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Efficient biomimetic catalytic epoxidation of polyene polymers by manganese porphyrins

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Abstract

Two polyene polymers, *cis*-polybutadiene and *cis*-polyisoprene, were transformed into polyepoxides under mild conditions. The epoxidation of these two polyene polymers is stereospecific, giving *cis*-epoxides as products. All factors controlling the reaction rate, such as the nature of the catalyst, the oxygen donor and the presence of bases as axial ligands, were studied. The optimum results were obtained when iodosylbenzene was used as the oxygen donor, Mn(TpFPP)Cl as the catalyst and imidazole as the axial ligand. Under these optimum conditions the turnover number was found to be 71. These results render this system promising for the epoxidation of polyene polymers in a more general way.

Keywords: Catalysis; Epoxidation; Polyene polymers; Manganese porphyrins

1. Introduction

The presence of one or more functional groups in polymers that contain non-conjugated double bonds can drive the production of new specialty polymer products [1]. For example, key connector groups catalytically placed on a polymer can aid in the attachment of other polymer chains or monomer groups in order to achieve the desired assembly. *cis*-1,4-Polybutadiene and *cis*-1,4-polyisoprene can be used as such starting polymers, in which one can introduce a functional group on each butadiene or isoprene unit. Such a functional group could be the epoxide, which is often prepared by transfer of an oxygen atom to unsaturated molecules. Epoxides are versatile intermediates in organic synthesis [2]. Polyepoxides are also able to react with inorganic surfaces containing hydroxyl groups through the formation of covalent bonds, whereas the remainder remain unreacted [3]. The unreacted epoxy groups can be used for further chemical modification, e.g. by reaction with nucleophiles [4]. Modification of inorganic and polymer surfaces to generate functional interfaces plays a significant role in microelectronic applications, affinity chromatography [5], immobilization of enzymes [6] and the design of antifouling surfaces [7].

In this report, we present the biomimetic catalytic transformation of two polyene polymers, *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene, into the corresponding polyepoxides (Fig. 1). Metalloporphyrins were used as catalysts in order to mimic cytochrome P-450, which is able to perform oxidation reactions at ambient temperature. Many groups have studied the catalytic epoxidation or

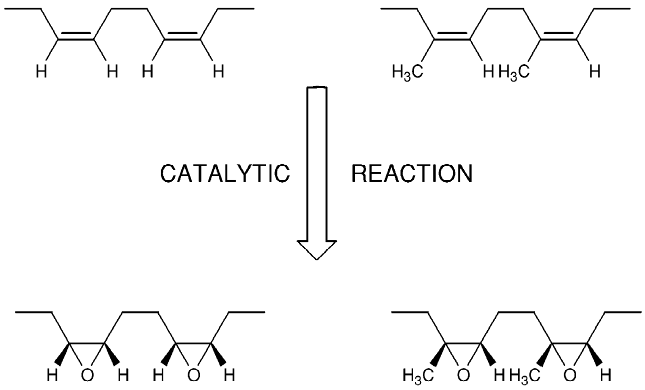

Fig. 1. Epoxidation reaction for *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene.

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hydroxylation of simple and relatively reactive molecules such as *cis*-cyclooctene [8], *cis*- and *trans*-stilbene [9–11], cyclohexadiene [10], styrene [11,12], etc. by metalloporphyrins [13]. As far as we know, this is the first time that the above polyene polymers have been used as substrates, as already mentioned in our preliminary work [14]. Iodosylbenzene [9,15,16], sodium hypochlorite [21], and, in a few cases, potassium persulfate [22] have been used as oxygen donors. The addition to the reaction mixture of substituted pyridines or amines considerably modifies the reaction rate. For this reason, a variety of bases have been used. In order to obtain robust catalysts and, consequently, perform high yield epoxidation reactions, substitution on the phenyl group of the porphyrin ring and/or at the β-pyrollic position is required. Today, there is a wide range of synthetic metalloporphyrins bearing steric or electronic effects and, in some cases, both. For all these reasons, the nature of the porphyrin ring, the oxygen donor, the presence of various substituted pyridines as well as all factors which could play a role in the studied reaction process were investigated and a systematic study was carried out.

2. Experimental

All solvents and reagents were purified by standard methods before use. For the identification of the reaction products, the polyepoxides of *cis*-polybutadiene and *cis*-polyisoprene were prepared independently by the action of *m*-CPBA and characterized by ^{1}H-NMR and ^{13}C-NMR. Iodosylbenzene was prepared according to a literature method [17] by the hydrolysis of iodobenzene diacetate with NaOH. Sodium hypochlorite was obtained from Riedel de Haën, ca. 12–13% Cl active, and titrated by the iodometric method (0.7 mol dm^{-3}, pH 10.5). Oxone (a mixed salt, $2KHSO_5$, $KHSO_4$, K_2SO_4) was obtained from Merck.

2.1. Porphyrin synthesis

All of the manganese porphyrins were prepared as described in the literature: Mn(TpFPP)Cl [18], Mn(TPyP)AcO [19], Mn(TDCPP)Cl [20], Mn(β-Cl$_8$TPP)Cl [21], Mn(TMP)Cl [20], and Mn(β-Br$_8$TMP)Cl [22].

Catalytic reactions were monitored by removing aliquots at specific time intervals (a number of identical reactions were running simultaneously with respect to the number of aliquots) and the product was quantified by integration of the vinylic protons of the starting polymer and the –CH– protons of the formed epoxide in ^{1}H-NMR spectra.

NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AMX 500 at 500 MHz for ^{1}H-NMR and 125 MHz for ^{13}C-NMR.

2.2. Epoxidation procedure

All reactions were carried out at room temperature in a 30 ml round bottle equipped with a stirring bar. Since catalytic reactions are not significantly affected by molecular oxygen, they were performed under air.

