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Some Observations on Complexes of a Cobalt Phthalocyanine with Poly(vinylamine) and Their Catalytic Activity in the Autoxidation of Thiols

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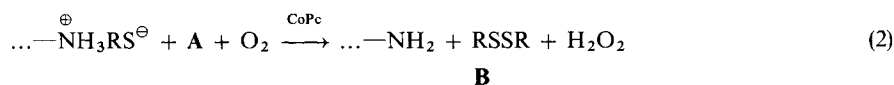
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SUMMARY:

Complexes of the tetrasodium salt of cobalt(II)-tetrasulfophthalocyanine and poly(vinylamine) were applied as bifunctional catalysts for the autoxidation of thiols to disulfides. Optical and catalytic experiments gave supporting evidence to the hypothesis, that the isolation of cobalt centers and the catalytic activity can be promoted by increasing the relative amount of polymeric base. It appeared that the specific catalytic activity of the polymeric catalysts depends on the number average degree of polymerization (\bar{P}_n) of the applied polymer samples. In particular at relatively high cobalt content, samples with comparatively low \bar{P}_n give more protection against aggregation of cobalt sites (i. e. inactivation) and, therefore, effect a higher specific catalytic activity. A statistical calculation, suitable to determine the distribution of cobalt sites over the polymeric coils, supports the interpretation of the experimental data.

Introduction

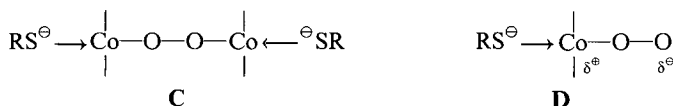
Metalphthalocyanines have attracted considerable interest because of their structural similarity with the naturally occurring porphyrins^{1,2)}. Metalporphyrins^{2,3)} and phthalocyanines^{4,5)} are well known oxidation catalysts, e. g. for thiols. An effective catalyst for the autoxidation of thiols should possess oxidation sites and basic sites in cooperative interaction^{6–8)}. In this paper such bifunctional catalysts composed of a water-soluble cobaltphthalocyanine (CoPc) and a polymeric base are described. The prepared polymeric catalysts are being tested for the autoxidation of thiols (**A**) to disulfides (**B**) in aqueous media.



In previous papers^{7,8)} we have shown that a particularly active catalytic system could be obtained using poly(vinylamine) (PVAm) as the polymeric base. It was suggested^{7,8)}, that two

phenomena, both inherently connected with the polymeric character of the base, can account for the observed high activity of these bifunctional catalysts. Firstly, a more effective cooperation between oxidation sites and basic sites can be achieved when using a polymeric base instead of a low molecular weight base. Taking into consideration the proposed mechanism of the reaction⁷⁾, an enhanced rate of oxidation due to this effect may be expected. Secondly, the shielding effect exerted by the polymer coils hinders undesirable dimerization reactions of CoPc molecules.

In case of conventional (i. e. polymer-free) CoPc-NaOH systems, in the presence of oxygen and substrate, dimerization reactions of CoPc molecules cannot be avoided and binuclear dioxygen adducts **C** are formed. These adducts are fairly stable, giving rise to a relatively low overall catalytic activity. On the other hand, in CoPc solutions in the presence of a sufficient excess of polymeric base, separation of cobalt centers may be achieved. In this case, the formation of the instable (i. e. reactive) mononuclear oxygen adduct **D** will be favoured during the oxidation reaction^{7,9)}, resulting in a relatively high overall reaction rate.



In the present contribution we wish to present further supporting experimental evidence to this hypothesis. For this purpose the results of catalytic experiments on the autoxidation of thiols with CoPc-PVAm catalysts were correlated with optical data on the CoPc-PVAm complexes. Because of the strongly complexing properties of PVAm towards CoPc, it might be expected that with increasing concentration of PVAm at a constant CoPc concentration, the formation of mononuclear CoPc species will be promoted. A statistical calculation on the distribution of CoPc over the PVAm chains confirms this presumption, and the results of this calculation are compared with the kinetic data obtained from catalytic experiments. Furthermore, from this statistical calculation a molecular weight dependence of the specific catalytic activity of the CoPc-PVAm systems might be expected. The results of the measurements on the influence of the number average molecular weight of the PVAm on the catalytic activity are presented and discussed.

