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Gaseous Products formed by γ-Irradiation of Poly(1,4-Butylene Terephthalate), Poly(Ethylene Terephthalate) and Poly(Ethylene 2,6-Naphthalenedicarboxylate)

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Summary

A comparative investigation of gaseous products formed by γ-irradiation of poly(1,4-butylene terephthalate), PBT; poly(ethylene terephthalate), PET; and poly(ethylene 2,6-naphthalenedicarboxylate), PEN has been performed. These polyesters were irradiated under vacuum at doses from 0.5 to 4 MGy. The gases formed were analyzed by gas chromatography - mass spectrometry, and their radiation-chemical yields (G) were calculated. Hydrogen, carbon monoxide and carbon dioxide, as the main products, and methane of low quantity were found after radiolysis of all polyesters studied. Other hydrocarbons such as ethane, propane, propene and n-butane were also detected in gases mixture resulted from irradiation of PBT. Traces of ethane were also registered in the radiolysis products of PET. Irradiation of PEN did not lead to formation of hydrocarbons other than methane. The total G values and compositions of the formed gaseous mixtures depended on chemical structure of the irradiated polyesters. Mechanism of gaseous products formation has been discussed.

Introduction

Interaction of high energy irradiation with polymers is accompanied, as a rule, by essential evolution of gaseous products. Gas evolution from many irradiated polymers has been investigated in details, and radiation-chemical yields (G) of the gases formed were compiled in the fundamental monographs on radiation chemistry (1,2). Information about yields and compositions of gases produced by polymers irradiation in combination with other data concerning irradiated polymers (IR and ESR spectra, fragmentation by thermal decomposition, swelling, mechanical properties etc) is useful for characterization of radiation stability of polymers and for explanation of mechanism of different radiation-chemical transformations in these materials: crosslinking, destruction and graft polymerization (1-3).

There are data about formation of carbon monoxide, carbon dioxide (main products), hydrogen and methane within a total G of 0.2-0.3 molecules/100 eV by γ-irradiation of poly(ethylene terephthalate), PET in vacuum (1). Besides, hydrogen, carbon monoxide and ethylene were evolved under 180 MeV Ag^- ion irradiation of PET but G values of these gases were not determined (4). It is known that PET is a polymer of medium radiation stability and it has a predominent tendency to radiation degradation (3). At present, there is an increasing interest to radiation processing of poly(1,4-butylene terephthalate), PBT and poly(ethylene 2,6-naphthalene-dicarboxylate), PEN – promising engineering plastics with good mechanical and thermal properties (5-10). It has been shown that PBT can be crosslinked by γ- or electron irradiation but in the presence of a crosslinking reagent (5). Higher chemical resistance of tracks formed in PEN

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by irradiation with the accelerated ions (Kr, Xe and Bi), compared to the virgin polymer, indicated crosslinking effects in irradiated PEN (9). But it seems to be no data about gas evolution from the irradiated PBT and PEN.

This work presents a comparative investigation of compositions and yields of gaseous products formed by radiation processing of PBT, PET and PEN.

Experimental

PBT, PET and PEN pellets (molecular weights of 2-3.5 $\cdot 10^5$) as well as phenol and tetrachloroethane were supplied by Aldrich Chemical Co.

20 g of each polyesters sample were introduced into a 100 ml cylindrical Pyrex reactor of a "T-form": one of branch tubes served for the pellets loading and the reactor pumping out, and the other one (closed by thin glass partition) – for the subsequent reactor connection to a gas chromatograph. The reactor with pellets was connected into a vacuum manifold and the air from the reactor and that absorbed in the pellets were pumped out for 1 hr at 10^{-7} bar. Then the branch tube was sealed under vacuum, and reactor was irradiated with a ^{60}Co γ-source (Gammabeam 651 PT, Nordion International Inc.) at doses from 0.5 to 4 MGy with a dose rate of 6 kGy/h. Fricke dosimeter was used to determine absorbed dose rate under the experimental conditions used. During irradiation of polymers, 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 with a HP quadrupole mass spectrometer (5989B) equipped with electron impact and chemical ionization modes. The reactor was connected to the chromatograph, the glass partition in the branch tube was broken with a special tool, and 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 × 0.32 mm I.D. PoraPlot Q fused-silica with a 2.5 m particle trap. The temperatures at the interfaces 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 the commercial spectral library Wiley 138K MS. 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.

The solubility of the irradiated PBT, PET and PEN pellets was tested in phenol/tetrachloroethane mixture of 40/60 weight ratio at 80^{0}C (11,12).

Results and discussion

The starting white-color pellets became dark with the irradiation dose, the most intensive darkening was observed for PBT.

