Synthesis of a highly efficient flame retardant utilizing plant-derived diphenolic acids and its application in polylactic acid

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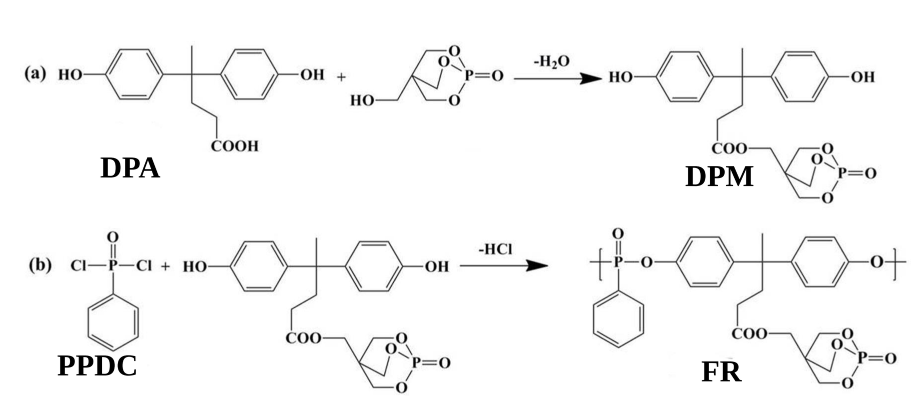
Background

- Growing concerns over petroleum depletion has led to immense interest in polymers that are derived from renewable feedstocks. Of particular interest, polylactic acid (PLA), derived from sugars and starches, is already approaching cost-competitive prices with petrochemical plastics and is produced on commercial volumes. However, similar to its petroleum-derived counterparts, the inflammable deficiency of PLA limits its further application. Therefore, the work rendering PLA with flame retardancy is of great significance.
- Among the flame retardant formulations, some methods have involved rendering PLA flame retardant by blending with other bio-based sources. However, this often required relatively high loadings of FR additives (i.e., at times > 40% by mass additive), which may deteriorate the comprehensive properties of the resulting composites. Thus, developing highly efficient green flame retardants is leading the next generation of flame retardant.

Synthesis route of FR

FR was synthesized via two steps

- First, the intermediate, DPA-based monomer (DPM) was synthesized through the esterification of DPA and PEPA
- Second, flame retardant (FR) was synthesized by the polycondensation between DPM and PPDC



