Mechanisms of Thermal Oxidation of Poly(bisphenol A carbonate)

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ABSTRACT: In the attempt to find evidence on the structure of the species produced in the thermal oxidative degradation of bisphenol A−polycarbonate (PC), two polycarbonate samples, one capped (incompletely) with phenyl groups at both ends (PC1) and the other one capped (incompletely) with *tert*-butyl phenyl groups at both ends (PC2), were used. The two PC samples were heated at 300 and 350 °C under atmospheric air for up to 180 min, producing a THF-insoluble gel at the longer heating times. The oxidative process was followed as a function of the exposure time by SEC, ^{1}H NMR, MALDI-TOF, and SEC/MALDI-TOF techniques. The SEC curves showed extensive degradation, up to the formation of very low molar mass oligomers. Highly valuable structural information on the thermally oxidized PC species was obtained by using MALDI-TOF mass spectrometry. The MALDI-TOF spectra of the thermally oxidized PC1 and PC2 samples showed the presence of polymer chains containing acetophenone, phenyl-substituted acetone, phenols, benzyl alcohol, and biphenyl terminal groups. Formation of acetophenone and phenol end groups was confirmed by ^{1}H NMR analysis. The mechanisms accounting for the formation of thermal oxidation products of PC involve the operation of several simultaneous reactions: (i) hydrolysis of carbonate groups of PC to form free bisphenol A end groups; (ii) oxidation of the isopropenyl groups of PC; (iii) oxidative coupling of phenols end groups to form biphenyl groups. The presence of biphenyl units among the thermal oxidation products confirmed the occurrence of cross-linking processes, which is responsible for the formation of the insoluble gel fraction. The MALDI-TOF analysis of the oxidation products of PC2 sample, capped with *tert*-butyl phenyl groups at both ends, unveiled a specific antioxidant action of these terminal groups, which are able to slow the rate of thermal oxidation of PC2 compared to PC1 sample.

Introduction

The thermal and oxidative degradation reactions occurring on poly(bisphenol A carbonate) (PC) have received continued attention,[1−14] since PC is an important engineering thermoplastic material which is subjected to injection molding operations at temperature above 300 °C.

At this temperature, thermal and oxidative degradation reactions are likely to occur, and therefore, the understanding of the overall process is of crucial importance.

Species formed in the thermal oxidation processes of many polymeric materials are often very reactive, do not accumulate, and are present only in minor amounts among the reaction products.

Because of this, conventional analytical techniques may be inadequate in establishing the structure of the oxidation products, and despite the sizable literature existing on the thermooxidative degradation of PC,[11−14] information on the species produced in the oxidation is still scarce and the structural assignments tentative.

Modern mass spectrometry offers the opportunity to explore the finest structural details in polymers.[15−17] Matrix-assisted laser desorption ionization−time-of-flight (MALDI−TOF) mass spectrometry provides mass-resolved spectra, which allow the detection of quite large molecules even in complex mixtures. The MALDI-TOF spectra originating from ions of intact polymer chains show enough resolution to allow the structural identification of oligomers up to 30 000 Da and above in some cases.[15−21]

The study of polymer degradation phenomena by MALDI-TOF[9,22−28] involves the collection of several MALDI-TOF spectra at different times and/or temperature to observe the structural changes induced by heat and light under an inert and/or oxidizing atmosphere. The partially degraded polymer sample can be directly analyzed, and the recorded MALDI-TOF spectrum arises from a mixture of nondegraded and degraded chains.

This opens new vistas in studying polymer degradation and deserves careful exploration, due to the relevance of these phenomena in everyday's practice.

We have recently reported on the thermal degradation of PC[9] and on the products of thermal oxidation of Nylon 6,[28] using MALDI-TOF as the main analytical technique.

On these occasions, we have remarked on the surprisingly high amount of structural information that can be extracted from the analysis of MALDI-TOF spectra of thermal or thermally oxidized polymers.

We have now performed the thermal oxidation of PC by heating at 300 and 350 °C in atmospheric air. Two polycarbonate samples, one capped (incompletely) with phenyl groups at both ends (PC1) and the other one capped (incompletely) with *tert*-butyl phenyl groups at both ends (PC2), were used. A THF-insoluble gel, corresponding to cross-linked polymer chains, was produced at longer heating times.

The oxidative process was followed as a function of the exposure time by SEC, ^{1}H NMR, MALDI-TOF, and SEC/MALDI-TOF techniques. The SEC curves showed

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Table 1. Thermal Oxidation Residue, THF Insoluble Residue, and Molar Mass Distribution Data of PC1 and PC2 Polycarbonate Samples Thermal Oxidized at 300 and 350 °C

temp (°C)	heating time (min)	oxidation residue[a]		insoluble residue[b]		PC1		PC2	
		PC1	PC2	PC1	PC2	M_w[c]	M_n[c]	M_w[c]	M_n[c]
	0	100	100	0	0	21000	16000	20000	13000
300	30	100	100	0	0	18800	13900	19200	11500
	60	100	100	0	0	18300	12100	18000	11000
	90	100	100	0.8	0	19000	11500	17000	10500
	120	100	100	3	0	17600	9800	16500	10500
	150	100	100	6.8	9.40	16800	9000	16000	9700
	180	100	100	13	13.90	15600	8400	15500	9300
350	15	100	100	0	0	15900	12000	10500	6500
	45	98.7	98	10	11.30	14400	7300	9300	5600
	60	97.7	98	14.7	13.65	9300	4450	8530	5000
	75	97	97	23.5	17.23	7880	4010	8000	4650
	90	96	97	24.5	16.00	6200	3730	7600	4000
	120	96	96	25	16.54	5500	2700	7000	3600
	150	95.5	95.5	25.6	19.77	5200	2350	5400	3000
	180	94.5	95	28.6	18.02	4900	2200	4900	2574

[a] Percent of residue with respect to the initial weight of samples. [b] Percent of THF-insoluble fractions obtained from the thermal oxidized residue. [c] Obtained by SEC/MALDI-TOF method (see Experimental Section).

extensive degradation, up to the formation of very low molar mass oligomers. The MALDI-TOF spectra of the thermally oxidized PC1 and PC2 samples showed the presence of polymer chains containing acetophenone, phenyl-substituted acetone, phenols, benzyl alcohol and biphenyl terminal groups. Formation of acetophenone and phenol end groups was confirmed by ^{1}H NMR analysis.

