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## Grafting Reactions onto Poly(organophosphazenes). 1. The Case of Poly[bis(4-isopropylphenoxy)phosphazene]-*g*-polystyrene Copolymers

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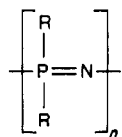
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**ABSTRACT:** In this paper we propose a method for grafting organic polymers onto polyphosphazene matrices, which is of general applicability for carbon-backboned polymers that are synthesized via radical initiation. As an example, we describe the grafting reaction of polystyrene onto poly[bis(4-isopropylphenoxy)phosphazene] to obtain poly[bis(4-isopropylphenoxy)phosphazene]-*g*-polystyrene copolymers. Gel permeation chromatography, fractional precipitation, thermal analysis, and X-ray diffraction studies performed on these materials indicated that the grafting reaction was successful, yielding comblike grafted copolymers attached to organic substituents on the polyphosphazene skeleton. Moreover, thermogravimetric analysis of the poly[bis(4-isopropylphenoxy)phosphazene]-*g*-polystyrene copolymers indicated that the thermal properties of these materials are different from those of the constituent homopolymers and blends and imply that they are considerably more thermally stable than pure polystyrene.

### Introduction

One of the most intriguing characteristics of the poly(organophosphazenes) (POP) may be recognized in the inorganic nature of their skeleton, which is formed by alternating nitrogen and phosphorus atoms, according to the general formula<sup>1</sup>



The presence of these atoms in the phosphazene polymer chain confers to this class of macromolecules interesting properties, namely, flame retardancy,<sup>2</sup> self-extinguishability,<sup>3,4</sup> resistance to high temperature,<sup>5</sup> low-temperature flexibility,<sup>6</sup> oil repellence,<sup>7</sup> biocompatibility,<sup>8</sup> etc., which make them suitable for use in several research and industrial applications.

Moreover, due to the very flexible synthetic method used for the preparation of the POP,<sup>1,6,9</sup> these properties may be significantly enhanced by a careful choice of the substituent group R to be bonded to the phosphorus atoms of the phosphazene chain.

In fact, substituent groups such as highly fluorinated alcohols impart to the corresponding POP very good

elastomeric characteristics, relevant mechanical and thermal stability, and very low flammability,<sup>10,11</sup> while POP substituted with aryloxy and alkoxy groups have been carefully evaluated as flame-retardant and smoke-suppressant additives for commercial carbon-backboned polymers<sup>3,4,12-15</sup> to prevent their combustion and to improve their thermal stability.

In recent years, however, alternative approaches to blends of POP with commercial polymers have been explored in an attempt to obtain improved formulations suitable for practical applications. These methods involve basically (1) copolymerization reactions of hexachlorocyclophosphazene (NPCl<sub>2</sub>)<sub>3</sub> with other monomers, with the aim of preparing linear polymers containing in the skeleton alternating blocks of the two reacting species, and (2) grafting reactions of industrially important polymers onto POP.

The first of these two possibilities has been investigated recently by Allcock,<sup>16</sup> who attempted the copolymerization at high temperature of hexachlorocyclophosphazene with hexamethylcyclotrioxane. Although some oligomeric species were detected in this reaction, no linear, soluble, high molecular weight copolymers containing -N=P- and -SiO- blocks were obtained.

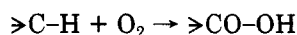
The second approach, which implies the preparation of grafted copolymers between POP and organic macro-

molecules, seems to be more attractive and suitable for further developments.

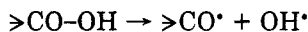
In fact, a recent patent by Brossas et al.<sup>17</sup> reported the grafting of several different polymers, namely, polystyrene, polybutadiene, and polyisoprene, onto poly(dichlorophosphazene), followed by substitution of the unreacted chlorine of the  $(\text{NPCl}_2)_n$  with 2,2,2-trifluoroethoxy groups. The resulting polymers seem to exhibit very good thermal stability and considerably high limiting oxygen index (LOI) values, implying excellent flame resistance.

Expanding upon this approach, we undertook a study on the possibility of grafting organic polymers onto POP, and we found a new method for achieving this goal.

