Synthesis and Characterization of Polymers with Pendent Phosphonate Groups

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Synopsis

Soluble chloromethylated polystyrene and its copolymers with vinylidene chloride as well as poly(phenyl oxides) brominated in the side chains and in the ring were synthesized and characterized in detail by NMR. The halogenated polymers were phosphonylated with alkyl phosphites. Uncrosslinked polymers with pendent phosphonate groups were prepared in the presence of etheral solvents, which solvate the ionic intermediates of the Arbuzov reaction. These polyphosphonates are highly hygroscopic and are soluble in a variety of solvents. Their T_g's are in the range of 50–175°C. Their thermal behavior was analyzed on the basis of thermogravimetric measurements combined with mass-spectrometric analysis. Poly(styrene phosphonate) seems to be the most stable, and its thermal decomposition starts at ~330°C. The polymeric phosphonates are compatible with an unusually large number of polymeric systems and seem to form "true" polymeric alloys with acetylcellulose.

INTRODUCTION

Phosphorus-containing polymers have attracted considerable interest over the past years, and several reviews were devoted to this subject.[1-3] The interest in these polymers was greatly enhanced in view of the role of organic phosphorus in imparting fire retardance to polymeric systems, either by itself or in combination with halogens.[4]

There have been two main approaches to the synthesis of such polymers: (1) direct polyaddition or condensation from P-containing monomers and (2) modification of existing macromolecules by reaction of a phosphatic reagent with some functional group contained in the chain.

Except for very few cases,[5] the polymerization of P-containing monomers invariably resulted either in intractable crosslinked systems or in low molecular weight polymers of poor mechanical properties.[1]

The modification of commercially available polymers by reaction with phosphorylating reagents was more successful and led in some cases to high MW products that may have important uses.[6] Phosphorylated polyethylene[7] and a phosphono acetal[8] based on poly(vinyl alcohol) are successful examples of this approach.

In previous publications from this Laboratory, work on metal ion[9] and water transport properties[10] of plasticized PVC membranes was reported,

TABLE I

Chloromethylation of Polystyrene and its Copolymers with Vinylidene Chloride at 25°C

Polymer	Styrene/vinylidene chloride in polymer	$(\eta)^a$	Polymer, g	ClCH$_2$OCH$_3$, ml	CS$_2$, ml	AlCl$_3$, g	ZnCl$_2$, g	Reaction time, hr	Cl in Polymer, %		Degree of chloromethylation	
									Before reaction	After reaction	I[b]	II[c]
Polystyrene	—	0.9098	10	12	50	2.5	—	5	—	22.3	0.95[d]	0.95
Polystyrene	—	0.9098	10	150	50	—	10	20	—	20.6	0.88[e]	0.86
Copolymer-1	0.84	0.0332	2.5	12	50	2.0	—	5	38.2	41.8	0.48	0.72
Copolymer-2	2.12	0.1303	2.5	2.5	120	1	—	5	22.3	26.0	0.25	0.20
Copolymer-2	2.12	0.1303	1.5	1.5	—	0.5	—	2	22.3	29.0	0.47	0.45
Copolymer-2	2.12	0.1303	1.5	1.5	—	—	0.5	4	22.3	29.7	0.53	0.42
Copolymer-3	1.63	0.3359	10	10	50	7	—	7.5	26.6	34.9	0.76	0.84
Copolymer-3	1.63	0.3359	10	10	50	11	—	11.5	26.6	39.0	1.05	1.26

[a] Intrinsic viscosity in toluene at 25°C.
[b] Calculated from the %Cl of the chloromethylated compound.
[c] Calculated from the % P after phosphorylation of the product.
[d] Gel fraction: 70% of polymer.
[e] Gel fraction: 1% of polymer.

the plasticizers being various esters of phosphonic and phosphoric acid. It was of interest to compare the transport properties of such membranes with those containing the ligand phosphoryl (PO) moiety that is covalently linked to the polymer backbone. For this purpose, it was necessary to prepare high molecular weight PO-containing and film-forming polymers. In view of the failure of previous attempts to achieve this aim by direct polymerization, we chose to arrive at such polymers by modification of easily available macromolecules. The phosphonylation of the polymeric backbone was achieved by an Arbuzov reaction.

The present work will describe the synthesis and characterization of several polymers of this kind, as well as some of their physical properties.

EXPERIMENTAL

Materials and Equipment

A commercial polystyrene had an intrinsic viscosity of $(\eta)^{25°}{}_{toluene} = 0.91$ dl^{-1}g; $M_n \approx 250,000$.

Copolymers of styrene and vinylidene chloride were prepared according to the procedure given in reference 11. Their composition and intrinsic viscosities are given in Table I.

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) (G.E. Grade 691-111): $[\eta]^{25°}{}_{toluene} = 0.51$ dl^{-1}g; $M_w \simeq 30,000$.

Trimethyl phosphite (TMP) ("Makhtheshim" Israel), technical grade, dried over sodium at room temperature and freshly distilled in argon atmosphere.

