# Preparation and reactivity of metal-containing monomers

## 46.* Copolymerization of vinylporphyrin metal complexes and the structure of the products

*A. D. Pomogailo,*[a]* *N. M. Bravaya,*[a] *V. F. Razumov,*[a] *I. S. Voloshanovskii,*[b] *N. A. Kitsenko,*[b] *V. V. Berezovskii,*[b] *A. I. Kuzaev,*[a] *and A. G. Ivanchenko*[a]

[a]*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,*
*142432 Chernogolovka, Moscow Region, Russian Federation.*
*Fax: 007 (096) 515 3588. E-mail: adpomog@icp.ac.ru*
[b]*I. I. Mechnikov Odessa State University,*
*2 ul. Petra Velikogo, 27000 Odessa, Ukraine*

The radical-induced copolymerization of *meso*-tetraphenylporphyrin monomers with the vinyl group in a benzene or pyrrole ring and their copper and zinc complexes with styrene and methyl methacrylate was studied. Porphyrin comonomers decrease the overall polymerization rate and the number-average molecular weight of the products formed compared to the weight of polystyrene obtained under similar conditions. The main reasons for termination of chain growth by vinylporphyrins were revealed, and some quantitative parameters of these reactions were obtained. IR and electronic absorption spectra of porphyrin-containing copolymers are discussed. According to the ESR spectra, the copper-containing centers in the copolymers are fairly remote from each other, and the metal-containing polymeric systems are magnetically dilute.

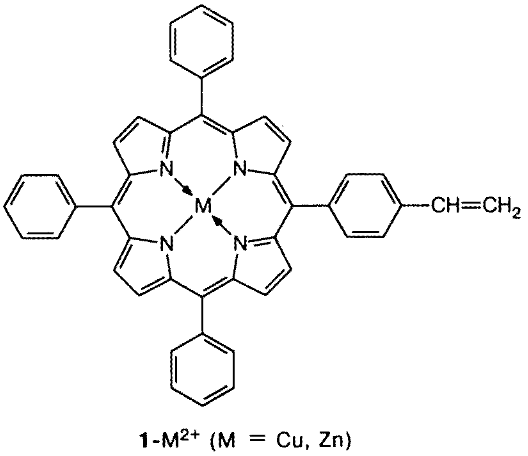
**Key words:** vinylporphyrins, metal-containing monomers, metal-containing polymers, copolymerization, metal-containing copolymers.

Interest in polymeric porphyrins and their macrocomplexes is related to the fact that this class of macroheterocyclic pigments includes such important natural compounds as chlorophylls; they are components of hemoglobins, cytochromes, and many enzymes (catalase, peroxidase, *etc.*). It is significant that in many cases porphyrins in natural systems are aggregated. For example, in the photosynthetic apparatus of green plants and bacteria, the chlorophyll dimer is one of the significant structural units of the photosynthetic reaction center,[1] and the energy of electron excitation due to absorption of a photon is transferred to the reaction center by a so-called light-collecting antenna, which is a structurally organized aggregate of several hundred chlorophyll molecules.[2]

Intense studies have been performed on various associated states of porphyrins, dimers or aggregates of higher orders that are spontaneously formed in concentrated solutions,[3–6] covalently linked dimeric porphyrin molecules,[7,8] and polymer molecules containing a porphyrin cycle.[9–12]

There are two main approaches to the preparation of porphyrin-containing polymers: polymer-analogous transformations (reactions of functional macroligands with the corresponding derivatives of porphyrins or their metal complexes) and copolymerization of porphyrin-containing monomers with traditional monomers. The latter direction is being developed less actively, and one of the reasons for this is the absence of convenient methods for the synthesis of this class of monomers.

A rather simple method has been described[13] for the preparation of *meso*-tetraphenylporphyrin monomers with a vinyl group in the benzene or pyrrole ring, 5-(4-vinylphenyl)-10,15,20-triphenylporphyrin (**1**), 2-vinyl-5,10,15,20-tetraphenylporphyrin (**2**) and copper- (**1**-$Cu^{2+}$ and **2**-$Cu^{2+}$) and zinc-containing (**1**-$Zn^{2+}$ and **2**-$Zn^{2+}$) complexes based on these porphyrins.

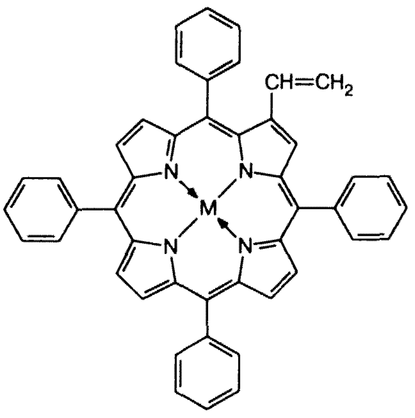


**1**-$M^{2+}$ (M = Cu, Zn)

---

* For Part 45, see *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2404 [*Russ. Chem. Bull.*, 1995, **44**, 1758 (Engl. Transl.)].

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2922—2929, December, 1996.



**2**-M$^{2+}$ (M = Cu, Zn)

The possibility in principle of preparing their copolymers with methyl methacrylate (MMA) and acrylonitrile has been shown.[14] However, neither the kinetic parameters of the process nor the structure and molecular-mass parameters of the products have been studied. This report is devoted to analysis of these problems.

