Macromolecules **1992,** *25,* 6605–6611

Main Chain Porphyrin Polymers. 2. Synthesis and Characterization of Some Copolyethers and Their Metal Derivatives†

Daniele Vitalini

Istituto per la Chimica e Tecnologia dei Materiali Polimerici, CNR, Viale A. Doria 6, 95125 Catania, Italy

Emilio Scamporrino*

Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

Received March 2, 1992; Revised Manuscript Received June 15, 1992

ABSTRACT: Polycondensation between mixtures of 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)-porphyrin (I) and Bisphenol A (BP-A) with dibromomethane was performed to obtain copolyethers III–VI which contain different amounts of porphyrin in the main chain. The resulting copolyethers were characterized by GPC, UV–visible, NMR, and FAB-MS analysis. Data on the inclusion of some transition metals in the porphyrin units of the copolymers are also reported.

Introduction

In the last few years the use of porphyrin systems in such fields as the chemical conversion of solar energy by photocatalytic or electrochemical reactions,[2–5] artificial oxygen carriers inspired by those in biological systems,[5–10] ion-selective membranes,[10–15] or new polymer metal catalytic systems[16–21] has attracted the interest of many researchers.

Several reports concerning polymers in which the metal-containing porphyrin units are bound as pendant groups are reported in the literature.[2,4,7,22,23] However, little information exists on the inclusion of porphyrin units along the main chain of polymeric materials and on the ability of porphyrin units to bind metal ions.

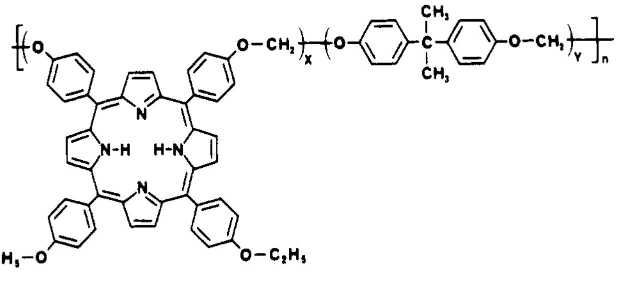
In a previous article[1] we reported the synthesis and characterization of some polyethers containing *meso*-tetraarylporphyrin units in the main chain. Data on the inclusion of transition metals (Co, Mn, Cu, Ni, Fe, and Zn) in the porphyrin units of the obtained polymers were also reported. Positive FAB-MS spectra of the polyethers treated with metal salts showed the presence of peaks corresponding to compounds in which the two NH hydrogen atoms of each porphyrin ring had been replaced by one metal atom.

In the present work we describe the synthesis and characterization of copolyethers III–VI which contain different amounts of porphyrin units (from 50% to 0.5%), obtained by condensation between dibromomethane and mixtures of 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)porphyrin (I) and Bisphenol A (BP-A) in different molar ratios. Also porphyrin I and Bisphenol A homopolyformals II and VII, respectively, were synthesized for comparison. The composition of each copolymer was determined by UV–visible spectrophotometry.

Data on experiments on the inclusion of transition metals in the porphyrin units by reaction between some copolyethers and cobalt(II) or copper(II) acetate are also reported.

Experimental Section

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



	x	*y*
polyether II	1.0	0
copolyether III	0.507	0.493
copolyether IV	0.16	0.84
copolyether V	0.045	0.955
copolyether VI	0.0051	0.9949
polyether VII	0	1.0

Porphyrin Monomer I Synthesis. A 5-g (7.37-mmol) sample of tetrakis(*p*-hydroxyphenyl)porphyrin and 2.4 g (60 mmol) of powdered NaOH in 200 mL of DMF are placed in a three-neck flask with a magnetic stirrer, a reflux condenser, and a tube for N_2 introduction. Then 2.4 g (22 mmol) of CH_3CH_2Br in 20 mL of DMF are slowly added to this stirred solution maintained at 70 °C under N_2 flow. After about 1 h, the solvent was distilled and the residue treated with diluted HCl to acid pH, washed with water, and dried under vacuo.

The 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-ethoxyphenyl)porphyrin (I) was then separated from the mixture according to the procedure described previously,[1] and its ^1H NMR and FAB mass spectrum coincide with those reported.[1]

Polyether and Copolyether Synthesis. Polyether II was synthesized according to the method described elsewhere[1,24] starting from porphyrin monomer I and dibromomethane. Into a 5-mL vial with a magnetic stirrer were placed 100 mg (0.136 mmol) of porphyrin I, 45 mg (3 times the stoichiometric amount) of powdered KOH, and 1.5 mL of *N*-methyl-2-pyrrolidone (NMP). The mixture was heated at 70 °C under stirring in an N_2 atmosphere to obtain homogeneous solution; then 0.5 mL of CH_2Br_2 (a large excess) was added and the vial closed hermetically. After 24 h the mixture was cooled and centrifuged and the insoluble material (polymer with higher molecular weight), after washing with H_2O/CH_3COOH solution and CH_3CH_2OH, was dried under vacuo (yield 30%). A low molecular weight fraction of polyether II was also obtained by pouring the NMP solution into 30 mL of ethanol/acetic acid (5:1) mixture. The precipitate was washed with hot water and ethanol and dried under vacuo at 70 °C (yield 40%).

