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## Main-Chain Porphyrin Polymers. 1. Synthesis and Characterization of Polyethers Containing Porphyrin Units and Their Metal Derivatives

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ABSTRACT: The synthesis of four polyethers (I–IV) containing *meso*-tetraarylporphyrin units in the main chain is described. Two monomers, 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)porphyrin ($M_1$) and 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-methoxyphenyl)porphyrin ($M_2$), obtained by partial ethylation or methylation of tetrakis(*p*-hydroxyphenyl)porphyrin, were carefully separated from the other reaction products and characterized by $^1H$ NMR and FABMS analyses. In order to obtain macromolecules having flexible connections among porphyrin units along the polymer chain, the monomers $M_1$ and $M_2$ were treated with linear aliphatic dichlorides or dibromides of different molecular weight. The polyethers I–IV obtained were characterized by GPC, $^1H$ and $^{13}C$ NMR, and FABMS analyses. Their thermal stabilities were also examined. FABMS data about the inclusion of transition metals [cobalt(II), manganese(II), and zinc(II)] in the porphyrin units of polyethers III and IV are also reported. Our data show that in all the porphyrin units the two NH hydrogen atoms are substituted by one metal transition atom. So, polymers having a porphyrin units/metal ions ratio of 1 are always obtained.

### Introduction

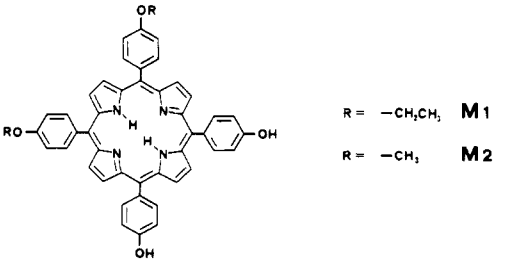
In recent years, polymeric materials containing macrocyclic units with the ability to bind transition metals have attracted much interest.[1-14]

Potential applications for these materials are found in the field of the chemical conversion of solar energy by photocatalytic or electrochemical reactions,[5,14-16] highly selective polymeric membranes,[3,4,9-11] polymer metal complexes used as immobilized catalysts,[16-20] and polymer liquid crystals.

Among the macrocyclic structures incorporated in the polymer chains, porphyrin and metalloporphyrin units have frequently been used especially for the construction of artificial oxygen carriers inspired by those in biological systems,[4,6,12-14,23] the development of new catalytic systems,[19-22] and the synthesis of new receptors able to bind amino acids (via metal-coordination and hydrogen-bonding interactions).[24,25]

There are two types of polymers in which the metal-containing units either are bound to the polymer as pendant groups or are part of the polymer main chain. Several examples of polymers belonging to the first type of materials have been reported in the literature.[5-8,14] In this paper we present the synthesis of four new polyethers (I–IV) in which porphyrin units are located in the backbone of the polymer chain.

The porphyrins used, 5,10-bis(*p*-hydroxyphenyl)-15,-20-bis(*p*-ethoxyphenyl)porphyrin and 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-methoxyphenyl)porphyrin (indicated in the text as $M_1$ and $M_2$, respectively), were prepared by partial ethylation or methylation of the 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrin. Polymers I–IV, having




flexible connections of different lengths between the porphyrin units, were obtained by the reaction of $M_1$ or $M_2$

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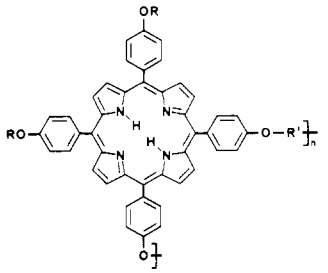
with suitable linear aliphatic dichlorides or dibromides in the presence of a phase-transfer agent. The polymers were characterized by GPC, $^1H$ and $^{13}C$ NMR, and FABMS[26-30] analyses.



R: $-CH_3$ ; R': $-CH_2-$ ; I

R: $-CH_3$ ; R': $-(CH_2)_6-$ ; II

R: $-CH_3$ ; R': $-(CH_2)_8-$ ; III

R: $-CH_2CH_3$ ; R': $-(CH_2)_6-$ ; IV

Data about the reaction between polymers III and IV and cobalt(II), manganese(II), or zinc(II) acetate are also reported.

## Experimental Section

**Materials.** All the solvents and the basic materials were commercial products appropriately purified before use.

**Porphyrin Monomer Synthesis.** The two monomers, 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)porphyrin ($M_1$) and 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-methoxyphenyl)porphyrin ($M_2$), were prepared by partial ethylation or methylation with an excess of $CH_3CH_2Br$ or $CH_3I$, respectively, of 5,10,15,20-tetrakis(*p*-hydroxyphenyl)porphyrin (obtained as described previously[31]).

Both monomers were synthesized and purified in the same way; we report the procedure adopted for $M_1$.