2.3. General procedure for oxidations using iodosylbenzene as oxygen donor

In a typical reaction the polyene polymer (0.926 mmol) was dissolved in 10 ml of CH_2Cl_2. Then 0.023 mmol of manganese porphyrin (Mn^{III}(Por)Cl) was added to the solution (the catalyst/polymer ratio was 2.5%). Finally, 0.6 g (2.85 mmol) of iodosylbenze was added to the stirred mixture. The reaction was monitored by ^{1}H-NMR. Stirring was stopped prior to the withdrawal of each aliquot (0.3 ml), the residue was dissolved in $CDCl_3$ and its ^{1}H-NMR spectrum was recorded.

2.4. Epoxidation of cis-polybutadiene in the presence of various bases

The same procedure was adopted as previously, except that, before the addition of iodosylbenzene, 0.345 mmol of various bases (base/catalyst ratio 15:1) was added to the reaction mixture.

2.5. General procedure for oxidations using sodium hypochlorite as oxygen donor

In a typical reaction the polyene polymer (0.926 mmol) was dissolved in 10 ml of CH_2Cl_2. To a solution of manganese porphyrin (0.023 mmol), benzyldimethyltetradecylammonium chloride (9.7 mg, 0.024 mmol) was added. Then 10 ml of sodium hypochlorite (7 mmol) was added to the reaction mixture. At specific time intervals, stirring was stopped, the two layers were separated, an aliquot (0.3 ml) was taken from the organic phase and was dried with anhydrous magnesium sulfate. Finally, the solvent was removed and the ^{1}H-NMR spectrum of the residue was obtained in $CDCl_3$.

2.6. General procedure for oxidations using $KHSO_5$ as oxygen donor

In a typical reaction, the polyene polymer (0.926 mmol) was dissolved in 10 ml of CH_2Cl_2. To a solution of manganese porphyrin (0.023 mmol), benzyldimethyltetradecylammonium chloride (9.7 mg, 0.024 mmol) was added. 1.7 g (2.76 mmol) $KHSO_5$ diluted in 20 ml of phosphate buffer 0.25 M, pH 7, was then added. At specific time intervals, stirring was stopped, the two layers were separated, an aliquot (0.3 ml) was taken from the organic phase and was dried with anhydrous magnesium

Table 1
^{1}H-NMR chemical shifts of *cis*-1,4-polybutadiene, *cis*-1,4-polyisoprene and the corresponding polyepoxides

Polymer	Chemical shift (ppm)		
	–CH–	–CH$_2$–	–CH$_3$
cis-Polybutadiene	5.3	2.0	
Polyepoxide	3, 2.8	1.7	
cis-Polyisoprene	5.15	2.07	1.7
Polyepoxide	2.8, 2.7	1.72	1.34

sulfate (see also general procedure). Finally, the solvent was removed, and the ^{1}H-NMR spectrum of the residue was obtained in CDCl$_3$.

Table 2
^{13}C-NMR chemical shifts of *cis*-1,4-polybutadiene, *cis*-1,4-polyisoprene and their polyepoxides

Polymer	Chemical shift (ppm)			
	–CH–		–CH$_2$–	–CH$_3$
cis-Polybutadiene	130.0		27.8	
Polyepoxide	56.5		24.7	
	–C–	–CH–		
cis-Polyisoprene	135.2	125.0	32.2, 26.4	23.4
Polyepoxide	60.4	64.7	29.5, 24.5	22

3. Results

3.1. Characterization of polyepoxides of cis-polybutadiene and cis-polyisoprene

The polyepoxides, which were produced by the epoxidation reaction of *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene, were fully characterized by ^{1}H-NMR, ^{13}C-NMR and FT-IR spectroscopies. The chemical shifts observed by ^{1}H- and ^{13}C-NMR data for the starting polymers as well as their polyepoxides are presented in Tables 1 and 2, respectively. For *cis*-polybutadiene (Fig. 2) the peak at 5.30 ppm, which is attributed to vinylic protons, is shifted to 3.00 and 2.80 ppm in the polyepoxide, and the peak at 2.00 ppm, which is attributed to –CH$_2$– protons, is shifted to 1.70 ppm in the polyepoxide. From the ^{13}C-NMR spectra (Fig. 3) we can observe that the methine carbons are shifted from 130 to 56.5 ppm in the polyepoxide. Similar results were also observed for the epoxidation reaction of *cis*-polyisoprene. According to the ^{1}H-NMR spectra (Fig. 4), the vinylic protons are shifted from 5.15 to 2.80 and 2.70 ppm, the peak at 2.07 ppm, which is attributed to methinic protons, is shifted to 1.72 ppm and the signal for the methyl protons is shifted from 1.70 to 1.34 ppm for the polyepoxide. From the ^{13}C-NMR spectra (Fig. 5) we can observe that the tertiary carbon and the methine carbons at 135.20 and 125.00 ppm in *cis*-polyisoprene are shifted to 60.40 and 64.70 ppm, respectively, for the polyepoxide. The above results are consistent with

