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# New Copoly(bisphenol-A)carbonates, Having Hydrophilic Porphyrin Units as End-Groups, Synthesized by Melt-Reacting Processes

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**Summary:** The synthesis of some poly(bisphenol-A)carbonates (PCs) containing hydrophilic porphyrin units as end groups, by thermal treatment of commercial PC and 5,10,15-tri{*p*[*ω*-methoxy-poly(oxyethylene)]phenyl}20(*p*-hydroxy phenyl)porphyrin (I) blends, is reported. A suitable choice of reaction temperature, molar composition and reaction time, allowing the extent of the outer-inner transesterification reactions, leads to a gradual insertion of porphyrin units in the polymer chains. The composition of the obtained materials was inferred by GPC and MALDI-TOF mass spectrometric analysis.

**Keywords:** hydrophilic porphyrin; MALDI-TOF mass spectrometry; polycarbonate

## Introduction

In recent years there has been a remarkable interest in the synthesis of porphyrin compounds for their potential use in such fields as the storage of solar energy, artificial oxygen transport[1] or, more recently, non-linear optical devices (such as optical switches, sensor protectors, light modulators, etc.) and synthetic biological receptors.[2] Often, for these applications, polymers are used as a matrix of the porphyrin compounds to form guest-host systems, but there is an increasing technological interest in the direct incorporation of active porphyrin units inside the polymeric chains in order to obtain high-performance materials.[3]

We have already reported the synthesis of some polyethers and copolyethers containing different amounts of tetra-arylporphyrin units in the main chain.[4] More recently, to overcome the difficulty in obtaining, by direct monomers condensation, copolycarbonates functionalized with fullerene or porphyrin units and having enough high molecular mass

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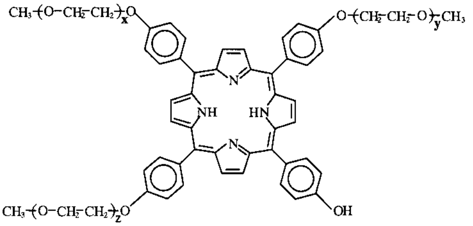
and homogeneous composition, a thermal activated transesterification process[5], starting from mixtures of preformed polycarbonates and suitable fullerene or porphyrin derivatives was tried. The same procedure was here adopted to bind hydrophilic 5,10,15-tri-{*p*-[*ω*-methoxy-poly(oxyethylene)]phenyl}-20-(*p*-hydroxyphenyl)porphyrin (I) units to polycarbonate chains, starting from suitable mixtures of commercial PC and porphyrin (I).

The structural characterization of the obtained copolymeric materials was performed by UV-visible, GPC and MALDI-TOF mass spectrometric analyses.



**I**

## Experimental Section

*Materials*: All solvents and basic materials were commercial products appropriately purified before use. Starting poly(bisphenol-A)carbonates were commercial products from General Electric (Lexan, L-220) and Aldrich (A-PC) while the 5,10,15tri{p[*ω*-methoxy-poly(oxyethylene)phenyl]}20(*p*-hydroxyphenyl)porphyrin (I) was prepared according to the procedure elsewhere described.[6]

*Thermal Treatment*: About 50mg of homogeneous mixtures of PC and porphyrin (I) were placed in different glass tubes that, after sealing under vacuum, were simultaneously immersed in a silicone oil bath maintained at 240°C and singly extracted after different times (from 7 min to 240 min). After cooling, the glass tubes were opened and the obtained materials dissolved in THF. Only for the quantitative determination of the porphyrin amount bonded to the polycarbonate, were these solutions analysed without any treatment; on the contrary, for the other characterizations, the residue recovered after precipitation in water was used. Unfortunately, the procedure adopted did not permit the complete separation of water-soluble compounds, so that little amounts of porphyrin (I) remained incorporated into the precipitate and revealed in the following analyses.

*GPC Analysis*: A PL-GPC 110 (Polymer Laboratories) thermostated system, equipped with two Mixed-D and one Mixed-E PL-gel 5µm columns and calibrated with polystyrene standards (Polymer Lab.), was used.

