

Copolymerization of 1-Oxo-2,6,7-trioxa-1-phosphabicyclo[2,2,2]oct-4-yl Methyl Acrylate and (10-Oxo-10-Hydro-9-Oxa-10-phosphaphenanthrene-10-yl) Methyl Acrylate with Styrene and Their Thermal Degradation Characteristics

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ABSTRACT: Two phosphorus-containing acrylates of 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2,2,2]oct-4-yl methyl acrylate and (10-oxo-10-hydro-9-oxa-10 λ ⁵-phosphaphenanthrene-10-yl) methyl acrylate were free-radical-copolymerized with styrene (St). The r_1 reactivity ratio values (related to the novel acrylates) were 0.342 and 0.225, respectively, and the r_2 reactivity ratio values (related to St) were 0.432 and 0.503, respectively. The thermal stability of the copolymers was tested by thermogravimetric analysis (TGA) in N₂ or air, and the ignitability was tested by measurements of UL-94 vertical combustion tests and the limiting oxygen index. The results of TGA and combustion tests indicated that the effect of flame retard-

ancy was determined by the nature of the phosphorus-containing substituent. Compared with the 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide based group, the 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2,2,2]oct-4-yl methol based group could enhance the ability of char formation with an antidripping effect. It is concluded that phosphorus-containing acrylates are potential flame-retarding monomers for styrenic polymers. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1032–1038, 2010

Key words: flame retardance; copolymerization; polystyrene

INTRODUCTION

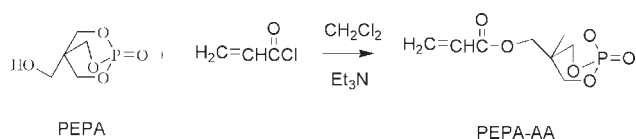
Nowadays, styrenic thermoplastics are widely used in the electronics industry and in construction materials. However, they are easily degraded and release large quantities of highly flammable and volatile monomeric and oligomeric fragments because of their poor thermal stability. Thus, even a small improvement in the flame retardancy of these materials would be popular with the government, consumers, and manufacturers. In the past decade, people have concentrated mainly on the development of phosphorus-containing species because they are environmentally friendly.^{1,2}

Although the phosphorus-containing moiety confers flame retardancy by crosslinking phosphate structures in a condensed phase in oxygen-containing polymer systems,¹ when it is used as an additive, the main mechanism of flame-retardant action of phosphorus incorporated into polystyrene occurs in the gas phase.³ Therefore, phosphorus-containing additives usually are used in typical concentrations of 20–40 wt % to confer flame retardancy to polysty-

rene; otherwise, they could result in adverse changes to the physical and mechanical properties of the polymer. Generally, when the flame-retardant groups are integral parts of macromolecules, not only the flame retardancy but also the stability are sufficiently improved to withstand processing conditions and resist migration or removal without affecting other polymer properties.^{4,5} Such an approach is readily adaptable to step-polymerization polymers such as polyesters and thermoset plastics such as epoxy resins.^{6–13} Remarkably, the flammability of polystyrenes with flame-retardant units covalently bonded to the polymer chain has been recently reported.^{3,5,14–16} The char residue of phosphorus-containing copolymers after combustion was substantial because of the condensed-phase flame-retardant action of phosphorus.³

1-Oxo-2,6,7-trioxa-1-phosphabicyclo[2,2,2]oct-4-yl methol (PEPA) is one of the most widely used phosphates applied as a protective, foamlike char former.^{17,18} 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is considered an efficient and environmentally friendly flame-retarding unit because of its high phosphorus content and rich aryl groups.¹⁹ However, little has been reported about the applications of their derivatives in styrenic polymers, although the works of Allen et al.²⁰ and Komori et al.²¹ on copolymerizations of styrene

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Scheme 1 Synthesis of PEPA-AA.

(St or M_1) with PEPA and DOPO derivatives are notable in this respect.

Encouraged by these findings, we synthesized two acrylate monomers: 1-oxo-2,6,7-trioxa-1-phosphabicyclo[2,2,2]oct-4-yl methyl acrylate (PEPA-AA) and (10-oxo-10-hydro-9-oxa-10 λ^5 -phosphaphenanthrene-10-yl) methyl acrylate (DOPO-CH₂O-AA). Additionally, PEPA-AA and DOPO-CH₂O-AA were copolymerized with St. The values of the reactivity ratios for free-radical copolymerization were determined initially. The copolymers were tested by thermogravimetric analysis (TGA) in N₂ or air for the analysis of their thermal stability.

