Flame-Retarded Polystyrene with Phosphorus- and Nitrogen-Containing Oligomer: Preparation and Thermal Properties

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ABSTRACT: A phosphorus- and nitrogen-containing compound (2-dimethylamino ethyl phenyl hydroxyethyl acrylate phosphate) and its oligomer (poly(2-dimethylamino ethyl phenyl hydroxyethyl acrylate phosphate), PDPHP) were synthesized and characterized. The polystyrene (PS) composites with various amounts of PDPHP were prepared by melt blending. The thermal stability of the PDPHP and PS composites was investigated by thermogravimetric analysis. The flame retardancy of the composites was evaluated using microscale combustion calorimeter and limiting oxygen index test. A Fourier transform infrared (FTIR) spectroscopy coupled with a thermogravimetric analyzer was also used to study the gas phase from the degradation of PS composites. The char residues of the PS composites containing 30 wt % PDPHP were analyzed by FTIR and scanning electron microscopy. The results suggest that the incorporation of PDPHP into PS can evidently enhance the char formation and improve the flame retardancy of virgin PS. The compact and coherent char formed during degradation was attributed to the enhancement of char quality and flame retardance. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 770–778, 2012

Key words: polystyrene; thermal properties; polymer blends; flame retardant; phosphorus

INTRODUCTION

Polystyrene (PS), with characteristics of low density, excellent mechanical durability, good chemical resistance, and convenience of processing and molding, has been widely applied in many fields such as electrical industries, building, transport, and so on. However, the high flammability and serious dripping during burning may cause fire hazards and thus limit its application in some areas. To improve its flame retardancy, halogen-containing flame retardants (FRs) such as decabromodiphenyl oxide (Deca), 1,2,5,6,9,10-hexabromocyclododecane, and so on were added into PS products in industrial community.[1,2] Unfortunately, it has been believed that some of halogenated compounds may affect the human health and environment because of the evolution of toxic gases and corrosive chemicals. Thus, in recent years, researchers have focused on exploiting environmental friendly halogen-free FRs for PS.[1,3–5]

Phosphorus-containing compounds, as halogen-free FRs, which mainly act on condensed flame-retardant mechanism, have received considerable attention.[6–10] For example, triphenyl phosphate (TPP), resorcinol bis(diphenyl phosphate) (RDP), and bisphenol A bis(diphenyl phosphate) are mostly well known and widely used to polycarbonate (PC), PC/ABS, and polyesters.[11,12] However, TPP has disadvantages of high volatility and mobility, and RDP suffers from handling problem because of its resin state. Apart from phosphorus-based FRs, various phosphorous-nitrogen (P-N) compounds were proposed to endow flame retardancy to polymers. Compared with phosphorus-based FRs, P-N compounds have higher thermal stability and lower toxic gases evolution.[13] Moreover, synergistic effect between phosphorus and nitrogen has been reported.[14,15] Ammonium polyphosphate (APP) is mostly widely

used P-N FR and known to act as an efficient acid source for intumescence in flame-retardant systems. However, the APP is mainly used in polypropylene or polyethylene because of its lower initial decomposition temperature.[16,17] Very recently, a novel P-N compound was prepared by Nguygen et al. in an attempt to develop a gas-phase mode FR.[18] According to the literature, the P-N FR based on phosphoramidate is much more efficient to the charrable polymer such as PC and PBT compared with other noncharrable polymers, for example, ABS. Furthermore, the authors also prepared a series of P-N compounds and investigated the thermal stabilities and flame retardancy of the compounds.[19] Nevertheless, most of the P-N FRs reported are mainly small molecular compounds, which have many drawbacks such as leaching and poor compatibility with polymer matrix in use. In comparison, oligomeric or polymeric FRs would overcome some shortcomings of low molecular phosphorus- and nitrogen-containing FRs and thus attract more and more attention.[20–22] Moreover, few studies of P-N oligomers flame retardarding PS have been reported.

In this article, phosphorus- and nitrogen-containing compound (2-dimethylamino ethyl phenyl hydroxyethyl acrylate phosphate, DPHP) and its oligomer (poly(2-dimethylamino ethyl phenyl hydroxyethyl acrylate phosphate), PDPHP) were synthesized and well characterized. The PS composites with various amounts of PDPHP were then prepared by melt blending. The thermal properties, flammability, and char-forming mechanism of the composites were investigated.

EXPERIMENT

Materials

Phenyl dichlorophosphate (PDCP) was purchased from Deheng Chemical Corp (Shijiazhuang, China) and was freshly distilled before use. Triethylamine (TEA), N,N-dimethylethanolamine, and hydroxyethyl acrylate (HEA) were obtained from the China Medicine (Group) Shanghai Chemical Reagent (Shanghai, China) and were purified by distillation. Tetrahydrofuran (THF) was refluxed with natrium for 10 h and was then distilled. The initiator, 2,2-azobisisobutyronitrile (AIBN), was purified by recrystallizing from methanol. PS with commercial name SH-65 was obtained from Soeps (Shantou, China). All of the other chemicals were used as received.

