Polymeric membranes: the role this support plays in the reactivity of the different generations of metalloporphyrins

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Abstract

In this work, we investigated the catalytic activity of representatives of the three generations of ironporphyrins, namely [5,10,15,20-tetraphenylporphyrin]iron(III) chloride (Fe(TPP)Cl), [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin]iron(III) chloride (Fe(TDCPP)Cl), and [5-mono(pentafluorophenyl)10,15,20-tris(2,6-dichlorophenyl)2,3,7,8,12,13,17,18-octachloroporphyrin] iron(III) (Fe(PCl$_8$)Cl), occluded in a polymeric film based on poly(dimethylsiloxane) (PDMS), in the oxidation of cyclohexane by iodosylbenzene. The catalytic results show the influence of the polymeric support on the reactivity of the three generations of metalloporphyrins, its importance in concentrating the substrate close to the catalytic site, and the protection it renders the catalyst against auto-oxidative destruction.
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1. Introduction

The application of new materials in biomimetical chemistry has been extensively studied in order to prepare catalysts that are more stable and selective under the employed reaction conditions. Another feature that is pursued in these catalysts is their easy recovery from the reaction media and the possibility of having them recycled. One example of such new materials is metalloporphyrins immobilized on, or entrapped in zeolites, mesoporous materials, and clays [1–4].

Metalloporphyrin systems have been studied as models for cytochrome P-450 for over 20 years [5–10]. The search for improved models has led to the design and synthesis of the first, second, and third generations of metalloporphyrins, which bear increasing substitution of hydrogen atoms for bulky, electron-withdrawing groups, on the *meso*-phenyl and

β-pyrrole rings of the porphyrin macrocycle [11,12]. Such substituents confer steric hindrance to the catalyst, avoiding its auto-oxidative destruction [13], and activate the catalytic species, generally a metallo-oxo porphyrin π-cation radical [Me^{IV}O(P$^{\bullet+}$)], making it more electrophilic and reactive towards the substrate [14,15]. Metalloporphyrin immobilization on solid supports offers numerous advantages, such as the prevention of catalyst self-destruction, increased regioselectivity in some reactions, and easy catalyst recovery and re-use [1–4]. Another advantage of supported metalloporphyrins is related to the possibility of their mimicking the protein cavity that is present in natural enzymes. It is well known that the steric effects imposed by the active site environment are responsible for the selectivity encountered within the biological systems [16,17].

Polymeric membranes have been considered innovative materials for metalloporphyrin immobilization. Such support presents many advantages concerning its affinity for reagents, which is the main property of polymers. The hydrophobic
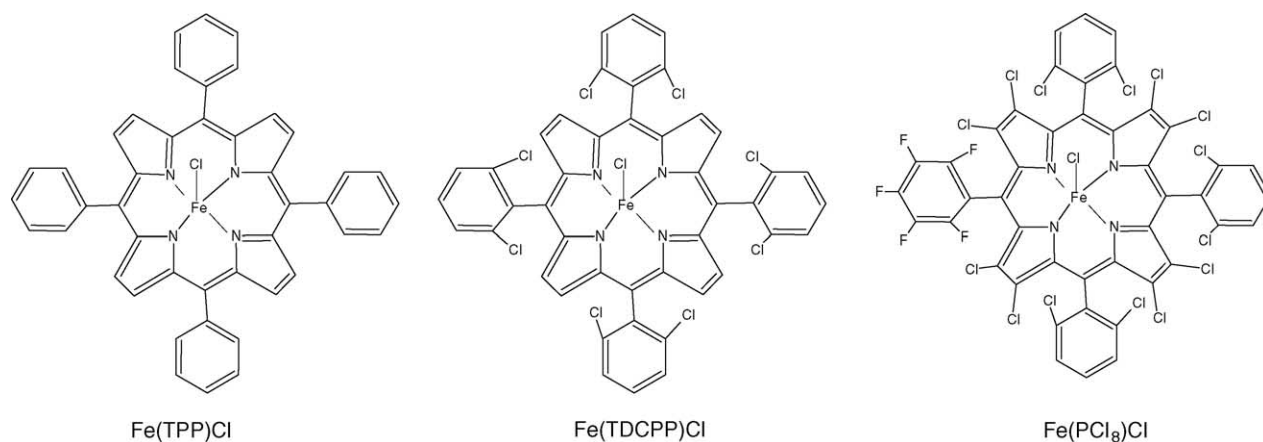