Experimental Section

Materials. Basic materials were commercial products appropriately purified before use. The PC1 sample was obtained by Sigma-Aldrich Chemical Co. and PC2 sample was from TEI JIN (Japan). 2-(4-Hydroxyphenilazo)benzoic acid (HABA) was purchased from Aldrich Chemical Co. and used as supplied.

Thermal Oxidative Degradation of PC. The thermal oxidation was carried out on molten PC samples in the presence of atmospheric air at 300 and 350 °C. First, 100 mg of sample was placed in a glass vessel and heated for 30, 45, 60, 90, 120, and 180 min in a electric furnace, without stirring. The oxidized PC samples were treated with THF and filtered. The THF soluble portions were dried and stored for the successive analyses, the solid residue were dried under vacuum and weighed. Residue values are reported in Table 1.

SEC Analysis and Molar Mass Determination. The analyses were performed on a Waters 600 A apparatus, equipped with five Ultrastyragel columns (7.8 × 300 mm) (in the order 10^5, 10^3, 500, 10^4, and 100 Å pore size) connected in series, and a Waters R401 differential refractometer. Then 90 μL of a $CHCl_3$ PC solution (0.5%) was injected and eluted with $CHCl_3$ at flow rate of 1 mL/min. The molar masses of PC samples were determined by the SEC/MALDI method.[18−21] Undegraded PC sample was fractionated to collect several equal volume fractions of about 0.165 mL each (corresponding to 12 drops). The molar mass of each collected fraction was determined by MALDI−TOF. The absolute calibration curves obtained by plotting the log M_w of some SEC selected fraction as a function of the corresponding elution volume allowed the calculation of molar masses of undegraded and thermally oxidized PC samples by the Polymer Lab Caliber software. The calculated data were reported in Table 1.

MALDI−TOF Analysis. MALDI−TOF mass spectra were obtained using a Voyager-DE STR instrument, equipped with a nitrogen laser emitting a 337 nm with a 3 ns pulse width and working in positive ion mode. The accelerating voltage was 20−25 kV, and the grid voltage and delay time (delayed extraction, time lag) were optimized for each sample to obtain

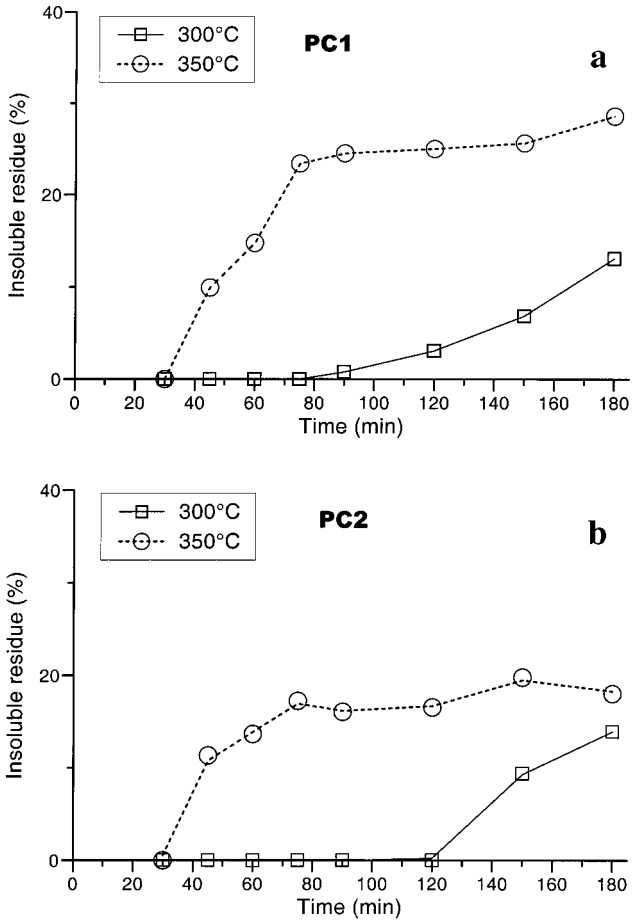


Figure 1. Percent of insoluble gel formed in the thermal oxidative degradation of (a) PC1 and (b) PC2 samples at 300 and 350 °C as a function of the heating time.

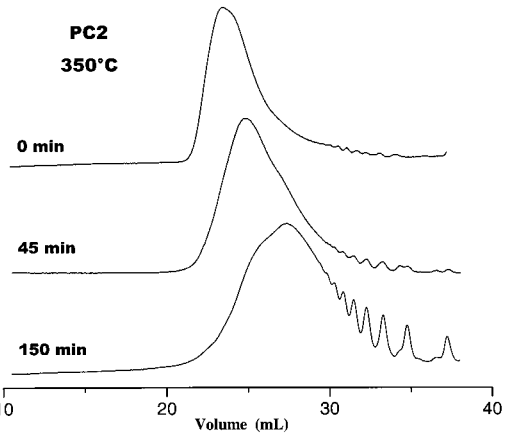


Figure 2. GPC traces of PC2 sample thermally oxidized at 350 °C for 0, 45, and 150 min.

the higher molar mass values. The laser irradiance was maintained slightly above threshold. The MALDI−TOF spectra in Figures 4 and 7 were recorded in linear mode. Although reflection MALDI−TOF spectra showed a higher resolution, they were not shown here because the intensity of the less abundant thermal oxidation products were close to the background noise level. The resolution of the MALDI spectra was about 1000 ($M/\Delta M$) and the accuracy of mass determination was about 0.02% for masses in the range 1000−5000.