In a three-neck flask equipped with a magnetic stirrer, a reflux condenser, and a tube for $N_2$ introduction were placed 6.78 g (0.001 mol) of tetrakis(*p*-hydroxyphenyl)porphyrin, 5.45 g (0.05 mol) of $CH_3CH_2Br$, 5.3 g (0.05 mol) of $Na_2CO_3$, and 300 mL of acetone. The mixture was stirred under refluxing conditions and $N_2$ flow and tested by thin-layer chromatography (TLC) and FABMS analyses at regular intervals. When the optimum diethoxy porphyrin derivative (two different isomers are formed) was formed, the reaction was stopped (after about 50 h) and the mixture chromatographed on silica gel under medium pressure (liquid chromatograph (LC), Büchi Model 681) using a solution of chloroform containing ethanol (from 0.5% to 3%) as eluant. Because the two 5,10- and 5,15-bis(hydroxyphenyl)porphyrin isomers were not well separated on this column, a second preparative LC was necessary for obtaining pure products. The separated compounds had the same molecular weight and composition [$C_{48}H_{38}N_4O_4$] determined by exact positive FABMS analysis as $(M + H)^+$ ions: 735.297 amu (calculated value, 735.297), but different $R_F$ (TLC) and mp (DSC) values: one, obtained in greater abundance, had $R_F$ 0.61 ($CHCl_3/C_2H_5OH$, 93/7) and mp 335 °C; the other, with $R_F$ 0.69, decomposed without melting at 420 °C.

The proton NMR spectra (in DMF-$d_7$) of the two isomers are reported in Figure 1 (the truncated peaks at 2.718, 2.886, and 8.0 ppm are due to DMF, and that at 3.50 ppm is due to $H_2O$). These two spectra appeared very similar except for the region corresponding to the pyrrole (about 9 ppm) and phenyl (between 7 and 8.5 ppm) proton resonances. On the basis of the greater molecular symmetry shown by the product having the NMR spectrum in Figure 1b, this isomer was identified as 5,15-bis(*p*-hydroxyphenyl)-10,20-bis(*p*-ethoxyphenyl)porphyrin. The other compound ($R_F$ 0.61 and mp 335 °C), obtained with a yield of about 10%, indicated as $M_1$ in the text, corresponds to 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)porphyrin and was used for polyether IV synthesis.

Proton chemical shifts (ppm) of $M_1$ (Figure 1a): $CH_3$, 1.528 (t, 6 H); $CH_2$, 4.311 (q, 4 H); CH phenyl, [7.309 (d, 4 H), 7.357 (d, 4 H), 8.091 (d, 4 H), 8.153 (d, 4 H)]; CH pyrrole, 8.930 (m, 8 H); OH, 10.195 (s, 2 H).

Proton chemical shifts (ppm) of the 5,15-isomer (Figure 1b): $CH_3$, 1.553 (t, 6 H); $CH_2$, 4.354 (q, 4 H); CH phenyl, [7.312 (d, 4 H), 7.407 (d, 4 H), 8.095 (d, 4 H), 8.187 (d, 4 H)]; CH pyrrole, 8.491 (dd, 8 H); OH, 10.210 (s, 2 H).

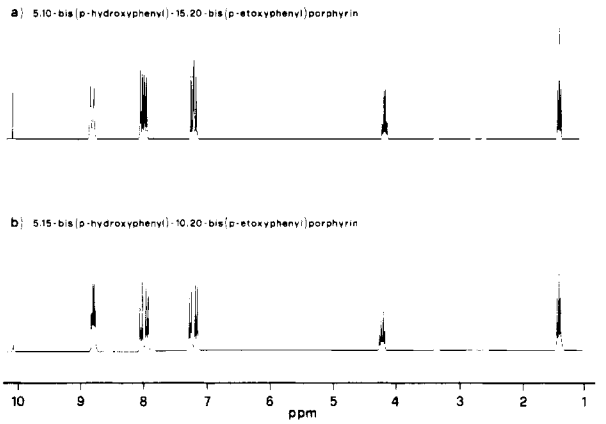



**Figure 1.** $^1H$ NMR spectra, recorded in DMF-$d_7$, of (a) 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)porphyrin ($M_1$) and (b) 5,15-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)-porphyrin. The truncated peaks are due to DMF and $H_2O$.

The 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-methoxyphenyl)-porphyrin [$M_2$, $C_{46}H_{34}N_4O_4$] was examined by exact positive FABMS analysis. The molecular weight, as $(M + H)^+$, was 707.267 amu (calculated value, 707.266). This compound was obtained with a yield of about 5% with respect to the tetrakis(*p*-hydroxyphenyl)porphyrin starting amount. It had an $R_F$ of 0.59 ($CHCl_3/C_2H_5OH$, 93/7); the corresponding 5,15-isomer had $R_F$ 0.67. $^1H$ NMR spectrum (shifts in ppm) in DMSO-$d_6$ of $M_2$: $CH_3$, 4.037 (s, 6 H); CH phenyl, [7.196 (d, 4 H), 7.366 (d, 4 H), 7.989 (d, 4 H), 8.108 (d, 4 H)]; CH pyrrole, 8.746 (m, 8 H); OH, 9.957 (s, 2 H).

**Polyether Synthesis.** Polyethers I and II were synthesized using porphyrin $M_2$ (0.1 mmol) and dichloromethane (in large excess) or 1,6-dichlorohexane (stoichiometric amount) in the presence of NaOH (0.4 mmol) and tetrabutylammonium bromide (TBAB) (0.2 mmol) as phase-transfer agent in a toluene/$H_2O$ mixture under stirring at about 100 °C for 24 h.[32,33] After distillation of solvents, the residue was solubilized in *N*-methyl-2-pyrrolidone (NMP), precipitated in water/acetic acid, washed with ethanol, and dried in vacuo. Yields were about 50% (polymer I) and 40% (polymer II).

