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Pyrolysis of γ-irradiated bisphenol-A polycarbonate

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Summary

A new approach to study the mechanism of radiation-induced degradation of polymeric materials based on the combined analysis of radiolytic gases and pyrolytic products from preirradiated polymers is proposed. Bisphenol-A polycarbonate (PC) was γ-irradiated under vacuum in the dose range from 0.125 to 1.0 MGy followed by its flash pyrolysis under an inert atmosphere coupled to GC-FTIR-MS. Pyrolyzed PC at 750°C released mainly carbon dioxide, methane, benzene, toluene, phenol and 4-methylphenol. The yields of some of these products linearly decrease or increase with absorbed dose. On the basis of this behavior and combining our previous data on gas evolution, we infer two main pathways of PC radiation-induced scission with equal probabilities: (a) carbonate bond and (b) aliphatic-aromatic bond ruptures.

Introduction

Bisphenol-A polycarbonate (PC) is an important engineering polymer bearing excellent mechanical properties, transparency and relatively high heat resistance. Ionizing radiation has been widely used to modify polymeric materials, and the mechanism of radiation-chemical transformations in some of them has been investigated in detail (1-5), but for PC this question has been not addressed appropriately. It is known that interaction of ionizing irradiation with PC results in its degradation (6-14). This process is accompanied by gas evolution from this polymer but data on the chemical composition and yields of gases were contradictory (6,7). Recently we have shown that PC irradiation is accompanied by the preferential release of carbon monoxide followed by minor production of hydrogen, carbon dioxide and methane (15). Gas analysis is a good indicator of the overall radiation-induced damage and is useful for the study of the mechanism of polymer transformations caused by irradiation. The interaction of gamma rays with PC could lead to bond cleavage in the carbonate and aliphatic groups resulting in the formation of gas molecules. In addition, electron spin resonance studies of the irradiated PC at 77 K have shown the formation of $–C_6H_4$-O·, $-C_6H_4$· and $-O-C_6H_4-C(CH_3)_2$· radicals (7). Recently, some attempts have been made to modify PC *via* radiation-grafting to introduce new functional groups into this polymer or to crosslink it in the presence of additives to improve the PC chemical resistance against organic solvents (16-18), but nature of active centers in irradiated PC and their contribution to contacts with compounds used for this polymer modification were not considered. These investigations will clearly benefit from a detailed mechanistic study of the chemical transformations and structural changes initiated by ionizing radiation on PC.

Pyrolysis - gas chromatography (Py-GC) is widely used for polymers characterization as a rapid and extremely sensitive technique of investigation that provides unique structural information for polymeric materials (19-22). Py-GC, in combination with mass spectrometry (MS), IR spectroscopy, size exclusion chromatography and nuclear magnetic resonance, was used for PC characterization (23-25). In addition direct Py-MS was employed for investigation of thermal fragmentation processes in PC (26-28). There are data on pyrolysis of irradiated polypropylene and irradiation resulted only in a change of the products distribution without formation of new compounds (29). Pyrolytic decomposition of irradiated, thermally aged poly(ethylene-co-tetrafluoroethylene) results in dehydrofluorination, formation of unsaturation, and hydrogen and fluorine migration (30).

To our knowledge, the Py-GC technique has not yet been used to characterize irradiated PC although it probably can provide relevant information on the chemical transformations induced and could also possibly contribute to the understanding of mechanism of chemical transformation in this irradiated polymer. In this work we apply quantitative pyrolysis-gas chromatography coupled to infrared spectroscopy and electron impact mass spectrometry to study the radiation-induced scission of PC.

Experimental

Irradiations of PC were conducted in the ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) located at the Institute of Nuclear Science of the National Autonomous University of Mexico. Fricke dosimeter was used to determine the absorbed dose rate under the experimental conditions used. PC pellets of about 2 mm thickness (10 g), supplied by General Electric Co (Lexan, LBW248), were introduced into a 100 ml cylindrical Pyrex reactor equipped with a high-vacuum stainless steel stopper. The reactor was then connected into a vacuum manifold and the air from the reactor and that absorbed in the pellets was pumped out for several hours until the vacuum pressure was maintained constant at 10^{-7} bar. Then the reactor was closed and irradiated at doses from 0.125 to 1.0 MGy with a dose rate of 7 kGy h^{-1}.

