EFFECTS OF 2,4-IONENES OF DIFFERENT MOLAR MASSES ON THE OXIDATIVE COUPLING OF THIOL CATALYZED BY COBALTPHTHALOCYANINE

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Abstract—A photometric method is developed for the determination of the molar mass of 2,4-ionene by attaching a chromophoric moiety to its end-groups. Molar mass determination of these polyelectrolytes by acid–base titration of the amine end-groups is also possible, and confirms the photometric method. The effects of molar mass of 2,4-ionenes on the oxidative coupling of 2-mercaptoethanol (ME) was studied in the presence of cobalt(II)phthalocyanine-tetra-sodium-sulphonate (CoTSPc). Monomeric analogues of 2,4-ionene showed no increase of reaction rate as compared with the polymer-free system. However, relatively low molar mass ionene ($\bar{M}_n = 1740$) showed a dramatic increase of reaction rate. The reactivity showed an optimum around pH = 8. Saturation kinetics (Michaelis–Menten kinetics) were observed. The calculated turnover number was 3200 sec^{-1} and 3600 sec^{-1} for $\bar{M}_n = 6600$ and $\bar{M}_n = 1740$, respectively. The stoichiometry of the reaction was disturbed at low thiol concentration.

INTRODUCTION

We have studied the effect of cationically charged polymers on the so-called Merox-process i.e. the oxidative coupling of thiols to disulphides in the presence of the catalyst, cobalt(II)phthalocyanine-tetra-sodium sulphonate (CoTSPc, **1**, Scheme 1)

activity [2, 3]. Two major effects are believed to cause this phenomenon: (1) coulombic interaction between the negative charge of the sulphonate groups of CoTSPc and the positive charge on the polymer
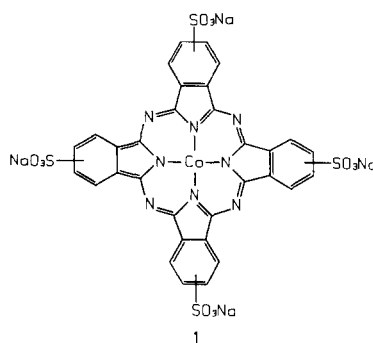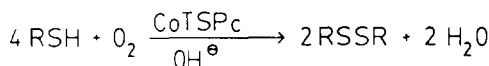
Scheme 1. Conventional (polymer free) thiol oxidation.
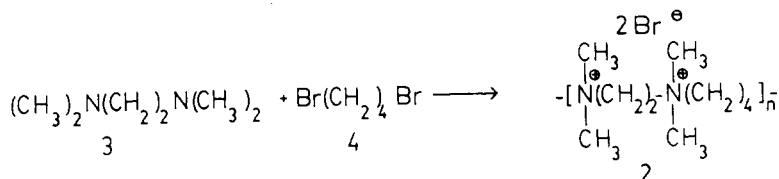
Scheme 2. Synthesis of 2,4-ionene.

[1, 2]. Especially poly(vinylamine) (PVAm) and 2,4-ionene, a poly(quaternary ammonium) salt (**2**, Scheme 2) were found to give a surprisingly high increase in reaction rate. Experiments showed that an increase of the positive charge density on the polymer chain resulted in an enhancement of the catalytic

backbone and (2) an increase of the degree of dissociation of the thiol in the cationically charged polymer domain, resulting in a locally enhanced thiolate anion concentration. In the case of PVAm also coordinative binding between the metal complex

and the polymer is assumed to occur [4, 5] and Michaelis–Menten kinetics in thiol and oxygen have been observed [6]. The reaction rates with both PVAm and 2,4-ionene showed an optimum around pH = 8 [2, 7], caused by two opposing effects on increasing the pH, viz. an increase of thiolate anion concentration and an increase of ionic strength. In the case of PVAm the collapse of the catalytic activity above the pH-optimum is also due to loss of polymer charge (deprotonation). Most interestingly, a molar mass dependence of the catalytic activity was observed in the case of PVAm [8]. Therefore, we describe in this paper our investigations on molar mass dependence of the catalytic activity and kinetics of ionene containing systems. The synthesis of 2,4-ionene involves a step reaction of *N,N,N',N'*-tetramethylethylenediamine (TMEDA, **3**) with 1,4-dibromobutane (**4**) (Scheme 2). In the literature, molar masses of these types of polymers have been determined by viscometry, light scattering and ultracentrifugation [9–11]. However, these methods are often complicated and laborious, due to the polyelectrolytic character of these polymers. Therefore, in this paper we present two relatively simple methods of determining molar masses of 2,4-ionenes, both based on the determination of amine end-groups of aminated 2,4-ionenes. The first method measures the

