Flame Retardance in Polyester Fabric Radiolytically Grafted with Bromostyrene

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Synopsis

Ionizing radiation was employed to graft bromostyrene (BSy) onto poly(ethylene terephthalate) (PET) fabric. The fire-retardant effect of the polymerized monomer on PET fabric was evaluated both by LOI tests and by DTA and TGA methods under conditions of controlled total combustion. The yields of HBr and BSy evolved during pyrolysis in the presence and absence of oxygen were determined. A linear correlation was found between ΔOI values and yields of HBr, and the implications of this finding are discussed. It is suggested on the strength of DTA and TGA results under total combustion conditions that the fire-retardant effect of poly(bromostyrene) manifests itself mainly by a physical-mode mechanism through a significant reduction in the release of flammable gases.

INTRODUCTION

In recent years there has been considerable interest in graft polymerization as a tool for achieving flame proofing of textiles¹ with special attention given to radiation grafting.²⁻⁴ It was pointed out that the radiation grafting method has two useful characteristics: it is a low energy consumption process, and it appears to have a potential for good fixation of flame retardants.⁵ However, investigation of the fire retardation mechanism when employing radiation-induced grafting has been limited to a small number of monomers and the mechanism of protection is still not well understood.

It is well known that bromine-bearing compounds are effective agents in suppressing burning of a variety of polymers. The brominated aromatic compounds are supposed to be more effective as retardants of poly(ethylene terephthalate) (PET) fabric flammability than aliphatic compounds.⁶ The better performance of the former most likely reflects the fact that the higher degradation temperature of aromatic compounds is a better match to the relatively high decomposition temperature of PET and thus may facilitate the retardant interference in the burning process. Several comparative studies of the effectiveness of aromatic vs. aliphatic brominated compounds have been published,⁷⁻⁹ and the superior retardant capability of the aromatic compounds is, by now, well established. It should be noted that the flame retardancy mechanism of the aromatic compounds is not yet fully understood. Moreover, some of these compounds undergo vaporization during thermal decomposition,⁷ and only a small fraction of them decompose to yield HBr, which has been assumed to be the active species in the flame inhibition reactions induced by brominated compounds.^{10,11} Thus the flame retardation mechanism of brominated aromatic compounds and the role of HBr warrant further investigation.

The aim of this work was to contribute to the understanding of the fire-retardation mechanism of brominated aromatic compounds on PET fabrics through an investigation of the bromostyrene (BSy) grafted PET system. This monomer was chosen because it is an aromatic compound with a simple structure and lends itself to fixation on the PET fabric by means of radiation-induced graft copolymerization. BSy has a relatively low bromine content (43.7%) and its C—Br aromatic bond is quite stable. Thus HBr generation during combustion of the treated fabric can be expected to be low. Nevertheless, it was hoped that these unfavorable features would be compensated to a significant extent by the fact that both PET and poly(bromostyrene) (PBSy) decompose thermally in the same temperature range, a fact that should enhance the efficiency of the fire retardant.⁸

EXPERIMENTAL

Materials

The polyester fabric (Argaman Inc., Yavne) used throughout this work was 4.1 oz/yd^2 , plain woven from 82 denier fibers, treated for fixation at 195°C and chemically cleaned and washed. BSy (Makhtheshim Ltd., Beer-Sheva) consisted of a 5/2 mixture of the para and ortho isomers. The monomer was vacuum distilled prior to use in order to remove the inhibitor. All other chemicals were reagent grade and were used without further purification.

Procedures

In the irradiation grafting experiments a 60 Co gamma cell with an average dose rate of 0.12 Mrad/h was used. The percent add-on in the sample was defined as the increase in weight of the sample divided by the weight of the nongrafted sample multiplied by 100. The percent grafted polymer in the sample was defined as the actual percent of grafted polymer relative to the overall weight of the sample. All samples were extracted for at least 100 h with tetrahydrofuran in a Sohxlet apparatus in order to remove all extractable homopolymer. The samples were dried in a vacuum oven for at least 16 h and kept in a vacuum desiccator over phosphorus pentoxide for at least 24 h before weighing and testing.