The samples for the MALDI analyses were prepared by mixing adequate volumes of the matrix solution (HABA, 0.1 M in THF) and polymer solution (2 mg/mL in THF) to obtain a 1:1 or 1:3 ratio (sample/matrix)v/v. 1 μL of a 0.1 M solution of sodium trifluoroacetate (NaTFA) in THF was added to aid

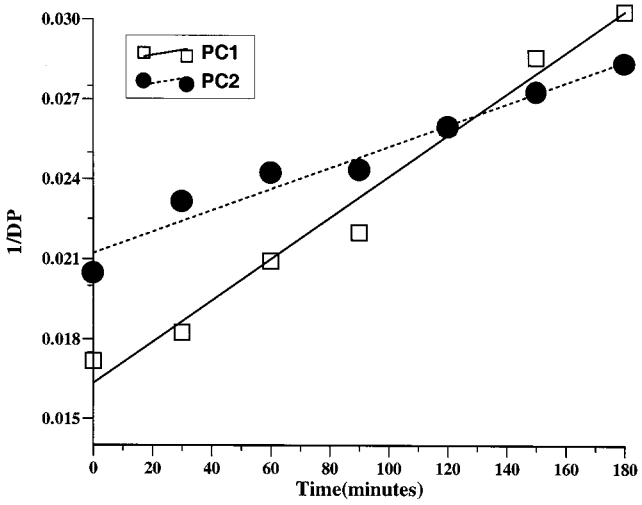


Figure 3. Inverse of degree of polymerization (1/DP) as a function of time of PC1 and PC2 samples thermooxidized at 300 °C.

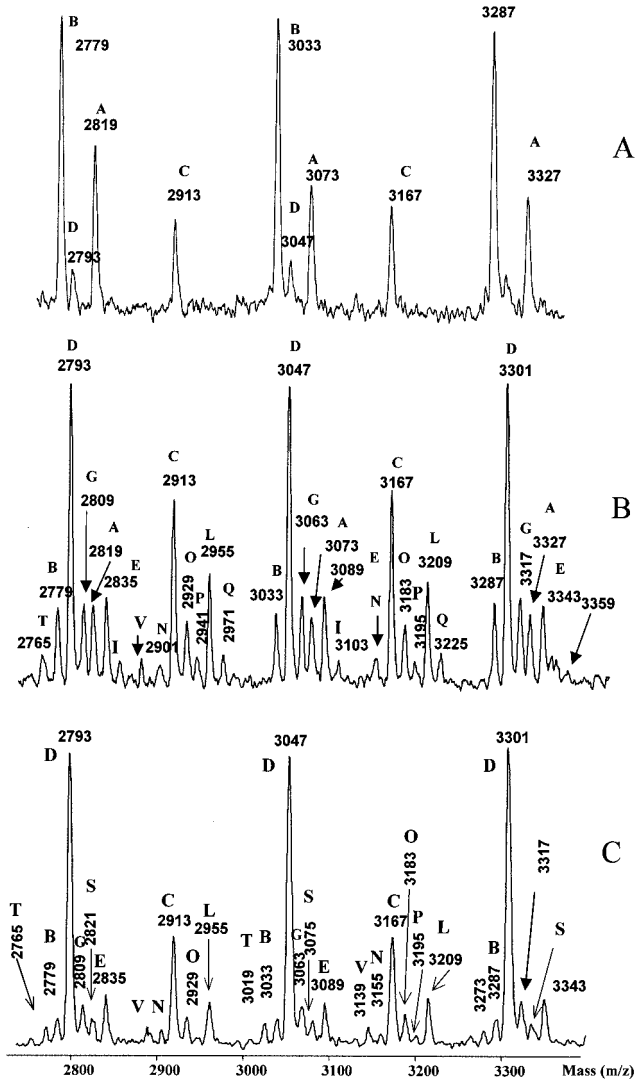


Figure 4. MALDI−TOF mass spectra, in the range 2800−3400 Da, of PC1 samples: (a) undegradated; themooxidized at 300 °C for (b) 90 and (c) 180 min.

cationization. Then 1 μL of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallization.

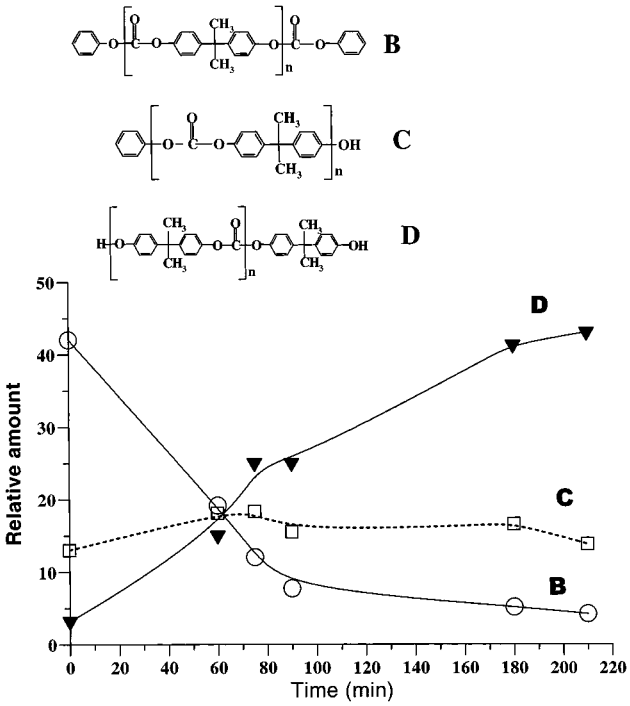


Figure 5. Relative amount vs heating time of species B, C, and D species as obtained from the MALDI spectra of thermooxidized PC1 sample at 300 °C.

The relative amount of species reported in Figures 5 and 6 was obtained as the ratio I_A/I_T, where I_A is the sum of the peaks intensity of each species in the mass range 2000−5000 and I_T corresponds to the sum of the intensity of all peaks appearing in the same mass range.

NMR Spectroscopy. ^{1}H NMR analyses were carried out at room temperature by a ^{UNITY}INOVA Varian instrument operating at 500 MHz using deuterated chloroform as solvent and tetramethylsilane as internal standard.

Results and Discussion

Two polycarbonate samples bearing two different types of chain ends, PC1 sample capped with phenyl groups and PC2 sample with *tert*-butyl-phenyl groups, were subjected to thermal oxidation by heating at 300 and 350 °C in atmospheric air up to 180 min.

At longer exposure times (Table 1) the thermooxidized samples showed gel formation and were subjected to extraction with THF, to have a soluble portion suitable for SEC, NMR, and MALDI−TOF analyses.

In Figure 1, parts a and b are reported the percent amount of THF-insoluble gel formed at 300 and 350 °C, respectively, as a function of the heating time. The amount of gel formed at 300 °C, after 180 min heating, is about 10% for both PC samples, but the gel formation onset is shifted at a higher heating time (150 min) in the PC2 sample with respect to the PC1 sample (90 min). This fact, together with the lower gel amount (20%) formed in PC2 at 350 °C, as compared to PC1 (30%), is taken as an indication that the cross-linking process is slightly slower in PC2.