Polyethers III and IV were similarly synthesized using 1,8-dibromooctane (0.1 mmol) and porphyrin $M_2$ (0.1 mmol) or 1,6-dibromohexane (0.1 mmol) and porphyrin $M_1$ (0.1 mmol), respectively, in the presence of KOH (0.4 mmol) and 18-crown-6 ether (0.2 mmol) as phase-transfer catalyst. The polymers, precipitated in an ethanol/acetic acid mixture, were collected by filtration, washed with ethanol, and dried under vacuo. Yields were in both cases about 60%.

**Metal Derivatives of Polyethers III and IV.** The zinc and manganese/polyether III derivatives were prepared as follows: to 20 mg of polyether III in 20 mL of NMP were added 40 mg (a large excess with respect to the stoichiometric amount) of zinc(II) or manganese(II) acetate. The mixture was maintained at about 70 °C under stirring for several hours. After distillation of the solvent, the residue was repeatedly washed with hot water to remove any trace of unbound metal.

In another series of experiments, polyether IV was treated in the way reported above with cobalt(II), copper(II), nickel(II), iron(II), barium(II), lead(II), or magnesium(II) acetate.

**GPC Analysis.** A Waters 6000A apparatus, equipped with four $\mu$-Styragel columns (in the order 1000-, 500-, 10 000-, and 100-Å pore size) attached in series, was used. The analyses were performed at 25 °C using $CHCl_3$ as eluant at a flow rate of 1 mL/min. The instrument was calibrated with a mixture of five polystyrene standards (Polysciences; molecular weights between 800 and 110 000 amu).

**$^1H$ NMR and $^{13}C$ NMR Analysis.** $^1H$ NMR and $^{13}C$ NMR spectra were obtained on a Bruker 250 A-CF spectrometer using DMF-$d_7$ or DMSO-$d_6$ as solvents and TMS as an internal reference.

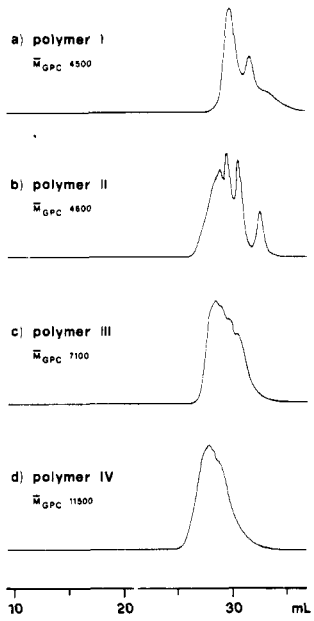



**Figure 2.** Gel permeation chromatograms ($CHCl_3$ as eluant) of polyethers I–IV (evolution volume for pure porphyrin $M_1$ and $M_2$ is 34.6 mL). The GPC-average molecular weight ($M_{GPC}$) values, measured with respect to polystyrene standards, are reported.

**Thermal Properties.** Thermogravimetric analyses were performed with a Perkin-Elmer TGS-2 apparatus in a $N_2$ atmosphere with a flow rate of 60 mL/min and a heating rate of 10 °C/min.

Differential scanning calorimetry (DSC) was performed to determine the melting point of the samples examined by using a Mettler DSC-20 instrument. The heating rate was 10 °C/min, under a $N_2$ atmosphere.

**FABMS Analysis.** FAB analyses were performed on a double-focusing Kratos MS 50S mass spectrometer equipped with the standard FAB source. The FAB gun (Ion Tech) was operated with a 7–8-keV xenon beam. The instrument was scanned from $m/z$ 4000 to 90, with a scan rate of 30 s/decade. The accelerating voltage was 8 kV. The mass resolution was approximately 4000. Mass spectra were recorded by using a UV oscillographic recorder. Spectra were obtained by using 3-nitrobenzyl alcohol (TNB) as a matrix.

Peak intensity values shown in the mass spectra represent the average of almost three different mass spectra.

B/E-FABMS were performed by using a linked scan unit.[34]

Exact mass measurements were performed on positive FAB mass spectra at 10 000 resolving power using TNB as an internal reference and by computer interpolation with the "Convert Masses" program of our DS 90 Kratos software.

## Results and Discussion

In order to obtain polymers having linear flexible connections of different lengths between the porphyrin units along the polymer chain, polyethers I–IV were synthesized by a condensation reaction between *meso*-bis(hydroxyphenyl)porphyrin $M_1$ or $M_2$ and dichloromethane, 1,6-dichlorohexane, 1,8-dibromooctane, or 1,6-dibromohexane.

In Figure 2 the GPC traces of the obtained polyethers ($CHCl_3$ used as eluant) are reported. The GPC-average molecular weight ($M_{GPC}$) values (measured with respect to polystyrene standards) lie between 4500 and 11 500 amu.

The weight loss curves (under a nitrogen atmosphere) of the four polymers are reported in Figure 3. The temperature of the maximum rate of polymer decomposition (PDT) appears for all at about 440 °C, and they all leave an abundant thermally stable residue, whose amount depends on the weight of the aliphatic connection among the porphyrin units present in each polymer. So, at 700 °C a residue amount of 71% is observed for polyether I (methylene), while a residue of only 42% is found for polyether III (octamethylene).

