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Autoxidation of thiols with tetrasodium cobalt(II)phthalocyaninetetrasulfonate, bound to poly(vinylamine), 3[a]

Dependence on molecular weight

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SUMMARY:
Polymeric catalysts consisting of cobalt(II)phthalocyanine, $CoPc(NaSO_3)_4$, coordinatively bound to poly(vinylamine) of various molecular weight, were used as oxidation catalysts in the conversion of thiols to disulfides. The molecular weight of the polymeric ligand, poly(vinyl-amine), largely affects the reaction rate below a critical polymer concentration of about 0,01 w/v %. The activation enthalpy $\Delta H_2^{\neq}$ does not depend on the degree of polymerization (DP) of the polymeric ligand and from visible light spectra it appears that electron transfer of the thiol-anion to Co(II) to yield Co(I) is favored when low instead of high molecular weight ligands are used. The observed catalytic oxidation rate of thiol is considerably higher for low molecular weight ligands (DP 20 – 40) in the low polymer concentration region. This may be attributed to a change in base strength in the micro-environment of $CoPc(NaSO_3)_4$ due to conformational differences between low and high molecular weight ligands, manifested at low polymer concentration. When the ligand has no polymeric character, e. g. 1,3-propanediamine, low catalytic activity is observed.

Introduction

Thiol oxidation is of great interest in industrial sweetening processes and in biological systems. It is well known[1] that beside other metal compounds specially tetrasodium cobalt(II)phthalocyanine-2,7,12,17-tetrasulfonate, $CoPc(NaSO_3)_4$, (Fig. 1) in alkali, possesses catalytic activity in the conversion of thiols to disulfides.

It was shown by other investigators in our institute that upon attachment of $CoPc(NaSO_3)_4$ to a basic polymeric ligand, the reaction rate increases strongly[2].

Our aim is to elucidate the role of the polymeric ligand in the increased catalytic action observed. As a model reaction the oxidation of 2-mercaptoethanol in water with molecular oxygen into 2,2′-dithiodiethanol is being studied using $CoPc(NaSO_3)_4$ attached to poly(vinylamine) (PVAm) as a catalyst.

In earlier communications we reported on the incorporation of $CoPc(NaSO_3)_4$ in the polymeric ligand PVAm[3], on the effect of pH on conformation and catalytic activity of the polymeric catalyst[4], and on other kinetic characteristics of this homo-

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[a] Part 2: cf. W. M. Brouwer, P. Piet, A. L. German, J. Mol. Catal. **22**, 297 (1984).
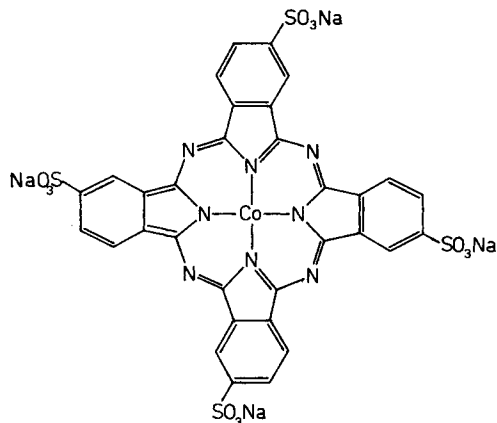
Fig. 1.   Chemical structure of tetrasodium cobalt(II)phthalo-cyanine-2,7,12,17-tetrasulfonate

geneous polymeric catalyst system[5]. It appeared that the polymeric catalyst exhibits an enzyme-like behaviour, including high activity (turnover number per Co site $3 \cdot 10^3$ s^{-1}).

The present study is concerned with the relation between molecular weight of the polymeric ligand and the catalytic activity. Recently, experimental results dealing with this peculiar, rarely observed, phenomenon have been published[6]. Now a more extended investigation is presented based on complementary experimental data.

Experimental part

Synthesis

Since monomeric vinylamine is very unstable, poly(vinylamine hydrochloride) (PVAmHCl) can only be prepared via a prepolymer. Several methods to prepare PVAmHCl are described in the literature[7 – 12]. We prepared PVAmHCl by hydrolysis of poly(*tert*-butyl N-vinylcarbamate) (PTBNVC) in 10 M HCl/ethanol, since this method was reported to yield linear PVAmHCl with 100% protonated amine groups. The monomer *tert*-butyl N-vinylcarbamate (TBNVC) was prepared starting from acryloyl chloride and proceeding via acryloyl azide, vinyl isocyanate to TBNVC. Basically we have used the procedure described by Hughes and St. Pierre[12], but some modifications were applied to increase the yield.

Reduction of reaction times as well as a direct distillation of vinyl isocyanate as soon as it is formed during the decomposition of acryloyl azide largely have contributed to a rise of the yield from 35% to 85% on the basis of acryloyl chloride.

Polymerization of dry TBNVC was carried out at 60 °C in benzene (dried on CaH$_2$) with 2,2'-azoisobutyronitrile (AIBN) as initiator. The product PTBNVC was precipitated in a stirred 20-fold excess of cold hexane.