A differential refractometer (DR, Polymer Laboratories) and an UV–Visible spectrophotometer (UV, Hewlett Packard series 1050, fixed at 421 nm), connected in parallel, were used as detectors. The amount of porphyrin (I) inserted in the modified PCs was determined comparing the relative intensities of the GPC signal due to the polymeric fraction and to the unreacted porphyrin (I) in unprecipitated mixtures (see *Thermal Treatment* part).

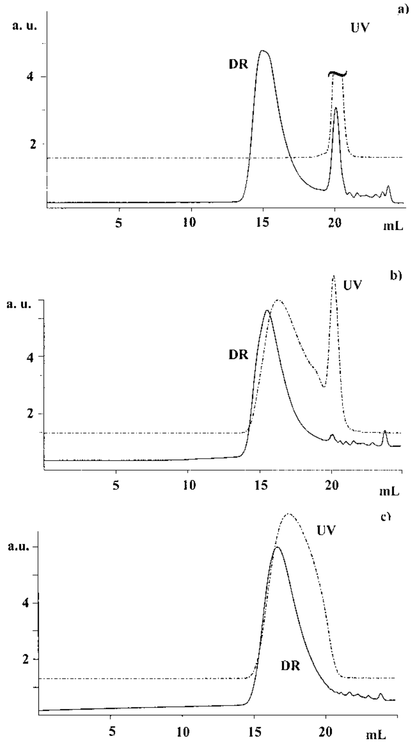
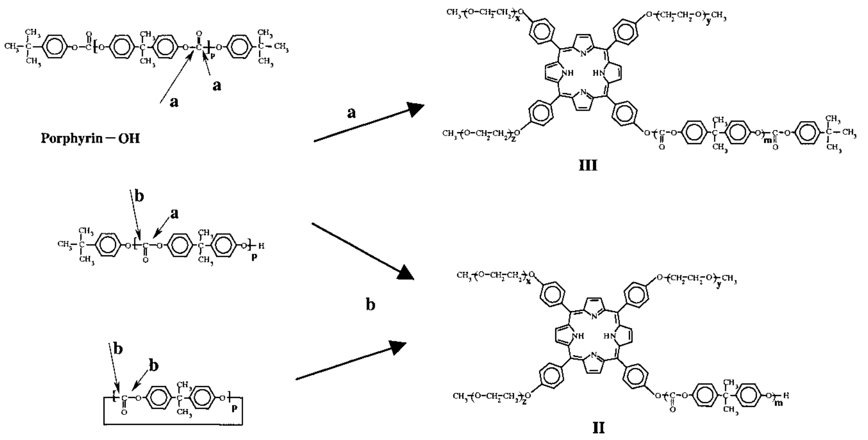


Figure 1: GPC traces, obtained using UV-visible (traces indicated as UV) and differential refractometer (traces indicated as DR) detectors connected in parallel, of the L-220/porphyrin I (10 wt.-%) mixture after 0 (a), 7 (b) and 120 min of heating at 240 °C.

*MALDI Mass Spectrometric Analysis*: The MALDI-TOF mass spectra were acquired by a Voyager DE-STR (PerSeptive Biosystem) using a simultaneous delay extraction procedure (20 kV applied after 233 ns with a potential gradient of 2545 V/mm) and detection in reflection mode. The m/z values reported in the spectra refer to the more abundant isotope of each element contained in the molecule.

## Results and Discussion

The GPC traces, recorded using both a DR and an UV spectrophotometer as detectors, of the starting mixture of L-220 and 10 wt.-% of porphyrin (I) (Figure $1_a$, in which the truncated peak corresponds to the saturated porphyrin signal) and the material obtained after a thermal treatment of 7 or 120 min (Figures $1_b$ and $1_c$, after precipitation in water, see Experimental Section) are compared in Figure 1. Because the DR detector reveals all the compounds eluted from the GPC column whereas the UV (set, in the present case, at 421 nm, maximum of the characteristic Soret absorption band of the porphyrin) only reveals compounds containing porphyrin units, the comparison between the two DR and UV traces in Figures $1_a$-$1_c$ allows the control of the actual porphyrination of the chains. So, in the UV traces of Figures $1_b$ and $1_c$, an increasing signal in correspondence of the polymer region can be noticed, while the peak due to the residual porphyrin (I), still present in the mixture, decreases up to almost disappearing at higher reaction times. At the same time, the shift toward higher elution times of the maximum of the DR traces indicates a gradual molecular mass reduction of the PC (Mp from 69000 Da to about 26000 Da).



