Macromolecules **1999,** *32,* 60−69

Synthesis and Characterization of Some Main Chain Porphyrin Copolyformals, Based on Bisphenol A and Long Linear Aliphatic Units, Having a Low Glass Transition Temperature

Daniele Vitalini* and Placido Mineo

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

Emilio Scamporrino

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

Received May 26, 1998; Revised Manuscript Received October 22, 1998

ABSTRACT: The synthesis of new high molecular mass copolyformals containing long linear aliphatic linkages and different amounts of porphyrin units in the main chain is described. The copolymers have been prepared by the condensation reaction between a large excess of dibromomethane and mixtures of 1,12-dodecanedi(bisphenol A) ether (**I**) or 1,20-eicosanedi(bisphenol A)ether (**II**) and 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-dodecanoxyphenyl)porphyrin (**III**) in different molar ratio. The structural characterization of the resulting copolyethers has been performed by NMR and MALDI−TOF analysis. The average molecular mass values of the copolyethers determined by GPC have been compared with those obtained by a recently developed off-line procedure of MALDI−TOF mass spectrum processing. Thermal properties of copolymers have also been examined. All collected data show that high molecular mass copolymers with a homogeneous arrangement of the porphyrin and aliphatic units along the molecular chains and with a glass transition temperature depending on the aliphatic content in the molecules have been obtained.

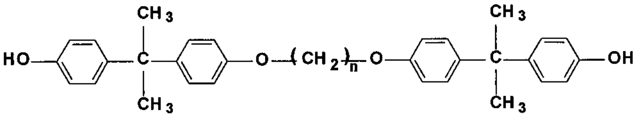
Introduction

In recent years porphyrin systems have been used in such fields as conversion and storage of solar energy by photocatalytic or electrochemical reactions,[1−6] photocatalytic oxidation of organic substrates,[7−9] and manufacture of nonlinear optical devices (like optical switches, sensor protectors, light modulators, etc.).[10−13] For many of these applications there is an interest to bind porphyrin units to a polymeric substrate in order to make their use easier.

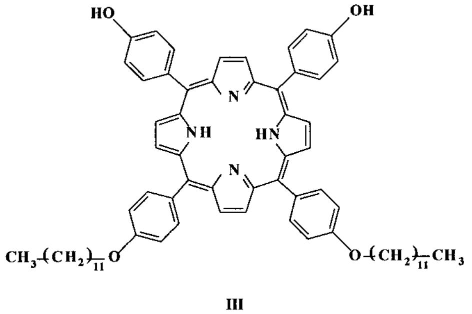
We have previously[14] synthesized some polyethers and copolyethers containing different amounts of porphyrin units in the main chain. At the present time these materials, as films, are under examination regarding their properties in the reverse saturable absorption (RSA)[13] and photocatalysis (in heterogeneous phase oxidations of organic substrates such as 1,3-diphenylisobenzofuran)[15] fields. Regarding this last case, preliminary experiments have shown that the porphyrin units maintain their redox properties also when inserted into macromolecular chains with the great advantage, with respect to low molecular mass porphyrin products, that the films can be rapidly extracted at any reaction time without leaving undesired degradation products in the solution. However, because of their high glass transition temperature (T_g) values, the examined bisphenol/porphyrin copolymer films are stiff and brittle so that they are difficult to handle.

To overcome this problem, we have inserted in the polymer chains, together with the porphyrin and bisphenol units, long linear aliphatic groups with the hope of lowering the T_g of the materials. In the present paper, we report the synthesis of these new copolymers and their chemical and thermal characterization.

Because aliphatic diols are much less reactive species with respect to aromatic ones (such as bisphenol A and porphyrin monomers), to obtain high molecular mass copolymers with a homogeneous arrangement of the aliphatic units along the copolymer chain, we have prepared two monomers, 1,12-bis(bisphenoxy-A)dodecane (**I**) and 1,20-bis(bisphenoxy-A)eicosane (**II**), in which the aliphatic groups are inserted between two bisphenol groups.



n = 12, **I**
n = 20, **II**



III

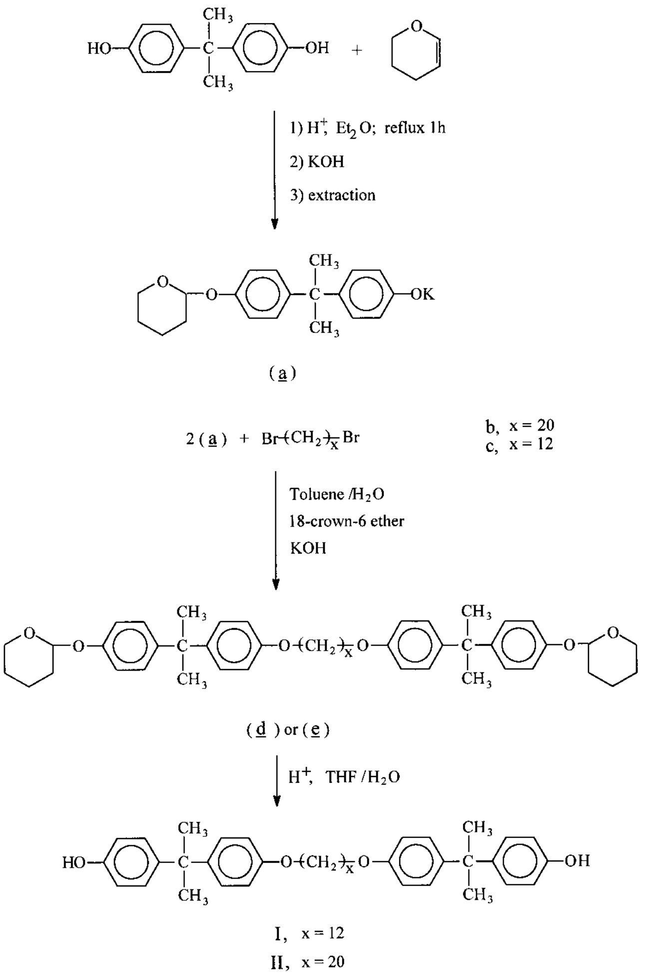
A new porphyrin monomer, 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-dodecanoxyphenyl)porphyrin (**III**), having two long aliphatic side groups which increase the

---

* Author for correspondence. Fax: 0039-95-221541. E-mail: dvitalini@dipchi.unict.it.

10.1021/ma980834q CCC: $18.00

Scheme 1



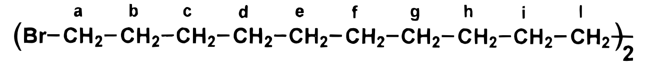
solubility of this compound and make its use easier, has also been synthesized.

By condensation reaction between dibromomethane and several mixtures of porphyrin **III** and compound **I** or **II** in different molar ratio, copolyformals **IV**−**VIII** (see Table 1) have been obtained. The polymeric materials have been characterized by NMR, DSC, GPC, and MALDI−TOF analyses. The obtained data show that the resulting materials have high molecular masses. It has also been verified that the insertion of the long aliphatic units in the polymer chains does not change the thermal stability of the copolymers, with respect to the totally aromatic ones, whereas their T_g decreases with the increase of the aliphatic amount present in the molecules.