In Figure 2 are shown the GPC traces of some thermally oxidized PC2 samples. The degradation process is already evident after 45 min exposure, and at 150 min, one observes prominent single peaks most likely due to dihydroxyl-terminated PC oligomers (see below).

The molar masses of the blank PC samples and those of the THF soluble fractions of thermally oxidized PC1

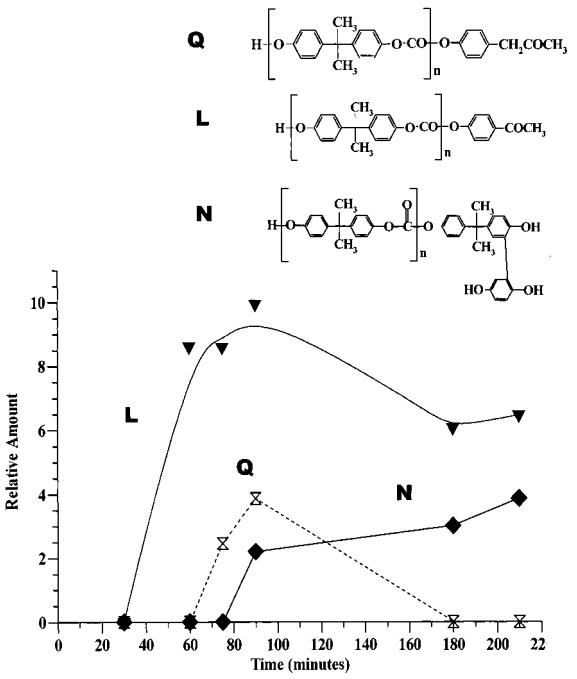


Figure 6. Relative amount vs heating time of species L, N, and Q species as obtained from the MALDI spectra of thermooxidized PC1 sample at 300 °C.

and PC2 samples were determined by the SEC/MALDI method.[18−21]

Data shown in Table 1 indicate that the degradation process is fairly extensive, producing a steady reduction of the molar mass with the reaction time.

The inverse polymerization degree (1/DP), shows a fair linearity against heating time for both PC samples thermally oxidized at 300 °C (Figure 3), indicating that the process proceeds by a random chain scission of the polymer molecules.[29,30]

The MALDI spectra of the pristine PC1 and PC2 samples have been already reported,[20] and therefore only expanded portions in the mass range 2000−4000 Da are presented here.

The MALDI spectrum of the PC1 sample, reported in Figure 4a, shows peaks belonging to four different mass series. The most intense peak series, at *m*/*z* 2779 + *n*254.2, is due to sodiated ions of PC1 chains terminated with phenyl groups at both ends (species B, Table 2).

A second series of peaks appearing with low intensity at *m*/*z* 2793 + *n*254.2, can be assigned to the sodiated ions of PC1 chains terminated with bisphenol A groups (BPA−OH) at both ends (species D, Table 2). A third series of peaks at *m*/*z* 2819 + *n*254.2 are due to sodiated ions of PC cyclic chains (species A, Table 2). The last series of peaks at *m*/*z* 2913 + *n*254.2, corresponds to sodiated ions of PC chains terminated with phenyl group at one end and a BPA−OH groups at the other end (species C, Table 2).

The MALDI mass spectra of PC1 heated at 300 °C in air for 90 and 180 min (Figure 4b-c) show an increased number of peaks with respect to the blank sample, indicating that the thermal oxidation reactions are producing several terminal groups.

The most intense peaks in the MALDI spectrum recorded after 90 min of heating (Figure 4b) are due to D species (Table 1), bearing BPA−OH groups at both ends. The intensity of the cyclic oligomers (species A)

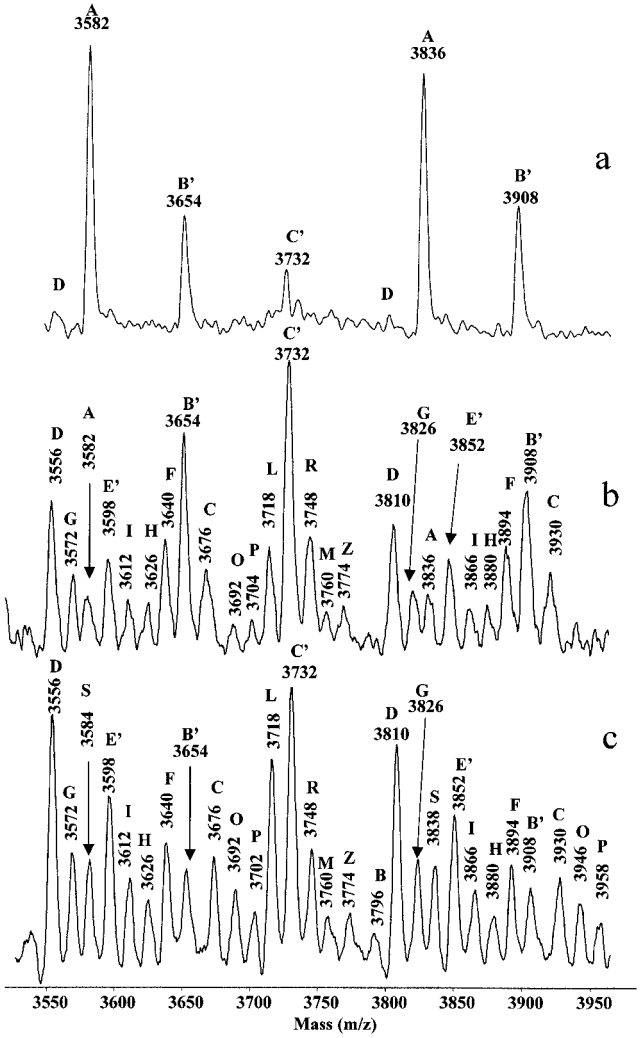


Figure 7. MALDI−TOF mass spectra, in the range 3500−4000 Da, of PC2 samples: (a) undegradated; thermooxidized at 300 °C for (b) 90 and (c) 180 min.

is strongly reduced whereas they disappear after 180 min of heating at 300 °C (Figure 4c). The phenyl-terminated oligomers (B species) appear with reduced intensity in both spectra in Figure 4b,c.

