

# Localized Radiation Grafting of Flame Retardants to Polyethylene Terephthalate. II. Vinyl Phosphonates

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## Synopsis

Six vinyl phosphonates have been synthesized and evaluated as grafts on poly(ethylene terephthalate) for their flame retardance properties. Diethylvinyl phosphonate was used as a model for phosphorus-containing flame retardants in developing the methodology for localizing flame retardants either on the surface of the filament or uniformly throughout it. 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 poly(diethyl vinyl phosphonate) was then correlated with its location in the filament. Other grafted phosphorus-containing flame retardants showed a range of efficiencies that depended not only upon the location of the graft within the filament but also upon the %P in the compound. The wide variations in flame retardance efficiencies of copolymers and terpolymers were attributed to large variations in the melt viscosity of the different grafted materials. The grafts showed only small changes in tenacity and large increases in elongation.

## INTRODUCTION

The studies of localized vinyl bromide grafting on poly(ethylene terephthalate) (PET) fibers and grafting of vinyl bromide copolymers and other bromine-containing monomers were described in a previous paper.<sup>1</sup> The work presented here deals with the synthesis of six functionally substituted phosphorus-containing monomers, their homo-, co-, and terpolymer grafting, and evaluation of the grafted materials. Diethyl and dimethyl vinyl phosphonates were grafted on PET fibers to investigate the effect of the graft distribution within the filament upon their flame retardance efficiency. Grafting of the other phosphorus-containing monomers showed a wide range of efficiencies that depended not only upon the location of the graft within the filament but also upon the %P content in the molecule.

## EXPERIMENTAL

### Monomer Synthesis

Six monomers were synthesized according to the literature references cited. The products were characterized by their boiling points and by elemental analysis. The formulae and analysis results are presented in Tables I and II, respectively.

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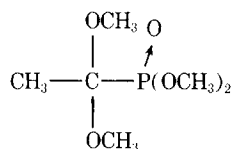
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TABLE I  
 Structural Formulae of the Compounds Synthesized

$\text{CH}_2=\text{CHC}(\text{O})\text{NHCH}_2\text{P}(\text{O})(\text{OCH}_3)_2$	$\text{CH}_2=\text{C}(\text{OCH}_3)\text{P}(\text{O})(\text{OCH}_3)_2$	$\text{CH}_2=\text{C}(\text{OCCH}_3)\text{P}(\text{O})(\text{OCH}_3)_2$
N-(dimethylphosphonomethyl)- acrylamide (I)	dimethyl 1-(methoxy)vinyl phosphonate (II)	dimethyl 1-(acetoxy)vinyl phosphonate (III)
$\text{CH}_2=\text{CHC}(\text{O})\text{COCH}_2\text{P}(\text{O})(\text{OCH}_3)_2$	$\text{CH}_2=\text{CHP}(\text{O})(\text{OCH}_3)_2$	$\text{CH}_2=\text{CHCH}_2\text{P}(\text{O})(\text{OCH}_3)_2$
dimethylphosphonomethyl acrylate (IV)	dimethyl vinyl phosphonate (V)	dimethyl allyl phosphonate (VI)

**N-(Dimethylphosphonomethyl)acrylamide (NDPA).** NDPA was prepared<sup>2,3</sup> directly from trimethyl phosphite (TMP) and N-methylolacrylamide (NMA). Solid NMA (mp 75–76.5 °C), recrystallized from ethyl acetate, was added in small increments to TMP (5:1 mole ratio) maintained at 65° ± 3°C and containing 2,6-di-*tert*-butyl-4-methylphenol (0.3 g/mole NMA) as a vinyl polymerization inhibitor. Elevated temperature was maintained for 70 min after addition to allow the reaction to go to completion. Partial stripping at reduced pressure was followed by vacuum filtration through sintered glass. After final stripping to terminal conditions of 60°C at 0.1 mm, NDPA was obtained as a colorless liquid residue in quantitative yield.

