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Synthesis and reactivity of metal-containing monomers

64.* Synthesis, structure, polymerization, and catalytic properties of the palladium and cobalt vinylporphyrin complexes

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2-Vinylporphyrin and its complexes with Pd^{II} and Co^{II} were synthesized and characterized by NMR, IR, and mass spectra. The palladium vinylporphyrin complexes are efficient metal-containing monomers in radical copolymerization with styrene. Palladium(II) in an amount of up to 1 mol.% can thus be introduced into the polymers. The synthesized polymeric Pd complexes perform the photosynthesized activation of dioxygen to the lowest excited singlet state, which is an active oxidizing agent for anthracene producing the 1,4-addition products. The monomeric and macromolecular cobalt complexes are chain-transfer catalysts in radical styrene polymerization.

Key words: vinylporphyrins, palladium vinylporphyrin complexes, cobalt vinylporphyrin complexes, metal-containing monomers, copolymerization, anthracene, photooxidation, anthracene *endo*-peroxide.

Metal-containing polymeric porphyrins and phthalocyanines find wide use as sensors, catalysts, and photocatalysts in organic synthesis.[2] Metal-containing porphyrin derivatives can be synthesized by the reactions of metal salts with porphyrin-containing polymers (polymer-analogous transformations) and by polycondensation and copolymerization of porphyrin-containing monomers. In the latter case, both the vinylporphyrin itself and its metal complexes are of interest as comonomers in radical copolymerization with traditional monomers (styrene, methyl methacrylate, acrylonitrile, acrylamide, *etc.*). This method has been described recently for the polymerization of vinylporphyrin monomers of copper and zinc[3,4] and the (acryloyloxyphenyl)amide complexes of zinc[5,6] and some other metals.[7] However, this method is used in practice rather rarely, mainly because convenient methods for the syntheses of the initial vinylporphyrins and their metal complexes are lacking. Two ways for the solution of this problem are known[7]: synthesis of porphyrins and metal porphyrins containing the vinyl group in the pyrrole or benzene ring. For this purpose, methods for assembling substituted porphyrin are used directly in the step of its formation, for instance, by consecutive reactions of porphyrin cycle formation, introduction of metal ions (Cu, Co), and synthesis of metal vinylporphyrin by the Wittig reaction[8] through the interaction of the corresponding aldehydes with triphenylmethylenephosphorane.

The present work deals with the synthesis and structure of potential vinylporphyrin (co)mononers that include the exocyclic double bond linked to the pyrrole ring and the catalytically active metals Pd and Co. Metal monomers of this type were studied in radical copolymerization with styrene, and the resulting products are catalysts of anthracene photooxidation with air oxygen to anthracene *endo*-peroxide.

Results and Discussion

The palladium complex with 2-vinyl-5,10,15,20-tetraphenylporphyrin (**1**) was synthesized by the Wittig reaction of the palladium 2-formyl-5,10,15,20-tetra-

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* For Part 63, see Ref. 1.

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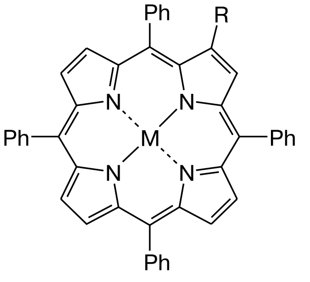
phenylporphyrin complex (**2**) with triphenylmethylenephosphorane generated from triphenylmethylphosphonium iodide by the potassium carbonate complex with crown ether 18-crown-6 in boiling methanol. The cobalt complex with 2-vinyl-5,10,15,20-tetraphenylporphyrin (**3**) was synthesized similarly from the cobalt 2-formyl-5,10,15,20-tetraphenylporphyrin complex (**4**) (method *A*). Aldehydes **2** and **4** were synthesized by the Vilsmeier formylation of the palladium (**5**) and cobalt (**6**) 5,10,15,20-tetraphenylporphyrin complexes, respectively.