Grafting via Preirradiation. The weighed fabric samples were placed in preirradiation grafting tubes equipped with breakseals, and evacuated to a pressure of 10^{-5} torr. The tubes were sealed and irradiated. Following irradiation, the monomer solution was placed in the sidearm connected to the breakseal. The solution was degassed by several freeze-thaw cycles, and evacuated to a pressure of 10^{-3} torr and sealed off. It was then added to the fabric by breaking the seal. Subsequently, the fabric and the solution were maintained in a thermostated bath, or an oven for various periods of time as shown in Table I.

Grafting by Simultaneous Irradiation of Fabric and Monomer. The weighed fabric sample and the monomer solution were placed in a grafting tube. The tube was degassed by freeze-thaw cycles to a pressure of 10^{-3} torr. It was

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PBSy (wt %)	Dose ^a (Mrad)	Reaction time ^b (h)
6.5	3.4	1.5 ^c
7.8	3.4	3c
12.6	6.7	13
12.7	6.3	17°
17.8	6.7	18°
19.3	8.9	17 ^d

TABLE I Grafting Conditions for PET Fabric Preirradiated and Grafted with PBSy

^a Preirradiation dose to the fabric carried out in vacuum.

^b All graft experiments were performed in 50 wt % solutions of BSy in methanol at 84°C.

^c The solution contained 0.2% by weight FeSO₄ for inhibition of homopolymerization.

^d The fabric was preswelled in DMF for 2 min at 140°C, rinsed in water, and dried before grafting. The grafting solution contained $5.34 \times 10^{-2}M$ H₂SO₄ to catalyze the grafting process.

sealed and then irradiated for a predetermined period.

Thermal Analysis. A DuPont-990 Thermal Analyzer with DTA-1200 moduli, and a DuPont-951 Thermogravimetric Analyzer were used. In the DTA experiments, the reference material was alumina and the enthalpy was calibrated by means of the known heat of melting of pure zinc. Every DTA-1200 experiment was performed at least three times in order to check the reproducibility of the results. The heating rate was 10°C/min in all experiments, and the flow rate of the purging gases was 50 mL/min.

HBr Analysis. The procedure for continuously monitoring the evolved HBr was described previously.¹²

Depolymerization. The extent of depolymerization was determined by bubbling the purged gas, leaving the TGA apparatus through a specially designed trap containing 8 mL of cyclohexane. Intact molecules of monomer formed during the thermal decomposition or combustion were trapped in the cyclohexane, and the solution was injected into an HP-5750 gas chromatograph equipped with a DC-200 20% Silicon Rubber 1/4-in. 8-ft column, and a flame ionization detector. The oven temperature was 150°C and the carrier gas was helium. Calibration was carried out with standard solutions of the monomer. The reliability of the method was checked by varying the amount of cyclohexane and the geometry of the trapping device. Good reproducibility of the monomer yields was obtained.

LOI Measurements. Oxygen index determinations were made with an apparatus built in the laboratory. The apparatus was designed according to Isaacs¹³ in accordance with ASTM-D2863-70¹⁴ requirements. In order to prevent melt dripping during the LOI test, the samples were sewed along their length with fiberglass thread as described by Nametz and Smith.¹⁵ The distance between the lines was $\frac{5}{8}$ in. and the density of the stitches was 6/in.

Microanalysis. The bromine content of grafted samples was determined according to the procedure proposed by Schoniger.¹⁶

RESULTS AND DISCUSSION

The PET fibers have a high aromatic ring content and a highly crystalline structure; thus they exhibit a high resistance to ionizing radiation. The G-value

U		
Dose (Mrad)	PBSy (wt %)	Br (wt %)
0.065	0	0
0.19	0	0
0.38	2.1	0.9
0.45	4.6	2
0.53	9.3	4.04
0.57	9.3	4.06
0.57	12.2	5.33 ^b
0.62	12.3	5.36
0.64	20.2	8.82 ^b
0.65	25.6	11.17 ^b
0.85	28.5	12.44
3.50	30.9	13.50 ^b

TABLE II Grafting Conditions for PET Fabric Grafted with PBSy by the Mutual Irradiation Method^a

^a In all the experiments the grafting solution was 30.5 wt % BSy in methanol.

^b Experimentally determined value of % bromine.

of the free radicals formed during γ -irradiation of PET is $0.02.^{17}$ (The *G*-value is the yield of product molecules formed per 100 eV of absorbed energy.) Therefore, PET fibers show a low tendency to undergo grafting and high doses of irradiation are necessary in order to achieve significant add-on levels. The graft copolymerization was carried out by one of two methods: preirradiation of the fabric or mutual irradiation of fabric and solvent. In both cases solutions of BSy in methanol were used.