Synthesis route of FR

Characterization of DPM and FR

1. DPM characterization

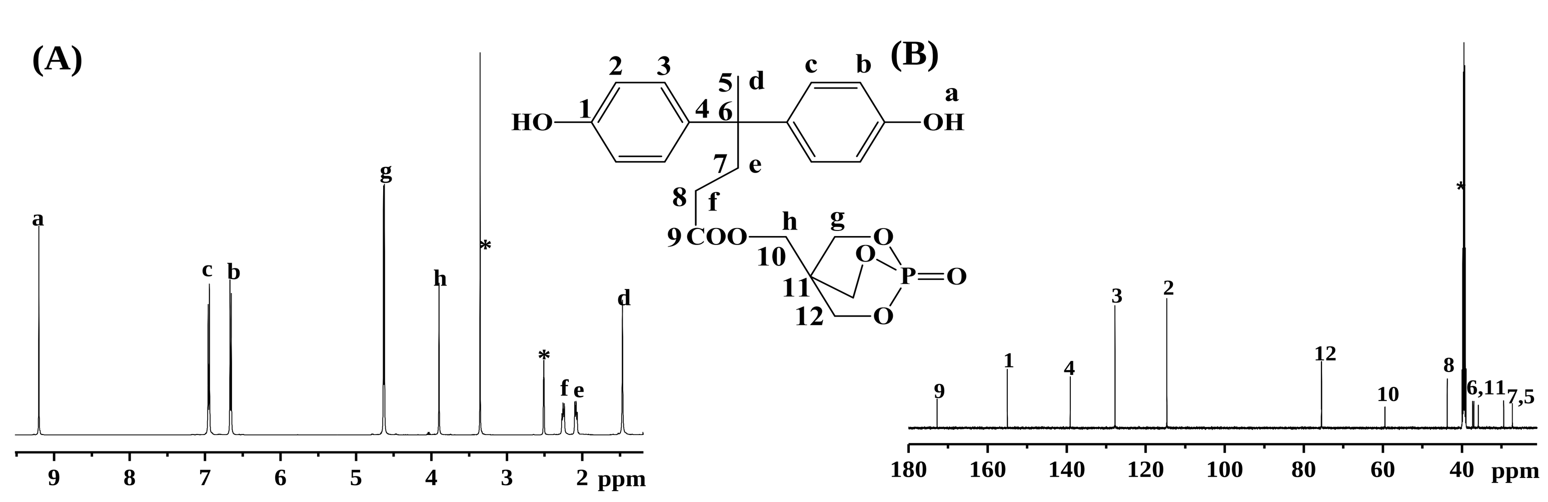


Figure 1. (A) ^{1}H NMR and (B) ^{13}C NMR spectra of DPM in DMSO-d6

2. FR characterization

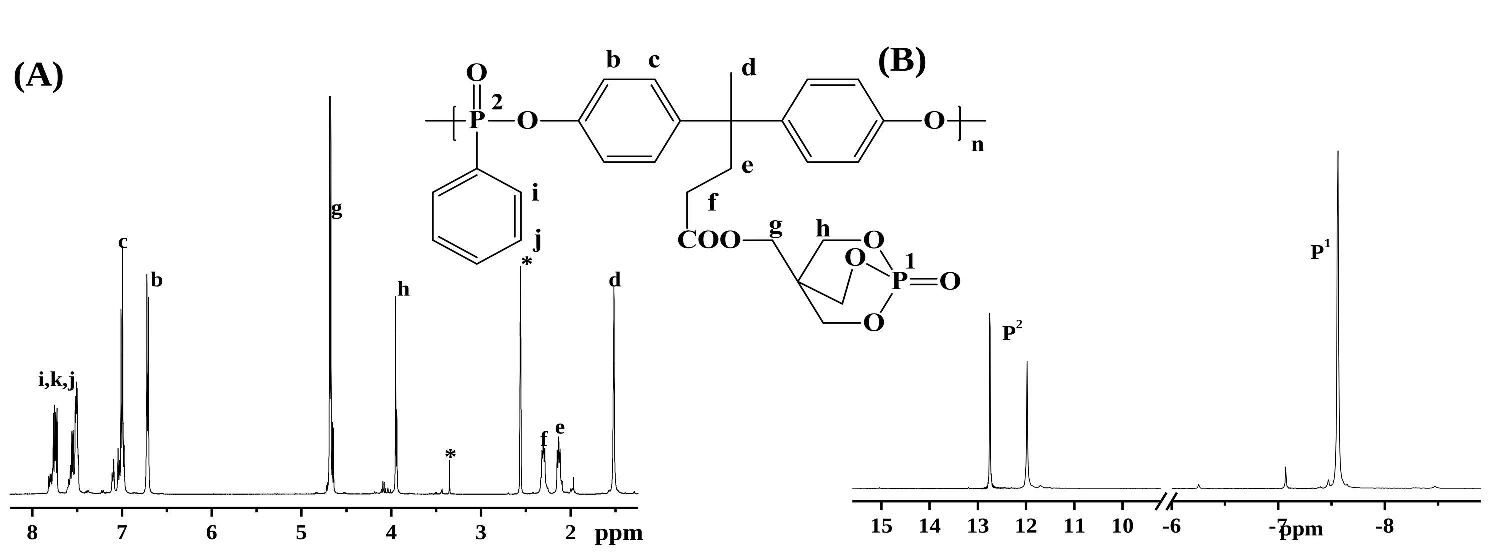


Figure 2. (A) ^{1}H NMR and (B) ^{31}P NMR spectra of FR in DMSO-d6

Flame retardant properties of PLA/FR

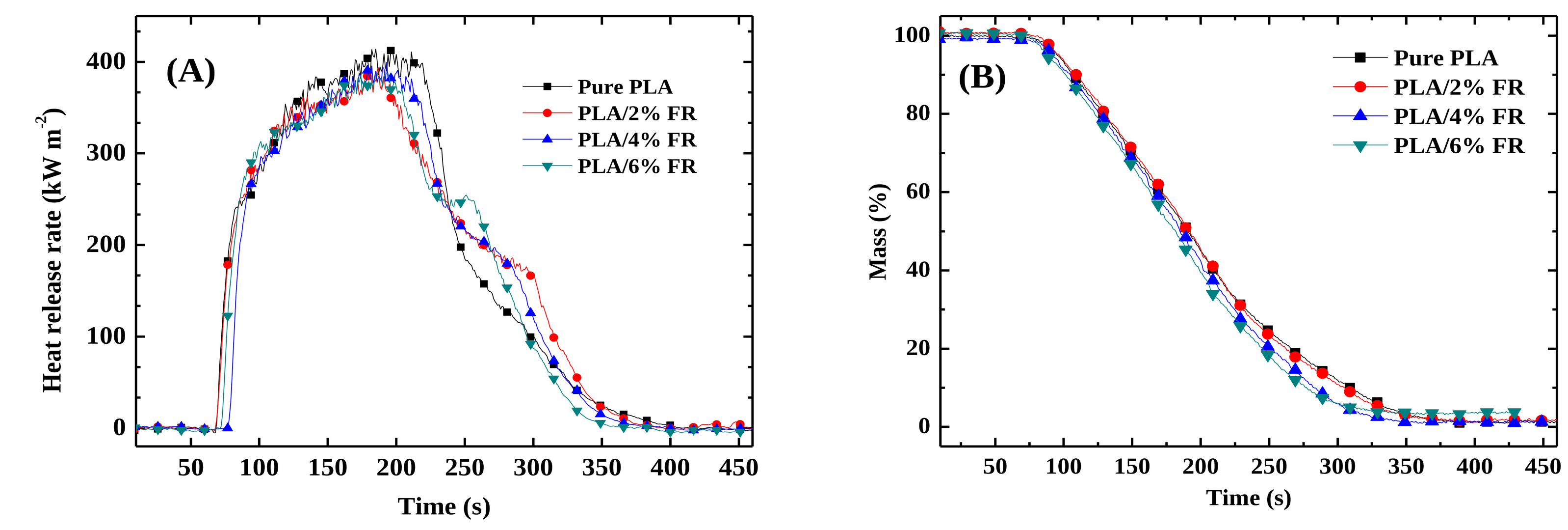


Figure 3. (A) HRR vs time curves of PLA and PLA/FR; (B) mass curves of PLA and PLA/FR

gas phase flame retardant mechanism

Sample	UL-94	LOI	Cone calorimetry				
			TTI (s)	PHRR (kW m^{-2})	THR (MJ m^{-2})	Residual Mass (wt%)	CO YIield (kg/kg)
PurePLA	NR	20.0	68±1	418±3	70±1	1.6±0.2	0.0073±0.0006
PLA2%FR	V2	28.8	68±1	394±14	69±1	2.5±0.1	0.0087±0.0005
PLA4%FR	V0	33.7	78±2	396±6	67±2	3.1±0.1	0.011±0.002
PLA6%FR	V0	35.3	74±1	388±6	66±1	3.5±0.2	0.016±0.001