Experimental Section

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

Synthesis of the Starting Compounds: The monocapped bisphenol A compound **a** reported in Scheme 1 was obtained according to the procedure described by Williams et al.[16] by reaction between bisphenol A (BPA) and dihydropyrane, with a yield of about 40%. ^{13}C NMR spectrum of **a** was in complete accord with previous data. 1,20-Dibromoeicosane (**b**, in Scheme 1) was prepared by an electrolytic procedure, like that used by Woolford et al.,[17] starting from 11-bromoundecanoic acid dissolved in MeOH, containing mol 5% of Na with respect to the acid, placed in an electrolytic cell. When the acid was dissolved, a current of about 1 amp at 50 V was passed for 24 h, at a temperature of about 30 °C, inverting the polarity of the Pt electrodes every 15 min to avoid the formation of residues on the electrodes. The mixture was then concentrated using a rotoevaporator, filtered to remove the blackish residue, and placed in a freezer. The formed precipitate was dissolved in 200 mL of ethyl ether and washed twice with 200 mL of water containing 20 g of Na_2CO_3 to remove any trace of unreacted product and then repeatedly with pure water. The solution was then dried over $CaCl_2$ and its volume reduced by a partial evaporation of the solvent; white crystals, having mp 66.6 °C (DSC determination) and MW 440 (exactly, from FAB−MS determination), were obtained by cooling. ^1H NMR and ^{13}C NMR spectra ($CDCl_3$) verified the structure of the product as 1,20-dibromoeicosane (**b**). Hydrogen atom assignments (shift): 3.408 (t, 4H, aCH_2), 1.854 (m, 4H, bCH_2), 1.412 (m, 4H, cCH_2), and 1.255 (intense broad signal, 32H, all the remaining methylene groups) ppm. Carbon atom shifts: 34.051 (aC), 32.831 (bC), 29.659 (intense broad signal, h−lC), 29.606 (gC), 29.529 (fC), 29.426 (eC), 28.758 (dC) and 28.167 (cC) ppm (as expected, some signals appear at higher fields due to the γ-effect induced by bromine).

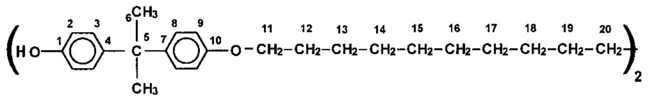


$$(\overset{a}{Br-CH_2}-\overset{b}{CH_2}-\overset{c}{CH_2}-\overset{d}{CH_2}-\overset{e}{CH_2}-\overset{f}{CH_2}-\overset{g}{CH_2}-\overset{h}{CH_2}-\overset{i}{CH_2}-\overset{l}{CH_2})_2$$

b

1,12-Dibromododecane (**c** in Scheme 1) was a commercial product.

Synthesis of the Monomers I and II: Compounds **I** and **II** were prepared in the same way according to Scheme 1. We report, as an example, the procedure adopted for the 1,20-bis(bisphenoxy-A)eicosane (**II**) synthesis. First, 6 g (0.018 mol) of potassium mono-capped bisphenol A salt (**a**) were dissolved in 30 mL of water containing 0.2 g of KOH and 4.75 g (0.018 mol) of 18-crown-6 ether. A solution of 3.8 g (0.0086 mol) of 1,20-dibromoeicosane (**b**) in 50 mL of toluene was added and the mixture maintained under vigorous stirring at 50 °C for 24 h. The organic solution was then recovered, repeatedly washed with water to remove any trace of salts and dried over $CaSO_4$. The residue obtained after distillation of the solvent was then recrystallized from ethyl ether and dried under vacuum. Then 3.9 g (yield about 50%) of compound **d** having mp 79.8 °C (DSC) and MW 902 (positive FAB−MS determination, molecular ion at *m/z* 925 as MNa^+) were obtained. The chemical structure of this compound was confirmed by NMR analysis. The compound (**d**) (1.95 g in 75 mL of THF) was then treated with 6N HCl (10 mL) under stirring for 24 h. The white residue obtained by precipitation in water (400 mL) was filtered, dissolved in ethyl ether and washed with water containing $NaHCO_3$ and purified by preparative LC (on silica gel using a mixture of cyclohexane/ethyl ether, 60:40, as eluant). The collected product (**II**) was further purified by recrystallization from ethyl ether: mp 101.3 °C (DSC) and MW 734 (exact FAB−MS determination); yield about 80%.



II

The ^1H NMR and ^{13}C NMR spectra ($CDCl_3$) of compound **II** are very similar to those of the intermediate (**d**). Proton signal assignments: two overlapped multiplets at about 7.08 ppm (4H, aromatic CH, 3 and 8), two multiplets centered at 6.77 and 6.68 ppm (4H, aromatic CH, 2 and 9), a weak signal at 4.60 ppm (hydroxyl group), a triplet centered at 3.916 ppm (4H, CH_2, 11), two broad multiplets centered at 1.747 and 1.41 ppm (8H, CH_2, 12 and 13), a singlet at 1.606 ppm (12H, CH_3, 6), and a large signal at about 1.263 (28H, the remaining CH_2, 14−20).

On the basis of ^1H-^{13}C chemical shift correlation map (HETCOR) and DEPT spectra the carbon signal assignments are: the 10 quaternary carbons at 157.025 and 153.328 (C1 and C10), 143.422 and 143.042 (C4 and C7), and 41.731 (C5) ppm; 16 tertiary carbons at 127.926 and 127.680 (C3 and C8) and 114.796 and 114.100 (C2 and C9) ppm; 20 secondary carbons at 66.201 (C11), 29.661 (C15−20), 29.573 (C14), 29.390 (C13), and 26.087 (C12) ppm; four primary carbons at 31.096 (C6) ppm.

The intermediate product (**e**) (mp 53 °C), obtained by reaction between the monocapped BPA (**a**) and 1,12-dibromododecane (**c**) (see Scheme 1), exhibits very similar ^{1}H NMR and ^{13}C NMR spectra to those of compound **d**. The corresponding dihydropyrane-free monomer **I** formed by hydrolysis has mp 101.4 °C and MW 622 (FAB mass spectrometric analysis). The chemical structure of this compound was confirmed by NMR analysis (its ^{1}H NMR and ^{13}C NMR spectra are very similar to those of monomer **II**, and the signal assignments are not reported here for brevity).

Porphyrin Monomer III Synthesis. 5,10-Bis(*p*-hydroxyphenyl)-15,20-bis(*p*-dodecanoxyphenyl)porphyrin (**III**) was prepared by partial condensation reaction between the sodium salt of tetrakis(*p*-hydroxyphenyl)porphyrin and 1-bromododecane according to the method described previously for similar compounds.[14] The obtained mixture of six products was chromatographed on silica gel column under medium pressure using a solution of chloroform containing 0.5% of ethanol as eluant.

The first product eluted from the column, having a mp of 137 °C and a MW of 1350 (determined by FAB−MS), corresponds to the totally substituted derivative, the tetrakis(*p*-dedecanoxyphenyl)porphyrin ($C_{92}H_{126}N_4O_4$), which structure was confirmed by NMR ($CDCl_3$) analysis (this compound was used for MALDI−TOF calibration, see further). Proton signal assignments: 8.864 ppm (s, 8H, pyrrole); 8.115 and 8.072 ppm (d, 8H, phenyl); 7.265 and 7.222 ppm (d, 8H, phenyl); 4.207 ppm (t, 8H, methylene in α position with respect to oxygen); 1.963 ppm (m, 8H, *β* methylene); 1.6−1.2 ppm (unresolved signal, 72 H, the remaining methylene units); 0.898 ppm (t, 12H, methyl groups); −2.745 ppm (s, 2H, NH pyrrole). Carbon signal assignments: 158.927, 146.331, 134.422, and 119.798 ppm (quaternary carbons); 135.586 and 112.665 ppm (phenyl tertiary carbons); 134.422 ppm (pyrrole tertiary carbons); 68.275 ppm (CH_2 in α position with respect to oxygen); 31.948, 29.727, 29.685, 29.535, 29.397, 26.233, and 22.723 ppm (the remaining methylene carbons); 14.154 ppm (methyl carbons).

The second product, having mp 117 °C and MW 1182 was identified as 5-(*p*-hydroxyphenyl)-10,15,20-tris(*p*-dodecanoxyphenyl)porphyrin.