of the activity and kinetics of catalytic systems based on 2,4-ionene.

EXPERIMENTAL

All chemicals and solvents were used as purchased unless mentioned otherwise. TMEDA, 1,4-dibromobutane and 2-mercaptoethanol were obtained from Fluka.

Synthesis of 2,4-ionene

2,4-Ionenes were synthesized according to the method of Rembaum *et al.* [9] with a few modifications. The reaction conditions were adapted in such a way as to accomplish the complete solution of the resulting polymer throughout the reaction.

A typical experiment: 4.063 g TMEDA (**3**) and 7.560 g 1.4-dibromobutane (**4**) (Scheme 2) were dissolved in 70 g water–dimethylformamide (DMF) (1/1, w/w) and placed in a waterbath at 40°C under N_2. After two or more days an excess of TMEDA was added to the reaction mixture in order to aminate the product. After two more days, the reaction mixture was precipitated in acetone. After filtration and washing with acetone, the product (**5**, Scheme 3) was dried under reduced pressure (0.1 kPa) at 50°C. Yields, determined by mass were between 90 and 100%. In order to obtain higher molar masses, reaction times (2–14 days), temperature (20–60°C) and solvent combinations [e.g. DMF/methanol (1/1, w/w) and DMF/water (4/1, w/w)] were varied. However, the use of these solvent combinations appeared to carry the risk of precipitation of polymer as polymerization proceeds.
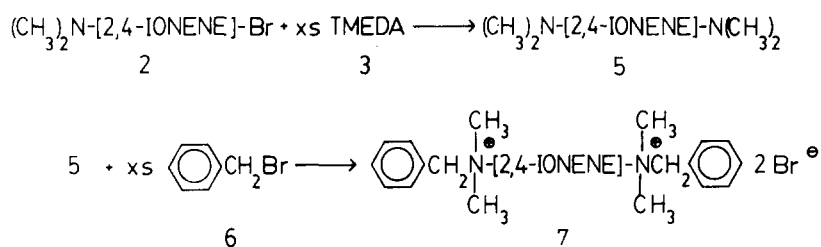
Scheme 3. Amination and benzylation of 2,4-ionene.
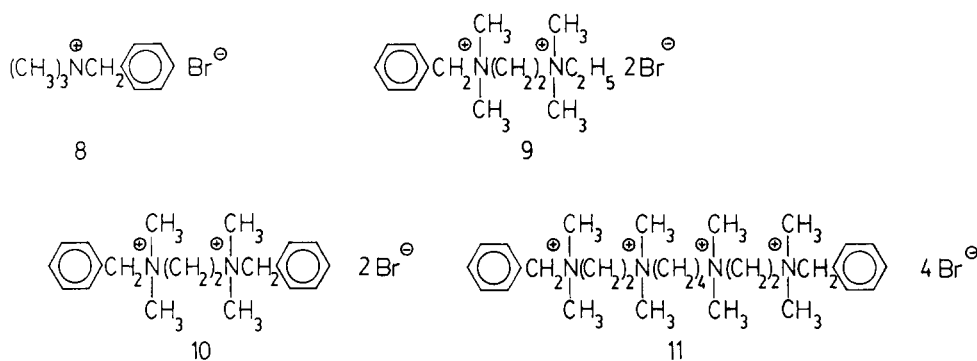
Scheme 4. Chemical structure of compounds used in Table 1.

u.v.-absorbance of a chromophore (a benzylic group), chemically bonded to the amine end-groups. The second method determines the amount of amine end-groups by direct acid–base titrations. These methods will be shown to be sufficiently accurate to determine the relatively small molar mass dependence