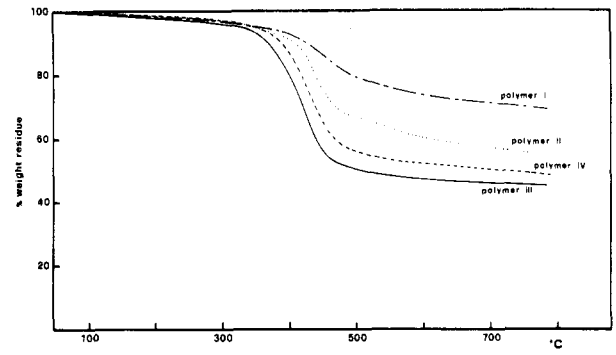



**Figure 3.** Percent weight loss curves of polyethers I–IV. TG experiments were done under $N_2$ flow (60 mL/min) with a heating rate of 10 °C/min.

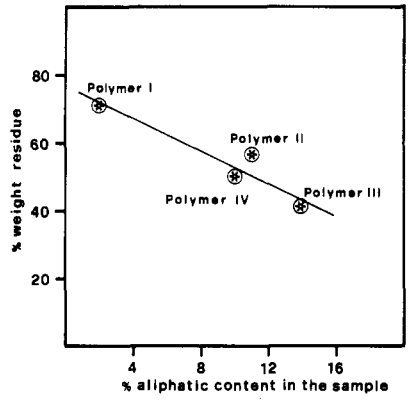



**Figure 4.** Plot of percent weight residue at 700 °C in TG experiments under a $N_2$ flow vs the corresponding percent aliphatic content (w/w) present in each polymer.

In Figure 4 the residue amounts (at 700 °C) are reported as a function of the percent aliphatic (methylene, hexamethylene, or octamethylene) content (w/w) present in each polymer. The good correlation obtained implies that similar thermal degradation processes are responsible for char formation. We have also ascertained that the thermal behavior of polyethers I–IV is little modified by the inclusion of metal atoms in the polymer porphyrin units.

The structural characterization of polyethers I–IV was attempted by $^1H$ NMR and $^{13}C$ NMR analyses.

The proton NMR spectra do not give significant results because of the very low resolution of the signals (data omitted for brevity). However, a shift of CH pyrrole and CH phenyl proton resonances, with inversion of their signals in the $^1H$ NMR spectra of polyethers with respect to those of the corresponding porphyrin monomers, can be pointed out.

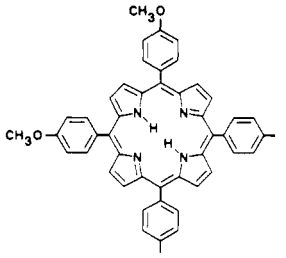
On the contrary, the $^{13}C$ NMR spectra of polymers appear more informative. In Figure 5, as an example, the $^{13}C$ NMR spectrum of polyether IV and that of porphyrin monomer $M_1$ are compared (the truncated peak at 39.5 ppm is due to DMSO).

Also in this case, a lower resolution is observed in the spectrum of the polymer (Figure 5a) than in that of the monomer (Figure 5b); so, in the region of the CH pyrrole and CH phenyl carbon resonances (between 110 and 170 ppm), 11 signals are found in Figure 5b ($M_1$) compared to only 8 in the spectrum of Figure 5a (polymer IV). Notwithstanding this, the signals in the zone of aliphatic CH carbon resonances (between 10 and 70 ppm) are diagnostic in confirming the polymer formation. In fact,

**Table I**
**Low Molecular Weight Oligomers Detected in the Positive FAB Mass Spectrum of Polyether I**

| structures[a] | m/z values of molecular ions with n = 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| [O—Porph—$OCH_2$]$_n$ [b] | | (719)[d] | 1437 | 2155 |
| H[O—Porph—$OCH_2$]$_n$OH [c] | | 736 | 1454 | 2172 |
| H[O—Porph—$OCH_2$]$_n$O—Porph—OH [c] | 706 | 1424 | 2142 | |

[a] In the reported structures, Porph =

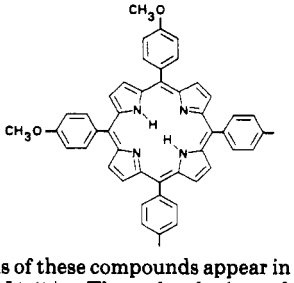


[b] The molecular ions of these oligomers appear in the positive FAB mass spectrum as $(M + 1)^+$. [c] The molecular ions of these oligomers appear in the positive FAB mass spectrum as $(M)^+$. [d] Peak originated by EI.

**Table II**
**Low Molecular Weight Compounds Detected in the Positive FAB Mass Spectrum of Polyether II**

| structures[a] | m/z values of molecular ions with n = 0 | 1 | 2 |
|---|---|---|---|
| [O—Porph—$O(CH_2)_6$]$_n$ [b] | | (789)[d] | 1577 |
| H[O—Porph—$O(CH_2)_6$]$_n$$O(CH_2)_4OH$ [b] | | 907 | |
| H[O—Porph—$O(CH_2)_6$]$_n$O—Porph—$OC_6H_9$ [c] | 762 | 1550 | |
| H[O—Porph—$O(CH_2)_6$]$_n$$OC_4H_9$ [b] | | 863 | 1651 |
| $C_4H_9$[O—Porph—$O(CH_2)_6$]$_n$$OC_4H_9$ [b] | | 819 | 1607 |
| $C_4H_9$[O—Porph—$O(CH_2)_6$]$_n$Cl [b] | | 881 | 1669 |
| HO[$(CH_2)_6$O—Porph—O]$_n$$(CH_2)_6$Cl [b] | | 924 | |
| Cl[$(CH_2)_6$O—Porph—O]$_n$$(CH_2)_6$Cl [b] | | 943 | |