The two following products eluted from the column, having different mp (119 and 184.5 °C, respectively) but the same positive FAB mass spectrum constituting essentially an intense molecular ion peak at *m*/*z* 1014, correspond to the two possible didodecanoxy-substituted porphyrin isomers ($C_{68}H_{78}N_4O_4$) detected as M^+.

The structural assignment of these products was made on the basis of their NMR spectra. Proton signal assignments (NMR recorded in DMSO-d_4 at 20 °C) for the third product eluted from the column are as follows: a singlet at 9.594 ppm (OH); two multiplets centered at 8.85 and 8.79 ppm (8H, pyrrole); two multiplets centered at 7.99 and 7.22 ppm (16H, phenyl); a triplet centered at 4.160 ppm (4H, methylene in α position with respect to oxygen atom); a multiplet centered at 1.82 ppm (4H, *β* methylene); a complex signal between 1.6 and 1.1 ppm (36H, the remaining methylene groups); a triplet centered at 0.849 ppm (6H, methyl groups); a singlet at −2.670 ppm (2H, NH pyrrole). Carbon signal assignments: 158.273, 157.010, 146.107, 145.881, 133.101, 131.619, 119.683, and 118.919 ppm (quaternary carbons); 134.812, 134.691, 113.525, and 112.658 ppm (tertiary phenyl carbons); 130.460 and 130.231 ppm (tertiary pyrrole carbons); 67.557 ppm (methylene in α position with respect to the oxygen); 30.688, 28.425, 28.390, 28.199, 28.055, 25.043, and 21.409 ppm (the remaining methylene carbons); 13.145 ppm (methyl carbons).

Proton signal assignments (NMR recorded in DMF-d_4 at 80 °C) for the fourth product eluted from the column are as follows: a singlet at 9.652 ppm (OH); a double doublet at 8.942, 8.918, 8.893, and 8.868 ppm (8H pyrrole); a double doublet at 8.157, 8.114, 8.079, and 8.036 ppm (8H phenyl); a double doublet at 7.390, 7.347, 7.325, and 7.282 ppm (8H phenyl); a triplet centered at 4.309 ppm (4H, methylene in α position with respect to the oxygen); a multiplet centered at 1.965 ppm (4H, *β* methylene); a complex signal between 1.7 and 1.1 ppm (36H, the remaining methylene groups); a triplet centered at 0.887 ppm (6H, methyl groups); a singlet at −2.534 ppm (2H, NH pyrrole). Carbon signal assignments: 160.158, 158.857, 147.881, 147.664, 135.012, 133.531, 121.166, and 120.608 ppm (quaternary carbons); 136.335, 136.283, 114.793, and 114.045 ppm (tertiary phenyl carbons); 131.725 and 131.540 ppm (tertiary pyrrole carbons); 69.269 ppm (methylene in α position with respect to the oxygen); 32.354, 30.075, 29.922, 29.736, 26.711, and 23.002 ppm (the remaining methylene carbons); 14.102 ppm (methyl carbons).

On the basis of the lesser symmetry of the signals between 7 and 9 ppm in the ^{1}H NMR spectrum of the third product eluted from the column (mp 119 °C) with respect to the fourth one, and considering also that it was obtained almost in a doubled yield with respect to the other, as expected due to its greater probability of formation,[14] this isomer was identified as 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-dodecanoxyphenyl)porphyrin (**III**). The other one turns out to be 5,15-bis(*p*-hydroxyphenyl)-10,20-bis(*p*-dodecanoxyphenyl)porphyrin. The following eluted products were not collected.

Copolyformal Synthesis. Copolymers were synthesized according to the method described elsewhere[14] using tetrabutylammonium bromide (TBAB) as phase-transfer agent. Copolyether **IV** was prepared by reaction between monomer **I** and dibromomethane. Copolyethers **V**−**VIII** were obtained starting from dibromomethane and mixtures of monomer **I** or **II** and suitable amounts of porphyrin monomer **III**. Copolyether **IX** was prepared by reaction between dibromomethane and a mixture of bisphenol A and porphyrin **III**.

GPC Analysis. A PL-GPC 110 (Polymer Laboratories) thermostated system, equipped with three PL-gel 5 *μ*m columns (two Mixed-D and one Mixed-E) attached in series, was used. The analyses were performed at 35 ± 0.1 °C using THF as eluant at a flow rate of 1 mL/min. A differential refractometer (Polymer Laboratories) was used as the detector. The instrument was calibrated with a mixture of five polystyrene standards (Polysciences; molecular masses between 2000 and 1200000 Da) using PL-Caliber GPC software for the determination of average molecular masses and Polydispersity of the polymer samples.

UV−Visible Spectrophotometric Analysis. UV−visible spectra of copolyethers were recorded on a Perkin-Elmer Model 330 spectrophotometer at room temperature using THF as solvent. The porphyrin content in each copolymer sample was evaluated by considering the absorption value at 424 nm (maximum absorption wavelength for porphyrin groups) using Beer's law and a molar absorption of 362 490 determined for porphyrin monomer **III**. The values obtained (an average of at least three different measurements) and, as a function of these data, the calculated composition of copolyethers **V**−**IX**, are reported in Table 1.

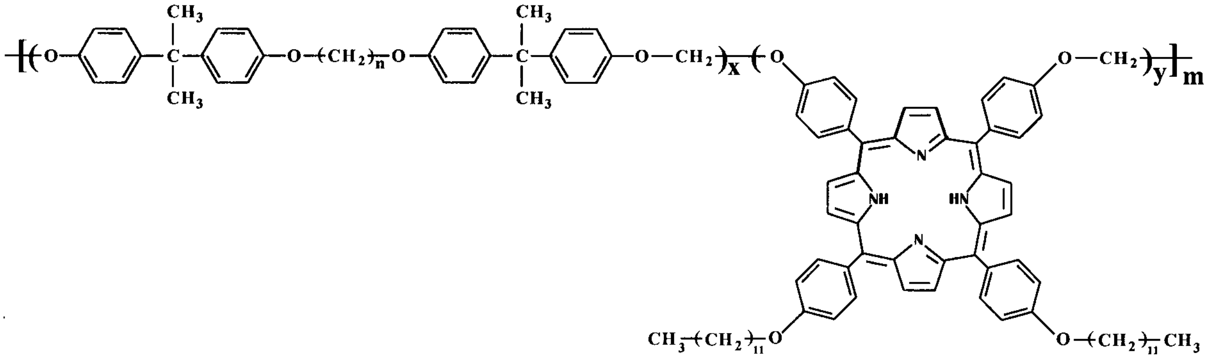
^{1}H NMR and ^{13}C NMR Analyses. ^{1}H NMR and ^{13}C NMR spectra were obtained on a AC 200 F Bruker spectrometer interfaced with an Aspect 3000 computer using the Bruker DISR 90 acquisition software. Samples were dissolved in DMSO-d_6, DMF-d_7, or $CDCl_3$ and the chemical shifts expressed in ppm by comparison with the signal of TMS used as an internal standard.

The DEPT 135° ^{13}C-spectra were acquired with the Bruker microprogram DEPT.AU. The ^{1}H−^{13}C chemical shift correlation experiment (HETCOR) data were acquired with the Bruker microprogram XHCORR.AU. Data points were zero-filled in F_1 and multiplied by an unshifted sine−bell function in F_1 and by an exponential function in F_2 before Fourier transformation.

