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Immobilization of Porphyrins on the Surface of Polypropylene Films Modified with Acrylic Acid

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Abstract—The process of immobilization of the aminoporphyrins: 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin (**I**), 5,10,15,20-tetra(*p*-aminophenyl)porphyrin (**II**), 5,15-di(*p*-aminophenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin (**III**), and a hydroxyporphyrin, 5,15-di(*p*-hydroxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin (**IV**) by attaching them to the surface of polypropylene materials activated by plasma and modified with acrylic acid. The grafting of acrylic acid on the activated polypropylene surface is shown to increase 2–3-fold the amount of immobilized porphyrin as compared with the porphyrin immobilization directly onto the plasma-activated polypropylene films.

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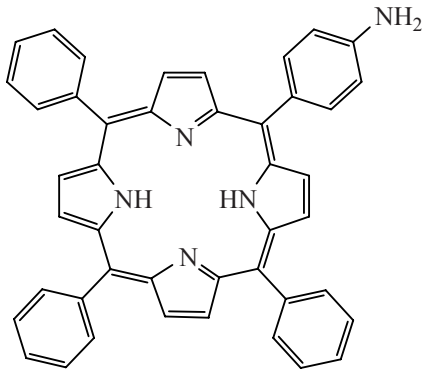
The main advantage of organic polymers as supports over mineral supports is the concentration of functional groups higher by an order of magnitude and capable of immobilization of various supramolecular structures [1]. Therefore now modification dominates of the properties of existing polymeric materials over the tendency of the synthesis of new polymers and development of new technological processes. For example, modification of the surface of polypropylene and materials based on it allows retaining the molecular mass characteristics of the polymer while changing in a required direction the chemical character of the macromolecular chains, aimed at imparting desired properties to the materials (surface activity, pores formation, ion exchange, etc.) [2–4].

Porphyrins with their high structural variety make it possible to apply them, on the one hand, as compounds capable to identify active functional groups and particles appearing on the material surface under the action of plasma, and, on the other hand, are catalytically and biologically active compounds allowing the creation of new materials for application in medicine, biotechnology, catalysis, and so on. In particular, the porphyrins bearing amino groups on the macrocycle periphery are very sensitive compounds toward the presence on the polymer surface of such groups as carboxy, halogens, etc. [5]. The porphyrin macromolecules are bulky, with the size much greater than the size of the polymer elementary unit, and therefore their immobilization on the surface of a polymeric carrier is restricted significantly owing to steric hindrances. However, this can be avoided or at least the process of immobilization can be facilitated by means of preliminary modificating the polymer surface with various monomers that can further play a role of a spacer.

A specific feature of a spacer as an object of investigation is its small absolute content in the sample. However, even at low grafting degree of the spacer group the surface capacity of the polymer increases resulting in higher efficiency of immobilization of bulky, sterically hindered molecules of porphyrins [1, 6–8].

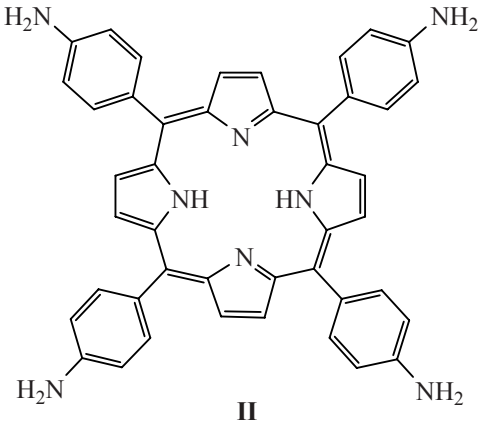
The aim of this work was the investigation of the process of immobilization of amino- and hydroxyporphyrins by attaching them to the surface of polypropylene film modified with acrylic acid. The grafting with acrylic acid was carried out by surface post-plasma graft copolymerization. In this work amino- and hydroxyporphyrins were examined (see the scheme).