Triethyl phosphite (TEP) (Fluka), treated as the TMP.

Chloromethyl ether (CME) (Fluka, Pract.).

Carbon disulfide (Fisher, Analar).

Tetrachloroethane (TCLE) (Fluka, Pract.).

Bis(2-ethoxyethyl) ether (diethyl carbitol, DEC) (Fluka, Pract.).

Aluminum trichloride (anhydrous finely ground before adding to reaction mixture) (Fluka, Puriss).

Zinc chloride (Fisher, sticks), melted on the bottom of the reaction flask until vapor evolution ceased, then cooled to form a thin layer on the wall of the flask.

N-Bromosuccinimide (NBS) (BDH, laboratory reagent).

An AIRAM mercury lamp, Type M4 HgSl, 160 W output, was used for the photochemical brominations.

Chloromethylation of Polystyrene and Styrene–Vinylidene Chloride Copolymers

The experimental conditions are summarized in Table I.

All reactions were carried out at 25°C. AlCl$_3$ or ZnCl$_2$ were used as catalysts. In the case of copolymers, gelation was not observed, provided the catalyst was added in small portions. With the high MW polystyrene, a gel-free product could be obtained only with ZnCl$_2$ as catalyst. The reaction was stopped by adding wet dioxane until the red color disappeared. The polymer was precipitated with methanol.

Bromination of poly(2,6-Dimethyl-1,4-phenylene Oxide) (PPO)

Procedure A. A substitution of 1 bromine atom in the aromatic ring is achieved at room temperature by adding dropwise 1 mole-equivalent of bromine to a 1% solution of PPO in CCl_4 or in chloroform.

Procedure B. A substitution of 1 bromine atom in the aromatic ring and 1 bromine atom in the side chain is achieved by adding dropwise at room temperature 1 mole-equivalent of bromine to 1% PPO in tetrachloroethane (TCLE), raising the temperature to reflux after evolution of HBr stopped, then illuminating the reaction mixture with a Hg lamp and adding dropwise (for 90 min) a second mole-equivalent of Br_2.

Side group bromination[12] without simultaneous ring substitution can be obtained with a low stationary bromine concentration and at a high reaction temperature. Under these conditions, the radical reaction takes precedence over the electrophilic attack.

Procedure C-1. A product containing 90% side chain-substituted monobromide and 10% bromine in the aromatic rings is obtained by dropwise addition of 1 mole-equivalent of bromine to a 0.1% solution of PPO in TCLE kept at reflux. Reflux is continued for 60 min after the addition of bromine was complete.

Good results are also obtained if N-bromosuccinimide (NBS) is used as brominating agent.[13]

Procedure C-2. NBS, 1.1 mole-equivalent, is suspended in a 0.5% solution of PPO in CCl_4. The reaction mixture is illuminated with a Hg lamp and refluxed for 6 hr.

Procedure D-1. NBS, 2.6 mole-equivalents, is suspended in a 0.6% solution of PPO in a CCl_4–chloroform mixture (3/1 W/W). The reaction mixture is illuminated with a Hg lamp and refluxed for 6 hr.

Procedure D-2. A side chain-substituted dibromide can also be prepared by dropwise addition of 2 mole-equivalents of bromine to a 0.1% solution of PPO in TCLE kept at reflux. After the addition of bromine is complete, the reaction mixture is refluxed for 60 min.

A product in which 2 hydrogen atoms in some of the methyl side groups were substituted by bromine (69.9% total Br) is obtained by modifications of procedure D-2.

Procedure E-1. Bromine, 4.2 mole-equivalents, is added dropwise to a 0.1% solution of PPO in TCLE kept at reflux. When the addition of bromine is complete, reflux of the reaction mixture is continued for 90 min while catalytic quantities (3–4 mg) of benzoyl peroxide are added at 15-min intervals.

Procedure E-2. Bromine, 2 mole-equivalents, are added dropwise to a 0.1% solution of PPO in TCLE kept at reflux. Reflux is continued after the addition of bromine is complete. The reaction mixture is illuminated with the Hg lamp, and 2 mole-equivalents of NBS are added. Reflux is continued for 6 hr.

Polymers are precipitated with pentane and purified by dissolution in methylene chloride, followed by reprecipitation.

Preparation of Polymeric Phosphonate Esters by the Michaelis-Arbuzov Reaction. Phosphonylation of Chloromethylated Polystyrene and Its Copolymers

Essentially no gel formation occurred when the following procedure was adopted: A 5% solution of the polymer in diethyl carbitol (DEC) was added dropwise within 2 hr to a refluxing mixture of equal volumes of TEP and DEC, under vigorous stirring. A slight precipitate was observed with each drop hitting the boiling solution which, however, disappeared almost immediately. The reaction mixture was refluxed for additional 2 hr after completing the addition of the polymer solution. The mixture was then poured into excess of pentane and the precipitated product was purified by dissolution in methylene chloride and reprecipitation with pentane.