Table 1. Composition, Viscosity, Thermal Stability, and Glass Transition Temperature of Copolyformals IV−IX

copolymer	η_{inh}[a]	% (w/w) content[b] porph	bisph	aliph	PDT[c]	T_g[d] (°C)	$\bar{M}_w$ (MWD) MALDI	GPC	univ calibr[e]
IV	1.82		66.2	33.8	425 (390)	37		336 000 (2.1)	162 400
V	0.54	3.9	63.6	32.5	425 (375)	37	157 000 (1.8)	197 400 (1.9)	
VI	1.81	3.6	54.2	42.2	430 (385)	15	148 000 (1.9)	303 880 (1.7)	163 100
VII	1.31	13.4	48.5	38.1	445 (410)	21	144 000 (1.8)	330 800 (1.9)	137 000
VIII	1.79	28.3	39.9	31.8	430 (400)	27	149 000 (1.6)	216 900 (1.4)	138 300
IX	0.55	8.9	79.5	11.6	435 (400)	91	141 000 (1.8)	171 350 (1.6)	120 200

[a] Inherent viscosity measurements were performed in THF at 35 °C. [b] The aliphatic (aliph), bisphenol (bisph), and porphyrin (porph) amounts (weight percent) contained in the copolymers were calculated on the basis of the porphyrin content in each sample valued spectrometrically (absorbances at 424 nm). [c] Temperature of maximum rate of polymer degradation from TG experiments under N_2 flow. The temperatures at which 2% of weight loss of material is observed are also reported in parentheses. [d] Glass transition temperature determined by DSC experiments. [e] Molecular masses determined on the basis of the universal calibration curve obtained using the GPC and inherent viscosity data (in THF) of polystyrene standards.



IV-VIII

Thermal Properties. Thermogravimetric analyses (TG) 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. The temperatures of maximum polymer degradation rate (PDT) of the examined polymers are reported in Table 1.

Differential scanning calorimetry (DSC) was performed to determine melting points and glass transition temperatures by using a Mettler DSC-20 instrument. The heating rate was 10 °C/min, under N_2 atmosphere.

Viscometry. Inherent viscosity of the copolymers **IV**−**IX** ($\eta_{\mathrm{inh}} = \ln \eta_r/c$, $c = 0.5$ g/L) was measured in a Desreux-Bishoff suspended level viscometer. The measurements were performed in THF at 35 °C; pertinent values are reported in Table 1.

FAB and MALDI−TOF Mass Spectrometric Analyses. FAB−MS analyses were performed on a double-focusing Kratos MS 50S mass spectrometer equipped with the standard FAB source. Xenon was used as the bombarding gas, with an energy of about 8 keV. The instrument was scanned from 4000 to 90 Da, with a scan rate of 30 s per decade. The accelerating voltage was 8 kV. The mass resolution was approximately 4000. Mass spectra were recorded by using an UV oscillographic recorder. Spectra were obtained by using 3-nitrobenzyl alcohol (TNB) as a matrix.

The MALDI−TOF mass spectra were acquired using a Bruker Reflex mass spectrometer equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash ADC (time base 8 or 16 ns); the laser irradiance was slightly above threshold (ca. 10^6 W/cm^2). The accelerating voltage was 30 kV. The detection was in the reflection mode (31.4 kV), using a double plate microchannel detector, or in the linear mode, using a High Mass detector (HI-MASS) with a low time resolution. It has a venetian-blind steel dynode that performs ion-to-electron conversion; the electrons pass through a 6000 V potential difference and hit first a single-plate microchannel detector and then a cesium iodide scintillator mounted at the entrance window of a photomultiplier. The conversion dynode enables the detection of high mass ions, and the scintillator avoids the detection saturation, thus providing a very wide dynamic range. MALDI spectra were obtained by using *trans*-3-indoleacrylic acid (IAA) as a matrix. In each MALDI experiment the sample was prepared by loading about 0.1 nmol of polymer and 40 μmol of matrix on the probe tip, using THF as a solvent. 5,10-Bis(*p*-dodecanoxyphenyl)-15,20-bis(*p*-hydroxyphenyl)porphyrin ($C_{68}H_{78}N_4O_4$, 1014 Da) and tetrakis(*p*-dodecanoxyphenyl)porphyrin ($C_{92}H_{126}N_4O_4$, 1350 Da) (synthesis reported above) were used as standards for m/z calibration. The m/z values reported in the spectra and in the text refer to values corresponding to ions containing the more abundant isotope of each element contained in the molecules.

The MALDI mass spectra were first processed with the XMASS program from Bruker and then with a computer program compiled in Quick Basic (version 4.5) using MS-DOS 6.22. Noise was removed from the spectra by use of a smoothing algorithm of the “moving window averaging” type.[18,19] To maintain a good mass resolution, especially in the low m/z value range, the centroid of the windows was calculated while changing the span of the moving windows proportionally to the mass range examined.[19] To remove the analog/digital offset contribution, the ordinate zero-baseline value was fixed to correspond with the least intense signal in each spectrum.[20,21] The quantitative response was corrected considering the MALDI−TOF mass spectrum obtained for an equimolar mixture of four poly(methyl methacrylate) (PMMA) standards (MWD = 1.04−1.07) having molecular masses of 4.7, 17, 48.6, and 95 kDa, using a recently reported calibration procedure[23] based on the following Gaussian function (eq 1):

$$Y_{\mathrm{cor}} = P_1 e^{-P_2 X} + P_3 e^{-P_4 X} \qquad (1)$$

Here $P_1 - P_4$ = experimentally determined parameters ($P_1 = 1.81410616$, $P_2 = 2.4431 \times 10^{-4}$, $P_3 = 0.29571478$, and $P_4 = 5.58 \times 10^{-6}$), $X = m/z$, and Y_{cor} = ion intensity correction factor.

Normalized MALDI−TOF spectra were obtained reporting for any m/z value the theoretical signal intensity (Y_{theor}) calculated as the ratio (eq 2) between the experimental intensity (Y_{exp}, after smoothing operation and subtraction of the offset contribution to the signal intensity) and the correct factor (Y_{cor}, deduced according to eq 1 for each experimental m/z value, X).

$$Y_{\mathrm{theor}} = Y_{\mathrm{exp}}/Y_{\mathrm{cor}} \qquad (2)$$

The MALDI−TOF mass spectra of copolyformals were also acquired using a Perseptive Voyager-DE MALDI−TOF mass spectrometer equipped with a delayed extraction system. Best results were obtained using an accelerating voltage of 25 kV with a grid voltage of 95% and a delay time of 1000 ns.

Results and Discussion

To obtain less stiff films of copolyformals containing porphyrin and bisphenol A units in the main chain, long linear aliphatic linkages [$-(CH_2)_{12}-$ or $-(CH_2)_{20}-$], able to lower the glass transition temperature (T_g) of the materials, were inserted in the polymer structure. Because aliphatic dioles are less reactive species than bisphenol A and porphyrin compounds, the direct condensation reaction between mixtures of these compounds and dibromomethane was avoided. As an alternative, two bisphenol terminated monomers (**I** and **II**), each containing an aliphatic linkage inside, were prepared. Moreover, to increase the porphyrin solubility, two long aliphatic groups were also attached to the porphyrin structure (monomer **III**). Copolyethers **IV**−**VIII** were then obtained by reactions between dibromomethane and mixtures of monomer **I** or **II** and porphyrin monomer **III**, in different molar ratios, in the presence of a phase transfer agent (see Experimental Section). By this procedure an homogeneous distribution of the aliphatic units along the polymer chain was obtained. A bisphenol/porphyrin copolyformal (**IX**), which does not contain any aliphatic units in the main chain except for the CH_2 linkages, was also prepared for comparison. The composition of copolyethers **IV**−**IX**, i.e., amounts of porphyrin, bisphenol A, and aliphatic groups present in each copolyether, is summarized in Table 1.

The GPC traces of copolyethers **IV**−**IX** (omitted for brevity) are very similar and they point out that each polymeric material contains a high molecular mass fraction and a little amount of low molecular mass oligomers. Pertinent average molecular mass (MW) values, calculated with respect to the signals of polystyrene standards, and polydispersity indexes (MWD) determined excluding in the computation the signal due to low molecular mass oligomers, are reported in Table 1. However, considering the difference in the chemical structure of our copolyethers and polystyrene, wrong values could be obtained; therefore, a recently developed off-line procedure for direct MW calculation by MALDI−TOF mass spectra of polymers was also applied.[20−22]

The method can be summarized in three points: (i) a variable smoothing necessary to improve the signal/noise ratio of the recorded spectrum but still maintaining a good resolution in the low m/z range; (ii) a subtraction of the misleading contribution to the signals introduced by the offset used in the spectrum recording; (iii) a quantitative response correction which renders the MALDI−TOF signal really representative of the abundance of the species in the sample.

