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# Influence of the Molecular Weight of Ionenes on the Cobaltphthalocyanine-Catalysed Autoxidation of Mercaptoethanol

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**Abstract:** In order to study the promoting effect of polycations on the cobalt(II)phthalocyanine-tetrasodiumsulphonate ( $\text{CoPc}(\text{NaSO}_3)_4$ )-catalysed autoxidation of thiols, it is imperative to know the molecular weight dependence of the polymer. Monodisperse oligomers can often supply a lot of information. To elucidate the mechanism of the promoting effect of 2,4-ionene, a poly(quaternary ammonium)salt, on the  $\text{CoPc}(\text{NaSO}_3)_4$ -catalysed autoxidation of 2-mercaptoethanol, a series of monodisperse 2,4-ionene oligomers were prepared. Trimeric 2,4-ionenes, containing two quaternary ammonium groups separated by four methylene groups, showed a high co-catalytic activity, and active Co-aggregates were detected with visible light spectroscopy. The spectroscopic behaviour was in close agreement with that of high molecular 2,4-ionene/ $\text{CoPc}(\text{NaSO}_3)_4$  complexes. In order to achieve this aggregation several oligomeric ionenes have to act concertedly. If the distance between the ionic sites is short, the trimer acts as a simple salt in stabilizing the aggregates. With respect to the catalytic activity the optimum polycation/catalyst ratio, expressed as the  $\text{N}^+/\text{Co}$  ratio, decreased with increasing chain length and reached a constant level of 50 at a 2,4-ionene nonamer. For the trimers and pentamers this ratio is affected by the type of end-group. All synthesized 2,4-ionene oligomers exhibited excellent co-catalytic properties at the optimum  $\text{N}^+/\text{Co}$  ratio, with maximum turnover frequencies of 4600 mol thiol/(mol Co s), i.e. 50 times higher than those obtained for the polymer-free system. In the case of monodisperse 2,4-ionene pentamer with bromo end-groups, double Michaelis–Menten kinetics were observed, as also was exhibited by high molecular weight ionene.

**Key words:** cobalt(II)phthalocyanine-tetrasodiumsulphonate, poly(quaternary ammonium)salt, oligomeric ionenes, thiol autoxidation, catalysis.

## INTRODUCTION

Polymers can exhibit considerable effects on various catalytic reactions. At present polymeric effects on the catalysed autoxidation of thiols to disulphides receive much attention.<sup>1–9</sup> In our group it has been found that several cationic polymers have large promoting effects on the thiol autoxidation, catalysed by cobalt(II)-

phthalocyanine-tetrasodiumsulphonate ( $\text{CoPc}(\text{NaSO}_3)_4$ ) (Fig. 1).<sup>10</sup>

Poly(quaternary ammonium)salts, the so-called ionenes, proved to be the most effective promoters for the  $\text{CoPc}(\text{NaSO}_3)_4$ -catalysed autoxidation of thiols. The highest rate enhancement, an increase by a factor of 50, has been reported for 2,4-ionene (Fig. 2). One reason for this increase is the effect of substrate enrichment, resulting in an increase in the local concentration of the thiolate anion, which is the reactive species. But also,

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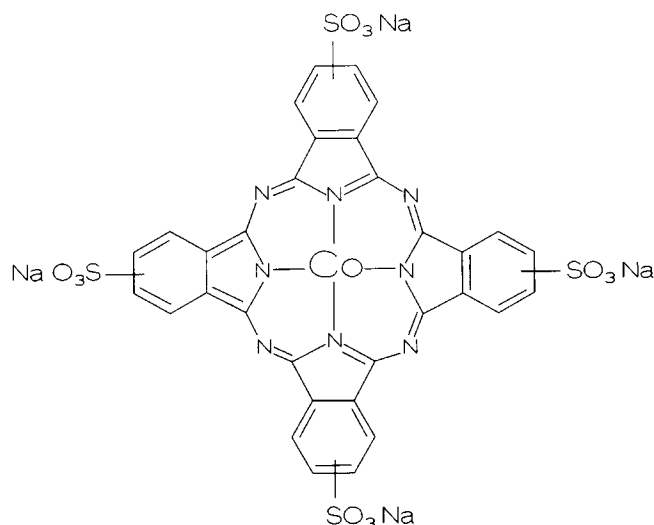


Fig. 1. Structure of cobalt(II)phthalocyanine-tetrasodium-sulphonate.

catalyst enrichment in the positively charged polymer domain plays an important role. Furthermore, the formation of the catalytically inactive oxygen bridged  $\mu$ -peroxy complex is strongly suppressed. Additionally, ionene induces dimerization and aggregation of the catalyst.<sup>11</sup>

So far, various types of ionenes have been investigated with regard to their effect on the dimerization of the catalyst as well as on the catalytic activity. Until now, little attention has been paid to the effect of the length of the ionene on the formation of the cobalt aggregates and the catalytic oxidation rates, because monodisperse 2,4-ionene oligomers were not available. Earlier attempts were made to determine the influence of the chain length of polyvinylamine as co-catalyst on the activity of the thiol oxidation. Brouwer *et al.*<sup>12</sup> observed a molecular weight dependence on the catalytic activity in the case of polyvinylamine. Van Streun *et al.*<sup>13</sup> attempted to study the effects of two different molecular weight 2,4-ionenes on the kinetics, but due to the small variation in the molecular weights, no significant influence could be observed.

