Thermal Decomposition Processes in Aromatic Polycarbonates Investigated by Mass Spectrometry

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ABSTRACT: The thermal decomposition pathways leading to the formation of volatile compounds and to char residue in poly(bisphenol A carbonate) (**PC**), poly(resorcinol carbonate) (**PRC**), and poly(hydroquinone carbonate) (**PHC**) have been investigated by mass spectrometry. The structure of the volatile compounds obtained in the temperature range 300−700 °C, by direct pyrolysis mass spectrometry (DPMS), suggests that these polycarbonates undergo thermal decomposition by a number of different pyrolysis processes. In the initial stage of the thermal degradation are generated cyclic oligomers by an intramolecular exchange reaction, whereas the evolution of CO_2 and H_2O is spread over all the pyrolysis temperature range, being responsible for the formation of ether bridges (decarboxylation) and phenolic end groups (hydrolysis). A disproportionation reaction of the BPA isopropylidene bridges of **PC** itself takes place at higher temperature yielding phenyl and isopropylidene end groups, whereas pyrolysis products containing dibenzofuran units are formed by dehydrogenation of ether units. The formation of compounds containing xanthone and fluorenone units, most likely generated by isomerization of the aromatic carbonate functional groups and successive condensation reaction, has also been observed. In an additional set of experiments, the isothermal pyrolysis of **PC** was achieved, isothermally, at 350 and 400 °C, and then the exhaustive and selective aminolysis of the carbonate functional groups, still present in the pyrolysis residue, has been performed. The aminolyzed residue was then analyzed by fast atom bombardment (FAB) mass spectrometry to detect the compounds eventually formed by molecular rearrangements of **PC** chains. The FAB-MS spectra showed the presence of compounds containing several consecutive xanthone and ether units, indicating that at this temperature the isomerization and the condensation processes leading to these structures are quite extensive. These units undergo aromatization and cross-linking processes, leading to a graphite-like charred residue as the temperature increases.

Introduction

The thermal decomposition processes occurring in poly(bisphenol A carbonate) (**PC**) have received continued attention in the literature,[1−18] due to the fact that this polymer is an important engineering thermoplastic material which is subjected to injection molding operations at temperature above 300 °C. At this temperature, degradation reactions are likely to occur, and therefore the understanding of its thermal behavior is of crucial importance in the end use application.

Furthermore, **PC** leaves about 20−30% residue at 800 °C, and there are no indications in the literature about its structure.

Davis and Golden[2−8] studied the isothermal pyrolysis of **PC**, in the temperature range 300−400 °C, and noticed, by intrinsic viscosity measurements, a decrease in the molecular weight of **PC** when it is thermally degraded in a sealed system,[2] whereas in a continuously evacuated system **PC** rapidly cross-links to form an insoluble gel.[3,5,8]

A rearrangement of the carbonate group to form a pendant carboxyl group, ortho to an ether link, which then leads to xanthone units and to a cross-linked structure with ester linkage between chains, has been hypothesized[7,8] on the basis of the structure of pyrolysis compounds obtained from diphenyl carbonate, a model compound.[6]

However, direct experimental evidence is not available in the literature about the formation of xanthones or other condensed structures formed during the heating of **PC**.

The thermal degradation of **PC** was also performed at higher temperature (500−850 °C) by flash pyrolysis GC/MS (Py-GC/MS),[9,12] but only small compounds (i.e., below the mass of the polymer repeat unit) such as H_2O, CO_2, bisphenol A, phenol, isopropenylphenol, and diphenyl carbonate were detected, because the higher molar mass compounds are not enough volatile to get through the GC column.

In fact, the detection of structurally significant thermal degradation products appears to be a problem associated with condensation polymers bearing large repeating units.

The mechanism of thermal cleavage of a polymer chain can be better inferred if larger primary pyrolysis products were detected, and therefore thermal degradation studies ought to focus on techniques such as direct pyrolysis mass spectrometry (DPMS),[13−25] which allow the detection of large primary products of pyrolysis.

Earlier DPMS studies on the thermal degradation of **PC**[10,13,16−18] and on poly(resorcinol carbonate) (**PRC**)[13] have established that, in the initial stage of thermal degradation (about 300−400 °C), the primary degradation products evolving from these polymers are cyclic oligomers formed by intramolecular exchange processes.

In these studies the volatile products were collected up to 450 °C, and therefore the pyrolysis compounds evolving at higher temperature (>500 °C), which might provide structural information on the pyrolysis residue of **PC** and **PRC**, were not detected.

DPMS experiments on some condensation polymers such as PPO and PEEK,[19] PPS,[20] and poly(xylilene

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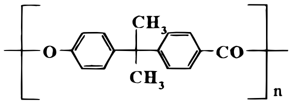
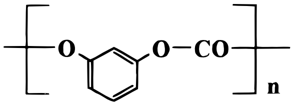
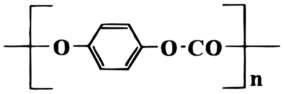
Table 1. Structure, Viscosity, Thermogravimetric, and Total Ion Current Data of the Three Aromatic Polycarbonates Studied

polymer		PDT[a] (°C)	TIC[b] (°C)	residue % (800 °C)	η_{inh}[c]
PC[d]		500	380	20	0.42[e]
PRC		380	360	18	0.1[f]
PHC		450	450	12	0.15[g]

[a] Temperature of maximum rate of polymer decomposition. [b] Total ion current maximum of DPMS curves. [c] $\eta_{inh} = \ln \eta_r/c$; $c = 0.5$ g/dL. [d] $M_w = 21\,500$; $M_n = 12\,400$; $M_w/M_n = 1.74$. [e] In chloroform. [f] In dimethylformamide. [g] In tetrachloroethane/phenol 40/60 (w/w).

sulfide)[21] have provided information about the structure of the pyrolysis residue and on the nature of the reactions leading to its formation, by analyzing the structure of the pyrolysis compounds evolved at higher temperature (500−700 °C).

Owing to this, we decided to investigate by DPMS the thermal decomposition of **PC** and for comparison that of other two aromatic polycarbonates, i.e., **PRC** and poly(hydroquinone carbonate) (**PHC**) (Table 1), exploring the higher temperature range (up to 700 °C).

In an additional set of experiments, the isothermal pyrolysis of **PC** was achieved by heating it at a given temperature (350 and 400 °C) and then performing the exhaustive and selective aminolysis of the carbonate functional groups still present in the pyrolysis residue. The aminolyzed residue was then analyzed by fast atom bombardment (FAB) mass spectrometry to detect the compounds eventually formed by molecular rearrangements of **PC** chains.

In these experiments the FAB mode was preferred to MALDI, because MALDI does not allow to analyze the region below 1000 Da, usually covered by the matrix clusters.

Experimental Section

Materials. Basic materials were commercial products appropriately purified before use. Poly(bisphenol A carbonate) (**PC**, Table 1) is a commercial product (Lexan L220) by General Electric. Poly(resorcinol carbonate) and poly(hydroquinone carbonate) (**PRC** and **PHC**, Table 1) were synthesized by interfacial polycondensation (as reported elsewhere),[13] starting from equimolar amounts of hydroquinone or resorcinol and their corresponding bis(chloroformate).