## Results and Discussion

*Copolymerization of **1**, **2**, and their metal complexes.* Let us mention first of all that no radical homopolymerization of the vinylporphyrins considered and their metal complexes initiated by 0.1—2.0% azobisisobutyronitrile (AIBN) occurs at 70 °C in 10 h. This can be a consequence of both steric (related to the bulkiness of the substituent at the double bond) and electronic (conjugation of the generated radical with the system of π-conjugated bonds of the planar macrocycle) factors. From this it follows that the rate constant of the addition of a porphyrin monomer to the radical formed from the monomer is equal to zero ($r_1$ = 0). At the same time, in the copolymerization with styrene, the rate constant of the addition of vinylporphyrin monomers to the styryl radical has a measurable value. It is impossible to obtain the overall copolymerization curve in "composition of the monomeric mixture—composition of the copolymer" ($M_2$—$m_2$) coordinates for two reasons. First, due to the low solubility of vinylporphyrin monomers in toluene it is impossible to achieve a high concentration of them in the monomeric mixture, and second, insoluble copolymers (CPM) form even at a small content of porphyrin units. As a result, the maximum concentration of units of **1** and **2** in CPM ($m_2$) was not greater than 1—2 mol.%.

In all cases, when vinylporphyrin monomers were added, the polymerization rate was lower than the homopolymerization rate of styrene (Figs. 1 and 2). This effect can be demonstrated by the data from Table 1 and by a comparison of the specific heat release during copolymerization of **2**-Cu$^{2+}$ with styrene (see Fig. 1).

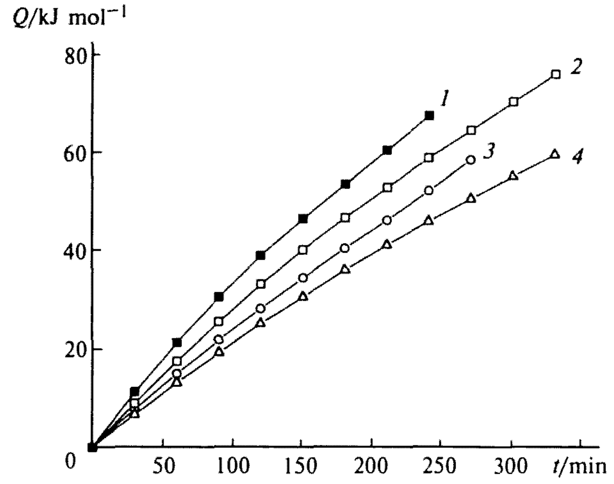


**Fig. 1.** Kinetics of specific heat release during radical polymerization of styrene (*1*) and its copolymerization with 0.1 (*2*), 0.5 (*3*), and 1.0 (*4*) mol.% of **2**-Cu$^{2+}$.

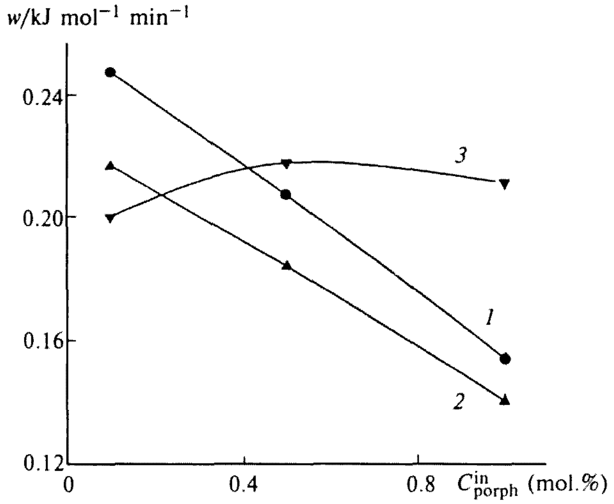


**Fig. 2.** Effect of concentrations of **1** (*1*), **1**-Cu$^{2+}$ (*2*), and **2**-Cu$^{2+}$ (*3*) on the rates of their copolymerization with styrene.

**Table 1.** Initial rates ($w_{\text{init}}$) of copolymerization and time of appearance of gel-effect ($t_{\text{init}}$) in styrene—vinylporphyrin systems

| Sample | $w_{\text{init}}$ /cal mol$^{-1}$ min$^{-1}$ | $t_{\text{init}}$/min |
|---|---|---|
| Styrene | 58.91 | 240 |
| Styrene + 0.1 mol.% **1** | 61.95 | 270 |
| Styrene + 0.5 mol.% **1** | 49.59 | 590 |
| Styrene + 1 mol.% **1** | 37.14 | 590 |
| Styrene + 0.1 mol.% **2**-Cu$^{2+}$ | 51.66 | |
| Styrene + 0.5 mol.% **2**-Cu$^{2+}$ | 43.91 | |
| Styrene + 1.0 mol.% **2**-Cu$^{2+}$ | 34.02 | |
| Styrene + 0.1 mol.% **1**-Cu$^{2+}$ | 47.66 | 220 |
| Styrene + 0.5 mol.% **1**-Cu$^{2+}$ | 52.07 | 200 |
| Styrene + 1.0 mol.% **1**-Cu$^{2+}$ | 50.79 | 180 |

**Table 2.** Comparison of content (molar fractions) of vinylporphyrin comonomers in the initial mixture ($M_2$) and porphyrin units in copolymers formed ($m_2$)

| System | $M_2$ | $m_2$ | Yield of copolymer (%) |
|---|---|---|---|
| Styrene—**1** | 0.001 | 0.0022 | 65 |
| Styrene—**1** | 0.005 | CPM insoluble | 72 |
| Styrene—**1** | 0.010 | (Ditto) | 70 |
| Styrene—**1**-$Cu^{2+}$ | 0.001 | 0.001 | 58 |
| Styrene—**1**-$Cu^{2+}$ | 0.005 | CPM insoluble | 62 |
| Styrene—**1**-$Cu^{2+}$ | 0.010 | (Ditto) | 68 |
| Styrene—**1**-$Zn^{2+}$ | 0.001 | 0.0008 | 56 |
| Styrene—**2**-$Cu^{2+}$ | 0.005 | 0.007 | 58 |
| Styrene—**2**-$Cu^{2+}$ | 0.010 | 0.011 | 54 |
| Styrene—**2**-$Cu^{2+}$ | 0.050 | 0.040 | 55 |
| Styrene—**2**-$Zn^{2+}$ | 0.001 | 0.001 | 63 |
| Styrene—**2**-$Zn^{2+}$ | 0.005 | 0.013 | 60 |
| Styrene—**2**-$Zn^{2+}$ | 0.010 | 0.010 | 55 |