Since we are able to prepare monodisperse oligomers of 2,4-ionene, which primarily have been used to obtain amphiphilic polystyrene-ionene diblock copolymers,<sup>14,15</sup> these well-defined oligomers can be used to study the influence of the molecular weight of 2,4-ionene on the thiol oxidation. Some types of low molecular weight ionene oligomers also have been used as

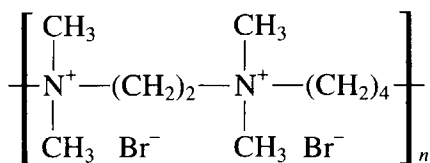


Fig. 2. Structure of 2,4-ionene.

model compounds in the X-ray analysis of crystal structures<sup>16,17</sup> and to study the formation of ionene polymers<sup>18</sup> and their surface tension properties.<sup>19</sup>

From a mechanistic point of view it is very important to know the minimum length of 2,4-ionene necessary to obtain the active aggregates of  $\text{CoPc}(\text{NaSO}_3)_4$ . In this paper we discuss the influence of the length of monodisperse 2,4-ionene oligomers and of 2,4-ionene polymers, prepared by step condensation polymerization, on the dimerization of the catalyst. Also, the resulting effects on the catalytic activity and the kinetics of these ionene promoted reactions are discussed.

## EXPERIMENTAL

### Synthesis of 2,4-ionene oligomers and polymers

A series of oligomeric 2,4-ionenes (Fig. 3) were synthesized following the procedures previously described.<sup>14,15</sup> The so-called Br-trimer (**1a**), a 2,4-ionene trimer with two quaternary ammonium groups and bromo end-groups, was prepared by reacting 11.4 g *N,N,N',N'*-tetramethylethylenediamine (TMEDA) (Janssen Chimica) with 317.5 g (a 15-fold excess over TMEDA) of 1,4-dibromobutane (Janssen Chimica) (both monomers were distilled and stored under argon before use) in 250 ml of methanol/dimethylformamide (DMF) (1/1, v/v) for 3 days at 40°C, followed by the purification procedure consisting of precipitation in acetone and washing with acetone. Subsequently, the N-terminated trimer of 2,4-ionene, the N-trimer (**1d**), was synthesized using the same reaction conditions: 18.2 g of 1,4-dibromobutane and 146.9 g of TMEDA (a 15-fold excess). The N-terminated pentamer (**1h**) was prepared by reacting the Br-trimer (**1a**) with a large excess (25-fold) of TMEDA in a mixture of DMF, CH<sub>3</sub>OH and water. In the same way after consecutive

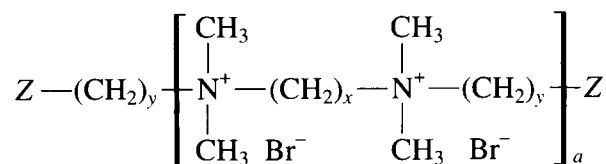


Fig. 3. Structures of the different monodisperse ionene oligomers.

	<i>a</i>	<i>x</i>	<i>y</i>	Z
<b>1a</b> : Br-trimer	1	2	4	Br
<b>1b</b> : H-trimer-2C	1	2	4	H
<b>1c</b> : H-trimer-3C	1	3	4	H
<b>1d</b> : N-trimer	1	4	2	N-(CH <sub>3</sub> ) <sub>2</sub>
<b>1e</b> : N-trimer-6C	1	6	2	N-(CH <sub>3</sub> ) <sub>2</sub>
<b>1f</b> : Br-pentamer	2	2	4	Br
<b>1g</b> : Br-nonamer	4	2	4	Br
<b>1h</b> : N-pentamer	2	4	2	N-(CH <sub>3</sub> ) <sub>2</sub>
<b>1i</b> : N-heptamer	3	4	2	N-(CH <sub>3</sub> ) <sub>2</sub>

steps, always using a 20-fold excess of one of the monomers, the different monodisperse oligomers of 2,4-ionene, i.e. Br-pentamer (**1f**), N-heptamer (**1i**) and Br-nonamer (**1g**), as shown in Table 1, were obtained.

Likewise, three other trimers were synthesized with two, three and six methylene groups between the positive charges, respectively. H-trimer-2C (**1b**) was prepared by reacting 1.7 g of TMEDA and 12.7 g of 1-monobromobutane (Janssen Chimica, 99%) (a six-fold excess over TMEDA) in 25 ml of methanol/DMF (1/1, v/v) for 3 days at 50°C. Following a similar procedure, H-trimer-3C (**1c**) was synthesized using the same reaction conditions: 1.9 g of *N,N,N',N'*-tetramethylpropanediamine (Janssen Chimica, 99%) and 11.0 g of 1-monobromobutane. N-trimer-6C (**1e**) was prepared by reacting 3.4 g of 1,6-dibromohexane (Fluka, 97%) and 17.1 g of TMEDA (a 10-fold excess) according to the same method.

The polymeric 2,4-ionenes were prepared according to the method developed by Rembaum *et al.*<sup>20</sup> All molecular weights were determined by titration of the tertiary amino end-groups of the ionene with HCl. Therefore, it was necessary to end-cap the Br-terminated oligomeric and polymeric ionenes with dimethyl-amino groups by reacting them with an excess of TMEDA in water for 1 day at 25°C.

#### Visible light spectroscopy

All VIS spectra were recorded on a Hewlett-Packard diode array 8451A spectrophotometer, using a 1-cm cell.