[a] In the reported structures, Porph =



[b] The molecular ions of these compounds appear in the positive FAB mass spectrum as $(M+1)^+$. [c] The molecular ions of these compounds appear in the positive FAB mass spectrum as $(M)^+$. [d] Peak originated by EI.

two signals at 63.301 and 14.853 ppm (due to the $OCH_2CH_3$ group) are found in the $^{13}C$ NMR spectrum of porphyrin monomer $M_1$ (Figure 5b), while five signals are present in that of polymer IV (Figure 5a): two, at 63.840 and 14.763 ppm, are due also in this case to the $OCH_2CH_3$ group; the others, at 68.140, 28.858, and 25.560 ppm, correspond to the carbon resonances of the $OCH_2CH_2CH_2CH_2CH_2O$ aliphatic connection between the porphyrin units in the polymer.

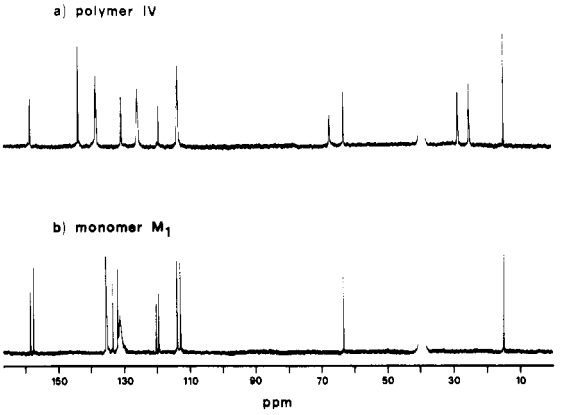



**Figure 5.** $^{13}C$ NMR spectra, recorded in DMSO-$d_6$, of (a) polymer IV and (b) 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)-porphyrin ($M_1$). The truncated peak is due to DMSO.

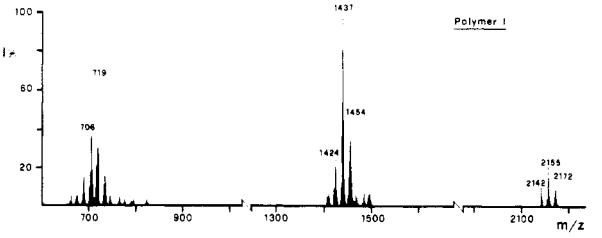



**Figure 6.** Positive FAB mass spectrum of polyether I.

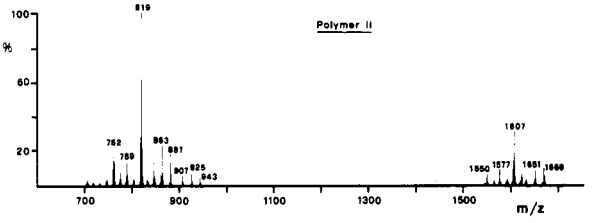



**Figure 7.** Positive FAB mass spectrum of polyether II.

For a better structural characterization of polyethers I–IV, the positive FAB mass spectra of the low molecular weight oligomers present in each sample were taken.

In Figure 6 the positive FAB mass spectrum of the low molecular weight oligomers present in the polyether I sample is reported.[26-30] The structures corresponding to the peaks appearing in the spectrum are reported in Table I.

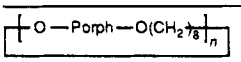
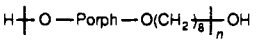
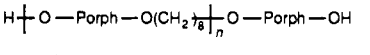
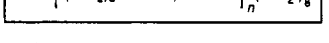
The spectrum is constituted essentially of three families of peaks. The peaks at m/z 1437 and 2155 of the series $719 + (n-1)718$, with $n = 2$ and 3, respectively, correspond to molecular ions [detected as $(M + 1)^+$] of dimer and trimer cyclic oligomers (Table I) formed in polymer synthesis according to eq 1.

$$ClCH_2[O—Porph—OCH_2]_n[O—Porph—O^-\ Na^+ \longrightarrow$$

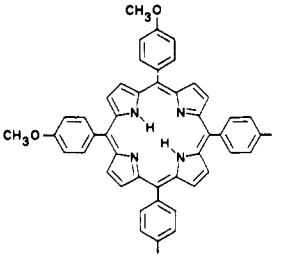
$$[CH_2[O—Porph—OCH_2]_n[O—Porph—O] + NaCl \quad (1)$$

The peak at m/z 719 (first term of the series, $n = 1$) must be considered a fragment formed by electron impact (EI) of oligomers having higher molecular weight (as evidenced by the B/E mass scan[34] of the peak at m/z 1437,

**Table III**
**Oligomers Present in the Polyether III and Their Zn or Mn Derivatives Detected in the Positive FAB Mass Spectra[a]**