As an example, the MALDI−TOF mass spectrum, acquired in linear mode, of copolyether **VI** after the above-described procedure, is reported in Figure 1a. In Figure 1b a graphic method to evaluate MW values is shown.[20−22] According to this method M_w and M_n values, calculated by fixing the lower mass limit of the mass spectrum at m/z 1000 (to minimize the matrix contribution) and the upper mass limit at different m/z values, were plotted as a function of the pertinent upper m/z values. The obtained curves exhibit a plateau in correspondence of which M_w = 148 000 and M_n = 79 500 were determined. Pertinent values obtained for all the copolyethers **IV**−**IX** are reported in Table 1. Comparing these data with those determined by GPC it can be observed that, as expected, the MW values of copolyethers obtained by MALDI are lower whereas MWD values are similar.

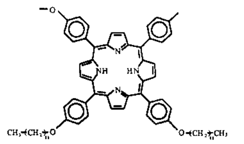
To ascertain the true MW values of the copolyformals, on the basis of the GPC and inherent viscosity data of polystyrene standards, a universal calibration curve was

Table 2. Compounds Present in the Copolyformals IV and V Detected in Their MALDI−TOF Mass Spectra

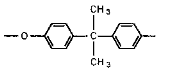
	Structures[a]	m/z (n) Values of Molecular ions (n = Number of Repeating Units in Each Structure)
(#)[b]	$\left[\mathrm{Bisph}-O-(CH_2)_{12}-\mathrm{Bisph}-O-CH_2\right]_n\ Na^+$	1925 (3), 2559 (4), 3193 (5), 3827 (6), 4461 (7), 5095 (8), 5729 (9), 6363 (10), 6997 (11), 7631 (12), 8265 (13), 8899 (14)
(*)	$\left[\mathrm{Porph}-O-CH_2\right]\left[\mathrm{Bisph}-O-(CH_2)_{12}-\mathrm{Bisph}-O-CH_2\right]_n\ ^+$	2294 (2), 2928 (3), 3562 (4), 4196 (5), 4830 (6), 5464 (7), 6098 (8), 6732 (9), 7366 (10)
(•)	$\left[\mathrm{Porph}-O-CH_2\right]_2\left[\mathrm{Bisph}-O-(CH_2)_{12}-\mathrm{Bisph}-O-CH_2\right]_n\ ^+$	2052 (0), 2686 (1), 3320 (2), 3954 (3), 4588 (4), 5222 (5)

a) Abbreviations in the reported structures:

Porph =



Bisph =



b) The symbols used in the mass spectra of the Figures **2** and **3** are reported in parenthesis.

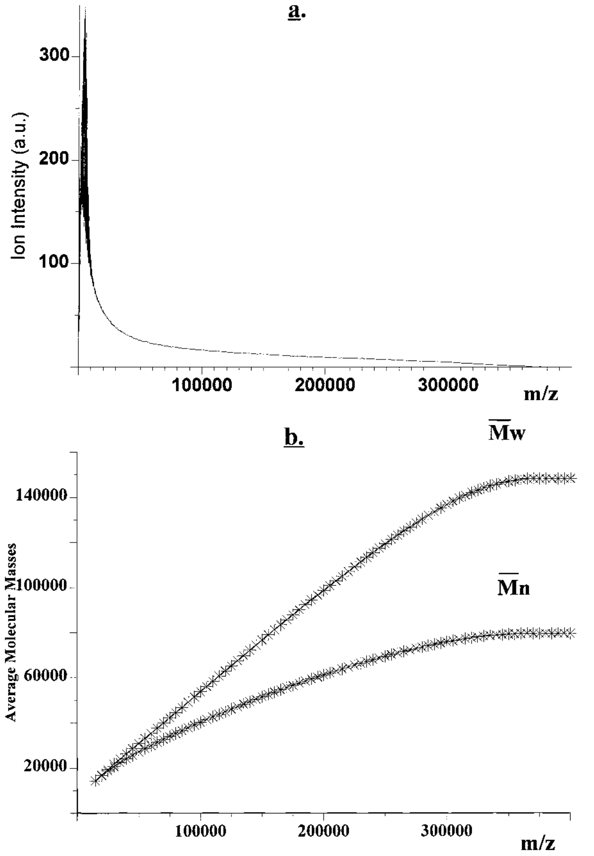


Figure 1. (a) Elaborated MALDI−TOF mass spectrum, obtained in linear mode, of copolyformal **VI**. (b) Molecular weight averages (M_w and Mn) of copolyformal **VI** calculated from its elaborated MALDI−TOF mass spectrum at different *m/z* upper limits and reported as a function of those *m/z* values.

also determined. The calculated MW values for the copolyformals, reported in Table 1, confirm the mass values provided by MALDI−TOF method.

The MALDI−TOF mass spectrometric analysis allowed also the structural characterization of copolyethers **IV**−**IX**. To have the highest mass resolution, necessary for a correct *m/z* molecular ion assignment of the species contained in each polymeric material, the following reported MALDI−TOF mass spectra were obtained using a reflection or delayed extraction procedure.

The MALDI spectrum of sample **IV** is reported in Figure 2. It consists essentially of a series of peaks at *m/z* *n*634 + 23 with *n* = 3−14, corresponding to molecular ions, as M_n(Na$^+$) (peaks due to M_n(K$^+$) ions also appear in the spectrum but with little intensity), of cyclic formals containing monomer **I** units whose structural assignments are given in Table 2 (compounds indicated as #).

The spectrum of copolyformal **V**, shown in Figure 3, presents three families of peaks corresponding to cyclic products whose structures are reported in Table 2. The most abundant series is of peaks at *m/z* 1026 + *n*634 with *n* = 2−10 (indicated as ∗ in Figure 3 and Table 2), due to molecular ions of cyclic products containing, in addition to monomer **I**, also one porphyrin **III** unit in the molecule and detected, as in previous cases, as M_n^+ (peaks due to M_n(Na$^+$) ions appear with very little intensity in the spectrum). Peaks of cyclic compounds containing only monomer **I** units are also present at *m/z* *n*634 + 23 with *n* = 3−7 (peaks detected as M_n(Na$^+$) and indicated as # in Figure 3 and Table 2). The other series of peaks at *m/z* 2052 + *n*634, with *n* = 0−5 (indicated as ● in Figure 3 and Table 2), is due to compounds, detected as M_n^+, containing two porphyrin units in each molecule.