Synthesis of 2-dimethylamino ethyl phenyl hydroxyethyl acrylate phosphate

PDCP (0.10 mol) was dissolved in 80-mL dry THF in a three-neck round flask equipped with a mechani-cal stirrer and a dropping funnel. After the mixture was cooled to about 0°C in an ice-salt bath, TEA (0.21 mol) was added into the reaction system. After 20 min of stirring, HEA (0.10 mol) dissolved in 20-mL THF was introduced dropwise over a period of 2 h and then kept isothermal for 3 h. Subsequently, a solution of N,N-dimethylethanolamine (0.10 mol) in 20-mL THF was added dropwise into the reaction mixture during 1 h and then kept isothermal for 3 h. Finally, the system was heated to room temperature and stirred for another 10 h. The solution was washed with saturated sodium chloride solution and filtered after the filtration of TEA hydrochloride. A very viscous yellow liquid (74% yield) was obtained after the removal of solvent under reduced pressure. The synthesis route was illustrated in Scheme 1.

^{1}H-NMR (CDCl$_3$, ppm; Fig. 1): δ7.20–6.85 (5H, Ar-H), 6.25 and 5.70 (2H, vinyl), 5.95 (1H, CH=CH$_2$), 4.20 (2H, —COO—CH$_2$—), 4.03 (2H, P—O—CH$_2$—), 3.83 (4H, —O—CH$_2$CH$_2$—N), 3.26 (6H, N—CH$_3$); ^{31}P-NMR (CDCl$_3$, ppm; Fig. 2), δ4.15 ppm (singlet peak); IR (KBr pellet, cm^{-1}; Fig. 3), 3038 (aromatic C—H), 1499 and 1593 (aromatic C=C), 2896 and 1407 (CH$_3$), 1720 (C=O), 1637 (vinyl), 1257 (P=O).

Preparation of poly(2-dimethylamino ethyl phenyl hydroxyethyl acrylate phosphate) oligomer

The preparation of PDPHP was carried out in a two-step process by the bulk radical polymerization. In a typical example, first, in a 100-mL round flask equipped with a magnetic stirrer, a N$_2$ inlet, and a condenser, DPHP (0.1 mol, 34.3 g) was introduced. The system was then heated to 90°C, and AIBN (68.6 mg, 0.2 wt %) was added to prepolymerized it. The mixture was cooled until a critical viscosity was reached. Subsequently, the mixture was poured into a cell made from PC plates. The cell was then placed in an air oven at 65°C for 20 h and 120°C for another 8 h to obtain light yellow solid. The oligomer was successfully prepared by disappearance of absorption peak at 1637 cm^{-1} (C=C) in the IR spectrum of the sample. A schematic reaction process was presented in Scheme 2.

Preparation of PS/PDPHP composites

The flame-retardant PS with various amounts of PDPHP were prepared on a two-roll mill at a temperature 185–190°C for 15 min. After mixing, the samples were hot pressed at about 195°C under 5 MPa for 10 min and under 12 Mpa for another 2 min into sheets. The sheets were then cut into small samples with suitable size according to the standard of limiting oxygen index (LOI) test. The composition of PS/PDPHP composites was listed in Table I.
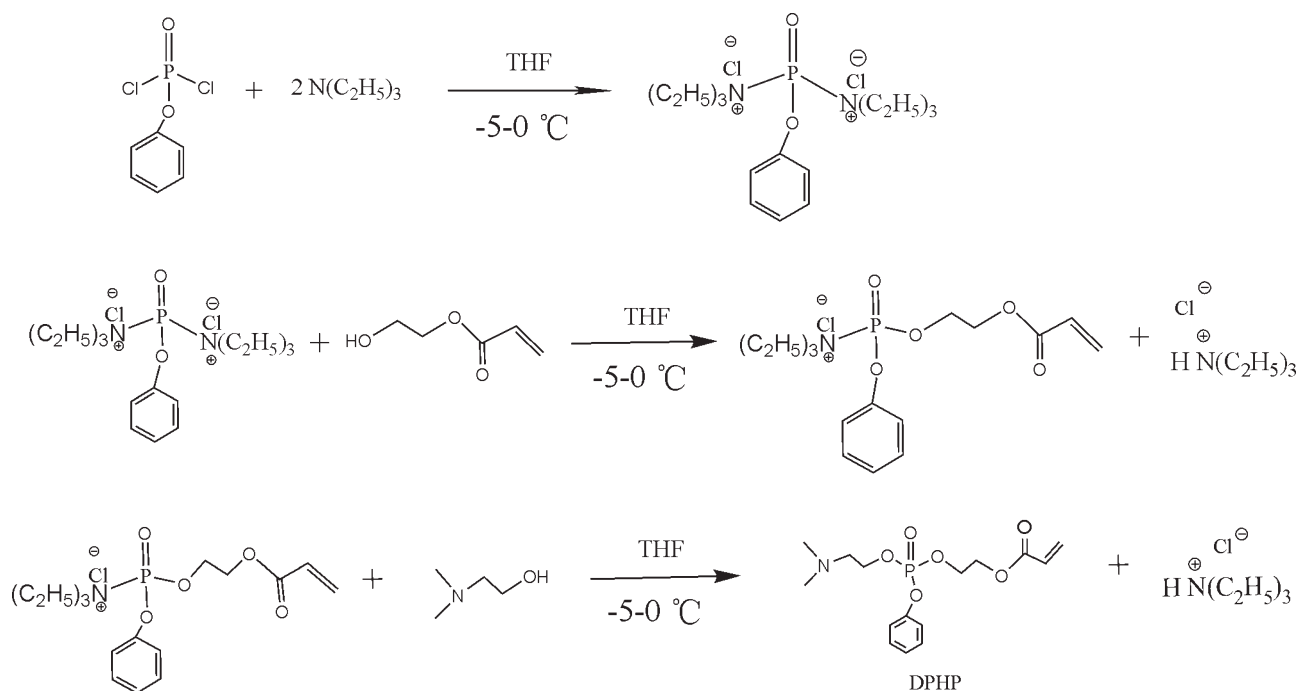
Scheme 1 Synthesis of DPHP.

