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Viscometric characterization of a polymeric catalyst for the autoxidation of thiols

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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(NaSO₃)₄) and poly(vinylamine) (PVAm). The incorporation of the CoPc(SO₃)²⁻ 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 CoPc(SO₃)²⁻ 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 method¹ with some minor modifications (\(M_n\text{,PVAm}=61.10^3\) 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(NaSO₃)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(NaSO₃)₄), (see Figure 1), attached to the weakly basic poly(vinylamine) (PVAm) appeared to be a very effective catalyst for the autoxidation of thiols⁴. It is prepared by mixing aqueous solutions of CoPc(NaSO₃)₄ and PVAm.

In order to elucidate the mode of incorporation of CoPc(NaSO₃)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(NaSO₃)₄ and other salts, which in contradistinction to CoPc(NaSO₃)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(NaSO₃)₄](image-url)
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. 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(NaS0₃)₄⁴⁻ ion. This is a strong indication that no multi-ligand intramolecular chelate formation occurs after addition of CoPc(NaS0₃)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. Consequently, the viscosity experiments support the view that only one axial position of the central metal atom of CoPc(NaS0₃)₄ is involved in the coordinative interaction with PVAm.

Schutten et al. 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 (circles) and (triangles) in Figure 3, accompanied by a distinct fall of pH. The polymer conformation is considerably affected by the pH, as reported earlier.²,⁸

The presence of CoPc(NaS0₃)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(NaS0₃)₄ to PVAm and the lower pH, caused by the presence of the substrate, are giving rise to an extended conformation.

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