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Catalyst systems based on immobilised porphyrins and metalloporphyrins

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Abstract. The key approaches to the preparation of catalysts based on porphyrins and porphyrin metal complexes immobilised on polymeric supports are analysed. The factors determining the catalytic activity of porphyrin-containing polymer systems are outlined. Processes catalysed by such systems are considered. The bibliography includes 99 references.

I. Introduction

The design of metal complex systems immobilised on various supports has been vigorously progressing in recent decades. The main principles of immobilisation of metal complexes (MC) have now been formulated and routes for the development of this line of research have been outlined.[1] It should be noted that the reactions of transition metal compounds with the support restrict their mobility, which affects the rates and, in some cases, also the mechanisms of catalysed reactions. This should be taken into account when preparing supported metal complex catalysts.

The design of immobilised catalysts with active sites having a known structure and environment contributes to better understanding of the mechanisms of catalytic transformations and allows theoretically substantiated choice of the catalysts and prediction of the catalytic effect. The immobilised catalysts should be stable and show reproducibility of functional properties; it is also required that they be readily separable from the reaction products.[2]

When homogeneous metal complexes are used as catalysts, the catalytic transformation occurs in the coordination sphere of the transition metal under 'steric participation' of ligands in electron density redistribution and formation of intermediate active complexes. It is generally considered that in this case, all metal complexes are identical and equally accessible to reactants. Meanwhile, the MC immobilised on supports (inorganic, polymeric, *etc*.) possess, generally speaking, different activities and some of the complexes can be inactive or even catalyse side reactions.[1, 2] However, immobilised systems have obvious advantages because they are more easily separated from products and recycled, which is especially important when dealing with fairly expensive metal porphyrins.

The problem of separation of catalysts from the reaction mixture is so acute that chemical processes based on homogeneous catalysts are seldom implemented in industry. Exceptions include the Ziegler – Natta catalysts (olefin polymerisation) and catalysts of the Wacker (ethylene oxidation to acetaldehyde) and Monsanto processes (methanol carbonylation to acetic acid).[3] Therefore, it can be understood why specialists have always looked for ways of developing catalysts of a new type that would combine the advantages of homogeneous and heterogeneous systems.

A new impetus for research along these lines was given by the discovery of unique catalytic properties for the systems prepared by grafting transition metal complexes to polymer supports. The knowledge coming from studies of the functional activity of MC in natural systems prompted the search for efficient heterogeneous catalyst systems to be focused on imparting certain mobility to the 'attached' catalytic sites. This is attained by immobilisation of functionalised MC on polymeric supports, which are most mobile. In what follows we restrict ourselves to considering this particular type of 'attachment'. This review discusses the set of problems associated with the development of catalyst systems based on immobilised porphyrins and metalloporphyrins (MP).

II. Immobilised metal complexes as fragments of natural systems

Fastening of low-molecular-weight compounds including MC to mineral or polymeric substrates and participation of these immobilised compounds in various processes are frequently encountered in animate and abiotic nature. The presence of ions in the inorganic natural sorbents occurring as parts of soils and natural sedimentary deposits dictates the dynamics of element redistribution in nature, ore-formation processes, the formation of carbon mineral products, and so on. The transport and assimilation of metal ions in animate

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nature determine almost all functions of native systems including enzymic, muscle, photosynthetic and other properties.[1,2]

In particular, porphyrin metal complexes catalyse biochemical processes that provide for the vital activity of organisms. The specific activity of natural hemoproteins containing a protoporphyrin complex of trivalent iron (oxidase, monooxygenase, haemoglobin, myoglobine) is determined first of all by the spatial arrangement of the side functional groups of the polypeptide chain in the vicinity of the active site. In the best-studied monooxygenases, namely, cytochromes P-450, which oxidise xenobiotics such as steroids and cholesterols, within the microsomal system of the liver, the central Fe(III) ion of the haem is coordinated to the imidazole group of histidine and the thiol group of cysteine. The removal of these amino acid residues from the cytochrome active site results in enzyme deactivation. However, it is believed that in the haemoglobin molecule, iron protoporphyrin responsible for oxygen binding and oxygen transport to all organs and tissues of living creatures is coordinated to the imidazole groups of two histidine molecules. It should be noted that oxygen does not react with iron if iron is not coordinated to imidazole groups. In addition, strong binding between the haem and a protein is due to acid – base interaction of the carboxy groups of porphyrin with the side groups of the polypeptide chain.[4,5]

As an example illustrating the possible conformational changes in the protein molecule in the vicinity of the metalloporphyrin active site, one can cite classical results of an X-ray diffraction study of ferro- and ferricytochrome *c* carried out by Dickerson and co-workers [6] with a resolution of 0.245 (ferrocytochrome) and 0.28 nm (ferricytochrome). Cytochrome *c* in mitochondrial membranes participates in the electron transport along the 'respiratory chain' and in oxidative phosphorylation of food, resulting in the synthesis of a versatile energy storage in the cell, namely, adenosine triphosphate (ATP), hydrolysis of which releases an energy of ~ 7 kcal mol^{-1}. The cytochtome *c* itself is a protein with a molecular mass of $\sim 123\,000$ containing 104 amino acid residues. Figure 1 sketches a stereoprojection of ferricytochrome *c*, indicating what types of rearrangement take place in this system during the reduction of the central ion of the haem.[7]

It can be seen from Fig. 1 that the haem is linked to cysteines-14 and -17 of the protein by covalent sulfide bonds and to the imidazole nitrogen atom of histidine-18 and the sulfur atom of methionine-80 by coordination bonds *via* iron. The nitrogen atom of the imidazole ring of histidine-18 is involved in the hydrogen bond with the carboxy group of proline-30. On reduction of ferricytochrome *c*, the globule undergoes severe conformational changes (Fig. 1 *b*), only 21 amino acid residues of 104 remaining unaffected. Thus, the coordination properties of MP toward covalent binding to the fragments of biological systems are realised under dynamic variability of the 'environment' of the central ion and the porphyrin ring plane. The nature controls the catalytic or other properties of small molecules by 'attaching' them to supports, which formally do not participate in the process but indirectly influence it through the formation of non-covalent (coordination and hydrogen) bonds. This often changes the process direction and efficiency.

One more example of conformational rearrangements in biological macromolecules upon metal binding refers to the antibiotic valinomycin, first synthesised by M M Shemyakin in 1963. Valinomycin belonging to the class of cyclic depsipeptides can bind alkali metal ions (in particular, potassium ions) to give positively charged lipophilic complexes and perform the catalytic transport of these ions through hydrophobic zones of biological membranes. During this process, the valinomycin molecule undergoes complex conformational rearrangements, as shown in Fig. 2.[8]

It should be emphasised that the knowledge of dynamic aspects of the functioning of complex systems *in vivo* is not only of purely scientific but also of practical interest (we have in view the practical line of studies on metal complex catalysis, in particular, catalysis involving MP). Apparently, for efficient use of metalloporphyrins for practical purposes, it is necessary to follow nature's example, that is, to put them on various macromolecular supports.

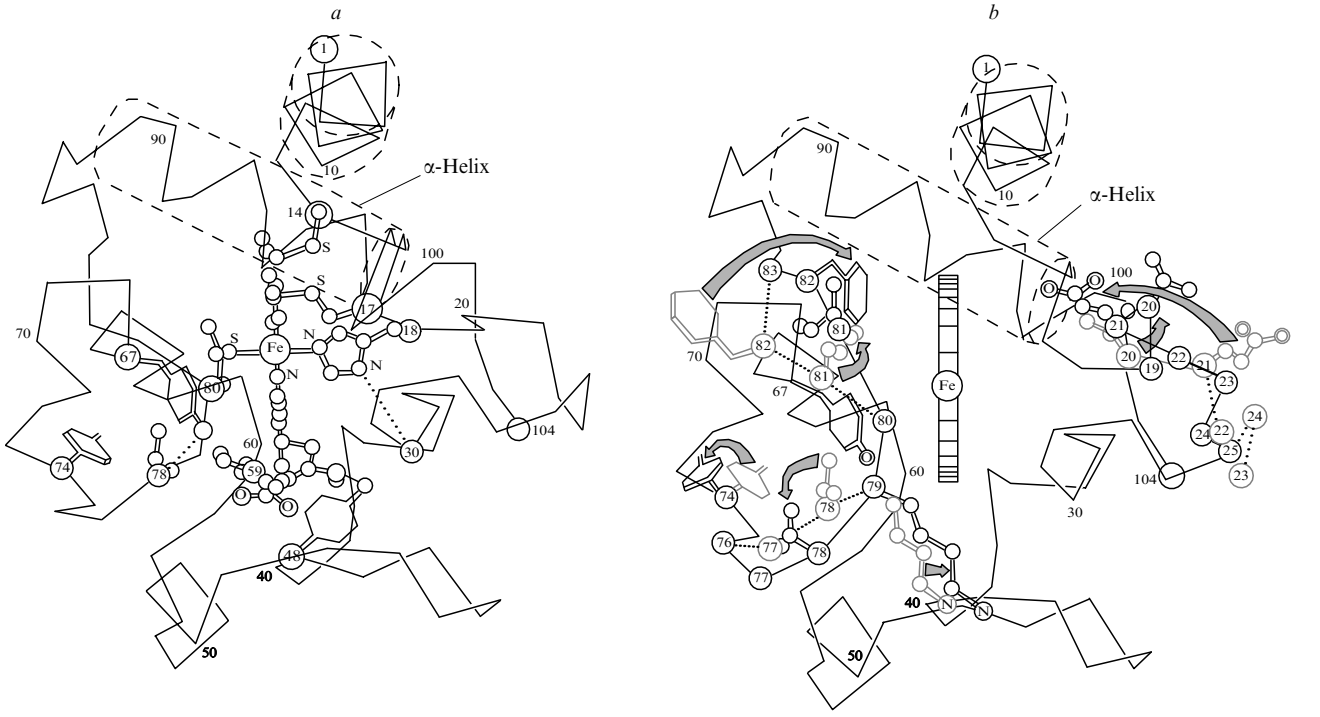


Figure 1. A stereoprojection of the schematically depicted molecule of ferricytochrome *c* (*a*) and main structural changes (shown by arrows) taking place upon reduction of ferricytochrome *c* (*b*).[7]

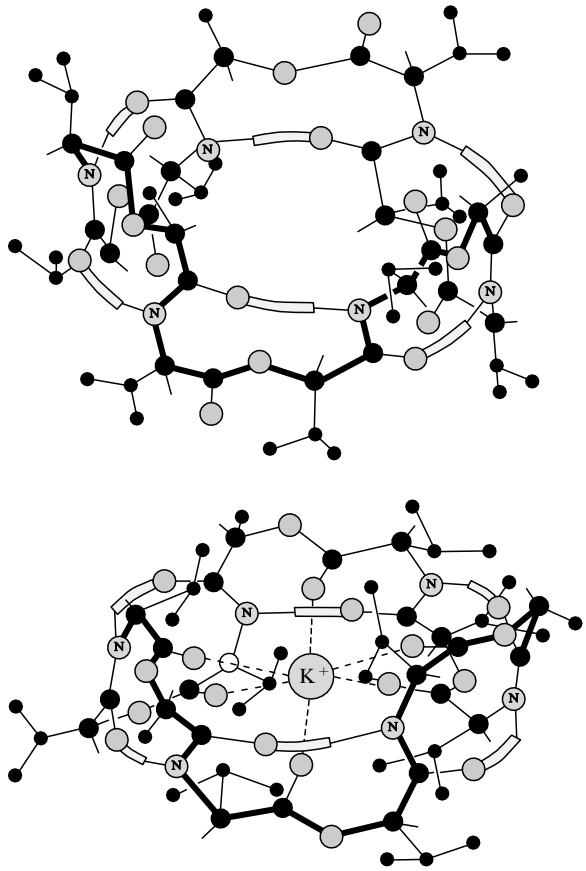


Figure 2. Conformational changes in the valinomycin molecule upon complex formation with the potassium ion.[8]

III. Immobilised metal complexes in catalysis

Apparently, the first attempts at using MC attached to a polymer support as catalysts date back to the late 1960s. By as soon as 1975, British Petroleum and Mobil Oil Corporation had received about 2000 patents for the use of such catalysts. The first publications devoted to the use of immobilised MP and metallophthalocyanines (MPc) in catalysis appeared 10 years later.[1]

Immobilisation may both decrease and increase the specific (per active site) efficiency of metal complexes as catalysts. In particular, poor solubility of transition metal complexes is often responsible for their low catalytic activity in homogeneous catalysis, while immobilisation of MC on polymer supports soluble in the given reaction medium can markedly increase the MC concentration in the solution and, hence, the efficiency in catalysis. The change in the catalytic activity upon immobilisation can be due to specific rearrangements of the polymer chain, the change in the stereochemical environment of the metal ion, *etc*., which take place in the reaction medium.

In the general case, immobilisation of metal complexes on a polymer sapport can redound to the combination of advantages and elimination of disadvantages of homogeneous and heterogeneous catalysts. Development of such catalyst systems is a fairly complicated task. In order to take advantage of the whole potential of the catalyst systems based on MC coupled with polymer supports, it is necessary to accumulate experience in selecting polymer supports and methods for grafting the MC. Moreover, in every stage of development of immobilised catalysts, one should take into account specific features of the interaction of MC with the macromolecular material.

Metalloenzymes are known to be polymers whose active sites incorporate transition metal complexes with porphyrins or other ligands. High catalytic activity of enzymes is due to the existence of a whole series of interrelated factors, first of all, to the enzyme–substrate structural compliance caused by enhanced affinity of some biopolymer fragments to the substrate. These fragments of protein macromolecules form a three-dimensional network around the active site, the shape and dimensions of the network being consistent with the substrate size. This promotes accumulation of the substrate near the active site (so-called substrate enrichment) and creates favourable orientation of the reactant molecules. In addition, enzymatic catalysis often involves so-called multicentre coordination, which arises upon additional activation of the substrate by functional groups of the biopolymer.[9]

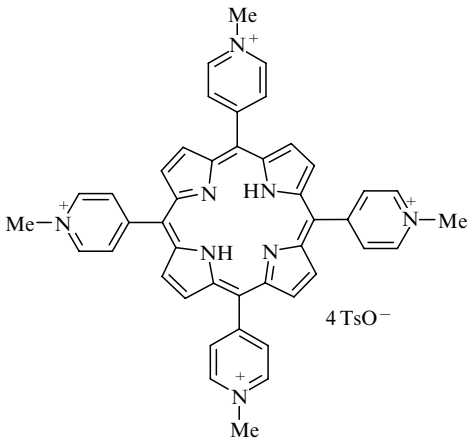
In the most general form, a polymer support suitable for chemical immobilisation of MC should meet the following requirements: (i) give a sufficient number of reactive functional groups; (ii) have a high specific (per unit volume) microporosity (iii) possess appropriate physical and mechanical properties; (iv) be chemically stable under catalysis conditions; and (v) be inert with respect to the reaction products. Depending on the type of catalytic process, polymer supports can be manufactured in different forms, in particular, as powders, granules, fibres, films (including membranes) or swollen gels. In terms of the degree of cross-linking of polymer supports, the metallopolymer catalysts (including those based on metal porphyrins) are classified into three groups — highly cross-linked beaded polymers approaching in properties inorganic substrates; lightly cross-linked swelling gel-type polymers; and linear soluble polymers whose macromolecular chain influences most appreciably the activity of the MC.