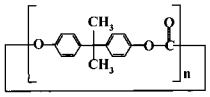
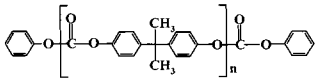
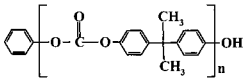
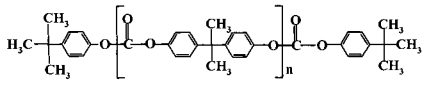
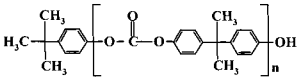
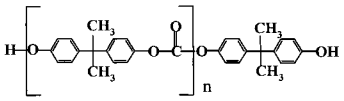
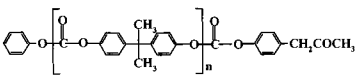
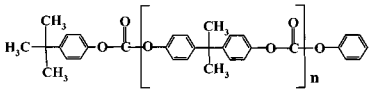
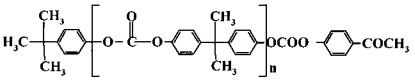
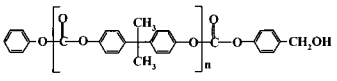
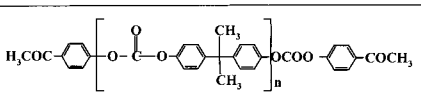
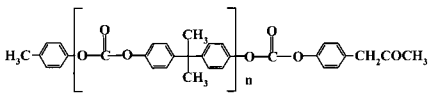
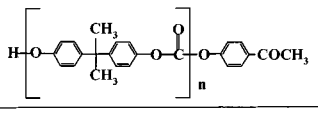
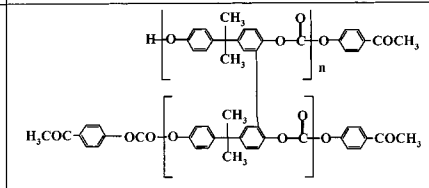
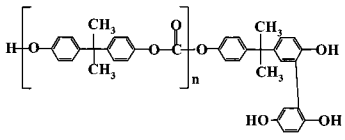
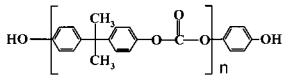
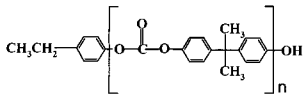
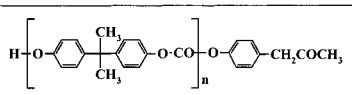
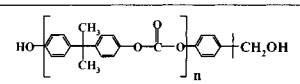
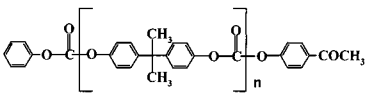
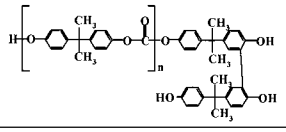
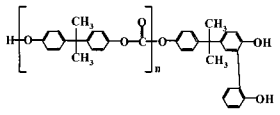
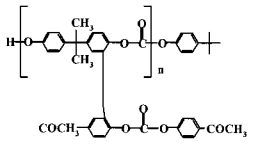
The assignment of species A (Figure 4c) to cyclic PC chains has been confirmed by the SEC/MALDI method. In fact, the MALDI spectra of the lower mass SEC fractions of 90 min thermally oxidized PC sample show a double distribution of peaks with the ratio of $M_{cycle}/M_{linear} = 1.2$, typical for the simultaneous presence of cyclic and linear oligomers.[20,21]

The large amount of PC1 chains containing BPA−OH as end groups (species D), is an indication that an extensive hydrolysis reaction of the carbonate functional groups, is occurring, either due to the atmospheric air moisture or to the water produced during the PC autoxidation which may also play a significant role.

The kinetics of the process is shown in Figure 5, in which the relative amount of the B, C and D species is reported as a function of the heating time. It can be noted the strong decrease of the intensity of species B, together with the corresponding increment of species D.

Instead, the amount of PC1 chains terminated with phenyl groups at one end and BPA−OH at the other end (C species) remains almost constant, presumably

Table 2. Structural Assignments of Sodiated Ions Appearing in the MALDI−TOF Spectra of Thermooxidized PC1 and PC2 Samples

Mass Series	Oligomers structures	n	M+ Na
A		11 12 13 14 15	2819 3073 3328 3582 3836
B		10 11 12	2779 3033 3287
C		11 12 14 15	2913 3167 3676 3930
B'		13 14	3654 3908
C'		14 15	3732 3986
D		10 11 12 13 14	2793 3047 3301 3556 3810
E		10 11 12	2835 3089 3343
E'		13 14	3598 3852
F		13 14	3640 3894
G		10 11 12 13 14	2809 3063 3317 3572 3826
H		13 14	3626 3880
I		11 12 13 14	2849 3103 3612 3866
L		11 12 14 15	2955 3209 3718 3972
M		12	3760
N		11 12	2901 3155
O		11 12 14	2929 3183 3692
P		11 12 14	2941 3195 3704
Q		11 12	2971 3225
R		14	3748
S		11 12 13 14	2821 3075 3584 3838
T		10 11	3019 3273
V		10 11	2885 3139
Z		13	3774

because these oligomers also arise from the hydrolysis degradation reaction of higher molar mass PC1 chains capped with phenyl groups at both ends (B species).