Thermogravimetry. A Perkin-Elmer thermal analyzer TGS-2 was used to determine the thermal stability of the polymers. Experiments were carried out on about 2 mg sample under nitrogen, at a flow rate of 60 mL/min and a heating rate of 10 °C/min, up to 800 °C. The temperature of maximum rate of polymer degradation (PDT) corresponds to the temperature (°C) at which DTG curves reach their maxima and are collected in Table 1.

Viscometry. Inherent viscosity values [$\eta_{inh} = \ln \eta_r/c$] were measured in a Desreux-Bishoff suspended level viscometer, maintaining the temperaure at 30 ± 0.01 °C. Viscometry data and solvents used are reported in Table 1.

Direct Pyrolysis Mass Spectrometry. Pyrolysis mass spectra were obtained using a VG TRIO 1000 QMD mass spectrometer using Lab-Base software. Pyrolysis was carried on about 10 μg of sample, placed on a glass tube, heated from 100 to 700 °C at heating rate of 10 °C/min by the water-cooled standard direct insertion probe for solid materials,. Mass spectral scans were made continuously with a cycle time of 3

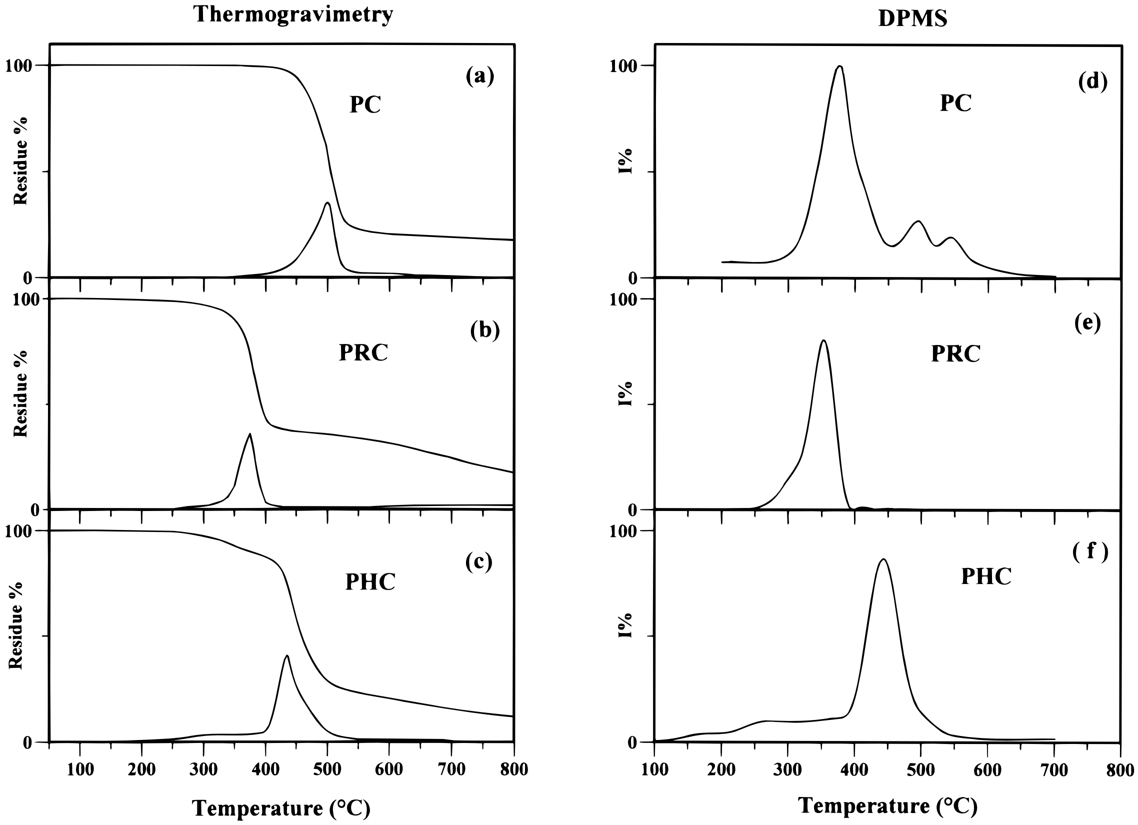
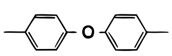
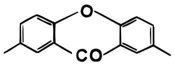
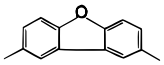
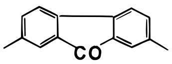
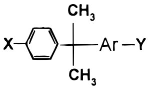
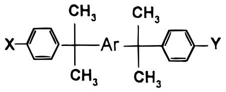
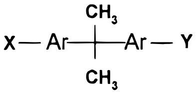
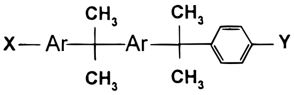
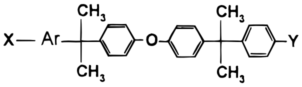


Figure 1. TG, DTG, and TIC curves of (a, d**)** **PC**, (b, e**)** **PRC**, and (c, f**)** **PHC**.

Table 2. Structural Assignments of Pyrolysis Compounds Evolved at 500 and 550 °C from Poly(bisphenol A carbonate)

Strucure	**Terminals**		**Ar**			
						
	X	**Y**	**M$^+$**	**M$^+$**	**M$^+$**	**M$^+$**
X–Ar–Y	H	H	-	196	168	-
	H	CH_3	184	210	-	-
	CH_3	CH_3	198	224	196	-
	CH_3	C_2H_5	212	238	210	-
	C_2H_5	C_2H_5	-	252	224	236
	C_2H_5	C_3H_7	-	-	238	250
	C_3H_7	C_3H_7	-	-	252	264
	H	C_3H_5	210	236	-	-
	CH_3	C_3H_5	224	250	-	-
	C_2H_5	C_3H_5	238	264	236	
	C_3H_7	C_3H_5	252	-	250	-
	C_3H_5	C_3H_5	250	276	-	-
	H	H	-	314	286	298
	H	CH_3	302	328	300	312
	H	C_2H_5	316	342	314	326
	H	C_3H_7	330	356	328	340
	H	C_2H_5	328	354	326	338
	OH	H	304	330	302	314
	OH	CH_3	318	344	316	328
	OH	C_2H_5	332	358	330	344
	OH	C_3H_7	-	-	344	356
	OH	C_2H_5	344	370	342	354
	H	H	406	432	404	416
	H	OH	422	448	420	432
	OH	OH	438	464	436	448
 $X{-}Ar{-}C(CH_3)_2{-}Ar{-}Y$	H	H		432	376	400
	H	CH_3		446	390	414
	CH_3	CH_3		460	404	428
	CH_3	C_2H_5		474	418	442
	C_2H_5	C_2H_5		488	432	456
	C_2H_5	C_3H_7		-	446	470
	C_3H_7	C_3H_7		-	460	484
	H	C_3H_5		472	416	440
	CH_3	C_3H_5		486	430	454
	C_2H_5	C_3H_5		-	444	468
	C_3H_7	C_3H_5		-	-	482
	C_3H_5	C_3H_5		-	458	480
	H	H		-	494	
	OH	H		566	-	
	H	CH_3		-	508	
	OH	CH_3		580	-	
	OH	C_3H_5		606	-	
	OH	H		540		
	OH	CH_3		554		

s, mass range 10−1000, and interscan time 3 s and stored. Electron impact (EI) mass spectra were obtained at 18 eV. The source temperature was 250 °C.