Scheme 1

These results can be considered evidence of the exchange reactions (Scheme 1); in particular, because porphyrin molecules only have one reactive hydroxyl group, they are bound to the PC molecules as end-groups.

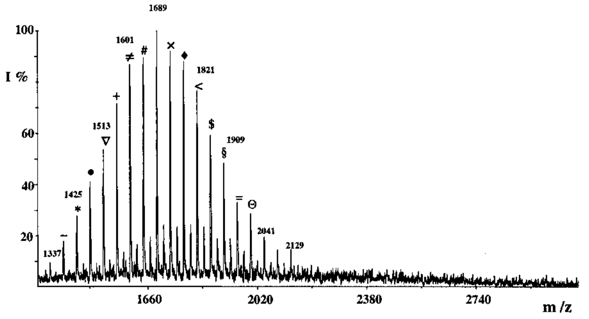


Figure 2: Positive MALDI-TOF mass spectrum of L-220/porphyrin I (10 wt.-%) mixture.

Furthermore, for the reacted 120 min material (Figure $1_c$), the DR and UV traces are similar, indicating a porphyrination of the PC molecules in all the polymer mass range. It was also verified that, varying the percent of porphyrin in the starting mixture, the reaction temperature and/or the melt-reaction time (data omitted for brevity), the extension of the exchange reaction, and then both the porphyrin amount inserted in the PC and its molecular mass reduction, can be controlled. In the case of the above discussed mixture, an insertion of about 4 wt-% of porphyrin units in the PC sample after 120 min of heating was ascertained (see Experimental Section).

To confirm the occurrence of the transesterification reactions, the structural characterization of the melt-mixed materials was achieved by means of MALDI-TOF mass spectrometric analysis. The positive MALDI mass spectrum of the starting polycarbonate L-220/I mixture and that of the obtained material after 120 min of heating are shown in Figure 2 and 3, respectively.

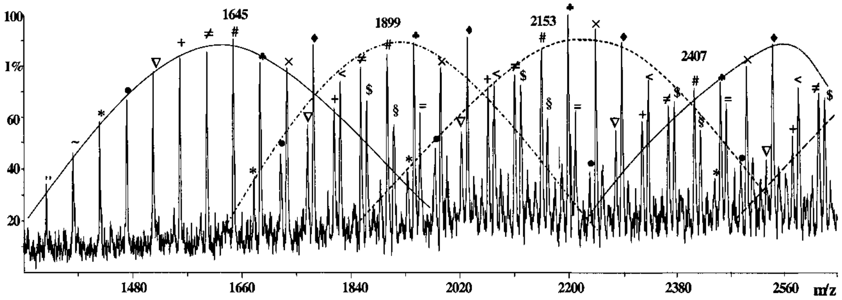


Figure 3: Positive MALDI-TOF mass spectrum of L-220/porphyrin I (10 wt.-%) mixture after 120 min of heating at 240 °C.

In the spectrum of Figure 2, the signals due to PC, because of both different ionization efficency and polydispersity of PC (d= 3.45) and porphyrin (I) (d=1.02), result too weak to be detected; as a consequence, the spectrum is almost coincident with that of the pure porphyrin (I) and presents a cluster of peaks, centred at about m/z 1700, at m/z values 721+n44 (with n=x+y+z= 14-32) corresponding to porphyrin (I) oligomers (detected as $MH^+$ ions) with a varying (x+y+z) number of ethylene glycol units in the three branches (for peak assignments see Table 1, column for m=0), whose first peak at m/z 1337 corresponds to the smaller porphyrin species with a total of 14 ethylene glycol units in the three branches. Weak signals due to porphyrin oligomers sodiated ions are also present in the spectrum at m/z values 743+n44 (n=14-32).

Remarkably, the MALDI-TOF mass spectrum of the mixture after 120 min of heating, reported in Figure 3, is very different. In fact, in addition to the peaks due to the unreacted porphyrin (I) oligomers, other families of peaks corresponding to molecules containing a porphyrin end-group and an increasing number of bisphenol-A carbonate units, formed by transesterification reactions reported in Scheme 1, are present in the spectrum.