This method, which is of general applicability for vinyl monomers that polymerize by radical initiation, implies the use of POP containing substituents having hydrogens bonded to tertiary carbons. Due to their high reactivity, these hydrogens can be easily peroxidized under mild experimental conditions to produce hydroperoxides supported by phosphazene matrices, according to the general reaction



From these hydroperoxide groups, radicals are successively generated by thermal and/or photochemical breaking of the hydroperoxide bond, according to the scheme



Radical species of this type are able to initiate the polymerization of vinyl monomers,<sup>18</sup> allowing in this way the growing of polymeric chains directly from the polyphosphazene skeleton.

As a typical polyphosphazene material suitable for this study, we selected poly[bis(4-isopropylphenoxy)phosphazene],  $[\text{NP}(\text{OC}_6\text{H}_4-i\text{-C}_3\text{H}_7)_2]_n$  (PIPP), due to the presence on the phenoxy moieties of two, easily peroxidized, isopropyl groups. As the grafting monomer, styrene (S) was selected.

In this paper we report on the grafting reaction of S onto PIPP together with some chemicophysical characterizations of the synthesized polystyrene (PS)-PIPP copolymers.

## Experimental Section

The dioxane used for the synthesis of PIPP, a C. Erba RPE solvent, was purified following previously reported methods,<sup>19</sup> dried by refluxing over Na/benzophenone complex, and distilled immediately prior to use. Tetrahydrofuran (THF), isopropylbenzene, and other solvents, were C. Erba analytical grade and were freshly distilled before use. Styrene monomer was flash distilled, dried over  $\text{CaH}_2$ , and stored in a freezer under nitrogen. Hexachlorocyclophosphazene was purchased from Inabata Co., Japan, and purified by means of multiple recrystallization from *n*-hexane followed by vacuum sublimations until a constant melting point of 114 °C was obtained.<sup>1</sup> 4-Isopropylphenol was obtained from Aldrich and purified by vacuum distillation.

The chemicophysical characterization of (1) poly[bis(4-isopropylphenoxy)phosphazene], (2) peroxidized PIPP, (3) polystyrene grafted onto PIPP (PIPP-*g*-PS), and (4) PS-PIPP blends in the same proportion of the grafted copolymer was performed with (i) a Perkin-Elmer Model 457 infrared spectrophotometer, (ii) a Waters GPC instrument equipped with refraction index and UV detectors and with  $\mu$ Styragel columns ( $10^3$ ,  $10^4$ ,  $10^5$ , and  $10^6$  Å), (iii) a Du Pont 990 DSC instrument (all runs were performed under nitrogen (50 mL/min flow)), (iv) a Siemens D-500 X-ray diffractometer for unoriented specimens, (v) a Kiessig camera for X-ray fiber patterns, and (vi) a Du Pont 951 thermogravimetric analyzer (heating rate 10 °C/min).

**Synthesis of Poly(dichlorophosphazene).** The synthesis of poly(dichlorophosphazene) was achieved by bulk thermal polymerization of hexachlorocyclophosphazene at 250 °C under vacuum, according to the literature.<sup>1</sup>

**Synthesis of PIPP.** In a 1000-mL round-bottomed, three-necked flask, equipped with a mechanical stirrer and an efficient condenser, 5 g (0.0431 mol, based on the repeating units) of poly(dichlorophosphazene)  $(\text{NPCl}_2)_n$  was dissolved in 150 mL of anhydrous dioxane and treated with the sodium salt of isopropylphenol, prepared by reacting a suspension of 16.55 g (0.3448 mol) of NaH 50% oil dispersion in dioxane with 46.96 g (0.3448 mol) of 4-isopropylphenol. To this mixture was added 1 g of tetrabutylammonium bromide to improve the efficiency of the substitution reaction of the  $(\text{NPCl}_2)_n$ .<sup>20</sup> The reaction mixture was stirred for 16 h at 80 °C and finally poured into excess water. The PIPP obtained in this way was purified by means of several dissolutions in THF and precipitations in water or methanol. The final yield of polymer was around 50%, as calculated on the starting amount of poly(dichlorophosphazene).