**Dimethyl 1-Methoxyvinyl Phosphonate (DMVP).** DMVP was prepared by the Golborn and Dever method.<sup>4,5</sup> Its precursor, dimethyl 1,1-dimethoxyethyl phosphonate (A), was prepared by adding phosphorus trichloride dropwise to a mixture of trimethyl orthoacetate, trimethyl phosphite, and zinc chloride (1 g/mole PCl<sub>3</sub>) maintained at -5° to 0°C. Vacuum distillation gave A in 81% yield. Elimination of methyl alcohol was accomplished by heating with sodium bicarbonate (2.5 g/mole) for 1 hr at 178°C and then 15 min at 180°–200°C. The desired monomer, DMVP, was obtained with 70% yield as a colorless liquid by vacuum distillation:



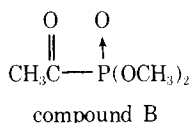
compound A

**Dimethyl 1-acetoxyvinyl Phosphonate (DAVP).** DAVP was prepared via the Golborn<sup>6</sup> route. Its precursor, dimethyl acetyl phosphonate (B), was conveniently prepared by dropwise addition of TMP to acetyl chloride at 0°C.

TABLE II  
 Analytical Data on Compounds Synthesized

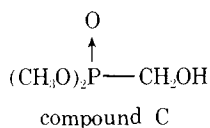
Com- pound	Formula	MW	% Carbon		% Hydrogen		% Phosphorus	
			Theory	Found	Theory	Found	Theory	Found
I	C <sub>6</sub> H <sub>12</sub> NO <sub>4</sub> P	193.14	37.31	37.23	6.26	6.46	16.04	15.74
II	C <sub>5</sub> H <sub>11</sub> O <sub>4</sub> P	166.12	36.15	35.98	6.68	6.67	18.65	18.43
III	C <sub>6</sub> H <sub>11</sub> O <sub>5</sub> P	194.12	37.12	36.94	5.71	5.78	15.96	15.96
IV	C <sub>6</sub> H <sub>11</sub> O <sub>5</sub> P	194.12	37.12	36.93	5.71	5.64	15.96	15.74
V	C <sub>4</sub> H <sub>9</sub> O <sub>3</sub> P	136.09	35.30	35.49	6.66	6.62	22.76	22.54
VI	C <sub>5</sub> H <sub>11</sub> O <sub>3</sub> P	150.12	40.00	39.80	7.39	7.26	20.63	20.51

Vacuum distillation gave B in 81% yield:



Compound B was then mixed in an equal molar amount with acetic anhydride and a 20% molar excess of pyridine under N<sub>2</sub>. The temperature was maintained at 25°C for 17 hr. The reaction mixture was then treated with methanol, neutralized with NaHCO<sub>3</sub>, and concentrated by stripping at ambient temperature. DAVP was extracted from the resulting paste with chloroform. The resulting solution was washed with small portions of water and stripped at ambient temperature giving DAVP in a 55% yield.



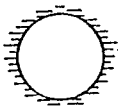
**Dimethyl Phosphonomethyl Acrylate (DPA).** DPA was prepared by acryloyl chloride esterification of dimethyl hydroxymethyl phosphonate (C), which was conveniently synthesized by a newly developed preparative procedure:



Compound C was prepared from dimethyl phosphite (DMP), aqueous formaldehyde (25% excess), and triethylamine (~20 ml/mole DMP) to drive the reaction quickly to completion. Triethylamine is added dropwise with caution to a stirred, cooled mixture of aqueous formaldehyde and DMP. No exotherm is observed until sufficient triethylamine is added to neutralize acid constituents. Thereafter, large quantities of free triethylamine must be avoided, especially in the early stages in order to maintain control of the reaction. When all DMP was consumed, volatiles were removed at reduced pressure to terminal conditions of 120°C at 0.15 mm, giving compound C as a colorless liquid residue in quantitative yield and of sufficiently purity for reaction with acryloyl chloride.

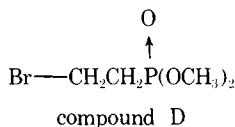
Acryloyl chloride in dry methylene chloride (1 l./mole) was added dropwise to a stirred and cooled (0°–5°C) mixture of compound C and triethylamine (10% excess). After warming to ambient temperature, triethylamine hydrochloride was separated by filtration. The solution was washed repeatedly with small portions of water, treated with anhydrous sodium carbonate, filtered, and

TABLE III  
 FR Location Versus Efficiency

	Solution Coating	Grafts	
			
DEVP OI	23.2	27.6	24.3
% FR	18	16	21
$OI_{\text{control}} = 20.4$			

stripped leaving DPA as a crude residue with a 65% yield. Distillation (88°C at 0.3 mm), using 0.5% hydroquinone as inhibitor, yielded pure DPA as a colorless liquid with 53% overall yield.