The time of the appearance of the gel-effect in the styrene—**1** system increases considerably (2.2 times), when the content of **1** increases from 0.1 to 0.5 mol.% (see Table 1) and there is a small decrease in the initial polymerization rate. At the same time, copolymerization of styrene with a metal-free vinylporphyrin monomer when the content of the latter is 0.5 mol.% in a mixture of comonomers results in the formation of THF-insoluble copolymers. Copolymerization of the corresponding metal-containing monomer (**1**-$Cu^{2+}$) with styrene occurs with a lower initial rate of polymerization of styrene than homopolymerization of styrene and there is a simultaneous decrease in the time of the appearance of the gel-effect. When the content of the vinylporphyrin comonomer in a mixture is ~0.5 mol.%, THF-insoluble copolymers are also formed. As the data from elemental and spectral analyses show, the composition of the CPM formed depends slightly on the nature and concentration of the porphyrin-containing comonomers (Table 2). No gel-effect was observed during copolymerization of styrene with metal-containing vinylporphyrin monomers **2**-$M^{2+}$ (M = Cu, Zn); the number-average and weight-average molecular weights of the CPM formed (Table 3) were typically lower than those of styrene and CPM based on styrene and monomer **1**.

The regularities observed along with the kinetic parameters of copolymerization and the molecular-mass and spectral parameters of the CPM obtained make it possible to draw some conclusions about the role of vinylporphyrin comonomers and the corresponding metal complexes in the main stages of the process, such as the growth and termination of polymer chains (see below).

*Molecular-weight parameters of CPM.* Copolymers of styrene with **2**-$M^{2+}$ as well as with **1** and **1**-$M^{+}$ when the concentrations of these units are low, are soluble in THF, which made it possible to determine their molecular-mass parameters (see Table 3). The analysis shows that there is a tendency for the number-average ($\bar{M}_n$) and weight-average ($\bar{M}_w$) molecular weights of the resulting products to decrease as the concentration of comonomers **2**-$Cu^{2+}$ and **2**-$Zn^{2+}$ increases. It is of interest that the molecular weights of CPM of styrene with these comonomers are approximately half that of the homopolymer of styrene and CPM of styrene with **1** when the content of the latter in the reaction mixture is low. In addition, according to GLC, a bimodal molecular-weight distribution is observed for CPM with **2**-$Cu^{2+}$ (Fig. 3). The proportion of the high-molecular weight fraction of CPM increases as the content of **2**-$Cu^{2+}$ in the monomeric mixture increases and reaches 40%. It is characteristic that this effect is not observed for CPM of styrene with **2**-$Zn^{2+}$.

A comparison of the kinetic data of the copolymerization of styrene with vinylporphyrin comonomers and

**Table 3.** Molecular-weight parameters of copolymers of styrene with porphyrins and their metal complexes

| Sample (content of copolymer, mol.%) | $\bar{M}_n$ | $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ | Proportion of high-molecular weight fraction (%) |
|---|---|---|---|---|
| Styrene | 145000 | 380000 | 2.62 | – |
| Styrene-**1** (0.1) | 143000 | 678000 | 4.74 | Absent |
| Styrene-**1** (0.5) | Insoluble | | | |
| Styrene-**1** (1.0) | Insoluble | | | |
| Styrene-**2**-$Cu^{2+}$ (0.5) | 77000 | 248000 | 3.22 | 0.6 |
| Styrene-**2**-$Cu^{2+}$ (1) | 68000 | 300000 | 4.41 | ~6 |
| Styrene-**2**-$Cu^{2+}$ (5) | 60000 | 180000 | 3.00 | ~40 |
| Styrene-**2**-$Zn^{2+}$ (0.1) | 106000 | 290000 | 2.73 | Absent |
| Styrene-**2**-$Zn^{2+}$ (0.5) | 45000 | 120000 | 2.66 | Absent |
| Styrene-**2**-$Zn^{2+}$ (1) | 50000 | 120000 | 2.40 | Absent |
| Styrene-**1**-$Cu^{2+}$ (0.1) | 140000 | 390000 | 2.78 | Absent |
| Styrene-**1**-$Cu^{2+}$ (0.5) | Insoluble | | | |
| Styrene-**1**-$Cu^{2+}$ (1) | Insoluble | | | |
| Styrene-**1**-$Zn^{2+}$ (0.1) | 128000 | 470000 | 3.67 | Absent |

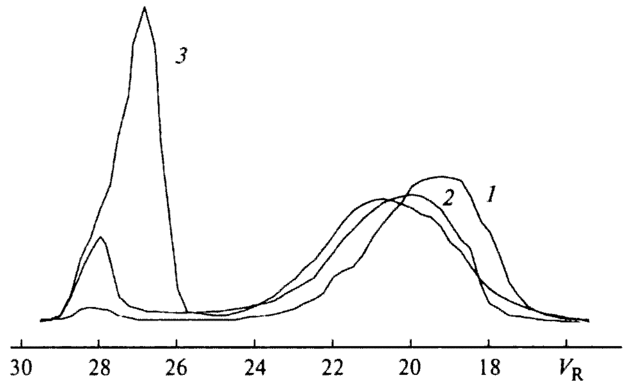


**Fig. 3.** Gel-chromatograms of copolymers of styrene with 0.1 (*1*), 0.5 (*2*), and 5.0% (*3*) of **2**-$Cu^{2+}$.

the analysis of the molecular-weight parameters of the CPM obtained allow us to suggest a mechanism of chain termination. The addition of a vinylporphyrin unit to the growing chain results in its monomolecular pseudotermination (restriction): a macroradical with a terminal porphyrin unit is stabilized by conjugation with the macrocycle (apparently, equally for derivatives **1** and **2**).