**Peroxidation of Isopropyl Groups in PIPP.** PIPP (1 g) was dissolved in 150 mL of freshly distilled isopropylbenzene and heated at 60 °C for 2 h in the presence of 200 mg of benzoyl peroxide, while air (5 L/h) was bubbled through the solution. The polymer was then recovered by precipitation in ethanol and purified by several dissolutions in THF and reprecipitations in acetone. This procedure was adopted in order to guarantee that all residual unreacted benzoyl peroxide and peroxidized isopropylbenzene were completely absent in the final polymer.

The analysis of the hydroperoxide groups was performed according to the method proposed by Carlsson and Wiles,<sup>21</sup> and it was found that the total amount of hydroperoxide groups was around 1 mol %, as calculated on the basis of the number of moles of isopropyl groups.

The peroxidized phosphazene polymer was stored under nitrogen in the dark in order to prevent undesirable side reactions. In spite of this precaution, however, some cross-linking of the peroxidized PIPP did occur after a few days, which indicated the high reactivity of the POOH functions on the polyphosphazene.<sup>22</sup>

**Grafting Reactions of PS onto Peroxidized PIPP.** Peroxidized PIPP (1 g) was dissolved in 20 g of carefully purified styrene monomer in a glass tube, and the tube was sealed under vacuum and heated at 80 °C for 16 h. The resulting polymer was dissolved in toluene, precipitated in ethanol, and subsequently dried under vacuum overnight.

**Fractional Precipitation.** PIPP-*g*-PS copolymer (250 mg) was dissolved in 25 mL of benzene and subsequently precipitated in a tenfold excess of acetone. The same procedure was used with a 3/1 mixture of PS (by radical polymerization) and PIPP. The resulting precipitates were analyzed by infrared spectroscopy.

**Infrared Characterization of the Copolymers.** IR characterization of PIPP and PS homopolymers and of PIPP-*g*-PS copolymers was performed on evaporated  $\text{CH}_2\text{Cl}_2$  solutions of these materials. The spectrum of PIPP is mainly characterized by vibrational frequencies at 1200–1250 ( $\text{P}=\text{N}$ ) and 950 ( $\text{P}-\text{O}-\text{C}$ )  $\text{cm}^{-1}$ . PS shows a band at 1200  $\text{cm}^{-1}$  which overlaps the PIPP bands. The presence of PIPP in the copolymer can be easily detected by the band at 950  $\text{cm}^{-1}$ . Other characteristic bands of PIPP in the graft copolymer are at 2955, 1500, 1100, 1020, and 830  $\text{cm}^{-1}$ .

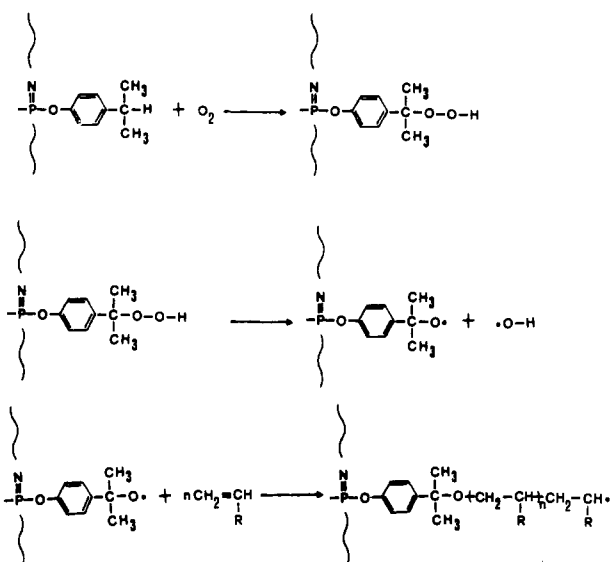
## Results and Discussion

**General Considerations.** In the Introduction we stressed the versatility of the substitutive synthetic approach used in the preparation of POP, which allows the synthesis of tailor-made polymers exhibiting remarkably different properties by varying the nature of the substituent groups on the phosphorus.<sup>1,6,23</sup>

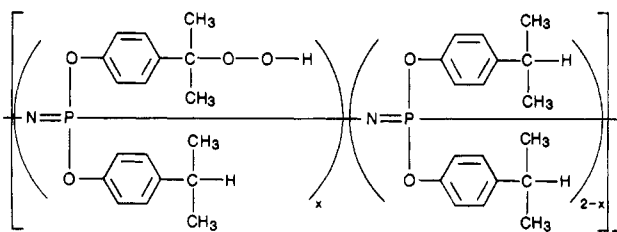
We now emphasize that a further possibility of substantially modifying the characteristics of already-synthesized phosphazene polymers and improving their technological potentialities may be achieved by performing a series of functionalization reactions on these side substituent moieties.

