Organic Polymers with Cyclophosphazene Side Groups: Influence of the Phosphazene on Physical Properties and Thermolysis

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Received October 5, 2000; Revised Manuscript Received March 8, 2001

ABSTRACT: Polystyrene and poly(methyl methacrylate) copolymers with cyclophosphazene side groups have been prepared by the reactions of azidocyclophosphazenes with diphenylstyrylphosphine residues in the copolymer structures. The cyclophosphazene pendent groups were present in from 1 to 100% of the monomer residues in polystyrene and from 2 to 20% of the repeating units in poly(methyl methacrylate). In both systems, the cyclophosphazene side units lowered the T_g roughly in proportion to their concentration in the macromolecules. The presence of ∼10% of cyclophosphazene-bearing monomer residues markedly reduces the combustibility of both polystyrene and poly(methyl methacrylate). The mechanism of fire retardance is discussed.

Introduction

The incorporation of phosphorus atoms into an organic polymer normally has the effect of decreasing its flammability.[1] Phosphazenes provide an excellent vehicle for the introduction of phosphorus into macromolecules. Cyclic phosphazene trimers have been incorporated into organic polymers in various ways. Allen[2] and Inoue[3] as well as others[4−6] have demonstrated the homo- and copolymerization of cyclotriphosphazenes that bear an unsaturated side group via addition polymerization. Others have incorporated cyclic trimers into condensation polymers using difunctional species.[7−10] The drawback to both of these approaches is the need to study the polymerization behavior of each individual phosphazene monomer, because the reactivity is affected both by the nature of the polymerizable group or groups and by the steric and electronic effects of the remaining side groups on the cyclic trimer.

Recently, we reported a novel method for the linkage of phosphazene cyclic trimers to preformed organic polymers.[11] In this method, poly(diphenyl-*p*-styrylphosphine) is treated with cyclotriphosphazenes that bear a single azido side group. The product polymer then had cyclic trimeric phosphazene rings linked to every repeating unit through a phosphinimine bond. Diphenyl-*p*-styrylphosphine (**1**) is known to copolymerize with styrene or methyl methacrylate,[12,13] and it is possible to produce both random and block copolymers with controlled molecular weights and comonomer distributions. Moreover, because **1** can be polymerized via free radical or anionic addition techniques, a wide range of conventional monomers should, in principle, copolymerize with it, with some reactions providing control of the chain length and molecular weight distribution. The side groups on the phosphazene ring can be varied over a wide range, and this allows fine-tuning of the properties of the polymer.

In the present work, we describe the reactions of cyclophosphazene azides with *copolymers* formed from diphenyl-*p*-styrylphosphine and either styrene or methyl methacrylate. The mole percentage of phosphinated styrene in the copolymers was varied from 1 to 100% for polystyrene and from 2 to 20% for PMMA, and the amount of phosphazene linked to each chain was then controlled directly by the percentage of the functionalized styryl unit present.

The incorporation of cyclic phosphazene trimers into organic polymers offers the possibility of changes to the physical properties and especially the prospect of decreasing the combustibility of the polymers.

Results and Discussion

Monomer **1** was homopolymerized anionically to yield poly(diphenyl-*p*-styrylphosphine). A series of copolymers of **1** with styrene or methyl methacrylate (MMA) were synthesized via free-radical addition techniques using AIBN as the initiator. In addition to molecular characterization by multinuclear NMR, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC) techniques, the polymers were examined by thermogravimetric analysis (TGA) and oxygen index (OI) methods.

Styrene-Based Copolymer Systems. The free-radical copolymerization of monomer **1** with styrene was accomplished in toluene as the solvent at 60 °C over a period of 40 h (Scheme 1). The monomer ratios in the styrene-based copolymers were very similar to those in the monomer feed ratios and are shown in Schemes 1 and 2. Integration of the ^{1}H NMR peaks was used to determine the mole percent incorporation of monomer **1**. The chemical shifts detected for the protons in each styrene copolymer were nearly identical. The different copolymers were indistinguishable by ^{31}P NMR spectroscopy.

Methyl Methacrylate (MMA)-Based Copolymer Systems. The free radical copolymerization of monomer **1** with MMA was carried out with dioxane as the solvent at 60 °C for 2 h. The ^{1}H NMR resonance signals for polymers **5a−d** were identical, except for a slight downfield shift of the aliphatic proton signals as the MMA percentage was increased. This shift is due to the shielding effect of the aromatic rings on the diphenyl-*p*-styrylphosphine units. This effect has also been noted for copolymers of MMA with styrene.[14] These copoly-

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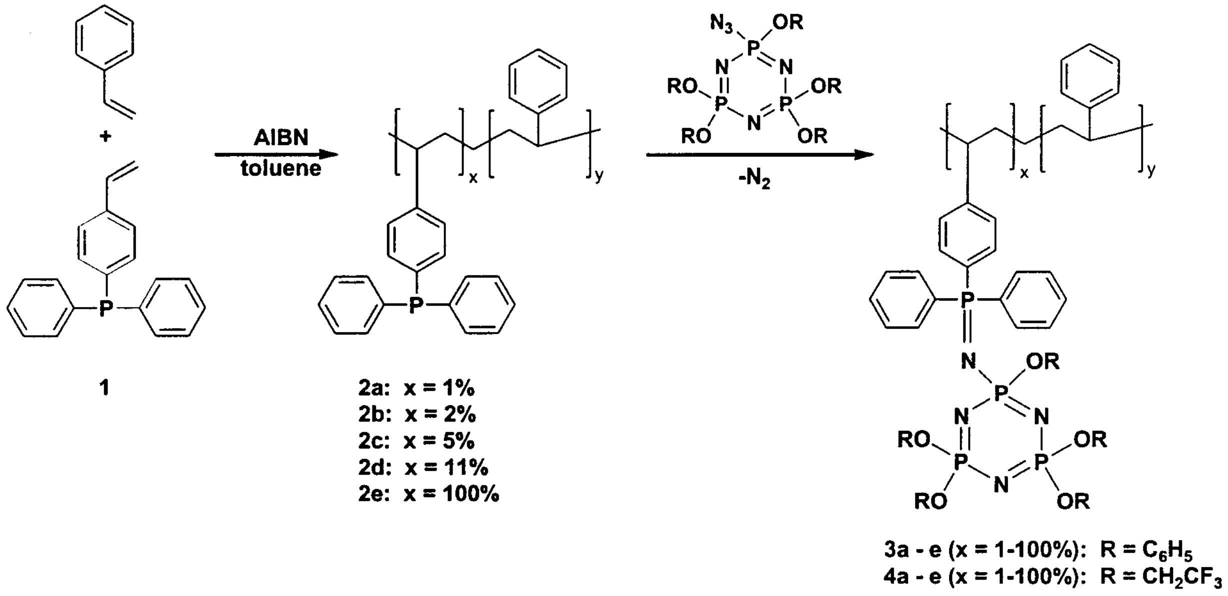
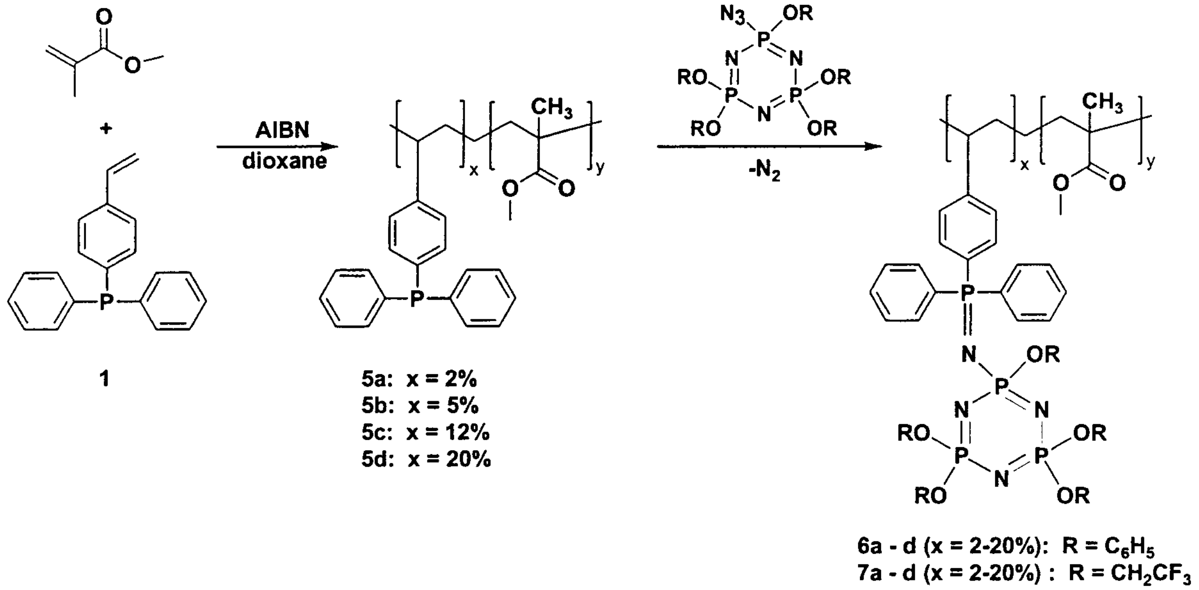
10.1021/ma001735r CCC: $20.00