IV. Types of binding of porphyrins immobilised on polymer supports

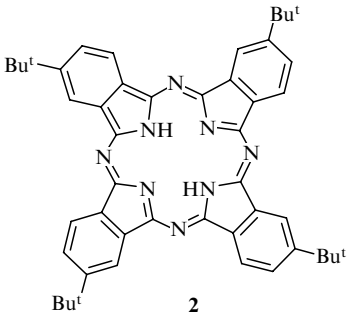
1. Physical binding of MP to a polymer support

The 'MP–polymer support' systems in which the components do not form chemical bonds are usually prepared either by dispersing a polycrystalline porphyrin in a solution of the polymer (in the case of insoluble porphyrins) or by co-dissolution of the polymer and porphyrin followed by casting on an appropriate surface and solvent evaporation to prepare a film, or by impregnating a finished polymer film by a solution of porphyrin.

For example, for the preparation of bactericide photoreactive systems that generate singlet oxygen, metal-free 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (**1**) as the tosylate was impregnated into regenerated cellulose films.[10,11] The films were 50 μm thick, the process was carried out in water or aqueous methanol at 50 °C.



1



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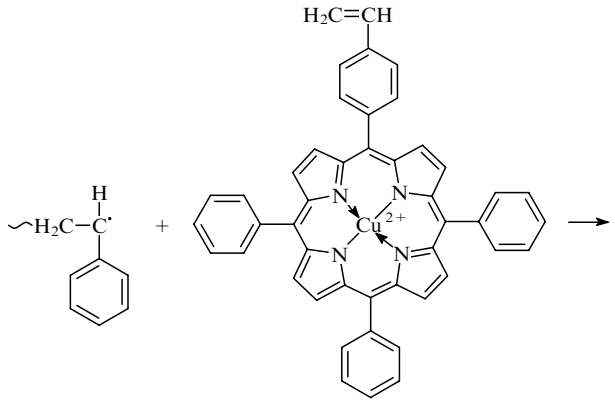
Films containing tetra(*tert*-butyl)phthalocyanine (**2**) were prepared by co-dissolution of phthalocyanine **2** and cellulose diacetate in wet acetone with subsequent casting on an appropriate surface.[11]

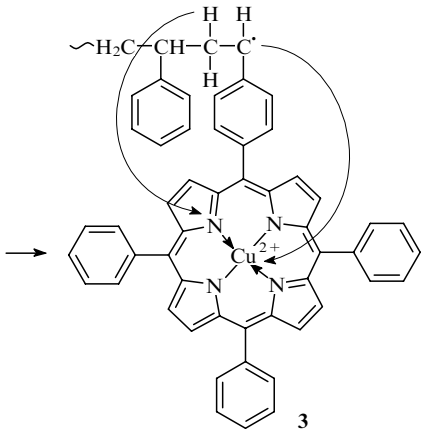
Vankelecom *et al.*[12–14] prepared porphyrin- and phthalocyanine-containing catalytically active membranes based on polydimethysiloxanes (PDMS) by dispersing a porphyrin or phthalocyanine catalyst pre-deposited on an inorganic support (zeolites with different degrees of porosity) in a PDMS solution followed by casting a polymer film. The key prerequisite for uniform distribution of the catalyst in the matrix is the use of relatively dilute solutions of the polymer. The resulting polymer systems catalyse the selective epoxidation of hydrocarbons on treatment with *tert*-butyl hydroperoxide.

The same researchers[15–17] proposed one more method for the preparation of porphyrin-containing membranes based on PDMS. To this end, a solution of the porphyrin complex of manganese or iron in dichloromethane was added to a mixture of prepolymer (RTV 615A) and a cross-linking agent (RTV 615B) in the same solvent. The mixture was stirred for 1 h at room temperature and left overnight. Polymerisation was carried out *in vacuo* at 150 °C. The catalyst systems prepared in this way proved to be efficient in epoxidation of enols and oxidation of alcohols to ketones.[15–17] It was stressed that these composite catalyst systems containing iron porphyrins can be regarded as simple models of cytochrome P-450.[18,19]

2. Covalently bound metalloporphyrins

Covalently bound metalloporphyrins are obtained most often by copolymerisation or polymerisation of porphyrin-containing monomers.[20–31] In particular, the synthesis of THF-soluble copolymers of styrene with methyl methacrylate or acrylonitrile and vinyltetraphenylporphyrin has been reported.[24–27] The scheme of preparation of copolymers **3** based on the vinylporphyrin complex of copper and styrene is shown below.

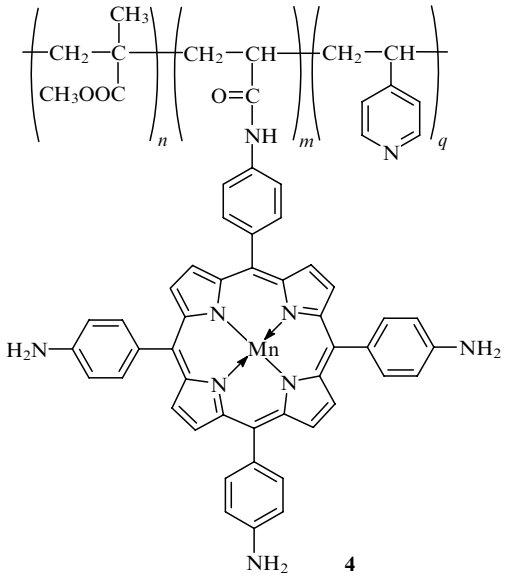




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Neither vinylporphyrins themselves nor their metal complexes undergo homopolymerisation, which is due to either steric (bulky porphyrin substituents) or electronic factors (conjugation of the growing radical with the π-system of the porphyrin). The above procedure was used to obtain copolymers containing zinc and copper tetraphenylporphyrins. The content of MP in the polymer was 1 mol % – 2 mol %, the molecular mass $M_w \approx 400\,000$. For increasing the content of porphyrin units in the copolymer, one should employ monomers in which the double bond is located far from the macrocycle.[28]

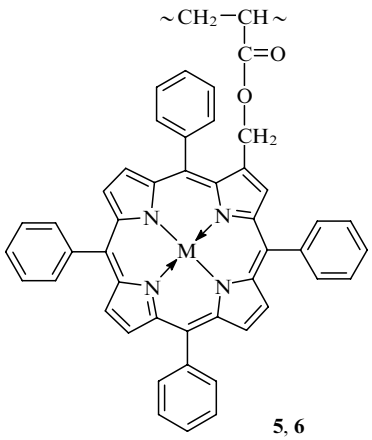
The synthesis of copolymers **4** soluble in chloroform, based on mono-*N*-acryloylated [tetra(*p*-aminophenyl)porphyrinato]manganese (TAPPMn), vinylpyridine and methyl methacrylate, has been reported.[29]



4

The content of TAPPMn in copolymer **4** was 3 mol % – 7 mol %, $M_w \approx (2.5 – 4.0) \times 10^4$.

Benzene- and chloroform-soluble polyacrylates **5**, **6** with $M_w \approx (0.7 – 2.0) \times 10^4$ containing copper and vanadyl tetraphenylporphyrins (TPPCu and TPPVO) have been prepared by radical polymerisation of the corresponding monomers.[30] It was found that the molar extinction coefficient for the Soret band is lower for the polymer than for the monomer and a new absorption band appears at 630 nm. This may be due to electronic interaction of the porphyrin rings with fragments of the polymer chain.



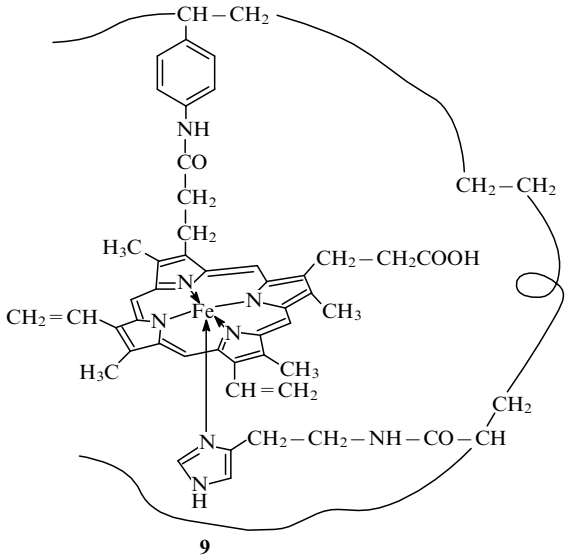
5, **6**

M = Cu^{2+} (TPPCu, **5**), VO^{2+} (TPPVO, **6**).

For the preparation of catalysts with controlled activity, one can use systems **7** and **8** formed upon polycondensation of pyrrole, sodium *o*-formylbenzenesulfonate and dipyrrolyletioporphyrin (Scheme 1).[31] Using this reaction, it is possible to introduce a definite amount of porphyrin into the polymer to obtain a non-conjugated (**7**) or polyconjugated (**8**) porphyrin-containing polymer.

After metallation, such systems can be active in decomposition of hydrogen peroxide, oxidation of phenol and other processes that take place in aqueous media.

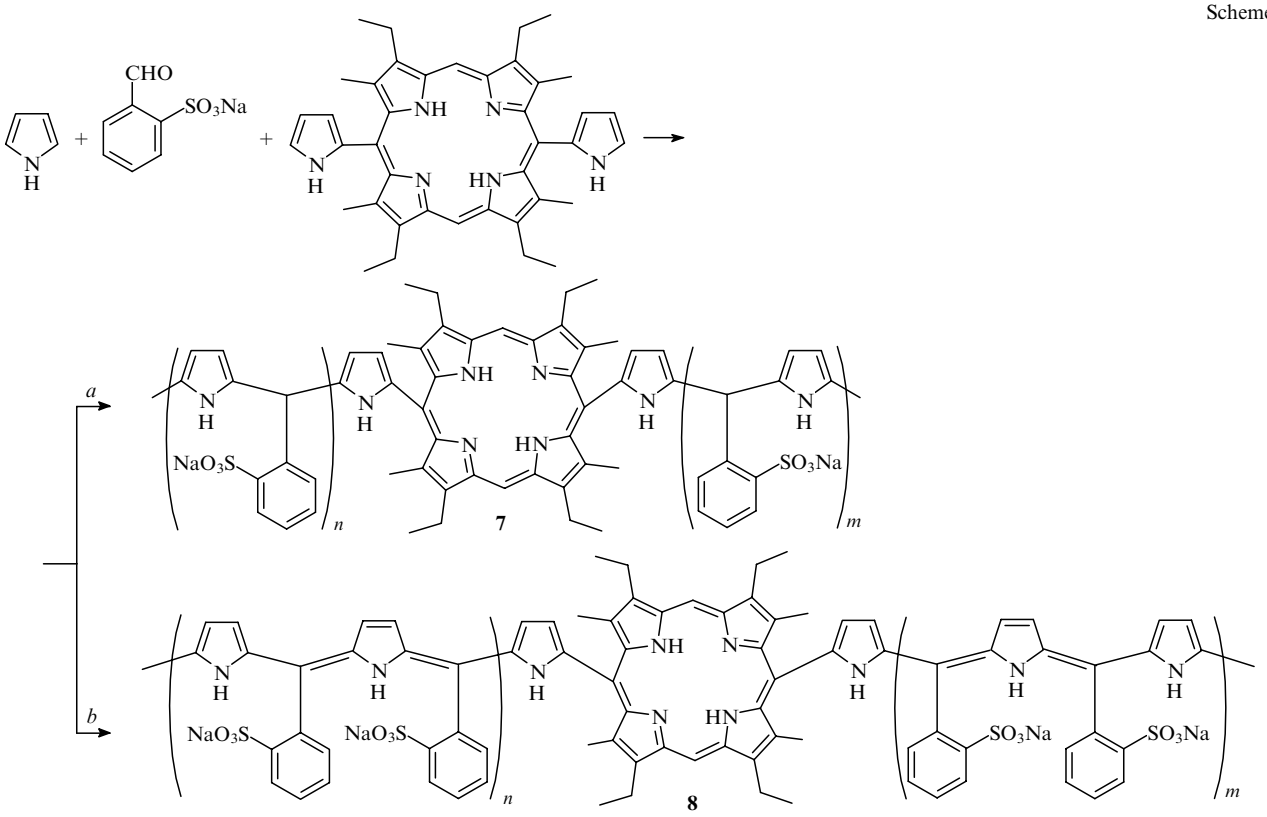
Mixed-type porphyrin-containing polymers (for example, **9**) have also been reported.[32] In these polymers, MP are linked to the polymer support by covalent bonds through substituents present in the pyrrole rings of the porphyrin ligand; the central metal ion in the MP is additionally coordinated by the functional groups of the polymer chain. Shown below is the structure of the polymer modified with hemin, which is bound to the polymer chain by both covalent and coordination bonds (compound **9**).[32]



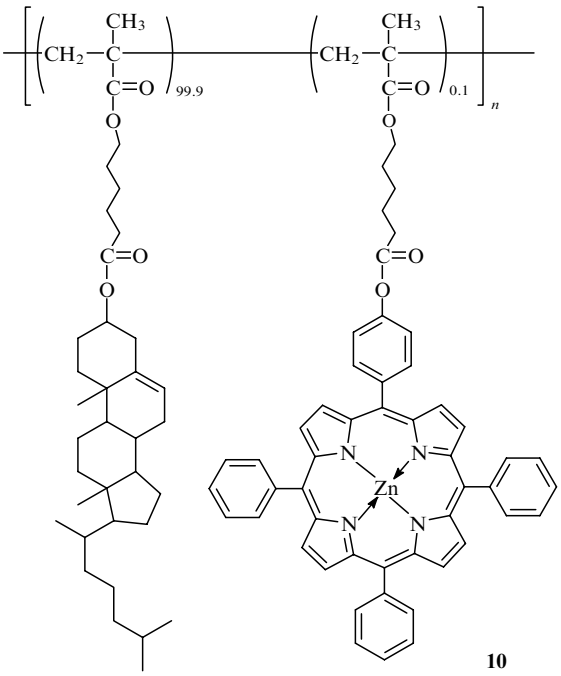
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Polymers **10**, containing zinc tetraphenylporphyrin (TPPZn) and cholesterol, were prepared by copolymerisation of (5-methacryloyloxyhexanoyloxyphenyl-10,15,20-triphenylporphyrinato)zinc with cholesteryl methacryloyloxyhexanoate.[33]

Scheme 1



(*a*) H^+ (Cat.), DMF, room temperature, N_2, 24 or 50 h; (*b*) H^+ (Cat.), DMF, room temperature, O_2, 6 days.