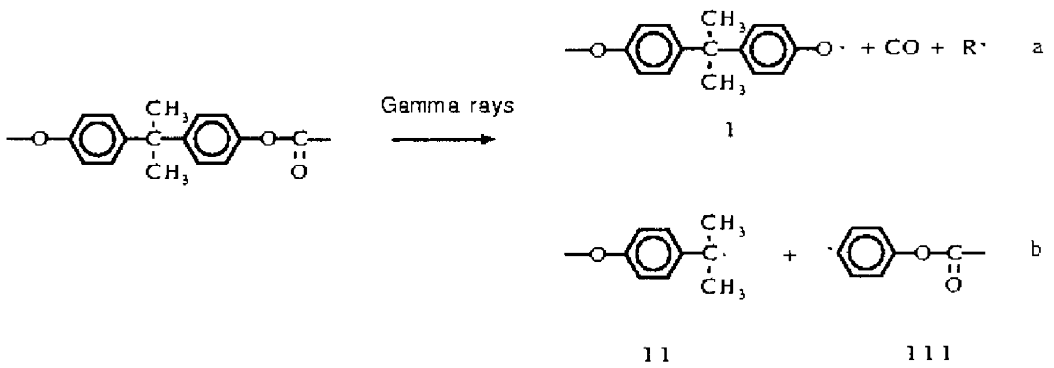
Analyses of pyrolyzates of blanks and irradiated PCs were performed using a Hewlett Packard (HP) gas chromatograph 5890 series interfaced in parallel with a HP FTIR-detector (model 5965) and a HP quadrupole mass spectrometer (5989B) operating in electron impact mode at 70 eV. The column used was a PoraPlot Q fused-silica 25 m long × 0.32 mm I.D. with a 2.5 m particle trap. The temperatures at the interfaces and in the FTIR flow cell were at 260°C. The carrier gas used was helium (chromatographic grade from Praxair, Inc.) with a flow of 1.2 ml min^{-1}.

Powder of irradiated and non-irradiated PCs (particles size of 60 μm) were made with a mill (Arthur H. Thomas Co, Scientific Apparatus, Philadelphia, PA). A portion of the powder (~1.5 mg) was loaded in a capillary quartz tube and held in place using small plugs of quartz wool. Each tube was then mounted in the center of a platinum coil filament-type pyrolyzer (CDS Pyroprobe2000). Atmospheric air was removed from the pyrolysis cavity by flushing a stream of helium (99.9999%) for 3 min. The polymers were subjected to a thermal treatment of 200°C for 10 seconds, then to 750°C with a heating rate of 10°C/ms, and finally holding this temperature for 60 seconds. The resulting pyrolyzed gases and votaliles were injected 60 seconds after pyrolysis into the injection port of the gas chromatograph by an automatic six-port gas-sampling valve. The pyrolyzer probe is mounted on the top of the injection port of the gas chromatograph. The pyrolyzer interface and the gas chromatograph injection port were maintained at 250°C. The column program temperature was isothermal at 60°C for 2 min, and then a rate of 10°C min^{-1} up to 240°C, and finally isothermal for 35 min. The mass analyzer was scanned from m/z 10 to 250 at a scan rate of 4.4 scan/s. The electron impact chamber and the quadrupole were maintained at 250°C and 100°C, respectively. The FTIR detector scanned from 4000 to 550 cm^{-1} at a rate of 1.6 scan/s.

The products were identified on the basis of their spectral properties with the help of two spectral libraries: Wiley 138K MS and EPA IR Vapor Phase Databases.