Experimental Part

Catalyst preparation

Poly(vinylamine) (PVAm): The preparation of this polymer has been described recently⁸⁾. The prepolymer poly(*tert*-butyl vinylcarbamate) (PtBVC) was prepared from the corresponding monomer under nitrogen in benzene with 2,2'-azoisobutyronitrile (AIBN), as initiator (reaction time: 10 h; $T=60^{\circ}\text{C}$)¹⁰⁾. Products (PtBVC) with different average degrees of polymerization (\bar{F}_n) were obtained by varying the amount of AIBN (see Tab. 1).

Tetrasodiumsalt of cobalt(II) 4,4',4'',4'''-tetrasulfophthalocyanine (CoTSPc): This compound was prepared as described in a previous paper⁷⁾.

Complexation of CoTSPc and PVAm: Aqueous solutions of PVAm and CoTSPc were simply mixed. The spontaneously formed complexes (see^{7,8)}) were used in the various measurements. All solutions were prepared with distilled and deionized water.

Tab. 1. Radical polymerization of *tert*-butyl vinylcarbamate^{a)}

Monomer weight in g	AIBN weight in g	Benzene volume in ml	\bar{P}_n
5,01	0,6573	55	50 ^{b)}
10,35	0,1155	55	570 ^{c)}
4,95	0,0057	30	1680 ^{c)}

a) Reaction conditions: see text.

b) Determined by vapor pressure osmometry (solvent: benzene; $T=45^\circ\text{C}$).

c) Determined by membrane osmometry (solvent: toluene; $T=37^\circ\text{C}$).

Catalytic activity measurements

Activity measurements were carried out in an all-glass, thermostated ($T=23^\circ\text{C}$), double-walled, Warburg apparatus provided with a mechanical (glass) stirrer. Water was used as solvent; unless otherwise stated the total reaction volume amounts to 75 ml. The substrate, 2-mercaptoethanol (Merck), was distilled before use and carefully kept under nitrogen. The reaction rate was determined by measuring the initial oxygen consumption rate at constant oxygen pressure ($p(\text{O}_2)=1\text{ atm}$) and a constant stirring speed (3000 r.p.m.).

Instrumentation

Number average molecular weights were determined with a Hewlett Packard High Speed Membrane Osmometer 502 and a Knauer Vapor Pressure Osmometer. Optical spectra were measured with quartz cuvettes by means of an Unicam SP 800 spectrophotometer.

Results

Visible light spectral measurements

It is well established, that the tetrasodiumsalt of cobalt(II) 4,4',4'',4'''-tetrasulfophthalocyanine (CoTSPc) in aqueous solution may exist in at least three forms: the mononuclear form, binuclear form and binuclear dioxygen adducts^{11,12}. At neutral pH, low ionic strength and low CoTSPc concentration an equilibrium between mononuclear and binuclear species prevails, whereas in alkaline medium the dioxygen adduct and the binuclear form of CoTSPc predominate. Our results of visible light measurements on CoTSPc in alkaline solutions of different basic strength (at constant CoTSPc concentration) are in accordance with data obtained from literature^{11,12} (see Fig. 1). With increasing NaOH concentration (under nitrogen) the concentration of binuclear species increases, as appears from the increasing peak at 16000 cm^{-1} .

When bubbling O_2 through these alkaline solutions the peak at 15000 cm^{-1} rapidly increases representing the formation of the binuclear dioxygen adduct. At higher NaOH concentrations, a faster formation of the latter adduct is observed.

Turning now to the CoTSPc-PVAm system it appears that the spectra in the presence of PVAm differ appreciably from the spectra recorded when using NaOH. The visible light spectra (see Fig. 2) recorded under nitrogen reveal that with increasing PVAm content at constant CoTSPc concentration, the peak at 16000 cm^{-1} diminishes and the peak at 14900 cm^{-1} increases. Evidently, with increasing PVAm concentration at constant CoTSPc content, the equilibrium between mononuclear and binuclear form is shifted to the mononuclear form.

When bubbling O_2 through the solutions of CoTSPc-PVAm complexes the peak at 14800 cm^{-1} increases indicating the formation of dioxygen adducts (see Fig. 2).

