

MECHANISM OF RADIATION-CHEMICAL AND PYROLYTIC TRANSFORMATIONS IN LEXAN®

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ABSTRACT

We report here a new approach to study the mechanism of radiation-chemical transformations in 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). Lexan® (bisphenol-A polycarbonate) was studied in the dose range from 0.125 to 1.0 MGy. Lexan irradiation was accompanied by the preferential release of carbon monoxide followed by minor production of hydrogen, carbon dioxide and methane. Pyrolyzed Lexan releases mainly carbon dioxide, methane, benzene, toluene, phenol and 4-methyl-phenol. On the basis of these results we suggest two main pathways of Lexan radiation-induced scission with equal probabilities: (a) carbonate bond and (b) aliphatic-aromatic bond ruptures.

Key Words: Lexan, radiolysis, flash pyrolysis, GC-FTIR-MS, mechanism of degradation.

RESUMEN

Reportamos una nueva metodología para estudiar el mecanismo de transformaciones por radiación en 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 la cromatografía de gases -espectroscopía de infrarrojo con transformada de Fourier- espectrometría de masas por impacto electrónico. El Lexan® (polycarbonato de bisfenol-A) fue estudiado en el rango de dosis de 0.125 a 1.0 MGy. La irradiación del Lexan estuvo acompañada por la liberación preferencial del monóxido de carbono seguida de una producción menor de hidrógeno, dióxido de carbono y metano. El Lexan 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 Lexan por radiación con igual probabilidad: (a) ruptura del enlace carbonato y (b) ruptura del enlace alifático-aromático.

Palabras Clave: Lexan, radiólisis, pirólisis instantánea, CG-IRTF-EM, mecanismo de degradación.

INTRODUCTION

Lexan® is the registered trademark for the bisphenol-A polycarbonate manufactured by General Electric Co. It 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 has been investigated in detail in

some of them¹⁻⁵, but for Lexan this question has not been appropriately addressed. It is known that the interaction of ionizing irradiation with Lexan results in its degradation⁶⁻¹². Electron spin resonance studies of PC at 77 K have shown the formation of $-C_6H_4-O\cdot$, $-C_6H_4\cdot$ and $-O-C_6H_4-C(CH_3)_2\cdot$ radicals⁷. Radiation-induced degradation is accompanied by gas evolution from this polymer but the results of the chemical composition and yields of gases were contradictory^{6,7}. Recently we have shown that the irradiation of Lexan was accompanied by the preferential release of carbon monoxide followed by minor

production of hydrogen, carbon dioxide and methane¹³. 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}. In addition some attempts have been made to modify Lexan via radiation grafting to introduce new functional groups into this polymer or to crosslink it in the presence of special additives to improve the chemical resistance of Lexan against organic solvents¹⁴⁻¹⁶, but nature of active centers in irradiated Lexan 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 Lexan.

Pyrolysis-gas chromatography (Py-GC) is widely used for polymer characterization as a rapid and extremely sensitive technique of investigation that provides unique structural information for polymeric materials¹⁷⁻²¹. Py-GC, in combination with mass spectrometry (MS), IR spectroscopy, size exclusion chromatography and nuclear magnetic resonance, was used for PC characterization^{22,23}. In addition direct Py-MS was employed for investigation of thermal fragmentation processes in Lexan²⁴⁻²⁶. 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 transformations in the irradiated Lexan.

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

MATERIAL AND METHODS

Lexan pellets (LBW248) of about 2 mm thickness were supplied by General Electric Co. 10 g of the pellets 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 in the ⁶⁰Co γ -source (Gammabeam 651 PT, Nordion International Inc.) at doses from 0.125 to 1.0 MGy with a dose rate of 7 kGy/h. Fricke dosimeter was used to determine the dose rate of irradiator under the experimental conditions used.

Analyses of gases and pyrolyzates of blanks and irradiated Lexan were performed using a Hewlett Packard (HP) gas chromatograph 5890 series interfaced in parallel with a HPFTIR-detector (model 5965) and a HP quadrupole mass spectrometer (5989B) operating in electron impact mode at 70 eV (Fig.1). The

column used was a PoraPlot Q fused-silica 25 m long x 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 Lexan were injected into the gas chromatograph by an automatic 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 FTIR 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 cm³ min⁻¹ capacity.

Powder of irradiated and non-irradiated Lexan (particles size of 60 μ m) 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 60 s. The resulting pyrolyzed gases and volatiles were injected 60 s after pyrolysis into the injection port of the gas chromatograph by an automatic port gas-sampling valve (Fig. 1). 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 138KMS and EPA IR Vapor Phase Databases.