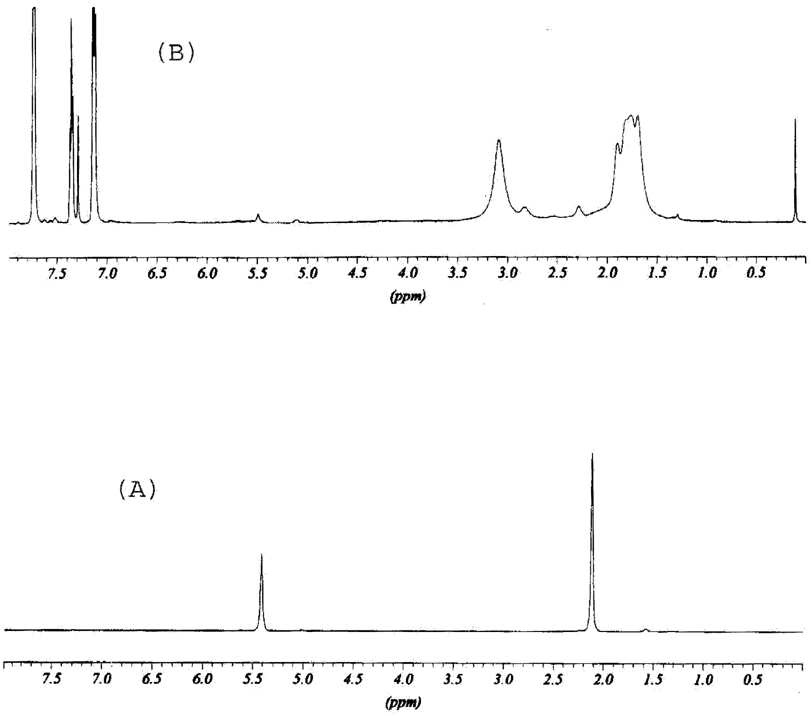

Fig. 2. ^{1}H-NMR spectra of (A) *cis*-1,4-polybutadiene and (B) *cis*-1,4-polybutadiene epoxide.

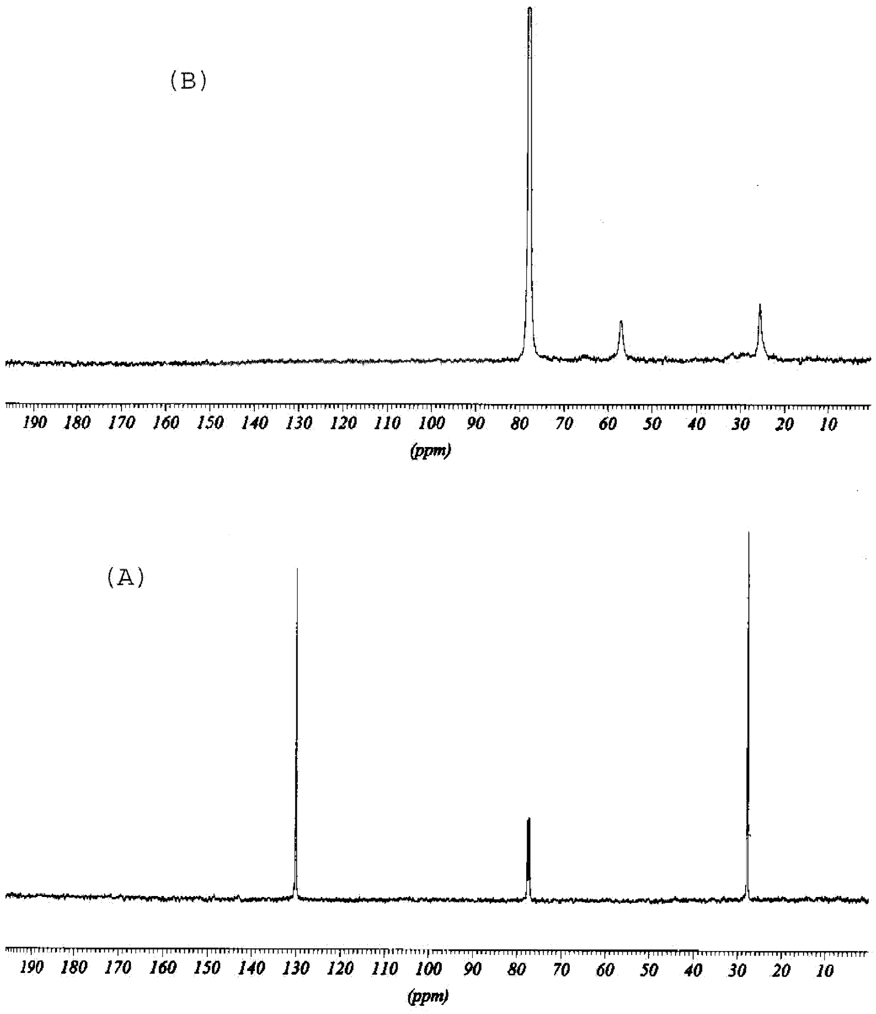

Fig. 3. ^{13}C-NMR spectra of (A) *cis*-1,4-polybutadiene and (B) *cis*-1,4-polybutadiene epoxide.

the FT-IR data. We will focus our attention on the expected symmetrical stretching, or ring breathing frequency, of the epoxy ring. All ring bonds, stretching and contracting in phase, were observed at 1272 and 1266 cm^{-1} for the corresponding epoxide of *cis*-polybutadiene and *cis*-polyisoprene, respectively. An additional band appears at 823 and 878 cm^{-1} for the epoxides of *cis*-polybutadiene and *cis*-polyisoprene, respectively, attributed to the asymmetrical ring stretch in which the C–C bond is stretched during contraction of the C–O bond. Finally, the C–H stretching vibrations of the epoxy rings were observed at 2967 and 2975 cm^{-1} for the same epoxides in the same order.

3.2. The role of various bases as the sixth ligand

The reaction rates for the formation of *cis*-polybutadiene epoxide in the presence of various bases during the epoxidation reaction are presented in Fig. 6. As can be seen, the addition of a base to the reaction mixture increases the reaction rate. In this case, iodosylbenzene was used as the oxygen donor and Mn(TPP)Cl as the catalyst. The base/catalyst ratio was 15:1. It should be noted that the addition of more than 15 equivalents of base, with respect to the catalyst, results in a lower conversion of the starting polymer [14]. Pyridine, imidazole, *N*-methylimidazole, pyridine, 4-tert-butyl-pyridine, 4-cyanopyridine, 2,6-dimethylpyridine, 3,5-dimethylpyridine, 4-hydroxypyridine and triethylamine were selected as bases for this study. Reactions with added base were compared with the reaction in which no base was present. All of the selected bases accelerate the epoxidation reaction, except for triethylamine. The best results were obtained when imidazole or *N*-methylimidazole was used as the corresponding base. In the above cases, after 40 min, a high yield transformation of the starting polymer to the polyepoxide (99 and 94.4% with imidazole and *N*-methylimidazole, respectively) was observed. 4-tert-Butylpyridine, which has been referred to as the best base in similar epoxidation reactions when using sodium hypochlorite [23] or potassium persulfate [24] as the oxygen donor, was still effective, but gave a poorer conversion of the polyene polymer to polyepoxides (89% after 4 h).