The results of preirradiation grafting experiments are summarized in Table I and those of irradiation in the presence of the monomer in Table II. It can be seen that much higher add-on percentages can be obtained by the latter method at lower radiation doses than by the former. Since a significant fire-retardant effect is observed only at relatively high add-on of grafted PBSy on PET, the mutual irradiation method was used preferentially throughout this study. The dependence of the percent of grafted PBSy on the irradiation dose for the mutual irradiation method is shown graphically in Figure 1. It can be seen that there



Fig. 1. Effect of dose on the amount of PBSy entrapment in samples of PET fabric grafted by the direct irradiation method. The grafting solution was 30.5% BSy in methanol.

is a short inhibition period, probably due to impurities or residual air, followed by a sharp increase in the percent add-on in the 0.5–0.7 Mrad range, and a leveling-off effect is observed at higher irradiation doses. In the mutual irradiation experiments, homopolymerization of the monomer was observed. The homopolymer yielded in experiments performed at doses higher than 0.6 Mrad swelled up in THF but did not dissolve in it, indicating that a crosslinked structure was formed. Therefore, it can be assumed that the PBSy grafted at doses higher than 0.6 Mrad is also partially crosslinked.

Flame Retardation in Controlled Oxygen Environment Combustion of PBSy-Grafted PET Fabric

Determination of the LOI of some of the samples described in Table II showed that the dependence of the LOI on the bromine content is not linear and the fire retardation effect is not pronounced. In order to obtain additional information on the effectiveness of PBSy in retarding the burning of PET, it was decided to evaluate the flame retardation under total combustion conditions. TGA and DTA methods were employed to follow the combustion and degradation pattern of the grafted samples. TGA thermograms of untreated PET fabric, PET grafted with 30.9% PBSy, and pure PBSy in an N₂ environment are shown in Figure 2. The TGA thermograms of PBSy grafted PET fabric in an O₂ environment are presented in Figure 3. Throughout this study an oxygen environment was used instead of air for the controlled combustion experiments. This procedure was adopted in order to obtain information on the fire-retardant effects of PBSy under conditions favoring total combustion. It should be noted that the TGA of a PET sample exposed to 3.5-Mrad irradiation yielded thermograms undistinguishable from those of untreated material.

The TGA experiments performed in an N_2 environment show that the beginning of decomposition of the grafted fabric compared with pure PET (see Fig.



Fig. 2. TGA thermogram in a N_2 environment, of untreated PET fabric (I), PET grafted with 30.9% PBSy in the sample (II), and pure PBSy (III).



Fig. 3. TGA curves of untreated PET fabric $(-\cdots -)$, pure PBSy $(-\cdots -)$, and PET fabric treated with different amounts of PBSy by the direct irradiation method [% PBSy (% Br) in PET]: (\ldots) 12.2% (5.3%); (--) 20.2% (8.8%); (--) 25.6% (11.2%); (--) 30.9% (13.5%). Experimental conditions: 20 mg samples, oxygen environment, 10°C/min heating rate.

2) is lower by approximately 50°C. This effect is reasonable in view of the finding that the decomposition temperature of pure PBSy is 415°C vs. 460°C for untreated PET fabric.

The thermal decomposition of untreated PET in an oxygen environment is essentially a combustion process. When compared with decomposition in the inert environment two characteristics of the combustion are observed: a lower temperature of the maximum decomposition rate by 50° C and a very sharp weight loss at this temperature. This weight loss is accompanied by self-ignition of the sample, and a high amount of heat is released, which causes a temporary loss of temperature control in the experiment. When loading PET fibers with PBSy, the combustion pattern is changed, and the decomposition temperature of the grafted samples is raised gradually to that found under a nitrogen environment (460°C).

The Influence of PBSy on the Flammability of PET Fabric

The effect of PBSy on the combustion of PET may be assessed from the TGA experiments by calculating the sharp weight loss accompanying the self-ignition in the range 425-450 °C. The results are presented in Table III. This sharp weight loss is due to the combustion of a flammable mixture formed during decomposition prior to ignition. This combustion causes a sharp rise in the temperature of the solid sample. The magnitude of the weight loss is of significance in assessing the interference activity of fire retardants on the formation of the flammable mixture¹⁸ and has a bearing on the flammability of the treated substrate in a confined space.