Acryloyl chloride (Fluka, practical grade) and *tert*-butyl alcohol (Merck, p. a.) were distilled prior to use. Sodium azide (Fluka, pure) was used as provided. Toluene (p. a.) and benzene (p. a.) were dried on CaH$_2$. AIBN (Fluka, pure) was recrystallized from diethyl ether. Hexane was practical grade and heptane was p. a.

Variation of molecular weight

Variation of molecular weight was achieved by changing the monomer/initiator ratio in the polymerization reaction of TBNVC. PTBNVC was precipitated in an excess of cold hexane.

The high molecular weight samples were isolated by filtration, but the products with a low degree of polymerization (DP) could only be successfully isolated by centrifugation of the white colloidal solutions during 10 min at 2000 r.p.m.

In order to obtain low molecular weight products, relatively large initiator concentrations had to be used. Unreacted initiator could be removed by redissolving the dried crude polymerization product in benzene and precipitation in hexane. All samples were purified twice in this way and afterwards washed with heptane p. a. The samples were dried at room temperature at 10^{-2} Pa. In Fig. 2 a gel permeation chromatogram of a low molecular product is shown before and after one purification step. Peak (2) originates from unreacted AIBN and disappears after further

Fig. 2. Gel permeation chromatogram of PTBNVC II; (a) crude polymerization product (dried), (b) purified (1 ×) polymerization product (dried). (1) PTBNVC; (2) AIBN. Conditions: 0,4 mg of PTBNVC II; mobile phase: THF; flow rate: 0,9 ml · min^{-1}; temp.: 23 °C. Method of detection: differential refractive increment (DRI). Columns: μ-styragle 10^2, 10^3, 10^4, 10^5 Å

retention   volume / ml
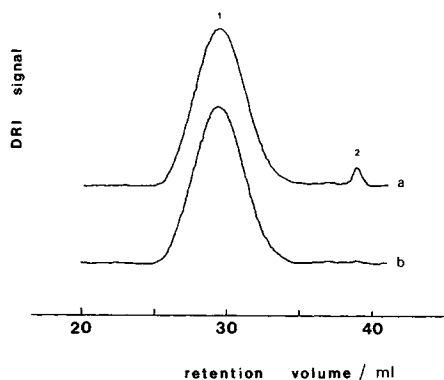
purification. By application of Benoit's universal calibration concept[13] the method of Mahabadi and O'Driscoll[14] was used for developing a GPC calibration curve for PTBNVC. The dispersity ($\bar{M}_w/\bar{M}_n$) appeared to have values between 2 and 2,5 for all samples.

A summary of the various polymerization conditions is shown in Tab. 1. The molecular weight of the PTBNVC samples was determined by membrane and vapour pressure osmometry and is also listed in Tab. 1. For the isolation of low molecular weight PVAmHCl centrifugation appeared to be imperative. The yields of both high and low molecular weight PVAmHCl were about 90 – 95% on the basis of PTBNVC.

Tab. 1. Polymerization conditions and number average molecular weight $\bar{M}_n$ of poly(tert-butyl N-vinylcarbamate) (PTBNVC)[a]

Sample	$\dfrac{c_{TBNVC}}{mol \cdot dm^{-3}}$	$\dfrac{c_{AIBN}}{mol \cdot dm^{-3}}$	$\dfrac{10^{-3} \cdot \bar{M}_n}{g \cdot mol^{-1}}$	DP[b]
I	0,54	0,050	3,3	23[c]
II	0,66	0,046	5,9	41[c]
III	1,01	0,043	8,7	61[c]
IV	1,00	0,030	22	154[d]
V	1,17	0,003	103	720[d]
VI	1,10	0,002	133	930[d]
VII	1,15	0,002	148	1 030[d]

[a] Conditions; solvent: benzene; temp.: 60 °C; reaction time: 20 h.
[b] After purifying twice.
[c] Obtained by vapour pressure osmometry.
[d] Obtained by membrane osmometry.

It has been reported that the average DP of PVAmHCl is somewhat larger than that of PTBNVC, which was ascribed to the probable loss of some low molecular weight material[15] in the precipitation step of hydrolyzed PTBNVC. However, with low molecular weight PTBNVC the yield of PVAmHCl was still about 90%, which may indicate that no severe fractionation occurs during the hydrolysis step.

Since the characterization of low molecular weight PVAmHCl is rather complicated (PVAmHCl is a polyelectrolyte and not soluble in apolar organic solvents) only the number average DP's of PTBNVC are given. The DP's of PVAmHCl may be somewhat higher.

Measurements

Potentiometric titrations: Solutions of PVAm were obtained by eluting 3% aqueous solutions of PVAmHCl through an Amberlite IRA 401 anion-exchange column. All eluents were tested for the absence of chloride by adding a silver nitrate/nitric acid solution, which proved that the exchange had been complete.

The concentration of amine groups in the PVAm solution was determined by potentiometric titration with HCl (Titrisol ampoules, Merck) in 2 M NaCl. A Radiometer Copenhagen titration equipment fitted with a GK 2401 B pH electrode was used.