Thermal Degradation Measurements

A Perkin-Elmer instrument containing the following components was used: (i) a thermobalance TGS-1, (ii) a differential scanning calorimeter DSC-1B, and (iii) a thermomechanical analyzer TMS-1.

The oven was modified by inserting a glass attachment that connected it to the input part of a Finnigan Model 1015 mass spectrometer. The pyrolysis fragments were carried by an argon stream.

RESULTS AND DISCUSSION

Chloromethylation

Chloromethylation of crosslinked polystyrene and its copolymers is a widely practiced industrial process.[14] As our objective was to obtain soluble P-containing polymers, crosslinking had to be avoided at any stage of the synthesis. This was particularly hard to achieve with the higher molecular weight polymers.

Jones[15] obtained a soluble chloromethylated polystyrene containing 17% Cl (theoretical value for monosubstitution, 23.4%) by using very diluted polymer solutions in chloromethyl ether, whereby the concurrent Friedel-Crafts (crosslinking) reaction is minimized. When CS_2 was used as solvent, only 15.5% Cl was introduced, while 25% of the product gelled. In all cases, $AlCl_3$ was used as catalyst.

As may be seen from our results, summarized in Table I, gelling of the product was practically suppressed when $ZnCl_2$ was used as catalyst instead of the more active $AlCl_3$. A product with over 20% chlorine was obtained.

With the copolymers, no gellation was encountered, because of smaller probability of concurrent alkylation. However, in this system some HCl elimination from the polymer backbone always took place:

$$-CH_2-CCl_2-CH\phi-CH_2 \xrightarrow{AlCl_3} -CH=CCl-CH\phi-CH_2- + HCl$$
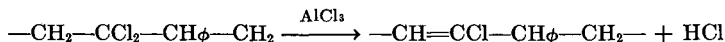
This is reflected by the difference in the apparent degree of substitution when calculated prior and after phosphonylation of the polymer (last two columns in the Table I).

TABLE II
Bromination of Poly(2,6-dimethyl-1,4-phenylene Oxide)

Procedure[a]	PPO, moles	Reagent, moles	Solvent	Br in polymer, %	Br in monounit (theoretical), %	Br atoms per phenyl group[b]	Br in side groups per monounit[b]		
							CH_2Br	$CHBr_2$	$CHBr_3$
A	0.82	1.0 Br_2	CCl_4	43.5	40	1.02	0	0	0
B	0.82	1.9 Br_2	TCLE	59	57	1.1[c]	1	0	0
C-1	0.09	0.1 Br_2	TCLE	41.5	40	0.1	0.9	0	0
C-2	0.41	0.5 NBS	CCl_4	38	40	0	0.9	0	0
D-1	0.50	1.3 NBS	$CHCl_3/CCl_4$ 25%/75%	60	57	0.2	1.7	0.1	0
D-2	0.045	0.9 Br_2	TCLE	57	57	0.1	1.9	0	0
E-1	0.5	2.1 Br_2	TCLE	66.9	—	0.1	1.0	0.5	0
E-2	0.5	1 Br_2 1 NBS	TCLE	70.1	—	0.1	1.0	0.5	0.17

[a] See procedures.
[b] Data based on NMR (cf. Table III).
[c] 69% Para and 31% ortho to the —CH_2Br group.

Bromination of PPO

Bromination of PPO may lead to a variety of products, depending on reaction conditions. Electrophilic monosubstitution in the phenyl ring is achieved spontaneously at room temperature, whereas methyl-group bromination is favored by a radical chain reaction.

In Table II are summarized the reaction conditions leading to the various products, which were not previously characterized in detail. The positions of the bromine atoms in the monounits (last four columns in Table II) were determined by NMR analysis (see Table III).

TABLE III
NMR Data

Monounit	Polymer designation	Type of H	Chemical shift, ppm
(2,6-dimethylphenylene oxide unit)	PPO	$-CH_3$	2.11
		$\phi-H$	6.55
(Br on ring; two CH_3)	PPOBr$_\phi$	$-CH_3$ (para)	2.03
		$-CH_3$ (ortho)	2.37
		$\phi-H$	6.15
(CH_3, CH_2Br)	PPOBr	$-CH_3$	2.11
		$-CH_2Br$	4.35
		$\phi-H$ para to CH_2Br	6.8
		$\phi-H$ ortho to CH_2Br	7.1
(CH_3, CH_2Br, Br)	PPOBrBr$_\phi$	$-CH_3$ (para)	2.03
		$-CH_3$ (ortho)	2.37
		$-CH_2Br$ (para)	4.3
		$-CH_2Br$ (ortho)	4.7
		$\phi-H$ para to CH_2Br	6.3
		$\phi-H$ ortho to CH_2Br	6.5
(CH_3, CH_2POCH_3)	PPOP$_{Me}$	$-CH_3$	2.11
		$-CH_2P$	2.85; 3.20 (doublet)
		$-OCH_3$	3.7
		$\phi-H$	6.5–7 (band)
(CH_2Cl on ring)	X[a]	$-CH_2Cl$	4.5
($CH_2-P(OCH_2CH_3)$)	PSP$_{Et}$	$-CH_3$	1.03–1.25 (band)
		$-CH_2P$	2.85; 3.2 (doublet)
		$-OCH_2-$	3.8–4.05 (band)

[a] Chloromethylated unit either of polystyrene or of its copolymers.

