Macromolecular effects on the oxidation of thiols : catalyzed by cobalt (II)phtalocyanine-tetra-sodium sulfonate attached to polyamines and polyammonium salts

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MACROMOLECULAR EFFECTS
on the
OXIDATION OF THIOLS

Catalyzed by
Cobalt(II)Phthalocyanine-Tetra-Sodium Sulfonate

Attached to
PolyAmines and PolyAmmonium Salts

W.M. BROUWER

MACROMOLECULAR EFFECTS ON THE OXIDATION OF THIOLS CATALYZED BY COBALT(II)PHTHALOCYANINE-TETRA-SODIUM SULFONATE ATTACHED TO POLYAMINES AND POLYAMMONIUM SALTS

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PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL EINDHOVEN, OP GEZAG VAN DE RECTOR MAGNIFICUS, PROF. DR. S. T. M. ACKERMANS, VOOR EEN COMMISSIE AANGEWEZEN DOOR HET COLLEGE VAN DEKANEN IN HET OPENBAAR TE VERDEDIGEN OP DINSDAG 11 SEPTEMBER 1984 TE 16.00 UUR

DOOR

WILFRIDUS MARIA BROUWER

GEBOREN TE ZEIST

Dit proefschrift is goedgekeurd door de
promotoren: Prof. Dr. Ir. A.L. German
Prof. Dr. R. Prins

CONTENTS

INTRODUCTION

General introduction

According to Ostwald's definition in 1901 (1), a catalyst changes the rate of a chemical reaction, without itself being consumed or altering the position of the final thermodynamic equilibrium. For this reason, rate enhancing catalysts are widely used in chemical processes in industry, enabling more efficient processes and offering new ways of preparing high quality products. Also in living organisms biocatalysts, then called enzymes, are operative and their high specificity and selectivity are subject to many investigations.

Polymers or macromolecules are long, thread-like molecules which in solution often exist as loosely wound coils, with average dimensions in the colloidal size range (2). In special cases, e.g. when the macromolecules bear charges, specific chain interactions may occur and rod-like or helix-like conformations become possible (3). Polymers may occur naturately, e.g. starch and proteins, or may be synthesized at a laboratory or industrial scale. Through special synthetic methods, developed in polymer chemistry, copolymers can be prepared with well-known composition and microstructure, tailor-made for widely different purposes.

Sometimes polymers possess catalytic activity in certain chemical reactions and are therefore called polymeric catalysts although this term may not be in complete accordance with Ostwald's definition, as was shown by Ise for polyelectrolyte catalysed reactions (4).

A well-known polymeric catalyst is polyvinylimidazole in the hydrolysis of nitrophenylesters (5). Here the cooperating, monomeric repeating units were found responsible for the catalytic action. In other polymeric catalysts, specific catalytic activity is obtained by the introduction of catalytically active functionalities either during polymerization, e.g. active monomers (6), or afterwards, e.g. transition metals in polymer metal complexes (7,8).

Often enzymes are essentially polymeric catalysts, although the latter term is commonly reserved for synthetic polymeric catalysts. It is therefore not surprising that many synthetic polymeric catalysts fulfil one or more criteria characteristic of enzyme catalysis (9): e.g. specificity, rate enhancement, saturation kinetics similar to Michaelis-Menten kinetics (10) and multi-functional catalysis. Some polymeric catalysts possess high intrinsic catalytic activity, comparable to enzymes and are called synzymes (from synthetic enzymes).

Hydrophobic interactions, electrostatic interactions or both are of prime importance in substrate binding, while the availability of suitable, generally base or acid groups in the appropriate ionic forms and orientations are necessary for catalysis. In order to allow more technical application, soluble polymeric catalysts need to be immobilized on solid supports, thus facilitating separation of the catalysts from the reaction solution and enabling its reuse. Many reviews on this topic appeared during the recent years (7,11-14).

Closely related to polymeric catalysis is the catalytic action of soaps in solution, i.e. micellar catalysis (15). Very recently an example of mixed polymeric and micellar catalysis, so-called polymer-surfactant complex catalysis was reported (18). These rather new possibilities in polymeric catalysis may be of great importance to industry, where progressively water continuous emulsions will replace the conventional reaction systems in which organic solvents are used.

The polymeric catalysts presented in this thesis are capable of oxidizing thiols with molecular oxygen to disulfides in aqueous media, exhibiting high selectivity.

Thiol catalysis plays an important role in oil sweetening used in the refining industry for rendering thiols harmless (19), the latter being invariably present in hydrocarbon distillates. Sometimes thiols are deliberately used in industrial processes, e.g. the addition of dodecanethiol as a chain length modifier in emulsion polymerization, but removal from the end product is often desirable because of their bad smell. In solving such problems highly effective thiol oxidation may offer a usefull approach. Finally, the formation and role of disulfide linkages in biological systems also stresses the importance of research on thiol oxidation (18).

All catalysts used in the present investigations contain the catalytically active cobalt(II)phthalocyanine-tetrasodium sulfonate (abbrev.: $CoPc(NaSO_3)_4$), a water soluble derivative of cobaltphthalocyanine. The latter is a thiol oxidation catalyst in the presence of base (19), and has a porphyrin-like structure similar to that of all kinds of biological redox systems such as haemoglobin and vitamin B_{12}. At present CoPc is being used in the oil refining industry.

From earlier work of Zwart (20) and Schutten (21) in the Catalysis and Polymer Chemistry departments of our institute, it appeared that attachment of this organometal compound to a basic polymer resulted in a large enhancement of the catalytic activity (22). It was suggested that prevention of dimerization of the $CoPc(NaSO_3)_4$ catalyst and enrichment of the weakly acidic substrate in the basic coils accounted for the enhanced catalytic activity of these multi-functional catalysts.

All polymeric ligands used in the investigations belong to the group of water soluble polyamines and polyquaternized ammonium salts, which are at present, apart from their known industrial importance (23), of great interest for their sometimes peculiar physicochemical behavior (24-27), their chemo-therapeutic properties (28,29) and their propensity to form polymer-metal chelates exhibiting oxygen binding ability (30). All these properties are undoubtedly related to the positive net charge these polymers bear specially at neutral pH. This polyelectrolyte character, as will appear from this thesis, also plays an important role in the polymer catalyzed thiol oxidation.

Aim and outline of this thesis

The aim of this thesis is to study the promoting effects of the polymeric ligand on the catalytic activity, including the commonly observed problem of partial deactivation when active polymeric catalysts are immobilized, and thiol oxidation in surfactant containing systems. The latter become of industrial importance.

The polymeric catalyst, mainly used in the investigations described in this thesis is $CoPc(NaSO_3)_4$ attached to poly(vinylamine). Overall coil dimensions and the effect of thiol addition hereon have been investigated by viscometry (Chapter I). Also the incorporation of the $CoPc(SO_3)_4^{4-}$ ion in the polymer was investigated. In Chapter II the pH dependence of the catalytic activity as well as its viscometric behavior is presented and discussed. Kinetic measurements on the oxidation of 2-mercaptoethanol are presented in Chapter III and the enzyme-like behavior of the polymeric catalyst is established. The molecular weight of poly(vinylamine) has been varied and its effect on catalytic activity and activation parameters has been investigated and discussed (Chapter IV). Copolymers of nearly randomly distributed vinylamine and vinylalcohol were synthesized (Chapter V) and used as polymeric ligands for $CoPc(NaSO_3)_4$ as described in Chapter VI, in order to obtain insight into the relationship between catalytic activity and amine group density in the polymeric ligands.
In Chapter VII the investigation has been extended to other thiols including the hydrophobic dodecanethiol and the use of surfactant in the thiol oxidation catalysis has been introduced. Features and drawbacks are discussed. In Chapter VIII other polycationic catalysts are investigated. Here the concepts basically developed in the Chapters II, III, VI and VII accounting for the enhanced polymer catalyst activity, will appear to have a more general applicability.
Finally, in Chapter IX, matrices of cross-linked poly(vinylamine) have been used as insoluble polymeric supports for $CoPc(NaSO_3)_4$. The effects

of several experimental parameters were measured, from which suggestions for further improvement of the immobilized catalyst systems have been deduced.

Chapters I-IX, corresponding to references 31-39, respectively, have been published already or will be published soon.
The co-authors, Ir. P.A.M. Traa and Ir. T.J.W. de Weerd have had a major part in the performance of the experiments as described in Chapter IX.

References

(1) W. Ostwald, *Phys. Z.*, 3 (1902), 313
(2) P.J. Flory, *Principles of Polymer Chemistry*, Ithaka, Cornell University Press, 1953
(3) C. Tanford, *Physical Chemistry of Macromolecules*, John Wiley, New York 1961
(4) N. Ise in A. Rembaum and E. Sélégny (eds), *Polyelectrolytes and their applications*, D. Reidel, Dordrecht, The Netherlands, 1975, p. 71
(5) C.G. Overberger, T.St. Pierre, N. Vorcheimer, J. Lee and S. Yaroslavsky, *J. Am. Chem. Soc.*, 87 (1965), 296
(6) H.C. Kiefer, W.I. Congdon, I.S. Scarpa and I.M. Klotz, *Proc. Nat. Acad. Sci. USA*, 69 (1972), 2155
(7) E. Tsuchida and H. Nishide, *Adv. Pol. Sci.*, 24 (1977), 1
(8) M. Kaneko and E. Tsuchida, *J. Polym. Sci. Macromol. Rev.*, 16 (1981), 397
(9) C.W. Warton, *Int. J. Biolog. Macromolecules*, 1 (1979), 3
(10) L. Michaelis and M.L. Menten, *Biochem. Z.*, 49 (1913), 333
(11) M.A. Kraus and A. Patchornik, *J. Polym. Sci. Macromol. Rev.*, 15 (1980), 55
(12) G. Manecke and W. Storck, *Angew. Chem.*, 90 (1978), 691
(13) A. Akelah and D.C. Sherrington, *Chem. Rev.*, 81 (1981), 557

(14) J.M.J. Fréchet, *Tetrahedron*, 37 (1981), 663

(15) J.H. Fendler and E.J. Fendler, *Catalysis in Micellar and Macromolecular Systems*, Academic Press, New York, 1975

(16) H.G.J. Visser, R.J.M. Nolte and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, 102 (1983), 417

(17) A.M. Oswald and T.J. Wallace in N. Kharasch and C.L. Meyers (eds) *The Chemistry of Organic Sulphur Compounds*, Vol 2, Pergamon, London, 1966, ch. 8

(18) P.C. Jocelyn, *Biochemistry of the SH group*, Academic Press, London, 1972

(19) N.N. Kundo and N.P. Keier, *Russ. J. Phys. Chem.*, 42 (1968), 707

(20) J. Zwart, *PhD Thesis*, University of Technology, Eindhoven, The Netherlands, 1978

(21) J.H. Schutten, *PhD Thesis*, University of Technology, Eindhoven, The Netherlands, 1981

(22) J.H. Schutten and J. Zwart, *J. Mol. Catal.*, 5 (1979), 109

(23) M.F. Hoover, *J. Macromol. Sci. Chem.*, A4 (1970), 1327

(24) R. Barbucci, V. Barone, P. Ferruti and L. Oliva, *J. Polym. Sci. Polym. Symp.*, 69 (1981), 49

(25) E.A. Lewis, J. Barkley and T.St. Pierre, *Macromolecules*, 14 (1981), 546

(26) P.L. Rinaldi, C. Yu and G.C. Levy, *Macromolecules*, 14 (1981), 551

(27) C.J. Bloys van Treslong and A.J. Staverman, *Recl. Trav. Chim. Pays-Bas*, 93 (1974), 171

(28) P. Ferruti in E.J. Goethals (ed), *Polymeric Amines and Ammonium salts*, Pergamon, Oxford, 1980

(29) H. Moroson and M. Rotman in A. Rembaum and E. Sélégny (eds), *Polyelectrolytes and their applications*, D. Reidel, Dordrecht, The Netherlands, 1975, p. 187

(30) E. Tsuchida, H. Nishide and H. Yoshioka, *Makromol. Chem. Rapid. Commun.*, 3 (1982), 161,693

(31) W.M. Brouwer, P. Piet and A.L. German, *Polym. Commun.*, 24 (1983), 216

(32) W.M. Brouwer, P. Piet and A.L. German, *Polym. Bull.*, 8 (1982), 245

(33) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.*, 22 (1984), 297

(34) W.M. Brouwer, P. Piet and A.L. German, *Makromol. Chem.*, 185 (1984), 363

(35) W.M. Brouwer, P. Piet and A.L. German, *J. Polym. Sci. Chem. Ed.*, accepted

(36) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.*, (1984), accepted

(37) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.*, accepted

(38) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.*, submitted

(39) W.M. Brouwer, P.A.M. Traa, T.J.W. de Weerd, P. Piet and A.L. German, *Angew. Makromol. Chem.*, submitted

Chapter I

Viscometric characterization of a polymeric catalyst for the autoxidation of thiols

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(*Received* 8 *October* 1982; *revised* 1 *December* 1982)

A polymeric catalyst for the oxidation of thiols to disulphides by molecular oxygen was prepared by mixing aqueous solutions of cobalt(II)phthalocyanine-tetra-sodiumsulphonate ($CoPc(NaSO_3)_4$) and poly(vinylamine) (PVAm). The incorporation of the $CoPc(SO_3)_4^{4-}$ ion in the polymer was investigated by viscometry. Conformational changes in the catalyst upon addition of substrate were studied. Only a single coordination site for the $CoPs(SO_3)_4^{4-}$ ions appeared to be occupied by a polymeric ligand and the addition of substrate to the polymeric catalyst resulted in a large extension of the polymer coil.

Keywords Thiol autoxidation; polymeric catalysis; poly(vinylamine); conformational changes; viscometric characterization

INTRODUCTION

Polymeric catalysts often shown an enhanced activity. Consequently, attention has been paid to the specific role of the polymer chain in this process. The apparent analogy with enzymatic reactions has stimulated attempts to gather knowledge about enzyme action from polymer catalysis studies, and *vice versa*. Polymers can be tailor-made, which offers the possibility of introducing several compositional and configurational effects that may influence the catalytic mechanism and thus reaction rate and specificity. In our laboratory a study is in progress on the catalytic autoxidation of thiols with molecular oxygen by polymeric catalysts. The viscometric characterization of one such catalyst is the subject of this report.

EXPERIMENTAL

PVAm HCl was synthesized by the Hart method[1] with some minor modifications ($\bar{M}_{n,\mathrm{PVAm}} = 61.10^3$ from membrane osmometry experiments in water, containing 0.01 N NaOH and 0.1 M NaCl). Aqueous solutions of PVAm were obtained by eluting a 3% solution of PVAm HCl through an Amberlite IRA-401 ion-exchange column. The equivalent amine concentration was determined by potentiometric titration with HCl solution (Merck, Titrisol ampoules) in the presence of 2 M NaCl. 2-Mercaptoethanol was purchased from Merck and distilled before use.

$CoPc(NaSO_3)_4$, kindly provided by Dr T. P. M. Beelen, was synthesized according to an adaptation by Zwart *et al.*[2] of the method by Weber and Busch[3]. Viscosity measurements on filtered solutions were carried out at (25.00 ± 0.05)°C in a Hewlett Packard automatic solution viscometer of the Ubbelohde type. All measurements were performed under a nitrogen gas atmosphere to prevent absorption of oxygen and carbon dioxide. Samples were prepared using nitrogen purged, sealed, ampoules and syringes. In those experiments where thiol was added, measurements were conducted twenty minutes after addition, since small time effects were observed. All salts mentioned were p.a.

pH measurements were performed with a Radiometer Copenhagen pH-meter (PHM 62), equipped with a GK 2401 B electrode.

RESULTS AND DISCUSSION

Cobalt(II)phthalocyanine-tetra-sodiumsulphonate ($CoPc(NaSO_3)_4$, (see *Figure 1*), attached to the weakly basic poly(vinylamine) (PVAm) appeared to be a very effective catalyst for the autoxidation of thiols to disulphides[4]. It is prepared by mixing aqueous solutions of $CoPc(NaSO_3)_4$ and PVAm.

In order to elucidate the mode of incorporation of $CoPc(NaSO_3)_4$ in the polymer chain, which may be an important factor determining high catalytic activity, the viscosity of aqueous solutions of PVAm has been measured upon addition of small amounts of $CoPc(NaSO_3)_4$ and other salts, which in contradistinction to $CoPc(NaSO_3)_4$, do not possess the propensity for interaction, other than ionogenic, with PVAm. The average charge number of the anions, *z*, varied between 2 and 4. It is apparent from *Figure 2* that the reduced viscosity decreases with increasing counter-ion charge *z*.

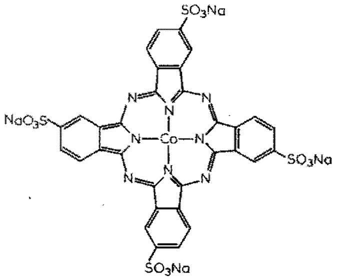

Figure 1 Structure of $CoPc(NaSO_3)_4$

0263-6476/83/070216-02$03.00

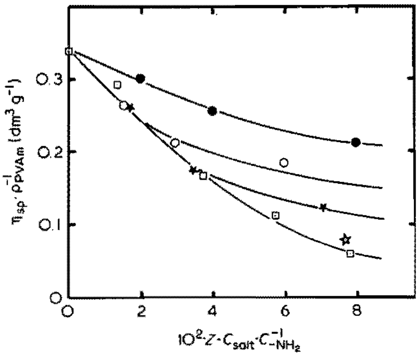

Figure 2 **Reduced viscosity of PVAm vs. the ratio of the total charge number of counter-ions (=$z.c_{salt}$) and molar amine concentration, c_{-NH_2}. Temperature 25.00±0.05°C; pH=10.3±0.1; c_{-NH_2}=16.4 mg eq dm^{-3}; $\bar{M}_{nPVAm}$=61000 g mol^{-1}; ● sodiumtartrate, z=2; ○ sodiumcitrate, z=3; ★ sodiumethylene-di-amino-tetra-acetate, z=3.5; ☆ potassium-hexa-cyanoferrate(II), z=4; □ CoPc(NaSO$_3$)$_4$, z=4**

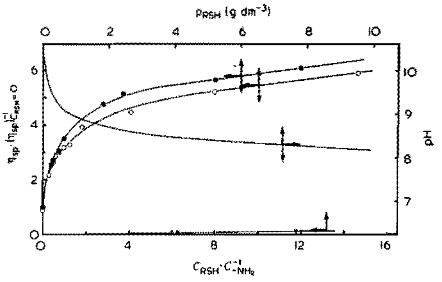

Figure 3 **Viscosity ratio of various solutions relative to a solution of PVAm vs. the molar ratio of thiol (RSH) and amine ligands. In all measurements c_{-NH_2}=8.4 mg eq dm^{-3} pH of the system and weight concentration of thiol (ρ_{RSH}) are also indicated on separate axes. $\bar{M}_{n,PVAm}$=61000 g mol^{-1}. Temperature 25.00 ±0.05°C. ● CoPc(NaSO$_3$)$_4$/NH$_2$=0; ○ CoPc(NaSO$_3$)$_4$/NH$_2$=10^{-3}; ★ RSH in water**

The addition of salt may be expected to affect the 'double-layer' between the slightly positively charged polymer chain and the negatively charged counter-ions. As a consequence, the presence of salt and in particular those possessing a high counter-ion charge will diminish the double-layer repulsion between separate chain segments, causing a shrinkage of the polymer coil and a decrease in viscosity. These phenomena have been observed in the interaction between charged colloidal particles[5]. Upon addition of the hexa-cyanoferrate(II)-ion, in which event no complexation between the central metal atom and amine ligands of the polymer is to be expected, the reduced viscosity of the PVAm solution shows a decrease similar to that observed in the case of addition of the equally charged CoPc(NaSO$_3$)$_4^{4-}$ ion. This is a strong indication that no multi-ligand intramolecular chelate formation occurs after addition of CoPc(NaSO$_3$)$_4$ to PVAm solutions. The formation of multi-ligand complexes between multi-dentate polymers and transition metal ions will invariably be accompanied by a sharp additional decrease in viscosity, due to the contraction of the polymer chain[6]. Consequently, the viscosity experiments support the view that only one axial position of the central metal atom of CoPc(NaSO$_3$)$_4$ is involved in the coordinative interaction with PVAm.

Schutten *et al.*[4] have performed e.s.r. measurements on the system CoPc(COOH)$_4$–PVAm in DMSO and obtained an e.s.r. signal quite typical of 5-coordinate cobalt complexes. The present viscosity measurements completely confirm these earlier findings and provide conclusive evidence of the proposed uniaxial coordination.

In order to obtain a better insight into the conformation of the catalyst during reaction, we have investigated the polymeric complex by monitoring the viscosity changes upon addition of substrate, viz. 2-mercaptoethanol (RSH).

Because RSH is a weak acid and PVAm a polybase, a pH change of the system upon addition of RSH could be expected. Thus the pH was monitored during addition of thiol to PVAm in a separate experiment (*Figure 3*). The following conclusions can be drawn:

The viscosity contribution of RSH itself in aqueous solution (marked with the asterisk) is low, as might be expected for a low molecular mass solute.

The viscosity of the PVAm solution increases dramatically upon addition of substrate (○) and (●) in *Figure 3*), accompanied by a distinct fall of pH. The polymer conformation is considerably affected by the pH, as reported earlier[7,8];

The presence of CoPc(NaSO$_3$)$_4$ only leads to a slightly lower (*ca.* 8%) viscosity curve, again indicating that no intramolecular chelates are formed.

Thus it may be concluded that during reaction the polymeric catalyst is freely accessible to reactants because the uniaxial coordination of CoPc(NaSO$_3$)$_4$ to PVAm and the lower pH, caused by the presence of the substrate, are giving rise to an extended conformation.

REFERENCES

1 Hughes, A. R. and St. Pierre, T. *Macromol. Synth.* 1977, **6**, 31
2 Zwart, J., Van der Weide, H. C., Bröker, N., Rummens, C., Schuit, G. C. A. and German, A. L. *J. Mol. Catal.* 1977–1978, **3**, 151
3 Weber, J. H. and Busch, P. H. *Inorg. Chem.* 1965, **4**, 469
4 Schutten, J. H. and Zwart, J. *J. Mol. Catal.* 1979, **5**, 109
5 Hiemenz, P. C. 'Principles of Colloid and Surface Chemistry', Marcel Dekker, Basel (1977), 352
6 Tsuchida, E. and Nishide, H. *Adv. Polym. Sci.* 1977, **24**, 1
7 Teyssie, Py., Decoene, C. and Teyssie, M. T. *Makromol. Chem.* 1965, **84**, 51
8 Brouwer, W. M., Piet, P. and German, A. L. *Polym. Bull.* 1982, **8**, 245

Polymer Bulletin 8, 245-251 (1982)

Polymer Bulletin

Chapter II

Autoxidation of Thiols with Cobalt (II) Phthalocyanine-Tetra-Sodium Sulfonate, Attached to Poly(Vinylamine)

1. pH and Viscometric Effects

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Summary

The oxidation of 2-mercaptoethanol with molecular oxygen in water with cobalt(II)phthalocyanine-tetra-sodium sulfonate attached to poly(vinylamine) has been investigated.

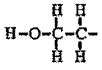
Specially attention was paid to the effect of pH and chain dimensions on polymer activity. The polymer catalyst possesses a large conformational freedom at neutral pH, but at higher pH a shrinkage of the polymer coil occurs and diffusion limitations cannot be excluded. The catalyst shows an enzyme-like behaviour in the autoxidation of thiol. Overall activation energies appear to decrease with increasing pH. At pH = 7.4, E_a = 61 KJ mole^{-1}; at pH = 9.5, E_a = 3 KJ mole^{-1}.

Electrostatic effects are of major importance in the chemical reactivity since they affect the local thiol-anion concentration in the close vicinity of the polymer attached oxidation sites.

Introduction

In our laboratory the autoxidation of 2-mercaptoethanol (RSH) with water soluble cobalt(II)phthalocyanine-tetra-sodium sulfonate ($CoPc(NaSO_3)_4$), attached to poly(vinylamine) (PVAm), has been investigated (SCHUTTEN and ZWART 1979; SCHUTTEN et al. 1979.).

$$4\ RSH + O_2 \xrightarrow[PVAm]{CoPc(NaSO_3)_4} 2\ RSSR + 2\ H_2O \qquad (1)$$

with R =

$$H{-}O{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}$$

The cobaltphthalocyanine is an organometallic compound, consisting of cobalt(II) incorporated in a porphyrin ring. The derivative used here ($CoPc(NaSO_3)_4$) carries four sulfonic groups, which makes it soluble in water. Thiol oxidation plays a role in biologic systems and is an important process in the desulferization of oil and natural gas.

It was suggested that the enhanced activity of the polymeric system in comparison with the system $CoPc(NaSO_3)_4/OH^-$ in the absence of PVAm mainly could be attributed to the high density of basic sites on the polymer, which increases the thiol-anion concentration, and to the polymeric coil structure, inhibiting the formation of binuclear oxo-adducts, which are , catalytically inactive (SCHUTTEN and ZWART 1979; SCHUTTEN et al. 1979.).

0170-0839/82/0008/0245/$01.40

From these previous investigations it appeared that addition of base affected the catalytic activity. Therefore, we have examined the specific effect of pH on the catalytic activity and on the conformation of the polymeric catalyst. For the latter purpose viscometry was used.
Moreover, overall activation energies have been determined. The results might elucidate some important aspects involved in the catalytic behaviour of the polymeric catalyst.

Experiments

Chemical reagents

All solutions were prepared with distilled water. PVAmHCl was purchased from Polysciences Inc. (Warrington U.S.A.), $\bar{M}_{w,\mathrm{PVAmHCl}}$ = 50,000-160,000 . Aquous solutions of PVAm were obtained by eluting a 3 % solution of PVAmHCl through an Amberlite IRA-401 ion-exchange column. The equivalent amine concentration (c_{-NH_2}) was determined by potentiometric titration with HCl solution (Merck, Titrisol ampoules) in the presence of 2 M NaCl.
$CoPc(NaSO_3)_4$ was kindly provided by Dr. T.P.M. Beelen, and was synthesised analogous to the method by WEBER and BUSCH (1965), as described elsewhere (ZWART et al. 1977).
2-Mercaptoethanol (Merck) was distilled before use. It was stored in the dark at 5 °C for periods not exceeding two weeks. All salts, mentioned in the text were p.a.

Viscosity

Measurements on filtered solutions were carried out at (25.00±0.05) °C in a Hewlett Packard automatic solution viscometer of the Ubbelohde type. All measurements were performed under a nitrogen gas atmosphere to prevent absorption of oxygen and carbon dioxide. Samples were prepared using nitrogen purged, sealed ampoules and syringes. In those experiments where thiol was added, measurements were conducted twenty minutes after addition, since small time effects were observed.

Catalyst preparation

The catalyst was prepared by mixing aqueous solutions of PVAm and $CoPc(NaSO_3)_4$. First the solution of PVAm was added, the solution of $CoPc(NaSO_3)_4$ immediately afterwards.
Then the desired pH was adjusted by addition of NaOH (0.3 N) or HCl-solution (0.01 N).
The mixture was degassed twice and saturated with oxygen in twenty minutes, while stirring vigorously.

Catalytical activity measurements

Activity measurements were carried out in an all-glass double-walled, thermostated Warburg apparatus, equipped with a powerful mechanical glass-stirrer, at constant pressure (0.1 MPa). Stirring speed was 2300 r.p.m. Although vigorous stirring appeared imperative, this stirring speed was not within a critical range, since a somewhat higher or lower stirring speed did not affect the oxygen uptake rate. Since even small amounts of salt largely affect the conformation of the polymeric catalyst in solution (see text), no buffer solutions but instead, sodium hydroxide and hydrochloric acid were used to adjust the pH. The Warburg apparatus was equipped with a

pH-electrode (Radiometer Copenhagen GK 2401 B) and the pH was measured 15 seconds after addition of thiol. During the first minute of reaction the pH hardly varied at pH $\geq$ 8.3, but a slight increase was observed at lower and intermediate values as a result of the conversion of thiol and the lower buffer capacity of the reaction system at these values.
Oxygen consumption rates were measured with a digital flow meter equipment (Inacom Veenendaal, The Netherlands).
The reaction was started by adding the substrate, 2-mercaptoethanol, to the reaction vessel with a syringe. Initial reaction rates were determined as the average O_2 consumption rate (normalized at 20 °C and 0.1 MPa) during the the first minute. Such a fast measurement is advantageous since the influence of catalyst deactivation, which occurs as the reaction progresses (ROLLMAN 1975.), can be neglected; besides, pH and substrate concentration remain practically constant.

Results and discussion

Conformation of the polymer complex in the presence of 2-mercaptoethanol

The reduced viscosity of aqueous solutions of PVAm with and without thiol were determined as a function of deliberately imposed pH changes, in order to obtain a better insight in the conformation of the catalyst as a function of pH. HCl (0.01 N) and NaOH (0.3 N) were used to adjust the pH at the desired values. The results are presented in Figure 1. This figure shows that the conformation of pure PVAm is drastically influenced by the pH. A maximum in viscosity is reached at pH = 6. When thiol is present the maximum is shifted to lower pH and above pH = 7 the viscosity collapses in comparison with the behaviour of the PVAm solution without thiol. The viscosity increase upon neutralization of the basic PVAm solutions can be explained considering an increasing mutual repulsion of neighbouring charged groups with increasing polymer charge thus causing a more expanded conformation (TEYSSIE et al. 1965; BLOYS VAN TRESLONG 1978.). Although polymer charge increases continuously with lower pH (BLOYS VAN TRESLONG 1978.), polymer coil dimensions do not. The occurrence of a maximum in chain dimensions may be due to a very stiff structure at intermediate pH, a conformation stabilized by

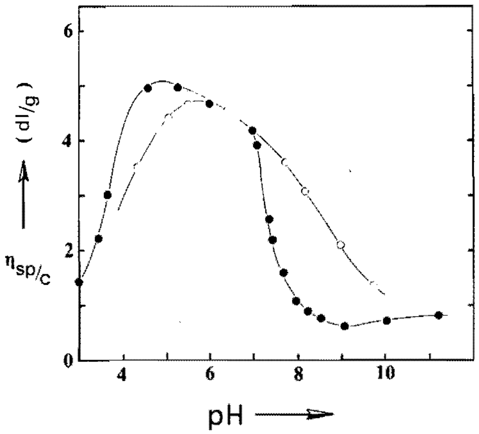


Figure 1.
Reduced viscosity of an aqueous solution of PVAm with (●) and without (○) thiol vs. pH. Polymer and thiol concentrations: c_{-NH_2} = 1 7 mgreq dm^{-3}, c_{RSH} = 0.186 mole dm^{-3}. Temperature: (25.00 ± 0.05) °C. pH was adjusted by addition of HCl or NaOH solutions

hydrogen bonding between neighbouring ammonium and amine groups (LEWIS et al. 1981; RINALDI et al.1981.)
When thiol is added the viscosity of the system is somewhat higher at low pH and the maximum is shifted significantly to lower pH (Figure 1). Probably this is caused by a specific counter-ion effect. The collapse of viscosity above pH = 7 in comparison with the PVAm solution without thiol must be attributed to the increased salt concentration in the bulk (Na^+RS^-) under these conditions and is caused by the dissociation of the weakly acid RSH (pK_a = 9.6 (JOCELYN 1972.)). The latter effect will result in a shielding of the polymeric charges which in turn causes a sharp decrease in viscosity.
The slight increase in viscosity beyond pH = 9 in Figure 1 must be due to increasing salt and base concentrations, while the polymer charge is minimal. From the above it must be concluded that the polymer catalyst is most expanded at intermediate pH and in the absence of salt, but conformational freedom is lost upon addition of even small amounts of base.