RESULTS AND DISCUSSION

Figure 2 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. 3-5). Hydrogen is not detected by our analytical platform and so we inferred its

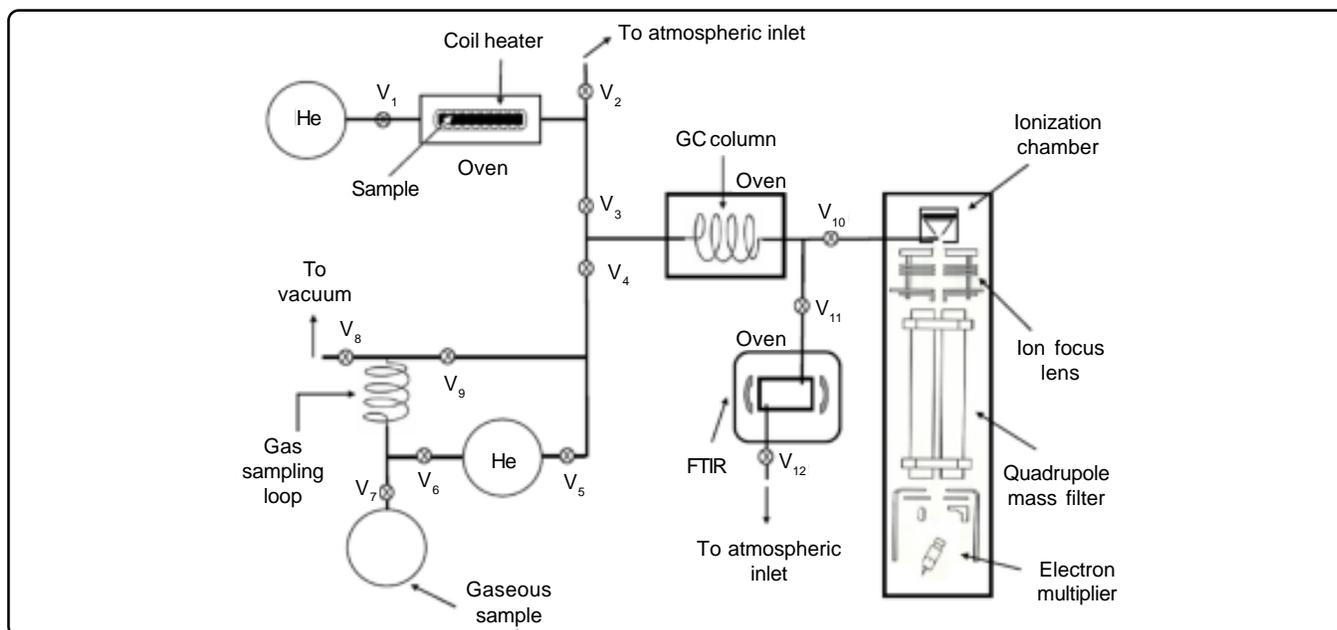


Figure 1. Schematic diagram for the analysis of gases and volatiles released by flash pyrolysis by gas chromatography coupled Fourier transform infrared spectroscopy and mass spectrometry.

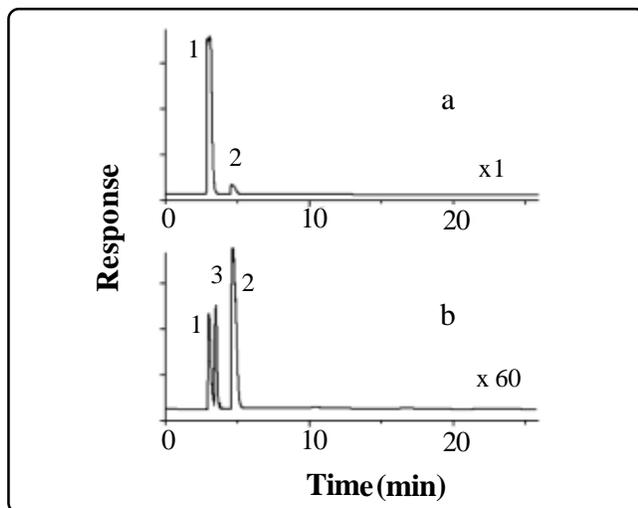


Figure 2. Reconstructed gas chromatogram of gases evolved from γ -irradiated Lexan (0.66 MGy). Ion 28 m/e (a), ion 16 m/e (b). Carbon monoxide (1), carbon dioxide (2), methane (3).

