Localized Radiation Grafting of Flame Retardants to Poly(ethylene Terephthalate). I. Bromine-Containing Monomers

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Synopsis

Vinyl bromide was used as a model for bromine-containing flame retardants in developing methodology for localizing flame retardants either on the surface of the filament, uniformly throughout it, or predominantly at the core. SEM–x-ray microprobe techniques were used in the verification of the location of the flame retardant in the filament. The flame retardance efficiency of PVBr was then correlated with its location in the filament. Grafting other bromine-containing flame retardants showed a wide range of efficiencies which depended not only upon the location of the graft within the filament but also upon the structure of the compound. For the various bromine homopolymer grafts, the apparent thermal stability of the graft and its flame retardance efficiency may be simply related to the alpha aliphatic hydrogen-to-bromine ratio. The lower this ratio is, the higher the efficiency. VBr copolymers and terpolymers showed wider variation in flame retardance efficiencies. This is attributed to large variations in melt viscosity of the different grafted materials. The grafts showed only small changes in their melting points and minimal changes in tenacity and stiffness. However, grafting induced large increases in the elongation.

INTRODUCTION

In an effort to obtain basic information which could be utilized in designing flame retardant systems for cotton/polyester blends, we chose model systems which should be applicable to a broad scope of blend compositions. Thus, the two basic flame-retarding elements—bromine and phosphorus—were represented by vinyl bromide (VBr) as the model for bromine-containing flame retardants and dimethyl and diethylvinyl phosphonates as the models for phosphorus-containing flame retardants. The work described here deals with grafting of the poly(vinyl bromide) (PVBr) compositions on poly(ethylene terephthalate) (PET) and the investigation of the effects of PVBr distribution within the grafted PET filament upon its flame retardance efficiency. Grafting of other bromine-containing flame retardants showed a wide range of efficiencies which depended not only upon the location of the graft within the filament but also upon the structure of the compound. The work conducted with the phosphorus-containing monomers will be described in part II of this series.

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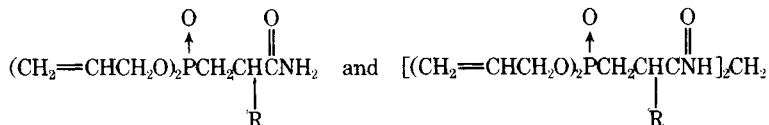
HISTORICAL

The first attempt at grafting a flame-retarding monomer, vinyl chloride, to PET appears to be that of Armstrong, Walsh, and Rutherford.[1] The objective of that work was to explore the modifications of fiber properties that might be possible by radiation grafting. Vapor-phase gamma-radiation grafting techniques were used, and under those conditions the general findings were that it was not possible to graft vinyl chloride to PET (best add-on reported 0.1%). The use of various radiation sensitizers did not help much; the best sensitizer found was acetic anhydride, which led to an add-on of 0.4%.

The first explicit descriptions of flame retarding of polyesters by radiation grafting techniques come from patent literature.[2-5] In the Farbwerke and Hoechst patent of 1971,[2] the use of diallyl 2,3-dibromopropyl phosphate and allyl bis(2,3-dibromopropyl) phosphate was claimed. In the Hooker Chemical Corp. patent of 1972,[3] six phosphonate acrylamides of the general structure

$$\begin{matrix} & O & O \\ & \parallel & \uparrow \\ CH_2 \!\!=\!\! & CCNCH_2P(OR'')_2 \\ & | \; | \\ & R \; R' \end{matrix}$$
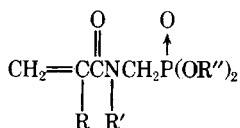
were claimed for flame-retarding cotton, cotton/polyester blends, and wool. In the Stauffer Chemical Co. patent of 1973,[4] a combination of two compounds of the following general structures is claimed:

$$\begin{matrix} & O & O \\ & \uparrow & \parallel \\ (CH_2\!\!=\!\!CHCH_2O)_2PCH_2CHCNH_2 \\ & | \\ & R \end{matrix} \quad \text{and} \quad \begin{matrix} & O & O \\ & \uparrow & \parallel \\ [(CH_2\!\!=\!\!CHCH_2O)_2PCH_2CHCNH]_2CH_2 \\ & | \\ & R \end{matrix}$$

In the Hooker Chemical Corp. patent of 1974,[5] the use of a family of compounds of the general structure

$$\begin{matrix} & O & O \\ & \parallel & \uparrow \\ CH_2\!\!=\!\!CCOCHP(OR'')_2 \\ & | \; | \\ & R \; R' \end{matrix}$$
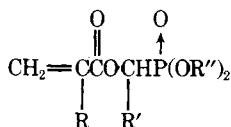
is claimed in the flame retarding of cellulosic, proteinaceous, and analogous man-made materials (polyester mentioned).

The only other openly described work that deals with radiation flame retarding of cotton/polyester blends appears to be that at North Carolina State University.[6] The monomers studied were Fyrol 76, Fyrol BB, bis(2,3-dibromopropyl) phosphate ester of hydroxyethyl methacrylate, and N-methylolacrylamide.

BACKGROUND

Swelling Agents

It was discovered in the early 1960's that grafting to cotton took place only when the cotton was sufficiently swollen to allow the monomer to diffuse to the

radical sites in the fiber. Thus, for example, effective grafting of styrene to cotton was very much dependent upon the water content in the system.[7] Subsequent studies with many different polymer–monomer grafting systems demonstrated the great importance of the swelling in radiation grafting. Diffusion in radiation grafting processes plays a dual role: (1) it controls the chain growth via diffusion of monomer to the growing chain end, and (2) it controls termination via diffusion (combination) of two polymeric species. This can lead, for example, to the well-known gel effect. Another consequence of diffusion control is that the grafting often tends to be concentrated in the surface regions, particularly in poorly swollen systems or in systems with high dose rates. Because one of the objectives of this work was the study of the effect of changing the location of the grafted flame retardant on properties, the swelling behavior of PET in different solvents was thus a very important factor.

Amorphous PET develops crystallinity after immersion in a number of different organic liquids at 25°C.[8–11] Although interaction of organic liquids with, and their diffusion into, amorphous PET have not been related quantitatively to the rate or final degree of crystallization induced in the polymer, it has been shown that liquids having a solubility parameter (δ) near the estimated δ of amorphous PET (10.7) induce appreciable crystallinity in the polymer. The use of total solubility parameter may not provide a sufficiently precise characterization of a solvent's capability to interact with PET. The work of Moore and Sheldon[8] showed that induced crystallization in unoriented amorphous PET and maxima of density changes were observed in solvents with total δ around 9.5 and 12.0. More recent work on longitudinal shrinkage and swelling volume of PET fibers evaluated in terms of the δ concept together with iodine displacement studies indicated that PET may be treated as an $(AB)_x$ alternating copolymer.[11] The A may be $-CO-\langle\bigcirc\rangle-$ with a δ value of 9.8, and B may be $-OCH_2CH_2OCO-$ with a δ value of 12.1. Thus, preferential interaction of a solvent with either of these two PET segments was demonstrated.