**Dimethyl Vinyl Phosphonate (DMeVP).** DMeVP was prepared by the Zenftman and Calder<sup>7</sup> route. Dimethyl phosphite was added dropwise to threefold 1,2-dibromoethane maintained at 110°–115°C. Stripping thereafter to 140°C at 0.2 mm gave poor yields (15%–30%) of dimethyl 2-bromoethyl phosphonate (D) based on starting trimethyl phosphite. Crude dimethyl 2-bromoethyl phosphonate (D) was dehydrobrominated with excess triethylamine. Reaction was run in benzene for 17 hr at ambient temperature. Insoluble triethylamine hydrobromide was removed by filtration, and the filtrate was refluxed for 1 hr to complete reaction. A second filtration followed by stripping, and distillation resulted in a 58% yield of dimethyl vinyl phosphonate (bp 33°C/0.2 torr).



**Dimethyl Allyl Phosphonate (DMAP).** DMAP was prepared conveniently by the procedure of Arbusov and Razumov.<sup>8</sup> TMP was heated 5 hr at 76°C with 2.9 moles allyl bromide. Unreacted allyl bromide was removed by distillation, and a 12-in. packed column was used to separate dimethyl methyl phosphonate prior to collecting DMAP (48%) at 43°C (0.1 torr).

**Diethyl Vinyl Phosphonate (DEVP).** Diethyl vinyl phosphonate was obtained from Polysciences, Inc., and was used as received.

**Substrate Grafted.** American Enka Co. polyester fiber; 150/96 S.D. polyester filament yarn; 0.35% TiO<sub>2</sub>; ~0.2% water-soluble finish.

**Grafting Techniques. Gamma Radiation.** The samples were degassed by three freeze-thaw cycles to at least 10<sup>-5</sup> torr. In most cases, the grafting was performed using a mutual irradiation technique in a small glass ampule at dose rates of 0.01–0.1 Mrad/hr. Following irradiation, the fiber samples were extracted with solvent for the homopolymers or copolymers, first at room temperature and then at a temperature of 70°–100°C. 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 were obtained following this drying procedure.

**Uniform Grafting.** The fibers were preswollen in ethylene dichloride at 70°C/0.5 hr, 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.

**Grafting in Presence of ZnCl<sub>2</sub>.** A 1:1 molar ratio of monomer:ZnCl<sub>2</sub> was prepared by dissolving the required amount of anhydrous ZnCl<sub>2</sub> in ethyl acetate with vigorous stirring; to this solution was added the monomer. The preswollen (DCE) fiber was treated with this solution, and the sample was sealed and grafted in the manner described above.

**Oxygen Index (OI).** A sample holder has been developed to evaluate fiber samples for OI. The procedure, as well as the validity of the technique, have been previously described.<sup>9</sup>

**Scanning Electron Microscopy and X-Ray Microprobe Analysis.** Thin cross sections of the grafted PET fibers were prepared by embedding the fibers 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. 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 conveniently record a specific heat-versus-temperature curve in a relatively short time. Melting is taken as the temperature at which the specific heat-versus-temperature curve goes through the maximum of the melting peak. Typically, 5–10 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 a 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.

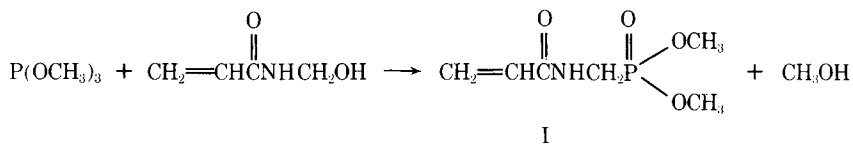
**Mechanical Properties.** Tenacity and elongation were determined on dried fibers (50°C, vacuum oven) in a Instron machine. The determinations were made on a sample with a gauge length of 1 in. at a gauge speed of 5 cm/min.

