Preparation of Functionalized Copolymers by Thermal Processes: Porphyrination and Fullerenation of a Commercial Polycarbonate

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ABSTRACT: The preparation of copolycarbonates containing porphyrin or fullerene units in the main chain is described. The syntheses were performed inserting the “special groups” in bisphenol A polycarbonate (PC) molecules by prolonged heating at 240 °C of PC mixtures with different amounts (5−30 wt %) of porphyrin or fullerene derivatives. To this end, four porphyrins with one or two phenolic [5-(*p*-hydroxyphenyl)-10,15,20-tris(*p*-decanoxyphenyl)porphyrin (**II**) and 5,15-bis(*p*-hydroxyphenyl)-10,-20-bis(*p*-decanoxyphenyl)porphyrin (**III**)] or alcoholic [5-[*p*-(11-hydroxy)undecanoxyphenyl]-10,15,20-tris-(*p*-dodecanoxyphenyl)porphyrin (**IV**) and 5,15-bis[*p*-(11-hydroxy)undecanoxyphenyl]-10,20-bis(*p*-dodecanoxyphenyl)porphyrin (**V**)] −OH groups and 61-(*p*-hydroxyphenyl)methano-1,2-fullerene[60] were prepared. Composition and structure of the obtained materials were inferred by GPC, UV−visible, and MALDI−TOF analysis. Our results suggest that thermal activated exchange reactions provoke a gradual and homogeneous porphyrination or fullerenation of the polymer chains in the entire mass range. It was also ascertained that, under our conditions, the outer−inner reactions produce only a moderate mass reduction of the PC.

Introduction

A large variety of new materials are under examination for the preparation of nonlinear optical devices (such as optical switches, sensor protectors, light modulators, etc.),[1] photocatalytic systems, liquid crystal applications, etc.[2−5] Often the properties of these materials are related to the presence of compounds, containing “special groups”, embedded in a support material to form guest−host systems.[1−10] Polymers are often used as a matrix, and recently there has been increasing technological interest in directly incorporating the active units in the polymer molecules, as side-chain or main-chain groups, to obtain high-performance materials.[5]

The synthesis of these polymers has attracted our interest, and in previous papers we have reported the synthesis and characterization of a few polyformals, polycarbonates and related copolymers containing different amounts of porphyrins,[11,12] Schiff-base metal complexes,[13] or fullerenes[14] in the main chain. Principal difficulties met in these syntheses were the preparation of reactive monomers and suitable procedures to obtain polymers with a high molecular mass and, in the copolymer cases, a homogeneous microstructure. However, the polymer formation was not always easy so that, in some cases, alternative procedures may be preferable.

In the present paper, we report the preliminary results of a work regarding the insertion of porphyrin and fullerene units in a bisphenol A polycarbonate (PC) through prolonged heating at 240 °C of PC mixtures with suitable compounds.

It is well-known that polymers with reactive groups inside the chains and/or at the chain ends (such as ester, amide, carbonate, etc.) can undergo exchange reactions when maintained at high temperature for long time (melt-mixing process); some detailed studies on these chemical reactions in the case of several polymer mixtures have been published.[15] The different mechanisms of exchange reactions that could happen according to the polymer composition [i.e., the direct reaction between functional groups located inside the polymer chains (inner−inner reactions) or the end groups attack on the inside functional linkages (outer−inner reactions)] have been underlined.

These thermal activated processes, of scarce significance in the case of homopolymers, become most important when mixtures of different polymers are processed because variable amounts of random, block, and/or graft copolymers (that often significantly change the chemical and physical properties of the blends) may be formed.

We have examined the possibility to insert fullerene and porphyrin units in the chains of a commercial polycarbonate (chosen for its excellent optical properties) by means of thermal activated outer−inner exchange reactions, because preliminary attempts to prepare copolycarbonates by direct condensation reaction of suitable monomers failed (or only material with a low molecular mass and little content of special units were obtained).

The occurrence of these exchange reactions was investigated by UV−visible, GPC, and MALDI−TOF mass spectrometric analyses.

Experimental Section

Materials. All solvents and basic materials were commercial products appropriately purified before use. Poly(bisphenol A carbonate) (PC) was a commercial product (Lexan L-220) from General Electric.

Synthesis of 1,12-Bis(bisphenoxy-A)dodecane (I). Compound **I** was synthesized starting from the potassium salt of the monodihydropyran derivative of bisphenol A and 1,12-dibromododecane, as reported elsewhere.[13]

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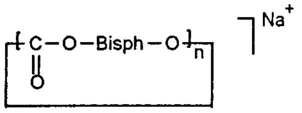
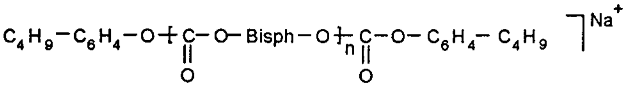
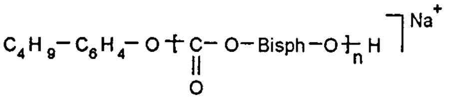
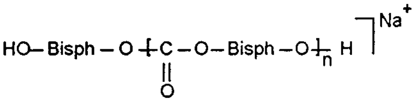
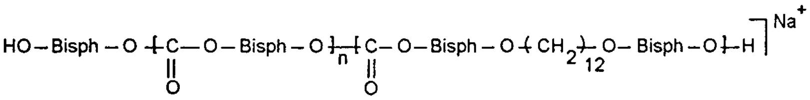
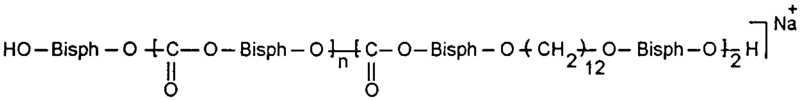
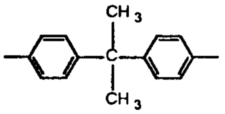
Table 1. Molecular Ions Detected in the *Positive*-MALDI−TOF Mass Spectra of PC Sample and Heated Mixtures of PC with Bisphenol A and Monomer I (see Figures 1, 3, and 4)

	Structures[a]	m /z Values of Molecular ions[b]
○	 $\left[\left(\underset{\underset{O}{\|}}{\mathrm{C}}-\mathrm{O-Bisph-O}\right)_n\right]\mathrm{Na}^+$	1547 + n 254
✖	 $\left[\mathrm{C_4H_9-C_6H_4-O}\left(\underset{\underset{O}{\|}}{\mathrm{C}}-\mathrm{O-Bisph-O}\right)_n\underset{\underset{O}{\|}}{\mathrm{C}}\mathrm{-O-C_6H_4-C_4H_9}\right]\mathrm{Na}^+$	1619 + n 254
●	 $\left[\mathrm{C_4H_9-C_6H_4-O}\left(\underset{\underset{O}{\|}}{\mathrm{C}}-\mathrm{O-Bisph-O}\right)_n\mathrm{H}\right]\mathrm{Na}^+$	1697 + n 254
✳	 $\left[\mathrm{HO-Bisph-O}\left(\underset{\underset{O}{\|}}{\mathrm{C}}-\mathrm{O-Bisph-O}\right)_n\mathrm{H}\right]\mathrm{Na}^+$	1521 + n 254
#	 $\left[\mathrm{HO-Bisph-O}\left(\underset{\underset{O}{\|}}{\mathrm{C}}-\mathrm{O-Bisph-O}\right)_n\left(\underset{\underset{O}{\|}}{\mathrm{C}}-\mathrm{O-Bisph-O}\left(\mathrm{CH_2}\right)_{12}\mathrm{O-Bisph-O}\right)\mathrm{-H}\right]\mathrm{Na}^+$	1661 + n 254
†	 $\left[\mathrm{HO-Bisph-O}\left(\underset{\underset{O}{\|}}{\mathrm{C}}-\mathrm{O-Bisph-O}\right)_n\left(\underset{\underset{O}{\|}}{\mathrm{C}}-\mathrm{O-Bisph-O}\left(\mathrm{CH_2}\right)_{12}\mathrm{O-Bisph-O}\right)_2\mathrm{H}\right]\mathrm{Na}^+$	1829 + n 254