Determination of molar mass

Photometric method. The aminated 2,4-ionene (**5**) was reacted with an excess of benzylbromide (**6**) (Scheme 3) in DMF/water (1/1, w/w) at 40°C under N_2 for two days. The product work-up was similar to that used for the aminated 2,4-ionenes. The u.v.-spectra were measured with a Hewlett–Packard 8451A diode array spectrophotometer at

25°C in a 0.4 M NaCl solution at $\lambda = 264$ nm. The slope of the plot of absorbance vs concentration of ionenes (in g/dm^3) gives the absorptivity (a, in 10 dm^2·g^{-1}).

Titration method. Titration of the aminated 2,4-ionenes was carried out in a 0.4 M NaCl solution under N$_2$. A 0.1 M HCl (Merck, Titrisol) solution was added until pH $\simeq$ 3 was reached. Then this solution was titrated with a 0.01 M NaOH solution (Merck, Titrisol). The pH was monitored with a combi-electrode (Radiometer, GK 2401B) connected to a digital pH meter (Radiometer PHM 82). From the equivalence points and the total mass of 2,4-ionene, the molar mass can be calculated.

Catalytic experiments. CoTSPc was synthesized by the method described by Weber and Bush [12]. The substrate, 2-mercaptoethanol (Scheme 1. R = CH$_2$CH$_2$OH, abbreviated as ME), was distilled before use. Activity measurements were carried out at constant O$_2$ pressure in an all-glass double-walled Warburg apparatus, equipped with a powerful mechanical glass stirrer. The stirring speed was maintained at 2500 rpm during the reaction. The Warburg apparatus was further equipped with a pH-electrode (Radiometer GK 2401B). The catalyst was prepared by adding an aqueous solution of CoTSPc to the reactor containing an aqueous ionene solution. Adjustments of pH were accomplished by adding minor amounts of a 0.01 M NaOH solution (Merck, Titrisol). The mixture was degassed twice and saturated with O$_2$. During the reaction the temperature was maintained at 25°C and the O$_2$ pressure at 100 kPa. After injecting ME into the reactor, a drop of pH was observed due to the acidity of the thiol. The oxygen uptake rate was monitored with a digital flowmeter (Inacom). The initial reaction rates were determined as the maximum oxygen consumption. The total reaction volume was 0.1 dm^3. The peroxide content of the reaction mixture was determined by iodometry as described by Vogel [14].

RESULTS AND DISCUSSION

Determination of the molar mass of 2,4-ionene by measuring the u.v.-absorbance of a chemically bonded chromophore (benzylbromide, 6, Scheme 3) requires the value of the molar absorptivity (ϵ, in 10 dm^2·mol^{-1}) of the chemically bonded benzylbromide. In addition, it should be proved experimentally that ϵ is independent of the length of the attached 2,4-ionene chain. In Table 1, where some chromophoric analogues of 2,4-ionene are listed, it is shown that ϵ is relatively insensitive to the chain length. We have chosen compound 11 as reference compound. From Lambert–Beer's law is follows that

$$M_{pol} = \epsilon_{ref}/a_{pol}$$

where M_{pol} is the molar mass of aminated 2,4-ionene (including its chromophoric end-groups) and a_{pol} is the absorptivity of the unknown ionene, calculated from the slope of the absorbance vs concentration curve (c in g·dm^{-3}). The latter measurement requires that 2,4-ionene is first aminated with TMEDA (3) leading to (5) and then reacted with the chromophore