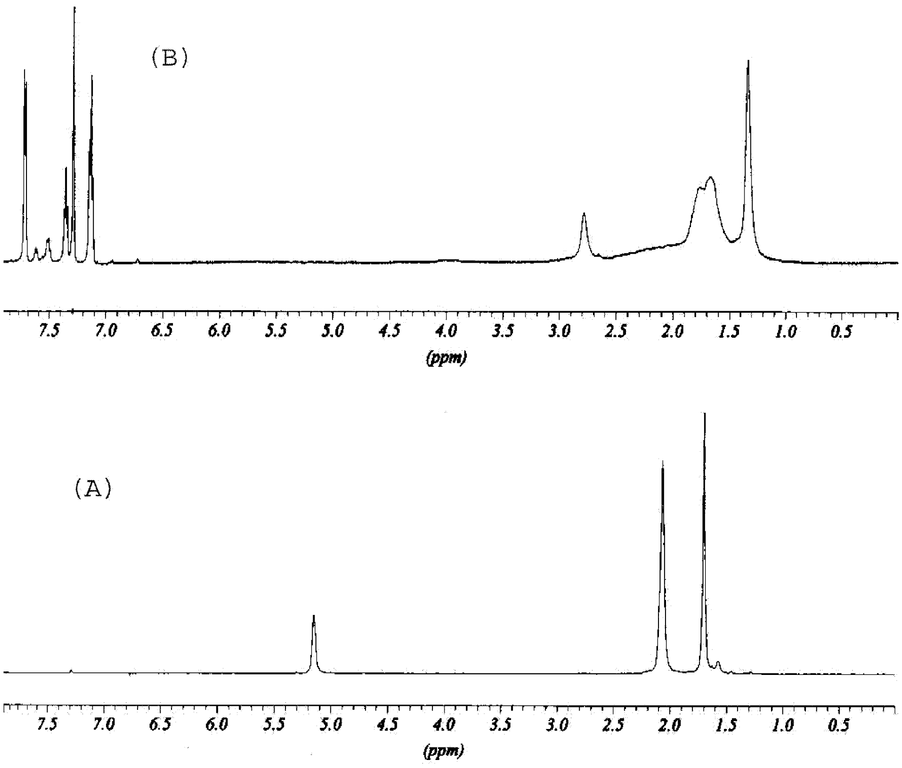

Fig. 4. ^{1}H-NMR spectra of (A) *cis*-1,4-polyisoprene and (B) *cis*-1,4-polyisoprene epoxide.

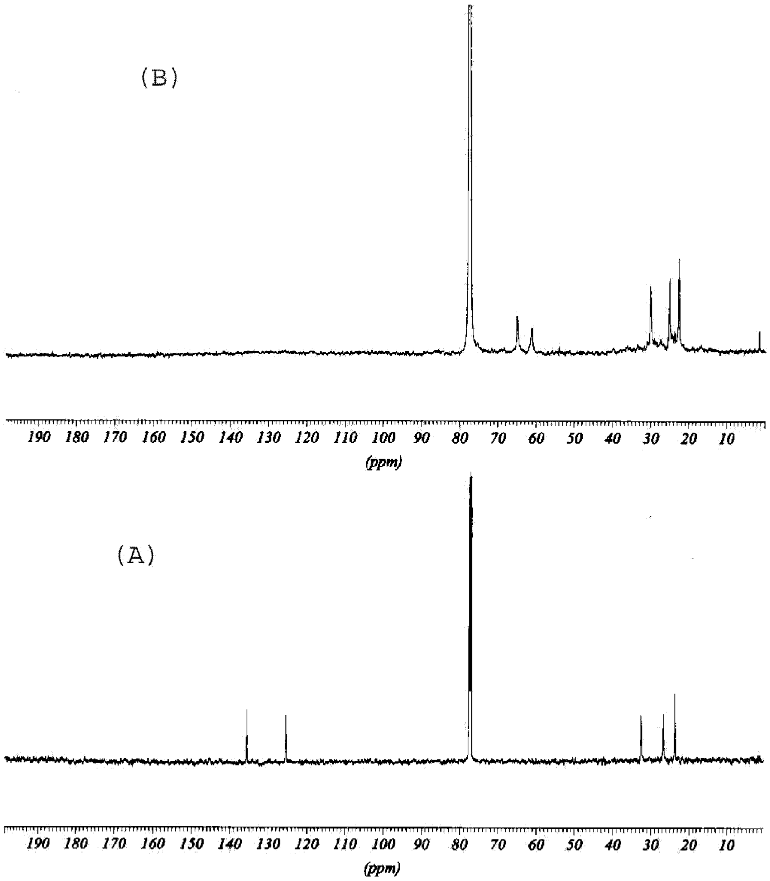

Fig. 5. ^{13}C-NMR spectra of (A) *cis*-1,4-polyisoprene and (B) *cis*-1,4-polyisoprene epoxide.