Scheme 1



Scheme 2



mers were also indistinguishable by ^{31}P NMR spectroscopy. The final copolymers had a higher mole percent incorporation of **1** than in the original monomer feed ratio as determined by ^{1}H NMR spectroscopy. These values were reproducible for given a monomer feed ratio from experiment to experiment.

Phosphinimine Formation: NMR Analysis. The various copolymers were then treated with the two azidophosphazenes, one with trifluoroethoxy and the other with phenoxy side groups, to generate the phosphinimine linkage. Reactions were carried out in refluxing toluene with an excess of the phosphazene azide. Complete conversion to the phosphinimine occurred under relatively mild conditions for each copolymer. The progress of individual reactions was monitored by ^{31}P NMR spectrometry. Diphenyl-*p*-styrylphosphine gives a singlet ^{31}P peak at −6 ppm. Reaction with the cyclic phosphazene azido trimers caused this peak to disappear as a new peak appeared downfield from the first, as the phosphazene was converted to a phosphinimine unit. Each reaction was considered to be complete when the phosphine peak could no longer be detected. The exact location of the new phosphinimine peak depends on the organic groups linked to the cyclic phosphazene trimer. The reaction between $N_3P_3(OCH_2CF_3)_5(N_3)$ and polymer **2e** is a convenient example. Spectrum C in Figure 1 represents the final product of this reaction. The phosphorus atom closest to the organic backbone, originally at −6 ppm (spectrum B), now appears at 13 ppm (spectrum C). The cyclophosphazene phosphorus atom originally bound to the azide unit shifts from near 17 ppm (spectrum A) to 11 ppm (spectrum C). The two phosphorus atoms furthest from the reaction center remain near 17 ppm (spectra A and C). A doublet is generated for these resonances due to splitting by the phosphorus atom originally bound to the azide. These chemical shifts are in good agreement with the results for small molecule analogues discussed in previous work.[15] The integration of spectrum C is 1:1:2 for the peaks at 11, 13, and 17 ppm, respectively, as expected for repeat units that contain four phosphorus atoms. The ^{31}P NMR spectrum for each styrene-based copoly-

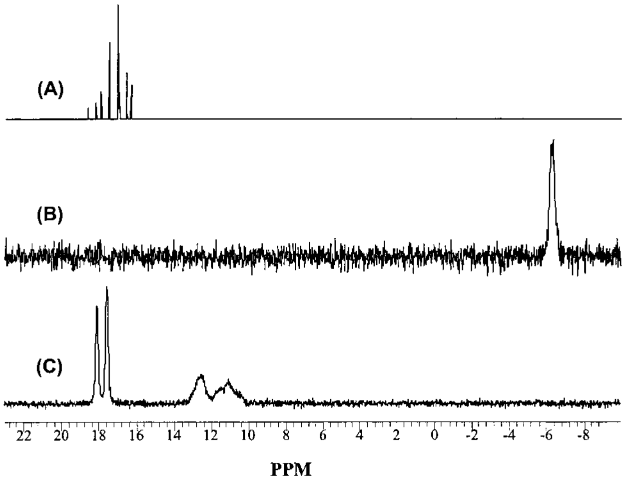


Figure 1. ^{31}P NMR spectra of (A) $N_3P_3(OCH_2CF_3)_5(N_3)$, (B) polydiphenyl-*p*-styrylphosphine, and (C) phosphinimine-modified product obtained from the reaction of $N_3P_3(OCH_2CF_3)_5(N_3)$ with poly(diphenyl-*p*-styrylphosphine).

Table 1. GPC Data for Styrene-Based Copolymer Systems

polymer	mol % **1**	M_n	PDI
polystyrene	0		
2a	1.0	47 000	1.8
2b	1.7	44 000	1.6
2c	4.8	43 000	1.4
2d	11.2	39 000	1.7
2e[a]	100	279 000	1.7
3a	1	52 000	1.6
3b	1.7	45 000	1.6
3c	4.8	49 000	1.4
3d	11.2	48 000	1.6
3e	100	965 000	1.6
4a	1.0	47 000	1.6
4b	1.7	47 000	1.6
4c	4.8	49 000	1.4
4d	11.2	54 000	1.4
4e	100	2 690 000	1.5

[a] Anionic polymerization.

mer was very similar to the spectrum of the corresponding homopolymer. In some cases, a small percentage (<5%) of the phosphine was oxidized during the isolation of the unmodified polymer. The oxidized phosphine has a ^{31}P NMR chemical shift near 24 ppm. This peak remained unchanged after the polymer had reacted with the azide compounds. Once formed, the phosphinimines were hydrolytically stable during several months exposure to the atmosphere and showed no evidence of decomposition when analyzed by ^{31}P NMR.

Gel Permeation Chromatography. Molecular weights for both the unmodified and the phosphazene-linked copolymer systems were estimated by gel permeation chromatography using polystyrene standards (Tables 1 and 2). The molecular weights of the phosphazene-bearing copolymers were generally higher than those of their unmodified counterparts. However, the increases in molecular weight did not correspond to the theoretical values predicted by assuming complete conversion from the phosphine to the phosphinimine. For example, polymer **2e** had an M_n of 279 000. The introduction of the trifluoroethoxy-substituted phosphazene cyclic trimer units would theoretically yield a polymer with an M_n of 903 000. The GPC suggested that **4e** had an M_n of 2 690 000, roughly 3 times larger than the calculated value. This could be due to the fact that gel permeation chromatography is influenced by the hydrodynamic volume of the different polymer systems, with the bulky side groups increasing this volume.