[a] The symbols are those used in the mass spectra of Figures 1, 3, and 4. In the structures "Bisph" corresponds to:



[b] The *m/z* value of the first peak reported in the spectra, for each family, is indicated.

Synthesis of Porphyrin Monomers II−V. 5-(*p*-Hydroxyphenyl)-10,15,20-tris(*p*-decanoxyphenyl)porphyrin (**II**) and 5,15-bis(*p*-hydroxyphenyl)-10,20-bis(*p*-decanoxyphenyl)porphyrin (**III**) were prepared by partial condensation reactions between the sodium salt of tetrakis(*p*-hydroxyphenyl)porphyrin and 1-bromodecane, according to the method described previously for similar compounds.[12,13] The obtained mixture of six products was chromatographed on a 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 143.6 °C and a MW of 1238 Da (determined by MALDI−TOF), corresponds to the totally substituted derivative, the tetrakis(*p*-decanoxyphenyl)porphyrin ($C_{84}H_{110}N_4O_4$) (yield 11% with respect to the starting porphyrin amount), whose structure was confirmed by NMR ($CDCl_3$). The second product, having mp 159.7 °C and MW 1098 Da, was identified as 5-(*p*-hydroxyphenyl)-10,15,20-tris(*p*-decanoxyphenyl)porphyrin (**II**) (yield 7% with respect to the starting porphyrin amount).

The two following products eluted from the column, having different mp (217.5 and 243.2 °C, respectively) but the same molecular weight of 958 Da, correspond to the two didecanoxy-substituted porphyrin isomers ($C_{64}H_{70}N_4O_4$). As in previous works,[12] it was possible to assign to each compound the correct structure on the basis of their NMR spectra; thus, the third eluted product proves to be 5,10-bis(*p*-hydroxyphenyl)-15,20-bis(*p*-decanoxyphenyl)porphyrin (yield 4% with respect to the starting porphyrin amount) while the fourth is 5,15-bis(*p*-hydroxyphenyl)-10,20-bis(*p*-decanoxyphenyl)porphyrin (**III**) (yield 2.5% with respect to the starting porphyrin amount; for NMR data see Supporting Information).

Analogously, 5-[*p*-(11-hydroxy)undecanoxyphenyl]-10,15,20-tris(*p*-dodecanoxyphenyl)porphyrin (**IV**) and 5,15-bis[*p*-(11-hydroxy)undecanoxyphenyl]-10,20-bis(*p*-dodecanoxyphenyl)-porphyrin (**V**) were synthesized starting from tetrakis(*p*-hydroxyphenyl)porphyrin and an equimolar mixture of 1-bromododecane and 11-bromo-1-undecanol.

Also in this case, the separation of the six obtained compounds was accomplished by chromatography. After the tetrakis(*p*-dodecanoxyphenyl)porphyrin (mp 137 °C, MW 1350 Da), the first product eluted from the column, 5-[*p*-(11-hydroxy)undecanoxyphenyl]-10,15,20-tris(*p*-dodecanoxyphenyl)-

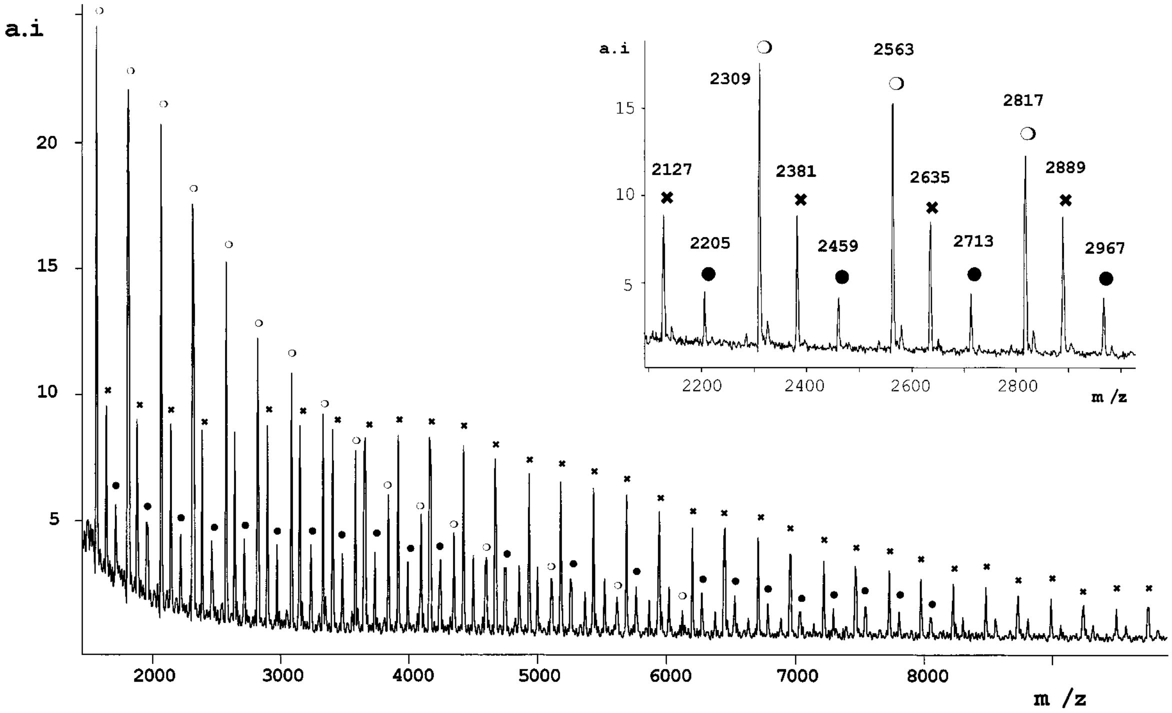


Figure 1. *Positive*-MALDI–TOF mass spectrum of pure polycarbonate (PC) (for the structural assignments, see Table 1).

