

Thermal and combustion characteristics of phosphorus and phosphorus/nitrogen-containing styrene monomers and oligomers

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Abstract Two series of styrene monomers, one with phosphorus-containing moieties as substituents and the other with substituents containing both phosphorus and nitrogen, have been prepared, characterized, and converted to oligomers. The oligomers contain, in the one case, phosphorus and, in the other, phosphorus and nitrogen. This provides the opportunity to not only assess the impact of the presence of phosphorus on the combustion characteristics of the oligomers but to determine whether or not this impact is enhanced by the presence of nitrogen. The level of residue from thermogravimetry and heat release rate during combustion suggest that the presence of nitrogen may have a small positive impact on the effectiveness of phosphorus flame retardants.

Keywords Flame retardant poly(styrene) · Phosphinated styrene monomers · Styrene phosphoramidates · Nonhalogen flame retardants

Introduction

Thermogravimetry (TG) has long been used as a component of the assessment of the effectiveness of flame-retarding additives in polymeric materials [1–10]. It can be utilized to determine the thermal degradation

characteristics of both the additive-free polymer and the flame retardant. More importantly, it can be used to determine the impact of the presence of the additive on the thermal degradation characteristics of the polymer. The onset temperature for degradation, an alteration of the mode of the decomposition in the presence of the additive, and the amount of the residual char formed may readily be determined using this technique. In particular, the char yield upon decomposition has been utilized as a first indicator of potential utility as a flame retardant for the additive. At higher temperature, TG can provide information about the decomposition of residual char. Most usually, TG is used in conjunction with several other techniques for an assessment of flame retardant activity. These often include a determination of limiting oxygen index, behavior in the UL-94 vertical burn test and/or cone calorimetric evaluation [10, 11]. More recently, pyrolysis combustion flow calorimetry (PCFC) has been used to obtain combustion data for polymeric materials containing flame retardant additives [1, 12–16]. This approach provides combustion calorimetric data using much smaller samples and at significantly lower cost than is possible with cone calorimetry. In this technique oxygen combustion calorimetry is used to measure both the rate of the heat release and the amount of heat released by complete combustion of fuel gasses generated by pyrolysis of a small (mg) sample of the flame-retarded material [18]. In this instance, the degradation and combustion characteristics of two sets of styrenic oligomers, one containing phosphorus and the other containing both phosphorus and nitrogen, have been determined using TG and PCFC. The change in the glass transition temperature (T_g) for the polymer upon incorporation of bulky pendant groups may be readily monitored using differential scanning calorimetry (DSC).

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Experimental

Materials

The preparation and characterization of styrene polymers containing phosphorus or nitrogen/phosphorus moieties as pendants has been described [19–21].

Thermogravimetry

TG was performed using a TA Instruments 2950 Hi-Res TG instrument interfaced with the Thermal Analyst 2100 control unit. Most generally, a heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ was used. Samples (5–10 mg) were contained in a standard platinum pan. The sample compartment was purged with dry nitrogen at 50 ml/min during analysis. TA Universal Analysis software was used for data analysis.

Differential scanning calorimetry

T_g 's were determined using a DSC Q 2000 (TA Instruments). The samples were contained in standard aluminum DSC pans. Samples were heated from -20 to $200\text{ }^{\circ}\text{C}$ in a nitrogen atmosphere at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. Duplicate analyses were obtained for each sample. The T_g 's were obtained from the second heating cycle, using TA Universal Analysis software. A pure iridium metal standard was used to determine a temperature-correction factor which was used for all runs.