The degree of protonation σ was calculated as follows:

$$\sigma = \frac{c_{H^+_{added}} - c_{H^+_{free}} + c_{OH^-_{free}}}{c_{-N}} \tag{1}$$

where $c_{H^+_{added}}$ is the proton concentration as resulting of added HCl; $c_{H^+_{free}}$ and $c_{OH^-_{free}}$ are the concentrations of free protons and hydroxyl ions measured in the titration vessel, respectively. c_{-N} is the concentration of titratable groups.

Osmometry: The molecular weight of the PTBNVC samples was determined by osmometry in toluene. For samples having molecular weights >20000 a Hewlett Packard 502 high speed membrane osmometer thermostatted at 37 °C was used; samples with lower molecular weights were measured on a Knauer vapour pressure osmometer at 60 °C. Calibration was carried out with sucrose-octaacetate (BDH) recrystallized twice from ethanol.

Viscometry: Viscometry measurements were performed with a Hewlett Packard 5901 B auto-viscometer of the Ubbelohde type at 25,00 °C . Solutions were filtered before measurements. The measurements with PVAm solutions were conducted in a nitrogen atmosphere.

Visible light spectroscopy: Visible light spectra were obtained at room temperature under the exclusion of oxygen with a Unicam SP 800 D Ultraviolet spectrophotometer suitable for absorbances between 0 – 2 units. For experiments in the low concentration region of CoPc(NaSO$_3$)$_4$ a Cary 14 spectrophotometer was used with absorbance unit scales of 0 – 0,1 and 0 – 0,2.

Catalytic activity measurements: CoPc(NaSO$_3$)$_4$, kindly provided by Dr. T. P. M. Beelen, was synthesised according to the method by Weber and Busch[16] as described by Zwart et al.[17]. 2-Mercaptoethanol (Merck) was distilled and stored in the dark at 5 °C for periods not exceeding two weeks. The thiol content was checked iodometrically before use and was found to be 99%. For every set of experiments freshly prepared stock solutions of CoPc(NaSO$_3$)$_4$ and PVAm were used. Catalytic activity experiments were carried out in an all-glass thermostatted Warburg apparatus, equipped with a mechanical glass-stirrer. Stirring speed was 2300 r.p.m. Oxygen consumption rates were measured with a digital flow-meter equipment (Inacom Veenendaal, The Netherlands).

The polymeric catalyst was prepared by adding an aqueous solution of CoPc(NaSO$_3$)$_4$ to a PVAm solution in water, resulting in a coordinatively bound polymer metal complex. The catalyst solution was degassed twice and saturated with oxygen in 20 min. The reaction was started by adding the 2-mercaptoethanol to the reaction vessel using a syringe. Initial reaction rates were calculated from the oxygen consumption during the first minute of reaction.

It was assumed that at a stirring speed of 2300 r.p.m. oxygen would not meet any transport limitations by going from the gas phase to the bulk during reaction, since an increase of stirring

speed did not increase the reaction rate. Moreover, the reaction rate appeared to be first order in polymeric catalyst over a wide concentration range[5], which corroborates the above assumption.

Results and discussion

Polymeric catalyst during reaction

In earlier investigations it was shown that PVAm exhibits polyelectrolyte character and that pH affects conformation and charge density of the polymer[4, 18, 19].

Under reaction conditions, this very pronounced polyelectrolyte character is present as is shown in Fig. 3 (■), where the reduced viscosity of the polymeric catalyst in the presence of thiol is shown as a function of polymeric catalyst concentration. The viscometric behaviour shown is characteristic of polyelectrolytes[20]. As a result, it can be expected that during reaction the polymeric catalyst is more easily accessible to reactants, due to the expanded conformation. This implies that transport limitations, due to coil diffusion, are not likely to occur. The viscometric behaviour of the polymeric catalyst during reaction is in sharp contrast to the behaviour of PVAm solutions where the marked polyelectrolyte character is suppressed in 0,1 M NaCl and 0,01 M NaOH (⊙ in Fig. 3).
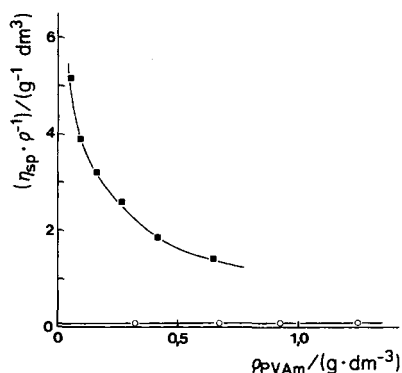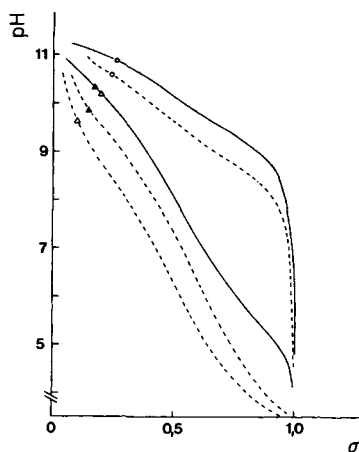