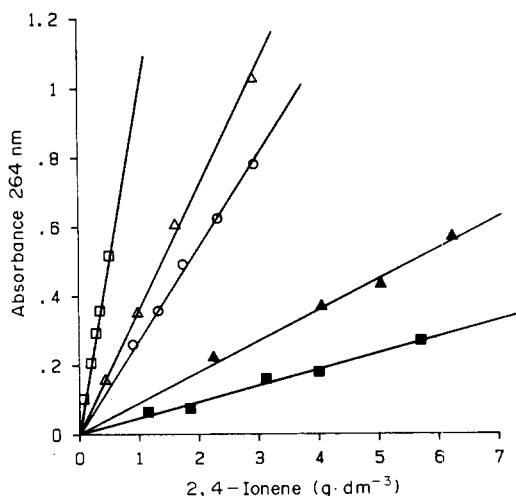Fig. 1. Absorbance ($\lambda = 264$ nm) vs concentration of the modified 2,4-ionene (g dm^{-3}) at 25°C, [NaCl] = 0.4 mol·dm^{-3}. □: Reference compound; △: $\bar{M}_n = 1800$; ○: $\bar{M}_n = 2750$; ▲: $\bar{M}_n = 8800$; ■: $\bar{M}_n = 16,600$.

benzylbromide (6) (Scheme 3). The calculated molar mass minus the molar mass of the benzylbromide groups gives the molar mass of the aminated 2,4-ionene. As in fact the total number of end-groups is measured, the calculated molar mass is the number-average molar mass ($\bar{M}_n$). Figure 1 shows absorbance vs concentration curves for several modified 2,4-ionenes. The linearity of the curves proves an important prerequisite, i.e. that Lambert–Beer's law is obeyed in the present case. An alternative method of determining the amount of end-groups of aminated 2,4-ionenes is acid–base titration. The molar mass calculated in this manner is again the number-average quantity and can therefore be compared with the results of the photometric method (Table 2). The two methods are in good agreement although the relative discrepancy tends to increase toward higher molar mass. The calculated molar masses of the ionenes, though relatively low, lie within the range of data reported in literature [9, 11].

Catalytic experiments. Figure 2 shows reactivity vs pH for 2,4-ionenes of different number-average molar mass ($\bar{M}_n = 1740$ and $\bar{M}_n = 6600$). Both curves show a broad maximum around pH = 8. The curves indicate an all-over lower activity for $\bar{M}_n = 6600$. The pH optimum suggests a dependence of the reactivity on the local thiolate anion concentration (pK_a (ME) = 9.6 [13]). The moderate decrease of reactivity above pH = 8 is thought to be caused by an increase of ionic strength of the reaction mixture, including competitive ion effects (RS$^-$ and OH$^-$). This effect is

Table 1. Molar absorptivity (ϵ) of various ionene analogues at $\lambda = 264$ nm (Scheme 4)

Compound	M	ϵ (10 dm^2·mol^{-1})
8	230	352
9	396	344
10	458	778*
11	790	761*

*Two chromophoric groups per molecule.

Table 2. Comparison between molar mass ($\bar{M}_n$) of aminated 2,4-ionenes determined by the photometric and titration methods

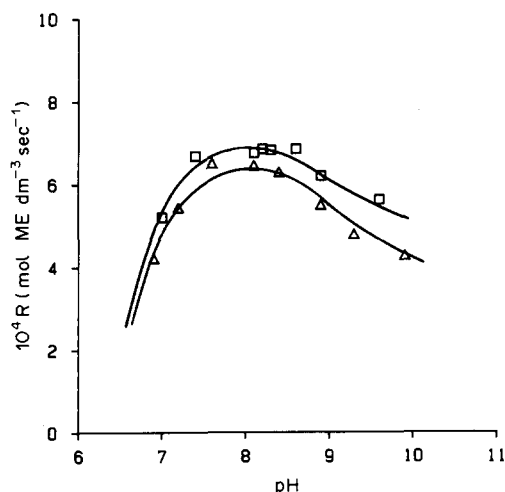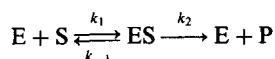| Photometric	Titration
1810	1740
2650	2750
8800	10,100
16,600	18,300