It can be seen from the data presented in Table III that approximately 90% of the PET sample disappears in one rapid burning stage in the 425–450°C range.

% PBSy	% wt loss on combustion			
in sample	Lower limit ^b	Upper limit ^c	Flammability range ^d	% Reduction in range
0	7.9	97.7	89.8	_
12.2	33.1	90.6	57.5	36
20.2	48.7	93.7	45	49.9
25.6	65	81.2	16.2	82
30.9	68.7	76.9	8.2	90.9

TABLE III Flammability Limits of the Gas Formed from PBSy-Grafted PET Fabric during Controlled Combustion in an Oxygen Environment^a

^a The data were calculated from results obtained in TGA experiments at a heating rate of 10°C/min in the range of 400–475°C.

 $^{\rm b}$ The lower limit specifies the weight loss at the onset of the rapid combustion step (with flame).

^c The upper limit specifies the weight loss at the end of the rapid combustion step (with flame).

^d Flammability range is the range of weight loss where the combustion is accompanied by flame.

Loading of the PET fabric with PBSy significantly depresses the fraction of the fabric that burns at this stage, and the flammability range is gradually diminished up to 30.9% PBSy, when no flame is observed. Thus it can be assumed that the PBSy influences the combustion reactions by depressing the flammable gas mixture available for burning. Such an interference is consistent with the assumption that PBSy suppresses the flame by a physical-mode mechanism proposed by Larsen¹⁹ in order to explain the flame-retardant activity of halogens on polymers.

Larsen assumes that the decrease in flammable gas mixture in bromine treated substrates is due to the fact that a part of the decomposition products are halogenated. These latter compounds have a significantly lower ΔH of combustion than nonhalogenated compounds. Thus, for example, the molar heat of combustion of benzene and bromobenzene is 781 and 628 kcal/mol, respectively. This difference between the heats of combustion becomes significantly larger when calculated per gram-weight, the corresponding values being 10 and 4 kcal/g.¹⁹ Thus the combustion of a halogenated compound subsequently lowers the mass of polymer volatilized into the gas phase. If the flame has to be sustained, a heat input into the system is needed in order to achieve a high enough rate of mass volatilization to maintain a flammable composition in the gas phase.

PBSy Decomposition Products Which May Affect the Combustion Retardation Mechanism

The TGA experiments were followed by trapping of products which may interfere with the oxidation processes in the gas phase. As mentioned earlier, during decomposition brominated compounds may yield HBr which can interfere in the early stages of the burning reaction by means of a radical trap mechanism.^{10,11} The amount of HBr produced during the thermal decomposition or combustion of the different samples was determined, and the results are shown graphically in Figure 4.



Fig. 4. The amount of HBr released during controlled thermal decomposition in nitrogen or combustion in oxygen vs. the amount of Br in the sample for PBSy-grafted PET fabric samples, heated up to 550°C at a rate of 10°C/min.

The HBr yields obtained by controlled heating in an oxygen environment are considerably higher than in nitrogen. The significance of the difference in the HBr release was confirmed by a statistical treatment of the results. However, the HBr yields obtained in an oxygen environment represent only 1-2% of the overall bromine content of the sample, and one must consider the possibility that other bromine-bearing decomposition species which constitute a much higher proportion of PBSy degradation may be involved in the combustion retardation mechanism.

It has been found that the major brominated decomposition product was BSy. The yields obtained for several samples are presented in Figure 5. The results show that depolymerization is a major pathway in the decomposition of grafted PBSy under N₂ and accounts for 50–54% of the PBSy in the sample. When the controlled heating is performed under oxygen, the yield of the trapped monomer is reduced to approximately 14–17% of the total PBSy in the sample. This reduction in the BSy released from the system could be due to combustion in the gas phase of a considerable part of the volatilized BSy. In this case, it can be assumed that the flammable gas mixture of burning PET fabric would be diluted by considerable amounts of BSy molecules which reduce the amount of heat released upon combustion. Thus, the relatively high amount of BSy evolved during thermal decomposition and the combustion of it in an oxygen environment



Fig. 5. Depolymerization of 30.9% PBSy grafted on PET fabric. Experimental conditions: TGA cell, heating up to 550°C at a rate of 10°C/min, N₂ or O₂ environment: (\Box) fraction of intact BSy molecules; (\blacksquare) fraction of decomposed BSy molecules; (\blacksquare) fraction of combusted BSy molecules.