For our studies of a special case of the effect of swelling agents on the grafting rates, we selected solvents with a narrower range of solubility parameters, namely, 10.6 to 10.8. We wanted to use reasonably good swelling agents, but not so good (either δ 9.5 or 12.1) that they would also induce maximum crystallinity and density changes in PET which would result in reduced monomer diffusion to the active sites and, hence, decreased grafting yield. The ease of grafting, in general, is a function of the degree of crystallinity.[12,13,14]

Radiation Sensitivity of PET

Polyesters in general are very stable toward radiation and show little tendency to undergo grafting. Free radicals form by γ-irradiation of PET with a $G(R\cdot)$ value of only 0.02.[15] This compares to polystyrene with $G(R\cdot)$ 0.7 and cellulose with $G(R\cdot)$ 1 to 6. It is not entirely clear why PET should form, by more than an order of magnitude, fewer free radicals than polystyrene does. Two types of free radicals were apparently generated: one was identified by ESR as
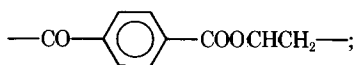
$$-CO-\langle\bigcirc\rangle-COOCHCH_2-;$$

TABLE I
Radiation Sensitizers Used in Grafting Acrylic Acid onto PET[16-19]

Radiation sensitizer	Add-on, %
None	2.8
Methylene chloride	36.4
Chloroform	32.3
Carbon tetrachloride	3.2
Ethylidene dichloride	33.1
Ethylene dichloride	34.1
1,1,1-Trichloroethane	4.1
1,1,2-Trichloroethane	41.8
1,1,1,2-Tetrachloroethane	20.8
1,1,2,2-Tetrachloroethane	33.8
Pentachloro ethane	29.3
cis-1,2-Dichloroethylene	31.3
trans-1,2-Dichloroethylene	32.0
Trichloroethylene	29.3
1,1,2,2-Tetrachloroethylene	38.5
n-Propyl chloride	19.4
Isopropyl chloride	33.1
n-Butyl chloride	32.2
Monochlorobenzene	41.4
o-Dichlorobenzene	37.8
Benzyl alcohol	2.0
Dimethylformamide	1.1
Dimethyl sulfoxide	0.7
Nitrobenzene	1.2
Formic acid	4.3

the other, a minor component (5–10%), was tentatively assigned the structure of
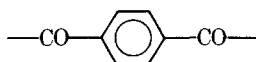
The use of radiation sensitizers in the grafting of PET was extensively investigated by Okada and co-workers.[16-19]   A list of the various sensitizers that they investigated is given in Table I.   They found that the best sensitizers were halogenated hydrocarbons which also acted as swelling agents and increased not only the per cent graft but also the grafting efficiency and grafting rate.   Presumably, this action was due to radiation-induced decomposition of the halogenated hydrocarbons into active free radicals which then participated in the chain reactions.   In addition to the sensitizers listed in Table I, we found vinyl bromide and vinylidene chloride, but not vinylidene bromide, to be excellent radiation sensitizers.

Localized Grafting

The radiation process can be varied in such a way as to change the location of the grafted polymer.   Diffusion of the monomer to the active sites and dose rate are the two important variables used to achieve localized grafting.   Since the monomer must diffuse into the fiber from the outside, the diffusion control also leads to control of the location of the graft.   Preswelling of the fiber not only
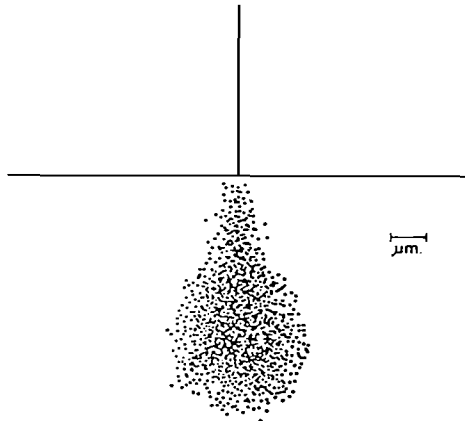
Fig. 1. Locus of scattered electrons.

increases the rate of diffusion of the monomer into the fiber but may also result in a higher initial monomer concentration in the fiber. By judicious control of the swelling conditions, the time of contact with the monomer, and the dose rate, it becomes possible to locate the graft at various depths in the fiber. In the work reported here, we have been able to concentrate the grafting of the flame retardants in three locations: surface only, uniformly throughout the fiber, and predominantly in the core of the fiber. The effect of the location of a flame retardant upon its flame retardance efficiency was then correlated.

Scanning Electron Microscopy and X-Ray Microprobe Analysis

To investigate the distribution of the grafted polymers across the section of a 13.5-μm PET filament by means of the intensity of characteristic peaks in the x-ray spectrum, a resolution of the order of about 1 μm is required. Since the intensity of characteristic x-rays given off by an element is affected by take-off angle (the angle between specimen surface and x-ray detector), it is required that the surface of a cross section be uniformly smooth if valid conclusions are to be drawn. In addition, the resolution of the scanning electron microscope, when emitted x-rays are used for imaging, is considerably worse than when secondary electrons are used. All x-rays excited by the electron beam, as it impinges on a bulk sample and is then scattered below the surface, can be equally effective in contributing to the image. The resolution is, therefore, determined by the locus of scattered electrons originating at the point of electron beam impingement on the surface. This locus turns out to be "pear shaped" with the narrow end at the surface and has a continuously increasing radius until the energy of scattered electrons becomes smaller than the excitation energy for characteristic x-rays from a given element (see Fig. 1). The maximum diameters of such pear-shaped scattering volumes may vary from about 4 to 16 μm depending on impinging electron energy, density of the matrix, and the element being imaged.[20,21] The scattering volume may have a depth of 10 μm or more. The resolution of x-rays can be increased by using 1- to 2-μm sections such that only the top of the pear-shaped volume can contribute to the image. For these two reasons—the need for a smooth surface and sections of fibers that are only 1–2

μm in thickness—the work described here was done on sections cut on an ultramicrotome from embedded fibers.