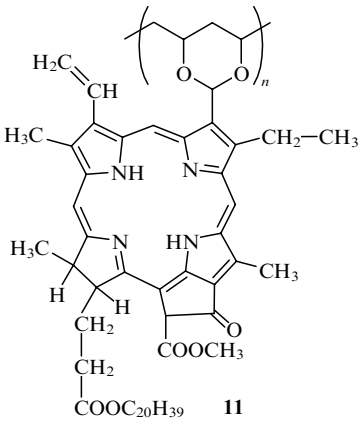


10

The content of TPPZn in polymers **10** was 0.1 mol %. It was suggested [33] that in this copolymer, the cholesterol residues are involved in electronic interactions, resulting in the formation of 'cavities' which accommodate the porphyrin fragments.

Polymer systems containing covalently bonded porphyrins can be obtained by treatment of polymers having functional groups (carboxy, amino, hydroxy) with porphyrins containing reactive substituents in the ring. Thus the reaction of low-molecular-mass poly(ethylene glycol) with mesoporphyrin IX containing carboxy groups afforded porphyrin-containing polymers efficient in the photogeneration of singlet oxygen.[34]

Some studies discuss the problems of polymer modification by metalloporphyrins. In particular, Govorov and co-workers [35–38] described the synthesis of polymeric catalysts based on poly(vinyl alcohol) (PVA) and a number of natural porphyrins, namely, pheophytin *b* (catalyst **11**), rhodin g_7, and their copper and cobalt complexes.



11

The resulting catalysts proved to be active in the decomposition of hydrogen peroxide in an aqueous medium.[35, 36]

A rather simple method for the preparation of porphyrin-containing insoluble polymers has been exemplified in tetra(aminophenyl)porphyrin (TAPP) modification of chloromethylated polystyrene [39] and polybenzaldehyde [40] cross-linked by divinylbenzene (Fig. 3). The subsequent metallation of these compounds by cobalt or aluminium salts resulted in the synthesis of polymeric MC used for reversible binding of molecular oxygen.

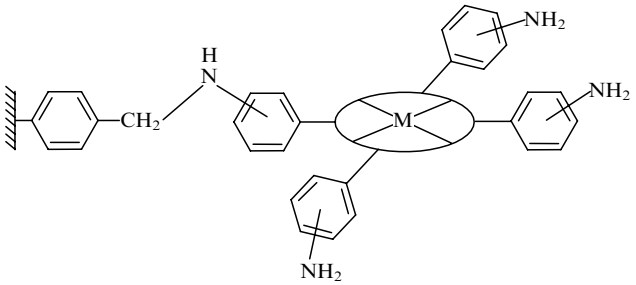
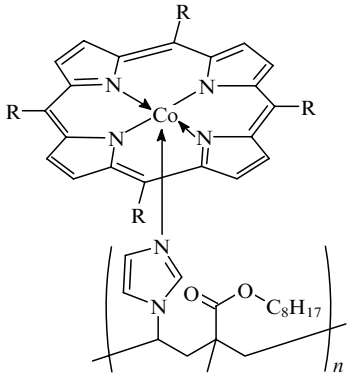


Figure 3. Structure of TAPP immobilised on chloromethylated polystyrene cross-linked by divinylbenzene.[39]

A similar method has been used to prepare polymeric catalysts on the basis of chloromethylated polystyrene and TAPPMn.[41] This catalyst proved to be active in the epoxidation of alkenes in the presence of imidazole or pyridine.

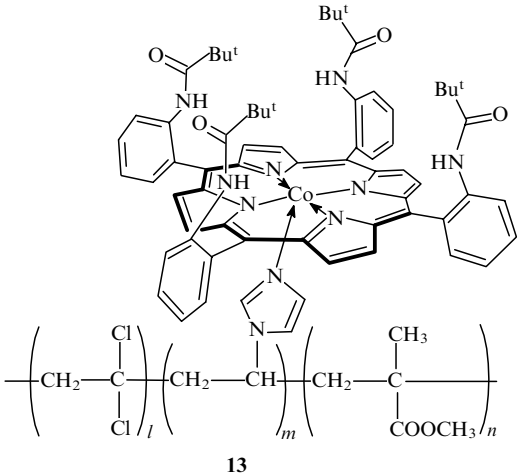
3. Metalloporphyrins bound to the polymer matrix by coordination bonds

The coordination of MP to polymers occurs most often through the central metal atom. Thus porphyrinatocobalt coordinated to the imidazole fragment of the octyl methacrylate – 1-vinylimidazole copolymer (polymer **12**) has been used to prepare oxygen permselective membranes.[42]



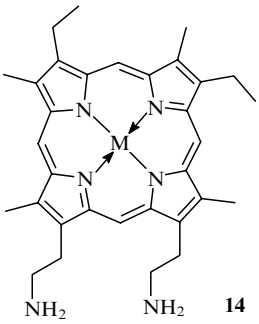
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The membranes were prepared from a solution of these compounds in acetone. The same researchers obtained copolymers **13** of vinylidene dichloride, methyl methacrylate and vinylimidazole containing porphyrinatocobalt immobilised through coordination bonds.[43] Membranes composed of this material were also oxygen permeable (the oxygen molecules were transferred through the membrane by the hopping mechanism).



13

Development of water-soluble polymeric catalysts based on metalloporphyrins is the subject of one more study of the same groups of researchers,[44] which describes the synthesis of micellar systems from aminoporphyrins (for example, etioporphyrin **14** containing amino groups).



14

These micellar systems are stabilised by polyelectrolytes [polyallylamine or poly(vinyl sulfate)] through the formation of donor–acceptor bonds (Fig. 4).

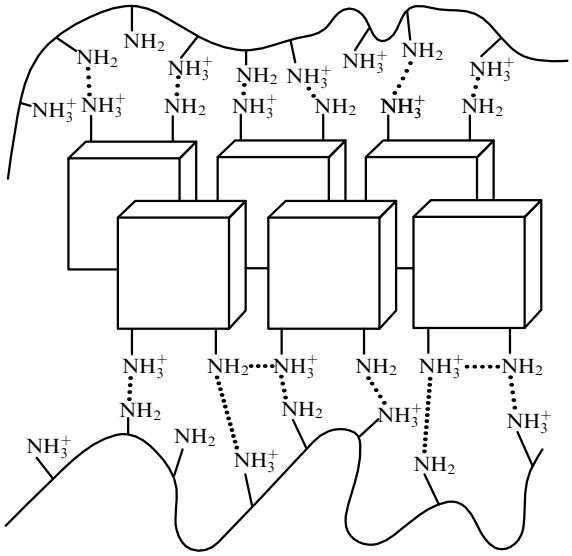
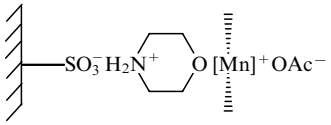


Figure 4. Structure of the complex formed by MP **14** and polyallylamine.[44]

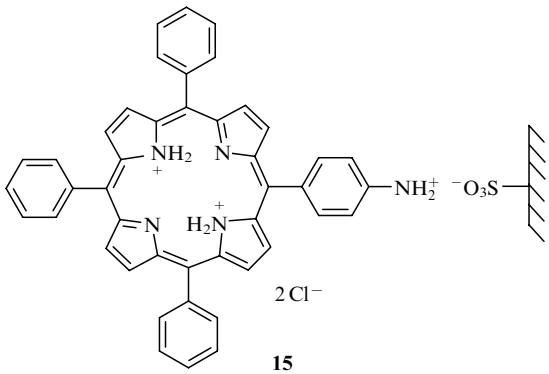
4. Polymeric catalysts with an ionic bond between metalloporphyrins and the matrix

The ionic interactions of MP with the polymer support can be found in the polymeric catalysts based on perfluorinated sulfonated cation exchange polymers (Nafion type) in the morpholine form and manganese porphyrins.[45–47] Manganese porphyrins are immobilised on a sulfonate cation exchange membrane of the Nafion type through a morpholine bridge.[45]



These systems exhibit catalytic activities toward hydroxylation of steroid alkenes in the presence of morpholine or imidazole.

It is noteworthy that metal-free porphyrins can also be fixed on sulfonate cation exchange materials (due to the formation of ionic bonds). For example, immobilisation of 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin (ATPP) in the protonated form on a sulfonate cation exchange matrix has given polymeric catalyst **15**,[47] active in the photogeneration of singlet oxygen.[46]



15

V. Catalyst systems with metalloporphyrins embedded in micelles

Owing to the low polarity and the presence of charged groups and bound water, the structurally organised micellar aggregates can be used as analogues of a protein globule.[48] For example, in oxidation of organic substrates by oxygen-containing compounds in the presence of metalloporphyrins, phospholipid vesicles have been used as structure-forming agents,[49] resulting in a pronounced increase in the degree of conversion and a change in the reaction regiospecificity. Metalloporphyrins embedded in micellar structures were found to exhibit monooxygenase activity,[50] typical of P-450 type enzymes. Borovkova *et al.*[50] studied the kinetics of catalytic oxidation of unsaturated hydrocarbons with a system MP–reducing agent ($NaBH_4$)–dioxygen in the presence of micelle-forming agents, namely, Surf I (cetyltrimethylammonium bromide in a heptane–chloroform–ethanol mixture) and Surf II [sodium bis(2-ethylhexyl)sulfosuccinate in a heptane–ethanol mixture]. These systems displayed an extremal dependence of the specific rate constant k_s for the non-chain oxidation of cholesterol, anthracene and substituted naphthalenes on the concentrations of Surf I and Surf II (Fig. 5 and 6), the k_s value increasing significantly upon variation of the Surf I and Surf II concentrations in the ranges 0.05–0.30 mol litre^{-1} and 0.1–1.0 mol litre^{-1}, respectively. In the absence of surfactants, a certain contribution to the k_s value is apparently made by

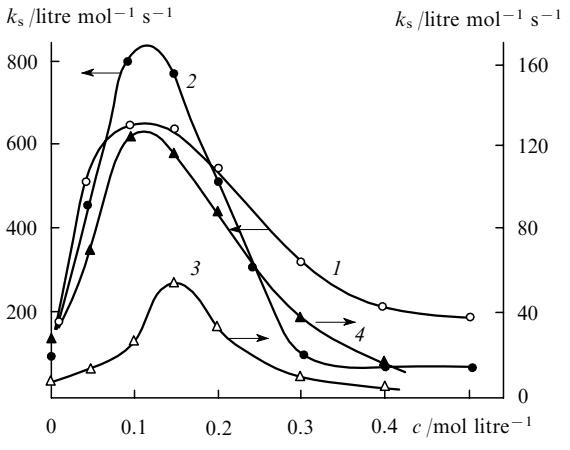


Figure 5. Dependences of k_s for oxidation of cholesterol (curves *1–3*) and anthracene (curve *4*) by the MP–$NaBH_4$–O_2 system on the concentration of Surf I in a chloroform–heptane mixture (1 : 1). MP = TPPMnCl (*1*, *2*, *4*) and TPPFeCl (*3*).[50]
The concentrations of cholesterol, anthracene, TPPMnCl, TPPFeCl and $NaBH_4$ were 2.2×10^{-3}, 4.3×10^{-3}, 6×10^{-5}, 1.3×10^{-4} and 0.1 mol litre^{-1}, respectively.

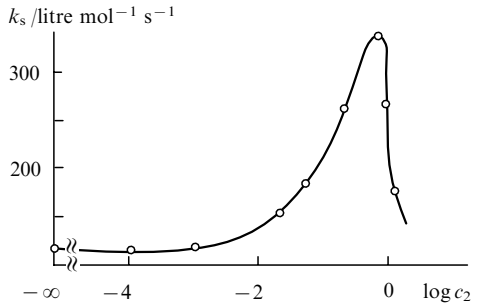


Figure 6. Dependence of k_s for the oxidation of cholesterol with the TPPMnCl – $NaBH_4$ – O_2 system on the concentration of Surf II.[50]
The concentrations of cholesterol, TPPMnCl and $NaBH_4$ were 2.2×10^{-3}, 6×10^{-5} and 0.1 mol litre^{-1}, respectively, and the concentration of EtOH was 2.65 vol.%.

diffusion restrictions; the reaction proceeds either in the diffusion or in the mixed diffusion and kinetic region.

The specific rate constant k_s in question was determined from the rate of formation of the product (v_p) at initial time instants

$$k_s = \frac{v_p}{[S][Cat]},$$

where $v_p = dQ/dt$ (Q is the concentration of the product, t is time), [S] and [Cat] are the substrate and catalyst concentrations, respectively. The catalysts used were tetraphenylporphyrin complexes with manganese, iron and cobalt (TPPMnCl, TPPFeCl and TPPCo). The manganese complex TPPMnCl was the most active in the oxidation of any of the studied substrates both in the presence and in the absence of surfactants. The specific rate constant for the non-chain oxidation of cholesterol increased 8 – 10-fold in the presence of Surf I and 10 – 18-fold in the presence of Surf II. The k_s value for the oxidation of anthracene increased by a factor of 5 – 8 when the system contained Surf I.

