Synthesis and Flame-Retardant Properties of Phosphorus-Containing Polymers Based on Poly(4-hydroxystyrene)

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SYNOPSIS

Phosphorus-containing polystyrene was obtained through incorporating phosphate groups onto poly(4-hydroxystyrene). This was achieved by esterification with diethylchlorophosphate. The phosphorylation was confirmed by IR, ^{1}H-NMR, and ^{31}P-NMR analysis. By varying the feeding ratios of the reactants, the phosphorus content in the polymers could be successfully tailored and gave values of 12.8 to 4.9% by weight. This was further corroborated by elemental analysis. Thermal characteristics and temporal stability of the phosphorylated polymers were evaluated by DSC and TGA. High char yields (64% by weight) and LOI values of 41 were found for these polymers. Such properties make these polymers useful in flame retardants. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The main drawback of organic polymeric materials in many applications is their flammability. Thus, the demand for flame-retardant polymeric materials steadily increases as a consequence of the increasing use of polymers in the home and other places. In the past years, studies on searching for ways to improve the flame retardance of polymeric materials have been reported.[1-13] A traditional technique of preparing flame-retardant polymers is to blend flame-retardant additives with polymeric materials. Bonding flame-retardant groups to polymer backbones, i.e., using a reactive flame retardant, has attracted much attention recently.[3-13] The use of a reactive flame retardant has the advantage of the permanent attachment of the flame retardant. This will lead to the requirement that a much smaller amount of flame retardant is required to reach a certain degree of flame retardancy. Consequently, a much smaller influence is brought upon the physical and mechanical properties of the polymers.[10,11]

In addition to the methods of preparing flame-retardant organic polymers, the development of novel flame-retardant compounds is a matter of high priority. With the consideration of avoiding the generation of toxic, corrosive, or halogenated gases in combustion, the trend is toward using nonhalogenated flame retardants. Consequently, phosphorous compounds are the material of choice for the flame retardation of organic polymers.[4-13] The burning of the phosphorus-containing flame retardants is mainly through a condensed-phase mechanism.[11] This mechanism leads to the production of a relatively incombustible carbonaceous char. Consequently, fewer toxic gases are released into the atmosphere. Furthermore, the flame-retardant efficiency of phosphorous compounds was reported to be better than equal-weighted halogenated compounds and could be further evened up when phosphorus is covalently bound to the polymers.[4-13] Among the several approaches of incorporating phosphorus into polymeric systems, copolymerization and polymer modification are considered to be highly promising.[3-5,9-10]

Chlorophosphate groups have been widely applied in the synthesis of phosphate derivatives with high conversion.[4-13] An example was to react chlorophosphates with some hydroxy-containing

compounds such as hydroxyethyl methacrylate (HEMA).[3,12] In this study, diethylchlorophosphate (DECP) was reacted with hydroxy-containing polymers: poly(4-hydroxystyrene) (PS-OH). Success in controlling the content of phosphorus was achieved. With a high degree of phosphorylation, the resulting polymers could be considered as an analog of polystyrene. Therefore, the polymers were considered to be more compatible in blending with polystyrene. Furthermore, the widely used index of the flame resistance, the limiting oxygen index (LOI), was chosen to examine the flammability.[14,15] A material is considered flammable as long as the LOI value ≤ 26.

EXPERIMENTAL

Materials

Poly(4-hydroxystyrene) (PS-OH, MW 9000–11,000) from Polyscience Inc. was used as received. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled prior to use. Triethylamine (TEA) was dried over potassium hydroxide and distilled prior to use. Diethylchlorophosphate (DECP) and copper(I) chloride from Aldrich Chemical Co. were used as received.

Phosphorylation of Polyhydroxystyrene

A typical reaction is described as follows: PS-OH (5.0 g) was dissolved in 60 mL of dry THF in a 250 mL round-bottom flask fitted with a magnetic stirrer. Distilled dry TEA (12.1 mL, 0.09 mol) was added and the system was cooled to 0°C. Cu_2Cl_2 (0.2 g) was also added, and then a solution of DECP (14.4 g, 0.0834 mol) in 30 mL THF was added dropwise over a period of 30 min. The system then became thick due to the precipitation of the amine hydrochloride. After maintaining it at 0°C for 2 h, the system was kept at room temperature overnight. The precipitant was filtered and washed with THF. The filtrate was washed with an ice aqueous solution (2%) of NaOH followed by distilled water. It was concentrated and then precipitated from methanol. The obtained product was reprecipitated twice more and then dried under a vacuum at 50°C.