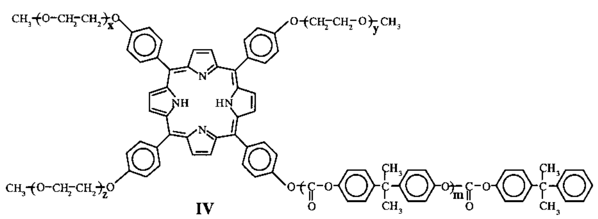
To facilitate the reading, homologous peaks (having the same x+y+z number of ethylene glycol in the branches) of each clusters are indicated with the same symbol used in Figure 2; so, as an example, the peaks indicated as # concern the family whose first peak at m/z 1645 corresponds to pure porphyrin with x+y+z= 21 ethylene glycol units in the three branches and the following peaks, at m/z values 1645+m254, to its derivatives (structure II, Scheme 1) with an increasing number of bisphenol-A carbonate units in the molecule (pertinent m/z values are reported in the line of Table 1 having m/z 1645 as first term). It can also be noticed that each series of peaks, whose m/z values appear in a same column of Table 1, due to PC molecules containing the same number of bisphenol-A carbonate units (*m* number on the top of each column) and a different porphyrin end-group (*i.e.*, porphyrin with a different x+y+z number of ethylene glycol units in the branches), form clusters (indicated with different traces in Figure 3) similar to that of the mixture of porphyrin oligomers in Figure 2, but whose maximum is progressively increased by 254 Da.

Table 1: Molecular Ions Detected in the Positive MALDI-TOF Mass Spectra of Melt-Mixed L-220/I and A-PC/I Mixtures

| Structures [a] | Symbol [b] | | m/z values of molecular ions (detected as $MH^+$) | | | | |
|---|---|---|---|---|---|---|---|
| | | m = | 0 | 1 | 2 | 3 | 4 |
| | | x+y+z = | | | | | |
| **II** | | 14 | **1337** | **1591** | **1845** | **2099** | **2353** |
| | ~ | 15 | **1381** | **1635** | **1889** | **2143** | **2397** |
| | * | 16 | **1425** | **1679** | **1933** | **2187** | **2441** |
| | • | 17 | **1469** | **1723** | **1977** | **2231** | **2485** |
| | ∇ | 18 | **1513** | **1767** | **2021** | **2275** | **2529** |
| | + | 19 | **1557** | **1811** | **2065** | **2319** | **2573** |
| | ≠ | 20 | **1601** | **1855** | **2109** | **2363** | **2617** |
| | # | 21 | **1645** | **1899** | **2153** | **2407** | **2661** |
| | ♣ | 22 | **1689** | **1943** | **2197** | **2451** | **2705** |
| | × | 23 | **1733** | **1987** | **2241** | **2495** | **2749** |
| | ♦ | 24 | **1777** | **2031** | **2285** | **2539** | **2793** |
| | < | 25 | **1821** | **2075** | **2329** | **2583** | **2837** |
| | $ | 26 | **1865** | **2119** | **2373** | **2627** | **2881** |
| | § | 27 | **1909** | **2163** | **2417** | **2671** | **2925** |
| | = | 28 | **1953** | **2207** | **2461** | **2715** | **2969** |
| | Θ | 29 | **1997** | **2251** | **2505** | **2759** | **3013** |
| | | 30 | **2041** | **2295** | **2549** | | |
| | | 31 | **2085** | **2339** | **2593** | | |
| | | 32 | **2129** | **2383** | | | |
| **IV** | **A** | 18 | **1751** | **2005** | **2259** | **2513** | **2767** |
| | **B** | 19 | **1795** | **2049** | **2303** | **2557** | **2811** |
| | **C** | 20 | **1839** | **2093** | **2347** | **2601** | **2855** |
| | **D** | 21 | **1883** | **2137** | **2391** | **2645** | **2899** |
| | **E** | 22 | **1927** | **2181** | **2435** | **2689** | **2943** |
| | **F** | 23 | **1971** | **2225** | **2479** | **2733** | **2987** |
| | **G** | 24 | **2015** | **2269** | **2523** | **2777** | **3031** |
| | **H** | 25 | **2059** | **2313** | **2567** | **2821** | **3075** |
| | **I** | 26 | **2103** | **2357** | **2611** | **2865** | |

a) In the MALDI-TOF mass spectra of L-220/I mixture, the m/z values of the ions having structure II and III are coincident (see text).
b) The symbols are the same used in the mass spectra of Figures 2-4.