Fig. 1. Ironporphyrins of 1st, 2nd and 3rd generation.

membrane acts as a barrier, isolating and controlling the access of both the substrate and the oxidant to the active site, thus avoiding the presence of excess polar substances in its vicinity, and rendering a hydrophobic environment for substrate binding. Therefore, polymeric membrane-immobilized metalloporphyrins can act as shape-selective catalysts where the polymer isolates the catalytic complex, avoiding its inactivation by aggregation or self-oxidative destruction [18].

Poly(dimethylsiloxane) (PDMS), a dense hydrophobic elastomer, is one of the most important polymers in the silicon chemistry because of its good thermal and chemical stabilities. It has been successfully applied to the immobilization of oxygenation catalysts, such as phthalocyanines in zeolite-Y, and epoxidation catalysts, such as Mn-salen [19–21].

In this work, we compare the catalytic activity of representatives of the three generations of ironporphyrins, namely [5,10,15,20-tetraphenylporphyrin]iron(III) chloride (Fe(TPP)Cl), [5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrin]iron(III) chloride (Fe(TDCPP)Cl), and [5-mono(pentafluorophenyl)10,15,20-tris(2,6-dichlorophenyl)2,3,7,8,12,13,17,18-octachloroporphyrin] iron(III) (Fe(PCl$_8$)Cl) (Fig. 1) occluded in a polymeric film based on poly(dimethylsiloxane) (PDMS), in the oxidation of cyclohexane by iodosylbenzene. These films belong to a class of hybrid organic–inorganic materials that present, apart from an hydrophobic component (PDMS, in this case), the polar clusters as cross-linking centers of PDMS chains. These clusters display a great number of functional Si−OH groups to promote condensation reaction with the Si−OH of the chain-end of PDMS. The design of such hybrid network is an alternative for the production of multi-functional materials with polar and apolar nano-domains which can lead to a vast number of applications, since the combination of the intrinsic properties of each compound results in solubility, viscosity, and thermal behavior that are distinct from those observed with the traditional polymeric systems. Our aim herein is to investigate the role of this new support in the reactivity of the different generations of encapsulated metalloporphyrins.

2. Experimental

2.1. Materials

All compounds used in this study were commercially available from Aldrich or Sigma and were of analytical grade purity unless otherwise stated. Dichloromethane was distilled and stored on 4 Å molecular sieves. Acetonitrile and methanol were stored on 3 Å molecular sieves. Iodosylbenzene (PhIO) was prepared by the hydrolysis of iodosylbenzene diacetate following the method of Sharefkin and Saltzman [22], and its purity was 96%, as determined by iodometric titration. Fe(TDCPP)Cl and Fe(TPP)Cl were purchased from Mid-Century and used as received. Pentaerythritholtriacrylate (PETA) and isopropanol were purchased from Aldrich. 2-Aminoethyl-3-aminopropyltrimethoxysilane (AS) and poly(dimethylsiloxane) (PDMS), both with molecular weight of ~2200 g mol^{-1}, were supplied by Dow Corning. The di-n-butyltindilauryl complex, 5 wt.% in hexane (Sn catalyst), and tetraethoxysilane (TEOS) were supplied by Gelest.

The free base H$_2$(PCl$_8$) was prepared by chlorination of zinc 5-(pentafluorophenyl)-10,15,20-tris(2,6-dichlorophenyl)porphyrin with N-chlorosuccinimide followed by demetallation with trifluoroacetic acid, as described previously [3,23]. Iron porphyrin, Fe(PCl$_8$)Cl, was obtained by metallation of the free ligand with iron(II) chloride dihydrate in acetonitrile. UV–vis (CH$_2$Cl$_2$), Fe(PCl$_8$)Cl: λ, nm (ε, $\times 10^2$ L mol^{-1} cm^{-1}): 394 (854); 440 (933); m/z [FAB$^+$]: 1239.566 [100% − relative abundance] corresponding to FeC$_{44}$H$_9$N$_4$F$_5$^{35}Cl$_{11}$^{37}Cl$_3$.