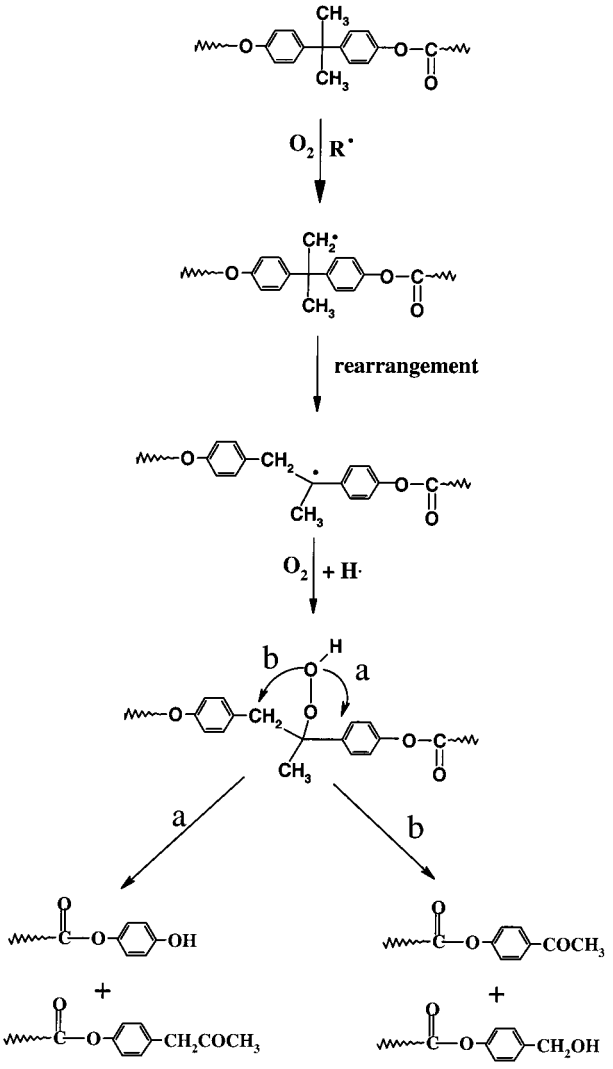
The structural assignment (Table 2) of the peaks labeled as E, I, Q in the MALDI spectra in Figure 4b-c, corresponds to thermal oxidation products with phenyl-substituted acetone end groups, whereas peaks O, V, N (Table 2) are assigned to oxidized PC1 chains containing phenol groups. All these species might arise through the hydroperoxide decomposition (Scheme 1, route a), as shall be discussed below.

Peaks L and S, assigned to oxidized PC1 chains bearing acetophenone chain ends (Table 2), are thought to be formed according to hydroperoxide decomposition (Scheme 1, route b), which also produces benzyl alcohol end groups (peak G, Table 2).

Peaks N, *T* and V (Table 2) are thought to correspond to species containing biphenyl units, most likely formed by the oxidative coupling of two phenyl rings of simple phenols and/or bisphenol A units (Scheme 3).[11,13]

This reaction creates biphenyl bridges between the linear PC chains, promoting the generation of char-like

Scheme 1. Thermal Oxidative Degradation Process of Poly(bisphenol A carbonate)



structures and the gel formation in the thermooxidative reaction.

In Figure 6 is reported the intensity of selected MALDI peaks related to representative compounds formed in the thermal oxidation process. The amount of oxidized species E and M increases steadily in the first part of the process and then tends to level for longer heating times, whereas the amount of Q species steadily decreases at longer heating time.

The leveling and/or decrease of oxidized species with time is only apparent, being related to the intervening cross-linking phenomena in the oxidation process. In fact, the cross-linked fraction (which contains a major portion of the oxidized products), becomes insoluble and cannot be detected by MALDI, since only the soluble material can be analyzed by MALDI.

In Figure 7a is reported the MALDI−TOF mass spectrum of the blank PC2 sample in the mass range 3500−4000Da, where cyclic oligomers (A) are the most intense peaks followed by the *tert*-butyl phenyl end-capped chains (B′) and by the PC2 chains (C′) containing one BPA−OH group at one end and a *tert*-butyl phenyl group at the other end. (Table 2). Species D, containing BPA−OH groups, at both ends (Table 2) is obtained in a very low amount in this PC sample.

The MALDI mass spectra of PC2 sample heated at 300 °C in air for 90 and 180 min (Figure 7b,c) show an increased number of peaks, most likely due to thermal oxidation.

After 90 min of heating, the most intense peaks in the MALDI spectrum (Figure 7b) are due to C′ and B′ species together with the D species, whereas the intensity of the cyclic species (A) is strongly reduced, indicating the presence of an extensive hydrolysis reaction. After 180 min of heating, the intensity of B′ species strongly decreases, peaks C′ and D become the most intense and the cyclic oligomers (A species) totally disappear.

The kinetics of the degradation process indicates that the intensity of A, B′, C′, and D species is very similar to that observed for PC1 sample and will not be reported for brevity; however, it should be pointed out that the hydrolysis process of the PC2 sample is significantly slower than that for the PC1 sample.

In fact, the intensity of B′ and C′ peaks corresponding to PC chains with free BPA−OH end groups (Figure 7b,c), is always higher than B and C peaks of PC1 sample (Figure 4b,c).

The structural assignments of the peaks appearing in the MALDI spectra in Figure 7b,c are listed in Table 2.

Peaks labeled by F, H, L, M, S, and Z, appearing with noticeable intensity, have been assigned to PC chains bearing acetophenone chain ends, produced according to Scheme 1 (route b).

The same oxidation pathway accounts for the presence of the G peaks corresponding to benzyl alcohol terminated PC chains.

Peaks E′ and I are due to species bearing phenyl-substituted acetone terminal groups, and peaks N and O are due to chains with phenol end groups, all generated according to Scheme 1 (route a).

Peaks M and Z in Figure 7b,c were assigned (Table 2) to species containing biphenyl bridges, formed by oxidative coupling of two aromatic rings.

The kinetics of formation of the oxidation products of PC2 sample is very similar to that observed for PC1 and will not be reported here for brevity.

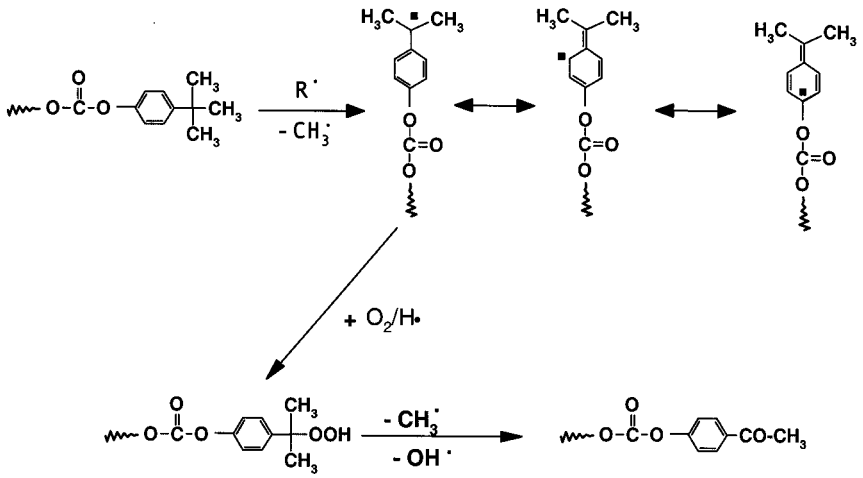
The presence of a higher amount of PC chains terminated with acetophenone end groups in the PC2 sample, as compared to PC1, might be ascribed to the different structure of the therminal groups. In fact, the *tert*-butyl moiety of PC2 chains may also undergo oxidation processes via the formation of a hydroperoxide, which can decompose[12] (Scheme 2) producing the same type of compounds formed in the thermal oxidation of isopropenyl groups (Scheme 1, route b). This hypothesis is also supported by the presence of the intense peaks R (Figure 7b,c) corresponding to a compound with methylol groups (Table 2) most likely formed in the initial stage of oxidation of *tert*-butyl chain ends.[12]