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. Fig. 6, as an example, shows this dependence. The radiation-chemical yields G (expressed as the number of molecules formed per 100 eV of energy absorbed) of gaseous products from irradiated Lexan were calculated, normalized to carbon monoxide and are reported in Table I. Thus, Lexan irradiation is accompanied by the preferential release of carbon monoxide followed by minor production of

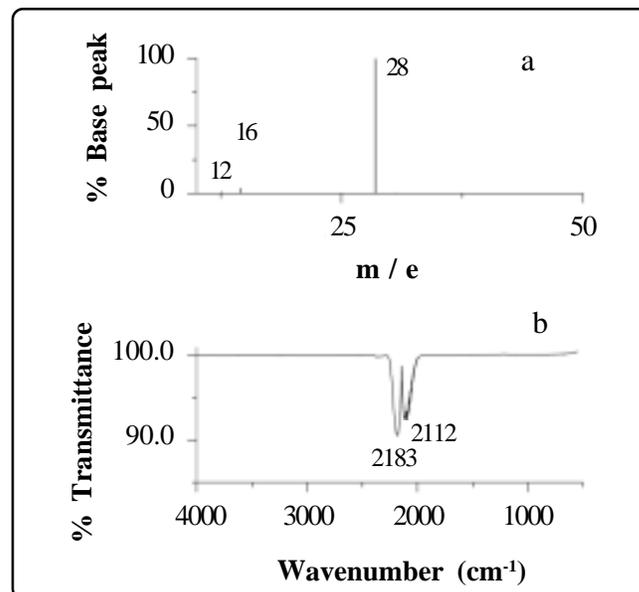


Figure 3. Mass spectrum (a) and infrared spectrum (b) of carbon monoxide formed from γ -irradiated Lexan.

hydrogen, carbon dioxide and methane. Our results are consistent with the data of Golden and Hazell⁶; nevertheless, the published results from Hama and Shinohara⁷ 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 Lexan 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

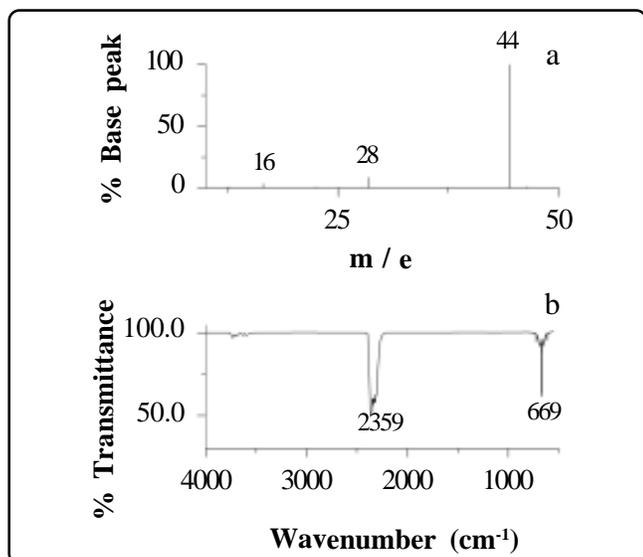


Figure 4. Mass spectrum (a) and infrared spectrum (b) of carbon dioxide formed from γ -irradiated Lexan.

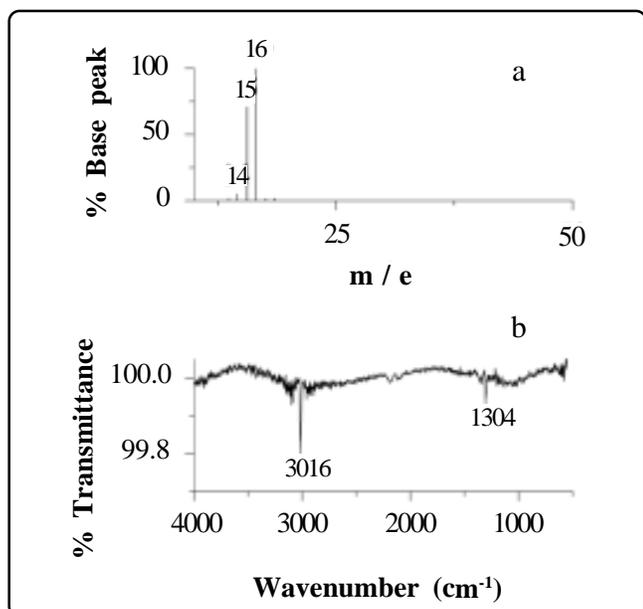


Figure 5. Mass spectrum (a) and infrared spectrum (b) of methane formed from γ -irradiated Lexan.