Isothermal Pyrolysis of PC and Aminolysis of the Pyrolysis Residue. Isothermal pyrolysis of the **PC** were performed in a thermogravimetric apparatus under nitrogen flow (60 mL/min). Typically, 2 mg of samples was heated for 1 h at 350 and 400 °C. The residue was added with 1 mL of THF, with a large excess (1:10 molar ratio) of piperidine and after 1 h, at room temperature, was dried by a nitrogen flow and finally redissolved with the minimum volume of THF.

FAB-MS. A double focusing Kratos MS 50S equipped with the standard FAB source operating with 20 kV cesium gun and a MASPEC II data system (from MS Service, Manchester) was used to obtain the FAB mass spectra. The instrument was scanned from *m*/*z* 3000 to 60, with a scan rate of 10 s/decade, with an accelerating voltage of 8 kV. The clusters of cesium iodide were used for the calibration of the raw FAB-MS spectra; a resolution of about 2000 ($M/\Delta M$) was obtained. A drop of the aminolyzed sample solution was placed on the stainless steel target end of the direct insertion FAB probe and mixed with 3-nitrobenzyl alcohol as liquid matrix. Peak intensity values shown in mass spectra represent the average of 10 mass spectra.

Results and Discussion

Thermal Degradation Behavior. The TG and DTG traces of the three aromatic polycarbonates (**PC, PRC, PHC**; Table 1), reported in Figure 1a−c, indicate that they possess different thermal stability. The TG and DTG curves of **PC** (Figure 1a) indicate that it is stable

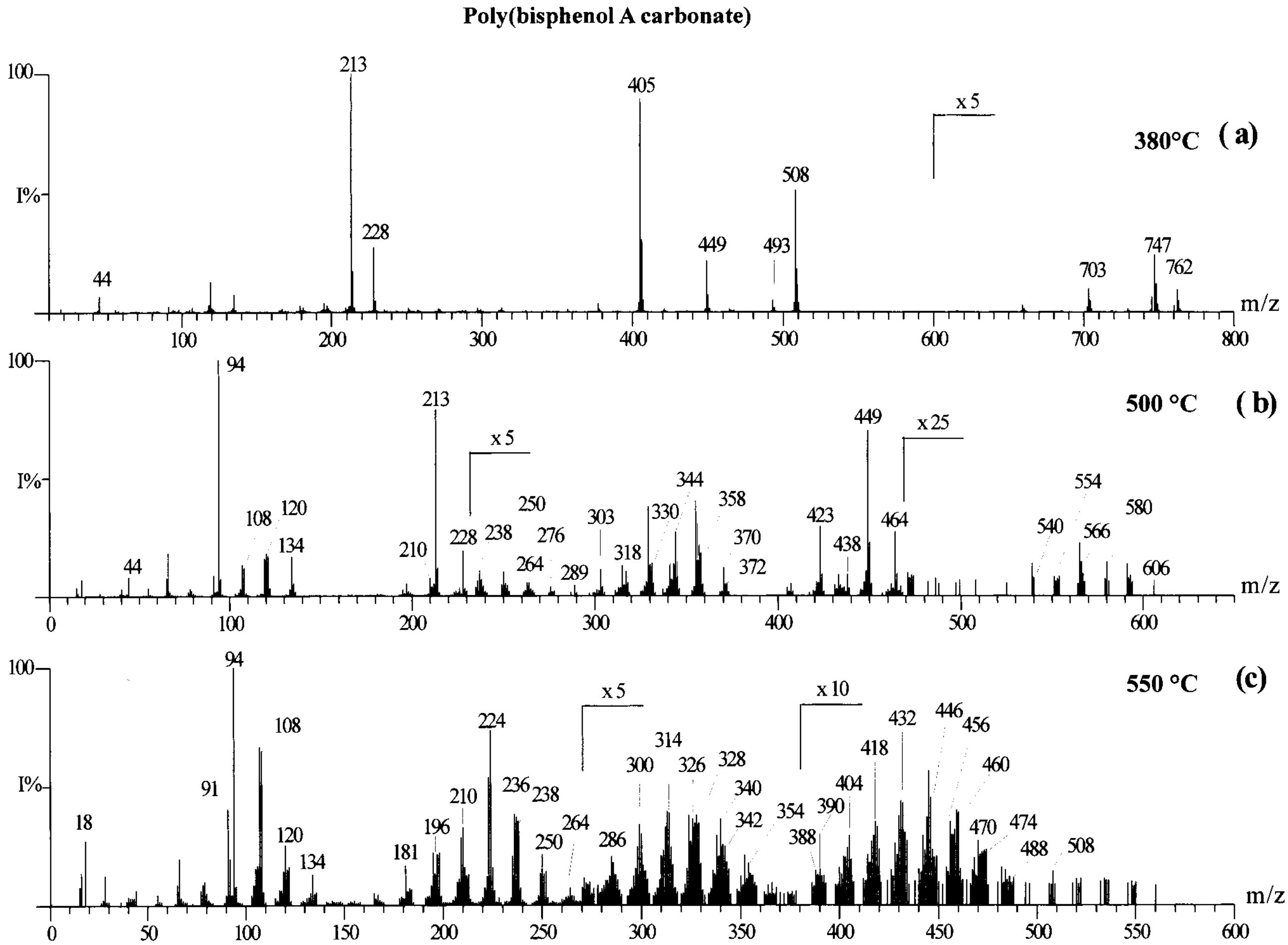


Figure 2. EI (18 eV) mass spectra of pyrolysis compounds obtained by DPMS of **PC** at a probe temperature of (a) 380, (b) 500, and (c) 550 °C.

up to 400 °C and decomposes in a single step with a PDT (see Experimental Section) of 500 °C, leaving 20% of residue at 800 °C. **PRC** is less thermal stable than **PC** (Figure 1b); it shows a PDT of about 380 °C and produces about 30% residue at 600 °C and 15% at 800 °C, whereas for **PHC** the thermal decomposition maximum is shifted to 450 °C, with 25% residue at 600 °C and 10% at 800 °C.

In Figure 1d–f are reported the total ion current (TIC) curves of the three aromatic polycarbonates **PC**, **PRC**, and **PHC**, respectively, obtained by DPMS. In this technique the polymer samples are heated inside the ion source of the MS with the same linear temperature program used in TG runs (10 °C/min), so that TIC curves resemble DTG ones.[13–24]

It can be noted in Figure 1d that the TIC curve of **PC** shows the presence of three peaks with the first maximum lowered at 380 °C, with respect to the maximum of the DTG curve, whereas the maximum of the other two peaks appear at 500 and 550 °C, respectively. The TIC maximum of **PRC** appears at 360 °C, and it is slightly shifted with respect to DTG maximum (380 °C), whereas the TIC curve of **PHC** has a shape very close to that of the DTG curve.