## RESULTS AND DISCUSSION

### Monomer Synthesis

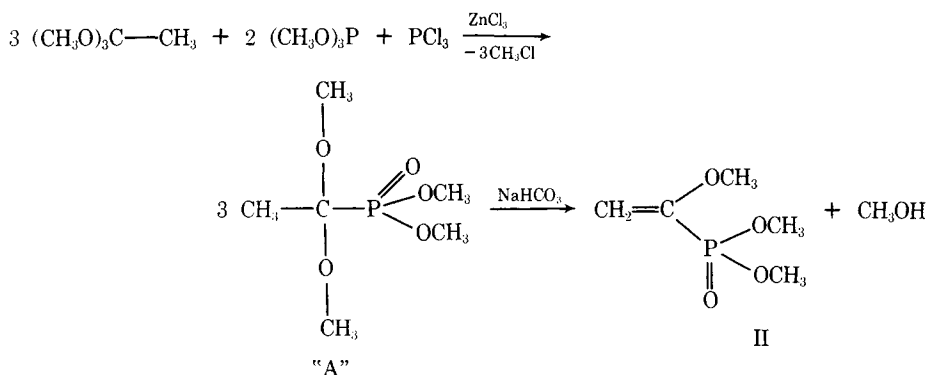
In addition to the procedures given in the experimental section, the following observations should be emphasized in the synthesis of the various monomers. The structural formulae of the monomers synthesized are given in Table I.

**Synthesis of NDPA.** This compound was prepared directly from trimethyl phosphite (TMP) and freshly recrystallized N-methylolacrylamide (NMA):



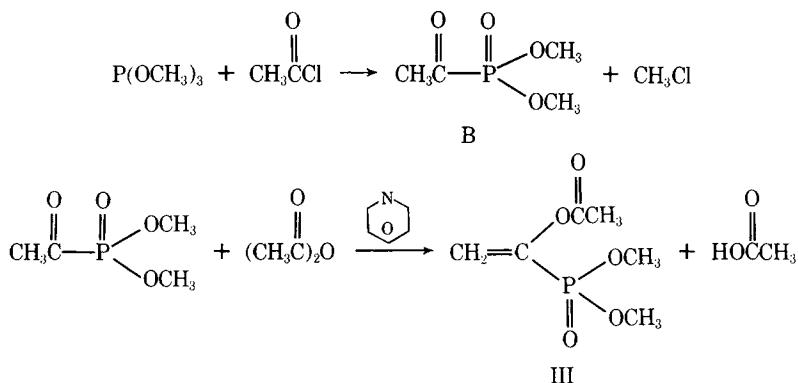
The NMA was added in increments to excess TMP maintained at  $65^\circ \pm 3^\circ\text{C}$ , and a quantitative yield of the product was obtained as a residue on stripping.

**DMVP.** This compound was prepared in the following reaction sequence:



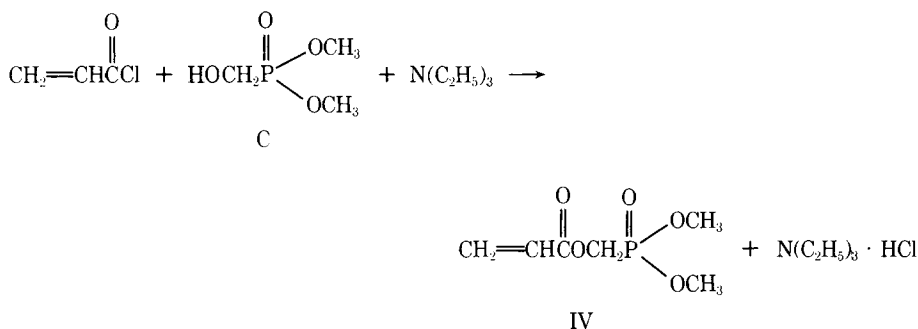
The reactants used were in the molar amounts indicated in the equation, and  $\text{ZnCl}_2$  was used in the amount of 1 g/mole of  $\text{PCl}_3$ . The product was obtained in an overall yield of 64%.

**DAVP.** This monomer was prepared as follows:



It was found that compound B would undergo enolacetylation at ambient temperature using acetic anhydride and pyridine. Efforts to isolate DAVP by vacuum distillation proved unsuccessful, so an involved procedure was used that resulted in significant losses of DAVP as a result of its alkaline hydrolysis and water solubility. Methanol was first added with cooling to consume unreacted acetic anhydride. Sodium bicarbonate followed by water was added to neutralize acetic acid. All volatiles were then removed at ambient temperature under high vacuum. DAVP was extracted from the resulting paste with chloroform and washed with small portions of water. DAVP was obtained on stripping at ambient temperature in 55% yield as a light-amber liquid.