Table 2. Copolymer Molecular Mass after 60 and 240 min of Heating at 240 °C and Amounts of Porphyrin or Fullerene Units Inserted in the PC Chains after 240 min of Heating

	Mp values after heating times[a]		
mixture	60 min	240 min	wt %[b]
PC	68 800	64 650	
PC/10 wt % BPA	32 100	26 700	
PC/10 wt % **I**	51 200	42 450	
PC/10 wt % **II**	52 150	35 400	6.1
PC/10 wt % **III**	43 300	32 450	7.8 (8.4)[c]
PC/30 wt % **III**	25 300	16 200	26.1
PC/10 wt % **IV**	55 350	30 650	6.3
PC/10 wt % **V**	43 900	29 400	8.8
PC/5 wt % **VI**	46 950	45 250	3.2

[a] Average molecular weight (as Mp) obtained by GPC traces calibrated with respect to polystyrene standards. [b] The amounts of porphyrin or fullerene units were determined by UV-visible GPC curves. [c] In parentheses is reported the porphyrin amount calculated spectrophotometrically by solution method adopting Beer's law.

porphyrin (**IV**) (mp 121.8 °C, MW 1352 Da, yield 8%), 5,10-bis[*p*-(11-hydroxy)undecanoxyphenyl]-15,20-bis(*p*-dodecanoxyphenyl)porphyrin (mp 133.6 °C, MW 1354 Da, yield 7%), and 5,15-bis[*p*-(11-hydroxy)undecanoxyphenyl]-10,20-bis(*p*-dodecanoxyphenyl)porphyrin (**V**) (mp 129.8 °C, MW 1354 Da, yield 4%) were eluted in the order. Because the two 5,10- and 5,15-bis[*p*-(11-hydroxy)undecanoxyphenyl]porphyrin derivatives were not well separated, two other preparative LC were necessary for obtaining pure products. All these compounds were characterized by MALDI–TOF mass spectrometry and NMR (the NMR spectra are similar to those of the other porphyrins previously reported and here, for brevity, only the ^{13}C NMR data of porphyrin **V** is reported as Supporting Information).

Synthesis of the Fullerene Monomer VI. The synthesis of 61-(*p*-hydroxyphenyl)methano-1,2-fullerene[60] (**VI**) was accomplished by hydrolysis of the 61-(*p*-methoxyphenyl)-methano-1,2-fullerene[60] (prepared as reported elsewhere)[15] in *o*-dichlorobenzene using an excess of BBr_3 in CH_2Cl_2. Compound **VI** (obtained with a yield of about 12% with respect to the starting fullerene amount) was characterized by *negative*-MALDI–TOF mass spectrometry (molecular ion at *m*/*z* 826 as M^-) and NMR, which agree with previous data.[15]

Thermal Treatments. To obtain homogeneous mixtures, the PC and suitable amounts of compounds **I**–**VI** were dissolved in THF, then evaporated under N_2 flow, and finally maintained under vacuum at 50 °C overnight. Each sample was then placed in a glass tube and sealed under vacuum. The tubes were then immersed simultaneously in a silicone oil bath maintained at 240 °C and singly extracted at different times (from 15 to 240 min). After cooling, the glass tubes were opened and the obtained materials, dissolved in THF, analyzed without further treatment; in a few cases, to remove the unreacted porphyrin derivative from the bulk, the material was extracted with ethanol by Soxhlet.

GPC Analysis. A PL-GPC 110 (Polymer Laboratories) thermostated system, equipped with three PL-gel 5 μm 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) and/or an UV–visible spectrometer (Hewlett-Packard series 1050), connected in parallel, were used as detectors. The instrument was calibrated with a mixture of 12 polystyrene standards (Polysciences; molecular masses between 2000 and 1200000) using PL-Caliber GPC software for the determination of average molecular masses and polydispersity of the polymer samples.

UV–Visible Spectrophotometric Analysis. The porphyrin or fullerene contents in the copolymers were calculated on the basis of the GPC trace recorded by a UV–visible detector, considering the absorption values at 425 or 328 nm, respectively, and comparing the polymer signal area with that of the unreacted chromophore. Pertinent values are reported in Table 2.

In some cases the chromofore content was also evaluated by solution measurements using a Shimadzu spectrophotometer model 1601 at room temperature using THF as solvent.

^{1}H NMR and ^{13}C NMR Analyses. ^{1}H NMR and ^{13}C NMR spectra were obtained on a $^{\mathrm{UNITY}}$INOVA Varian instrument operating at 500 (^{1}H) and 125 (^{13}C) MHz and using VNMR for software acquisition and processing. Samples were dissolved in $CDCl_3$, and the chemical shifts expressed in ppm by comparison with the signal of TMS used as an internal standard.

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

MALDI−TOF Mass Spectrometric Analysis. The MALDI−TOF mass spectra were acquired by a Perseptive Voyager DE-STR using a simultaneous delay extraction procedure (20 kV applied after 233 ns with a potential gradient of 2545 V/mm and a wire voltage of 200 V) and detection in reflection mode. The instrument was equipped with a nitrogen laser (emission at 337 nm for 3 ns) and a flash AD converter (time base 2 ns).

In each MALDI experiment, the sample was prepared by loading about 0.05 nmol of polymer and 80 μmol of matrix (*trans*-3-indoleacrylic acid, IAA) on the sample plate, using THF as a solvent. For *positive*-MALDI−TOF mass spectra, both 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) were used as standards for *m/z* calibration. Instead, for *m/z negative*-MALDI−TOF spectra calibration, 61-(*p*-methoxyphenyl)methano-1,2-fullerene[60] ($C_{68}H_8O$, 840 Da) and 61,61-bis(*p*-methoxyphenyl)-methano-1,2-fullerene[60] ($C_{76}H_{16}O_2$, 960 Da) were used as standards.

The *m/z* values reported in the spectra and in the text are those corresponding to ions containing the more abundant isotope of each element present in the molecules. In *positive*-MALDI−TOF mass spectra, peaks corresponding to molecular ions of bisphenolcarbonates appear essentially as M_nNa^+. Differently, porphyrin derivatives are detected as M_nH^+ ions and, with minor intensity, as $M_n{}^+$ and M_nNa^+ [examining the MALDI mass spectra of some porphyrin model compounds, the following relative abundance of the species was found: M^+ (17%), MH^+ (100%), and MNa^+ (9%)].

Results and Discussion

The positive MALDI−TOF mass spectrum of the commercial PC used in this work is shown in Figure 1. The spectrum presents three families of peaks whose structural assignments are given in Table 1 (see also the insert in Figure 1).

The peaks at *m/z* 1547 + *n*254 (indicated as ○), which appear with higher intensity in the first zone of the spectrum, correspond to molecular ions of cyclic product detected as M_nNa^+. The other two series of peaks (also detected as M_nNa^+) at *m/z* 1697 + *n*254 (indicated as ●) and *m/z* 1619 + *n*254 (indicated as ×) are due to open-chain compounds having, respectively, a bisphenoxy-A end group and a *tert*-butylphenoxy end group or both *tert*-butylphenoxy end groups. The presence of these last compounds points out that the 4-*tert*-butylphenol, a molecular terminator, was used as a molecular mass regulator in the synthesis of the PC.

To verify the stability of pure PC to protracted heating, several pure samples of this polymer were heated for increasing times at 240 °C and the obtained materials examined by GPC and MALDI−TOF techniques. The obtained data, omitted here for brevity, showed that both the chemical composition and the molecular mass of the polymeric material remain almost unchanged after thermal treatments up to 240 min (maximum experimented time).