Results and Discussion

In our previous work (15) we analyzed gases evolved from γ-irradiated PC and calculated their radiation-chemical yields (G) expressed as the number of molecules produced per 100 eV of the absorbed energy. These values were: 1.00 (total gases), 0.87 (carbon monoxide), 0.08 (hydrogen), 0.04 (carbon dioxide) and 0.006 (methane). These yields were normalized to carbon monoxide and are reported in Table 1. From the gas analysis data it is evident that carbon monoxide, the main gaseous product, results from the carbonate bond rupture of PC (Scheme 1, channel a) and that decarboxylation is not important. The radiation effect on the aliphatic group could result in bond cleavage in the following regions:1) hydrogen-aliphatic carbon, 2) aliphatic carbon-aliphatic carbon, and 3) aromatic carbon-aliphatic carbon. The radicals formed by case 1 and 2 would lead to the formation of molecular hydrogen and methane, respectively. From our gas analysis it is clear that these two processes are not important. Case 3 is supported by ESR (7) in which these radicals are formed



Scheme 1

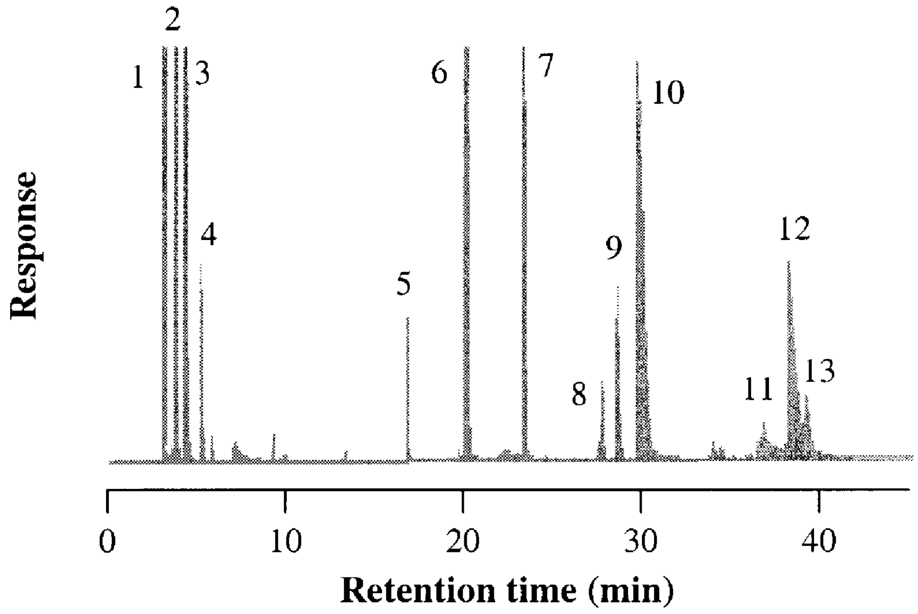


Figure 1. Reconstructed gas chromatogram of γ-irradiated PC (0.66 MGy) subjected to pyrolysis. 1. traces of air; 2. Methane; 3. Carbon dioxide; 4. Ethene; 5. Cyclopentadiene; 6. Benzene; 7. Toluene; 8. Dimethyl-benzene; 9. Vinyl-benzene; 10. Phenol; 11. Ethenylmethylbenzene; 12. 4-Methylphenol; and 13. 1-Propynylbenzene.

in channel b: $-O-C_6H_4-C(CH_3)_2\cdot$ and $-C_6H_4\cdot$; but their final stable products are not found in the gas phase. Pyrolyzates of irradiated and non-irradiated PC are essentially similar in the type of products formed. Fig. 1 shows a typical gas chromatogram of an irradiated PC that was reconstructed by mass spectrometry. The main products of both irradiated and non-irradiated PC are carbon dioxide, methane, benzene, toluene, phenol and 4-methyl-phenol. These compounds were identified on the basis of their MS and IR spectra. As examples Figs. 2 and 3 show the IR and MS spectra, respectively for phenol and 4-methylphenol.

Table 1. Normalized yields of gases from irradiated PC.

Compound	Normalized yields*
Carbon monoxide	1.0
Hydrogen	0.09
Carbon dioxide	0.05
Methane	0.007

*to carbon monoxide.

Other minor products shown in Fig. 1 were only identified by MS due to their low yield of production and the low sensitivity of the IR detector in comparison with the MS. Larger molecules (*e.g.*, bisphenol-A) were not detected because they were retained in the GC column. Analytical pyrolysis-GC-FTIR-MS shows however some quantitative differences between the yields of these main products.