Figure 1 shows chromatograms of the gaseous products formed from the irradiated PBT. Carbon monoxide and carbon dioxide were the main products followed by five hydrocarbons of low concentration. These carbon oxides (main products), methane and ethane (minor products) were found also in chromatogram of gases evolved from the irradiated PET. But only carbon oxides and methane were detected in the case of PEN. Thus, the chromatograms of products formed by irradiation of these polyesters differed in the minor products detected. The identity of all these compounds was confirmed by electron impact mass spectrometry at 70 eV (Fig.2). Hydrogen was

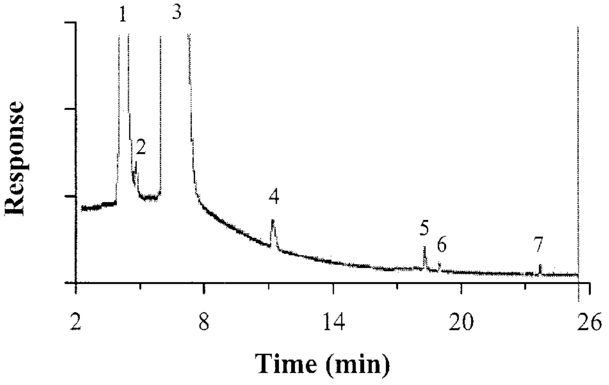

Figure 1. Reconstructed gas chromatograms of products arising from γ-irradiated PBT at 2.5 MGy. 1. Carbon monoxide; 2. Methane; 3. Carbon dioxide; 4. Ethane; 5. Propane; 6. Propene; and 7. n-Butane.

not detected by the chromatograms, and yields of this gas were calculated from the difference between measurements of total gas pressures and analysis of gases from GC-MS.

Total yields of gases evolved from all these polyesters increased with the absorbed dose (Fig.3).

It should be noted that total G values of gases from the irradiated PBT, PET and PEN (Table 1) were approximately 30-150 –fold less as compared with irradiated polyolefines or polyacrylates (1,2). It is known that polymers, containing aromatic groups, are more stable against radiation in contrast to the other ones due to dissipation of ionizing radiation energy in these groups. The resonance electronic structure of aromatic rings allows a large fraction of the energy of excited molecules to be channeled to relatively low-energy excited states that have a low probability of these molecules dissociation. Besides, the aromatic groups can also act as traps for the energy absorbed by other parts of molecules (2,3). Thus, aromatic groups in polymers decrease efficiency of all radiation-chemical transformation, including gas evolution, in irradiated polymers.

A considerable difference in total yields of gases from irradiated PBT, PET and PEN can be explained by the presence of different aromatic and aliphatic groups in these polymers. Naphthalene and its derivatives are known as the very active antirads (protectors) which increase radiation resistance of polymers (3). Apparently, naphthalene groups of PEN exert a higher protective effect than phenylene groups of PET that explains an essential dufference in amounts of gases evolved from these irradiated polymers. As to PBT and PET, which have the same phenylene groups, a higher yield of gases from the former polymer was conditioned, probably, by the different hydrocarbon chains.

Table 1 shows that hydrogen was the predominant product, and, obviously, it is produced mainly due to H radicals abstraction from the aliphatic groups of the polyesters. Besides, it is possible to assume that some part of hydrogen is produced by radiolysis of hydrocarbons formed in the gas phase but this contribution is difficult to estimate. It is known that hydrogen yield from the irradiated aromatic compounds is approximately 15-fold lower as compared with aliphatic ones

(2), and, in our case, contribution of hydrogen from phenylene and naphthalene groups practically did not affect the total yield of this gas. It is clear, that carbon monoxide and carbon dioxide were produced by the chains breaking through ester bond rupture. These products were found earlier by irradiation of polyesters as well as polyacrylates an polycarbonates (1,2,13). Difference in yields of hydrogen at the same yields of carbon oxides for PBT and PET may be explained by the longer aliphatic chains in PBT. In this case, the protecting efficiency is less, probably, with increase in distance from the phenylene groups. The analogous effect was found by irradiation of aromatic hydrocarbons with different length of side aliphatic chains (14). Traces of methane and other hydrocarbons appeared, to all probability, by ruptures in aliphatic chains in the polyesters. In spite of a very low yield of these compounds we were able to estimate a contribution of the detected products to the total hydrocarbons yield (Table 2). The individual

