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Phosphonate-Functionalized Polypropylenes: Single-Component Flame Retardants

Alexander Evans, Louis J. Morris, Zoë R. Turner, and Dermot O'Hare*

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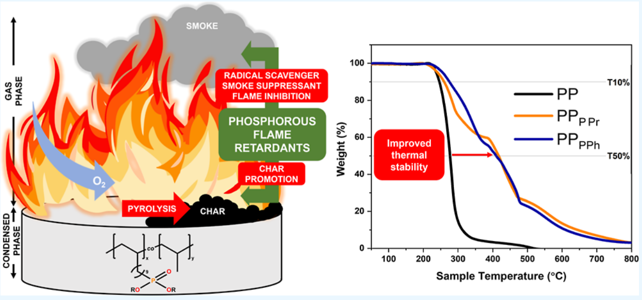

ABSTRACT: Phosphonate-modified polypropylenes ($\mathbf{PP_R}$; R = PPr, $P(O)(O^iPr)_2$; PPh, $P(O)(OPh)_2$) have been prepared via a two-step synthesis and display enhanced thermal stability, offering potential as compatible single-component flame-retardant additives for PP systems. PP typically displays high flammability and poor fire resistance, which consequently restricts applications. Solution-phase copolymerization of propylene and 11-bromo-1-undecene using commercial *rac*-ethylenebis(indenyl)zirconium dichloride afforded poly(propylene)-*co*-(11-bromo-1-undecene) with tunable comonomer incorporation levels up to 8.1 mol %. Solvent-free, quantitative, postmodification of pendent bromine with phosphite esters yielded alkyl ($\mathbf{PP_{PPr}}$) and aryl ($\mathbf{PP_{PPh}}$) phosphonate-modified PPs. Increased thermal stability (higher $T_{10\%}$, $T_{50\%}$, T_{max}, and % residue at 700 °C) in a synthetic air atmosphere was determined by thermogravimetric analysis with respect to **PP**. Microscale combustion calorimetry of both $\mathbf{PP_{PPr}}$ and $\mathbf{PP_{PPh}}$ indicates lower values of heat release capacity, peak heat release rate, and total heat release compared to that of **PP**, indicating enhanced flame retardancy. Both $\mathbf{PP_{PPr}}$ and $\mathbf{PP_{PPh}}$ can be easily blended with **PP** at $\mathbf{PP}$:$\mathbf{PP_R}$ weight ratios of 80:20, 90:10, 95:5, and 99:1, respectively. The polymer blends demonstrated higher thermal stability than the homopolymer, and so such PP-compatible $\mathbf{PP_R}$ offers an alternate strategy for improving the flame-retardant properties of PP-based materials, which circumvents additive leaching while limiting disruption to the mechanical strength of the base PP material.

KEYWORDS: *flame retardant, polypropylene, functional polymer, thermal analysis, phosphonate-modified, copolymers*

INTRODUCTION

Polyolefins are ubiquitous in everyday life. Since its inception,[1] polypropylene (PP) has been one of the most manufactured polymers in the world, second only to polyethylene (PE).[2] Desirable chemical and mechanical resistance, low toxicity, relative ease of processability, and low production costs have led to widespread utilization in a plethora of applications. Despite this, pristine PP exhibits poor fire resistance as characterized by limiting oxygen index (LOI), heat release rate (HRR), and flame exposure tests (UL 94);[3−5] thus, restricting its use in a number of applications subject to fire safety standards.[6,7]

The flame retardancy of polymers is traditionally improved through the additive use of halogenated compounds, often in conjunction with inorganic materials such as aluminum trihydroxide (ATH), magnesium hydroxide, and antimony trioxide.[8] However, many brominated and chlorinated chemicals have proven to be highly persistent, bioaccumulative, and toxic to animals and humans.[9−12] Development of halogen-free systems,[13] phosphorus-based flame retardant (FR) systems in particular,[14] has been the subject of more intense investigation in order to circumvent these environmental concerns while still providing the desired material properties.

The effectiveness of phosphorus-based FR systems can be attributed to their chemical versatility, low required loadings, and multiple mechanisms by which flammability is reduced in both the condensed and gas phase.[15−19] Char formation in the condensed phase is stimulated by phosphorus moieties such as phosphite esters ($PO(OR)_3$), phosphonates ($PO(OR)_2R$), and phosphinates ($PO(OR)R_2$), which act as acid precursors and lead to esterification and dehydration. This mechanism serves to blockade oxygen from the substrate while additionally preventing the formation of flammable gases.[20] Further improved FR characteristics can be gained from tandem gas-phase mechanisms, whereby $PO^\cdot$ acts as a radical scavenger during combustion.[21,22]

Common commercial nonhalogenated FR additives for polyolefin systems are typically based on phosphorus, boron, inorganic hydroxides, silicon, and nitrogen-based additives, which are introduced to polymer matrices during process-

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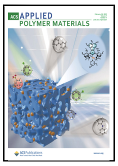