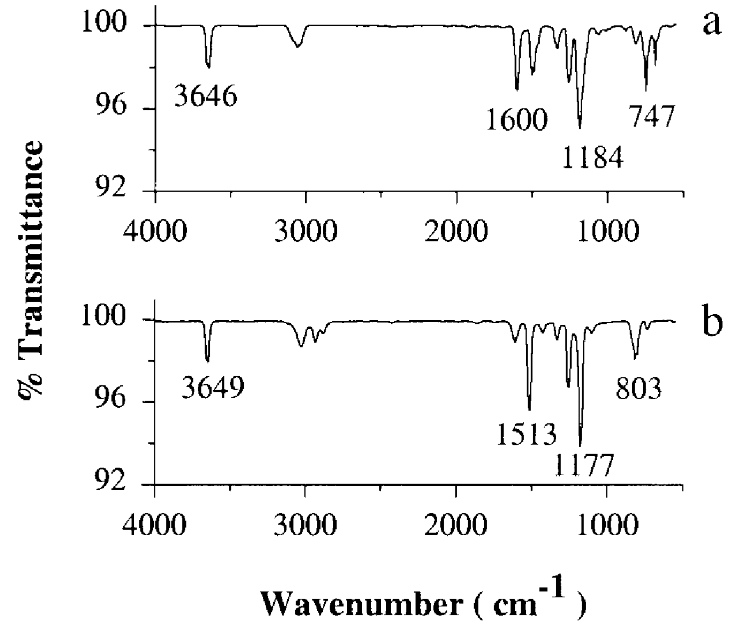


Figure 2. Infrared spectra of (a) phenol, and (b) 4-methylphenol formed by pyrolysis at 750°C of γ-irradiated PC at 0.5 MGy (4 cm^{-1} resolution).

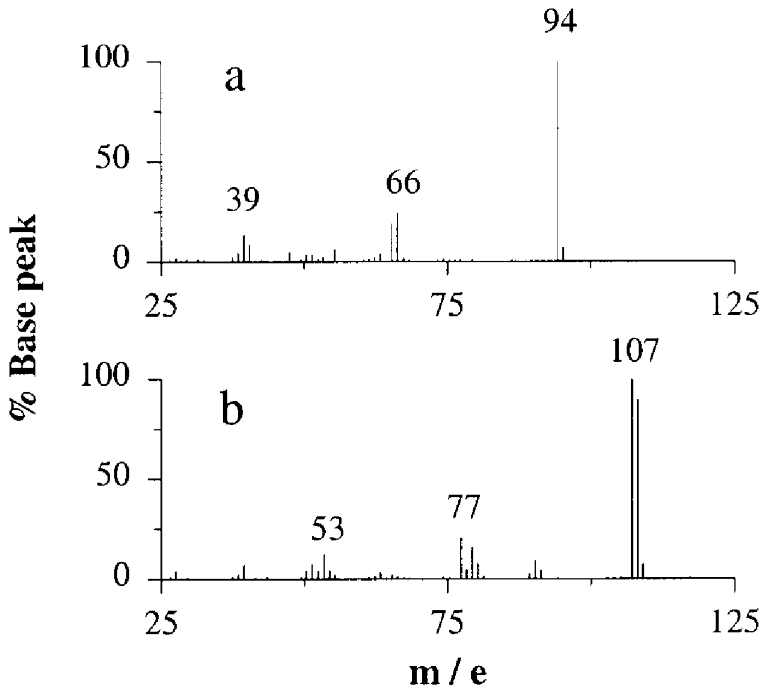


Figure 3. Mass spectra pattern of (a) phenol, and (b) 4-methylphenol formed by pyrolysis at 750°C of γ-irradiated PC at 0.5 MGy.