EXPERIMENTAL

Materials

PEPA was prepared from pentaerythritol with phosphorus oxychloride, and (10-oxo-10-hydro-9-oxa-10 λ^5 -phosphaphenanthrene-10-yl) methanol (DOPO-CH₂-OH) was prepared by the method suggested by Shieh and Wang.⁹ Acryloyl chloride was synthesized from acrylic acid with benzoyl chloride. Benzoyl peroxide (BPO) was recrystallized from chloroform and methanol. Triethylamine, St, 1,2-dichloroethane, and dichloromethane were purchased from the Guoyao Group of Chemical Reagents, Ltd. (Shenyang, China). All the solvents were purified by distillation over calcium hydride before being used. The other reagents were used as received.

Measurements

The Fourier transform infrared (FTIR) spectra were recorded with a Nicolet (USA) 20DXB FTIR spectrophotometer. ¹H-NMR spectra were measured with a Bruker (Switzerland) Unity 400 NMR spectrometer at room temperature with tetramethylsilane as an internal reference. The weight-average molecular weights of the polymers were estimated with gel permeation chromatography (201, Waters, USA) with polystyrene as the calibration standard. The samples were run in tetrahydrofuran at a concentration of 5 mg/mL and at a flow rate of 1 cm³/min. Differential scanning calorimetry (DSC) analysis was implemented for DSC studies with a Mettler (Germany) DSC30. TGA was completed with a TGA/SDTA851 thermal analyzer at a scanning rate of 10°C/min in air or in N₂ from 50 to 500°C. The limiting oxygen index (LOI) was obtained according to ISO4589-1984. A CZF-2 UL-94 flame test

station (Jingrui Ltd., Co., Ningbo, China) was used for the UL-94 vertical test.

Synthesis of PEPA-AA

1-oxo-2,6,7-trioxa-1-phosphabicyclo[2,2,2] oct-4-yl methyl acrylate PEPA-AA (M_2) was prepared via the route shown in Scheme 1. PEPA (54.0 g, 0.3 mol) was dispersed in 200 mL of dichloromethane, and 42.0 mL (0.3 mol) of triethylamine was placed into a 500-mL flask equipped with a thermometer, an electromagnetic stirrer, a condenser, and a feeding funnel. After the temperature decreased to -10°C, 27.2 g (0.3 mol) of acryloyl chloride in 100 mL of dichloromethane was added at -10°C dropwise. The reactive system completed the esterification at this temperature for 2 h and then at the ambient temperature for another 6 h. After filtration, a buff powder was obtained. The product was purified by recrystallization from water/methanol and then dried *in vacuo* at 50°C for 12 h. The final product was a white powder with a yield of 80% and a melting point of 160–162°C. The structure was characterized with FTIR, ¹H-NMR, and ³¹P-NMR measurements (Figs. 1 and 2).

FTIR (KBr, cm⁻¹): 1729 (C=O), 1618 (C=C), 1312 (P=O), 1270 (C—O—C), 1038 (P—O—C). ¹H-NMR (400 MHz, CDCl₃, δ , ppm): 4.03 (s, 2H), 4.62 (d, 6H), 5.96 (d, 1H), 6.48 (d, 1H), 6.13 (m, 1H). ³¹P-NMR (400 MHz, CDCl₃, δ , ppm): -8.14 (s).

Synthesis of DOPO-CH₂O-AA

Scheme 2 shows the synthesis of DOPO-CH₂O-AA. DOPO-CH₂-OH (49.2 g, 0.2 mol), which was synthesized from DOPO and formaldehyde in alcohol according to a previous article⁹; triethylamine (22.3 g, 0.22 mol), and 200 mL of dichloromethane were fed into a round-bottom flask equipped with a