Table 2. GPC Data for MMA Copolymer Systems

polymer	mol % **1**	M_n	PDI
PMMA	0		
5a	2	133 000	2.0
5b	5	140 000	1.9
5c	12	146 000	1.8
5d	20	142 000	1.8
6a	2	137 000	2.0
6b	5	140 000	1.9
6c	12	195 000	1.7
6d	20	339 000	1.8
7a	2	136 000	2.3
7b	5	130 000	2.2
7c	12	238 000	1.6
7d	20	219 000	1.8

Glass Transition Temperatures. DSC analysis provides an insight into the polymer microstructure as well as the mechanical properties of the copolymer systems. A single glass transition temperature (T_g) was detected for each cyclophosphazene-substituted copolymer examined, as well as for the copolymers linked with diphenyl-*p*-styrylphosphine only. This suggests a random copolymer microstructure of the type normally obtained in free-radical polymerizations. A block structure would generate two or three T_g's.

The T_g's of the phosphinated styrene copolymers were higher than that of polystyrene and increased with increasing incorporation of diphenyl-*p*-styrylphosphine, presumably due to the bulk and rigidity of the phosphine-containing monomer. However, the T_g's of the cyclophosphazene-substituted copolymers were lower than those of polystyrene or the corresponding phosphinated copolymers. For example, polystyrene has a T_g of 98 °C. The T_g of the phosphinated polymer **2d** is at 112 °C. Incorporation of the cyclophosphazene lowered the T_g to 83 °C for the fluoroalkoxy phosphinimine and to 85 °C for the aryloxy phosphinimine. It seems likely that phosphazene cyclic trimers pendent to the polymer backbone increase the free volume of the system, thereby decreasing the T_g's. The two different phosphazene trimers had very similar effects on T_g's of the copolymers despite the extreme bulkiness of the aryloxy cyclophosphazene units.

Increasing amounts of diphenyl-*p*-styrylphosphine in the MMA-based copolymers decreased the T_g slightly. This small effect reflects the similarities between the T_g's of the PMMA and homopolymers of **1**. The cyclophosphazene units had a much more pronounced effect on the physical properties. A loading of only 10% of the phosphazene trimer units lowered the T_g by 30−40 °C.

Thermal Stability. The thermal stability of a polymer has a significant, though not necessarily direct, influence on the fire resistance of that material. The thermal stabilities of these polymers were estimated by TGA techniques using a nitrogen atmosphere and a heating rate of 10 °C/min. One of the main questions of interest is the temperature at which a polymer has lost 5% of its original weight ($T_{5\%}$). Another factor is the weight of the ceramic-like residue, or "char", that remains at a given temperature, defined in terms of the percentage of the original weight. All residue yields reported were essentially unchanged after the system was heated from the specified temperature to 800 °C. Although decomposition temperatures and residue yields, as determined by TGA, cannot be used directly to predict flammability, they do give an indication of the

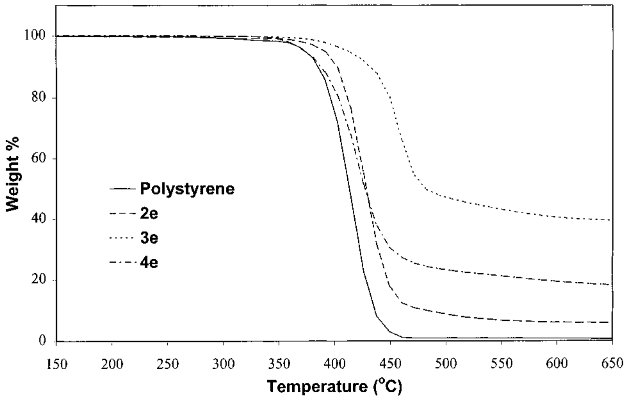


Figure 2. TGA curves for polystyrene-based polymers with 100% phosphine and cyclophosphazene side groups.

Table 3. Thermal Properties of Polystyrene and Derivatives

polymer	T_g (°C)	$T_{5\%}$ (°C)	char at 650 (wt %)
polystyrene	98	374	0.7
2e	117	391	5.9
3e	69	412	39.5
4e	54	373	18.2

tendency of a material to produce volatile compounds and highly cross-linked residues at high temperatures. In some cases, the volatile species can inhibit combustion by quenching the free-radical reactions within a flame, a process referred to as vapor phase flame retardance.[16] However, for most organic polymers without flame-retardant modification, the volatile compounds from pyrolysis are flammable and act as fuel for the sustained burning of the polymer. Inhibition of the release of these volatiles, as indicated by an increase in $T_{5\%}$ or in the char yield, can often decrease the flammability of a material by reducing the supply of fuel to the flame.[17] Flame-retardant action of this type is said to occur by a condensed phase mechanism.

Styrene-Based Polymer Systems. The weight-loss curves for polysytrene, poly(diphenyl-*p*-styrylphosphine) (**2e**), and the polymers with phosphazenes linked to every repeat unit (**3e**, **4e**) are shown in Figure 2, and the weight loss data are given in Table 3. Pure polystyrene shows a $T_{5\%}$ at 374 °C. A single-step decomposition follows, leaving less than 1% of the original material as a nonvolatile residue at 450 °C. Polystyrene depolymerizes thermally by random chain scission into a mixture of styrene monomer, dimer, and trimer.[18] All these products can act as fuel for combustion. Polymer **2e** and its phosphazene-modified derivatives **3e** and **4e** show a similar one-step weight loss. The main effect of the presence of phosphazene species is to increase the amount of nonvolatile residue formed at high temperatures. The aryloxy phosphazene derivative **3e** yields twice as much nonvolatile residue as the trifluoroethoxy phosphazene derivative **4e**.

TGA curves for the polystyrene copolymers with 10 mol % comonomer **1** and for copolymers **4a**−**d** show the one-step weight loss that is characteristic of pure polystyrene. Phosphazene derivatives **3** and **4** show no improvement in $T_{5\%}$ at the 10% loading and actually decrease the initial thermal stability at lower incorporation levels. This effect is slightly more pronounced for the trifluoroethoxy derivatives. However, for both types of phosphazenes, the amount of nonvolatile residue increases with increased concentration of phosphazene cyclic trimer in the copolymer. Again, the residue from the aryloxy derivatives is roughly double that from the corresponding trifluoroethoxy derivatives. These TGA curves can be found in the Supporting Information.

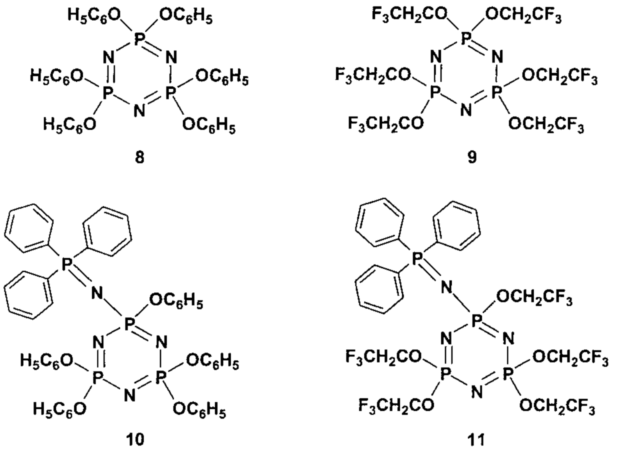


Figure 3. Phosphazene cyclic trimers used in polymer−oligomer blends and as model compounds.