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† For part 1 see ref 1.

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Table I
Thermal Stability (PDT),[a] Average Molecular Weight (M_{GPC}),[b] and Composition of the Polymeric Materials II–VII Investigated

sample	M_{GPC}	PDT (°C)	porphyrin (x) and Bisphenol A (y) content	
			theoretical[c]	found[d]
polyether II	6300	480	$x = 100, y = 0$	$x = 100, y = 0$
copolyether III	14 000	420	$x = 50, y = 50$	$x = 50.7, y = 49.3$
copolyether IV	15 000	450	$x = 20, y = 80$	$x = 16, y = 84$
copolyether V	60 000–3200	460	$x = 5, y = 95$	$x = 4.5, y = 95.5$
copolyether VI	125 000–4100	455	$x = 0.5, y = 99.5$	$x = 0.51, y = 99.49$
polyether VII	110 000–3100	450	$x = 0, y = 100$	$x = 0, y = 100$
polyether VII[e]	40 000–1000			

[a] TG experiments under N_2, flow rate 60 mL/min, heating rate 10 °C/min. [b] M_{GPC} values measured with respect to polystyrene standards in correspondence to the maxima of the GPC curves. [c] Theoretical molar percent contents inferred on the basis of the composition of the starting monomeric mixture used in the synthesis. [d] Porphyrin contents (molar percent) were valuated spectrometrically by considering the absorbances at 424 nm. [e] Polyether VII sample synthesized as described in Experimental Section using only a trace of TBAB.

Copolyether III was synthesized in the same way as polymer II starting from a mixture of porphyrin monomer I (125 mg, 0.17 mmol), Bisphenol A (39 mg, 0.17 mmol), KOH (0.68 mmol), and CH_2Br_2 (1 mL, a large excess). The mixture was stirred in a closed vial under N_2 at 70 °C for 24 h and then poured into 30 mL of ethanol containing 5 mL of acetic acid. The precipitated copolymer was collected by centrifuging, washed with hot water and ethanol, and dried under vacuo (yield 45%).

Copolymers IV–VI and Polyether VII were prepared using tetrabutylammonium bromide (TBAB) as phase-transfer agent according to the method described by Williams et al.,[24] starting from CH_2Br_2 and a 20/80, 5/95, 0.5/99.5, or 0/100 (molar ratio) porphyrin monomer I/BP-A mixture. As an example, we report the procedure adopted for copolymer IV: In a 5-mL vial with a magnetic stirrer, a mixture of 50 mg (0.068 mmol) of porphyrin monomer I and 62 mg (0.272 mmol) of BP-A was placed together with 68 mg (1.7 mmol) of NaOH, 109 mg (0.34 mmol) of TBAB, and 3 mL of a toluene/H_2O (2:1) mixture. The mixture was heated at 80 °C under stirring; then 1 mL of CH_2Br_2 (a large excess) was added and the vial closed hermetically under N_2. After 24 h the reaction was stopped and the polymer collected in the same way described for copolymer III (yield 60%).

Increasing the BP-A amount in the starting mixture, higher yields were obtained: 90% for copolymer V and almost 100% for copolymer VI and polymer VII.

Metal Derivatives of Copolyethers IV–VI. The metal–copolyether derivatives were prepared as follows: 40 mg (a large excess with respect to the stoichiometric amount) of cobalt(II) or copper(II) acetate were added to 20 mg of copolymer in 2 mL of NMP. Each mixture was maintained at about 70 °C under stirring for 6 h. After distillation of the solvent, the residue was repeatedly washed with hot water to remove any trace of unbound metal.

GPC Analysis. A Water 6000 A apparatus, equipped with four micro-Styragel columns (in the order 1000-, 500-, 10000-, 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. A differential refractometer Model R 401 from Waters was used as the detector. The instrument was calibrated with a mixture of five polystyrene standards (Polysciences: molecular weight between 800 and 200 000) for the M_{GPC} determination of the polymer samples.

^{1}H NMR and ^{13}C NMR Analysis. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker 200 A-CF spectrometer using DMF-d_7, DMSO-d_6, or $CDCl_3$ as solvent.

Thermal Properties. Thermogravimetric analyses were performed with a Perkin-Elmer TGS-2 apparatus in an N_2 atmosphere, flow rate 60 mL/min and heating rate 10 °C/min. The temperature of the maximum rate of polymer decomposition (PDT) appears for all at about 450 °C (Table I).