In this paper we describe the case of a phosphazene material, poly[bis(4-isopropylphenoxy)phosphazene]  $[\text{NP}(\text{OC}_6\text{H}_4-i\text{-C}_3\text{H}_7)_2]_n$ , which lends itself nicely to this type of modification. This polymer, in fact, exhibits at least three important and valuable attributes: (1) the presence

Scheme I



of a phenoxy moiety having an isopropyl function, which can be easily peroxidized to produce a new, highly reactive, polyphosphazene, having the general formula



(2) improved thermal stability, in comparison with other aryloxy-substituted phosphazene polymers of the same series, according to Goldfarb et al.,<sup>24</sup> and (3) a noticeable degree of flame resistance, as indicated by a LOI of 23.4, and a reduced tendency to evolve smoke in comparison to alkoxy-substituted POP, as reported by Quinn et al.<sup>3</sup>

These facts are very interesting because they offer the possibility of introducing onto a valuable phosphazene substrate hydroperoxide functions, thereby dramatically changing the characteristics and the reactivity of the original PIPP.<sup>22</sup>

Hydroperoxide functions, once introduced into a polymeric system, are known to decompose, both thermally and photochemically,<sup>25</sup> bringing about (1) cross-linking reactions and insolubilization, (2) chain scissions and degradation, and (3) formation of very reactive radical sites, suitable for grafting reactions of vinyl-like polymers.<sup>18</sup>

We took advantage of the above-mentioned facts and studied the grafting reactions of vinyl polymers onto the peroxidized PIPP, having in mind proposing a novel, innovative, method for (1) synthesizing a new class of polyphosphazene materials and (2) improving the thermal stability of commercially valuable organic polymers.

As a suitable monomer to be grafted onto PIPP, we chose styrene, since polystyrene has broad commercial utilization and may be considered as a typical example of an organic polymer prepared via radical initiation of an olefinic monomer.

**Synthesis of PIPP-g-PS Copolymers.** The overall reaction sequence that was adopted for grafting PS onto PIPP is summarized in Scheme I. In Scheme I, the isopropyl group in the phenoxy moiety is peroxidized in the presence of benzoyl peroxide to introduce hydroperoxide functions into the phosphazene matrix. The successive

Table I  
Peroxidation Reaction of PIPP under Various  
Experimental Conditions

run	oxidation time, h	temp, °C	% benzoyl peroxide <sup>a</sup>	% polymer peroxidation
1	2	60	20	0.3
2	2	60	30	0.4
3	2	85	20	cross-linking
4	2	60	20	1.0

<sup>a</sup>By weight over the polymer.

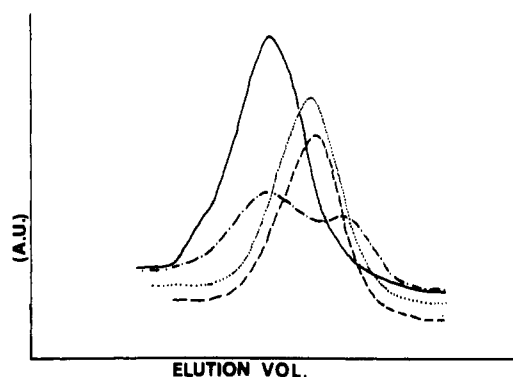


Figure 1. GPC chromatograms of PS (···), blend (---), peroxidized PIPP (— · —), and PIPP-g-PS copolymer (—) (see text).

breaking of these groups in the presence of styrene monomer allows the onset of a radical polymerization and the growing of organic polymeric chains from the polyphosphazene macroradical sites. PS homopolymer, concurrently formed in the reaction mixture, is separated from the grafted copolymer by its selective precipitation in acetone.