In Figure 4a−c the mass spectra of copolyethers **VI**−**VIII**, which contain monomer **II** (i.e.: eicoisane derivative) and different amounts of porphyrin **III** (between 2.7 and 23 mol %), are compared. The peak assignments are reported in Table 3. The spectra are constituted essentially by peaks corresponding to cyclic oligomers, detected as M_n^+ ions, containing, in addition to monomer **II**, one (peaks at *m/z* 1772 + *n*746 indicated as ∗ in Figures 4 and Table 3), two (peaks at *m/z* 2052 + *n*746, indicated as ● in Figure 4 and Table 3), three (peaks at *m/z* 3078 + *n*746, indicated as ◊ in Figure 4 and Table 3) or four (peaks at *m/z* 4104 + *n*746, indicated as + in Figure 4 and Table 3) porphyrin units in the molecules,

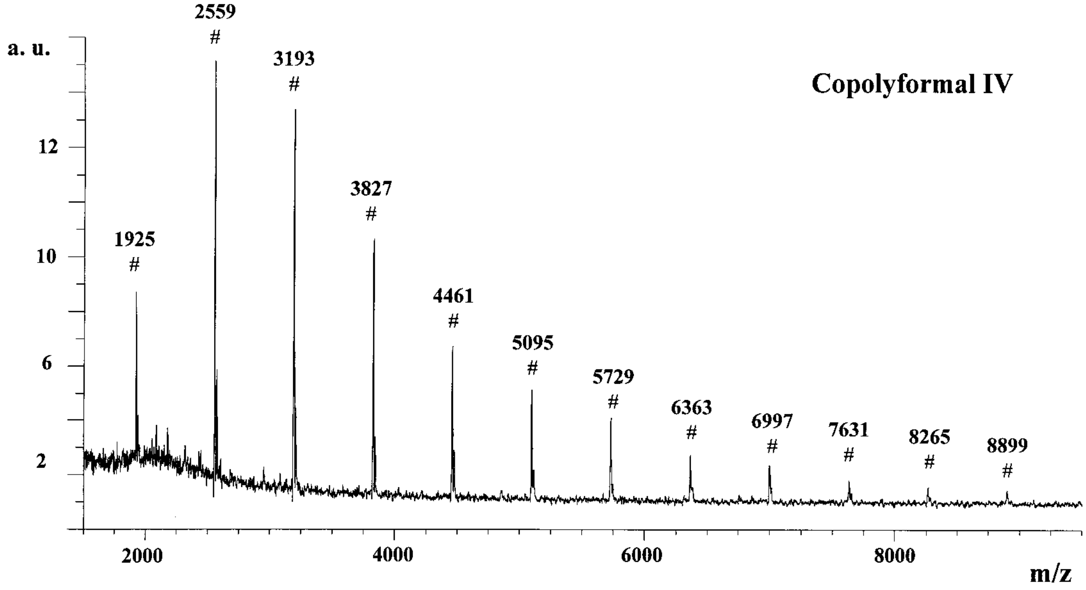


Figure 2. Positive MALDI−TOF mass spectrum, obtained in reflection mode, of copolyformal **IV** (for the structural assignments see Table 2).

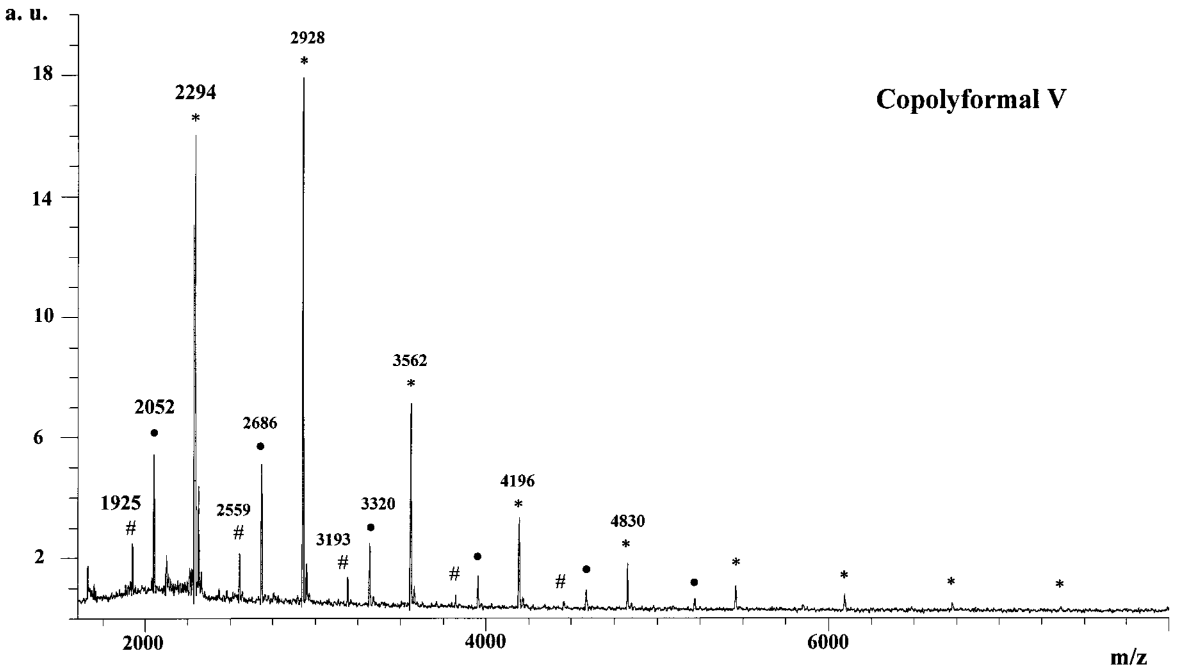


Figure 3. Positive MALDI–TOF mass spectrum, obtained in reflection mode, of copolyformal **V** (for the structural assignments see Table 2).

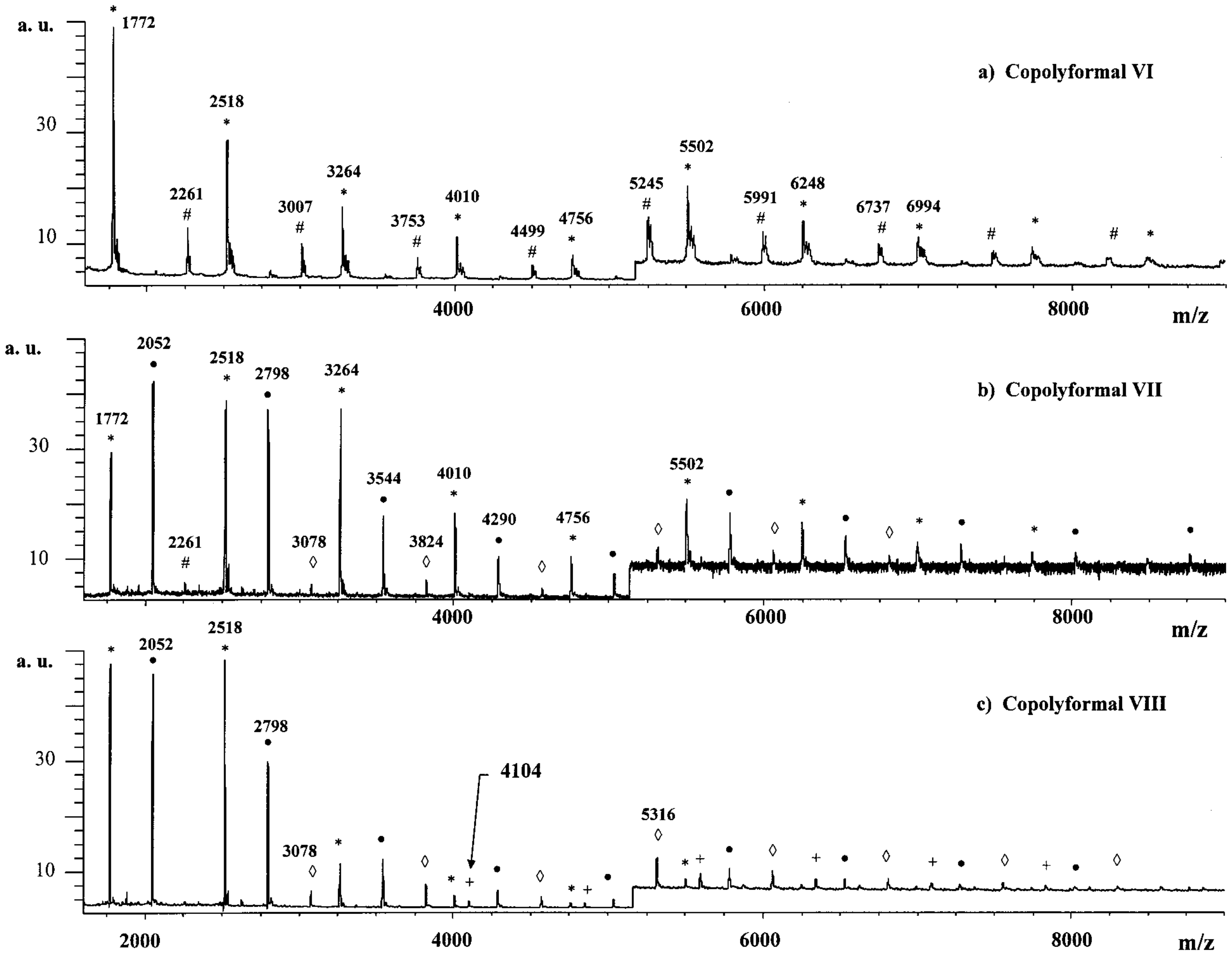


Figure 4. Positive MALDI–TOF mass spectra, obtained in reflection mode: (a) copolyformal **VI**; (b) copolyformal **VII**; (c) copolyformal **VIII** (for the structural assignments see Table 3).