**DPA.** This monomer was prepared as follows:



Attempted preparation of compound C proved unsuccessful using conditions similar to those used in the preparation of diisopropyl hydroxymethyl phosphonate.<sup>10</sup> Presumably, hydrolysis and methylation of dimethyl phosphite were competing reactions when aqueous formaldehyde was used. Hydrolysis transformed dimethylphosphite into monoethyl phosphite and phosphorous acid. These acids neutralized the triethylamine catalyst, making hydrolysis the predominant reaction.

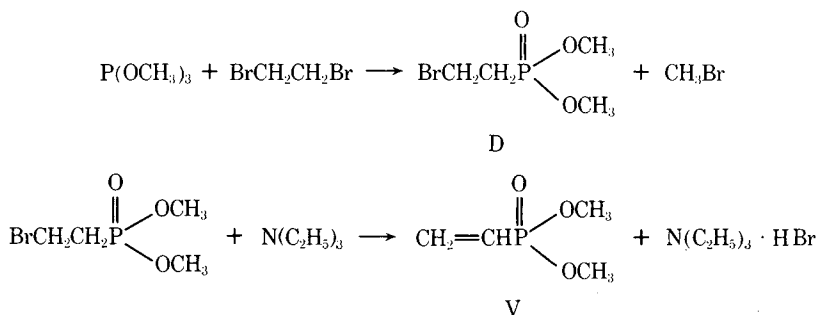
Suitable reaction conditions were found which minimized hydrolysis of dimethyl phosphite and resulted in a successful synthesis. The reaction temperature was maintained in the 20°–25°C range instead of the reported 40° and 90°C reaction temperatures used by Golborn<sup>10</sup> for preparation of diisopropyl hydroxymethyl phosphonate. A 25% molar excess of formaldehyde, along with triethylamine, was used to drive reaction quickly to completion, thereby limiting contact time of dimethyl phosphite with water.

The technique used involved cautious, dropwise addition of triethylamine to a stirred and externally cooled mixture of aqueous formaldehyde and dimethyl phosphite. No exotherm was observed until sufficient triethylamine was added to neutralize acid constituents. Thereafter large quantities of free triethylamine *must be avoided* in order to maintain control of the reaction. This is especially true early in the reaction when dilution of reactants by product is not extensive.

The reaction is conveniently monitored by observing the disappearance of dimethyl phosphite using NMR (disappearance of the response located at 0.88  $\delta$  which is one resonance of the doublet ( $J = 697$  Hz) for the hydrogen attached to phosphorus in dimethyl phosphite).

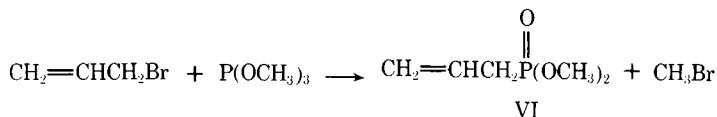
Crude dimethyl hydroxymethyl phosphonate obtained by stripping under high vacuum was of adequate purity for subsequent esterification with acrylyl chloride using triethylamine as acid acceptor. Crude yield of DPA was 65% after significant losses occurred during water washings to remove triethylamine hydrochloride. Distillation using hydroquinone inhibitor gave DPA in 53% overall yield based on starting dimethyl phosphite.

**DMeVP.** This monomer was prepared by the following reaction sequence:



The Arbusov reaction of trimethyl phosphite with a threefold excess of 1,2-dibromoethane resulted in poor yields (15–30%) of dimethyl 2-bromoethyl phosphonate (D). The major reaction product was dimethyl methylphosphonate, formed by the methyl bromide-catalyzed isomerization of trimethylphosphite.

**DMAP.** This compound was prepared directly from excess allyl bromide and trimethyl phosphite:



### Grafting Techniques

Four of the seven phosphonates studied presented some special problems, and these will be discussed below.

**NDPA.** When  $\gamma$ -irradiated in a mutual recipe in aqueous solution, this monomer homopolymerized in a manner that was hard to control. The product which was obtained was highly crosslinked, as indicated by swelling tests on homopolymerized samples. Thus, for grafting purposes we had to use two-step postirradiation techniques in order to control the add-ons. By preirradiating the fiber (or fabric) with as low a total dose as 2 Mrads and subsequently combining it with an aqueous (or organic solvent) solution of NDPA, add-ons as low as 4% could be obtained.