Since polymers have no vapor pressure, their thermal decomposition temperature should not be affected by vacuum pyrolysis; in fact, the TIC curves recorded in DPMS experiments usually reproduce the DTG curves.[13–24]

Therefore, the strong lowering of the TIC maximum of **PC** with respect to DTG curve and the small difference observed for **PRC** are somehow surprising, although similar observations have appeared in the case of poly(alkyl isocyanate)[26] and of aliphatic poly(thiocarbonate)s,[27] which also form cyclic oligomers by pyrolysis.

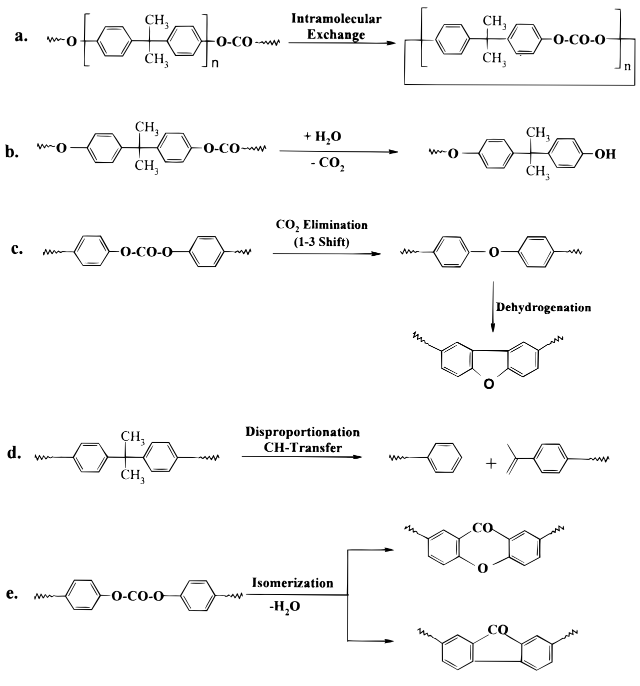
A plausible hypothesis to explain this fact is that the cyclization process occurring in polycarbonates[13,22] can be considered as a reversible depolymerization reaction which obeys the laws that rule the ceiling temperature concept, including its dependence from the reaction pressure.[28]

Structure of the Pyrolysis Compounds and Thermal Degradation Pathways. In Figure 2a–c are reported the EI mass spectra of the pyrolysis compounds of **PC**, evolved at 380, 500, and 550 °C (i.e., at the top of the three TIC maxima in Figure 1d); each spectrum contains different series of peaks whose structural assignments are given in Table 2.

As observed in previous studies,[10,13,16–18] the EI mass spectrum (Figure 2a) of pyrolysis compounds recorded at 380 °C (temperature of the first TIC maximum) shows the ions at *m*/*z* 508 and *m*/*z* 762, corresponding to cyclic dimer and trimer of **PC**, respectively, whereas the remaining peaks in the spectrum are due to CO_2 and methyl loss by EI fragmentation from the cycles.

In the EI mass spectrum recorded at 500 °C (second degradation step) (Figure 2b) can be identified the ions corresponding to phenol (*m*/*z* 94) (base peak), methylphenol (*m*/*z* 108), isopropylidenephenol (*m*/*z* 134), and bisphenol A (*m*/*z* 228). The ions at *m*/*z* 210 and *m*/*z* 250 are due to para-substituted diphenyl ethers with one and two isopropylidene end units, respectively (Table

Scheme 1. Thermal Degradation Processes Occurring in Poly(bisphenol A carbonate)



2). The ions at *m*/*z* 318, 332, and 438 are due to ethers containing an intact bisphenol A unit (Table 2). The latter ions can be better identified by the presence in the spectrum of the more intense (M−15) ions at *m*/*z* 303, 317, and 423, due to methyl loss from BPA units.

The ions at *m*/*z* 276, *m*/*z* 358, *m*/*z* 370, *m*/*z* 372, and *m*/*z* 464 can be assigned to pyrolysis compounds with xanthone units (Table 2), whereas the ions at *m*/*z* 566, 580, and 606 (appearing in the spectrum with low intensity) clearly correspond to pyrolysis compounds containing two xanthone units. The ions at *m*/*z* 540 and *m*/*z* 554 can be identified as pyrolysis compounds containing both xanthone and ether units (Table 2).

The mass spectrum in Figure 2c, corresponding to the pyrolysis compounds evolved at 550 °C (the third degradation step), also shows the presence of phenol (*m*/*z* 94) (base peak), methylphenol (*m*/*z* 108), and isopropylidenephenol (*m*/*z* 134) as in the previous spectrum, but at higher masses the presence of several clusters of peaks is observed.

The intense ions at *m*/*z* 196, 210, 224, 236, 250, and 264 cannot be assigned to pyrolysis compounds with a unique structure due to isobaries, but anyway they have (in alternative) xanthone or ether or dibenzofuran or fluorenone structures (Table 2).

The ions at *m*/*z* 286, 300, 390, 404, 418, 420, 430, 444, and 458 can be unequivocally assigned to pyrolysis compounds bearing dibenzofuran structure (Table 2).

The ions at *m*/*z* 312, 340, 338, 400, 414, 428, 442, 456, 468, 470, and 484 can be unequivocally assigned to pyrolysis compounds with fluorenone structure (Table 2).

The structure of the decomposition compounds evolved over the temperature range (300−700 °C) suggests that **PC** undergoes thermal decomposition by a number of different pyrolysis processes (Scheme 1a−e), which can be recognized through the inspection of the time−temperature resolved evolution profiles of some pertinent pyrolysis compounds of **PC** (Figure 3a−h).

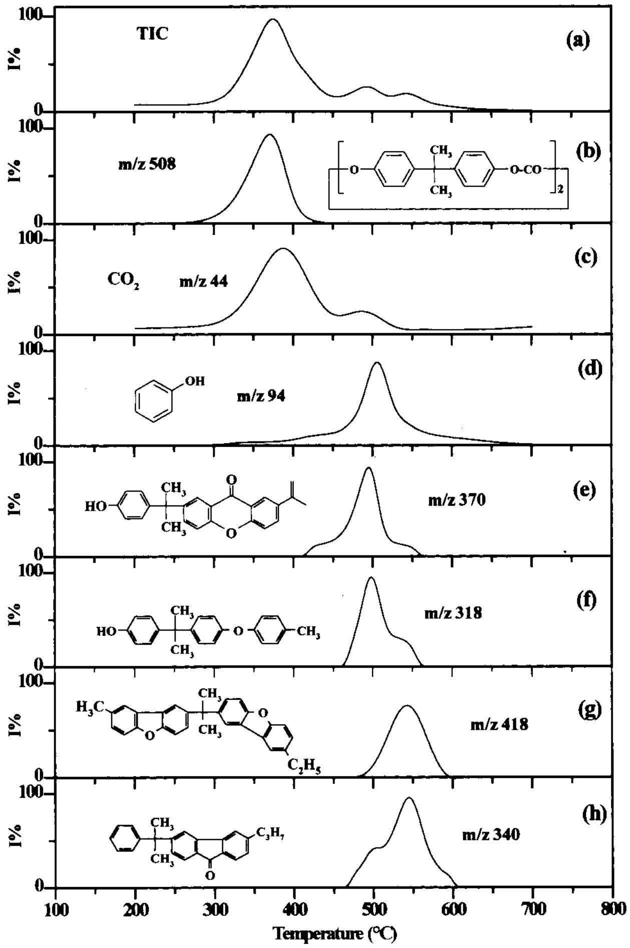


Figure 3. TIC curve and time−temperature resolved profiles of some selected molecular ions obtained in the DPMS of **PC**.