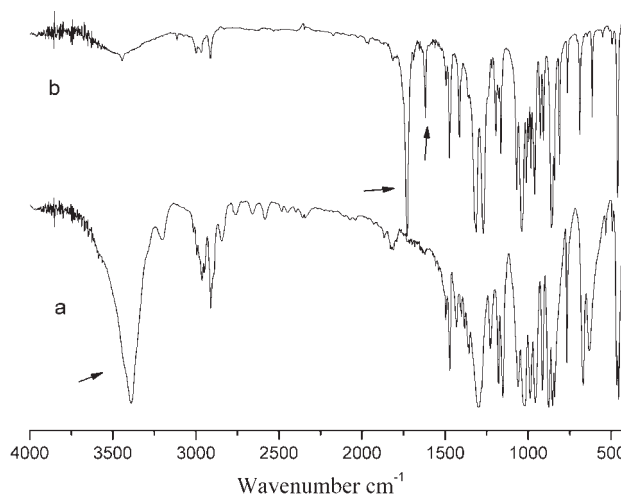


Figure 1 FTIR spectra of (a) PEPA and (b) PEPA-AA.

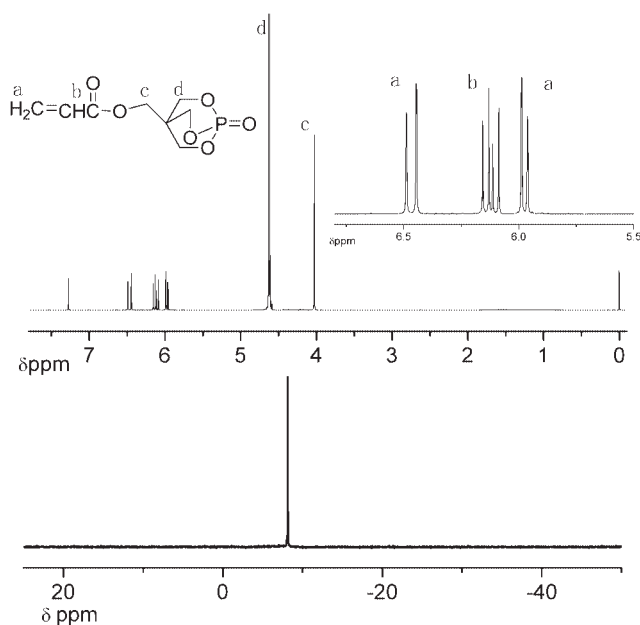
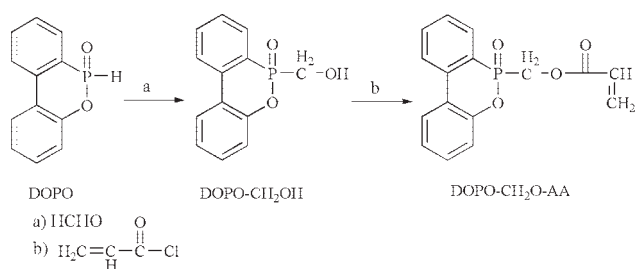


Figure 2 (a) ^1H -NMR and (b) ^{31}P -NMR spectra of PEPA-AA.

thermometer, an electromagnetic stirrer, a condenser, and a feeding funnel. The reaction mixture was cooled to -20°C under stirring, and then acryloyl chloride (20.0 g, 0.22 mol) in 50 mL of dichloromethane was added dropwise over a period of 3.5 h at -20°C . After that, the reaction mixture was maintained at -10°C for an additional 2 h and then at the ambient temperature for another 6 h. The mixture was washed with water and a 5% NaOH solution several times until the organic phase was neutralized. The crude product was obtained after dichloromethane evaporated. The product was purified by column chromatography on SiO_2 with ethyl acetate as the eluent to produce DOPO- $\text{CH}_2\text{O-AA}$. The yield was 84%, and the melting point was 75°C . The structure was characterized with FTIR, ^1H -NMR, and ^{31}P -NMR measurements (Figs. 3 and 4).

FTIR (KBr, cm^{-1}): 1735 (C=O), 1632 (C=C), 802 (C=C-H), 1236, 1167 (C-O-C), 924 (C-C=O). ^1H -NMR (400 MHz, CDCl_3 , δ , ppm): 4.78 (m, 2H), 5.64 (d, 1H), 5.78 (m, 1H), 6.00 (d, 1H), 7.26 (m, 2H), 7.37 (t, 1H), 7.55 (m, 1H), 7.73 (t, 1H), 7.93 (m, 1H), 8.00, 8.28 (m, 2H). ^{31}P -NMR (400 MHz, CDCl_3 , δ , ppm): 28.16 (s).