Furthermore, the presence of the *tert*-butyl capping groups in PC2 sample might be also able to generate resonance-stabilized radicals acting as antioxidant agents (Scheme 2). This might explain the different rate of gel formation and molar mass decreases of PC2 sample with respect to PC1 sample (Figures 1 and 2).

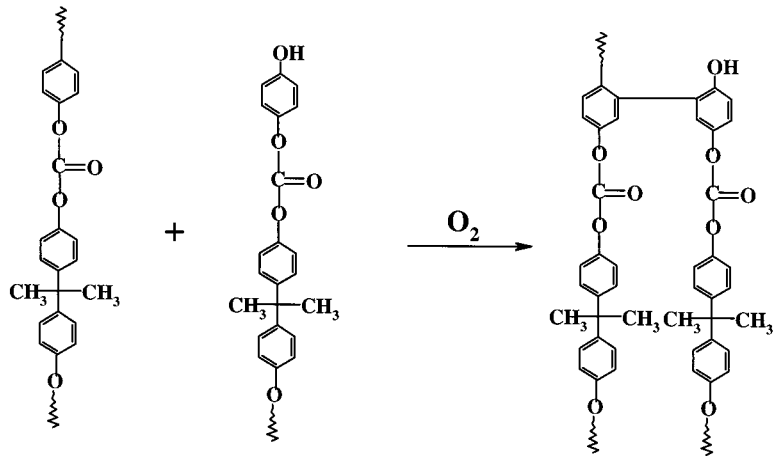
The thermal oxidation process of sample PC2 was also investigated by 500 MHz ^{1}NMR analysis.

In parts a−c of Figure 8 are reported the ^{1}H NMR spectra of the PC2 sample thermooxidized at 300° for

Scheme 2



Scheme 3



180 min (Figure 8b) and at 350 °C for 120 min (Figure 8c), respectively. Because of the low amount of chain ends, the NMR spectra have been expanded and only the spectral regions in which appear end groups signals are shown here.

The singlet peak at 2.6 ppm (methyl protons) and the two multiplets centered at 8.02 and 8.25 ppm (aromatic protons) correspond to the acetophenone terminal groups (Figure 3b,c).

The two multiplets centered at 6.65 and 7.05 ppm are due to aromatic protons of BPA−OH therminal groups (Figure 8b,c).

The singlet peaks appearing in the interval between 4.89 and 4.95 ppm (Figures 8b,c), can be assigned to the OH protons of the BPA−OH terminal groups. The latter assignment was confirmed by the ^{1}H NMR spectrum of a sample constituted of low molar mass PC oligomers terminated with BPA−OH at both ends (Figure 8d).

The NMR spectra therefore nicely confirm the formation of acetophenone and phenoxy end groups, which were among the several oxidation products detected by the MALDI analysis reported above.

Thermal Oxidation Mechanisms. Thermal oxidation pathways of PC were first proposed by Factor et al.[11,13] These workers analyzed the base hydrolysis products derived from a PC sample that was oven-aged at 140 °C, and found *p*-hydroxybenzoic acid and *p*-hydroxybenzophenone among the hydrolysis products.

In principle, base hydrolysis might catalyze rearrangement reactions of the pristine oxidation products, and the temperature used is rather low in order to simulate the oxidation and degradation processes occurring in the processing conditions of PC. In fact, degradation processes operating on PC are a function of the temperature.[8,9]

The present oxidation studies were carried out at 300 and 350 °C in order to simulate closely the PC processing conditions.

Pure oxidation is not the only reaction occurring when the PC samples are processed above 300 °C.

Hydrolyses of PC chains induced by the contact with atmospheric air and also the Schmitt−Kolbe isomerization of the carbonate group are also occurring.[2−14]

The mechanisms accounting for the thermal oxidation products of PC up to 350 °C involve at least the following: (i) oxidation and decomposition of the isopropenyl groups of BPA (Scheme 1); (ii) cross-linking reactions through the oxidative coupling of BPA units to form biphenyl groups (Scheme 3).

The MALDI data presented above support a primary oxidation mechanism leading to the initial formation of methylene radicals which undergo rearrangement to a more stable benzylic radical.

The subsequent reaction with oxygen produces a hydroperoxide intermediate, which may decompose by two parallel pathways (Scheme 1, routes a and b).

All the four kinds of end groups predicted by this reaction scheme have been detected by MALDI (Table