Combining the results represented in Figs. 1 and 2, it can be concluded that binuclear adduct formation in the relevant CoTSPc solutions (i. e. under nitrogen) is promoted by increasing the amount of alkaline base and is hindered by increasing the amount of polymeric base. On the other hand, it still appears to be possible that for a given CoTSPc concentration in a PVAm so-

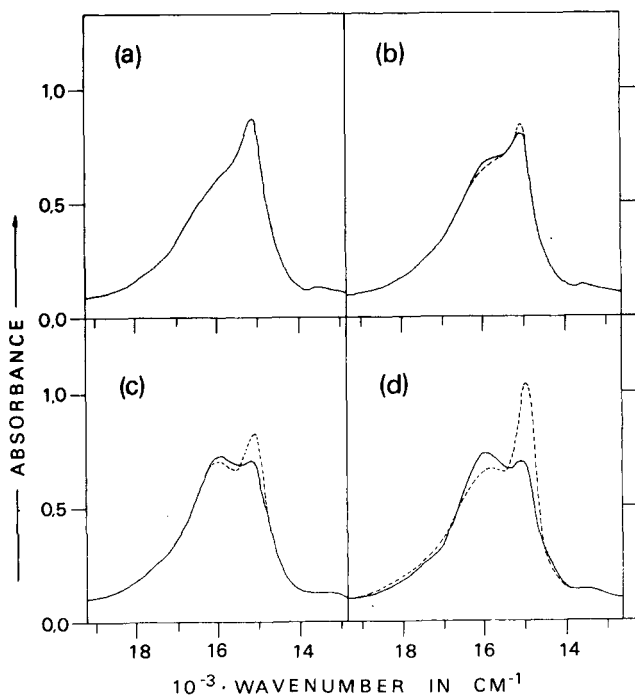


Fig. 1. Visible light absorption spectra of $2,5\ \mu\text{mol/l}$ CoTSPc solutions at ambient temperature (solvent: water; optical path length: 50 mm) in the presence of (a): no base, (b): $2,5\ \text{mmol/l}$ NaOH, (c): $10,0\ \text{mmol/l}$ NaOH, (d): $25,0\ \text{mmol/l}$ NaOH. Spectra after $0,5\ \text{h}$ flushing with purified nitrogen (—) and thereafter $1\ \text{h}$ flushing with oxygen (---)

lution, more dimeric CoTSPc species are present than in an alkaline solution containing the same amount of basic groups. This effect can be ascribed to the high local concentration of basic groups (i. e. coordinative sites) within the polymeric coil due to the specific non-homogeneous features of dilute polymer solutions^{7,8}. This phenomenon causes a relatively high concentration of CoTSPc molecules within the polymeric coils, which promotes the formation of binuclear CoTSPc species. Evidently, the latter effect is most distinct when relatively low PVAm amounts are used. With increasing PVAm content this effect becomes less important due to the increasing shielding effect exerted by the polymer molecules.

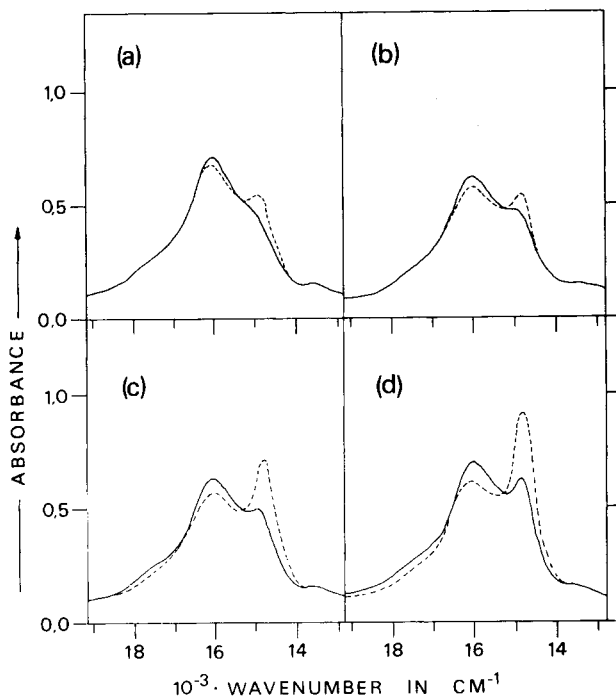


Fig. 2. Visible light absorption spectra of $2,5 \mu\text{mol/l}$ CoTSPc solutions at ambient temperature (solvent: water; optical path length: 50 mm) in the presence of PVAm ($\bar{P}_n = 570$). (a): 2,5 mmol/l amine, (b): 5,0 mmol/l amine, (c): 10,0 mmol/l amine, (d): 25,0 mmol/l amine. Spectra after 0,5 h flushing with purified nitrogen (—) and thereafter 1 h flushing with oxygen (---)

Catalytic activity measurements

In Fig. 3 the results of the catalytic experiments carried out with PVAm samples of different average degrees of polymerization are shown. It appears that the specific catalytic activity of CoTSPc-PVAm complexes for the autoxidation of thiols as a function of the amine content (at constant CoTSPc concentration) depends on the average molecular weight of the PVAm sample applied. To our knowledge, this is the first time such a molecular weight dependence of the catalytic activity of polymeric catalysts was found.