The evolution profile of the cyclic dimer (ion at *m*/*z* 508, Figure 3b) is included within the first TIC maximum, indicating that, at the onset of the thermal degradation, **PC** mainly decomposes through an intramolecular exchange reaction to yield cyclic oligomers (Scheme 1a).

In the first decomposition stage the evolution of CO_2 is also observed (Figure 3c), due in great part to electron impact fragmentation processes and to the hydrolytic cleavage of the carbonate group, which leads to the formation of hydroxyl-terminated oligomers and CO_2 (Scheme 1b).

The evolution of CO_2 is also observed in the second degradation step, most likely due to an intramolecular (1−3 shift) CO_2 elimination (Scheme 1c), yielding compounds with diphenyl ether linkages (ion at *m*/*z* 318, Figure 3f), which undergo dehydrogenation at higher temperature (ion at *m*/*z* 418, Figure 3g) to yield dibenzofuran units (Scheme 1c).

A disproportionation reaction of the bisphenol A unit (Scheme 1d), with consequent polymer chain cleavage, accounts for the formation of pyrolysis compounds with phenyl and isopropylidene end groups, such as phenol (ion at *m*/*z* 94, Figure 3d) and isopropylidene phenol.

The formation of compounds containing xanthone units is observed in the second decomposition step (ion at *m*/*z* 370, Figure 3e) through an isomerization of the carbonate group (Scheme 1e). The latter rearrangement has been postulated[7,8] to occur via the isomerization of the carbonate group to form aryloxybenzoic acids,

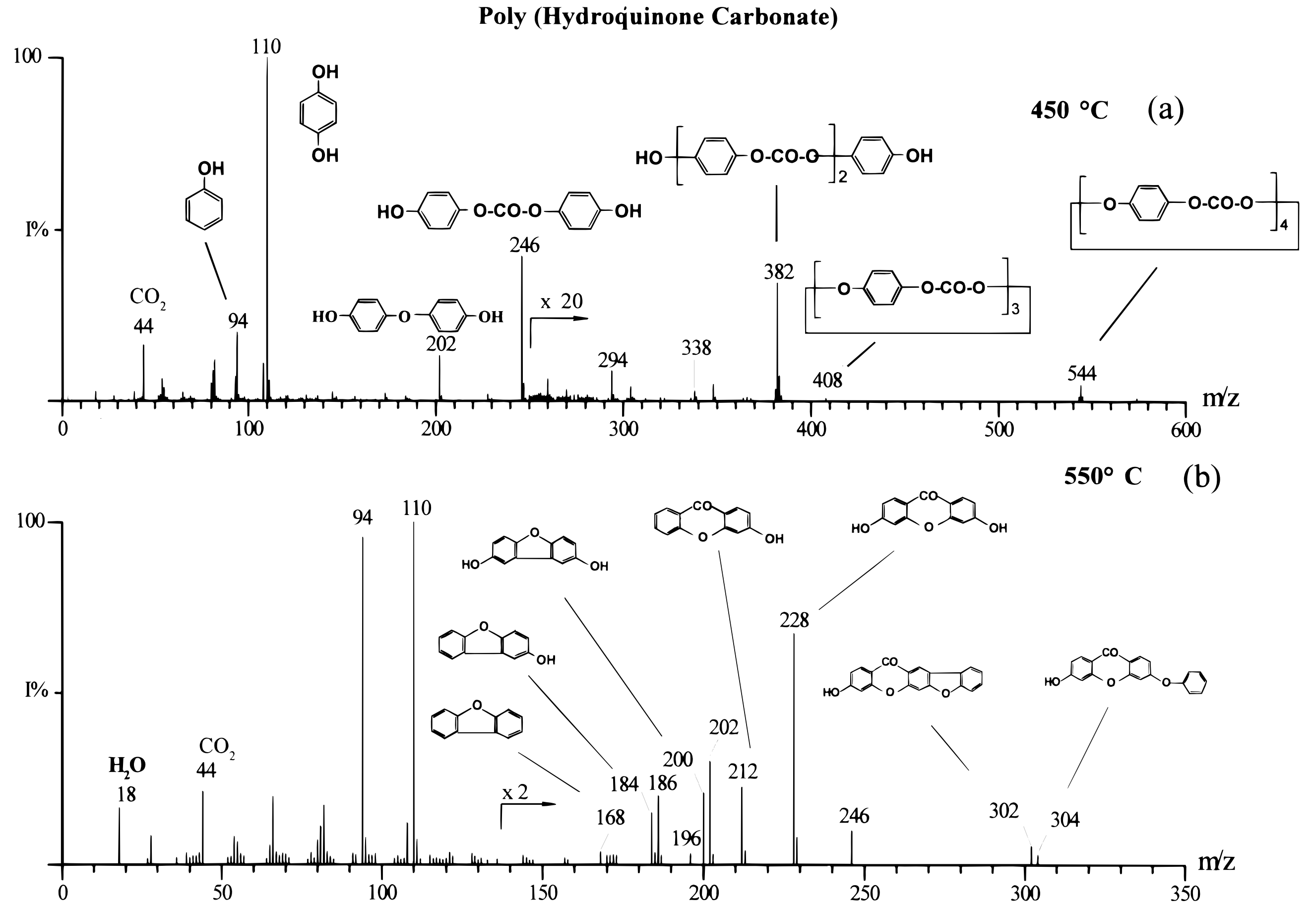
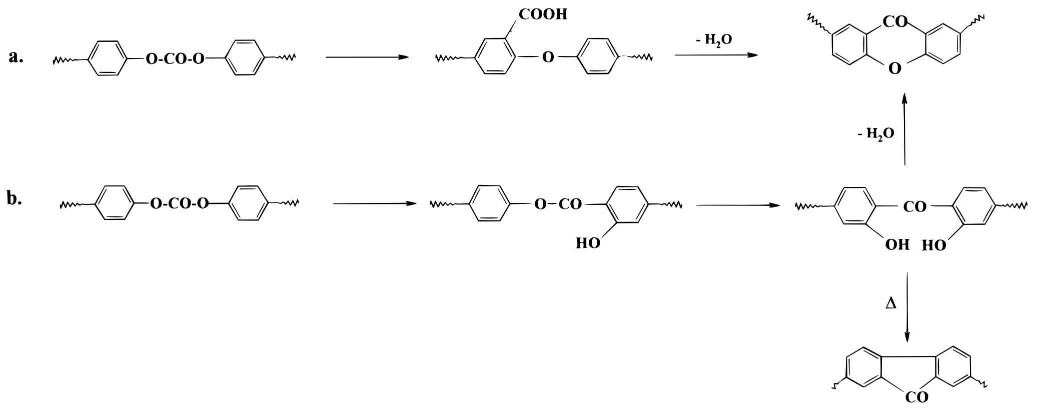


Figure 4. EI (18 eV) mass spectra of pyrolysis compounds obtained by DPMS of **PHC** at a probe temperature of (a) 450 and (b) 550 °C.