EXPERIMENTAL

Materials

Substrate Grafted. American Enka Co. polyester fiber; 150/96 S.D. polyester filament yarn; 0.35% TiO_2; ~0.2% water soluble finish. Information on the original draw ratio and crystallinity of the yarn was not available to us.

Bromine Compounds Grafted. Vinylbromide (VBr); vinylidene bromide (VBr_2); 2,3-dibromopropyl acrylate (DBPA); 2,3-dibromopropyl methacrylate (DBPM); 2,4,6-tribromophenyl methacrylate (TBPM); 2,4,6-tribromophenyl acrylate (TBPA); tribromoneopentyl acrylate (TNPA); 2,2,2-tribromoethyl acrylate (TBEA); 2-(2,4,6-tribromophenoxy)ethyl acrylate (TBPOEA); bisacrylate of 2-hydroxyethyl ether of tetrabromobisphenol A (BABA-50). VBr and VBr_2 were supplied courtesy of Ethyl Corporation; DBPA, DBPM, BABA-50, and TBPOEA were courtesy of Great Lakes Chemical Corp.; TBPM and TBPA were courtesy of Hooker Chemical Corp., and TNPA and TBEA were purchased from Polysciences, Inc., and used as received.

Techniques

Grafting Technique. Gamma Radiation. A series of initial investigations showed no discernible differences in the per cent weight gain obtained with scoured and unscoured yarns; thus, all subsequent work was carried out on unscoured samples. The samples were degassed by means of three freeze–thaw cycles to at least 10^{-5} torr. In most cases, the grafting (Co-60 source) was performed using a mutual irradiation technique in a small glass ampule at dose rates of from 0.01 to 0.1 Mrad/hr. Following irradiation, the fiber samples were extracted with solvent for the homopolymers or copolymers, first at room temperature and then at elevated temperature. The extracted fibers were vacuum dried at constant weight and stored in a desiccator for subsequent evaluation. The data for weight gain achieved during grafting was obtained following this drying procedure.

FR Localization Techniques. Surface coating. Approximately 10% solution of the compound in THF was used. After immersing the fibers in the solution, they were dried in a vacuum oven at 50°C/16 hr. **Uniform grafting.** The fibers were preswollen in ethylene dichloride at 70°C/½ hr, then placed in the flame retardant solution for about 2 hr, and then irradiated. **Surface grafting.** Fibers were placed in the flame retardant solution and immediately irradiated. **Core VBr grafting.** Fibers were preswollen in ethylene dichloride at 70°C/½ hr, then placed in vinyl bromide for about 2 hr. The excess VBr was decanted and the swollen fiber frozen to −78°C. Next, the tube was opened to the atmosphere and then placed in the γ-radiation source.

Oxygen Index. Since the samples in the initial phase of this work were in the form of individual yarns or fibers, it was necessary to develop a modified technique for measuring the oxygen index (*OI*) of these materials. The development of the sample holder and the procedure for measuring the *OI* have been
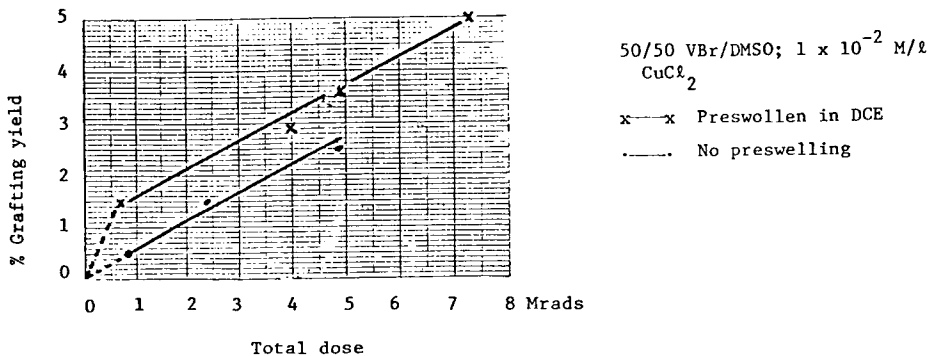
50/50 VBr/DMSO; 1×10^{-2} M/ℓ
CuCℓ$_2$

x⎯⎯x Preswollen in DCE

.⎯⎯. No preswelling

Fig. 2. Percent grafting yield vs total dose.

described.[22] The procedure permitted not only the determination of the *OI* values, but also an estimation of the char yield as the material burned in the tester. This procedure was also applied to the evaluation of the various grafted fabric samples.

Scanning Electron Microscopy and X-Ray Microprobe Analysis. Thin cross sections of the grafted PET fibers were prepared by embedding in an epoxy or poly(methyl methacrylate) resin and sectioning with a Reichert "Omu2" ultramicrotome using a glass knife. The epoxy yielded the better sections. The sections were floated off onto water during the sectioning and then transferred to a drop of water on a carbon stub using an eyelash. The water droplet on the stub was then evaporated and the section examined in the scanning electron microscope. No coating was required.

Differential Scanning Calorimetry. The DSC instrument used in this work was a Perkin-Elmer Model DSC-1. The instrument allows one to record a specific heat-versus-temperature curve in a relatively short time and convenient manner. The melting was taken as the temperature at which the specific heat-versus-temperature curve goes through the maximum of the melting peak. Typically, 5 to 10 mg of cut fiber sample was sealed in an aluminum cup, and an empty aluminum cup was used in the other sample holder. The instrument was operated at 10°C/min heating rate.

Thermogravimetric Analysis. Typically, 10-mg samples were used in a quartz pan provided with the instrument. The analyses were conducted in a nitrogen atmosphere (26 ml/min) at a programmed heating rate of 5°C/min.

RESULTS AND DISCUSSION

Polyester fiber

Vinyl Bromide Grafts

Effect of Dose. When VBr is grafted from a dimethyl sulfoxide solution at room temperature, the percent graft increases linearly with dose (time) and without any induction period (see Fig. 2). Preswelling the fibers in ethylene dichloride at 70°C/½ hr produced a parallel dependence of weight gain on total dose, but displaced 1% higher on the weight gain axis.