As the carrier polymer we used commercial polymeric film of isotactic polypropylene with biaxial orientation (technical specifications TU RB



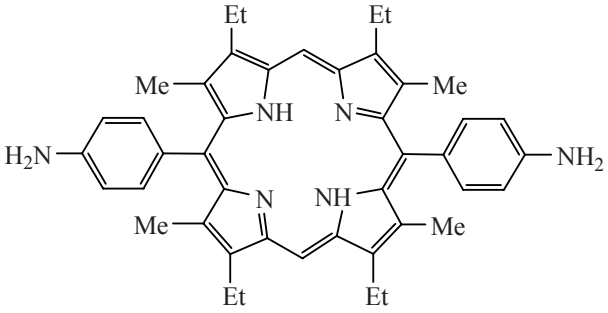
I

5-(*p*-aminophenyl)-10,15,20-triphenylpor-phyrin



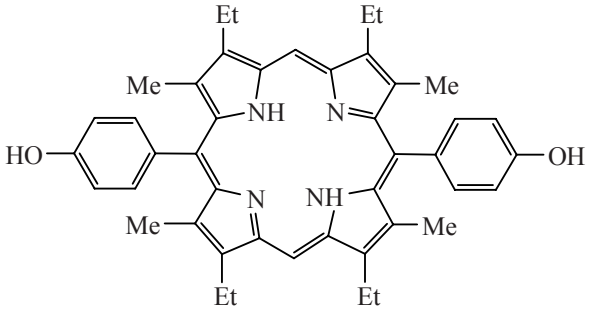
II

5,10,15,20-tetra(*p*-aminophenyl)porphyrin



III

5,15-di-(*p*-aminophenyl)-3,7,13,17-tetramethyl-2,8,12,18- tetraethylporphyrin



IV

,15-di(*p*-hydroxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin

00204079.164-97), with molecular mass 400,000 to 700,000, thickness 20 μm.

The surface of the polymeric samples was preliminary activated by exposure to the low pressure plasma in oxygen or argon atmosphere either in the active zone of the plasma or in the zone of the flowing afterglow plasma, as well as in the system of plasma–solution, under atmospheric pressure, according to procedures in [7, 8].

For the creation of a spacer group for immobilization of porphyrins we used acrylic acid. The acrylic acid grafting on the polypropylene film was carried out by surface post-plasma copolymerization with the polypropylene along the procedure in [9].

Further experiments on the spacer grafting were carried out only with the polypropylene samples with the surface activated with low-temperature oxygen plasma in active zone of the plasma or in the area of flow charge afterglow (P = 30 Pa, I_p = 20 μA, t = 90 s), and in the argon plasma (P = 300 Pa, I_p = 20 μA, t = 5 min). For graft-copolymerization of acrylic acid with polypropylene we used 25% aqueous solution of the acid. We observed that at this concentration practically did not form acrylic oligomers that increased the degree of conversion of the acrylic acid in the working solution and retard the process of graft-copolymerizetion, while amount of acrylic acid on the carrier polymer surface was maximal as was also confirmed in [10].

The surface layer composition of the parent and surface-modified polypropylene was investigated by IR spectroscopy in the mode of attenuated total reflection (ATR) (also called multiple internal reflectance).

A special feature of absorption spectra of porphyrins is the presence of characteristic Soret band whose extinction coefficients are so high that allow registration of even very small amount of porphyrin in the examined sample (as low as 10^{-7} mol l^{-1}).

As has been shown in [9], the preliminary activation by plasma results in effective grafting of

Table 1. Effect of conditions of the polypropylene modification on the surface concentration of 5,10,15,20-tetra(*p*-aminophenyl)porphyrin **II**

Conditions of modification		$N_S \times 10^{-13}$, cm^{-2}	
Preliminary activation of polymer	Conditions of co-polymerization	A[a]	B[b]
Without activation	–	2.79	Traces
O_2, charge zone	–	2.70	0.58
O_2, afterglow	–	2.26	0.77
Ar, charge zone	–	2.65	0.63
O_2, charge zone	acrylic acid	2.46	1.44
O_2, afterglow	acrylic acid	2.07	1.01
Ar, charge zone	acrylic acid	2.79	1.64
O_2, charge zone	acrylic acid+H_2O_2	1.88	1.20
O_2, afterglow	acrylic acid+H_2O_2	2.94	2.02
Ar, charge zone	acrylic acid+H_2O_2	3.56	2.79

[a] A is a film with immobilized porphyrin, B is the same film after washing with chloroform.

acrylic acid on the polypropylene film surface. The acrylic acid grafting as a spacer group on the surface of activated by plasma polypropylene allows (1) to increase surface capacity of the carrier polymer and (2) to increase the distance between the polymeric support and the compounds that should be immobilized. Principally, this allows the application as an object of immobilization complicated porphyrin derivatives with bulky reactive groups on the macrocyle periphery.