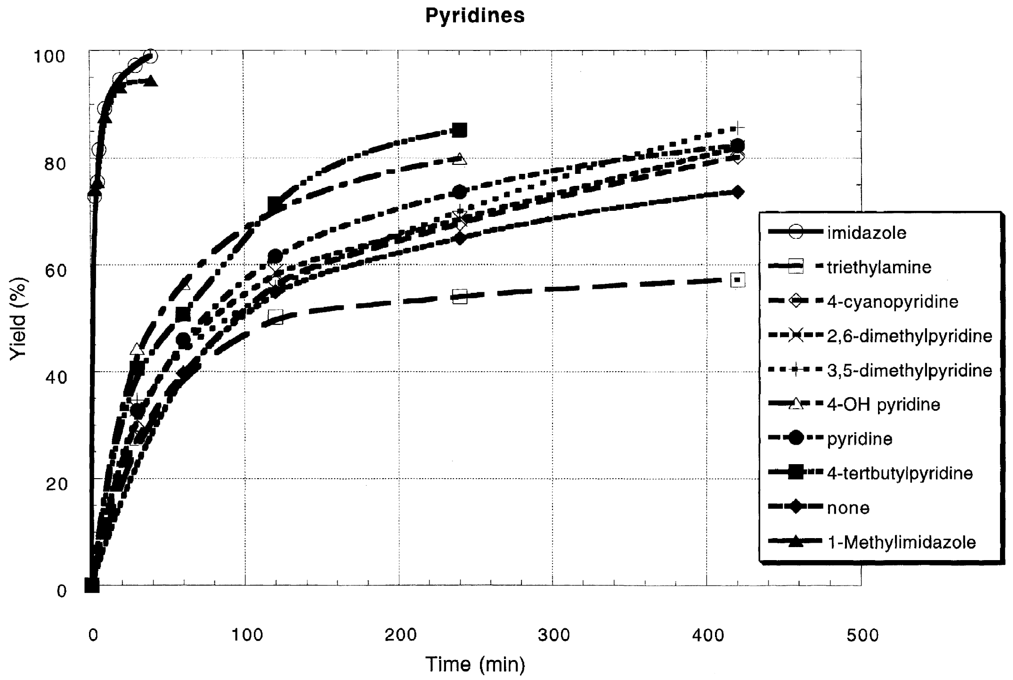

Fig. 6. Comparison of the rates of epoxidation of *cis*-1,4-polybutadiene by PhIO in CH_2Cl_2 catalyzed by Mn(TPP)Cl in the presence of various amines.

3.3. Effect on the catalytic reaction of substitution of the porphyrin ring

As has already been reported [14], the first generation of manganese porphyrins are more effective catalysts than the analogous iron and chromium porphyrins for the epoxidation reaction of *cis*-polybutadiene or *cis*-polyisoprene. The final conversion rates obtained for both polyene polymers and all catalysts are presented in Table 3. The reaction rates for the formation of *cis*-polybutadiene and *cis*-polyisoprene epoxides by different manganese porphyrins are presented in Figs. 7 and 9, respectively. The catalyst/polyene polymer ratio for all reactions was fixed at 2.5%. The epoxidation rate of *cis*-polybutadiene was slower than that of *cis*-polyisoprene. The best catalyst for both polymers turned out to be Mn(TpFPP)Cl porphyrin. With this catalyst, the yield of polyepoxide was 99.4% after 60 min for *cis*-polybutadiene, and 100% after 30 min for *cis*-polyisoprene. Interesting results were also obtained when Mn(TPyP)AcO and Mn(TMP)Cl were used as catalysts. The first catalyst is effective in yielding a high transformation of polyene polymers to the corresponding polyepoxides in a short time. The latter catalyst gave a poorer conversion. This catalyst, Mn(TMP)Cl, was reported to be the most robust catalyst with a high stereo specificity for the epoxidation of alkenes such as *cis*-stilbene [25], but this was not the case in our catalytic transformation.

Table 3
Yield of *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene polyepoxides from the oxidation of starting polymers by PhIO in CH_2Cl_2 catalyzed by different manganese porphyrins

Catalyst	Polyepoxide yield (%)	
	cis-Polybutadiene	*cis*-Polyisoprene
Mn(TPP)Cl	73.7 (420)[a]	97.4 (420)
Mn(TPyP)AcO	99.4 (300)	91.6 (120)
Mn(TMP)Cl	54 (420)	68.2 (420)
Mn(TpFPP)Cl	99.4 (60)	100 (30)
Mn(β-Cl_8TPP)Cl	88.7 (350)	90.7 (180)
Mn(TDCPP)Cl	81.4 (420)	90.2 (420)
Mn(Tm-MePP)Cl	75.1 (420)	95.1 (420)
Mn(β-Br_8TMP)Cl	70.6 (420)	89.2 420)

[a] Reaction time (min) in parentheses.

3.4. Influence of the oxygen donor

After determining the best catalyst for the epoxidation reaction (Mn(TpFPP)Cl), we studied its behavior with three different oxygen donors, iodosylbenzene, sodium hypochlorite and potassium persulfate. Also, an axial ligand with the best performance was used in each case. For all experiments, the catalyst/*cis*-polybutadiene ratio was 1% and the base/catalyst ratio was fixed at 15:1. When iodosylbenzene was used as the oxygen donor, the turnover number was 71. The turnover number decreased to 39 when potassium persulfate was used as the oxygen donor and to 6 in the case of sodium hypochlorite.