Scheme 2 Synthesis of DOPO- $\text{CH}_2\text{O-AA}$.

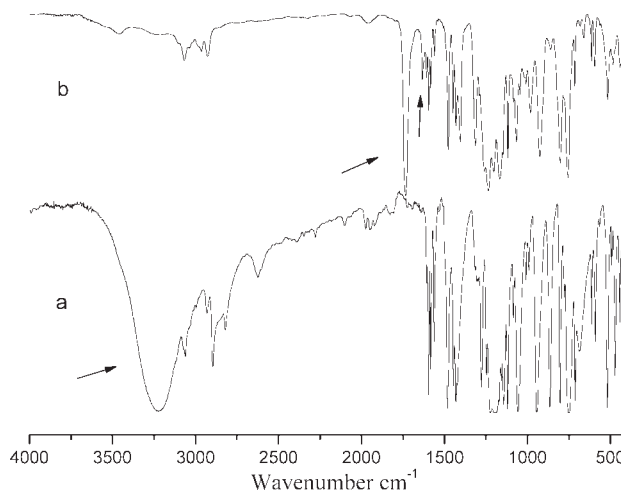


Figure 3 FTIR spectra of (a) DOPO- CH_2OH and (b) DOPO- $\text{CH}_2\text{O-AA}$.

General procedure for free-radical polymerizations in solution

Both small-scale and larger scale polymerizations were performed in solutions of the monomers at 90°C with BPO as the initiator (Scheme 3) under N_2 . After the required reaction periods, the copolymers were precipitated from the reaction mixture in an excess of methanol. The copolymers were collected by filtration and vacuum-dried. The gel permeation chromatography analysis of the copolymers showed that the number-average molecular weights ranged from 11,000 to 18,000 with polydispersity indices of approximately 2. The ^1H -NMR spectra of the

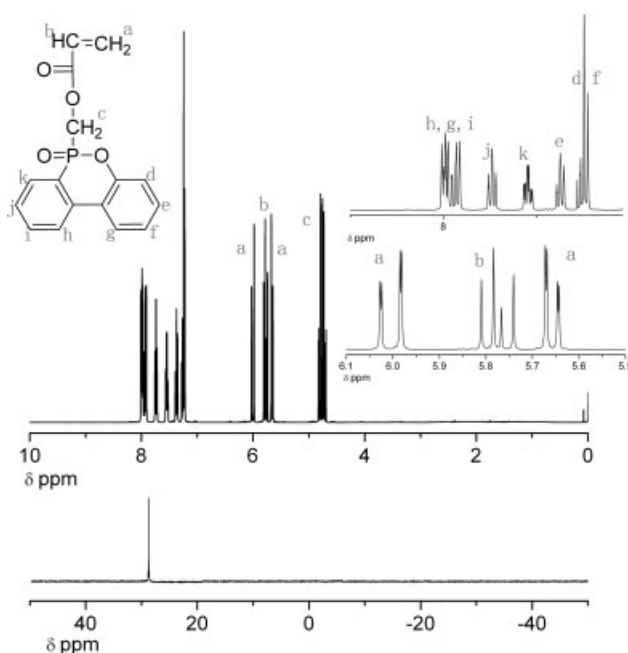
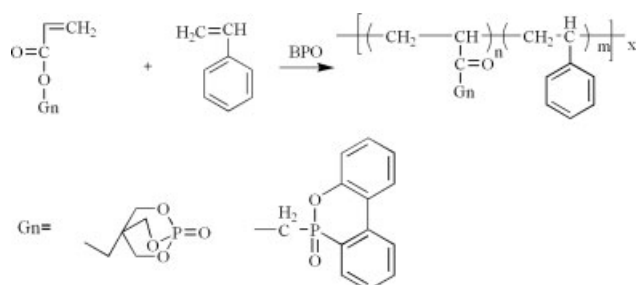


Figure 4 (a) ^1H -NMR and (b) ^{31}P -NMR spectra of DOPO- $\text{CH}_2\text{O-AA}$.



Scheme 3 Copolymerization of St (M_1) with PEPA-based and DOPO-based acrylates (M_2).

polymers were almost identical and differed only in the relative signal intensities (Fig. 5).