Fig. 2. Dependence of catalytic activity on pH
[CoTSPc] = 2×10^{-7} mol·dm^{-3}; [ME] = 0.14 mol·dm^{-3};
[ME] = 0.14 mol·dm^{-3}, [N$^+$] = 10^{-3} mol·dm^{-3}, 25°C. □:
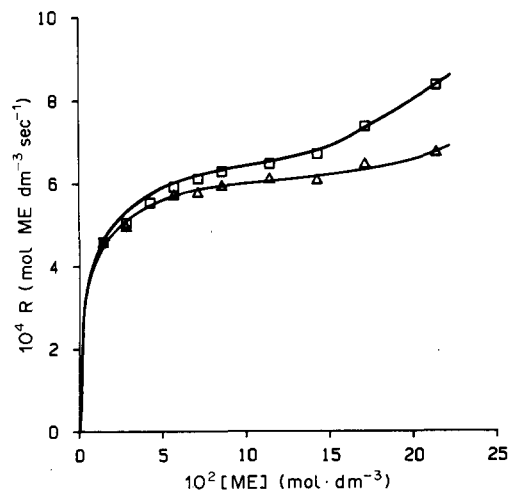$\bar{M}_n$ = 1740; △: $\bar{M}_n$ = 6600.

Fig. 3. Catalytic activity as a function of the substrate
(2-mercaptoethanol) concentration. [CoTSPc] = $2 \times$
10^{-7} mol·dm^{-3}, pH = 8.2 [N$^+$] = 10^{-3} mol·dm^{-3}; 25°C,
□: $\bar{M}_n$ = 1740; △: $\bar{M}_n$ = 6600.

less pronounced than in the case of PVAm [2]. The latter can be explained by the fact that PVAm in contrast to the ionenes suffers from coil deprotonation as pH increases [8]. The reactivity of the monomeric analogues of 2,4-ionene and the conventional system (without polymer) are listed in Table 3. Comparing reaction rates in Table 3 and Fig. 2, it can be seen that a minimum cationic charge density on the polymer backbone is required to increase catalytic activity. Similar molar mass dependence was observed for PVAm [8]. Only a few quaternary ammonium groups are involved in binding the cobalt complex to the polymer backbone. The residual quaternary ammonium groups of the backbone are available to create a cationic polymer domain thus increasing the local thiolate anion concentration. For PVAm, the dependence of the reaction rate on thiol concentration can be described by Michaelis–Menten kinetics [6]:

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

in which E stands for catalyst (CoTSPc), S for substrate (mercaptoethanol) and P for products (disulfide). It can be derived that

$$R = \frac{k_2[E_0][S]}{K_M + [S]}$$

which can be rewritten as

$$R^{-1} = (k_2 \cdot [E_0])^{-1} + K_M(k_2 \cdot E_0)^{-1} \cdot [S]^{-1}$$

where R stands for the reaction rate (expressed in mol ME·dm^{-3}·sec^{-1}), K_M for the Michaelis constant $[(k_{-1} + k_2)/k_1]$ and [E_0] for the initial catalyst concentration. K_s is the substrate binding constant $(k_1/k_{-1}) \cdot k_2$ is also called the turnover number (dimension sec^{-1}) In Fig. 3 the reactivity is plotted vs the thiol concentration. It appears that a plateau is reached at relatively low thiol concentration, whereas deviations from saturation behaviour are observed for high thiol concentrations (>0.15 mol·dm^{-3}). Any possible deviation from Michaelis–Menten kinetics should manifest itself in the non-linearity of the so-called Lineweaver–Burk plot, i.e. a double reciprocal plot of reactivity vs thiol concentration as shown in Fig. 4. In spite of some non-linearity, it seems justified to draw some major conclusions from these curves. From the slope, the turnover number and Michaelis constant can be estimated, both are listed in Table 4. Assuming that $k_2 \ll k_{-1}$ i.e.