1—12

	M	R
1	Pd	$CH{=}CH_2$
2	Pd	CHO
3	Co	$CH{=}CH_2$
4	Co	CHO
5	Pd	H
6	Co	H
7	Cu	H
8	Cu	CHO
9	2 H	CHO
10	2 H	$CH{=}CH_2$
11	Cu	$CH{=}CH_2$
12	Zn	H

Alternatively, cobalt complex **3** was synthesized through consecutive transformations *via* method *B*. The copper complex with 5,10,15,20-tetraphenylporphyrin (**7**) was formylated according to Vilsmeier,[7] and the demetallation of the resulting copper 2-formyl-5,10,15,20-tetraphenylporphyrin complex (**8**) *via* the known procedure[8] afforded 2-formyl-5,10,15,20-tetraphenylporphyrin (**9**). The latter was transformed by the Wittig reaction[9] into 2-vinyl-5,10,15,20-tetraphenylporphyrin (**10**) under the conditions close to those described[3] for the synthesis of the copper complex with (2-vinyl-5,10,15,20-tetraphenyl)porphyrin (**11**). Vinylporphyrin **10** has been synthesized earlier[10] as an intermediate product during the study of transformations in the reaction of the zinc 5,10,15,20-tetraphenylporphyrin complex (**12**) with methyl diazoacetate. As in the procedure described, the method proposed for the synthesis of vinylporphyrin **10** is also three-step but provides the higher yields of both target vinylporphyrin **10** and intermediate porphyrins **8** and **9**. Unlike the method[10] in which methyl diazoacetate and lithium borohydride were used, we applied more safe and available reagents ($[Ph_3PMe]I$, PhLi]). Meanwhile, intermediate porphyrins (**7**, **9**) are more stable, can easily be isolated and purified, and are more workable than vinylporphyrin **10**. The reaction of free base vinylporphyrin **10** with cobalt acetate in a chloroform—acetic acid mixture afforded cobalt complex **3**. The first route for the synthesis of vinylporphyrin including the Wittig olefination of aldehyde **4** is more preferential than the alternative synthesis from complex **7**, because it requires less time, is shorter by one step, and, which is the main, yields target compound **3** by 18—20% more. The reaction of free base **10** with palladium salts affords mixtures of products containing no metal vinylporphyrin **1**. When a metal is introduced into the coordination cavity of vinylporphyrin **10** according to this method, a π-complex with the palladium salt containing the double bond of the vinyl group is formed in parallel and undergoes further transformations. It is known that the alkene complexes with the palladium salts are rather reactive. In particular, they are oxidized with air oxygen and alkylate aromatic compounds. It can be assumed that attempts of direct introduction of Pd atoms into vinylporphyrin **10** give the palladium complexes with the products of oxidation of the vinyl group, alkylation of the phenyl cycle adjacent to the vinyl group, another porphyrin molecule, another solvent molecule, and also products of other reactions.

Unlike the porphyrin containing one vinyl group in the benzene ring of 5-(4-vinylporphyrin)-10,15,20-triphenylporphyrin, whose structure has been determined[3] by X-ray diffraction analysis, we failed to grow crystals of **1**, **3**, and **10** appropriate for X-ray study. Therefore, the structures of these products were determined by IR spectroscopy, NMR, and mass spectrometry. The main characteristics of synthesized 2-vinyl-5,10,15,20-tetraphenylporphyrin and its complexes with palladium and cobalt are given in Tables 1 and 2.

The ^1H NMR spectra exhibit multiplets from aromatic pyrrolic protons at δ 8.88—8.68 and two multiplets from the Ph protons at δ 8.21—8.03 and 7.84—7.66. The vinylic protons are observed at δ 6.42 (ddd, H_f), 5.82 (dd), and 5.09 (dd). Quantification of the spectra shows 30 protons of the following types: seven protons H_d, $H_{d'}$, $H_{d''}$, and H_e; eight protons H_c and $H_{c'}$; four protons H_a and $H_{a'}$; eight protons H_b and $H_{b'}$; one protons H_f; one proton H_h; and one proton H_g. The spin-spin coupling constant values of the vinylic protons of compounds **1** and **10** differ by 0.1—0.5 Hz. The spectrum of unsubstituted vinylporphyrin **10** contains two more protons from the NH groups. As known,[11] due to magnetic screening of the protons arranged inside the cycle (N—H protons), their signal in the ^1H NMR spectrum undergoes an

Table 1. Elemental compositions and molecular ions of synthesized compounds **1**, **3**, and **10**