$^1\text{H-NMR}$ of copolymer of PEPA-AA and styrene poly(PEPA-AA-co-St) (400 MHz, hexadeuterated dimethyl sulfoxide, δ , ppm): 7.6–6.4 (H benzene ring), 2.3–1.0 (H main chain), 4.47 (H–PEPA). $^1\text{H-NMR}$ of copolymer of DOPO-CH₂O-AA and styrene poly(DOPO-CH₂O-AA-co-St) (400 MHz, hexadeuterated dimethyl sulfoxide, δ , ppm): 0.5–2.1 (H main chain), 4.0–5.0 (–CH₂O–), 5.8–8.4 (H benzene ring).

RESULTS AND DISCUSSION

Polymerization

The copolymerizations were performed via the general procedure. The structures of the polymers were confirmed with $^1\text{H-NMR}$. The reactivity ratios for free radicals (r_1 and r_2) were estimated with the slope–intercept method. Therefore, the conversion of small-scale polymerizations had to be kept less than 10%. Here PEPA-AA and DOPO-CH₂O-AA are defined as M_2 . In the $^1\text{H-NMR}$ spectrum of poly(PEPA-AA-co-St) [Fig. 5(a)], the signals occurring at 7.6–6.4 ppm are assigned to a benzene ring, which testifies to the content of St. The peak at 4.47 ppm represents the hydrogen of the bicyclic structure in PEPA. In Figure 5(b), the signals from 4.0 to 5.0

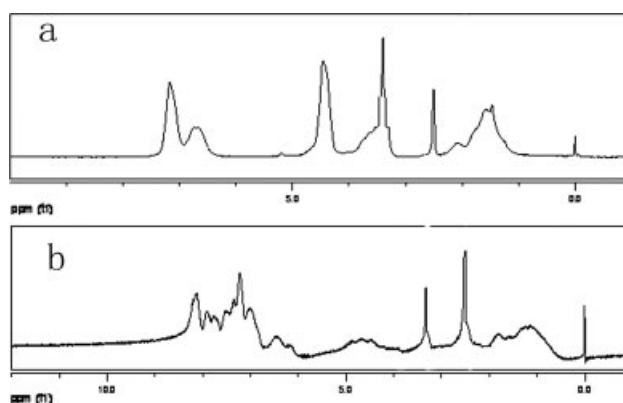


Figure 5 $^1\text{H-NMR}$ spectra of (a) poly(PEPA-AA-co-St) and (b) poly(DOPO-CH₂O-AA-co-St).

ppm represent the methylene protons of –CH₂O– of the pendent group in poly(DOPO-CH₂O-AA-co-St), which testifies to the content of DOPO-CH₂O-AA. The signals occurring at 5.8–8.4 ppm can be assigned to the benzene ring protons of St and DOPO. Therefore, the copolymer composition (F_1) was calculated with the following equations:

$$\frac{F_1}{1 - F_1} = \frac{d[M_1]}{d[M_2]} = \frac{\frac{1}{5} \left(\sum_{6.4\text{ppm}}^{7.6\text{ppm}} H \right)}{\frac{1}{6} \left(\sum_{4.47\text{ppm}} H \right)} \quad (1)$$

$$\frac{F_1}{1 - F_1} = \frac{d[M_1]}{d[M_2]} = \frac{\frac{1}{5} \left(\sum_{5.8\text{ppm}}^{8.4\text{ppm}} H - 4 \sum_{4.0\text{ppm}}^{5.0\text{ppm}} H \right)}{\frac{1}{2} \sum_{4.0\text{ppm}}^{5.0\text{ppm}} H} \quad (2)$$

where $1/5 \left(\sum_{6.4\text{ppm}}^{7.6\text{ppm}} H \right)$ and $1/6 \left(\sum_{4.47\text{ppm}} H \right)$ represent the molar ratios of St and PEPA-AA in poly(PEPA-AA-co-St). Similarly, $1/5 \left(\sum_{5.8\text{ppm}}^{8.4\text{ppm}} H - 4 \sum_{4.0\text{ppm}}^{5.0\text{ppm}} H \right)$ and $1/2 \left(\sum_{4.0\text{ppm}}^{5.0\text{ppm}} H \right)$ represent the molar ratios of St and DOPO-CH₂O-AA in poly(DOPO-CH₂O-AA-co-St). Here, H means proton peak integral in NMR spectra.