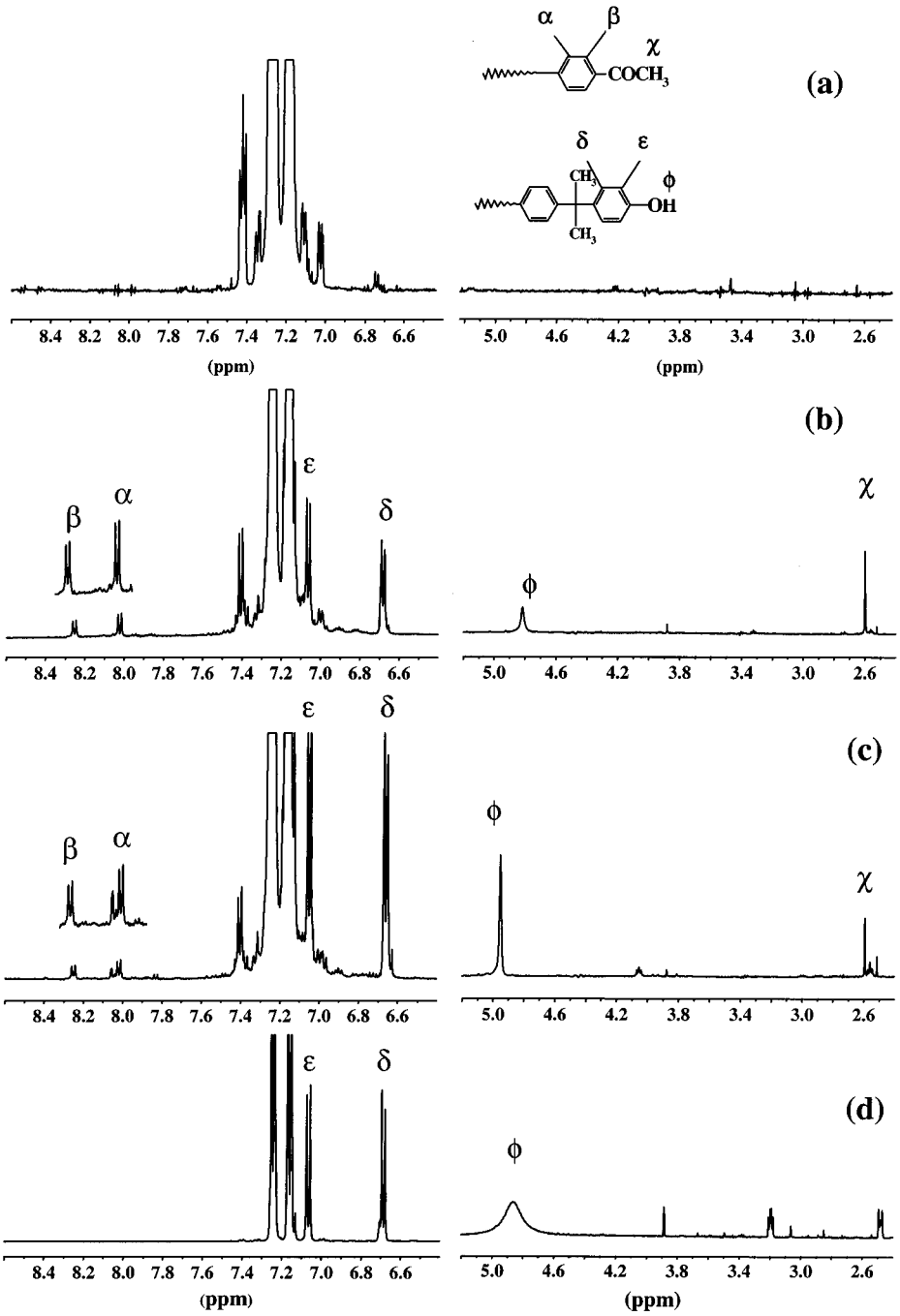


Figure 8. ^{1}H NMR spectra of PC2 samples: (a) undegraded; (b) thermooxidized at 300 °C for 180 min; (c) thermooxidized at 350 °C for 120 min; (d) low molar mass PC sample terminated with BPA−OH groups at both ends.

2), so that the overall process depicted in Scheme 1 is in general agreement with the original proposal of Factor et al.[11,13]

Also, the presence in the PC2 sample of a higher amount of PC chains terminated with acetophenone end groups, as compared to PC1, can be explained by Scheme 1.

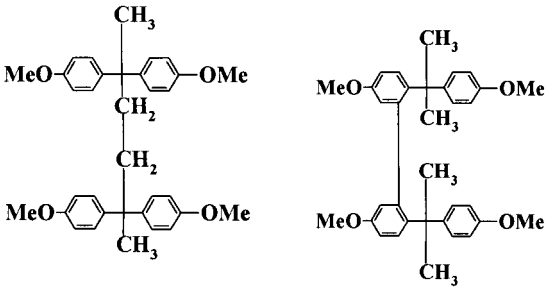
In fact, the *tert*-butyl moiety of PC2 chains may also undergo oxidation processes via a methyl loss and the formation of a hydroperoxide, which can decompose[12] (Scheme 2) producing the same type of compounds as formed in the thermal oxidation of isopropenyl groups (Scheme 1, route b).

The *tert*-butyl capping groups in PC2 might be able to generate resonance-stabilized isopropyl radicals (Scheme 2), which can act as antioxidant agents, helping rationalizing also the different rate of gel formation and molar mass decrease of PC2 with respect to the PC1 sample (Figures 1 and 2).

The presence of compounds containing biphenyl units among the oxidation products of PC, was also reported by Factor et al.,[11,13] and we have detected in the MALDI spectra five PC oligomers possessing structures which would indicate the presence of biphenyl units along the chain (Table 2).

Quite recently, however, Tsuge et al.[14] analyzed by reactive pyrolysis GC/MS at 400 °C some thermally oxidized PC samples and detected some reactive pyrolysis products containing doubled bisphenolA units that they assigned to the coupling of two methyl radicals formed from the oxidation of the ispropylidene bridges.

The structures proposed by Tsuge et al. (**1**)[14] are isomeric with the those containing biphenyl units (**2**).



1 **2**

From a detailed analysis (omitted for brevity) of the electron impact spectra reported in the paper of Tsuge et al.,[14] we find no basis to support their proposal and prefer to retain the biphenyl assignment for the structures detected by the MALDI spectra.

Conclusion

The data collected in our study show that the thermal oxidative degradation processes produce a sensible reduction of the molar mass of the PC samples, with formation of phenyl-substituted acetone, acetophenone, benzyl alcohol, biphenyl, and phenols as PC chain ends.

It should be remarked that, for the first time, the MALDI mass spectra allowed the determination of the species predicted from the thermal oxidation mechanism in Scheme 1, whereas in previous studies[11,13,14] some of these compounds had escaped detection.

The detection of PC oligomers containing biphenyl units is an indication of the oxidative pathways contributing to the gel formation.

The accurate MALDI analysis of the oxidation products of PC2 sample, capped with *tert*-butyl phenyl groups at both ends, unveiled the antioxidant action of these terminal groups, which are able to slow the rate of thermal oxidation of PC2 (Scheme 2).

The results presented here show that highly valuable structural information on the thermal oxidation products of PC can be obtained by matrix-assisted laser desorption ionization (MALDI) mass spectrometry.

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