The Phosphonylation Reaction

Phosphonylation of active halide-containing compounds by alkyl phosphites is well documented,[16] and the synthesis of macromolecular phosphonates via the Arbuzov reaction has been reported.[17,18] However, an inherent difficulty in applying this reaction to a polymer system is due to gellation and formation of insoluble products. Two stages are recognized in this reaction[16]:
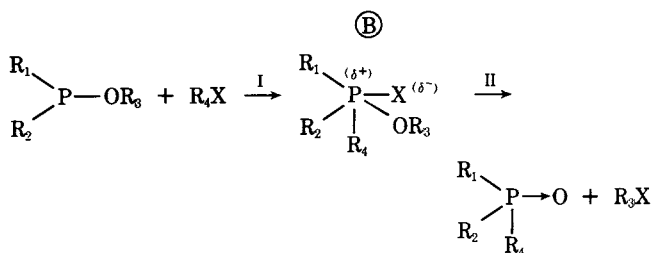
Stage I is facilitated by the nucleophilicity of R_1 and R_2, which enhances the stability of the ionic intermediate. By the same token, step II is slowed down by such substituents.

In our case, the alkylating agent was either triethyl or trimethyl phosphite. An insoluble gel was formed even if a very diluted solution of chloromethylated polystyrene in TEP ($\sim 1\%$) was slowly added to TEP at reflux temperature. However, gelation could be nearly completely eliminated by using a high-boiling polydentate ether as diluent.

In a manner analogous to gelation during the chloromethylation reaction, crosslink formation in the present case probably occurs by the following route:
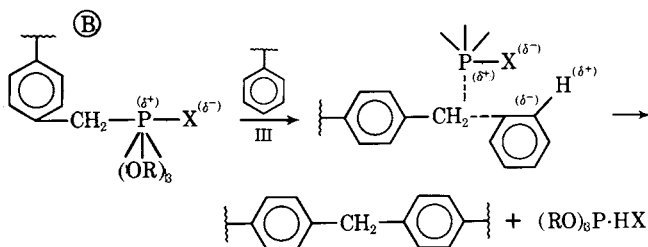
The probablity of this reaction increases under conditions of poor solubility (molecular aggregation) and a high concentration of a strong nucleophile. Solvation of the ionic intermediate B by an electron-donating polydentate etheral solvent (DEC) protects it effectively from intermolecular collisions with phenyl groups, which are required by the crosslinking reaction III, and thus enhances the probability of a molecular rearrangement (reaction II), leading to the final product.

Apparently, the bulky polydentate molecule provides a more effective solvation shell for the ionic intermediate B than TEP molecules. Such a behavior can easily be rationalized on entropy grounds. Indeed, poly-

TABLE IV
Phosphonylation[a] of Chloromethylated Polystyrene and its Copolymers

Parent polymer[b]	Solvent	Cl in reacting polymer, %	Cl in product polymer, %	P, %	Gel, %	Designation of product
Polystyrene	TEP	22.3	1.5	10.9	85	PSP
Copolymer-1	TEP	41.8	26.9	7.6	none	COP-1
Copolymer-2	TEP	26.0	24.0	1.8	none	COP-2
Copolymer-2	TEP	29.0	15.7	6.5	40	COP-2
Copolymer-2	TEP	34.9	24.5	6.1	90	COP-2
Polystyrene	DEC+TEP	20.6	—	11.0	1.5	PSP
Copolymer-3	DEC+TEP	34.9	15.1	9.2	none	COP-3
Copolymer-3	DEC+TEP	39.0	9.1	10.5	none	COP-3

[a] A solution of the chloromethylated parent polymer in the solvent was added dropwise to a refluxing solvent.

[b] See Table I.

dentate ethers were shown to act as powerful solvating agents for cations.[19-21]

The results of phosphonylation of the various precursor polymers are summarized in Tables IV and V, respectively.

Physical Properties of the Polymeric Phosphonates

The polyphosphonates, listed in Tables IV and V, produced coherent films when cast from a variety of solvents such as dioxane, THF, or chlorinated hydrocarbons. All polymers had glass transition temperatures (T_g) above room temperature, and most of them produced rigid, rather brittle films. The only exception was PPOBrP, which had a tensile strength of ~ 4 kg/mm², while PPOP had a tensile strength ~ 1 kg/mm². (The idealized formulae of these polymers are given in column 1, Table V.) The elongation at break did not exceed 5% in any case. Since these polymers were not intended to be used as such but as polymeric additives to other polymers, the following physical properties seemed of particular interest: (i) water absorption; (ii) thermal behavior; (iii) compatibility with various polymers and plasticizers.