whose intensities in each spectrum change as a consequence of the porphyrin content in the copolyformal. Thus, in the spectrum of copolyether **VIII** (Figure 4c), which contain 23% of porphyrin, peaks due to cyclic species having three or four porphyrin units in the molecule are well observed. A few peaks (indicated as # in Figure 4 and Table 3), which correspond to oligomers containing only bisphenol A units, appear

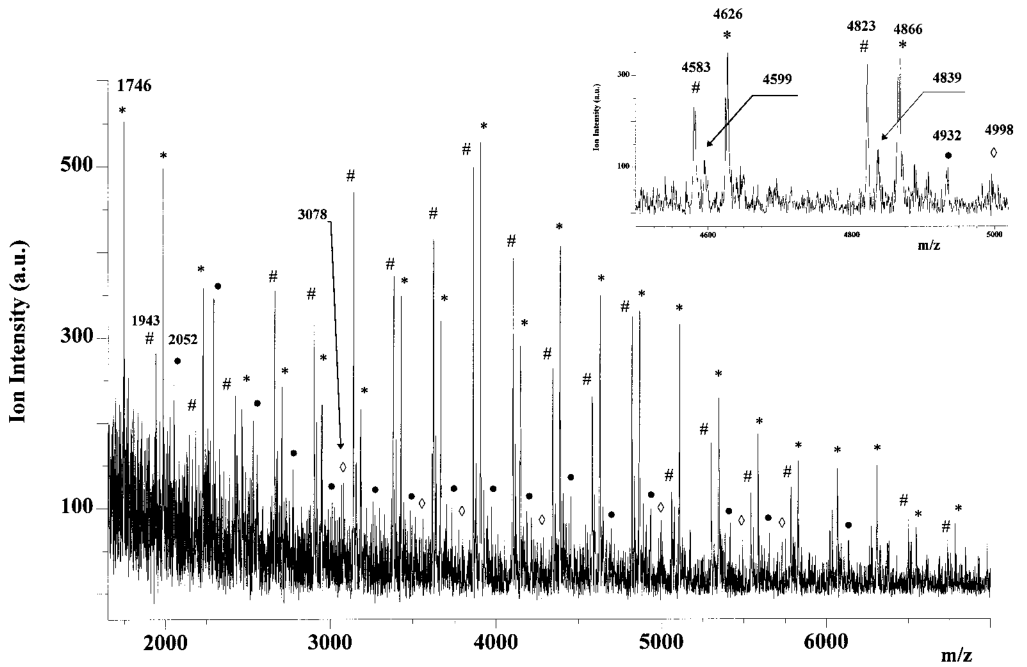


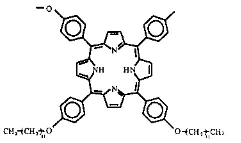
Figure 5. Positive MALDI–TOF mass spectrum, obtained using a delayed extraction procedure, of copolyformal **IX** (for the structural assignments see Table 4).

Table 3. Compounds Present in the Copolyformals VI–VIII Detected in Their MALDI–TOF Mass Spectra

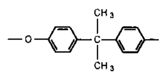
	Structures[a]	m/z (n) Values of Molecular ions (n = Number of Repeating Units in Each Structure)
(#)[b]	$[\text{Bisph–O}(\text{CH}_2)_{20}\text{Bisph–O–CH}_2]_n\ \text{Na}^+$	2261 (3), 3007 (4), 3753 (5), 4499 (5), 5245 (6), 5991 (7), 6737 (8), 7483 (9), 8229 (10)
(*)	$[\text{Porph–O–CH}_2][\text{Bisph–O}(\text{CH}_2)_{20}\text{Bisph–O–CH}_2]_n\ ^+$	1772 (1), 2518 (2), 3264 (3), 4010 (4), 4756 (5), 5502 (6), 6248 (7), 6994 (8), 7740 (9), 8486 (10)
(•)	$[\text{Porph–O–CH}_2]_2[\text{Bisph–O}(\text{CH}_2)_{20}\text{Bisph–O–CH}_2]_n\ ^+$	2052 (0), 2798 (1), 3544 (2), 4290 (3), 5036 (4), 5782 (5), 6528 (6), 7274 (7), 8020 (8), 8766 (9)
(◊)	$[\text{Porph–O–CH}_2]_3[\text{Bisph–O}(\text{CH}_2)_{20}\text{Bisph–O–CH}_2]_n\ ^+$	3078 (0), 3824 (1), 4570 (2), 5316 (3), 6062 (4), 6808 (5)
(+)	$[\text{Porph–O–CH}_2]_4[\text{Bisph–O}(\text{CH}_2)_{20}\text{Bisph–O–CH}_2]_n\ ^+$	4104 (0), 4850 (1), 5596 (2)

a) Abbreviations in the reported structures:

Porph =



Bisph =



b) The symbols used in the mass spectra of Figure 4 are reported in parenthesis.

with very low intensity at *m*/*z* *n*746 + 23 (*n* = 3–11) only in the spectrum of Figure 4a.

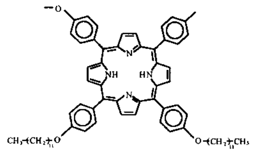
The MALDI–TOF mass spectrum of copolyformal **IX**, which only contains bisphenol A (97.7 mol %) and porphyrin (2.3 mol %) units, is reported in Figure 5. One can notice the high mass accuracy in the spectrum, obtained using a delayed extraction procedure (see also the inset in Figure 5; calculated mass resolution is 2660 fwhm at about *m*/*z* 5000). All the peaks were identified as due to cyclic oligomers, and their structural assignments are summarized in Table 4. Briefly, the two most abundant series are constituted by peaks at *m*/*z* *n*240 + 23 (with *n* = 8–16, peaks indicated as #) and at *m*/*z* 1026 + *n*240 (with *n* = 3–20, peaks indicated as ∗) corresponding to the molecular ions of oligomers containing only an increasing number of bisphenol A units (ions detected as $M_n(Na^+)$, peaks due to $M_n(K^+)$ ions are also observed in the spectrum) or bisphenol A and one

Table 4. Compounds Present in the Copolyformal IX Detected in Its MALDI–TOF Mass Spectrum

