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MALDI−TOF Investigation of Polymer Degradation. Pyrolysis of Poly(bisphenol A carbonate)

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ABSTRACT: The MALDI−TOF technique allows the detection of intact polymer molecules up to high masses and therefore offers the opportunity to study directly the thermal degradation processes occurring in polymeric materials by analyzing conveniently exposed (i.e., partially degraded) polymer samples. This opens new vistas in polymer analysis and deserves careful exploration, due to the relevance of polymer degradation phenomena in everyday practice.The thermal decomposition of poly(bisphenol A carbonate) (PC) has been investigated by heating isothermally at 300, 350, 400, and 450 °C and subsequent analysis of the pyrolysis residue by means of MALDI mass spectrometry. The MALDI mass spectra of the pyrolysis residues obtained at 300 °C showed a progressive reduction of the abundance of cyclic oligomers, whereas the relative abundance of the other compounds was unaffected. At 350 °C, the occurrence of an extensive hydrolysis reaction was responsible for the degradation of cycles and linear chains bearing *tert*-butylphenyl carbonate end groups with subsequent formation of abundant open chain PC oligomers with phenol end groups. Furthermore, at these two temperatures, cyclic oligomers never disappear in the MALDI spectra, even at higher heating time (60 min), suggesting the presence of an equilibrium between the rate of cleavage and the rate of formation of cycles. PC chains terminated with phenol groups at both ends, together with pyrolyzed chains bearing phenyl and isopropylidene end groups, generated by the disproportionation of the aliphatic bridge of bisphenol A, were observed in the MALDI spectra of pyrolysis residue obtained at 400 °C. Condensed aromatic compounds such as xanthones, which are considered to be the precursors of a graphite-like structure of the charred residue, were also detected in the MALDI spectra of PC samples heated at 400 °C and they became the most intense species at 450 °C. The PC samples heated at temperature higher than 450 °C consisted of insoluble carbonaceous materials not suitable for MALDI analysis.

Introduction

The thermal degradation of poly(bisphenol A carbonate) (PC) has received continued attention,[1−9] since this 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.

We have recently reported[6] a direct pyrolysis mass spectrometry (DPMS) investigation of the thermal degradation products evolving from PC and wish now to discuss the results of an analogous study performed by following the thermal degradation reaction by means of the MALDI−TOF technique.

Because of the importance of the information obtainable, DPMS has been widely applied to the analysis of polymer decomposition products,[6,10−12] whereas the development of MALDI−TOF for the analysis of polymers[13−15] offers now the opportunity to study directly the thermal degradation processes occurring in polymeric materials by analyzing conveniently exposed (i.e., partially degraded) samples.[16]

Application of the MALDI−TOF technique to these problems may open new vistas in polymer analysis and deserves careful exploration, due to the relevance of polymer degradation phenomena in everyday's practice.

Contrary to the traditional GC/MS[7−9] and DPMS[6,10−12] methods, which are capable of detecting only compounds of relatively low masses produced by pyrolysis of polymeric materials, the MALDI technique provides mass-resolved spectra which allow the detection of oligomers up to 30 000 Da and above.[13−15]

The study of the thermal degradation phenomena by MALDI involves the partial degradation of a polymeric sample by keeping it under inert or oxidizing atmosphere at a certain temperature and then collecting MALDI−TOF spectra of the sample to observe the structural changes induced by the heat and/or oxygen. The polymer molecules of the partially degraded polymer sample are detected without any further fragmentation, generating a mass spectrum which may consist of a mixture of undegraded and degraded chains.

This *off-line* method of analysis suffers an important limitation; i.e., only the soluble part of the polymer residue generated in the degradation processes can be analyzed, and this also limits the upper temperature of thermal degradation or the specific conditions at which the formation of a totally insoluble residue is observed. Furthermore, the thermal degradation of a polymer sample is performed for prolonged time at atmospheric pressure so that only the most thermally stable thermal degradation products may survive to the heating.

DPMS,[6,10−12] being performed on-line and in a continuously evacuated system, provides very short transport times of the pyrolysis compounds from the hot zone and may then complement the MALDI data by supply-