#### Catalytic activity measurements

CoPc(NaSO<sub>3</sub>)<sub>4</sub> was prepared according to a slight adaptation by Zwart *et al.*<sup>21</sup> of the method described by

Weber & Busch.<sup>22</sup> 2-Mercaptoethanol (98%, Janssen Chimica) was distilled prior to use, stored in the dark and kept under argon atmosphere in sealed flasks. The catalytic thiol autoxidations were carried out batchwise as reported previously,<sup>11</sup> in an all-glass double-walled Warburg apparatus, equipped with a powerful mechanical glass stirrer (stirring speed 2600 rpm) and thermostatted at 25.0 ± 0.5°C. The catalyst was prepared by adding an aqueous CoPc(NaSO<sub>3</sub>)<sub>4</sub> solution to the reactor containing an aqueous ionene solution. The pH was adjusted by the addition of a KOH solution to the reaction mixture (100 ml) just before the addition of 2-mercaptoethanol (ME). The initial reaction rate was measured immediately after ME was added. Reaction rate was measured by monitoring the oxygen uptake rate with a digital mass flow controller (Inacom Veenendaal), keeping the oxygen pressure constant at 10<sup>5</sup> ± 50 Pa.

## RESULTS AND DISCUSSION

#### Visible light spectroscopy

It is known that CoPc(NaSO<sub>3</sub>)<sub>4</sub> in aqueous solution occurs in its monomeric as well as in its dimeric form, with absorption maxima in the visible light spectrum at 662 nm and 628 nm, respectively.<sup>23,24</sup> Visible light spectroscopy shows that addition of 2,4-ionene to a catalyst solution dramatically affects the dimer-monomer equilibrium. Van Welzen *et al.* demonstrated that after the addition of 2,4-ionene to a CoPc(NaSO<sub>3</sub>)<sub>4</sub> solution the dimeric form is favoured over the monomeric form.<sup>11</sup> This aggregation of the catalyst was attributed to the suppression of charge repulsion between the four-fold negatively charged CoPc(NaSO<sub>3</sub>)<sub>4</sub> on addition of the cationic polymer. Even further aggregation was demon-

TABLE 1. Molecular weights of the different oligomeric and polymeric ionenes prepared

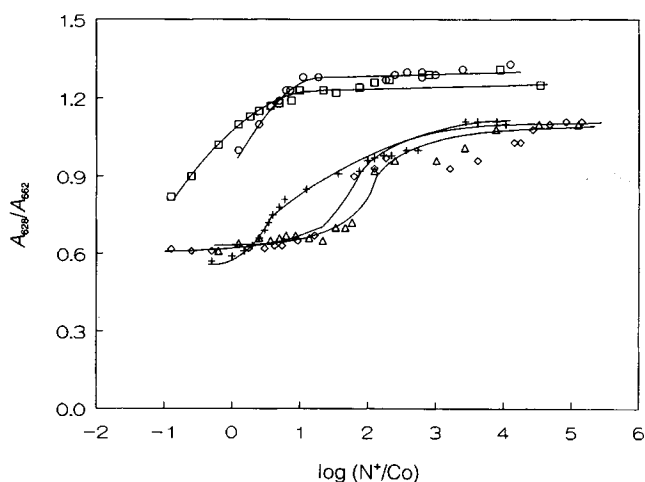
	End-group	$\bar{M}_n$ (theoretical) (g mol <sup>-1</sup> )	$\bar{M}_n$ (experimental) (g mol <sup>-1</sup> )
Br-trimer ( <b>1a</b> )	Br	548	589
N-trimer ( <b>1d</b> )	N	448	459
Br-pentamer ( <b>1f</b> )	Br	880	954
N-pentamer ( <b>1h</b> )	N	780	865
N-heptamer ( <b>1i</b> )	N	1113	1196
Br-nonamer ( <b>1g</b> )	Br	1544	1645
H-trimer-2C ( <b>1b</b> )	H	390	<sup>a</sup>
H-trimer-3C ( <b>1c</b> )	H	404	<sup>a</sup>
N-trimer-6C ( <b>1e</b> )	N	476	492
2,4-ionene	Br	—	1648
2,4-ionene	N	—	3500
2,4-ionene	N	—	6200
2,4-ionene	N	—	22000

<sup>a</sup> Titration showed the absence of dimethyl-amino groups.

strated by a shift to shorter wavelength (620–622 nm). This dimerization, leading to suppression of the inactive  $\mu$ -peroxo complex (674 nm), and substrate enrichment in the presence of 2,4-ionene result in a tremendous increase in the catalytic oxidation rate of 2-mercaptoethanol.<sup>10</sup>

The new method of preparing monodisperse oligomeric 2,4-ionenes<sup>14,15</sup> enables us to determine the minimum chain length of 2,4-ionene required for the formation of dimers of the catalyst. The VIS experiments described above were all performed with a high molecular weight 2,4-ionene ( $\bar{M}_n = 22\,000\text{ g mol}^{-1}$ ). We have now prepared several monodisperse oligomeric ionenes (**1a–i**) and polymeric 2,4-ionenes, which are given in Table 1. As can be seen, the molecular weights of these monodisperse oligomers of 2,4-ionene are in very good agreement with the theoretical values. Despite many reaction steps low dispersities can be retained.