2.2. Preparation of the polymeric membranes

The synthetic procedure followed for the obtention of polymeric membranes (PM), and of polymeric membranes containing encapsulated ironporphyrin started from the first-generation dendrimeric units prepared in situ from PETA (2.6 wt.%) and AS (7.7 wt.%), by the addition-type Michael

reaction. These dendrimers act as cross-linkable centers in the preparation of the PDMS network, making it a self-supported film. In these films, the amount of PDMS was 79.7 wt.%, and TEOS (10 wt.%) was present as co-cross-link. The membranes were obtained using isopropanol (10 mL) as solvent, by mixing the reagents for 30 min at 40 °C, in the presence of Sn catalyst [24]. Afterwards, 10 mL dichloromethane was added, followed by the addition of a volume of catalyst solution in dichloromethane that was enough to provide 0.02 wt.% iron porphyrin in relation to the total mass of the polymeric membrane. The mixtures were cast on Teflon® Petri dishes for 10 days. The samples were then dried at 50 °C, in a vacuum oven, for 48 h, resulting in the Fe(TPP)Cl-PM, Fe(TDCPP)Cl-PM and Fe(PCl$_8$)Cl-PM membranes with 0.02 wt.% catalyst.

2.3. Sorption measurements

The sorption of cyclohexane, the oxidation product (cyclohexanol) and the solvents (methanol and dichloromethane) in the polymeric membrane were investigated by dipping 50 mg of the membrane into the appropriate liquid. After 24 h of immersion, the swollen membrane was weighted again after the removal of the excess liquid. The supernatant was analyzed by UV–vis spectrum in order to check if the metalloporphyrin had leached from the membrane during the sorption experiments.

2.4. Oxidation reactions

The encapsulated iron(III)porphyrin (FeP) (7.0×10^{-9} mol, 40 mg membrane containing FeP 0.02 wt.%) or iron(III)porphyrin in homogeneous solution (7.0×10^{-9} mol) was stirred with cyclohexane and iodosylbenzene in dichloromethane:methanol (1:1). The catalyst:substrate:oxidant molar ratio was 1:2000:4000, in the case of condition 1; and for condition 2, the catalyst:oxidant:substrate molar ratio was 1:4000:990.000. After 24 h, the membrane was removed, the internal standard was added, and the products were analyzed by GC. All the reactions were carried out at room temperature with magnetic stirring. After the reactions, the membranes were immersed in dichloromethane for 24 h in order to extract the oxidized products that could remain inside the polymer. The extracts were analyzed by GC. Control reactions were carried out in the same conditions, using the membrane containing no iron(III)porphyrin.

2.5. Instrumentation

UV–vis spectra were obtained on a Hewlett-Packard 8452, diode array spectrometer. The spectra were recorded in 10 mm path length quartz cells (Hellma). The spectra of the occluded catalysts were registered by maintaining the membrane directly in the optical way, using the membrane containing no iron porphyrin as reference.

GC analysis was performed on a Varian 3400 CX chromatograph with a hydrogen flame ionization detector using a DB-wax (1 μm thickness) megabore column (30 m × 0.538 mm). Nitrogen was used as the carrier gas. The results were recorded and processed on a Varian workstation.

The morphology of the membranes was analyzed by scanning electron microscopy (SEM) using a JEOL-JSM T-300 microscope, operating at 20 kV. The observed surface was obtained by coating the cryogenic fracture with a thin gold layer.