**DMVP and DAVP.** These monomers could not be grafted to any significant add-ons in a mutual recipe using  $\gamma$ -irradiation at total doses of 6 Mrads. However, they both could be grafted to achieve add-ons above 20% by combining them with ethyl acetate solutions of anhydrous  $\text{ZnCl}_2$  (1:1 molar ratio). This technique was found to lead to improved add-ons with a number of other formulations which were hard to graft, for example, those containing vinylidene bromide or bis(2-chloroethyl) vinyl phosphonate (Fyrol Bis-Beta).

**DMAP.** This monomer could not be grafted with add-ons above 3% because of the great propensity of the allyl group for chain transfer.

**Localized Grafting.** Both DEVP and DMeVP were grafted uniformly and at the surface of PET fibers. Poly(DEVP) was also solution (THF) coated for comparative evaluation in the OI test. The distribution of DEVP grafts across the PET fiber cross section was determined in a semiquantitative fashion using an x-ray microprobe attachment to the scanning electron microscope. The phosphorus distribution in fiber cross sections are depicted in Figures 1–4.



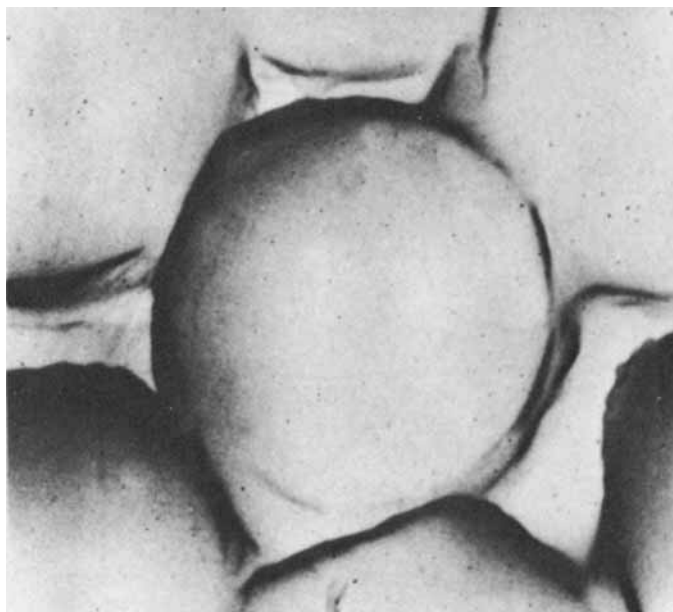


Fig. 1. Secondary electron image of surface P(DEVP) grafted polyester.

Figures 2 and 4 clearly show the different phosphorus distributions in the two substrates. Similar photomicrographs (indicating different graft distribution) were obtained for DMeVP.

#### **OI Versus Location of the Graft**

The OI-versus-location data are summarized in Table III. The placement of poly(DEVP) in the interior and more uniformly in fibers enhanced its flame

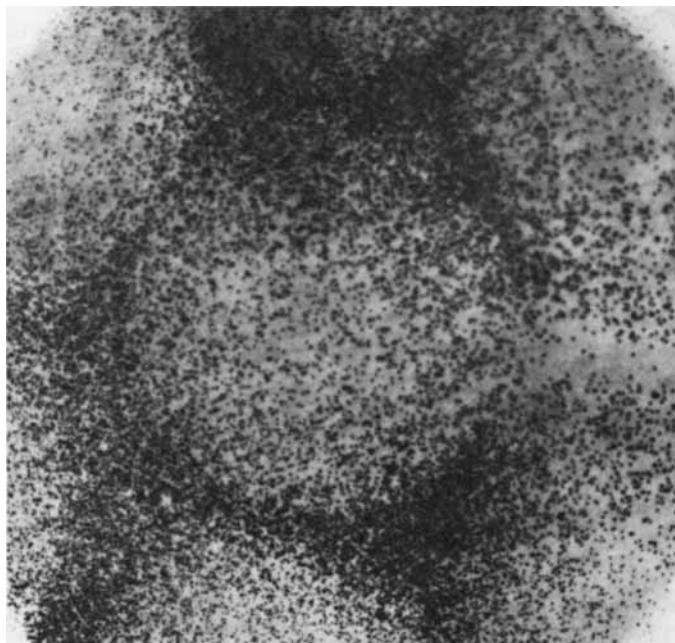


Fig. 2. Phosphorus distribution from sample in Figure 1.