Contrarily, the data relative to mixtures of PC with 10 wt % of bisphenol A (BPA) or 1,12-bis(bisphenoxy-A)dodecane (**I**) indicate, after 240 min of heating, an evident modification of the polymer. The GPC traces of Figure 2, in fact, show a reduction in the molecular mass from 69 900 Da (GPC Mp value) of the starting PC (Figure 2a) to 42450 Da, in the case of the mixture with **I** (Figure 2b), and 26700 Da in that with BPA (Figure 2c). Also the chemical composition of the polymer was changed; in fact, comparing the MALDI spectrum of the PC/BPA mixture after 240 min of heating (Figure 3) with that of pure PC (Figure 1), it can be observed that, as expected, the peaks of the cycles (○) and those of the open-chain compounds with both *tert*-butylphenoxy end groups (×) have a minor abundance, while the peaks of the open-chain products with a bisphenoxy and a *tert*-butylphenoxy end groups (●) are of higher intensity. Furthermore, a new family of intense peaks, corresponding to compounds with both bisphenoxy end groups (indicated as $*$, see also Table 1), appears in the spectrum.

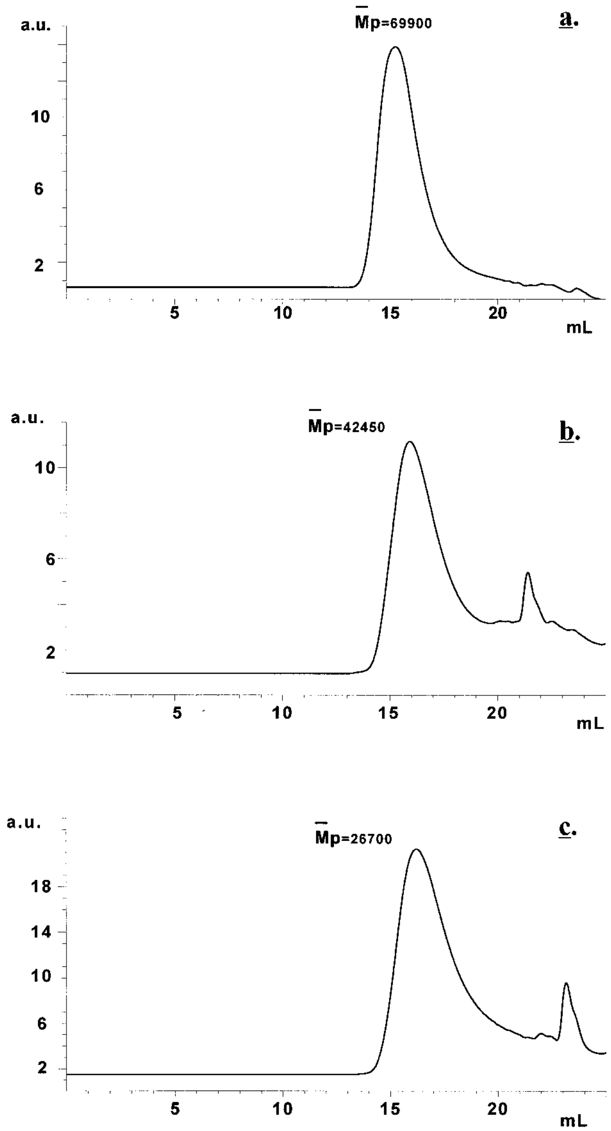
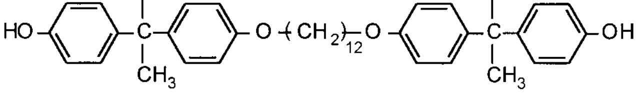


Figure 2. GPC traces of pure PC (a), PC/**I** (10 wt %) (b), and PC/BPA (10 wt %) (c) mixtures after 240 min of heating at 240 °C.



I

These data are diagnostic in confirming the occurrence of exchange reactions. In fact, the attack of the active hydroxyl BPA groups on the carbonate linkages

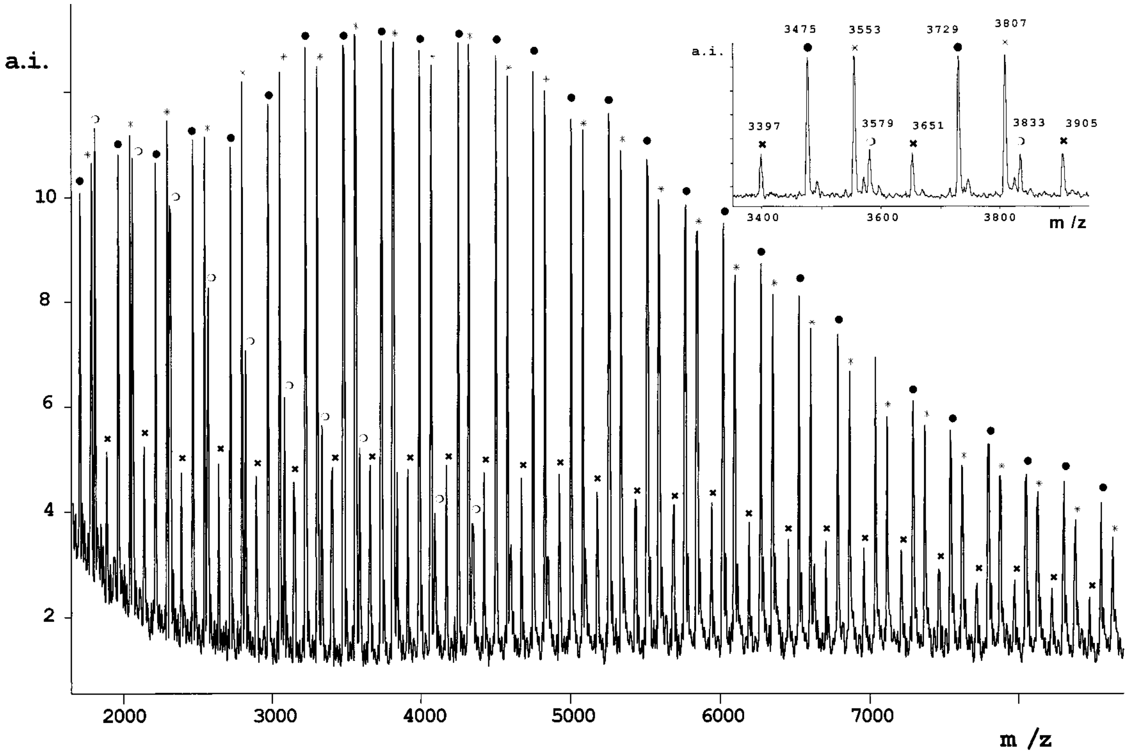


Figure 3. *Positive*-MALDI−TOF mass spectrum of PC/BPA (10 wt %) mixture after 240 min of heating at 240 °C) (for the structural assignments see Table 1).