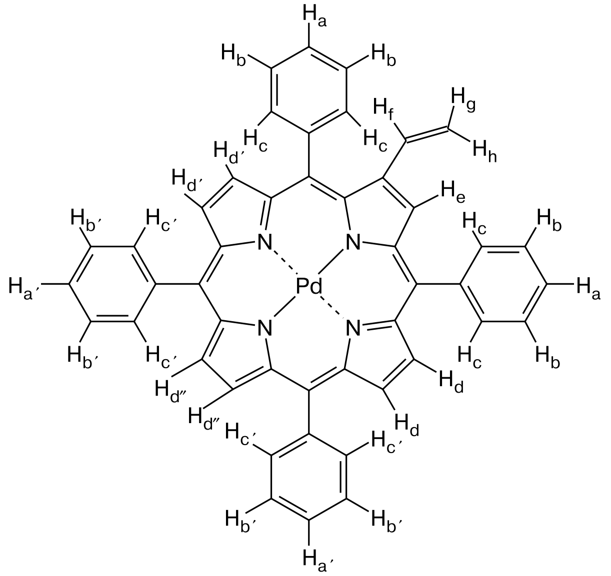
Compound	Found/Calculated (%) C	H	N	M	Molecular formula	$[M]^+$, found/calculated
1	73.22* 72.88	3.88* 3.55	6.92* 6.42	14.35* 13.91	$C_{46}H_{30}N_4Pd$	745 745.19
3	79.19 78.88	4.30 3.90	8.03 7.55	8.46 8.99	$C_{46}H_{30}CoN_4$	697 697.7
10	86.25 86.96	5.00 5.11	8.75 8.01	—	$C_{46}H_{32}N_4$	640 640.79

* Average of several independent parallel determinations.

Table 2. Spectral characteristics of synthesized compounds **1**, **3**, and **10**

Compound	^{1}H NMR (CDCl$_3$), δ (*J*/Hz)	IR spectrum, ν/cm^{-1}	UV—Vis spectrum (DMF), λ/nm (logε)
1	8.88—8.68 (m, 7 H, H_d, $H_{d'}$, $H_{d''}$, pyrrole); 8.21—8.03 (m, 8 H, H_c, $H_{c'}$, Ph); 7.84—7.66 (m, 12 H, H_a, $H_{a'}$, H_b, $H_{b'}$, Ph); 6.42 (dd, 1 H, H_f, CH=CH$_2$, *J* = 1.0, *J* = 10.8, *J* = 17.1); 5.82 (d, 1 H, H_h, CH=CH$_2$, *J* = 2.0, *J* = 17.1); 5.09 (d, 1 H, H_g, CH=CH$_2$, *J* = 2.4, *J* = 10.8)	700, 715, 750, 795 (δ, benzene ring + pyrrole); 910 (δ(=CH$_2$)); 980, 1010, 1070, 1175, 1350, 1440 (δ(CCH) + ν(C—C), benzene ring); 1485 (ν(C=C—C=N), pyrrole); 1595 (ν(CC) + δ(CCH), benzene ring)	418 (5.53), 527 (4.71)
3	—	700, 720, 750, 792 (δ, benzene ring + pyrrole); 905 (δ(=CH$_2$)); 995, 1000 (CCH, benzene ring); 1070, 1175, 1350, 1345, 1440 (ν(CC) + δ(CCH), benzene ring); 1487 (ν(C=C—C=N), pyrrole); 1595 (ν(CC) + δ(CCH), benzene ring)	421 (5.22), 538 (4.54)
10	8.90—8.69 (m, 7 H, H_d, $H_{d'}$, $H_{d''}$, pyrrole); 8.21—8.03 (m, 8 H, H_c, $H_{c'}$, Ph); 7.81—7.21 (m, 12 H, H_a, $H_{a'}$, H_b, $H_{b'}$, Ph); 6.44 (dd, 1 H, H_f, CH=CH$_2$, *J* = 0.5, *J* = 10.5, *J* = 17.0); 5.95 (d, 1 H, H_h, CH=CH$_2$, *J* = 1.8, *J* = 17.2); 5.18 (d, 1 H, H_g, CH=CH$_2$, *J* = 1.7, *J* = 10.7); –2.7 (s, 2 H, NH)	698, 730, 760, 795 (δ, benzene ring + pyrrole); 985 (δ(=CH$_2$)); 998 (CCH); 1065 (benzene ring); 1170, 1345, 1440, 1465 (ν(CC) + δ(CCH), benzene ring); 1487 (ν(C=C—C=N), pyrrole); 1595 (ν(CC) + δ(CCH), benzene ring)	427 (5.48), 526 (4.59)

upfield shift by 11 ppm. For instance, the chemical shifts of protons of the N—H groups in the porphyrin and ethylporphyrin are –3.76 and –3.34 ppm, respectively. In the case of vinylporphyrin **10**, this shift is –2.7 ppm. Note that their integral intensity corresponds to 1.92 protons, probably, due to the deuterioexchange that occurs with the solvent (CDCl$_3$).