Tables 1 and 2 contain the data on the immobilization of porphyrins on the modified surface of polypropylene. It is seen from Table 1 that grafting of acrylic acid onto the polypropylene surface allows to immobilize 2–3-fold more molecules of porphyrin **II** (on account of increasing the surface capacity of polymeric support) as compared to non-grafted surface. Similar results were obtained with porphyrins **I** and **III**. We also have to note that the increase in the number of peripheral amino groups from one to four leads to an increase in the surface concentration by an order of magnitude. This fact shows that the concentration of active functional groups on the surface of the modified polypropylene is high enough. Apparently, all the studied porphyrin derivatives except **I** fit to the surface by their whole planes. Any other orientation would exclude the observed effect of *trans* amino groups.

Table 2. Effect of conditions of the polypropylene film modification on the surface concentration of 5,15-di(*p*-hydroxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrin **IV**

Conditions of co-polymerization with acrylic acid	$N_S \times 10^{-13}$, cm^{-2}			
	System plasma–solution	Ar, charge zone	O_2, charge zone	O_2, after-glow
Without initiator	1.6	0	0	0
In the presence of conc. H_2SO_4	2.9	3.9	4.3	0
In the presence of $FeSO_4 \cdot 7H_2O$	5.5	3.1	4.0	3.2

Table 2 contains the data on immobilization of porphyrin **III** on the modified polypropylene surface. It is noteworthy that this porphyrin does not form strong bonds with the surface of the modified film. This porphyrin is removed completely at washing the film with chloroform. This is not surprising, because in this case the interaction of porphyrin with acrylic acid grafted on the polypropylene film surface is restricted to hydrogen bonding and dispersion forces. Therefore the data on the surface porphyrin concentration correspond to the moment directly after immobilization, without washing with chloroform is shown bellow.

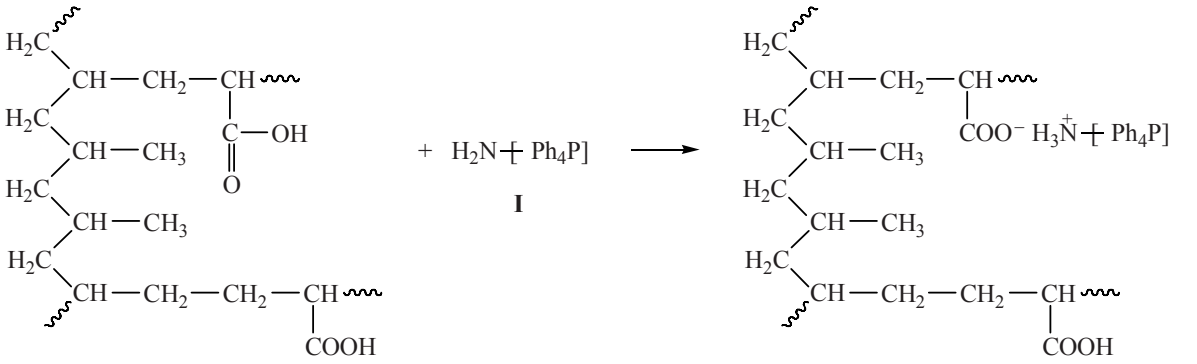
Porphyrin	H_2MAPP	H_2TAPP	H_2DAP	H_2DO
Area, Å^2	214	223	212	216

The comparison of the results of spectroscopic investigation by IR ATR and electron spectroscopy in UV-VIS region of the products of graft-copolymerization of acrylic acid with polypropylene film and the products of subsequent immobilization of 5,10,15,20-tetra(*p*-aminophenyl)porphyrin **II** shows that the quantity of surface carboxylic groups and the content of porphyrin on the polypropylene surface are related to each other (see figure).

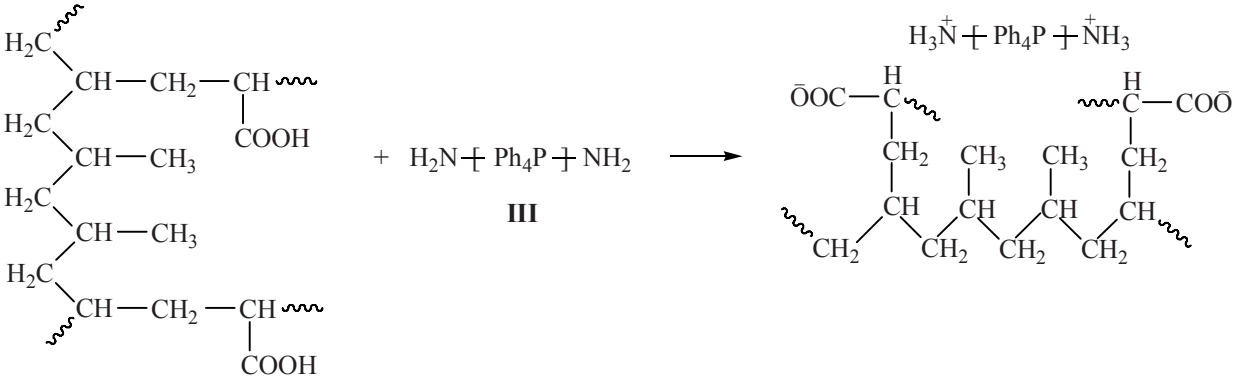
Proceeding from the data obtained, the following schemes of immobilization of porphyrins can be proposed: (a) Ionic type (for aminoporphyrins) and (b) hydrogen bonding (for hydroxyporphyrins).