Effect of Dimethyl Sulfoxide (DMSO) Concentration. The effect of the concentration of DMSO (as well as that of hexamethylphosphoramide, HMPA)

TABLE II
Effect of Temperature on Grafting of VBr

Grafting temp., °C	Total dose, Mrads	Grafting yield, %
−194	2.7	2.0
−64	2.1	8.2
−44	2.5	9.9
~24 (R.T.)	2.3	9.1
+81	2.4	17.7

TABLE III
Effect of Swelling Agent on Grafting Yield

Swelling agent	δ	Grafting yield, %
—	—	9.1
Morpholine	10.8	3.6
Dimethylacetamide	10.8	4.3
Propionitrile	10.7	5.1
Dimethyl phthalate	10.7	5.8
Dimethylformamide	10.6	4.7
n-Butanol	10.6	9.1

TABLE IV
Radiation Sensitizers/Swelling Agents Studied

	Boiling point, °C	δ
Methylene chloride	40	9.7
Chloroform	61	9.3
Carbon tetrachloride	77	8.5
Ethylene dichloride	84	9.8
1,1,1-Trichloroethane	71	8.8
1,1,2,2-Tetrachloroethane	130	9.7
Chlorobenzene	132	9.5
Bromobenzene	152	9.9
Bromonaphthalene	281	10.6
Methylene bromide	97	12.4
p-Chlorotoluene	162	8.8
n-Butyl chloride	68	8.1

on the grafting of neat vinyl bromide was similar to that on the grafting of styrene on polyester.[12,13] The addition of a small amount of DMSO (or HMPA) increased the grafting yield considerably, followed by a gradual decrease with increasing concentration. Typical grafting yields (%) at room temperature for the following DMSO concentrations (moles/l.) (total dose 4.80 Mrads) were as follows: 0.5 mole/l., 9%; 1.0 mole/l., 11%; 2.0 moles/l., 8%; 4.0 moles/l., 5%; 8.1 moles/l., 2.5%.

TABLE V
Effect of Radiation Sensitizers

Radiation sensitizer	Total dose Mrads	Grafting yield, %
Methylene bromide	2.3	19.1
Bromobenzene	4.7	14.0
1,1,2,2-Tetrachloroethane	2.2	13.0

Effect of Monomer Structure on *OI*

Graft type	Grafting yield, %	*OI*	Bromine, %
TBPM	13.5	32.5	8.1
VBr$_2$	9.4	28.6	8.1
VBr	10.8	24.7	8.1

Effect of Temperature. The effect of temperature on the grafting of VBr (neat, no preswelling of the fiber) is illustrated in Table II. It can be seen that, within the temperature range explored, there is a maximum in the grafting yield at +81°C. The maximum reached in the vicinity of the glass transition temperature of PET is understandable, as it has been observed before.[12,13] Conceivably, a still higher yield may be achievable above the glass transition temperature.

Effect of Swelling Agents. A series of experiments were conducted using different swelling agents to explore their effect upon grafting yield. The swelling agents used, their δ values, and grafting yield at room temperature, at total dose of 2.3 Mrads, are illustrated in Table III. The swelling agents were used in approximately 1:100 (by weight) ratio of fiber to swelling agent. None of these swelling agents improved grafting yield above that of grafting VBr neat. We believe the decreased grafting yield with these swelling agents is due to their efficient induction of crystallinity and density changes in the amorphous regions of PET. There is at least one correlation that has been observed before, and that is pertinent here. It was found that dimethyl phthalate induced in amorphous PET an equilibrium crystallinity of 41.7%, while n-butanol induced one of only 4.2%.[8] Our grafting yields in these two solvents agree at least qualitatively with the induced crystallinity-decreased grafting yield hypothesis.

Effect of Radiation Sensitizers/Swelling Agents. A list of the various halogenated organic solvents that we investigated as radiation sensitizers/swelling agents is given in Table IV. In general, the effect of the best radiation sensitizers was that of increasing the grafting yield of PVBr. Some typical data are illustrated in Table V. The radiation sensitizers were used in approximately 1:100 (by weight) ratio of fiber to radiation sensitizer during the preswelling step. Subsequently, the excess radiation sensitizer was decanted off. However, the effect of these compounds on VBr grafting is not very pronounced because VBr itself is a radiolytically labile molecule and therefore acts as a self-sensitizer. The effect of these compounds is much more remarkable when used in formulations with monomers that are difficult to graft (e.g., certain vinyl phosphonates).
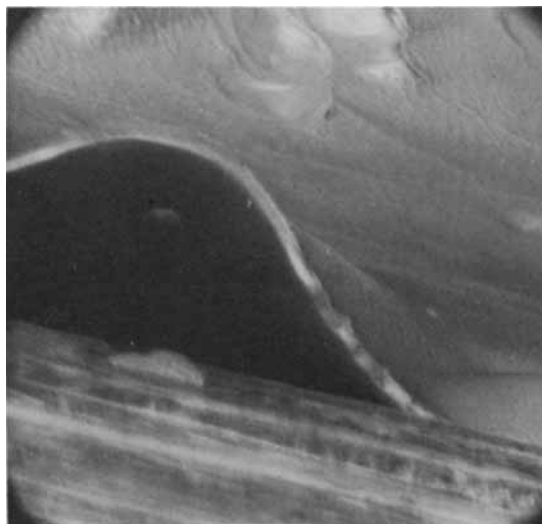
Fig. 3. Thickness of sectioned embedding medium.

Scanning Electron Microscopy and X-Ray Microprobe Analysis. The distribution of VBr grafts across the PET fiber cross section was determined in a semiquantitative fashion using an x-ray microprobe attachment to the scanning electron microscope. In Figures 5–15 are depicted the bromine distributions in the fiber cross section. Figure 3 shows the thickness (1 μm) of the embedding medium after sectioning and the fiber cross sections are seen in the top of the photograph. In some of the sections, part of some fiber would break loose from the embedding medium revealing the thickness of the fiber cross section. This is depicted in Figure 4, where the fiber cross section is shown to be 1 μm. Figure 5 is a secondary electron image of a cross section of PVBr-coated filament. The thickness of the coating is seen to be 1–2 μm. Figure 6 depicts the energy spectrum for x-rays emitted from the cross section shown in Figure 5. The L_α bro-
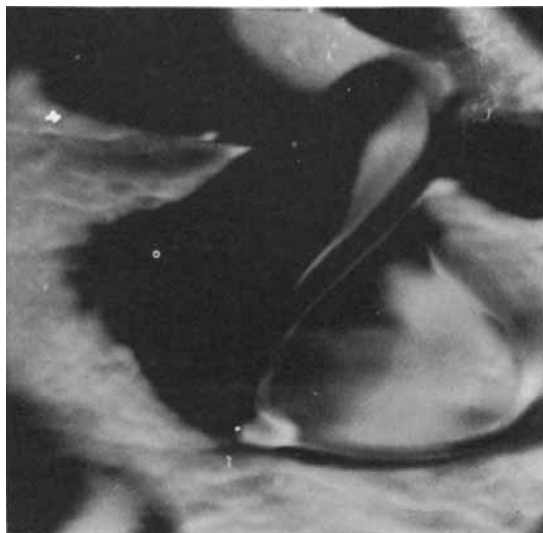
Fig. 4. Thickness of fiber cross section.
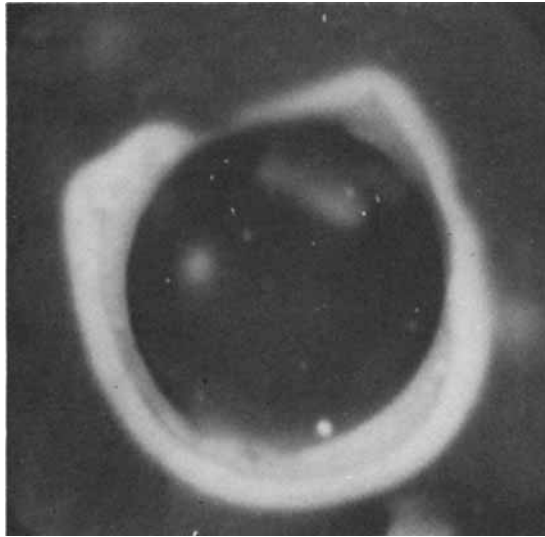
Fig. 5. Secondary electron image of a PVBr-coated filament.