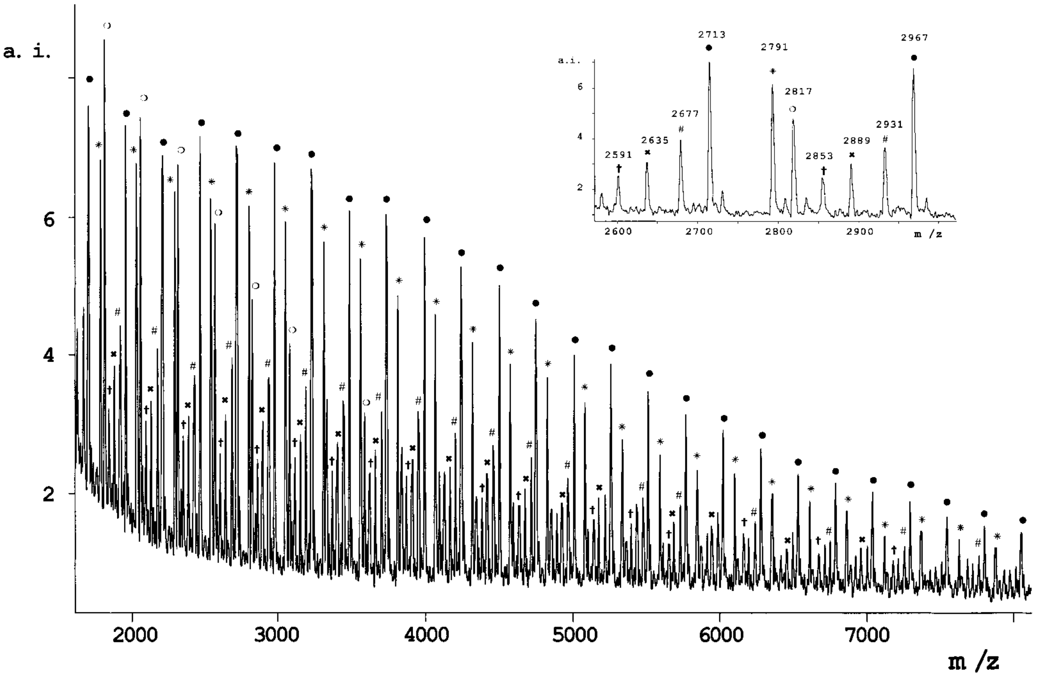


Figure 4. *Positive*-MALDI−TOF mass spectrum of PC/**I** (10 wt %) mixture after 240 min of heating at 240 °C (for the structural assignments see Table 1).

provokes: the ring opening of cyclic species, responsible for the amount reduction of the (○) species; the breaking of the open-chain molecules which has as a consequence the intensity reduction of the (×) peaks and the appearance of those (∗), absent in the starting and heated PC samples, with a resulting partial lowering of the polymer molecular mass (Table 2).

The occurrence of the outer−inner reactions is still more evident on examining the MALDI spectrum of PC/**I** mixture after 240 min of heating, shown in Figure 4. In fact, besides the above-discussed changes in the peaks composition, peaks corresponding to compounds with one or two hydroxyl end groups (indicated as # and †; for structural assignments see Table 1) and containing one or two 1,12-bis(bisphenoxy-A)dodecane units (probably as end groups) are observed in the spectrum.

Since the PC molecular mass is moderately reduced (Table 2), we considered the possibility to adopt a melt-mixing procedure for the insertion of complex units in PC chains to get polymeric materials otherwise of

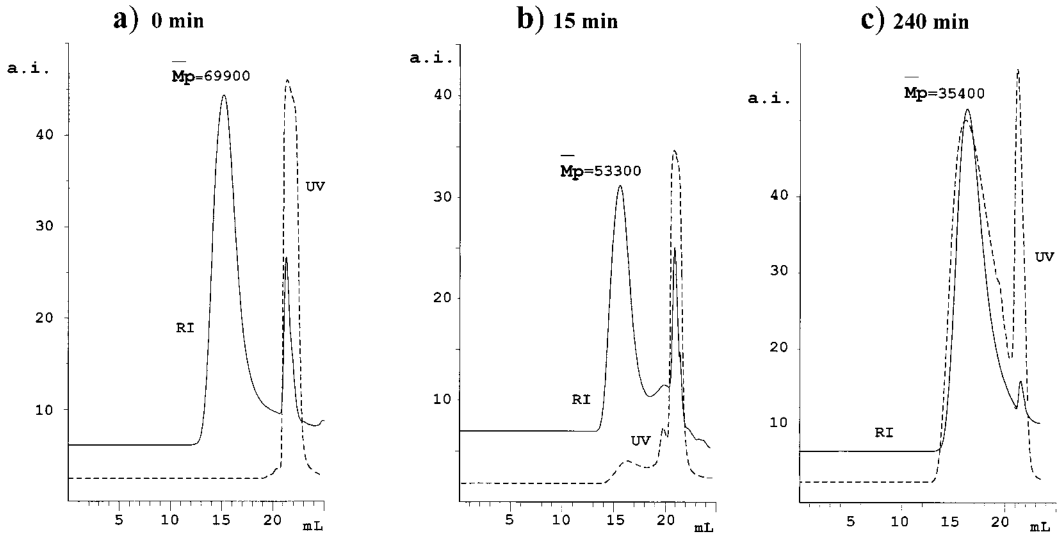
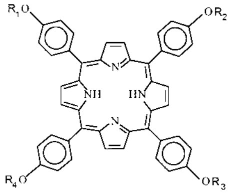


Figure 5. GPC traces, obtained using both UV−visible (traces indicated as UV) and differential refractometer (traces indicated as RI) detectors connected in parallel, of the PC/porphyrin **II** (10 wt %) mixture after 0 (a), 15 (b), and 240 (c) min of heating at 240 °C.

difficult preparation. As an example, the results of experiments with some porphyrins and a fullerene derivative are reported here.

Four porphyrins with one or two phenolic (**II** and **III**) or alcoholic (**IV** and **V**) −OH were prepared as reported in the Experimental Section. Mixtures between PC and these products were heated at 240 °C and maintained at this temperature up to 240 min.



	R_1	R_2	R_3	R_4
II	$C_{10}H_{21}$	$C_{10}H_{21}$	$C_{10}H_{21}$	H
III	$C_{10}H_{21}$	H	$C_{10}H_{21}$	H
IV	$C_{12}H_{25}$	$C_{12}H_{25}$	$C_{12}H_{25}$	$C_{11}H_{22}OH$
V	$C_{12}H_{25}$	$C_{11}H_{22}OH$	$C_{12}H_{25}$	$C_{11}H_{22}OH$

The GPC traces of the materials obtained after 0−240 min of heating of the PC mixture with 10 wt % of porphyrin **II** are reported in Figure 5. Because these porphyrin units have a characteristic band of light absorption at 425 nm, the homogeneous porphyrin arrangement in all the mass range of the PC macromolecules was followed by using, besides the differential refractometer, an UV−visible detector (set at 425 nm). So, in the case of the starting mixture, the refractive index trace (RI in Figure 5a) shows a large curve due to the polymer component (Mp = 69 900 Da) and a peak at higher elution volume due to the porphyrin. Differently, the UV−visible trace (UV in Figure 5a) only shows the peak of the porphyrin because the bisphenolcarbonate linkages do not absorb at 425 nm.

After 15 min of heating, the maximum of the GPC polymer trace (Figure 5b) is shifted slightly toward a lower molecular mass value (Mp = 53 300), and on the basis of the UV−visible trace it can be seen that a little portion of polymer has incorporated porphyrin units in the chains. At the reaction time of 240 min (Figure 5c), on the contrary, RI and UV−visible traces are very similar; although a reduction of the polymer molecular mass (Mp = 35400) is observed, these data point out the considerable quantity of porphyrin units inserted in the polymer and their homogeneous concentration in all the molecular mass range.