The electronic spectra of all samples contain the intense Soret band at λ = 418 (for palladium derivative **1**) and 421 nm (for cobalt complex **3**) and the Q band with a considerably lower intensity at λ = 527 (**1**) and 538 nm (**3**). For vinylporphyrin **10** containing no metal, these bands are observed at λ = 427 and 526 nm, respectively.

In the IR spectra of compounds **1**, **3**, and **10**, we could not detect the band of stretching vibrations of the C=C bond in the characteristic region of 1650—1630 cm^{-1}. This is caused by both the low molar absorption coefficient of this nonpolar bond and the low relative content of vinyl groups compared to other atomic groups of the macrocyclic ligand. Certain hindrance can also be created by water traces, because the band of bending vibrations of the H$_2$O molecule lies in the region of stretching vibrations of the C=C bond. However, the presence of the vinyl group in compounds **1**, **3**, and **10** is indicated by the band at 900 cm^{-1} assigned to the δ(CCH) bending vibrations of the C=CH$_2$ group. The assignment of this band to vibrations of the vinyl group is favored by its absence in the spectrum of the cobalt complex with tetraphenylporphyrin. The shape of the broad band at 900 cm^{-1} in the IR spectra of the compounds under study differs substantially from those of other absorption bands with a small width and the Lorentz contour, which is characteristic of the spectra of molecular crystals. The broadening of the band of the vinyl group can be caused by conformational polymorphism due to rotation about the C—C bond connecting this group with the porphyrin macrocycle and to superposition of the absorption bands of several rotamers stabilized by the intermolecular interaction in the crystal lattice. As can be seen from the data in Table 2, metal incorporation into the macrocycle cavity exerts virtually no effect on vibrational frequencies of the groups arranged at the periphery of the Ph rings. This can be related to the shift of the Ph rings from the conjugation plane in the system of pyrrole rings, which has been found[12] by X-ray diffraction analysis. At the same time, complex formation increases the vibrational frequencies of the system of the conjugated C=C—C=N π-bonds in the pyrrole cycles by 20—25 cm^{-1} (see Table 2). This is probably caused by the elimination of lone electron pairs of the N atoms from the nonbonding orbitals of the pyrrole cycles due to their interaction with the metal atom and formation of the M—N bond.

All mass spectra contain peaks of molecular ions as the major peaks and a series of low-intensity impurity peaks, which is caused by a higher sensitivity of the method to the substances under study; some samples were analyzed using the consecutive connection of two mass spectrometers (MS/MS).

Copolymerization of styrene with monomers 1, 3, and 10. The rate of copolymerization of vinylporphyrin monomers **1**, **3**, and **10** and the molecular-weight characteristics are lower compared to those for styrene homopolymerization (Table 3). The palladium content in the copolymer depends on the composition of the monomeric mixture and ranges from 0.1 to 1.0 mol.%. Note that vinylporphyrin **10** containing no metal induces inhibition of styrene polymerization to a less extent than palladium complex **1** does (Fig. 1).

The UV spectra of the monomeric and polymeric palladium complexes are indiscernible, indicating no interaction between the porphyrin subunits with each other in solution.[4]

With an increase in the initiator concentration (Fig. 2), the copolymerization rate of both comonomers **1** and **10** increases.

The average numerical molecular weight of the copolymers decreases with an increase in the fraction of comonomers **1** and **10** in a monomeric mixture and with an increase in the initiator concentration (Table 4).

Comparison of the kinetic data and molecular-weight distribution of the synthesized copolymers with vinylporphyrin monomers **1** and **10** suggests some mechanistic features of chain termination in these polymerized systems. It is most probable that incorporation of the vinylporphyrin unit into the growing chain produces monomolecular pseudo-termination: the macroradical with the terminal porphyrin unit is stabilized due to conjugation with the electronic system of the porphyrin cycle. A similar phenomenon has been observed earlier for styrene copolymerization with the Cu^{II} and Co^{II} complexes containing pyrrolylmethyleneiminopropene[13] and for copolymerization of the copper and zinc vinylporphyrins

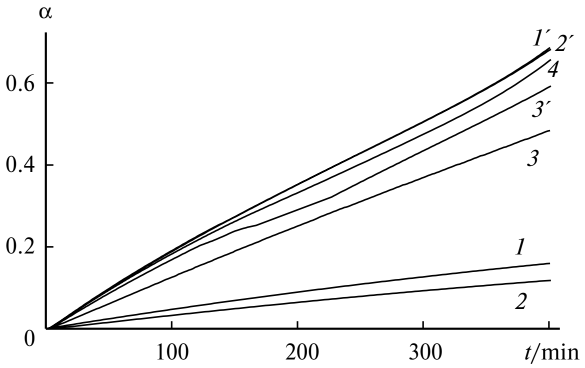


Fig. 1. Kinetic curves of styrene copolymerization with compounds **1** (*1—3*) and **10** (*1′—3′*) at the concentration of the vinylporphyrin copolymers 0.1 (*1*, *1′*), 0.5 (*2*, *2′*), and 1.0 wt.% (*3*, *3′*); *4*, styrene homopolymerization. Copolymerization conditions: T = 70 °C, 0.6 wt.% AIBN, in block; α is conversion.