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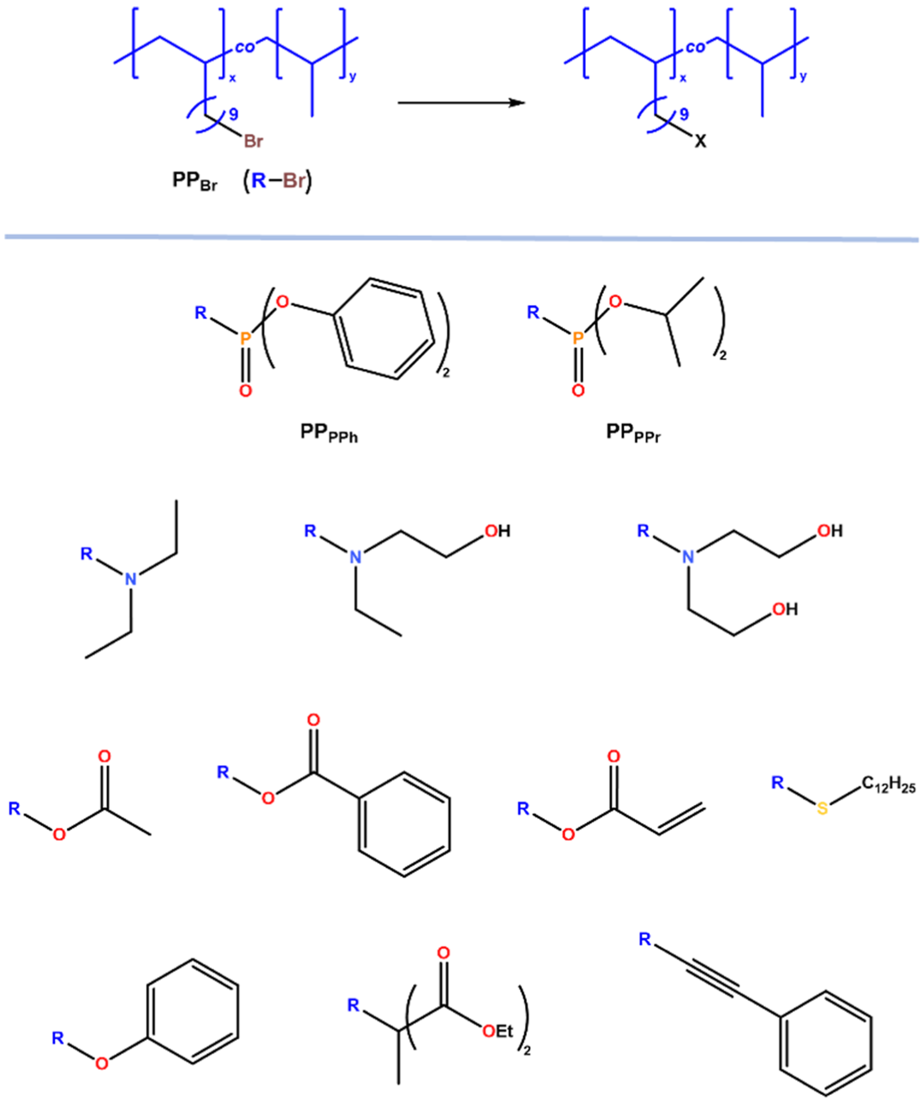
Scheme 1. **Recently Reported Synthetic Strategy for the Postmodification of PP_{Br} Yielding a Variety of Modified PPs, Including PP_{PPh} and PP_{PPr}[36]**



ing.[5,23−26] Undesirable consequences of physical mixing include the resulting blends being prone to migration and ultimately leaching,[27] or severely disrupted mechanical properties due to poor chemical and physical compatibility within the polymer matrix.[28] Chemical incorporation of FR functionality directly into the polymer through copolymerization has the potential to provide good FR properties at low comonomer loadings,[29,30] avoiding migration and leaching while providing good mechanical performance. For example, phosphorus moieties have been incorporated via radical polymerization in styrene[29] and (meth)acrylate systems[27,31,32] or Pd-catalyzed copolymerization with ethylene[33] yielding promising results.

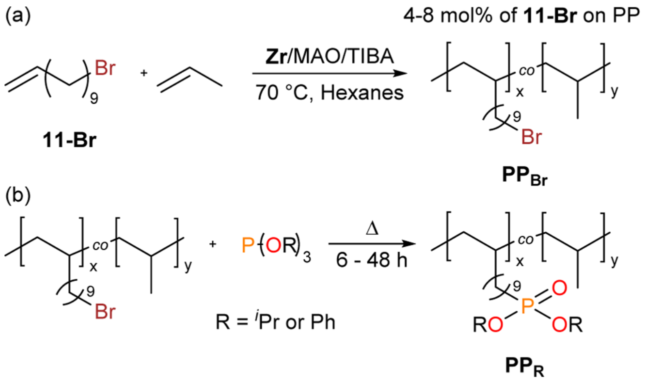
Polyolefin postmodification via traditional small-molecule nucleophilic substitution chemistry presents solubility and purity complications and is subsequently less developed.[34,35] We have recently reported a two-step methodology for the preparation of a diverse range of functionalized PPs via quantitative postmodification of a brominated copolymer (Scheme 1).

Phosphonate-functionalized PP with aryl or alkyl phosphite esters (**PP_R**; R = PPr, $P(O)(O^iPr)_2$; PPh, $P(O)(OPh)_2$) was highlighted as having potential FR properties as a consequence of increased thermal stability, indicated by thermogravimetric analysis (TGA).[36] Herein, we build on our previous results regarding phosphonate-modified polymers, offering a more comprehensive study of the materials. Both **PP_{PPr}** and **PP_{PPh}** have been fully characterized, focusing on thermal stability and their FR efficacy, and displayed significantly improved thermal stability and FR properties when blended with pristine PP. This highlighting their potential use as PP-compatible additives which are halogen-free avoid additive leaching and the disruption of polymer mechanical properties, which is a feature of high loadings of inorganic materials.

■ RESULTS AND DISCUSSION

Solution-Phase Copolymerization of Propylene and Bromoalkenes. The brominated copolymer poly(propylene)-*co*-(11-bromo-1-undecene) (**PP_{Br}**) was first prepared by copolymerization of propylene and 11-bromo-1-undecene (**11-Br**) using a commercially available catalyst, *rac*-ethylenebis(indenyl)zirconium dichloride (**Zr**) (Scheme 2a). Subsequent copolymer postmodification was carried out with triisopropyl phosphite ($P(O^iPr_3)$) and triphenyl phosphite

Scheme 2. Synthesis of Phosphonate-Functionalized Polypropylenes by (a) Copolymerization and Subsequent (b) Postmodification



($P(OPh_3)$) according to a previously reported work (Scheme 2b).[36]