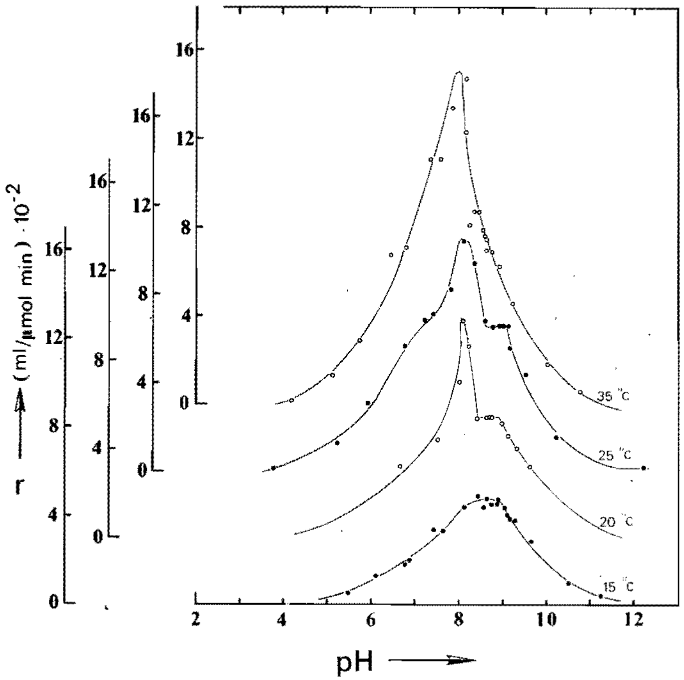


Figure 2.
Catalytic activity of polymeric systems at 15, 20, 25 and 35 °C vs. pH. c_{-NH_2} = 1.7 mgreq dm^{-3}; $c_{CoPc(NaSO_3)_4}$ = 1.9 10^{-7} mole dm^{-3}. Reaction volume = 101 ml. Added thiol: 18.5 mmole. r in ml O_2/µmole $CoPc(NaSO_3)_4$ min

Catalytic activity experiments

Because the solubility of the polymeric catalyst is not restricted by the pH, we were able to investigate the effect of the pH on the catalytic activity. The effect of temperature on the activity-pH plots has been determined at 15, 20, 25 and 35 °C. This is shown in Figure 2. At each temperature level a maximum in reaction rate is observed at pH 8-9, depending on temperature. Such behaviour has often been observed in enzymatic reactions and generally is explained by assuming that acid as well as basic sites are playing a role in most enzyme-substrate interaction mechanisms (TANFORD 1961.). However, our polymeric catalyst carries only basic sites, and therefore this explanation does not hold for the present system. Here polymer charge and the presence of counter-ions other than RS^- are considered to be important. It was reported that the charge on the polymer chain decreases with increasing pH (BLOYS VAN TRESLONG 1978).
Below pH = 7.4, when HCl has been added to adjust the pH, more competing counter-ions are present (i.e. Cl^-) and the local thiol-anion concentration in the close vicinity of the polymer chain is supposed to decrease and so is the reaction rate. Beyond pH = 7.4 the thiol-anion concentration in the bulk increases considerably due to the weakly acid character of RSH.
A slight increase in pH above 7.4 does not necessarily mean that polymer charge decreases in the relevant catalytic systems, because ionic strength is increased by Na^+RS^-, which enhances polymer charge to some extent (BLOYS VAN TRESLONG 1978.). Thus at pH values slightly higher than 7.4 the local thiol-anion concentration near the polymer chain may be somewhat enhanced and so is the reaction rate. At still higher pH, polymer charge decreases and hydroxyl-ion concentration increases and a reduction of reaction rate must be expected, although the bulk thiol-anion concentration is still increasing.
The considerations above are summarized in Table 1.

Table 1.

Synopsis of some important parameters in the pH-dependent behaviour of the catalytic activity.

	Lower pH (<7.4)	Intermediate pH (7.4-8)	Higher pH (>8)
polymer charge	++++	+++	+
"strange" counter-anions other than RS^-	yes (Cl^-)	no	yes (OH^-)
c_{RS^-} in close vicinity of the polymer chain	+	+++	+
c_{RS^-} in the bulk	+	++	++++
catalytical activity, r	+	+++	+

From the above it seems that the course of the reaction rate curves can be explained in terms of a variation of the local thiol-anion concentration in the close vicinity of the polymer chain.
Further supporting evidence to this hypothesis, has been provided by the occurrence of a saturation effect in the relationship between reaction rate and thiol concentration and by the occurrence of a distinct fall in

activity upon addition of inert salt. The latter can be explained by a considerable decrease of thiol-anions in the near vicinity of the polymer chain because of repulsive forces between competitive anions (Cl^-) and shielding of the chain charge.

The observed temperature dependence of the reaction rate curves in Figure 2 was a motive to determine the activation energies accurately, by measurements performed in a range chosen from Figure 2, viz. 5-45 °C at pH = 7.4, 8.75 and 9.5. Activation energies, E_a, are given in Table 2.

Table 2.

Activation energies at different pH.

pH	E_a (KJ $mole^{-1}$)
7.4	61 ± 7
8.75	19 ± 3
9.5	2.5 ± 2

In Figure 2 a shoulder appears between pH = 8.5 and 9 at lower temperatures. This peculiar behaviour may indicate that two mechanisms are operative with different activation energies and different pH optima. In earlier investigations the formation of considerable amounts of hydrogen peroxide at neutral pH was reported (SCHUTTEN and BEELEN 1980.). The concentration H_2O_2 decreased rapidly upon addition of small amounts of base which was attributed to a fast base catalysed reduction of the hydrogen peroxide by thiols. However, in the light of the present findings the occurrence of two pH-dependent mechanisms may also explain this phenomenon.
On the other hand, diffusion limitation may not be excluded, particularly at higher pH. In the presence of thiol, the polymer coil shrinks considerably upon addition of base (Figure 1). Therefore transport limitations of reactants or the product, which has larger dimensions, may be easily encountered. The apparent activation energy for diffusion of counter-ions and uncharged molecules in swollen resins amounts to about 20 KJ $mole^{-1}$ (MEARES 1968.), which is not in conflict with the present experimental observations. In order to elucidate the phenomenon of the pH dependent activation energies additional kinetic investigations are required.

Conclusions

Some final conclusions may be drawn. The polymeric catalyst exhibits an enzyme-like behaviour in the autoxidation of 2-mercaptoethanol, in contradistinction to the system with $CoPc(NaSO_3)_4$ as a catalyst in the absence of polymers (ZWART et al. 1977.).
The maximum rate is reached at pH = 8-9, depending on temperature. The polymeric catalyst possesses a large conformational freedom at neutral pH and electrostatic effects are of great importance in the catalytic activity, because these effects will influence the local thiol-anion concentration in the close vicinity of the oxidation sites.
The pH-dependence of activation energies may be explained by assuming two pH-dependent mechanisms with different activation energies to occur. On the other hand the polymer coil is considerably contracted at high pH values and the occurrence of diffusion controlled reactions cannot be excluded.

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References

BLOYS VAN TRESLONG, C.J.: Recl. Trav. Chim. Pays-Bas 97 (1), 13 (1978)
HUGHES, A.R. and St. PIERRE, T.: Macromol. Synth. 6, 31 (1977)
JOCELYN, P.C.: Biochemistry of the SH-group, New York, Academic Press (1972)
LEWIS, E.A., BARKLEY, J., St PIERRE, T.: Macromolecules 14, 546 (1981)
MEARES, P. in Diffusion in Polymers, New York, Academic Press (1968)
RINALDI, P.L., CHIN YU and LEVY, G.C.: Macromolecules 14, 551 (1981)
ROLLMAN, L.D.: J. Am. Chem. Soc. 97, 2132 (1975)
SCHUTTEN, J.H. and ZWART, J.: J. Mol. Catal. 5, 9 (1979)
SCHUTTEN, J.H., PIET, P. and GERMAN, A.L.: Makromol. Chem. 180, 2341 (1979)
SCHUTTEN, J.H. and BEELEN, T.P.M.: J. Mol. Catal. 10, 85 (1980)
TANFORD, Ch., Physical chemistry of macromolecules, New York, John Wiley & Sons Inc. (1961)
TEYSSIE, Ph., DECOENE, C. and TEYSSIE, M.T.: Makromol. Chem. 84, 51 (1965)
WEBER, J.H. and BUSCH, P.H.: Inorg. Chem. 4, 469 (1965)
ZWART, J., WEIDE, H.C. v/d, BROKER, N., RUMMENS, C., SCHUIT, G.C.A. and GERMAN, A.L.: J. Mol. Catal. 3, 151 (1977-1978)

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Chapter III

AUTOXIDATION OF THIOLS WITH COBALT(II) PHTHALOCYANINE TETRASODIUM SULFONATE ATTACHED TO POLY(VINYLAMINE). 2. KINETIC MEASUREMENTS

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Summary

A kinetic study is presented of the autoxidation of 2-mercaptoethanol using cobalt(II) phthalocyanine tetrasodium sulfonate attached to poly(vinylamine) as a catalyst.

The main products appear to be 2,2′-dithiobis(ethanol) and hydrogen peroxide; the measured oxygen consumption was found to be in balance with the theoretical one, based on the exclusive formation of these compounds. The catalytic system exhibits a large activity and Michaelis–Menten kinetics are obeyed with respect to substrate concentration and oxygen pressure. The reaction rate was first order in polymeric catalyst.

Upon addition of salt a severe decrease in activity was observed. A comparison of the activation energies in the presence and absence of salt suggests that the local thiol anion concentration in the vicinity of the oxidation sites is lowered upon salt addition. Although an entropy change cannot be excluded, this may explain the fall in reactivity.

Addition of radical scavengers also led to a decrease in the reaction rate, indicating that radicals are reaction intermediates. Overall, the polymeric catalyst exhibits an enzyme-like behaviour and resembles the catalytic action of vitamin B_{12} in the oxidation of thiols.

Introduction

During the past two decades much attention has been paid to the autoxidation of thiols using transition metal containing compounds as catalysts. Some of these investigations [1] originated from a wish to develop catalysts which could be used for the desulfurization of natural gas and oil. Other surveys [2, 3] dealt with the enzymatic conversion of thiols in order to clarify thiol metabolism in biological systems. It has been found that cobalt(II) phthalocyanine (CoPc) [4] in the presence of alkali is a very good catalyst for the conversion of thiols to disulfides, the alkali increasing the

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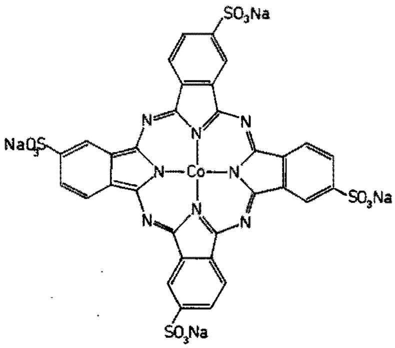

Fig. 1. Structure of $CoPc(NaSO_3)_4$.

concentration of thiol anions which are the reactive species in the system. In many papers emphasis was laid on reaction kinetics and re-use of the catalysts. However large differences in kinetic behaviour were observed between homogeneous systems where CoPc derivatives in alkaline media were used as the catalyst [5, 6] and systems where CoPc was immobilized on porous solid supports [6, 7].

In our laboratory systems are being investigated where $CoPc(NaSO_3)_4$ (Fig. 1) is attached to basic polymers by complexation. In particular, the water-soluble poly(vinylamine) (PVAm) appears to be a very good promotor in the autoxidation of 2-mercaptoethanol (RSH) [8]. Thus, relative to the aqueous system $CoPc(NaSO_3)_4/OH^-$, the bifunctional polymeric system appears to be *ca.* 30 times more active. Our aim is to elucidate the contribution of the polymeric ligand to this increased catalytic action, and in order to achieve this systems with other basic polymers are being investigated.

We found earlier [9] that the coil conformation of the polymer prevents the formation of catalytically inactive dimeric oxo adducts of $CoPc(NaSO_3)_4$, and that the basic functionalities were an excellent substitute for the alkali commonly used in the homogeneous system with $CoPc(NaSO_3)_4$ [8]. Recently we have investigated the conformation of the polymeric catalyst during reaction and examined the influence of pH on the conformation of the polymeric catalyst and its reaction rate [10]. We now present a kinetic study of this polymeric system, the results being discussed in relation to data obtained from homogeneous and immobilized systems.

Experimental

Chemical reagents

PVAmHCl was purchased from Polysciences Inc. (Warrington U.S.A.; $\bar{M}_n(PVAm) = 5 \times 10^4$ g mol^{-1}, from viscosity experiments in water containing 0.01 N NaOH and 0.1 M NaCl [11]). Aqueous solutions of PVAm were obtained by eluting a 3% solution of PVAmHCl through an Amberlite IRA-

401 anion exchange column. The equivalent amine concentration was determined by potentiometric titration with HCl solution (Merck, Titrisol ampoules) in 2 M NaCl (p.a.). $CoPc(NaSO_3)_4$ (kindly provided by Dr. T.P.M. Beelen) had been synthesised by a method analogous to that of Weber and Busch [12] as described by Zwart *et al.* [5]. 2-Mercaptoethanol was distilled before use and stored in the dark at 5 °C for periods not exceeding two weeks. The thiol content after storage was checked by iodometric titration [13] and was found 99% pure. Distilled water was used throughout.

Catalyst preparation

The catalyst was prepared by mixing aqueous solutions of PVAm and $CoPc(NaSO_3)_4$, resulting in a polymer–organometal complex. The solution of PVAm was initially added to the reaction vessel and the solution of $CoPc(NaSO_3)_4$ immediately afterwards. The mixture was degassed twice and saturated with oxygen over a period of 20 min while stirring vigorously.

Catalytic activity measurements

The reaction rate was determined by monitoring the oxygen consumption during the oxidation reaction.

Activity measurements were carried out at constant pressure in an all-glass double-walled thermostated Warburg apparatus, equipped with a powerful mechanical glass stirrer. Oxygen pressure was adjustable. A stirring speed of 2300 r.p.m. was maintained, although this was not critical since a somewhat higher or lower stirring speed did not affect the oxygen uptake. However at oxygen uptake rates exceeding 25 - 30 ml min^{-1}, for a reaction volume of 0.1 dm^3 and oxygen pressure of 35 kPa, transport limitation problems occurred.

The Warburg apparatus was equipped with a pH electrode (Radiometer Copenhagen GK 2401 B), the pH being measured 15 s after addition of thiol. Calibrated buffer solutions were employed to check that this type of electrode was not harmed by the presence of thiol. Oxygen consumption rates were measured with a digital flowmeter (Inacom Veenendaal, The Netherlands).

The reaction was started by adding the substrate, 2-mercaptoethanol, to the reaction vessel by means of a syringe. Initial reaction rates were determined as the average consumption during the first minute.

Analysis of the H_2O_2 content

The hydrogen peroxide level in the reaction mixture was analysed by iodometric titration [14].

Results and discussion

Oxygen mass balance

Earlier studies of the autoxidation of thiols [5, 15] have investigated whether disulfide was formed exclusively as the reaction product; in other words if the conversion obeyed eqn. (4) in Scheme 1. This reaction appears to be the principal one, but in some cases H_2O_2 could be also detected in the reaction mixture [3, 5]. Thus in the system $CoPc(NaSO_3)_4$/PVAm the existence of H_2O_2 at neutral pH was demonstrated spectrophotometrically [16].

$$2RSH + O_2 \longrightarrow RSSR + H_2O_2 \tag{1}$$

$$2RSH + H_2O_2 \longrightarrow RSSR + 2H_2O \tag{2}$$

$$(1) - (2){:}\ 2H_2O + O_2 \longrightarrow 2H_2O_2 \tag{3}$$

$$(1) + (2){:}\ 4RSH + O_2 \longrightarrow 2RSSR + 2H_2O \tag{4}$$

Scheme 1. Overall reactions in the oxidation of 2-mercaptoethanol.

In order to check the oxygen mass balance for the $CoPc(NaSO_3)_4$/PVAm system, the total oxygen consumption for complete conversion, *i.e.* the integral of the oxygen uptake curve in Fig. 2, was measured and the peroxide content was determined iodometrically. From the weight of added substrate and from the remaining hydrogen peroxide content after oxygen consumption had stopped, *i.e.* after complete conversion of RSH, the corresponding moles of oxygen were calculated using eqns. (3) and (4) in succession (Scheme 1). The sum of these should be compared with the measured oxygen consumption, see Table 1. From a consideration of the stoichiometry of eqns. (3) and (4) in Scheme 1 and the results in Table 1 it appears that mainly RSSR, and to a lesser extent H_2O_2, are formed during the catalytic oxidation of RSH, the hydrogen peroxide possibly as an intermediate product*.

It has been shown [16] that, in the absence of PVAm and at neutral pH, $CoPc(NaSO_3)_4$ decomposes rather slowly in the presence of H_2O_2. As stated above, initial reaction rates have been obtained in this study from the oxygen consumption during the first minute of reaction on the basis that over such short periods of time no substantial decomposition of the catalyst will occur. However, the existence of an oxygen mass balance does not rule out the formation of very small amounts of sulfur-containing acids arising from the relatively high H_2O_2 levels during reaction. These acids were assumed to be responsible for catalyst deactivation during successive runs [16].

In some cases [5, 15] the presence of some RSH has been reported after oxygen consumption has stopped. However, in these studies, the detection of residual thiol (which has a strong smell even as extremely small traces) was not possible after cessation of the oxygen uptake. Furthermore,

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***If reaction 2 occurs more slowly than reaction 1, some H_2O_2 will remain after the thiol is converted to RSSR. At this stage it is not possible to verify whether RSSR is formed exclusively through reactions 1 and 2 proceeding consecutively or via a mechanism involving several simultaneously occurring reactions.**

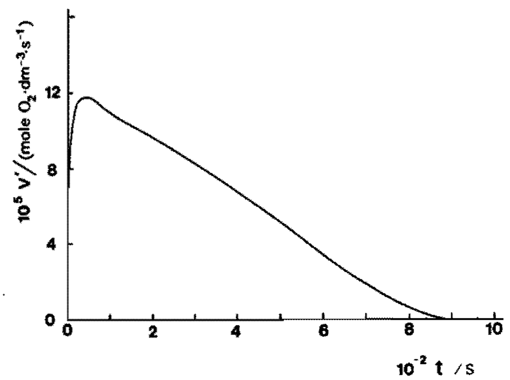

Fig. 2. Oxygen uptake rate v' plotted against time. $c_{\mathrm{CoPc(NaSO_3)_4}} = 1.92 \times 10^{-7}$ M; $c_{\mathrm{-NH_2}} = 1.5 \times 10^{-3}$ N; [added thiol] = 18.5 mmol; reaction volume = 0.101 dm^3; $T = 25.0 \pm 0.1$ °C; pH = 7.4; $P_{O_2} = 100$ kPa.

TABLE 1

Oxygen mass balance in the oxidation of 2-mercaptoethanol

Amount of product (mmol)[a]	Amount of O_2 consumed (mmol)		Mole fraction of O_2 (%)
RSH converted (a) 18.558	O_2 (RSSR) (a/4)	4.640	87.3 ± 1.8[b]
H_2O_2 remaining (b) 1.307	O_2 (H_2O_2) (b/2)	0.654	12.3 ± 0.6
	O_2 (total calc.)	5.293	99.6 ± 1.8
	O_2 (total meas.)	5.315	100.0

[a] Data after complete conversion of RSH.

[b] Average of four experiments; errors within 95% confidence limit.

because of the method of analysis employed for H_2O_2, any unconverted thiol would also react with iodine to yield RSSR, and thus not affect the calculated total oxygen consumption.

Effect of thiol concentration

The relationship between the reaction rate and the thiol concentration at a pH value of 7.2, a temperature of 25.0 °C and a Co/NH$_2$ mole ratio of 3.9×10^{-4} is shown in Fig. 3(a). At high concentrations a saturation effect is observed. Michaelis–Menten kinetics [17, 18] (Scheme 2) appear to be obeyed, and the rate constants k_2 and K_m have been calculated from a Lineweaver–Burk plot, *i.e.* a double reciprocal plot of the initial reaction rate v against the initial substrate concentration [Fig. 3(b)].

From the intercept in Fig. 3(b) and the total catalyst concentration, the turn-over number of the enzyme–substrate complex, *i.e.* the catalytic con-

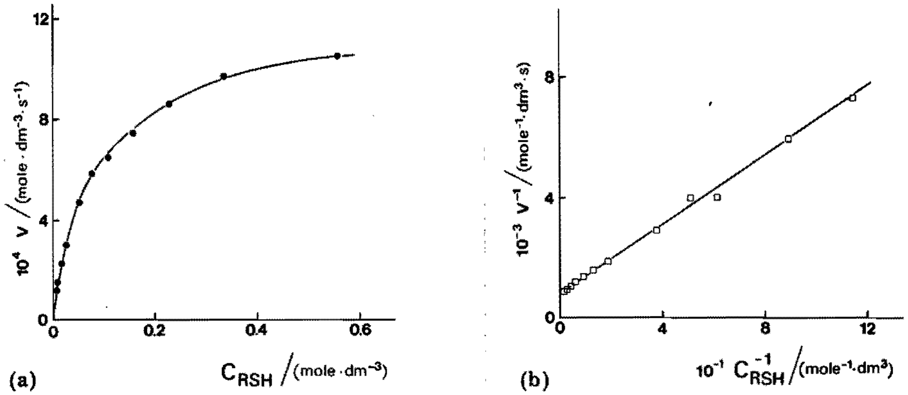

Fig. 3. (a) Reaction rate v plotted against the thiol concentration. $c_{\mathrm{CoPc(NaSO_3)_4}} = 3.7 \times 10^{-7}$ M; $c_{\mathrm{-NH_2}} = 0.95 \times 10^{-3}$ N; reaction volume = 0.105 dm^3; $T = 25.0 \pm 0.1$ °C; pH = 7.2; $P_{\mathrm{O_2}} = 100$ kPa. The reaction rate v is expressed in mol RSH dm^{-3} s^{-1}, calculated on the basis of the stoichiometry of eqn. (4). (b) Lineweaver–Burk plot. Reaction conditions as given for Fig. 3(a).

stant, can be calculated from eqn. (7) of Scheme 2 and has the value $k_2 = 1.6 \times 10^3$ s^{-1}. Similarly, from the slope in Fig. 3(b) and v_s it follows that $K_m = 0.07$ mol dm^{-3}.

$$\mathrm{E + S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \xrightarrow{k_2} \mathrm{E + P} \tag{5}$$

$$\frac{1}{v} = \frac{1}{v_s} + \frac{K_m}{v_s} \cdot \frac{1}{c_{\mathrm{RSH}}} \tag{6}$$

$$v_s = k_2 \cdot E_0 \tag{7}$$

$$K_m = \frac{k_{-1} + k_2}{k_1} \tag{8}$$

$$K_s = \frac{k_1}{k_{-1}}$$

Scheme 2. Summary of Michaelis–Menten kinetics. In this scheme v_s is the maximum reaction rate at $c_{\mathrm{RSH}} = \infty$; K_m is the Michaelis–Menten constant; K_s is the equilibrium constant for substrate binding; and E_0 is the concentration of added catalyst.

The occurrence of a saturation effect for the catalytic activity upon addition of excess substrate, which is common in enzymatic reactions, has also been observed in other systems involving polymeric catalysts [19], indicating that a complex is formed between the substrate and the catalyst before the actual reaction takes place.

The observed value of k_2 is remarkably high for a polymeric catalyst, while the value of K_m is in the usual range. Values of k_2 normally lie in the range 10^{-3} - 10^{-1} s^{-1} and $K_m \simeq 10^{-4}$ - 1 mol dm^{-3} for polymeric catalysts obeying Michaelis–Menten kinetics [19 - 21]. The value of the turnover number for a polymeric catalyst observed in this work is of a magnitude which is only commonly encountered with enzymes.

Effect of ionic strength

Figure 4 illustrates the catalytic activity at a pH value of 7.2 and a temperature of 25.0 °C as a function of the ionic strength μ (added NaCl). The addition of small amounts of salt leads to a severe reduction in the reaction rate. This behaviour may be explained by the considerable decrease in the concentration of the thiol anion (RS^-) adjacent to the polymer chain caused by repulsive forces between competitive anions (Cl^-) and shielding of the charge on the chain. Moreover, upon addition of salt the polymeric coils shrink considerably due to shielding of the chain charge, and this is reflected in a decreasing viscosity for solutions of the polymeric catalyst [22]. Hence, the occurrence of transport limitations of reactants, which would cause a lower (apparent) reaction rate, cannot be excluded. Similar electrostatic effects have been observed for other polymeric catalysts in aqueous solutions. Pecht *et al.* [23] have investigated the oxidation of ascorbate and other negatively charged ions with molecular oxygen in the presence of a copper(II)–poly(histidine) catalyst, the addition of salt again causing the reaction rate to diminish. Tsuchida *et al.* [24] have also reported that an increase of anion concentration caused by the addition of neutral salt led to a decrease of reaction rate in the electron transfer reactions of cobalt(III)–poly(4-vinylpyridine) complexes.

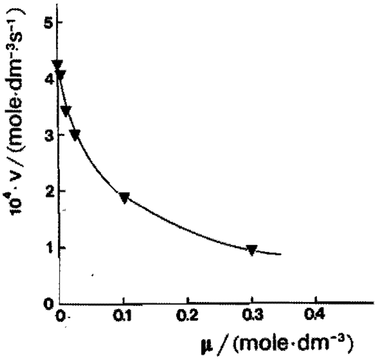

Fig. 4. Reaction rate as a function of the ionic strength (NaCl). pH = 7.2. Other reaction conditions as listed for Fig. 2.

Effect of temperature

In order to adduce further supporting evidence for the hypothesis that addition of salt lowers the local substrate concentration (RS^-), the temperature dependence of the reaction rate has been measured at $\mu = 0$ and $\mu = 0.1$ between 5 and 45 °C, at a fixed catalyst concentration and pH. Because the reaction rate largely depends upon the pH value of the system [10], this was controlled by addition of small amounts of HCl or NaOH to compensate for the thermal dissociation affects.

Plots of $\ln v$ against the reciprocal of the temperature are shown in Fig. 5, the overall activation energies being listed in Table 2. In the calculation of the activation energies, measurements above 40 °C were not taken into account since limitations of oxygen transport were observed at such temperatures. The difference in activation energy at $\mu = 0$ and $\mu = 0.1$ is small; however, the decrease in activity shown in Fig. 4 is quite large. For this reason the observed decrease in chemical reactivity must arise from a smaller activation entropy, smaller local reactant concentrations or both. At this stage of the investigation it is not yet possible to distinguish clearly between these effects since ionic strength and chain conformation may also affect the activation entropy. We have shown earlier [10] that at intermediate pH values no direct correlation exists between the conformation of the catalyst and reaction rate; however, this does not entirely exclude the

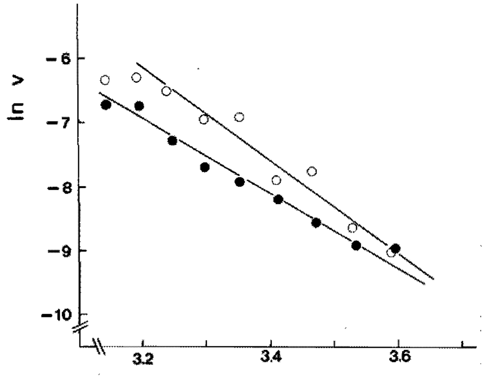

Fig. 5. A plot of ln v against the reciprocal of the temperature for different ionic strengths (NaCl). pH = 7.3 ± 0.1; other reaction conditions as listed for Fig. 2; ○: $\mu = 0$; ●: $\mu = 0.1$.

TABLE 2

Activation energies, E_a, at different ionic strengths

pH	μ (mol dm^{-3})	E_a (kJ mol^{-1})
7.4	0	61 ± 7
7.2	0.1	49 ± 2

occurrence of a change in the conformational activation entropy. Hence, irrespective of the fact that the polymeric catalyst conformation is strongly influenced by salt addition, it is to be expected that a lower thiol concentration rather than a lower activation entropy will have the greater effect upon the reaction rate.

Effect of catalyst concentration

Important kinetic features have been obtained by investigating whether k_2 (eqn. (7), Scheme 2) and K_m (eqn. (8), Scheme 2) remain constant when the catalyst concentration is varied. Since variations in the Co/NH_2 ratio affect the reaction rate [9], this ratio was kept constant at 1.3×10^{-4} during the first set of experiments. Since polymer concentration varies, the pH value was controlled by the addition of small amounts of NaOH and was kept constant at 7.4. Lineweaver–Burk plots have been composed for several concentrations of the polymeric catalyst [Fig. 6(a)] and values of v_s, K_m and k_2 determined (see Table 3). The reaction rate at infinite substrate concentration, v_s, is plotted against catalyst concentration in Fig. 6(b). From the slope in Fig. 6(b) k_2 was derived: $k_2 = 2.8 \times 10^3$ s^{-1}. The linear relationship found is in full accordance with eqn. (7) in Scheme 2. Also K_m does not change significantly within experimental error.

The higher value of k_2 at lower Co/NH_2 ratios ($k_2 = 1.6 \times 10^3$ and 2.8×10^3 s^{-1} at Co/$NH_2 = 3.9 \times 10^{-4}$ and 1.3×10^{-4}, respectively) may be ascribed to effects arising from different bulk pH values at the two ratios employed. Evidently, the calculated values of k_2 are apparent values, since the effective catalyst concentration diminishes at higher Co/NH_2 ratios. On this basis, an absolute value of k_2 should be obtained on extrapolation to Co/NH_2 = 0.

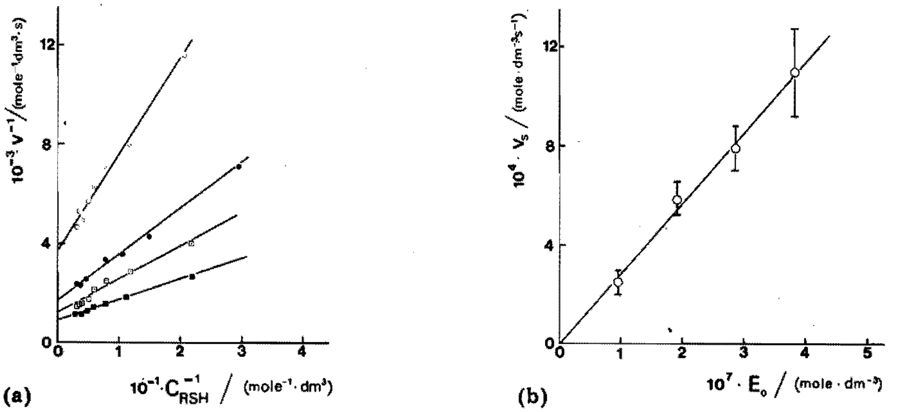

Fig. 6. (a) Lineweaver–Burk plots for several catalyst concentrations. Co/NH_2 = 1.28 × 10^{-4}; pH = 7.4; reaction volume = 0.101 dm^3; T = 25.0 ± 0.1 °C; P_{O_2} = 100 kPa; ○: E_0 = 0.96 × 10^{-7} M; ●: E_0 = 1.92 × 10^{-7} M; □: E_0 = 2.87 × 10^{-7} M; ■: E_0 = 3.83 × 10^{-7} M. (b) Plot of the reaction rates at infinite substrate concentration against the catalyst concentration, E_0, expressed as mol CoPc($NaSO_3$)$_4$ dm^{-3}. Reaction conditions as listed for Fig. 6(a). Experimental errors are within 95% confidence limits.