The differences in the thermal degradation of the cyclophosphazene-modified copolymers are a result of the chemical characteristics of the side groups. Because the two phosphazene cyclic trimers themselves have approximately equal molar masses, copolymers **3a**−**e** and **4a**−**e** contain almost identical concentrations by weight of phosphazene for a given mole percent loading. The behavior of the small molecules, hexa(phenoxy)cyclotriphosphazene and hexa(trifluoroethoxy)cyclotriphosphazene (compounds **8** and **9** in Figure 3, respectively), at elevated temperatures has been well documented.[19−21] In an inert atmosphere, **9** volatilizes at 300 °C without significant decomposition. However, compound **8** does not begin to volatilize until 400 °C under identical conditions, and this process competes with a cross-linking reaction that links cyclic trimeric rings into a cyclomatrix material. In the polymers examined here, this cross-linking reaction probably occurs during the main weight loss step as detected by TGA. Compound **9** has both a higher volatility and a reduced tendency to undergo cross-linking reactions than **8**. Thus, smaller amounts of residue are generated from the trifluoroethoxy derivatives. It is also possible that the phosphazenes inhibit radical depolymerization reactions by physically diluting the polymer matrix.

Methyl Methacrylate-Based Polymer Systems. The TGA curves for the poly(methyl methacrylate) copolymers with 20 mol % comonomer **1** incorporation are shown in Figure 4, and data for copolymers **5a**−**d**, **6a**−**d**, and **7a**−**d** (with phosphazene) are given in Table 4. Pure poly(methyl methacrylate) (PMMA) has $T_{5\%}$ at 252 °C, more than 100 °C below that of polystyrene. Minimal nonvolatile residue is left by 400 °C as PMMA depolymerizes almost completely to the monomer.[22] The copolymer of MMA with 20 mol % comonomer **1** (**5d)** (no phosphazene) shows a two-step weight loss. The first step begins at a temperature close to that for PMMA, but only 15% of the original weight is lost in this step. The second step, which occurs closer to the $T_{5\%}$ of poly(diphenyl-*p*-styrylphosphine), leaves slightly less than 20% of the original weight at 650 °C. Dramatic increases in $T_{5\%}$ occur following incorporation of the phosphazenes into the polymer side groups. The two-step weight loss found for **5d** is not detected for the 20% phosphazene derivatives. However, the lower loadings of phos-

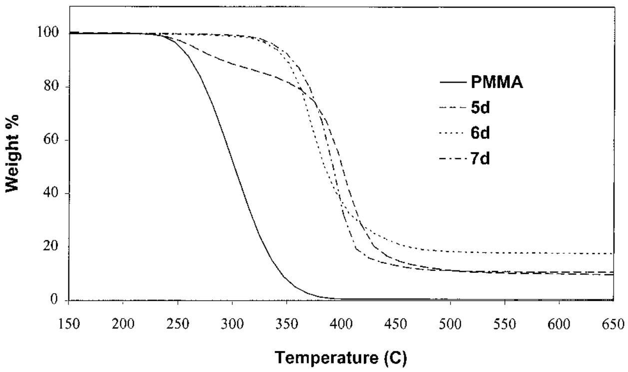


Figure 4. TGA curves for poly(methyl methacrylate)-based copolymers showing the effects of changing the side groups from those of pure PMMA to those of the 20% phosphine and cyclophosphazene derivatives.

Table 4. Thermal Properties and Flammability of Copolymers Containing 10 mol % Comonomer

polymer	T_g (°C)	$T_{5\%}$ (°C)	char at 650 (wt %)	OI
polystyrene	98	374	0.7	22
2d	112	364	0.8	22
3d	85	376	18.7	33
4d	83	377	7.1	28
PMMA	127	252	0.5	17
5c	123	264	9.6	20
6c	83	337	17.6	22
7c	90	341	10.5	27

phazenes in **6a**–**d** cause a slight weight loss before the main decomposition step. The TGA curves for **6a**–**d** are in the Supporting Information. The residue yields for the phosphazene-functionalized copolymers are reduced by roughly 30% relative to their polystyrene copolymer counterparts.

Poly(methyl methacrylate) produced by free radical addition has been shown to degrade by a two-step mechanism.[22] The first step involves depolymerization from the chain ends and occurs between 220 and 300 °C. This is followed by random chain cleavage at temperatures between 320 and 350 °C. This polymer can be stabilized to higher temperatures simply by the incorporation of an organic comonomer such as styrene or various alkyl acrylates. The presence of the comonomer inhibits the depolymerization of PMMA by blocking the unzipping process that generally begins at the chain ends.[22] The thermal degradation behavior detected for **5d** is consistent with this mechanism. The strong influence of the phosphine on the formation of nonvolatile residue is probably due to a reaction of the phosphorus(III) species with the carbonyl groups of the MMA to produce phosphorus esters.[23] Copolymer **6d** and **7d** contain no phosphorus(III), and residue formation is probably due to the same mechanism that operates in the polystyrene copolymers. This mechanism is sensitive to the polymer matrix as is evidenced by the lower yield of residue for the PMMA copolymers. However, the presence of the phosphazene does serve to inhibit the initial depolymerization of PMMA from the chain ends.

Model Compound Studies. To further understand the thermal degradation of these copolymers, pyrolysis studies of model compounds **10** and **11** were undertaken. Heating of compound **10** in nitrogen to 400 °C gave an insoluble, glassy residue. Heating to temperatures of 200 and 300 °C resulted in the formation of the same solid residue beneath a layer of clear oil. This oil had the same characteristics as **10**, as did the volatiles collected from the pyrolysis. Compound **11** gave no residue or volatiles below 400 °C. Analysis by ^{31}P and ^{1}H NMR spectroscopy indicated no change from the original spectrum.

The ability of **10** to volatilize without fragmentation or rearrangement indicates that it can act as a vapor phase flame retardant, as has been observed for **9**.[24] Once depolymerization of the polymer backbone has occurred, the comonomer **1** is liberated and can undergo simultaneous cross-linking and volatilization. Hexaphenoxycyclotriphosphazene is known to undergo cross-linking reactions only above 400 °C. As seen here, no observable rearrangement or volatilization occurs below this temperature. Even after depolymerization of the backbone, the aromatic phosphazene comonomer will not vaporize into a flame front but will enhance the ceramic char formation through cross-linking reactions.

Fire Resistance. The flammabilities of the copolymers of styrene with 10 mol % comonomer **1** (**2d**) and its cyclophosphazene-modified derivatives (**3d** and **4d**) as well as the copolymers of MMA with 10 mol % comonomer **1** (**5c**) and its cyclophosphazene-modified derivatives (**6c** and **7c**) were examined by a modification of oxygen index (OI) analysis. These results were compared to the flammabilities of pure polystyrene and poly(methyl methacrylate). The OI is defined as the concentration of oxygen necessary to sustain the flaming combustion of a material in a controlled nitrogen and oxygen atmosphere. Thus, an OI of 20 suggests that the material will burn in the atmosphere. Materials with high OI values are considered to be more flame resistant since more oxygen is necessary to sustain a burning flame. The modified method employed here has been shown to yield reproducible results which are useful for comparing the effects of flame-retardant treatments within a specific polymer system.[25,26] The copolymers containing approximately 10 mol % comonomer **1** (**2**–**4d**, **5**–**7c**) should give the most practical indication of the effectiveness of phosphazene modification for improving the fire resistance of these polymers.