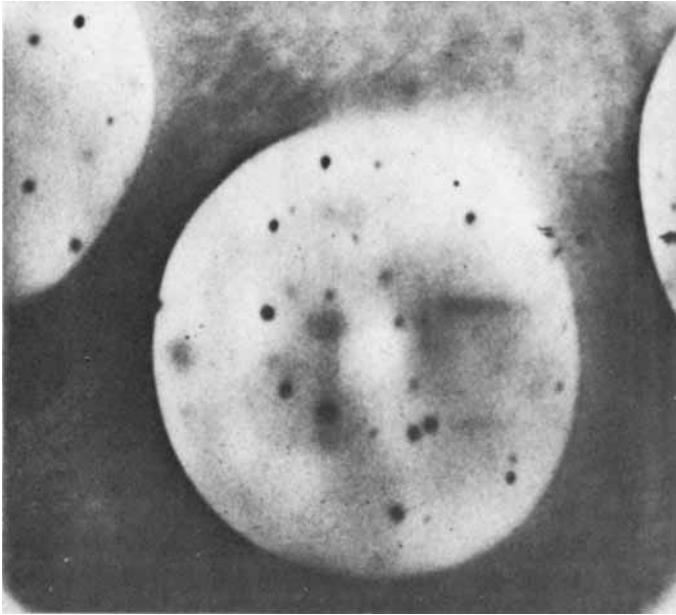


Fig. 3. Secondary electron image of uniformly P(DEVP) grafted polyester.

retardance efficiency. Surface grafting was a poor second, and solution deposition of the polymer led to its least efficient utilization. These correlations are identical to those found for poly(vinyl bromide).<sup>1</sup> TGA analysis of the poly-(DEVP) grafts indicated that they were no more thermally stable than those of poly(vinyl bromide). Thus, it would seem that factors that delay the volatilization of the phosphorus source from PET will increase its flame retardance efficiency.

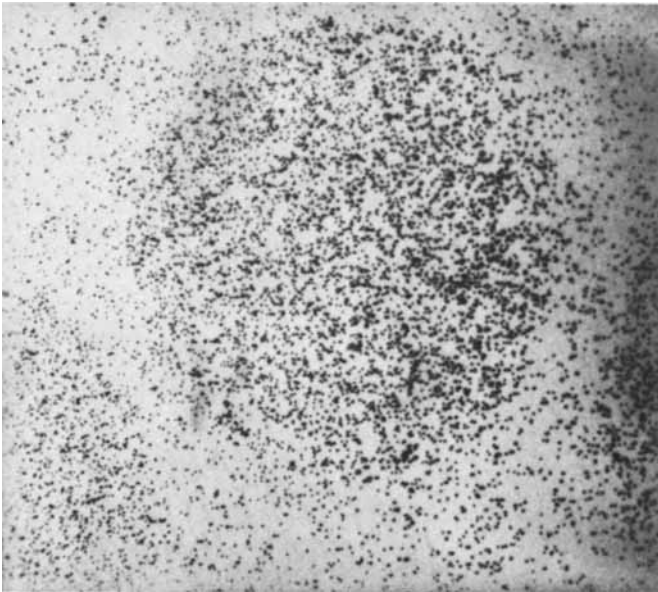
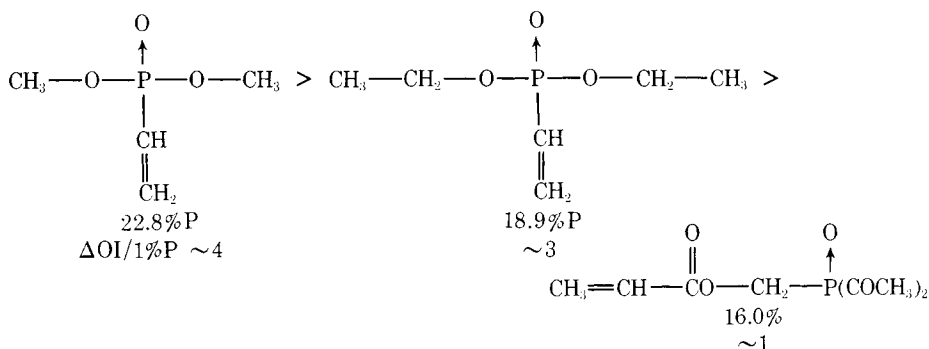


Fig. 4. Phosphorus distribution from sample in Figure 3.

