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Phosphinimine Modification of Organic Polymers

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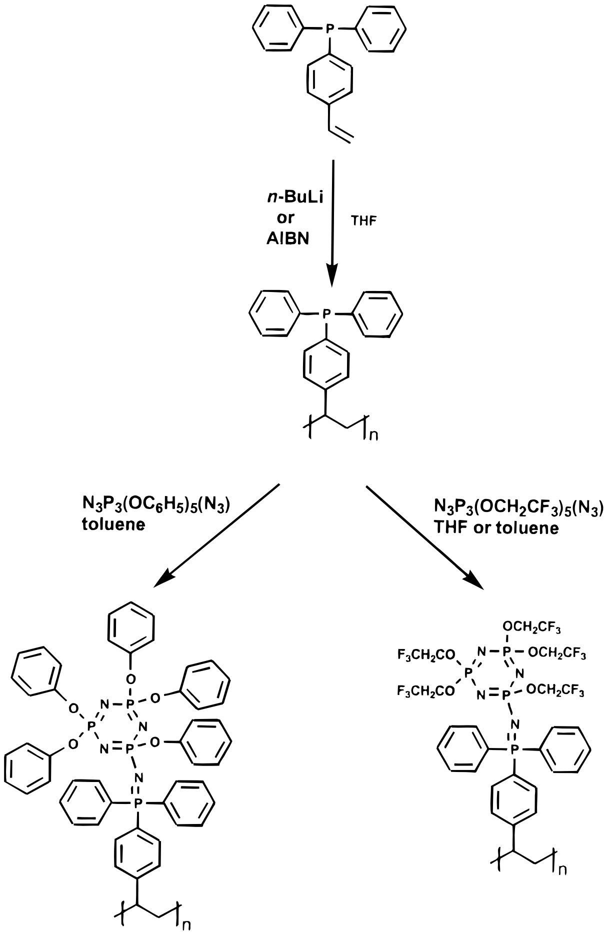
Introduction. The incorporation of phosphorus-containing components into organic polymers is a subject of general interest because such systems offer the promise of fire retardance and enhanced thermal stability as well as resistance to oxidation by molecular oxygen.[1,2] Numerous methods have been explored to synthesize such hybrid macromolecules. For example, poly(vinylphosphine oxides) have been examined in some detail.[3] However, the linkage of phosphorus−nitrogen compounds to organic polymers offers some special advantages because of the synergistic fire retardance of phosphorus and nitrogen[4] and the overall stability under ambient conditions of species such as phosphazenes.

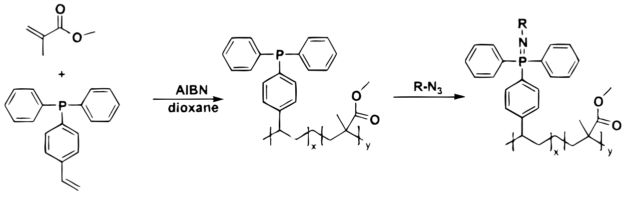
Small-molecule cyclic or linear phosphazenes can be incorporated into polymers in several ways. First, phosphazene rings may be linked through organic groups to yield cyclo−linear materials. These polymers incorporate a cyclic phosphazene trimer or tetramer directly into the backbone.[1,2,5−13] Of special interest are cyclo−linear species that are linked together via azide coupling reactions.[9,10] However, the difficulty involved in synthesizing high molecular weight polymers of this type and the poor control of the molecular weight are major drawbacks. These problems can be solved by using a second approach, where vinyl or allyl compounds that bear cyclic phosphazene side groups are subjected to free radical addition polymerization or copolymerization to yield organic polymers with cyclophosphazene side groups.[14] In this case, the phosphazene ring is incorporated as a pendent side group rather than as part of the polymer backbone. Similar species have recently been prepared in our program though the ring-opening metathesis polymerization of norbornenes with cyclic phosphazene side units.[15]

Here we describe an alternative approach in which polystyrene with diphenylphosphine pendent units (poly(diphenyl-*p*-styrylphosphine)) is allowed to react with cyclic phosphazene azides. This process couples the cyclic phosphazene to the polystyrene through a P═N−P (phosphinimine) linkage (Scheme 1). Such reactions occur readily under mild conditions.[16] Furthermore, the properties of the resultant polymers may be tailored by varying the nature of the phosphazene. Diphenyl-*p*-styrylphosphine polymerizes via anionic or free-radical methods.[17] This allows a wide variety of comonomers to be used for property modification. Here we describe coupling reactions between the azidophosphazenes and copolymers of diphenyl-*p*-styrylphosphine with styrene or methyl methacrylate (Scheme 2). In addition, we demonstrate that phosphoryl units can be linked to the phosphinated polystyrene by treatment with diphenylphosphoryl azide.