mine emission line was used for mapping the bromine distribution in the cross section. Figure 7 shows the parts in the cross section from which the x rays were emitted and, hence, the location of the bromine atoms. In order to ascertain that such a map actually indicated the site of bromine atoms and not an especially favorable topography at the boundaries of the fiber for emission of all x rays, a map was obtained with a "window" corresponding to background. Such a map is depicted in Figure 8 and is featureless. The above-described procedure was routinely followed on all subsequent samples analyzed. For the purposes of this paper, we will present only the photographs of secondary electron images and the corresponding element distribution maps.

Figures 9 and 10 show the secondary electron image and the bromine L_α map for uniformly VBr-grafted samples. Figures 11 and 12 clearly show that the PVBr graft is localized at the surface of the filament. Figure 13 is the secondary electron image of a core-grafted sample. The percent grafting yield in this case
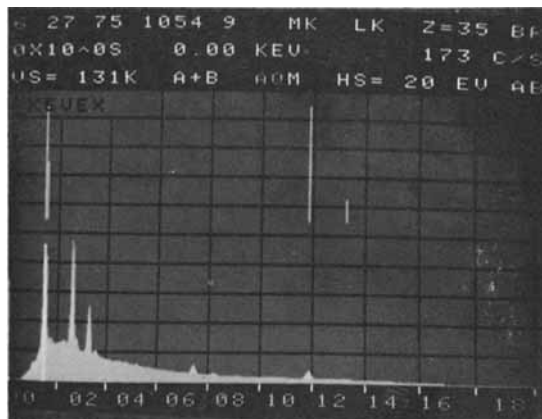
Fig. 6. Energy spectrum for x rays emitted from sample in Figure 5.
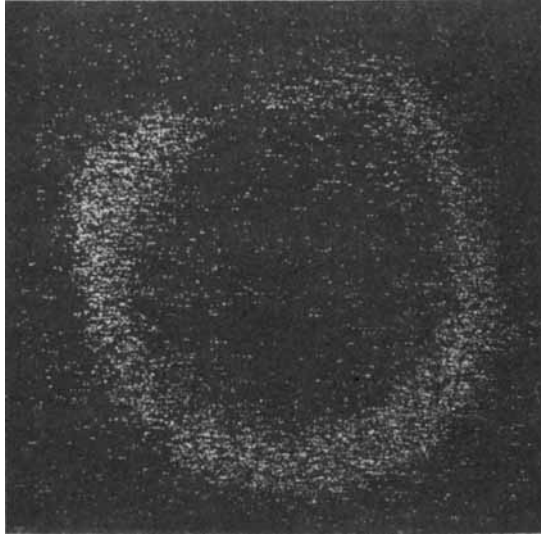
Fig. 7. Bromine distribution from sample in Figure 5.

was only 1.2%. Figure 14 dipicts the energy spectrum for x rays emitted from the cross section. Because of the low bromine concentration, mapping would require extremely long times to obtain reasonable photographs. Thus, to obtain the distribution of bromine across the fiber cross section, x-ray counts were obtained from 1-μm^2 areas at the center of the fiber and from four points 1 μm from the edge of the filament. Both L_α and K_α peaks were used and corrected for background, and the total counts under these peaks were recorded. In order to correct for possible variations in incident beam intensity, these counts were corrected for variations in the total count from 0 to 20 kV, consisting mostly of Bremsstrahlung. The results are depicted schematically in Figure 15. Four locations 1 μm from the edge of the filament yielded 73 to 85% of the bromine
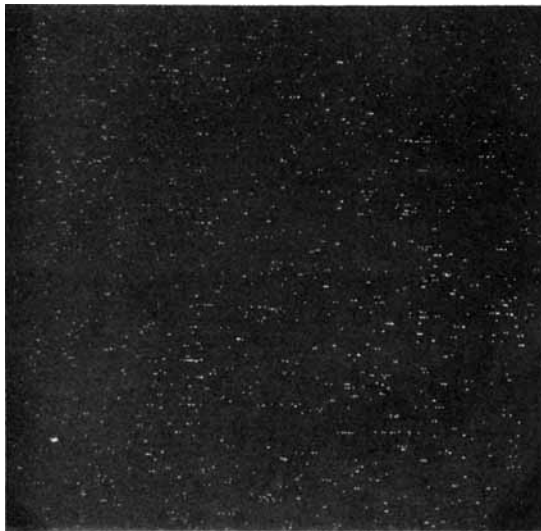
Fig. 8. Background from sample in Figure 5.
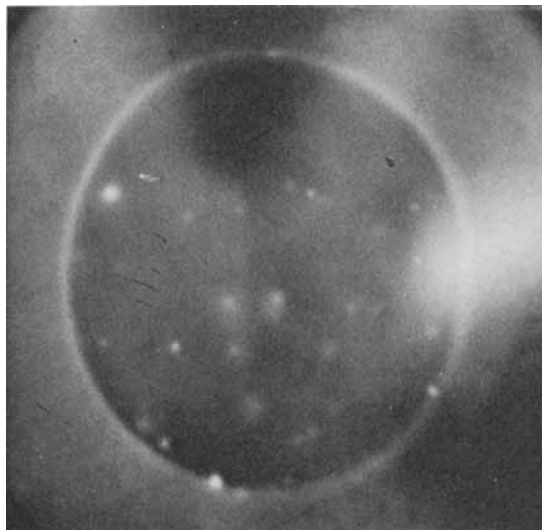
Fig. 9. Secondary image of uniformly PVBr-grafted polyester.

count at the center of the filament. Presumably, the closer the site of x-ray emission to the edge of the fiber, the lower the count would be relative to that at the center.