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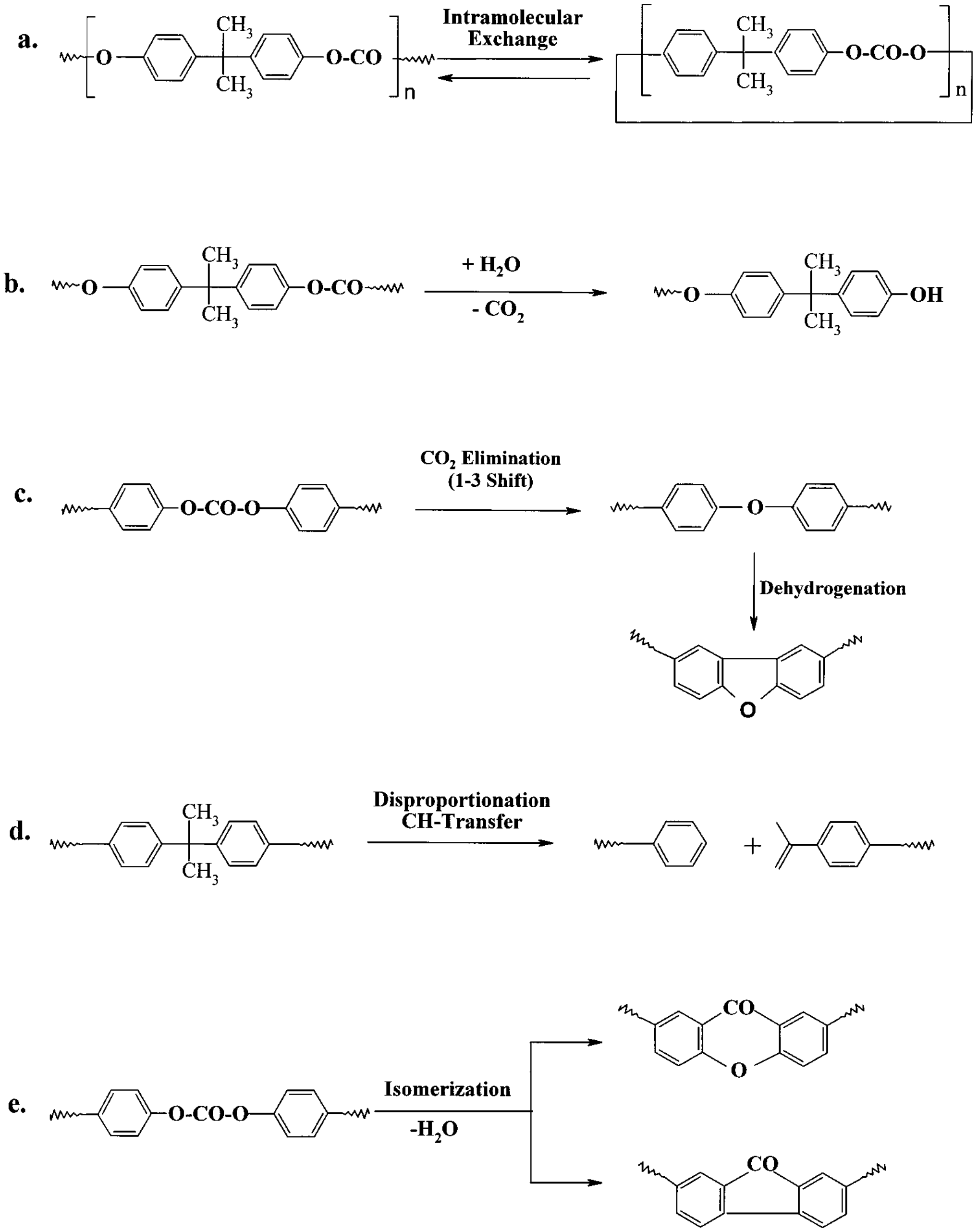
Scheme 1. Thermal Degradation Processes Occurring in Poly(bisphenol A carbonate)



ing information on less thermal stable pyrolysis products and on compounds generated at temperatures at which the pyrolysis residue becomes insoluble and therefore inaccessible to the MALDI analysis.

Furthermore, DPMS[6] allows fractionation and continuous monitoring of the effluents, and it becomes therefore easier, with respect to the MALDI method, in detecting the less abundant pyrolysis products eventually formed.

Earlier DPMS studies[5,6] established that, in the initial stage (about 400 °C), the primary thermal degradation products evolving from PC are cyclic oligomers formed by intramolecular exchange processes (Scheme 1).

Recently,[6] DPMS studies, performed up to a temperature of 700 °C, have produced evidence that a rearrangement of the carbonate group leads to the formation of xanthones and of other condensed structures formed during the heating of PC (Scheme 1).

However, the DPMS of PC had, of necessity, to be performed in a vacuum, whereas in real world applications polymers are exposed to normal pressure conditions and to oxygen, which can be expected to induce major changes in the structure of polymer chains.

We have now performed the isothermal pyrolysis of PC by heating it at a fixed temperature (300, 350, 400, and 450 °C) under a nitrogen stream, and MALDI−TOF spectra of these thermal treated PC samples have been taken and analyzed.

Kinetic studies of PC isothermal pyrolysis were possible, monitoring the diverse molecular species present by means of the MALDI spectra of partially degraded samples. The results obtained by this MALDI investigation nicely complement the previous DPMS studies.[6]

In a future effort, we shall report on a MALDI−TOF study on the early stages of the thermooxidation processes occurring in PC.