The products formed upon oxidation of cholesterol and anthracene were the same (3β,5α-cholestanediol and 9,10-anthraquinone, respectively) as those formed in the absence of surfactants in the reaction mixture,[51] while the ratio of the oxidation products of 2,6-dimethylnaphthalene and 2-methylnaphthalene (epoxytetralins and dihydroxytetralins) changed from 1 : 1 (without a surfactant) to 2 : 3 (with a surfactant).

The concentrations of Surf I and Surf II corresponding to a sharp increase in k_s were substantially higher than the critical micelle concentrations (CMC's) for both surfactants. Reverse micelles were formed with the polar tails of the surfactant molecules directed inwards. The observed extremal pattern of dependences $k_s = k_s$([surfactant]) can be attributed to redistribution of the catalyst and substrate molecules between the organic and micellar phases.[52] An increase in the surfactant concentration is accompanied by an increase in the concentration of micelles and efficient accumulation of the substrate and the catalyst in the micelle bulk, which entails an increase in k_s (see Figs 5 and 6). Upon further increase in the surfactant concentration to values an order of magnitude greater than the CMC, phase separation with destruction of the reverse micelles starts in the reaction mixture, and process kinetics returns to the initial regime (observed in the absence of a surfactant).

The validity of the qualitative conclusions concerning the extremal dependence of k_s on c is also supported by the observed extremal dependence of k_s for the oxidation of cholesterol on the concentration of MP for surfactant concentrations exceeding the CMC (Fig. 7, curves *1* and *2*) and by the fact that k_s almost does not depend on the MP concentration when no surfactant is present (Fig. 7, curve *3*).

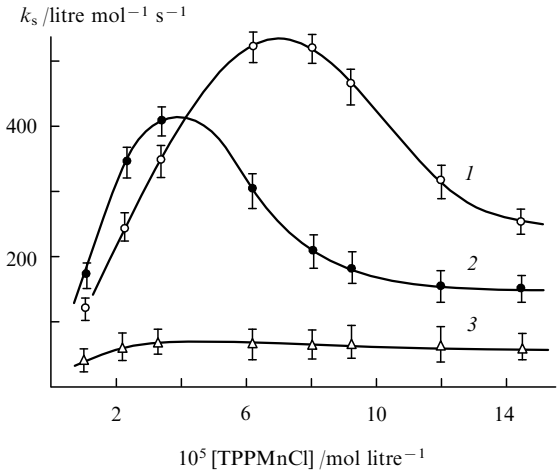


Figure 7. Dependence of k_s for the oxidation of cholesterol with the TPPMnCl – $NaBH_4$ – O_2 system on the concentration of TPPMnCl in the presence of Surf II (curve *1*), Surf I (curve *2*) and in the absence of surfactants (curve *3*) (in heptane).[50]
The concentrations of Surf I, Surf II and cholesterol were 0.05, 0.5 and 2.2×10^{-3} mol litre^{-1}, respectively, the concentration of EtOH was 2.65 (*1*) and 4.42 vol.% (*2*, *3*).

It is also evident that some concentration limit should exist for embedding of substrate molecules into the micellar phase. This is indicated by the dependences of the observed rate of cholesterol oxidation v_p in the presence of micelle-forming agents of both types on the cholesterol concentration shown in Fig. 8. The fact that the kinetic curves reach a stationary level (unlike the linear dependence of u_p on the cholesterol concentration in the absence of a surfactant) demonstrates the saturation effect in substrate embedding into the micelles.

The dependence of k_s values for these oxidation processes on the content of an aliphatic alcohol (or water) in the reaction mixture also deserves attention (Fig. 9). The necessity of introducing an alcohol (polar component) into the reaction mixture is due to the fact that sodium tetrahydroborate is insoluble in nonpolar

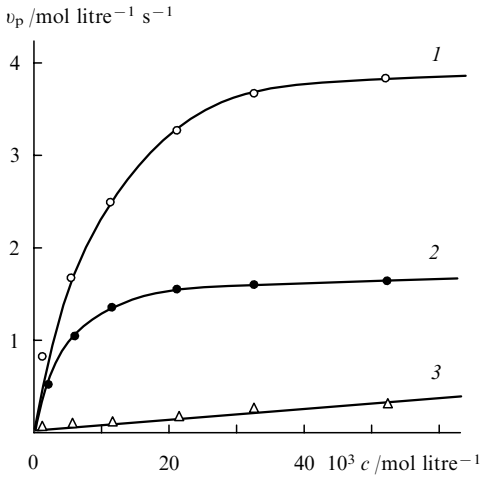


Figure 8. Rate of cholesterol oxidation v_p with the TPPMnCl – $NaBH_4$ – O_2 system *vs.* cholesterol concentration in the presence of Surf I (curve *1*), Surf II (curve *2*) and in the absence of surfactants (curve *3*) in a chloroform – heptane mixture (1 : 1).[50]
The concentrations of Surf I, Surf II and TPPMnCl were 0.05, 0.5 and 6×10^{-5} mol litre^{-1}, respectively; the concentration of EtOH was 2.65 vol.%.

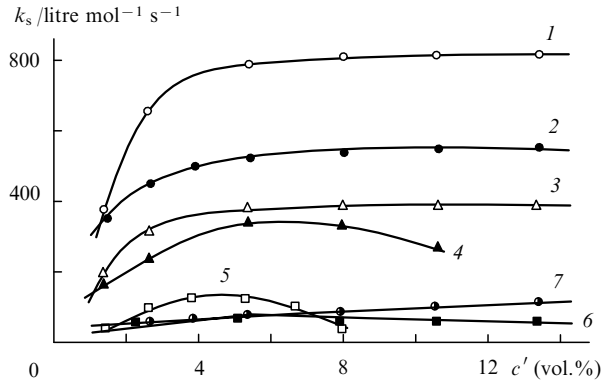


Figure 9. Dependences of k_s for cholesterol oxidation with the TPPMnCl–$NaBH_4$–O_2 system on the alcohol (or water) concentration (c') in the presence of Surf II (curves *1*–*6*) and in the absence of Surf II (curve *7*). The introduced alcohol (or water) used: ethanol (*1*–*3*), propan-2-ol (*4*), water (*5*), n-butanol (*6*).[50]
The concentrations of cholesterol and TPPMnCl were 2.2×10^{-3} and 6×10^{-5} mol litre^{-1}, respectively, the concentration of Surf II was 0.2 (*1*), 0.1 (*2*), 0.05 (*3*–*6*) and 0 (*7*, in heptane) mol litre^{-1}.

solvents or chloroform. Depending on the nature of the alcohol, its concentration in the reaction mixture was 2.5 vol.%–3.0 vol. % . An increase in the content of alcohol (water) in the system resulted in a lower stability and a smaller size of the reverse micelles.

It was found that the rate of oxidation of cholesterol in the presence of Surf II decreases in the following sequence of the polar components added to the system: ethanol > propan-2-ol > n-butanol > methanol > water. The low k_s values observed with water and methanol are due to fast destruction of the reducing agent and loss in its activity.

It was also shown that the introduction of Surf I into the reaction system increases k_s for the oxidation of anthracene and the degree of its conversion (k_s increases 5–6-fold and the degree of conversion increases to 100%). Studies on the oxidation of substituted naphthalenes showed that the presence of reverse micelles formed by Surf I increases the specific rate constant for the oxidation of 2-methylnaphthalene in the presence of TPPCo by a factor of 4–6, and for 2,6-dimethylnaphthalene, this factor is 6–8. Simultaneously, the degrees of conversion increase from 10% to 30% and from 30% to 80%, respectively. The ratio of the oxidation products somewhat changes due to an increase in the yield of dihydroxy derivatives of tetralins (with respect to epoxy alcohols).

A significant feature found for the oxidation of hydrocarbons in the presence of surfactants is the substantial increase in the stability of the active form of the catalyst, which is more pronounced in the presence of Surf I than Surf II. It has been shown[50] for the oxidation of cholesterol in the presence of TPPMnCl that the turnover number of TPPMnCl until its complete decomposition ('discoloration') increased from 20–25 to 240–250 in the presence of Surf II and from 35–40 to 860–870 in the presence of Surf I. These data attest to a decrease in the rate of catalyst destruction. Apparently, this is related to a decrease in the probability that the intermediate complex $[MP]^{2+}$–O_2–substrate involved in the oxidation[51] would react with the hydroperoxide adducts formed during the reaction.

The above data provide grounds for treating MP solubilised by reverse micelles as a new type of porphyrin-containing catalyst for non-chain oxidation of alkenes characterised by enhanced efficiency and stability compared to monomer analogues.

VI. Catalytic activity of soluble and insoluble polymeric systems with immobilised porphyrins and their metal complexes

The catalytic activity of non-immobilised MP in the chain oxidation of unsaturated hydrocarbons by dioxygen in the presence of reducing agents has been described.[51] It was shown that the Mn^{3+} and Fe^{3+} porphyrin complexes in the presence of sodium tetrahydroborate are efficient catalysts of the following reactions:

— regioselective oxidation of mono-, di- and trisubstituted aliphatic and trisubstituted steroid alkenes to ketones and secondary (or tertiary) alcohols (in the case of Δ^5-steroid alkenes, the reaction proceeds with 100% stereo- and regioselectivities);

— oxidation of anthracene, its alkylated and phenylated derivatives and phenanthrene to the corresponding quinones; and

— oxidation of alkyl- and phenyl-substituted naphthalenes to dihydroxy- and epoxy-derivatives of tetralin.

A mechanism for the catalytic action of MP has been proposed. The mechanism is underlain by the view which implies the formation of an intermediate ternary complex MP–O_2–substrate where dioxygen is activated to a singlet-like state. Within the framework of this mechanism, it became possible to describe the whole set of data obtained for reactions of this type. New methods for the oxidation of cholesterol to 3β,5α-cholestanediol (a new reaction in the chemistry of steroids) and oxidation of C_4–C_6 alkenes to tertiary alcohols have been developed.

1. Porphyrin-containing polymeric systems in the catalytic oxidation of steroid alkenes by dioxygen in the presence of reducing agents

This Section considers the results of studies[29,45,46] dealing with oxidation of steroid alkenes with MP catalysts immobilised on polymers in the presence of sodium tetrahydroborate. The oxidation of these substrates by dioxygen was carried out in ethanol or its mixture with chloroform. The effective rate constants k_{ef} were found from the kinetic curves for oxygen absorption by the reaction system at the initial instants.

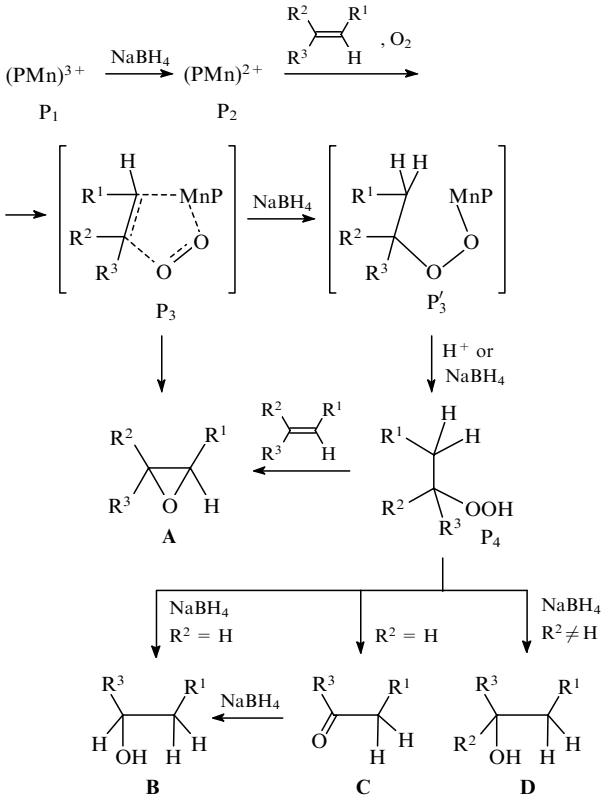
a. Oxidation of cholesterol in the presence of soluble polymeric catalyst systems

Soluble polymeric catalysts (PC) containing PMn were prepared by copolymerisation of methacrylates with the *N*-acryloyl derivative based on [tetra(*p*-aminophenyl)porphyrinato]manganese (PMn-AA) (the product of reaction between acryloyl chloride and TAPPMnOAc). The copolymers obtained in this way proved to be active catalysts for the oxidation of steroid alkenes (cholesterol, androstene). However, aliphatic, dienic, and fused aromatic hydrocarbons (ethylene, propylene, hex-1-ene, hex-2-ene, isoprene, anthracene and its derivatives or substituted naphthalenes) were not oxidised in the presence of these soluble PC. It was shown that oxidation of cholesterol to 3β,5α-cholestanediol in the presence of soluble PC and $NaBH_4$ proceeds *via* the formation of cholesterol hydroperoxide, like oxidation in the presence of non-immobilised PMn,[51] *i.e.*, the oxidation mechanism can be considered to remain the same on passing to soluble PC.

The scheme of catalytic action of MP in the presence of a reducing agent proposed in a number of studies[51,53–55] assumes the formation of an intermediate complex containing, apart from the reduced MP and dioxygen, a substrate molecule. It is significant that dioxygen and the alkene are coordinated on one side of the plane of the porphyrin ring. The possibility of this coordination is determined by the ability of the central ion of the MP occurring in the high-spin state to emerge from the plane of the porphyrin macrocycle by a distance of up to 0.05 nm. Previously, the existence of intermediate ternary complexes of this type has been postulated in the discussion of the oxidation mechanism of substrates involving haem enzymes.

It was assumed that the first stage ($P_1 \rightarrow P_2$) of the catalytic process (Scheme 2) is the reduction of the central ion in the MP molecule. The possible scheme of hydroxylation of substituted alkenes with the $PMn-O_2$ system in the presence of sodium tetrahydroborate is presented below.[51]

Scheme 2



The reaction of the reduced form of the catalyst (P_2) with the alkene and dioxygen molecules ensures the regioselectivity of the process and results in the intermediate product P_3. Subsequently, under the action of the reducing agent, complex P_3 is converted into final products (**A**–**D**), possibly, *via* intermediate compounds P'_3 and P_4. Depending on the alkene structure and the oxidation conditions, this can give ketones and secondary or tertiary alcohols. In the case of trisubstituted alkenes, the intermediate adduct P_3 with the tertiary carbon atom can be converted under the action of sodium tetrahydroborate (in particular, *via* hydroperoxide P_4) directly into tertiary alcohol. If complex P_3 contains a secondary carbon atom, *i.e.*, the initial alkene is disubstituted ($R^2 = H$), the hydroperoxide P_4 can either disproportionate to give ketones or be reduced on treatment with $NaBH_4$ to give secondary alcohols. According to this scheme, epoxides can be produced by two routes, namely, by disproportionation of the intermediate complex P_3 (this process predominates in the absence of hydride reducing agents) and by the reaction of hydroperoxide P_4 with a second alkene molecule (epoxidation of alkenes with hydroperoxides is a well-known reaction). Table 1 presents the effective 'specific' rate constants k_s for the oxidation of cholesterol related to the concentration of PC (for soluble PC) and the low-molecular-mass analogue (TAPPMnOAc) (*i.e.*, per catalyst molecule): $k_s = \upsilon_p/([MP] \times [substrate])$, where υ_p is the rate of transformation of cholesterol during the initial instants.