Measurements and characterization

^{1}H and ^{31}P nuclear magnetic resonance (NMR) spectra were obtained by a Varian NMR system (300 MHz) at room temperature with CDCl$_3$ as the solvent. Fourier transform infrared (FTIR) spectroscopy was performed with a Nicolet 6700 spectrometer (Nicolet Instrument, WI) using KBr pellets.

The thermal properties of the samples were performed on a TGA Q5000 thermal gravimetric analyzer (TA instruments) with nitrogen at a heating rate of 20°C/min. The flammability data of the samples were obtained from a Govmak MCC-2 Microscale Combustion Calorimeter (MCC). LOI was measured using a LOI testing device according to ASTM D2863 (the specimen size: $100 \times 6.5 \times 3.0$ mm^3). The degradation products of the samples were analyzed by FTIR coupled with a thermogravimetric analyzer (TG-IR), operating in nitrogen at a heating rate of 20°C/min. Scanning electron microscopy (SEM) images of the char residues were obtained with a SEM (Inspect S, FEI, USA).

RESULTS AND DISCUSSION

Thermal stability of PDPHP

Figure 4 shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of virgin PDPHP evaluated in nitrogen and air, respectively. The TG curve obtained in nitrogen reveals significant degradation of PDPHP between 200 and 300°C, and the degradation rate decelerates when the temperature exceeds 300°C. The char yields are almost
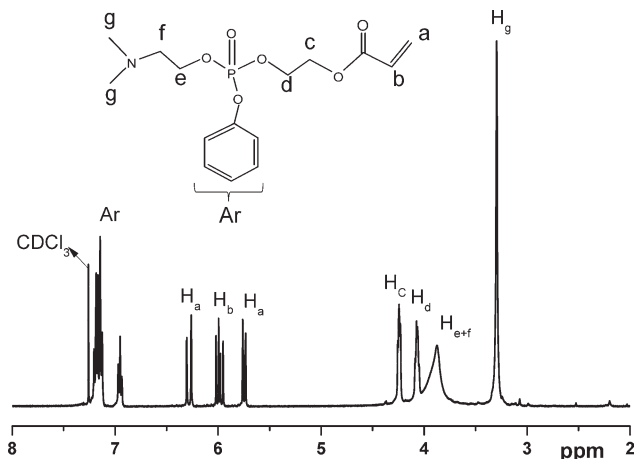

Figure 1 The ^{1}H-NMR spectrum of DPHP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
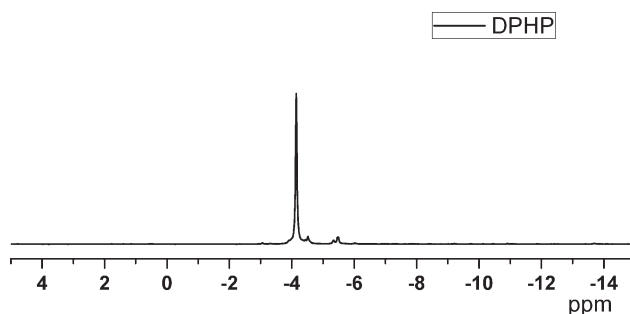

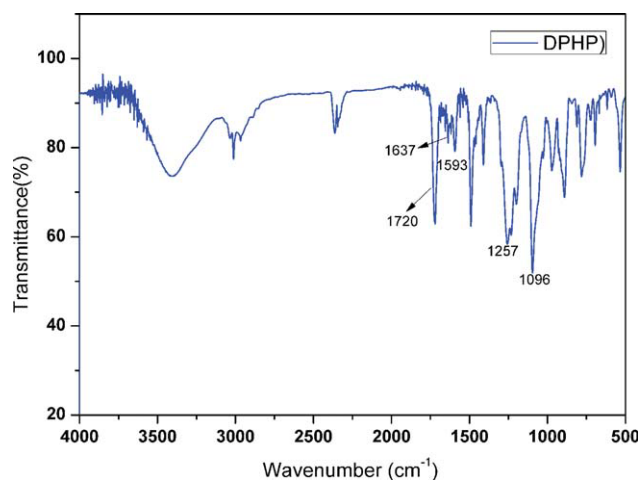**Figure 2** The ^{31}P-NMR spectrum of DPHP.