Experimental Section

Materials. Basic materials were commercial products appropriately purified before use. The PC sample (Lexan 220)

Table 1. Pyrolysis Residue and Molar Masses of PC Samples Heated for Several Times at 300, 350, 400, and 450 °C

temperature (°C)	heating time (min)	residue[a] (%)	soluble residue[b] (%)	M_w[c]	M_n[c]
	0			26 000	13 200
300	15	100	100	26 500	15 500
	30	100	100	29 000	17 400
	45	100	100	29 200	15 800
	60	99.5	100	31 400	16 300
350	5	100	100	29 700	16 300
	15	94	100	30 800	17 950
	30	98	100	32 000	16 100
	45	97	100	32 700	17 600
	60	97	100	30 600	17 000
400	15	97	30		
	30	84	30		
	45	82	5		
	60	74	5		
450	15	36	traces		

[a] % of residue with respect to the initial weight of PC samples as obtained by thermogravimetry. [b] % of THF soluble fractions extracted from the pyrolysis residue. [c] Obtained by calibration of the SEC/MALDI method (see Experimental Section).

was a commercial product obtained by General Electric. 2-(4-Hydroxyphenylazo)benzoic acid (HABA) was purchased from Aldrich Chemical CO (Italy) and used as supplied.

Isothermal Pyrolysis of PC. Isothermal pyrolysis of PC were performed in a thermogravimetric apparatus under nitrogen flow (60 mL/min). Typically, 8 mg of samples were heated for 15, 30, 45, and 60 min at 300, 350, and 400 °C. Isothermal pyrolysis at 450 °C was carried out for 15 min. The pyrolyzed samples were dissolved in THF and the soluble portions were analyzed by MALDI−TOF.

SEC Analysis and Fractionation. The analyses were performed on a Waters 600 A apparatus, equipped with five Ultrastyragel columns (7.8 × 300 nm) (in the order 10^5, 10^3, 500, 10^4, and 100 Å pore size) connected in series and a Waters R401 differential refractometer. Injection volume was 90 μL of a (0.5% in $CHCl_3$) solution. The flow rate was 1 mL/min. The fractionation of the undegraded PC sample was performed by collecting several equal volume fractions (about 90) corresponding to about 0,165 μL (12 drops).

MALDI−TOF Analysis. PerSeptive Biosystems Voyager-DE STR and Voyager-DE were used to perform the matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI−TOF MS) analysis of the pyrolysis products of PC samples. The two MALDI−TOF instruments were equipped with a nitrogen laser emitting at 337 nm with a 3 ns pulse width and working in positive mode. Accelerating voltage (20−25 kV), grid voltage and delay time (delayed extraction, time lag) were optimized for each sample. The laser irradiance was maintained slightly above the threshold. Some of the spectra were recorded in reflectron mode by using the Voyager-DE STR, which gave a mass resolution of about $3000M/\Delta M$. The samples for the MALDI analyses were prepared by mixing adequate volumes of the matrix solution (HABA, 0.1 M in THF) and of polymer solution (2 mg/mL in THF) to obtain a 1:1 or 1:3 ratio (sample/matrix) v/v. Other matrixes were also experienced, and gave MALDI spectra almost comparable with those obtained with HABA. However, a better mass resolution was obtained with HABA as a matrix.

Typically, 1 μL of every sample/matrix solution was spotted on the samples plate and allowed to slowly evaporate in order to improve the crystallization.

Molar Mass Calculations. The molar masses of the unfractionated polymer samples were calculated from the SEC curves by Polymer Lab Caliber software using the absolute calibration curves obtained by plotting the log M_w of each SEC selected fraction (calculated from the MALDI−TOF spectra) as a function of the corresponding elution volume. The molar mass distribution data obtained for the undegraded and degraded PC samples are reported in Table 1.

Results and Discussion

The isothermal pyrolysis of PC was performed by heating the samples at a constant temperature (300, 350, 400, and 450 °C) under inert atmosphere, for 15, 30, 45, and 60 min, respectively. The residue obtained after 1 h of heating was nearly 100% at 300 °C, 95% at 350 °C, and 70% at 400 °C, whereas after $^1/_2$ h of heating at 450 °C the residue was about 36%, with respect to the initial sample weight (Table 1).

Since the MALDI method requires a solution of the sample in an appropriate solvent, the heated PC samples were extracted with THF in order to obtain a soluble fraction suitable for the MALDI analysis.