TABLE 3

Values of v_s, K_m and k_2 as a function of the catalyst concentration E_0

$10^7 E_0$ (mol dm^{-3})	10^4Co/NH$_2$	$10^4 v_s$ (mol dm^{-3} s^{-1})	K_m (mol dm^{-3})	$10^{-3} k_2$ (s^{-1})
0.96	1.3	2.7 ± 0.5	0.11 ± 0.02	2.8 ± 0.6[a,c]
1.92	1.3	5.9 ± 0.8	0.11 ± 0.01	3.1 ± 0.4[a]
2.87	1.3	7.9 ± 0.9	0.09 ± 0.01	2.8 ± 0.3[a]
3.83	1.3	10.9 ± 1.9	0.08 ± 0.01	2.9 ± 0.5[a]
3.71	3.9	5.9 ± 0.9	0.07 ± 0.01	1.6 ± 0.3[b]

[a] Calculated from the data in Fig. 6(a).
[b] Calculated from the data in Fig. 3(b).
[c] All errors are within 95% confidence limits.

The value of K_m, however, is apparently not very sensitive to the Co/NH$_2$ ratio (see Table 3); obviously K_m is not dependent on the polymer concentration over the range studied.

Effect of oxygen pressure

The effect of oxygen pressure on reaction rate was investigated over the pressure range 10 - 100 kPa at fixed substrate concentration. The results are shown in Fig. 7(a). The occurrence of a saturation effect and the linear nature of the Lineweaver–Burk plot [Fig. 7(b)] indicate that Michaelis–Menten kinetics may apply to the rate dependence on oxygen pressure.

Special attention has been paid to the possibility of oxygen transport limitations to the reaction. A somewhat faster or slower stirring speed does not affect the oxygen uptake rate, even over the low pressure region, although the reaction rate was more dependent on oxygen pressure over this

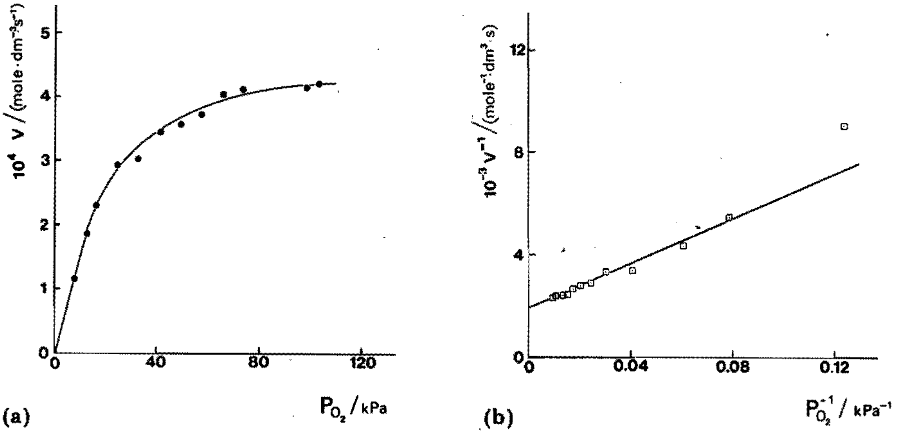

Fig. 7. (a) A plot of the reaction rate against the oxygen pressure. Reaction conditions as listed for Fig. 2. (b) Lineweaver–Burk plot for results depicted in Fig. 7(a).

latter region [see Fig. 7(a)]. What is important, however, is that even at the low pressure of 24 kPa the reaction rate remained first order in the catalyst concentration, as found earlier at a pressure of 100 kPa. These observations exclude the possible occurrence of transport limitations on the passage of oxygen from the gas phase into the bulk solution.

Effect of the addition of p-benzoquinone

The addition of 13 mg of *p*-benzoquinone to the reaction vessel (containing 1.5 g of thiol) caused an 80% decrease in the rate of reaction. Although it is possible that *p*-benzoquinone may take a direct part in the oxidation of the thiol, it is more likely that radical intermediates are involved in the reaction process thus explaining why such a small quantity of free radical scavenger can have such a large effect on the reaction rate.

General discussion

The polymeric catalyst possesses many enzyme-like characteristics:

(1) Michaelis–Menten kinetics with respect to RSH.

(2) A dependence of the reaction rate on pH with a maximum rate at a pH value of 8 - 9 [10].

(3) First order kinetics with respect to catalyst concentration.

(4) A relatively high turnover number ($k_2 \simeq 2 - 3 \times 10^3\ s^{-1}$).

The activation energy is similar to the values observed in the autoxidation of RSH by vitamin B_{12}, the latter system exhibiting the same kinetics as the present polymeric system [15].

The occurrence of a saturation effect in the relationship between the reaction rate and oxygen pressure in the present system indicates that, in contrast to the homogeneous system $CoPc(NaSO_3)_4/OH^-$, the amount of catalytically inactive binuclear oxo adducts of $CoPc(NaSO_3)_4$ is not increased by higher oxygen pressures. This confirms again that the $CoPc(NaSO_3)_4$ sites are effectively shielded from other oxidation sites on the polymer surface.

A comparison of the $CoPc(NaSO_3)_4$/PVAm system with the homogeneous $CoPc(NaSO_3)_4/OH^-$ system reveals that the kinetics of the two systems are entirely different. The latter system appeared to have a positive, nearly first order, dependence on RS^- [25], the reaction rate decreasing with increasing oxygen pressure [25] and increasing upon addition of comparable amounts of salt [26]. Furthermore, in the conventional system the reaction rate was relatively low and the binuclear oxo-adduct content high [9]. The existence of H_2O_2 was never established, probably because the high pH value caused a rapid conversion of the peroxide [16].

Immobilized conventional systems containing $CoPc(NaSO_3)_4$ behave differently from the polymeric catalysts reported here. For the former systems, the influence of RSH on the reaction rate varies from being almost linear for porous chloromethylated polystyrene, cross-linked with divinylbenzene [7], to the existence of saturation kinetics for cellulose anion-exchange resins [6]. In all cases reported, the activity for these immobilized systems is much lower than that observed for the $CoPc(NaSO_3)_4$/PVAm system.

Obviously, the freely accessible polymer conformation and the special polymeric features of PVAm, such as the basicity of the amine ligands and complexation properties towards $CoPc(NaSO_3)_4$, act together to provide a much more efficient catalytic system.

Acknowledgements

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References

1 A. H. Oswald and T. J. Wallace, in N. Kharasch and C. L. Meyers (eds.), *The Chemistry of Organic Sulphur Compounds*, Vol. 2, Pergamon, London, 1966, Chap. 8.
2 D. S. Tarbell, in N. Kharasch (ed.), *Organic Sulfur Compounds*, Vol. 1, Pergamon, London, 1961, Chap. 10.
3 P. C. Jocelyn, *Biochemistry of the SH Group*, Academic, London, 1972, Chap. 4.
4 N. N. Kundo and N. P. Keier, *Russ. J. Phys. Chem.*, *42* (1968) 707.
5 J. Zwart, H. C. van der Weide, N. Bröker, C. Rummens, G. C. A. Schuit and A. L. German, *J. Mol. Catal.*, *1* (1977 - 1978) 151.
6 A. Skorobogaty and T. D. Smith, *J. Mol. Catal.*, *16* (1982) 131.
7 L. D. Rollmann, *J. Am. Chem. Soc.*, *97* (1974) 2132.
8 J. H. Schutten and J. Zwart, *J. Mol. Catal.*, *5* (1979) 109.
9 J. H. Schutten, P. Piet and A. L. German, *Makromol. Chem.*, *180* (1979) 2341.
10 W. M. Brouwer, P. Piet and A. L. German, *Polym. Bull.*, *8* (1982) 245.
11 C. J. Bloys van Treslong and C. F. H. Morra, *Recl. Trav. Chim. Pays-Bas*, *94* (1975) 101.
12 J. H. Weber and P. H. Busch, *Inorg. Chem.*, *4* (1965) 469.
13 J. P. Danehy and J. A. Kreuz, *J. Am. Chem. Soc.*, *83* (1961) 1109.
14 L. Meites (ed.), *Handbook of Analytical Chemistry*, 1st Ed., McGraw-Hill, London, 1963, Sections 3-65 and 3-69.
15 J. L. Peel, *Biochem. J.*, *88* (1963) 296.
16 J. H. Schutten and T. P. M. Beelen, *J. Mol. Catal.*, *10* (1980) 85.
17 L. Michaelis and M. L. Menten, *Biochem. Z.*, *49* (1913) 333.
18 A. Cornish Bowden, *Fundamentals of Enzyme Kinetics*, Butterworths, London, 1979.
19 C. W. Warton, *Int. J. Biolog. Macromol.*, *1* (1979) 3.
20 H. Shirai, A. Maruyama, K. Kobayashi and N. Hojo, *J. Polym. Sci., Polym. Lett. Ed.*, *17* (1979) 661.
21 A. J. Schouten, D. Noordegraaf, A. P. Jekel and G. Challa, *J. Mol. Catal.*, *5* (1979) 331.
22 W. M. Brouwer, P. Piet and A. L. German, *Polym. Commun.*, *24* (1983) 216.
23 I. Pecht, A. Levitzki and M. Anbar, *J. Am. Chem. Soc.*, *89* (1967) 1587.
24 E. Tsuchida, Y. Karino, H. Nishida and Y. Kurimara, *Makromol. Chem.*, *175* (1974) 161.
25 J. Zwart, *Ph.D. Thesis*, Eindhoven University of Technology, 1978.
26 J. H. Schutten, *Ph.D. Thesis*, Eindhoven University of Technology, 1981.

Makromol. Chem. **185**, *363 – 375 (1984)*

Chapter IV

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(vinylamine), largely affects the reaction rate below a critical polymer concentration of about 0,01 w/v %. The activation enthalpy $\Delta H_2^{\ddagger}$ 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).

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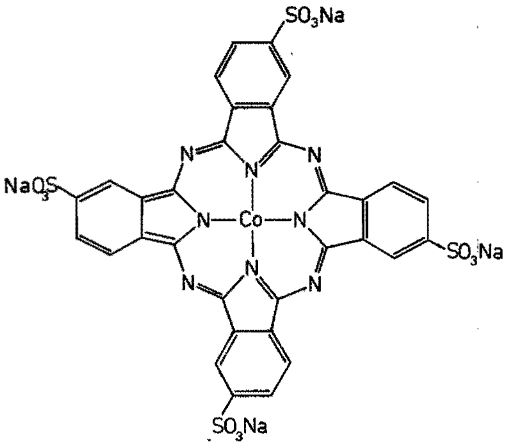

Fig. 1. Chemical structure of tetrasodium cobalt(II)phthalocyanine-2,7,12,17-tetrasulfonate

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 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 ($\overline{M}_w/\overline{M}_n$) appeared to have values between 2 and 2,5 for all samples.

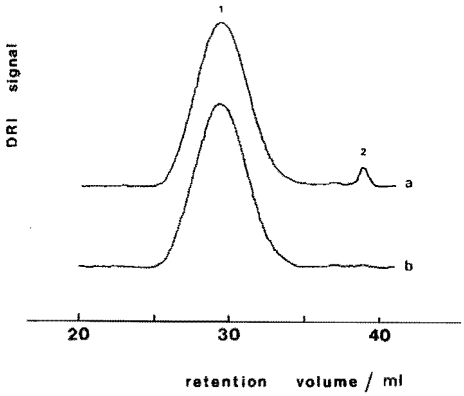

Fig. 2. Gel permeation chromatogram of PTBNVC II; (a) crude polymerization product (dried), (b) purified (1 ×) polymerization product (dried). (1) PTBNVC; (2) AIBN. Conditions: 0,4 mg of PTBNVC II; mobile phase: THF; flow rate: 0,9 ml · min^{-1}; temp.: 23 °C. Method of detection: differential refractive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

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 $\overline{M}_n$ of poly(*tert*-butyl *N*-vinylcarbamate) (PTBNVC)[a)]

Sample	$\frac{c_{TBNVC}}{mol \cdot dm^{-3}}$	$\frac{c_{AIBN}}{mol \cdot dm^{-3}}$	$\frac{10^{-3} \cdot \overline{M}_n}{g \cdot mol^{-1}}$	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:

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

where $c_{\mathrm{H}^+_{\mathrm{added}}}$ is the proton concentration as resulting of added HCl; $c_{\mathrm{H}^+_{\mathrm{free}}}$ and $c_{\mathrm{OH}^-_{\mathrm{free}}}$ are the concentrations of free protons and hydroxyl ions measured in the titration vessel, respectively. $c_{-\mathrm{N}}$ 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 autoviscometer 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 $\mathrm{CoPc(NaSO_3)_4}$ a Cary 14 spectrophotometer was used with absorbance unit scales of 0 – 0,1 and 0 – 0,2.

Catalytic activity measurements: $\mathrm{CoPc(NaSO_3)_4}$, 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 $\mathrm{CoPc(NaSO_3)_4}$ 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 $\mathrm{CoPc(NaSO_3)_4}$ 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).

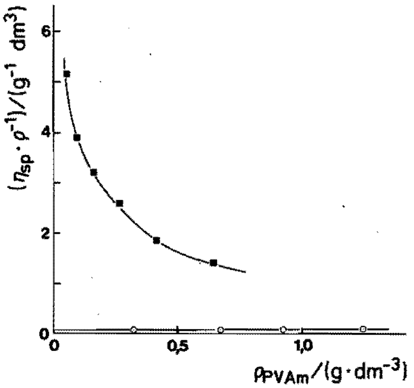

Fig. 3

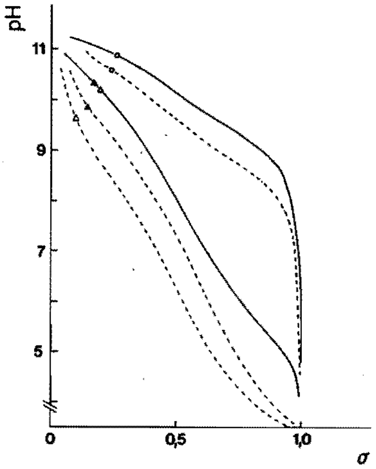

Fig. 4

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; $\overline{M}_{n,PVAm} = 5 \cdot 10^4\ g \cdot mol^{-1}$

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]:

$$\mathrm{E} + \mathrm{S} \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} \mathrm{ES} \xrightarrow[k_2]{} \mathrm{E} + \mathrm{P} \qquad (2)$$

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

$$\frac{1}{v} = \frac{1}{k_2[\mathrm{E}_0]} + \frac{K_m}{k_2[\mathrm{E}_0][\mathrm{S}]} \qquad (3)$$

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

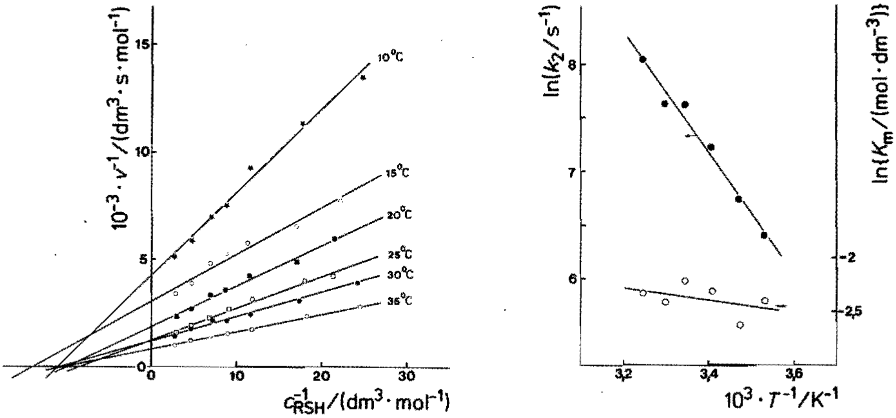

Fig. 5a

Fig. 5b

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

constant K_m can be obtained. In Fig. 5b the Arrhenius plots are shown containing the values of k_2 and K_m derived from Fig. 5a. From the slope the (activation) enthalpies were calculated: $\Delta H_2^{\neq} = (47 \pm 4)\ \mathrm{kJ\cdot mol^{-1}}$ and $\Delta H_\mathrm{m}\ (= -\Delta H_\mathrm{s}$ for $k_2 < k_{-1}) = (5 \pm 5)\ \mathrm{kJ\cdot mol^{-1}}$, and from the intercept at $T^{-1} = 0$ the (activation) entropies are obtained: $\Delta S_2^{\neq} = (-34 \pm 10)\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ and $\Delta S_\mathrm{m}\ (= -\Delta S_\mathrm{s}$ for $k_2 < k_{-1}) = (-3 \pm 15)\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$. 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 $\mathrm{mol\cdot dm^{-3}}$). 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 $\ln\{v(1 + K_\mathrm{m}^{298}/[\mathrm{S}])/[\mathrm{E_0}]\}$ ($\approx \ln k_2$) 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	$\Delta H_2^{\ddagger}$ / $\mathrm{kJ \cdot mol^{-1}}$	$\Delta S_2^{\ddagger}$ / $\mathrm{J \cdot mol^{-1} \cdot K^{-1}}$	$\Delta G_2^{\ddagger}$ a) / $\mathrm{kJ \cdot mol^{-1}}$	$10^{-3} \cdot k_2$ / $\mathrm{s^{-1}}$	K_m / $\mathrm{mol \cdot dm^{-3}}$
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 $\Delta S_2^{\ddagger}$.

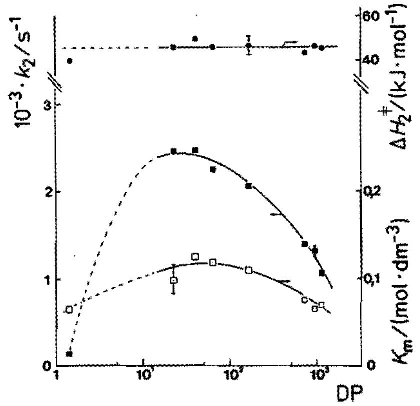

Fig. 6

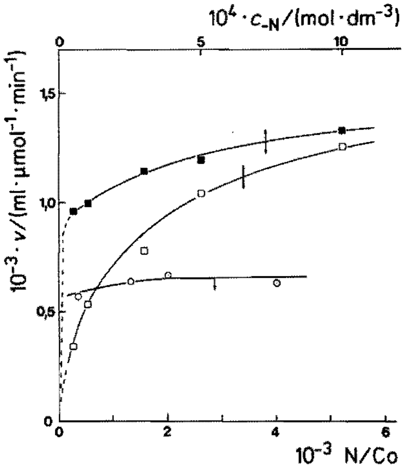

Fig. 7

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. (□): K_m^{298}; (■): k_2^{298}; (●): $\Delta H_2^{\ddagger 298}$. $c_{-N} = 3{,}8 \cdot 10^{-5}\ \mathrm{mol \cdot dm^{-3}}$, N/Co = 100; pH = 5,7

Fig. 7. Catalytic activity (expressed in ml oxygen consumed per minute per μmole $\mathrm{CoPc(NaSO_3)_4}$) of polymeric catalysts at various compositions vs. N/Co ratio. (■): DP = 23, $c_{\mathrm{CoPc(NaSO_3)_4}} = 1{,}9 \cdot 10^{-7}\ \mathrm{mol \cdot dm^{-3}}$, c_{-N} variable. (□): DP = 1030, $c_{\mathrm{CoPc(NaSO_3)_4}} = 1{,}9 \cdot 10^{-7}\ \mathrm{mol \cdot dm^{-3}}$, c_{-N} variable. (○): DP = 1030, $c_{-N} = 10^{-4}\ \mathrm{mol \cdot dm^{-3}}$, $c_{\mathrm{CoPc(NaSO_3)_4}}$ variable, ionic strength was kept constant with catalytically inactive $\mathrm{K_4Fe(CN)_6}$ at $5{,}7 \cdot 10^{-6}\ \mathrm{mol \cdot dm^{-3}}$. $c_{\mathrm{RSH}} = 0{,}37\ \mathrm{mol \cdot dm^{-3}}$

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 $\mathrm{CoPc(NaSO_3)_4/OH^-}$ system[2].

Assuming that $k_2 \ll k_{-1}$ ($K_m^{-1} \approx K_s$) the slight molecular weight dependence of K_m demonstrates that the formation of an active enzyme-substrate complex is not affected strongly by the higher base strength occurring in low molecular weight PVAm (Fig. 4).

From Fig. 6 it is unequivocally shown that $\Delta H_2^{\neq}$ 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 (■). The curves (⊡) and (■) are in full agreement with those published by Schutten[6]. 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 · dm^{-3}

and pH = 7,0 at $c_{-N} = 10^{-3}$ mol · 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).

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

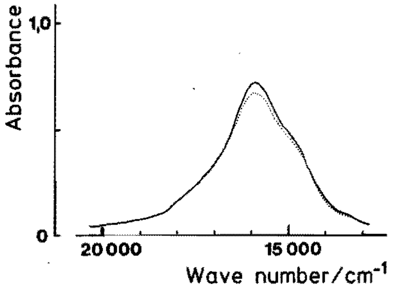

Fig. 8

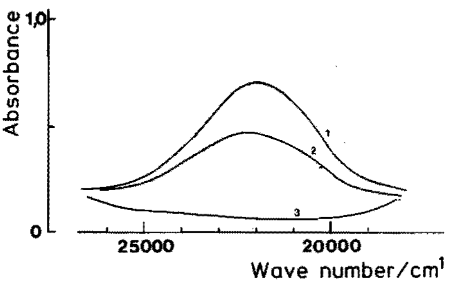

Fig. 9

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 · dm^{-3}, $c_{CoPc(NaSO_3)_4} = 4 \cdot 10^{-6}$ mol · dm^{-3}; path length b = 50 mm; (———) DP = 23; (······) 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 · dm^{-3}; (2): 1,3-PDA, $c_{-N} = 2 \cdot 10^{-3}$ mol · dm^{-3}; (3): no base. Nitrogen atmosphere. $c_{CoPc(NaSO_3)_4} = 2 \cdot 10^{-5}$ mol · dm^{-3}, c_{RSH} = 0,07 mol · dm^{-3}, b = 10 mm

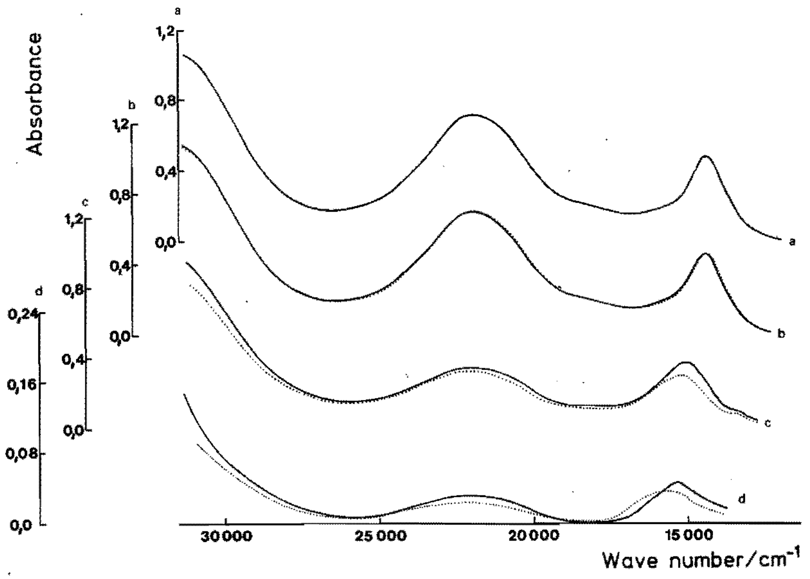

Fig. 10. Visible light spectra of the interaction product of $CoPc(NaSO_3)_4$ and RSH in the presence of PVAm of different molecular weight. Nitrogen atmosphere, N/Co = 100; c_{RSH} = 0,07 mol · dm^{-3}. (———) DP = 23; (······) DP = 930. (a) Conc. of N-groups $c_{-N} = 10^{-2}$ mol · dm^{-3}, path length b = 2 mm; (b) $c_{-N} = 2 \cdot 10^{-3}$ mol · dm^{-3}, b = 10 mm; (c) $c_{-N} = 4 \cdot 10^{-4}$ mol · dm^{-3}, b = 50 mm; (d) $c_{-N} = 8 \cdot 10^{-5}$ mol · 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 · 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 · 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 · 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 $\Delta H_2^{\neq}$ 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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1) N. N. Kundo, N. P. Keier, Russ. J. Phys. Chem. **42,** 707 (1968)
2) J. H. Schutten, J. Zwart, J. Mol. Catal. **5,** 109 (1979)

[3] W. M. Brouwer, P. Piet, A. L. German, Polym. Commun. **24**, 216 (1983)
[4] W. M. Brouwer, P. Piet, A. L. German, Polym. Bull. **8**, 245 (1982)
[5] W. M. Brouwer, P. Piet, A. L. German, J. Mol. Catal. **22**, 297 (1984)
[6] J. H. Schutten, P. Piet, A. L. German, Makromol. Chem. **180**, 2341 (1979)
[7] D. D. Reynolds, W. O. Kenyon, J. Am. Chem. Soc. **69**, 911 (1947)
[8] E. Bayer, K. Gecheler, K. Weingärtner, Makromol. Chem. **181**, 585 (1980)
[9] H. Tanaka, R. Senju, Bull. Chem. Soc. Jap. **19**, 2821 (1976)
[10] D. J. Dawson, R. D. Gless, R. E. Wingard Jr., J. Am. Chem. Soc. **98**, 5996 (1976)
[11] R. Hart, Makromol. Chem. **32**, 51 (1959); J. Polym. Sci. **29**, 629 (1958)
[12] A. R. Hughes, T. St. Pierre, Macromol. Synth. **6**, 31 (1977)
[13] P. Grubisic, P. Rempp, H. Benoit, J. Polym. Sci., Part B **5**, 753 (1967)
[14] H. K. Mahabadi, K. F. O'Driscoll, J. Appl. Polym. Sci. **21**, 1283 (1977)
[15] C. J. Bloys van Treslong, C. F. H. Morra, Rec. J. R. Neth. Chem. Soc. **94**, 101 (1975)
[16] J. H. Weber, P. H. Busch, Inorg. Chem. **4**, 469 (1965)
[17] J. Zwart, H. C. van de Weide, N. Bröker, C. Rummens, G. C. A. Schuit, A. L. German, J. Mol. Catal. **3**, 151 (1977 – 1978)
[18] Ph. Teyssie, C. Decoene, M. T. Teyssie, Makromol. Chem. **84**, 51 (1965)
[19] C. J. Bloys van Treslong, Recl. Trav. Chim. Pays-Bas **97**, 13 (1978)
[20] Ch. Tanford, "Physical Chemistry of Macromolecules", John Wiley, New York 1961
[21] E. A. Lewis, J. Barkley, T. St. Pierre, Macromolecules **14**, 546 (1981)
[22] P. L. Rinaldi, Chin Yu, G. C. Levy, Macromolecules **14**, 551 (1981)
[23] E.g. A. Cornish-Bowden, "Fundamentals of enzyme kinetics", Butterworths, London 1979
[24] M. Nagasawa, A. Takahashi, in "Light scattering from polymer solutions", ed. by M. B. Huglin, Academic Press, London/New York 1972, ch. 16
[25] E. Tsuchida, H. Nishide, Adv. Polym. Sci. **24**, 1 (1977)
[26] M. J. Stillman, A. J. Thomson, J. Chem. Soc., Faraday Trans. II **70**, 790 (1974)
[27] B. B. Wayland, J. C. Swartz, Inorg. Chim. Acta **23**, 221 (1977)
[28] F. Nome, J. H. Fendler, J. Chem. Soc., Dalton Trans. **1976**, 1212

Chapter V

COPOLYMERS OF VINYLAMINE AND VINYLALCOHOL BY ACID HYDROLYSIS OF POLY(N-VINYL-TERT-BUTYLCARBAMATE-CO-VINYLACETATE).

Evaluation of reactivity ratios.

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Summary

Copolymers of vinylamine and vinylalcohol have been prepared by hydrolysis of poly(N-vinyl-tert-butylcarbamate-co-vinylacetate) in 1:1 v/v % ethanol/HCl mixtures at room temperature.

Reactivity ratios of the monomers N-vinyl-tert-butylcarbamate (1) and vinylacetate (2) have been calculated from monomer feed and copolymer composition data, according to the methods of Fineman-Ross and Kelen-Tüdös, yielding $r_1 = 1.14 \pm 0.05$, $r_2 = 0.47 \pm 0.07$ *and* $r_1 = 1.12 \pm 0.07$, $r_2 = 0.46 \pm 0.03$, *respectively.*

From these values the average sequence length distribution of monomer units was derived showing that in the reaction of N-vinyl-tert-butyl-

carbamate and vinylacetate nearly Bernouillian (i.e. purely random) copolymers are formed, with a slight tendency toward alternation.

Introduction

The polymeric amine with the simplest chemical structure is undoubtedly poly(vinylamine) and although its synthesis is rather laborious, it can be prepared according to one of the synthetic routes already known (1-5).

Some important features of these polymers are their water solubility, complexation properties toward transition metal-ions (6), rather high basicity of the amine groups ($pK_a(-NH_3^+) \approx 9$) (7) and the ability of easy reaction with all kinds of electrophilic compounds, such as dyes (4). The pH dependent basicity of amine groups is of fundamental scientific interest (8).

In our laboratory poly(vinylamine) is being used as a functional polymeric ligand of a thiol oxidation catalyst. Application of this polymeric base instead of NaOH was found to increase catalytic activity 50-fold (9). It appeared from viscosity (10), pH (11) and kinetic (12) measurements that the amine group basicity, polymer charge and conformation largely affected catalytic activity. Combination of these properties with other desirable functionalities can be achieved by appropriate copolymerization. Selection of the synthetic route will depend on the nature of the comonomer.

Copolymers of vinylamine and a suitable uncharged comonomer seem to offer the opportunity to investigate the effect of base group density within the polymer chain on catalytic activity. For this purpose copolymers with either randomly distributed vinylamine units or alternating monomer units are preferred to block copolymers.

Until now, to our knowledge, the synthesis of only two water soluble vinyl copolymers containing vinylamine has been reported: copolymers of vinylamine with sodium vinylsulfonate, containing cationic and anionic functionalities in water (13), and copolymers of vinylamine with vinylalcohol containing only cationic functionalities. The latter copolymers were prepared first by Nikolayev (14) starting from copolymers of vinylphthalimide and vinylacetate, which could be aminolysed and hydrolysed, respectively, with hydrazine hydrate. Decomposition of the formed phthalylhydrazide salt of vinylamine was achieved in hydrochloric acid according to the method of Reynolds and Kenyon (1). Very recently, a new way of preparing copolymers of vinylamine and vinylalcohol, by acid hydrolysis of copolymers of N-vinyl-tert-butylcarbamate (NVTBC) and vinylacetate (VAc), based on the Hart synthesis of polyvinylamine (15) was outlined briefly by Bloys van Treslong and Jansen (16).