4. Discussion

The polyepoxides were unique products of the described epoxidation reaction by various manganese metalloporphyrins and oxygen donors, as no side products were

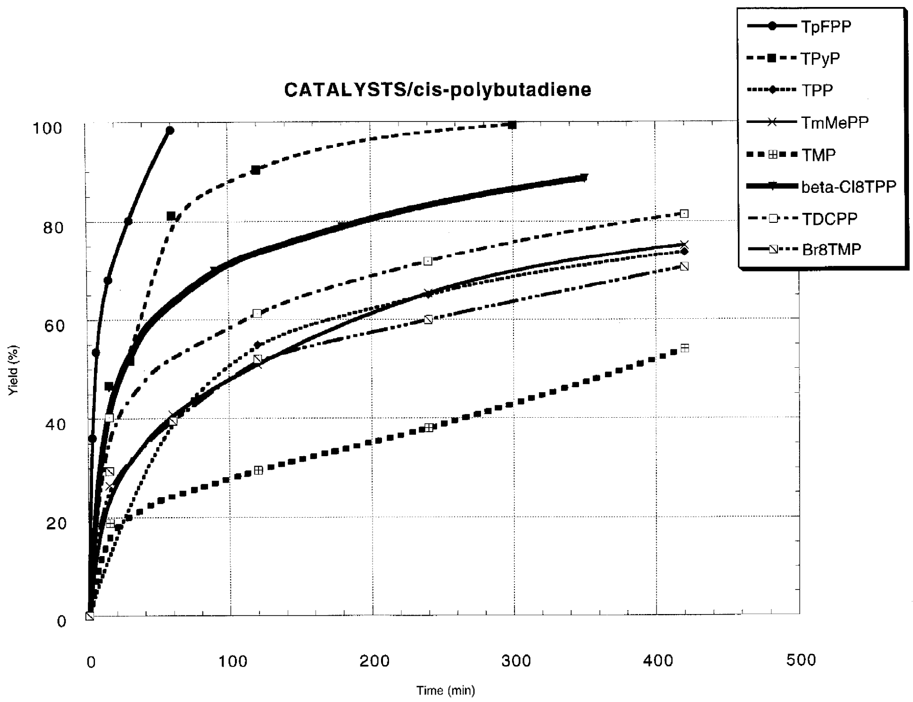

Fig. 7. Comparison of the epoxidation rates of *cis*-1,4-polybutadiene by PhIO in CH_2Cl_2 catalyzed by different manganese porphyrins.

detected by NMR spectroscopy. The epoxidation reactions of *cis*-polybutadiene and *cis*-polyisoprene are stereospecific. The only product which was observed was the *cis*-polyepoxide. The presence of epoxides in the structure of the oxidized polyene polymers was confirmed mainly on the basis of the ^{13}C-NMR spectra of these polymers, which exhibit characteristic resonances in the region 55–65 ppm, corresponding to epoxy carbon atoms. In the case of *cis*-polybutadiene, the peak at 56.5 ppm is characteristic of *cis*-polyepoxide (the *trans*-polyepoxide shows a resonance peak at 58.5 ppm) [26]. When *cis*-polyisoprene was used as the substrate, only the *cis*-polyepoxide was observed as the epoxy carbon at 64.7 ppm, with the epoxy carbon for the *trans*-polyepoxide appearing at 63.5 ppm [26]. It is interesting to note that the order of quaternary and tertiary carbons is reversed from that of the corresponding olefinic carbons. Presumably, this reversal results from the hybridization change with the attendant modification of steric and electronic factors [26].

The addition of small amounts of pyridine strongly increases the reaction rate and the overall turnover for the described transformation, as also reported by Meunier and coworkers [27]. The role of pyridine is essentially to act as the sixth ligand (proximal effect), as has been demonstrated in the case of NaOCl/Mn porphyrin epoxidation using porphyrins with a pyridine or an imidazole covalently linked to the tetrapyrrole macrocycle by two arms [27]. Fig. 6 presents the formation of the polyepoxide of *cis*-polybutadiene as a function of time by the addition of an axial base, using Mn(TPP)Cl and PhIO as the catalyst and the oxygen donor, respectively. As can be seen, the epoxidation reaction depends both on electronic and steric factors. Therefore, the presence of bulky substituents on the pyridine ring at positions 2 and 6 results in a decrease in the reaction rate (compare 2,6-dimethylpyridine with pyridine). When the substituents are more distant from the pyridine nitrogen, the reaction rate increases again (compare 3,5-dimethylpyridine with 2,6-dimethylpyridine). Also, the presence of an electron-donating group at position 4 of the pyridine ring, e.g. 4-tert-butyl, or a hydroxyl group increases the rate of the epoxidation reaction (compare 4-tert-butyl-pyridine and 4-hydroxypyridine with pyridine). Opposite results were obtained when this group was an electron-withdrawing group (compare 4-cyanopyridine with 4-tert-butyl-pyridine and pyridine). The best results were obtained when imidazole or *N*-methylimidazole were used as axial bases. With these ligands the transformation of polymers to the polyepoxide was achieved in about 40 min. It is interesting to note that these ligands cannot be used when NaOCl [23] or $KHSO_5$ [24] is used as the oxygen donor. Similar results were obtained when NaOCl was used as the oxygen donor and imidazole was held in a proximal position by a covalent linkage to the porphyrin ring [27].

Following the discovery that metalloporphyrins are able to mimic the catalytic activity of cytochrome P-450, there was an increase in interest in the synthesis of new catalysts that are robust towards self-oxidative destruction and μ-oxo dimerization, in order to achieve a high turnover number. Since the selectivity of metalloporphyrin-catalyzed oxidations relies largely on the steric and electronic effects of the group attached to the macrocycle, substituents were introduced on the phenyl group of the porphyrin ring or at the β-pyrrolic position in order to introduce a steric effect provided by the macrocycle. In this study, we performed the epoxidation reaction of *cis*-polybutadiene (Fig. 7) and *cis*-polyisoprene (Fig. 9) with manganese porphyrins, which possess a steric or an electronic effect, or both. Iodosylbenzene used as the oxygen donor in combination with manganese porphyrins gives the best results [14].

Comparing the epoxidation of the polymers, one observes that *cis*-polyisoprene is more active than *cis*-polybutadiene. This is in accordance with the fact that an electrophilic high valent metal-oxo species is formed as a reactive intermediate and electron-rich olefins are more reactive than non-substituted olefins [28].