Instrumental Analysis

IR spectra were recorded with KBr powder using a Perkin-Elmer 842 infrared spectrophotometer. ^{1}H- and ^{31}P-NMR spectra were recorded with a Bruker

MSL-300 (300 MHz) NMR spectrometer using DMSO-d_6 as the solvent. The elemental analysis was performed by an F002 Heraeus CHN-O Rapid elemental analyzer with acetanilide as a standard. The phosphorus contents of the polymers were determined by phosphorus elemental analysis via a Micro Digestion Apparatus with a spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded with a Seiko DSC 5200 at a heating rate of 10°C/min under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed by a DuPont 951 thermogravimetric analyzer at a heating rate 10°C/min under a nitrogen or air atmosphere with a flowing rate of 50 mL/min. LOI values were measured on a Stanton Redcroft flame meter by a modified method: Powder samples (500 mg) were placed in a glass cup (diameter 25.6 mm; height 4.5 mm) situated in the middle of the chimney. The flame was applied from the top of the chimney for 10 s. The flow rate ($N_2 + O_2$) was maintained at 17 L/min. The percentage of oxygen in the O_2 and N_2 mixture just sufficient to sustain the flame was taken as the LOI.[7]

RESULTS AND DISCUSSION

The synthesis of phosphorus-containing polymers was performed by reacting DECP with PS-OH (Scheme 1). DECP reacting with HEMA under this reaction has been reported to have a 100% conversion.[3] A conversion higher than 95% was also obtained in the present study, in spite of using a polymer as the reactant. This high conversion in the
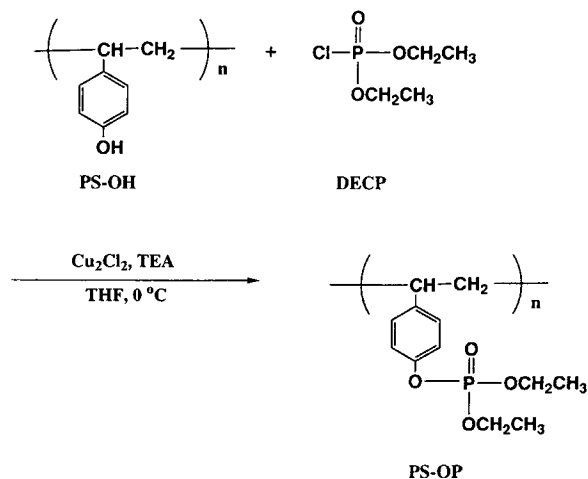
Scheme 1 Phosphorylation of poly(4-hydroxystyrene) (PS-OH).
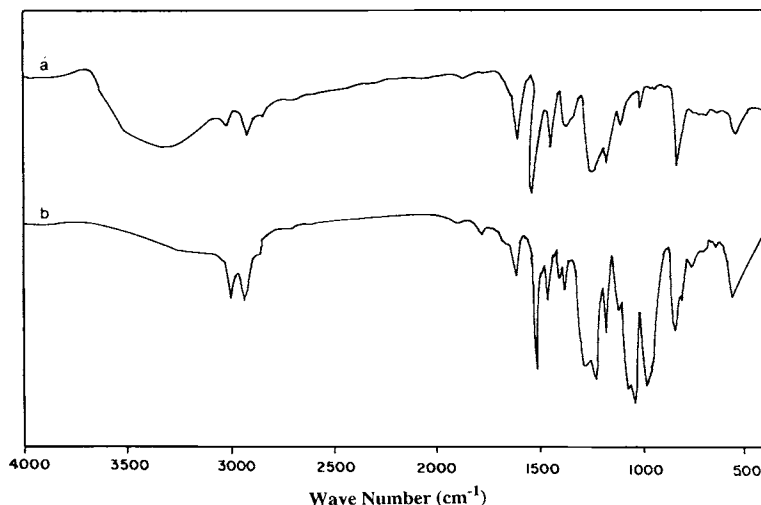
Figure 1 IR spectra of PS-OH (a) before and (b) after phosphorylation (PS-OP-I) by DECP.

reaction reveals not only that the phosphorus content of the resulting polymers could reach a large value (about 12.5% by weight), but also that the phosphorus content of the resulting polymers can be controlled via varying the feed ratios of the reactants.