The synthetic route they described is an important contribution to making these copolymers more accessible to further investigations. Unfortunately, only few copolymerization data were presented prohibiting accurate calculation of the reactivity ratios of the pre-monomers. Therefore, we followed their preparation method succesfully (minor modifications) determining the copolymer reactivity ratios of the monomers from completive data, in order to get insight into the randomness of these very hygroscopic copolymers.

Experimental

Synthesis of the pre-copolymers

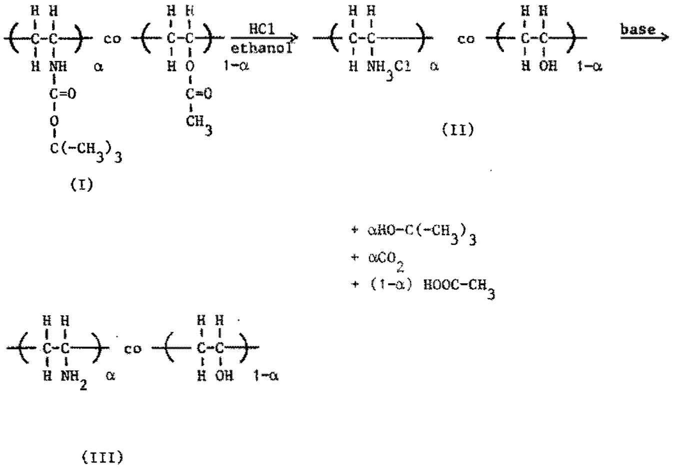
NVTBC was synthesised according to the Hart method (15), with some minor modifications (17). After drying thoroughly, the white, powdery NVTBC was purified by sublimation at 54°C at 1 kPa pressure. Regarding the highly poisonous character of NVTBC - in aquo the toxic hydrolysis product ethylenimine is formed - all manipulations with this reagent were carried out under an efficient fume hood. VAc (kindly provided by DSM) was vacuum distilled before use.

Copolymerization of NVTBC and VAc was carried out in benzene (Merck pro analysi, dried on CaH$_2$) at 60°C for 6 hr with α,α'-azoisobutyronitrile as initiator under nitrogen. The pre-copolymers were isolated by precipitating the reaction product in a 20 fold excess of ice-cold n-hexane. After drying, the copolymers were purified by redissolution in toluene and precipitation in n-hexane, followed by washing with n-heptane (pro analysi) in order to remove residual initiator. The purified copolymers (I)(Scheme 1) were dried at 0.1 Pa, at 35°C.

Number average molecular weights ($\bar{M}_n$) were determined in toluene at 37°C with a Hewlett Packard 502 high speed membrane osmometer, $\bar{M}_n$ lying in the range of 30,000 - 75,000 g mole^{-1}.

The molar fraction of NVTBC units in the copolymer, α, was calculated either from the nitrogen content, obtained from elemental analysis or from the relative peak intensity of the methyl protons of the tert-butyl group in the ^{1}H NMR spectrum (Although the methylene peaks (a and b in Fig. 3) are fully separated, these peaks were nevertheless considered too small for proper analysis)

Scheme 1



Hydrolysis of copolymers

Two gram of (I) was dissolved in absolute ethanol and added to a stirred 500 ml round bottom flask by means of a dropping funnel. Then it was mixed with an equal amount of concentrated HCl, added in the same manner, while the temperature was controlled not to exceed 30°C. The mixtures were stirred at room temperature for 48 h. From copolymers (II), with $\alpha > 70\%$ (type A), white, brittle precipitates were formed. From copolymers with α-values in the range 0.5-0.7 (type B), white clotty precipitates were obtained after a few hours of reaction, while from reaction mixtures containing copolymers with a lower value of α (type C), no precipitation was observed.

Isolation of hydrolysed copolymers

Copolymers (II) of type A and B were isolated by filtration, washed with cold absolute ethanol, and dried under vacuum at room temperature. These products appeared to be very hygroscopic. Reaction mixtures containing copolymer (II) of type C were diluted with 100 ml of water, neutralized by hydrated sodium carbonate, and followed by removal of the alcohol fraction by rotary evaporation at 50°C. These solutions, mostly containing precipitated NaCl, were ultrafiltrated with distilled water (Diaflow Membrane YM-10, sharp cutoff: 10,000 MW), until no chloride could be detected in the eluent with a $AgNO_3/HNO_3$ test solution. It appeared that ultrafiltration was a safe and effective way of purification.

After eluting solutions of (II) through an Amberlite IRA 401 anion exchange resin in the OH^- form, solutions of deprotonated copolymers (III) were obtained. These copolymers were precipitated by pouring aqueous solutions of (III) into acetone.

Analysis

Samples for IR spectra were prepared by evaporation of some drops of a methanolic solution of (III) on a KBr disk. Polymers (I) were dispersed in a KBr disk. Characteristic absorptions of (III) occur at 3400 cm^{-1} (OH, NH_2); 2950 cm^{-1} (CH_2, CH); 1620 cm^{-1} (NH_2); 1470 cm^{-1} (CH_2, CH); 1100 cm^{-1} (CH) and 850 cm^{-1} (C-C).

Potentiometric titration of copolymers (III) were performed with HCl (0.03 N) in the presence of 2 M NaCl. Titration times were not shorter than 20 min, for reasons of reproducibility.

Results and Discussion

Features of synthesis

Complete hydrolysis of poly(N-vinyl-tert-butylcarbamate-co-vinylacetate) could be obtained after 48 h of reaction in a mixture of 1:1 v/v % ethanol/concentrated HCl at room temperature. The hydrolysis of tert-butylcarbamate is completed within ½ h $^{(5)}$, but the hydrolysis of the acetate is rather slow under these conditions. The rate of hydrolysis of the acetate group could be followed by monitoring the decrease in the -C=0 band intensity at 1750 cm^{-1} in the IR spectra of the copolymers (Fig. 1). It is shown that after 20 h of reaction

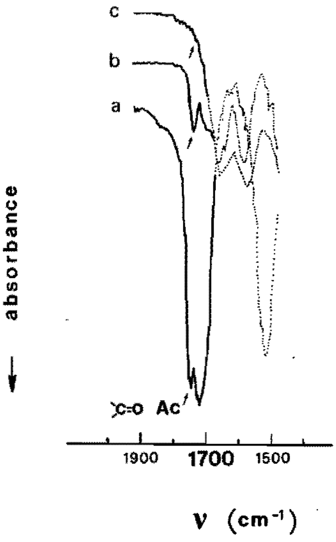


Figure 1: IR spectra of (I) ($\alpha = 0.56$) after hydrolysis during (a): 0 h, (b): 20 h, (c): 48 h. Arrows indicate the carbonyl group of the acetate moiety at 1750 cm^{-1}.

(b in Fig. 1) almost all VAc is hydrolysed and after 48 h the reaction is complete.

Copolymers (II) were only soluble in water, but the deprotonated forms (III) were very soluble in both water and the lower alcohols in agreement with Nikolayev $^{(14)}$.

Basicity of the amine groups

Copolymers (III) were subjected to potentiometric titration experiments with HCl in 2 M NaCl. The results are shown in Fig. 2, revealing that the individual amine groups possess a higher basicity as the amine group content in the copolymers is lower. This behaviour can be

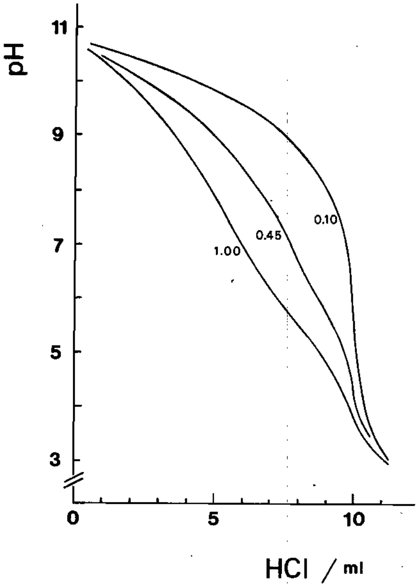


Figure 2: Potentiometric titrations of copolymers (III) with 0.03 N HCl in 2 M NaCl. Solutions contain 0.3 mmole of amine groups. α-values are given in the figure.

explained by assuming a decreased nearest neighbour interaction when the amine groups find themselves more isolated in the polymer chain at low α values. On the grounds of these experimental observations, copolymers with a high degree of randomness or alternation are expected to be formed. In the following section this inference will be confirmed by measuring the copolymer reactivity ratios. The titration behaviour, shown in Fig. 2, is in qualitative agreement with the titration experiments performed by Bloys van Treslong et al. (16) and by Kimura et al. (18) on copolymers (III) prepared according to the Hart method (5) and the Nikolayev method (14), respectively.

Reactivity ratios of NVTBC and VAc in benzene

The dependence of copolymer composition on the monomer feed has been evaluated for initial molar monomer feed ratios, q_0, in the range 0.05-4. Total conversion was mostly 15% but never exceeded 30%, to avoid large shifts in the monomer feed ratio.

Copolymer compositions were calculated from elemental analysis (C,H,N) of the purified, dried copolymers (I). For some of these copolymers the composition was determined from the methyl proton peak intensity of the tert-butyl group of (I) in the ^1H NMR spectrum (shown in Fig. 3 for $\alpha = 0.43$). In Table 1 values of α, obtained from NMR and elemental analysis data are given, showing that within experimental error the NMR data are in good agreement with the elemental analysis results.

The reactivity ratios of monomers (1) and (2) have been evaluated according to the methods of Fineman-Ross (19) and Kelen-Tüdös (20). These methods were selected on the grounds of experimental convenience, since in the present case, copolymer compositional analysis data appeared to be available much more easily and accurately than monomer feed data during the polymerization.

In the Fineman-Ross method the parameters $F = \frac{(\bar{q})^2}{x}$ and $G = \bar{q}(x - 1)/x$ are evaluated, where $\bar{q}$ = the average ratio of molar

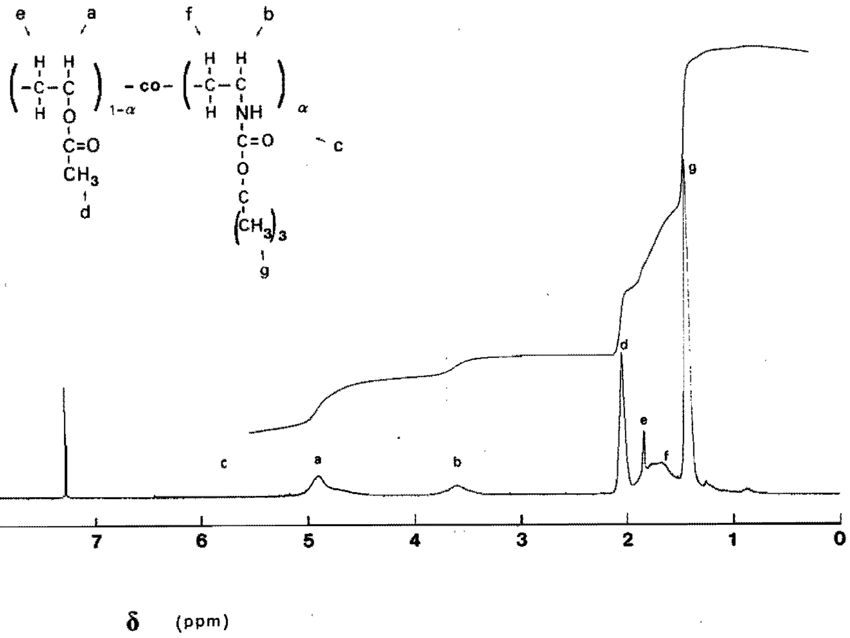


Figure 3: ^{1}H NMR spectrum of (I) (α = 0.43) in $CDCl_3$ with $CHCl_3$ as internal standard. Peaks correspond to the hydrogen atoms indicated.

Table 1: Comparison of copolymer compositional determination by elemental analysis (C,H,N) and ^{1}H NMR.

Molefraction of NVTBC in monomer feed	α(CHN) (a)	α(^{1}H NMR) (b)
0.80	0.84 ± 0.05	0.83 ± 0.06
0.59	0.67 ± 0.04	0.74 ± 0.05
0.31	0.43 ± 0.03	0.44 ± 0.03
0.18	0.33 ± 0.02	0.30 ± 0.02
0.13	0.20 ± 0.01	0.21 ± 0.02

(a) Nitrogen content of (I) has been used

(b) Methyl proton peak intensity of the tert-butyl group in (I) has been used

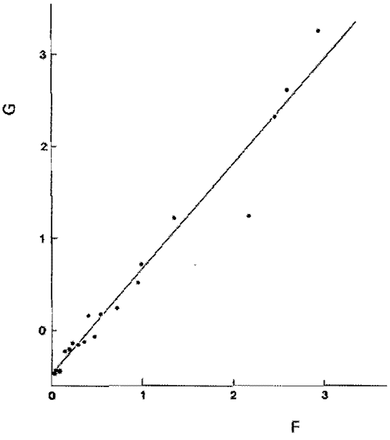


Figure 4: Fineman-Ross plot; the intercept gives $-r_2$, the slope gives r_1.

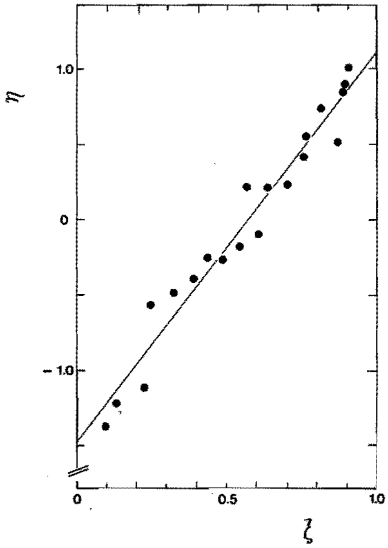


Figure 5: Kelen-Tüdös plot; the intercept at $\xi = 0$ gives $\frac{-r_2}{\beta}$, the intercept at $\xi = 1$ gives r_1. $\beta = 0.31$.

concentrations of monomers (1) and (2), and x = the molar ratio of these monomers in the copolymers. This analysis is shown in Fig. 4. In the calculations, q_0 instead of $\bar{q}$ has been used, since simulation experiments (21) show that for the present pair of r-values and degree of conversion any possible deviations of these r-values, introduced by substituting q_0 for $\bar{q}$, will be within the error intervals given for the Fineman-Ross method. Moreover, in Fig. 4 the experimental points derived from relatively high conversion (30%) experiments do not deviate significantly more from the drawn linear fit than do the points pertaining to lower conversion experiments. In the method designed by Kelen-Tüdös for low conversion, the experimental points are symmetrized by introducing the parameter $\beta = (F_{min} F_{max})^{\frac{1}{2}}$ in the dependent variable $\xi = F(\beta + F)$ and $\eta = G(\beta + F)$. According to the latter method, data contained in Fig. 4 have been replotted in Fig. 5. Reactivity ratios calculated from Fig. 4 and 5 are given in Table 2, which shows that the results of both methods are in good agreement. Obviously, the effect on r_1 and r_2 of symmetrization of the experimental points as occurs in the Kelen-Tüdös method is negligible. The values of r_1 and r_2 found here (1.14 ± 0.05 and 0.47 ± 0.05, respectively) deviate considerably from the values recently reported by Bloys van Treslong et al. (16), viz. 1.8 ± 0.2 and 0.76 ± 0.11, respectively.

Table 2: Reactivity ratios of NVTBC and VAc in benzene, calculated according to the methods of Fineman and Ross (F-R) and Kelen and Tüdös (K-T).

Method of data analysis	r_1	r_2
F - R	1.14 ± 0.05	0.47 ± 0.07
K - T	1.12 ± 0.07	0.46 ± 0.03

However, their experimental points do not seriously conflict with ours as would appear from plotting their data in Fig. 4. The main reason for the discrepancy in the reactivity ratio values is that although the latter authors used a calculation method essentially the same as the Fineman Ross procedure (19) only few experimental points within a very narrow range of monomer feed ratios were available, not enough for determining the reactivity ratios sufficient accurately.

While summarizing, more accurate reactivity ratios will be obtained when using more experimental data, obtained from copolymerization experiments over a wider range of monomer feed compositions. If possible, the copolymer compositional analysis should be confirmed by a second technique. On these grounds, we believe our present data to be the more reliable.

Sequence distribution

The distribution of monomer units in the copolymer is directly related to the reactivity ratios, the latter being measures of the probability of occurrence of homogeneous sequences of either monomer unit. In order to get insight into the randomness of the monomer unit distribution along the polymer chain, the relative numbers of amine-amine, amine-alcohol, and alcohol-alcohol neighbouring groups as well as the number average sequence length of either monomer have been calculated (22) and compared with a situation of Bernouillian distributed, i.e. purely randomly, sequenced monomer units. In Table 3 the results are listed for a copolymer with $\alpha = 0.43$.

A more sensitive indicator of deviations from the Bernouillian distribution is the so-called monomer dispersity index, MD, which is defined as $100/\bar{\ell}$ where $\bar{\ell}$ is the number average sequence length (23). An MD value of 100 would indicate that all vinylamine units occur isolated in alcohol-amine-alcohol sequences. Any value below 100 is indicative of the occurrence of contiguous amine-amine units.
In Fig. 6 values of MD of vinylamine units for copolymers formed

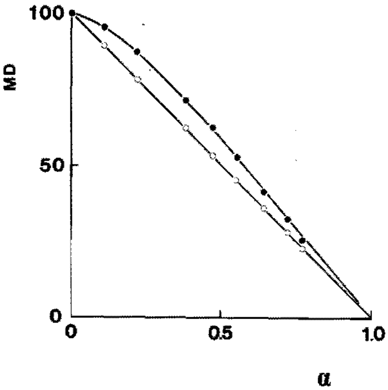


Figure 6: Monomer dispersity of vinylamine units versus α.
(●) in the presently synthesised copolymers
(o) in hypothetical Bernouillian type copolymers

Table 3: Calculated diad abundance and number average sequence length in one of the present copolymers as compared with a hypothetical Bernouillian type copolymer (α = 0.43).

		present copolymer [b]	perfectly Bernouillian sequenced copolymer
diad abundance (%) [a]	11	15	18
	12 + 21	57	49
	22	29	32
sequence length [a]	$\bar{\ell}_1$	1.51	1.75
	$\bar{\ell}_2$	2.00	2.33

[a] 1 = vinylamine unit; 2 = vinylalcohol unit

[b] $r_1 = 1.12$; $r_2 = 0.46$; $q_0 = 0.46$

according to the present pair of r-values as well as for a hypothetical perfect Bernouillian type copolymer have been plotted versus the copolymer composition α. From the calculations (Table 3 and Fig. 6) it may be concluded that in the reaction of NVTBC with VAc random copolymers are formed with a slight tendency toward alternation. These copolymers are therefore eminently suitable as polymeric ligands in a study on the relation between base density within a polymeric thiol oxidation catalyst and catalytic activity. The results of this study will be reported separately.

Acknowledgements

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References

(1) Reynolds, D.D. and Kenyon, W.O., *J. Am. Chem. Soc.* , 69 (1947), 911

(2) Bayer, E., Gecheler, K. and Weingärtner, K., *Makromol. Chem.* , 181 (1980), 585

(3) Tanaka, H. and Senju, R., *Bull. Chem. Soc. Jpn.* , 19 (1976), 2821

(4) Dawson, D.J., Gless, R.D., Wingard Jr, R.E., *J. Am. Chem. Soc.*, 98, (19), (1976), 5996

(5) Hart, R., *Makromol. Chem.* , 32 (1959), 51 and *J. Polym. Sci.*, 29 (1958), 629

(6) Teyssié, Ph., Decoene, C., Teyssié, M.T., *Makromol. Chem.* , 84 (1965), 51

(7) Bloys van Treslong, C.J. and Staverman, A.J., *Recl. Trav. Chim. Pays-Bas*, 97 (1), (1978), 13

(8) Katachalsky, A., Mazur, J. and Spitnik, P., *J. Polym. Sci.* , 23 (1957), 513

(9) Schutten, J.H. and Zwart, J., *J. Mol. Catal.*, 5 (1979), 9

(10) Brouwer, W.M., Piet, P. and German, A.L., *Polymer Commun.* , 24 (1983), 216

(11) Brouwer, W.M., Piet, P. and German, A.L., *Polym. Bull.* , 8 (1982), 245

(12) Brouwer, W.M., Piet, P. and German, A.L., *J. Mol. Catal.* , 22 (1984), 297

(13) Kronstadt, M. Dawson, D.J. and Dubin, P.L., *Polym. Prepr. Am. Chem. Soc.* 19 (1), (1978), 280

(14) Nikolayev, A.F., Ushakov, S.N., Vishnevetskaya, L.P. and Voronova, N.A., *Vysokomol. soyed.*, 5 (4), (1963), 547 English translation: *Polym. Sci. USSR*, 4 (1963), 1221

(15) Hughes, A.R. and St. Pierre, T., *Macromol. Synth.* , 6 (1977), 31

(16) Bloys van Treslong, C.J. and Jansen, B.J., *Eur. Polym. J.* 19 (1983), 131

(17) Brouwer, W.M., Piet, P. and German, A.L., *Makromol. Chem.*, 185, (1984), 363

(18) Kimura, K., Inaki, Y. and Takemoto, K., *Makromol. Chem.* 176 (1975), 2225

(19) Fineman, M. and Ross, S.D., *J. Polym. Sci.*, 5 (1950), 259

(20) Kelen, T. and Tüdös, F., *J. Macromol. Sci. Chem.*, A9 (1975), 1

(21) Hautus, F.L.M., Linssen, H.N. and German, A.L., to be published in J. Polym. Sci.

(22) Harwood, H.J. and Ritchey, W.M., *J. Polym. Sci. Polym. Lett. Ed.* 2 (1964), 601

(23) Hsieh, E.T. and Randall, J.C., *Macromolecules*, 15 (1982), 1402

Chapter VI

AUTOXIDATION OF THIOLS WITH COBALT(II) PHTHALOCYANINE TETRASODIUM SULFONATE ATTACHED TO POLY(VINYLAMINE).

4. Influence of base density within the polymeric ligand.

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Summary

Water soluble, polymeric catalysts consisting of cobalt (II)phthalocyanine-tetrasodium sulfonate, coordinatively bound to poly(vinylamine-co-vinylalcohol) have been used in the oxidation by oxygen of 2-mercaptoethanol to its corresponding disulfide.

An increase of the intrinsic activity of the catalytic sites was observed for increasing ethylamine (base group) content in the copolymers, while constant activation enthalpies indicated that the reaction mechanism remained unchanged.

From potentiometric titrations of the basic copolymers with hydrochloride and from catalytic activity measurements it could be deduced that reaction rate varied linearly with the mole fraction of charged monomeric units in these copolymers.

A reaction scheme has been proposed, suggesting that the thiol-anion is involved in the rate limiting step.

The present polymeric catalyst and Vit B_{12} *were found to show similarities in their oxidation behaviour toward thiols.*

Introduction

During the last decennia many papers concerning the oxidation of thiols have been published as its great importance in oil sweetening and biological processes became apparent.

Many catalysts are known for the oxidation of thiols, whereas especially porphyrins and phthalocyanines appeared to be useful catalysts (1,2). It has been shown that Vit B_{12}, containing cobalt within a porphyrin related structure, also catalyses the oxidation of thiols (3).

In our laboratory we are using cobalt(II)phthalocyanine-tetra-sodium sulfonate ($CoPc(NaSO_3)_4$, Fig. 1) attached to poly(vinylamine) (PVAm), as a polymeric catalyst in the oxidation of 2-mercaptoethanol (RSH), causing a fifty-fold enhancement of reaction rate in comparison to polymer free $CoPc(NaSO_3)_4$ solutions. In the presence of 1,3 propane-diamine, which may be regarded as the monomeric analog of PVAm, reaction rate appeared to be also much lower compared with the polymer attached $CoPc(NaSO_3)_4$ system (4). It has been shown from

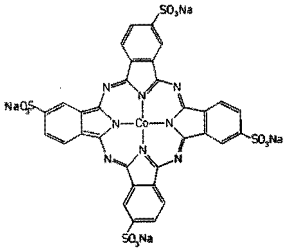


Figure 1: Chemical structure of $CoPc(NaSO_3)_4$.

viscosity (5) and ESR measurements (6) that the metal centre of $CoPc(NaSO_3)_4$ is coordinated by five nitrogen atoms at most, when attached to PVAm. However, the importance of Coulombic attraction between the fourfold negatively charged $CoPc(SO_3)_4^{4-}$ ion and the positively charged PVAm must not be ruled out and may also contribute to the bonding.

So far, little is known of the detailed kinetics of the thiol oxidation by polymer bound $CoPc(NaSO_3)_4$. Only a few studies with porphyrins and phthalocyanines attached to polymers and polymeric sorbents have been published (7,8).

In order to reveal the essence of the observed enhanced activity when using $CoPc(NaSO_3)_4$ attached to PVAm as a catalyst the relations between catalytic activity on the one hand and pH, viscosity, reactant and catalyst concentrations, temperature and ionic strength on the other hand were investigated (9,10). Kinetic resemblance was found with the action of Vit B_{12} derivatives in the oxidation of thiols. Recently we have shown that the enhanced basicity of low molecular weight PVAm with respect to high molecular weight PVAm caused an increase in reaction rate. Local thiol-anion concentration in the vicinity of the oxidation sites was assumed to be enhanced by the more basic character of low molecular weight PVAm (4).

Now the effect of local base strength has been investigated by varying the amine group density within the polymer chain, by intercalation of non-charged spacer groups of variable length. For this purpose we have synthesised random copolymers of vinylamine and vinylalcohol (PVAm-co-VAL).

Experimental

Copolymers of vinylamine and vinylalcohol have been synthesised by acid hydrolysis of poly(N-vinyl-tert-butylcarbamate-co-vinylacetate) (PNVTBC-co-VAc) as described elsewhere (11).
Different molefractions of ethylenamine, α, in the copolymers could be obtained by varying the initial monomer feed ratio of N-vinyl-tert-butylcarbamate and vinylacetate. The total conversion was controlled not to exceed 30%, in order to prevent heterogeneous copolymer formation.

Values of α were obtained from elemental analysis (N-content) of the pre-copolymers. The number average molecular weight of these polymers was determined in toluene with a Hewlett Packard 502 high speed membrane osmometer operating at 37°C.
In Table 1 monomer feed, copolymer composition data, number average molecular weights and degree of polymerization (D.P.) have been listed.

After hydrolysis and elution through an anion-exchange column (Amberlite IRA-401), stock solutions of copolymers were stored under nitrogen, to prevent absorption of CO_2.

Table 1: Feed-copolymer compositional data, number average molecular weight and degree of polymerization (DP) for the copolymerization of NVTBC with VAc in benzene at 60°C.

Sample	Molefraction of NVTBC in the feed	Molefraction of NVTBC in the copolymer (=α)	$\frac{10^{-3}.\bar{M}_n}{g\ mole^{-1}}$	DP
I	1.00	1.00	22	154
II	0.77	0.81	50	378
III	0.66	0.73	40	313
IV	0.56	0.63	40	328
V	0.45	0.56	33	280
VI	0.35	0.45	32	287
VII	0.26	0.39	27	364
VIII	0.13	0.20	69	708
IX	0.06	0.10	75	951
X[a]	-	-	72	1636

[a] Poly(vinylalcohol) obtained from Koch Light Laboratories England

The molar N-group concentration (c_{-N}) was determined by potentiometric titration with HCL (0.03 N) in 2 M NaCl.

Catalytic activity measurements were carried out isobarically in an all-glass thermostated Warburg apparatus, equipped with a mechanical glass-stirrer. Oxygen consumption rates were measured with a digital flow meter equipment.

The polymeric catalyst was prepared by adding an aqueous solution of $CoPc(NaSO_3)_4$ to a copolymer solution in water, resulting in a coordinatively bound polymer complex. $CoPc(NaSO_3)_4$ concentration was $1.9\ 10^{-7}$ M under reaction conditions. The catalyst solution was degassed twice and saturated with oxygen. The reaction was started by adding the 2-mercaptoethanol to the reaction vessel with a syringe. Initial reaction rates were calculated from the oxygen consumption during the first minute of reaction. Limitations of oxygen transport from the gas phase to the liquid were precluded by operating at a high stirring speed, viz 2300 r.p.m., as described earlier (9).

Results and Discussion

Previous investigations (9) have shown that the oxidation of 2-mercaptoethanol catalysed by PVAm bound $CoPc(NaSO_3)_4$ can be described by Michaelis-Menten kinetics (12) which means that in the reaction mechanism the rate determining step takes place subsequent to enzyme-substrate complex formation:

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

$$v = k_2\ [ES] \qquad [1]$$

where [E] = unbound enzyme, [ES] = enzyme-substrate complex and P = product. A plot of reciprocal reaction rate versus reciprocal substrate concentrations [S], a so-called Lineweaver-Burk plot, yields $(k_2.[E_0])^{-1}$ as intercept, and extrapolation to $v^{-1} = 0$ yields $-K_m^{-1}$ as abscissa:

$$\frac{1}{v} = \frac{1}{k_2[E_0]} + \frac{K_m}{k_2[E_0]} \cdot \frac{1}{[S]} \qquad [2]$$

where $K_m = \dfrac{k_{-1} + k_2}{k_1}$ (for $k_2 << k_{-1}$: $K_m \cong \dfrac{1}{K_s} = \dfrac{k_{-1}}{k_1}$) and

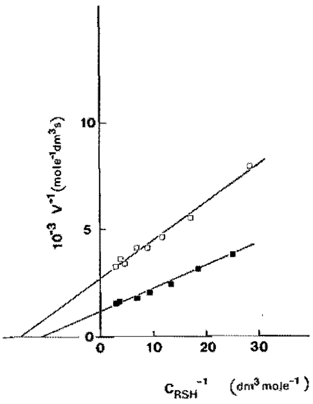
$[E_0]$ = total enzyme concentration, i.e. $c_{CoPc(NaSO_3)_4}$.
This type of kinetics has been observed with respect to both reactants, i.e. thiol and oxygen. At O_2 pressures above 0,1 MPa ($\cong 5 \, . \, K_{m,O_2}$) the saturation plateau was reached as no further pressure dependence was observed (9).

For the present polymer VIII ($\alpha = 0.20$) we have verified the reaction rate to be independent of oxygen pressure around 0.1 MPa (at 0.06 MPa reaction rate was 90% of that at 0.1 MPa). All experiments reported in this paper, therefore, have been performed at 0.1 MPa oxygen pressure, while fairly high polymer concentrations have been used to avoid any effects of the molecular weight of the polymers on reaction rate (4).

For copolymers of different amine content (II, $\alpha = 0.81$, VIII, $\alpha = 0.20$ and IX, $\alpha = 0.10$) the apparent reaction constants k_2 and K_m have been evaluated from Lineweaver-Burk plots, shown in Fig. 2 for II and VIII, according to eq. 2.

In Fig. 3 Arrhenius plots are shown for copolymers II and VIII. It has been shown earlier (10) that ΔH_m is small in comparison to $\Delta H_2^{\neq}$, therefore the overall activation enthalpy virtually equals $\Delta H_2^{\neq}$ at high thiol concentrations, as can be derived from eq. 2.

