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A comparative radiation degradation of some aromatic polyesters

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Summary

A comparative investigation of radiation degradation of poly(1,4-butylene terephthalate), PBT; poly(ethylene terephthalate), PET; and poly(ethylene 2,6-naphthalene-dicarboxylate), PEN, was carried out. These polyesters were irradiated under vacuum at doses from 0.5 to 4 MGy. Data on solubility of the irradiated polyesters revealed absence of cross-linking. Molecular weights of PBT and PET decreased noticeably after irradiation, and radiation-chemical yields of destruction were quantified. NMR and UV spectra revealed changes in molecular structure upon irradiation of PBT. Efficiency and mechanism of radiation degradation of PBT, PET and PEN were discussed.

Keywords:

Polyesters, Gamma-irradiation, Gas formation, Degradation, Radiation-chemical yields

Introduction

Interaction of high energy irradiation with polymers results, as a rule, in the formation of gaseous products accompanied by polymer crosslinking (the formation of intermolecular bonds), degradation (the scission of bonds in the main polymer chain and in side chains) and some other secondary processes. These transformations and their radiation-chemical yields have been investigated and calculated, respectively, for many polymers; these data are compiled in monographs on radiation chemistry [1-3]. Information about yields and composition of gases produced by polymer irradiation in combination with data concerning irradiated polymers (changes in molecular weights, swelling, different spectral characteristics, etc) is useful to explain the mechanisms and efficiency of radiation-chemical transformations in these materials. It should be stressed that the evaluation of polymers radiation stability (resistance to irradiation) is of great importance in nuclear engineering (nuclear reactors, radioisotope installations), electron and other particles accelerators, or in devices operating under outer-space conditions [2-5].

It is known that poly(ethylene terephthalate), PET is the most widely used thermoplastic polyester, and it has a medium stability upon irradiation with a predominant tendency to degrade. The value of the absorbed dose of gamma irradiation at which it shows noticeable degradation is about 1 MGy [6]. Recently, the irradiation stability of PET at 3 MeV proton dose was analyzed [7]. There is a number of publications concerning effect of irradiation on poly(1,4-butylene terephthalate), PBT and poly(ethylene 2,6-naphthalene-dicarboxylate), PEN, which are engineering plastics with good mechanical and thermal properties [8-14]. It has been shown that PBT can be crosslinked by gamma or electron irradiation in the presence of crosslinking reagents. Compared to the starting polymer, a substantial chemical resistance due to crosslinking was observed in PEN samples irradiated with accelerated ions (Kr, Xe and Bi). It has been shown earlier that radiolysis of terephthalate and naphthalate aliphatic polyesters resulted in formation of aromatic and aliphatic radicals [15]. G values of these radicals increased with the length of the aliphatic chains, and yields for the terephthalate-based polyesters were higher than those of the corresponding naphthalate-based polyesters.

It is interesting to compare an efficiency of radiation-chemical transformations in PET, PBT and PEN and relate them to their chemical structure. Recently, we investigated the comparative yields and compositions of gaseous products formed by gamma-irradiation of PET, PBT and PEN [16]. These gases were analyzed by gas chromatography - mass spectrometry. We have found that yields and compositions of the formed gaseous mixtures depended on chemical structure of the irradiated polyesters. However, changes in the molecular weights and in other structural characteristics of these irradiated materials were not considered.

This work presents a comparative investigation of radiation degradation of PBT, PET and PEN, based on the analysis of the gaseous products upon irradiation of these polyesters, changes in molecular weights and spectral characteristics of the irradiated polyesters.

Experimental

PBT, PET and PEN pellets, phenol and solvents (tetrachloroethane, m-cresol, deuterated trifluoroacetic acid, and deuterated chloroform) were supplied by Aldrich Chemical Co.

20 g of each polyester sample were 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 the absorbed dose rate under the experimental conditions used.

Solubility of the starting and irradiated PBT, PET and PEN pellets was tested in phenol/tetrachloroethane mixture of 40/60 weight ratio at 80°C [17,18].

Molecular weights of the starting and irradiated polyesters were determined in a Waters GPC High-Temperature chromatograph with a HT Styragel 6E column. The system was calibrated with a polystyrene TSK standard (TOSOH, Japan). The tests were performed using 0.05 g/ml of polymer solution in m-cresol at 135°C.