Table VI lists data on water absorption by film strips of the various polymers cast from solution, when equilibrated at 21°C with water. It may be seen from these data that, while the parent polymers absorb very little water, their phosphonate derivatives are quite hydrophilic and water absorption increases with P content. A striking feature is the tremendous increase in the water absorption of COP when its P content exceeds 6.5%. At this point, the film becomes opaque, apparently due to microphase separation of water, but it remains intact and does not desintegrate.

It is known[22-24] that the phosphoryl oxygen forms hydrogen bonds with water, and the bond energy in a hydrate of tributyl phosphate is about 5 kcal/mole. For the more basic oxygen in a phosphonate, the hydrogen
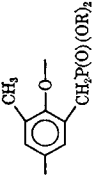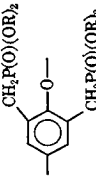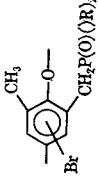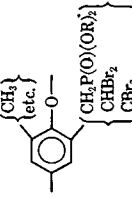
TABLE V
Phosphonylated PPO Derivatives
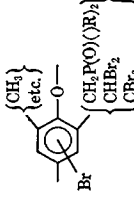
Monounit	Polymer designation	P atoms per monounit	Br atoms per monounit	Solubility
[structure: CH_3, O, $CH_2P(O)(OR)_2$]	PPOP	0.5–1.3	0–0.25	soluble in THF, chlorinated solvents, alcohols, ketones
[structure: $CH_2P(O)(OR)_2$, O, $CH_2P(O)(OR)_2$]	PPOP₂	1.4–2.0	0–0.50	Same as above
[structure: CH_3, O, $CH_2P(O)(OR)_2$, Br]	PPOBr$_\phi$P	1.0–1.3	1.0–1.25	same as above, except ketones
[structure: $\{CH_3$ etc.$\}$, O, $\{CH_2P(O)(OR)_2$, $CHBr_2$, $CBr_3\}$]	PPOPBr	1.0–1.3	1.0–2.0	same as above, except alcohols
[structure: $\{CH_3$ etc.$\}$, O, $\{CH_2P(O)(OR)_2$, $CHBr_2$, $CBr_3\}$, Br]	PPOPBr₂P	1.0–1.3	1.0–3.5	same as above

TABLE VI
Water Absorption by Polymeric Phosphonates at 21°C

Polymer designation[a]	P, %	Cl, %	Br, %	T_g, °C	Water absorbed, $(w_{H_2O}/w_{dry\ film}) \times 100$
Polystyrene	0	0	0	99	<1
PSP	8	0	0	96.5	40
Copolymer	0	26.6	0	50	<1
COP-3	1.2	24.5	0	50	17
COP-3	3.7	20.5	0	48	22
COP-3	6.5	15.5	0	47	35
COP-3	8.6	10.5	0	46	315
PPO	0	0	0	210	<1
PPOP	9.5	0	9	120	38
PPOBrϕP	10.5	0	33	175	20

[a] See Tables IV and V; ~100-μ-thick film strips were dried in vacuo at 45°C for 7 days, then immersed in water at 21°C for 7 days.

bond energy is 7–8 kcal/mole. Water absorbed by the polymer exerts a strong plasticizing effect, and the T_g of the system decreases. The sudden manifold increase in the water uptake of COP, when the P content is increased over 6.5%, is probably due to the collapse of the glassy state as the value of T_g decreases below that of the equilibration temperature of 21°C. This is confirmed by the observation that, when a COP film having a P content of 6.5% was warmed in a water bath at a rate of 5°C/hr, its water content went up suddenly to 180% of its dry weight when the bath temperature reached 36°C. At this stage, the film became rubbery. It reversibly returned to its former state when the temperature was lowered again.

The correlation between water absorption and the glass transition temperature was also demonstrated by experiments with PPOP plasticized with a hydrophobic plasticizer, a liquid vinyl chloride telomer (TVC) (Prepared in this laboratory by M. Asscher and H. Rosin to whom the authors are indebted). While such plasticizers cause a decrease in water absorption when incorporated into a hydrophilic polymer,[25] the addition, in our case, of 15% (w/w) of TVC to PPOP caused a decrease of the T_g to 18°C and an *increase* in the water uptake of up to 86%.

The reversible water absorption by the polymeric phosphonates may be of practical importance. Since they impart flame retardance to polymer compositions (v.i.), their hydrophilic character may render them attractive as additives to certain fibers.[26]