OI versus **PVBr Location.** *OI* -versus-PVBr location data are summarized in Figure 16. Although the per cent add-on varied greatly, the correlation seems clear. The placement of the PVBr in the interior of the fiber enhanced its flame retardance efficiency the most, followed by uniform grafting and then surface grafting. Thus, these results indicate that better flame retardance results might be obtained if penetration of the PET filament is achieved. The less thermally stable a flame retardant is (e.g., PVBr), the more efficient it becomes and the more it is incorporated in the core of the filament. Thus, in general, it would
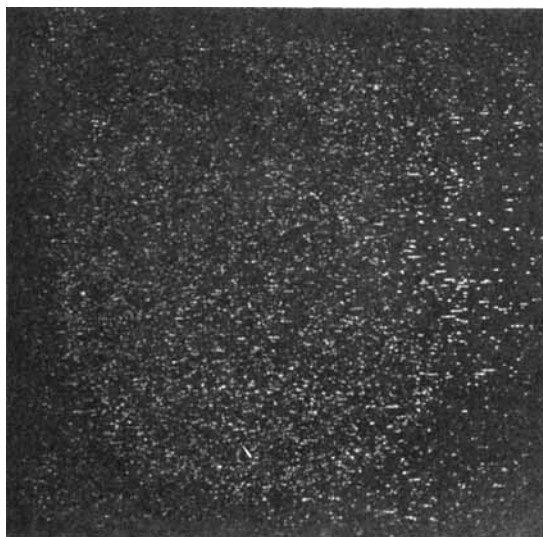
Fig. 10. Bromine distribution from sample in Figure 9.
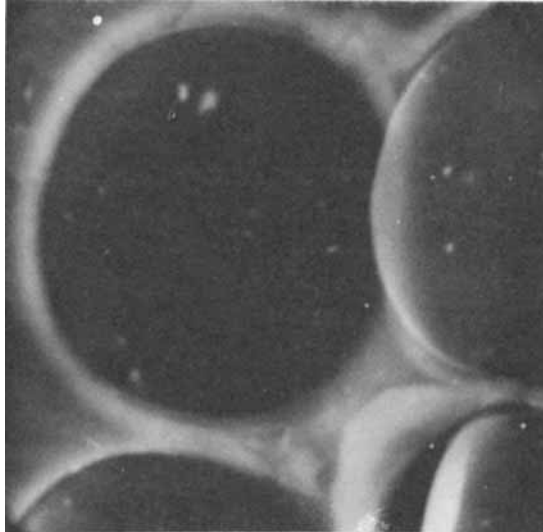
Fig. 11. Secondary electron image of surface PVBr-grafted polyester.

seem that factors which will delay the volatilization of the bromine from the flame front will increase its efficiency.

***OI* versus PVBr Grafting Yield.** Data on uniformly grafted PVBr grafting yield versus *OI* is depicted in Figure 17. The initial rapid increase in *OI* with percent grafting yield starts to slow down after about 10% PVBr content. The results would seem to indicate that the maximum *OI* achievable with PVBr on PET is in the vicinity of 27. The last two points on the graph for 20.3 and 24.4% grafting yields represent PVBr grafts that also contain sulfur—0.5 and 1.8%, respectively. The sulfur must have come from the SO_2 pretreatment of the fibers for these two grafts and is probably incorporated as a SO_2–VBr copolymer. Thus, these two points are left outside the general trend of the data. However,
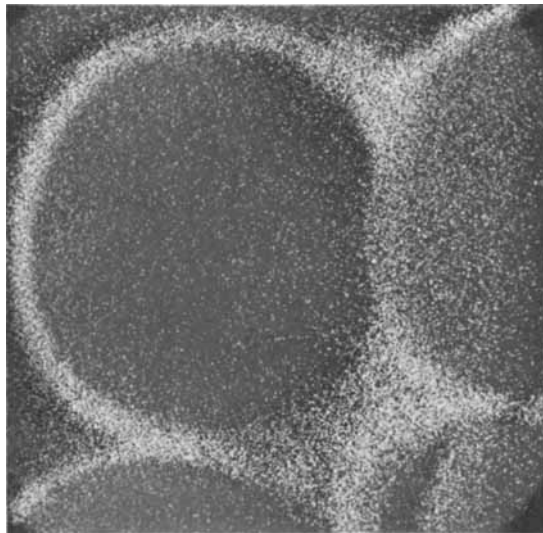
Fig. 12. Bromine distribution from sample in Figure 11.
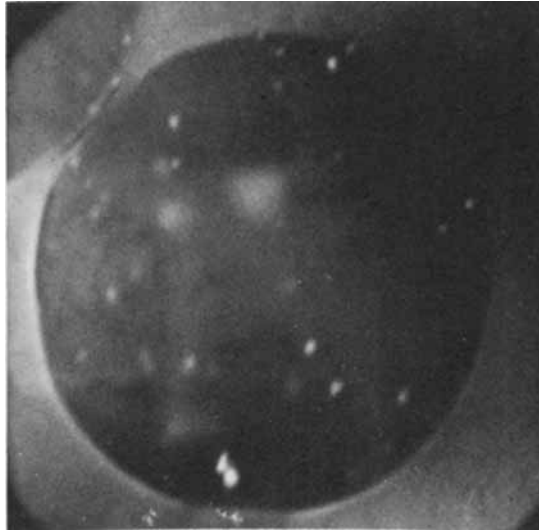
Fig. 13. Secondary electron image of core PVBr-grafted polyester.

they do perhaps indicate that incorporation of sulfur in this type of a graft leads to increased *OI* beyond that achievable by bromine.

Other Bromine-Containing Monomer Grafts

A variety of other bromine-containing monomers have been studied, both by themselves and in various combinations. In general, the acrylates grafted the easiest, and usually their rate of grafting had to be moderated. Next in the ease of grafting were the methacrylates, followed by vinyl bromide and then vinylidene bromide, which was the most difficult to graft. The bisacrylate of 2-hydroxyethyl ether of tetrabromobisphenol A was found to be a very efficient crosslinking agent in our grafting formulations. The *OI* data obtained with the uniformly grafted homopolymers showed a wide range of efficiencies; examples are shown in Table V.