FAB-MS Analysis. FAB mass spectrometric 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 5000 to 90, with a scan rate of 30 s/decade. The accelerating voltage was 8 kV. 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 at least three different mass spectra.

UV–Visible Spectrophotometric and Fluorometric Analysis. UV–visible spectra of polymers II and VII, copolymers III–VI, and their metal derivatives, were recorded on a Perkin-Elmer Model 330 spectrophotometer using NMP as solvent. The fluorescence spectra were obtained with a Perkin-Elmer MPF 44E spectrofluorometer.

Results and Discussion

In order to obtain copolymers having different amounts of porphyrin units along the polymer chain, copolyethers III–VI were synthesized by a condensation reaction between dibromomethane and mixtures of 5,10-bis(p-hydroxyphenyl)-15,20-bis(p-ethoxyphenyl)porphyrin (I) and Bisphenol A in different molar ratios. For comparison, polyethers II and VII were also synthesized.

The GPC-average molecular weight (M_{GPC}) values of the polymeric material obtained (estimated considering the elution volumes corresponding to the maxima on the GPC traces, with respect to polystyrene standards) lie between 6300 and 160 000. Pertinent values are reported in Table I.

In the cases of copolyethers V and VI and polyether VII two M_{GPC} values are reported in Table I because the corresponding GPC curves, Figure 1a–c, show two well-separated peaks. The two eluted fractions were collected separately and, after evaporation of the solvent, the residues were analyzed by IR and positive FAB mass spectrometry.

For each polymeric sample the IR spectra of the two residues (omitted for brevity) appear very similar. The only difference is in a broad band centered at about 3300 cm^{-1} (characteristic of hydroxy groups) present in the spectrum of the fraction at lower elution volume (corresponding to products with higher molecular weight), which is absent in the IR spectrum of the fraction at higher elution volume (due to oligomers).

The FAB mass spectra of the residues at higher elution volume (omitted for brevity) show a series of intense peaks corresponding to molecular ions of oligomers having a cyclic structure. The FAB mass spectra of the residues at lower elution volume, on the contrary, do not show peaks, because this fraction is constituted from products having too high a molecular weight to be detected by our mass spectrometer.

However, considering the presence of hydroxyl groups (IR spectrum), it may be that the fraction at lower elution volume is essentially made up of macromolecules having open-chain structures.

It may be noted that the molecular weight distribution of Figure 1a–c is exhibited by polymeric samples prepared

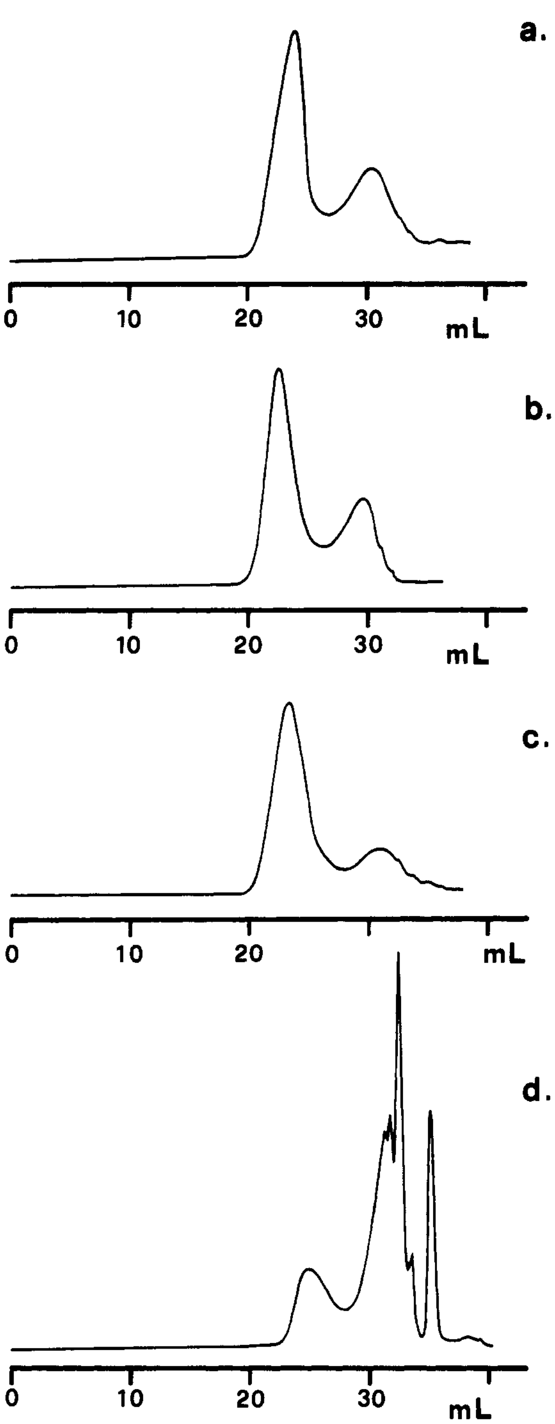


Figure 1. Gel permeation chromatograms ($CHCl_3$ as eluant) of (a) copolyether V, (b) copolyether VI, (c) polyether VII, and (d) polyether VII synthesized in presence of only a trace of TBAB.

using TBAB as phase-transfer agent (see Experimental Section).