The copolymerization of propylene and **11-Br** was carried out, and the results are summarized in Table 1. Successful incorporation of a comonomer was identified by the presence of -C***H***$_2$Br (δ = 3.49 ppm) and -C***H***$_2$CH$_2$Br (δ = 1.97 ppm) in ^{1}H NMR spectra and C−Br stretching frequency (721 cm^{-1}) in the FT-IR spectrum, 3.99−8.12 mol % as judged by NMR spectroscopy (Figures S1−S3); the enchainment levels of the comonomer were consistent with previously reported examples of olefin copolymerization with ω-halo-1-alkenes.[37,38]

All copolymers exhibited a monomodal M_n distribution by SEC (Figures S4) with narrow molar-mass dispersities ($Đ_m$) (1.7−2.2). Under a given set of conditions, the copolymer M_n is lower than PP (Table 1, entry 1; 13 600 g mol^{-1} and entry 2; 5000 g mol^{-1}) but displays a narrower $Đ_m$; however, changing [**11-Br**] had little impact on M_n or $Đ_m$. The reduction of copolymer M_n could be attributed to the chain-transfer reactions induced by the spatial active site of **Zr**. Additionally, chain transfer to aluminum alkyl, β-H transfer to metals and monomers are also significant in **Zr** polymerization.[37,39] Competing coordination of **11-Br** and propylene to the metal center may accelerate chain-transfer reactions, further decreasing copolymer M_n.

Postpolymerization Modification of Bromine-Functionalized PP Using Phosphite Esters. Our previously reported studies provide evidence of the C−Br bond transformation to C−P[36] via the Michaelis Arbuzov reaction.[40−42] DSC, SEC, and NMR spectroscopic characterization were found to be fully consistent with the phosphonate group being covalently bound to the polymer and quantitatively converted (Figures S5, S7, and S8). The reaction of $\mathbf{PP_{Br}}$ with neat triisopropyl phosphite ($P(O^iPr)_3$) or triphenyl phosphite ($P(OPh)_3$) led to corresponding PP-phosphonates ($\mathbf{PP_{PPr}}$ and $\mathbf{PP_{PPh}}$; Table 2 and Scheme 2b). Full conversion was achieved within 6 and 48 h, respectively, as confirmed by ^{1}H NMR spectroscopy through the absence of the methylene protons adjacent to the bromide (Figures S7 and S8), irrespective of incorporation levels. Complementary convection-compensated diffusion experiments support the modifier−polymer coupling with key modifier ^{1}H NMR resonances (e.g., $\mathbf{PP_{PPr}}$ = δ 4.80−4.68 ppm − OC***H***Me$_2$ and $\mathbf{PP_{PPh}}$ = 7.39−7.23 ppm − OAr***H***) displaying the same diffusion coefficient to that of polymer backbone resonances ($\mathbf{PP_{PPr}}$ = 2.8 × 10^{-6} cm^2 s^{-1} and $\mathbf{PP_{PPh}}$ = 2.1 × 10^{-6} cm^2 s^{-1}; Figures 1A,B and S1).

Monomodal SEC distributions were observed for the modified polymers with consistent $Đ_m$ values with the parent copolymer (Figure S6). However, a significant deviation between $M_{n,th}$ and $M_{n,SEC}$ (Table S1) was evidenced and can be attributed to altered polymer polarity affecting the polymer−column interaction. Since the Mark−Houwink correlation is not known for functionalized PP, the presence of the polar group is likely to affect the radius of gyration in solution;[43] however, it is assumed that the backbone chain length is unchanged during postpolymerization modification. Quantitative Br analysis evidenced removal of the Br functionality in $\mathbf{PP_{PPr}}$ and $\mathbf{PP_{PPh}}$ (Table 2, entries 5 and 8), 0.23 ± 0.2 and 0.12 ± 0.1 wt % brominated comonomer, respectively; postmodification. $\mathbf{PP_{Br}}$ (Table 1, entry 4) exhibited 23.7 ± 3.7 wt % comonomer incorporation level, which tracks with 18.7 wt % incorporation as determined by ^{1}H NMR spectroscopy.

DSC (Table 2: entries 5−7) revealed decreased crystallinity (27−11%) and lower melting temperatures (T_m = 89−77 °C; S23) for $\mathbf{PP_{PPr}}$ compared to the corresponding $\mathbf{PP_{Br}}$. Conversely to $\mathbf{PP_{PPr}}$, DSC traces of $\mathbf{PP_{PPh}}$ (Table 2: entries 8−10) exhibited increased crystallinity (32−24%) and T_m (95−76 °C) (Figure S5) versus the corresponding $\mathbf{PP_{Br}}$, possibly due to a decrease in entropy due to $\pi-\pi$ stacking of the phenyl groups.

Thermal Stability Studies of Phosphonate-Functionalized PP. TGA is widely employed to assess thermal stability and decomposition temperatures for FR polymeric materials.[41,42,44] TGAs were performed between 50 and 800 °C under a synthetic air atmosphere (20:80 O_2/N_2) with a heating rate of 20 °C min^{-1} (Figure 2 and Table 2). Polymers were evaluated by the temperatures at 10% and 50% weight loss ($T_{10\%}$ and $T_{50\%}$) and the temperature of maximum rates of weight loss (T_{max}). Additionally, the solid residual char yields at 700 °C were recorded as a measure of the phosphonate activity in the condensed phase. Notably, polymers exhibited comparable $T_{50\%}$ and T_{max} under an N_2 atmosphere (Figure

Table 1. Copolymerization Optimization Data of Propylene and 11-Br[a]

entry	**11-Br** (mM)	activity[b]	productivity[c]	yield (g)	incorporation[d] (mol %)	M_n[e,f] (g mol^{-1})	$Đ_m$[e]	T_m[g] (°C)	crystallinity[g] (%)
1	0	5467	26.1	6.53	0.00	13 600	2.2	114	44
2	91	1686	8.1	2.01	3.98	5000	1.9	90	43
3	137	1594	7.6	1.90	6.63	4500	1.7	81	41
4	182	1025	4.9	1.22	8.12	5200	1.7	78	18