It follows from Table 1 that immobilisation can result in a substantial increase in the 'specific' TAPPMnOAc activity. This increase in the rate constants can be related to an increase in the local concentration of cholesterol near the active site caused by the participation of the macromolecular chain of the polymer catalyst in the effective sorption of the substrate. Evidently, in this case, the PC macromolecules should be sufficiently flexible. Indeed, an increase in the chain rigidity caused by introduction of a large amount of PMn into the polymer chain entails a decrease in the specific catalytic activity of copolymers based on MMA and PMn-AA, while the PC based on 4-vinylpyridine and PMn-AA, which exists in solution as a rigid solvated structure, is virtually inert in this process. However, the introduction of MMA fragments into this PC increases the catalytic activity of the resulting terpolymer. The copolymers of PMn-AA with BMA and OMA do not exhibit a catalytic activity, possibly due to the shielding of the MP active sites by bulky side groups of the polymer support.

Table 1. Kinetic parameters of oxidation of cholesterol by dioxygen in the presence of copolymers of various acrylates and vinylpyridine (VP) with PMn-AA in a chloroform – ethanol mixture (1 : 1) at room temperature.[27]

Second monomer [a]	[PMn] (mass %)	10^5 [PMn] /mol litre^{-1}	$10^5\,\upsilon_p$ /mol litre^{-1} s^{-1}	k_s /litre mol^{-1} s^{-1}
MMA	0.3	1.87	1.14	60.9
MMA	1.0	6.14	1.90	32.4
MMA	3.5	21.8	2.21	10.1
BMA	0.5	3.12	0.31	9.8
OMA	0.1	0.62	0.01	1.6
4-VP	0.4	2.5	0.01	0.4
4-VP – MMA	0.6	3.74	0.47	12.7
Alkylated 4-VP – MMA	0.6	3.74	0.12	3.18
TAPPMnOAc (see [b])	100	125	1.95	1.52

Note. The cholesterol and $NaBH_4$ concentrations were 1×10^{-2} and 5.5×10^{-2} mol litre^{-1}, respectively.
[a] Designations: MMA is methyl methacrylate, BMA is butyl methacrylate, OMA is octyl methacrylate, 4-VP is 4-vinylpyridine; [b] non-immobilised complex.

The temperature dependence of the effective rate constant for the oxidation of cholesterol in the presence of PMn-AA copolymers with MMA and BMA passes through a maximum at about room temperature (Fig. 10, curves *1* and *2*). It should be noted that upon a decrease in the molecular mass of the synthesised PC

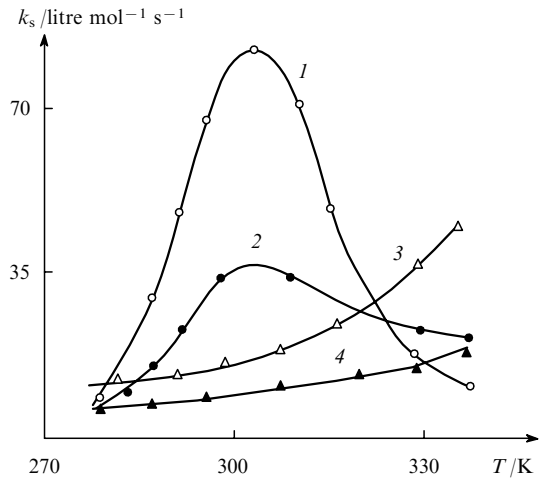


Figure 10. Temperature dependences of the rate constant for the oxidation of cholesterol in the presence of $NaBH_4$ and copolymers of PMn-AA with MMA (curves *1*, *3*) and BMA (curve *2*) and also in the presence of non-immobilised TAPPMnOAc (curve *4*).
The concentrations of cholesterol and $NaBH_4$ were 1×10^{-2} and 5.4×10^{-2} mol litre^{-1}, respectively. The concentrations of copolymers in relation to PMn were 1.8×10^{-5} (MMA) and 3.1×10^{-5} mol litre^{-1} (BMA).
The molecular mass of MMA-based copolymers was 29 000 (curve *1*) and 7 000 (curve *3*).

(transition to oligomers), the k_s decreases and the temperature dependence acquires the Arrhenius form (curve *3* in Fig. 10).

This non-monotonic behaviour of k_s implies the possibility of temperature-induced conformational transitions in the system. In particular, this may be the rearrangement of the secondary structure of the polymer caused by the formation of hydrogen bonds. These processes are completed over a certain temperature range. Usually, rearrangements of this type are described using a cooperativity parameter depending on temperature (in the above-indicated temperature range) according to an activation law and defined as the equilibrium constant of the formation of one rupture in the sequence of hydrogen bonds. In the same temperature range, the intrinsic viscosity of the system (η) should also change according to the equation

$$\eta = \eta_0 \exp \frac{E}{RT} ,$$

where E is the activation energy for viscous flow. Indeed, the $\eta(T)$ dependences observed experimentally for the MMA copolymer with PMn-AA (the content of PMn was 0.3%), like those for poly(methyl methacrylate), were 'rectified' in the appropriate coordinates.[29] It is noteworthy that the introduction of 0.3% of porphyrin-containing groups in the copolymer changes the activation energy for viscous flow from 25.2 (for PMMA) to 50.4 kJ mol^{-1} (for the PMn-AA copolymer).

b. Catalytic oxidation of cholesterol, substituted anthracene hydrocarbons and phenanthrene in the presence of metalloporphyrins immobilised on a perfluorinated sulfonate cation exchange copolymer

The insoluble PC containing MP were prepared by copolymerisation of methyl methacrylate with PMn-AA in the presence of a cross-linking agent (divinylbenzene) and by immobilisation of a number of monomeric PMn [P = TPP, tetra(*p*-methoxyphenyl)-porphyrin (TMPP) and hematoporphyrin (HP)] on insoluble polymeric supports at room temperature from solutions in dioxane in the presence of heterocyclic nitrogenous bases. Table 2 presents the data on the chemical structures and activities of the catalysts.

The insoluble copolymers of MMA and PMn-AA containing 3 mass % – 5 mass % of TAPPMnOAc proved to be inert toward oxidation of cholesterol. The introduced PMn were easily washed out from the polymer matrices based on butadiene – styrene (**21**, **22**) and divinylbenzene – styrene (**19**, **20**) copolymers (see Table 2) under reaction conditions in a chloroform – ethanol solution. The low catalytic activity of the copolymers obtained by copolymerisation of PMn-AA with MMA or DVB (PC **23** – **25** in Table 2) became somewhat higher for lower degrees of cross-linking. This fact can be attributed to low accessibility of active sites of the catalyst in the cross-linked copolymer because the corresponding soluble PC (MMA copolymers with PMn-AA) exhibited high catalytic activities.

Catalysts **17** prepared by immobilisation of PMn on insoluble perfluorinated (sulfonate) cation exchange polymer films MF-4SK in the morpholine form manufactured at the scientific-production association Plastpolymer (St-Petersburg) exhibited a high catalytic activity towards the oxidation of cholesterol and anthracene. However, aliphatic alkenes were not oxidised in the presence of these catalysts. Note that if the central ion of the MP was linked to ionogenic groups of copolymers as a counter-ion, immobilisation resulted in the loss of the catalytic activity of PMn. This loss of activity can be attributed to the 'rigid' localisation of the Mn^{3+} in the vicinity of the ionogenic groups of the copolymers, which can prevent the reduction of the central ion and activation of oxygen. The 'rigid' fixing can be avoided by performing coordination of PMn through a bifunctional bridge, *i.e.*, heterocyclic nitrogenous base (morpholine, imidazole, piperazine). This type of immobilisation took place in the transformation of the sulfonate cation exchange copolymer into the morpholinium form (this process was monitored by IR spectroscopy based on the appearance of an absorption band at 3060 cm^{-1} corresponding to the protonated form of morpholine in the spectra of copolymers) with subsequent treatment of this copolymer with a solution of PMn in dioxane (the absorption

Table 2. Some properties of insoluble polymeric catalysts.

Polymeric support	X (Y)	PC	Percentage of PMn washed out in 30 min	Content of PMn (mass %)	k_s /litre mol^{-1} s^{-1}
$-(CF_2-CF_2)_n-(CF_2-CF(OCF_2O(CF_2)_2SO_3^-X))_m-$ (MP-4SK)	H^+	**16**	–	2.5	10^{-5}
	morpholine [a]	**17**	–	3.0	28 – 30
$-(CF_2-CF_2)_n-(CF_2-CF(OCF_2O(CF_2)_2COO^-X))_m-$	H^+		–	3.0	10^{-5}
	morpholine [a]	**18**	15 – 20	3.0	see [b]
$-(CH_2-CH(C_6H_4CH=CH_2))_n-(CH_2-CH(C_6H_4SO_3^-X))_m-$	H^+	**19**	2	2.5	10^{-3}
	morpholine [a]	**20**	20 – 25	2.0	see [b]
$-(CH_2-CH(CH=CH_2))_n-(CH_2-CH(C_6H_4SO_3^-X))_m-$	H^+	**21**	3 – 4	2.5	10^{-3}
	morpholine [a]	**22**	20 – 25	2.5	see [b]
$-(CH_2-C(CH_3)(COOCH_3))_n-(CH_2-CH(CONHTPPMn))_m-Y_l$	(0.1% DVB) [c]	**23**	–	1.2	10^{-3}
	(0.3% DVB) [c]	**24**	–	1.5	10^{-3}
	(0.6% DVB) [c]	**25**	–	2.0	10^{-4}

[a] Morpholine in the protonated form. [b] In experiments in which more than 5% of PMn contained in the PC passed to the solution, the k_s value was not calculated. [c] DVB is divinylbenzene.

band of the morpholinium ion was retained in the IR spectra of the copolymers).

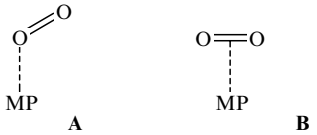
The ability of the MF-4SK copolymer to bind PMn without the loss of catalytic properties of porphyrin is apparently due to the presence of fluorine-containing fragments in the α-position with respect to the SO_3^- groups, which causes migration of the electron density to the α-carbon atoms and thus enhances the acid properties of the copolymer sulfonic groups. In addition, the hydrophobicity of the fluorocarbon framework prevents the penetration of the polar solvent molecules into the diffusion channels of the copolymer;[56] as a consequence, the solvation environment of the ionogenic groups of MF-4SK differs substantially from that of the sulfo groups in other copolymers. The MF-4SK copolymer, unlike butadiene–styrene and divinylbenzene–styrene rubbers, has a rather ordered structure of simply connected channels along which the diffusion transfer of partially solvated ions and molecules takes place. This may stipulate high efficiency of the transfer of the initial reactants and products in MF-4SK along this system of channels.

Experimental data related to the kinetics of oxidation of cholesterol by dioxygen in the presence of the MF-4SK polymeric catalyst and $NaBH_4$ are presented in Table 3.

It can be seen that the rate constants for the oxidation of cholesterol (k_s) in the presence of monomeric and immobilised PMn are of the same order of magnitude but for insoluble PC, the overall yield of the product per catalytic site markedly increases due to the increase in the turnover number (μ) of the catalyst. This parameter introduced during generalisation of the formal Michaelis–Menten kinetics [51] characterises the number of product molecules formed per 'catalyst molecule' throughout the whole process until the catalyst has completely decomposed, which necessarily takes place due to oxidative destruction processes. As regards the data presented in Table 3, note that, whereas the rate constant for cholesterol oxidation in the presence of monomeric PMn is affected substantially by the nature of the substituents in the porphyrin macrocycle, in the case of immobilised HPMn and TPPMn, the k_s values are virtually the same. It has been shown above that the rate constants for the oxidation of substrates in the presence of soluble PC in a homogeneous catalytic process increase due to the 'polymeric effect', namely, due to the involvement of polymeric fragments in effective sorption of the substrate. However, a substantial increase in the turnover number of the insoluble PC (10–100-fold compared to that of monomeric HPMn) is apparently indicative of a substantially lower susceptibility of immobilised PMn to destruction.

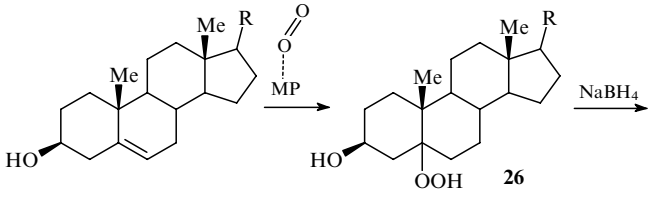
The destruction processes that take place during the catalytic action of monomeric PMn and PFe and soluble PC containing them proceed apparently through bimolecular reaction of the reduced catalyst (P_2) with oxygen adducts (P_3 and P_3') or with the intermediate compound P_4 (see Scheme 2), resulting in cleavage of the conjugation chain of the porphyrin ring. With the above-described coordination of PMn near the sulfo groups of the polymer matrix, these bimolecular destruction processes occur at a considerably lower rate, which is responsible for the longer service life of insoluble PC. It should be emphasised that the aggregative state of the catalyst may dictate the route of oxidation.[57] Indeed, cholesterol is oxidised to 3β,5α-cholestanediol in the presence of both soluble monomeric PMn and insoluble PC, while anthracene is oxidised to anthraquinone in the presence of monomeric PMn, but only anthracene endoperoxide is formed in the presence of insoluble PC containing PMn. Alkyl-substituted anthracenes and phenanthrene are oxidised in a similar way (*i.e.*, to endoperoxides).