Styrene-Based Polymer Systems. As measured by this method, polystyrene has an OI of 22. Incorporation of 10 mol % phosphine does not improve the fire resistance of the polymer at all. Significant increases in flame resistance are observed following incorporation of phosphazene rings into the side groups. The fluorinated derivative **4d** has an OI of 28, and the aromatic derivative **3d** has an OI of 33. For these polystyrene copolymers, fire resistance correlates with the formation of nonvolatile residue at high temperatures as measured by TGA. The elemental compositions of the residues left after combustion are shown in Table 5 in terms of molar ratios of phosphorus to carbon, phosphorus to nitrogen, and phosphorus to fluorine. The phosphazene-containing copolymers show dramatic increases in P/C in the range of 400% for **3d** and 170% for **4d**. Because the phosphorus atoms are preferentially incorporated into the char, a condensed phase mechanism is probably responsible for part of the fire retardance of these copolymers.

Both of the phosphazene-containing copolymers show increases in the ratio of phosphorus to nitrogen (P/N) in the residue relative to the original material. Also, **4d** shows a 300% increase in the ratio of phosphorus to fluorine (P/F) following combustion, which indicates that side groups on the phosphazene rings are eliminated during this process. These increases in P/N and P/F

Table 5. Elemental Composition of Chars from Combustion of Polystyrene Copolymers and Blends

	2d		**3d**		**4d**		**8** blend		**9** blend	
molar ratio	calcd	char	calcd	char	calcd	char	calcd	char	calcd	char
P/C	0.011	0.017	0.032	0.161	0.039	0.106	0.021	0.112	0.024	0.003
P/N			1.00	1.77	1.00	2.37	1.00	3.40	1.00	1.40
P/F					0.266	1.10			0.167	0.333

Table 6. Elemental Composition of Chars from Combustion of Poly(methyl methacrylate) Copolymers and Blends

	5c		**6c**		**7c**		**8** blend		**9** blend	
molar ratio	calcd	char	calcd	char	calcd	char	calcd	char	calcd	char
P/C	0.015	0.031	0.042	0.200	0.053	0.100	0.028	0.033	0.035	0.020
P/N			1.00	5.90	1.00	2.20	1.00	1.08	1.00	0.95
P/F					0.269	0.909			0.167	0.141

show that significant rearrangements of the phosphazenes occur under oxidizing conditions at high temperatures. Both nitrogen-containing compounds and halogenated compounds can act as vapor phase flame retardants, thus enhancing the total flame-retardant effect of the phosphazene species.[16] However, the vapor phase effect of the fluorine in **4d** does not compensate for the lack of a condensed phase flame retardance.

Flammability studies were also conducted on physical blends (alloys) of polystyrene with 33 wt % of small molecules **8** or **9**. These blends had approximately the same loading by weight of phosphazene as the corresponding 10 mol % phosphorus-bearing copolymers. The blend with **8** was optically clear, indicating good miscibility of the additive with the polymer. Analysis by DSC showed a T_g of 50 °C. A lack of compatibility between polystyrene and **9** was indicated by a visible phase separation after casting of a film. For this blend, a T_g at 97 °C was detected, as was a melting transition at 50 °C for **9**. The flammabilities of these blends were greatly reduced relative to the analogous copolymers **3d** and **4d**. The OI of the blend with small molecule **8** was 45, and that of the blend with **9** was 35. Apparently, the flame-retardant effects of the phosphazenes are increased if the additive is not bound to the polymer matrix. In the case of the blend with **9**, fire retardance seems to be due almost exclusively to a vapor phase mechanism.

Methyl Methacrylate-Based Polymer Systems. Poly(methyl methacrylate) had an OI of 17 in our studies, which indicates a high level of combustibility. In this case, incorporation of 10 mol % diphenyl-*p*-styrylphosphine slightly improved the fire resistance as reflected in an increase in the OI to 20. The addition of the small-molecule phosphazenes improved the flame resistance further, but without any correlation with the amount of residue formation (Table 6). In fact, the aryloxy derivative **6c** increases the OI to only 22 even though it yields the highest residue (TGA) of the copolymers of MMA with 10 mol % comonomer **1** (**5c**) and its phosphazene-modified derivatives (**6c** and **7c**). The fluorinated derivative **7c** had an OI of 27, similar to that of the polystyrene copolymer. A vapor phase mechanism thus seems to be dominant for this system.[27]

The trifluoroethoxyphosphazene is expected to be more effective for quenching the radicals present in the flame, due to both its higher volatility than that of the phenoxy phosphazene and the presence of large amounts of halogen in the side groups. Fluorine-containing compounds have been shown to be effective at quenching radicals in a flame (although they are less effective than chlorinated or brominated species).[27] This is supported by the elemental ratios of phosphorus to carbon, phosphorus to nitrogen, and phosphorus to fluorine in the combustion residues, as shown in Table 6. The residue from the aryloxy phosphazene derivative **6c** showed an increase in the P/C ratio that was equal to that of its polystyrene analogue **3d**, but a comparable flame-retardant effect was not detected. The residue from **7c** showed an increase in P/C of only 88%, roughly half of the increase seen for its polystyrene copolymer counterpart **4d**. Thus, for the trifluoroethoxy system, more phosphazene is released into the flame front from the PMMA copolymer than from the polystyrene copolymer. The increase in vapor phase flame retardance compensates for the reduced residue formation.

Unlike the polystyrene system, the blending of PMMA with **8** and **9** did not dramatically increase the fire resistance. Both phosphazene cyclic trimers are miscible with PMMA as evidenced by the formation of clear films and by presence of single T_g's at 60 °C for the blend with **8** and 55 °C for the blend with **9**. The OI for both blends was 24. The presence of small molecule phosphazene cyclic trimers as additives rather than as covalently bound comonomers has a negligible effect on the degradation mechanism of PMMA. Without a comonomer present to inhibit the chain scission reactions, the majority of the flame-retardant activity must occur through the action of the phosphazene cyclic trimer in the vapor phase. Because both **8** and **9** volatilize above the temperature at which PMMA depolymerizes, there is less likelihood of an interaction in the vapor phase between the phosphazene flame retardant and the combustion of MMA monomer. Elemental analysis of the residues from these blends gave no evidence for rearrangement reactions of the phosphazene trimers because the P/N and P/F ratios were not changed significantly. The differences in volatility of the phosphazenes provided an explanation for the observation that the blend with **8** showed a slight increase in phosphorus−carbon ratio, and the blend with **9** shows a decrease.

Conclusions

The covalent incorporation of cyclophosphazene trimers into organic copolymers via phosphinimine formation is an effective method to generate new polymer structures from a wide range of organic polymers. This technique allows for control of the structure and properties of the copolymers by variation of both the ratio of functionalized comonomers to nonfunctionalized comonomers and the choice of different cosubstituents on the cyclic phosphazene unit. Many other cosubstituents are accessible in addition to the trifluoroethoxy and phenoxy groups discussed here. Because this method relies on the controlled modification of preformed organic polymers, the effects of phosphazene structure on the properties of the copolymers can be analyzed in a more straightforward manner than has been possible previously.

Pendent phosphazene cyclic trimers inhibit the thermal degradation of polystyrene by increasing the ceramic char yield at high temperatures through cross-linking reactions. Their effect on the decomposition of PMMA becomes manifest as an increase in the temperature at which volatile compounds are released. The fire resistance of polystyrene is improved due to a condensed phase mechanism, and the aryloxy phosphazene is more effective than the trifluoroethoxy phosphazene in this system. This pattern is reversed for PMMA, where vapor phase flame quenching effects are dominant. The fluorinated cyclic phosphazene covalently bound to the polymer is the most effective in this case. Although unbound cyclic phosphazenes incorporated into the organic polymers are also effective fire retardants, the possibility that they may diffuse from the polymer over time provides an argument for the use of the chemically bonded species.