Assuming the prevalent termination of growing chains by vinylporphyrin units and based on the analysis of the molecular-weight parameters of CPM, we estimated the relative rate constant ($C_s$) for the restriction of the growing polymer chains using the known correlation:

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

where $\bar{P}_0$ and $\bar{P}_n$ are the mean degrees of polymerization in the absence and in the presence of restricting agents; $C_{porph}$ is the concentration of the vinylporphyrin monomer, $C_s = K_t/K_g$, $K_g$ and $K_t$ are the rate constants for chain growth and termination. This estimation gives $C_s$ equal to $2.0 \cdot 10^{-3}$ and $2.7 \cdot 10^{-3}$ for monomers **2**-$Cu^{2+}$ and **2**-$Zn^{2+}$, respectively (Fig. 4).

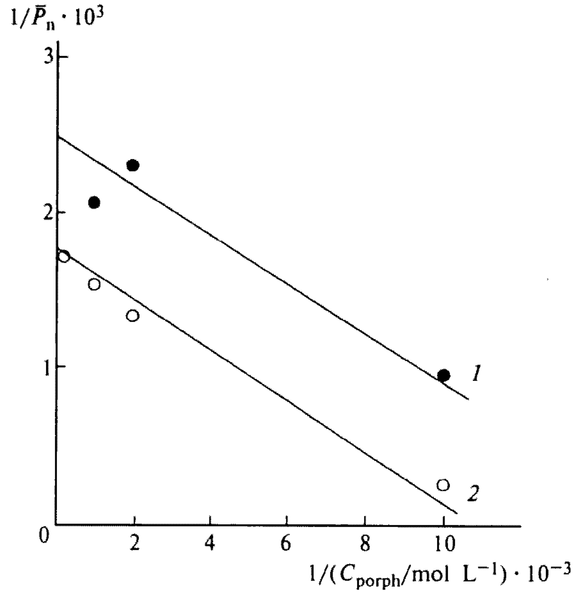
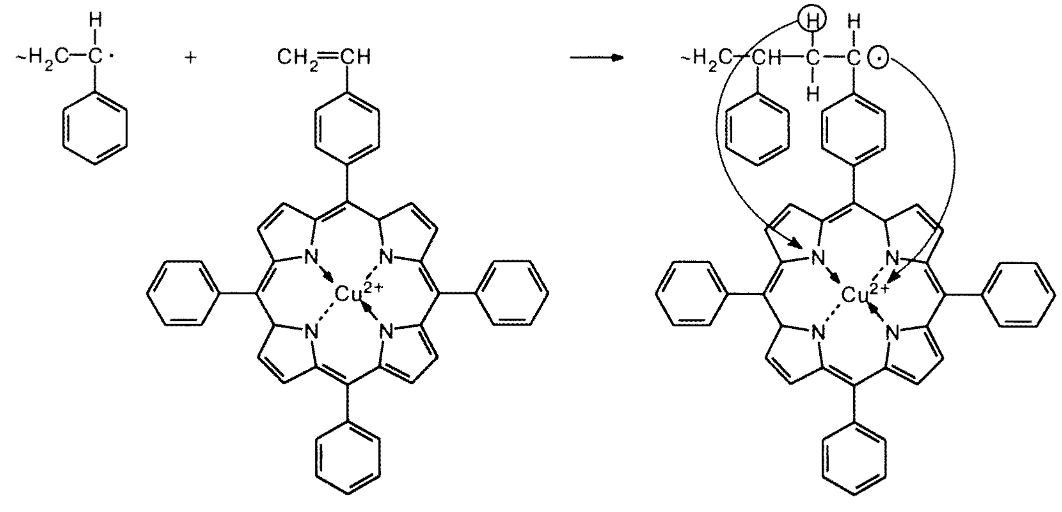


**Fig. 4.** Dependence of the inverse average degree of polymerization on the inverse concentration of **2**-$Zn^{2+}$ (*1*) and **2**-$Cu^{2+}$ (*2*).

In the copolymerization of metal-containing monomers with a developed coplanar system of π-electrons, especially those containing metal ions with comparatively low values of standard electrode potentials (for example, $E^0(Cu^{2+} \rightarrow Cu^+) = 0.15$ V), chain termination occurs due to intramolecular electron transfer in redox reactions along the system of π-electrons (the degenerate chain transfer type). A proton of the vinyl group is simultaneously eliminated and is likely added to the nitrogen atom of the porphyrin cycle (Scheme 1).

A similar mechanism of chain termination was observed[15] for the first time in the copolymerization of styrene with $Cu^{2+}$ and $Co^{2+}$ complexes of pyrrolylmethyleneiminopropene or pyrrolylmethyleneiminostyrene.

**Scheme 1**



An interesting phenomenon of catalytic chain transfer to the monomer was observed[16] for radical polymerization of vinyl monomers, in particular, MMA, in the presence of metalloporphyrins (MP). It is caused by conjugated reactions of dehydrogenation of the growing radical and hydrogenation of the monomer (Scheme 2).

**Scheme 2**

$$\mathrm{R^{\cdot} + MP \longrightarrow R_{-H} + H\text{-}MP^{\cdot}}$$

$$\mathrm{H\text{-}MP^{\cdot} + MMA \longrightarrow H\text{-}MMA^{\cdot} + MP}$$

The rate of chain transfer in a MMA—$Co^{2+}P$ system (P is porphyrin) is $10^7$ times greater than that of polymerization of MMA in the absence of MP. It is noteworthy that only $Co^{2+}P$ is an effective regulator of the chain length. Replacement of $Co^{2+}$ by ions of other metals (Zn, Cu, Mn, Cr, Ni, Pd) results only in a weak regulatory effect. Probably, in the case of the considered $Cu^{2+}$ and $Zn^{2+}$ complexes with **1** or **2**, this effect is even less pronounced.