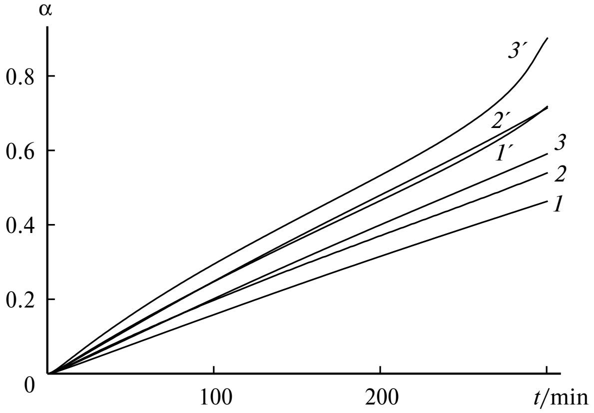


Fig. 2. Kinetic curves of styrene copolymerization with compounds **1** (*1—3*) and **10** (*1′—3′*) at the AIBN concentration 1.0 (*1*, *1′*), 1.5 (*2*, *2′*), and 2.0 wt.% (*3*, *3′*). Copolymerization conditions: T = 70 °C, in block, content of compounds **1** and **10** in the monomeric mixture 0.1 mol.%; α is conversion.

Table 3. Molecular-weight distribution of the styrene copolymers with compounds **1** and **10** with a varied amount of comonomers **1** and **10** in the comonomer mixture*

C (mol.%)	**1**					**10**				
	M_n	M_w	M_z	M_w/M_n	M_z/M_w	M_n	M_w	M_z	M_w/M_n	M_z/M_w
0	81000	329000	840000	4.06	10.38	81000	329000	840000	4.06	2.56
0.1	64000	360000	946000	5.63	2.63	40400	363000	1800000	8.99	4.96
0.5	43000	202000	1000000	4.71	2.29	15250	56000	454000	3.67	8.11
1.0	7300	34600	1000000	4.75	2.90	8400	23000	95000	2.74	4.13

* Copolymerization conditions: T = 70 °C, AIBN (0.5%), in block.

Table 4. Molecular-weight distribution of the styrene copolymers with compounds **1** and **10** with a varied initiator amount*

C_{AIBN} (wt.%)	**1**					**10**				
	M_n	M_w	M_z	M_w/M_n	M_z/M_n	M_n	M_w	M_z	M_w/M_n	M_z/M_n
0.1 (PP-11)	106000	416000	790000	3.92	1.9	—	—	—	—	—
0.6	—	—	—	—	—	40400	363000	1800000	8.99	4.96
1.0 (PP-15)	84000	252000	461000	3.00	3.03	36500	316000	1951000	8.66	6.17
1.5	30000	131000	387000	4.36	2.95	29400	247000	1454000	8.40	5.89
2.0 (PP-19)	24000	93600	288000	3.90	2.86	23200	196000	1414000	8.45	7.21

* Conditions: $T = 70$ °C, concentration of the comonomer in the comonomer mixture 0.1 mol.%.

with styrene and methyl methacrylate.[4] Using the known equation

$$1/\bar{P}_n = 1/\bar{P}_0 + C_s/C_{porph}$$

($\bar{P}_0$ and $\bar{P}_n$ are the average degrees of polymerization in the absence and presence of restriction agents, respectively; C_{porph} is the concentration of the vinylporphyrin monomer; $C_s = k_t/k_{gr}$, k_{gr}, and k_t are the rate constnts of chain growth and termination), we can conclude that vinylporphyrin **10** containing no metal is a more efficient chain-transfer carrier to the monomer ($C_s = 11.2 \cdot 10^{-3}$) than Pd-containing complex **1** ($C_s = 7.3 \cdot 10^{-3}$).