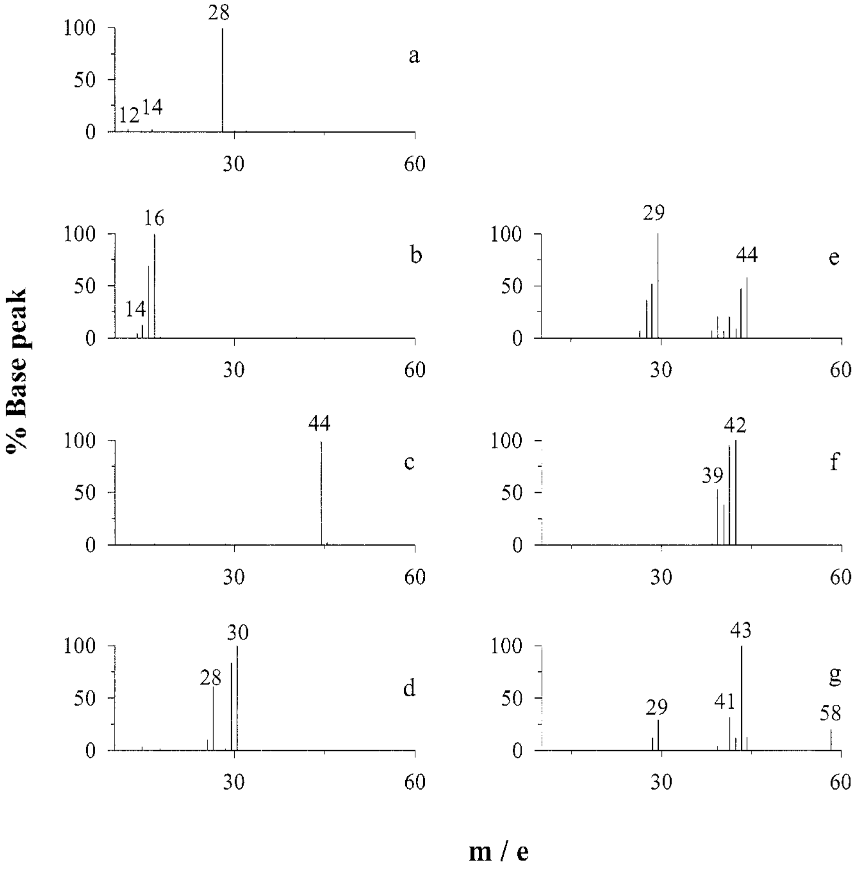

Figure 2. Mass spectra pattern of (a) Carbon monoxide; (b) Methane; (c) Carbon dioxide; (d) Ethane; (e) Propane; (f) Propene; and (g) n-Butane formed from PBT irradiated at 2.5 MGy.

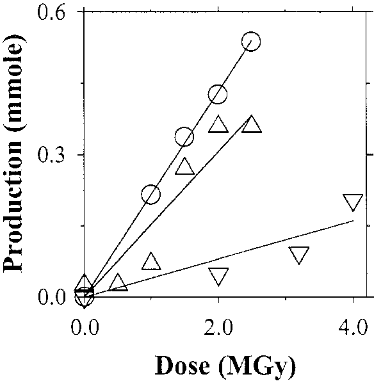

Figure 3. Total yields of gases from irradiated PBT (O), PET (△), and PEN (▽) as a function of dose.

Table 1. G values of gases (molecules/100 eV) from irradiated polymers

Compound	PBT	PET	PEN
Total	0.11	0.07	0.02
Hydrogen	0.09	0.04	0.02
Carbon monoxide	0.01	0.01	0.001
Carbon dioxide	0.01	0.01	0.002
Methane	0.0001	0.01	0.0001
Other hydrocarbons	0.0002	0.0001	Not detected

Table 2. Contribution of hydrocarbons (%) to their total yield

Compound	PBT	PET
Methane	33	99.9
Ethane	36	0.1
Propene	18	Not detected
Propane	10	Not detected
n-Butane	3	Not detected

yields of these compounds showed that abstraction of the aliphatic fragments in full length was unlikely.

According to our data on composition and yields of gaseous products evolved from the irradiated PBT and PET, it was possible to assume that not only degradation but also a crosslinking of these polymer occurred. The ester bonds rupture, accompanied by the carbon oxides evolution, will result in destruction (scission) of macromolecules, and contribution of the aliphatic chains scission to destruction of these polyesters is insignificant. But radicals that appear by the hydrogen abstraction from the aliphatic groups of our polyesters, could form intermolecular crosslinks. However a gel fraction was not found by the test of the irradiated polyesters solubility that indicated absence of radiation crosslinking in the polyesters under given conditions of irradiation. Low total yield of gases from the irradiated PEN testifies high radiation stability of this polymer, and essential radiation-chemical transformations in it are unlikely even at high absorbed doses of some MGy.

Conclusion

γ-Irradiation of PBT, PET and PEN resulted in formation of different gases. The main gaseous product was hydrogen followed by carbon monoxide, carbon dioxide and traces of methane, ethane, propane, propene and n-butane. The total G values of gases evolved from the PBT, PET and PEN were equal to 0.1, 0.07 and 0.02 molecules/100 eV, respectively, that indicate a different radiation stability of these polymers. These values and compositions of the formed gaseous mixtures depended on chemical structure of the irradiated polyesters.

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