The pyrolysis residues of the samples heated at 300 and 350 °C were totally soluble in THF, and their molar masses (obtained by the SEC/MALDI method, see Experimental Section)[15] reveal a slight increase as a function of the heating time, most likely due to heat-promoted post-polymerization processes (Table 1). In contrast, the pyrolysis residue of the PC samples heated at 400 °C is in part composed of an insoluble carbonaceous material and of a THF-soluble portion whose amount decreases from 30% to 5% (with respect to the total pyrolysis residue) as the heating time increases (Table 1). On heating at 450 °C, only traces of soluble materials were obtained, almost near the lower limit of sensitivity of the MALDI method. At higher temperatures, the pyrolysis residues of PC were totally insoluble, thus preventing the application of MALDI analysis.

The MALDI spectrum of the unheated PC sample (in the mass rage 1000−12000 Da) is reported in Figure 1, in which well-resolved peaks are detectable. The inset expansion shows the presence of peaks belonging to four mass series corresponding to species **A**−**D** assigned in Table 2, which desorb either as sodiated and potassiated ions.

The cyclic oligomers contained in the unheated PC sample (species **A**, Table 2) are the most intense species at low masses and their intensity decreases rapidly with size (peaks marked with circles, Figure 1), whereas peaks corresponding to open chain oligomers bearing *tert*-butylphenyl carbonate groups at both ends (species **B**, Table 2) become the most intense, starting from about 4000 Da. The peaks corresponding to the mass series *C* (Table 2), which contain *tert*-butylphenyl carbonate at one end and a phenol group at the other end, are also present in the spectrum with sizable intensity, whereas peaks corresponding to PC chains terminated with phenol groups at both ends were detected in trace amount (mass series *D*, Table 2).

In Figure 2 is reported the MALDI mass spectrum of a PC sample heated for 1 h at 300 °C, showing that the intensity of cyclic oligomers is drastically reduced with respect to the unheated PC sample (see inset expansion), and that the relative intensity of the other three mass series does not show sizable changes. This fact indicates that at 300 °C either the hydrolytic cleavage of the cyclic oligomers of PC and/or the polymerization of the cyclic oligomer to higher molar mass linear products may be hypothesized.

In Figures 3−5 are compared the relative intensities of the peaks corresponding to the four mass series identified in Table 2 and appearing in the MALDI spectra of PC samples heated at 300, 350,and 400 °C, respectively, as a function of the heating time. It can

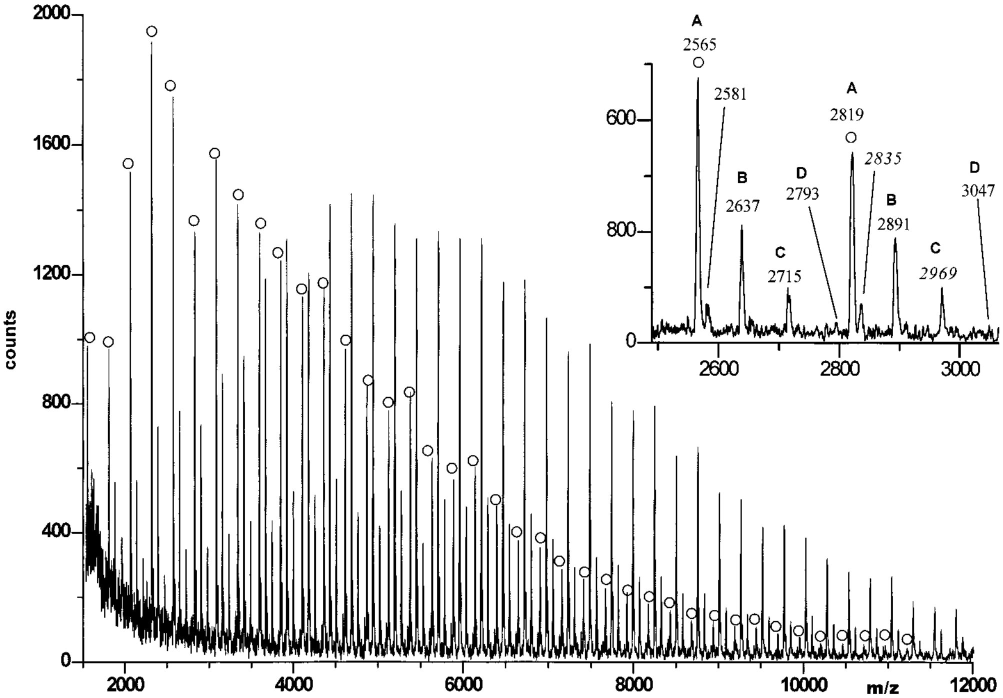


Figure 1. MALDI−TOF mass spectrum on unheated PC sample. Peaks labeled with circles correspond to cyclic oligomers.