The chemical structures of the polymers were characterized by IR, NMR, and elemental analysis. The IR spectra of the obtained polymers are shown in Figure 1. The spectra show strong absorption at 1273 cm^{-1} (—P$=$O), 1166 and 966 cm^{-1} (—P—O—Ph), and 1030 cm^{-1} (—P—O—C—).[4,5] This reveals the formation of the phosphate

structure and sequentially confirms the phosphorylation of PS-OH. The structure of the obtained polymers was also confirmed by ^{1}H-NMR (Fig. 2). The board peak at δ = 6.67 ppm corresponding to the aromatic protons of PS-OH shifted to δ = 6.62 and 7.10 ppm after phosphorylation. The peak at δ = 9.18 ppm corresponding to the Ph—O$\underline{H}$ proton also disappeared after phosphorylation. These above results support the occurrence of the esterification reaction on the hydroxy groups. The characteristic absorption which determined the structure of the resulting polymers are described as follows: δ = 1.04 ppm (—C$\underline{H}_3$), δ = 1.40 ppm (PhCH—C$\underline{H}_2$), δ
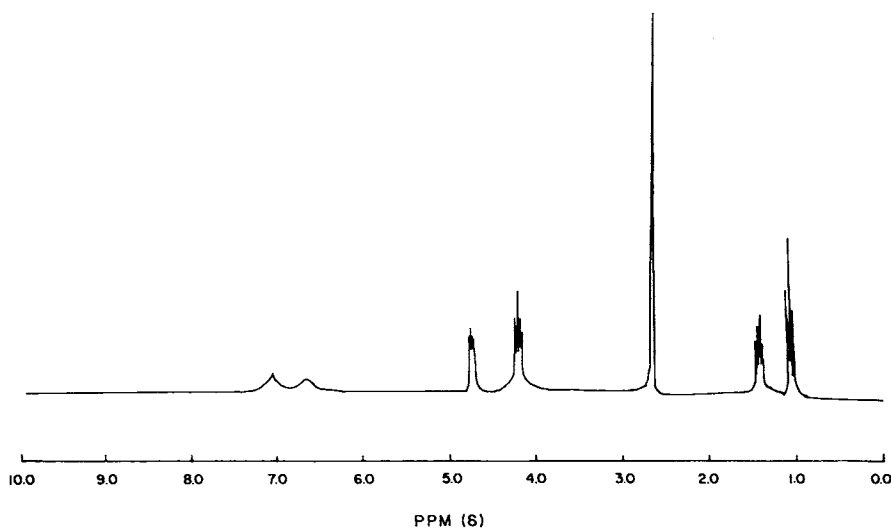

Figure 2 ^{1}H-NMR spectrum of PS-OP-I.
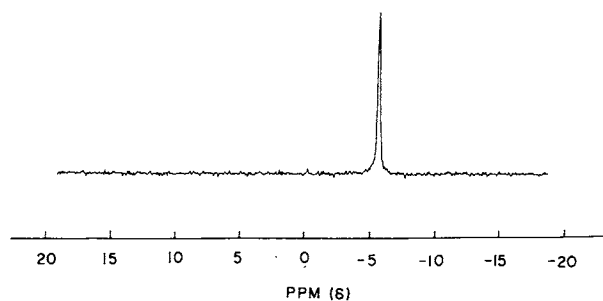
Figure 3 ^{31}P-NMR spectrum of PS-OP-I.

δ = 4.23 ppm ($-$OC$\underline{H}_2$CH$_3$), δ = 4.67 ppm (PhC$\underline{H}-$CH$_2$), and δ = 6.62 and 7.10 ppm (aromatic protons). Furthermore, the ^{31}P-NMR spectra of all these polymers show a peak at around δ = $-$5.20 ppm (Fig. 3), thereby confirming that the respective polymers were obtained.

As mentioned above, polymers with various phosphorus contents could be obtained through varying feeding ratios of DECP/PS-OH. Some analytical data of the resulting polymers are summarized in Table I. Elemental analysis results agree with the values calculated from the predicted compositions of the polymers. Polymers with various phosphorus contents, from 12 to 4.8%, were obtained. This further confirms the success in controlling the ratios of phosphorylation of the polymer, i.e., the phosphorus content of the polymers.