Figure 3 The FTIR spectrum of DPHP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

constant as the temperature exceeds 500°C. In air condition, it has been found that the thermal degradation behavior of PDPHP is not changed, as the TG curve is analogous to that in nitrogen. However, it is very interesting that the char residues at high temperature in air atmosphere are much higher than those in nitrogen. For example, the char residues under air and nitrogen present about 32.8 and 28.3 wt % at 600°C, respectively. The result indicates the oxygen in air plays an important role in char formation during the thermal degradation of PDPHP. In our previous study, a phosphorous- and nitrogen-containing monomer was incorporated into PS backbone via radical copolymerization.[23] Similarly, it was found that the thermal stability of the copolymer evaluated in air condition, was higher than that in nitrogen. However, Wang and coworkers prepared a phosphorus-containing polymer with a similar structure.[24] They found that the thermal stability of the polymer at high temperature in air atmosphere was much lower than that in nitrogen due to the oxidation of char residue. The results suggest that the introduction of nitrogen element into a phosphorus-containing molecule can enhance the char formation

and thus improve the thermal stability at higher temperature. This may give us some useful viewpoint on synthesis of FR with high char residue and antioxidation effect.

In DTG curves, the temperature at which the rate of volatilization reached a maximum is designated by T_{max}. From the DTG curves, it can be observed that the PDPHP mainly undergoes two-step thermal degradation in both nitrogen and air, as confirmed by two peaks in the DTG curves. The first significant region at around 260°C can be attributed to the decomposition of the phosphate and pyrolysis of alkyl chain and acrylate, while the second degradation region at around 370°C may be due to the decomposition of aromatic structure and formation of poly(phosphoric acid) char.[25] It is noticeable that no peak is observed in the high-temperature region from the DTG curve in air, suggesting the char formed is rather thermally stable.

Thermogravimetric analysis of PS composites with PDPHP

The TG curves of PS and PS with various amounts of PDPHP are shown in Figure 5. The detailed TG and DTG data, such as the temperature at which 5% ($T_{5\%}$) weight loss, the char residues (600°C), and the temperature of maximum weight loss rate (T_{max}) for the samples, are summarized in Table I. The virgin PS decomposes significantly between 350 and 450°C, caused by a chain scissoring then by a depolymerization and formation of styrene monomer, oligomers, and some volatiles.[26] As can be seen from Figure 5 and Table I, the thermal degradation behaviors of PS composites are not affected evidently with the incorporation of PDHPD. The $T_{5\%}$ of the samples decreases along with the PDPHP increases, which can be attributed to the early mass loss of the PDPHP FR. Moreover, because of the high charring character of the PDHPD, the char formation of the samples in nitrogen increases with increasing the PDPHP content. For example, the virgin PS leaves negligible char above 500°C, but the PS composites
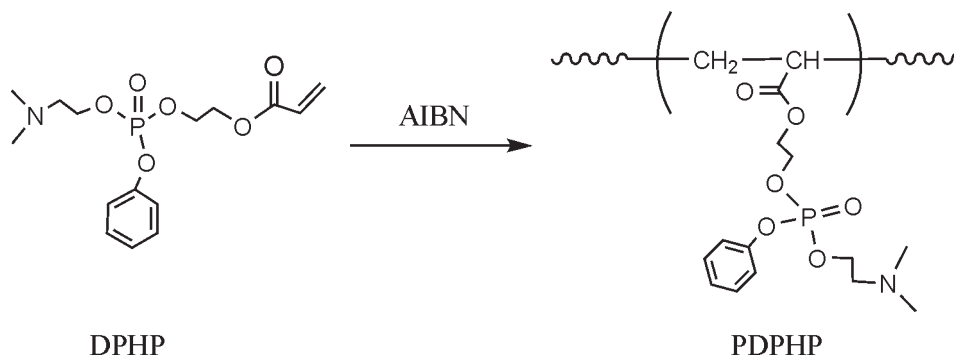
DPHP   PDPHP

Scheme 2 The preparation of PDPHP oligomer.

Sample	Components (%)		$T_{5\%}$ (°C)	Char residues (600°C, wt %)	T_{max}
	PS	PDPHP			
PS	100	0	386	0.5	433
PS-a1	90	10	289	3.6	439
PS-a2	80	20	261	6.0	444
PS-a3	70	30	248	8.7	446

containing 30 wt % PDPHP yield as high as 8.7% char residues at 600°C. In comparison with $T_{5\%}$, the T_{max} of PS composites slightly increases in nitrogen compared with that of virgin PS, indicating the thermal enhancing effect of PDPHP at higher temperature. The char yielded makes a great contribution to the enhancement in thermal stability at high temperature. As the char formation can act as a mass transport barrier and heat insulator between the bulk PS matrix and the surface where degradation happens. In consequence, all the PS composites containing PDPHP exhibit higher thermal stability and char residues at high temperature.