3. Results and discussion

3.1. Characterization of the occluded catalyst

The polymeric membrane used was a PDMS-based membrane, cross-linked by polar first-generation dendrimers. TEOS units also acted as co-cross-linkable centers. Indeed, the resulting polymeric membrane displayed a well-defined glass transition at approximately −120 °C, due to relaxation of the PDMS chains [24,25]. Since the ironporphyrins were soluble in the medium where the membranes were prepared, the occluded catalysts were homogeneously dispersed into the PDMS chains, resulting in completely homogenous and transparent membranes. Fe(TPP)Cl, Fe(TDCPP)Cl, and Fe(PCl$_8$)Cl iron(III)porphyrins (Fig. 1) were successfully encapsulated in the membranes, as shown by the UV–vis spectra of the materials, which display Soret bands at 414, 424, and 488 nm for Fe(TPP)Cl-PM, Fe(TDCPP)Cl-PM, and Fe(PCl$_8$)Cl-PM, respectively (Fig. 2). The absorption of Fe(TDCPP)Cl-PM and Fe(PCl$_8$)Cl-PM are red-shifted, if compared to the parent iron(III)porphyrins in dichloromethane solution (416 and 440 nm, respectively). Significant changes are normally observed when these iron porphyrins are immobilized on solid supports [26], and they can be attributed to the distortion of the porphyrin ring provoked by the support. Distortions in the porphyrin ring planarity lead to a destabilization of the HOMO, but not of the LUMO orbital, resulting in a decrease in the HOMO–LUMO energy gap, which is responsible for the red-shift of the Soret band [27,3]. No shift was observed in the Soret band of occluded Fe(TPP)Cl (412 nm). This is because this less robust ironporphyrin can fit better in the membrane cavity without any distortion of the porphyrin ring.

The cryogenic fractures observed on the surface of the dense membranes both in the presence and in the absence of the occluded complexes showed similar and homogeneous patterns, without any morphological detail in the higher magnification micrography, as can be seen in Fig. 3A for Fe(TDCPP)Cl-PM. In the lower magnification micrography (Fig. 3B), a rough surface was observed, due to the cryogenic fracture typical of PDMS membranes.

The affinity of reagents and products for the membrane phase can be easily determined by measuring the sorption of the compounds in the membrane. The more a polymer swells
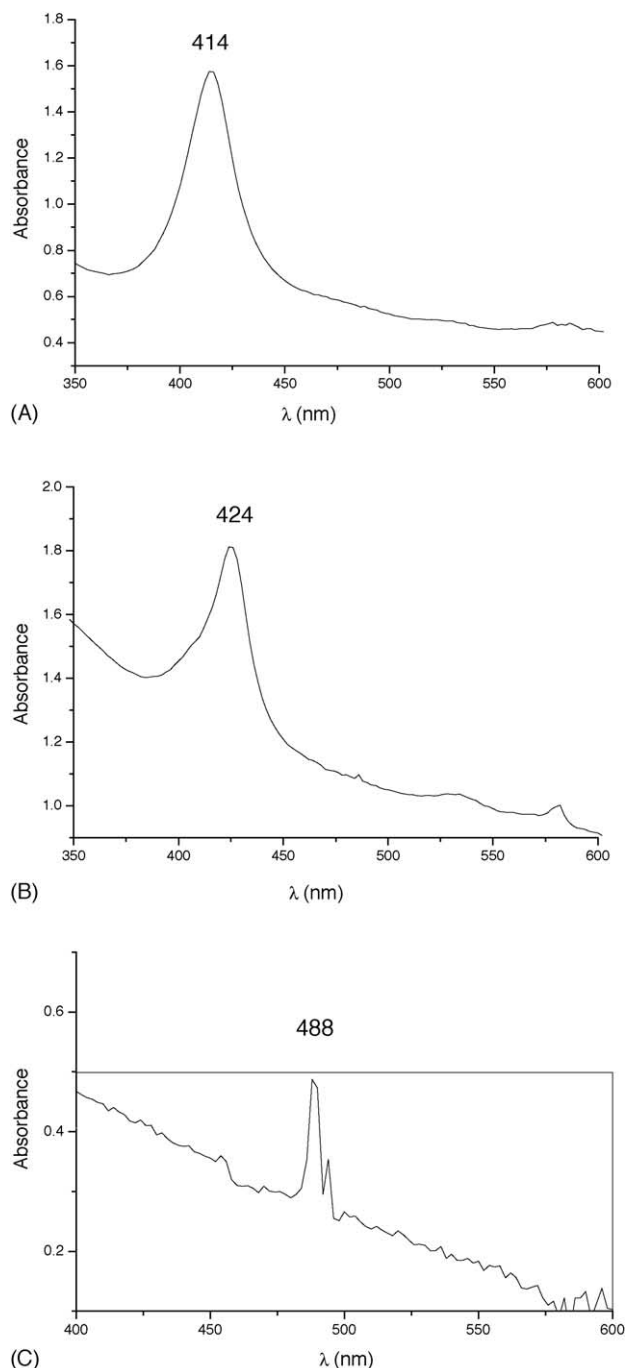
Fig. 2. UV–vis spectra of the (A) Fe(TPP)Cl-PM, (B) Fe(TDCPP)Cl-PM, and (C) Fe(PCl$_8$)Cl-PM. The membrane without ironporphyrin was used as reference.