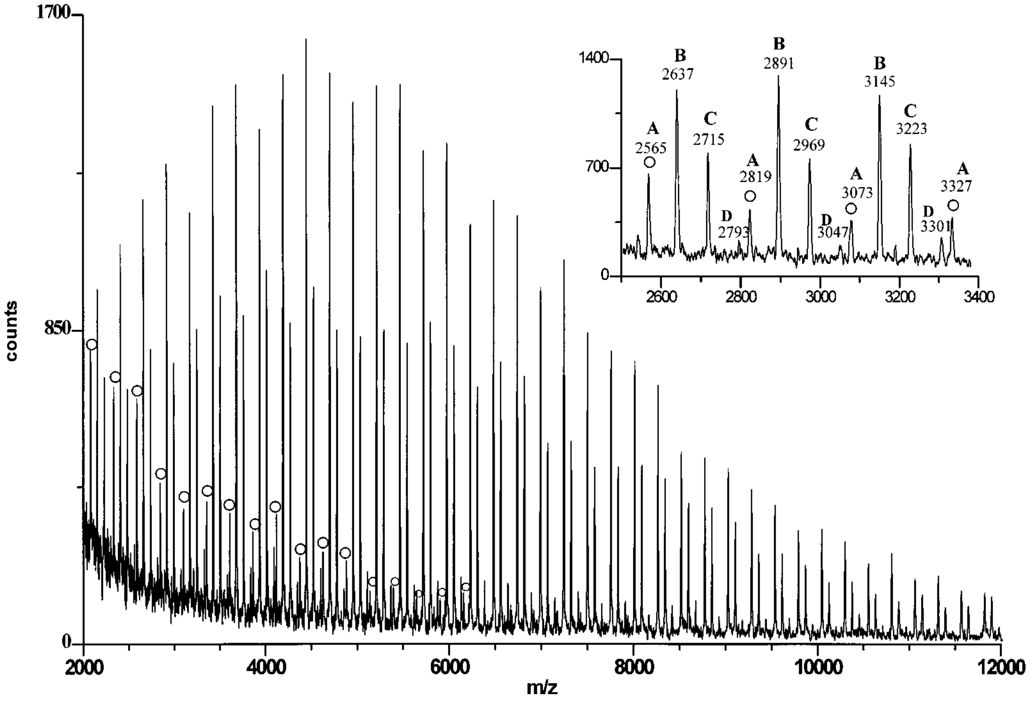
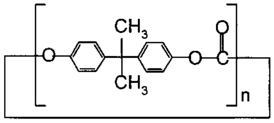
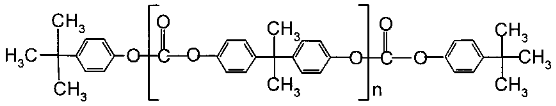
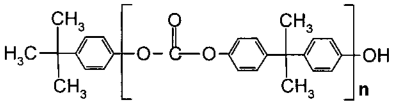
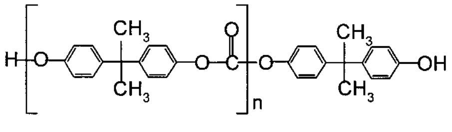
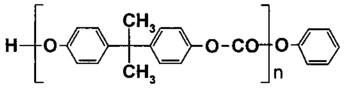
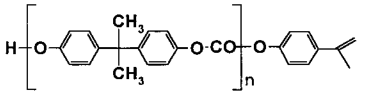
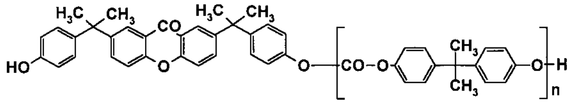
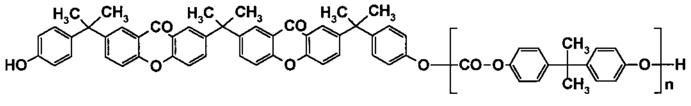
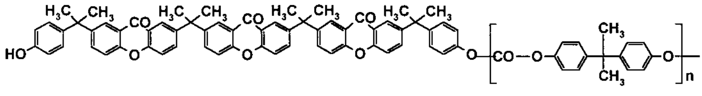


Figure 2. MALDI−TOF mass spectrum of the soluble fraction extracted from the pyrolysis residue of PC obtained after heating for 1 h at 300 °C. Peaks labeled with circles correspond to cyclic oligomers.

be noted that whereas the heating at 300 °C (Figure 3) causes a progressive reduction of the abundance of cyclic oligomers, leaving unaffected the abundance of the other compounds, at 350 °C (Figure 4) a marked change in the relative intensities of the open chain PC oligomers as the heating time increases is observed. The MALDI spectrum obtained after heating the sample at 350 °C for 15 min (Figure 4), closely resembles that of the PC residue obtained at 300 °C for 1 h. However, already after 30 min of heating at 350 °C (Figure 4), the intensity of the mass series **C** and **D** (Table 2) due to phenol-terminated oligomers shows a significant increase. The increased intensity of the species C and D may be due to hydrolysis of higher molar mass *tert*-butylphenyl capped chains and/or transesterification reactions with free *tert*-butylphenol previously produced by hydrolysis of a *tert*-butylphenyl end cap.