Values of $\Delta H_2^{\neq\,298}$, $\Delta S_2^{\neq\,298}$, k_2^{298} and K_m^{298} have been listed in Table 2. This table shows that a four fold increase in amine group



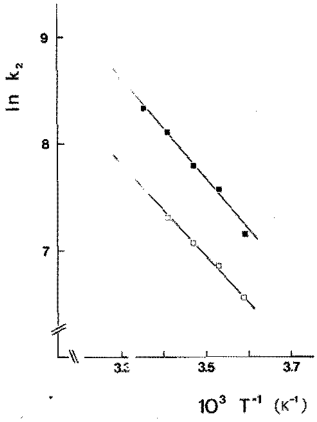


Figure 2: Lineweaver-Burk plots for systems containing copolymers [illegible] (α = 0.81, ■) and VIII (α = 0.20, □). c_{-N} = 1.5 10^{-3} M; $c_{CoPc(NaSO_3)_4}$ = 1.9 10^{-7} M. pH = 7.8. pH adjusted with NaOH (0.1 N).

Figure 3: Arrhenius plots of k_2. Copolymers as in Fig. 2. c_{RSH} = 0.34 M, other concentrations and pH as given in Fig. 2. The value of k_2 has been approximated by

$$\frac{v}{c_{CoPc(NaSO_3)_4}} \cdot \left(1 + \frac{K_m^{298}}{c_{RSH}}\right)$$

Table 2: Effect of amine content in PVAm-co-VAl on some important reaction parameters at 298 K.

α	$\frac{\Delta H_2^{\neq}}{\text{kJ mole}^{-1}}$	$\frac{\Delta S_2^{\neq}}{\text{J mole}^{-1}\ \text{K}^{-1}}$	$\frac{10^{-3} k_2}{s^{-1}}$	$\frac{K_m}{\text{mole dm}^{-3}}$
1.00	43 ± 4	- 39 ± 10	4.5 ± 0.6	0.10 ± 0.01
0.81	39 ± 4	- 53 ± 10	4.4 ± 0.5	0.09 ± 0.01
0.63	42 ± 4	- 44 ± 10	3.7 ± 0.4	0.08 ± 0.01
0.39	36 ± 4	- 68 ± 10	2.4 ± 0.4	0.[illegible]8 ± 0.01
0.20	36 ± 4	- 70 ± 10	1.9 ± 0.3	0.07 ± 0.01
0.10	41 ± 4	- 57 ± 10	1.2 ± 0.2	0.[illegible]8 ± 0.01

content in the polymer chain ($\alpha = 0.20$ to $\alpha = 0.81$) causes a two fold increase in the intrinsic activity of the catalytic sites, indicated by the values of k_2. The values of K_m remain unchanged and no significant dependence of $\Delta H_2^{\neq}$ on α is being observed. As a result, it may be inferred that the reaction mechanism remains unaltered when varying base density in the polymer chain, and the apparent change in k_2 must be attributed to a change in apparent activation entropy $\Delta S_2^{\neq}$, including local concentrations (i.e. nearby the catalytic sites) of reactants involved in the rate determining step. Unfortunately, $\Delta H_2^{\neq}$ cannot be determined with an accuracy sufficient to avoid overlap of the error intervals of $\Delta S_2^{\neq}$. As a consequence, the changes in $\Delta S_2^{\neq}$, though plausible, cannot be evidenced conclusively.

Since K_m hardly alters when k_2 changes almost four fold, it seems that $k_2 < k_{-1}$ and no dramatic change in the apparent value of K_s is to be expected when increasing base density in the polymeric ligand.

In order to find a relation between a polymeric parameter and the observed catalytic activity, reaction rates have been measured at rather high thiol concentrations ($c_{-RSH} = 0.3$ M, i.e. $3\text{-}4.K_m$) for all copolymers. At these relatively high thiol concentrations, changes in reaction rate in fact reflect changes in k_2. Ethylenamine unit concentration was fixed at $c_{-N} = 1.5$ mM (except for polymer X) and pH was maintained at 7.8.

Fig. 4 (●) shows reaction rate as a function of α in the polymer chain. It is clearly shown that in the absence of basic amine groups ($\alpha = 0$) reaction rate is virtually zero and reaction rate does not increase linearly with α but instead levels off with increasing values of α. It might be suggested that the sequence distribution of vinylamine units in the copolymer is related to the observed pattern of catalytic activity. This was investigated by calculating the number average block length $\bar{\ell}$ (13) of ethylenamine sequences in the copolymers with various α, from the monomer feed and copolymer composition data given in Table 1, and the reactivity ratios of NVTBC and VAc in benzene. The latter were determined as described elsewhere (11) and found to

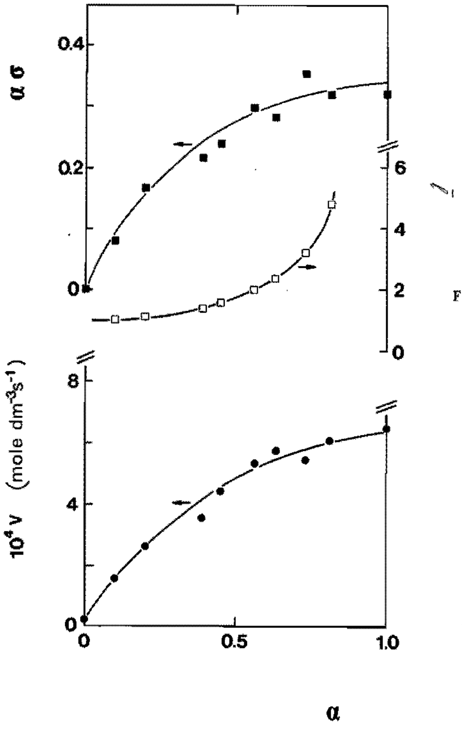


Figure 4: Various important parameters versus the mole fraction of ethylenamine units in the polymeric ligand, α.(.) Reaction rate, v (expressed in converted thiol $dm^{-3}s^{-1}$, calculated from the oxygen consumption assuming that 1 mole O_2 reacts with 4 moles of RSH to H_2O and RSSR) c_{RSH} = 0.28 M. Other concentrations and pH as given in Fig. 2.

(□) Number average block length, $\bar{\ell}$, of ethylenamine units in PVAm-co-VAl, calculated from the reactivity ratios of NVTBC and VAc and from the data in Table 1.

(■) Mole fraction of charged monomeric units, $\alpha.\sigma$, in PVAm-co-VAl derived from potentiometric titrations of the copolymers. c_{-N} = 0.01 M, pH = 7.8.

be r_{NVTBC} = 1.12 and r_{VAc} = 0.46 under the relevant conditions. In Fig. 4 (□) the results are shown, revealing that the course of the catalytic activity versus α does not coincide with the dependence of $\bar{\ell}$ on α.

Another important polymeric parameter may be the degree of charge on the polymer, since this is expected mainly to determine the local concentration of thiolate ions by electrostatic attraction between RS^- and the positively charged polymer chain.

The pH as a function of the degree of protonation, σ, of the amine groups in the copolymers has been determined by potentiometric titrations of all of the basic copolymer solutions (c_{-N} = 0.01 M) with HCl (0.03 N) at 22 ± 1°C in the absence of salt. The complete titrations were extended over a period of at least 20 minutes. The degree of of protonation, σ, was calculated as follows:

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

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

Fig. 5 shows the pH versus σ at four values of α (For the sake of clarity not all curves have been drawn). Evidently the intrinsic basicity of the amine groups increases with decreasing α, which must be attributed to a decreased nearest neighbour interaction when the amine groups find themselves more separated in copolymers with a high vinylalcohol content (14). In Fig. 4 (□) this degree of separation of

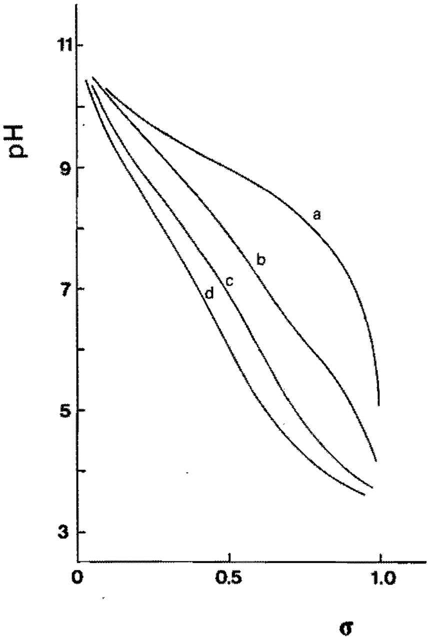


Figure 5: pH versus the mole fraction of charged amine groups, σ, for $\alpha = 0.20$ (a); $\alpha = 0.45$ (b); $\alpha = 0.81$ (c) and $\alpha = 1.00$ (d). Curves have been derived from potentiometric titrations with HCl (0.03 N); $c_{-N} = 0.01$ M.

amine groups is shown by the occurrence of the asymptote $\bar{\ell} = 1$ when α adopts low values. Nonetheless, $\bar{\ell}$ is only a qualitative measure for the degree of separation since amine group interactions are not exclusively of the nearest neighbour type.

It can easily be seen that the degree of charge on the copolymer chain (i.e. the mole fraction of charged monomeric units) at a certain pH value is represented by α.σ. In Fig. 4 (■) α.σ. is plotted versus α at pH = 7.8., being the pH during the catalytic activity measurements. The resemblance between the curves of α.σ. versus α, Fig. 4 (■), and v versus α, Fig. 4 (●) is striking. This conformity is confirmed by Fig. 6, where reaction rate is shown to vary linearly with polymer charge. The polymeric catalyst in reaction solution, the latter containing a large excess of thiol with respect to amine groups, may be regarded as a concatenation of positively charged rod-like segments, surrounded by a diffuse double layer of negatively charged counter ions, i.e. thiolate ions. Accordingly, the local thiolate ion concentration in the vicinity of the oxidation sites ($CoPc(SO_3)_4^{4-}$) is governed by the polymer charge.

In view of the observed linear increase of reaction rate with polymer charge it seems therefore that the thiol anion is involved in the rate determining step.

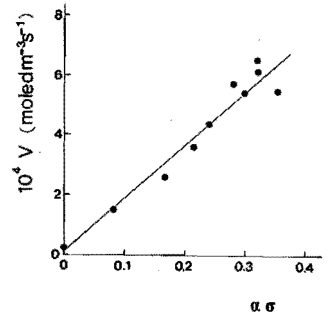


Figure 6: Reaction rate, v, versus the mole fraction of positively charged monomeric units in the copolymers, α.σ, derived from Fig. 4.

On the other hand the complexation of $CoPc(SO_3)_4^{4-}$ to the charged polymer chain may also depend on polymer charge. From ultrafiltration experiments with PVAm solutions containing $CoPc(NaSO_3)_4$ (Co/N = 1: 200) it appeared, however, that blue $CoPc(SO_3)_4^{4-}$ could not be rinsed out. This behaviour appeared to be independent of the pH in the range pH = 4-11 and as a consequence independent of the polymer charge. This in contrast with the polymer free $CoPc(NaSO_3)_4$ solutions, which passed the membrane easily.

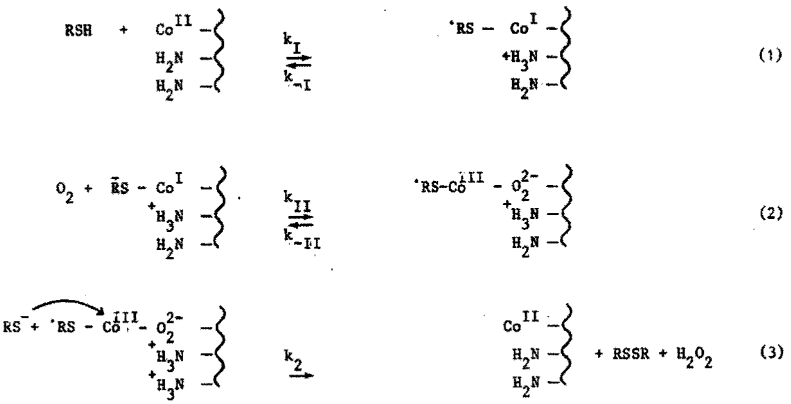
From these observations it may be inferred that due to the large excess of amine ligands with respect to Co as well as the high charge of the $CoPc(SO_3)_4^{4-}$ ion, practically all $CoPc(SO_3)_4^{4-}$ will be present in the polymer domain under the relevant conditions.

It is also not probable that the rate dependence on the ethylamine mole fraction in the polymeric ligand can be explained from axial coordination effects, since the $CoPc(NaSO_3)_4$ in monomeric 1,3 propanediamine solution appeared to be much less active than the polymer attached $CoPc(NaSO_3)_4$.

Another polymeric property, related with polymer charge is the polymer conformation. It may be assumed that the expansion of the polymer chain is enhanced by increasing chain charge. Conformation may affect catalytic activity, but neither transport limitations of reactants or products by coil diffusion nor a change of the reaction mechanism is to be expected in the light of the observed constancy of $\Delta H_2^{\neq}$ even at low α values.

According to the foregoing experimental observations a preliminary reaction scheme may be proposed as shown in Scheme 1 eq. 1-3. This scheme is consistent with the observed Michaelis-Menten kinetics in thiol and oxygen, although the rate limiting step (eq. 3 in scheme 1) is first order in local thiolate ion concentration. It may be assumed that at neutral pH this local concentration is not affected very much by the thiol concentration in the bulk and therefore Michaelis-Menten kinetics in thiol is still observed. Another interesting feature, following from the observed Michaelis-Menten kinetics with respect to

Scheme 1



Co = $CoPc(NaSO_3)_4$
$\}$ = polymer backbone
$k_I \cdot k_{II} = k_1$
$k_{-I} \cdot k_{-II} = k_{-1}$

thiol is that obviously not thiolate but thiol interacts mainly with the metal centre (eq. 1, scheme 1). This is not so unexpected since the electrostatic repulsion between the thiolate ion and the four fold negatively charged $CoPc(SO_3)_4^{4-}$ may hinder the approach of the metal centre by RS^-, although the negative charge of the $CoPc(SO_3)_4^{4-}$ will be shielded by the positive polymeric charge to some extent. Probably fast proton abstraction will be concomitant with or subsequent to complex formation. In this train of thought it can be understood that the nucleophilic attack by RS^- according to eq. 3 in scheme 1 will be rate determining.

Similar kinetic observations have been made by Nome and Fendler (15) in the investigation of the oxidation of 1-cysteine by Vit B_{12a}. They showed the equilibrium formation of a cysteine-Vit B_{12a} complex prior to the rate-limiting step and the rate constant k_2 appeared to increase linearly with cysteine concentration at fixed pH, while k_2 increased exponentially with increasing pH, clearly indicating that the rate determining step was first order in cysteinate ion.

The formation of H_2O_2 (eq. 3 in scheme 1) in the polymeric catalyst system at neutral pH has been shown earlier (16,8), although it has not been proven to occur stoichiometrically with the formation of RSSR, probably due to further reaction of H_2O_2 with thiol. Recently Jacobsen (17) unequivocally has shown that in the aquocobinamid (a Vit B_{12} derivative) catalyzed oxidation of various thiols H_2O_2 was formed stoichiometrically with RSSR.

Obviously, in the oxidation of thiols to disulfides the polymeric catalyst and Vit B_{12} have many kinetic features in common, which may be partially attributed to the similarities in environment of the metal centres in both catalysts (18). A study, further revealing the polymeric effects in the polymeric catalysis of thiols is in progress.

Conclusions

In this investigation dealing with the effect of base density in the polymeric ligand on the catalytic activity of a water soluble polymeric catalyst in the oxidation of thiols it has been shown that:

- there is no direct relation between base group block length and the intrinsic activity of the catalytic sites;
- the apparent rate determining constant k_2 varies linearly with the charge on the polymer chain, while K_m is not affected significantly;
- within the experimental error the activation enthalpy $\Delta H_2^{\neq}$ does not change with the amine content in the copolymer inferring that the reaction mechanism remains unaffected when varying base density within the polymeric ligand;
- it becomes plausible that the thiol anion is involved in the rate determining step (eq. 3, scheme 1) and that mainly RSH instead of RS^- is involved in the complex formation step (eq. 1, scheme 1);
- $CoPc(NaSO_3)_4$ attached to PVAm shows kinetical resemblance with Vit B_{12a} in the oxidation of thiols to disulfides.

Acknowledgements

The authors are indebted to Prof. L.A.A.E. Sluyterman, Prof. R. Prins and Dr. T.P.M. Beelen for stimulating discussions and for a critical reading of the manuscript for this paper.

References

(1) Gleim, W.K.T. and Urban, P., *U.S. Patent* 2,966,453; Dec. 27, 1960

(2) Urban, P., *U.S. Patent* 3,039,855; June 19, 1962

(3) Peel, J.L., *Biochem. J.* 88 (1963), 296

(4) Brouwer, W.M., Piet, P, and German, A.L., *Makromol. Chem.* 185 (1984), 363

(5) Brouwer, W.M., Piet, P. and German, A.L., *Polymer Commun.* 24 (1983), 216

(6) Schutten, J.H. and Zwart, J., *J. Mol. Catal.* 5 (1979), 109

(7) Rollman, L.D., *J. Am. Chem. Soc.* 97 (8) (1975), 2132

(8) Skorobogaty, A. and Smith, T.D., *J. Mol. Catal.* 16 (1982), 131

(9) Brouwer, W.M., Piet, P. and German, A.L., *J. Mol. Catal.* 22 (1984), 297

(10) Brouwer, W.M., Piet, P. and German, A.L., *Polym. Bull.* 8 (1982), 245

(11) Brouwer, W.M., Piet, P. and German, A.L., *J. Polym. Sci., Chem. Ed.* accepted for publication

(12) e.g. Cornish-Bowden, A., *Fundamentals of enzyme kinetics*, Butterworths London 1979

(13) Harwood, H.J. and Ritchey, W.M., *J. Polym. Sci. Pol. Lett. Ed.* 2 (1964), 601

(14) Katchalsky, A., Mazur, J. and Spitnik, P., *J. Polymer Sci.* 23 (1957), 513

(15) Nome, F. and Fendler, J.H., *J.C.S. Dalton* (1976), 1212

(16) Schutten, J.H. and Beelen, T.P.M., *J. Mol. Catal.* 10 (1980), 85

(17) Jacobsen, D.W., *Inorg. Chim. Acta* 79 (1983), 193

(18) Pratt, J.M., *Inorganic Chemistry of Vitamin* B_{12} Academic Press, London, New York 1972

Chapter VII

AUTOXIDATION OF THIOLS WITH COBALT(II) PHTHALOCYANINE TETRASODIUM SULFONATE ATTACHED TO POLY(VINYLAMINE).

5. Effect of surfactant and thiol variation.

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Summary

The autoxidation of various thiols, viz. 2-mercaptoethanol (ME), 3-mercapto-1,2-propanediol (MP), mercaptoacetic acid (MA) and dodecylmercaptan (DM) with cobalt(II)phthalocyanine-tetrasodium sulfonate (CoPc(NaSO$_3$*)*$_4$*) as a catalyst in the absence and presence of the basic poly(vinylamine) has been determined.*

Differences among the oxidation rates of the various thiols are discussed qualitatively in terms of pK$_{SH}$*, charge, water solubility and size of the substrates.*

The effect of anionic, nonionic and cationic surfactant on the oxidation rate of these thiols is investigated. In the absence of polymer the effect of various types of surfactant is small for the hydrophilic ME, MP and MA. However, for DM a micellar, catalytic effect *of cationic surfactant is observed, whereas anionic surfactant retards the reaction.*

When CoPc($NaSO_3$)$_4$ is used in the presence of poly(vinylamine) large differences are observed between the effects of various types of surfactant on the oxidation rate of ME. Nonionic surfactant does not affect the high reaction rate, whereas cationic and anionic surfactants appear to diminish the rate considerably, even at concentrations far below the critical micelle concentration. These effects are discussed in terms of interactions between the polymer catalyst and surfactant. Furthermore, similarities and differences between polymeric catalysis and micellar catalysis in thiol oxidation are shown.

Introduction

The oxidation of thiols to disulfides is an important process in oil sweetening and in biological systems.

Among the catalysts known for this autoxidation (1) cobaltphthalocyanines in alkali appeared to be very efficient (2). Attachment of the water soluble cobaltphthalocyanine-tetrasodium sulfonate (CoPc($NaSO_3$)$_4$, see Fig 1) to the basic poly(vinylamine) (PVAm) resulted in a 30-50 fold enhancement of the oxidation rate of 2-mercaptoethanol (ME) in water compared with the CoPc($NaSO_3$)$_4$/OH^- system(3).

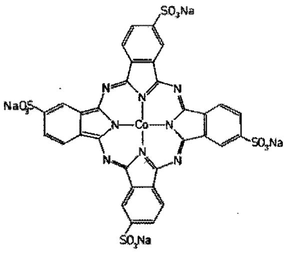


Figure 1: Chemical structure of CoPc($NaSO_3$)$_4$.

The promoting power of the PVAm could be ascribed to prevention of dimerization of the $CoPc(NaSO_3)_4$ catalyst on the one hand and enrichment of both the weakly acidic substrate and the $CoPc(NaSO_3)_4$ in the basic coils on the other hand. In several papers the effect of pH (4,5), molecular weight (6), polymer chain charge (7), ionic strength and substrate concentration (8) on reaction rate were reported. In all these investigations ME was used as substrate, serving as a model for other thiols. In the present paper we extend our investigation to some other thiols, i.e. 3-mercapto-1,2-propanediol (MP), mercaptoacetic acid (MA) and dodecylmercaptan (DM), the latter being sparingly soluble in water. The catalytic activity of both the conventional system ($CoPc(NaSO_3)_4/OH^-$) and the polymeric system ($CoPc$-$(NaSO_3)_4$/PVAm) in the conversion of these thiols is tested.

Furthermore, for both catalyst systems the effect of surfactants on the reaction rate is studied, since the conversion of smelly thiols (they can be scented in ppb) in surfactant containing reaction systems is an important issue in industry, that forms a challenge in particular for chemists working in the field of polymeric and micellar catalysis.

Some of the results concerning the effect of surfactants on polyelectrolyte catalysis may be valid for other polyelectrolyte catalyst systems, provided only electrostatic interactions are playing a role in the catalysis.

Experimental

Hexadecyltrimethylammoniumbromide (CTAB, Fluka, purum), sodiumdodecylsulfate (SDS, Fluka, purissimum) and poly(oxyethylene) 30-nonylphenol (Antarox CO-880, GAF, abbrev.: A-CO-880) were used as supplied.

Aqueous solutions of poly(vinylaminehydrochloride) (3% w/v; Polysciences Inc. Warrington U.S.A., $\bar{M}_n = 5\ 10^4$ g mole $^{-1}$, from viscosity experiments in water containing 0.01 N NaOH and 0.1 M NaCl (9)) were eluted through an Amberlite IRA 401 anion exchange column to remove the chloride. The PVAm solutions thus obtained were stored under nitrogen to prevent absorption of CO_2.

2-Mercaptoethanol and dodecylmercaptan were distilled; the 3-mercapto-1,2-propanediol and mercaptoacetic acid were used as supplied. Their purity (> 99%) was determined iodometrically prior to use. $CoPc(NaSO_3)_4$ (kindly provided by Dr. T.P.M. Beelen) had been synthesised by a method analogous to that of Weber and Busch (10) as described by Zwart et al. (11).

Initial reaction rates were determined by monitoring the oxygen consumption during the first minute of reaction. The measurements were carried out at 25°C as described previously (8).

The polymeric catalyst was prepared by mixing aqueous solutions of PVAm and $CoPc(NaSO_3)_4$ resulting in a polymer-organometal complex. The mixture was degassed twice and saturated with oxygen over a period of 20 min while stirring vigorously. The reaction was started by adding the substrate to the reaction vessel by means of a syringe.

In the micellar catalyst system the substrate was added after degassing and saturating the soap mixture with oxygen. The reaction was started 30 s hereafter by adding the $CoPc(NaSO_3)_4$ catalyst, thus obtaining best reproducibility.

The turbidity τ during turbidimetric titration of the polymeric catalyst with SDS in the presence of ME was obtained from transmission measurements: $\tau = (\log I_0/I)/b$ where I_0 and I are the intensities of the incident and transmitted light, respectively; and b is the optical path length of the cell used. A Carl Zeiss PMQ II spectrophotometer operating at 600 nm wavelength was used with 1 cm cells.

Viscosity measurements on filtered solutions were carried out at 25.0°C in a Hewlett Packard automatic solution viscometer of the Ubbelohde type. Measurements were conducted twenty minutes after addition of the thiol, since small time effects were observed.

Results and Discussion

The $CoPc(NaSO_3)_4/OH^-$ catalyst system

Effect of thiol variation

In several papers attention was paid to $CoPc(NaSO_3)_4$ in alkaline medium as a catalyst for the autoxidation of ME (3,11,12). The alkali was needed to enhance the dissociation of the weakly acidic thiol producing thiol anions, the latter generally being regarded as the reactive species.

In order to get insight into the differences among the reactivities of the various thiols, as well as to compare this catalyst system with those containing surfactant or polymer, the reaction rate at optimal pH was measured for ME, MP, MA and DM. The results are listed in Table 1, column 3-4. The negative logarithm of the dissociation constants of the sulfhydryl group of these thiols is listed in column 2.

Obviously the pH optimum increases with increasing pK_{SH}, which corroborates the assumption that the thiol anions play a dominant role in the reaction mechanism. Moreover, for the almost equally acidic substrates ME and MP practically equal pH optima and reaction rates are observed. The oxidation rate of MA is considerably lower and only slightly dependent on pH. Probably the pH dependent dissociation of the carboxylic acid group will contribute to this behaviour, since at lower pH the low thiol anion concentration and at higher pH the high ionic charge (-2) will hinder a fast autoxidation. A similar rate difference has been observed in the Vit B_{12} catalysed oxidation of ME and MA (16).

The oxidation rate of DM is low in comparison with the other thiols, probably due to lower water solubility and the large size of the substrate.

Table 1.

Thiol	pK_{SH}	$CoPc(NaSO_3)_4/OH^-$ [a] optimal pH	v without surfactant ($ml\ \mu mol^{-1} min^{-1}$)	$v_{r,SDS}$ [f] anion.	$v_{r,A\text{-}CO\text{-}880}$ [f] nonion.	$v_{r,CTAB}$ [f] cation.	$CoPc(NaSO_3)_4/PVAm$ [a] optimal pH	v_r [g]
2-mercaptoethanol (ME)	9.6 [b]	10	38	0.9	0.4	0.3	8	28
3-mercapto-1,2-propanediol (MP)	9.7 [c]	10	40	1.1	0.7	0.3	8	14
mercaptoacetic acid (MA)	10.4 [b]	10-11 [e]	21	0.8	0.8	0.8	9 [e]	5
dodecylmercaptan (DM)	11 [d]	13	4	0.0	0.6	23	-	0

[a] Duplicate measurements. Thiolconcentration: c_{RSH} = 0.19 M. Initial rates determined at pH optimum. v_r is expressed relative to the rate in the corresponding surfactant free $CoPc(NaSO_3)_4/OH^-$ system. Rate expressed in ml O_2/ μmol $CoPc(NaSO_3)_4$.min.

[b] ref. 13

[c] ref. 14

[d] estimation by ref. 15

[e] Reaction rate is only slightly dependent on the pH

[f] Surfactant concentrations: c_{surf} = 0.01 M. SDS= sodiumdodecylsulfate; A-CO-880 = poly(oxyethylene)30-nonylphenol; CTAB = cetyltrimethylammoniumbromide

[g] Polymer concentration (repeating units): c_{-N} = 1.5 10^{-3} M

Effect of surfactant

The effect of surfactant on the thiol oxidation was investigated at the pH optimum. An anionic, a nonionic and a cationic surfactant were used, viz. sodiumdodecylsulfate (SDS), poly(oxyethylene) 30-nonylphenol (A-CO-880) and hexadecyltrimethylammoniumbromide (CTAB) at 0.01 M. In Table 1, column 5-7 the relative rates v_r compared with the surfactant free system (column 4) are listed. For the water soluble ME, MP and MA mostly a slight decrement of reaction rate occurs irrespective of surfactant type in comparison with the corresponding surfactant free reaction systems.

However, for the DM containing system an anionic surfactant retards the reaction; a nonionic surfactant acts rather indifferently, whereas a cationic surfactant causes a large enhancement. The latter observations are indicative of the occurrence of a so-called micellar catalysis in the oxidation of DM. The micellar catalytic action was first explained by Hartley (17) using simple electrostatic considerations: anionic micelles will retard reaction rates involving anions, whereas cationic micelles will cause the opposite effect. However, since for the present thiols only a micellar effect is observed for the long chain thiol DM, it seems that here also other than electrostatic, i.e. hydrophobic interactions, are playing a role.

The influence of thiol and surfactant concentration as well as the effect of ionic additives on the oxidation rate of DM by micellar catalysis will be the subject of the next subsection.

Micellar catalysis in the oxidation of dodecylmercaptan

The effect of thiol concentration on the cationic micelle catalysed oxidation rate of DM appears to be of the saturation type and can be described with the Michaelis-Menten concept (18). This means that the rate determining reaction step takes place subsequent to substrate-catalyst complex formation:

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

Accordingly, linear plots of reciprocal initial reaction rate versus reciprocal substrate concentration are obtained (so-called Lineweaver-Burk plots):

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

where v = initial reaction rate, $[E_0]$ = the total catalyst concentration, E = unbound catalyst, P = product(s), [S] = initial substrate concentration and $K_m = \frac{k_{-1} + k_2}{k_1}$ with $K_s = \frac{k_1}{k_{-1}}$ ($\cong K_m^{-1}$ for $k_2 << k_{-1}$). In Fig. 2 the Lineweaver-Burk plot is shown for the DM oxidation and in Table 2 the turn-over number k_2 and the Michaelis constant K_m are listed. These values will be discussed in relation with those obtained in the system $CoPc(NaSO_3)_4$/PVAm in the next section.

In Fig. 3 the oxidation rate of DM is shown as a function of surfactant concentration. DM concentration is $4\ 10^{-2}$ M. Nonionic and anionic surfactant retard reaction rate. The rate enhancing effect of CTAB, in comparison with the surfactant free system $CoPc(NaSO_3)_4/OH^-$, exhibits a maximum at $c_{CTAB} = 4\ 10^{-3}$ M. A maximum often has been observed in micellar catalysis (19) and was explained by solubilization of reactive anions in cationic micelles, thus making them less active. In the present case it is possible that at this surfactant concentration part of the catalytically active anions, $CoPc(SO_3)_4^{4-}$, are solubilized in the cationic micelles, thus accounting for the decrease in rate at CTAB concentrations larger than $4\ 10^{-3}$ M (Fig. 3●).

The effect of ionic additives, viz NaCl, Na benzoate and SDS, on the oxidation rate of DM is shown in Fig. 4. CTAB concentration was $3.8\ 10^{-3}$ M. It is obvious that NaCl, a salt with a small anion, hardly affects the reaction rate. The more hydrophobic benzoate ion has more influence and the effect of SDS is dramatic. The latter substance

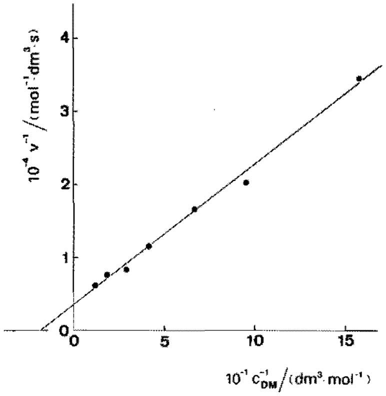


Figure 2: Lineweaver-Burk plot for the oxidation of DM, catalysed by cationic micelles (CTAB) at pH = 13.
$c_{CoPc(NaSO_3)_4} = 3.8\ 10^{-7}$ M and $c_{CTAB} = 3.8\ 10^{-3}$ M.