Experimental Section

Instruments. ^{31}P and ^{1}H NMR spectra were recorded with use of a Bruker AMX-360 NMR operated at 146 and 360 MHz, respectively. ^{1}H NMR spectra are referenced to tetramethylsilane. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. The ^{31}P NMR spectra were proton-decoupled. Molecular weights were estimated with a Hewlett-Packard HP1090 gel permeation chromatograph equipped with a HP-1037A refractive index detector and a Polymer Laboratories PL gel 10 μm column calibrated with polystyrene standards (Waters). Samples were eluted with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate in THF. Thermal weight loss measurements of the polyphosphazenes were made using a Perkin-Elmer TGA-7 under an atmosphere of dry nitrogen at a flow rate of 30 cm^3/min using a heating rate of 10 °C/min. Glass transition temperatures were measured using a Perkin-Elmer DSC-7 system.

Synthesis of Compound 1. This material was synthesized following a method described in the literature.[12]

Synthesis of $N_3P_3(OC_6H_5)_5N_3$ and $N_3P_3(OCH_2CF_3)_5N_3$. The synthesis of these materials in our lab is described in a previous publication.[15]

Anionic Polymerization of Monomer 1. Comonomer **1** (1.00 g, 3.5×10^{-3} mol) was dissolved in 20 mL of distilled THF and cooled to −78 °C. Butyllithium (2.5 M in hexane, 0.007 mL, 1.7×10^{-5} mol) was added to the reaction flask via syringe. The reaction immediately changed from a clear, colorless solution to a clear, red solution. After stirring for 30 min at −78 °C, 2 mL of methanol was added to quench the reaction. The reaction instantaneously changed from the red solution back to a clear colorless solution. The polymer was purified by multiple precipitations from THF into methanol (2 times) and hexanes (2 times). The resultant white powder was characterized by multinuclear NMR and gel permeation chromatography. ^{31}P NMR (CD_2Cl_2): $\delta = 6.3$ (s, 1P). ^{1}H NMR (CD_2Cl_2): $\delta = 7.7-6.7$ (bm, 12H), 6.5−6.1 (bs, 2H), 2.0−0.9 (bm, 3H).

Free-Radical Polymerization of Monomer 1. Monomer **1** (1.0 g, 3.5 mol) and AIBN (1.4 mol %) were dissolved in distilled THF (20 mL) and stirred under argon. The reaction was heated to reflux for 12 h. The polymer was purified using the same technique as employed above. Multinuclear NMR spectra of the resultant white polymer were indistinguishable from the polymer polymerized via the anionic route. ^{31}P NMR (CD_2Cl_2): $\delta = 6.3$ (s, 1P). ^{1}H NMR (CD_2Cl_2): $\delta = 7.7-6.7$ (bm, 12H), 6.5−6.1 (bs, 2H), 2.0−0.9 (bm, 3H).

Reaction of $N_3P_3(OCH_2CF_3)_5N_3$ with Poly(diphenyl-*p*-styrylphosphine). Poly(diphenyl-*p*-phosphine) (0.5 g, 1.7×10^{-3} mol repeat units) and $N_3P_3(OC_2F_3)_5N_3$ (1.75 g, 2.6×10^{-3} mol) were heated to reflux in toluene (100 mL) and stirred for 48 h. The polymer was purified by precipitations into hexanes (3 times) followed by Soxhlet extraction with hexanes for 48 h. The resultant white polymer was characterized by multinuclear NMR, elemental analysis, and GPC. ^{31}P NMR (THF-*d*$_8$): $\delta = 17.8$ (d, 2P), 12.6 (bm, 1P), 11.1 (bm, 1P). ^{1}H NMR (THF-*d*$_8$): $\delta = 8.0-7.1$ (bm, 12H), 7.1−6.1 (bs, 2H), 4.7−4.4 (bs, 4H), 4.4−4.0 (bs, 6H), 2.1−0.9 (bm, 3H). Elemental analysis calculated for $C_{30}H_{27}F_{15}N_4O_5P_4$ (%): C, 38.62; H, 2.92; F, 30.57; N, 6.01; P, 13.29. Found: C, 39.33; H, 2.82; F, 30.77; N, 5.84; P, 12.31.

Reaction of $N_3P_3(OC_6H_5)_5N_3$ with Poly(dipheny-*p*-styrylphosphine). Poly(diphenyl-*p*-phosphine) (0.5 g, 1.7×10^{-3} mol repeat units) and $N_3P_3(OC_6H_5)_5N_3$ (1.67 g, 2.6×10^{-3} mol) were heated to reflux in toluene (100 mL). The reaction was stirred for 72 h. The reaction mixture was concentrated and precipitated into methanol. The polymer was then precipitated from THF into hexanes (2 times) followed by Soxhlet extraction with hexanes for 48 h. The resultant polymer was characterized by multinuclear NMR and gel permeation chromatography. ^{31}P NMR (CD_2Cl_2): $\delta = 11.3-9.7$ (bs, 1P), 8.7−7.4 (overlapping bs, 2P), 7.4−5.7 (bm, 1P). ^{1}H NMR (CD_2Cl_2): $\delta = 7.6-5.7$ (overlapping bm, 39H), 2.0−0.8 (bs, 3H).

Copolymerizations of Comonomer 1 with Styrene. General Synthesis Procedure. Comonomer **1** was dissolved in freshly distilled toluene under an atmosphere of argon. Styrene was added to the reaction flask via syringe followed by addition of AIBN (0.0057 g/g total monomer feed). The reactions were then heated to 60 °C. During the polymerization, the viscosity of the reaction mixtures noticeably increased. After 40 h, the reactions were precipitated into MeOH. The resultant white polymers were then precipitated into hexanes (2 times) to finish the purification. The copolymers were analyzed by multinuclear NMR, GPC, and DSC. The compositions of the purified copolymers were very close to that of the initial monomer feed and were determined by comparing the ^{1}H NMR integration of the aryl protons to that of the alkyl protons. Typical chemical shifts for both ^{1}H and ^{31}P NMR are demonstrated with polymer **2a**. Monomer feed ratio (styrene: comonomer **1**), $\%_{mol}$ incorporation of comonomer **1**, and DSC results (when available) are given for each polymer.

(i) **Polymer 2a.** ^{31}P NMR (CD_2Cl_2): $\delta = -5.9$ (s, 1P, (C_6H_4)-$P(C_6H_5)_2$). ^{1}H NMR (CD_2Cl_2): $\delta = 7.6-6.2$ (br m, ArH), 2.3−0.9 (br m, C*H* and C*H*$_2$). Monomer feed ratio (styrene:monomer **1**): 99:1; mol % comonomer **1** incorporated: 1.

(ii) **Polymer 2b.** Monomer feed ratio (styrene:comonomer **1**): 98:2, mol % monomer **1** incorporated: 2.

(iii) **Polymer 2c.** Monomer feed ratio (styrene:comonomer **1**): 95:5, mol % monomer **1** incorporated: 5.

(iv) **Polymer 2d.** Monomer feed ratio (styrene:comonomer **1**): 90:10, mol % monomer **1** incorporated: 11.