The formation of large amounts of cyclic oligomers in the synthesis of polyethers is well-known; on the other hand it has already been reported that the TBAB catalyzes the formation of high molecular weight polymers. Thus, the presence in the GPC curve of both high molecular weights and oligomers as two separated fractions is justified. On the contrary, the polymers prepared in NMP solution without TBAB (polymers II–IV, Table I, and the same polymers V–VII, data do not reported) only show a broad GPC peak due to the presence of low molecular weight polymer together with cyclic oligomers. Moreover, according to the data of Williams et al.,[24] when the synthesis of polyether VII was carried out in the presence of only a trace (1/20 molar ratio) of TBAB, the corresponding GPC curve (Figure 1d) shows an extremely high content of cyclic oligomers.

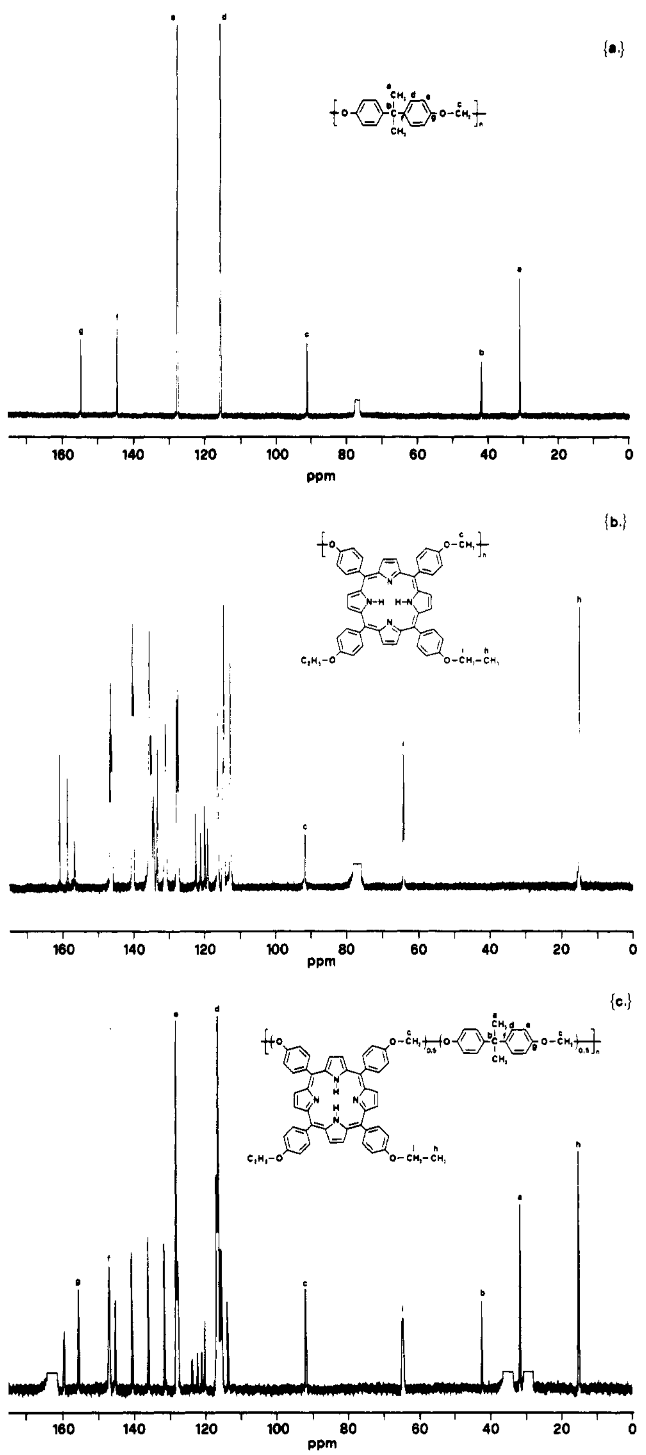


Figure 2. ^{13}C NMR spectra of (a) polyether VII, (b) polyether II (both recorded in $CDCl_3$), and (c) copolyether III (recorded in DMF-d_7). The truncated peaks are due to solvents.

The porphyrin content in each copolymer was evaluated spectrometrically by considering the absorption value at 424 nm (maximum absorption wavelength for porphyrin groups) by using Beer's law and a molar absorptivity of 362 490, determined for homopolyether II (in NMP solution).