[a] Conditions: *rac*-ethylenebis(indenyl)zirconium dichloride ([**Zr**] = 0.024 mM), MAO used as a cocatalyst and a scavenger with [Al]$_0$:[**Zr**]$_0$ = 1000:1. Molar ratio of [TIBA]$_0$:[**11-Br**]$_0$ = 1:10, 0.5 mL of toluene, 49.5 mL of hexanes, propylene 2 bar, polymerization time = 30 min, and polymerization temperature = 70 °C. Polymerization and analysis were performed in duplicate, and mean values are reported. [b] kg$_{PP}$ mol$_{Zr}^{-1}$ h^{-1} bar^{-1}. [c] kg$_{PP}$ g$_{Zr}^{-1}$ h. [d] Determined by ^{1}H NMR spectroscopy. [e] Determined by SEC. [f] g mol^{-1}. [g] Determined by DSC.

Table 2. Thermal Characterization Data of Polymers

entry	functionality	incorporation[a] (mol %)	T_m[b] (°C)	crystallinity[b] (%)	$T_{10\%}$[c] (°C)	$T_{50\%}$[c] (°C)	residue[c,d]	$T_{max\ (1)}$[c] (°C)	$T_{max\ (2)}$[c] (°C)
1	**PP$_{Br}$**	0.00	111	38	246	277		275	
2	**PP$_{Br}$**	3.99	91	27	295	362		369	
3		6.84	83	22	294	376		380	
4		7.98	77	19	302	380		388	
5	**PP$_{PPr}$**	3.99	89	27	260	417	6.9	277	440
6		6.84	77	20	274	438	6.9	281	443
7		7.98	77	11	273	437	9.4	279	443
8	**PP$_{PPh}$**	3.99	95	32	275	409	5.1	337	456
9		6.84	84	24	304	450	5.8	346	458
10		7.98	76	26	323	452	6.6	346	458

[a]Determined by ^{1}H NMR spectroscopy. [b]Determined by DSC. [c]TGAs were performed between 50 and 800 °C under a synthetic air atmosphere (20:80 O_2/N_2) with a heating rate of 20 °C min^{-1} with values reported in °C. [d]Residue (%) at 700 °C.

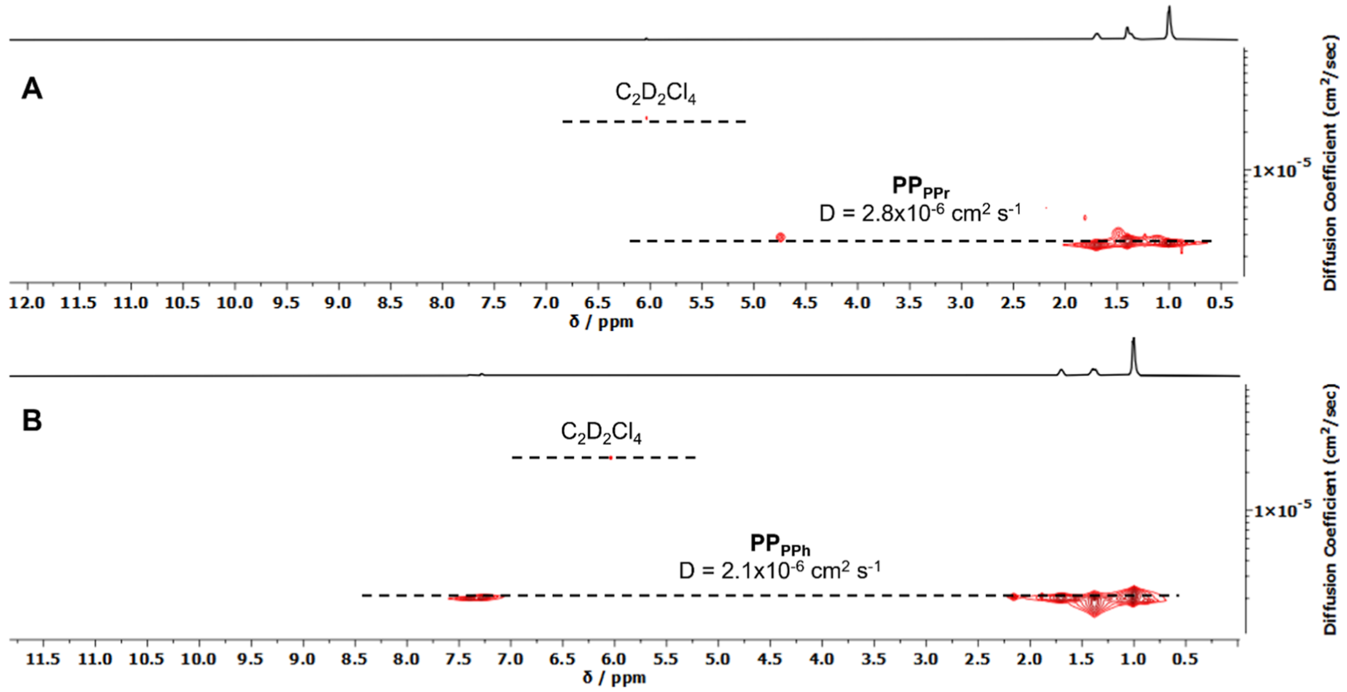


Figure 1. DOSY ^{1}H NMR spectra (500 MHz, $C_2D_2Cl_4$, 393 K) of (A) **PP$_{PPr}$** and (B) **PP$_{PPh}$**.

S9), highlighting the impact of functionalization on the suppression of oxidative decomposition rather than purely altered thermal stability.