TABLE I
 f_1 and F_1 Data in the Copolymerizations

Sample	St (M_1 ; g)	PEPA-AA (M_2 ; g)	DOPO-CH ₂ O-AA (M_2 ; g)	f_1	Time (min)	Conversion (%)	F_1
1	0.452	0.113		0.9	40	7.8	0.820
2	0.452	0.254		0.8	55	6.9	0.725
3	0.452	0.436		0.7	65	5.4	0.6595
4	0.452	0.407		0.6	65	5.7	0.573
5	0.452	0.508		0.4	65	4.7	0.475
6	18.90	35.1		0.55	600	98.7	0.580
7	0.832		0.6	0.8	15	8.2	0.718
8	0.728		0.9	0.7	15	6.4	0.667
9	0.624		1.2	0.6	20	6.5	0.585
10	0.520		1.5	0.5	20	6.2	0.565
11	0.416		1.8	0.4	30	4.7	0.512
12	0.390		4.5	0.2	40	4.3	0.370
13	21.70		37.0	0.63	600	96.8	0.640

f_1 is the mol ratio of M_1 in the monomer.

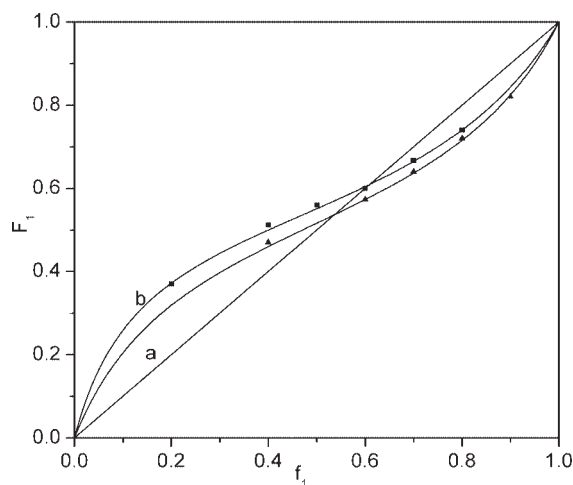


Figure 6 Copolymer composition curves of (a) St (M_1) of PEPA-AA (M_2) and (b) DOPO-CH₂O-AA (M_2).

The ratios of the monomers and copolymer compositions are listed in Table I, and the copolymer composition curve is shown in Figure 6. The copolymerization reactivity ratios and the confidence intervals were calculated and related to the polarity (e) and the resonance effect (Q) in the Q - e scheme; they are listed in Table II. St (M_1) is considered the standard monomer ($Q_1 = 1.0$ and $e_1 = -0.8$). The results show the characteristics of nonideal copolymerization with an azeotropic point. Therefore, to obtain a random copolymer with a steady composition, larger scale copolymerization was performed according to the calculated azeotropic point of the copolymer composition. The copolymer was precipitated from the reaction mixture in an excess of methanol after 10 h. ¹H-NMR data in Table I show that the copolymer compositions were 0.58 and 0.64. They approximately reached the calculated results. These copolymers, obtained according to the azeotropic points, were examined with flame testing and investigated with TGA.

Flammability properties

The results of flame testing are listed in Table III. Both copolymers presented a self-extinguishing

TABLE II
Copolymerization Parameters for the Free-Radical Copolymerization of St (M_1) with PEPA-AA or DOPO-CH₂O-AA (M_2)

M_2	r_1	r_2	e_2	Q_2	Azeotropic point
PEPA-AA	0.432	0.342	0.476	0.766	0.55
DOPO-CH ₂ O-AA	0.503	0.225	0.476	0.413	0.63

property. After the combustion of UL-94, poly(PEPA-AA-*co*-St) generated substantial charring residue. This is characteristic of the condensed-phase flame-retardant action of phosphorus.³ The char formation limits the release of combustible gases and decreases the thermal conductivity of burning materials, consequently retarding the flammability of the materials.¹⁹ The LOI of poly(PEPA-AA-*co*-St) reached 27.0% because of the flame-retardant action in the condensed phase.