The values obtained (an average of at least three different measurements) were compared in Table I with the theoretical values inferred on the basis of the molar ratio of the starting monomeric mixtures used in the syntheses. They correspond well. Furthermore, examining separately the two GPC fractions of copolyethers V and VI, we have ascertained that the porphyrin content

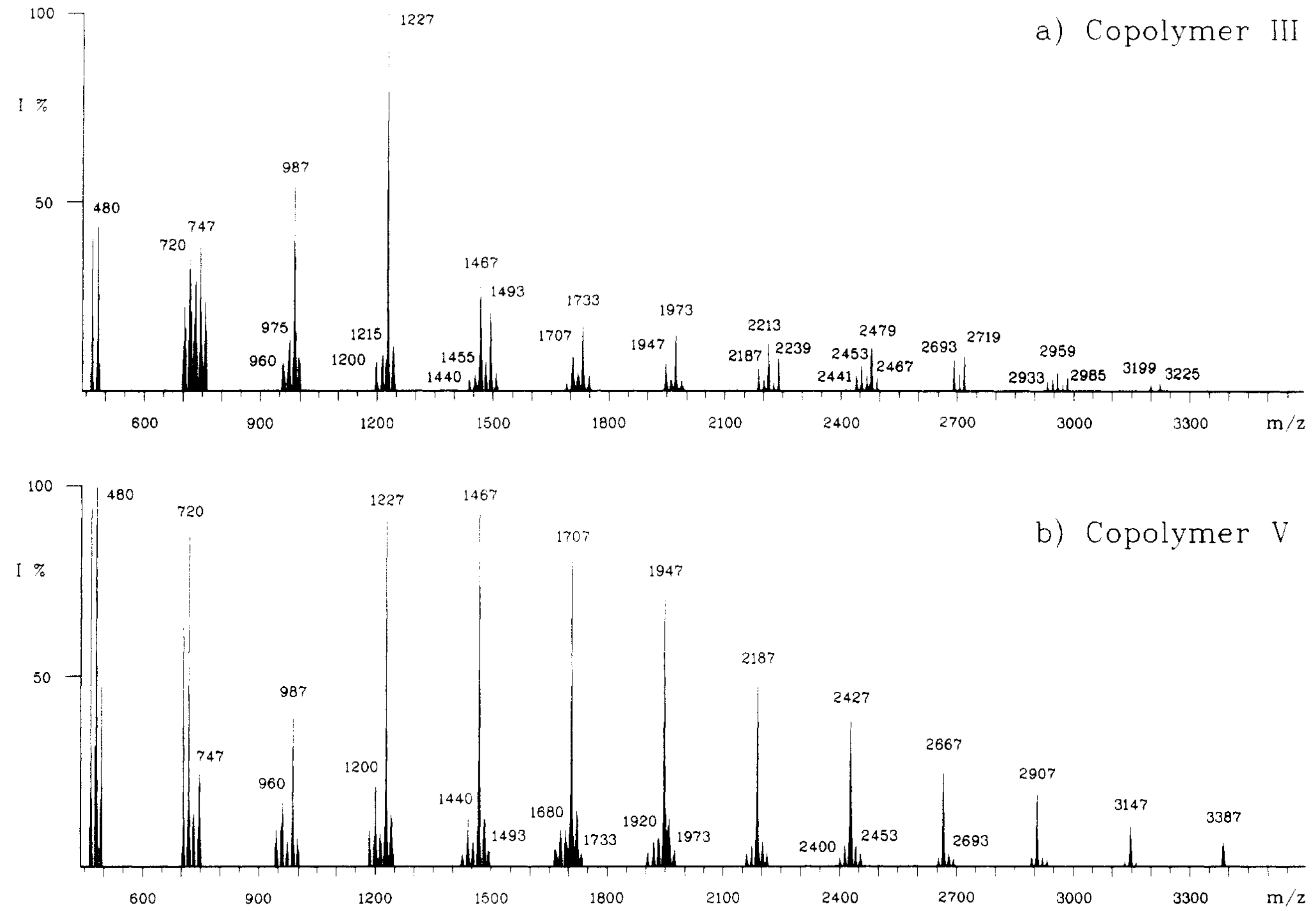
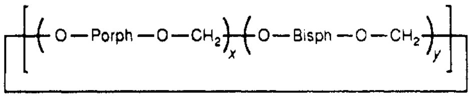
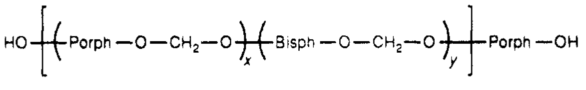


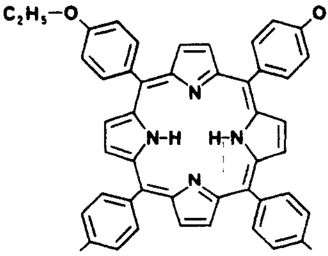
Figure 3. Positive FAB mass spectra of (a) copolyether III (containing 50.7% of porphyrin units) and (b) copolyether V (containing 4.5% of porphyrin units).