The whole set of results can be easily interpreted within the framework of the above Scheme 2 accordng to which oxygen reacts with reduced MP at initial stages of the process and then the ternary intermediate complex, MP–O_2–substrate, is produced. According to Scheme 2, no noticeable transfer of charge or spin density to oxygen takes place in the adducts formed from PMn and PFe with O_2, and oxygen passes into a reactive singlet-like state.[58] For the oxygen adducts PMn^{2+} and PFe^{2+}, two alternative structures were proposed, one with the terminal tilted attachment of the dioxygen molecule to the MP (structure **A**) where the Mn and Fe cations are linked to only one of the oxygen atoms and the M–O–O angle is 120° and the other, with a symmetrical arrangement of oxygen (structure **B**) with the central cation coordinated to the oxygen double bond.



According to quantum-chemical calculations,[58] structure **A** is energetically favourable for isolated complexes. However, the complexes are stabilised in solutions due to solvation effects and the proportions of forms **A** and **B** do not necessarily correlate with the quantum-chemical estimates; therefore, in the general case, both structures should be taken into account.

When a catalytic reaction is carried out in a polar solvating solvent, the probability of interaction between the substrate and the catalyst in form **A** or **B** depends obviously on the nature of the substrate. The polar cholesterol molecules (dipole moment $\mu_C = 1.99$ D) should be coordinated preferably near complexes of type **A**. This type of interaction is responsible for the subsequent formation of 5α-hydroperoxycholesterol (**26**), which then reacts with sodium tetrahydroborate, being reduced to alcohol **27**.

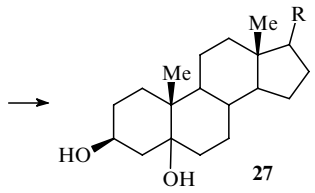


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Table 3. Kinetic parameters of cholesterol oxidation in the presence of PMn immobilised on perfluorinated sulfonate copolymer MF-4SK and monomeric PMn in ethanol at 20 °C.[45]

Catalyst system	10^2 [Cholesterol] /mol litre^{-1}	k_s /litre mol^{-1} s^{-1}	$10^{-2}\mu$	Degree of conversion (%)
TMPPMnOAc	4.0	9	2	96
Immobilised TMPPMnOAc *	8.0	26	400	95
TPPMnOAc	4.0	8	2	95
Immobilised TPPMnOAc *	8.0	26	400	96
HPMnOAc	2.5	0.5	1.2	80
Immobilised HPMnOAc *	8.0	30	400	96

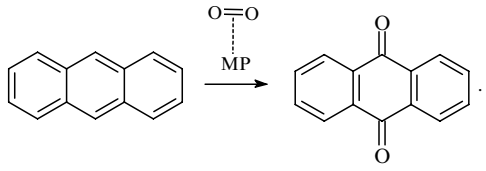
Note. The concentrations of $NaBH_4$ and PMn were 5×10^{-2} and 2.5×10^{-3} mol litre^{-1}, respectively. In the case of insoluble polymeric catalysts (asterisked), the conventional concentration [PMn] corresponding to the amount of PMn contained in the polymer per ml of the reaction mixture was calculated.



27

R = $CH(CH_3)(CH_2)_3CH(CH_3)_2$.

For the symmetrical anthracene molecules, having an extensive system of π-conjugation, the coordination and the formation of the intermediate ternary complex with form **B** of the catalyst are apparently more energetically favourable, although the content of this form in the solution may be lower than that of form **A**. Anthraquinone is produced according to the following scheme



An activated transition of form **A** into form **B** upon coordination of anthracene near the $MP-O_2$ complex is also possible. It is clear that for cholesterol the formation of this product is completely ruled out. However, at high PMn concentrations where the proportion of form **A** markedly increases, anthracene can also react with the 'asymmetrical' form of the oxygen adduct $PMnO_2$, which leads to the appearance of anthracene endoperoxide in the reaction system. This is also facilitated by the large bulk of the $PMnO_2$ complex with a tilted orientation of oxygen (form **A**).

When PMn is immobilised on insoluble polymer supports, the symmetry of the molecular fields of the above-described complexes decreases, which would suppress even more strongly the formation of symmetrical oxygen adducts (**B**), *i.e.*, the probability of formation of the corresponding oxidation products would diminish. Indeed, it has been noted above that oxidation of anthracene on insoluble immobilised PMn gives only anthracene endoperoxide.

2. Immobilised porphyrins and their metal complexes in hydroxylation, decomposition of hydrogen peroxide, electrooxidation, reversible binding of substrates, epoxidation and photocatalysis

Examples of the title processes catalysed by immobilised porphyrins and metalloporphyrins are given in Table 4. This list of reactions should be considered as a supplement (with some refinement) to the information on these reactions considered in the previous review.[59]

Let us discuss in more detail the processes included in Table 4.

It has been shown that immobilisation of phaeophytin *b* and its cobalt and copper derivatives on PVA yields active catalyst systems used for H_2O_2 decomposition.[36, 37] The catalytic activities of phaeophytin and its metal complexes in aqueous solutions of H_2O_2 are nearly equal. In the absence of porphyrin, with cobalt chloride dispersed in PVA, the reaction does not proceed. Cobalt complexes of phaeophytin dispersed in water do not initiate the reaction either. The mechanisms of these processes have not yet been elucidated; however, it has been suggested[36, 37] that the

Table 4. Examples of processes catalysed by immobilised porphyrins and their metal complexes.

Catalysed process	Catalyst system [a]	Type of binding	Ref.
Decomposition of hydrogen peroxide	phaeophytin *b* (**11**), rhodin g_7, their Co and Cu complexes immobilised on poly(vinyl alcohol)	covalent	36, 37
Epoxidation of alkenes	TAPPMn (**4**) immobilised on chloromethylated polystyrene cross-linked by divinylbenzene	"	41
Photooxidation of hydrocarbons	$TPPFe^{III}$ – Nafion	ionic	60
Hydroxylation of cholesterol and alkenes	copolymers of TAPPMn with methacrylates (methyl, butyl, octyl) and 4-vinylpyridine	covalent	29
	TPPMn (TMPPMn or HPMn) – morpholine – Nafion	ionic	45, 46
Hydroxylation of aniline and oxidation of alkenes	$TPPFe^{III}$ – poly(γ-methyl-L-glutamate)	covalent	61
Electrooxidation of NO	glassy carbon electrode – polymeric TMHPP – Nafion	physical adsorption	62
Reversible oxygen binding	PCo – vinylimidazole copolymer with octyl methacrylate (sensor system)	coordination	42
	$H_2TPP(2\text{-}NHCOBu^t)_4$ – copolymer of vinylidene chloride, vinylimidazole and methyl methacrylate	"	43
	TAPPCo immobilised on chloromethylated polystyrene cross-linked by divinylbenzene	covalent	39
Photogeneration of singlet oxygen	TMPP tosylate (**1**) – regenerated cellulose	physical adsorption	10
	$TMPPPd^{II}$ – $TDCPPFe^{III}$ – Nafion	ionic	60
	MATPP (**15**) – Nafion	"	47
	(tetrapyridylporphyrinato)tin – silica	physical adsorption	63
Photoinduced modelling of oxygenase activity	TPPFe – Nafion	ionic	64

[a] Designations: TAPP is 5,10,15,20-tetra(*p*-aminophenyl)porphyrin; TMHPP is tetrakis(3-methoxy-4-hydroxyphenyl)porphyrin, TMPP is tetrakis(*N*-methylpyridinium-4-yl)porphyrin, TDCPP is tetrakis(2,6-dichlorophenyl)porphyrin, MATPP is 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin.

mechanisms of decomposition of H_2O_2 in the presence of phaeophytin and its metal complexes are different.

The epoxidation of alkenes[41] takes place with the participation of sodium periodate in acetonitrile in the presence of imidazole or another nitrogenous base. Due to the high degree of matrix cross-linking, the immobilised TAPPMn behaves as a typical heterogeneous catalyst where only near-surface layers are active. Immobilisation increases markedly the catalyst stability against degradation in the presence of sodium periodate, which is a strong oxidant. The degree of conversion reaches 95%.

The oxidation of a mixture of cyclohexene and cyclohexane by dioxygen on exposure to sunlight at 20 °C under atmospheric pressure has been studied.[60] In addition to the $TPPFe^{III}$ – Nafion system, the researchers used also chlorinated or fluorinated analogues of porphyrinatoiron immobilised on Nafion. The porphyrins were added to the reaction mixture after swelling of the resin in a mixture of dichloromethane and ethanol. The immobilisation of $TPPFe^{III}$ was found to result in a growth of the photocatalytic activity and stability of the catalyst. The ratio of the products formed in the catalytic reaction differed somewhat (from that obtained in the oxidation in the presence of non-immobilised porphyrinatoiron).

The covalent binding of TPPFe to poly(γ-methyl L-glutamate) afforded polymeric catalysts active in hydroxylation of aniline on treatment with hydrogen peroxide and in the oxidation of alkenes.[61] Immobilisation was carried out in aqueous methanol. The catalyst obtained in this way was much more active than non-immobilised analogues.

Cizewski *et al.*[62] developed a sensor device for determination of nitrogen oxide based on its anodic oxidation. The catalyst was prepared by successive deposition *via* electropolymerisation of tetrakis(4-hydroxy-3-methoxyphenyl)porphyrin (or its nickel complex) and Nafion film layers onto the surface of a glassy carbon electrode. The oxidation proceeded throughout the whole bulk of the film. The limit of determination of nitrogen oxide by this method was 10^{-4} mol litre^{-1}.

It should be noted that metalloporphyrins and metallophthalocyanines deposited on graphite or carbon electrodes are often used in electrooxidation or electroreduction processes (for example, proton to hydrogen). The use of Nafion films containing metalloporphyrins, in particular TPPCo, for coating the electrodes increases the efficiency of this process.[65–68]

Membrane systems selectively permeable for oxygen have been prepared using cobalt porphyrin complexes and polymer supports.[39, 42, 43] The polymeric systems based on vinylimidazole copolymers proved to be most efficient. The introduction of Co into the polymer increased the membrane permeability by a factor of 25. The ratio of the oxygen and nitrogen permeability coefficients of the membranes reached several hundreds.

The photogeneration of singlet oxygen upon photoexcitation of regenerated cellulose films containing adsorption-bound porphyrins has been studied.[10] The photogeneration of singlet oxygen to the gas phase has been studied in the presence of protonated MATPP immobilised on the Nafion film and on quartz[47] and in the presence of (tetrapyridylporphyrinato)tin supported on silica gel.[63] The process was more efficient with MATPP immobilised on a polymer support. The efficiency of generation of singlet oxygen was found to increase with an increase in the temperature of the support. The TPPFe immobilised on the Nafion film was used to model the oxygenase activity exhibited by the system on photoexcitation.[64]

To summarise the data, it can be stated that immobilisation of MP on insoluble polymeric supports results most often in a higher stability of the catalyst. This may also change the selectivity and increase the efficiency of the catalysed processes compared to the processes taking place in the presence of free MP. If the substrate is a bulky molecule, as is the case for hydroxylation of cholesterol, the MP molecule should retain some mobility during the catalytic transformation. However, in other cases, there is no need for MP mobility (the case of photogeneration of singlet oxygen on MATPP immobilised on Nafion).

Some publications deal with the redox reactions taking place in metalloporphyrin (Co, Zn, Mn, *etc.*) molecules immobilised on poly-4-vinylpyridine and Nafion. In this case, polymeric films with immobilised MP were applied on glass electrodes,[69–73] which were immersed into an electrolyte solution. The electrochemical charge transfer to the polymeric film was studied in a three-electrode system.

VII. Photochemical processes involving deposited layers of porphyrins

In recent years, the possibilities of functional use of not only porphyrin-containing polymer systems but also molecular aggregates and supramolecular ensembles formed with participation of porphyrin molecules and metalloporphyrins have been found. Scanning probe microscopy (SPM) and its versions — scanning tunnelling (STM), atomic-force (AFM) and scanning magnetic (SMM) microscopies — allow one not only to examine the arising structures at the atomic and subatomic levels but also to transfer and isolate separate molecules on a solid surface.[74–78] These techniques cover the scale from fractions of a nanometre to several micrometres. The appropriate instruments allow one to control the 'assembly' and the structural organisation of molecular and supramolecular ensembles. In particular, recently STM has been used to elucidate the supramolecular aggregation on the surface of gold of the molecules of substituted tetraphenylporphyrin containing cyanophenyl substituents, which initiate the aggregation. This aggregation gave di-, tri- and tetrameric (*cis* and *trans*) aggregates.[79] The STM technique was also used to visualise *in situ* the process of formation of highly ordered structures of tetramethylpyridiniumporphyrin (in the form of tosylate) on an iodine-modified gold surface.[80] The process was performed in 0.1 M solutions of perchloric acid.

The new potential of nanotechnology can be associated with the use of deposited molecular layers formed under self-assembly conditions where the structural organisation of the layers (for nanometre to fractions of micrometre levels) is dictated by the structure of the molecules and interactions between them. Porphyrins and related molecules can be used for deposition, as they are capable of aggregation upon both precipitation from solutions and sputtering onto various substrates. In this Section, we present the results of investigation of the structure of vacuum deposited layers of tetraphenylporphyrin and some of its derivatives over a broad range of surface concentrations N_{tot} ($N_{tot} \approx 10^{-11}$–10^{-9} mol cm^{-2}) of deposited molecules.[81] These layers proved to be functionally active for generation of the singlet oxygen $^1O_2$ to the gas phase upon the photosensitised excitation of the molecular oxygen $^3O_2$ adsorbed on the deposited TPP layer. The rate of generation of $^1O_2$ depended on the structure of deposited layers on scales of about fractions of a micrometre. The conclusions concerning the structure of porphyrin layers on different spatial scales were drawn from the micrographs obtained by transmission electron and atomic-force microscopy. The recent interest in the photogeneration of singlet oxygen to various media is related to the possibility of initiating the photosensitised oxidation of biologically active substrates and to the problem of photodynamic therapy in medicine.

Here, it is pertinent to note that SPM analysis of the surface structure is based on the processing of digitised 'roughness profiles' along the scans obtained from a surface section with characteristic dimensions ranging from tens of nanometres to tens of micrometres. As a rule, the results are represented as images of fragments of the surface structure (for example, molecular aggregates) or the general surface morphology under conditions of 'model highlighting';[82, 83] the appearance of images can depend appreciably on the type of this highlighting and, at the operator's option, pictures different in kind (from the Carpathians to the Himalayas) can be obtained from the same section of the surface.