Thermal Behavior

The thermal behavior (in argon) of various polymeric phosphonates and of their parent polymers is shown in Figure 1. If we choose as a criterion for pyrolytic stability the highest temperature at which no weight loss takes place under a standard heating procedure, then PSP appears as the most
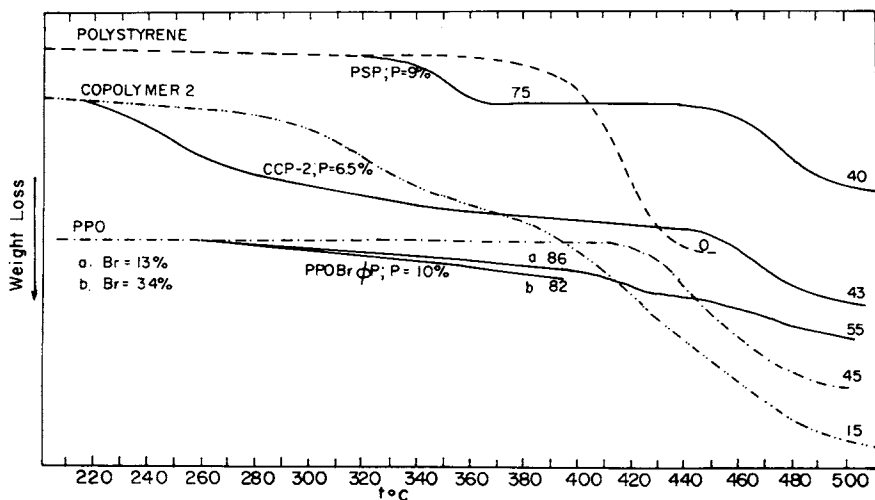
Fig. 1. Thermogravimetric analysis of various polyphosphonates and their parent polymers: (−.−.−.−.−.−) parent polymer; (————) polyphosphonate. The numbers above the curves indicate the remaining weight in %: (a) POBrϕP with 13% Br; (b) PPOBrϕP with 34% Br. Rate of Scan: 16°C/min. Flow of argon: 18 cc/min.

stable, the COP polymer would be rated as least stable, while the PPO derivatives occupy an intermediate position.

The thermal behavior of a typical PSP (∼9%P) is shown in greater detail in Figure 2, where a concurrant mass-spectrometric (MS) analysis of the decomposition products is also given. The material is stable till about 330°C, at which point a sudden weight decrease of 24.5% occurs. The endothermic peak is due to evolution of fragments from the ethyl ester group, with the value $m/e = 27$ (C_2H_3) being very prominent (Fig. 2). Another prominent peak is that of $m/e = 31$, whose intensity reaches a sharp maximum at 350°C. An interesting feature of the TG analysis of PSP is the firm plateau of the curve in the range of 350° to 450°C. A catastrophic decomposition of the polymer backbone takes place only above 450°C; a similar decomposition of the parent polymer appears at a much lower temperature (∼410°C). Since the first weight drop is accompanied by an almost quantitative loss of one etoxy and one ethyl group, the stable plateau (Fig. 1) is probably due to the formation of a crosslinked network such as
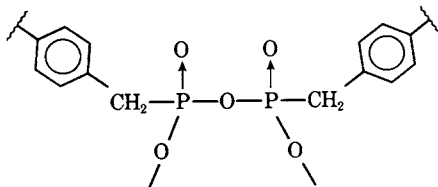
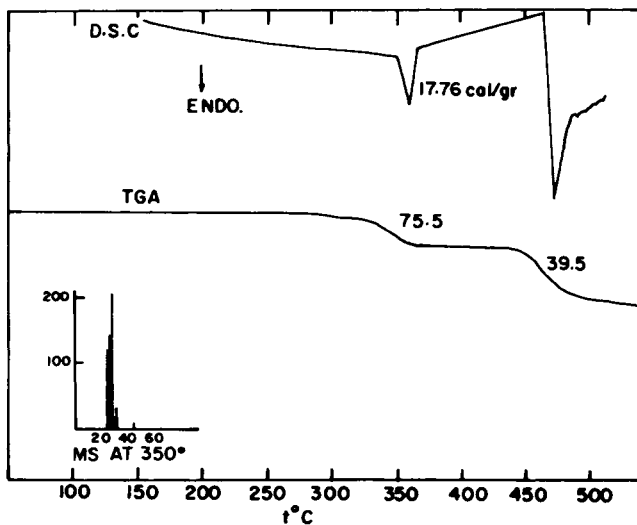whose stability far exceeds that of the parent polymer.