Phosphinimine Formation with Styrene Copolymer Systems. General Synthesis Procedure. The copolymer was dissolved in freshly distilled toluene under an atmosphere of argon. The azido phosphazene trimer (2 equiv/mol phosphine incorporated) was then added to the reaction flask. The reactions were heated to reflux, and their progress was monitored by ^{31}P NMR. Reactions were generally complete within 72 h. Purification of the reaction product began with first concentrating the reaction mixture via rotoevaporation followed by precipitation into MeOH. The polymers were then precipitated from THF into MeOH (1 time) and hexanes (2 times) followed by Soxhlet extraction with hexanes for 48 h. The polymers were characterized by multinuclear NMR, GPC, and DSC. Typical chemical shifts for both ^{1}H and ^{31}P NMR are illustrated using polymers 3a and 4a. GPC and DSC results (when available) are in Tables 1 and 3.

(i) **Polymer 3a.** ^{31}P NMR (CD_2Cl_2): $\delta = 10.4$ (d, 1P, (C_6H_4)-$(C_6H_5)_2P{=}N-$), 8.4 (d, 2P, $P(OC_6H_5)_2$), 10.2 (m, ring *P* bound to phosphinimine). ^{1}H NMR (CD_2Cl_2): $\delta = 7.7-6.2$ (m, ArH), 2.6−0.9 (m, C*H* and C*H*$_2$).

(ii) **Polymer 4a.** ^{31}P NMR (CD_2Cl_2): $\delta = 17.7$ (d, 2P, $P(OCH_2CF_3)_2$), 13.7 (d, 1P, $(C_6H_4)(C_6H_5)_2P{=}N-$), 10.2 (m, 1P, ring *P* bound to phosphinimine). ^{1}H NMR (CD_2Cl_2): $\delta = 7.9-6.5$ (br m, ArH), 4.6−3.8 (br m, OCH_2CF_3), 2.6−1.2 (br m, C*H* and CH_2).

Copolymerizations of Comonomer 1 with Methyl Methacrylate. General Synthesis Procedure. Polymers **5a**−**5d** were all prepared in a similar manner. The following preparation of is typical. Methyl methacrylate, comonomer **1**, and AIBN (g AIBN/g total monomer feed = 0.0057) were added in a Schlenk flask under an atmosphere of argon. Dioxane was added, and the flask was placed into a 60 °C water bath and stirred for 2 h. The resultant copolymer was precipitated into methanol, redissolved in dioxane, and precipitated in hexanes (2 times). The polymers were characterized by multinuclear NMR spectroscopy, GPC, and DSC. The actual compositions of the copolymers differed from that of the monomer feed and were determined by ^{1}H NMR spectroscopy. The ratio of the integration of the protons from the aromatic rings to the α-CH_3 hydrogen atoms was used to determine the mole percent of comonomer **1** in each copolymer. Typical chemical shifts for both ^{1}H and ^{31}P NMR are demonstrated using polymer **5a**. Monomer feed ratios and mole percent comonomer **1** incorporated into the copolymers are listed below. GPC and DSC data (when available) are given in Tables 1 and 3.

(i) **Polymer 5a.** ^{31}P NMR (CD_2Cl_2): δ (ppm) −5.90 (s, 1P). ^{1}H NMR (CD_2Cl_2): δ (ppm) 6.7−7.3 (ArH), 2.0−3.6 (OCH_3), 1.1−2.0 (C*H* and CH_2), 0.3−1.1 (α-CH_3).

Monomer feed ratio (MMA:monomer **1**): 99:1; mol % comonomer **1** incorporated: 2.

(ii) **Polymer 5b.** Monomer feed ratio (MMA:comonomer **1**): 98:2; mol % comonomer **1** incorporated: 5.

(iii) **Polymer 5c.** Monomer feed ratio (MMA:comonomer **1**): 95:5; mol % comonomer **1** incorporated: 12.

(iv) **Polymer 5d.** Monomer feed ratio (MMA:comonomer **1**): 90:10; mol % comonomer **1** incorporated: 20.

Phosphinimine Formation with Methyl Methacrylate-Based Copolymer Systems. General Synthesis Procedure. Polymers **6a**−**d** and **7a**−**d** were all prepared in a similar manner. The following preparation is typical. Polymer **5d** and the phosphazene azide compound (1.5 equiv with respect to mol % **1** incorporated) were heated to reflux in dioxane for 72 h. The resultant polymer was purified by precipitating in hexanes (2 times) and dried under vacuum. Polymers were characterized by multinuclear NMR spectroscopy, GPC, and DSC. ^{1}H and ^{31}P NMR spectra were very similar for all methyl methacrylate-based copolymers modified with both phosphazene azides. Typical chemical shifts are demonstrated with polymers **6d** and **7d**. GPC and DSC data (when available) are given in Tables 2 and 3.

(i) **Polymer 6d.** ^{31}P NMR (CD_2Cl_2): δ (ppm) 10.2 (d, 1P, $(C_6H_4)(C_6H_5)_2P{=}N-$), 8.4 (d, 2P, $(C_6H_5O)_2P$), 6.0 (m, 1P, ring *P* bound to phosphinimine). ^{1}H NMR (CD_2Cl_2): δ (ppm) 6.7−7.5 (m, ArH), 2.0−3.6 (OCH_3), 1.1−2.0 (C*H* and CH_2), 0.3−1.1 (m, α-CH_3).

(ii) **Polymer 7d.** ^{31}P NMR (CD_2Cl_2): δ (ppm) 17.6 (d, 2P, $(CF_3CH_2O)_2P$), 13.4 (d, br, 1P, $(C_6H_4)(C_6H_5)_2P{=}N-$), 10.3 (m, 1P, ring *P* bound to phosphinimine). ^{1}H NMR (CD_2Cl_2): δ (ppm) 7.1−7.5 (ArH), 3.7−4.7 (m, CF_3CH_2O), 2.0−3.6 (OCH_3), 1.1−2.0 (C*H* and CH_2), 0.3−1.1 (m, α-CH_3).

Pyrolysis of Model Compounds. Compounds **10** and **11** were prepared as described previously.[15] These were heated in the thermogravimetric analyzer under conditions identical to the TGA studies (30 cm^3/min N_2 flow; 10 °C min heating rate). The volatiles were collected from the furnace vent on Tenax adsorbent packed inside a Pyrex tube. Suction on the vent was maintained with a Q-Max sampling pump (Supelco). The tubes were subsequently flushed with ethyl acetate to remove the volatile compounds. The residue left in the sample pan as well as the extracts from the tubes were analyzed by ^{31}P and ^{1}H NMR spectroscopy.

Preparation of Polymer/Cyclic Trimeric Phosphazene Blends. Compounds **8** and **9** were prepared as described previously.[28] Blends prepared from mixtures of 3.33 g of polymer (polystyrene or PMMA) and 1.67 g of phosphazene (**8** or **9**) were dissolved in methyl ethyl ketone (MEK). The solutions had a total volume of 50 mL and were cast into molds measuring 22.5 cm × 17.5 cm. Slow evaporation of the solvent was obtained by covering both the mold and a reservoir of pure MEK with a loose covering of foil. The resultant blends containing 33 wt % phosphazene cyclic trimer were dried under vacuum to remove any residual solvent.

Combustion Analysis. Modified oxygen indices were obtained through the use of a procedure developed for powdered samples. Following the techniques of Catala and Brossas[25] and of Reghunadhan Nair, Clouet, and Guilbert,[26] a glass cup containing 200 mg of polymer powder was suspended in inside an oxygen index instrument. This instrument was constructed according to the specifications of standard ASTM-D-2863-91. An atmosphere of nitrogen and oxygen of controlled composition was maintained with a purge flow of 17 L/min. A typical sample was then exposed to a propane flame for 10 s to ignite the polymer. The oxygen index (OI) was the concentration of oxygen necessary to sustain the combustion of the ignited polymer for exactly 30 s. In addition, the chars from the combustion of the copolymers and blends were analyzed for elemental composition. Elemental analyses were provided by Quantitative Technologies, Inc., Whitehouse, NJ.