The phosphonate-modified polypropylenes **PP$_{PPr}$** and **PP$_{PPh}$** displayed significantly increased thermal stability compared to that of **PP$_{Br}$** and **PP**, according to TGA and derivative thermogravimetry (DTG) plots (Figure 2a–d and Table 2). A two-step thermal oxidative degradation process was observed for the phosphonate-modified copolymers, in contrast to the one-step degradation of **PP** and **PP$_{Br}$**. Decomposition of the phosphonate moieties occur during the first stage, as shown by the peaks at 275 °C (**PP$_{PPr}$**) and 338 °C (**PP$_{PPh}$**) in the DTG. The higher $T_{10\%}$ of **PP$_{PPh}$** compared to **PP$_{PPr}$** (323 vs 273 °C; Table 2, entries 7 and 10) is attributed to a stronger P–O–C linkage induced by the aromatic substituents in the former, which delays the first decomposition stage.[45,46] This is further supported by TGA carried out on **PP$_{PPr}$** under a N_2 atmosphere where the first of two degradation steps was attributed to P–O–C bond scission, compared with the singular degradation step of **PP$_{PPh}$** (Figure S9). During this process, formation of the carbonaceous char layer serves to shield the material from oxygen and prevent the formation of flammable gases.[16] This provokes the second decomposition stage to be at a significantly elevated temperature compared to **PP**. Evaluating $T_{50\%}$ of **PP$_{PPr}$** (Table 2, entries 5–7) and **PP$_{PPh}$** (Table 2, entries 8–10) against **PP** (Table 2, entry 1) confirms improvement between 140–160 and 132–175 °C, respectively. Importantly, improved thermal stability against the brominated copolymers (Table 2, entries 2–4) by 47–72 °C validates beneficial characteristics of phosphonate postmodification. Increased incorporation levels in both **PP$_{PPr}$** and **PP$_{PPh}$** correlated to increased thermal stability with respect to $T_{50\%}$ and T_{max}; however, plateauing at >6.8 mol % incorporation suggests a limit in the maximum efficiency. Although $T_{50\%}$ and T_{max} showed no improvement at highest incorporation levels, the residual char for both **PP$_{PPr}$** and **PP$_{PPh}$** continued to increase. **PP$_{PPr}$** (Table 2, entry 7) afforded the highest char yield (9.4%), whereas **PP$_{PPh}$** observed the highest $T_{50\%}$ (452 °C) and T_{max} (458 °C; Table 2, entry 10).

Flammability Studies of Phosphonate-Functionalized PP. Microscale combustion calorimetry (MCC) is a thermal analysis method for predicting flame resistance and fire

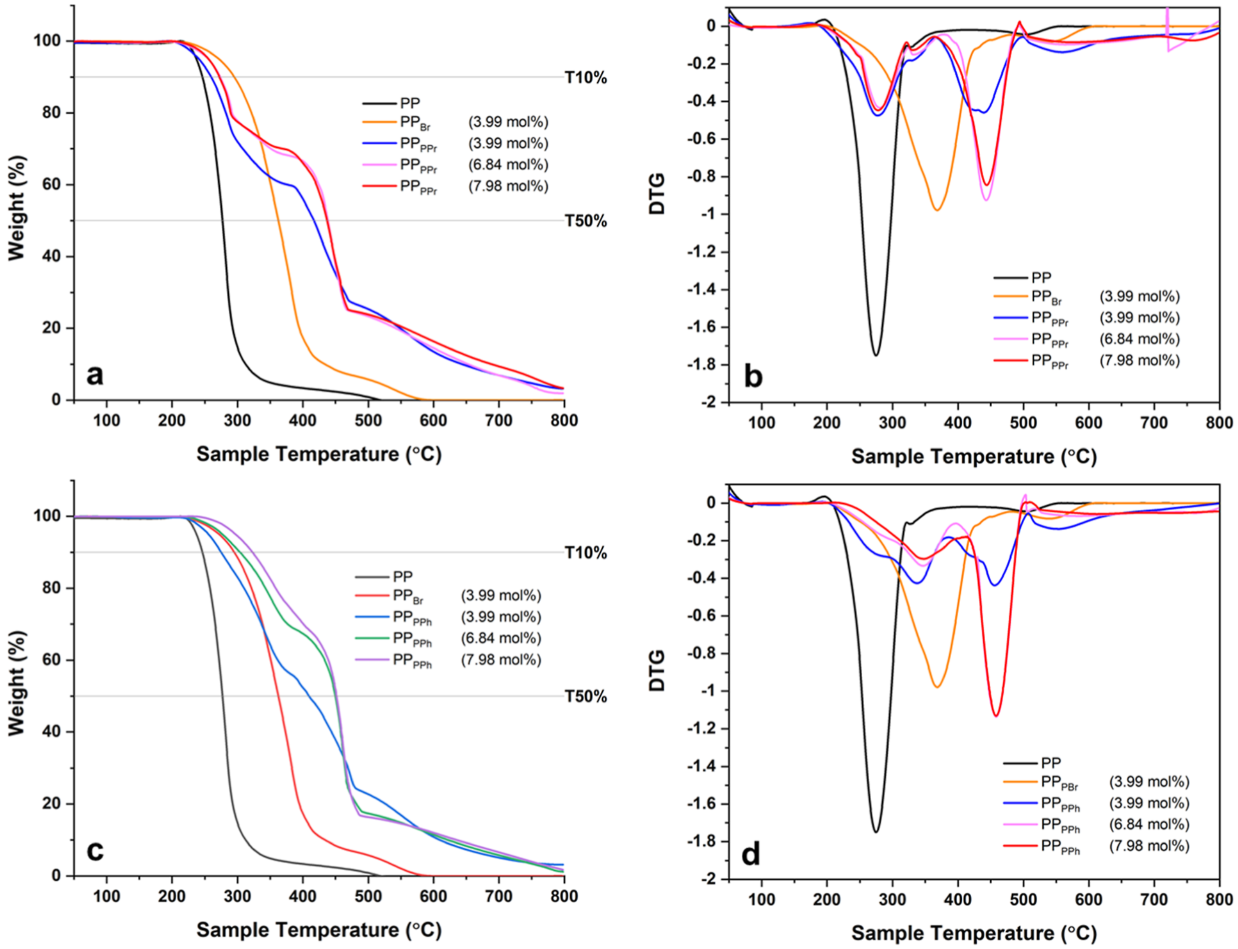


Figure 2. TGA curves and DTG plots of $\mathbf{PP_{PPr}}$ (a,b) and $\mathbf{PP_{PPh}}$ (c,d) under a synthetic air atmosphere (20:80 O_2/N_2) with a heating rate of 20 °C min^{-1}.