Fig. 2. Thermal analysis of PSP in argon atmosphere: rate of scan: 16°C/min; flow of argon: 18 cm³/min; MS is mass spectrometry. The numbers above the TGA curve indicate the remaining weight in per cent.
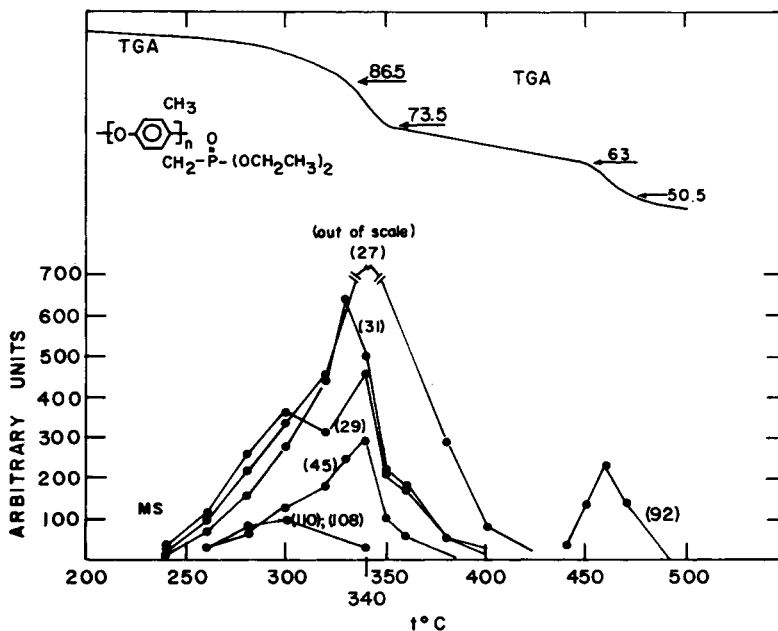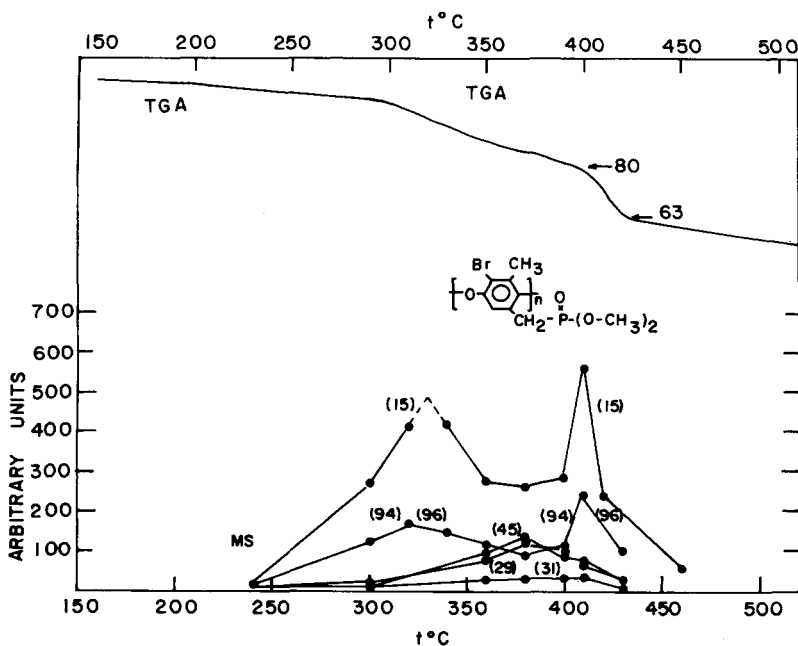

Fig. 3. Thermogravimetric curve and mass-spectral analysis of the decomposition products of PPOP$_{Et}$. Numbers in parentheses indicate the mass number of the fragment: (27)—C$_2$H$_3$; (29)—C$_2$H$_5$, CHO; (31)—CH$_3$O; (45)—C$_2$H$_5$O; (92)—C$_7$H$_8$; (108) and (110)—C$_2$H$_5$Br. The numbers above the TGA curve indicate the remaining weight in per cent.

Fig. 4. Thermogravimetric curve and mass-spectral analysis of the decomposition products of PPOBrϕP. Numbers in parentheses indicate the mass number of the fragment: (15)–CH$_3$; (29)–C$_2$H$_5$, CHO; (31)–CH$_3$O; (45)–C$_2$H$_5$O; (94) and (96)–CH$_3$Br.

On the basis of the comparison between the thermal·behavior of the polystyrene and of PSP, one would expect that PPOP$_{Et}$ should maintain constant weight up to well over 320°C, because of a basic similarity in structure to PSP. (The subscript Me or Et designates a methyl or ethyl phosphonate moiety, respectively.) In fact, it begins to lose weight already at 270°C (Fig. 3). Moreover, before it reaches the sudden drop at 350°C (same as in the case of PSP), its weight decreases gradually (~13.5% loss). In both cases, MS analysis shows maxima at 350°C for the same peaks (m/e = 27, 31, 45) and, in the case of PPOP$_{Et}$, distinct peaks at m/e = 110 and at m/e = 108 (associated with C$_2$H$_5$Br) appear at 270°C. This is due to "Arbuzov-unreacted" bromine left in the molecule (elemental analysis P = 10.1%, Br = 9.66%) which causes destabilization by furnishing bromine radicals at an early stage. The peak m/e = 92 (C$_7$H$_8$) at 470°C is due to an aromatic fragment, indicating the collapse of the main chain. It may be deduced that a PPOP, if completely devoid of unreacted side-group bromine (which we did not succeed in preparing), would show a stability similar to that of PSP.

Introduction of bromine into the benzene ring causes some further destabilization of the polymer, as may be seen from the thermal analysis of PPOBrP$_{Me}$ (Fig. 4). The peaks of m/e = 15 (CH$_3$), m/e = 94 and 96 (CH$_3$Br) exhibit a double maximum: at 320°C, where it is derived from the side-group bromine (as in the previous case), and at 420°C, due to elimina-

tion of aromatic Br. The second maximum coincides with that of $m/e = 79$ and 81, which are indicative of elemental Br. Up to 300°C, both PPOP and PPOBrP show adequate stability for incorporation into certain polymer systems.