With the above said in mind we estimate a degree of surface filling with the porphyrins. The area of porphyrins molecules is calculated by the methods of molecular mechanics (MM+ force field) using Hyper Chem (version 7) program.

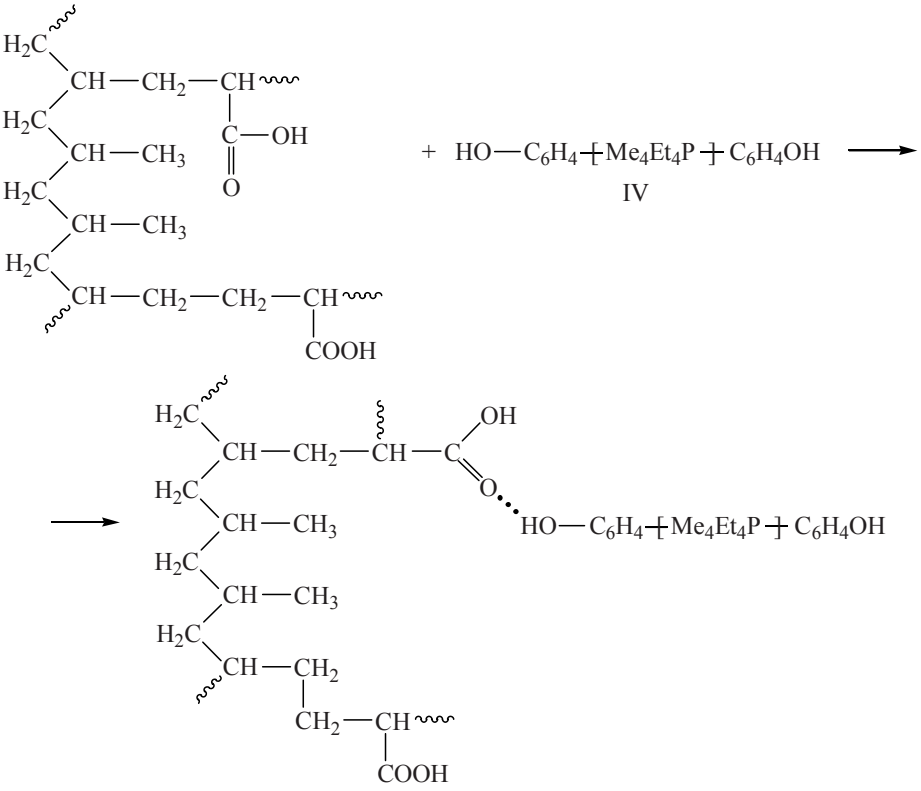
(a)

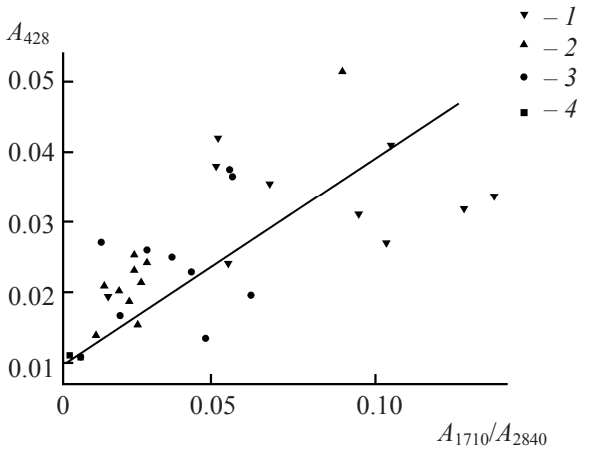


P is tetraphenylporphyrins.