The inspection of Figures 3 and 4 indicates that peaks corresponding to cyclic oligomers never disappear in the MALDI spectra obtained at 300 and 350 °C, as should be expected if the hydrolysis reaction were the only process taking place at these temperatures. The persistence of peaks due to cyclic oligomers in the MALDI spectra can be justified by assuming the presence of an equilibrium between the rate of cleavage and the rate of formation of cycles (Scheme 1a).

Table 2. Structural Assignments of the Peaks Appearing in the Inset Sections of the MALDI Spectra in Figures 1−4 Relative to Undegraded and Degraded PC Samples at 300, 350, 400, and 450 °C

Mass Series	Oligomers structures	n	M	
			Na^+	K^+
A		10 11 12	2565 2819 3073	2581 2837 3089
B		10 11 12	2637 2891 3145	2653 2907 3161
C		10 11 12	2715 2969 3223	
D		10 11 12	2793 3047 3301	
E		10	2659	
F		10	2699	
G		9 10 11	2775 3029 3283	
H		8 9 10	2757 3011 3265	
I		7 8 9	2739 2993 3247	

This result is in agreement with the data illustrated in our previous DPMS studies on PC degradation,[5,6] in which it has been shown that cyclic oligomers are generated by an intramolecular exchange reaction (Scheme 1a), in the initial stages of the thermal degradation (300−350 °C).

The MALDI mass spectra of the soluble fractions of the PC residues obtained at 400 °C (Figure 5) show that, after 15 min of heating, either cyclic and *tert*-butylphenyl carbonate terminated linear oligomers (Table 2; species **A** and **B**, respectively) are almost absent, whereas PC chains terminated with phenol groups at one end (species C, Table 2) appear with greatly reduced intensity. On the contrary, PC oligomers bearing phenol groups at both ends (species **D**, Table 2) become the most intense peaks in the spectrum in Figure 5, implying that at this temperature hydrolytic processes (Scheme 1b) occur at a high rate. The hydrolysis process may be due to the residual water in the starting PC sample and/or to the water that may be formed in situ during the pyrolysis processes such as condensation, fragmentation, and/or displacement reactions of phenol groups.

Two peaks (marked as **E** and **F** in Figure 5) appear at *m*/*z* 2659 and 2699 in the MALDI spectra obtained after heating the sample at 400 °C for 15 and 30 min, and they can be assigned to linear PC oligomers bearing phenol groups at one end and phenyl and/or isopropylidene groups to the other ends (mass series **E** and **F**, respectively, Table 2). Their presence can be accounted for by the disproportionation reaction of bisphenol A units (Scheme 1d) with consequent polymer chain cleavage and formation of pyrolysis compounds with phenyl and isopropylidene end groups.[5] Remarkably, these two peaks are no longer detectable in the spectra of the soluble fraction of PC residue obtained at higher heating times (60 min), presumably because these species undergo cross-linking and produce insoluble carbonaceous residues.

Another pyrolysis process is detectable from the MALDI spectra of the soluble materials obtained at 400 °C. In the spectrum obtained after heating 15 min, is present a strong peak at *m*/*z* 2775 (marked as **G** in Figure 5), which is located 18 mass units lower than peak **D**, and it can be assigned to PC oligomers

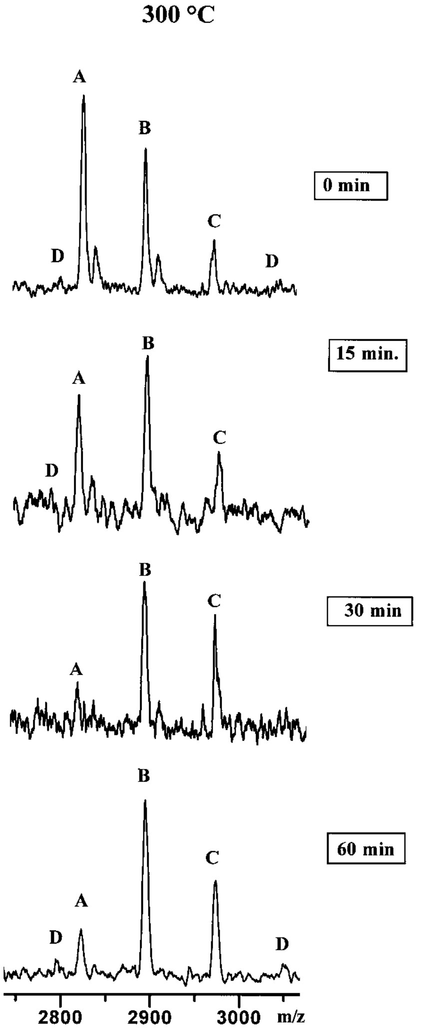


Figure 3. MALDI–TOF mass spectra of the soluble fraction extracted from the pyrolysis residue of PC obtained after heating for 15, 30, and 60 min at 300 °C.