Fig. 3   Fig. 4

Fig. 3. Reduced viscosity, η_{sp}/ρ, of aqueous solutions of poly(vinylamine) (PVAm) vs. polymer mass concentration, ρ. (■): PVAm in the presence of $CoPc(NaSO_3)_4$ (N/Co = $7{,}7 \cdot 10^3$) and 2-mercaptoethanol ($c_{RSH} = 0{,}19$ mol $\cdot$ dm^{-3}); (⊙): PVAm in 0,1 M NaCl and 0,01 M NaOH; temp. 25,0 °C; $\bar{M}_{n,PVAm} = 5 \cdot 10^4$ g $\cdot$ mol^{-1}

Fig. 4. pH vs. degree of charge, σ. PVAm DP = 23 (▲); PVAm DP = 720 (△); 1,3-PDA (○). (— — —): no salt; (———)· in 2 M NaCl. Conc. of titratable groups $c_{-N} = 0{,}01$ mol $\cdot$ dm^{-3}, temp. 22 °C

Degree of charge of the polymeric catalyst

The effect of pH and ionic strength on the degree of charge of PVAm of various DP was determined by potentiometric titration of basic polymer solutions with HCl in the presence and absence of 2 M NaCl. In Fig. 4 titration curves are shown for PVAm with DP = 23 (▲) and 720 (△) and for 1,3-propanediamine (1,3-PDA) (○), which may be regarded as the low molecular weight analog of PVAm with a DP of 1,5. The curves in Fig. 4 clearly show that (1) the low molecular weight analog of PVAm (○) is more basic than PVAm itself, probably due to nearest neighbour interactions between the amine groups, present in PVAm[21,22], but almost absent in 1,3-PDA; (2) in the absence of salt (− − −) the pK_a of the polymeric amine groups is higher for the low molecular weight PVAm (▲), but at high ionic strength (———), where the polyelectrolyte character is suppressed, this molecular weight dependence disappears; (3) salt increases base strength of both PVAm and 1,3-PDA, and (4) under reaction conditions (bulk pH 5,8 − 7,5, depending on the amine/thiol ratio) the PVAm is 50 − 70% charged, but for 1,3-PDA the degree of protonation will be about 95%.

This means that PVAm possesses a larger quantity of free amine groups, able to form complexes with the $CoPc(SO_3)_4^{4-}$ ions, than 1,3-PDA does, while in both cases a large amount of thiol anions will be present as counterions near the protonated, charged amine groups. In the polymer many counterions are present in the close vicinity of $CoPc(SO_3)_4^{4-}$, attached to the polymer, which is not the case for 1,3-PDA.

Catalytic experiments

In order to investigate the dependence of reaction rate on the number average DP of PVAm and in order to prove whether enthalpic or entropic effects are dominant, catalytic activities and activation energies were determined for each polymer at rather low polymer concentrations.

We have found earlier[5] that the dependence of the reaction rate on the thiol concentration can be described by Michaelis-Menten kinetics[23]:

$$E + S \; \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} \; ES \; \xrightarrow{k_2} \; E + P \tag{2}$$

in which E stands for catalyst, S for substrate (RSH), and P for products. Assuming steady state kinetics it can be derived that

$$\frac{1}{v} = \frac{1}{k_2[E_0]} + \frac{K_m}{k_2[E_0][S]} \tag{3}$$

where v is the initial rate, $[E_0]$ and $[S]$ are the initial concentrations of $CoPc(NaSO_3)_4$ and RSH, k_2 is the rate determining rate constant, $K_m = (k_{-1} + k_2)/k_1$ is the Michaelis-Menten constant, and $K_s = k_1/k_{-1}$ is the equilibrium constant for substrate binding. For polymer IV Lineweaver-Burk plots in the temperature interval 10 − 35 °C are shown in Fig. 5a. From the intercept, slope, and polymer catalyst concentrations the values of the turnover number k_2 and the Michaelis-Menten
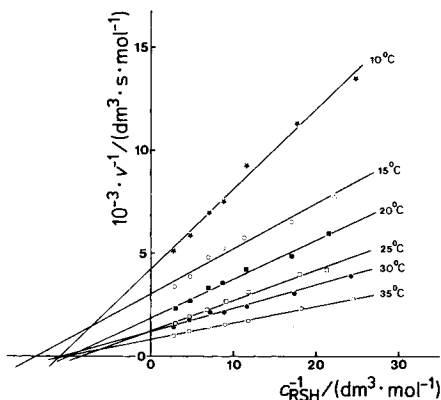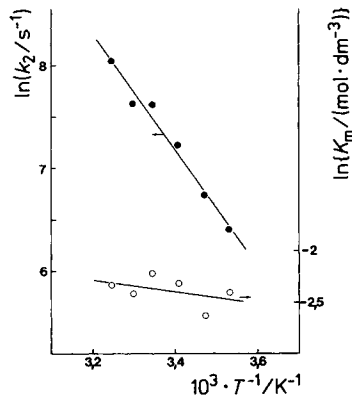
Fig. 5 a   Fig. 5 b