Unfortunately, the unambiguous structural characterisation of these materials was impossible because the m/z value of each peak in the mass spectra corresponds to two expected modified PC molecules (Scheme 1) having the same number of bisphenol-A units but different end-groups: *i.e.*, a porphyrin and a hydroxyl-bisphenoxy group (structure II) or a porphyrin oligomer with four ethylene glycol units less in the branches and a tert-butylphenoxy unit (structure III).


IV

In the attempt to distinguish the two different species and ascertain the presence of compounds like II, III or both, the melt-reacting experiments were made again using an Aldrich polycarbonate (A-PC) which, as shown in a previous work,[5b] has 4-cumylphenoxy end-groups instead of the *tert*-butylphenoxy present in the L-220.

A significant portion of the MALDI mass spectrum of the A-PC/I mixture after 120 min of heating at 240°C is reported in Figure 4. Besides the peaks due to unreacted porphyrin oligomers (at m/z values 723+n44, with n=x+y+z) and to PC species with a porphyrin and an hydroxyl-bisphenoxy end-groups (at m/z 723+n44+m254, structure II), a new series of peaks at m/z 723+n44+m254+238 (indicated with letters), due to species having the structure IV with a porphyrin and a 4-cumylphenoxy as end-groups and an increasing number of bisphenol-A carbonate units in the molecule (for the structural assignments see Table 1), is present in the spectrum. So, as an example, the porphyrin of

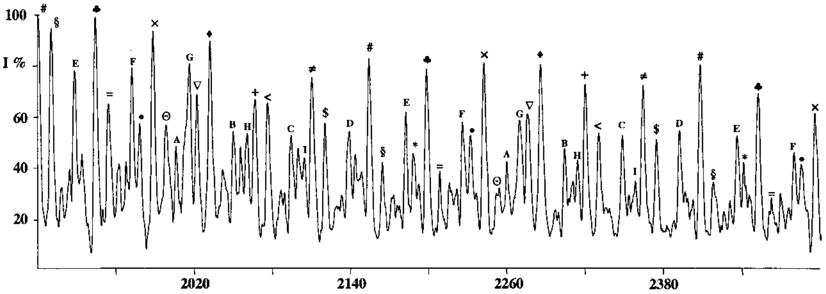


Figure 4: Positive MALDI-TOF mass spectrum of A-PC/porphyrin I (10 wt.-%) mixture after120 min of heating at 240 °C.

molecular mass 1689 (containing x+y+z= 22 ethylene glycol units and indicated as ♣ in the spectrum, see Table 1) is the progenitor of the two series at m/z 1943, 2197, 2451, etc. (having structure II, indicated as ♣) and at m/z 1927, 2181, 2435, etc. (having structure IV, indicated as E).

It can be observed that, at high reaction times, the species with the structure II appear more intense than those having structure IV in all the mass range of the spectrum, whereas, in the spectra at lower reaction times (omitted for brevity), the intensities of the two series of peaks are comparable. This factor may be explained by considering the unchanging number of 4-cumylphenoxy end-groups present in the PC with respect to the progressively increasing numbers of hydroxyl end-groups, consequent to the insertion of porphyrin units (see Scheme 1), as a function of the reaction times.

Summarising our data, it can be observed that exchange reactions, occurring at 240°C between molecules of commercial poly(bisphenol-A)carbonates (L-220 or A-PC capped with tert-butylphenoxy or 4-cumylphenoxy groups, respectively) and the porphyrin (I), allowed the formation of poly(bisphenol-A)carbonates having hydrophilic porphyrin units as end-groups.

The MALDI mass spectra (omitted for brevity) of the water soluble fraction of A-PC/I and L-220/I mixtures heated 120 min (about 10% of the starting PC/I mixtures), showed the presence of peaks only up to about m/z 3000 due to lower molecular mass PCs having two (I) units or one (I) unit and a hydroxyl-bisphenoxy group as end-groups.

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