In order to study the molar weight dependence on the aggregation phenomenon we measured the absorbances at 628 nm and 662 nm of the oligomers of 2,4-ionene by varying the ionene/ $\text{CoPc}(\text{NaSO}_3)_4$  ratio, expressed as the  $\text{N}^+/\text{Co}$  ratio. It appeared from earlier experiments that this ratio is a measure of the relative amount of aggregated cobalt species.<sup>11</sup> The effect of varying the  $\text{N}^+/\text{Co}$  ratio for the Br-trimer (**1a**) on the ratio of both absorbances is given in Fig. 4. An increase in the dimer over monomer ratio can be seen, but no sharp increase, characteristic of a high molecular weight 2,4-ionene at an  $\text{N}^+/\text{Co}$  ratio of 4, can be detected. The only effect which can be observed is increasing aggregation of the cobalt complex due to increasing Br-trimer (**1a**) concentration. Obviously, the Br-trimer (**1a**) is unable to stabilize the dimers as effectively as does the polymeric ionene. The spectroscopic behaviour



**Fig. 4.** Ratio of absorbances at 628 nm and 662 nm as a function of the  $\text{N}^+/\text{Co}$  ratio for Br-trimer (**1a**) (+), N-trimer (**1d**) (O), H-trimer-2C (**1b**) ( $\Delta$ ), H-trimer-3C (**1c**) ( $\diamond$ ) and N-trimer-6C (**1e**) ( $\square$ ).  $[\text{CoPc}(\text{NaSO}_3)_4] = 2 \times 10^{-6}\text{ mol dm}^{-3}$ .

looks more or less like the earlier reported<sup>11,25</sup> effect of adding a simple salt.

Additionally, we measured both absorbances also for the other 2,4-ionene trimer, i.e. the N-trimer (**1d**). Looking at the results in Fig. 4, a quite different behaviour can be observed. These results obtained are quite similar to those found for the high molecular weight 2,4-ionene.<sup>11</sup> As  $\text{N}^+/\text{Co}$  increases from 0 to 4, it appears that the dimer/monomer ratio increases. At  $\text{N}^+/\text{Co} = 4$  a discontinuity in the plot arises, which suggests the formation of an ionene/ $\text{CoPc}(\text{NaSO}_3)_4$  complex with fixed stoichiometry. Above an  $\text{N}^+/\text{Co}$  ratio of 4 (i.e.  $\log(\text{N}^+/\text{Co}) = 0.6$ ) a relatively high  $A_{628}/A_{662}$  ratio is found, which remains constant even after increasing the N-trimer (**1d**) concentration: the existing complex is not further affected. This implies that the N-trimer (**1d**) stabilizes the dimeric form better than does the Br-trimer (**1a**), which can be ascribed to the difference in the distance between the quaternary ammonium groups in both trimers, i.e. approximately 4.1 Å and 6.1 Å for the Br-trimer (**1a**) and N-trimer (**1d**), respectively.

In order to elucidate the role of the distance between the two quaternary ammonium groups, we synthesized oligomeric ionenes with two, three, and six methylene groups between the ionic sites, respectively. A similar structure of the H-trimer-2C (**1b**) as compared with the Br-trimer (**1a**), explains the analogous spectroscopic behaviour (Fig. 4). In addition, the H-trimer-3C (**1c**), where the positive charges are separated by three methylene groups (distance 5.3 Å), is also unable to induce aggregation. By contrast, the N-trimer-6C (**1e**) stimulates the aggregation of  $\text{CoPc}(\text{NaSO}_3)_4$ . Therefore, it is interesting to notice that a critical minimum distance of four methylene groups between the positive charges in an ionene trimer is required, in order to obtain a spectroscopic behaviour closely resembling that of the high molecular weight 2,4-ionenes. Apparently, a trimer where the distance between the quaternary ammonium groups is shorter than 6.1 Å cannot stabilize a dimer of  $\text{CoPc}(\text{NaSO}_3)_4$  because only one of the two positive charges per trimer chain is capable of interacting with one negative charge of the catalyst. On the other hand, in the case of the N-trimers (**1d**), due to a larger distance between the ionic sites, the two quaternary ammonium groups can compensate the charges of two  $\text{CoPc}(\text{NaSO}_3)_4$  molecules, and hence a dimer can be formed.

Looking at the results for the N-pentamer (**1h**) and Br-pentamer (**1f**) (Fig. 5), both containing four quaternary ammonium groups, the spectroscopic behaviour is in agreement with that of high molecular weight 2,4-ionenes. The ratio of absorbances at 628 nm and 662 nm increases until a discontinuity arises at an  $\text{N}^+/\text{Co}$  ratio of 4, after which further addition of 2,4-ionene does not affect this ratio. A similar spectroscopic behaviour has been determined for the N-heptamer (**1i**) and Br-nonamer (**1g**).