Styrene polymerization in the presence of cobalt complex **3** differs basically from polymerization in the presence of palladium complex **1** by both the kinetics of the process and the structure and molecular weight of the polymerization products, which is related to phenomena of catalytic chain transfer and catalytic inhibition.[14] Omitting detailed kinetic analysis, we would like to mention that the sharp decrease in the molecular weight of the polymerization products with an increase in the content of compound **3** favors catalytic chain transfer. For instance, for the content of 1 mol.% compound **3** in the comonomeric mixture (0.5 wt.% AIBN, $T = 70$ °C), the degree of polymerization (in essence, oligomerization) of styrene is only 4—5 ($M_n = 420$, $M_w = 520$, $M_z = 680$, $M_w/M_n = 1.23$, $M_z/M_w = 1.30$). The resulting oligomers (P_n) have the structure H—$(CH_2—CHPh)_n$—CH=CHPh.

The presence of the terminal C=C bonds indicates that the catalysis of chain transfer to the monomer (M) proceeds through H atom abstraction from the methylene group of the growing macroradical by the metal complex (CoL) *via* the "ping-pong" mechanism with a change in the valent state $Co^{II} \rightleftharpoons Co^{III}$ according to Scheme 1.

Scheme 1

$$H—(CH_2—CHPh)_n—CH_2—HPhC^{\cdot} + CoL \longrightarrow P_n + HCoL$$

$$M + HCoL \longrightarrow R + CoL$$

Photooxidation of anthracene by compounds 1, 3, and 10. The ability of porphyrins and metal porphyrins to catalyze photochemical reactions is well known. They produce transformation of a dioxygen molecule into the lowest excited singlet state $^1\Delta_g$ due to quenching of their lowest excited electron states by dioxygen in organic solvents (see, *e.g.*, Ref. 15). In turn, singlet oxygen is an active oxidizing agent capable of interacting, in particular, with condensed hydrocarbons, for example, with anthracene, to form 1,4-addition products.[16]

Although processes of quenching by molecular oxygen of the excited electronic states of metal porphyrin complexes of different metals have been studied in rather detail, the properties of monomeric and polymeric complexes **1**, **3**, and **10** in the photosensibilized generation of $^1O_2$ have not been studied earlier.

The absorption spectra of a system **1**—anthracene upon irradiation with the light of the wavelength λ = 300—400 nm are shown in Fig. 3 as an example. As can be seen, the exciting light is absorbed by anthracene only, the absorbance of complex **1** remains unchanged during irradiation, and the absorption intensity at 300—400 nm decreases without changing the spectral shape. Similar absorption spectra are observed for a **10**—anthracene system. The rate of decreasing the anthracene concentration (C/mol L^{-1} s^{-1}) during irradiation was determined by a change in the absorbance in the absorption maximum of the most intense band at λ = 349 nm using the formula $V = \Delta C/\Delta\tau$. The changes observed in the absorption spectra are related to the oxidation of anthracene to form its *endo*-peroxide, which absorbs the light in the region of λ < 300 nm. After absorption of a photon, molecules **1** and **10** are transformed into the triplet state due to intersystem crossing, and the triplet state is quenched by dissolved air oxygen.[17—19] As a result, an excited molecule of singlet dioxygen and a molecule of **1** or **10** in the ground state are formed. The appeared singlet dioxygen reacts (k is the rate constant of this reaction) with anthracene to form anthracene *endo*-peroxide or deactivates (Scheme 2).

The oxidation rates of anthracene by air oxygen and quantum yields (Φ_A) in the presence of the monomeric and polymeric palladium-containing porphyrin complexes and their analogs free of metal are presented in Tables 5 and 6. As can be seen from the data in Table 5, the specific rates of anthracene oxidation (rates based on the

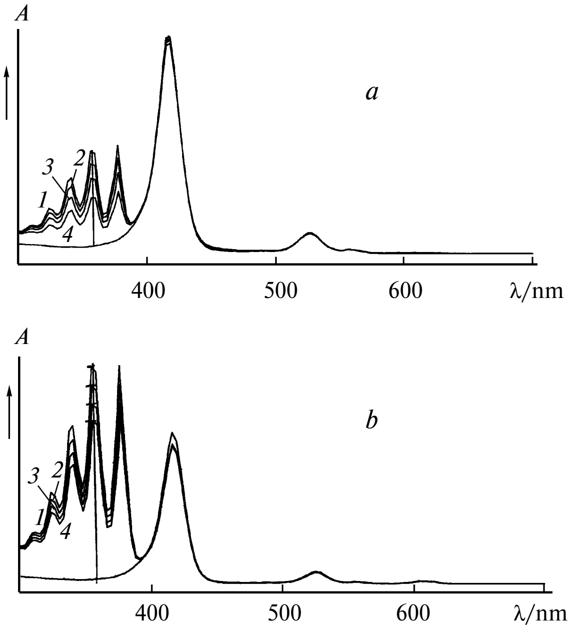
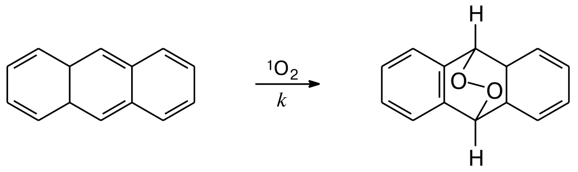