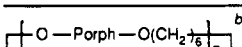
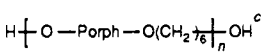
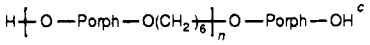
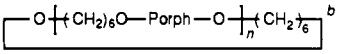
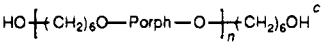
| structures | *m/z* values of molecular ions of polyether III with *n* = | | | | *m/z* values of molecular ions of[f] Zn derivatives with *n* = | | | *m/z* values of molecular ions of Mn derivatives with *n* = | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 0 | 1 | 2 | 0 | 1 | 2 |
|  | | (816)[c] | 1632 | 2448 | | (878)[c,d] | 1694,[d] 1756[e] | | 869[d] | 1738[e] |
|  | | 834 | 1650 | 2466 | | 896[d] | 1712,[d] 1774[e] | | 887[d] | 1756[e] |
|  | 706 | 1522 | | | 768[d] | | | 759[d] | | |
|  | | 944 | 1760 | 2576 | | 1006[d] | 1884[e] | | 997[d] | 1866[e] |
|  | | 962 | 1778 | 2594 | | 1024[d] | 1902[e] | | 1015[d] | 1884[e] |

[a] All the molecular ions appear in the positive FAB mass spectra as $(M)^+$. [b] In the reported structures, Porph =

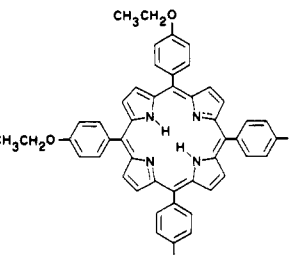


[c] Peaks originated by EI. [d] Compounds having one Zn or Mn atom in the molecule. [e] Compounds having two Zn or Mn atoms in the molecule. [f] The *m/z* values of these compounds are referred to the most abundant isotope of the Zn (atomic mass 64, natural abundance 48.6%).

**Table IV**
**Oligomers Present in the Polyether IV and Their Cobalt Derivatives Detected in the Positive FAB Mass Spectra**

| structures[a] | *m/z* values of molecular ions of pure polyether IV, with *n* = | | | | | *m/z* values of molecular ions of[e] polyether IV Co derivatives, with *n* = | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 | 0 | 1 | 2 | 3 | 4 |
|  [b] | | (817)[d] | 1633 | 2449 | 3265 | | (874)[d] | 1747 | 2620 | 3493 |
|  [c] | | 834 | 1650 | 2466 | 3282 | | 891 | 1764 | 2637 | 3510 |
|  [c] | 734 | 1550 | | | | 791 | 1664 | | | |
|  [b] | | 917 | 1733 | 2549 | 3365 | | 974 | 1847 | 2720 | 3593 |
|  [c] | | 934 | 1750 | 2566 | 3382 | | 991 | 1864 | 2737 | 3610 |

[a] In the reported structures, Porph =



[b] The molecular ions of these oligomers appear in the positive FAB mass spectra as $(M+1)^+$. [c] The molecular ions of these oligomers appear in the positive FAB mass spectra as $(M)^+$. [d] Peaks originated by EI. [e] In these oligomers, all the porphyrin units contain one cobalt atom.

not reported for brevity) because the formation of the cyclic structure is hindered.[35,36]

The other two series of peaks at *m/z* values of 736 + (*n* − 1)718 (*n* = 1–3) and 706 + *n*718 (*n* = 0–2), detected as $(M)^+$, correspond to open-chain oligomers having hydroxy end groups (Table I).

The positive FAB mass spectrum of polyether II is shown in Figure 7. The peak assignments are reported in Table II.

A peak corresponding to the molecular ion of the cyclic dimer appears at *m/z* 1577, as $(M + 1)^+$. The peak at *m/z* 789, as in the preceding case, in an EI fragment (B/E analysis). Inspection of Figure 7 and Table II reveals that many of the peaks in the spectrum correspond to unexpected compounds having one or two butyl end groups. The presence of these low molecular weight products in polyether II can be explained by the competitive reaction between the butyl group of the tetrabutylammonium bromide (TBAB), used as a phase-transfer agent in the synthesis and present in great excess with respect to 1,6-dichlorohexane, and the porphyrin hydroxy groups. This reaction is also responsible for the low yield of polymeric