Compatibility

The compatibility of polymeric systems is rather limited because of the negligible entropy gain due to the mixing of the polymeric molecules.[27] As a result, only very few polymer mixtures were recognized as "true" blends.[28] While in some applications, intimate blending of the polymeric components is not important (or even undesirable, e.g., in the case of high impact polystyrene), in other cases (fibers, film) it may be of great importance.

As may be seen from data collected in Table VII the polymeric phosphonates are compatible with a large number of other polymers. In view of their high phosphorous and halogen content, they may be of commercial importance as fire-retarding additives as well as membrane-forming materials.[26]

Three criteria were used in assessing compatibility: (i) glass transition temperature (T_g); (ii) leaching with solvents, and (iii) electron microscopy.

The T_g criterion has been applied before, and the following equation was suggested[27]:

$$T_g(\text{alloy}) = W_1(T_{g_1} - T_{g_2}) + T_{g_2} \tag{1}$$

where W_1 is the weight fraction of component 1. According to this equation, a single T_g is expected for a "true" alloy, its value depending on the weight fractions of the alloy components.

In Figure 5, the T_{g_1} of the polymeric alloys of varying compositions of cellulose acetate (Eastman 394–45) and COP (7%P, 14.5%Cl, $[\eta]^{25}_{\text{toluene}} = 0.135$) are plotted against the weight fraction of COP. Results are in excellent agreement with those predicted by eq. (1).

The nonseparation between alloy components by leaching with a solvent that dissolves one of the components but does not affect the other is a less clear-cut requirement for an alloy. Clearly, one cannot expect this to hold over the whole range of compositions, and an arbitrary limit has to be set for this test. In the present work, the standard test involved the immersion for 1 hr into a boiling solvent of a 100-μ-thick 200-mg film strip which contains 50% by weight of each component. The solvent is chosen such that, under identical conditions, it would dissolve films comprising only one of the two components of the alloy within a few minutes. A loss of weight smaller than 0.5% was regarded as acceptable.

Morphologic homogeneity can also be defined only with qualification. No phase heterogeneity could be seen, down to a resolution of 200 Å, when alloys of cellulose acetate with PPOBrP [1/1 and 0.75/0.25 (w/w)] were examined in a scanning electron microscope. To enhance the scattering

Solution in DMF

	Copolymer	Poly-styrene	PPO	HEC	PAN	CA	COP	PSP	PPOP	PPOBrP
Copolymer		+	+	/	/	-	+	+	+-	-
Polystyrene	+		+	/	/	-	+-	+	+-	-
PPO	+	+		/	/	+-	+	+-	+	/
HEC	/	/	/		+=	+	+	+	+	+
PAN	/	/	/	+=		+=	+	+	+	+
CA	-	-	+-	/	/		+	+	+	+
COP	+	+-	+	/	/	+		+	+	+
PSP	+	+	+-	/	/	+	+		+	+
PROP	+-	+-	+	/	/	+	+	+		+
PPOBrP	-	-		/	/	+	+	+	+	

Solution in Dioxane, Chloroform

Legend:

- /   One of the polymers is insoluble in this solvent
- +   Compatible in this solvent
- +-   Compatible within certain limits of concentration
- +=   Homogeneous in solution, but phase separated when film is cast
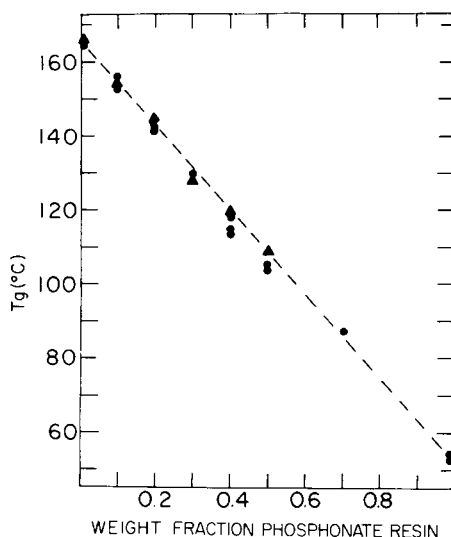- +   Compatible accordingly to the Tg and "leaching" criteria (cf. discussion)

Fig. 5. Glass transition temperature of CA/COP alloys. (●) alloy immediately after casting; (▲) alloy after 1 hr in 1:1, benzene–cyclohexane at reflux.

effect above that imparted by the presence of Br atoms, the film samples were exposed to solutions containing $1M$ $UO_2(NO_3)_2$ and $3M$ $NaNO_3$ at pH 2, whereby the polymer absorbed uranyl ions by virtue of the phosphonate ligands.[29] The secondary electron technique was applied for the inspection of such films.

According to the above criteria of compatibility, the results seem to indicate that "true" polymeric alloys are, indeed, formed by blending polyphosphonates with cellulose acetate.

The application of the Hildebrand solubility parameters concept to the formation of polymeric alloys will be discussed elsewhere.

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