Another mechanism of monomolecular termination of the polymer chain is also possible for Cu-containing vinylporphyrin monomers. The initiator of radical polymerization, AIBN, can, in principle, coordinate as an extraligand to the central copper ion, and their concentrations under copolymerization conditions are comparable. Probably, this extracoordination results in the formation of very strong complexes that may be stable even in the CPM formed. Moreover, extracoordination of radicals appearing during polymerization that can participate in reactions of both intra- and intermolecular termination of polymer chains cannot also be excluded. Previously, we have shown[17] the possibility of chain termination involving Ti-coordinated radicals in the copolymerization of Ti-containing monomers with styrene. The IR and ESR spectra of the CPM formed and the IR spectra of the products of the reaction of **2**-$Cu^{2+}$ with AIBN indicate that there is a significant probability of the occurrence of this coordination (the shift of the absorption frequency of vibrations of the nitrile group from 2244 in AIBN to 2268 $cm^{-1}$ in the product).

*Spectral parameters of porphyrin-containing CPM.* All groups of absorption bands typical of the initial monomers are in the IR spectra of CPM based on metal complexes of vinylporphyrins. The skeletal vibrations of the pyrrole rings of the porphyrin cycle (1492—1495, 1458—1461, 1603—1604 $cm^{-1}$) are weak and not pronounced at all in the case of CPM based on metal-free analogs. The out-of-plane vibrations of the pyrrole rings (780 and 766 $cm^{-1}$, shoulder) correspond to the absorption band at 791 $cm^{-1}$ for **1** and its metal complexes. The formation of metal complexes has almost no effect on the state of the C—H bonds[18] in the pyrrole ring.

Significant information on the structure of porphyrin-containing chains with paramagnetic metal ions can be obtained by the ESR method. For example, it is by this method that it has been shown[12] that the complete disappearance of the fine structure from the $Cu^{2+}$ ions in methyl methacrylate—porphyrin copolymers and the much lesser change in the spectra of acrylate—porphyrin copolymers are associated with the fact that in the first case the distance between the centers of the porphyrin cycles is shorter. The ESR spectra of magnetically dilute systems of CPM of styrene with **1**-$Cu^{2+}$ and **2**-$Cu^{2+}$ have four almost equidistant lines caused by splitting at the $Cu^{2+}$ nucleus, $S = 3/2$. The spectra of a solution of **2**-$Cu^{2+}$ in toluene and its CPM with styrene are shown in Fig. 5. Since an unpaired electron is surrounded by the four equivalent nuclei of the nitrogen atoms of the porphyrin cycle, the hyperfine splitting observed (9 lines) from the nitrogen nuclei ($S = 1$) is more pronounced in the components of the spectrum of $Cu^{2+}$, which are in a stronger field. The relationship of the intensities is close to binomial. The ESR spectra of the **1**-$Cu^{2+}$ and **2**-$Cu^{2+}$ monomers are almost identical ($g_{\parallel} = 2.12$, $a_{\parallel} = 100$ G, $g_{\perp} = 2.01$, $a_N \gg 16.9$ G) and nearly coincide with the ESR spectra of $Cu^{2+}$-etioporphyrin.[19] The ESR spectra of CPM of styrene with **2**-$Cu^{2+}$ (toluene solutions) and of CPM with **1**-$Cu^{2+}$ (insoluble) (see Table 2) are the superposition of the spectra of two types of copper complexes ($g_{\parallel} = 2.18$, $g_{\perp_1} = 2.04$, $g_{\perp_2} = 1.98$). The second of them likely corresponds to the extracoordinated $Cu^{2+}$ complex, while no additional splitting is observed at the nitrogen nucleus of the fifth ligand probably due to its remoteness from the metal ion.

Analysis of ESR spectra also indicates that the dipole-dipole or exchange interaction between paramagnetic copper ions, which would result in broadening or exchange narrowing of the spectra and their transformation into a singlet spectrum, is absent both in solutions of the initial $Cu^{2+}$ complexes and in CPM. Thus, in the region of concentrations of CPM solutions studied,