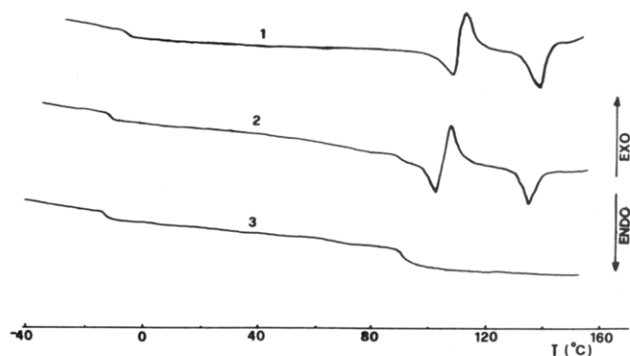
Consider now the initial peroxidation step of PIPP together with the growing reaction of PS chains as described in Scheme I: Table I reports the results of the peroxidation of PIPP as a function of both time and temperature of the reaction. All runs were performed in isopropylbenzene with a concentration of PIPP of 70 mg/mL and flow of air of 5 L/h.

As can be seen from the data in Table I, the degree of oxidation is strongly dependent on the temperature, in the sense that higher oxidation temperatures (85 °C) induce cross-linking of PIPP. So, in order to prevent cross-linking of the polymer, it was necessary to have a low oxidation temperature. It was also found that the peroxidation reaction is strongly dependent on the nature of the solvent used for this process, as demonstrated by other authors.<sup>18</sup>

The peroxidized PIPP, obtained as described above, was dissolved in pure styrene (initial PS/PIPP = 20/1) and allowed to react with this monomer for 16 h at 80 °C. The final PIPP-g-PS grafted copolymer exhibited a PS/PIPP ratio in the range 3/1 to 3.5/1, as determined by weighing the product after polymerization.

Fractional precipitation, gel permeation chromatography, DSC, and X-ray diffraction analyses demonstrated the success of the grafting reaction of PS onto PIPP.

**Gel Permeation Chromatography and Fractional Precipitation.** Figure 1 shows a comparison of GPC chromatograms of (1) PS obtained by radical polymerization with benzoyl peroxide as initiator, (2) a blend in a 3/1 ratio of the PS and the peroxidized PIPP, (3) peroxidized PIPP (showing a bimodal distribution of molecular weight), and (4) the crude PIPP-g-PS copolymer obtained in run 1 (PS/PIPP = 3/1). As can be seen, the PIPP-g-PS graft copolymer curve shows an elution volume slightly less than the higher molecular weight peak of the peroxidized PIPP. Moreover, the low molecular weight



**Figure 2.** DSC analysis of PIPP (1, heating rate 5 °C/min), PIPP/PS blend (2, heating rate 5 °C/min), and PIPP-g-PS copolymer (3, heating rate 20 °C/min).

peak of the peroxidized PIPP disappears. Both of these facts point toward an increase of the molecular weight of this material and may offer an indication of the formation of the graft copolymer.

However, the presence of some PS homopolymer cannot be excluded on this basis. In order to be sure of this, the following separation procedure was adopted: 250 mg of the blend, whose GPC curve is illustrated in Figure 1, was dissolved in 25 mL of benzene and subsequently precipitated in a tenfold excess of acetone. The resulting suspension was refluxed for 2 h. After the mixture cooled, a solid polymer precipitated (25% of the initial weight), which, after IR investigation, was found to be PS homopolymer only. The corresponding filtrate was a suspension of PS and PIPP. Under these conditions, the PIPP homopolymer does not precipitate from the solution.

The same procedure was used with the crude copolymer obtained by the grafting reaction. After refluxing and cooling, a solution instead of a suspension was obtained, and the precipitate (90% of the initial weight) analyzed by IR was found to be a mixture of PS and PIPP in almost the same composition as the pristine material.