(b)





Dependence of porphyrin **II** surface concentration on the quantity of carboxylic groups on the polypropylene surface (*1*) activation in argon plasma, (*2*) activation in O_2 (flow afterglow), (*3*) activation in O_2 (charge zone), and (*4*) non-activated sample. A_{428} is optical density of the Soret band of porphyrin **II**, A_{1710} is optical density at the maximum of stretching vibrations of CH_2 groups in polypropylene at 1710 cm^{-1}, A_{2840} is optical density at the maximum of the band of proper vibrations of CH_2 groups in polypropylene at 2840 cm^{-1}.

If for porphyrin **I**: $\varepsilon = 3.12\times10^5$ l mol^{-1} cm^{-1}, then $A/\varepsilon = 0.1/(12\times3.12\times10^5) = 2.67\times10^{-8}$ mol cm l^{-1}. For the surface density of the particles we obtain: $N_s = (A/\varepsilon)N_A\times10^{-3} = 1.6\times10^{13}$ cm^{-2}. Let effective area of porphyrin molecule, $S = 223$ $Å^2$, then the mono-layer capacity $(1/S) = 4.5\times10^{13}$ cm^{-2}. This means that the number of porphyrin macromolecules attached chemically to the modified polypropylene film surface can achieve 1/3 of the capacity of sorption monolayer. The quantity of physically adsorbed porphyrin is 5–10 times more, therewith the porphyrin molecules immobilized on the surface are not in associated form.

This fact is of principal significance for the creation of new complex materials based on porphyrins. The porphyrins are known to possess a high activity (e.g., catalytic activity) only in the nonassociated form. Therefore for achieving certain effect it is important to provide reasonable density of distribution on the polymeric carrier surface of the immobilized porphyrins.

Taking all the above said into account we emphasize the following factors influencing the creation of the materials with the porphyrins immobilized on surface:

– activation of the polypropylene film surface leads to modification of its chemical composition (formation of oxygen-containing groups of different nature, of double C=C bonds, etc.);

– grafting a monomer of vinyl series (acrylic acid) promotes increase of the adsorption surface area of the polymeric carrier, the grafted molecules of acrylic acid can behave as spacers for the further immobilization of functional compounds such as porphyrins or their analogs;

– choice of the porphyrins to be immobilized and the grafted monomers depends on the functional properties of the material finally obtained (catalyst, biomedical preparation and so on) and the carier polymer structure.

Thus, immobilization of porphyrins on the surface of polypropylene films modified with acrylic acid is a promising pathway for creation of heterogenic catalysts of new generation (for various oxidation – reduction processes), for creation of the materials generating singlet oxygen into gas phase (photodynamic cancer therapy, including diagnostics and treatment), and can serve as a model for creation of new materials possessing medico-biological activity as well.

EXPERIMENTAL

The IR measurements were carried out on a Nicolet Avatar 360 FT-IR ESP spectrometer using crystalline ZnSe prism for multiple internal reflectance. The beam angle of incidence to the interphase frontier was 45°, number of reflexes 12. The spectra were registered with accumulation of the signals of 32 scans. The spectra were registered in the range of wave number from 400 to 4000 cm^{-1}. The porphyrins studied were presented by prof. A.S. Semeikin.

The immobilization of porphyrins by bonding to the modified polypropylene was carried out from solutions in chloroform with the porphyrin concentration 3×10^{-4} mol l^{-1} for 3 to 24 h at the temperature 18±2°C.

The results of immobilization of the porphyrins were examined by measuring electronic absorption spectra on a Perkin Elmer Lambda 20 scanning UV/VIS spectrophotometer. The accuracy of wavelength value ±0.1 nm, wavelength reproduction ±0.05 nm, photometric reproductivity ± 0.003 nm. For enhancing the level of effective signal were used packages of 4 to 6 films.

The spectra were registered after treatment of the film in a porphyrin solution followed by washing with

chloroform for removing the molecules attached to the surface by weak forces of physical adsorption. The surface concentration of immobilized macromolecules was determined from the optical density of characteristic bands assuming equality of the sections of photo-absorption of the molecules in solution and on the polymer surface. For prophyrins were used the Soret bands: **I**, λ_{max}= 406 nm, ε = 200.9× 10^3 l mol^{-1} cm^{-1}, **II**, λ_{max} = 428 nm, ε = 312.5× 10^3 l mol^{-1} cm^{-1}, **III,** λ_{max} = 412 nm, ε = 247 × 10^3 l mol^{-1} cm^{-1}, **IV**, λ_{max} = 408,95 нм, ε = 260 × 10^3 l mol^{-1} cm^{-1}.

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