Table 3. MCC Data of Propylene (Co)polymers[a]

entry	functionality	incorporation (mol %)	HRC (J g^{-1} K^{-1})	pHRR (W g^{-1})	THR (kJ g^{-1})	T_{pHRR} (°C)
1	$\mathbf{PP_{Br}}$	0.00	1245.2 (47.2)	1047.2 (24.6)	48.3 (4.4)	468.5 (1.7)
2	$\mathbf{PP_{Br}}$	3.98	577.2 (126.2)	501.5 (113.0)	43.6 (4.4)	428.0 (5.7)
4		8.12	715.8 (55.9)	615.6 (53.4)	41.5 (2.9)	430.0 (0.4)
5	$\mathbf{PP_{PPr}}$	3.98	812.1 (79.6)	688.3 (54.3)	39.9 (3.8)	470.9 (2.6)
7		8.12	911.4 (8.8)	778.9 (3.9)	42.5 (3.6)	473.8 (1.0)
8	$\mathbf{PP_{PPh}}$	3.98	949.3 (23.5)	840.9 (10.9)	43.6 (1.7)	473.6 (2.3)
10		8.12	975.9 (24.8)	832.2 (18.7)	41.8 (0.5)	470.0 (1.2)

[a] Each sample repeated in triplicate and error, one standard deviation, shown in brackets (σ).

behavior of flame-retardant materials, commonly utilized as a screening tool. The MCC method directly measures the heat of combustion of the gases evolved during controlled heating of milligram-sized samples.[47] MCC was carried out in triplicate for **PP**, $\mathbf{PP_{Br}}$, $\mathbf{PP_{PPr}}$, and $\mathbf{PP_{PPh}}$ of 4 and 8 mol % functionality (Figures S10 and S11); the averaged values for heat release capacity (HRC), peak heat release rate (pHRR), total heat release (THR), and temperature at pHRR (T_{pHRR}) with accompanying errors are summarized in Table 3 and illustrated in Figure 3.

PP yields high values concerning HRC (1245.2 J g^{-1} K), pHRR (1047.2 W g^{-1}), and THR (48.3 kJ g^{-1}), indicating substantial release of flammable products; these values are consistent with those reported in the literature.[47−49] Improved HRC and pHRR of $\mathbf{PP_{PPr}}$ (36 and 34%, respectively) and $\mathbf{PP_{PPh}}$ (24 and 20%, respectively) for 4 mol % incorporated polymers compared with PP indicate that incorporation of the phosphonate group increases the flame retardancy performance. Increased performance was not attained via increased incorporation levels, as suggested by TGA, despite improvements to HRC and pHRR of $\mathbf{PP_{PPr}}$ (27 and 26%, respectively) and $\mathbf{PP_{PPh}}$ (22 and 21%, respectively) for 8 mol % incorporated polymers compared with **PP**. This is surprising and implies an alternate contributing effect, perhaps attributable to polymer molecular weight given the low M_n; this trend was likewise observed for both $\mathbf{PP_{Br}}$ samples. Comparing both modified polymers to their parent $\mathbf{PP_{Br}}$, we can isolate the effect of increasing modifier incorporation. The HRC of $\mathbf{PP_{PPr}}$ and $\mathbf{PP_{PPh}}$ with respect to $\mathbf{PP_{Br}}$ was observed to be higher in all instances, but the difference was minimized for samples with

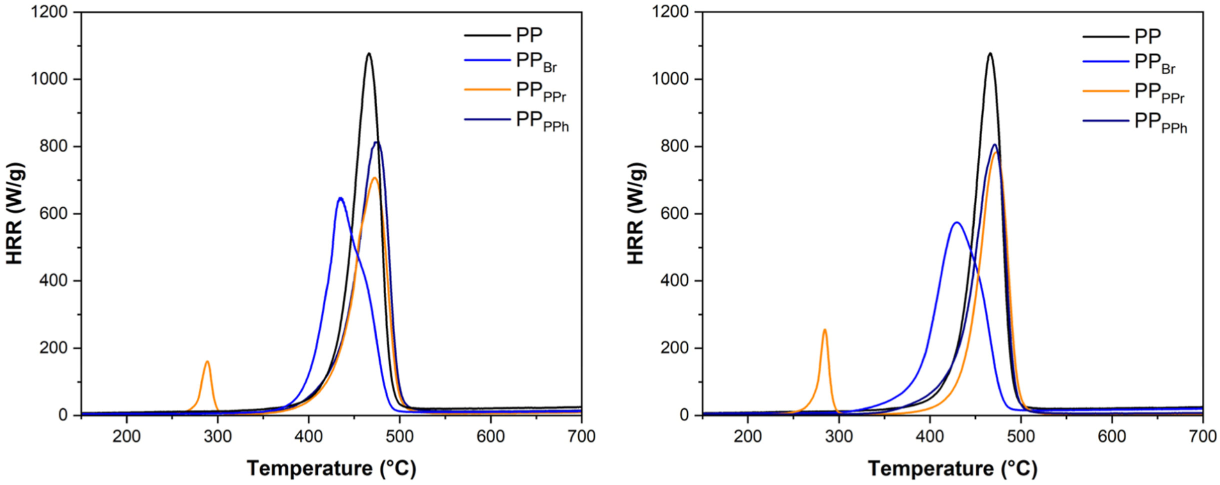


Figure 3. Representative MCC of **PP**, **PP_{Br}**, **PP_{PPr}**, and **PP_{PPh}** at 3.98 (left) and 8.12 mol % incorporation (right).