From data of this type, it soon became obvious that the efficiencies of the
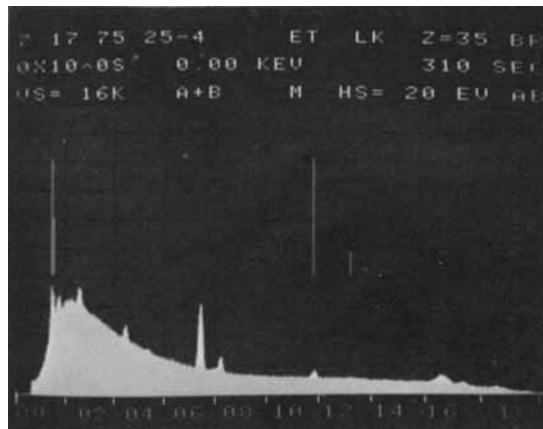
Fig. 14. Energy spectrum for x rays emitted from sample in Figure 13.
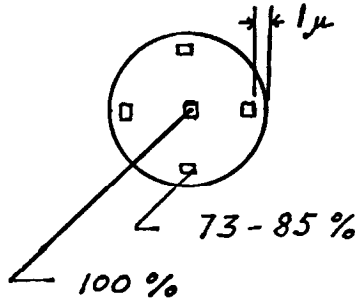
Fig. 15. X-ray count for sample in Figure 13.

	Solution Coating	Uniform Graft	Surface Graft	Core Graft
OI	25.2	26.3	23.5	21.9
%F.R.	55	18.8	18.8	1.2

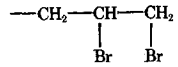|		Uniform Graft	Surface Graft	
OI		21.9	21.9	
%F.R.		1.2	2.5	

Control = 20.4

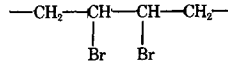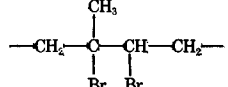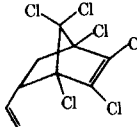Fig. 16. *OI* vs PVBr location.
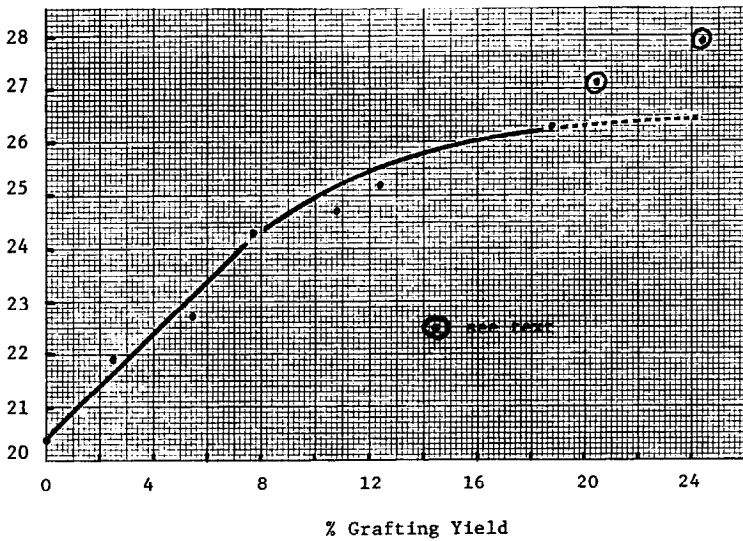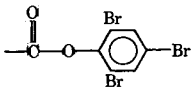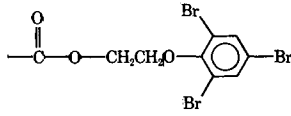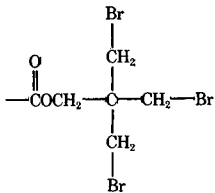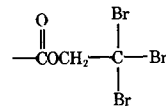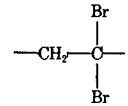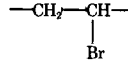
% Grafting Yield

Fig. 17. *OI* vs PVBr percent grafting yield.

TABLE VI
Alpha Aliphatic Hydrogen-to-Bromine Ratio Versus
Thermal Stability Versus FR Efficiency

Compound	H/Br	Dec. pt., °C	$\Delta OI/1\%$ Br
(structure: benzoate ester with 2,4,6-tribromophenyl — O=C–O–C6H2(Br)(Br)–Br)	0	303	1.5
(structure: O=C–O–CH2CH2O–C6H2(Br)(Br)–Br, tribromophenoxy ethyl ester)	0	—	1.2
(structure: O=C–OCH2–C(CH2Br)(CH2Br)–CH2Br)	0	300	—
(structure: O=C–OCH2–C(Br)(Br)–Br)	2/3	220	1.1
(structure: –CH2–C(Br)(Br)–)	1	204	1.0
(structure: –CH2–CH(Br)–)	2	150	0.5
(structure: –CH2–CH(Br)–CH2, with Br Br)	2.5	132	(0.2)
(structure: –CH2–CH(Br)–CH(Br)–CH2–)	3	127	—
(structure: –CH2–C(CH3)(Br)–CH(Br)–CH2–)	4	122	—

various flame retardants varied quite widely depending upon the structures of the compounds in addition to the location of the graft within the filament. A further correlation between the flame retardance efficiency and the structure of a compound and its thermal stability was noticed once a detailed analysis of the TGA data of the various grafted samples was undertaken. A summary of these data is given in Table VI. In the case of various bromine homopolymer grafts, the apparent thermal stability of the graft and its flame retardance efficiency may be simply related to the alpha aliphatic hydrogen-to-bromine ratio. The lower this ratio is, the higher the efficiency. The most efficient flame retardants appear to be those with no alpha aliphatic hydrogens to bromine. Note the large drop in thermal stability of the graft as soon as alpha aliphatic hydrogens are introduced: neopentyl acrylate versus tribromoethyl acrylate. The
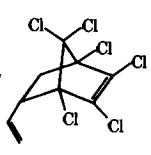
TABLE VII
OI of VBr Copolymers

Copolymer		Grafting yield, %	*OI*
VBr/CH$_2$=C—OCH$_3$ 　　　　$\|$ 　　　P(OCH$_3$)$_3$ 　　　　↓ 　　　　O	(1:1)	3.9	>30.1
O 　　　　　　　　$\|$ VBr/CH$_2$=O—OCCH$_3$ 　　　　$\|$ 　　　P(OCH$_3$)$_2$ 　　　　↓ 　　　　O	(4:1)	2.3	28.6
O　　O 　　　　$\|$　　↑ VBr/CH$_2$=CHCOCH$_2$P(OCH$_3$)$_2$	(7:3)	14.4	27.6
Cl　Cl 　　Cl 　　　Cl VBr/ 　　　　 　　Cl　Cl	(1:1)	1.8	33.5
O 　　　　$\|$ VBr/CH$_2$=CHCN HCH$_2$OH	(1:1)	62	22.7
O 　　　　　　↑ VBr/ClCH$_2$CH$_2$OPOCH$_2$CH$_2$Cl 　　　　$\|$ 　　　　CH 　　　　$\|$ 　　　　CH$_2$	(1:1)	6.9	28.3
O 　　　↑ VBr/(O—P—R)$_n$ 　　　$\|$ 　　　CH 　　　$\|$ 　　　CH$_2$	(2:1)	17.0	27.9

second large drop in thermal stability occurs as soon as more than one alpha hydrogen per bromine atom is introduced: vinylidene bromide versus vinyl bromide.