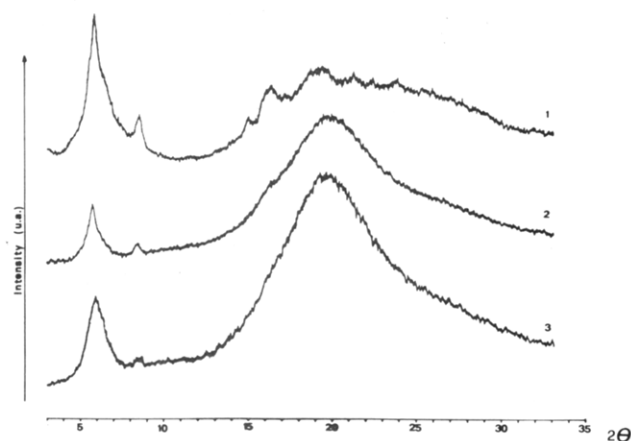
From the above considerations, it may be concluded that PS homopolymer, if present, is less than 10%.

**Thermal Analysis.** Figure 2 displays DSC scans of PIPP, PIPP/PS blend, and PIPP-g-PS copolymer. The thermal behavior of PIPP (scan 1) was previously investigated and is described elsewhere.<sup>26</sup> It mainly consists of an endothermic peak ( $T_g$ ) at 0 °C, an endothermic peak at 110 °C immediately followed by an exothermic peak at 115 °C, and finally by another endothermic peak at 140 °C. This last peak corresponds to a crystalline-mesomorphic phase transition, while the previous peaks detect the crystalline phase transformations, clearly elucidated by X-ray diffraction analysis (see below). No endothermic peak attributable to melting could be determined before decomposition, as commonly observed in other poly(organophosphazenes)<sup>27</sup>.

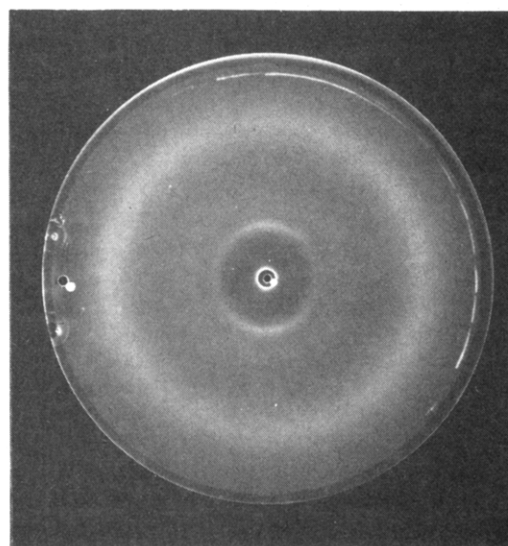
Scan 2, of the blend, is characterized by the overlap of the two constituent homopolymer thermograms, i.e., all PIPP peaks and the  $T_g$  endotherm of PS around 90 °C. It is worth noting that  $T_g$  of PS and other PIPP peaks are shifted toward lower temperature, such a decrease being already found in other two-component blends.<sup>28</sup>

The copolymer DSC (scan 3) reveals only the presence of the glass transition temperature of the two constituent homopolymers, with a marked decrease of PS  $T_g$  in the first scan (subsequent scans indicate the  $T_g$  around 90 °C). This shift has already been observed in other copolymers.<sup>29,30</sup>

**X-ray Diffraction Analysis.** Figure 3 shows X-ray diffraction patterns performed in toluene solution cast



**Figure 3.** X-ray diffraction patterns of PIPP (1), PIPP/PS blend and (2), PIPP-g-PS copolymer (3).



**Figure 4.** Fiber diffraction pattern of PIPP-g-PS copolymer stretched 400% at ~110 °C.

films of PIPP, PS/PIPP blend, and PIPP-g-PS copolymer (1, 2, and 3, respectively). The amorphous bump of PS in 2 and 3 and also the relatively sharp peaks of PIPP are evident.

Recently, a detailed structural analysis on PIPP<sup>31</sup> revealed the existence of two crystalline phases, aside from a high-temperature mesomorphic phase, consistent with DSC findings.<sup>26</sup> In spite of the apparent similarity of patterns 2 and 3, a remarkable increase of half-width of the low  $2\theta$  angle equatorial peaks is detected, indicating reduced PIPP microdomain dimensions in the copolymer.