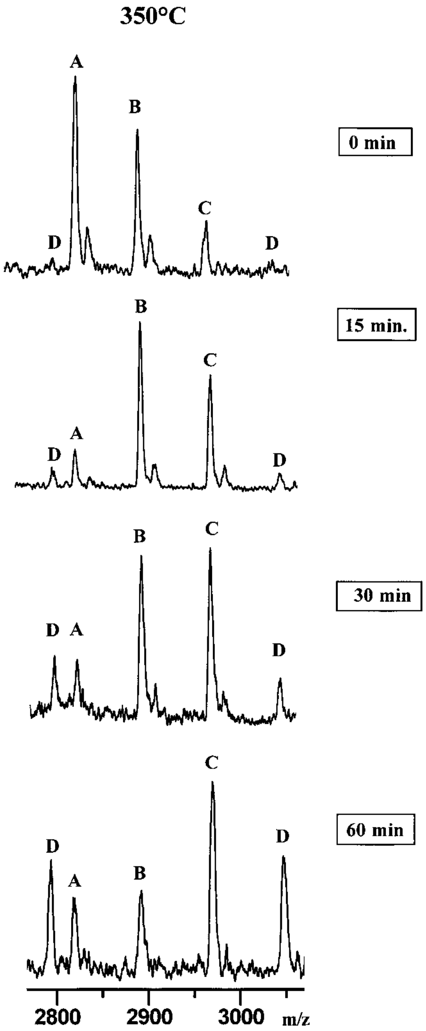


Figure 4. MALDI–TOF mass spectra of the soluble fraction extracted from the pyrolysis residue of PC obtained after heating for 15, 30, and 60 min at 350 °C.

terminated with phenol groups at both ends and containing one xanthone unit along the chain (species **G**, Table 2).

The formation of pyrolysis compounds containing xanthone units during the thermal degradation of PC has been also detected in the previous DPMS study,[5] and it is thought to occur by a thermal rearrangement (Scheme 1e) taking place in parallel to other pyrolysis processes.

Further heating of PC samples at 400 °C increases the amount of PC oligomers containing one xanthone unit (peak G, Figures 3–5) and induces the formation of more xanthone units along the same chain, as indicated by the presence of the two additional peaks H and I in the MALDI spectra taken after 30 and 60 min (Table 2; species **H** and **I**).

The thermal treatment of a PC sample for $^1/_2$ h at 450 °C produced an extensive weight loss (about 64% of its initial weight), and only trace amounts of the pyrolysis residue are soluble in THF (Table 1). We are therefore near the limit of the applicability of the MALDI method to the structural analysis of the PC pyrolysis products.

The MALDI spectrum of the THF soluble fraction (Figure 6) shows that the spectral pattern is drastically changed with respect to the cases reported in Figures 1–5, and it consists of a series of sharp multiplets, which correspond (see inset expansion) to PC chains terminated with OH phenol at both ends, incorporating zero, one, two, and three xanthone groups (Table 2).

It is interesting to note that PC chains containing xanthone units are now preponderant in Figure 6. It is therefore likely that the insoluble pyrolysis residue, which could not be analyzed by MALDI, will also contain a considerable amount of xanthone units trapped in the three-dimensional network.

Several thermal degradation processes (Scheme 1) have been ascertained to occur in PC, when this polymer was pyrolyzed by DPMS using a gradual heating from room temperature up to 700 °C.[6]

The seven new structural units produced in the pyrolysis (Scheme 1) may be incorporated within the pyrolyzed PC chains (diphenyl ether, dibenzofuran, fluorenone, xanthone), or may appear as end groups (phenol, phenyl, isopropylidene).

Some of the above structural units (diphenyl ether, dibenzofuran, fluorenone) were not detected in the present MALDI study. This fact can be explained by taking into account that these species may be the less abundant ones and might remain embedded in the mass spectrum background noise. Alternately, they might be generated at temperatures higher than 450 °C, and therefore they cannot be detected by the MALDI method since they may remain trapped in the insoluble carbonaceous residue.