Poly(DOPO-CH₂O-AA-*co*-St) exhibited obvious drippings during UL-94 testing. It is thought that the drippings could take the heat off the polymer's surface. Besides, the phosphorus-containing groups prevented the release of highly flammable and volatile monomeric and oligomeric fragments. The LOI of poly(DOPO-CH₂O-AA-*co*-St) was lower than that of poly(PEPA-AA-*co*-St) because of the scarce char formation. This indicates that the DOPO group was less effective at promoting (acid-catalyzed) crosslinking in the polymer because of its weaker phosphonic acid property.

Thermal decomposition analysis

The DSC curves obtained for the various samples under N₂ are presented in Figure 7. PS underwent single-stage endothermic decomposition from 400 to 460°C. The DSC curves for the two copolymers indicate that the breakdown of the phosphorus-containing components was exothermic.³ The heat flow maximum for the samples corresponded closely to the mass loss maxima observed for these samples in the thermogravimetry (TG) experiments (Fig. 8).

TABLE III
Flame Test Results for the Copolymers

Copolymer	LOI (%)	UL-94 test			
		First ignition (s) ^a	Second ignition (s) ^a	Observed dripping ^b	UL-94 rating
Poly(PEPA-AA- <i>co</i> -St)	27.0	<1	<1	No	V-0
Poly(DOPO-CH ₂ O-AA- <i>co</i> -St)	24.2	2	2	Yes	V-2

^a The average time to self-extinguishing after ignition for 10 separate tests on 10 separate samples.

^b Indicates that molten plastic did (yes) or did not (no) drip onto the cotton patch underneath the bar during the UL-94 test.

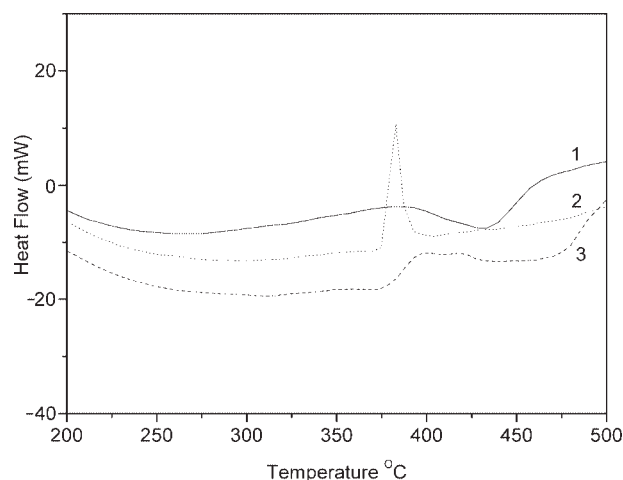


Figure 7 DSC curves of (1) polystyrene, (2) poly(PEPA-AA-co-St), and (3) poly(DOPO-CH₂O-AA-co-St) in N₂ at heating rate of 10 °C/min.

It is proposed that the charring residue on pyrolysis is linearly proportional to the oxygen index of halogen-free polymers.²² The char formation will limit the release of combustible gases and decrease the thermal conductivity of the burning materials, and this will consequently retard the flammability of the materials. Phosphorus-containing structures can alter thermal decomposition by increasing the releasing yield of carbon rather than CO or CO₂. In our work, thermal analysis showed that the decomposition process was substantially changed by the incorporation of PEPA-based or DOPO-based groups into the polystyrene polymers (see Figs. 8 and 9). Table IV shows that the residue at 500 °C of the PEPA-based polymer was more than that of the DOPO-

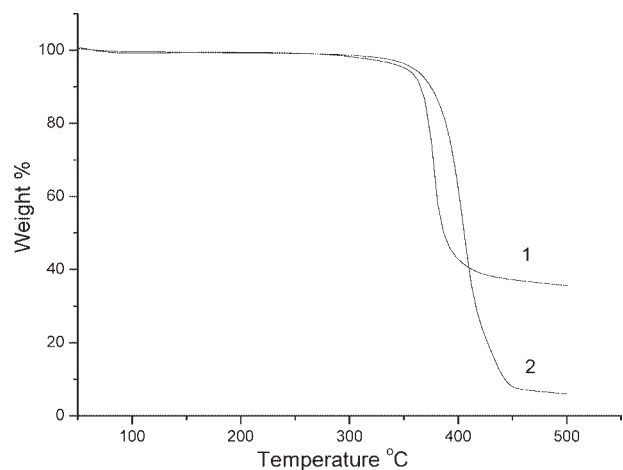


Figure 8 TGA curves of (1) poly(PEPA-AA-co-St) and (2) poly(DOPO-CH₂O-AA-co-St) in N₂ at heating rate of 10 °C/min.