Furthermore, Fig. 3 reveals that the specific catalytic activity of CoTSPc-PVAm complexes for the autoxidation of 2-mercaptoethanol increases with increasing amine content (at constant CoTSPc concentration). It has already been shown by visible light spectral measurements (see Fig. 2) that the formation of the binuclear adduct of the CoTSPc is hindered by increasing the PVAm content (at constant CoTSPc content). Thus, it may be concluded that the enhanced catalytic activity (see Fig. 3) on increasing the PVAm concentration (at constant CoTSPc concentration) is effected by a reduced number of dimeric species.

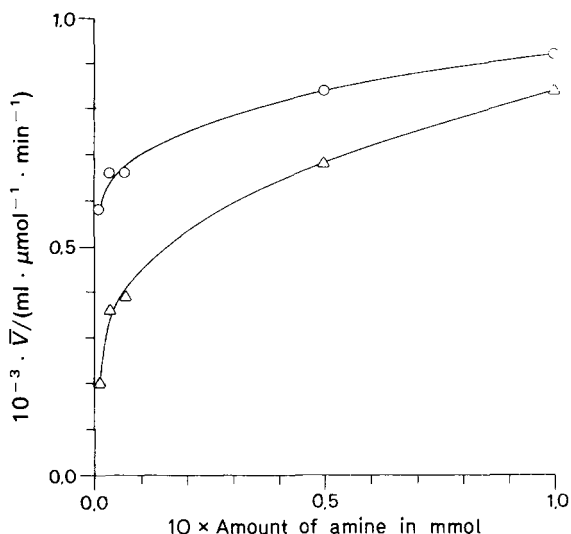


Fig. 3. The average catalytic activity of CoTSPc-PVAm complexes (\bar{v}) (ml of O₂ and μmol of Co) as a function of the amine content (at constant CoTSPc content of 10^{-8} mol) for PVAm samples with $\bar{P}_n = 50$ (○) and $\bar{P}_n = 1680$ (△). Measurements carried out in triplicate; substrate: 2-mercaptoethanol (1 ml, 14,25 mmol); time of complexation: 40 min

From Tab. 2 it becomes evident that the specific catalytic activity of the CoTSPc-PVAm catalyst decreases with increasing CoTSPc concentration (at constant amine content). This result can be explained by taking into account the relatively decreasing amount of mononuclear species on increasing the CoTSPc concentration (at constant PVAm content).

Tab. 2. Catalytic activity of polyvinylamine-cobaltphthalocyanine complexes; [Amine] = 4 mmol · dm⁻³ ^{a)}

$\frac{10^6 \cdot [\text{CoPc}]}{\text{mol} \cdot \text{dm}^{-3}}$	$\frac{10^{-3} \cdot \bar{v}}{\text{ml} \cdot \mu\text{mol}^{-1} \cdot \text{min}^{-1}}$ ^{b)}
0,08	2,37
0,4	1,05
0,8	0,89
4,0	0,29
8,0	0,21

^{a)} Reaction conditions: see Exptl. Part. Total reaction volume: 11 ml. A PVAm sample with $\bar{P}_n = 570$ was used; substrate: 2-mercaptoethanol (1 ml, 14,25 mmol); time of complexation: 24 h.

^{b)} \bar{v} = specific rate (ml of O₂ and μmol of Co).

Discussion

In recent years polymer-bonded metallocporphyrins have been studied as model systems for enzymes as for instance cytochrome P₄₅₀, myoglobin and hemoglobin¹³). Iron(II)-porphyrins in proteins can bind and activate molecular oxygen for oxidations of various substrates^{13,14}). However, in solution and in the presence of oxygen iron(II)-porphyrins are rapidly oxidized to the iron(III) state¹⁵). Up to now, three methods have been described in the literature¹⁶) to avoid this

irreversible dimeric oxidation of iron(II)-porphyrins: 1) steric restriction preventing dimerization, of the metalporphyrins, 2) low temperature causing slower irreversible oxidation and 3) rigid surfaces preventing dimeric oxidation of anchored metalporphyrins.