Scheme 2. Alternative Isomerization Condensation Processes Leading to Xanthones and Fluorenones



ultimately leading to the formation of xanthone units along the chain (Scheme 2a). An alternative pathway, a Fries rearrangement (Scheme 2b), would explain the formation of xanthone units and may also provide a plausible route to the formation of compounds containing fluorenone units which are evolved in the third degradation step (ion at *m*/*z* 340, Figure 3h).

To double-check the mechanistic hypotheses made on the basis of the thermal decomposition behavior of **PC,** the thermal decomposition of two aromatic polycarbonates **PHC** and **PRC** (Table 1) was also studied by DPMS, on the assumption that the latters should decompose through processes similar to **PC**.

Although the TIC curves of **PRC** and **PHC** (Figure 1e,f) show only one TIC maximum located below 500 °C, the mass spectra recorded at higher temperature (about 550 °C) show the evolution of several pyrolysis compounds in correspondence to the slight weight loss observed by TG (Figure 1b,c).

In Figure 4a is reported the EI mass spectrum of pyrolysis products of **PHC** evolved at 450 °C. There can be identified two series of intense ions at *m*/*z* 110, 246, 382 and 202, 294, 338, which are due to linear oligomers most likely generated from the hydrolysis and decarboxylation of the polymer backbone. The ions at *m*/*z* 408 and *m*/*z* 544 corresponding to the cyclic trimer and tetramer are also present in the spectrum, although in trace amounts.

In the EI mass spectrum recorded at high temperature (550 °C, Figure 4b) are present the peaks at *m*/*z*

196, 212, and 228, corresponding to pyrolysis compounds having the xanthone structure, and the peaks at *m*/*z* 168, 184, and 200, related to dibenzofuran structure. The ions at *m*/*z* 302 and 304 are due to pyrolysis compounds containing one xanthone unit with a dibenzofuran or an ether moiety, respectively.

In Figure 5a–g are reported the evolution profiles of representative compounds evolving in the DPMS of **PHC**, and it can be clearly seen that CO_2 and the pyrolysis compounds formed by hydrolysis (ion at *m*/*z* 246) and by decarboxylation (ion at *m*/*z* 202), are isochronous with the TIC curve. The cycles (ion at *m*/*z* 544) are also generated in the initial stage of the pyrolysis, whereas xanthones (ion at *m*/*z* 228) and dibenzofurans (ion at *m*/*z* 200) are evolved in the later stages.

The formation of pyrolysis compounds bearing xanthone and dibenzofuran units can be accounted for by similar mechanistic pathways drawn for **PC** in Schemes 1 and 2.

The EI mass spectrum of **PRC** obtained at 360 °C is dominated, in the higher mass region, by peaks corresponding to the cyclic trimer, tetramer, and pentamer, at *m*/*z* 408, 544, and 680, respectively (i.e., the cyclization process is strongly influenced by molecular geometry and conformation). The ions at *m*/*z* 110 and 246 formed by hydrolysis of the **PRC** chain are present in the spectrum together with the ions at *m*/*z* 636, 500, 368, 276, and 202, arising form dercarboxylation of cycles and from open-chain pyrolysis compounds.

At higher temperature (500 °C, Figure 6b), the cyclic oligomers disappear, and four xanthone-containing compounds at *m*/*z* 196, 212, 228, and 304 are present together with two dibenzofuran-containing compounds at *m*/*z* 168 and 184.

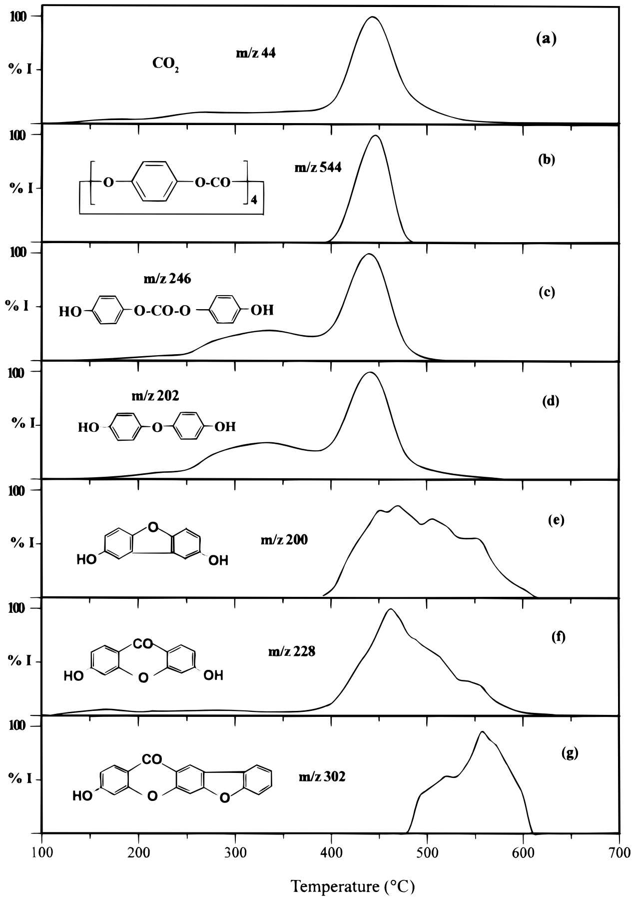


Figure 5. Time–temperature resolved profiles of the molecular ions at *m*/*z* 44, 544, 246, 202, 200, 228, and 302 obtained in the DP-MS of **PHC**.