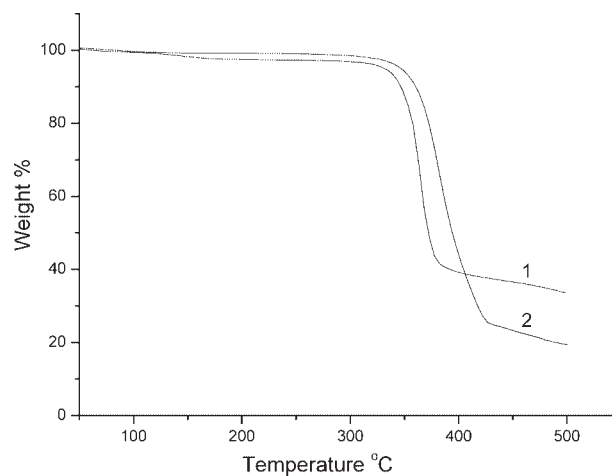


Figure 9 TGA curves of (1) poly(PEPA-AA-co-St) and (2) poly(DOPO-CH₂O-AA-co-St) in air at heating rate of 10 °C/min.

based polymer in an atmosphere of N₂ or air, and this agreed with the results of the ignition tests.

Poly(PEPA-AA-co-St) was found to have excellent thermal stability from the TG curve of decomposition in N₂ (Fig. 8). There was 5% weight loss at 350 °C, and the main thermal event occurred in the range of 360–380 °C with 60% weight loss. The thermal degradation curve of poly(DOPO-CH₂O-AA-co-St) exhibited the main stage of decomposition from 375 to 440 °C with 90% weight loss. The TG experiments showed that the weight loss for both copolymers began at lower temperatures in air than in N₂. In air, the initial weight loss (5%) for poly(PEPA-AA-co-St) and poly(DOPO-CH₂O-AA-co-St) occurred about 20 and 15 °C lower than in N₂, respectively, and this demonstrated that the presence of oxygen had an accelerating effect on the polymer degradation. However, the residues of TG experiments observed for the PEPA-based polymer and DOPO-based polymer were not equally affected by the change in atmosphere. At 500 °C, poly(PEPA-AA-co-St) left a substantial residue of 33 wt % in N₂, as much as in air. The DOPO-based polymer showed only 6% residues in N₂ but 19% residues in air. This further verified that oxygen had an accelerating effect on the acid-catalyzed crosslinking actions in the polymer.

Phosphates are well known to enhance charring production because of phosphoric acid formation, which enhances char formation in the polymer. DOPO could form the weaker phosphonic acid instead of phosphoric acid. This weaker acid would be less effective at promoting (acid-catalyzed) char formation in the polymer. This was consistent with the reduced residue. The greater increase in the poly(DOPO-CH₂O-AA-co-St) residue in air might

TABLE IV
TGA Data of the Copolymers

Copolymer	In N ₂			In air		
	<i>T</i> _{onset} (°C)	<i>T</i> _{max} (°C)	Residue at 500°C (%)	<i>T</i> _{onset} (°C)	<i>T</i> _{max} (°C)	Residue at 500°C (%)
Poly(PEPA-AA-co-St)	350	375	36.0	330	368	34.6
Poly(DOPO-CH ₂ O-AA-co-St)	361	402	6.2	346	382	19.3

*T*_{onset} = initial decomposition temperature of 5% weight loss; *T*_{max} = maximum weight loss temperature.

have been partly due to the oxidation of phosphonic acid to phosphoric acid in the polymer in air. On the other hand, the presence of oxygen increased the crosslinking phosphate structures during the thermal oxidative degradation of poly(DOPO-CH₂O-AA-co-St).

CONCLUSIONS

The ignition test results and TGA data for the copolymers show that the PEPA group is more suitable for flame-retarded non-oxygen polymeric systems in the condensed phase in comparison with the DOPO group. The study suggests that the effect of flame retardancy depends on the nature of the phosphorus-containing substituent. Clearly, further studies should investigate the combustion process and copolymerization of PEPA-AA and DOPO-CH₂O-AA with other monomers.

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