Radiation-chemical yields of the polyesters degradation (G_d) are calculated using the Charlesby equation [3]:

$$G_d = 9.65 \cdot 10^3 \,(1/M_{n1} - 1/M_{n0}) / D$$

where G_d stands for scission/100 eV, D is the absorbed dose (MGy), M_{n0} and M_{n1} are the number-average molecular weights of the starting and irradiated polymers, respectively.

NMR measurements were performed at ambient probe temperature using 5 mm sample tubes. Solution ^{1}H and spectra of the $CDCl_3$ / CF_3COOD mixture (70/30 by volume) were recorded using a Varian Gemini 200 and a Varian Unity *Plus* 300 spectrometer.

UV-visible spectra were recorded in a CARY 400 Varian Spectrometer using 0.01g/dL of polymer solution in a phenol-tetrachloroethane mixture (40/60 by weight) at room temperature.

Results and discussion

Table 1 presents data obtained in our previous work on gaseous products formed upon irradiation of these polyesters [16]. The Table 1 is given here for the visual comparison of efficiencies both gases yields and chemical transformations in the irradiated PBT, PET and PEN. The wide difference in total gas yields 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 well known as radiation-resistant compounds (protectors) [2,3]. Apparently, naphthalene groups of PEN have a higher protective effect than the phenylene groups that explains the essentially lower yield of gases evolved from this irradiated polyester. With regard to PBT and PET, which have the same phenylene groups, the larger hydrogen yield from the former is related to the longer aliphatic chains. It is clear that carbon monoxide and carbon dioxide are produced by ester bond rupture. These products can also be found by irradiation of polyacrylates or polycarbonates [1,3,19]. In addition, it was shown that radiolysis of terephthalate and naphthalate polyesters give rise to aromatic radicals formation [15], which confirms the mechanism of chain breaking in polyesters.

According to data on composition and yields of gaseous products evolved from irradiated PBT, PET and PEN, it is likely that degradation and crosslinking reactions occur simultaneously. The ester bond rupture detected by carbon oxides production

Table 1. Radiation-chemical yields of gases (molecules/100 eV) produced upon polyesters irradiation

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	0.001	0.01	0.0001
Other hydrocarbons	0.002	0.0001	Not detected
Contribution of hydrocarbons (%) to their total yield			
Methane (%)	33	99	
Ethane (%)	36	1	
Propene (%)	18	Not detected	
Propane (%)	10	Not detected	
n-Butane (%)	3	Not detected	

leads to the reduction of molecular weight due to macrochain scissions. The contribution of the aliphatic chains rupture to polymer degradation was essentially less. However, radicals resulting from hydrogen extraction from the polyester aliphatic groups maybe lead to intermolecular crosslinking. Nevertheless, no gel fraction was detected in the solubility test of the irradiated polyesters, which indicates absence of crosslinking.

In PET and PBT, the number-average molecular-weight (M_n) decreases upon irradiation (Table 2). In contrast, M_n practically does not decrease in irradiated PEN. Thus, the naphthalene groups of this polyester have a higher protective effect against its chains breaking under given conditions of irradiation. G_d of irradiated PET was determined elsewhere, with values of 0.07 and 0.17 [20] to 0.4 [21], which are in agreement with those found in the present study. However, data on G_d presented in this work for irradiated PBT has not been reported before.

^{1}H NMR spectra of the starting PBT and irradiated samples are shown in the Figure 1. Irradiation leads to a decrease in the number of aliphatic protons appearing at 2.13 and