Fig. 5. (a) Lineweaver-Burk plots for various temperatures in the interval $10-35\,^{\circ}\mathrm{C}$ for polymer IV. v expressed in $\mathrm{mol}_{RSH} \cdot \mathrm{dm}^{-3} \cdot \mathrm{s}^{-1}$. $c_{-N} = 3,8 \cdot 10^{-5}\ \mathrm{mol} \cdot \mathrm{dm}^{-3}$, N/Co = 100; pH = 5,7; (b) Arrhenius plots for k_2 (■) and K_m (○)

constant K_m can be obtained. In Fig. 5 b the Arrhenius plots are shown containing the values of k_2 and K_m derived from Fig. 5 a. From the slope the (activation) enthalpies were calculated: $\Delta H_2^{\neq} = (47 \pm 4)\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$ and $\Delta H_m\ (= -\Delta H_s$ for $k_2 < k_{-1}) = (5 \pm 5)\ \mathrm{kJ} \cdot \mathrm{mol}^{-1}$, and from the intercept at $T^{-1} = 0$ the (activation) entropies are obtained: $\Delta S_2^{\neq} = (-34 \pm 10)\ \mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$ and $\Delta S_m\ (= -\Delta S_s$ for $k_2 < k_{-1}) = (-3 \pm 15)\ \mathrm{J} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$. Evidently $\Delta H_2^{\neq}$ is about 10 times larger than ΔH_m.

Since determination of $\Delta H_2^{\neq}$ in this way is quite laborious, while the precision in determination of K_m values is poor, activation energies for polymeric catalysts with polymeric ligands of various molecular weight were obtained from experiments performed at different temperatures at constant large thiol concentration. ([S] = 0,37 $\mathrm{mol} \cdot \mathrm{dm}^{-3}$). Since $\Delta H_2^{\neq}$ is so much larger than ΔH_m and since [S] is several times larger than K_m, the activation energies obtained in this way are almost equal to the values of $\Delta H_2^{\neq}$. For all polymeric ligands of different DP Lineweaver-Burk plots at 298 K were drawn in order to obtain the kinetic constants k_2^{298} and K_m^{298}. All these parameters thus obtained including $\Delta S_2^{\neq}$ (obtained from the intercept of a plot of $\ln\{v(1 + K_m^{298}/[S])/[E_0]\}$ ($\approx \ln k_2$) vs. T^{-1}) and $\Delta G_2^{\neq}$ ($= \Delta H_2^{\neq} - T\Delta S_2^{\neq}$) at 298 K are listed in Tab. 2.

It must be mentioned that 1,3-PDA exhibits Michaelis-Menten kinetics with respect to thiol, but that a curved Arrhenius plot is obtained (with increasing temperature reaction rate increases less than expected). The value of $\Delta H_2^{\neq 298}$ must therefore be regarded with some reserve. In Fig. 6 values of K_m, k_2, and $\Delta H_2^{\neq}$ at 298 K are shown as a function of DP. These values and specially K_m and k_2 depend not only on temperature but also on other reaction conditions such as pH and ionic strength. The figure clearly demonstrates the occurrence of a maximum in k_2 and K_m at a number average DP around 40. If the length of the polymeric ligand decreases from the

Tab. 2. Activation parameters and reaction constants at 298 K

Sample	DP	$\Delta H_2^{\ddagger}$	$\Delta S_2^{\ddagger}$	$\Delta G_2^{\ddagger}$ a)	$10^{-3} \cdot k_2$	K_m
		$kJ \cdot mol^{-1}$	$J \cdot mol^{-1} \cdot K^{-1}$	$kJ \cdot mol^{-1}$	s^{-1}	$mol \cdot dm^{-3}$
1,3-PDA	1,5	40	−78	63,2	0,1	0,06
I	23	47	−31	55,8	2,5	0,10
II	41	50	−17	55,6	2,5	0,13
III	61	46	−34	56,0	2,3	0,12
IV	154	47	−34	57,0	2,1	0,11
V	720	43	−46	57,1	1,4	0,08
VI	930	47	−36	57,2	1,3	0,07
VII	1 030	46	−41	57,9	1,1	0,07

a) $\Delta G_2^{\ddagger}$ calculated from unrounded values of $\Delta H_2^{\ddagger}$ and $\Delta S_2^{\ddagger}$.
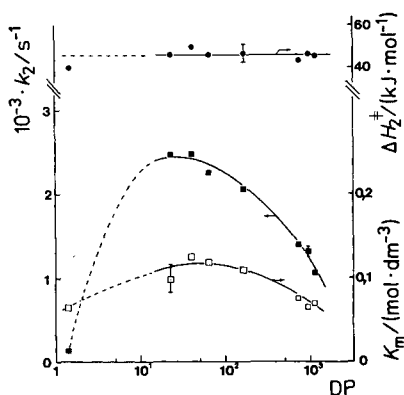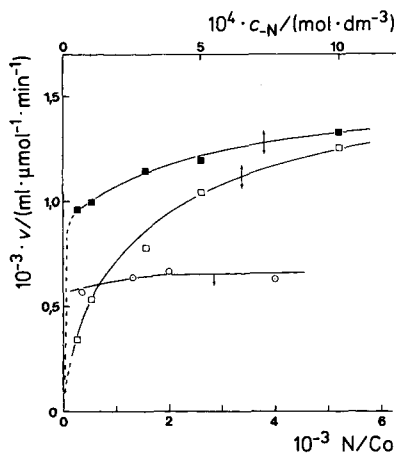
Fig. 6   Fig. 7