Scheme 1. Phosphinimine Modification of Poly(diphenyl-*p*-styrylphosphine)



Scheme 2. Phosphinimine Modification of Methyl Methacrylate-Based Copolymers



Experimental Section. Poly(diphenyl-*p*-styrylphosphine) was synthesized by both anionic and free-radical addition polymerization processes. *n*-Butyllithium was employed as the initiator for the anionic polymerization in THF at −78 °C. The reactions were complete within 0.5 h. The polymers were deactivated by quenching with methanol and were allowed to warm to room temperature. The polymer was purified by multiple precipitations from THF into methanol and hexanes. The resultant white powder was dried under vacuum and was characterized by gel permeation chromatography (vs polystyrene standards), elemental analysis, and multinuclear NMR (^{1}H and ^{31}P). The free-radical polymerization of the same para-substituted styrene occurred readily in refluxing THF using AIBN as an initiator. The resultant polymer is similar to the one formed by the anionic polymerization route although, as expected,

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Table 1. GPC Analysis of Phosphinimine Modified Polymers

	initiator	M_n	M_w/M_n	phosphazene azide	M_n	M_w/M_n
phosphine1[a]	BuLi	279 000	1.66	TFE	2 700 000	1.54
phosphine 1[a]	BuLi	279 000	1.66	phenoxy	965 000	1.57
phosphine/styrene[b]	AIBN	38 900	1.66	TFE	54 400	1.42
phosphine/styrene[b]	AIBN	38 900	1.66	phenoxy	47 500	1.61
phosphine/MMA[c]	AIBN	142 000	1.78	TFE	219 000	1.77
phosphine/MMA[c]	AIBN	142 000	1.78	phenoxy	339 000	1.76

[a] Poly(diphenyl-*p*-styrylphosphine). [b] Copolymer comprised of 10% diphenyl-*p*-styrylphosphine/90% styrene. [c] Copolymer comprised of 20% diphenyl-*p*-styrylphosphine/80% methyl methacrylate.

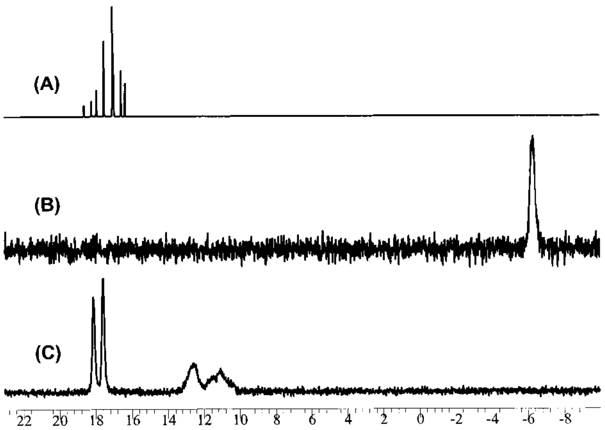

Figure 1. ^{31}P NMR spectra of (A) $N_3P_3(OCH_2CF_3)_5(N_3)$, (B) poly(diphenyl-*p*-styrylphosphine), and (C) phosphinimine modified product obtained from the reaction of $N_3P_3(OCH_2CF_3)_5(N_3)$ with poly(diphenyl-*p*-styrylphosphine).

the polydispersity is slightly higher (2.23 vs 1.69). Copolymers of diphenyl-*p*-styrylphosphine with both styrene and methyl methacrylate were synthesized using the free-radical route, and they were purified in a similar way.