A similar behavior was also observed for the other PC/porphyrin mixtures and the Mp values of the polymeric materials obtained after heating are summarized in Table 2. As expected, when monohydroxyl product **II** or **IV** was used, a lower reduction of Mp, with respect to the case of the dihydroxylporphyrin **III** or **V**, was observed. Moreover, it can be also noticed that the final molecular mass (after 240 min of heating) remains beyond 25 000 Da for all the mixtures.

The porphyrin contents in the polymers were evaluated spectrophotometrically by considering the absorption values at 425 nm in the GPC traces; in few cases, the data were verified by solution measurements after extraction with ethanol of the unreacted porphyrin from the sample. Considering the pertinent values reported in Table 2, it appears that a large amount of porphyrin is bound to the macromolecules after 240 min of heating.

A fine structural characterization of the obtained materials by MALDI−TOF mass spectrometric analysis was attempted to confirm the insertion of porphyrin units in the polymeric chains.

As an example, we report here the case of the PC mixture containing 10 wt % of porphyrin **IV**. In the MALDI−TOF mass spectra of the mixtures heated to about 60 min (omitted for brevity) little intense peaks corresponding to products containing a porphyrin unit in the molecule also appear besides the peaks observed in the PC spectrum of Figure 1. On the contrary, the spectrum of the sample after 240 min of heating (Figure 6), essentially consists of intense peaks at m/z 2037 + n254 (indicated as ◇), m/z 2115 + n254 (indicated as ▲) and, with less abundance, m/z 2731 + n254 (indicated as ☆) which correspond (see Table 3) to three families of products having a *tert*-butylphenoxy and a porphyrin, a porphyrin and a bisphenol, or two porphyrins as end groups, detected as M_nH^+ ions (also lower intense peaks due to M_n^+ and M_nNa^+ ions appear in the spectrum, see Experimental Section); on the contrary, peaks due to products containing only BPA units [especially those of the cyclic products (○) and those having two *tert*-butylphenoxy end groups (×), see also Table 1] have very little intensity.

These data, obtained also for PC/porphyrin **II** mix-

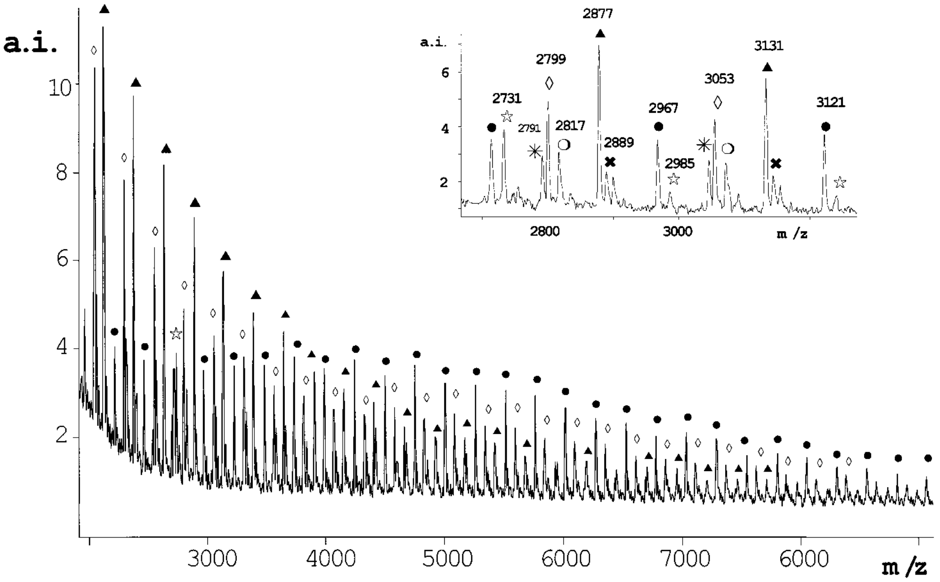
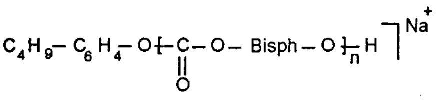
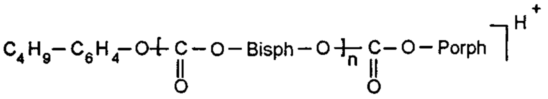
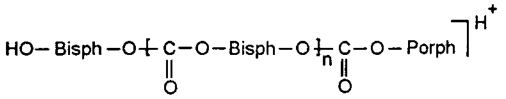
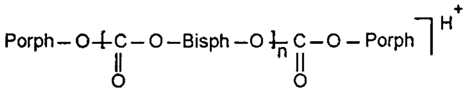
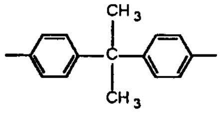


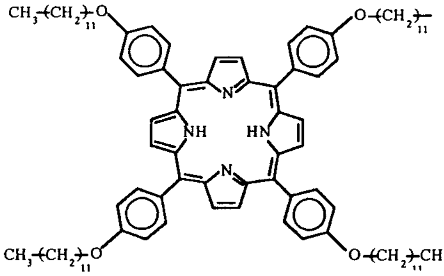
Figure 6. *Positive*-MALDI–TOF mass spectrum of PC/porphyrin **IV** (10 wt %) mixture after 240 min of heating at 240 °C (for the structural assignments, see Table 3).

Table 3. Molecular Ions Detected in the *Positive*-MALDI–TOF Mass Spectra of Heated Mixtures of PC and Porphyrin Monomer IV (see Figure 6)

	Structures[a]	m/z Values of Molecular Ions[b]
●	 $\left[C_4H_9-C_6H_4-O\left(\underset{\underset{O}{\|}}{C}-O-\text{Bisph}-O\right)_n H\right]Na^+$	1443 + n 254
◊	 $\left[C_4H_9-C_6H_4-O\left(\underset{\underset{O}{\|}}{C}-O-\text{Bisph}-O\right)_n\underset{\underset{O}{\|}}{C}-O-\text{Porph}\right]H^+$	2037 + n 254
▲	 $\left[HO-\text{Bisph}-O\left(\underset{\underset{O}{\|}}{C}-O-\text{Bisph}-O\right)_n\underset{\underset{O}{\|}}{C}-O-\text{Porph}\right]H^+$	2115 + n 254
☆	 $\left[\text{Porph}-O\left(\underset{\underset{O}{\|}}{C}-O-\text{Bisph}-O\right)_n\underset{\underset{O}{\|}}{C}-O-\text{Porph}\right]H^+$	2731 + n 254

[a] The symbols are those used in the mass spectrum of Figure 6. Abbreviations in the structures are

Bisph = 

Porph = 

[b] The *m*/*z* value of the first peak reported in the spectrum, for each family, is indicated.

ture, are in agreement with those expected considering that porphyrins **II** and **IV**, having only an hydroxyl group, can be subjected to only one exchange reaction, so they can be exclusively bound as end groups.