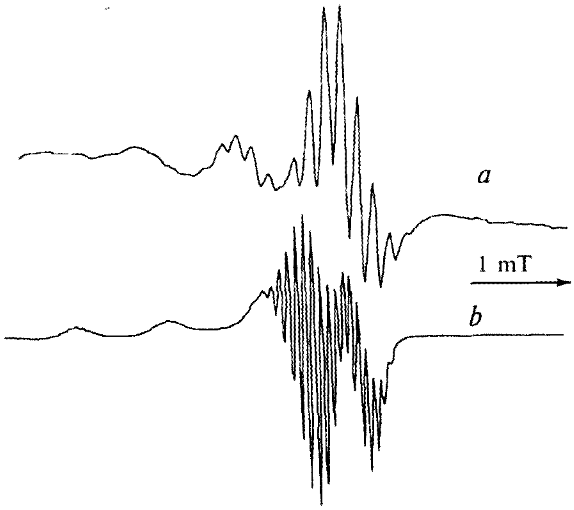


**Fig. 5.** ESR spectra of **2**-$Cu^{2+}$ (*a*) and its copolymer with styrene (*b*).

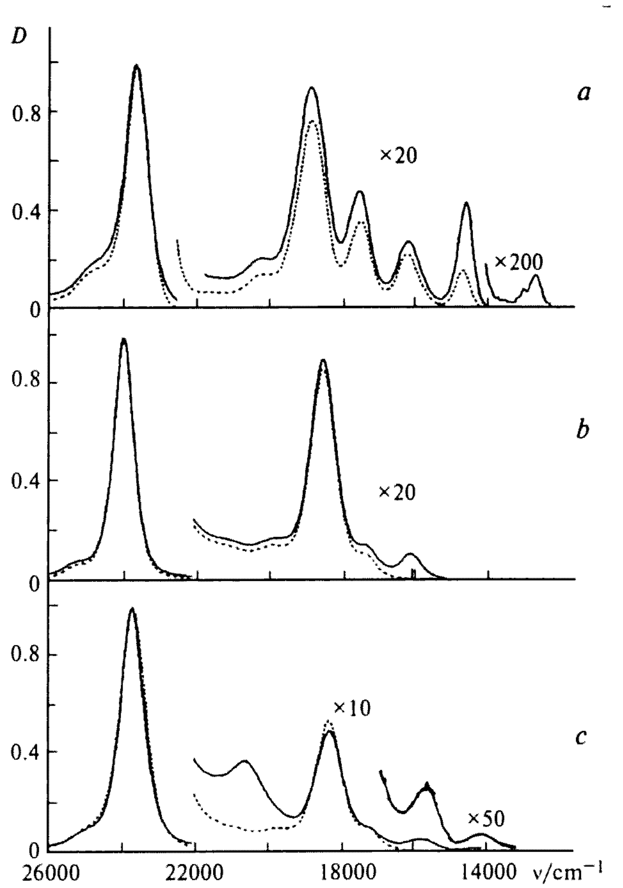


**Fig. 6.** Absorption spectra of styrene copolymers with vinylporphyrins: content 0.1 mol.% of **1** (*a*); 0.5 mol.% of **1**-Cu$^{2+}$ (*b*); and 0.5 mol.% of **2**-Cu$^{2+}$ (*c*). Spectra are normed to $D_{max}$ of the Soret band.

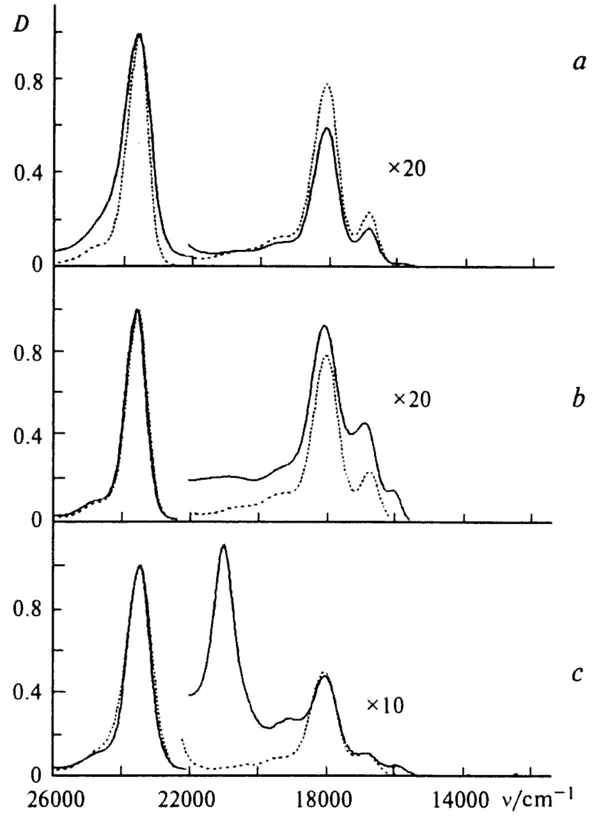


**Fig. 7.** Absorption spectra of copolymers with porphyrin-containing monomers: methyl methacrylate with an equimolar amount of **1**-Zn$^{2+}$ (*a*); styrene with 0.1 mol.% of **1**-Zn$^{2+}$ (*b*), and styrene with 0.1 mol.% of **2**-Zn$^{2+}$ (*c*).

Cu$^{2+}$-containing centers are fairly remote from each other, and the system is magnetically dilute. The estimation of the lower boundary of the average distance between immobilized isolated copper(II) complexes by the method described previously[20] gives the value $r_{isol}$ > 22—15 Å.

The electronic absorption spectra of metal-free CPM and Cu-containing CPM of vinylporphyrins with styrene are presented in Fig. 6, the spectra of Zn-containing CPM are presented in Fig. 7, and the positions of the maxima of the bands and their intensities are listed in Table 4. The absorption spectra of the corresponding porphyrin-containing monomers are presented by dotted lines in each diagram for comparison. The vibrational structure of the $Q_x$ and $Q_y$ bands is well resolved, and an intense Soret band is observed in the absorption spectrum of **1**. Changes in the spectrum of the corresponding CPM with styrene involve only redistribution of the intensities of the $Q$ bands: the intensity of the $Q_x$ band (0—0) is approximately twice as high, and the intensity of the $Q_y$ band (0—1) is somewhat lower. Similar spectral changes were observed[10] in the preparation of a 5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphyrin homopolymer. It should be mentioned that the electronic interactions of metal-free porphyrins result, as a rule, in insignificant changes in their absorption spectra, and this is true not only for polymeric systems, but also for covalently linked porphyrins. For example, in the study of di- and pentamers of tetraphenylporphyrins covalently linked through common phenyl rings it was established[7] that the changes in the absorption spectra of even these products mainly involve the transformation of the Soret band, while the shape of the $Q$ band remains almost unchanged. This is likely typical of the planar (or nearly planar) arrangement of porphyrin cycles. New additional $Q$ bands are observed for the sandwich-type dimer structures that can be obtained in concentrated porphyrin solutions.[3—6]

CPM of **1** with styrene are characterized by the appearance of a new weak long-wave band with a maximum at 13500 cm$^{-1}$ (see Fig. 6, *a*), whose intensity depends on the content of **1**. The positions and shapes of the other $Q$ bands remain unchanged, and the Soret band broadens insignificantly. These results agree with the data[12] of the study of homopolymers of copper 5-(4-acryloyloxyphenyl)- and 5-(4-methacryloyloxyphenyl)-10,15,20-triphenylporphyrinates. In the first