(i) **Polymer 2d.** Elemental analysis calculated for $C_{80}H_{83}P$ (%): C, 89.9; H, 7.3; P, 2.8. Found for char: C, 86.81; H, 7.03; P, 3.75.

(ii) **Polymer 3d.** Elemental analysis calculated for $C_{113}H_{105}F_{15}N_4O_5P_4$ (%): C, 78.8; H, 6.1; N, 3.2; P, 7.2. Found for char: C, 44.36; H, 3.66; N, 4.70; P, 18.42.

(iii) **Polymer 4d.** Elemental analysis calculated for $C_{93}H_{90}F_{15}N_4O_5P_4$ (%): C, 63.8; H, 5.2; F, 16.2; N, 3.2; P, 7.0. Found for char: C, 49.44; H, 3.74; F, 7.88; N, 2.58; P, 13.52.

(iv) **Polymer 5c.** Elemental analysis calculated for $C_{57}H_{76}O_{15}P$ (%): C, 69.8; H, 7.2; P, 4.5. Found for char: C, 72.60; H, 6.43; P, 5.89.

(v) **Polymer 6c.** Elemental analysis calculated for $C_{87}H_{101}N_4O_{20}P_4$ (%): C, 38.62; H, 2.92; F, 30.57; N, 6.01; P, 13.29. Found for char: C, 41.07; H, 3.14; N, 1.61; P, 20.97.

(vi) **Polymer 7c.** Elemental analysis calculated for $C_{67}H_{86}F_{15}N_4O_{20}P_4$ (%): C, 38.62; H, 2.92; F, 30.57; N, 6.01; P, 13.29. Found for char: C, 49.81; H, 4.59; F, 8.46; N, 2.59; P, 12.41.

(vii) **Polystyrene/8 Blend.** Elemental analysis calculated for $C_{108}H_{102}N_3O_6P_3$ (%): C, 82.3; H, 6.6; N, 2.0; P, 4.5. Found for char: C, 51.52; H, 4.85; N, 1.96; P, 14.93.

(viii) **Polystyrene/9 Blend.** Elemental analysis calculated for $C_{84}H_{84}F_{18}N_3O_6P_3$ (%): C, 68.1; H, 5.7; F, 15.6; N, 1.9; P, 4.2. Found for char: C, 88.64; H, 7.45; F, 1.08; N, 0.25; P, 0.75.

(ix) **PMMA/8 Blend.** Elemental analysis calculated for $C_{107}H_{143}N_3O_{35}P_3$ (%): C, 60.6; H, 6.8; N, 2.0; P, 4.4. Found for char: C, 57.75; H, 6.86; N, 2.04; P, 4.85.

(x) **PMMA/9 Blend.** Elemental analysis calculated for $C_{86}H_{131}F_{18}N_3O_{36}P_3$ (%): C, 46.4; H, 5.9; F, 15.5; N, 1.9; P, 4.2. Found for char: C, 51.16; H, 6.69; F, 11.77; N, 1.29; P, 2.70.

Acknowledgment. We thank the Federal Aviation Administration through Grant 99-G-0013 for the support of this work.

Supporting Information Available: Figure S-1 showing TGA curves for polystyrene and polymers **2d, 3d,** and **4d**, Figure S-2 showing the TGA curves for polystyrene, **4a, 4b, 4c,** and **4d**, and Figure S-3 showing the TGA curves for poly(methyl methacrylate), **6a, 6b, 6c,** and **6d**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Green, J. *J. Fire Sci.* **1996**, *14*, 353−366.
(2) Allen, C. W. *Trends Polym. Sci.* **1994**, *2*, 342−349.
(3) Inoue, K.; Kaneyuki, S.; Tanigaki, T. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 145−148.
(4) Bosscher, G.; Wieringa, R. H.; Jenkel, A. P.; van de Grampel, J. C. *J. Inorg. Organomet. Polym.* **1996**, *6*, 255−265.
(5) Selveraj, I. I.; Chandrasekhar, V. *Polymer* **1997**, *38*, 3617−3623.
(6) Allcock, H. R.; Laredo, W. L.; deDenus, C. R.; Taylor, J. P. *Macromolecules* **1999**, *32*, 7719−7725.

(7) Dez, I.; Henry, N.; De Jaeger, R. *Polym. Degrad. Stab.* **1999**, *64*, 433−437.

(8) Tunca, U.; Hizal, G. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1227−1232.

(9) Radhakrishnan Nair, P.; Reghunadhan Nair, C. P.; Francis, D. J. *Eur. Polym. J.* **1996**, *32*, 1415−1420.

(10) Chen-Yang, Y. W.; Chuang, Y. H. *Phosphorus Sulfur Silicon* **1993**, *76*, 261−264.

(11) Hartle, T. J.; Sunderland, N. J.; McIntosh, M. B.; Allcock, H. R. *Macromolecules* **2000**, *33*, 4307−4309.

(12) Rabinowitz, R.; Marcus, R.; Pellon, J. *J. Polym. Sci., Part A* **1964**, *2*, 1233−1240.

(13) Rabinowitz, R.; Marcus, R.; Pellon, J. *J. Polym. Sci., Part A* **1964**, *2*, 1241−1249.

(14) San Roman, J.; Madruga, E. L.; Del Puerto, M. A. *Angew. Makromol. Chem.* **1979**, *78*, 129.

(15) Allcock, H. R.; McIntosh, M. B.; Hartle, T. J. *Inorg. Chem.* **1999**, *38*, 5535.

(16) Lewin, M. In *Fire Retardancy of Polymers: The Use of Intumescence*; Le Bras, M., et al., Eds.; The Royal Society of Chemistry: Cambridge, UK, 1998.

(17) Cullis, C. F.; Hirschler, M. M. *Polymer* **1983**, *24*, 834−840.

(18) McNeill, I. C.; Zulfiqar, M.; Kousar, T. *Polym. Degrad. Stab.* **1990**, *28*, 131−151.

(19) Maynard, S. J.; Sharp, T. R.; Haw, J. F. *Macromolecules* **1991**, *24*, 2794−2799.

(20) Allcock, H. R.; McDonnell, G. S.; Riding, G. H.; Manners, I. *Chem. Mater.* **1990**, *2*, 425−432.

(21) Peddada, S. V.; Magill, J. H. *Macromolecules* **1983**, *16*, 1258−1264.

(22) McNeill, I. C. *Eur. Polym. J.* **1968**, *4*, 21−30.

(23) Brown, C. E.; Wilkie, C. A.; Smukalla, J.; Cody, R. B., Jr.; Kinsinger, J. A. *J. Polym. Sci., Part A* **1986**, *24*, 1297−1311.

(24) Allen, C. W. *J. Fire Sci.* **1993**, *11*, 320−328.

(25) Catala, J.-M.; Brossas, J. *Proc. 18th Int. Conf. Org. Coat. Sci. Technol.* **1992**, 87−99.

(26) Reghunadhan Nair, C. P.; Clouet, G.; Guilbert, Y. *Polym. Degrad. Stab.* **1989**, *26*, 305−331.

(27) Green, J. *J. Fire Sci.* **1996**, *14*, 426−442.

(28) Allcock, H. R. *Phosphorus−Nitrogen Compounds*; Academic Press: New York, 1972.

MA001735R