Pyrolysis combustion flow calorimetry

PCFC was performed using a Govmark microscale combustion calorimeter. PCFC measures the rate at which the heat of combustion of the fuel gasses is released by a solid during controlled pyrolysis in an inert gas stream. The fuel gasses are then mixed with excess oxygen and completely oxidized at high temperature, and the instantaneous heat of combustion of the flowing gas stream is measured by oxygen consumption calorimetry, which is subsequently used to determine the heat of combustion of the pyrolysis products. For this method, small polymer samples (1–10 mg) were dried for at least 8 h at $75\text{ }^{\circ}\text{C}$ in a convection oven and held in a desiccant chamber until testing. The samples were heated at a constant rate ($1\text{ }^{\circ}\text{C sec}^{-1}$) from 150 to $700\text{ }^{\circ}\text{C}$. The volatile pyrolysis products generated during the temperature ramp were swept from the pyrolyzer into the combustion chamber ($900\text{ }^{\circ}\text{C}$) by nitrogen gas flowing at $80\text{ cm}^3\text{ min}^{-1}$ to which was added $20\text{ cm}^3\text{ min}^{-1}$ of pure oxygen. Combustion gasses were scrubbed to remove carbon dioxide, water, and acid gasses (if any), and the gas stream passed through a flow meter and oxygen analyzer. Deconvolution of the oxygen

consumption signal was performed during the test, and the heat release rate was calculated in watts per gram of sample.

Results and discussion

Flame retardants containing phosphorus as an active component are increasingly of interest as the regulatory pressure to avoid the use of organohalogen flame retardants continues to grow. Organohalogen compounds are highly effective gas-phase flame retardants but are persistent in the environment, tend to bioaccumulate, and may present potential health risks. Organophosphorus compounds are, in the main, solid-phase active and promote the formation of a protective char on the surface of a polymeric material in a combustion environment. This prevents heat feedback from the flame to sustain polymer pyrolysis and the formation of fuel fragments. Numerous organophosphorus compounds of varied structure serve as effective flame retardants [21–27]. Further, it has often been suggested that the flame retardant activity of these compounds is enhanced in the presence of nitrogen compounds [28–40]. To assess the impact of the presence of nitrogen on the flame-retarding properties of phosphorus compounds two sets of substituted styrene oligomers, one containing phosphorus and the other containing both phosphorus and nitrogen have been examined using TG and PCFC. The polymers are listed in Table 1. Since these polymers contain the flame-retarding moieties as an integral part of the monomer units which get covalently incorporated into the structure there is no opportunity for blooming to the surface and loss during processing [41].

The level of elemental phosphorus and nitrogen for these polymers is displayed in Table 2.

The T_g for these polymers (Table 3) are generally higher than for poly(styrene). This may be reflective of strong intermolecular interactions between the polar groups pendant to the polymer main chain.

Thermal decomposition of the polymers bearing only phosphorus-containing pendants is depicted in Fig. 1.

As can be seen, the onset temperature for degradation is higher for the polymers with phosphorus-containing pendant groups than for unsubstituted poly(styrene). Further, the residue from degradation of the phosphorus-containing polymer is significantly greater (16–27 % of the initial sample mass) than for the degradation of unsubstituted poly(styrene) (0 %). The degradation of the polymers bearing pendant groups containing both phosphorus and nitrogen is depicted in Fig. 2. Again, the onset temperature for degradation of the polymers with phosphorus/nitrogen-containing pendant groups is generally higher than that for unsubstituted poly(styrene). Degradation of these polymers

Table 1 Styrene polymers containing phosphorus- or phosphorus/nitrogen flame-retarding units

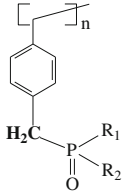
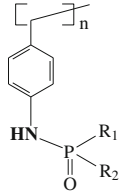
			
Homopolymer code name		Homopolymer code name	
R ₁ = R ₂ = OCH ₃	HPM ₁	R ₁ = R ₂ = OCH ₃	HPM ₅
R ₁ = R ₂ = OC ₂ H ₅	HPM ₂	R ₁ = R ₂ = OC ₂ H ₅	HPM ₆
R ₁ = R ₂ = OC ₆ H ₅	HPM ₃	R ₁ = R ₂ = OC ₆ H ₅	HPM ₇
R ₁ , R ₂ = DOPO	HPM ₄	R ₁ , R ₂ = DOPO	HPM ₈