Thermal analysis was performed using DSC and TGA. A glass transition temperature was found from the resulting DSC thermograms. The glass transition temperature of the phosphorylated polymer PS-OP-I (see Table I) was found to be 90°C. This glass transition temperature was lower than that of the unphosphorylated PS-OH (145°C). The hydroxyl

groups of PS-OH were eliminated by phosphorylation. Thus, the density of hydrogen bonding of the polymers decreases after phosphorylation, and, consequently, the T_g's of the polymers decrease. Therefore, the T_g's of these phosphorylated PS-OH were observed to be dependent on the ratios of phosphorylation (Table I). The higher ratio of phosphorylation would lead to the lower T_g of the polymer and vice versa.

TGA traces of PS-OH before and after phosphorylation in N$_2$ are shown in Figure 4. For PS-OH, weight loss occurred at 363°C and a fast degradation was observed at 399°C. After being phosphorylated (PS-OP-I), the polymer began to lose weight at 242°C and then a two-stage weight loss process was observed, one at 292°C and the other at 457°C. Since the phosphate pendant group would not affect the thermal stability of the polystyrene backbone, the relatively poor thermal stability of phosphorylated PS-OH (e.g., PS-OP-I) is thus due to the fact that the decomposition is triggered by the pendant groups. Therefore, the first step of degradation in PS-OP-I should be originated from the decomposition of some phosphate compounds. Bond cleavages and elimination of some carbon/oxygen compounds in this degradation led to some weight loss. Nevertheless, some amount of char was obtained from the formation of phosphorus–carbon bonds. Subsequently, crosslinking carbonization of the char occurred at the second step of degradation.[5,7] Thus, the phosphorylation led this polymer to give one additional step of weight loss. This weight loss was coming from the decomposition of pendant phosphate groups. Moreover, the decomposition of polystyrene backbones was also shifted to high temperatures. Furthermore, a high char yield of 64% was found at 850°C under N$_2$ for PS-OP-I. This im-

Table I Characterization of Phosphorylated Polymers

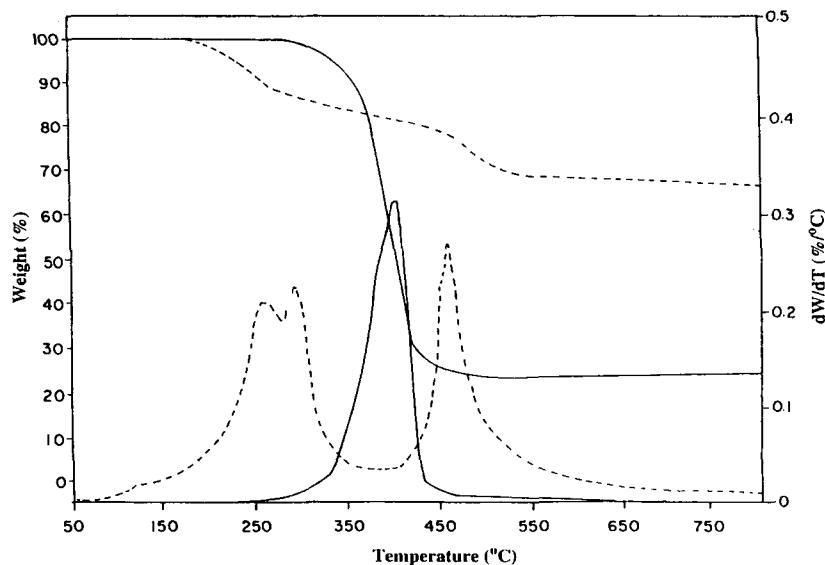| Samples	Phosphorus Content (Wt %)	Phosphorylation Ratio (Mol/Mol %)	Elemental Analysis (Calcd) (%)		T_g (°C)
			C	O	
PS-OP-I	12.79	95	60.75 (61.51)	26.14 (26.76)	90
PS-OP-II	8.21	46	67.95 (68.17)	21.68 (21.96)	100
PS-OP-III	7.08	37	69.01 (69.82)	19.94 (20.72)	112
PS-OP-IV	4.97	23	72.68 (72.97)	18.03 (18.43)	140

Figure 4   TG and DTG analysis of (———) PS-OH and (- - -) PS-OP-I in N_2.

plies that the polymer is effective in flame resistance. While in air (Fig. 5), PS-OH exhibited a two-stage weight loss process, whereas phosphorylated polymer PS-OP-I showed a three-stage process. The second step of weight loss of PS-OH could be owed to the occurrence of oxidation, since it could not be seen while in N_2. The oxidation was also found in TGA traces of PS-OP-I as the third step of weight loss beginning at around 590°C. Furthermore, the decomposition temperatures of the first two stages of weight loss in air are very close to those in N_2.