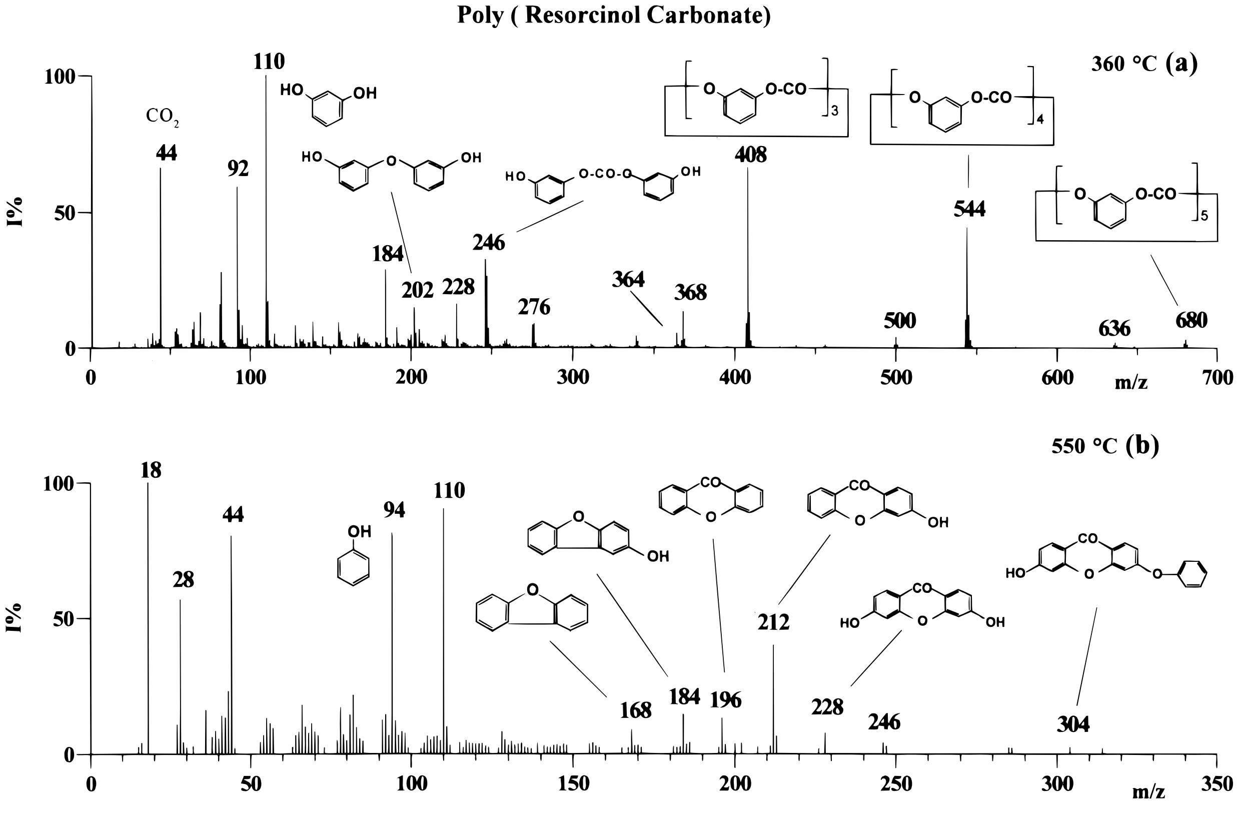


Figure 6. EI (18 eV) mass spectra of pyrolysis compounds obtained by DPMS of **PRC** at a probe temperature of (a) 360 and (b) 570 °C.

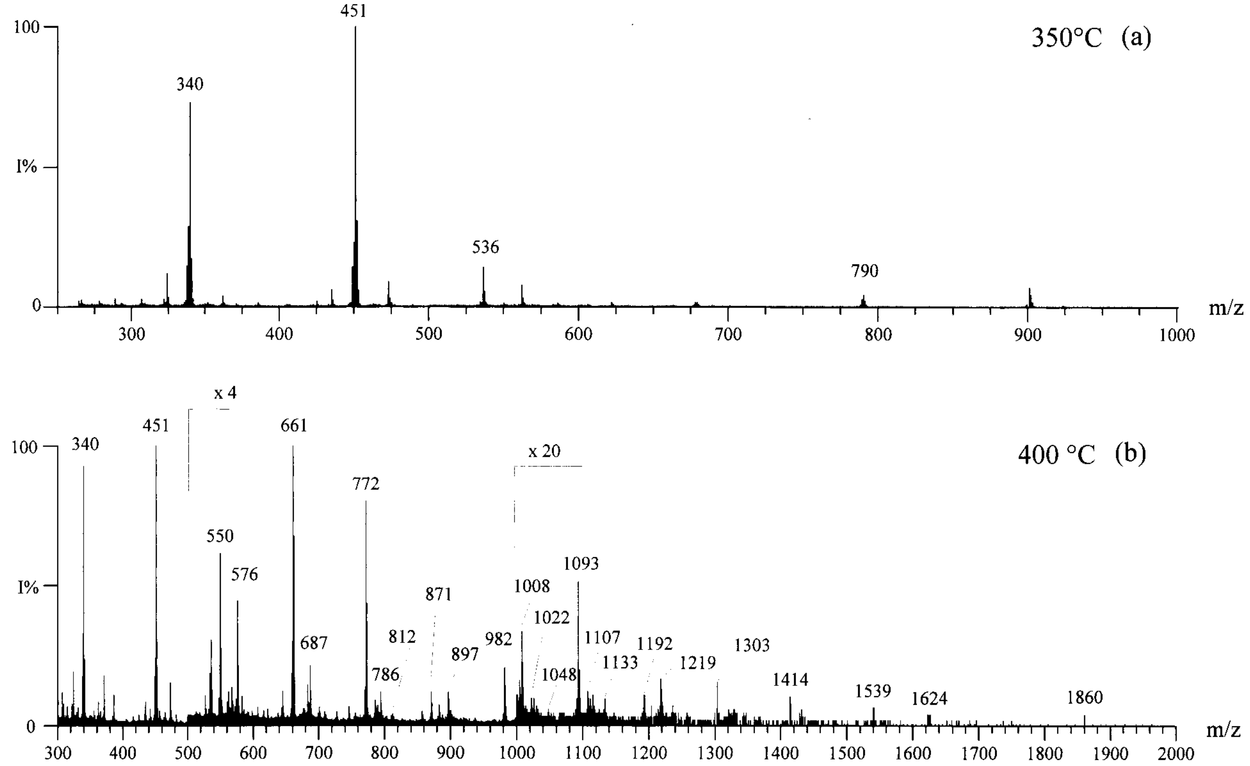


Figure 7. FAB mass spectra of the aminolyzed residue of **PC** samples after thermal degradation at (a) 350 and (b) 400 °C for 1 h.

The evolution profiles of representative compounds evolving in the DPMS of **PRC** reflect the pattern seen above for **PHC** and are not reported here for brevity.

Remarkably, ions at *m/z* 184 and *m/z* 228, corresponding to dibenzofurans and xanthones (Figure 6b), are also present in the spectrum recorded at 360 °C (Figure 6a), indicating that the dehydrogenation of ether units and the isomerization of the polycabonate backbone (Scheme 2) take place at lower temperature with respect to **PC** and **PHC**, most likely due to the meta structure of the resorcinol moiety.

Therefore, the DPMS experiments with **PHC** and **PRC** show that the formation of xanthone and dibenzofuran units is a characteristic thermal decomposition process of aromatic polycarbonates and also confirm the assignments and the mechanistic pathways drawn for **PC**.

Analysis of the Aminolysed Pyrolysis Residue of PC by FAB-MS. In DPMS experiments, the formulation of a thermal degradation mechanism is performed through the analysis of the structure of the volatile pyrolysis products evolved from the gradually heated polymer system.

Being based on the evolved products analysis, DPMS cannot give information on the structure of the involatile charred residue eventually formed during the pyrolysis process.

The isothermal pyrolysis of **PC**, followed by the fast atom bombardment (FAB) MS analysis of the aminolyzed pyrolysis residue, was also performed here in order to draw direct information on the structure of pyrolysis residue.

The pyrolysis was achieved by heating two **PC** samples at a constant temperature (350 and 400 °C) for 1 h in a TG apparatus, under nitrogen flow; the residue was 95% at 350 °C and 70% at 400 °C.