in a determined solvent, the higher its affinity for this compound. The ability of the membrane to adsorb the solvent and substrates is essential to establish the reaction conditions in the catalytic studies. The sorption values after 24 h of swelling for the compounds of interest in our study are shown in Fig. 4.

Dichloromethane, which is the solvent used in this study, is more readily adsorbed by these hydrophobic materials than cyclohexane. These results are reflected in the catalytic pro-

file of the encapsulated catalysts, as there is competition between this solvent and the substrate for the catalytic center. Methanol and cyclohexanol do not swell the membranes significantly.

No leaching of the catalysts was observed in any of the supernatants, proving that the catalysts are maintained inside the membranes.

3.2. Catalytic studies

The catalytic activity of the three generations of polymeric membrane-occluded metalloporphyrins was evaluated by using cyclohexane as substrate, and iodosylbenzene as oxidant. Taking into account the affinity of the support for the reagents, two reaction conditions were employed. In condition 1, a catalyst:substrate:oxidant molar ratio of 1:2000:4000 was used, which corresponds to 1.5×10^{-5} mol substrate in 1.5 mL solvent. Such condition employed highly diluted substrate in the reaction medium, since our aim was to evaluate the ability of the support in concentrating apolar reagents in its interior. Moreover, as the oxidant is polar and could be poorly sorbed into the membrane, it was used in excess in order to favor its sorption by the dragging effect.

A catalyst:oxidant:substrate molar ratio of 1:4000:990.000 was employed in condition 2, corresponding to a 1:1 cyclohexane:dichloromethane/methanol volume ratio. Such condition aimed at favoring the sorption of cyclohexane with respect to the solvent dichloromethane, since the latter displays higher affinity for the polymeric support (Fig. 4).

The membrane-occluded iron(III)porphyrins Fe(TDCPP)Cl and Fe(TPP)Cl presented excellent efficiency for cyclohexane oxidation, in the condition of highly diluted substrate (condition 1), as shown in Table 1, leading to 42 and 37 turnovers of oxidized products, respectively (Table 1, entries 4 and 5). These ironporphyrins were not efficient catalysts for cyclohexane oxidation in homogeneous solution, in the same experimental condition (Table 1, entries 1 and 2). This is because the low substrate concentration and the low substrate/oxidant molar ratio favor competitive reactions, such as solvent oxidation, PhIO disproportionation, among others, in homogeneous systems. These results show the great ability of the polymeric support in concentrating the apolar substrate in the vicinity of the catalyst active site, even at diluted concentrations, and considering that one of the reaction solvents (dichloromethane) presents higher affinity for the membrane than the substrate itself and undergoes preferable sorption (Fig. 4).