The analysis of evolved gas products

The TG-FTIR technique is a useful tool in dynamical analysis as it monitors continuously both the time-dependant evolution of the gases and the weight of the residue. It has been widely used in polymer thermal degradation, which can make a great contribution to the understanding of thermal degradation mechanism.[27,28] Figure 6 shows the gas phase 3D TG-FTIR spectra of virgin PS and PS composites containing 30 wt % PDPHP (PS-a3) at a heating rate of 20°C/min in nitrogen. It appears that there is no significant difference in the gas phase between the

two samples, except for the absorption band observed at 2356 cm^{-1} in the PS-a3 sample. To further investigate the composition evolved in the gas phase of the PS, the FTIR spectrum of PS selected at 24.5 min was plotted in Figure 7. The absorption bands at 3073, 1597, 773, and 698 cm^{-1} are assigned to aromatic compounds, and the absorption band observed at 1597 cm^{-1} is attributed to alkenyl units. According to a recent investigation, the decomposed products of PS under nitrogen are mainly monomer, dimer, and trimer of phenyl alkenyl.[29] In comparison, Figure 8 shows the FTIR spectra of gases evolved from the degradation of PS-a3 under nitrogen atmosphere at various time. Considering the TGA results and Figure 7, it can be concluded that the degradation before 18.5 min is mainly due to the degradation of PDPHP. The initial degradation products at 8 min from the PS-a3 sample are almost CO_2 exclusively noticeable from IR bands at around 2356 cm^{-1}, which may be attributed to the scissions of unstable P—O—C structure. With the time (also temperature) increasing, the bands at 2965 and 2785 cm^{-1} observed as the time reaches 14.5 min are assigned to the C—H vibrations of alkane compounds. Moreover, the band observed at 1054 cm^{-1} may be due to the stretching vibration of C—N.
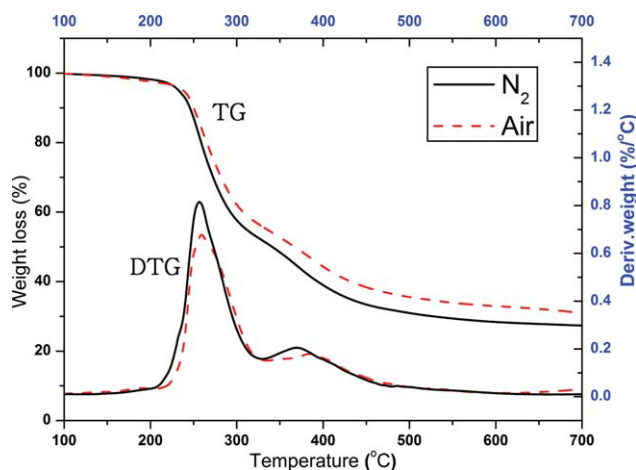

Figure 4 TG and DTG curves of PDPHP in nitrogen and air atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
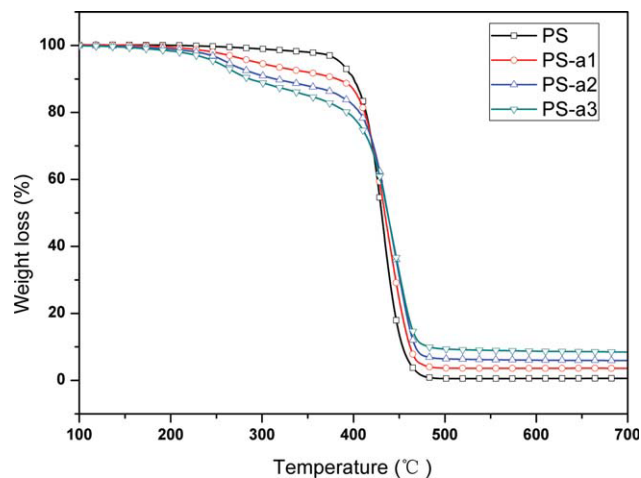

Figure 5 TG curves of PS and PS with various PDPHP additions in nitrogen at a heating rate of 20°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
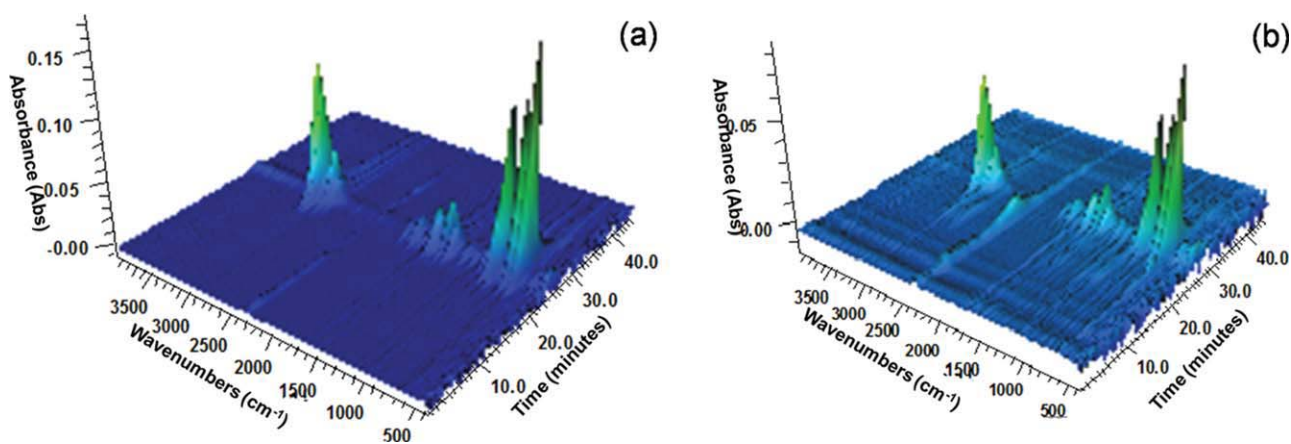
Figure 6 The 3D FTIR spectra of evolved products for (a) virgin PS and (b) PS-a3 under nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