Fig. 6. Dependence of Michaelis-Menten constant K_m, rate constant k_2, and activation enthalpy $\Delta H_2^{\ddagger}$ on the degree of polymerization (DP) of the polymeric ligand, at 298 K. ($\square$): K_m^{298}; ($\blacksquare$): k_2^{298}; ($\bullet$): $\Delta H_2^{\ddagger 298}$. $c_{-N} = 3,8 \cdot 10^{-5}$ mol $\cdot$ dm^{-3}, N/Co = 100; pH = 5,7

Fig. 7. Catalytic activity (expressed in ml oxygen consumed per minute per μmole CoPc(NaSO$_3$)$_4$) of polymeric catalysts at various compositions vs. N/Co ratio. ($\blacksquare$): DP = 23, $c_{CoPc(NaSO_3)_4} = 1,9 \cdot 10^{-7}$ mol $\cdot$ dm^{-3}, c_{-N} variable. ($\square$): DP = 1 030, $c_{CoPc(NaSO_3)_4} = 1,9 \cdot 10^{-7}$ mol $\cdot$ dm^{-3}, c_{-N} variable. ($\bigcirc$): DP = 1 030, $c_{-N} = 10^{-4}$ mol $\cdot$ dm^{-3}, $c_{CoPc(NaSO_3)_4}$ variable, ionic strength was kept constant with catalytically inactive K$_4$Fe(CN)$_6$ at $5,7 \cdot 10^{-6}$ mol $\cdot$ dm^{-3}. $c_{RSH} = 0,37$ mol $\cdot$ dm^{-3}

maximum value an increase of the reaction constants k_2 and K_m can be observed up to about 40 − 20 monomeric units. The values of k_2 and K_m for 1,3-PDA (DP = 1,5), where polymeric effects are absent, are very low in comparison with the polymeric systems, but nevertheless reactivity is still about 3 times larger than for the conventional CoPc(NaSO$_3$)$_4$/OH$^-$ system[2].

Assuming that $k_2 \ll k_{-1} (K_m^{-1} \approx K_s)$ the molecular weight dependence of K_m may be attributed to the higher base strength occurring in low molecular weight PVAm (Fig. 4), which favours proton abstraction from RSH in the formation of an active enzyme-substrate complex.

From Fig. 6 it is unequivocally shown that $\Delta H_2^{\ddagger}$ does not depend on DP which strongly indicates that the reaction mechanism does not change when using polymeric ligands of different chain length. Therefore, the observed change in k_2 must be attributed to a change in local reactant concentrations, effective catalyst concentration, or activation entropy.

The local base strength in the vicinity of the catalytic sites enhances the local concentration of thiol anions, being the reactive species. From Fig. 4 it was shown that in low molecular weight PVAm basicity is higher than in high molecular weight PVAm, so this would account qualitatively for the observed molecular weight dependence. Moreover, at low polymer concentration differences in coil density[24] may enlarge these differences.

The effective catalyst concentration will be maximum when all the $CoPc(NaSO_3)_4$ is present in the monomeric form, since dimeric and oligomeric $CoPc(NaSO_3)_4$ are less catalytically active. It is known that steric protection against dimerization reactions can be achieved by the attachment of metalloporphyrins in low concentration to polymers[25]. Nonetheless, it has to be investigated whether the distribution of $CoPc(NaSO_3)_4$ among separate coils — the concentration of the latter will be higher for lower DP ligands at the same bulk concentration of monomeric units — affects the amount of monomeric $CoPc(NaSO_3)_4$. In other words it must be verified whether the catalytic activity depends on the N/Co ratio in the polymeric catalyst solution.

In Fig. 7 reaction rate is shown versus the N/Co ratio. The latter was varied by changing the $CoPc(NaSO_3)_4$ concentration at constant PVAm concentration and constant ionic strength for DP = 1030, (⊙), or alternatively by changing the PVAm concentration at constant $CoPc(NaSO_3)_4$ concentration for DP = 1030 (⊡) and for DP = 23 (■). From a comparison of the curves (⊙) and (⊡) in Fig. 7 it may be inferred that at these $CoPc(NaSO_3)_4$ concentrations not the N/Co ratio and thus the distribution among the separate coils is important but merely polymer concentration governs reaction rate. It may therefore be expected that the effective catalyst concentration will not be affected by the molecular weight of the polymeric ligand either. Curves (⊡) and (■) in Fig. 7 clearly show that (1) the molecular weight dependence of reaction rate becomes more pronounced at lower polymer concentrations and (2) that enhanced reaction rates are observed as polymer concentration increases. According to the former observation the effect of molecular weight on catalytic activity is more pronounced when the polymeric chains exist in an isolated fashion and chain interpenetration is practically absent.