This indicates that these phosphorylated polymers are thermally stable under air, and the decomposition process of pendant phosphate groups does not involve oxygen.[7] However, the oxidation brought about a further weight loss at temperatures higher than 590°C and thus reduced the char yield to 23% at 850°C. For PS-OH, no char residue was observed after being heated at 850°C in air. The effect of phosphorylation on increasing char yield and flame retardance was further confirmed.
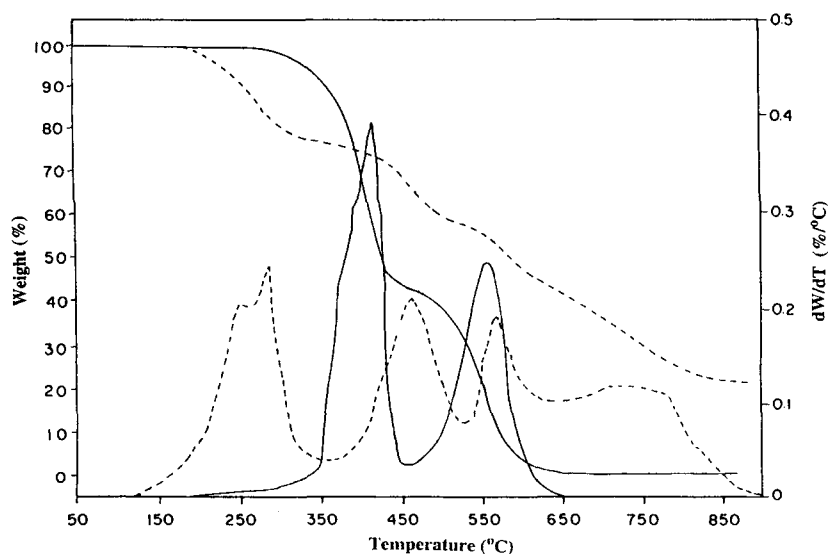
More TGA thermograms of phosphorylated

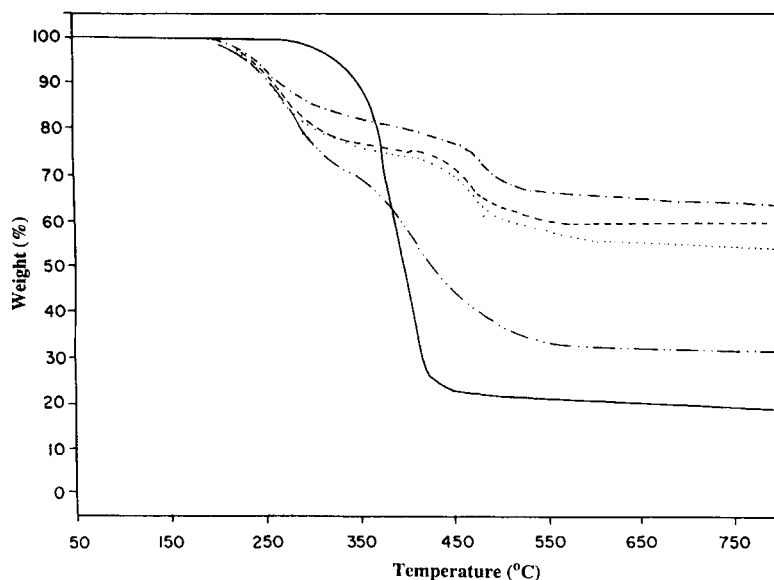**Figure 5**   TG and DTG analysis of (———) PS-OH and (- - -) PS-OP-I in air.