For the epoxidation of *cis*-polybutadiene (Fig. 7), the order of efficiency for manganese porphyrins is

$$\begin{aligned}\mathrm{Mn(TpFPP)Cl} &> \mathrm{Mn(TPyP)AcO} > \mathrm{Mn(\beta\text{-}Cl_8TPP)Cl}\\ &> \mathrm{Mn(TDCPP)Cl} > \mathrm{Mn(Tm\text{-}MePP)Cl}\\ &> \mathrm{Mn(TPP)Cl} > \mathrm{Mn(\beta\text{-}Br_8TMP)Cl}\\ &> \mathrm{Mn(TMP)Cl}\end{aligned}$$

As we can see, the most effective catalyst is Mn(TpFPP)Cl. Using this catalyst, we observed almost complete transformation of *cis*-polybutadiene to the corresponding epoxide. This catalyst has been reported [29,30] to exhibit extremely high stability as well as catalytic reactivity. In addition to Mn(TpFPP)Cl, Mn(TPyP)AcO also presents a high catalytic reactivity. The porphyrin ring of tetrapyridylporphyrin possesses almost the same structure as TPP, the only difference being the presence of a nitrogen atom in the *para*-position instead of a carbon atom. When using Mn(TPyP)AcO, we observed a 90.4% conversion of *cis*-polybutadiene to the polyepoxide after 2 h, instead of 50.9% with Mn(TPP)Cl. A possible explanation for this enormous difference is that the nitrogen atoms of the phenyl group can coordinate to the central metal atom of another porphyrin molecule and can play the role of an axial ligand, stabilizing the reactive intermediate while simultaneously increasing the reaction rate (Fig. 8). The introduction of halogen substituents in the porphyrin ring results in an increase of the epoxidation rate. However, two porphyrins with the same number of halogen atoms, but in different positions, TDCPP (at positions 2,6 of the phenyl ring) and β-Cl$_8$TPP (at β-pyrrolic positions), exhibit different catalytic actions. Better results were obtained with β-Cl$_8$TPP (70% epoxide yield after 90 min in comparison with 61.2% epoxide yield after 120 min for TDCPP). Concerning the catalytic action of β-substituted porphyrins, it has been reported [31] that the presence of electron-withdrawing substituents at the β-pyrrolic position results in an increase of the reactivity of the intermediate manganese-oxo species which is formed during this catalytic reaction. Also, it has been reported [21] that β-halogen porphyrins possess increased stability towards intermolecular oxidative destruction. This is due to the high oxidation potentials compared with non-β-substituent tetraphenyl porphyrins [21]. On the contrary, the introduction of a bulky group at the *ortho*-position on the phenyl group, for example a methyl group, results in a decrease of the catalytic action of the manganese porphyrin. When using Mn(TMP)Cl, the reaction time of transformation to epoxides for most olefins [25] is about half of that of the reaction with Mn(TPP)Cl as catalyst. With Mn(TMP)Cl as catalyst, a large increase in the reaction rates was found [25], together with product selectivity and stereoselectivity. One possible explanation for this is that the steric hindrance due to the *ortho*-methyl group on the phenyl substituents is sufficient to reduce the possibility of transfer of the electrophilic oxygen atom from one manganese porphyrin to another in the bimolecular decomposition process. This is not, however, the case for the epoxidation of *cis*-polybutadiene. Thus, after 7 h with Mn(TMP)Cl as catalyst, a polyepoxide yield of only 54% was observed, whereas Mn(TPP)Cl gave a yield of 73.7% after the same time. This decrease in catalytic activity of Mn(TMP)Cl is not due to the fact that bimolecular oxidative destruction is taking place, as only a minor portion of the catalyst is destroyed after 7 h (according to time-resolved UV–visible data, under the same experimental conditions). One possible explanation is that the bulky methyl group at the *ortho*-position does not allow the approach of the polyene polymer to the man-

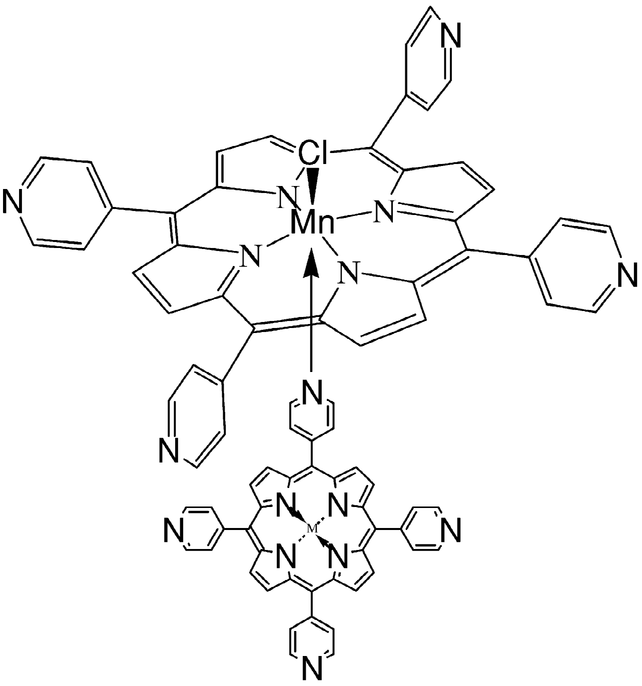

Fig. 8. The action of the catalyst, tetrapyridylporphyrin, as base.