These results suggest that the second volatilized product can be identified as $RN(CH_3)$, where R is an alkane group. Meanwhile, a weak band at around 1743 cm^{-1} indicates the evolution of some compounds containing carbonyl. To clearly understand the change of these formative products, the relationship between intensity of characteristic peak and time for evolved alkane, aromatic compounds, CO_2, and carbonyl compounds is plotted in Figure 9. It can be seen that the formation of CO_2 occurs almost in the whole degradation process and can be divided into two sections of 5–10 min and 15–25 min. As discussed in previous section, the thermal degradation of PDHDP mainly undergoes two steps in nitrogen. Thus, it is not difficult to speculate that the CO_2 was produced during both the two degradation process. The alkane and aromatic compounds were significantly formed between 20 and 30 min, mainly caused by the decomposition of PS. From the results of Figures 8 and 9, it is concluded that the volatil-

ized products for thermal decomposition of PDPHP are alkane, carbon dioxide, and carbonyl compounds.

Flammability

The flame retardancy of the samples was evaluated by LOI and MCC test, and the results were presented in Figure 10 and Table II. The MCC is a new and rapid method developed by Walters and Lyon, and it has many advantages on evaluation of polymer flammability compared with other large-scale calorimetry methods.[30,31] The most important parameter obtained in the test is heat release capacity (HRC), defined as the maximum amount of heat released per unit mass per degree Kelvin, is viewed as an inherent material property and a good
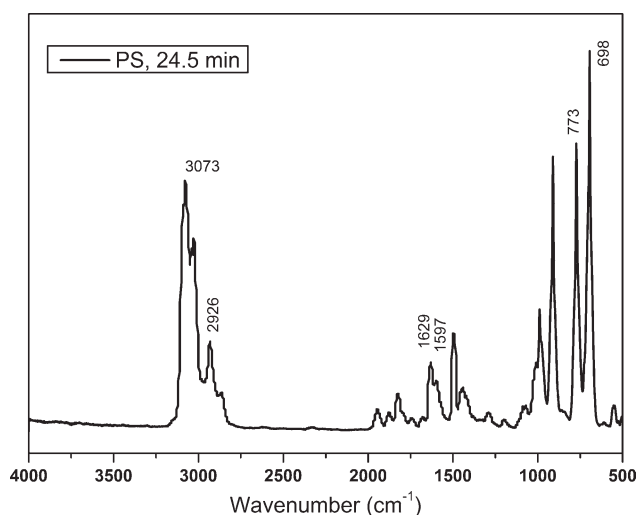

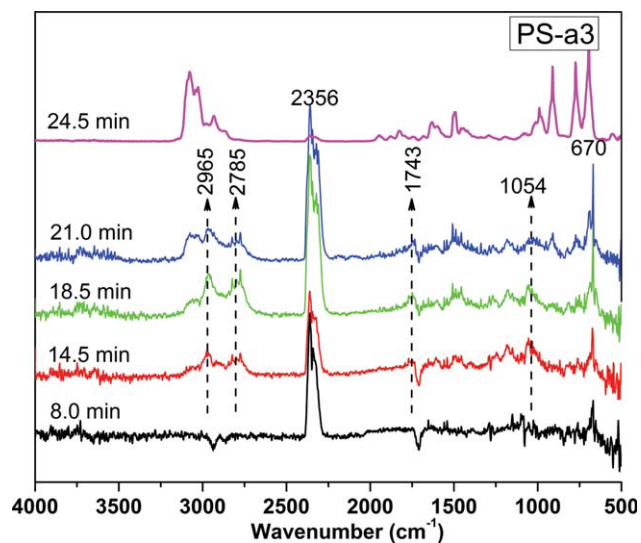**Figure 7** The FTIR spectrum of evolved products of virgin PS at 24.5 min.

Figure 8 FTIR spectra of evolved products at various time during the thermal degradation of PS-a3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
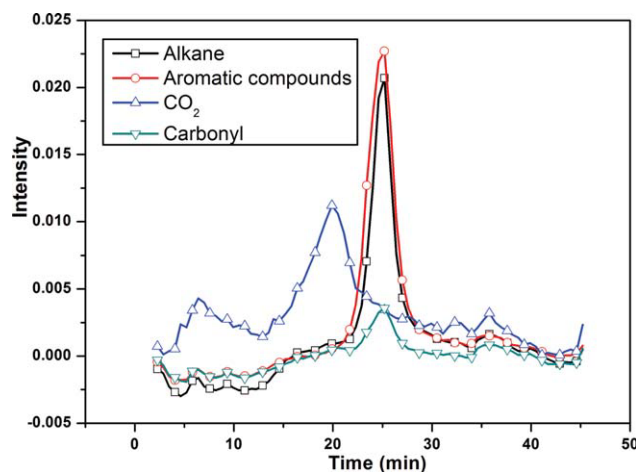
Figure 9 Relationship between intensity of characteristic peak and time for volatilized alkane, aromatic compounds, CO_2 and carbonyl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

predictor of flammability.[32] As shown in Figure 10 and Table II, the combustion of decomposed products of PDPHP mainly occurs between 220 and 350°C, and it has rather low flammability because of low HRC and (total heat release) THR. With the incorporation of PDPHP, the HRC and THR are evidently reduced. For instance, with the increase of PDPHP content from 0 to 30 wt %, a decrease of HRC from 729 J/K·g to 465 J/K·g and a decrease of THR from 35.8 to 29.3 kJ/g were observed. Generally, there are two main factors that can determine the value of HRC, one is the maximum mass loss rate (MMLR) and the other is the heat of combustion of the decomposed products at T_{max}. As can be seen from Table II, the incorporation of PDPHP into PS can obviously decrease the MMLR of PS matrix, and