Figure 6 TGA thermograms of phosphorylated polymers in N₂: (———) PS-OH; (– · –) PS-OP-I; (– – –) PS-OP-II; (· · · · ·) PS-OP-III; (– · · –) PS-OP-IV.

polymers with various phosphorus contents are shown as Figures 6 and 7. Polymers with various phosphorus contents showed similar weight loss behavior. However, it is noteworthy that the weight loss percents of the first-stage weight loss decreased with increasing phosphorus content of the polymers, whereas the char yield ratios increased as the phosphorus content of the polymers increased. As mentioned earlier, the first-stage weight loss is brought about by the decomposition of pendant phosphate groups. The high phosphorus content would form a more phosphorous-rich residue during decomposi-
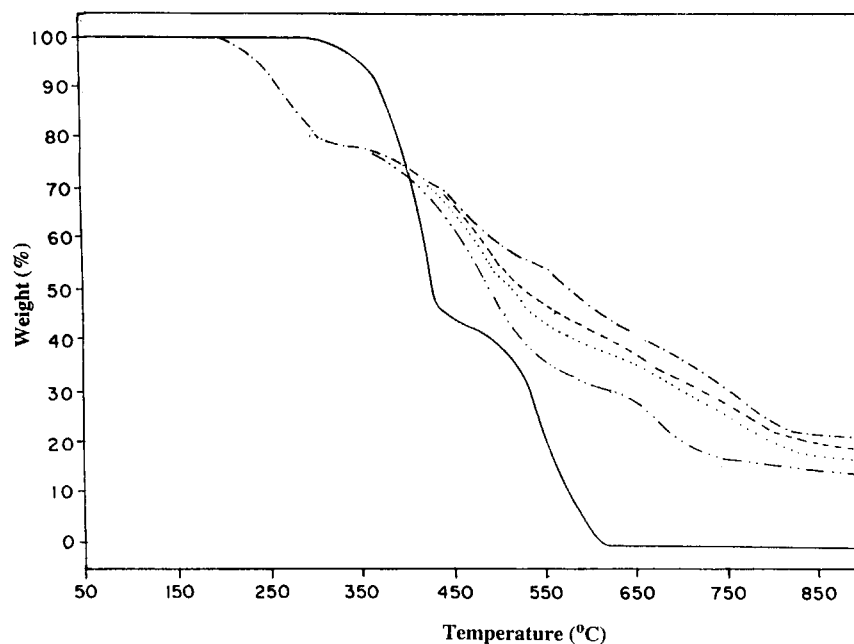

Figure 7 TGA thermograms of phosphorylated polymers in air: (———) PS-OH; (– · –) PS-OP-I; (– – –) PS-OP-II; (· · · ·) PS-OP-III; (– · · –) PS-OP-IV.

Table II Thermogravimetric and LOI Data of the Phosphorylated Polymers

| Samples | Specific Temperatures of Weight Loss from TGA (°C) | | | | | | | | Char % at 850°C | | LOI |
| | 1% Loss | | Step 1 | | Step 2 | | Step 3 | | | | |
	Air	N₂	Air	N₂	Air	N₂	Air	N₂	Air	N₂	
PS-OH	347	350	399	398	532	—	—	—	0	18	18
PS-OP-I	221	242	289	292	463	457	591	—	23	64	41
PS-OP-II	224	244	260	257	485	466	590	—	21	61	33
PS-OP-III	221	238	269	254	471	482	614	—	19	58	30
PS-OP-IV	220	247	279	286	508	460	594	—	16	35	25

tion, thereby resulting in high char yields. This also indicates that the flame-retardant effect of DECP involves a condensed-phase mechanism.[11] During combustion, a phosphorous-rich incombustible char layer would form on the surface of the polymer to block the advancing flame. Such a mechanism in flame retardation was also reported in some other phosphorous-based flame-retardant systems.[11,16]

The LOI data presented in Table II indicates that LOI values increased steadily with increasing phosphorus content in the phosphorylated PS-OH samples. This indicates that the incorporation of DECP has a significant effect upon the flame retardance of the polymers.

CONCLUSION

The incorporation of phosphorus into poly(4-hydroxystyrene) was achieved via a chemical modification. This phosphorylation can be performed by means of a polymer reaction. The phosphorus content of the resulting polymers could be tailored via varying the feeding ratios of the reactants. High char yields and LOI values of these obtained polymers indicated that phosphorylation exhibited a great effect upon improving the flame retardance of poly(4-hydroxystyrene). TGA investigation showed that this flame-retardant effect results mainly from a condensed-phase mechanism. The resulting phosphorylated polymers could be utilized as a flame retardant in polystyrene-based materials.

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