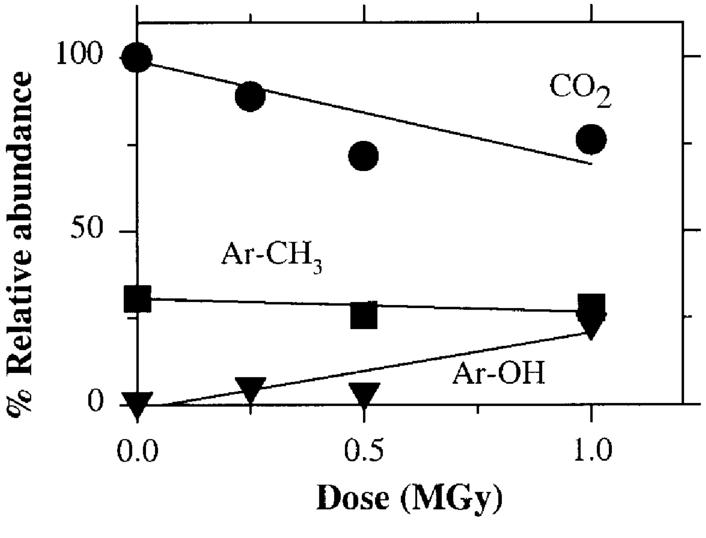


Figure 4. Dependence of the relative abundance of pyrolyzates as a function of dose.

Table 2. Production rate of main pyrolytic products of γ-irradiated PC.

Compound	Normalized rate*
Carbon dioxide	-1.0
Methane	-1.0
Benzene	0.0
Toluene	0.0
Phenol	1.1
4-Methylphenol	1.2

*to carbon dioxide. A negative or positive value implies depletion or enhancement, respectively; whereas a zero value means no alteration with dose.

Figure 4 shows the concentration trends for some selected compounds as a function of radiation dose. We found three general trends as a function of dose: enhancement, depletion and no change. The slopes of the major products from pyrolyzates of PC normalized to that of carbon dioxide are given in Table 2. Both carbon dioxide and methane decrease as a function of dose with the same slope suggesting that the same probability of radiation-induced damage occurred on both the carbonate and the methyl groups of PC. The chemical yields of benzene and toluene were not affected by radiation treatment followed by pyrolysis. This indicates that the aromatic ring is not cleaved from the backbone of PC by radiolysis whereas those of phenol and 4-methylphenol increase roughly the same slope with radiation dose. It must be emphasized that the slopes of depletion for carbon dioxide and methane are roughly equal in magnitude to those of enhancement for phenol and 4-methylphenol suggesting that these chemical transformations occur with a one-to-one stoichiometry. The depletion of carbon dioxide from pyrolysis of irradiated samples is consistent with the evolution of carbon monoxide during radiolysis of PC according to channel a. Decarboxylation is not a significant process in irradiated PC since the yield of carbon dioxide is quite low. The resulting radical (I) very likely recombines with hydrogen atoms producing a phenol fragment. This product will enhance the production of phenol due to the aliphatic-aromatic bond cleavage upon pyrolysis.

The depletion of methane from pyrolysis of irradiated samples may seem to be in contradiction with gas analysis data since it is found in low quantities in irradiated PC. However, it can be explained satisfactory by subsequent chemical transformations of radicals II and III in channel b leading to the formation of vinylbenzene and phenol fragments. Upon pyrolysis we detected an enhancement of phenol and 4-methyphenol in irradiated PC but not of vinylbenzene. The latter was detected in a very low yield probably due to its polymerization at elevated temperatures. It is possible to conceive that 4-methylphenol could result from the decomposition of radical II upon pyrolysis. Combining the results from both gases and pyrolysates we infer that channels a and b occur with equal probabilities and are the main channels of radiation-induced scission of PC. To our knowledge, this method is promising in the field of radiation chemistry of polymers and has the advantage of no laborious chemical manipulation of the sample after irradiation.

Conclusion

Pyrolysis of irradiated PC resulted in formation of different products that exhibited a dose-dependence. The yields of carbon dioxide and methane decrease linearly with absorbed dose whereas those of phenol and 4-methylphenol increase. The yields of benzene and toluene are unaffected by irradiation. The combination of gas and pyrolyzate products from irradiated PC enabled us to better understand the mechanism of gamma radiation-induced scission of bisphenol-A polycarbonate. Our results are relevant for the purposeful modification of PC by radiation grafting, block-copolymerization and crosslinking.

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