Fig. 6. DTA curves of untreated PET fabric, pure PBSy, and PET fabric treated with different amounts of PBSy by the direct irradiation method. Experimental conditions: 2 mg samples, oxygen environment, 10°C/min heating rate.

could impart fire retardation consistent with the physical-mode mechanism proposed by Larsen.¹⁹

The Influence of PBSy on the Heat of Combustion of PET Fabric

In view of the arguments presented above, it was of interest to carry out direct measurements of the heat of combustion of PBSy, PET, and PBSy-grafted PET. This was done by the DTA technique. The curves obtained are presented in Figure 6. It can be seen that the controlled combustion of PET fabric in oxygen occurs in three distinct stages: (a) in the range of $270-400^{\circ}$ C, (b) in the range $400-480^{\circ}$ C, and (c) in the range of $480-550^{\circ}$ C. From a comparison of the patterns of DTA and TGA thermograms under these conditions, the following assumptions can be made concerning the characteristics of the decomposition and combustion stages. Stage (a) may be attributed to surface exothermic oxidative reactions similar to those found by Tkac²⁰ in the preflame zone of burning



Fig. 7. ΔH Combustion of PBSy-grafted PET fabric vs. % bromine in the sample [(0) values obtained by microanalysis: (Δ) values calculated from graft percent)]. Experimental conditions: DTA, oxygen environment, heating to 600°C at a rate of 10°C/min.

polypropylene in the range 250–450°C. Stage (b) is assumed to represent the combustion of gaseous species evolved in the main decomposition of PET fabric, while stage (c) is supposed to be related to the combustion of the carbonaceous char. Stage (a) disappears when the PET samples are grafted with PBSy, even at 2% loading. The second stage gradually diminishes when the PBSy load increases; however, the third stage is not affected by the presence of PBSy in the sample.

The heat of combustion data of PET samples, derived from DTA curves using the procedure outlined in the Experimental section, were plotted as a function of bromine content (see Fig. 7). Nontreated PET fabric samples yield ΔH combustion values of 3.84 kcal/g. This value compares favorably with 3.27^{21} and 4.1 kcal/g²² determined by isoperibol calorimetry in an air environment. It can be seen in Figure 7 that the influence of PBSy on PET fabric combustion (with our experimental setup) is characterized by two stages: the initial one in which ΔH combustion is reduced by one-third already at about 2% PBSy in the sample, and a second stage in which a gradual decrease in ΔH combustion occurs at the higher PBSy loadings.

In terms of the physical-mode fire-retardation mechanism proposed by Larsen, PBSy may be seen as a depressing agent for heat evolution during combustion of PET. From DTA curves (see Fig. 6) we obtained the values 3.84 and 0.7 kcal/g for ΔH combustion of PET and PBSy, respectively. The molar values are 565 and 128 kcal/mol, respectively. Thus, PBSy seems to be a more effective heat of combustion depressing agent for PET than bromobenzene is for benzene.¹⁹

It should be noted that superficially there appears to be a contradiction between the very significant reduction of ΔH combustion observed already at the lowest loading of PBSy on PET and the flammability range data presented earlier, which does not show a similar initial effect. This contradiction is, however, not real, since the initially high reduction of ΔH combustion occurs in the flameless stage (a) in the temperature range of 270-400°C, while the



Fig. 8. LOI vs. % bromine in the sample for PET grafted with PBSy by the direct irradiation method.

flammability range data relate to stage (b) which occurs in the range 400–480°C and is accompanied by flame.

Flame Retardation in LOI Tests of PBSy-Grafted PET Fabric

The LOI values for PET grafted with PBSy by the direct irradiation method are presented graphically in Figure 8. The dependence of LOI on the % bromine in the sample is nonlinear and appears to be related to the amount of HBr released during controlled thermal decomposition (Fig. 4), suggesting a possible correlation between the LOI and the amount of HBr released under these conditions. In order to check the validity of such a relationship, the mean value of HBr released in TGA runs in N₂ was calculated for each of the samples containing different amounts of PBSy. In addition, Δ LOI values were derived for each sample, and these results are plotted in Figure 9.



Fig. 9. Δ LOI vs. amount of HBr released during thermal decomposition in N₂ of PET fabric grafted with PBSy by the direct irradiation method. HBr was trapped at the exit of the TGA apparatus when heating at 10°C/min up to 550°C.