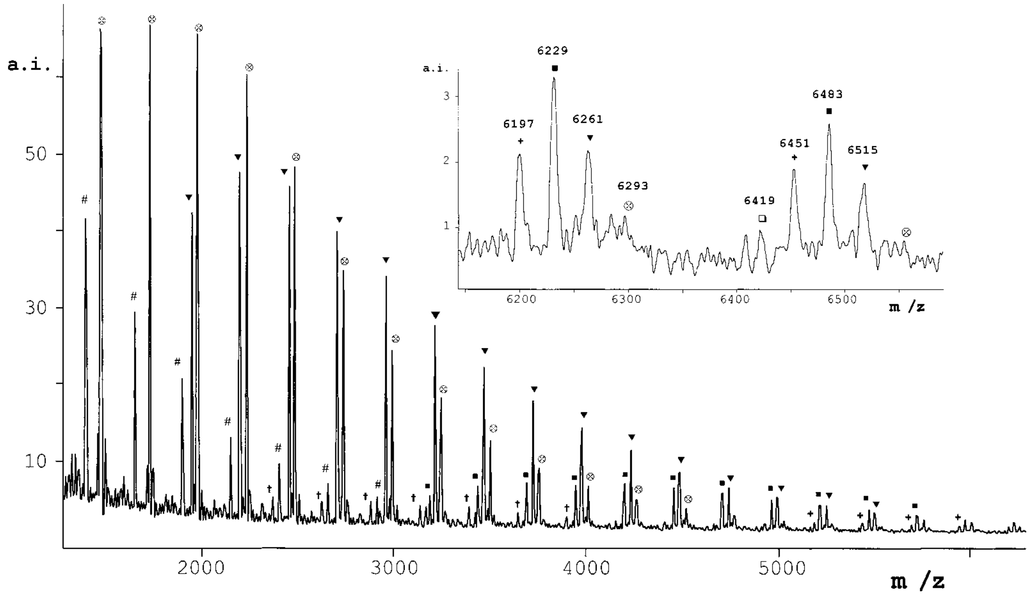


Figure 7. *Positive*-MALDI–TOF mass spectrum of PC/porphyrin **III** (30 wt %) mixture after 240 min of heating at 240 °C (for the structural assignments see Table 4).

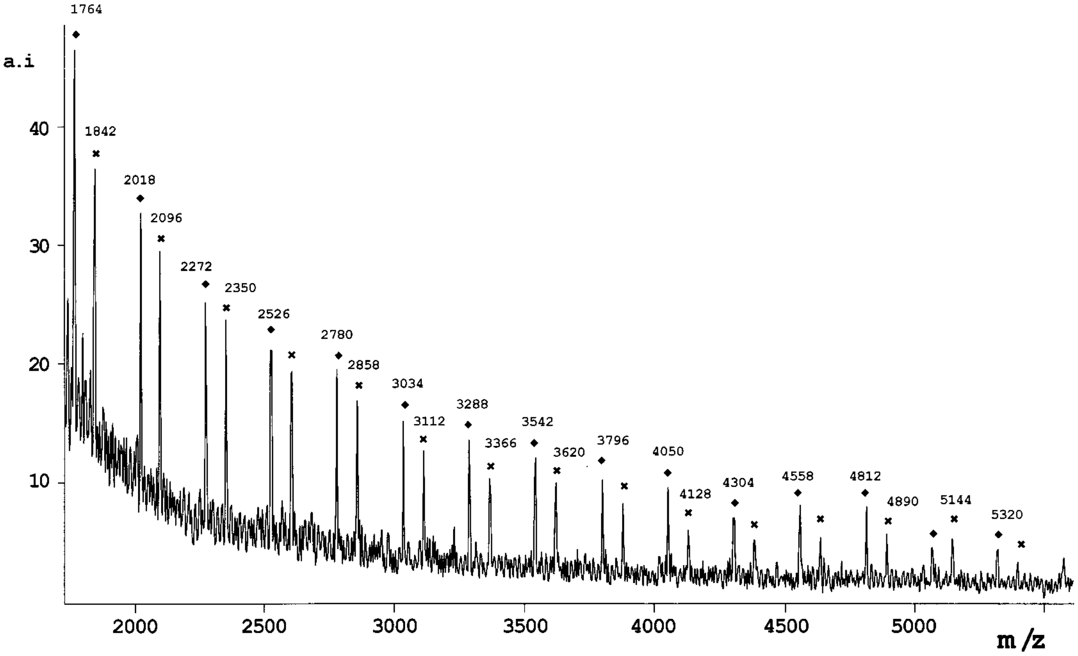
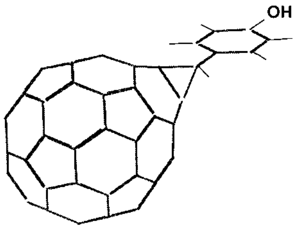


Figure 8. *Negative*-MALDI–TOF mass spectrum of PC/fullerene **VI** (5 wt %) mixture after 240 min of heating at 240 °C.

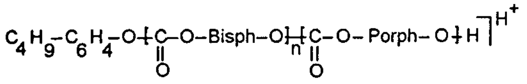
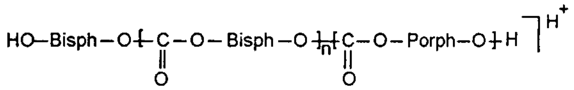
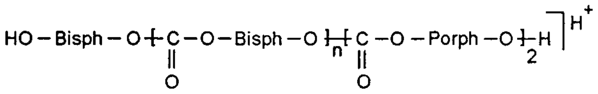
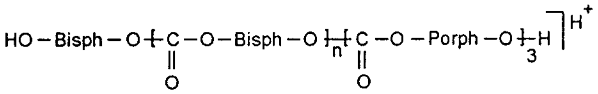
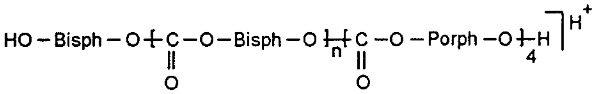
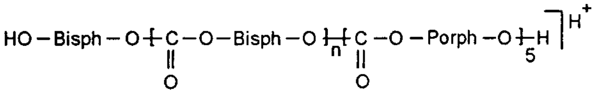
On the contrary, in the case of porphyrins **III** and **V**, having two hydroxyl groups, more exchange reactions are possible so that copolymeric species with more than two porphyrin units in the chain can be formed. However, in the MALDI mass spectra of PC mixtures with 10 wt % of porphyrin **III** or **V** (data omitted for brevity), probably due to the low porphyrin content, peaks concerning this last kind of compounds are not detected. To investigate this fact, PC mixtures with 30 wt % of porphyrin **III** were also examined. As expected, in the MALDI spectrum of the mixture after 240 min of heating (Figure 7), peaks due to pure bisphenol A carbonates are almost absent. The spectrum consists of intense peaks due to compounds containing one (at *m/z* 1213 + *n*254 and 1135 + *n*254, indicated as # and ⊗, respectively) or two (at *m/z* 1943 + *n*254, indicated as ▼) porphyrin units, but families of peaks with three (at *m/z* 2927 + *n*254, indicated as ■), four (at *m/z* 3911 + *n*254, indicated as +) or five (at *m/z* 4895 + *n*254, indicated as □) porphyrin units [these last appearing with higher intensity at higher mass (see also insert in Figure 7)], whose structural assignments are given in Table 4, are also present.