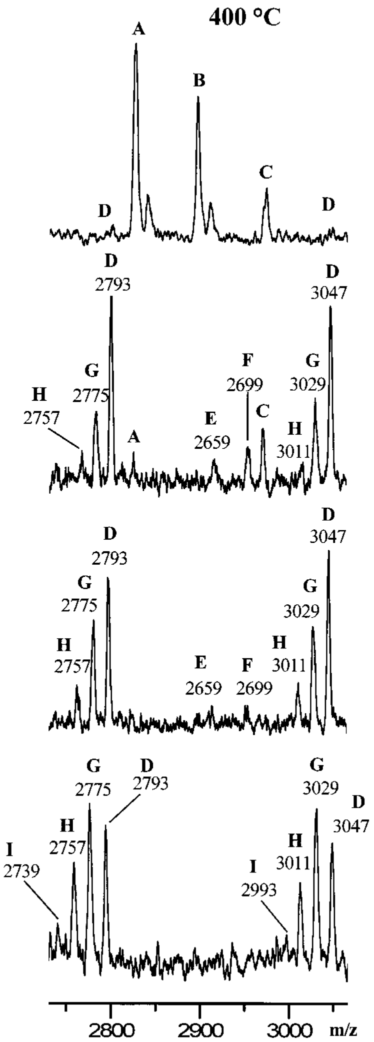


Figure 5. MALDI−TOF mass spectra of the soluble fraction extracted from the pyrolysis residue of PC obtained after heating for 15, 30, and 60 min at 400 °C.

In DPMS the thermal degradation is performed under vacuum by a gradual heating (10 °C/min) of the sample, under continuous removal of the pyrolysis products, which are therefore fractionated and revealed in temperature−time-resolved experiments. This of course facilitates the detection of minor components in the mixture of the pyrolysis products.

MALDI spectra provide instead an estimate of the relative amounts of all the compounds produced in the pyrolysis processes, which are not volatile at that specific heating temperature. Therefore, the overall structural information obtained on the pyrolysis of PC suggests that the PC pyrolysis residue consists of thermal rearranged sequences which 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, PES and PEK,[17] PPS,[18] and polyxylilene sulfide[19] which show a marked tendency to produce a graphite-like pyrolysis residue.

The data reported here show that, using isothermal pyrolysis followed by MALDI analysis, it is possible to gain detailed information on the structure of the pyrolysis residue of PC by the detection of sizable oligomer chains (up to 25−50 mers, and above) produced in the heating process at atmospheric pressure (under nitrogen stream).

Furthermore, our results suggest that, in studies concerning the thermal degradation of polymers, the MALDI technique should be best used in parallel with the DPMS method, the latter being unique in obtaining structural information on intractable, insoluble materials.

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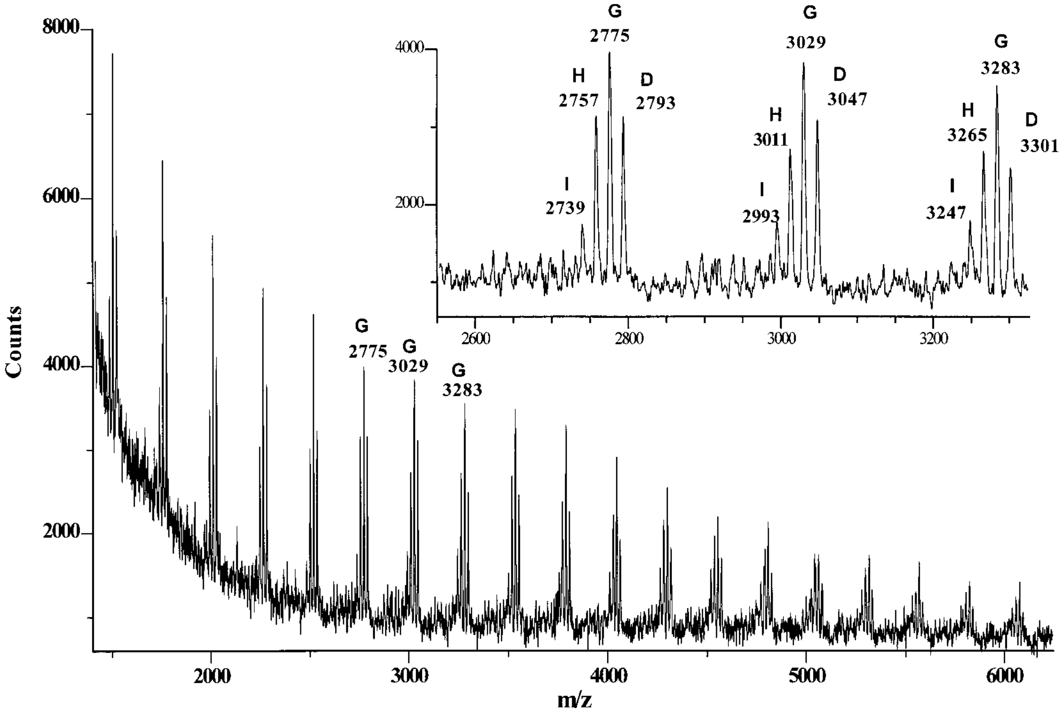

Figure 6. MALDI−TOF mass spectrum of the soluble fraction extracted from the pyrolysis residue of PC obtained after heating for $^{1}/_{2}$ h at 450 °C.

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