Pendent cyclic phosphazene trimers were linked to the polymer by the addition of an excess of the appropriate phosphazene azide to a solution of the poly(diphenyl-*p*-styrylphosphine). Tetrahydrofuran, dioxane, and toluene were found to be suitable reaction solvents. The reactions were monitored by ^{31}P NMR spectrometry. Complete conversion to the phosphinimine was generally detected within 72 h at reflux. The resultant polymers were purified by multiple precipitations from THF into methanol and hexanes followed by Soxhlet extraction with hexanes for 48 h. The identity of the white polymer was confirmed by multinuclear NMR and elemental analysis. Molecular weights were estimated by GPC relative to polystyrene standards. A similar approach was utilized for linkage of phosphoryl azides to the polymer backbone.

Results and Discussion. The linkage of the cyclophosphazene to the polystyrene appeared to be quantitative. Reactions were followed by ^{31}P NMR to monitor their progress. Poly(diphenyl-*p*-styrylphosphine) generates a singlet peak near −6 ppm in ^{31}P NMR spectra. Addition of the phosphazene azide causes this singlet to disappear and a new peak corresponding to the phosphinimine to appear. The location of this new peak is dependent on the nature of the cosubstituents on the cyclic phosphazene azide. Reactions were determined to be complete when the peak at −6 ppm could no longer be detected. This also is indicative of near quantitative conversion to the phosphinimine. A change in location of the chemical shift corresponding to the phosphorus within the phosphazene ring originally bound to the azide was also detected when either $N_3P_3(OC_6H_5)_5(N_3)$ or $N_3P_3(OCH_2CF_3)_5(N_3)$ reacted with the phosphinated polystyrene. Figure 1 shows the ^{31}P NMR spectra of the reactants and the purified product from the reaction of poly(diphenyl-*p*-styrylphosphine) with $N_3P_3(OCH_2CF_3)_5(N_3)$. Spectrum C is the final product. The phosphorus atom closest to the polymer backbone undergoes a shift from −6 to 11 ppm. The phosphorus originally bound to the azide shifts from near 17 to 13 ppm. These peaks are broad, and their splitting is obscured due to their proximity to the polymer backbone. The two phosphorus atoms furthest from the reaction center remain near 17 ppm. A doublet is generated due to the splitting from the phosphorus originally bound to the azide. These chemical shifts are in good agreement with the results for small molecule analogues discussed in a previous work.[18] Integration of spectrum C is 1:1:2, moving downfield as expected for the repeat unit containing four phosphorus atoms. Starting materials were not detected by ^{31}P NMR spectroscopy after purification. The purity of the final polymers was also verified by ^{1}H NMR spectra and elemental analysis.

Further evidence for the coupling process comes from gel permeation chromatography results. Table 1 shows GPC-derived data from a representative sample of poly(diphenyl-*p*-styrylphosphine) polymerized anionically as well as from products from the free-radical-initiated copolymerizations of diphenyl-*p*-styrylphosphine with both styrene and methyl methacrylate. Data are also shown for the above polymers after treatment with the alkoxy and aryloxy phosphazene azides.

In most instances, the M_n of the polymer is increased dramatically after reaction with the phosphazene azide. However, the increase in molecular weight does not correspond to theoretical values for the modified polymers based on the molecular weights of the phosphine-containing polymers. This is probably due to the fact that gel permeation chromatography is not an absolute method for determining molecular weight and does not take into account the microstructure of different polymers. A small decrease in polydispersity was also detected. This was attributed to the loss of lower molecular weight species during the purification procedure.

Molecular weights as high as 10^6 have been achieved for the phosphinimine-modified organic polymers. Also, some molecular weight control was possible using the anionic polymerization approach.

Conclusions. Cyclic phosphazene trimers can be linked to phosphinated organic polymers in near-quantitative yield. Because diphenyl-*p*-styrylphosphine can be polymerized by free-radical or anionic techniques, it should be possible to form copolymers with a wide variety of organic monomers, and use of the chemistry discussed here provides access to a wide range of phosphazene-linked styrene copolymers. Moreover, the use of phosphazene cyclic trimers with two or three azide groups may be an efficient means to achieve polymer cross-linking under relatively mild conditions. The coupling reaction with phosphoryl azides provides an additional method for the incorporation of phosphorus into organic polymers.

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Supporting Information Available: Text detailing the synthesis, purification, and characterization (^{1}H and ^{31}P NMR and GPC data) of the products discussed. This material is available free of charge via the Internet at http://pubs.acs.org.

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