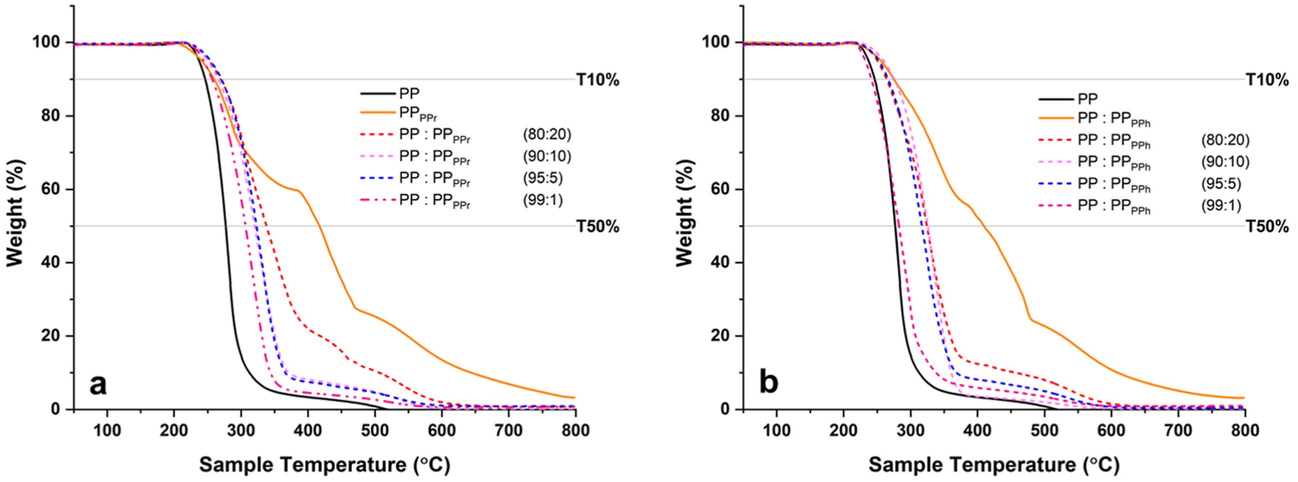


Figure 4. TGA thermographs of **PP_{PPr}** (4 mol %) (a) and **PP_{PPh}** (4 mol %) (b) and associated blends with **PP** under a synthetic air atmosphere (20:80 O_2/N_2) with a heating rate of 20 °C min^{-1}.

Table 4. Thermal Characterization Data of Polymer Blends[a]

sample	wt %	T_m[b] (°C)	crystallinity[b] (%)	$T_{10\%}$[c]	$T_{50\%}$[c]	residue[c,d]	$T_{max\ (1)}$[c]	$T_{max\ (2)}$[c]
PP_{xx}		111	38	246	277		275	
PP_{PPr}		89	27	260	417	6.94	277	440
PP_{PPh}		95	32	275	409	5.11	337	456
PP: **PP_{PPr}**	80:20	108	30	270	338	0.80	312	450
	90:10	109	50	266	320	0.00	327	
	95:5	111	33	271	323	0.87	329	
	99:1	113	38	257	307	0.62	312	
PP: **PP_{PPh}**	80:20	115	27	264	324	0.74	329	
	90:10	114	35	276	326	0.02	333	
	95:5	113	33	267	317	0.40	319	
	99:1	112	36	242	282	0.91	281	
PP: ATH	80:20	109	26	256	297	14.03	290	
PP: ATH: **PP_{PPr}**	80:10:10	112	32	265	315	7.58	311	
PP: ATH: **PP_{PPh}**	80:10:10	113	31	259	308	6.41	307	
PP: LDH	80:20	109	30	265	315	5.68	311	
PP: LDH: **PP_{PPr}**	80:10:10	110	27	260	312	3.36	313	
PP: LDH: **PP_{PPh}**	80:10:10	114	28	273	325	6.34	324	

[a] **PP_{PPr}** and **PP_{PPh}** phosphonate incorporation 4 mol %. [b] Determined by DSC. [c] TGAs were performed between 50 and 800 °C under a synthetic air atmosphere (20:80 O_2/N_2) with a heating rate of 20 °C min^{-1} with values reported in °C. [d] Residue (%) at 700 °C.

higher incorporation (41 and 64% vs 27 and 36%, respectively). Given that the mechanism of action for the phosphonated samples largely relies on the surface effects brought on by the char layer formation, increasing the proportion of modifier likely prompts this response. Highlighting the effect of M_n on MCC test results, synthesis of high M_n $\mathbf{PP_R}$ could contribute substantially to further improving the flammability performance. Preliminary synthesis of a modified high M_n PP (M_n = 54 300 g mol^{-1}, 6.2 mol %) supports this, evidencing an increased $T_{50\%}$ (477 °C) (Figure S21) vs $T_{50\%}$ = 438 °C for $\mathbf{PP_{PPr}}$ (7.98 mol %).

Heat release profile for $\mathbf{PP_{PPr}}$ suggests a two-step decomposition pathway in line with observed TGA data under oxidative conditions, while a single decomposition peak was observed for the remaining polymers. $\mathbf{PP_{Br}}$ provides evidence of a substantial drop in HRC (54%) and pHRR (52%) but also exhibits significant error and peak broadness compared to the other materials. This implies an inconsistent FR mechanism compared with both $\mathbf{PP_{PPr}}$ and $\mathbf{PP_{PPh}}$, all of which display lower errors.

HRC can be utilized to predict the fire behavior and flame resistance of flame-retardant polymers.[47] Given that the HRC of both $\mathbf{PP_{PPr}}$ and $\mathbf{PP_{PPh}}$ is >400 J g^{-1} K^{-1}, they are still currently characterized as flammable; plastics with HRC above 400 J g^{-1} K^{-1} typically will continue to burn after a brief exposure to a small flame and correlate to an LOI below 21% or Underwriters Laboratory HB rating.[6] MCC has been shown to correlate well to the fire properties of homopolymers; however, Stoliarov et al. have highlighted that MCC cannot be solely used to accurately assess polymer flame retardancy for a broad range of chemical compositions.[50] Consequently, further evaluation by alternate methods, preferably at a larger scale, should be undertaken to more accurately determine the material FR characteristics.