Table 2: Reaction constants in the oxidation of various thiols.

Thiol	pH	$\frac{10^{-2}k_2}{s^{-1}}$	$\frac{K_m}{\text{mole dm}^{-3}}$
2-mercaptoethanol (ME)[a]	7.4	31 ± 4	0.11 ± 0.01
3-mercapto-1,2-propanediol (MP)[a]	7.4	20 ± 3	0.05 ± 0.01
dodecylmercaptan (DM)[b]	13	3.9 ± 0.5	0.06 ± 0.01

[a] in polymeric system; $CoPc(NaSO_3)_4$/PVAm; $c_{CoPc(NaSO_3)_4} = 1.9\ 10^{-7}$M;
$c_{-N} = 1.5\ 10^{-3}$ M; T = 25.0°C

[b] in micellar system; $CoPc(NaSO_3)_4$/CTAB; $c_{CoPc(NaSO_3)_4} = 3.8\ 10^{-7}$ M;
$c_{CTAB} = 3.8\ 10^{-3}$ M; T = 25.0°C

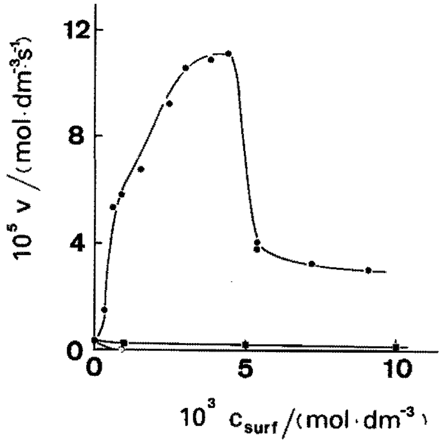


Figure 3: Effect of surfactant concentration on the initial oxidation rate, v, of DM (polymer absent). (●) CTAB, (○) SDS, (■) A-CO-880.
$c_{CoPc(NaSO_3)_4} = 3.8\ 10^{-7}$ M; $c_{DT} = 0.04$ M; pH = 13

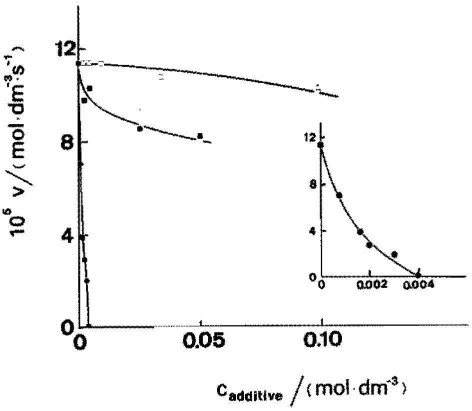


Figure 4: Effect of ionic additives on the initial oxidation rate of DM in a cationic micellar (CTAB) catalyst system at pH = 13. (□) NaCl, (■) Na benzoate, (●) SDS (also shown in the inset). Reaction conditions as given in Fig. 3; c_{CTAB} = 3.8 10^{-3} M.

may be assumed to be entirely mixed up with CTAB in the micelles. The inset in Fig. 4 shows that a complete loss of catalytic activity occurs at equally molar amounts of SDS and CTAB, viz. 3.8 10^{-3} M. The micelles may then be assumed to have zero net charge, and no catalytic activity is detected anymore.

From Fig. 4 it becomes clear that small, polar anions have little effect and large, hydrophobic anions have a large retarding effect on the micellar oxidation rate thus emphasizing that both hydrophobic and electrostatic effects play a role in micellar catalytic activity. The importance of electrostatic as well as hydrophobic interactions in micellar catalysis was earlier stressed by other investigators (19,20).

In contradistinction to the here observed small effect of NaCl on reaction rate in the micellar catalytical system, addition of NaCl in the polymeric catalytical system caused a considerable decrease in rate (8), emphasizing the importance of solely electrostatic interactions between substrate and catalyst in pure polyelectrolyte catalysis, where hydrophobic functionalities are absent.

The $CoPc(NaSO_3)_4$/PVAm catalyst system

Effect of thiol variation

Complexation of $CoPc(NaSO_3)_4$ with aqueous basic PVAm yields a catalyst exhibiting a much higher activity and considerably lower pH optimum than the polymer free $CoPc(NaSO_3)_4$ system (Table 1, column 8-9). The occurrence of an optimum at lower pH can be qualitatively explained by the high concentration of basic groups within the polymeric coils at intermediate pH values in the bulk. For ME the pH-dependency of the oxidation rate has been investigated and discussed in more detail previously (4).

It is striking that, using the polymeric catalyst system, different oxidation rates are found for ME and MP, whereas no significant difference was found in the case of the polymer free catalyst system (see Table 1). In previous investigations on polymeric catalytical systems it was shown that the Michaelis-Menten concept could be applied to describe the effect of ME concentration on reaction rate (6-8). This concept also appears to be applicable to the oxidation of MP with the polymeric catalyst. In Fig. 5 Lineweaver-Burk plots are shown for both ME (★) and MP (●) at pH = 7.4. In Table 2 the values of k_2 and K_m are listed. Different values of k_2 and K_m are observed for the substrates ME and MP. It seems that the complex formation constant K_s ($\cong K_m^{-1}$) is larger for MP, but the apparent intrinsic activity of the catalytic sites is lower. Since both substrates possess practically identical dissociation constants, the observed differences in k_2 and K_m must originate from

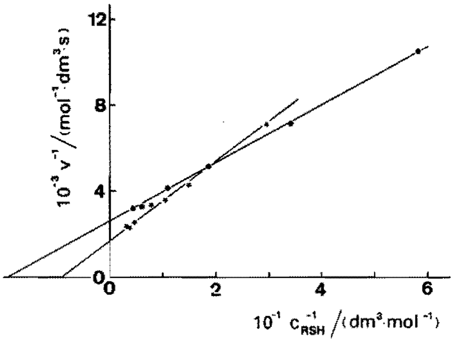


Figure 5: Lineweaver-Burk plots for the polymer catalysed oxidation of ME (✱) and MP (●) at pH = 7.4. $c_{CoPc(NaSO_3)_4} = 1.9\ 10^{-7}$ M; $c_{-N} = 1.5\ 10^{-3}$ M.

differences in size.

For DM, oxidized in the micellar catalyst system, the value of K_m is in the same range as for ME and MP in the polymeric catalytical system (see Table 2). It may therefore be inferred that the substrate-catalyst formation equilibrium is not affected very much by the environment of $CoPc(SO_3)_4^{4-}$ (whether polymeric or micellar).

The turn-over number k_2 found for DM in the micellar system is lower than k_2 observed for ME and MP in the polymeric catalyst system. These differences must be ascribed to differences in reactivity of the substrates, since also in the surfactant and polymer free catalyst system, $CoPc(NaSO_3)_4/OH^-$, the oxidation rate of DM was ten times lower than that of ME and MP.

MA shows rather low oxidation activity in the polymeric catalyst system, probably due to (1) competition between carboxylate and thiolate for a site on the catalyst and (2) electrostatic attraction between the negatively charged reaction product (due to the COO^- moieties) and the positively charged polymeric catalyst.

With DM as a substrate, no detectable catalytic activity is observed in the polymeric catalyst system. After stirring a PVAm solution containing DM, flocculation phenomena are observed. Probably DM, being rather hydrophobic, will be rejected by the water phase and interact relatively strongly within the polymeric region. Therefore, DM may not be converted under these conditions.

Effect of surfactant

In order to elucidate the effect of surfactants on the behaviour of polyelectrolyte catalysts in thiol oxidation, the oxidation rate of ME in the polymeric catalyst system was measured upon the addition of increasing amounts of SDS, A-CO-880 and CTAB.

In Fig. 6 (□) the initial oxidation rate of ME is plotted versus the logarithm of the SDS concentration. Polymer concentration (repeating units) is 1.5 10^{-3} M. Initially, reaction rate is slightly enhanced, a maximum occuring at SDS/-N = 0.2; adding more of the anionic surfactant

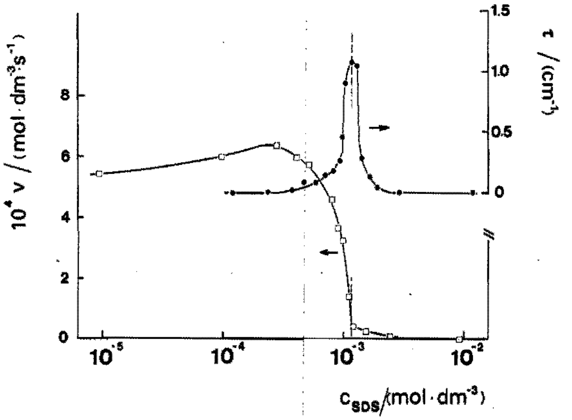
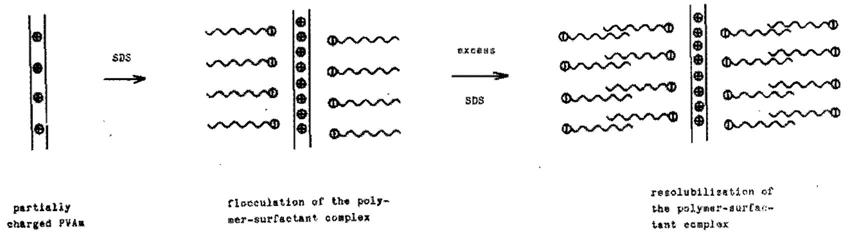


Figure 6: Effect of SDS concentration on the initial oxidation rate, v, of ME (polymer catalysed) (□) and on the turbidity, τ, of the reaction solution (●).
$c_{CoPc(NaSO_3)_4}$ = 1.9 10^{-7} M; c_{-N} = 1.5 10^{-3} M; c_{ME} = 0.19 M; pH = 7.6

causes a sharp decrease in reaction rate with an inflection point at SDS/-N = 0.8. Beyond this point reaction rate is very low. This tremendous effect of anionic surfactant on reaction rate occurs far below the critical micelle concentration (cmc) of SDS ($\text{cmc}_{\text{SDS}} = 8\ 10^{-3}$ M (21)). The decrease in rate is accompanied by the occurrence of turbidity of the reaction solution.

In separate experiments the polymeric catalyst solution in the presence of ME was titrated turbidimetrically with SDS (● in Fig. 6). A maximum in turbidity was observed at SDS/-N = 0.8. Addition of more SDS let to complete transparency of the solution, but catalytic activity, as shown in Fig. 6 (□), further decreased, though slowly. The increased turbidity is caused by flocculation (22) of the polymeric catalyst upon addition of SDS and can be explained by adsorption of SDS onto the positively charged polymer. Addition of excess SDS resolubilizes the polymer-surfactant complex (see Scheme 1) and the polymer solution becomes transparent again. Similar adsorption phenomena were observed for the interaction of ionic surfactants with oppositely charged polymers (23,24) or latices (25), although phase separation and resolubilization of the flocculated complexes were not always reported. Analogous to colloid titrations of cationic polymers with anionic ones

Scheme 1: Interaction of anionic SDS with positively charged PVAm.



(see for example (26)) the surfactant-polymer interactions cited above seem to occur stoichiometrically on the basis of charge.

Application of this concept to the present observations makes it plausible that (1) the catalyst is 80% charged (on the basis of repeating units), and (2) the inflection point in Fig. 6 (□), where the reaction rate becomes negligible, occurs at zero net charge of the polymer-surfactant complex. The latter result (2) is in complete agreement with our recent findings concerning the relation between the net polymer charge and reaction rate in copolymers of vinylamine and vinylalcohol (7). In addition, the hydrophobic mantle, formed by SDS (Scheme 1), will expel ionic substrate out of the polymer domain. The value found here for the polymer charge (80%) at pH = 7.6 is higher than that found earlier from potentiometric titrations, viz. 40% (6). Probably due to an effective screening by the dodecylsulfate counter-ions, PVAm behaves like a stronger polyelectrolyte and a higher degree of protonation is tolerated. This may also account for the initial slight increase of reaction rate at low SDS/-N ratios, where the rate enhancing electrostatic effect still dominates the rate retarding effect of the diffuse hydrophobic mantle. The same discrepancy was observed in poly(ethylenimine). From colloid and potentiometric titrations the polymer charge at pH = 6.5 was found to be 65% and 32%, respectively (26).

During the preparation of this paper, preliminary results were published by Visser et al. concerning the enhancement of the catalytic activity of imidazole containing polymers of isocyanides in the hydrolysis of 2,4-dinitrophenyl acetate upon the addition of cationic surfactant (27). At the relevant pH values the polymer was negatively charged. They found similar phenomena of precipitation and resolubilization of the polymer-surfactant complex as well as an increase of chain charge when adding the surfactant. The increase of reaction rate was partially attributed to the hydrophobic mantle enhancing the local (hydrophobic) substrate concentration in the vicinity of the catalytical polymeric functions.

From these observations it may be inferred that in polyelectrolyte-surfactant complexes the hydrophobic surfactant mantle may enhance or retard reaction rate, depending on the hydrophobicity of the substrate.

In view of these findings with SDS, adsorbing on the PVAm, it is conceivable that DM also strongly adsorbs on the polymer, which accounts for the observed flocculation of PVAm in the presence of DM, as mentioned in the preceding section.

In Fig. 7 the effect of the nonionic surfactant A-CO-880 on the oxidation rate of ME is shown, clearly indicating that catalytic activity is maintained. Obviously this charged polymeric catalyst is indifferent toward nonionic surfactant.

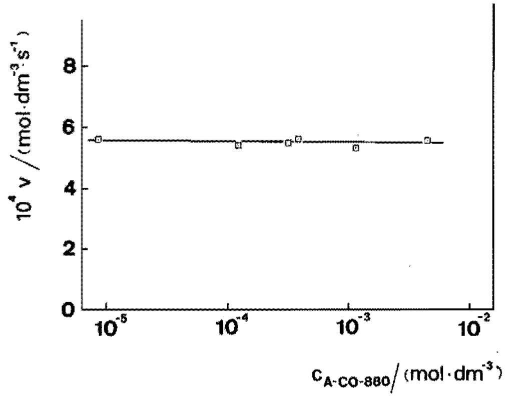


Figure 7: Effect of A-CO-880 concentration on the initial oxidation rate, v, of ME (polymer catalysed) (□). Other reaction conditions as in Fig. 6.

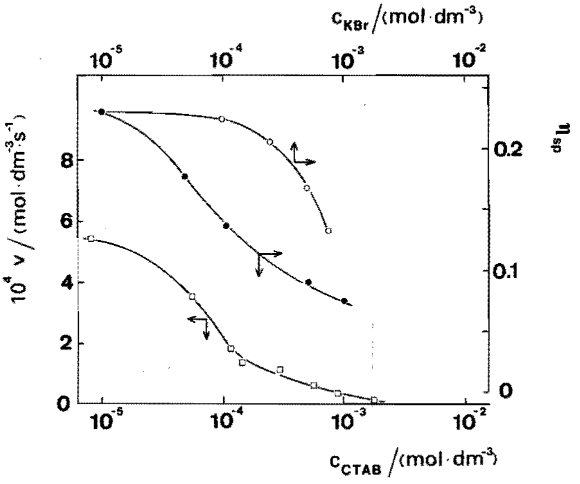


Figure 8: Effect of CTAB concentration on the initial oxidation rate, v, of ME (polymer catalysed) (□) and on the specific viscosity of the polymer containing reaction solution, η_{sp}, (●). As a reference the effect on η_{sp} of a simple 1:1 electrolyte (KBr) is shown (o). Other reaction conditions as in Fig. 6.

The effect of the cationic CTAB on the oxidation rate of ME is shown in Fig. 8 (□). Polymer concentration is 1.5 10^{-3} M. A decline in reaction rate is observed starting at very low concentrations of surfactant (c_{CTAB} << cmc_{CTAB} = 9 10^{-4} M (28)). Since the charges of surfactant and polymer have the same sign, direct polymer-surfactant interactions such as adsorption are less probable. However, monitoring the specific viscosity of the polymeric catalyst solution in the presence of CTAB (Fig. 8 (●)) and of KBr, as a reference (Fig. 8 (o)), clearly shows that in low concentrations CTAB has a marked effect on viscosity, whereas a simple 1:1 electrolyte (KBr) exhibits no drastic effect. Obviously, CTAB has a more charge shielding effect than KBr.

The great sensitivity of catalytic activity to small amounts of CTAB may be due to interactions directly with the $CoPc(SO_3)_4^{4-}$ moiety.

General Discussion

As follows from the observations above, thiols can be oxidized until scentlessness with high rates using polyelectrolyte or micellar catalysts. In order to select the proper catalyst system for the appropriate substrate, it may be useful to devide the thiol substrates into a polar and a hydrophobic group. Table 3 shows the catalytic activity expected for these types of substrate in the various catalyst systems. The hydrophobic substrates are best oxidized in a cationic micellar system, whereas the polar thiols are oxidized very rapidly with a positively charged polymeric catalyst (see also Scheme 2). In the latter catalyst system nonionic surfactant will not affect reaction rate, even when present in large concentrations. Other types of

Table 3: Schematic representation of the activity of various catalytical systems for polar and hydrophobic thiols.

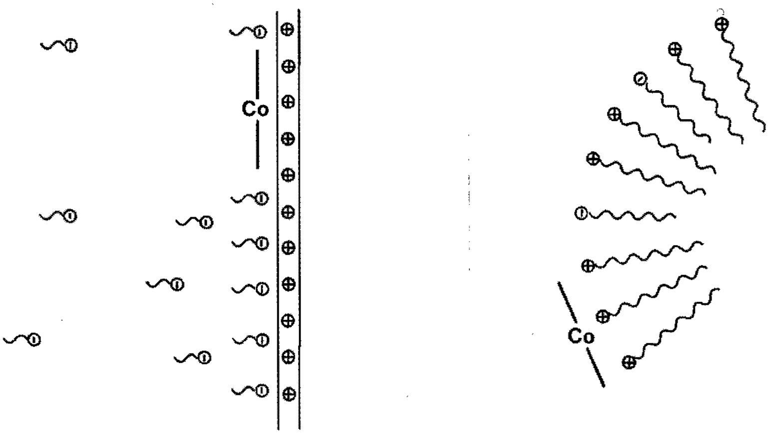
Thiol type	$CoPc(NaSO_3)_4/OH^-$				$CoPc(NaSO_3)_4/PVAm$			
	no surf	anion.	nonion.	cation.	no surf	anion.[a)]	nonion.[a)]	cation.[a)]
polar	0	0	0	0	+	-	+	-
hydrophobic	0	-	-	+	-	-	-	-

a) $c_{surf} < c_{polymer}$

+ large enhancement of reaction rate
0 no significant change of reaction rate
- retardation of reaction rate

in comparison with the surfactant and polymer free system $CoPc(NaSO_3)_4/OH^-$

Scheme 2: Schematic representation of thiols in polymeric and micellar catalysis.



(a)

ME in cationic polymeric catalysis (PVAm)

(b)

DM in cationic micellar catalysis (CTAB)

surfactant will diminish rate, aspecially at higher surfactant concentrations due to surfactant interactions with the polymer catalyst.

Several catalytic effects have been reported in this paper and though in most cases sound explanations for these observations could be presented, some of them are preliminary and require further investigations, viz.:

(1) The origin of the maximum in the plot of DM oxidation rate versus CTAB concentration (Fig. 3)

(2) The rate retarding effect of cationic surfactant on the cationic polymeric catalytic acitivity (Fig. 8). Does it originate from surfactant interaction with the $CoPc(SO_3)_4^{4-}$ moiety?

(3) The precise cause of relatively low DM conversion rate in polymer and micelle free, aqueous $CoPc(NaSO_3)_4$ solutions; which effect

dominates rate: the low water solubility, its large size or the high pK_a?

(4) The low oxidation rate of MA in the polymeric system. Is it mainly caused by (i) competition between the COO^- and RS^- moiety for coordination with the phthalocyanine, (ii) a slow product release from the polymeric domain, due to electrostatic attraction or by (iii) an enhancement of ionic strength due to the twofold negatively charged product?

Unfortunately, these points could not be elucidated as yet.

Till now, in thiol oxidation catalysis most attention has been paid to the (polymeric) catalysis of polar thiols. However, in many industrial systems the oxidation of more hydrophobic thiols is relevant and therefore more attention has to be paid to catalyst systems, capable of oxidizing these substrates. Micellar systems, where both electrostatic and hydrophobic interactions are playing a role, will be most promising for this purpose.

Conclusions

- Good water soluble thiols can be oxidized at high rates when $CoPc(NaSO_3)_4$ as a catalyst is used in the presence of the basic PVAm. For the sparingly water soluble, amphipolar DM no catalytic effect was observed in this catalyst system.
- The oxidation rate of DM is largely enhanced when $CoPc(NaSO_3)_4$ is used in alkaline medium in the presence of cationic micelles. Anionic micelles retard the reaction and nonionic micelles retard to a lesser extent. The oxidation rate of the good water soluble thiols is, however, only slightly affected by addition of surfactants.
- In the cationic polyelectrolyte catalysis of ME anionic surfactant retards the reaction rate due to adsorption at the polymer chain, thus decreasing the net charge on the polymer and increasing hydrophobicity in the neighbourhood of the catalytic sites. Nonionic

surfactant does not affect catalytic activity, while cationic surfactant diminishes reaction rate, possibly due to interaction with $CoPc(NaSO_3)_4$.

- In the present polymeric catalyst system electrostatic interactions dominate, whereas in the micellar catalyst system also hydrophobic interactions between substrate and micelle play an important role.

References

(1) A.H. Oswald and T.J. Wallace, in N. Kharasch and C.L. Meyers (eds), *The Chemistry of Organic Sulphur compounds*, Vol 2, Pergamon, London, 1966, ch. 8
(2) N.N. Kundo and N.P. Keier, *Russ. J. Phys. Chem.*, 42 (1968), 707
(3) J.H. Schutten and J. Zwart, *J. Mol. Catal.* 5 (1979), 109
(4) W.M. Brouwer, P. Piet and A.L. German, *Polym. Bull.*, 8 (1982), 245
(5) ibid , *Polym. Commun.*, 24 (1983), 216
(6) ibid , *Makromol. Chem.*, 185 (1984), 363
(7) ibid , *J. Mol. Catal.*, accepted
(8) ibid , *J. Mol. Catal.*, 22 (1984), 297
(9) C.J. Bloys van Treslong and C.F.H. Morra, *Recl. Trav. Chim. Pays-Bas* 94 (1975), 101
(10) J.H. Weber and P.H. Busch, *Inorg. Chem.*, 4 (1965), 469
(11) J. Zwart, H.C. van der Weide, N. Bröker, C. Rummens, G.C.A. Schuit and A.L. German, *J. Mol. Catal.*, 1 (1977-1978), 151
(12) A. Skorobogaty and T.D. Smith, *J. Mol. Catal.*, 16 (1982), 131
(13) J.P. Danehy and C.J. Noel, *J. Am. Chem. Soc.*, 82 (1960), 2511
(14) B. Sjöberg, *Ber. Dtsch. Chem. Ges.*, 75 (1942), 18
(15) I.M. Kolthoff and I.K. Miller, *J. Am. Chem. Soc.*, 73 (1951), 5118
(16) J.L. Peel, *Biochem. J.*, 88 (1963) 296
(17) G.S. Hartley, *Trans. Faraday Soc.*, 30 (1934), 444
(18) L. Michaelis and M.L. Menten, *Biochem. Z.*, 49 (1913), 333

(19) J.H. Fendler and E.J. Fendler: *Catalysis in Micellar and Macromolecular systems*, Academic Press 1975

(20) N. Ise in A. Rembaum and E. Sélégny (eds): *Polyelectrolytes and Their Applications*, Reidel, Dordrecht 1975, p. 71

(21) J.N. Philips and K.J. Mysels, *J. Phys. Chem.*, 59 (1955), 325

(22) I.D. Robb in E.H. Lucassen-Reynders (ed): *Anionic Surfactants: Physical Chemistry of Surfactant action*, surfactant science series Vol 11, Marcel Dekker, New York, Basel 1981, ch. 3

(23) J.W.A. van den Berg and A.J. Staverman, *Recl. Trav. Chim. Pays Bas*, 91 (1972), 1151

(24) E.D. Goddard and R.B. Hannan, *J. Colloid Interface Sci.*, 55 (1976), 73

(25) B.W. Greene, *J. Colloid Interface Sci.*, 43 (1973), 449

(26) D. Horn in E.J. Goethals (ed): *Polymeric Amines and Ammonium Salts*, Pergamon Press 1979, p. 333

(27) H.G.J. Visser, R.J.M. Nolte and W. Drenth, *Recl. Trav. Chim. Pays-Bas*, 102 (1983), 417

(28) P. Mukerjee and K.J. Mysels: *CMC of Aqueous Systems* National Standard Reference and Data System; Washington 1971

Chapter VIII

THE PROMOTING ROLE OF POLYCATIONS IN IN THE COBALT(II)PHTHALOCYANINE TETRASODIUM SULFONATE CATALYZED THIOL OXIDATION.

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Summary

The oxidation of 2-mercaptoethanol with polymer bound cobalt(II)-phthalocyanine catalysts was investigated. Poly(vinylamine) (PVAm), poly(ethylenimine) (PEI), poly(L-lysine) (PLL) and 2,4-, 2,6- and 2,10-ionenehydroxide were used as polymeric ligands. All polymeric ligands appeared to enhance reaction rate considerably as compared with their monomeric analogs and they exhibited similar behavior towards the effect of salt and pH. Reaction rate appeared to increase almost linearly with the linear charge density on the ionenes, which is consistent with recent findings for copolymers of vinylamine and vinylalcohol.

Mainly three parameters seem to provide the enhanced polycationic catalytic effect: a high linear charge density on the polymer, a large

amount of base groups in the polymer domain and a low ionic strength in the reaction solution. Moreover, comparison of the linear charge density, catalytic activity and activation parameters of the ionene catalysts with those obtained earlier for the vinylamine-vinylalcohol copolymers shows that the presence of hydrophilic side groups has a promoting effect on the oxidation of the hydrophilic thiol.

From catalyst reuse experiments it appeared that the polyamine catalysts (PVAm, PEI and PLL) have poor stability, but the ionene hydroxides can be reused many times, probably due to the chemical inertness of the quaternary ammonium groups in the ionenes.

Introduction

Cobalt(II)phthalocyanine is a well known catalyst for the oxidation of thiols to disulfides (1):

$$4\ RSH + O_2 \longrightarrow 2\ RSSR + 2\ H_2O$$

Attachment of the water soluble cobalt(II)phthalocyanine-tetrasodium sulfonate ($CoPc(NaSO_3)_4$, Fig. 1) to poly(vinylamine) (PVAm) caused a large rate enhancement compared with the monomeric analog 1,3 propanediamine (2). For this particular polymeric catalyst system the effect

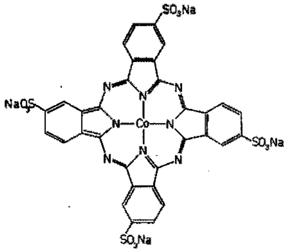


Fig. 1: Chemical structure of cobalt(II)phthalocyanine-tetrasodium sulfonate.

of pH (3), ionic strength, substrate concentration, oxygen pressure, temperature (4), and molecular weight of the polymeric ligand (2) on the oxidation rate of 2-mercaptoethanol (RSH) to 2,2 dithio-diethanol (RSSR) was investigated. The polymeric catalyst exhibited an enzyme-like behavior, e.g. Michaelis-Menten kinetics (Scheme 1) with respect to thiol and oxygen and a bell shaped pH dependence.

Scheme 1.

$$E + S + O_2 \rightleftarrows O_2\text{-}E\text{-}S \longrightarrow E + P$$

E stands for polymer bound $CoPc(NaSO_3)_4$; S for substrate (thiol) and P for products

The enhanced polymeric catalyst activity was partially attributed to prevention of dimerization of $CoPc(NaSO_3)_4$ by the basic polymer coils and to enrichment of these coils with thiol-anions, the reactive species. The polymer attachment of $CoPc(SO_3)_4^{4-}$ was attributed to coordinative and Coulombic interaction with the polymer (5,6).

From catalytic experiments using copolymers of vinylamine and vinylalcohol as polymeric ligands, it could be deduced that reaction rate depended linearly on the positive charge density on these ligands (7).

In order to check the more general validity of the concepts used to account for the catalytic behavior of the $CoPc(NaSO_3)_4$/PVAm catalyst (i.e. polymer charge density and basic groups as the most important parameters determining polymeric catalytic activity), the present investigation is focused at other types of basic polymers.

Branched poly(ethylenimine) (PEI), poly(L-lysine) (PLL) and poly(ammoniumhydroxides), also known as ionenes (8) have been introduced as ligands for $CoPc(NaSO_3)_4$. The results will be compared and discussed with those obtained from the $CoPc(NaSO_3)_4$/PVAm catalyst system. Finally, the performance of the various polymeric catalysts in reuse experiments is tested.

Experimental

Poly(vinylamine HCl) (Polysciences Inc.), poly(ethylenimine) (Fluka) and poly(L-lysine) (Polysciences Inc.) were used without further fractionation or purification. 2,4-, 2,6- and 2,10-ionenes were prepared in mixtures of equivolumes of dimethylformamide and methanol, containing stoichiometric amounts of tetramethylethanediamine and dibromo-butane, -hexane and -decane (3 mole dm^{-3}), respectively. The solutions were left undisturbed at roomtemperature for 2 weeks. The polymers were precipitated in acetone, filtered and purified by repeated dissolution in water and precipitation in acetone. The final products were dried at 50°C under vacuum. Carbon, nitrogen and hydrogen analysis indicated that the samples had the desired composition. As determination of the molecular weights of the ionenes by vapor pressure or membrane osmometry fails (9), the intrinsic viscosity values at 25°C in 0.4 M KBr were used to roughly estimate the molecular weights. For 2,4-, 2,6- and 2,10-ionenebromides, $[\eta]$ was 0.08, 0.08 and 0.06 dl g^{-1}, respectively. The molecular weights were estimated, using the Mark-Houwink constants for 3,4-ionenebromide (10) leading to $\bar{M}_{w\ 2,4-} = \bar{M}_{w\ 2,6-} = 10^4$ g $mole^{-1}$ and $\bar{M}_{w\ 2,10-} = 6\ 10^3$ g $mole^{-1}$.

All polymers were eluted through an Amberlite 401 IRA anionexchange column, in order to obtain the amine form of the polyamines or the hydroxide form of the ionenebromides. After elution, the polymers were kept under nitrogen. Polymer concentrations, expressed in the monomolar concentration of ionizable or ionized groups, were determined by potentiometric titration in 2 M NaCl, with the exception of PEI, where such method failed (11). In this case the concentration was used as provided by the purchaser.

Potentiometric titrations were carried out under nitrogen with HCl (titrisol ampoules, Merck). A Radiometer Copenhagen titration equipment fitted with a GK 2401 B pH electrode was used. Titration times were not shorter than 20 min in order to obtain reproducible results.

The degree of ionization (i.e. protonation) of the polyamines was calculated as follows:

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

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

For analysis of the H_2O_2 content iodometric titration was used as described previously (4).

