Navarro González, Rafael; Aliev, Roustam

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Investigación

Mechanism of radiation-induced degradation of bisphenol-A polycarbonate

Rafael Navarro-González[†] and Roustam Aliev[*]

Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Ciudad Universitaria, Apartado Postal 70-543, México 04510, D.F. Phone: (52) 5622-4674 (ext 261); Fax: (52) 5616-2233; E-mail: aliev@nuclecu.unam.mx

Abstract. We report here 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 by flash pyrolysis coupled to gas chromatography —Fourier transformed infrared spectroscopy— mass spectrometry with electron impact mode (GC-FTIR-MS). Bisphenol-A polycarbonate (PC) was studied in the dose range from 0.125 to 1.0 MGy. PC irradiation was accompanied by the preferential release of carbon monoxide followed by minor production of hydrogen, carbon dioxide and methane. Pyrolyzed PC releases mainly carbon dioxide, methane, benzene, toluene, phenol and 4-methyl-phenol. On the basis of these results we suggest two main pathways of PC radiation-induced scission with equal probabilities: (a) carbonate bond and (b) aliphatic-aromatic bond ruptures.
Keywords: Polycarbonate, radiolysis, flash pyrolysis, GC-FTIR-MS, mechanism of degradation.

Resumen. Reportamos una nueva metodología para estudiar el mecanismo de degradación por radiación de materiales poliméricos basada en el análisis combinado de los gases de origen radiolítico, y los productos pirolíticos, generados mediante la pirólisis rápida de polímeros pre-irradiados, acoplado a cromatografía de gases —espectroscopía de infrarrojo con transformada de Fourier— espectrometría de masas por impacto electrónico. El policarbonato de bisfenol-A (PC) fue estudiado en el rango de dosis de 0.125 a 1.0 MGy. La irradiación del PC estuvo acompañada por la liberación preferencial del monóxido de carbono seguida de una producción menor de hidrógeno, dióxido de carbono y metano. El PC pirolizado liberó principalmente dióxido de carbono, metano, benceno, tolueno y 4-metilfenol. Con base en los resultados obtenidos sugerimos dos vías principales para la incisión del PC por radiación con igual probabilidad: (a) ruptura del enlace carbonato y (b) ruptura del enlace alifático-aromático.
**Palabras clave:** Policarbonato, radiólisis, pirólisis instantánea, CG-IRTF-EM, mecanismo de degradación.

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 [6-12]. Electron spin resonance studies of PC at 77 K have shown the formation of $-C_6H_4-O\times$, $-C_6H_4\times$ and $-O-C_6H_4-C(CH_3)_2\times$ radicals [7]. Radiation-induced degradation 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 [13]. 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 [3,4]. 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 for PC to improve the chemical resistance against organic solvents [14-16], 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 [17-19]. Py-GC, in combination with mass spectrometry (MS), IR spectroscopy, size exclusion chromatography and nuclear magnetic resonance, was used for PC characterization [20, 21]. In addition direct Py-MS was employed for investigation of thermal fragmentation processes in PC [22-24]. To our knowledge this technique has not been used previously to characterize irradiated polymeric materials 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 the irradiated PC.
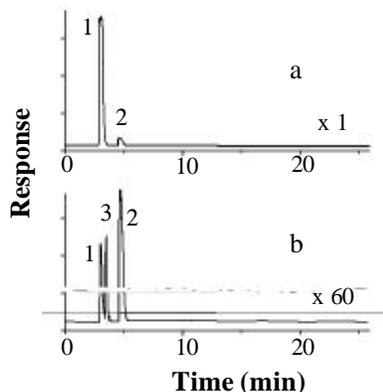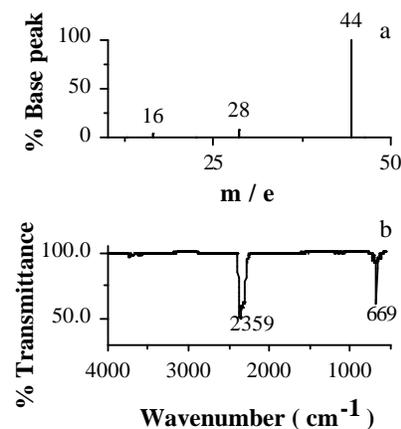
Fig. 1. Reconstructed gas chromatogram of gases evolved from γ-irradiated PC (0.66 MGy). Ion 28 m/e (a), ion 16 m/e (b). Carbon monoxide (1), carbon dioxide (2), methane (3).
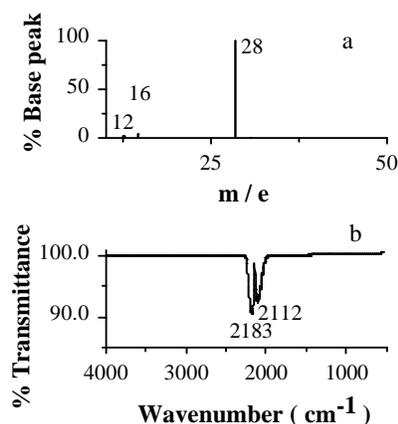
Fig. 2. Mass spectrum (a) and infrared spectum (b) of carbon monoxide formed from γ-irradiated PC.