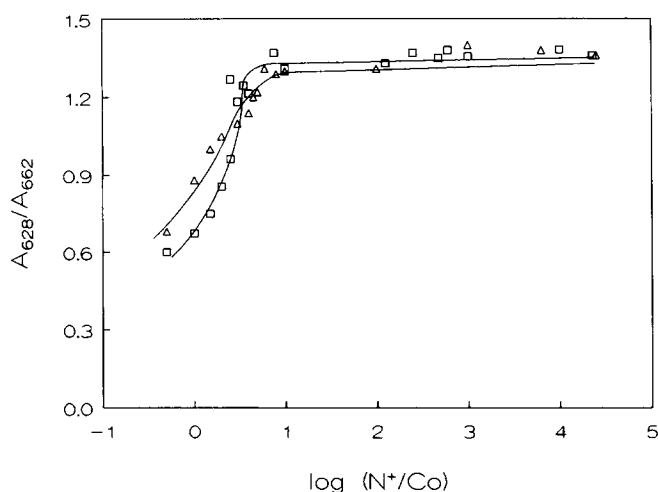


Fig. 5. Ratio of absorbances at 628 nm and 662 nm as a function of the  $N^+/Co$  ratio for Br-pentamer (1f) ( $\Delta$ ) and N-pentamer (1h) ( $\square$ ).  $[CoPc(NaSO_3)_4] = 2 \times 10^{-6} \text{ mol dm}^{-3}$ .

With respect to the formation of a Co-dimer, in principle eight positive charges are required to counterbalance the negative charges of the dimer. At an  $N^+/Co$  ratio of 4, eight positive charges of the ionene just match the opposite charge on the dimeric complex. Until now this was thought to be characteristic of ionene polymers only.<sup>11</sup> Hence, it can be inferred that in the case of trimers, where the relevant distance is at least four methylene groups, and both pentamers, several oligomeric ionene chains collectively contribute to the stabilization of dimers of  $CoPc(NaSO_3)_4$ . Recently, the same effect has also been observed in the phase-transfer catalysed oxidation of 1-dodecanethiol, applying an amphiphilic polystyrene-ionene diblock copolymer as co-catalyst.<sup>14</sup> In the latter system, several 2,4-ionene segments with a block length of four quaternary ammonium groups extending in the water-phase, have been found to cooperatively stabilize the  $CoPc(NaSO_3)_4$  aggregates.

#### Catalytic activity measurements

As reported before, the 2-mercaptoethanol oxidation rate is a function of the co-catalyst concentration.<sup>10</sup> When the catalyst concentration is kept constant and the ionene concentration is varied, a maximum in the activity rises at about  $N^+/Co = 200$  for a high molecular weight 2,4-ionene.<sup>10</sup> Van Streun *et al.* examined two different 2,4-ionenes of molecular weights  $1740 \text{ g mol}^{-1}$  and  $6600 \text{ g mol}^{-1}$ , respectively, and found not only similar maximum catalytic activities, but also identical optimum  $N^+/Co$  ratios for both polymers.<sup>13</sup>

The question now arises whether the monodisperse oligomers of 2,4-ionene will exhibit a similar characteristic behaviour with respect to the optimum  $N^+/Co$  ratio and corresponding catalytic activities. It is already known that the monomeric analogue of 2,4-ionene,

tetramethylammoniumhydroxide, shows no increase in reaction rate compared with the polymer-free system.<sup>26</sup> In addition, Schutten found enhanced catalytic activities at extremely high salt concentrations, where only dimerization occurs and no substrate enrichment takes place, and as a consequence lower reaction rates compared with those when using ionenes were observed.<sup>27</sup>

We measured the oxidation rate as a function of the concentrations of Br-trimer (1a) and N-trimer (1d) (Fig. 6). At very high  $N^+$ -concentrations an optimum is reached for both trimers and the same high reaction rates are achieved. This high reaction rate is attributed to aggregation of the catalyst induced by high trimer concentrations, leading to the same relative amount of  $CoPc(NaSO_3)_4$ -dimers for both trimers. Furthermore, it appears that these high  $N^+$ -concentrations are necessary to achieve substrate enrichment of the thiolate anions in the positively charged oligomer domain.

The effect of varying the  $N^+$ -concentrations in the Br-pentamer (1f) and N-pentamer (1h) promoted mercaptoethanol autoxidation is depicted in Fig. 7. The low activities at low pentamer concentrations are caused by the absence of substrate enrichment, an effect that disappears upon raising the co-catalyst concentration. After an optimum  $N^+/Co$  ratio has been reached, further increase in the pentamer concentration leads to a decrease in activity as a result of a decrease in the local thiolate anion concentration at the catalytically active site and simultaneous competition between bromide and hydroxide counterions on the one hand, and thiolate anions on the other. It can be concluded that apart from a higher optimum  $N^+/Co$  ratio, the pentamers behave like high molecular weight 2,4-ionene.

Additionally, we have determined the oxidation rates as a function of the concentration of N-heptamer (1i), Br-nonamer (1g) and other polymeric 2,4-ionenes, com-