Steric protection against dimerization reactions can for instance be achieved by the attachment of metalporphyrins in low concentration to soluble polymers¹³; the porphyrin-complex then virtually behaves as in solution at infinite dilution. We have applied this method for analogous reasons using poly(vinylamine) (PVAm) as a polymeric ligand for cobalt(II)-tetrasulfophthalocyanine (CoTSPc). This polymeric base can give protection against the dimerization reactions normally occurring in homogeneous polymer-free CoTSPc solutions and can promote the formation of the highly reactive mononuclear oxygen adduct of CoTSPc (D). It may be assumed that binuclear CoTSPc species cannot be formed when only one CoTSPc unit is present in each PVAm coil. Therefore, it can be expected that an optimal overall catalytic activity is obtained, when all CoTSPc molecules are found isolated in separate polymeric coils⁷.

A simple statistical calculation suitable to determine the distribution of CoTSPc over the PVAm coils will now be presented. Because of the very dilute PVAm solutions (<0,05 weight-% of polymer) in which the catalytic experiments are performed, it can be assumed that each PVAm coil contains only one polymer molecule (i. e. no entanglements). In the following statistical treatment the polymer chains are considered as polyfunctional units in which every functional group ($-\text{NH}_2$) has the same reactivity, independent of its environment. When equilibrium is established there will be a binominal distribution of CoTSPc over the amine groups. In case of PVAm with one functional group at each monomeric unit and with a mole ratio of CoTSPc to amine groups q ($q < 1$) the mole fraction of chains with degree of polymerization i , and k CoTSPc molecules in each chain can be expressed as:

$$x_{i,k} = \frac{i!}{(i-k)!(k)!} q^k (1-q)^{i-k} \quad (3)$$

PVAm was prepared via a radical polymerization of *tert*-butyl vinylcarbamate with AIBN as initiator (see Exptl. Part). As under these conditions the termination step most probably occurs by disproportionation, a Flory-distribution of the degree of polymerization¹⁷ of the instantaneously formed polymer molecules may be expected. The mole fraction of polymer chains with degree of polymerization i is then given by:

$$x_i = p^{i-1} (1-p) \quad (4)$$

where $p = 1 - 1/\bar{P}_n$ (\bar{P}_n = the number average degree of polymerization). Combining Eqs. (3) and (4), the mole fraction of PVAm chains with k molecules CoTSPc can be described as:

$$x_{\text{pol},k} = \sum_{i=k}^{\infty} \frac{i!}{(i-k)!(k)!} q^k (1-q)^{i-k} p^{i-1} (1-p) \quad (5)$$

For $k \geq 1$ and $q < 1$ Eq. (5) can be recast as:

$$x_{\text{pol},k} = \frac{(1-p)p^{k-1}q^k}{(1-p+pq)^{k+1}} \quad (6)$$

The number of CoTSPc molecules on PVAm chains with k molecules CoTSPc is $k \cdot x_{\text{pol},k}$ times the total number of PVAm chains (N). The total number of CoTSPc molecules is $q \cdot \bar{P}_n$ times the total number of PVAm chains (N). Based on these considerations one can calculate the mole fraction of CoTSPc on PVAm chains with k molecules CoTSPc ($x_{\text{Co},k}$):

$$x_{\text{Co},k} = \frac{x_{\text{pol},k} \cdot k \cdot N}{q \cdot \bar{P}_n \cdot N} \quad (7)$$

Using Eq. (6) and $\bar{P}_n = 1/(1-p)$ in Eq. (7), yields:

$$x_{\text{Co},k} = \frac{k(1-p)^2(pq)^{k-1}}{(1-p+pq)^{k+1}} \quad (8)$$

Eq. (8) holds for $k \geq 1$ and $q < 1$.

In reality, each amine group of PVAm will not react independently of its environment. It should be expected that any CoTSPc molecule will interact with more than one amine group of the polymer. This behavior can be accounted for by introducing a statistical chain element of N monomeric units as complexing moiety rather than a single monomeric unit. However, for small values of q the effects of this modification appear to be negligible.

The above statistical calculation supports the interpretation of the measured molecular weight dependence of the specific catalytic activity of CoTSPc-PVAm complexes for the autoxidation of thiols. It will be obvious from the calculated data presented in Tab. 3 that in the case

Tab. 3. Calculated amount of isolated CoTSPc molecules ($x_{\text{Co},1}$) and the specific catalytic activity of CoTSPc-PVAm complexes^{a)}