Fig. 3. Mass spectrum (a) and infrared spectum (b) of carbon dioxide formed from γ-irradiated PC.

In this work we apply these two analytical tools to study the radiation-induced scission of PC: gas analysis and quantitative pyrolysis-gas chromatography coupled to infrared spectroscopy and electron impact mass spectrometry.

Experimental

Irradiations of PC were conducted in the ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.). Fricke dosimeter was used to determine the dose rate of irradiator 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.

Analyses of gases and 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}.

The gases produced by gamma irradiation of PC were injected into the gas chromatograph by an automatic six-port gas-sampling valve with a gas loop of 2 mL. The column program temperature was isothermal at 30 °C for 4 min, and then a rate of 13 °C min^{-1} up to 240 °C, and finally isothermal for 5.62 min. The mass analyzer was scanned from m/z 10 to 100 at a scan rate of 8.6 scan/s. The electron impact chamber and the quadrupole were maintained at 200 °C and 100 °C, respectively. The FT infrared detector scanned from 4000 to 550 cm^{-1} at a rate of 1.6 scan/s. Calibration curves of standard gases were prepared in helium at various mixing ratios using a Linde mass flow measuring and control gas blending console (FM4660) equipped with fast response mass flow control modules (FRC) of 20 cm^3 min^{-1} capacity.

Powder of irradiated and non-irradiated PCs (particles size of 60 mm) were made with a mill (Arthur H. Thomas Co, Scientific Apparatus, Philadelphia, PA). A portion of this 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 s, then to 750 °C with a heating rate of 10 °C/ms, and finally holding this temperature for

Table 1. Yields of gases from irradiated PC.

| Compound	G	Normalized yields*	
		This work	Ref. 6
Carbon monoxide	0.87	1.0	1.0
Hydrogen	0.08	0.09	0.03
Carbon dioxide	0.04	0.05	0.2
Methane	0.006	0.007	—
Oxygen		—	0.001

*to carbon monoxide.

60 s. The resulting pyrolyzed gases and votaliles were injected 60 s 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 138 K MS and EPA IR Vapor Phase Databases.