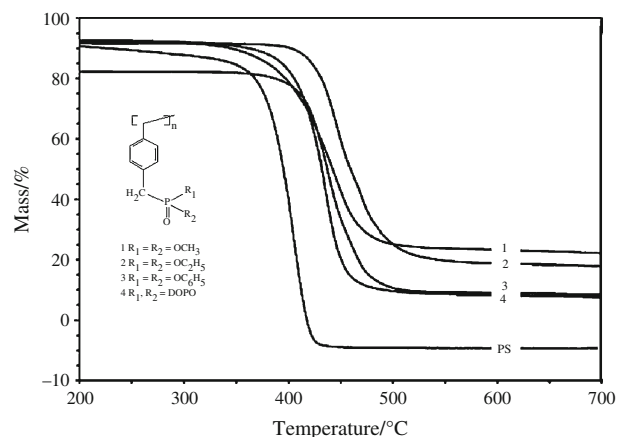
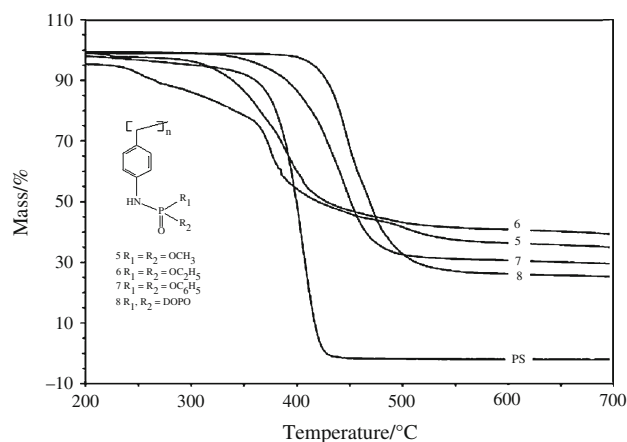
Table 2 Phosphorus and nitrogen content in styrene polymers containing modified phenyl units

Polymer	Phosphorus content/%	Nitrogen content/%
HPM ₁	13.7	0
HPM ₂	12.2	0
HPM ₃	8.9	0
HPM ₄	9.3	0
HPM ₅	13.6	6.2
HPM ₆	12.1	5.5
HPM ₇	8.9	4.0
HPM ₈	9.9	4.2

Table 3 Glass transition temperatures for poly(styrene) and phosphorus and phosphorus/nitrogen-containing styrenic polymers

Polymer	T _g /°C
HPM ₁	122.4
HPM ₂	130.2
HPM ₃	–
HPM ₄	153.4
PS	102
HPM ₅	131.5
HPM ₆	132.4
HPM ₇	136.1
HPM ₈	126.2
PS	102

also leads to significant levels of residual material (25–40 % of the initial sample mass). Not only is the level of residue much higher than that for unsubstituted poly(styrene) but is significantly greater than that for degradation of polymers with pendant groups containing only phosphorus. Based on these simple observations, it would seem that the beneficial impact of phosphorus on the thermal stability of poly(styrene) is strongly enhanced by

**Fig. 1** Thermal degradation of styrene polymers bearing phosphorus-containing pendant groups**Fig. 2** Thermal degradation of styrene polymers bearing pendant groups, containing both phosphorus and nitrogen

the presence of nitrogen. Data for the degradation of both sets of polymers are displayed in Table 4.