$10^2 \cdot q$ ^{b)}	$\bar{P}_n = 50$		$\bar{P}_n = 1680$	
	$x_{\text{Co},1}$ ^{c)} in %	$10^{-2} \cdot \bar{v}$ ^{d)} $\text{ml} \cdot \mu\text{mol}^{-1} \cdot \text{min}^{-1}$	$x_{\text{Co},1}$ ^{c)} in %	$10^{-2} \cdot \bar{v}$ ^{d)} $\text{ml} \cdot \mu\text{mol}^{-1} \cdot \text{min}^{-1}$
1	45,04	5,8	0,32	2,0
0,2	82,95	6,6	5,27	3,6
0,1	90,88	6,6	13,93	3,9
0,02	98,07	8,4	56,04	6,8
0,01	99,03	9,2	73,31	8,4

^{a)} Reaction conditions: see Exptl. Part. Always 10^{-8} mol of CoTSPc was used. Substrate: 2-mercaptoethanol (1 ml, 14,25 mmol); time of complexation: 40 min.

^{b)} $q = [\text{CoTSPc}]/[\text{Amine}]$.

^{c)} $x_{\text{Co},1}$ = mole fraction of CoTSPc in PVAm coils, containing one CoTSPc molecule (calc. with Eq. (8)).

^{d)} \bar{v} = Average specific rate, measurements carried out in triplicate (ml of O_2 and μmol of Co).

of the lower average molecular weight PVAm sample ($\bar{P}_n = 50$) a rather high percentage of isolated CoTSPc molecules ($x_{\text{Co},1}$) occurs, which decreases only slowly with increasing q ($[\text{CoTSPc}]/[\text{Amine}]$) ratios. In contradistinction to this behavior, the higher average molecular weight sample ($\bar{P}_n = 1680$) contains a high percentage of polymeric coils with a single CoTSPc molecule only when the value of q is low. Under these conditions the number of iso-

lated CoTSPc molecules decreases very rapidly as q increases. This implies that at relatively high CoTSPc contents the low molecular weight sample is expected to protect the CoTSPc better from dimerization reactions than does the high molecular weight sample. Since, as stated before, the catalytic activity is predominantly originating from the mononuclear CoTSPc species, a relatively high CoTSPc content should lead to a higher specific activity when a comparatively low molecular weight PVAm sample is used. This hypothesis was confirmed by the experimental results presented in Fig. 3 and Tab. 3.

Since it has been found that non-polymeric amines were able to provide only a low catalytic activity⁷⁾, it can be inferred that there should exist a minimal \bar{P}_n value necessary to protect the CoTSPc efficiently against dimerization reactions. Up to now such a minimally required \bar{P}_n value could not be determined.

It becomes evident that the above statistical calculation can be useful to a better understanding of the catalytic behavior of CoTSPc-PVAm complexes. Moreover, this calculation can also be applied to related problems, for instance in the field of polymer attached metals and other metal complexes.

It may be expected that the concentration of basic groups ($[N]_{\text{coil}}$) and consequently the concentration of substrate molecules in the polymeric coil ($[RS^{\ominus}]_{\text{coil}}$) depend also on the \bar{P}_n of the applied PVAm samples. When very dilute PVAm solutions are considered in the absence of CoTSPc, and all polyelectrolyte characteristics have been suppressed adequately, $[N]_{\text{coil}}$ is inversely proportional to the intrinsic viscosity of the polymer solution $[\eta]$ ¹⁸⁾. Furthermore, from the Mark-Houwink relation it is known that $[\eta]$ is related to the molecular weight of the polymer sample according to $[\eta] = K \cdot M^a$ ($0,7 < a < 0,9$). Thus, it will be obvious that $[N]_{\text{coil}}$ is inversely proportional to $M^{0,7}$ up to $M^{0,9}$. It may be assumed that the polyelectrolyte behavior is sufficiently suppressed in the presence of an excess of the substrate (2-mercaptoethanol). It can then be calculated, using the above relationship, that in the absence of CoTSPc, $[N]_{\text{coil}}$ and consequently $[RS^{\ominus}]_{\text{coil}}$ are at least 10 times higher when using the sample with low \bar{P}_n ($\bar{P}_n = 50$) instead of the sample with high \bar{P}_n ($\bar{P}_n = 1680$). However, the presence of a CoTSPc molecule will strongly disturb the conformation of a PVAm coil in solution. Because of the strongly complexing properties of CoTSPc towards polymer-bound RS^{\ominus} , it may be expected that a CoTSPc molecule is able to create a typical surrounding by RS^{\ominus} species practically independent of the \bar{P}_n of the polymer sample. Hence, it becomes rather unlikely that the molecular weight dependence of $[RS^{\ominus}]_{\text{coil}}$ influences the measured initial catalytic activity.

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