Table II
Compounds Present in the Copolymer III–VI Samples, Detected in the Positive FAB Mass Spectra[a]

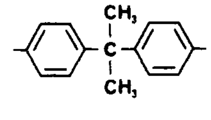
		molecular ions (*m/z*) for *y* =										
structures[b]	*x*	0	1	2	3	4	5	6	7	8	9	10
	0			480	720	960	1200	1440	1680	1920	2160	2400
	1	747	987	1227	1467	1707	1947	2187	2427	2667	2907	3147
	2	1493	1733	1973	2213	2453	2693	2933				
	3	2239	2479	2719	2959	3199						
	4	2985	3225									
	0	735	975	1215	1455							
	1	1481	1721	1961	2201	2441						
	2	2227	2467	2707	2947							

[a] The molecular ions of the products containing porphyrin units appear as $(M + 1)^+$; those containing only Bisphenol A units appear as M^+. [b] Abbreviations in the reported structures:

Porph =



Bisph =



is only a little more abundant in the fraction of the oligomers (i.e. 5.6% against 3.8% for copolymer V, with respect to 5.1% for the original material).

The structural characterization of polyethers and copolyethers II–VII was attempted by ^{1}H NMR and ^{13}C NMR analyses. Apart from polyether VII, the proton NMR spectra do not give significant results because of the very low resolution of the porphyrin hydrogen signals (data ommitted for brevity).

On the contrary, the ^{13}C NMR spectra of the polymer samples appear more informative.

In Figure 2a the ^{13}C NMR spectrum of polyether VII is reported. The signal at 30.983 ppm has been assigned to the two carbons indicated by a in the formula in Figure 2a (methyl group); the one at 41.839 ppm (a quaternary carbon, peak absent in the DEPT spectrum), to the b carbon. The signal at 91.184 ppm corresponds to a secondary carbon (negative peak in the DEPT spectrum), and therefore it was assigned to the c carbon (formal group).

The remaining signals were assigned to the phenyl carbons; in particular, those at 115.761 and 127.798 ppm