Flame retardant mechanism

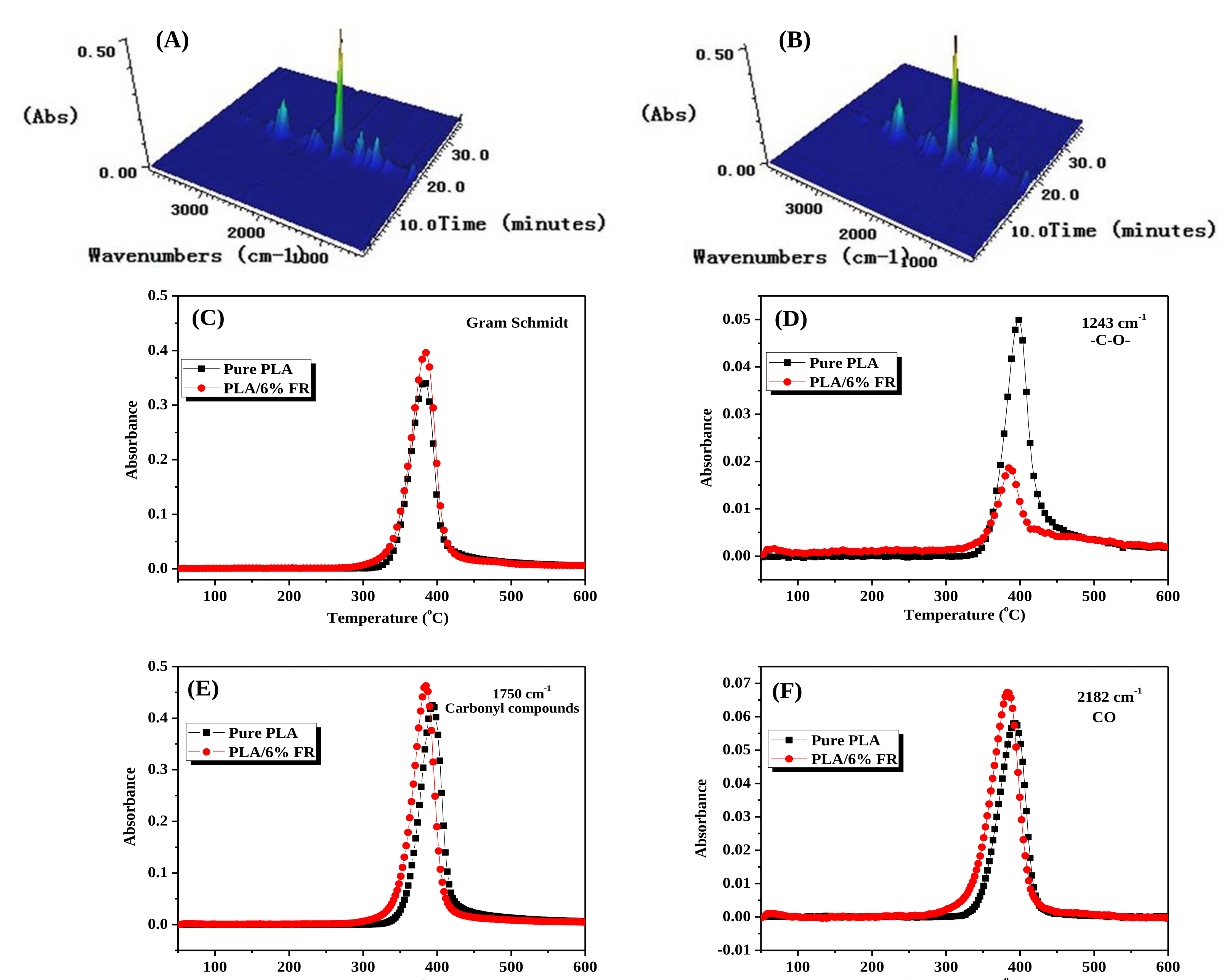


Figure 4. (A) 3-D image of TGA-FTIR results of PLA, (B) 3-D image of TGA-FTIR results of PLA/6%FR. (C) Gram−Schmidt curves vs temperature of PLA and PLA/6%FR. (D) Absorbance at 1244 cm^{-1} vs temperature curves of PLA and PLA/6%FR. (E) Absorbance of carbonyl compounds vs temperature curves of PLA and PLA/6%FR. (F) Absorbance of carbon monoxide vs temperature curves of PLA and PLA/6%FR

Conclusion

- The bio-based FR developed herein is blended with PLA, the resulting material exhibits flame-extinguishing characteristics and achieves UL-94 V0 ratings at low FR loadings (<4% by mass)
- Use of the bio-based flame retardants described herein yields flame retardant PLA containing up to 95% by mass of its constituent components are both bio-derived and formed from commodity bio-based chemicals (i.e., lactic acid and diphenolic acid)

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