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Gaseous products formed by γ-irradiation of bisphenol-A polycarbonate

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Summary

Bisphenol-A polycarbonate (PC) was γ-irradiated under vacuum at doses from 125 to 1000 kGy. Gases formed were analyzed by gas chromatography - mass spectrometry, and their radiation-chemical yields (G) were calculated. The total G value of gases was equal to 1.00 molec/100 eV, and main products of PC radiolysis were carbon monoxide and hydrogen, their G = 0.87 and 0.08, respectively. Traces of methane, carbon dioxide, acetaldehyde and acetone were detected at doses above 300 kGy. It has been found that acetaldehyde and acetone were produced practically by radiolysis of carbon monoxide - hydrogen mixture evolved from the irradiated PC. Mechanism of gaseous products formation by the PC irradiation has been discussed.

Introduction

Effects of ionizing radiation on properties of bisphenol-A polycarbonate (PC) have been investigated by many workers (1-8). It has been shown that PC irradiation results in its degradation and accompanies by changes in mechanical, electrical and optical properties of this polymer. Gas evolution by the PC irradiation has been reported also (1,2), mainly carbon monoxide and carbon dioxide were formed but data on their yields were contradictory; besides, some amounts of hydrogen and oxygen were detected. Other gases evolved from irradiated PC or compounds formed probably from primary gases by their radiolysis were not identified. It should be noted that gas evolution from many irradiated polymers was investigated in details (9-11) but data for irradiated PC were not compiled in these fundamental monographs. Apparently, gas formation by radiolysis of this polymer was studied insufficiently. Information about gas evolution in combination with other data concerning irradiated polymers (IR spectroscopy, electron spin resonance, fragmentation by thermal decomposition etc) can be useful for explanation of mechanism of different radiation-chemical transformations in these materials: destruction, crosslinking, graft polymerization, block copolymerization.

This work presents new data on composition and yields of gaseous products formed by radiation processing of PC.

Experimental

10 g of PC pellets (Lexon, LBW248), supplied by General Electric Co, were introduced into a 100 ml cylindrical Pyrex reactor equipped with a high-vacuum stainless steal stopper. The reactor was then connected into a vacuum manifold and the air from the

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reactor and that absorbed in the pellets were pumped out for 1 hr at 10^{-7} bar. Then the reactor was closed and irradiated with a ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) at doses from 125 to 1000 kGy with a dose rate of 7 kGy/h. Fricke dosimeter was used to determine absorbed dose rate under the experimental conditions used. During irradiation of PC, gas molecules were released and accumulated inside the reactor.

Analyses of irradiated samples and blanks 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) equipped with electron impact and chemical ionization modes. The gases were injected into the gas chromatograph by an automatic six-port gas-sampling valve with a gas loop of 2 ml. The column used was a 25 m x 0.32 mm I.D. PoraPlot Q fused-silica with a 2.5 m particle trap. The temperatures at the interfaces and in the FTIR flow cell were at 260°C. 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 carrier gas used was helium (chromatographic grade from Praxair, Inc.) with a flow of 1.2 ml min^{-1}. The products were identified on the basis of their retention times using standards and their spectral properties. In addition, their spectra were also compared with two commercial spectral libraries: Wiley 138K MS and EPA IR Vapor Phase Databases. Yields of gases were derived from calibration curves of standard gases diluted 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.

Results and discussion

Colourless pellets of the starting PC became yellow and then brown with increasing dose. Decrease in weight of irradiated pellets, as compared with the starting ones, changed from 0.08 to 0.4% within the doses used. In earlier studies it was found that starting molecular weight of this PC decreased from 18,000 to 5,800 after γ-irradiation to a dose of 400 kGy (12). These results suggested the formation of gas products from PC and its strong chains scission.