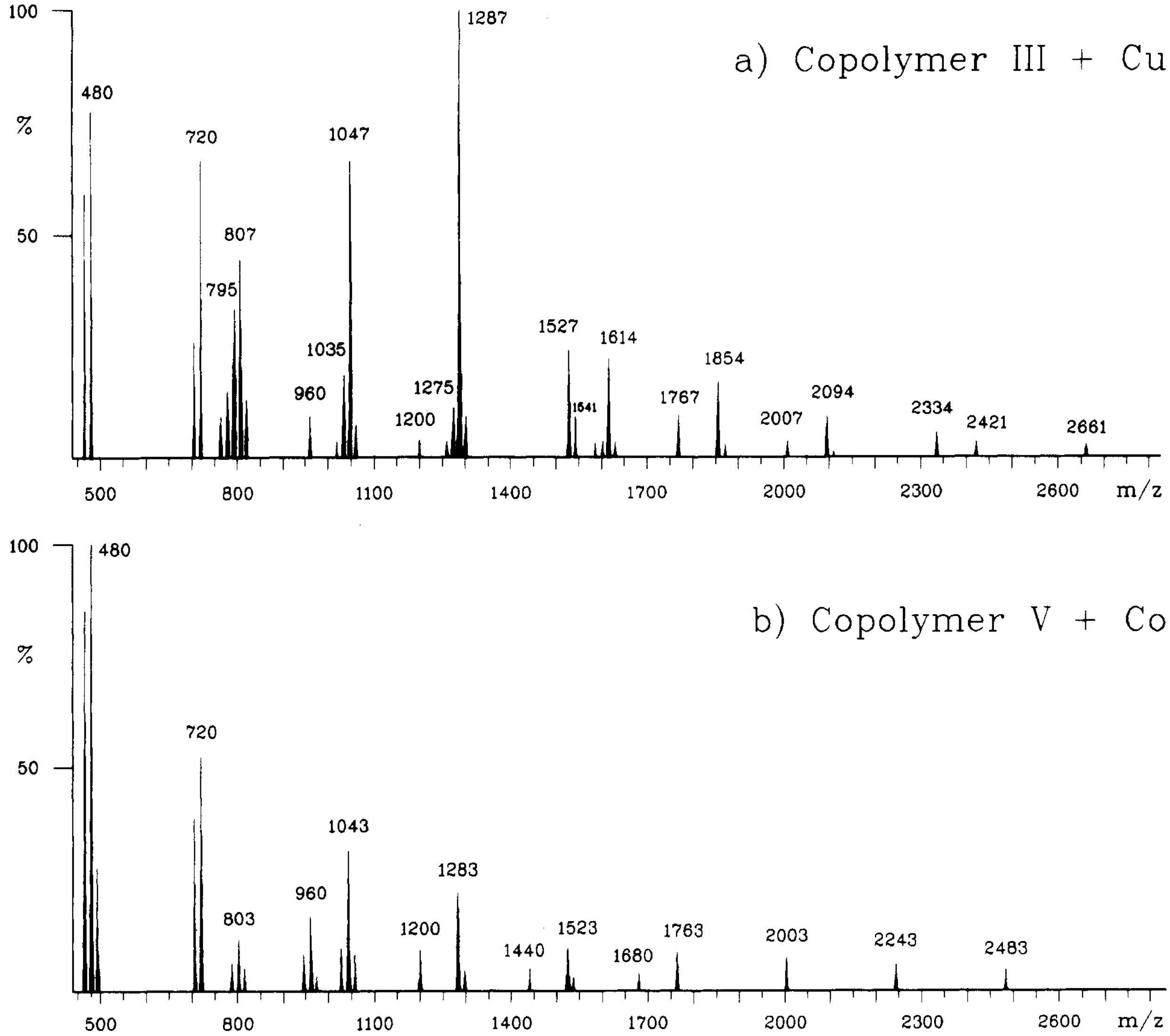


Figure 4. Positive FAB mass spectra of (a) copolyether III after reaction with copper(II) acetate and (b) copolyether V after reaction with cobalt(II) acetate.

(tertiary carbons) to the d and e carbons and those at 144.661 and 154.859 ppm (quaternary carbons) to the f and g carbons, respectively.

The ^{13}C NMR spectrum of polyether II, reported in Figure 2b, presents a large number of signals, and their assignments are very difficult. However, the three signals at 14.958, 64.112, and 91.855 ppm can certainly be assigned to the h, i, and c aliphatic carbons (see formula in Figure 2b), respectively. The remaining signals having higher chemical shifts (between 110 and 160 ppm) correspond to the porphyrin aromatic carbons.

In Figure 2c the ^{13}C NMR spectrum of copolyether III, containing almost 50% of both porphyrin and Bisphenol A units (see Table I), is reported.

As expected by comparing the spectrum of Figure 2c with the spectra of polyethers VII and II (Figure 2a,b), it may be observed that the spectrum of the copolymer presents both the series of signals detected in the spectra of the pure polyethers.

The presence of these signals is diagnostic in confirming copolymer formation, although there is no quantitative information. On the basis of the assignments made above for polyethers II and VII, the signals in the zone of aliphatic carbon resonances (between 10 and 100 ppm) and those due to the aromatic carbons of BP-A were identified (see formula in Figure 2c).

Copolymers IV–VI also exhibit ^{13}C NMR spectra (omitted for brevity) similar to that of Figure 2c, though the signals due to porphyrin linkages appear less and less intense as a consequence of the low porphyrin unit content in the copolymer (especially in copolymer VI).

For a better structural characterization of copolyethers III–VI FAB mass spectra of each sample were taken.[25]

In Figure 3 positive FAB mass spectra of copolyether III and V are reported. The structures corresponding to the peaks in the spectra are shown in Table II.

The spectrum of copolyether III (Figure 3a) presents two families of peaks. The most abundant series is of peaks at m/z $(746x + 240y) + 1$ with $x = 1–4$ (porphyrin units) and $y = 1–11$ (Bisphenol A units), corresponding to the molecular ions (as MH^+) of cyclic structure products (see Table II). Peaks at m/z $240y$ (with $y = 2–10$) due to cyclic products (as M^+) containing only Bisphenol A units and at m/z $746x + 1$ (with $x = 2–4$, Table II) containing only porphyrin units (as MH^+) are also present.

The other series of peaks, which appears with low intensity at m/z $735 + 746x + 240y$, corresponds to open chain compounds (as MH^+) having Bisphenol A and/or porphyrin end groups (Table II).

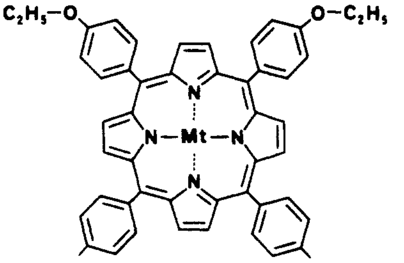
Although the molar composition of copolymer III is almost 50/50 (Table I), among the open chain products detected in the spectrum of Figure 3a, the signals of those having porphyrin end groups (Table II) are more intense. Furthermore, peaks corresponding to products having only porphyrin units are present, but no peaks of products

Table III
Compounds Present in the Copolymers III and V Treated with Copper and Cobalt Acetate, Respectively, Detected in the Positive FAB Mass Spectra[a]