The only cyclohexane oxidation product obtained when the reaction was catalyzed by Fe(TPP)Cl-PM or Fe(TDCPP)Cl-PM was cyclohexanol. The high selectivity for the alcohol indicates that the oxidation mechanisms probably involve the same catalytic species as the one observed in homogeneous solution, the high valent metal-oxo porphyrin π-cation radical, ($^{\bullet+}$P)Fe^{IV}=O, which is formed from the reaction between the oxidant and the iron(III)porphyrin
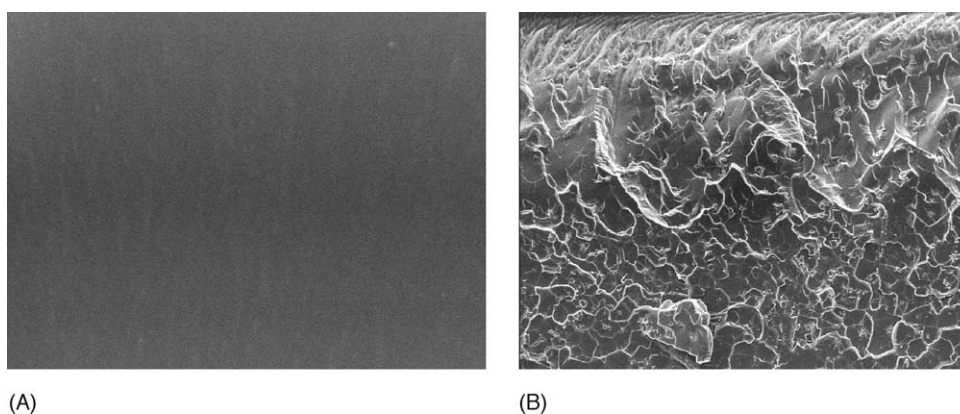
Fig. 3. Cryogenic surface fracture micrographies of the Fe(TDCPP)Cl occluded-polymeric membrane at different magnification: (A) ×3500; (B) ×75.
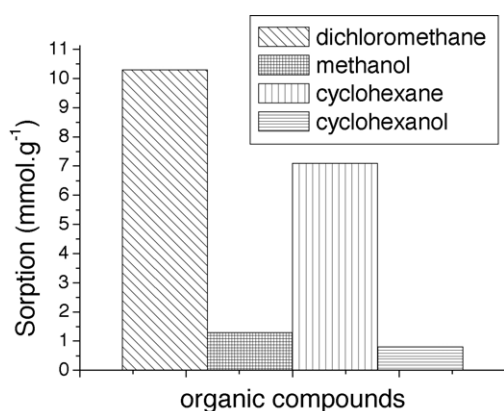

Fig. 4. Room-temperature sorption measurements for dichloromethane, methanol, cyclohexanol, and cyclohexane in FeP-PM.

[14,15]. After being produced, cyclohexanol is quickly expelled from the hydrophobic membrane, as can be inferred from its low sorption value (Fig. 4), avoiding its further oxidation to the corresponding ketone. This was confirmed by the absence of the alcohol in the dichloromethane extracts after the reaction.

In the case of Fe(PCl$_8$)Cl-PM, a third-generation metalloporphyrin, no product was formed in condition 1 (Table 1, entry 6). Although the polymeric membrane is capable of concentrating the substrate in the surroundings of the catalytic site, the eight additional chloro substituents in the β-pyrrole positions of this ironporphyrin ring offer great steric hindrance to the approach of cyclohexane. Moreover, as shown by its UV–vis spectrum, this bulky ironporphyrin presents a distorted ring when it is present between the polymer chains, a factor that may disfavor the interaction between the catalyst and the oxidant, or the catalyst and the substrate.

The catalytic results obtained with the Fe(TPP)Cl-PM system show the benefits of designing new materials for catalyst immobilization. In diluted condition (condition 1), this first-generation ironporphyrin led to the same catalytic efficiency as the second-generation ironporphyrin Fe(TDCPP)Cl-PM, which is known to be a very efficient catalyst in homogeneous solution, according to the literature [28–31]. In solution, total destruction of Fe(TPP)Cl was observed in the reaction conditions employed in this work, as seen from solution bleaching. The Fe(TPP)Cl-PM system, however, kept the same coloring after the oxidation reactions, indicating that the porphyrin

Table 1
Results obtained for the cyclohexane oxidation reactions by PhIO catalyzed by FeP in homogeneous systems or by FeP-PM