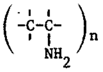
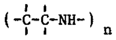
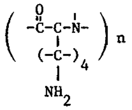
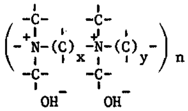
The polymeric catalysts were prepared by mixing aqueous solutions of $CoPc(NaSO_3)_4$ and polymer, resulting in a polymer attached organometal complex. Catalytic measurements were carried out in a Warburg apparatus, equipped with a mechanical stirrer and a digital oxygen flow meter. Initial rates were calculated from the oxygen consumption during the first minute of reaction. The pH was adjusted by adding HCl (0.01 M) or NaOH (0.3 M). A more detailed description was previously published (4).

Results and Discussion

Ionized state of the polymers

In Table 1 the chemical structures of the basic polymers used in the investigation have been summarized. During the catalytic experiments with the polymeric catalysts, the pH attained values between 7 and 8, due to the large excess of the weakly acidic thiol to basic polymer groups $(c_{RSH}/c_{-N} \approx 200)$. In this pH region all polymers used bear positive charges, as may appear from the titration plots shown in Fig. 2. For the polyamines (PEI, PVAm and PLL) the degree of ionization

Table 1: Polymers used in the investigation.

polymer	abbreviation	chemical structure	molecular weight g mole^{-1}	charge density parameter λ.[a]
poly(vinylamine)	PVAm	 $\left(-C-C(NH_2)-\right)_n$	$\bar{M}_n = 5.10^4$	0.99
poly(ethylenimine)	PEI	 $(-C-C-NH-)_n$	$\bar{M}_w = 5.10^4$	0.45
poly(L-lysine)	PLL	 $\left(-\overset{O}{\overset{\|}{C}}-C-N-\right)_n$, $(-C-)_4-NH_2$	-	1.42
poly(ammoniumhydroxide)	x,y-ionene	 $\left(-\overset{+}{N}(-C-)_2-(C)_x-\overset{+}{N}(-C-)_2-(C)_y-\right)_n\ OH^-\ OH^-$	$\bar{M}_w \approx 1.10^4$	2,4- :1.45 2,6- :1.15 2,10- :0.82

[a] at pH = 7.8

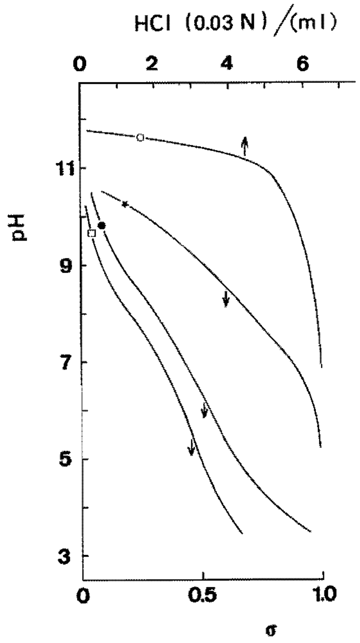


Fig. 2: Titration plots of basic polymers.
polyamines: pH vs. degree of protonation,
σ (lower scale) 2,4-ionenehydroxide: pH vs.
amount of added HCl (upper scale)
○ 2,4-ionenehydroxide, $c_{-N} = 6\ 10^{-3}$ M.
✱ poly(L-lysine), $c_{-N} = 10^{-3}$ M.
● poly(vinylamine), $c_{-N} = 10^{-2}$ M.
□ poly(ethylenimine), $c_{-N} = 1.6\ 10^{-2}$ M.

is dependent on the pH, in contradistinction to the ionene hydroxide polymers, which bear permanent charges. Titration of the latter reveals a strong base - strong acid titration behavior, as expected.

Polymer catalytic effects

In order to investigate the catalytical effects of these polymers on the oxidation of 2-mercaptoethanol, the oxidation rates of polymer attached $CoPc(NaSO_3)_4$ were compared with the oxidation rates of $CoPc(NaSO_3)_4$ in the presence of the monomeric analogs (see Table 2). From the results of these experiments rather important conclusions can be drawn:

(1) It is obvious that polymeric effects cause the observed rate enhancement. Moreover, the observation that all polycations presently

Table 2: Comparison of the catalytic activity of polymeric catalysts with their monomeric analogs at pH = 8, 298 K and c_{RSH} = 0.19 mole dm^{-3}.

polymer	10^4 reaction rate polymer bound CoPc-$(NaSO_3)_4$ mole . dm^{-3} . s^{-1}	monomeric analog	10^5 reaction rate $CoPc(NaSO_3)_4$ in the presence of monomeric analog mole . dm^{-3} . s^{-1}	k/k*
poly(vinylamine)	5.9	1,3 propanediamine	2.5	23
poly(L-lysine)	3.5	L-lysine	2.7	13
poly(ethylenimine)	1.9	dimethylamine	1.7	11
2,4-ionene	6.7	tetra-methylammoniumhydroxide	1.7	40

[a] k and k* are the reaction constants in the presence and absence of polymer, respectively. $k = v/c_{CoPc(NaSO_3)_4}$, where v is the reaction rate and c is concentration

investigated, exhibit large enhancements of the catalytic activity, provided that also basic functionalities are present, is indicative of a real polyelectrolyte catalysis, in which the long range interactions between substrate and polymer dominate. The precise polymer structure, viz. the location of charge (whether in or outside the main chain) or the kind of base group (amine or OH^-), seems to be of minor importance.

(2) Although axial coordination effects of the metal centre in $CoPc(NaSO_3)_4$ may occur in polyamines (5), these effects do not seem to play an important role in the mechanism of polymeric catalysis since the 2,4-ionene exhibits a very large rate enhancement, whereas it lacks any coordination ability. Moreover, the monomeric amines, possessing coordination abilities, nevertheless exhibit a comparatively low activity.

(3) Due to the absence of lone pair electrons in the ionenes, effects

of hydrogen bonding taking part in the substrate-polymer binding, can be ruled out here.

(4) All polymeric catalysts investigated exhibit a high apparent activity. Turnover numbers are in the range 1-4 . $10^3 s^{-1}$

Effect of salt

The effect of salt (NaCl) on the catalytic activity was investigated for the 2,4 ionene, PVAm and PEI (Fig. 3). An increase in ionic strength results in a decrease in reaction rate for all cations investigated. The result may indicate the importance of electrostatic effects occurring in the polymeric catalysis. The larger effect of salt on the activity of polycations of higher charge density corroborates this assumption. However, an increase in ionic strength might also cause a contraction of the polymer coils, eventually lowering the accessibility of the catalytic sites for the reactants. Although the effect of diffusional limitations did not reflect significantly in the overall activation energies (4) for the $CoPc(NaSO_3)_4$/PVAm catalyst, this effect cannot be entirely excluded.

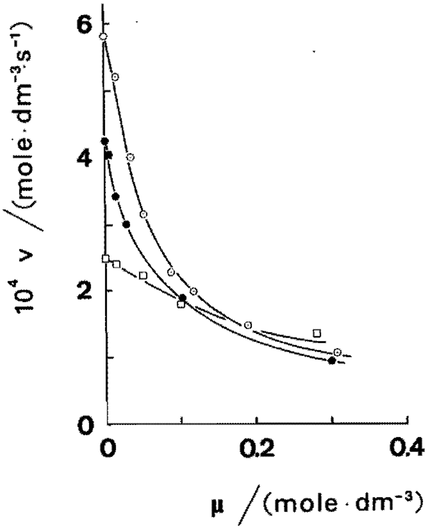


Fig. 3: Effect of ionic strength (NaCl) on the polymeric catalyst activity. $c_{CoPc(NaSO_3)_4} = 1.9\ 10^{-7}$ M, $c_{-N} = 10^{-3}$ M, $c_{RSH} = 0.19$ M.

○ 2,4-ionenehydroxide, pH = 7.5

● poly(vinylamine), pH = 7.2

□ poly(ethylenimine), pH = 7.0

Effect of polymer charge

In a recent paper (7), a linear increase in reaction rate with increasing polymer charge density was found when copolymers of vinylamine and vinylalcohol were used as polymeric ligands for $CoPc(NaSO_3)_4$. In order to check whether this behavior is a more general characteristic of other polycationic thiol oxidation catalysts as well, the effect of the charge density of the 2,4-, 2,6-, and 2,10-ionenes on the reaction rate was investigated. For the sake of comparison of the results with those previously obtained for the vinylamine-vinylalcohol copolymers (7), the dimensionless linear charge density parameter (λ) of the polycations was calculated, according to the rigid rod cell model for polyelectrolytes proposed by Katchalsky (12). The values of λ have been calculated from eq. 3 and some are listed in Table 1.

$$\lambda = \frac{\sigma\ e^2}{4\pi\ \varepsilon\ b\ kT} \qquad [3]$$

where e = proton charge, σ = degree of ionization of the polymer, $\sigma = 1$ for ionenes, $\sigma = 0.35$ for PVAm at pH = 7.8, see Fig. 2; ε = dielectric constant; b = average linear distance between ionizable (ionized) groups; kT = the Boltzmann term; all symbols should be expressed in SI units; in cgs units the factor 4π should be omitted.

In Fig. 4 the results are shown, revealing that also for the ionene polymers an almost linear relationship is observed between reaction rate and polymer charge density. However, the shift between the data obtained from the ionenes and those from the amine-alcohol copolymers in Fig. 4 indicates that at constant pH reaction rates are not solely determined by charge density. The observed shift may be explained by the difference in polarity of the chain segments between the charges on the main chain. The copolymers possess very

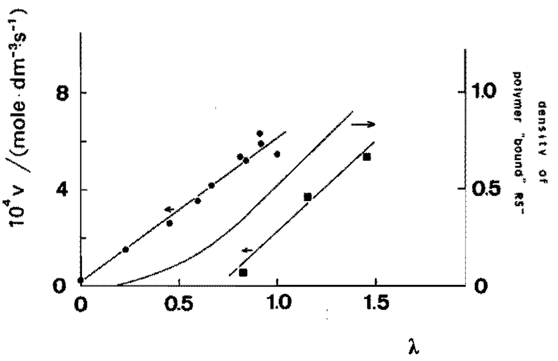


Fig. 4: Reaction rate v as a function of the linear charge density λ on the polycationic ligands. c_{RSH} = 0.3 M.

- ● copolymers of vinylamine and vinylalcohol, pH = 7.8, data obtained from ref. 7.
- ■ ionenes, pH = 7.4

On the right vertical axis the calculated polymer "bound" counterion density (RS^-) as a function of λ is shown. This was calculated with: $RS^-_{\text{"bound"}} = (1 - \phi_p).\lambda$, where ϕ_p is the osmotic coefficient; $1 - \phi_p$ reflects the mole fraction of polymer "bound" counterions either by condensation or by the effect of Debye-Hückel interactions on the uncondensed counterions (12).

hydrophilic chain segments (amine and alcohol residues), whereas the ionenes have hydrophobic alkyl segments. This may account for the observed minimal charge density of the ionenes required to exhibit a catalytic effect.

In Fig. 4 also the calculated polymer "bound" counterion (RS^-) density is plotted versus the charge density on the polymer (λ), using polyelectrolyte theories for salt free solutions (12). It reveals that the rate enhancement by polycations equipped with basic functionalities can be qualitatively explained from the enhanced local concentration of thiolanions * in the vicinity of the polymer attached oxidation sites ($CoPc(SO_3)_4^{4-}$) resulting in an enhanced collision frequency. However, desolvation effects of reactants and activated complex, generally observed in all kinds of systems in which a number of charges is confined to a small space *, should also be considered in order to account for the observations presented (13,14)**.

This proposed desolvation of the activated complex should be reflected by the values of the activation entropy. In Table 3 rate constants and activation parameters have been listed for some differently charged copolymers and for ionenes. The increase of $\Delta S^{\neq}_{298}$ observed for both polymer types when polymer charge density increases is consistent with both concepts accounting for the observed rate enhancement: enhanced local substrate concentration and increased desolvation of the activated complex by the high electrostatic potential of the macro-ions. However, for the amine-alcohol copolymers the increase in activation entropy is very moderate with respect to the ionenes, where $\Delta S^{\neq}_{298}$ is increased at the expense of a low activation enthalpy. Within the concept of dehydration of the activated complex, these differences in entropy increment may be explained from the increased hydrophobic effects occurring in the ionene polymers when charge density decreases and the alkyl segments get longer. In this line of thought it might be expected that the differences in dehydration of the activated complex showing up in the $\Delta S^{\neq}_{298}$ values, would be more pronounced for the ionenes than for the copolymers, the latter

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* In accord to these explanations we recently observed a cationic micellar catalytic effect for the oxidation of dodecanethiol (15).

** For various copolymers of vinylamine and vinylalcohol it was verified that $CoPc(SO_3)_4^{4-}$ was bound to these differently charged copolymers and hence a detachment of $CoPc(NaSO_3)_4$ could not account for the observations, shown in Fig. 4.

Table 3: Activation parameters for the oxidation of thiols in the presence of polycations at 298 K and pH = 7.8.

polymer	λ	k/k*	$\Delta G^{\neq}$ kJ mole^{-1}	$\Delta H^{\neq}$ kJ mole^{-1}	$\Delta S^{\neq}$ J mole^{-1}K^{-1}
PVAm-co-Al					
α = 0.20 [b]	0.51	9.5 [c]	56.9	36 ± 4 [a]	- 70 ± 10[a]
α = 0.39	0.67	12	56.3	36 [a]	- 68 [a]
α = 0.81	0.99	22	54.8	39 [a]	- 53 [a]
ionenes					
2,10-	0.82	4 [d]	61.1	11 ± 3	-168 ± 8
2,6-	1.15	28	56.3	25	-105
2,4-	1.45	40	55.4	38	- 58

[a] Data obtained from ref. 7.

[b] α = mole fraction of ethylenamine units in the copolymer

[c] $k^*_{1,3\ \text{propanediamine}} = 2\ 10^2\ s^{-1}$; values of k and k* obtained from extrapolation to $c_{RSH} = \infty$

[d] $k^*_{\text{tetramethylammonium OH}} = 83\ s^{-1}$, $c_{RSH} = 0.19$ mole dm^{-3}

being hydrophilic even at very low polymer charge density. In view of these considerations, the hydrophobic, activation entropy lowering effects of the ionenes should vanish when the alkyl chain segments become very short and the charge density becomes very high as in the 2,4-ionene. In fact, the similar activation entropy values found for the 2,4-ionene ($\Delta S^{\neq}_{298}$ = -58 J mole $^{-1}$K^{-1}) and the vinylamine-vinylalcohol copolymer (α = 0.81) ($\Delta S^{\neq}_{298}$ = -53 J mole $^{-1}$K^{-1}) corroborate this hypothesis.

Effect of pH

A change in the pH of the reaction medium will seriously affect important parameters establishing catalytic activity, e.g. the amount of basic groups in the polymer domain and thus the amount of thiolanions, the polymer charge (with the exception of the ionenes) and the ionic strength in the reaction medium. Also the polymer coil conformation will be affected.

In Fig. 5 the effect of pH on the catalytic activity of the various polymeric ligands is shown. More or less bell-shaped curves are found as often observed for enzymes (16), where both basic and acidic sites take part in the reaction. The importance of basic sites (and thus of RS^-) in the catalyzed oxidation of thiols is reflected by the increase of rate for pH > 4 in Fig. 5. All polymers exhibit an optimum and at higher pH the reaction rates are lower. For the polyamines this rate retarding effect is more drastic than for the 2,4-ionene. This can be explained by realizing that the polyamines loose their charge at higher pH (Fig. 2), whereas the ionene keeps it charge, thus favoring a higher catalytic activity (as can be deduced from Fig. 4).

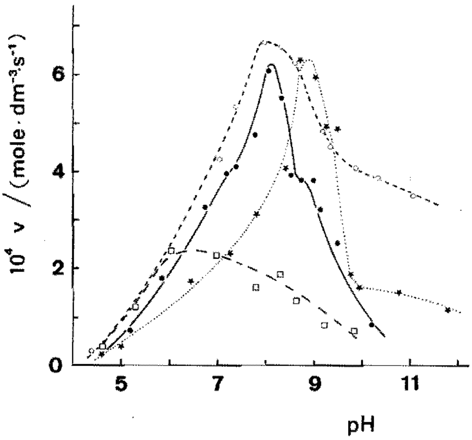

Fig. 5: Dependence of the catalytic activity of various polycationic catalysts on pH. $c_{CoPc(NaSO_3)_4} = 1.9\ 10^{-7}$ M, $c_{RSH} = 0.19$ M.

○ 2,4-ionenehydroxide, $c_{-N} = 10^{-3}$ M

✱ poly(L-lysine), $c_{-N} = 10^{-4}$ M

● poly(vinylamine), $c_{-N} = 10^{-3}$ M

□ poly(ethylenimine), $c_{-N} = 10^{-3}$ M

The increase in hydroxyl ion concentration at higher pH, will cause a rate retardation for all polycations, as could be expected from Fig. 3, although the bulk RS^- concentration increases, due to dissociation of the weakly acid RSH. The pH optima, observed for the polyamines in Fig. 5, are in the order PEI < PVAm < PLL. This can be explained by the basicity of the amine groups, which also increases in the order PEI < PVAm < PLL, as shown in Fig. 2. In other words, at pH = 6, which is the pH optimum for PEI, the polymer environment of PLL would be to acidic to exhibit optimal activity and therefore the pH optimum for the latter is shifted to higher pH.

Reuse of catalysts

Other workers in our institute found earlier that the $CoPc(NaSO_3)_4$/PVAm catalyst stability was poor $^{(17)}$. This deactivation was related to the formation of H_2O_2 during reaction. Apart from the well known destruction of $CoPc(NaSO_3)_4$ by H_2O_2 they showed that during reaction small amounts of sulfur containing oxo-acids were formed, which caused protonation of the amine groups of PVAm thus causing a drift in the pH from the optimal value. In our catalyst reuse tests the latter effect was ruled out by adjusting the pH (pH = 8) before each run, thus titrating the small amounts of acids formed.

In Fig. 6 the catalystperformance during successive runs is shown, revealing that the polyamines still exhibit poor stability under the present conditions, whereas the 2,4-ionene shows a much better performance. Nevertheless, the oxygen mass balance (Table 4) shows that in both the PVAm and the ionene system H_2O_2 and sulfur containing oxo-acids are formed. This makes it plausible that during oxidation the polymeric amine groups are chemically attacked, whereas the quaternary ammonium groups of the ionenes are not. Indeed there is evidence* that the main

* Mixtures of PVAm and RSSR yield a thiol odour soon after mixing, moreover they discolor an iodine solution after acidifying, whereas a blank of RSSR in water does not.

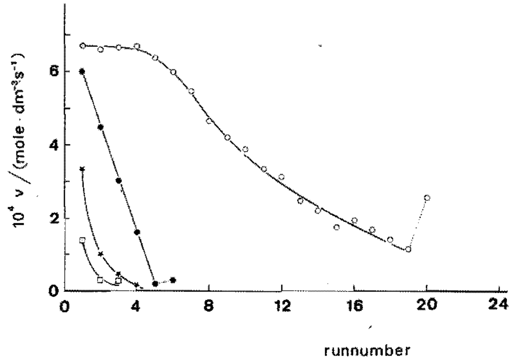

Fig. 6: Stability of polymeric thiol oxidation catalysts in reuse experiments. $c_{-N} = 10^{-3}$ M, $c_{CoPc(NaSO_3)_4} = 1.9\ 10^{-7}$ M. pH = 8. After cessation of oxygen consumption, fresh thiol (0.19 M) was added and the pH was adjusted to 8.
O 2,4-ionenehydroxide, ✱ poly(L-lysine), ● poly(vinylamine), □ poly(ethylenimine). ....: fresh portion of $CoPc(NaSO_3)_4$ is added ($1.9\ 10^{-7}$ M).

Table 4: Oxygen mass balance in the polymer catalysed oxidation of 2-mercaptoethanol.

process	$CoPc(NaSO_3)_4$/PVAm [a], mole fraction of O_2 (%) [c]		$CoPc(NaSO_3)_4$/2,4-ionene [b], mole fraction of O_2 (%) [c]	
RSH conversion to RSSR [d]		87.3 ± 1.8 [g]		84.5 ± 1.2 [g]
H_2O_2 production [e]		12.3 ± 0.6		15.4 ± 1.6
sulfur containing oxo-acids [f]		< 1.1		< 1.2
	total calc.	100.7 ± 1.8	total calc.	101.1 ± 2.0
	total meas.	100.0	total meas.	100.0

[a] pH = 7.4, data obtained from ref. 4.

[b] pH = 7.4

[c] Data after complete conversion of RSH

[d] Obtained from the stoichiometry of the reaction: $4RSH + O_2 \rightarrow 2RSSR + 2H_2O$, the weight of RSH was used.

[e] Obtained from the stoichiometry of the reaction: $O_2 + 2H_2O \rightarrow 2H_2O_2$, the amount of H_2O_2 was determined by iodometric titration.

[f] Maximum value obtained from the stoichiometry of the reaction: $2RSSR + 5O_2 + 2H_2O \rightarrow 4RSO_3H$, the amount of acids formed during reaction were determined by titration with NaOH till constant pH.

[g] Average of four experiments; errors within 95% confidence limit.

deactivation of the polyamine catalysts is caused by nucleophilic cleavage of the reaction product, RSSR, by primary or secondary amines yielding sulfenamides and thiol (18,19), thus destroying the charge and base functionalities of the polyamines. The ionenes, where nucleophilic groups are absent, will be inert to this poisoning. Therefore, in this latter case the main cause of deactivation will be the destruction of $CoPc(NaSO_3)_4$ by H_2O_2. This is confirmed by the observation that addition of fresh $CoPc(NaSO_3)_4$ solution to the PVAm catalyst after 4 runs does not increase catalytic activity significantly (Fig. 6), whereas addition of the same to the 2,4-ionene catalyst, results in a considerable recovery of catalytic activity, even after 19 runs. The significance of this observation is even greater when considering the accumulation of dialcohol (RSSR) in the reaction mixture (up to 25 v/v %) which in itself should be expected to lower the rate considerably (20).

Conclusions

- Cationic, basic polymers exhibit a large, rate enhancing effect on the $CoPc(NaSO_3)_4$ catalyzed oxidation of 2-mercaptoethanol, as compared with their monomeric analogs.
- Electrostatic effects play a dominant role in the catalysis; reaction rate varies linearly with the linear charge density on the polycation, and salt has a rate retarding effect.

  Hydrophilic side groups of the polymers have a promoting effect. An increased local concentration of thiolanions in the vicinity of the oxidation sites and dehydration effects of the activated complex account for the observed rate constants and activation parameters.
- Although axial coordination of the $CoPc(NaSO_3)_4$ by the polymeric ligand moiety may occur (e.g. in PVAm) it becomes improbable that

this accounts for the polymeric catalytic effect since the polycation 2,4-ionene, which has no coordination abilities toward $CoPc(NaSO_3)_4$, also exhibits a very pronounced enhancement of reaction rate.

- $CoPc(NaSO_3)_4$ attached to polycations, equipped with quaternary ammonium groups exhibits a very improved catalyst stability in reuse experiments as compared with polyamines.

References

(1) N.N. Kundo and N.P. Keier, *Russ. J. Phys. Chem.*, 42 (1968), 707

(2) W.M. Brouwer, P. Piet and A.L. German, *Makromol. Chem.* 185 (1984), 363

(3) W.M. Brouwer, P. Piet and A.L. German, *Polym. Bull.* 8 (1982), 245

(4) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.* 22 (1984), 297

(5) J.H. Schutten and J. Zwart, *J. Mol. Catal.* 5 (1979), 109

(6) W.M. Brouwer, P. Piet and A.L. German, *Polymer Commun.* 24 (1983), 21

(7) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.*, accepted for publication

(8) A. Rembaum, W. Baumgartner and E. Eisenberg, *J. Polym. Sci. Lett. E.* 6 (1968), 159

(9) E. Bortel, A. Kochanowski, W. Gozdechi and H. Koztowska, *Makromol. Chem.* 182 (1981), 3099

(10) H. Noguchi and A. Rembaum, *Macromolecules*, 5 (1972), 261

(11) C.J. Bloys van Treslong and A.J. Staverman, *Recl. Trav. Chim. Pays-Bas*, 93 (1974), 171

(12) A. Katchalsky, *Pure Appl. Chem.*, 26 (1971), 327

(13) N. Ise in A. Rembaum and E. Sélégny (eds): *Polyelectrolytes and their Applications*, D. Reidel Dordrecht, The Netherlands 1975, p. 71

(14) N. Ise, T. Okubo and S. Kunugi, *Acc. Chem. Res.*, 15 (1982), 171

(15) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.*, accepted for publication

(16) Ch. Tanford, *Physical Chemistry of Macromolecules*, New York, John Wiley, 1961

(17) J.H. Schutten and T.P.M. Beelen, *J. Mol. Catal.*, 10 (1981), 85

(18) H. Al-Rawi, K.A. Stacey, R.H. Weatherhead and A. Williams, *J.C.S. Perkin II*, (1978), 663

(19) R.H. Weatherhead, K.A. Stacey and A. Williams, *J.C.S. Perkin II* (1978),800

(20) J.H. Schutten, *Ph.D. thesis*, University of Technology, Eindhoven, The Netherlands, 1981

Chapter IX

AUTOXIDATION OF THIOLS WITH COBALT(II) PHTHALOCYANINE TETRASODIUM SULFONATE ATTACHED TO POLY(VINYLAMINE).

6. Immobilized catalysts by cross-linking of poly(vinylamine).

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Summary

Poly(vinylamine), being both carrier and promotor of the thiol oxidation catalyst cobalt(II)phthalocyanine-tetrasodium sulfonate ($CoPc(NaSO_3)_4$)*, was cross-linked with* α,α'*-dichloro-p-xylene, thus yielding porous hydrophilic networks.*

The effects of experimental parameters such as stirring speed, particle size, degree of cross-linking, distribution of catalytic sites ($CoPc(NaSO_3)_4$) *in the catalyst particles, pH, temperature, and thiol concentration were investigated.*

Reaction rates observed for the immobilized catalyst systems, appeared to be 4-30 times lower as compared with the water soluble *polymeric catalyst system, but still higher than the polymer free* $CoPc(NaSO_3)_4$ *catalyst.*

At a stirring speed around 3.10^3 *rpm not mass transfer from the bulk to the catalyst particles but intra-particle diffusion limits reaction rate. Accordingly, an uncross-linked polymeric catalyst anchored to silica, with catalytic sites situated close to the particle surface, exhibited comparatively high activity, i.e. only four times lower than the soluble polymeric catalyst.*

In addition, the heterogeneous catalyst systems showed resemblance in kinetic behavior with the soluble polymeric thiol oxidation catalyst.

Introduction

Immobilization of active soluble macromolecular catalysts is an important topic in the field of polymeric catalysis, as it offers the possibility of easy separation of the catalyst from the reaction products. Many reviews on heterogeneous polymer supported catalysis have been published (1-4).

In general the apparent catalytic activity diminished tremendously after immobilization. In many cases this decrease in rate was ascribed to the occurrence of a rate limitation by matrix diffusion or to specific effects of the carrier itself, e.g. steric hindrance, microenvironmental effects etc.

In this paper the effect of immobilization of the very active polymeric thiol oxidation catalyst cobalt(II)phthalocyanine-tetrasodium sulfonate ($CoPc(NaSO_3)_4$, Fig. 1), bound to poly(vinylamine) (PVAm), has been examined for its catalytic activity. Immobilization was achieved by cross-linking the functional polymeric promotor, PVAm, thus serving as both insoluble support and catalyst promotor. When immobilizing in this manner, specific rate retarding effects originating from a "foreign" carrier surface were thought to be reduced or absent.

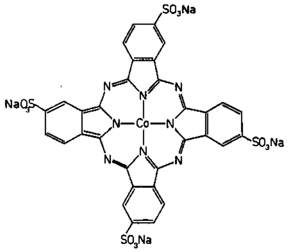


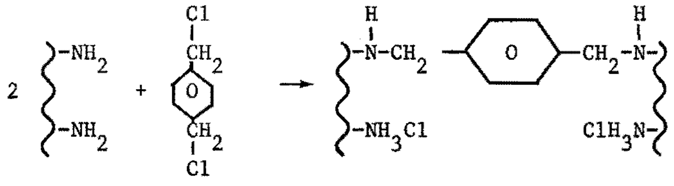
Fig. 1: Chemical structure of $CoPc(NaSO_3)_4$.

The effects of several experimental parameters on reaction rate have been investigated and from these results conditions have been formulated to obtain optimal activity of immobilized thiol oxidation catalysts.

Experimental

Cross-linking of poly(vinylamine)

All reagents were obtained commercially and used as supplied. Cross-link reactions of poly(vinylamine) (PVAmHCl, Polysciences; $\bar{M}_n = 5\ 10^4$ g mole^{-1}) and α,α'-dichloro-p-xylene (Fluka) were carried out in a 1:1 v/v mixture of methanol and water at 60°C during 5 h (see eq. 1). Polymer concentration (repeating units) was 1 mole kg^{-1}, reaction volume 8 ml.



[1]

I II

The crude resin so obtained was washed with 100 ml $NaOH_{aq}$ (5.10^{-3} M) and a large excess of distilled water, in order to remove chloride and caustic, respectively. Hereafter, the highly swollen resin was washed with acetone, pulverized and dried at 40°C at 10 Pa. The degree of cross-linking was in the range 1-20%, as determined by potentiometric titration.

Swelling behavior

The degree of swelling of the resin was determined after equilibration of the resin particles with distilled water. The samples were isolated by filtration under suction, until separation of water had ceased. Immediately afterwards, the weight of the highly swollen samples was determined.

Titration experiments

The basicity of the amine groups was determined by potentiometric titration of the dried resins with HCl (0.01 M) in 2 M NaCl. A PHM 62 pH meter (Radiometer Copenhagen) fitted with a GK 2401 B electrode was used. In order to prevent absorption of atmospheric CO_2, the titration vessel was carefully kept under a stream of nitrogen. The titrant was added in small portions (1 ml) and the pH was measured 25 min after each addition, when constant pH levels were attained.

Degree of cross-linking

The degree of cross-linking (DC) is defined as the molar ratio of cross-linker (c) and polymeric repeating units (p) *:

$$DC = \frac{c}{p} \cdot 100 \ (\%) \qquad [2]$$

For the experimental determination of the degree of cross-linking, potentiometric titrations with 0.1 M HCl on freshly prepared, crude resins were performed directly in the reaction vessel.

Anchorage of poly(vinylamine) to silica

Macroporous silica (Merckogel 1000) was used; particle size: 63-125 μm; specific surface by BET absorption: 17.3 m^2/g; average pore radius: 55nm.
The functional silane, γ-glycidoxy-n-propyl trimethoxy-silane (Union Carbide Silane A-187) was kindly supplied by mr. A. Graal, Contivema B.V.

At first the silica was treated with the functional silane in water at room temperature for 6 h (silane/silica = 1:20 w/w). Unreacted silane was removed by washing with water and acetone successively. One gram of pretreated silica was added to 4.5 mmol of aqueous PVAm. After standing for 24 h at room temperature, the particles were washed thoroughly with water and acetone, and dried at reduced pressure (10 Pa). Elemental analysis of the PVAm coated silica: 0.21% N; 0.63% C, which means that the ratio of polymer repeating units: silane = 4:1.
The $CoPc(NaSO_3)_4$ solution was added to the PVAm coated silica particles in the reaction vessel just before the kinetic measurements.

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* If all amine groups of I are cross-linked by II, the percentage of cross-linking is 50.