**Table 4.** Positions of absorption bands ($\nu$/cm$^{-1}$) of monomers and copolymers with styrene and their intensities (in parentheses)

| Compound | Type of compound (content of comonomer, %) | Soret region | *Q*-bands | New bands of copolymers |
|---|---|---|---|---|
| **1** | Monomer | 23750 | 19300 (0.04), 18110 (0.02), 16800 (0.01), 15400 (0.007) | |
| | Copolymer (0.1) | 23750 (1.00) | 19300 (0.045), 18100 (0.025), 16800 (0.015), 15400 (0.02) | 13500 (0.0007) |
| **1**-Cu$^{2+}$ | Monomer | 23900 (1.00) | 18400 (0.04), 17300 (0.005) | |
| | Copolymer (0.1) | 23900 (1.00) | 18400 (0.04), 17300 (0.007) | 16000 (0.005) |
| **2**-Cu$^{2+}$ | Monomer | 23700 (1.00) | 18300 (0.05), 17300 (0.01) | |
| | Copolymer (0.5) | 23700 (1.00) | 18300 (0.05), 17300 (0.015) | 20600 (0.04), 15800 (0.005), 14200 (0.001) |
| | Copolymer (1) | 23700 (1.00) | 18300 (0.056), 17300 (0.016) | 20600 (0.03), 15800 (0.03), 14200 (0.0005) |
| **1**-Zn$^{2+}$ | Monomer | 23440 (1.00) | 18000 (0.064), 16700 (0.022) | |
| | Copolymer (0.1) | 23440 (1.00) | 18000 (0.05), 16800 (0.04) | 20700 (0.01), 16000 (0.007) |
| **2**-Zn$^{2+}$ | Monomer | 23440 (1.00) | 17800 (0.05), 16600 (0.01) | |
| | Copolymer (0.1) | 23440 (1.00) | 18000 (0.05), 16800 (0.01) | 21000 (0.11), 19100 (0.03), 15900 (0.004) |
| | Copolymer (0.5) | 23400 (1.00) | 18000 (0.06), 16800 (0.016) | 21000 (0.012), 19100 (0.025), 15900 (0.003) |
| | Copolymer (1) | 23440 (1.00) | 18000 (0.08), 16800 (0.03) | 21000 (0.14), 19100 (0.04), 15900 (0.002) |

case, as in the present work, the appearance of a new long-wave *Q* band was observed along with broadening of the Soret band and an insignificant (20 cm$^{-1}$) hypsochromic shift. In the second case, the *Q* bands do not change, but the Soret band broadens considerably and shifts to the short-wave region. The absence of a new long-wave *Q* band is explained[12] by the fact that the electronic interaction of porphyrin cycles with fragments of the chain of the first polymer are stronger than the interaction with the second polymer, which is believed to be associated with the difference in the conformational structures of these polymers.

The interpretation of the absorption spectra of dimeric complexes even at a qualitative level is impossible when their geometric structures are unknown.[21–24] Therefore, the interpretation of the absorption spectra of porphyrin-containing CPM is most often restricted to qualitative comparative analysis.[18] It can only be assumed that the absorption spectra observed are the superposition of the spectra of porphyrin units that do not interact, and of porphyrin units that are arranged close to each other, and their geometry should be similar to that occurring in the homopolymerization of the Cu$^{2+}$ 5-(4-acryloyloxyphenyl)-10,15,20-triphenylporphyrin complex mentioned above. It can be assumed from the mechanism of termination of growing chains considered above that the probability of the incorporation of two consecutive units of a vinylporphyrin comonomer into the chain is very low, and the dimeric pair is most likely formed due to the specific conformation of the CPM macromolecule.

For CPM of styrene and monomers based on **1**, the shape and position of the Soret band change very insignificantly (a short-wave shift of the maximum by ~50 cm$^{-1}$ is observed), but the *Q* bands change significantly. This is especially noticeable for monomers based on **2**. In this case, an intense band (20600 cm$^{-1}$ for **2**-Cu$^{2+}$ and 21000 cm$^{-1}$ for **2**-Zn$^{2+}$) appears in the region between the *Q* bands and the Soret band along with an additional weak band (15800 and 14200 cm$^{-1}$ for **2**-Cu$^{2+}$ and 15900 cm$^{-1}$ for **2**-Zn$^{2+}$). As far as we know, there is no similar band in the spectra of the porphyrin-containing polymeric systems described previously or of porphyrin dimers in concentrated solutions. Since this band appears for CPM containing both **2**-Cu$^{2+}$ and **2**-Zn$^{2+}$, it cannot be excluded that it originates from the specific conformation of the chain caused by the addition of porphyrin units *via* the pyrrole cycle. The intensity of this band, like that of the new long-wave band, increases as the molar fraction of porphyrin units in CPM decreases (see Table 4).

Thus, the porphyrin-containing monomers studied with Zn$^{2+}$ or Cu$^{2+}$ ions within the macrocycles are of interest for the preparation of (metallo)porphyrin CPM. Even small numbers of units of these monomers introduced into the polymer chain have a substantial effect on the molecular-weight parameters and probably exert a modifying action on the conformation of the chains that are being formed. The microstructure of these CPM and the areas of their application will be the subjects of further studies.

## Experimental

Synthesis and characterization of porphyrin-containing monomers have been described previously.[13] Styrene was preliminarily freed from the stabilizing agent by washing with an ethanolic solution of KOH, dried with anhydrous $CaCl_2$, and repeatedly distilled *in vacuo*. Methyl methacrylate was washed with a 5% $Na_2CO_3$ solution and then with water to a neutral reaction, dried with anhydrous $Na_2SO_4$, and distilled, b.p. 80 °C (100 Torr), $n_D^{20}$ 1.450.

Azobisisobutyronitrile was recrystallized twice from MeOH, m.p. 103 °C. THF, toluene, $CHCl_3$, and EtOH were purified and dehydrated by conventional procedures.[25]

Radical copolymerization of vinylporphyrin monomers was performed in glass tubes at 60 °C in toluene. Calculated amounts of monomers and the initiator (0.5—2.0%) were preliminarily evacuated at the temperature of liquid nitrogen, and the tubes were sealed *in vacuo* after several freezing—thawing cycles. Time of polymerization ranged from 30 to 600 min depending on the composition of the monomeric mixture. The CPM that formed were precipitated with EtOH (20 vol.), in which vinylporphyrin monomers are highly soluble, washed repeatedly with EtOH, dried to constant weight, and analyzed. The content of a metal was determined by the atomic-absorption method on a "Saturn" instrument.