The increase of reaction rate as polymer concentration becomes higher can be ascribed to the increase in bulk pH (observed: pH = 5,8 at $c_{-N} = 5 \cdot 10^{-5} \, mol \cdot dm^{-3}$

and pH $= 7,0$ at $c_{-N} = 10^{-3}$ mol $\cdot$ dm^{-3}) which will on itself increase reaction rate as we have shown earlier[*)4)].

While summarizing the above observations, i. e. the constancy of $\Delta H_2^{\neq}$ over a wide molecular weight range, the independence of reaction rate on the CoPc(NaSO$_3$)$_4$ distribution among the polymer coils, and the higher basicity of amine groups in low molecular weight PVAm, it becomes plausible that the essence of the molecular weight dependence observed for the present polymeric catalyst, is explained by the differences in local base strength in low and high molecular weight PVAm.

Visible light spectroscopy

From the catalytic experiments it was inferred that the effective catalyst concentration, i. e. amount of monomeric CoPc(NaSO$_3$)$_4$ was not affected seriously by the molecular weight of the polymeric ligand. VIS experiments will conform this conclusion. In Fig. 8 the visible light spectra of CoPc(NaSO$_3$)$_4$ in the presence of low and high molecular weight PVAm at rather low polymer concentrations are shown. It reveals that the intensity of both the monomer (14900 cm^{-1}) and dimer (16000 cm^{-1}) peak of CoPc(NaSO$_3$)$_4$ is slightly lower in the case of high molecular weight PVAm. If a molecular weight dependent dimerization of CoPc(NaSO$_3$)$_4$ would play an important role, the intensity of the dimer peak should have increased relative to the monomer peak for the larger DP sample. Such behaviour, however, has not been observed. The observed slight difference between the spectra may be caused by a changing micro-environment of CoPc(NaSO$_3$)$_4$ when attached to polymers of different molecular weight. At much higher PVAm concentrations no difference in spectra was observed.

The effect of local base concentration on the visible light spectra of CoPc(NaSO$_3$)$_4$ in the presence of thiol is shown in Fig. 9. Equimolar ligand solutions of 1,3-PDA and PVAm were used as base. The band at 22000 cm^{-1} is only observed when base is present and must be assigned to metal-to-ligand charge transfer transitions of Co(I)[26]. This means that reduction of CoPc(NaSO$_3$)$_4$ only takes place in the presence of base. Indeed no catalytic activity is observed when RSH is present in the absence of any base. For other systems involving transition metal compounds such as Fe(III)/ myoglobine[27] and Vit B$_{12a}$[28] in the presence of thiols, similar spectroscopic observations have been made. The reduction of the metal centre solely occurred when, apart from the base involved in the complexation of this centre, extra base was added.

In Fig. 9 a band of much lower intensity at 22000 cm^{-1} is observed for 1,3-PDA in comparison with PVAm giving supporting evidence that the base concentration in the vicinity of the oxidation sites, which will be much higher for the polymer, dominates the reduction of these sites. These spectroscopic observations agree with the lower reaction rate observed for 1,3-PDA in comparison with PVAm (Fig. 6).

[*)] In order to perform pH-stat measurements, we deliberately did not make use of buffer solutions, since salt largely affects reaction rate.

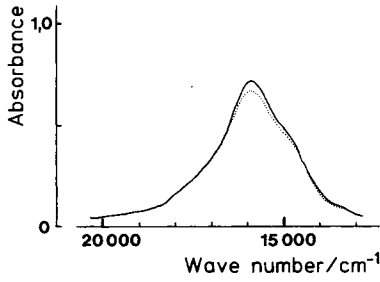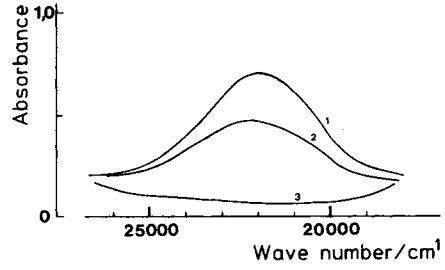Fig. 8   Fig. 9

Fig. 8. Visible light spectra of $CoPc(NaSO_3)_4$ in aqueous PVAm solution under nitrogen atmosphere. Conc. of N-groups c_{-N} = $4 \cdot 10^{-4}$ mol $\cdot$ dm^{-3}, $c_{CoPc(NaSO_3)_4}$ = $4 \cdot 10^{-6}$ mol $\cdot$ dm^{-3}; path length b = 50 mm; (———) DP = 23; ($\cdots\cdots$) DP = 930