Table 3. Reactivity of some monomeric analogues of 2,4-ionene, and of the conventional system. Conditions are as follows: pH = 8.2; [CoTSPc] = 2×10^{-7} mol·dm^{-3}; [ME] = 0.14 mol·dm^{-3}; [N$^+$] = 10^{-3} mol·dm^{-3} (except for the conventional system); 25°C

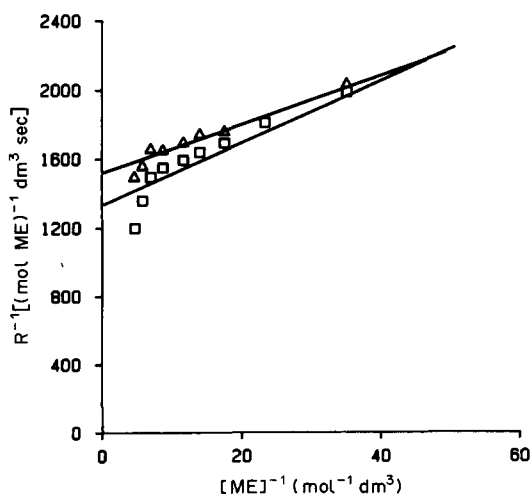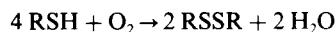| System	10^4 Reaction rate (mol ME dm^{-3}·sec^{-1})
Tetra methylammonium-hydroxide	0.29
N,N'-diethyl-N,N,N',N'-tetramethyl ethylene diammonium dibromide	0.29
OH$^-$ (conventional)	0.27

Fig. 4. Lineweaver–Burk plot. Reaction conditions as for Fig. 3.

Table 4. Comparison between the turnover numbers (k_2) and Michaelis constants (K_M) of 2,4-ionene and PVAm containing systems. Reaction conditions are as in Table 3

	k_2 (sec^{-1})	$10^3 \cdot K_M$ (mol·dm^{-3})
2,4-ionene $\bar{M}_n = 1740$	3700 ± 200	11.3 ± 2.3
$\bar{M}_n = 6600$	3300 ± 200	6.8 ± 1.4
PVAm $\bar{M}_n = 3 \times 10^4$	2800 ± 200	90.0 ± 20

$K_M \simeq K_s^{-1}$, the smaller Michaelis constants for the ionenes indicate a stronger substrate binding as compared with PVAm. The reactivity vs the cobalt complex concentration is shown in Fig. 5. The observed linearity indicates the absence of mass transport limitations (identical reaction conditions were used). The slopes of the curves, i.e. the turnover numbers, are 3600 sec^{-1} and 3200 sec^{-1} for $\bar{M}_n = 1740$ and $\bar{M}_n = 6600$, respectively, and confirm the k_2 data from the Lineweaver–Burk plots. The effect of ionene concentration on the catalytic activity is shown in Fig. 6. The ionene concentration is expressed as [N$^+$], calculated from the nitrogen content of 2,4-ionene determined by elemental analysis (i.e. 8.37%). Apparently, a minimum ionene concentration is required to enhance the reaction rate. As expected, further increase of the ionene concentration will diminish the thiolate anion concentration locally, i.e. around the active centre. In Scheme 1 the overall reaction equation is presented, which according to earlier work in our laboratory [6] results from:

$$2 \text{ RSH} + O_2 \rightarrow \text{RSSR} + H_2O_2 \qquad (a)$$

$$\underline{2 \text{ RSH} + H_2O_2 \rightarrow \text{RSSR} + 2H_2O} \qquad (b)$$

$$4 \text{ RSH} + O_2 \rightarrow 2 \text{ RSSR} + 2 H_2O$$

The stoichiometry of the reaction can be checked by measuring the peroxide content after the reaction by iodometry [14]. The results are listed in Table 5. The high residual peroxide content (relative to the initial thiol content) at low thiol concentration is very striking. Apparently, under these conditions, the thiol
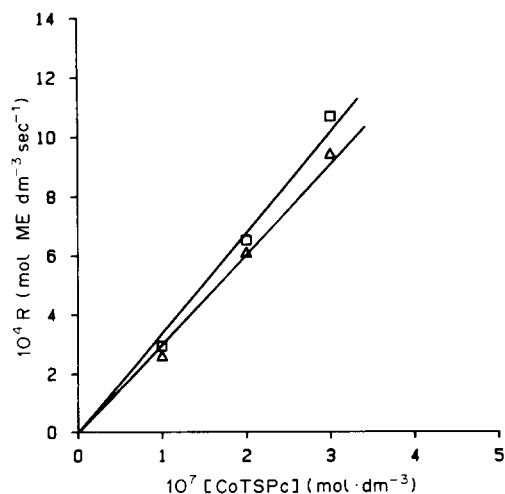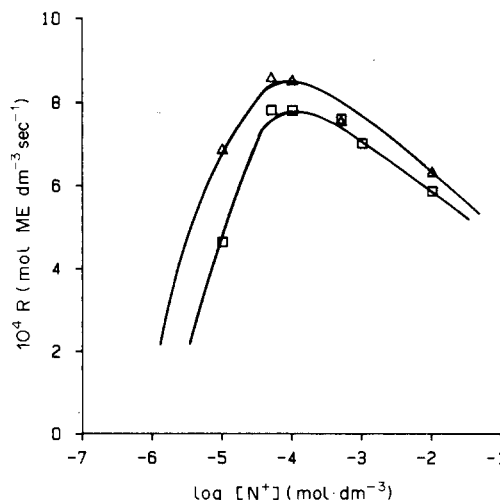