WAXS patterns obtained around 130 °C<sup>26</sup> on copolymer samples are essentially unaltered compared with patterns recorded at room temperature, clearly demonstrating that no phase transition has occurred. To confirm the above results, an X-ray fiber pattern of cast copolymer film stretched 400% at ~100 °C (above the PS  $T_g$ ) is reported (Figure 4). In fact, some orientation of PIPP (equatorial archings) and the amorphous halo of PS are evident, but no crystalline phase of PIPP could be detected. The PIPP part of the spectrum is strictly reminiscent of the pattern of the mesomorphic phase obtained above 140 °C.<sup>31,26</sup>

In conclusion, we should infer for PIPP the formation of a phase close to the mesomorphic one directly from the solution at room temperature, in order to account for the results consistently obtained from different techniques. This hypothesis is particularly reliable on the basis of the fact that the actual grafting of PS chains onto PIPP

Table II  
Percent Weight Loss by TGA<sup>a</sup>

temp, °C	PIPP-g-PS copolymer	PIPP	PS by radical polymerization	PIPP/PS blend
150	0.1	0	1.6	2.4
200	2.5	0	4.1	3.8
250	3.8	0	5.8	4.0
300	5.0	0	8.3	11.0
350	11.3	1.9	22.5	63.0
400	37.5	5.4	78.5	74.0

<sup>a</sup> Heating rate 10 °C/min in air.

backbone gives necessarily rise to a comblike structure, topologically hindered, which prevents the organization of PIPP chains into a phase exhibiting a higher order than the mesomorphic one.

All of the above-mentioned characterizations point toward the success of the grafting reaction of the PS onto the PIPP.

**Thermogravimetric Characterization of the Copolymers.** We also investigated the thermal behavior of the PIPP-g-PS copolymers, both in air and under nitrogen, and we compared the obtained results with those measured for the pure PS and PIPP homopolymers and blends.

In Table II the weight loss of PS, PS/PIPP blend, and PIPP-g-PS copolymer at various temperatures is reported. From these data, the following seem evident: (1) PS is considerably less thermally stable than PIPP; in fact, the temperatures observed for 50% weight loss are 360 °C for PS and 428 °C for PIPP in air. (2) Grafting PS chains onto PIPP increases the thermal stability of the organic polymer both under nitrogen and in air.

It is interesting to note that the weight loss rate of the blend increases significantly over 300 °C, i.e., the temperature range in which PIPP melting is expected to occur.

**Final Remarks.** It was stressed in the Experimental Section that the high reactivity of the hydroperoxide groups in the peroxidized PIPP results in the cross-linking of this material within a few days after the peroxidation. It should be mentioned, moreover, that the same problem, although to a lesser extent, was found in the PIPP-g-PS copolymers.

This fact seems to indicate that not all the hydroperoxide in the peroxidized PIPP is consumed during the grafting reaction of styrene monomer on this material and that the residual, unreacted >CO-OH functions in PIPP-g-PS may decompose successively to form >CO• radicals, whose coupling induces the cross-linking of the copolymers.

To circumvent this, the only possibility seems to be to minimize the amount of residual >CO-OH groups in the PIPP-g-PS copolymers. This may be achieved by (1) improving the yield of hydroperoxide breaking when the peroxidized PIPP is in the presence of styrene monomer, (2) strictly controlling the experimental conditions of the peroxidation reaction of the polyphosphazene substrate, in order to introduce in the PIPP only the correct amount of hydroperoxides necessary for grafting the vinyl monomer, and (3) decreasing the number of peroxidizable sites in the polyphosphazene matrix, without depressing sig-

nificantly the final grafting ability of the material. This may be easily achieved by using, for instance, polyphosphazene copolymers containing two different substituents, only one of which bears hydrogen atoms bonded to tertiary carbons. Possible candidates for this task may be (2,2,2-trifluoroethoxy)phosphazene-(4-isopropylphenoxy)phosphazene copolymers.

Research in this direction is in progress and will be reported in a forthcoming paper.

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**Registry No.** PS, 9003-53-6.

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