Polymer Compounding with PP and Inorganic FR Additives. **PP** was blended with 20, 10, 5, or 1 wt % $\mathbf{PP_{PPr}}$ or $\mathbf{PP_{PPh}}$ and assessed against blends containing inorganic FR additives, ATH or FR layered double hydroxide (LDH) (FR-LDH), by DSC and TGA under an air atmosphere (Figure 4a,b, Table 4, Figures S9 and S12, and Tables S2−S3).

TGA data on the polymer blends (Figure 4 and Table 4) show a minor increase in $T_{10\%}$, $T_{50\%}$, and T_{max} values compared to **PP**, for 1 wt % blends of the 4 mol % phosphonate-modified copolymer. This effect is more pronounced at loadings >5 wt %. This clearly demonstrates that very low overall phosphonate loadings could be highly effective in imparting PP with tunable FR properties while mitigating any degradation in mechanical properties. ATH is used as an FR additive in commercial polyethylene formulations for electrical applications due to the endothermic decomposition and liberation of water vapor between 220 and 400 °C. This slows the combustion process, diluting the flammable gases and shielding the polymer surface from oxygen.[51] Given low melt processing temperatures (<200 °C) for blending, synthesized (co)polymer blends with ATH were investigated. Synergies between ATH and phosphorus have been extensively investigated due to different FR mechanisms of action.[52−55] Blending **PP** with $\mathbf{PP_{PPr}}$ or $\mathbf{PP_{PPh}}$ and inorganic FR additives ATH or LDH (80:10:10 wt %, respectively), however, afforded no significant improvement in thermal stability by TGA, compared to pure phosphonate copolymers (Table 4). This is unsurprising given the high loading of ATH (>35 wt %) typically required to elicit a significant response. Such high inorganic contents result in a significant trade-off between flame retardancy and mechanical properties.[28] By contrast, the low required loading of, as propylene copolymers similar in chemistry to pure PP, should limit the impact on mechanical properties, making phosphonate copolymers a promising alternative.

■ CONCLUSIONS

Synthesis and characterization of a range of phosphonate-functionalized PP via quantitative postmodification of $\mathbf{PP_{Br}}$ with aryl and alkyl phosphite esters under neat conditions have been achieved. Significantly improved thermal stability of the phosphonate-PP was evidenced by TGA in a synthetic air atmosphere when compared to unmodified **PP**, evaluated by T_{max}, $T_{10\%}$, $T_{50\%}$, and residual char residue at 700 °C. Modified polymers exhibited a two-stage oxidative degradation, while a single decomposition step was observed for **PP**. MCC values of both $\mathbf{PP_{PPr}}$ and $\mathbf{PP_{PPh}}$ indicate lower values of HRC, pHRR, and THR compared to those of **PP**, indicating enhanced flame retardancy. Polymer blending of **PP** and $\mathbf{PP_{PPr}}$ or $\mathbf{PP_{PPh}}$ demonstrated that very low copolymer loadings (≥1 wt %) elicited improved thermal stability compared to the homopolymer. While no significant improvement in thermal stability was identified with blends including ATH or FR-LDH, at similar loadings, the phosphonate-functionalized polymers outperformed the commercial inorganic additives.

These single-component FR materials hold promise over commonly utilized FR additives, removing toxicity and environmental concerns of halogenated additives, not requiring high loadings of inorganic materials that compromise polymer mechanical properties, and by being resistant to leaching by virtue of the covalent tethering of the phosphonate group. Additionally, the ability to readily synthesize alternate functionalized PP and to further increase comonomer incorporation can now be investigated to further boost polyolefin FR efficacy.

■ EXPERIMENTAL DATA

General (Co)polymer Synthesis and Characterization. General procedure for the solution-phase copolymerization of propylene with bromoalkenes and subsequent postmodification of poly(propylene)-*co*-(11-bromo-1-undecene) with triisopropyl phosphite or triphenyl phosphite was carried out according to the literature.[36]

General Procedure for Polymer Compounding. In a vial with a magnetic stirrer bar, phosphite-postmodified poly(propylene)-*co*-(11-bromo-1-undecene) was combined with poly(propylene) in a known ratio by weight and melted in xylenes (5 mL) at 120 °C. The blend was subsequently precipitated in acidified methanol (2 wt % HCl) before being collected by filtration, washed with methanol (20 mL) and then acetone (2 × 20 mL), and dried in vacuo at 40 °C to a constant weight.

General Procedure for Polymer Compounding with Inorganic FR Additives. Phosphite-postmodified poly(propylene)-*co*-(11-bromo-1-undecene) was combined with PP and aluminium trihydroxide (ATH) or LDH, in known ratios by weight, in a vial with a magnetic stirrer bar. The mixture was melted in xylenes (5 mL) at 120 °C and precipitated in acidified methanol (2 wt % HCl) before being collected by filtration, washed with methanol (20 mL) and then acetone (2 × 20 mL), and dried in vacuo at 40 °C to a constant weight.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsapm.4c03706.

Polymer characterization, thermal stability data, and MCC data (PDF)

AUTHOR INFORMATION

Corresponding Author

Dermot O'Hare − *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, OX1 3TA Oxford, U.K.;* orcid.org/0000-0001-8054-8751;
Email: dermot.ohare@chem.ox.ac.uk

Authors

Alexander Evans − *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, OX1 3TA Oxford, U.K.*
Louis J. Morris − *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, OX1 3TA Oxford, U.K.*
Zoë R. Turner − *Chemistry Research Laboratory, Department of Chemistry, University of Oxford, OX1 3TA Oxford, U.K.;* orcid.org/0000-0003-2044-9203

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsapm.4c03706

Author Contributions

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Notes

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