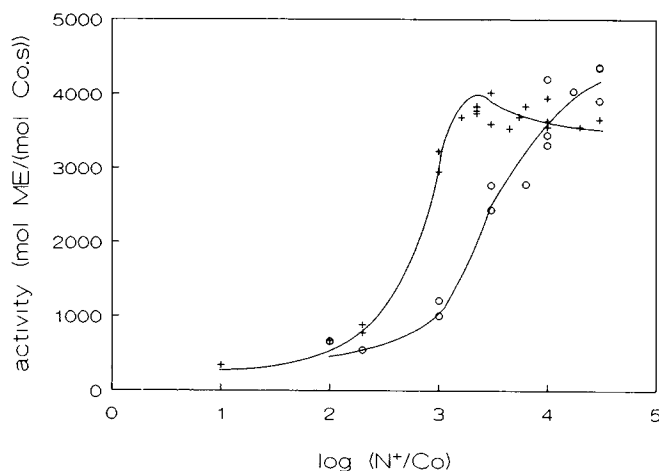
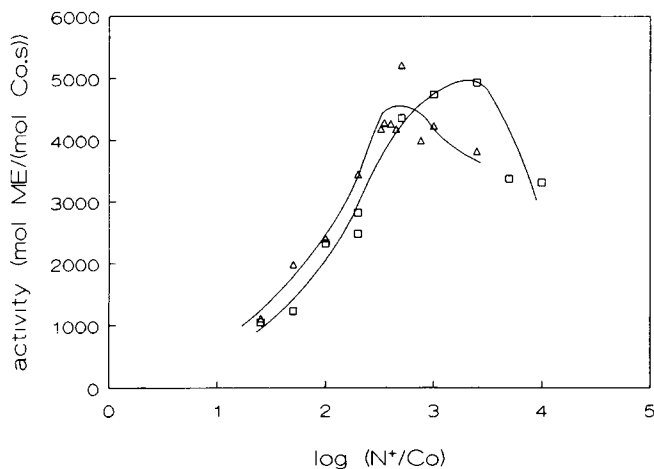
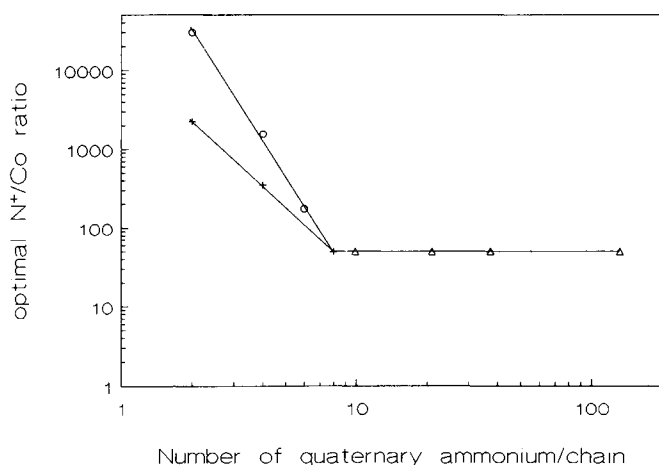


Fig. 6. Effect of  $N^+/Co$  ratio on the thiol oxidation rate.  $[CoPc(NaSO_3)_4] = 2 \times 10^{-7} \text{ mol dm}^{-3}$ ,  $\text{pH} = 9.0$ ,  $[ME] = 0.072 \text{ mol dm}^{-3}$ . (+) Br-trimer (1a); (O) N-trimer (1d).



**Fig. 7.** Effect of  $N^+/Co$  ratio on the thiol oxidation rate.  $[CoPc(NaSO_3)_4] = 2 \times 10^{-7} \text{ mol dm}^{-3}$ ,  $pH = 9.0$ ,  $[ME] = 0.072 \text{ mol dm}^{-3}$ . ( $\Delta$ ) Br-pentamer (**1f**); ( $\square$ ) N-pentamer (**1b**).

prising the whole range of molecular weights given in Table 1. The optimum  $N^+/Co$  ratios of the various polyelectrolytes as a function of the number of quaternary ammonium groups per chain are presented in Fig. 8. Two important conclusions can be drawn from this figure. First, the optimum  $N^+/Co$  ratio is a function of the chain length of 2,4-ionene. This ratio decreases with increase in the polycation length until a value of 50 is reached; this value is already reached for the Br-nonomer (**1g**), with eight positive charges. The higher optimum  $N^+/Co$  ratio for smaller oligomer lengths has to be attributed to the higher  $N^+$ -concentrations necessary to achieve an effective substrate enrichment. Moreover, the tertiary-amino-terminated oligomers show higher optimum  $N^+/Co$  ratios compared with the Br-



**Fig. 8.** Optimum  $N^+/Co$  ratio as a function of number of quaternary ammonium groups per chain.  $[CoPc(NaSO_3)_4] = 2 \times 10^{-7} \text{ mol dm}^{-3}$ ,  $pH = 9.0$ ,  $[ME] = 0.072 \text{ mol dm}^{-3}$ . (+) Br-terminated monodisperse oligomers; (O) N-terminated monodisperse oligomers; ( $\Delta$ ) polymeric 2,4-ionenes.

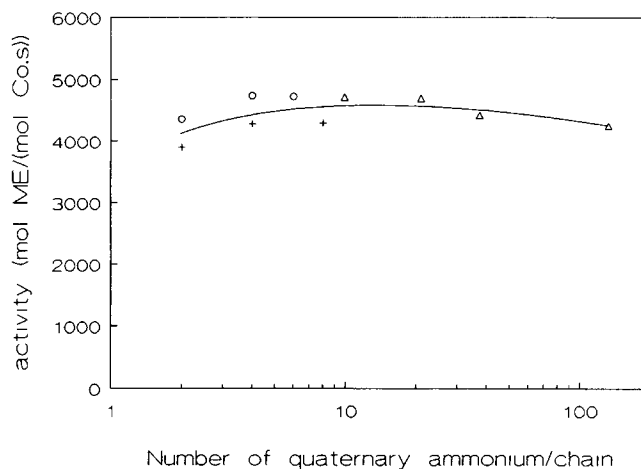
terminated oligomers with an equal number of quaternary ammonium groups. Presumably, in solution the more hydrophobic butyl-bromide end-groups form hydrophobic domains, resulting in higher local oligomer concentrations: hence, more effective substrate enrichment is reached at a lower overall  $N^+$ -concentration. A similar influence of the hydrophobicity of the end-group of the Br-terminated oligomers has been observed in the 1-dodecanethiol oxidation. In that case the Br-terminated trimers and pentamers, in contrast to the N-terminated oligomers, showed a promoting effect as a result of their hydrophobic interaction with the hydrophobic thiol.<sup>28</sup>

The catalytic activities at these optimum  $N^+/Co$  ratios are depicted in Fig. 9. It clearly shows that the maximum reaction rates are nearly independent of the molecular weights of 2,4-ionene oligomers and polymers, and remain practically constant around 4600 mol ME/(mol  $CoPc(NaSO_3)_4$  s). It should be emphasized, however, that this value is 50 times higher than that for the polymer-free system.