Fig.1 shows selective-ion chromatograms of the gaseous products formed. Carbon monoxide was the main product followed by carbon dioxide and methane. The other compounds had a very low concentration in the gas mixture analyzed. The identity of these compounds was confirmed by electron impact mass spectrometry at 70 eV and/or by FTIR spectroscopy (Figs. 2 and 3). Acetaldehyde and acetone could not be identified by infrared spectroscopy due to their very low concentrations. Total yield of gases as well as yields of carbon monoxide, carbon dioxide and methane increased with the absorbed dose (Fig.4). The hydrogen yield was calculated from the difference between measurements of total gas pressure and analysis of gases from GC-MS. Radiation-chemical yields (G) of gaseous products formed by the PC irradiation are reported in Table 1. It should by noted that hydrogen yield from PC was approximately 10-fold higher or lower as compared with irradiated polymers containing aromatic groups, e.g. polystyrene and poly(ethylene terephthalate), or with polyolefins, respectively (9-11).

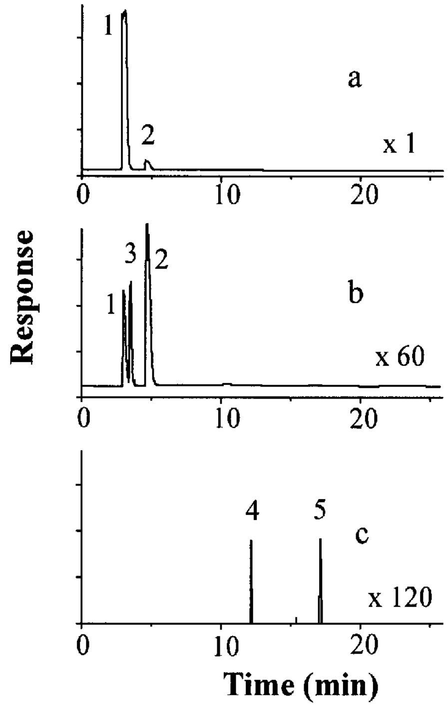

Figure 1. Reconstructed single-ion gas chromatograms of products arising from γ-irradiated PC at 664 kGy. (a) ion 28 m/e, (b) ion 16 m/e and (c) ion 43. Peak identifications: 1. Carbon monoxide; 2. Carbon dioxide; 3. Methane; 4. Acetaldehyde; and 5. Acetone.

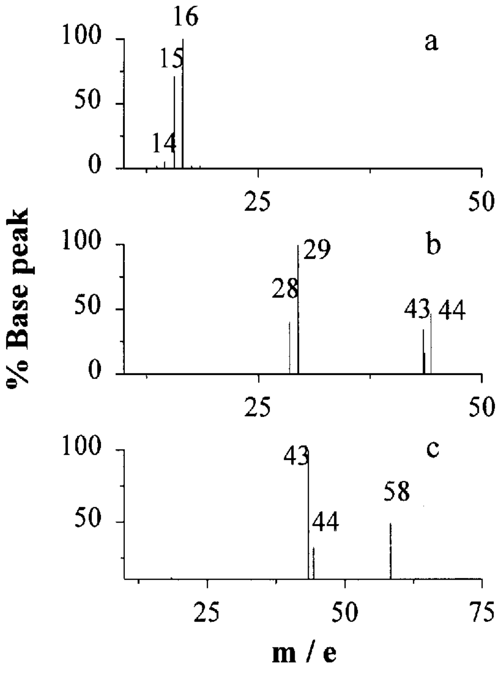

Figure 2. Mass spectra pattern of (a) methane, (b) acetaldehyde, and (c) acetone formed from PC irradiated at 500 kGy.

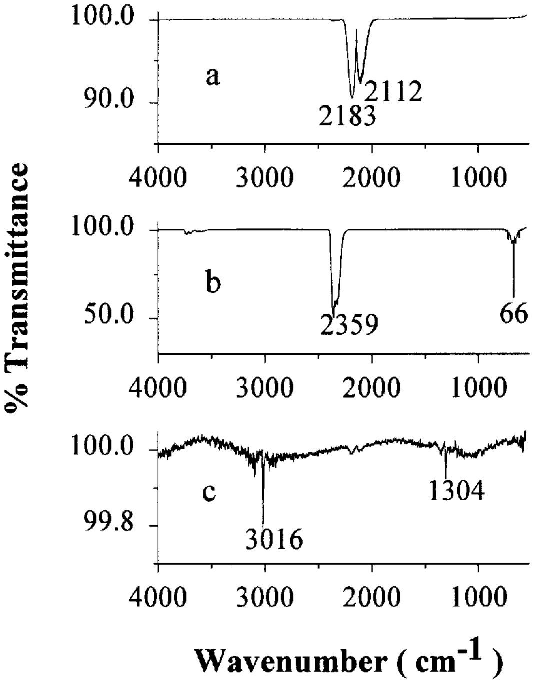

Figure 3. Infrared spectra of (a) carbon monoxide, (b) carbon dioxide, and (c) methane formed from PC irradiated at 375 kGy (4 cm^{-1} resolution).