		Cu–polymer III derivatives molecular ions (*m/z*) for *y* =						Co–polymer V derivatives molecular ions (*m/z*) for *y* =							
compounds[b]	*x*	0	1	2	3	4	5	0	1	2	3	4	5	6	7
$\left[\left(O-Porph-O-CH_2 \right)_x \left(O-Bisph-O-CH_2 \right)_y \right]$	0			480	720	960	1200			480	720	960	1200	1440	
	1	807	1047	1287	1527	1767	2007	803	1043	1283	1523	1763	2003	2243	2483
	2	1614	1854	2094	2334										
	3	2421	2661												
$HO-\left[\left(Porph-O-CH_2-O \right)_x \left(Bisph-O-CH_2-O \right)_y \right]-Porph-OH$	0	795	1035	1275											
	1	1541													

[a] All the molecular ions appear as M^+. The *m/z* values of the copper derivatives are referred to the most abundant isotope of Cu (atomic mass 63, natural abundance 65%). [b] Abbreviations in the reported structures (Mt corresponds to Cu or Co):

Porph =



containing only BP-A units are found. Considering that in the FAB mass spectra only preformed oligomers are detected, a possible explanation is that the Bisphenol A units are more reactive than the porphyrin groups: as a consequence, the molecules having Bisphenol A end groups, and not forming cyclic oligomers, have a greater probability of forming higher molecular weight compounds by way of an intramolecular process. In fact, as above reported for copolymer V, higher porphyrin content is present in the polymeric GPC fraction at lower molecular weight.

In the FAB mass spectra of copolymer V (Figure 3b) and copolymer VI (so similar to the former as to be omitted for brevity), containing 5% and 0.5% porphyrin units (see Table I), peaks mainly corresponding to cyclic compounds having Bisphenol A units appear, as expected (Figure 3b and Table II). However, peaks corresponding to cyclic products also having one porphyrin unit in the molecule are present with high intensity, notwithstanding the low content of porphyrin in the copolymer sample.

In order to ascertain if the porphyrin units along the copolymer chain maintain the same ability to exchange the two NH hydrogen atoms with transition metals as do the corresponding homopolyethers,[1] experiments treating the copolyethers with either cobalt(II) or copper(II) acetate were performed.

For a quantitative measure of the metal incorporated into each metal-treated copolymer, we attempted the elemental analysis of the samples but, as in the homopolymer case,[1] the obtained results were uncertain, especially for copolymers containing lower molar percent of porphyrin.

Because the metal inclusion causes a marked change in the fluorescence properties of porphyrin rings, comparing the fluorescence spectra of pure and metal-treated copolymers, information on the amount of unsubstituted porphyrin may be obtained. In all the examined cases, the signal due to free porphyrin in the spectra of metal-treated samples (omitted for brevity) is negligible.

The metal–copolymer derivatives obtained were also analyzed by FAB mass spectrometry.

In Figure 4a the positive mass spectrum of the reaction products formed between copolymer III and $(CH_3COO)_2Cu$ is reported. The spectrum appears less rich in peaks with respect to that of pure copolymer III (Figure 3a). However, by comparison of the two spectra, it may be observed that the peaks corresponding to pure oligomers (Table II) have been replaced by peaks due to compounds in which the two NH hydrogen atoms of each porphyrin unit have been replaced by one copper atom (Table III); on the contrary, the peaks corresponding to compounds having only Bisphenol A units (series at *m/z* 240*y*) appear at the same *m/z* values. So, for example, in the spectrum of the metal-treated sample (Figure 4a), the peaks at *m/z* 2421 and 2661 correspond to compounds in which the three porphyrin units contain three copper atoms (Table III). Besides, the copper being present in nature with two isotopes (at 63 and 65 amu), the metal derivatives are detected in the FAB mass spectra as complex clusters.

In Figure 4b the positive FAB mass spectrum of the reaction products between copolymer V and $(CH_3COO)_2Co$ is shown. Also in this case, by comparison of this spectrum with that of pure copolymer V (Figure 3b), it may be noted that the peaks corresponding to products containing porphyrin units have shifted at higher *m/z* values, pointing to the exchange of the two NH hydrogen atoms with a cobalt.

Acknowledgment. Partial financial support from the Italian Ministry of University and Scientific and Technological Research and a financial contribution from the "Progetto Finalizzato Chimica Fine 2" (CNR, Rome) are gratefully acknowledged. We are grateful to Miss G. Schilirò for her help in this work.

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Registry No. I, 138489-83-5; II (copolymer), 143330-80-7; II (SRU), 143330-85-2; III (copolymer), 143330-79-4; (BPA)(CH_2Br_2) (copolymer), 66987-36-8; (BPA)(CH_2Br_2) (SRU), 66983-33-3; CH_3CH_2Br, 74-96-4; tetrakis(*p*-hydroxyphenol)porphyrin, 51094-17-8.