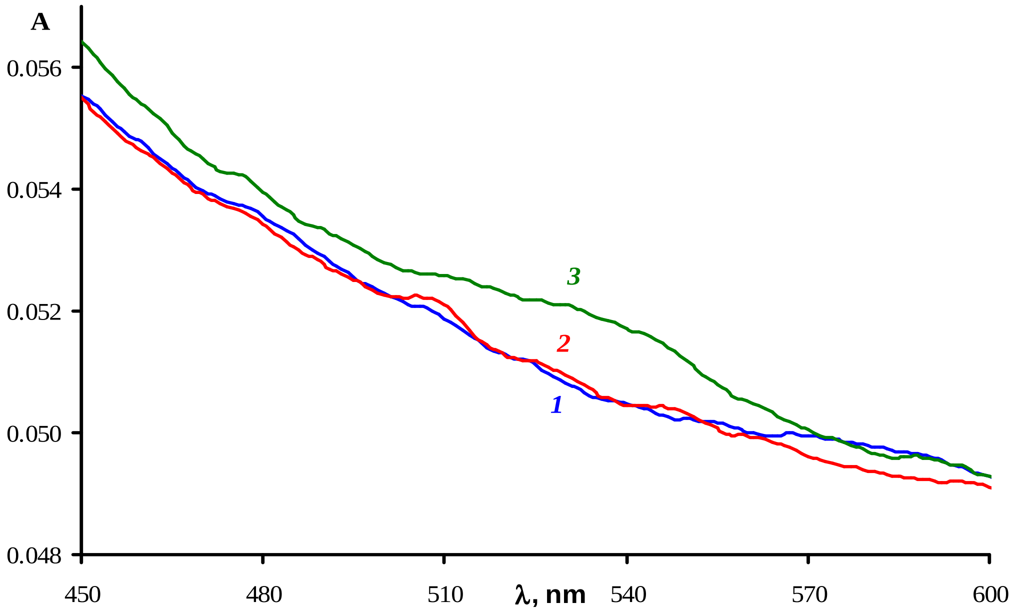


Figure 3. Sample PET modified by TBO - 2-azidobenzoic acid. **1** - PET, **2** - PET without irradiation, **3** - PET irradiated for 30 min.

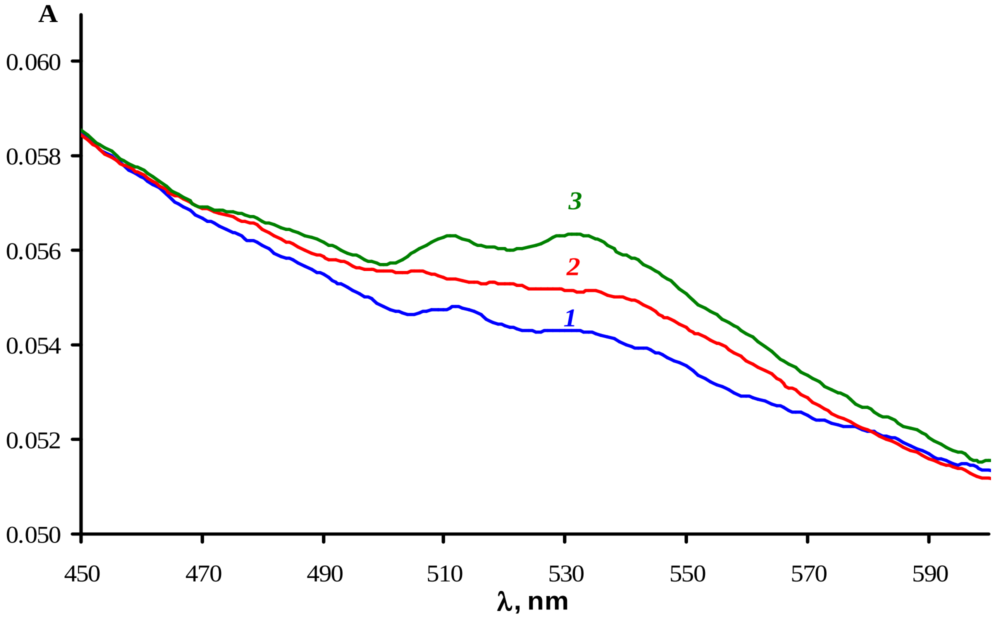


Figure 4. Sample PET modified by TBO - 3-azidobenzoic acid. **1**-PET, **2** - PET without irradiation, **3** - PET irradiated for 30 min.

