Polymer–metal complexes, based on poly(itaconic acid ester) derivatives, as catalysts for the decomposition of hydrogen peroxide

J. M. G. Cowie and N. M. A. Wadi
Department of Chemistry, University of Stirling, Stirling FK9 4LA, Scotland
(Received 15 October 1984)

Poly(methyl itaconates) and poly(heptyl itaconates), modified with ethylene diamine (EN) and tetraethylene pentamine (TETRAEN) side chains, were complexed with cobalt and copper ions, and their efficiencies as catalysts for the decomposition of hydrogen peroxide were assessed. All the polymer complexes studied were found to be active catalysts, but it was observed that the polymers with TETRAEN side chain, when complexed with $CoCl_2$ and $CuCl_2$ were less efficient than polymers with EN side chains which were complexed with *trans*-dichlorobis(ethylenediamine) cobalt(III) chloride, *trans*-$[Co(EN)_2Cl_2]Cl$. One feature of interest was that when the alkyl side chain of the poly itaconate was heptyl the rate of decomposition of hydrogen peroxide was faster than when the alkyl group was methyl.

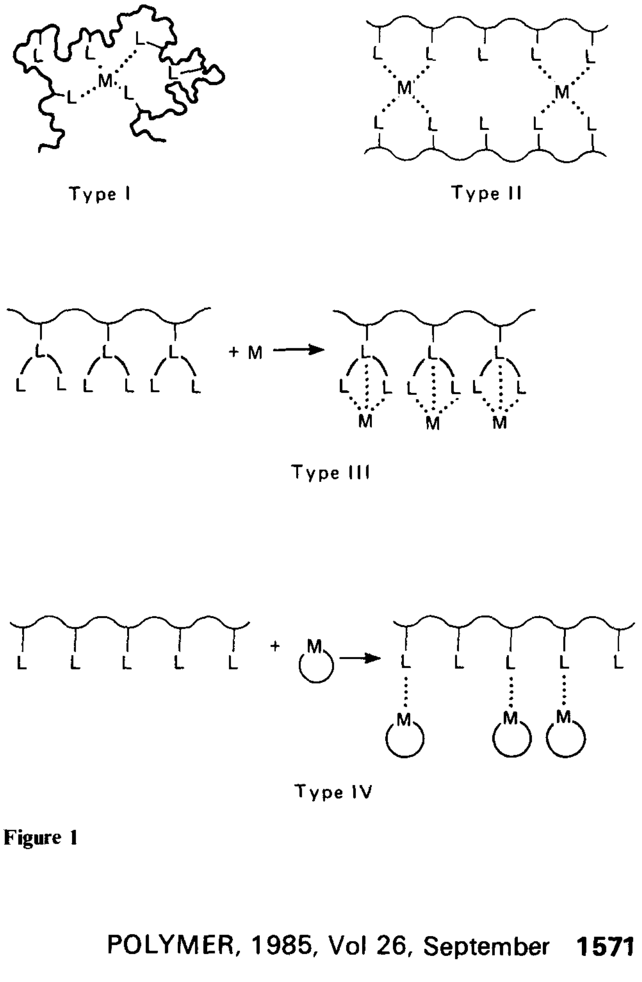
(Keywords: polymer–metal complexes; catalysis; poly(alkyl itaconate); hydrogen peroxide decomposition)

INTRODUCTION

The synthesis of poly(alkyl itaconates) with pendant ethylene amine chains, $-NH(CH_2CH_2NH)_xH$ where $x = 1, 2, 3$ and 4, and their interaction with some metal ions to form polymer metal complexes have been described in previous publications[1,2]. The binding of metal ions by polymer ligands is certainly one aspect of interest and the ion binding power of polystyrene, modified with similar ethylene amine groups, has also been reported by Shambu *et al.*[3]. There is, however, a second and perhaps more intriguing area to explore, namely the ability of many of these complexes to promote or catalyse certain types of reaction. Thus cobalt(III) and chromium(III) complexes attached to poly(vinyl pyridine) can promote the oxidative coupling of phenols[4]. Thio salts can be oxidized[5] by copper(II) chelates of poly(4-vinyl pyridine); cobalt(II) phthalocyanine complexes bound to poly(vinylamine) catalyse thiol oxidation[6] and iron(III) phthalocyanine complexes attached to polystyrene have catalase-like activity[7]. These are only a few examples in what is a constantly expanding field of study. Consequently, it was decided to test some of the polymer–metal complexes formed previously and to prepare others.