Results and discussion

Figure 1 shows that carbon monoxide is the main radiolytic gas with traces of carbon dioxide and methane. The identity of these compounds was confirmed by electron impact mass spectrometry and FTIR spectroscopy (Figs. 2-4). Hydrogen is not detected by our analytical platform and so we inferred its yield from the difference between measurements of total gas pressure and the analysis of gases from GC-MS. The total yield of gases derived from gas pressure measurements as well as those detected by the GC-MS-FTIR system increases linearly with the absorbed dose. Figure 5, as an example, shows this dependence. The radiation-chemical yields (G expressed as the number of molecules formed per 100 eV abosrbed) of gaseous products from irradiated PC were calcu-
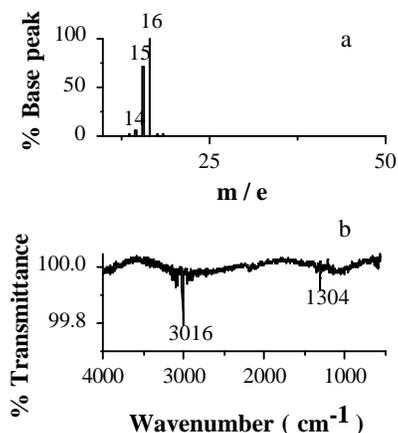
Fig. 4. Mass spectrum (a) and infrared spectum (b) of methane formed from γ-irradiated PC.
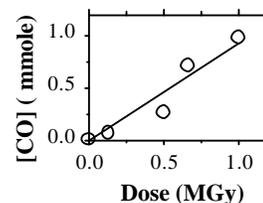
Fig. 5. Yield of carbon monoxide from γ-irradiated PC as a function of dose.
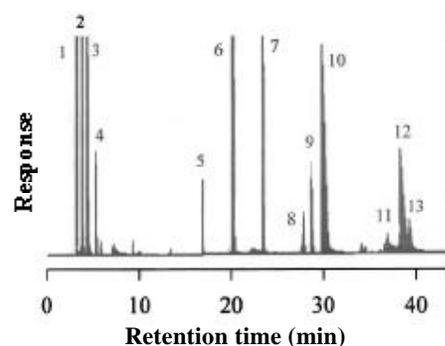
Fig. 6. Reconstructed gas chromatogram of gamma irradiated PC (0.66 MGy) subjected to pyrolysis. Traces of air (1), methane (2) carbon dioxide (3), ethene (4), cyclopentadiene (5), benzene (6), toluene (7), dimethylbenzene (8), vinylbenzene (9), phenol (10), ethenylmethylbenzene (11), 4-methylphenol (12) and 1-pronynylbenzene (13).
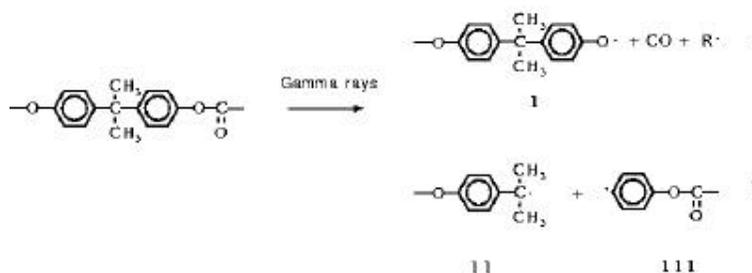
Scheme 1
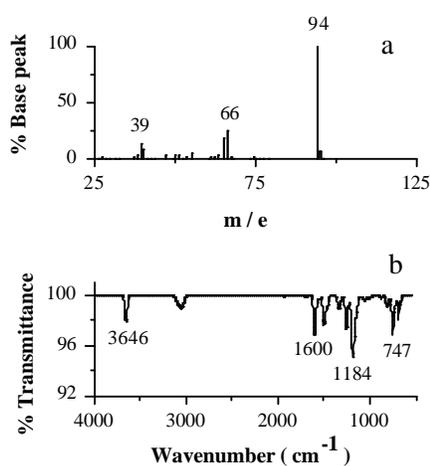
Fig. 7. Mass spectrum (a) and infrared spectrum (b) of phenol formed by pyrolysis of γ-irradiated PC.
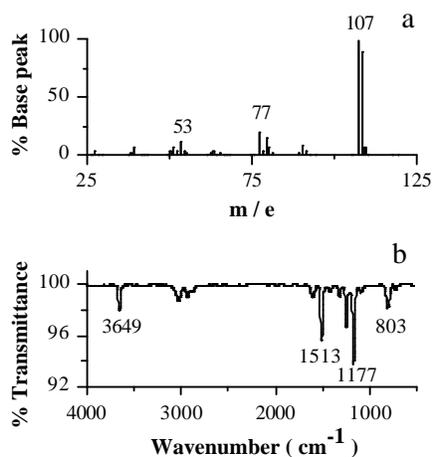
Fig. 8. Mass spectrum (a) and infrared spectrum (b) of 4-methylphenol formed by pyrolysis of γ-irradiated PC.
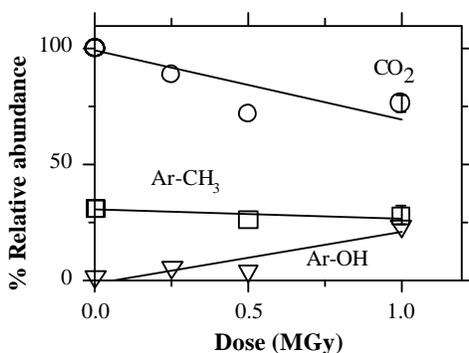
Fig. 9. Dependence of the relative abundance of pyrolyzates as a function of dose.

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.

lated, normalized to carbon monoxide and are reported in Table 1. Thus, PC irradiation is accompanied by the preferential release of carbon monoxide followed by minor production of hydrogen, carbon dioxide and methane. Our results are consistent with the data of Golden and Hazell [6]; nevertheless, the published results from Hama and Shinohara [7] are in contradiction in that they found significantly more carbon dioxide (about 0.5 relative to carbon monoxide). The possible reason for these contradictory findings is the presence of absorbed oxygen in PC due to insufficient pumping. 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 in channel b: $-O-C_6H_4-C(CH_3)_2 \times$ and $-C_6H_4 \times$ 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. 6 shows a typical gas chromatogram of an irradiated PC which 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, figures 7 and 8 show the MS and IR for phenol and 4-methylphenol. Other minor products shown in figure 6 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. Analytical pyrolysis-GC-FTIR-MS shows however some quantitative differences between the yields of these main products. Figure 9 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 the 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 4-methylphenol fragments, respectively. Upon pyrolysis we detected an enhancement of 4-methyphenol in irradiated PC but not of vinylbenzene. The latter was detected in very low yield probably due to its polymerization at elevated temperatures. Combining the results from both gases and pyrolysates we conclude that channels a and b occur with equal probabilities and are the main channels of radiation-induced scission of PC.

Conclusions

γ-Irradiation of PC resulted in formation of different gases, and their yields increased linearly with the absorbed dose. The main product was carbon monoxide with the radiation-chemical yield of 0.87. Pyrolysis of irradiated PC resulted also in formation of different products. The yields of carbon dioxide and methane decreased linearly with absorbed dose whereas those of phenol and 4-methylphenol increased. The yields of benzene and toluene were unaffected by irradiation. The combination of gas and pyrolyzate products from irradiated PC enabled us to deduce the mechanism of gamma radiation-induced scission of bisphenol-A polycarbonate. 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. Our results are relevant for the purposeful modification of PC by radiation grafting, block-copolymerization and crosslinking.

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