It can be noticed that, when porphyrin **V** (alcoholic OH) was used instead of **III** (phenolic OH) under the



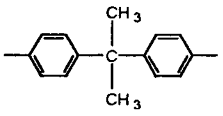
VI

Table 4. Molecular Ions Detected in the *Positive*-MALDI−TOF Mass Spectra of Heated Mixtures of PC and Porphyrin Monomer III (see Figure 7)

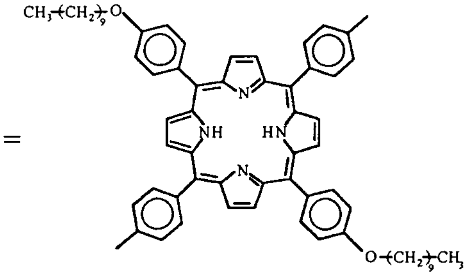
	Structures [a]	m/z Values of Molecular ions [b]
⊗	 $\left[C_4H_9-C_6H_4-O\left(\underset{\overset{\|}{O}}{C}-O-Bisph-O\right)_n\underset{\overset{\|}{O}}{C}-O-Porph-O-H\right]H^+$	1135 + n 254
#	 $\left[HO-Bisph-O\left(\underset{\overset{\|}{O}}{C}-O-Bisph-O\right)_n\underset{\overset{\|}{O}}{C}-O-Porph-O-H\right]H^+$	1213 + n 254
▼	 $\left[HO-Bisph-O\left[\left(\underset{\overset{\|}{O}}{C}-O-Bisph-O\right)_n\underset{\overset{\|}{O}}{C}-O-Porph-O\right]_2H\right]H^+$	1943 + n 254
■	 $\left[HO-Bisph-O\left[\left(\underset{\overset{\|}{O}}{C}-O-Bisph-O\right)_n\underset{\overset{\|}{O}}{C}-O-Porph-O\right]_3H\right]H^+$	2927 + n 254
✚	 $\left[HO-Bisph-O\left[\left(\underset{\overset{\|}{O}}{C}-O-Bisph-O\right)_n\underset{\overset{\|}{O}}{C}-O-Porph-O\right]_4H\right]H^+$	3911 + n 254
□	 $\left[HO-Bisph-O\left[\left(\underset{\overset{\|}{O}}{C}-O-Bisph-O\right)_n\underset{\overset{\|}{O}}{C}-O-Porph-O\right]_5H\right]H^+$	4895 + n 254

[a] The symbols are as those used in the mass spectrum of Figure 7. Abbreviations in the structures are

Bisph =



Porf =



[b] The *m*/*z* values of the first peak reported in the spectrum, for each family, are indicated.

same conditions of heating time and temperature, only small traces of compounds with three porphyrin units in the macromolecules were found in the MALDI mass spectra.

Another objective was the insertion of fullerene units in PC molecules. With this aim, 61-(*p*-hydroxyphenyl)-methano-1,2-fullerene[60] was prepared and PC mixtures with 5 wt % of this compound were heated analogously to the porphyrin experiments.

As expected, the UV traces of the GPC analyses (omitted for brevity) indicate a gradual fullerenation of PC macromolecules as a function of the heating time and a moderate reduction of the molecular mass as a consequence of the chain cleavage induced by the exchange reactions (Table 2). The fullerene content in the polymeric material after 240 min was 3.2 wt %.

The structural characterization of the materials after heating was achieved by inspection of both *positive*- and *negative*-MALDI−TOF mass spectra. The positive spectra result very similar to those of pure PC (Figure 3) and no peak due to compounds containing fullerene units is observed.

On the contrary, as in previous cases, due to the easier detection as negative ions of fullerene derivatives, the *negative*-MALDI spectra of the fullerenated polycarbonate shows only peaks of fullerenated species. As an example, the spectrum of the mixture heated for 240 min is shown in Figure 8. Two series of peaks appearing at m/z 1764 + n254 (indicated as ◆) and m/z 1842 + n254 (indicated as ×), correspond to molecular ions of products having a fullerene and a *tert*-butylphenoxy or an hydroxyl end groups, respectively, detected as M_n^-.

In conclusion, the data presented here show that copolycarbonates containing special units (likewise porphyrin and fullerene) in the main chain can be prepared through controlled melt-mixing processes in which mixtures of a preformed polycarbonate and reactive monomers are heated at 240 °C for a suitable time. The repeated outer−inner reactions cause a homogeneous monomer insertion in the polymer chains. As a consequence, the polymer molecular mass decreases, but starting from moderate amounts of monomer or reducing the heating time of the mixture, this effect can be limited.

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Supporting Information Available: Figures showing ^{1}H NMR and ^{13}C NMR spectra of porphyrin **III** (Figure 1S and 2S) and the ^{13}C NMR spectrum of porphyrin **V** (Figure 3S). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) See for example: (a) *Molecular Nonlinear Optics: Materials, Physic and Devices*; Zyss, J., Ed.; Accademic Press: Boston MA 1993. (b) *Polymers for Second-Order Nonlinear Optics*; Lindsay, G. A., Singer, K. D., Eds.; ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995. (c) *Introduction to Nonlinear Optcal Effects in Molecules and Polymers*; Prasad, N. P., Williams, D. J., Eds.; Wiley: New York, 1991. (d) *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; Electrochemical Society: Pennington, NJ, 1997; Vol. 4.

(2) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(3) Jefford, C. W. *Chem. Soc. Rev.* **1993**, 59.

(4) *Side Chain Liquid Crystal Polymers*; McArdle, C. B., Ed.; Blackie and Son Ltd: Glasgow, Scotland, 1989.

(5) *Electrical and Optical Polymer Systems*; Wise, D. L., Wnek, G. E., Trantolo, D. J., Cooper, T. M., Gresser, J. D., Eds.; Marcel Dekker: New York, 1998.

(6) Bao, Z.; Yu, L. *Trip* **1995**, *3*, 159.

(7) Weder, C.; Neuenschwander, P.; Suter, U. W.; Pretre, P.; Zaatz, P.; Gönter, P. *Macromolecules* **1995**, *28*, 2377.

(8) White, K. M.; Francis, C. V.; Isackson, A. J. *Macromolecules* **1994**, *27*, 3619.

(9) Miller, R. D.; et al. In *Photonic and Optoelectronic Polymers*; Jenekhe, S. A., Wynne, K. J., Eds.; ACS Symposium Series 672; American Chemical Society: Washington, DC, 1997; p 100.

(10) Döbler, M.; Weber, C.; Ahumada, O.; Neue, N.; Sckander, P.; Suter, U. W.; Follonier, S.; Boschard, C.; Günter, P. *Macromolecules* **1998**, *31*, 7676.

(11) Scamporrino, E.; Vitalini, D. *Macromolecules* **1992**, *25*, 1625: *25*, 6605.

(12) Vitalini, D.; Mineo, P.; Scamporrino, E. *Macromolecules* **1999**, *32*, 60.

(13) Vitalini, D.; Mineo, P.; DiBella, S.; Fragalà, I.; Maravigna, P.; Scamporrino, E. *Macromolecules* **1996**, *29*, 4478.

(14) Scamporrino, E.; Vitalini, D.; Mineo, P. *Macromolecules* **1999**, *32*, 4247.

(15) Montaudo, G.; Puglisi, C.; Samperi, F. In *Transreactions in Condensation Polymers*; Fakirov, S., Ed.; Wiley-VCH: Weinheim, Germany, 1999.

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