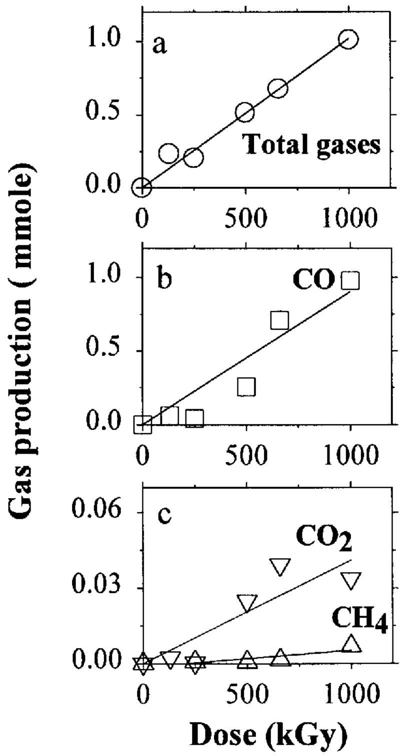

Figure 4. Yields of major (a and b) and minor (c) products from irradiated PC as a function of dose.

Table 1. Radiation-chemical yields of gases from irradiated PC

Compound	Identification	G (molec/100 eV)
Total	Gas pressure	1.00
Carbon monoxide	MS + FTIR	0.87
Hydrogen		0.08
Carbon dioxide	MS + FTIR	0.04
Methane	MS + FTIR	0.006
Acetaldehyde	MS	0.00002
Acetone	MS	0.00002

Thus, PC irradiation is accompanied by essential yields of carbon monoxide and hydrogen. These data differ essentially from results reported earlier (1,2). Apparently, carbon monoxide and carbon dioxide are produced by the PC chain breaking through carbonate bond rupture, and hydrogen is formed due to H radicals abstraction from methyl groups of this polymer. Mechanism of these gases formation corresponds to data based on IR investigation of irradiated PC (5). Appearance of methane traces can be explained by abstraction of methyl radicals from the polymer chain to a low extent with their following recombination with H radicals.

It is possible to assume that acetaldehyde, acetone and some part of methane are formed due to radiolysis of the gases evolved by the PC irradiation. Small quantities of methane and formic aldehyde were detected earlier by the carbon monoxide - hydrogen mixture irradiation with fission fragments from $^{235}U_3O_8$ (13). To verify this assumption, γ-irradiation of these gases mixture with amounts and molar ratio corresponding to yields of these gases from the irradiated PC was carried out at 1000 kGy. This experiment resulted in formation of appreciable quantities of methane, acetaldehyde and acetone. Yield of methane was equal to 0.2 µmole, *i.e.,* essentially less than by PC irradiation at this dose (Fig. 4c). Nevertheless, acetaldehyde and acetone were formed in amounts comparable with their yields found by the PC irradiation (0.02 µmole). These data supports the contention that methane results from the irradiated PC mainly, but radiolysis of the carbon monoxide - hydrogen mixture is responsible for the acetaldehyde and acetone formation.

Conclusion

γ-Irradiation of PC resulted in formation of different gases. It has been found that their total G = 1.00 molec/100 eV, and main gaseous products of PC radiolysis were carbon monoxide and hydrogen, their G = 0.87 and 0.08, respectively. Traces of methane, carbon dioxide, acetaldehyde and acetone were detected at doses above 300 kGy. Carbon monoxide, hydrogen, carbon dioxide and methane (main part) evolved from the irradiated PC but acetaldehyde and acetone were produced by radiolysis of carbon monoxide - hydrogen mixture in the gas phase.

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