Several general types of polymer–metal complex can be distinguished in which the ligands are pendant to the main chain and examples of these are shown schematically in *Figure 1*. Type I and type II complexes are similar in that single ligand binding sites occur spaced along the polymer chain and complexing can then take place either by inter- or intramolecular binding of the metal ion or indeed both may occur. For chains with multicentred ligands, not necessarily of the conformation shown schematically as type III, binding of the metal may involve only one ligand or several and again crosslinking is possible. The polyitaconate ligands reported previously[2] were both single and multicentred and in the latter there was evidence of significant crosslinking in the systems.

The type IV polymer–metal complexes are distinguishable from the type I and type II only in so far as the metal is introduced as a preformed complex, normally with only one labile binding site, which can be attached singly to a pendant polymer ligand. In some cases the preformed complex can be attached to a monomer which is subsequently polymerized to give the polymer catalyst[9], but it



Type I
Type II
Type III
Type IV

Figure 1

0032-3861/85/101571-04$03.00

is also possible to attach it directly to the poly ligand although the efficiency may not be 100%.

The decomposition of hydrogen peroxide is a convenient model reaction to use for the testing of certain types of catalyst, and it is known that the complex *trans*-dichlorobis(ethylenediamine) cobalt(III) chloride acts as a catalyst for this system. As this can be used with the appropriate polyitaconate ligand structure to form a type IV complex, it should provide an interesting comparison with any catalytic potential the type III complexes might have.

EXPERIMENTAL

Preparation of polyligands

Copolymers based on alkyl esters of itaconic acid were prepared as described previously[9]. Two samples were derived from poly(monomethyl-co-dimethyl itaconate) containing 10.5 mol% of the monoester; the first (PMI–EN) was fully substituted with ethylene diamine (EN) and in the second (PMI–TETRAEN) the modification of the acid groups was with tetraethylenepentamine (TETRA–EN). A second series was prepared using poly(mono-n-heptyl-co-di-n-heptyl itaconate) with 13 mol% of the monoester units in the chain, which were modified with EN (PHpI–EN) and TETRA–EN (PHpI–TETRAEN).

Polymer–metal complex formation (Type III)

The samples modified with TETRA–EN were dissolved in chloroform and solutions of copper(II) chloride or cobalt(II) chloride in (1:1) mixtures of methanol and chloroform were added. The mixtures were stirred for 24 h then the complexes were isolated by precipitation with methanol. These will be referred to as type III complexes. In the case of the polymer–copper(II) complex, the colour was blue, whereas the polymer–cobalt(II) complex was red.

Preparation of trans-*dichloro(bisethylenediamine) cobalt(III) chloride,* trans-$[Co(EN)_2Cl_2]Cl$

The synthetic procedure used was that described by Krishnamurthy[10].

Preparation of complexes from polymer and trans-$[Co(EN)_2Cl_2]Cl$

Two polymer complexes were prepared by reacting *trans* $[Co(EN)_2Cl_2]Cl$ with (PMI–EN) and (PHpI–EN). The polyligand was dissolved in chloroform and a solution of the cobalt complex was added. The reaction mixture was stirred for 24 h at room temperature during which time the colour changed from green to pink. The resulting polymer–metal complexes were isolated by precipitation with methanol. It is thought that the polymer-complex is formed by elimination of Cl^- by the nitrogen on the pendant EN chain as shown in *Figure 2* and the complexes, designated type IV, will be represented as *trans*-$[Co(EN)_2(PMI–EN)Cl]Cl_2$ and *trans*-$[Co(EN)_2(PHpI–EN)Cl]Cl_2$.

Decomposition of hydrogen peroxide

The activity of the polymer–metal complexes as catalysts for the decomposition of H_2O_2 was assessed by titrating residual H_2O_2 in the reaction mixture with potassium permanganate solution. The conditions used were: aqueous hydrogen peroxide solutions of concentration 4×10^{-4} mol dm^{-3}, thermostatted at 313 K, were mixed with amounts of polymer catalyst equivalent to 4.65×10^{-5} mol dm^{-3} of metal ion. The polymer complexes were not water soluble and the heterogeneous reaction was stirred throughout. Each reaction was then acidified and titrated with 0.02 M $KMnO_4$ at various time intervals up to 9 h, to determine residual H_2O_2.