Fig. 3. Electronic absorption spectra of the reaction mixtures for anthracene (A) oxidation in the presence of compound **1** (*a*) and the copolymer of compound **1** with styrene PP-15 (*b*). Conditions: solvent $CHCl_3$, concentration of compound **1** — $1 \cdot 10^{-5}$ mol L^{-1} (*a*) and $2.7 \cdot 10^{-4}$ mol L^{-1} (*b*), $C_A = 1.46 \cdot 10^{-5}$ mol L^{-1} (DRSh-1000, ZhS-12), reaction duration (*a*): 0 (*1*), 2 (*2*), 5 (*3*), and 10 min (*4*); (*b*): 0 (*1*), 5 (*2*), 10 (*3*), and 15 min (*4*).

Scheme 2



Pd^{II} concentration) and the quantum yields of the reaction in the presence of metal-polymeric systems and their analogs free of metal are comparable. However, taking into account that the isolation of the polymeric catalyst from the reaction mixture is rather simple and the catalyst can repeatedly be used (unique feature of the polymer-immobilized catalyst[20]), we can see its obvious advantages. No oxidation of anthracene occurs in the presence of polystyrene, which is the major component of the copolymers, and complex **3**. The cobalt-containing vinylporphyrin complex decomposes only with a rate of 9.2% during 5 min (DRSh-1000 lamp, ZhS-18 filter).

Experimental

Triphenylmethylphosphonium iodide was synthesized as described earlier.[3] References to the preparation of the earlier synthesized porphyrins (**2**, **4—9**) are given in Results and Discussion.

Palladium 2-vinyl-5,10,15,20-tetraphenylporphyrinate (1). A mixture of aldehyde **2** (0.5 g, 0.669 mmol), triphenylmethylphosphonium iodide (1.893 g, 4.683 mmol), potassium carbonate (1.11 g, 8.028 mmol), and 18-crown-6 (25 mg) in anhydrous benzene (100 mL) was refluxed for 18 h under argon and then cooled and filtered through a layer of Al_2O_3 (III activity grade, 3 cm). The filtrate was concentrated to a saturated solution, which was chromatographed on a column with silica gel (2.5×40 cm) using benzene as the eluent. The fractions containing vinylporphyrin **1** were combined and evaporated to dryness, and the residue was crystallized from a $CHCl_3$—MeOH (1 : 3) mixture. The yield was 0.389 g (78%).

Cobalt 2-vinyl-5,10,15,20-tetraphenylporphyrinate (3). ***A.*** Complex **3** was synthesized similarly to palladium complex **1** for 10 h in a yield of 0.351 g (75%) from aldehyde **4** (0.469 g, 0.669 mmol), triphenylmethylphosphonium iodide (1.893 g, 4.683 mmol), potassium carbonate (1.11 g, 8.028 mmol), and 18-crown-6 (25 mg) in anhydrous benzene (70 mL).

B. A solution of cobalt(II) acetate (0.237 g, 0.95 mmol) in acetic acid (25 mL) was added with stirring to a solution of free base **10** (0.5 g, 0.778 mmol) in chloroform (50 mL). The resulting mixture was refluxed for 30 min, cooled, and washed with water (3×50 mL). The chloroformic solution of complex **3** was concentrated to a volume of 15 mL, and boiling methanol (45 mL) was added. Evaporation was continued until a precipitate began to form, and then the reaction mixture was cooled

Table 5. Kinetic parameters of the photooxidation of anthracene ($1.46 \cdot 10^{-4}$ mol L^{-1}) in chloroform in the presence of compound **10**, polystyrene (PS), and copolymers of compound **10** with styrene (PP)

Compound	$[\mathbf{10}] \cdot 10^6$ /mol L^{-1}	$C^a \cdot 10^5$ /g mL^{-1}	$v^b = (\Delta C/\Delta\tau) \cdot 10^8$ /mol L^{-1} s^{-1}	$w_{sp}{}^c \cdot 10^2$ /mol L^{-1} s^{-1} (mol of **10**)$^{-1}$	$\Phi_A{}^d \cdot 10^2$
10	3.7	—	7.49	2.02	0.33
PS	—	2.9	—		—
PP-1	3.01	3.8	5.06	1.33	0.27
PP-2	2.01	5.2	3.36	0.65	0.27
PP-3	1.15	14.5	1.95	1.34	0.27

[a] Copolymer concentration.