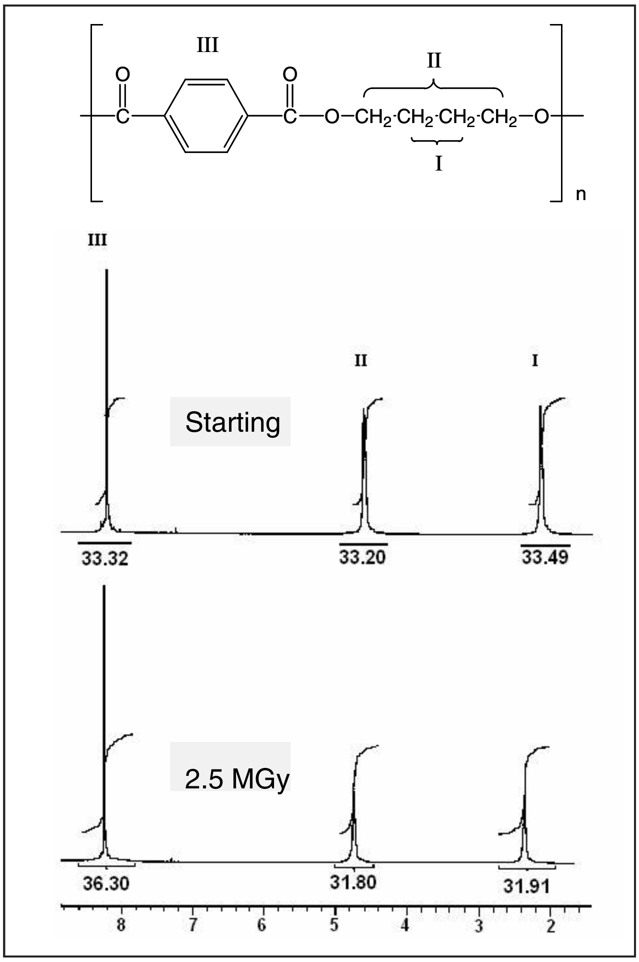

Figure 1. ^{1}H-NMR spectra of the starting and irradiated PBT.

Table 2. Radiation-chemical yields of the polyester degradation

Polyester	Dose (MGy)	M_n	G_d
PBT	0	28600	0.14
	2.5	14200	
PET	0	33800	0.23
	2.5	11100	

4.61 ppm. This can be ascribed to free radical formation resulting from C-H bond rupture in the aliphatic moieties. The formation of such radicals was detected previously by EPR [15]. Besides, UV spectra (Figure 2) revealed an increasing absorbance in the region of 300-350 nm that may be explained by formation of unsaturated bonds along the aliphatic groups of irradiated PBT. Formation of such bonds by radiolysis of polyethylene and some other polymers was reported by other authors [3]. But NMR and UV spectra of the starting and irradiated PET and PEN were practically the same. Thus, higher hydrogen yield by the PBT radiolysis was confirmed by the spectral data.

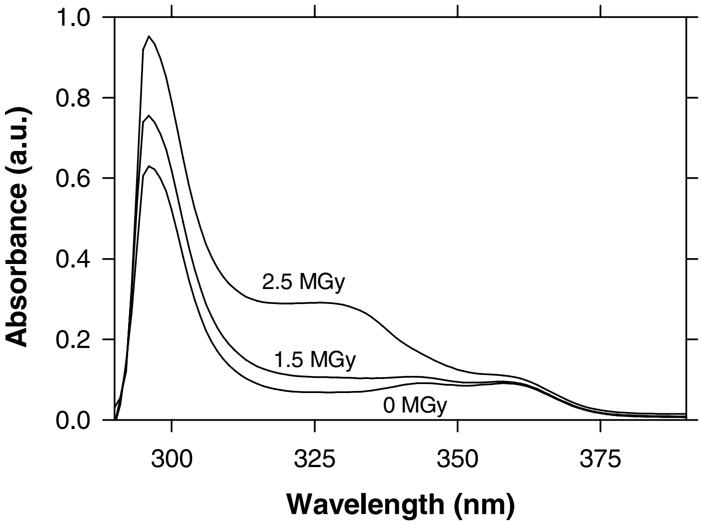

Figure 2. UV spectra of the starting and irradiated PBT.

Conclusions

Gamma-irradiation of PBT, PET and PEN resulted in different yields and compositions of the formed gaseous mixtures. Radiolysis of PBT and PET leads to a decrease in their molecular weights, with G_d values equal to 0.14 and 0.23, respectively. The spectral data reveal a decrease (with respect to starting PBT) in the number of aliphatic protons and formation of unsaturated bonds in aliphatic groups of irradiated PBT. Thus, results indicate different efficiency of radiation degradation occurring in these polyesters depending on their chemical structure. A low gas yield in the irradiated PEN, together with absence of molecular weight changes after irradiation, evidences the high irradiation stability of this polyester.

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