Catalyst preparation

Active thiol oxidation catalysts could be obtained by adding a very dilute blue solution of $CoPc(NaSO_3)_4$ to the polymeric functional carriers, causing the latter to take on a deep blue color. The bonding of $CoPc(SO_3)_4^{4-}$ to the polymer has been studied earlier and appeared to be caused by Coulombic and coordinative interaction (5).

In the case of cross-linked PVAm particles, two types of catalysts were used. Type A was obtained by adding the $CoPc(NaSO_3)_4$ solution *after* cross-linking of PVAm; in the preparation of type B, $CoPc(NaSO_3)_4$ was added to PVAm *before* the cross-linking took place. It is expected that the former procedure (Type A) leads to the occurrence of $CoPc(NaSO_3)_4$ sites on the particle surface, whereas the latter procedure (Type B) yields a homogeneous distribution of $CoPc(NaSO_3)_4$ sites within the catalyst particles.

$CoPc(NaSO_3)_4$ appeared to be tightly bound and could not be rinsed out. The ratio Co/N in the resins was in the range 0.001-0.002.

Catalytic activity measurements

Catalytic measurements were carried out in a double-walled thermostated Warburg apparatus, equipped with an all-glass mechanical stirrer (maximum speed 4000 rpm). Initial reaction rates were determined by measuring the oxygen uptake during the first minute of reaction. Rates were expressed either in ml O_2/µmol Co, min or in mole RSH/dm^3,s, in the latter case stoichiometry was assumed according to the reaction:

$$4\ RSH + O_2 \longrightarrow 2\ RSSR + 2\ H_2O \qquad [3]$$

Unless otherwise stated, the initial thiol concentration was 0.19 M and the temperature 25°C. Oxygen pressure was 0.1 MPa. The pH was adjusted with NaOH (1 M) or HCl (0.1 M). Measurements were carried out as described elsewhere in detail (6).

Results and Discussion

Catalyst preparation

In order to get insight into the effectiveness of the cross-linking reaction, potentiometric titration experiments with HCl were performed. Under a few assumptions the (experimental) degree of cross-linking (DC) could be obtained from these data. From the molar amount of HCl (t), required to reach the equivalence point and the molar amount of polymer repeating units, (p), the DC was calculated with eq. 4:

$$DC = \frac{p - t}{4p} \cdot 100\ (\%) \qquad [4]$$

Here the following assumptions were made:
(1) only primary amines can be titrated, as the basicity of the secondary amine groups, formed in the cross-link reaction (eq. 1) will be strongly reduced due to the electron withdrawing character of the aromatic moiety of the cross-linker $^{(7,8)}$, and (2) no further reaction of secondary amine groups to tertiary or quaternary amines is taking place. Thus, addition of c moles of cross-linker will cause a decrease of 4c of titratible primary amine groups according to eq. 1. In Table 1 the titration results and the theoretical and observed DC, calculated according to eq. 2 and 4, respectively, are shown. The DC values obtained from the titration experiments are in very good agreement with the theoretical values, which indicates that the cross-link reaction proceeds quantitatively within 5 h and justifies the assumptions made in the calculation of the experimental DC according to eq. 4

Table 1: Comparison of theoretical and observed degree of cross-linking.

$\frac{10^4\ c}{\text{mole}}$	$\frac{10^3\ p}{\text{mole}}$	$\frac{10^3\ t}{\text{mole}}$	theoretical degree of cross-linking [a]	observed degree of cross-linking [b]
0.234	1.97	1.88	1.2	1.1 ± 0.2 [c]
1.24	1.81	1.35	6.8	6.4 ± 0.4
2.66	2.52	1.51	10.5	10.0 ± 1.0

[a] According to equation 2.

[b] According to equation 4.

[c] Error interval based on the uncertainty in the determination of the equivalence point.

Basicity of amine groups in cross-linked resins

In Fig. 2 the titration diagrams (pH vs. the degree of protonation of the titratible groups) are shown of a monomeric amine: 1,3 propanediamine (1,3 PDA), poly(vinylamine) (PVAm) and cross-linked PVAm (DC: 2.5, 10 and 20%). From the figure it appears that the basicity of the amine groups is reduced in PVAm and even more in cross-linked PVAm, with respect to the monomeric analog 1,3 PDA. This effect may be explained by taking into account neighbour interactions between adjacent amine groups, causing a lower, pH dependent, basicity of the amine groups (9). The electron withdrawing properties of the cross-linker will contribute to this lower basicity level as well. A similar decrease of basicity as the DC of the networks increases was observed by Bolto et al. for poly(diallylamine) networks (8).

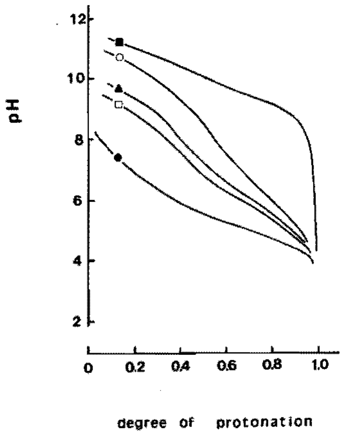


Fig. 2: Titration plots (pH versus degree of protonation of titratible base groups) of polyamines in 2 M NaCl.
■ 1,3-propanediamine; o PVAm; cross-linked PVAm, ▲ DC = 2,5%, □ DC = 10%, ● DC = 20%

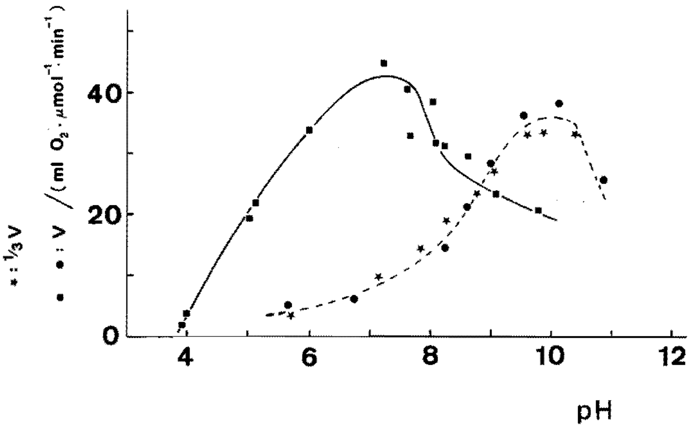


Fig. 3: pH dependence of catalytic activity.
■ CoPc$(NaSO_3)_4$/cross-linked PVAm (type B, DC = 4%):
✱ CoPc$(NaSO_3)_4$/1,3-propanediamine/OH^-; ● CoPc$(NaSO_3)_4$/OH^-

pH dependence of reaction rate

In Fig. 3(■) the pH dependence of the oxidation rate of RSH with catalyst type B (homogeneously distributed CoPc(NaSO$_3$)$_4$ in the cross-linked PVAm matrix) is shown. An optimal reaction rate is observed at pH = 7.5. In the polymer free systems CoPc(NaSO$_3$)$_4$/1,3 PDA/OH$^-$ (★) and CoPc(NaSO$_3$)$_4$/OH$^-$ (● in Fig. 3) an optimal catalytic activity is found at pH = 10. The CoPc(NaSO$_3$)$_4$/1,3 PDA/OH$^-$ system is about 3 times as active as the CoPc(NaSO$_3$)$_4$/OH$^-$ system which is in agreement with previous findings (10).

A similar shift in pH optimum as compared with the polymer free systems was earlier observed for the CoPc(NaSO$_3$)$_4$/PVAm (DC=0) system with an optimal activity at pH = 8 (11). This phenomenon was discussed in terms of changes in chain charge and local substrate concentrations, caused by the pH dependent basicity of the amine groups.

Accessibility of CoPc(NaSO$_3$)$_4$ sites and degree of cross-linking of the particles

As described in the Experimental section, two types of cross-linked particles were investigated. Type A was prepared by adding CoPc(NaSO$_3$)$_4$ *after* cross-linking of PVAm, in contrast with type B, where CoPc(NaSO$_3$)$_4$ was added *before* cross-linking of PVAm. The apparent catalytic acitivity of the sites in both catalyst types, and the effect of the degree of cross-linking on the water swellibility and on the activity of catalysts A and B was investigated. The results are shown in Fig. 4. System A appears to be at least three times more active than system B, measured at the same DC. From this result it may be inferred that in system A most of the large, square planar, rigid CoPc(NaSO$_3$)$_4^{4-}$ moieties are attached to the polymer matrix close to the particle surface while in system B the CoPc(SO$_3$)$_4^{4-}$ will be homogeneously distributed in the cross-linked particle. This is shown schematically in Fig. 5. The rate

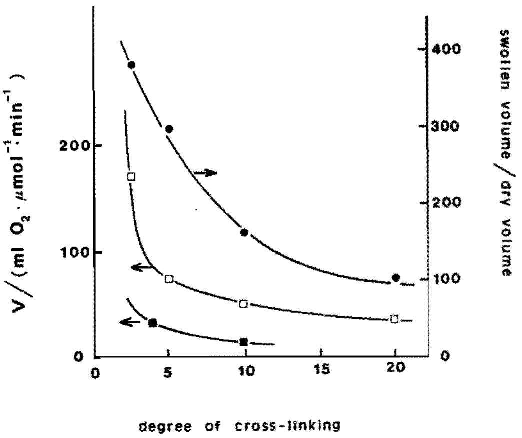


Fig. 4: Effect of the degree of cross-linking of PVAm on its swellibility (●) and on the catalytic activity, v, of catalyst type A (□) and B (■).

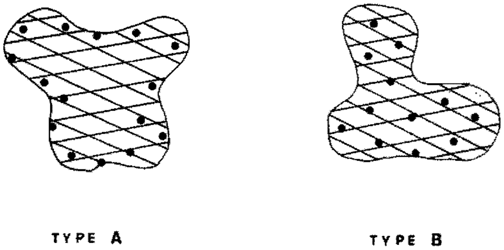


Fig. 5: Schematic representation of a cross-section of cross-linked PVAm. A: $CoPc(NaSO_3)_4$ added *after* cross-linking; B: $CoPc(NaSO_3)_4$ added *before* cross-linking.

difference between A and B may then be explained by the occurrence of a rate limiting intra-particle diffusion, which should be more pronounced in system B than in system A.

As expected, the degree of swelling increases as the degree of cross-linking decreases (see Fig. 4). The water swellibility is very high due to the presence of polar, charged groups in the polymeric matrix.

The catalytic activity follows curves of similar shape (□ for system A and ■ for system B in Fig. 4). This behavior is also indicative of a rate limiting matrix diffusion process, although the lower basicity (see Fig. 2) and thus the network charge at higher DC, may also contribute to the rate retardation (12).

Stirring speed and particle size

Variation around the high stirring rate applied (3.10^3 rpm) caused no significant change in reaction rate for both systems A and B. This indicates that reaction rate is not limited by mass transfer to or from the catalyst particles. The effect of the particle size of catalysts A and B was also measured. Two particle sizes, about 60 and 10 µm (obtained from scanning electron micrographs), were investigated. When using the small particles, no significant change could be observed in system A, but for system B the rate increased over 35%, indicating that the rate limiting effect of matrix diffusion in system B will be larger than in system A, which is consistent with the schematic representation in Fig. 5.

The observed effects of experimental parameters on the reaction rate have been summarized in Table 2a. The effects expected when mass transfer, intrinsic reactivity, or both intrinsic reactivity and matrix diffusion limit rate, are shown in Table 2b (13-15). It becomes evident that all experimental observations indicate that reaction rate is limited by both matrix diffusion and intrinsic reactivity.

Table 2a: Effect of experimental parameters on reaction rate in cross-linked PVAm catalyst systems.

stirring speed	particle size	degree of cross-linking	distribution of catalytic sites
independent	dependent [a)]	dependent	dependent

a) For catalyst type A this dependency was very small.

Table 2b: Effect of experimental parameters on rate-limiting processes.

process	stirring speed	particle size	degree of cross-linking	distribution of catalytic sites
mass transfer	dependent	dependent	independent	independent
intrinsic reactivity	independent	independent	uncertain	independent
matrix diffusion and intrinsic reactivity	independent	dependent	dependent	dependent

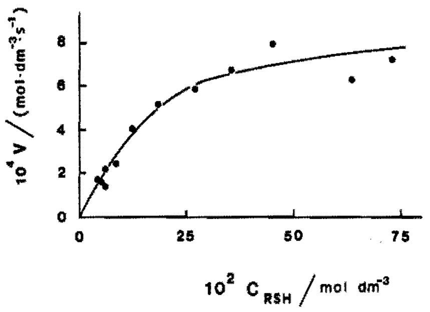
Activation energy

The importance of intra-particle diffusion in these cross-linked systems may also appear from an analysis of the apparent activation energies. If matrix diffusion is rate limiting, the observed activation energy will be lower than the true activation energy (13-15). The latter will be observed when the intrinsic reaction rate is low as compared with the matrix diffusion rate. Table 3 shows the observed activation energies at pH = 8 in the soluble polymeric catalyst system and in the cross-linked systems A and B (DC = 4.9%). The Table shows that rate limitation by matrix diffusion is more pronounced in system B than in system A, suggesting a larger diffusion path in the case of catalyst B. These findings support our explanation of the other phenomena observed.

Table 3: Apparent activation energy and intra-particle diffusion index x for several catalyst systems. [a)]

Catalyst support for $CoPc(NaSO_3)_4$	degree of cross-linking	$\frac{E^{\neq}_{app}}{kJ\ mole^{-1}}$
soluble PVAm	0	40 ± 4
catalyst type A	4.9	33 ± 4
catalyst type B	4.9	24 ± 2

a) At pH = 8



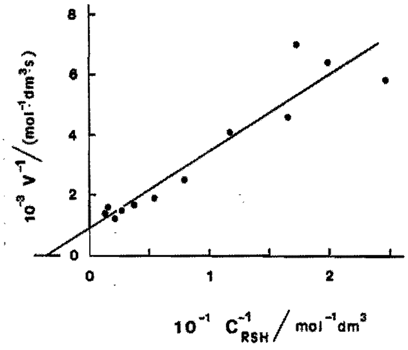


Fig. 6a: Effect of 2-mercaptoethanol concentration (RSH) on reaction rate.

Fig. 6b: Lineweaver-Burk plot. Data from Fig. 6a.

Thiol concentration

Initial reaction rates were determined for different initial thiol concentrations ranging from 0.04-0.7 M. Fig. 6a shows the results. The Michaelis-Menten kinetic concept (16) appears to be applicable to these data, implying a rate law of the type

$$v = \frac{k_2 \cdot E_0}{1 + \frac{K_m}{S}} \qquad [7]$$

where E_0 = the total catalyst concentration ($CoPc(NaSO_3)_4$), S = the initial substrate concentration, k_2 = the rate determining reaction constant and K_m is the Michaelis constant. From the Lineweaver-Burk plot in Fig. 6b, the apparent values of k_2 and K_m have been derived and are listed in Table 4, together with the parameters for the soluble polymeric catalyst system, found previously (6). The significantly

Table 4: Kinetic parameters for soluble and cross-linked $CoPc(NaSO_3)_4$/PVAm catalysts

Catalyst support for $CoPc(NaSO_3)_4$	pH	$\frac{K_m}{\text{mole dm}^{-3}}$	$\frac{10^{-2}\,k_2}{s^{-1}}$
catalyst type B	8.0	0.3 ± 0.1	1.2 ± 0.2
soluble PVAm	7.4	0.09 ± 0.02	28 ± 4

larger value of K_m as well as the lower value of k_2 in the immobilized system B may be due to diffusional resistance, causing a lower local substrate concentration in the vicinity of the catalytic sites as compared with the soluble polymeric catalyst system.

Silica anchored polymeric catalysts

From all these observations it may be deduced that the catalytic sites ($CoPc(NaSO_3)_4$), situated at or nearby the outer surface of the cross-linked polymeric particle, are the most effective ones, since then reaction rate is hardly limited by matrix diffusion. This ineffectiveness of the catalyst interior prompted us to substitute this inner part by an inert substance e.g. silica.

A silica anchored $CoPc(NaSO_3)_4$/PVAm catalyst was synthesized and characterized (see Experimental) and its activity (see Table 5) was

Table 5: Initial reaction rate and pH optimum for several catalyst systems.

Catalyst support for $CoPc(NaSO_3)_4$	pH optimum	10^{-2} initial rate [a) ml/μmol, min
OH^-	10	0.1
catalyst type B (DC = 4%)	7.5	0.3
catalyst type A (DC = 2.5%)	- [b)	1.6
silica anchored PVAm	8	2.7
soluble PVAm	8	10.6

[a) At pH = 8.2; c_{RSH} = 0.19 mole dm^{-3}

[b) Not determined

found to be even higher than observed for system A, but nevertheless less active than the soluble non-cross-linked polymeric system. Thus, an improved accessibility of the catalytic sites lead to an enhanced reaction rate as compared to system A, but decelerated it as compared with the polymeric catalyst system, due to multi-anchoring of the PVAm onto the silanized surface, thus lowering conformational freedom and accessibility or due to a specific effect of the silica surface (17). It seems therefore that a polymeric catalyst anchored by a single link on a small rigid inert carrier particle as shown recently by Verlaan et al. (18), will offer an approach to an even more active, immobilized polymeric catalyst.

Conclusions

- α,α'-dichloro-p-xylene appeared to be an efficient cross-linker of PVAm. The reaction proceeds almost quantitatively under the applied conditions.
- The main effect introduced by cross-linking the very active water soluble polymeric catalyst, $CoPc(NaSO_3)_4$/PVAm, is the occurrence of a rate limitation by matrix diffusion. At the applied stirring speed (3.10^3 rpm) rate limitation by mass transfer in bulk has not been observed. Therefore, more active immobilized catalysts of this type will only be obtained, when the accessibility to the very active catalytic sites is improved, as is the case for a silica anchored macromolecular catalyst.
- As expected, kinetic resemblance has been found between the soluble polymeric catalyst system, $CoPc(NaSO_3)_4$/PVAm, and the insoluble cross-linked polymeric catalyst: e.g. Michaelis-Menten kinetics in thiol and a shift of the optimal pH value from that of the polymer free systems.

References

(1) J.M.J. Fréchet, *Tetrahedron*, 37 (1981), 663

(2) G. Manecke and W. Storck, *Angew. Chem.*, 90 (1978), 691

(3) M.A. Kraus and A. Patchornik, *J. Polym. Sci., Makromol. Rev.*, 15 (1980), 55

(4) A. Akelah and D.C. Sherrington, *Chem. Rev.*, 81 (1981), 557

(5) W.M. Brouwer, P. Piet and A.L. German, *Polym. Commun.*, 24 (1983), 216

(6) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.*, 22 (1984), 297

(7) D. D. Perrin, *Dissociation Constants of Organic Bases in Aqueous solution*, Butterworths London, 1965

(8) B.A. Bolto and K.H. Eppinger, *J. Macromol. Sci. Chem.* A17 (1982), 175

(9) A. Katchalsky, J. Mazur and P. Spitnik, *J. Polym. Sci.*, 23 (1957), 513

(10) W.M. Brouwer, P. Piet and A.L. German, *Makromol. Chem.*, 185 (1984), 363

(11) W.M. Brouwer, P. Piet and A.L. German, *Polym. Bull.*, 8 (1982), 245

(12) W.M. Brouwer, P. Piet and A.L. German, *J. Mol. Catal.*, accepted for publication

(13) C.N. Satterfield and T.K. Sherwood, *The role of diffusion in Catalysis*, Addison-Wesley Publ. Co., 1963

(14) J.M. Thomas and W.J. Thomas, *Introduction to the Principles of Heterogeneous Catalysis*, Academic Press, New York, 1967, ch. 4

(15) F. Helfferich, *Ion Exchange*, Mc Graw-Hill, New York, 1962, ch. 11

(16) L. Michaelis and M.L. Menten, *Biochem. Z.*, 49 (1913), 333

(17) A. Akelah, *Br. Polym. J.*, 13 (1981), 107

(18) J.P.J. Verlaan, J.P.C. Bootsma and G. Challa, *J. Mol. Catal.*, 14 (1982), 211

SUMMARY

This thesis describes an investigation of the rate enhancing effect of basic polymers on the oxidation of thiols to disulfides, with cobalt(II)phthalocyanine-tetrasodium sulfonate ($CoPc(NaSO_3)_4$) as a catalyst. A 20-50 fold acceleration of rate was observed when using $CoPc(NaSO_3)_4$ bound to basic polymers instead of bound to monomeric analogs.

The conversion of 2-mercaptoethanol is governed by three important parameters, each largely affecting polymeric catalyst activity: basicity, polymer charge density and ionic strength.

Basic groups are needed to dissociate the weakly acidic thiol thus supplying thiol-anions which are generally considered as the reactive species (Ch. I). The importance of basic groups is also reflected by the molecular weight dependence of catalytic activity observed for $CoPc(NaSO_3)_4$/poly(vinylamine) catalysts. A low molecular weight poly(vinylamine) appears to be more active than a high molecular weight poly(vinylamine), which corresponds to the higher basicity of the amine groups in the low molecular weight polymers as compared with those with higher molecular weights (Ch. IV).

Catalytic activity appears to increase almost linearly with the cationic polymer charge density for copolymers of vinylamine and vinylalcohol (Ch. VI) and poly(quaternary ammonium salts) (Ch. VIII). The electrostatic attraction between the cationic polymer and the thiol-anions play an important role in the enhancement of the local thiol-anion concentration in the vicinity of the catalytic sites. In addition, dehydration of the activated complex may be facilitated, thus enhancing reaction rate.

Reaction rate is considerably diminished by increasing ionic strength, which can be explained by the shielding effect of salt on the electrostatic field of the macro-ions. For the same reason the polymer coil shrinks upon the addition of salt, but analysis of the

activation energies does not indicate the occurrence of rate limiting diffusion (Ch. II).

The importance of basicity, polymer charge density and ionic strength is also reflected by a strong rate dependence on pH (Ch. I and II).

Another polymeric feature responsible for high rates is the isolation of CoPc$(NaSO_3)_4$ sites by the polymeric coils, thus preventing the formation of catalytically inactive dimeric adducts. Accordingly, a first order rate dependence on polymer catalyst concentration was found (Ch. III).

Kinetic investigations show resemblance between these polymeric catalysts and enzymes, viz. Michaelis-Menten kinetics toward thiol and oxygen, a bell shaped rate dependence on pH and high turn-over numbers.

In the conversion of the hydrophobic dodecylmercaptan, not only cationic charge, but also hydrophobic binding sites in the catalyst domain seem to be important since this thiol, in contradistinction to 2-mercaptoethanol, can be converted catalytically in cationic micelles. Anionic micelles retard the reaction and a nonionic surfactant acts rather indifferently (Ch. VII). These results have lead to the conclusion that future polymeric catalysts suitable for the dodecylmercaptan oxidation should not only possess cationic charge and basic sites, but also hydrophobic binding sites.

The stability of the polymeric thiol oxidation catalysts in successive runs is rather poor in the case of poly(amines), but very good when poly(ammonium salts) are used as polymeric ligands. This has been attributed to the chemical inertness of the quaternary ammonium groups with respect to primary and secondary amine groups. These amine groups are probably attacked by the disulfides formed in the reaction (Ch. VIII).

The effect of immobilization of the CoPc$(NaSO_3)_4$ on solid supports of cross-linked poly(vinylamine) was investigated (Ch. IX). Despite the fact that the resins are highly swollen in water, a rate limiting matrix diffusion occurs. This problem is inherent to the high intrinsic activity of the present catalysts. Anchorage to silica supports shows a promising enhancement.

SAMENVATTING

In dit proefschrift wordt een onderzoek beschreven naar het snelheidsverhogende effect van basische polymeren op de oxydatie van thiolen in disulfiden, waarbij kobalt(II)ftalocyanine-tetra-natrium sulfonaat ($CoPc(NaSO_3)_4$) als katalysator wordt gebruikt.

Een 20 tot 50 voudige snelheidstoename werd waargenomen wanneer $CoPc(NaSO_3)_4$ werd gebruikt dat aan basische polymeren was gebonden i.p.v. aan de monomere analogi.

De omzetting van 2-mercaptoethanol wordt beheerst door drie belangrijke parameters, die elk afzonderlijk de polymere katalytische activiteit sterk beïnvloeden: basischiteit, ladingsdichtheid op het polymeer en ionsterkte.

Basische groepen zijn nodig om het zwakzure thiol te dissociëren, waarbij thiolanionen vrijkomen, welke in het algemeen als de reactieve deeltjes beschouwd worden (H. I). Het belang van basische groepen komt ook naar voren in de molecuulgewichtsafhankelijkheid van de katalytische activiteit van $CoPc(NaSO_3)_4$/poly(vinylamine) katalysatoren. Een poly(vinylamine) met een laag molecuulgewicht blijkt actiever te zijn dan een poly(vinylamine) met een hoog molecuulgewicht, wat overeenkomt met de hogere basischiteit van de amine groepen in polymeren met een laag molecuulgewicht vergeleken met die met hogere molecuulgewichten.

Bij copolymeren van vinylamine en vinylalcohol (H. VI) en poly(quaternaire ammoniumzouten) (H. VIII) blijkt de katalytische activiteit nagenoeg lineair met de kationische ladingsdichtheid op het polymeer toe te nemen. De electrostatische aantrekking tussen het kationische polymeer en de thiolanionen speelt een belangrijke rol in de verhoging van de lokale thiolanion concentratie in de nabijheid van de katalytisch actieve plaatsen. Bovendien kan dehydratatie van het geactiveerd complex vergemakkelijkt worden, waardoor ook de reactie snelheid verhoogd wordt.

De reactiesnelheid wordt aanmerkelijk verlaagd bij toenemende ionsterkte, hetgeen verklaard kan worden door het afschermende effect van zout op het electrostatische veld van de macroionen. Om dezelfde reden krimpt de polymere kluwen door het toevoegen van zout, maar een analyse van de activeringsenergie duidt niet op het optreden van een snelheidslimitering t.g.v. diffusie.

Het belang van basischiteit, ladingsdichtheid en ionsterkte komt ook tot uiting in de sterke afhankelijkheid van de reactiesnelheid van de pH (H. I en II).

Een andere functie van het polymeer is de afscherming van $CoPc(NaSO_3)_4$ door de polymere kluwens, waardoor de vorming van katalytisch inactieve dimere adducten wordt voorkomen. Dienovereenkomstig werd een eerste orde snelheidsafhankelijkheid van de polymere katalysatorconcentratie waargenomen (H. III).

Het kinetisch gedrag van deze polymere katalysatoren vertoont gelijkenis met dat van enzymen, nl. Michaelis-Menten kinetiek jegens thiol en zuurstof, een klokvormige snelheidsafhankelijkheid van de pH en hoge turn-over nummers.

Bij de omzetting van het hydrofobe dodecylmercaptaan, lijkt niet alleen kationische lading maar ook de aanwezigheid van hydrofobe bindingsplaatsen in het katalysator domein van belang want dit thiol kan katalytisch omgezet worden in kationische micellen, in tegenstelling tot 2-mercaptoethanol. Anionische micellen vertragen de reactie en een nonionisch surfactant heeft nagenoeg geen katalytisch effect (H. VII). Op grond van deze resultaten kan worden geconcludeerd dat toekomstige polymere katalysatoren die geschikt zijn voor de oxidatie van dodecylmercaptaan, niet alleen kationische lading en basische groepen maar ook hydrofobe bindingsmogelijkheden moeten bezitten.

De stabiliteit van de polymere thioloxydatiekatalysatoren is nogal slecht in het geval van poly(aminen), maar bijzonder goed indien poly(quaternaire ammoniumzouten) worden gebruikt als polymere liganden.

Deze waarnemingen zijn toegeschreven aan de chemische inertheid van de quaternaire ammoniumgroepen in vergelijking met primaire en secundaire amine groepen. Deze aminegroepen worden vermoedelijk door het disulfde, dat tijdens de reactie wordt gevormd, aangetast (H. VIII).

Het effect van immobilisatie van CoPc$(NaSO_3)_4$ op vaste dragers van vernet poly(vinylamine) werd onderzocht (H. IX).
Ondanks het feit dat het drager-hars sterk gezwollen is in water, treedt een snelheidslimiterende matrixdiffusie op. Dit probleem is inherent aan de hoge intrinsieke activiteit van de onderhavige katalysatoren. Verankering aan silicadragers toont een veelbelovende verbetering.

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bijvak: chemische technologie (Prof.drs. H.S. van der Baan, Eindhoven)

Betrekking:

Vanaf 15 juli 1981 is hij werkzaam in de rang van wetenschappelijk assistent bij de vakgroep Chemische Technologie van de Technische Hogeschool Eindhoven. Hier werd in de groep van Prof.dr.ir. A.L. German het onderzoek uitgevoerd dat is beschreven in dit proefschrift.

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Stellingen

1. Indien Kimura, Inaki en Takemoto zo nauwkeurig de samenstelling van het copolymeer en de monomeer voeding kunnen bepalen als zij opgeven, dan is de copolymerisatie reactie tussen vinylftaalimide en vinylacetaat niet te beschrijven met het Alfrey-Mayo model.

   K. Kimura, Y. Inaki, K. Takemoto, Makromol. Chem. *176* *(1975), 2225*
   T. Alfrey, Jr., G. Goldfinger, J. Chem. Phys., *12* *(1944), 205*
   F.R. Mayo, F.M. Lewis, J. Am. Chem. Soc., *66* *(1944), 1594*

2. De door Bansal e.a. opgestelde hypothese voor het verband tussen alcohol ketenlengte en de alcohol-zeep verhouding in het water-olie grensvlak in olie continue micro-emulsies, is blijkens metingen aan olie continue micro-emulsies bestaande uit water, tolueen, natriumdodecylsulfaat en alkylalcohol niet algemeen toepasbaar.

   V.K. Bansal, K. Chinnaswamy, C. Ramachandran, D.O. Shah, J. Coll. Interface Sci., *72* *(1979), 524*
   A.M. Cazabat, D. Langevin, J. Chem. Phys., *74* *(1981), 3148*

3. Bij het complexeringsgedrag van overgangsmetaalionen in deels geladen polyamines waarbij chelaatvorming optreedt, speelt de electrostatische repulsie tussen metaalion en polyion geen belangrijke rol.

   H. Nishide, E. Tsuchida, Makromol. Chem. *177* *(1976), 2295*
   E.A. Bekturov, S.E. Kudaibergenov, G.M. Zhaimina, Polymer *24* *(1983), 607*

4. Narkis en Joseph verwaarlozen ten onrechte het optreden van afschuiving als plastisch deformatie mechanisme bij de interpretatie van het spannings-rek gedrag van met glasbollen gevulde glasachtige polymeren tijdens trek-experimenten.

   M. Narkis, E. Joseph, Intern. J. Polymeric Mater., *6* *(1977), 1*

5. Op grond van het anomale, pH-afhankelijke viscositeitsgedrag van een polyvinylamine oplossing in water zijn de door Beckwith e.a. gekozen pH waarden waarbij de diameter van vernette polyvinylamine deeltjes en zo de zwelgraad wordt bepaald, niet de meest geschikte om veranderingen in deze zwelgraad vast te stellen.

C.J. Bloys van Treslong, Recl. Trav. Chim. Pays-Bas, 97 (1978), 13
P.L.M. Beckwith, D. Fornasiero, T. Hörr, K. Rye, T. Kurucsev, Polymer Commun., 25 (1984), 18

6. De snel stijgende verkoop van huiscomputers kan niet verklaard worden door een sterke behoefte van de consument aan de prestaties die het product thuis kan leveren.

7. Natuurbehoud is conservatisme.

Eindhoven, 11 september 1984 W.M. Brouwer