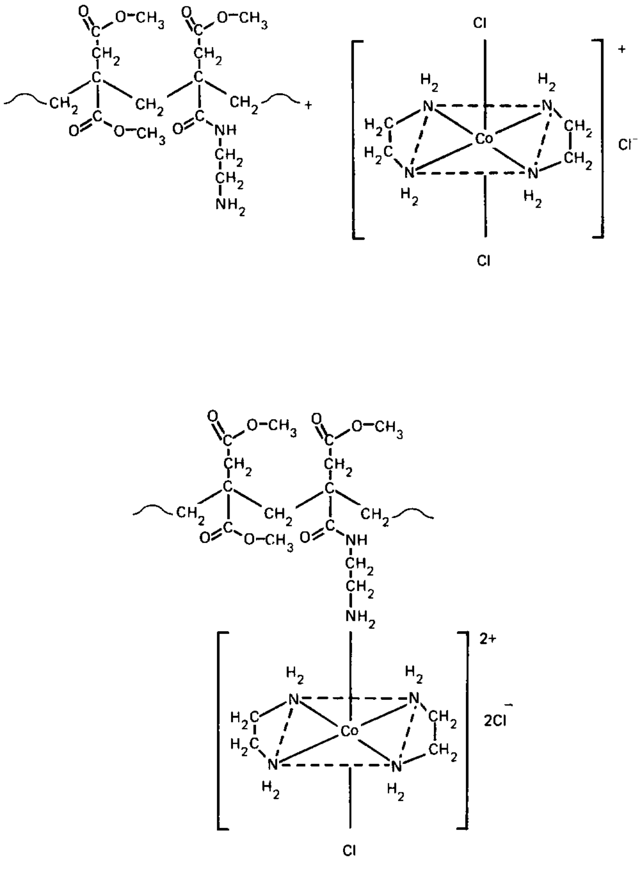


Figure 2

RESULTS AND DISCUSSION

The polymer–metal complexes were analysed by elemental analysis and in the case of the type IV complexes the degree of coordination, X, was also determined. This is defined as the mole ratio of the [metal complex] to that of the [repeating unit of the polymer chain] and was found to be $X = 0.5$ for *trans* $[Co(EN)_2(PMI–EN)Cl]Cl_2$ and $X = 0.3$ for *trans* $[Co(EN)_2(PHpI–EN)Cl]Cl_2$.

Tsuchida *et al.*[11,12] observed that for pendant cobalt(III) complexes attached to poly(vinyl pyridine) the value of X was rarely larger tha 0.68 and varied with the complex, the polymer type, and the time of the reaction. The lower value of X for the (PHpI–EN) ligand may reflect the greater steric hindrance to metal complex formation imposed by the longer heptyl side chains on the approach of the bulky *trans*$[Co(EN)_2Cl_2]Cl$.

When the polymer ligands react with these preformed metal complexes the structure of the product is reasonably approximated by that shown in *Figure 2*, but it is much more difficult to comment on the structures formed when $CoCl_2$ and $CuCl_2$ react with the polymers containing TETRAEN chains. Antonelli *et al.*[13] proposed that when cobalt(III) complexes interacted with poly(ethylene imine), (PEI), the polymer chain coordinated with the

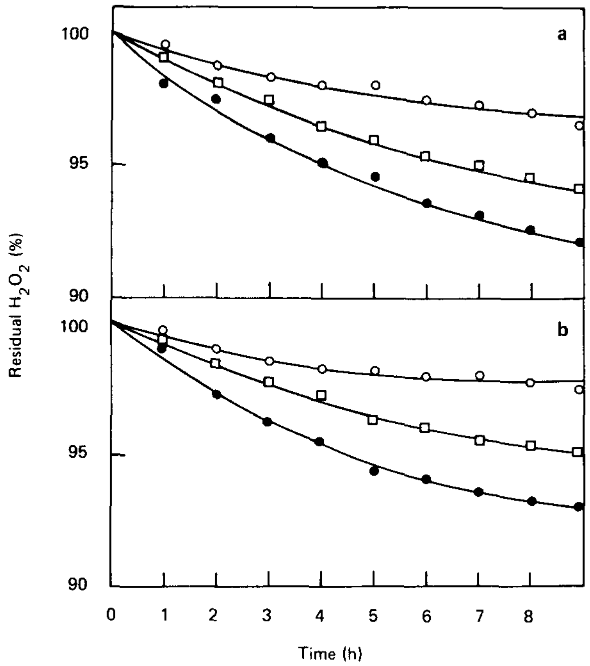


Figure 3 Residual H_2O_2 in the reaction as a function of time for: (a) $CoCl_2$ (○); (PMI–TETRAEN)-$CoCl_2$ (□); and (PHpI-TETRAEN)-$CoCl_2$ (●); (b) $CuCl_2$ (○); (PMI–TETRAEN)-$CuCl_2$ (□); and (PHpI–TETRAEN)-$CuCl_2$ (●)