The pyrolysis residue was then subjected to degradation with piperidine, which selectively reacts (at room temperature) with the carbonate functional groups of **PC**.

This procedure leads to compounds with hydroxyl and urethane end groups, and the structural units eventually formed by molecular rearrangements of the **PC** chains (ethers, xanthones, dibenzofurans, fluorenones) will not be degraded by piperidine.

The resulting aminolyzed pyrolysis residue obtained, after pyrolysis of **PC** at 350 and 400 °C, was analyzed by FAB MS; the corresponding mass spectra are shown in Figure 7a,b, respectively, and the structural assignments of the peaks appearing in these spectra are reported in Table 3.

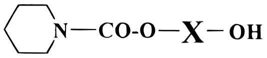
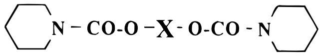
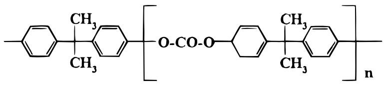
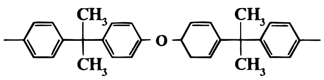
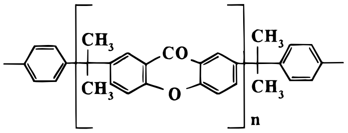
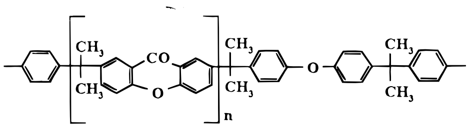
The aminolyzed residue of **PC** heated at 350 °C (Figure 7a) shows the presence of two major peaks at *m/z* 340 and *m/z* 451, corresponding to the protonated molecular ions of a bisphenol A unit with one and two piperidine−urethane linkages, respectively (Table 3).

The other peaks present at higher masses in this spectrum are quite weak and are due to the adduct of the ion at *m/z* 451 with piperidine (ion at *m/z* 536) and to the ion at *m/z* 790 assigned to a compound with piperidine−urethane end groups still containing a repeat unit of **PC** not aminolyzed (Table 3). The remaining peaks in this spectrum are due to ions originated from FAB fragmentation.

These data, together with the observation of the little weight loss (5%), indicate that at 350 °C the thermal degradation of **PC** occurs only to a minor extent.

In the FAB MS spectrum of the aminolyzed residue of **PC** heated at 400 °C (Figure 7b) are present the intense peaks at *m/z* 340 and *m/z* 451, originating from to the total aminolysis of the unrearranged **PC** backbone, together with peaks at higher masses that were

Table 3. Molecular Ions Detected by FAB-MS Analysis of the Aminolyzed Residue Obtained after Heating PC at 350 and 400 °C

STRUCTURES											
			MH^{+} [a]						MH^{+} [a]		
X		MH^{+}	+ 1 Pip	+ 2 Pip	+3 Pip	+4 Pip		MH^{+}	+ 1 Pip	+ 2 Pip	+3 Pip
		340					*n* = 0	451	536		
							n = 1		790		
		550						661			
	*n* = 1	576	661				*n* = 1	687	772		
	n = 2	812	897	982			*n* = 2	-	1008	1093	
	n = 3	1048	1133	1218	1303		*n* = 3	-	-	-	1414
	n = 4	-	-	-	1539	1624					
	*n* = 1	786	871				*n* = 1	897	982		
	n = 2	1022	1107	1192			*n* = 2	1133	1218	1303	
							n = 3	-	-	1540	1624
							n = 4	-	-	-	1860

[a] The protonated molecular ions are desorbed as adducts with piperidine; compounds with xanthone units add one molecule of piperidine for each xanthone unit.

missing in the previous FAB spectrum. Peaks at *m*/*z* 550 and *m*/*z* 661 correspond to piperidine−urethane compounds containing one ether unit (Table 3) which arise from the CO_2 elimination reaction from **PC** backbone (Scheme 1c), whereas peaks at *m*/*z* 576, 687, 786, 812, 897, 1022, 1048, and 1133 correspond to compounds containing up to three xanthone units (Table 3), generated from the isomerization reaction of **PC** backbone (Scheme 2).

Remarkably, compounds containing xanthone units also appear in the FAB spectrum (Figure 7b) as adducts containing one molecule of piperidine for each xanthone unit (Table 3); thus, the ions at *m*/*z* 1093, 1414, and 1624 correspond to compounds containing two, three, and four xanthone units, respectively, containing a number of piperidine molecules, as adducts, equal to xanthone units (Table 3).

The analysis of the FAB MS spectrum in Figure 7b, concerning the aminolyzed residue of **PC** degraded at 400 °C, nicely confirms the results obtained in the DPMS experiments of the polycarbonate sample investigated and indicates that already at this temperature the xanthone and ether units are extensively formed along the **PC** backbone. These units are thermally stable and accumulate in the residue, whereas cyclic oligomers are volatilized.

Conclusion

The existing flash pyrolysis GC/MS data on **PC**[9,12] do not report peaks beyond *m*/*z* 228, corresponding to a bisphenol A unit generated in the thermal cleavage of the polymer, and therefore it is not possible to deduce from them a complete pattern of the thermal decomposition processes occurring in the pyrolysis of **PC**.

The data collected in this work show that (using appropriate techniques such as DPMS and isothermal pyrolysis followed by FAB MS analysis) it is possible to gain detailed information on the complex thermal degradation processes occurring in aromatic polycarbonates (**PC, PHC, PRC**) (Schemes 1 and 2), to elucidate the structure of the char residue produced in the pyrolysis of this class of polymers and to probe the mechanism of char formation.

In the initial stage of the thermal degradation of these polycarbonates are generated cyclic oligomers by an intramolecular exchange reaction. This is a typical degradation pathway of polymers containing reactive functional groups in the backbone which are capable of promoting exchange processes.

The evolution of CO_2 and H_2O is spread over all the pyrolysis temperature range, being responsible for the formation of ether bridges (by decarboxylation) and phenolic end groups (by hydrolysis).

At higher temperature (500−700 °C) other decomposition reactions are observed with formation of linear open chain compounds whose structure is originated from molecular rearrangements or decomposition of the polycarbonates structural unit.

A disproportionation reaction of the BPA isopropylidene bridges of **PC** itself takes place at this temperature, yielding phenyl and isopropylidene end groups, whereas pyrolysis products containing dibenzofuran units are formed by the dehydrogenation of ether units. Compounds containing xanthone and fluorenone units are most likely generated by isomerization of the aromatic carbonate functional groups and successive condensation.

The analysis of the pyrolysis residue of **PC** obtained at 400 °C shows the presence of several consecutive xanthone units, indicating that at this temperature the isomerization and condensation processes are quite extensive.

Therefore, the pyrolysis residue can be considered as constituted by long ether/xanthone sequences that undergo aromatization and cross-linking processes, leading to a graphite-like charred residue as the temperature increases, analogous to several other bridged polyaromatics such as PPO and PEEK,[19] PPS,[20] and poly(xylilene sulfide)[21] which show a marked tendency to produce graphite-like pyrolysis residue.

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