No routine and generally accepted methods for the processing of digitised data in order to derive parameters generally characterising the key features and peculiarities of the surface under study have been developed as yet. The purely statistical processing methods giving the average roughness and the corresponding variances and semiinvariants are barely used now, because they do not provide information on a significant feature of the structures, namely, the correlations in the spatial organisation of fragments with different spatial scales. The Mandelbrot fractal dimension[84,85] proved to be inadequate for correct representation of the differences between complex surface structures. New prospects for parametrisation have appeared due to flicker-noise spectroscopy (FNS),[86–88] which is based on the views on the information significance of the irregularities in real structures ('spikes', 'jumps' and discontinuities of derivatives) on different spatial scales and the degree of correlation of these irregularities (connectivity) over the surface.

Photogeneration of singlet oxygen to the gas phase was studied in an all-soldered glass setup[81] in the presence of tetraphenylporphyrin and other porphyrin photosensitisers. Porphyrins were sputtered onto quartz plates with an area of 20 cm^2. The surface concentration of porphyrin was determined from the intensity of the Soret band in the electronic spectra of solutions of TPP in chloroform recorded after washing the porphyrin off the surface of quartz plates. The lowest detectable surface concentration was 5×10^{-12} mol cm^{-2}. The $^1O_2$ concentration was determined using semiconductor sensors.[47] The working pressure of dioxygen in the setup was maintained at 0.1 Torr. A DRSh-500 mercury lamp with a BS-8 light filter was used as the light source. The efficiency of photogeneration of singlet oxygen was estimated from the steady-state concentration c_S of singlet oxygen in the setup bulk under continuous photoexcitation of the system (in the absence of a photosensitiser deposited on quartz, no generation of singlet oxygen was detected upon photoexcitation). The data were presented as the reduced bulk concentrations $c_{S_0}^{red} = c_S/c_{S_0}$, the concentration of singlet oxygen formed in the setup at a temperature of 20 °C being taken as c_{S_0}. The c_{S_0} value was estimated using decomposition of 9,10-diphenylanthracene endoperoxide yielding a controlled amount of $^1O_2$.[89] According to this estimate, $c_{S_0} \approx 10^{-13}$ mol cm^{-3} ($\sim10^{11}$ particles cm^{-3}).

Electron microscopy data were obtained using a JEM-2000 EX-II transmission electron microscope. The samples were prepared by depositing TPP on a NaCl single crystal and then carbon replicas were formed from the deposited surface. The generation of singlet oxygen was studied for samples prepared by depositing TPP onto quartz. The surface reliefes were analysed for TPP layers deposited onto mica plates. A Solver P47 atomic force microscope (NT-MDT, Zelenograd) was used. The studies were carried out in the semicontact mode, the surface concentration of porphyrin (N_{tot}) being varied in the range of 10^{-11}–10^{-9} mol cm^{-2}. Electronic absorption spectra were recorded on a Specord UV-VIS spectrophotometer.

Figure 11 presents the dependence of the efficiency of generation of singlet oxygen on the overall surface concentration of TPP. It can be seen that this dependence has a broad maximum in the concentration range $N_{tot} \approx (4–12)\times10^{-11}$ mol cm^{-2}. The photosensitised generation of singlet oxygen is known to start with excitation of the sensitiser molecules and includes several steps.[90] Under experimental conditions, the surface layer of the deposited porphyrin films exists in the stationary photoexcitation state in which electronic-vibrational transitions take place in the molecular-crystalline fragments of the porphyrin layer. The porphyrin molecules in the initial singlet state $^1\Pi$ pass into the excited $^1\Pi^*$ states upon photon absorption. Under the conditions of electronic-vibrational transitions, intersystem crossing becomes possible in the molecular-crystalline fragments giving excited porphyrin molecules in the $^3\Pi^*$ triplet spin state. The photosensitisation of the triplet $^3O_2$ molecules, which are coordinated most probably near the porphyrin macrocycles, can be accomplished through these excited states. In this case, the oxygen

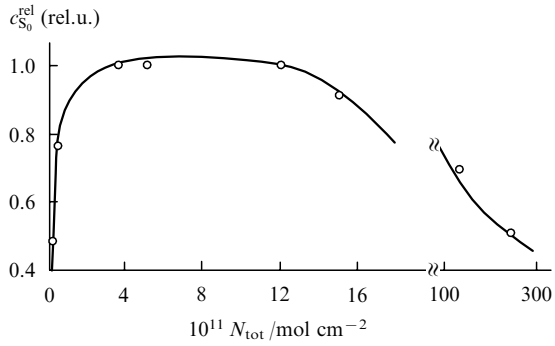


Figure 11. Efficiency of generation of singlet oxygen by deposited TPP layers at different average surface concentrations of porphyrin.

molecules $^1O_2$ in the singlet excited state formed upon energy transfer are also coordinated at the porphyrin molecules. This means that the generation of singlet oxygen to the gas phase is possible only in the case where the characteristic time of desorption of the coordinated $^1O_2$ molecules does not exceed their deactivation time in the coordinated state.

Within the framework of a formal kinetic scheme, from which some of the above-described intermediate steps have been eliminated, the process of $^1O_2$ generation to the gas phase induced by a light quantum $h\nu$ can be represented as the following set of transitions:

$$^1\Pi + h\nu \xrightarrow{k_1} {}^3\Pi^*, \quad (1)$$

$$^3\Pi^* + {}^3O_2 \xrightarrow{k_2} {}^1\Pi + {}^1O_2, \quad (2)$$

$$^3\Pi^* \xrightarrow{k_3} {}^1\Pi, \quad (3)$$

$$^1O_2 \xrightarrow{k_4} {}^3O_2. \quad (4)$$

Here k_1, k_2, k_3 and k_4 are the rate constants for processes (1)–(4), respectively, namely, the formation of porphyrin molecules in the triplet spin state $^3\Pi^*$, generation of the $^1O_2$ molecule to the gas phase, deactivation of the porphyrin molecule in the $^3\Pi^*$ state and deactivation of the $^1O_2$ molecule on the surface sites, in the chamber bulk and on the chamber walls. It is evident *a priori* that chemical transformations (1)–(3) occur on the surface of the porphyrin film; therefore, the rate of these chemical processes should be determined by the surface concentrations of the reactants. However, to simplify the subsequent analysis and to obtain analysable final relations, we shall write the equations of formal kinetics for the concentrations of oxygen molecules in the singlet and triplet states (c_S and c_T) in the gas phase assuming that the necessary equilibrium between the adsorbed and free forms of oxygen is attained over a short period of time. Therefore, all constants appearing in the set of equations of formal kinetics should be taken as effective values. In the stationary case, this set assumes the form

$$\frac{dN^*}{dt} = k_1 wN - k_2 c_T N^* - k_3 N^* = 0, \quad (5)$$

$$\frac{dc_S}{dt} = k_2 c_T N^* - k_4 c_S = 0, \quad (6)$$

$$N_0 = N + N^*, \quad (7)$$

$$c_0 = c_T + c_S, \quad (8)$$

where w is the parameter characterising energy absorption by the deposited layer under photoexcitation conditions (determined by the product of the incident luminous flux, the extinction coefficient and the effective thickness of the absorbing layer); N and N^* are the surface concentrations of the porphyrin molecules in the $^1\Pi$ and $^3\Pi^*$ states, respectively, efficiently involved in the photo-

generation of singlet oxygen; N_0 is the overall surface concentration of the TPP molecules participating in the photosensitised generation of singlet oxygen; and c_0 is the total concentration of oxygen in the gas phase.

The solution of the set of equations (5)–(8) for the steady-state concentration c_S in the gas phase has the form

$$c_S = \frac{k_1 k_2 w N_0 c_0}{k_3 k_4 + k_1 w(k_4 + k_2 N_0) + k_2 k_4 c_0}. \quad (9)$$

It is worth noting that under the experimental conditions, $c_S/c_T \approx 10^{-4}$, which implies fulfilment of the inequality

$$\frac{k_1 k_2 w N_0}{k_3 k_4 + k_1 w(k_4 + k_2 N) + k_2 k_4 c_0} \ll 1. \quad (10)$$

When comparing the obtained expression (9) with the experimentally observed dependence $c_S = c_S(N_{tot})$, one should take into account the effective dependence of the rate constants k_1, k_2, k_3 and k_4 on N_0. It is natural to suggest that $N_0 = \theta N_{tot}$, where θ is the fraction of porphyrin molecules participating in photosensitisation processes. Before discussing these dependences, we shall consider the experimental results of analysis of the structure of porphyrin polymolecular layers formed upon vapour deposition of porphyrin on a quartz substrate.

With low concentrations of the deposited TPP ($N_{tot} \ll 10^{-9}$ mol cm^{-2}), porphyrin islands are formed on the mica and quartz surfaces, the number and the dimensions of the islands being different for different N_{tot}. As follows from the transmission electron microscopy data, when $N_{tot} = 1.8 \times 10^{-11}$ mol cm^{-2}, TPP forms particles with linear dimensions 15–50 nm, the distances between them being greater than the particle size by a large factor. The increase in the surface concentration of TPP to 4.1×10^{-11} mol cm^{-2} results in the growth of both the dimensions of porphyrin particles (30–100 nm) and their number per unit area. Further increase in N_{tot} to 1.5×10^{-10} mol cm^{-2} induces mainly an increase in the linear dimensions of the islands to 100–150 nm. Figure 12 shows typical images of the porphyrin islands for $N_{tot} = 4.1 \times 10^{-11}$ mol cm^{-2}. These micrographs demonstrate that the particles formed are inhomogeneous as regards both their internal structure and the elevation above the support level. When $N_{tot} > 10^{-9}$ mol cm^{-2}, continuous porphyrin layers are formed.

The tentative inferences concerning the crystal structure of porphyrin 'macroislands' were drawn from analysis of the X-ray diffraction patterns obtained using an electron microscope in the microdiffraction mode.[81]

When N_{tot} is low and the deposited layer is mainly composed of small islands, these islands (the seeds for larger aggregates) are crystalline. As the island dimensions increase (with an increase in the surface concentration of porphyrin), the proportion of the amorphous component increases (the number of crystal reflections located on concentric circles diminishes and the amorphous halo grows). When the islands grow to their maximum size, the crystalline component becomes less pronounced. Presumably, the growth of the islands ceases when the crystalline seeds have been coated by an amorphous layer of porphyrin. Thus, upon an increase in the surface concentration N_{tot}, the overall degree of the layer crystallinity decreases and, hence, the degree of amorphisation increases.

The conclusions drawn about the morphology of the deposited TPP layers are confirmed by the data from atomic-force microscopy. The results are presented in Fig. 13 *a*–*c*, which show the typical surface reliefs of deposited TPP for different surface concentrations N_{tot}. The formation of a TPP layer on the support starts with the appearance of relatively small particles with a height of up to 5 nm. When the surface concentration of porphyrin increases to $N_{tot} = 2.0 \times 10^{-11}$ mol cm^{-2}, the height of some aggregates of porphyrin molecules reaches 80 nm, the diameter being 10–50 nm (Fig. 13 *a*), which is in line with the electron microscopy data. Further increase in N_{tot} induces mainly an increase in the number of new (small) seed islands formed on the defects of the mica surface, while the growth of particle height virtually ceases. As the surface concentration reaches $N_{tot} \approx 10^{-9}$ mol cm^{-2}, bridges between the separate aggregates of TPP molecules appear, which gives rise to a continuous layer (Fig. 13 *b*). Figure 13 *c* shows an enlarged image of a surface section obtained at $N_{tot} = 1.5 \times 10^{-12}$ mol cm^{-2} with a separate large porphyrin particle. It can be clearly seen in the relief that the particle is non-uniform in height.

The atomic-force microscopy data were processed in terms of a special programme of flicker-noise parametrisation of chaotic surfaces.[86, 91, 92] The parameters used for the quantitative description of the surface included the average roughness height of the surface h, the correlation length L_1 for the types of surface irregularities (jumps), and the dimensionless parameter n, which is a factor of Fourier spectra in the flicker-noise section describing the rate of loss of the correlation links in the sequence of spike-type irregularities. Table 5 presents the calculated flicker-noise parameters.

The structural features of the porphyrin (TPP) layers deposited on NaCl identified on the basis of electron-microscopy images of the layers recorded at different surface concentrations of TPP, including the high surface concentrations N_{tot} (the region of

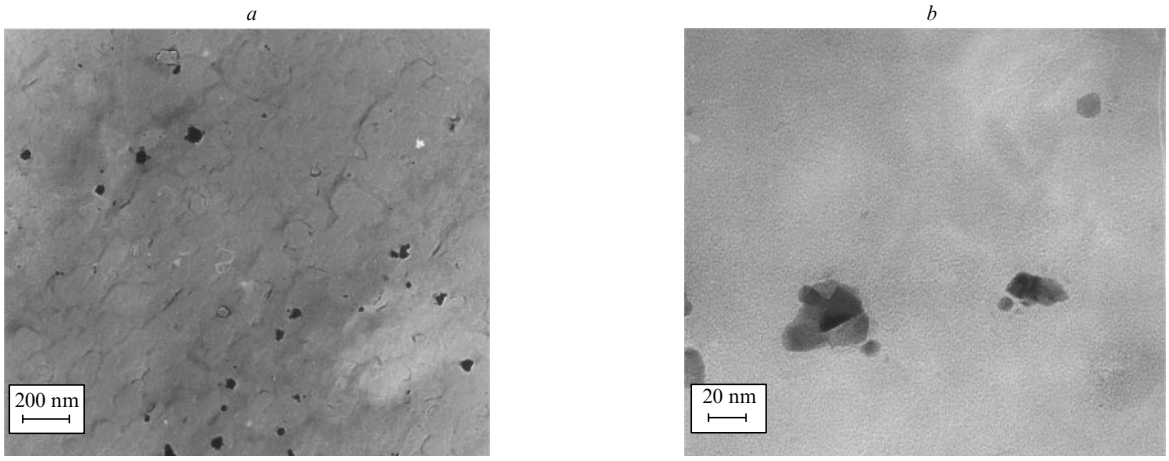


Figure 12. Typical electron micrographs of samples of deposited TPP at a surface concentration of 4.1×10^{-11} mol cm^{-2}. Magnification (*a*) × 50 000, (*b*) × 500 000.