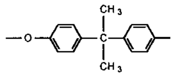
Structures [a]	m/z (n) Values of Molecular ions (*n* = Number of Repeating Units in Each Structure)
(#) [b] $\left[\left[\text{Bisph–O–CH}_2 \right]_n \right] \text{Na}^+$	1943 (8), 2183 (9), 2423 (10), 2663 (11),2903 (12), 3143 (13), 3383 (14), 3623 (15), 3863 (16), 4103 (17), 4343 (18), 4583 (19), 4823 (20), 5063 (21), 5303 (22), 5543 (23), 5783 (24), 6023 (25), 6263 (26), 6503 (27), 6743 (28)
(*) $\left[\left[\text{Porph–O–CH}_2 \right] \left[\text{Bisph–O–CH}_2 \right]_n \right]^+$	2226 (5), 2466 (6), 2706 (7), 2946 (8), 3186 (9), 3426 (10), 3666(11), 3906 (12), 4146 (13), 4386 (14), 4626 (15) 4866 (16), 5106 (17), 5346 (18), 5586 (19), 5826 (20), 6066 (21), 6306 (22), 6546 (23), 6786 (24)
(•) $\left[\left[\text{Porph–O–CH}_2 \right]_2 \left[\text{Bisph–O–CH}_2 \right]_n \right]^+$	2052 (0), 2292 (1), 2532 (2), 2772 (3), 3012 (4), 3252 (5), 3492 (6), 3732 (7), 3972 (8), 4212 (9), 4452 (10), 4692 (11), 4932 (12), 5172(13), 5412 (14), 5652 (15), 5892 (16), 6132 (17), 6372 (18)
(◊) $\left[\left[\text{Porph–O–CH}_2 \right]_3 \left[\text{Bisph–O–CH}_2 \right]_n \right]^+$	3078 (0), 3318 (1), 3558 (2), 3798 (3), 4038 (4), 4278 (5), 4518 (6), 4758 (7), 4998 (8), 5238 (9), 5478 (10)

a) Abbreviations in the reported structures:

Porph =



Bisph =



b) The symbols used in the mass spectrum of Figure **5** are reported in parenthesis.

porphyrin unit in each molecule (ions detected as M_n^+). Two other series of peaks, which appear with low intensity at m/z 2052 + n240 (with n = 0–17, peaks indicated as ●) and at m/z 3078 + n240 (with n = 0–7, peaks indicated as ◊), are due to oligomers containing two or three porphyrin units in each molecule.

The weight loss curves of copolyethers **IV**–**IX** (omitted for brevity) show that these materials have a similar thermal decomposition behavior (under N_2) so that the presence of the long aliphatic linkages along the polymer chains does not play a considerable role. All these polymers decompose in one stage exhibiting a temperature of maximum polymer degradation rate between 425 and 445 °C (PDT values in Table 1), and only for copolymers **VIII** and **IX** was a moderate thermally stable residue (about 14% and 26%, respectively, measured at 700 °C) observed.

On the contrary, the glass transition temperature (T_g) is remarkably influenced by the aliphatic content in each polymer. In Figure 6 the T_g values of copolyethers **IV**–**IX** are plotted with respect to the aliphatic content in each material (data reported in Table 1). As expected, the T_g value decreases when the aliphatic content in the polymer main chains increases, varying from 91 °C of the less flexible bisphenol/porphyrin copolyformal **IX** to 15 °C of the copolyether **VI**. It can be also noticed that, although copolyethers **IV**, **V** and **VIII** contain a similar aliphatic amount (see Table 1), the T_g of copolyether **VIII** is lower than those for **IV** and **V**, probably

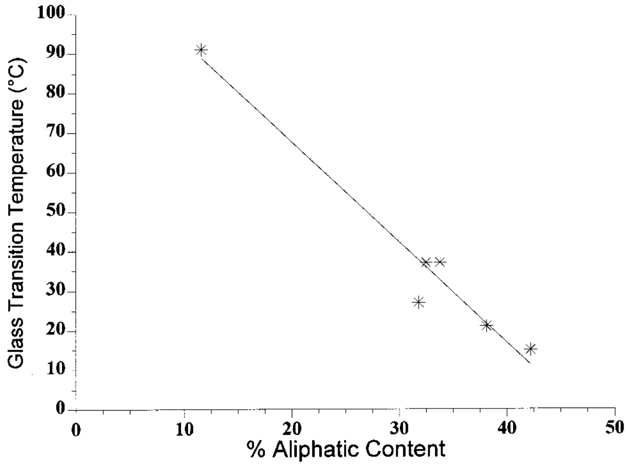


Figure 6. Glass transition temperature values of copolyformals **IV**–**IX** as a function of the aliphatic content (weight percent) in each sample.

as a consequence of longer aliphatic units (eicosane) present in this copolyether.

In conclusion, the data presented here show that, starting from porphyrin **III** and monomer **I** or **II**, in which a long linear aliphatic unit (dodecane or eicosane) is inserted between two bisphenol A units, high molecular mass copolymers **IV**−**VIII** were prepared. Because of the synthesis procedure adopted (a large excess of dibromomethane), these copolyformals are mainly constituted of cyclic macromolecules. The presence of the aliphatic linkages, homogeneously inserted along the polymer chains, has an insignificant effect on the thermal stability of the copolymers, whereas their glass transition temperatures are remarkably lowered with respect to that of copolyformal **IX** containing only bisphenol and porphyrin units. It was also found that copolyethers **VI**−**VIII** exhibit lower T_g values than **IV** and **V** as a consequence of the greater polymer chain flexibility induced by eicosane units with respect to dodecane ones.

Acknowledgment. Partial financial support from the Italian Ministry of University and Scientific and Technological Research and CNR-Rome are gratefully acknowledged.

References and Notes

(1) Kamogawa, H. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2317.
(2) King, R. B.; Sweet, E. M. *J. Org. Chem.* **1979**, *44*, 383.
(3) Nango, M.; Dannhauser, T.; Huang, D.; Spears, K.; Morrison, L.; Loach, P. A. *Macromolecules* **1984**, *17*, 1898.
(4) Kamogawa, H.; Inoue, H.; Nanasawa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2209.
(5) Milgrom, L. R. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2535.
(6) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.
(7) Fox, M. A.; Chanon, M. *Photoinduced Electrontransfer*; Elsevier: Oxford, 1988; Chapter 5.
(8) Bell, J. A.; MacGillivray, J. D. *J. Chem. Educ.* **1974**, *51*, 677.
(9) Jefford, C. W. *Chem. Soc. Rev.* 1993, p 59.
(10) *Molecular Nonlinear Optics: Materials, Physic and Devices*; Zyss, J., Ed.; Academic Press: Boston MA, 1993.
(11) Prasad, N. P.; Williams, D. J. *Introduction to Nonlinear Optcal Effects in Molecules and Polymers*; Wiley: New York, 1991.
(12) *Polymers for Second-Order Nonlinear Optics*; Lindsay, G. A., Singer, K. D., Eds., ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995.
(13) Vinodgopal, K.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 5053.
(14) Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 1625 and 6605.
(15) Scamporrino, E.; Vitalini, D.; Mineo, P. Work in progress.
(16) Williams, F. J.; Hay, A. S.; Relles, H. M.; Carnahan, J. C.; Loucks, G. R.; Boulette, B. M.; Donahue, P. E.; Johnson, D. S. In *New Monomers and Polymers*; Culbertson, B. M., Pittiman, C. U., Jr., Eds.; Plenum Press: New York 1984; p 90.
(17) Woolford, R. G. *Can. J. Chem.* **1962**, *40*, 1846.
(18) Cotter, R. G. *Time-of-Flight Mass Spectrometry*; ACS Symposium Series 549; American Chemical Society: Washington, DC, 1994; p 183.
(19) Sharaf, M. A.; Illman, D. L.; Kowalski, B. R. in "*Chemometrics*", Vol. 82 in Chemical Analysis, Elving, P. J. and Winefordner, J. D. Eds, **1986**, p 102.
(20) Vitalini, D.; Mineo, P.; Scamporrino, E. *Macromolecules* **1997**, *30*, 5285. *Rapid Commun. Mass Spectrom.* **1996**, *10*, 1551.
(21) Scamporrino, E.; Vitalini, D. In *Recent Advances in Mass Spectrometry of Polymers*; Pethrick, R. A., Ed.; J. Wiley & Sons: New York, 1998, in press.
(22) Scamporrino, E.; Vitalini, D.; Mineo, P. *Rapid Commun. Mass Spectrom.* 1998, *12*, 646.

MA980834Q