Compounda	Heat reduction $\Delta OI/\%$ Br (cal/g % Br) Ref. 1			
		((0), g / (-))		
TBPMA ^b	1.5		9	
TBPOEA ^b	1.2	-	9	
OBBPc	0.4 ^d	129 ^f	7	
DBDPO°	0.4^{d}	122 ^f	7	
TBBPAC	0.4 ^d	107 ^f	7	
BSy ^b	0.48 ^e	119 ^g	this study	

 TABLE IV

 ΔΟΙ/% Br and Combustion Heat Reduction for PET Fabric Treated with Various Brominated Aromatic Compounds

^a TBPMA = 2,4,6-tribromophenyl methacrylate; TBPOEA = 2-(2,4,6-tribromophenoxy) ethyl acrylate; OBBP = octabromobiphenyl; DBDPO = decabromodiphenylene oxyde; TBBPA = tetrabromobisphenol A.

^b Radiation grafted.

^c Applied by addition method.

^d Calculated from data in Ref. 7.

• $\Delta OI/\%$ Br is not constant: the value shown refers to samples containing $\ge 8\%$ Br.

^f Measured with an isoperibol calorimeter in an air environment.

^g Measured with a DTA apparatus in an oxygen environment.

It can be seen from Figure 9 that a very good linear relationship exists between Δ LOI and the amount of HBr released during controlled thermal decomposition under N₂. No similar relationship was found for Δ LOI vs. HBr released in an oxygen environment. Thus, it would appear that the PET decomposition reactions occurring during the LOI tests exhibit a pattern comparable to that observed in pyrolysis rather than combustion reactions. A similar assumption has been made by Granzow et al.,²³ who studied the effect of red phosphorus on the decomposition of PET. These authors proposed that the contribution of a thermooxidative pathway under burning conditions of the LOI test is negligible. It is of interest to note that Richard et al.²⁴ found that in the flame of a burning PET rod, 63% of the gas was N_2 and only 1.5% was O_2 . A similar observation was reported regarding the flame of burning poly(methyl methacrylate).²⁵ Thus it could be assumed that LOI measurements may be significantly affected by the presence of small amounts of HBr evolved in the temperature range of the decomposition of the substrate. Such an effect would not be expected under conditions of "oxygen-rich" combustion where small amounts of HBr would not be able to compete effectively with O_2 in the chain propagation reactions.

Relative Fire-Retardant Efficiency of PBSy

In Table IV a summary of the fire-retardation efficiencies of several brominated aromatic compounds grafted on PET fabrics are shown. The $\Delta OI/\%$ Br ratios compiled in Table IV show that PBSy is about as efficient as OBBP, DBDPO, and TBBPA, the latter two compounds representing commercial fire-retarding agents. Common to these compounds is the small amount of HBr produced during combustion and a substantial release of intact bromoaromatic molecules.⁷ In light of the argument presented earlier, the low rate of HBr generation very likely accounts for the low $\Delta OI/\%$ Br ratios. One is tempted to assume that the significantly higher $\Delta OI/\%$ Br ratios exhibited by PTBPMA and PTBPOEA could possibly reflect the tendency of the latter compounds to significant HBr or other bromine-bearing molecular fragment evolution, which can effectively interfere with the chain oxidation reactions in the course of the LOI tests.

The TGA and DTA results of this work suggest significant effectiveness of PBSy in flame retardation of PET, both by increasing the temperature of the onset of burning and by decreasing the flammable gas mixture. The heat reduction data (see Table IV), though derived by a different technique from that employed by McNeill⁷ give a heat of combustion value which is comparable to those of OBBP, DBDPO, and TBBPA. Thus, we tend to assume that, in spite of the rather low $\Delta OI/\%$ Br values exhibited by PBSy, as well OBBP, DBDPO, and TBBPA, all these compounds may be considered quite effective fire-retardant agents for PET.

CONCLUSIONS

The fire-retardation potential of PBSy grafted on PET fibers was determined by LOI, TGA, and DTA techniques. HBr and BSy yields formed during pyrolysis were determined. A linear correlation was found between ΔOI values and yields of HBr supporting a picture of a candlelike, oxygen-poor combustion process in the course of LOI tests.

It is proposed that the major contribution of PBSy to fire retardation occurs via a physical-mode mechanism by reducing the volatilization of flammable gases. This mechanism is not reflected under the conditions of LOI tests.

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