Fig. 9. Visible light spectra of the interaction product of $CoPc(NaSO_3)_4$ and RSH in the presence of (1): PVAm, DP = 930, c_{-N} = $2 \cdot 10^{-3}$ mol $\cdot$ dm^{-3}; (2): 1,3-PDA, c_{-N} = $2 \cdot 10^{-3}$ mol $\cdot$ dm^{-3}; (3): no base. Nitrogen atmosphere. $c_{CoPc(NaSO_3)_4}$ = $2 \cdot 10^{-5}$ mol $\cdot$ dm^{-3}, c_{RSH} = 0,07 mol $\cdot$ dm^{-3}, b = 10 mm
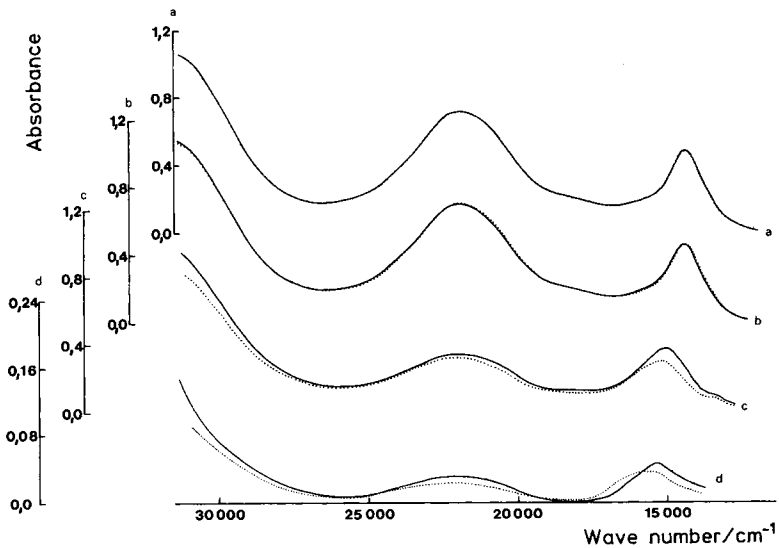

Fig. 10. Visible light spectra of the interaction product of $CoPc(NaSO_3)_4$ and RSH in the presence of PVAm of different molecular weight. Nitrogen atmosphere, N/Co = 100; c_{RSH} = 0,07 mol $\cdot$ dm^{-3}. (———) DP = 23; ($\cdots\cdots$) DP = 930. (a) Conc. of N-groups c_{-N} = 10^{-2} mol $\cdot$ dm^{-3}, path length b = 2 mm; (b) c_{-N} = $2 \cdot 10^{-3}$ mol $\cdot$ dm^{-3}, b = 10 mm; (c) c_{-N} = $4 \cdot 10^{-4}$ mol $\cdot$ dm^{-3}, b = 50 mm; (d) c_{-N} = $8 \cdot 10^{-5}$ mol $\cdot$ dm^{-3}, b = 50 mm

The influence of polymer concentration and molecular weight on the visible light spectra of $CoPc(NaSO_3)_4$ in the presence of thiol is shown in Fig. 10. Amine group concentration was varied between 10^{-2} and $8 \cdot 10^{-5}$ mol $\cdot$ dm^{-3}. N/Co ratio and thiol concentration were kept constant. Fig. 10 demonstrates that at N-group concentrations larger than $2 \cdot 10^{-3}$ mol $\cdot$ dm^{-3} the spectra with the low and high molecular weight PVAm are identical. But below this critical concentration the spectra differ more when concentration is lowered. The 22000 cm^{-1} band intensity indicates that more $CoPc(NaSO_3)_4$ exists in the reduced state when low molecular weight ligands are used. Obviously, a significant molecular weight dependent micro-environmental change of the oxidation sites is observed only at N-group concentrations lower than $2 \cdot 10^{-3}$ mol $\cdot$ dm^{-3} (0,01 w/v %). These spectroscopic observations are in qualitative agreement with the difference in reactivity between catalysts with low and high molecular weight PVAm (see Fig. 7).

Conclusions

At low polymer concentrations ($<0,01$ w/v %) the reaction rate is largely affected by the molecular weight of the polymeric ligand of the catalyst.

Catalysts with polymeric ligands possess higher catalytic activity than in case of a basic ligand without polymeric character (1,3-PDA). However, the polymeric ligand with the lowest molecular weight provides the highest activity.

Neither the activation enthalpy ΔH_2^+ nor the effective catalyst concentration seems to be dependent on the DP of the ligands. Potentiometric titrations show that the amine groups in low molecular weight PVAm are more basic in comparison with the high molecular weight PVAm. From these observations it becomes plausible that local base concentration and thus local thiol anion concentration in the vicinity of the oxidation sites are molecular weight dependent and form the essence of the observed molecular weight dependence of reaction rate. At low polymer concentrations when the polymer chains may be assumed to exist in an isolated fashion these molecular weight dependent effects are more pronounced.

Visible light spectra of $CoPc(NaSO_3)_4$ in the presence of 1,3-PDA and PVAm solutions suggest that specially the local base strength in the vicinity of the oxidation sites dominates the amount of reduced catalyst. This may also account for the observed differences in the spectra of low and high molecular weight ligands, i.e. larger amount of polymeric catalyst in the reduced state for low than for high molecular weight ligands. The spectra were in qualitative agreement with the observed differences in catalytic activity.

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