Lexan (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 ESR⁷ in which these radicals are formed in channel b: $-\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2\cdot$ and $-\text{C}_6\text{H}_4\cdot$; but their final stable products are not found in the gas phase.

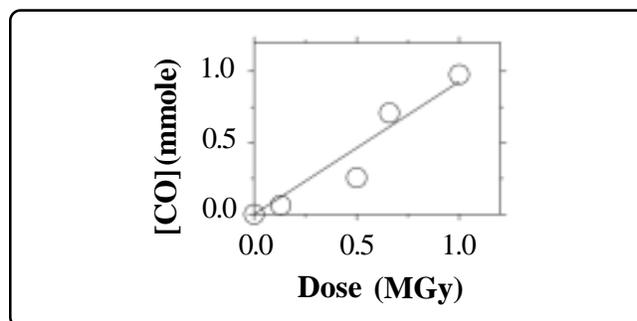


Figure 6. Yield of carbon monoxide from γ -irradiated Lexan as a function of dose.

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

Table I. Yields of gases from irradiated Lexan.

Pyrolyzates of irradiated and non-irradiated Lexan are essentially similar in the type of products formed. Figure 7 shows a typical gas chromatogram of an irradiated Lexan which was reconstructed by mass spectrometry. The main products of both irradiated and non-irradiated Lexan 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 8 and 9 show the MS and IR for phenol and 4-methylphenol. Other minor products shown in Figure 7 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 10 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 II. 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 Lexan. 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 Lexan by radiolysis whereas those of phenol and 4-methylphenol increase roughly the same slope with radiation dose. It must be emphasized

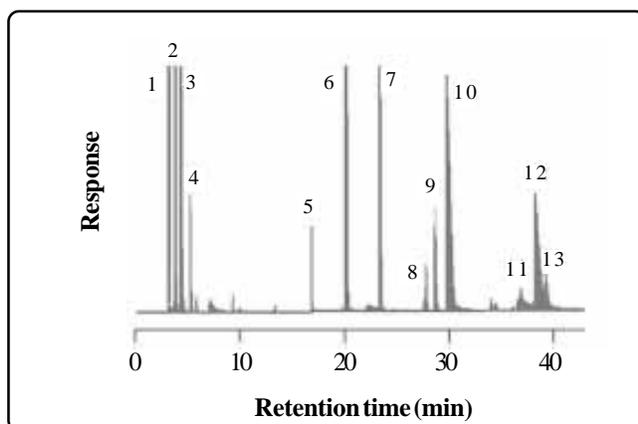
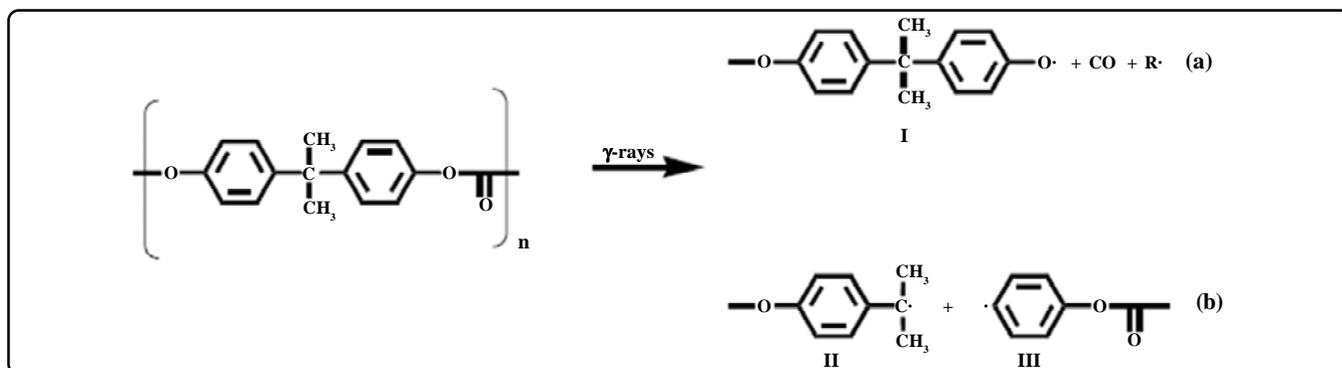


Figure 7. Reconstructed gas chromatogram of gamma irradiated Lexan (0.66 MGy) subjected to pyrolysis. Traces of air (1), methane (2) carbon dioxide (3), ethene (4), cyclopentadiene (5), benzene (6), toluene (7), dimethylbenzene (8), vinylbenzene (9), phenol (10), ethenylmethylbenzene (11), 4-methylphenol (12) and 1-pronnylbenzene (13).