metal ion to give an octahedral complex with approximately one cobalt(III) ion per ten nitrogens. There is evidence of both crosslinking and ion clustering[2] in (PHpI–TETRAEN)–cobalt(II) and copper(II) complexes and it is likely that coordination is octahedral or pseudo-octahedral but that more than one TETRAEN chain will be involved in the complex.

Decomposition of H_2O_2 using type III complexes

The reactions, which were heterogeneous, could be followed by plotting the % residual H_2O_2 in the system as a function of time. The collected data for (PMI–TETRAEN)-$CoCl_2$, (PMI–TETRAEN)–$CuCl_2$, (PHpI–TETRAEN)–$CoCl_2$ and (PHpI–TETRAEN)–$CuCl_2$ are summarized in *Figures 3*(*a*) and *3*(*b*). In the presence of either $CoCl_2$ or $CuCl_2$ without polymer, there is a small but detectable decomposition reaction. When the metals are complexed with the polymer ligands there is a significant increase in the reaction rate indicating that the polymer–metal complexes are more effective catalysts. There is a small difference in reaction rate between the copper and cobalt complexes where the cobalt is marginally more efficient and this may reflect the fact that copper chelates tend to be more stable than their cobalt counterparts[14]. One interesting feature of these reactions is that the rate of H_2O_2 decomposition in the presence of the (PHpI–TETRAEN)–metal complexes is noticeably faster than in the presence of the methyl counterparts. This suggests that the alkyl side chains have some influence on the course of the reaction.

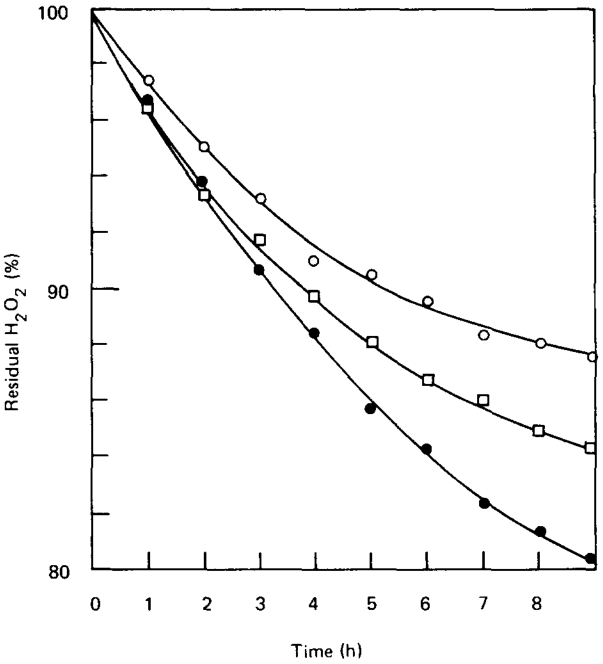


Figure 4 Rate of decomposition of H_2O_2 by (○) *trans*-[Co(EN)$_2$Cl$_2$]Cl; (□) *trans*-[Co(EN)$_2$(PMI–EN)Cl]Cl$_2$; (●) *trans*-[Co(EN)$_2$(PHpI–EN)Cl]Cl$_2$

Reactions using type IV catalysts

A comparison can now be made between the type III catalysts prepared by the random reaction of metal ions in oxidation state (II) with the polymer ligands, and the catalysts made using the preformed metal(III) complexes. The data are displayed in *Figure 4* for the heterogeneous reactions involving the polymer complexes and are compared with the homogeneous reaction using the *trans*-[Co(EN)$_2$Cl$_2$]Cl alone. This shows that the unattached *trans*[Co(EN$_2$)Cl$_2$]Cl is a better catalyst than any of the type III systems if the difference between the homogeneous and the heterogeneous nature of the reactions is ignored. More important is the observation that both the *trans*[Co(EN)$_2$(PMI–EN)Cl]Cl$_2$ and *trans*[Co(EN)$_2$(PHpI–EN)Cl]Cl$_2$ stimulate a more rapid decomposition of H_2O_2 than the unattached complex. This is clear evidence that attaching the metal complex to a polymer ligand leads to considerable enhancement of the catalytic action. This is in accord with Sasaki and Matsunata[15] who found that cobalt–dimethyl glyoxime complexes were more active in the decomposition of H_2O_2 when attached to poly(vinyl pyridine).