Kinetic studies of copolymerization were based on measurements of the rate of heat release in the isothermal regime on a differential automated DAK-1-1 microcalorimeter.

Absorption spectra of porphyrin-containing CPM and of the initial monomers (solutions in $CHCl_3$) were recorded on a Specord M-40 spectrophotometer, and IR spectra were recorded on a Specord IR-75 instrument. Molecular-weight parameters of CPM were determined by gel permeation chromatography in THF on a Waters-200 instrument equipped with Styrogel columns with exclusion limits of $10^3$, 500, and 200 Å (Set A) and $3 \cdot 10^3$, $3 \cdot 10^4$, and $3 \cdot 10^5$ Å (Set B). The calibrating dependence was obtained using monodisperse polystyrene standards (Waters). ESR spectra of $Cu^{2+}$-containing CPM were recorded at the temperature of liquid nitrogen on an SE/X-2544 radiospectrometer (Radiopan), the UHF power was 10 dW, the magnetic field modulation was 4 G, and the range was 2000 G.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09089) and the International Science Foundation (Grants NJB 000 and NJB 300).

## References

1. R. K. Clayton, *Photosynthesis*, Univ. Press, Cambridge, 1980.
2. A. Yu. Borisov, *Mol. biologiya*, 1986, **20**, 902 [*Mol. Biol.*, 1986, **20** (Engl. Transl.)].
3. S. S. Dvornikov, A. N. Sevchenko, K. N. Solov'ev, and M. P. Tsvirko, *Optika i spektroskopiya* [*Optics and Spectroscopy*], 1976, **41**, 424 (in Russian).
4. S. S. Dvornikov and M. P. Tsvirko, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, 1975, **39**, 2316 (in Russian).
5. M. P. Tsvirko and K. N. Solov'ev, *Zh. Prikl. Spektroskop.* [*Sov. J. Appl. Spectrosc.*], 1974, **20**, 115 (in Russian).
6. S. S. Dvornikov, K. N. Solov'ev, and M. P. Tsvirko, *Zh. Prikl. Spektroskop.* [*Sov. J. Appl. Spectrosc.*], 1983, **38**, 798 (in Russian).
7. S. Eriksson, B. Kallebring, S. Larsson, J. Martensson, and O. Wennerstorm, *Chem. Phys.*, 1990, **146**, 165.
8. L. P. Brivina, S. F. Ginzburg, and G. V. Ponomarev, *Zh. Prikl. Spektroskop.* [*Sov. J. Appl. Spectrosc.*], 1978, **29**, 691 (in Russian).
9. H. Aota, H. Fujii, A. Harada, and M. Kamachi, *Chem. Lett.*, 1990, 823.
10. M. Kamachi, X. S. Cheng, T. Kida, A. Kajiwara, M. Shibasaka, and S. Nagata, *Macromolecules*, 1987, **20**, 2665.
11. H. Aota, Y. Itai, A. Matsumoto, and M. Kamachi, *Chem. Lett.*, 1994, 2043.
12. N. Watanabe, X. S. Cheng, A. Harada, M. Kamachi, H. Nakaajama, W. Mori, and M. Kishita, *Polymer J.*, 1989, **21**, No. 8, 633.
13. N. A. Kitsenko, Yu. V. Ishkov, I. S. Voloshanovskii, Z. G. Aliev, and A. D. Pomogailo, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 1827 [*Russ. Chem. Bull.*, 1995, **44**, 1758 (Engl. Transl.)].
14. I. S. Voloshanovskii, N. A. Kitsenko, Yu. V. Ishkov, and A. Merz, *Ukr. Polym. J.*, 1995, **4**, 50 (in Russian).
15. T. Tomono, K. Honda, and E. Tsuchida, *J. Polym. Sci.: Polym. Chem. Ed.*, 1974, **12**, 1243.
16. B. R. Smirnov, I. S. Morozova, L. M. Pushchaeva, A. P. Marchenko, and N. S. Enikolopyan, *Dokl. Akad. Nauk SSSR*, 1980, **255**, 609 [*Dokl. Chem.*, 1980, **255** (Engl. Transl.)].
17. G. I. Dzhardimalieva, A. O. Tonoyan, A. D. Pomogailo, and S. P. Davtyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, 1744 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1987, **36**, 1612 (Engl. Transl.)].
18. *Porfiriny: struktura, svoistva, sintez* [*Porphyrins: Structure, Properties, and Synthesis*], Ed. N. S. Enikolopov, Nauka, Moscow, 1985, 333 pp. (in Russian).
19. E. M. Roberts and W. S. Koski, *J. Am. Chem. Soc.*, 1960, **82**, 3006.
20. A. T. Nikitaev, A. D. Pomogailo, N. D. Golubeva, and I. N. Ivleva, *Kinet. Katal.*, 1986, **27**, 709 [*Kinet. Catal.*, 1986, **27** (Engl. Transl.)].
21. R. Fulton and M. Gouterman, *J. Chem. Phys.*, 1964, **41**, 2280.
22. M. Gouterman, D. Holten, and E. Liberman, *Chem. Phys.*, 1977, **25**, 139.
23. C. A. Hunter, J. R. M. Sanders, and A. J. Stone, *Chem. Phys.*, 1989, **133**, 395.
24. A. Pakhamov, S. Ekbundit, C. H. Lin, R. C. Alden, and S. H. Lin, *J. Luminescence*, 1995, **63**, 129.
25. Yu. K. Yur'ev, *Prakticheskie raboty po organicheskoi khimii* [*Practical Works on Organic Chemistry*], MGU, Moscow, 1964, **1**, 419 pp. (in Russian).

*Received November 21, 1995;*
*in revised form September 15, 1996*