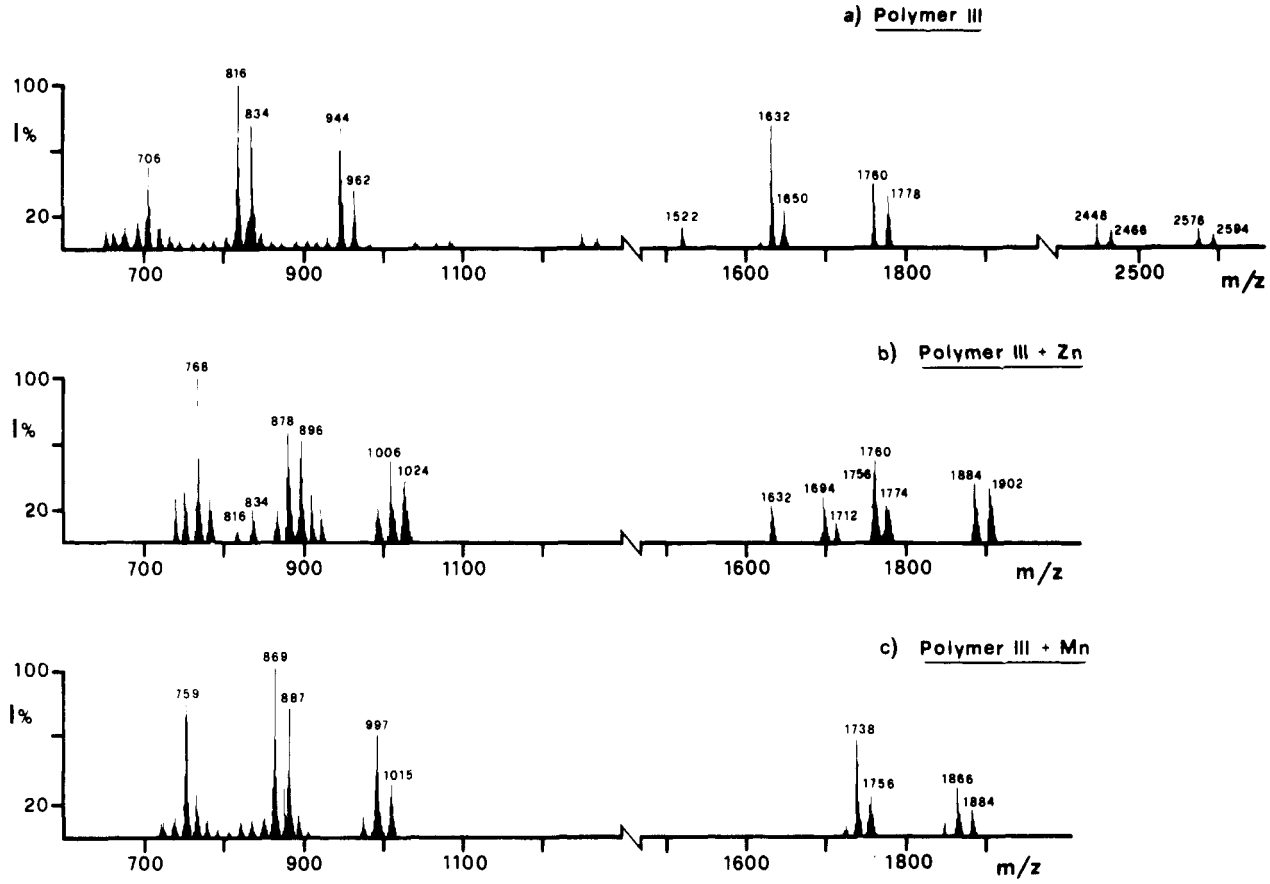



**Figure 8.** Positive FAB mass spectra of (a) pure polyether III, (b) polyether III after reaction with zinc(II) acetate, and (c) polyether III after reaction with manganese(II) acetate.

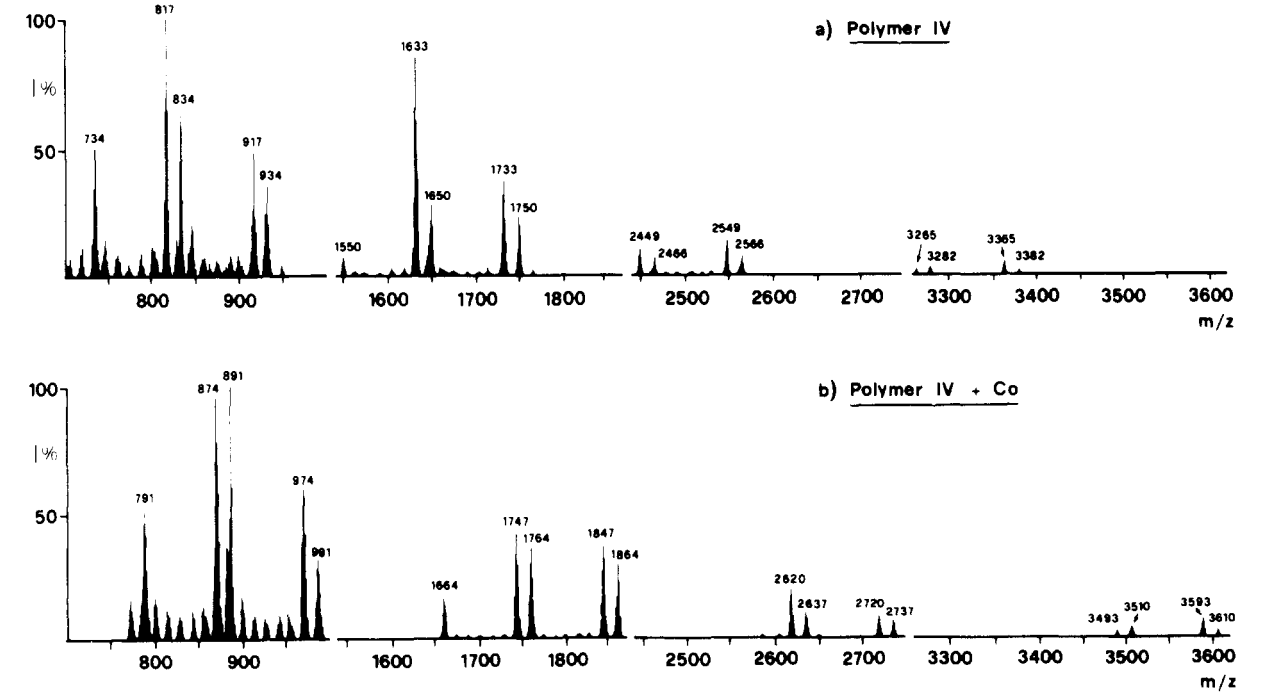



**Figure 9.** Positive FAB mass spectra of (a) pure polyether IV and (b) polyether IV after reaction with cobalt(II) acetate.

material (40%). In order to avoid this negative reaction, in the synthesis of polyether III the porphyrin monomer $M_2$ was treated with 1,8-dibromooctane using 18-crown-6 ether (instead of TBAB) as a phase-transfer agent.