Entry	Catalyst	C-ol (Ton)	C-one (Ton)	Total Ton	C-ol/C-one ratio
1	Fe(TPP)Cl (homogeneous solution)[a]	nd	nd	nd	–
2	Fe(TDCPP)Cl (homogeneous solution)[a]	nd	nd	nd	–
3	Fe(PCl$_8$)Cl (homogeneous solution)[a]	nd	nd	nd	–
4	Fe(TPP)Cl-PM[a]	37	nd	37	–
5	Fe(TDCPP)Cl-PM[a]	42	nd	42	–
6	Fe(PCl$_8$)Cl-PM[a]	nd	nd	–	–
7	Fe(TPP)Cl (homogeneous solution)[b]	395	316	711	1.3
8	Fe(TDCPP)Cl (homogeneous solution)[b]	570	445	1015	1.3
9	Fe(PCl$_8$)Cl (homogeneous solution)[b]	1152	530	1682	2
10	Fe(TPP)Cl-PM[b]	313	195	508	1.6
11	Fe(TDCPP)Cl-PM[b]	605	375	980	1.6
12	Fe(PCl$_8$)Cl-PM[b]	443	242	685	1.8

[a] Condition 1 – 1500 μL DCM: MeOH (1:1); – 2 μL cyclohexane (1.5×10^{-5} mol).

[b] Condition 2 – 750 μL DCM: MeOH (1:1); – 750 μL cyclohexane (6.9×10^{-3} mol); nd: not detected; C-ol: cyclohexanol; C-one: cyclohexanone; Ton: mol product/mol FeP (turnover number). Blank reactions (only PM was used): nd.

structure remained unchanged throughout the reaction. The polymer is, therefore, efficiently acting to avoid oxidative self-destruction, one of the problems encountered when first-generation metalloporphyrins are used in oxidation reactions in homogeneous solution [7].

The results obtained for cyclohexane oxidation carried out in excess substrate (condition 2) were different from those obtained in condition 1. In homogeneous solution, the presence of excess substrate disfavors the occurrence of the competitive reactions, leading to high turnover numbers (Table 1, entries 7–9). The observed catalytic efficiency was Fe(PCl$_8$)Cl > Fe(TDCPP)Cl > Fe(TPP)Cl, which is expected since an increase in the number of electron-withdrawing substituents in the periphery of the porphyrin ring improves catalyst performance by increasing the electrophilicity of the active species [32–35].

In the case of immobilized ironporphyrins, the small piece of the membrane that is used in the reactions has limited substrate and/or oxidant sorption capacity, which seems to be the limiting reaction factor at higher substrate concentrations. This fact explains the lower turnover numbers obtained for the heterogeneous systems in this condition (685, 980, and 508 for Fe(PCl$_8$)Cl-PM, Fe(TDCPP)Cl-PM, and Fe(TPP)Cl-PM, respectively, Table 1, entries 10–12), if compared to those obtained in homogeneous solution. In this condition, Fe(TDCPP)Cl-PM was more efficient than Fe(PCl$_8$)Cl-PM because of the greater steric hindrance of the latter catalyst within the membrane, as discussed previously. Fe(TDCPP)Cl-PM was also more efficient than Fe(TPP)Cl-PM, different from what occurs in condition 1. In this case, the excess substrate shows these complexes have different intrinsic reactivity.

It is important to note that the selectivity for cyclohexanol is higher with the occluded catalyst than with the less robust porphyrins in homogeneous solution (Table 1, entries 10 and 11 versus 7 and 8), showing that the hydrophobic membrane does play a role in selecting the substrate by its polarity, which is a role similar to that of the protein matrix in P-450 enzymes.

4. Conclusions

Three generations of metalloporphyrins have been successfully occluded in a new polymeric material, with little or no alteration in their geometry. Despite the typical limitations of heterogeneous systems, the catalytic results show that the support presents great ability in concentrating the reagents next to the catalyst, especially in diluted conditions. Such feature is responsible for controlling both the substrate access to the active site and the reactivity of the active species, leading to selective oxidation reactions. Moreover, the support acts as a good model for the protein cavity of cytochrome P-450, preventing inactivation of first-generation catalysts, such as Fe(TPP)Cl, and enhancing their catalytic efficiency which, in such systems, is similar to that of the second-generation

metalloporphyrin and higher than that of the third-generation catalyst.

The catalytic results obtained with these systems show that polymeric membranes of different polarity and environment can be designed, aiming at the selective oxidation of other substrates.

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