TABLE II
Detailed MCC Data of PDPHP, PS, and PS Composites with Various PDPHP Additions

Sample	HRC[a] (J/K·g)	THR[a] (kJ/g)	LOI (%)	MMLR[b] (%/°C)
PDPHP	147	14.1	–	0.81
PS	729	35.8	19.5	2.24
PS-a1	537	33.1	20.5	1.67
PS-a2	497	30.6	21.5	1.49
PS-a3	465	29.3	22.5	1.39

[a] MCC results.
[b] MMLR: (maximum mass loss rate), obtained from DTG data in nitrogen.

thus it is not surprising that all the samples containing PDPHP exhibit lower flammability.

The flame retardancy of the samples was also measured by LOI test, which is an important and representative parameter for evaluating the flame-retardant properties of a certain polymer material. The digital photos of the samples after LOI test and the LOI values are presented in Figure 11 and Table II. The virgin PS exhibits a low LOI of 19.5, owing to the serious dripping during combustion. When various amounts of PDPHP were added, the LOI values slightly increase with the increase of PDPHP addition. Despite the char enhancement and antidripping effect of the PDPHP in PS matrix revealed in Figure 11, it is disappointingly found during the tests that the char yielded was not firm enough to restrain the dripping at higher oxygen concentration. Therefore, how to eliminate the melt dripping and enhance the
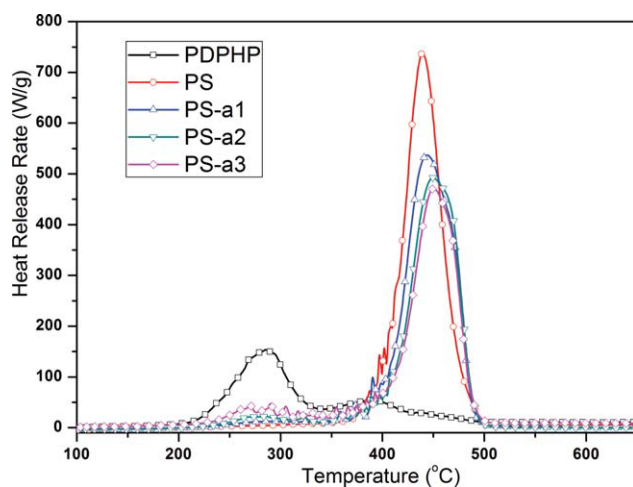

Figure 10 MCC curves of PDPHP, PS, and PS composites with various PDPHP additions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
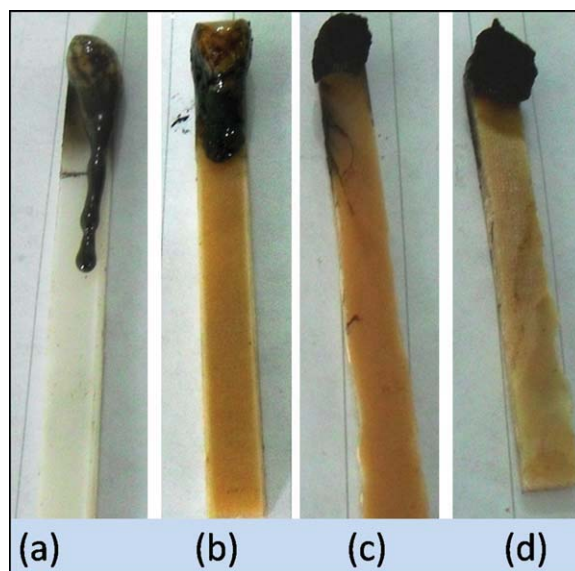

Figure 11 Digital photos of the samples after LOI test, (a) PS; (b) PS-a1; (c) PS-a2; (d) PS-a3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
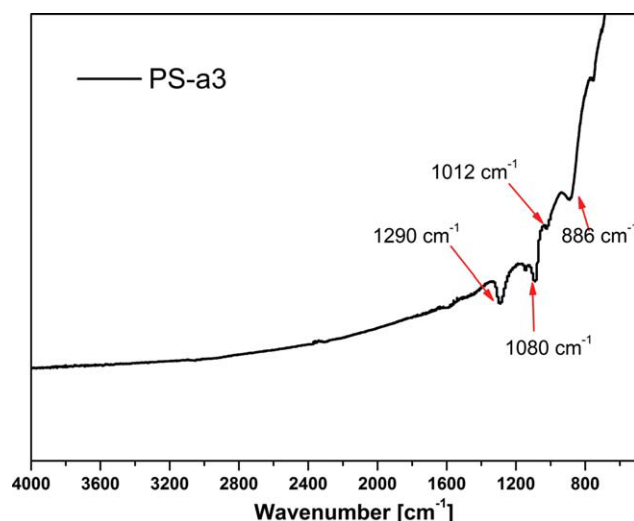
Figure 12 The FTIR spectrum of char residues for PS-a3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

char formation of PS during burning become the key points for nonhalogen flame retarding PS.