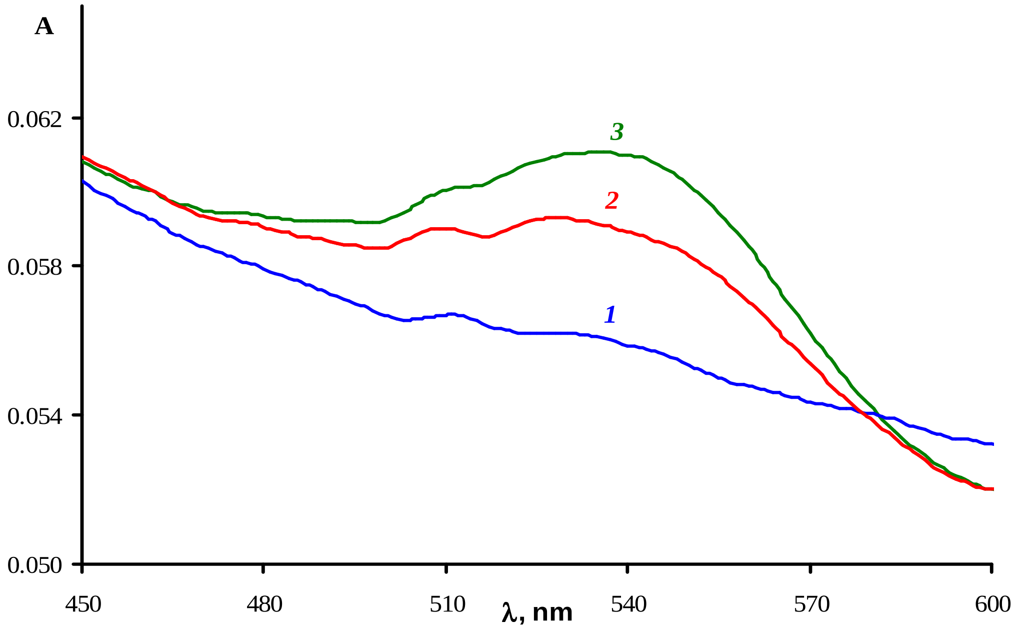


Figure 5 . Sample PET modified by TBO- 4 -azidobenzoic acid: **1**- PET , **2** - PET without irradiation , **3** - PET irradiated for 30 min.

Since it was found that the most effective modifier is TBO - 4-azidobenzoic acid, then there were determined the optimum conditions of the modification. For this purpose we prepare a series of the solutions of TBO - 4- azidobenzoic acid in acetonitrile with a concentration of 2×10^{-4} M and $2{,}5\times10^{-3}$ M, 1×10^{-3} M and the UV spectra of the PET film before and after the photochemical modification with different exposure times were obtained.

For the interpreting of the results we plotted the curve of the irradiation time on the optical density at an analytical wavelength of modified PET samples (Figure 6). Analytical wavelength was found 540 nm and corresponds to the maximum absorption of TBO- 4 - azidobenzoic acid.

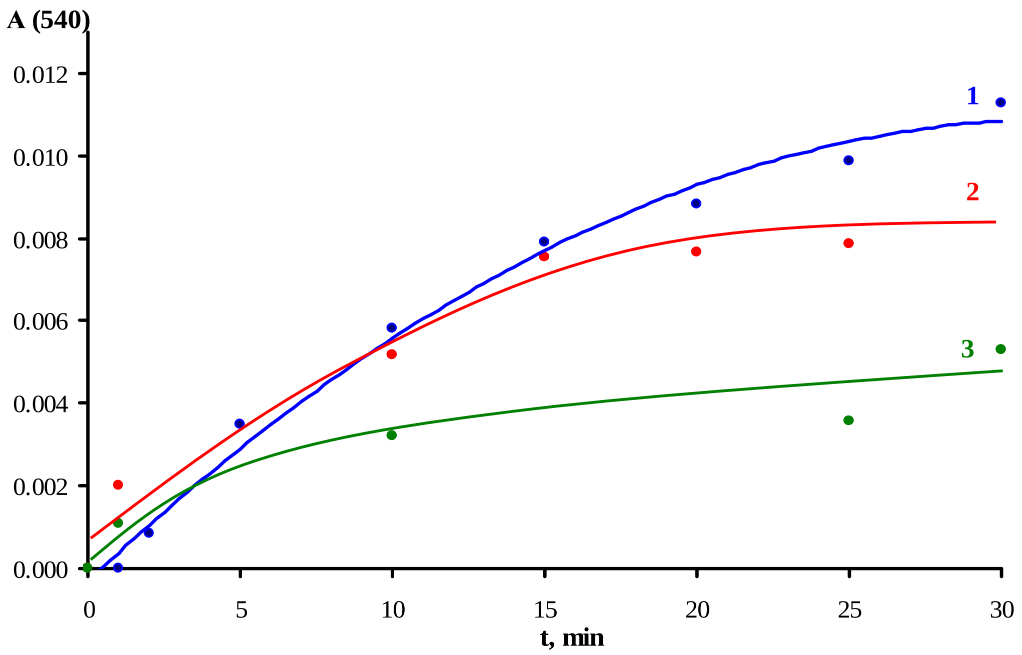


Figure 6. The dependence the optical density at an analytical wavelength of modified PET samples on irradiation time. Concentrations of solutions are **1**– 1×10^{-3} M, **2**– 2.5×10^{-3} M, and **3** – 2×10^{-4} M.

From the analysis of the curves it was founded that the concentration 1 × 10^{-3} M of TBO-4 -azidobenzoic acid was optimum for the most effective modification of PET surface. At higher concentrations, the deeply colored solution was obtained, and it was acted as an inner filter, and the portion of radiation reached the sample decreased, thereby reducing the efficiency of modification. In solutions of low concentrations there was observed a decrease of the modification quality, due to the increased probability of occurrence of intramolecular reactions typical for the singlet nitrene. Time of photochemical modification was 30 min. Increase of time led to the formation of secondary products of the photolysis TBO - 4 -azidobenzoic acid, the proportion of "grafted" molecules of TBO - 4 -azidobenzoic acid onto the PET surface remain constant.

Thus, in this study a series of the bifunctional dyes capable to form a covalent connection with PET was synthesized, the technique of modification, and the optimal conditions for photochemical modification such as the concentration of TBO-4-azidobenzoic acid is 1×10^{-3} M and the exposure time 30 min were established.

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