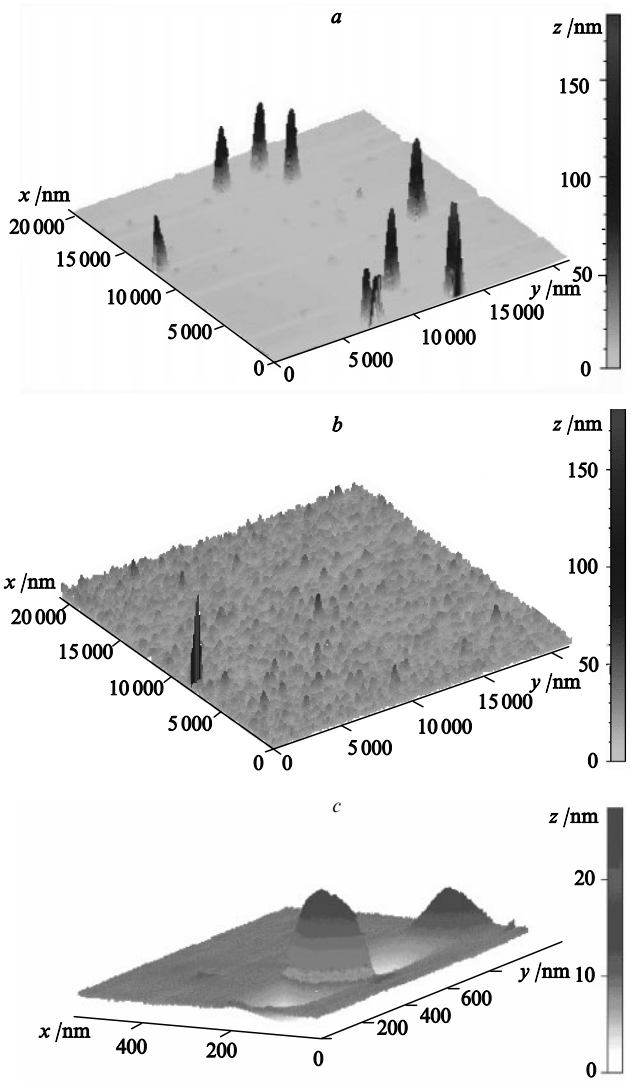


Figure 13. Typical surface reliefs of deposited TPP (*a*, *b*) and a separate island of deposited TPP (*c*).
Dimensions of sections: 20×20 μm (*a*, *b*) and 600×1000 nm (*c*). The surface concentrations of TPP were 2.0×10^{-11} (*a*), 1.3×10^{-9} (*b*), 1.5×10^{-12} mol cm^{-2} (*c*).

continuous layer) are in good agreement with the structural features of mica-deposited TPP layers determined using atomic-force microscopy data on scales of tens and hundreds of nanometres. In other words, the structure of deposited porphyrin layers on submicro- and microscopic scales is determined to a higher extent by the interaction of the porphyrin molecules with one another and, to a lower extent, by the effect of the support (quartz or mica). This conclusion is very significant for the subsequent analysis because the photosensitised generation of singlet oxygen to the gas phase was studied taking TPP layers deposited on quartz as an example. In view of the foregoing, we assume that the pattern of variation of the flicker-noise parameters following an increase in N_{tot}, revealed in analysis of the structure of mica-deposited porphyrin layers, is similar to the pattern of variation of the corresponding parameters of the layers deposited on quartz.

In the analysis, we shall proceed from the data presented in Table 5, which demonstrate how the parameters L_1 and n, which characterise, on the nanometre and submicrometre scales, the structural organisation of the molecular crystals of porphyrins formed upon sputtering onto the quartz support, depend on the surface concentration N_{tot} of porphyrin. In particular, the decrease in the correlation length L_1 and the increase in the

Table 5. Quantitative parameters of deposited TPP layers characterised by flicker-noise spectroscopy.

N_{tot} /mol cm^{-2}	L_1 /μm	n	h /μm
5.2×10^{-11}	0.332	2.85	0.0182
1.3×10^{-9}	0.190	2.86	0.0236
2.4×10^{-9}	0.0623	3.32	0.0316

parameter n with an increase in N_{tot} in the film continuity region attest to the loss of correlation relationships in the film structure following an increase in the surface concentration of porphyrin. This fact may be responsible for the experimentally observed (see Fig. 11) decrease in the rate of generation of singlet oxygen to the gas phase with an increase in N_{tot} in the region of high surface concentrations ($N_{tot} > 10^{-10}$–10^{-9} mol cm^{-2}).

It has been noted above that the formation and the subsequent desorption of $^1O_2$ occur under continuous excitation of the deposited crystalline porphyrin layers. The experimental data obtained in recent years, most often using scanning atomic-force and tunnelling microscopy, confirmed the earlier hypotheses [93, 94] concerning the substantial length of the solid-phase surface regions (from several nanometres to hundreds of nanometres) involved in structural rearrangements after chemisorption of simple gases (H_2, O_2) and the relative retardation (to times of $\sim 10^{-11}$ s or longer) of the relevant electronic and conformational rearrangements.[95, 96]

As applied to the problem we are considering, this means that the structural features of the molecular crystalline porphyrin layers identified on nanometre scales by FNS analysis of atomic-force microscopy data [91, 92] and determining the transfer of the electronic-vibrational excitation in the surface layers can affect the rate of $^1O_2$ generation to a vacuum upon photoactivation of the surface layers of porphyrin crystals. In particular, a decrease in the degree of correlation of fragments of the crystal structure of the surface layers determined by a decrease in L_1 and an increase in n may be expected to result in lower effective rate constants k_1 and k_2, whereas the constants k_3 and k_4 may, on the contrary, increase [see reactions (1)–(4)]. These assumptions, which imply the introduction of effective dependences $k_i = k_i(N_0)$, because the parameters L_1 and n vary with N_{tot} according to a known pattern (see Table 5), provide a natural interpretation for the concentration dependences $c_S = c_S(N_{tot})$ for the steady-state $^1O_2$ concentration presented in Fig. 11 (linear increase in c_S at low N_{tot}, reaching a maximum and a decrease at high N_{tot}) and allow one to estimate the parameters appearing in Eqn (9).

The correlation of the flicker-noise parameters with the surface concentration, which reflects quantitatively the degree of chaotisation of the deposited layer, is in full conformity with the trend of the rate of generation of singlet oxygen to decrease. Attention is drawn first of all by the non-trivial character of the result obtained, in particular, under the conditions of photoexcitation of deposited TPP layers considered here, the rate of generation of singlet oxygen is determined by the structural features of such layers revealed on scales exceeding by two orders of magnitude the proper atomic scale (fractions of a nanometre). Thus, in the heterogeneous photogeneration of $^1O_2$, the crucial role is played by the dynamics of redistribution and accumulation of the excitation energy of polymolecular porphyrin layers with the formation of local dynamic fluctuations sufficient for the generation of singlet oxygen molecules followed by their injection to the gas medium.

In connection with this result, we would like to note the following. The problems associated with the role of heterogeneity of the surface structure at the atomic or molecular level in heterogeneous catalysis have long been debated in the literature. From Temkin's standpoint (cited from Ref. 97), the surface of a heterogeneous catalyst is inhomogeneous in the adsorption capacity. According to Ostrovskii,[98, 99] the surface involved in heterogeneous catalysis is effectively 'homogeneous' in reactivity

of the chemisorbed phase ('chemadphase'), which is largely due to the diffusion transfer of components over the surface. Both suggestions are hypothetical because they are based on analysis of the kinetics of heterogeneous catalytic transformations (in particular, for the synthesis of ammonia) rather than on direct experiments on the measurement of surface diffusion or identification of surface heterogeneity on the basis of reactivity on the atomic level. The more so, because the formal kinetics equations give in both cases the same or similar dependences (see Ref. 98). The concept we develop here concerning the role of dynamic rearrangements of the surface (upon photoexcitation under conditions of heterogeneous catalysis) in the formation of local excitations determining the kinetics of chemical reactions and the efficiency of sorption–desorption processes, actually 'reconciles' these opposite viewpoints. Indeed, the effects of structural rearrangements with reorganisation of metastable fragments of a real surface with external excitation actually 'homogenise' the surface with dimensions of tens or hundreds of nanometres with respect to the kinetics of chemical processes taking place on this surface even when the surface is initially heterogeneous on the atomic level.

In conclusion, it should be noted that photosensitised generation of $^1O_2$ upon photoexcitation of deposited layers proved to be dependent on the chemical structure of the porphyrin molecules. This is demonstrated in Fig. 14, which presents the data on the steady-state concentrations of the singlet oxygen in the gas phase under conditions of photoexcitation of deposited layers of different porphyrins with the surface concentrations $N_{tot} \approx 10^{-11}$–10^{-9} mol cm^{-2} corresponding to the maximum $^1O_2$ generation upon photoexcitation of TPP.

The reduced values of the steady-state concentrations are related to the corresponding value of the concentration of singlet oxygen upon TPP photoexcitation. It follows from Fig. 14 that the efficiency of generation of $^1O_2$ on the photoexcitation of different porphyrins can differ by an order of magnitude: the lowest activity is found for deuterioporphyrin, while the highest one is found for dicarboranylporphyrins CP3 and CP2.[81] The apparent paradox of this result lies in the fact that the dicarboranylporphyrins CP3 and CP2, which form the most active deposited layers, were obtained by introducing carborane substituents into deuterioporphyrin molecules, which not only form the 'least active' layers for the photogeneration of $^1O_2$ but also demonstrate the least photosensitising activity (of all the porphyrins we studied) in the generation of singlet oxygen in homogeneous processes.[81]

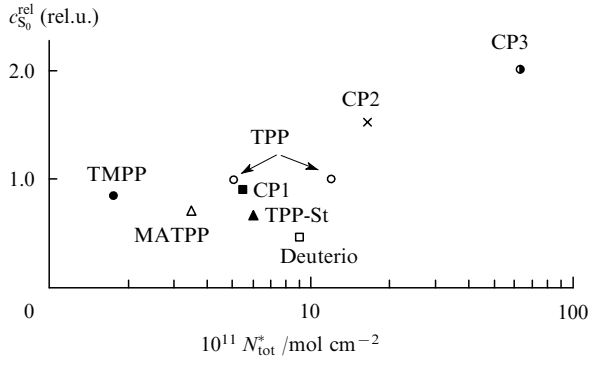


Figure 14. Comparative chart of the efficiency of generation of singlet oxygen by various porphyrins.
The following abbreviations are used: TPP is tetraphenylporphyrin, TMPP is tetra(*p*-methoxyphenyl)porphyrin, MATPP is 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin, TPP-St is 5-(*p*-stearoylaminophenyl)-10,15,20-triphenylporphyrin, Deuterio is dimethyl ether of deuterioporphyrin, CP1 is l,3,5,8-tetramethyl-2,4-divinyl-6(7)-[(2-benzyloxycarbonyl)ethyl]-7(6)-[2-(*m*-carboran-9-yl)oxycarbonylethyl]porphyrin, CP2 is l,3,5,8-tetramethyl-6,7-di[2-(*o*-carboran-3-yl)carbamoylethyl]porphyrin, CP3 is l,3,5,8-tetramethyl-6,7-di[2-(*m*-carboran-9-yl)methoxycarbonylethyl]porphyrin.[51]

The resolution of this paradox can be attributed to the specific structural organisation of porphyrin layers on the nanometre and submicrometre levels produced by packing of the porphyrin molecules deposited on a support under slow deposition conditions. Here, it is pertinent to note that the change in the angle (to 45°) at which the flux of porphyrin molecules is directed on the support has virtually no influence on the efficiency of the resulting layers towards photosensitised generation of singlet oxygen. This means that with the deposition conditions used, one can speak about realisation of quasi-steady-state conditions for the formation of film structure on different spatial scales, where the critical role is played by steric factors and intermolecular interactions. Evidently, the relatively bulky carboranyl substituents in the porphyrin molecules (especially in CP2 and CP3, whose molecules contain two such substituents) favoured the formation of less dense and 'more organised' (less 'chaotised') structures of deposited films under conditions of slow quasi-equilibrium deposition where a great free space ensured the possibility of more equilibrated adjustment of the porphyrin molecules getting on the surface to the structure of the layer. It is noteworthy that elucidation of the features of generation of singlet oxygen to the gas phase upon photoexcitation of deposited layers of various porphyrins allows a targeted search for efficient porphyrin-containing sensitising systems for liquid-phase oxidation of organic compounds.

VIII. Conclusion

The development of efficient catalytic systems based on immobilised metal complexes of porphyrins for specified chemical processes is faced with two types of problem. First of all, it is necessary to know the dynamics of an elementary catalytic event with allowance for all the key factors that influence the process kinetics (here, we mean the influence of electronic and conformation structures of MP, including the type of the central ion and side groups, the environment, and the dynamics of its fragments). Evidently, homogeneous catalyst systems based on MP and the systems with MP immobilised on soluble polymer supports should serve as model systems for the kinetic studies. It is necessary to take into account the role of the solvent and the functional groups (for example, amino acids) of the polymer in the catalytic activity of these systems. Recall that an amino acid residue (histidine) localised in place of one of the haem axial ligands regulates the enzymic activity of cytochrome *c*. A solvent that solvates the MP molecules can also affect appreciably the specific (per MP molecule) catalytic activity due to specific 'heterogeneity' of the solvation shell formed.

The second type of problem encountered in the development of immobilised metalloporphyrin systems is associated with elucidation of the role of the polymeric surrounding of MP. Although immobilisation of MP on a polymeric support results in all cases in lower mobility of the environment fragments near the MP, the choice of the matrix for immobilisation (polymers with functional groups, gels) leaves a place for variation of the local mobility of such fragments. The main point is to understand what positive effects can be attained and what type of labile environment (polar groups, amino acid residues, *etc.*) should be created.

A decrease in the mobility of fragments of the environment in the vicinity of the porphyrin ligand can bring about positive effects, in particular, decrease the probability that destructive factors would occur in the vicinity of the porphyrin ring. Perhaps, this accounts for the substantial increase (compared to the homogeneous case) in the turnover number of PMn immobilised on Nafion film until its degradation during non-chain hydroxylation of cholesterol.

It can be suggested that the search for new efficient porphyrin-containing polymeric systems will also continue along other routes. In our opinion, the main avenue of this research should be development of a fairly controllable labile environment of the porphyrin ligand — in conformity with the key principles of functioning of natural systems.

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