In Figure 8a the positive FAB mass spectrum of polyether III is shown and the structural assignment of the most abundant peaks present in the spectrum is reported in Table III.

The series of peaks at $m/z$ 816 + $(n - 1)$816 (with $n$ = 2 and 3) correspond to cyclic oligomers (see Table III); the peak at $m/z$ 816 ($n$ = 1) is due to EI fragmentation (B/E analysis). Also the peaks at $m/z$ 944 + $(n-1)$816 [detected in the spectrum as $(M)^+$] correspond to ions having a cyclic structure as shown in Table III; in this case, the presence of two octamethylene groups in the molecule permits the

formation also of the first term of this series (peak at $m/z$ 944).[35]

The other three series of peaks at $m/z$ values of 706 + $n$816, 834 + ($n$ − 1)816, and 962 + ($n$ − 1)816 correspond to open-chain oligomers having hydroxy end groups (see Table III).

The FAB mass spectrum of polyether IV is shown in Figure 9a. The structural assignments for the most intense peaks are given in Table IV.

Two series of peaks corresponding to ions having a cyclic structure [detected as $(M + 1)^+$] appear in the spectrum at $m/z$ 817 + ($n$ − 1)816 (1633, 2449, and 3265) and $m/z$ 917 + ($n$ − 1)816 (917, 1733, 2549, and 3365), respectively (Table IV). The peak at $m/z$ 917, because of the long aliphatic connection [−O$(CH_2)_6$O$(CH_2)_6$O−] between two porphyrin units, may also have a cyclic structure (Table IV).[35]

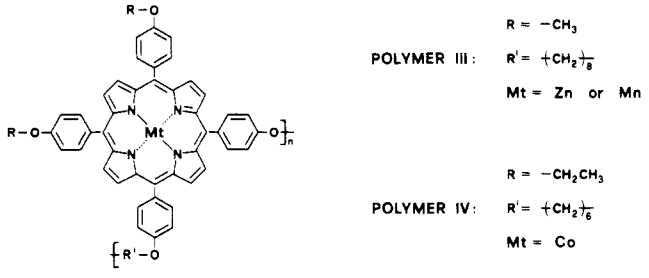
The families of peaks at $m/z$ 834 + ($n$ − 1)816, 734 + $n$816, and 934 + ($n$ − 1)816 correspond to molecular ions, detected as $(M)^+$, of open-chain oligomers having hydroxy end groups (Table IV).

Some experiments on the inclusion of transition metals in the porphyrin units present in polymers III and IV were performed treating the polymers with either cobalt(II), manganese(II), or zinc(II) acetate.

To confirm the formation of the porphyrin metal derivatives, we attempted the elemental analyses of the purified samples, but the results obtained were uncertain about the actual substitution of the two NH hydrogen atoms of each porphyrin unit with one metal atom.

In order to ascertain the formation of the metalloporphyrin polymer derivatives, we took FAB mass spectra of the obtained reaction products.

FAB mass spectra of the low molecular weight oligomers present in the polyether III sample after reaction with $(CH_3COO)_2Zn$ (reaction time 30 min) and $(CH_3COO)_2Mn$ (reaction time 24 h) are reported in parts b and c of Figure 8, respectively. Upon comparison of these spectra with that of the corresponding pure polymer (Figure 8a), a series of drastic changes may be noted. The peaks due to pure oligomers (Figure 8a and first section of Table III) appear with very little intensity in the Zn spectrum (Figure 8b) and are absent in the Mn spectrum (Figure 8c). These peaks have been replaced by those corresponding to metal derivatives (second and third section of Table III) in which the two NH hydrogen atoms of the porphyrin rings have been replaced by Zn or Mn atoms as indicated in the following formula:




In the case of the sample treated with zinc acetate, because of the short reaction time, not all the porphyrin units included a metal atom. However, we have verified that at longer reaction times (24 h) a complete substitution of the NH hydrogen atoms with Zn is obtained (data omitted for brevity).

The FAB mass spectrum of the reaction products formed between polymer IV and $(CH_3COO)_2Co$ after 24 h of reaction is reported in Figure 9b. Also in this case, comparing this spectrum with that of pure polymer IV (Figure 9a), it may be observed that the peaks corresponding to pure oligomers (series at $m/z$ 817 + $n$816, 917 + $n$816, 834 + $n$816, 734 + $n$816, and 937 + $n$816 in Figure 9a and the first section of Table IV) have been replaced by peaks due to compounds in which the two NH hydrogen atoms of each porphyrin unit have been replaced by cobalt atoms (second section of Tbale IV); so, for example, each compound corresponding to higher molecular weight peaks detected in the FAB mass spectrum (Figure 9b) at $m/z$ 3493, 3510, 3593, and 3610 (in which four porphyrin groups are present) contains four cobalt atoms.

We have also recorded the FAB mass spectra of the reaction products between polyether III or IV with other metal acetates; the results show that in the Ni(II), Fe(II), and Cu(II) cases the metal is easily bound to porphyrin units, while in those of Ba(II), Mg(II), and Pb(II), peaks corresponding to metal derivative products are not found in the mass spectra (data not reported for brevity).

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