#### Kinetics

The  $CoPc(NaSO_3)_4$ -catalysed oxidative coupling of ME gives rise to an enzyme-like kinetic behaviour. Double substrate Michaelis-Menten kinetics have been observed earlier when using cationic polymers as co-catalysts.<sup>29</sup> In the present investigation we have compared the kinetic behaviour of a Br-pentamer (**1f**) with that of a high molecular weight 2,4-ionene.

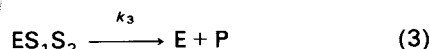
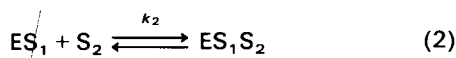
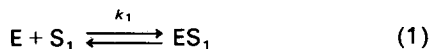
In order to study intrinsic kinetics mass transfer limitations have to be ruled out. The linear dependence of the catalytic activity on the catalyst concentration



**Fig. 9.** Maximum catalytic activities at the optimum  $N^+/Co$  ratios as a function of the number of quaternary ammonium groups per chain.  $[CoPc(NaSO_3)_4] = 2 \times 10^{-7} \text{ mol dm}^{-3}$ ,  $pH = 9.0$ ,  $[ME] = 0.072 \text{ mol dm}^{-3}$ . (+) Br-terminated monodisperse oligomers; (O) N-terminated monodisperse oligomers; ( $\Delta$ ) polymeric 2,4-ionenes.

( $N^+/Co$  ratio is constant for the Br-pentamer (**1f**) (Fig. 10)) clearly indicates the absence of mass transfer limitations in the present case.

The kinetics of the oxidative coupling of ME can be described as a two-substrate Michaelis–Menten kinetic model,<sup>8</sup> as presented in Scheme 1.



Scheme 1

with  $E = CoPc(NaSO_3)_4$ ,  $S_1 = ME$ ,  $S_2 = O_2$ , and  $P = 2,2'$ -dithiodiethanol. At a constant oxygen concentration the rate of thiol oxidation ( $R$ ) is given by

$$R = \frac{k'[CoPc(NaSO_3)_4][ME]}{K'_M + [ME]} \quad (4)$$

with  $k' = 4(k_3[O_2])(C_2 + [O_2])$ , the minimum turnover frequency for thiol conversion, at 0.1 MPa  $O_2$  and saturation in thiol,  $K'_M = (C_2[O_2] + C_4)/(C_3 + [O_2])$  the apparent Michaelis constant,  $C_2 = (k_{-2} + k_3)/k_2$ ,  $C_3 = k_3/k_1$ ,  $C_4 = k_{-1}/k_1$ . The dependence of reaction rate on the thiol concentration at optimum pH and  $[N^+]$  conditions is depicted in Fig. 11 for the Br-pentamer (**1f**) and two 2,4-ionenes with number-average molecular weights of 6200 and 22000  $g\ mol^{-1}$ , respectively. Saturation behaviour typical of enzyme-like kinetics can be observed. Minimum turnover frequencies and apparent Michaelis constants were determined from the Lineweaver–Burk plots (Fig. 12). These constants, indicative of the activity of the catalytic system, are listed in Table 2. As can be seen, no large discrepancies can be detected between the different ionenes, so it can be con-

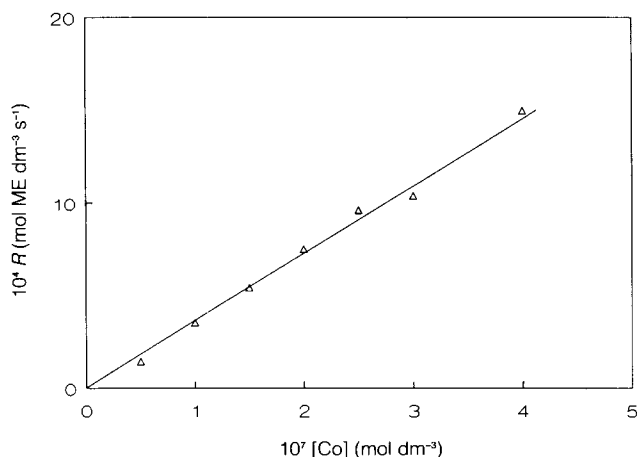


Fig. 10. Reaction rate as a function of the catalyst concentration at constant  $N^+/Co$  ratio.  $N^+/Co = 350$ ,  $pH = 9.0$ ,  $[ME] = 0.072\ mol\ dm^{-3}$ ; ( $\Delta$ ) Br-pentamer (**1f**).