[b] Reaction rate.

[c] Specific rate.

[d] Quantum yield of the reaction.

Table 6. Kinetic parameters of the photooxidation of anthracene ($1.46 \cdot 10^{-4}$ mol L^{-1}) in chloroform in the presence of compound **1** and its copolymers with styrene (PP)

Compound	[Pd] $\cdot 10^5$ /mol L^{-1}	$C^a \cdot 10^4$ /g mL^{-1}	$v^b = (\Delta C/\Delta\tau) \cdot 10^7$ /mol L^{-1} s^{-1}	$w_{sp}{}^c \cdot 10^2$ /mol L^{-1} s^{-1} (mol of Pd)$^{-1}$	$\Phi_A{}^d \cdot 10^2$
1	1.0	—	1.39	1.39	0.19
PP-11	0.43	2.16	0.60	1.40	0.18
PP-15	0.27	2.61	0.47	1.74	0.22
PP-19	0.24	2.70	0.39	1.63	2.00

[a] Copolymer concentration.
[b] Reaction rate.
[c] Specific rate.
[d] Quantum yield of the reaction.

down. The precipitate that formed was filtered off, washed with methanol, water, and methanol again, and dried at 110 °C. The yield was 0.523 g (96%).

Electronic absorption spectra were recorded on Perkin—Elmer Lambda 2 and Specord M-40 spectrophotometers (solvent DMF, concentration 10^{-6}—10^{-4} mol L^{-1}). ^{1}H NMR spectra were obtained on a DPX-200 NMR FT-IR spectrometer in $CDCl_3$ at room temperature (internal standard Me_4Si). Mass spectra were measured on a Varian MAT CH-5 instrument. TLC analysis was carried out on Silufol plates for free bases and on Silufol UV-254 plates in the case of the complexes. For column chromatography Al_2O_3 (III activity grade) and silica gel L 40/100 were used.

Copolymerization of vinylporphyrins **1**, **3**, and **10** with styrene was conducted in the bulk. Styrene was pre-washed from the stabilizer with an alcoholic solution of KOH, dried above anhydrous $CaCl_2$, and distilled *in vacuo*. The concentration ratios of the monomers were determined by the low solubility of the palladium or cobalt complexes and 2-vinyl-5,10,15,20-tetraphenylporphyrin in styrene (bulk polymerization) and ranged from 0.1 to 1 wt.%. Azobisisobutyronitrile (AIBN) in the amount from 0.5 to 2 wt.% of the sum of monomers was used as the initiator. The kinetics of copolymerization (70 °C) was monitored by calorimetry. The copolymer that formed (after 300—400 min) was precipitated, multiply washed with EtOH, dried until a constant weight was achieved, and analyzed. The metal content was determined by the atomic absorption method on a Saturn instrument. The composition of copolymers containing no metal was calculated from the nitrogen content.

IR spectra were recorded on Specord IR-75 and Perkin—Elmer Spektrum 1000 instruments (KBr pellets).

Molecular-weight characteristics of copolymers were determined by gel permeation chromatography in THF on a Waters-200 instrument equipped with styrogel columns with different exposure limits.

The photooxidation of anthracene was carried out in a chloroformic solution by air oxygen in a glass cell (l = 1 cm) upon irradiation with the light from a DRSh-1000 mercury lamp equipped with a water filter and the corresponding glass light filters (without additional oxygen purging) according to earlier[17—19] described procedures. The incident light intensity was measured on an IMO-2 power meter. The oxidation kinetics was monitored by a change in the anthracene concentration, which was determined by a decrease in the absorbance of the absorption bands of anthracene at 300—400 nm. Electronic absorption spectra were recorded on a Genesys^{TM} 2 instrument.

Quantum yields of anthracene photooxidation (Φ_A) in the presence of the catalysts (vinylporphyrin and its monomeric and polymeric metal complexes) were determined as the ratio of the number of anthracene molecules oxidized at the initial moments (calculated from the linear region of the kinetic curves) to the number of photons absorbed by the catalyst during this time.

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