Again the polymer complex with the heptyl side chains was more effective in decomposing H_2O_2 than the methyl counterpart. While there are differences in the degree of coordination between the two polymer–metal complexes used, the metal content in the reaction was always kept constant. Thus the only other distinction between the two catalyst environments could be the variation in the relative amounts of uncoordinated EN groups in the chains. The effect of the polymer-ligands themselves, without any metal present, on the decomposition of H_2O_2 was investigated but no reaction could be detected. This means that the polymer ligands themselves are inert as catalysts and the only influence that the EN chains might have on the reaction is to create a different environment for the complex when attached to the chain. This is one possibility but another is that the differences arise from the steric restrictions imposed by the large heptyl side chains on or around the active moiety. This may either cause a weakening of the bonding in the complex which could produce a more reactive system, or it might involve cage effects in which the longer heptyl chains tend to trap the H_2O_2 molecules in the vicinity of the active catalyst site for longer than normal. An explanation based on steric effects seems more likely in the light of the results with the type III complexes, but the precise mechanism is as yet unresolved.

CONCLUSIONS

Polyitaconates with pendant ethylene amine chains, when coordinated with copper or cobalt ions, produce both type III and type IV complexes which catalyse the decomposition of hydrogen peroxide. The length of the alkyl side chain in the polyitaconate–metal complex influences the effectiveness of the catalytic action. Polymer complexes based on chains with heptyl side groups always decomposed H_2O_2 more rapidly than those with methyl groups, when similar complex types were compared. It was found that in order of increasing catalytic efficiency, the systems studied were: (PMI–TETRAEN)-$CuCl_2$ < (PMI–TETRAEN)-$CoCl_2$ < (PhpI–TETRAEN)-$CuCl_2$ < (PhpI–TETRAEN)$CoCl_2$ < *trans*-[Co(EN)$_2$Cl$_2$]Cl < *trans*[Co(EN)$_2$(PMI–EN)Cl]Cl$_2$ < *trans*[Co(EN)$_2$(PHpI–EN)Cl[Cl$_2$]. The precise role of the polymer chain in enhancing the catalytic activity remains unresolved at present but further work is in progress to elucidate this point.

unresolved at present but further work is in progress to elucidate this point.

REFERENCES

1 Cowie, J. M. G. and Wadi, N. M. A. *Eur. Polym. J.* 1985, **17**, 27
2 Cowie, J. M. G. and Wadi, N. M. A. *Polymer* 1985, **26**, 0000
3 Shambhu, M. B., Theodorakis, M. C. and Digenis, G. *J. Polym. Sci., Polym. Chem. Edn.* 1977, **15**, 525
4 Tsuchida, E., Kaneko, M. and Nishide, H. *Makromol. Chem.* 1973, **164**, 203
5 Chanda, M., O'Driscoll, K. F. and Rempel, G. L. *J. Catal.* 1980, **61**, 533
6 Schutten, J. H., Piet, P. and German, A. L. *Makromol. Chem.* 1979, **180**, 2341
7 Shirai, H., Maruyama, H., Kobayashi, K., Hojo, N. and Urushido,K. *Makromol. Chem.* 1980, **181**, 565, 575
8 Osada, Y. *Makromol. Chem.* 1975, **176**, 1893
9 Cowie, J. M. G. and Haq, Z. *Eur. Polym. J.* 1977, **13**, 745
10 Krishnamurthy, M. *J. Inorg. Nucl. Chem.* 1972, **34**, 3915
11 Tsuchida, E., Nishide, H. and Takeshita, M. *Makromol. Chem.* 1974, **175**, 2293
12 Nishide, H., Hata, S. and Tsuchida, E. *Makromol. Chem.* 1978, **179**, 1445
13 Antonelli, M. L., Bucci, R., Carunchio, V. and Cernia, E. *J. Polym. Sci., Polym. Lett. Edn.* 1980, **18**, 179
14 Tsuchida, E. and Nishide, H. *Adv. Polym. Sci.* 1977, **24**, 1
15 Sasaki, T. and Matsunaga, F. *Bull. Chem. Soc. Jpn.* 1968, **41**, 2440