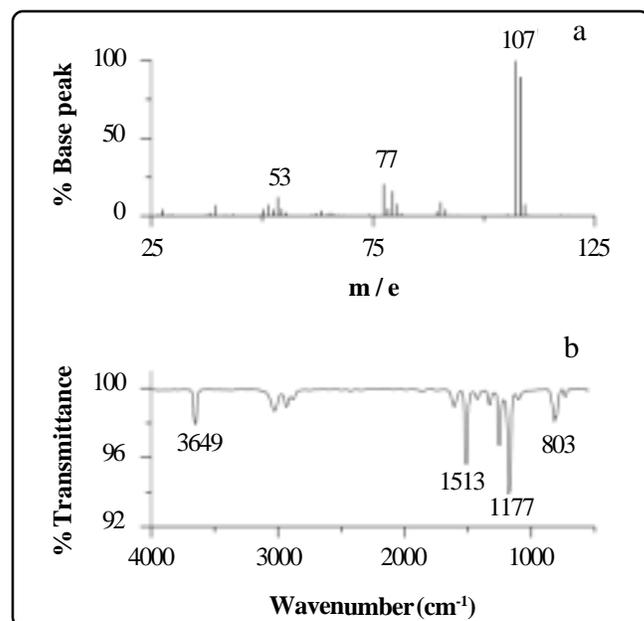


Figure 9. Mass spectrum (a) and infrared spectrum (b) of 4-methylphenol formed by pyrolysis of γ -irradiated Lexan.

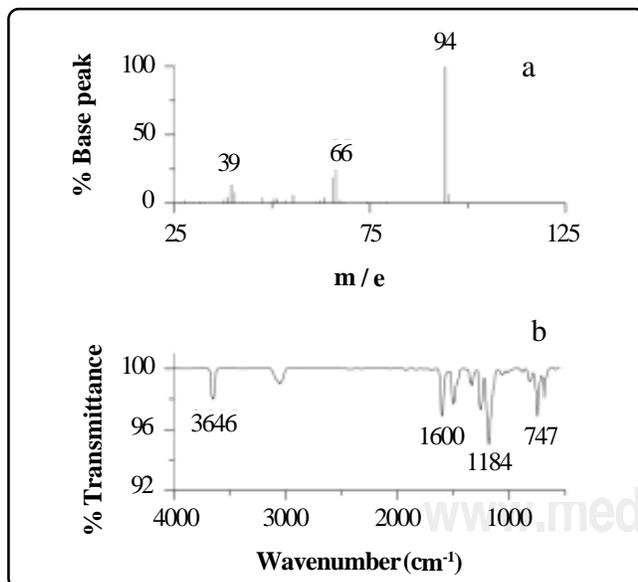


Figure 8. Mass spectrum (a) and Infrared spectrum (b) of phenol formed by pyrolysis of γ -irradiated Lexan.

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 Lexan according to channel a. Decarboxylation is not a significant process in irradiated Lexan 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 Lexan. However, it can be

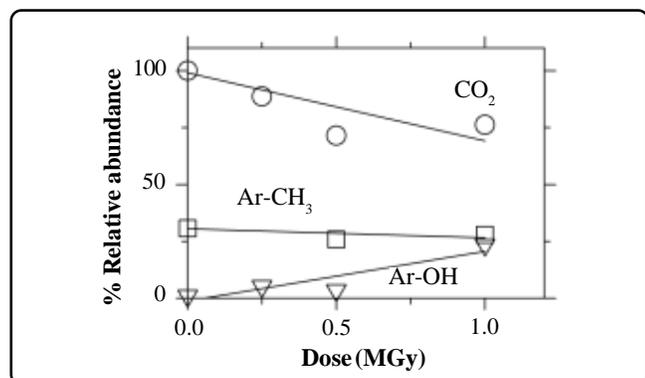


Figure 10. Dependence of the relative abundance of pyrolyzates as a function of dose.

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.

Table II. Production rate of main pyrolytic products of γ -irradiated Lexan.

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-methylphenol in irradiated Lexan 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 pyrolyzates we conclude that channels a and b occur with equal probabilities and are the main channels of radiation-induced scission of Lexan.

CONCLUSIONS

γ -Irradiation of Lexan 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 Lexan 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 Lexan enabled us to deduce the mechanism of gamma radiation-induced scission of this 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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