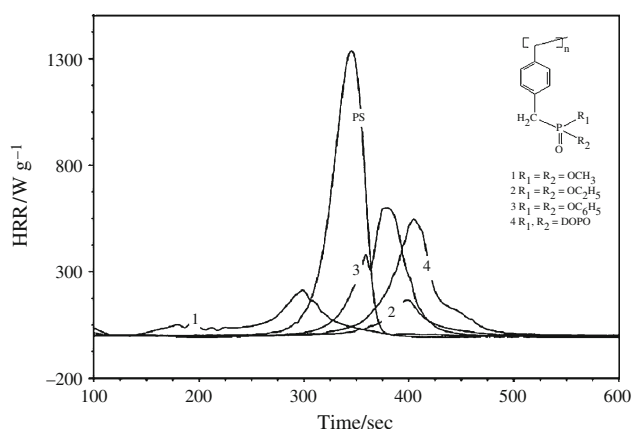
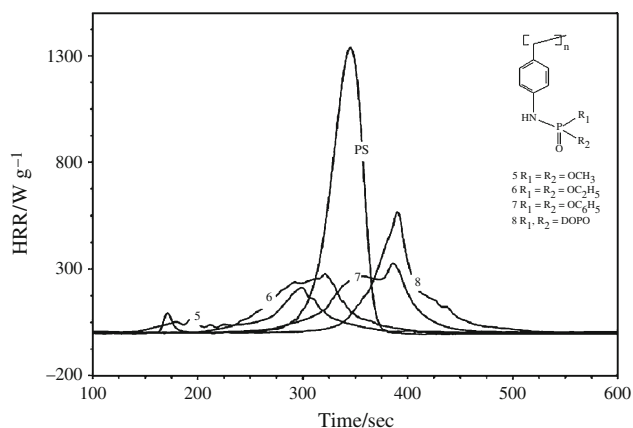
A reflection of the impact of the presence of the pendant groups on the combustion of the polymers is provided by

Table 4 Thermal degradation data for the polymers from phosphorus- and phosphorus/nitrogen-containing monomers

Sample	$T_{\text{onset}}/^{\circ}\text{C}$	Mass loss/%	Residue at 600 $^{\circ}\text{C}$ /%
HPM ₁	254	64.2	26.9
HPM ₂	293	69.9	20.2
HPM ₃	412	84.4	15.6
HPM ₄	416	83.6	16.3
PS	384	100	0
HPM ₅	206	63.6	36.4
HPM ₆	220	59.2	40.8
HPM ₇	391	68.7	31.3
HPM ₈	426	72.8	26.2
PS	384	100	0

Table 5 Heat release (HR) values for the combustion of the homopolymers from phosphorus- and phosphorus/nitrogen-containing monomers

Homopolymer	HR/kJ g ⁻¹
HPM1	25.8
HPM2	27.9
HPM3	28.3
HPM4	26.6
PS	42.4
HPM5	14.1
HPM6	22.6
HPM7	22.9
HPM8	25.2
PS	42.4

**Fig. 3** Heat release rate for the combustion of styrene polymers bearing phosphorus-containing pendant groups**Fig. 4** Heat release rate for the combustion of styrene polymers bearing phosphorus/nitrogen-containing pendant groups

the data from PCFC [17]. Plots of heat release rates versus time for polymers are displayed in Figs. 3 and 4.

First, it is apparent that the presence of phosphorus in the polymer dramatically alters heat release rate for combustion of the polymer. As may be seen from the plots in

Fig. 4, this impact is enhanced by the presence of nitrogen in the phosphorus/nitrogen-containing pendant groups.

Heat release values for the polymers are collected in Table 5. The heat release values for the combustion of polymers containing both phosphorus and nitrogen are marginally smaller than those for the polymers containing only phosphorus.

Conclusions

The thermal degradation and combustion characteristics for two sets of styrene polymers, one containing phosphorus and the other containing both phosphorus and nitrogen, have been evaluated using TG and PCFC. TG suggests that the presence of nitrogen changes the impact of the phosphorus on the stability of the polymers (higher onset temperature for degradation and significantly higher levels of residue after decomposition). In addition, polymers containing both phosphorus and nitrogen display somewhat depressed combustion heat release rates compared to those containing only phosphorus. These results support the suggestion that the impact of phosphorus compounds acting as flame retardants is enhanced in the presence of nitrogen compounds. However, the impact observed for these polymers is small and may not be reflective of a general phenomenon.

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