Char residues analysis

To further understand the char forming mechanism of PDPHP, the PS-a3 was heated in a muffle furnace at 600°C for 15 min, and the char residues were then collected and investigated using FTIR and SEM. Figure 12 shows the FTIR spectrum of the char residues. The absorption peak at 1290 cm^{-1} was assigned to the stretching vibration of P=O group of phosphate. A weak peak observed at around 1012 cm^{-1} may be due to the stretching vibration of P—O—C and PO_2/PO_3 in phosphate-carbon complexes.[33] The peaks at 1080 and 886 cm^{-1} can be attributed to the asymmetric and symmetric stretch-

ing vibrations of P—O—P bonds.[34] The results imply that the phosphate groups can be linked each other by two ways. One is linked by sharing an oxygen atom, and the other is linked by sharing a C—O—C group. Therefore, the P—O—P can be considered as a linker linking another phosphate or C—O—P group. As a result, char residues with complex crosslink-structure were formed.

The char residues were also studied by SEM. Two images with two magnifications of PS-a3 were shown in Figure 13. It seems that the surface of the char at lower magnification is smooth and a few small bubbles scatter on the surface. When observed in higher magnification, the surface of the char appears to present a coherent and compact layer, although the char seems to be much more rough compared with that observed in lower magnification. The char formation with compact and coherent structure not only reduces the production of flammable volatiles but also maintains a coherent flame and heat barrier between the igniting sources and underlying materials. Thus, it is not surprising that a sharp decrease for peak HRR of PS-a3 is observed in the MCC test.

CONCLUSIONS

A phosphorus- and nitrogen-containing compound (DPHP) and its oligomer (PDPHP) were successfully prepared and well characterized. The PDPHP undergoes two-step thermal degradation in both nitrogen and air and yields about 30 wt % char formation at 600°C. The char residues of PDPHP at high temperature, evaluated in air atmosphere, are higher than that in nitrogen, indicating the oxygen in air plays a crucial role during the char formation. The PS composites containing various amounts of PDPHP exhibit enhanced char residues and lower initial
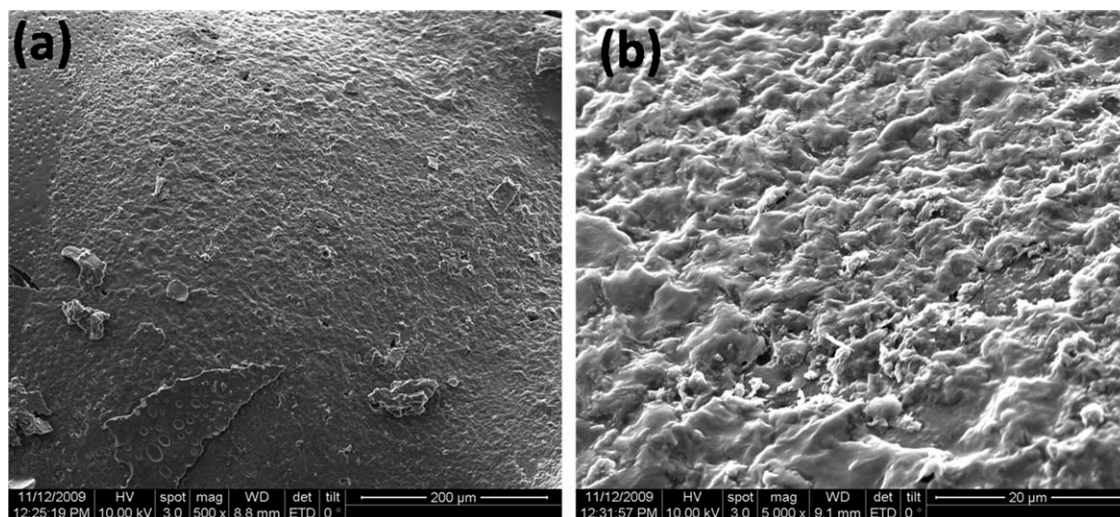

Figure 13 The SEM micrographs of char residues for PS-a3: (a) 500 magnification and (b) 5000 magnification.

decomposition temperature when compared with virgin PS from the TGA data. The TG-FTIR results indicate that the volatilized products of PDPHP are alkane, CO_2, aromatic compounds, and a few carbonyls. In the MCC test, the PS composites containing PDPHP exhibit significant reduction in the HRC and THR, indicating lower flammability when compared with virgin PS. Moreover, the incorporation of PDPHP can also increase the LOI value. From the SEM, it can be observed that the surface of the char residues is compact and coherent. The FTIR results suggest that the char residues contain mainly complex crosslink structure, which were consisted of phosphate sharing by an oxygen atom and P—O—C group. The compact char formed during the degradation of the PDPHP makes a great contribution to the enhancement of flame retardance of PS composites.

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