VBr Copolymers

Various VBr copolymers in various weight ratios have also been investigated. A set of copolymers, with the charged monomer weight ratios indicated, is given in Table VII. The flame retardance efficiencies of different copolymers range even more widely than those of the homopolymer grafts. When dealing with copolymer grafts, we believe that large variations in melt viscosity of the different grafted materials are predominantly responsible for the large variations in the apparent efficiencies. That this may be so can be easily seen in the large variations in the "viscosity" of the melt of the fiber in the *OI* determination. Grafts with high oxygen indices tend to have very low "viscosity" melts that easily run away from the flame front. This was most pronounced with the methoxyvinyl

TABLE VIII
OI of VBr Terpolymers

Terpolymer	Grafting yield, %	*OI*
VBr/VCl$_2$/CH$_2$=C—OCH$_3$ P(OCH$_3$)$_2$ O	4.2	>29.4
VBr/CH$_2$=C—OCCH$_3$ P(OCH$_3$)$_2$ O	2.8	30.6
VBr/VCl$_2$/CH$_2$=CHCOCH$_2$P(OCH$_3$)$_2$	25.9	27.6
VBr/ClCH$_2$CH$_2$OPOCH$_2$CH$_2$Cl/ CH CH$_2$	13.8	32.8
VBr/ClCH$_2$CH$_2$OPOCH$_2$CH$_2$Cl/CH$_2$=CHCN HCH$_2$P(OCH$_3$)$_2$ CH CH$_2$	3.1	25.5

and acetoxyvinyl phosphonate and the butadiene–hexachlorocyclopentadiene adduct copolymers, which therefore tended to have unusually high *OI* values.
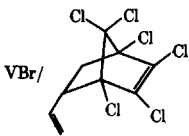
VBr Terpolymers

A set of VBr terpolymers, all charged in a 1:1:1 weight ratio, is given in Table VIII. The same conclusions apply to these grafts as the copolymer grafts. Incorporation of vinylidene chloride did not seem to contribute to increased *OI*. In general, the terpolymer compositions that we looked at did not seem to have any advantages over the copolymer compositions.

TABLE IX
Tenacity and Elongation Versus Percent PVBr Grafting Yield

Grafting yield, %	Tenacity, g/den	Elongation at yield point, %
—	4.4	38
2.9	4.5	92
5.5	4.3	90
7.6	4.8	82
10.7	4.8	73
17.7	4.5	84
20.3	3.9	94
24.4	4.6	120

TABLE X
Tenacity and Elongation Versus Copolymer Graft

Copolymer	Grafting yield, %	Tenacity, g/den	Elongation at yield point, %
None	—	4.40	38
VBr/CH₂=C—OCH₃ with P(OCH₃)₂ and O (see structure)	(1:1)	3.9	4.73	101
VBr/CH₂=C—OCCH₃ with P(OCH₃)₂ and O (see structure)	(4:1)	2.3	4.60	83
VBr/CH₂=CHCOCH₂P(OCH₃)₂ (see structure)	(7:3)	14.4	4.73	84
VBr/ (chlorinated bicyclic structure)	(1:1)	1.8	4.40	•87
VBr/ClCH₂CH₂OPOCH₂CH₂Cl with CH and CH₂ (see structure)	(1:1)	6.9	4.60	84
VBr/(−O—P—R−)ₙ with CH and CH₂ (see structure)	(2:1)	17.0	4.40	78

Properties

Melting Point versus Type of Graft

In general, the various grafts that we examined, regardless of the grafting yield (up to about 30%), showed only a small decrease or increase in the melting point. The one trend that was always noticed was that grafting VBr either as a homopolymer or as a copolymer always resulted in a decrease in the melting point.

Tenacity and Elongation versus Type of Graft

Selected data on tenacity and elongation versus percent grafting yield of PVBr are given in Table IX, and that versus type of copolymer grafts is given in Table X. From all of our work, two generalizations can be made: (1) grafting produced minimal changes in tenacity and stiffness, and (2) in practically all cases grafting induced large increases (up to 120% to yield point, and up to 150% total) in the elongation. These results would suggest that the main grafting occurred in the

amorphous regions of the substrate, with only a few changes in the crystalline regions. In the case of PVBr grafts from 2.9% to about 20% grafting yield, the elongation varied from 73 to 94%. The 24.4% graft, which also contained 1.8% sulfur, had a jump in elongation at yield point to 120%, with a small increase in tenacity (4.60 g/den). In the case of different copolymer grafts, again the elongation at yield point varied between 78 and 101% and a small increase in tenacity in most cases. Considering the low grafting yields, the elongation values are remarkable in most cases.

These increases in elongation are difficult to explain, but have appeared consistently in all our grafting work. Presumably, the small decreases in crystallinity which inevitably must accompany grafting plus the "plasticization" of the noncrystalline regions cause the increased elongation. Further work is needed with regard to these unexpected results.

CONCLUSIONS

Vinyl bromide can be graft copolymerized either at the surface, uniformly throughout, or predominantly at the core of the polyester filament. The core location for the PVBr was the most efficient in its utilization, followed by uniform and then surface location. Grafting of other bromine-containing flame retardants showed that their flame retardance efficiencies depended not only upon the location of the graft within the filament but also upon the structure of the compound. For the various bromine homopolymer grafts, their apparent thermal stabilities and their flame retardance efficiencies could be related to the alpha aliphatic hydrogen-to-bromine ratio in the repeating unit of the graft. The lower this ratio was, the higher the thermal stability and the higher the efficiency. For VBr copolymer and terpolymer grafts, the apparent very large variations in flame retardance efficiencies were attributed to large variations in melt viscosity of the grafts.

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