### Homopolymer, Copolymer, and Terpolymer Grafts

Some of the homo-, co-, and terpolymer graft data are recorded in Tables IV-VI. The increase in OI per %P in the homopolymer grafts of DMeVP, DEVP, and DPA followed the %P content in the monomer; the higher the %P, the higher the OI.



These were the only monomers that underwent facile polymerization. DMVP and DAVP required  $\text{ZnCl}_2$  complexion before grafting and led to highly melt viscosity-modified products, and the DMAP could not be grafted above 3% add-on. Thus, these monomers cannot be included in the above generalization. Since the phosphorus functionality was not changed in these monomers, it is reasonable that the OI would follow the %P in the molecule for this is also related to the "fuel content" (hydrocarbon) of the molecule. With copolymer and terpolymer grafts, there were large variations in the OI data and seemingly little correlation with the % add-on values. These large variations may result from variations in melt viscosity that were observed in the OI test. Grafts with high oxygen indices tend to have very low "viscosity" melts that easily run away from the flame front. This was especially noticeable with monomer formulations involving DMVP or DAVP as one of the components. These same observations were noted before with various halogen-containing grafts.<sup>1</sup> Homo- and copolymer grafts showed only a minor ( $1^\circ$ - $3^\circ\text{C}$ ) increase or decrease in the melting point.

### Mechanical Behavior of the Grafts

The tenacity and elongation data are given in Tables IV-VI. The tenacity data indicated little variation from the value of the base fiber (4.4 g/den) with grafting. However, in most examined cases, the elongation at yield had increased from 67 to 102 versus 38% percent for the base fiber. These results are similar to those observed with bromine-containing grafts. Presumably, the large in-

TABLE IV  
Properties of Homopolymer Grafts (Uniform)

Composition	% Add-on	OI	Tenacity, g/den	Elongation, % Y.P.
DMVP	27	27.1	4.7	84
DAVP	12	24.7	4.3	102
DMeVP	5	25.2	—	—
DEVP	15	27.6	—	—
DPA	28	26.7	4.4	79
NDPA	10	28.3	3.8	67
DMAP	3	21.8	—	—
Control	0	20.4	4.4	38

TABLE V  
Properties of Copolymer Grafts (Uniform)

Composition	% Add-on	OI	Tenacity, g/den	Elongation, % Y.P.
DMVP/VCl <sub>2</sub> (1:2 by wt)	17	26.7	5.0	82
DMVP/acrylamide (2:1)	20	27.9	4.5	72
DAVP/VCl <sub>2</sub> (1:1)	20	22.2	4.0	65
DAVP/acrylamide (2:1)	9	28.3	4.7	84
DPA/VBr (7:3)	14	27.6	4.7	84
DPA/VBr <sub>2</sub> (1:1)	15	28.6	4.7	82
NDPA/VBr <sub>2</sub> (1:1)	3	29.0	3.3	64
NDPA/Fyrol BB (1:1)	2	21.4	4.8	93
Control	0	20.4	4.4	38

TABLE VI  
Properties of Terpolymer Grafts (Uniform)

Composition	% Add-on	OI	Tenacity, g/den	Elongation, % Y.P.
DMVP/VCl <sub>2</sub> /VBr (1:1:1 by wt)	4	29.4	4.8	94
DAVP/VCl <sub>2</sub> /VBr <sub>2</sub> (1:1:1)	3	31.4	4.7	99
DAVP/VCl <sub>2</sub> /VBR (1:1:1)	3	30.6	4.5	86
DPA/VBr/VCl <sub>2</sub> (4:3:3)	18	27.6	5.0	85
NDPA/Fyrol BB/VBr (3:3:1)	3	25.5	4.3	87
NDPA/VBr <sub>2</sub> /VCl <sub>2</sub> (3:2:2)	3	27.9	3.8	67
Control	0	20.4	4.4	38

creases in elongation with little effect upon tenacity are due to a "plasticization" effect of the noncrystalline regions as a result of the grafting. However, further work is needed to elucidate this mechanism.

## CONCLUSIONS

Six vinyl phosphonates have been synthesized, and the flame retardance properties of these grafts on PET have been evaluated. The flame retardance efficiency of DMeVP, DEVP, and DPA homopolymer grafts appear to follow the %P in the monomer—the higher the P content, the higher the OI.

Diethyl or dimethyl vinyl phosphonate can be grafted either at the surface or uniformly throughout the PET fiber. The uniformly grafted fibers have higher OI values than surface grafted ones, and solution coating appeared to be the least efficient.

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