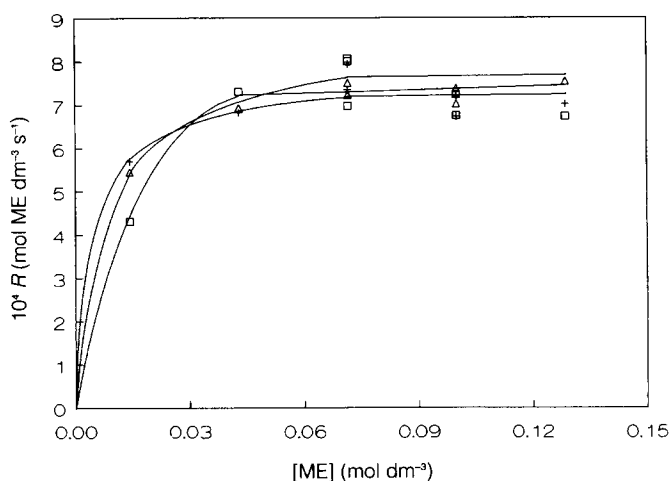


Fig. 11. Catalytic activity as a function of substrate (ME) concentration.  $[CoPc(NaSO_3)_4] = 2 \times 10^{-7}\ mol\ dm^{-3}$ ,  $pH = 9.0$ ,  $[ME] = 0.072\ mol\ dm^{-3}$ . ( $\Delta$ ) Br-pentamer (**1f**)  $[N^+] = 7 \times 10^{-5}\ mol\ dm^{-3}$ ; (+) 2,4-ionene ( $\bar{M}_n = 6200\ g\ mol^{-1}$ )  $[N^+] = 10^{-5}\ mol\ dm^{-3}$ ; ( $\square$ ) 2,4-ionene ( $\bar{M}_n = 22000\ g\ mol^{-1}$ )  $[N^+] = 10^{-5}\ mol\ dm^{-3}$ .

cluded that the mechanism of the 2,4-ionene promoted catalytic oxidation of ME is independent of the polymer chain length.

The insight acquired on the minimum critical chain length provides the basis for the preparation of ideal diblock copolymers, with well-defined block lengths, that will act as effective promoters in the phase-transfer catalysed oxidation of 1-dodecanethiol. Until now it was assumed that it was essential to apply long and flexible ionene chains in order to stabilize the active aggregates of the catalyst. This concept has to be amended in the case of mercaptoethanol autoxidation, since a number of short oligomeric ionene chains are also capable of stabilizing the  $CoPc(NaSO_3)_4$  aggregates. On the other hand, in immobilized systems, for example lattices carrying catalytic groups, it might still

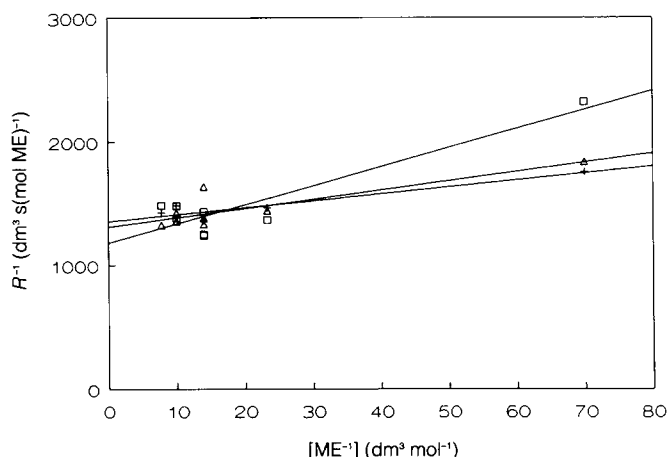


Fig. 12. Lineweaver–Burk plots of the catalytic systems under study. For experimental conditions see Fig. 11.



**TABLE 2. Minimum turnover frequencies and apparent Michaelis constants of the catalytic systems under study. Experimental conditions as in Fig. 11**

	$\bar{M}_n$ (g mol <sup>-1</sup> )	$k'_2$ (mol ME (mol CoPc(NaSO <sub>3</sub> ) <sub>4</sub> s) <sup>-1</sup> )	$10^3 K'_M$ (mol ME dm <sup>-3</sup> )
Br-pentamer (1f)	880	3750	5.4
2,4-ionene	6200	3700	4.1
2,4-ionene	22000	4150	12.4

be required to have long cationic tails. In those cases it will be more difficult for fixed short chains to contribute collectively to the stabilization of catalytically active aggregates, especially when the N<sup>+</sup>-concentration at the latex surface is low.

## CONCLUSIONS

Visible light spectroscopy experiments showed aggregation of CoPc(NaSO<sub>3</sub>)<sub>4</sub> when using relatively low molecular weight 2,4-ionene. Trimeric oligomers, in which the two positive charges are separated by at least four methylene groups, induced aggregation in a way similar to that occurring in high molecular weight 2,4-ionene. The optimum N<sup>+</sup>/Co ratio is very high for the smaller oligomers, because only at those high values can effective substrate enrichment be achieved. The hydrophobicity of the end-groups of the oligomers plays an important role in attaining the optimum co-catalytic activity. It may be inferred that the formation of hydrophobic domains, consisting of butyl-bromide end-groups, shifts the optimum N<sup>+</sup>/Co ratio of the Br-terminated oligomers to lower values. The final co-catalyst activity at optimum N<sup>+</sup>/Co ratio is very high for all 2,4-ionenes and is independent of molecular weight and type of end-group.

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