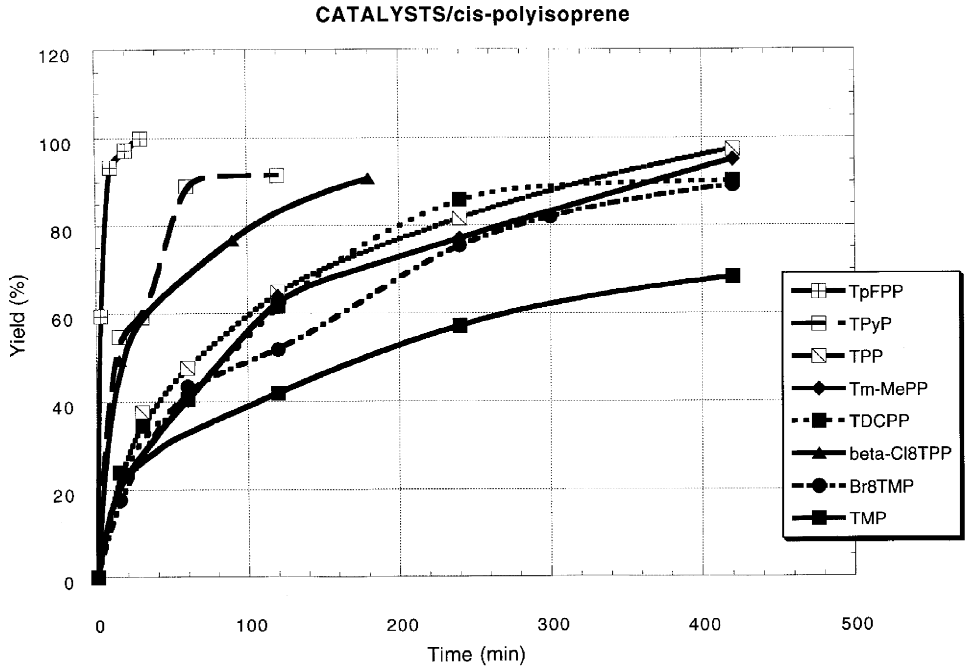

Fig. 9. Comparison of the rates of epoxidation of *cis*-1,4-polyisoprene by PhIO in CH_2Cl_2 catalyzed by different manganese porphyrins.

ganese-oxo species. The introduction of eight bromo substituents at the β-pyrollic position of the TMP ligand results in an increase of the epoxidation rate (70.6% after 7 h for the Mn(β-Br_8TMP)Cl derivative).

For the epoxidation of *cis*-polyisoprene (Fig. 9) the order of efficacy for manganese porphyrins is

$$\begin{aligned}&\mathrm{Mn(TpFPP)Cl} > \mathrm{Mn(TPyP)AcO} > \mathrm{Mn(}\beta\text{-}\mathrm{Cl_8TPP)Cl}\\&\quad > \mathrm{Mn(TPP)Cl} > \mathrm{Mn(Tm\text{-}MePP)Cl}\\&\quad > \mathrm{Mn(TDCPP)Cl} > \mathrm{Mn(}\beta\text{-}\mathrm{Br_8TMP)Cl}\\&\quad > \mathrm{Mn(TMP)Cl}\end{aligned}$$

As in the case of *cis*-polybutadiene and for the epoxidation of *cis*-polyisoprene, the most effective catalysts are the Mn(TpFPP)Cl and Mn(TPyP)AcO derivatives. For the other catalysts the introduction of bulky substituents to the phenyl group results in a decrease of the reaction rate. A possible explanation for this is that the presence of the methyl group of *cis*-polyisoprene creates additional stereochemical hindrance. As a result, the approach of *cis*-polyisoprene to the reactive manganese-oxo species becomes more difficult.

Similar results were obtained when NaOCl and $KHSO_5$ were used as oxygen donors (data not shown), but, in these cases, the reaction rates were slower than that when PhIO was used as the oxygen donor. For example, when Mn(TpFPP)Cl and NaOCl were used as catalyst and oxygen donor, respectively, after 1.5 h the polyepoxide yield was 97.5%, whereas when $KHSO_5$ was used as the oxygen donor, after 1 h the polyepoxide yield was 88%.

4. Conclusions

Manganese porphyrins are capable of efficiently performing polyene polymer epoxidation reactions, under mild conditions, with a variety of oxygen donors and with high reaction rates as well as overall turnover numbers. The epoxidation of polyene polymers is stereospecific. The chemical behavior of metalloporphyrins depends on the nature of the oxygen donor. Imidazole can be used as a free ligand and gives the best results when PhIO is used as the oxygen donor, in contrast to when NaOCl and $KHSO_5$ are used as oxygen donors. The introduction of bulky substituents to the phenyl group or electron-withdrawing substituents at the β-pyrollic position to produce stable oxidation catalyst is not an independent criterion for an efficient catalytic system. Such factors must be in balance as in the case of Mn(TpFPP)Cl, which is the best catalyst. Further work is under way to introduce other chemical groups to polyepoxides in order to produce specific polymers.

5. Abbreviations

PhIO	iodosylbenzene
NaOCl	sodium hypochlorite
$KHSO_5$	potassium persulfate
Mn(TPP)Cl	5,10,15,20-tetraphenylporphyrinato manganese(III) chloride
Mn(TDCPP)Cl	5,10,15,20-tetra(2,6-dichlorophenyl)-porphyrinato manganese(III) chloride

Mn(TpFPP)Cl	5,10,15,20-tetra(pentafluorophenyl)porphyrinato manganese(III) chloride
Mn(TPyP)AcO	5,10,15,20-tetrapyridylporphyrinato manganese(III) acetate
Mn(TMP)Cl	5,10,15,20-tetra(2,4,6-trimethylphenyl)porphyrinato manganese(III) chloride
Mn(Tm-MeP)Cl	5,10,15,20-tetra(2-methylphenyl)porphyrinato manganese(III) chloride
Mn(β-Cl$_8$TPP)Cl	2,3,7,8,12,13,17,18-octachloro-5,10,15,20-tetraphenylporphyrinato manganese(III) chloride
Mn(β-Br$_8$TMP)Cl	2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetra(2,4,6-trimethylphenyl)porphyrinato manganese(III) chloride

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