Fig. 6. Catalytic activity vs ionene concentration (expressed in [N$^+$], see text), pH = 8.2; [CoTSPc] = 2×10^{-7} mol·dm^{-3}, [ME] = 0.14 mol·dm^{-3}, 25°C, □: $\bar{M}_n = 1740$; △: $\bar{M}_n = 6600$.

and peroxide concentrations in the bulk are too low for the second oxidation step (b) to occur. This unfortunately effects the stoichiometry of the reaction. The observed (apparent) reaction rate, as calculated from the measured oxygen uptake and the assumed stoichiometry of the overall reaction, will be higher than the "true" reaction rate based on thiol conversion, in particular at low thiol concentrations. This will influence the Lineweaver–Burk plot in such a way that the "true" constants, k_2 and K_M, will be smaller and greater, respectively, than the calculated (apparent) ones. These deviations are negligible at thiol concentrations used throughout the present kinetic investigation, i.e. 0.14 mol·dm^{-3}.

CONCLUSIONS

The photometric and titration techniques correspond well and are satisfactory methods of determining the molar mass of 2,4-ionene. The latter polyelectrolyte shows a behaviour similar to PVAm in the catalytic oxidation of thiols in the presence of CoTSPc. Advantages of the ionene containing system over the PVAm containing system are: (1) larger turnover numbers (3200–3600 sec^{-1}), (2) smaller Michaelis constants [(6.8–11.3) × 10^{-3} mol·dm^{-3}] indicative of a stronger substrate-binding, and (3) a pH independent cationic charge on the polymer backbone, providing high activity over a wider pH range. Monomeric analogues of 2,4-ionene showed no increase of the catalytic activity as compared with

Fig. 5. Catalytic activity vs CoTSPc concentration. [N$^+$] = 10^{-3} mol·dm^{-3}; pH = 8.3, [ME] = 0.14 mol·dm^{-3}; 25°C, □: $\bar{M}_n = 1740$; △: $\bar{M}_n = 6600$.

Table 5. Residual peroxide content of the reaction mixture. Reaction conditions as described in Table 3

RSH (mol)	$\bar{M}_n = 1740$ H$_2$O$_2$ (mol)	% a*	$\bar{M}_n = 6600$ H$_2$O$_2$ (mol)	% a*
1.4 × 10^{-3}	5.63 × 10^{-4}	79.5	5.12 × 10^{-4}	73.2
1.4 × 10^{-2}	5.35 × 10^{-4}	7.6	4.41 × 10^{-4}	6.3
2.1 × 10^{-2}	2.56 × 10^{-4}	2.4	2.60 × 10^{-4}	2.5

*Percentage of thiol reacting with oxygen only, i.e. thiol consumption during the first step (a).

the conventional (polymer-free) system. However, relatively low molar mass ionene ($\bar{M}_n = 1740$) appeared to enhance the reaction rate dramatically. Evidently, a minimum cationic charge density on the polymer backbone is necessary to induce the observed rate accelerations. The residual peroxide content at low thiol concentration, as determined by iodometry, is relatively high, indicating that the assumed overall stoichiometry of the reaction is disturbed at low thiol concentration.

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