



## A STUDY OF THE INFLUENCE OF THE CHEMICAL ENVIRONMENTS OF P- AND N-CONTAINING GROUPS ON THE FIRE RETARDANCE OF POLYSTYRENE

Baby, A., Tretsiakova-McNally, S., Joseph, P., Arun, M., & Zhang, J. (2023). *A STUDY OF THE INFLUENCE OF THE CHEMICAL ENVIRONMENTS OF P- AND N-CONTAINING GROUPS ON THE FIRE RETARDANCE OF POLYSTYRENE*. 287. Paper presented at 19th European Meeting on Fire Retardant Polymeric Materials, Zurich, Dubendorf, Switzerland.

[Link to publication record in Ulster University Research Portal](#)

### Publication Status:

Published (in print/issue): 26/06/2023

### Document Version

Publisher's PDF, also known as Version of record

### General rights

Copyright for the publications made accessible via Ulster University's Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

### Take down policy

The Research Portal is Ulster University's institutional repository that provides access to Ulster's research outputs. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact [pure-support@ulster.ac.uk](mailto:pure-support@ulster.ac.uk).

## P65- A STUDY OF THE INFLUENCE OF THE CHEMICAL ENVIRONMENTS OF P- AND N-CONTAINING GROUPS ON THE FIRE RETARDANCE OF POLYSTYRENE

**Aloshy Baby<sup>a</sup>, Svetlana Tretsiakova-McNally<sup>a</sup>, Paul Joseph<sup>b</sup>, Malavika Arun<sup>b</sup> and Jianping Zhang<sup>a</sup>**

<sup>a</sup>*Belfast School of Architecture and the Built Environment, Ulster University, 2-24 York Street, Belfast BT15 1AP, Northern Ireland, UK; [baby-a1@ulster.ac.uk](mailto:baby-a1@ulster.ac.uk)*

<sup>b</sup>*Institute of Sustainable Industries and Liveable Cities, Victoria University, PO Box 14428, Melbourne 8001, Victoria, Australia*

**Main message:** The primary strategies to improve the fire retardance of styrene-based polymers are largely reliant on the use of halogenated fire retardants, which are considered as hazardous to the public health and environment. Hence, many halogen-based fire retardants have already been withdrawn from the products used as construction elements in built environments. Amongst the possible halogen-free alternatives, P- and N-containing compounds have gained great attention owing to their excellent fire-retarding efficiencies and environmentally benign attributes. The current paper is focused on the chemical modification of polystyrene with P- and N-containing moieties, and the characterisation of the modified materials with regard to their thermal degradation characteristics and combustion attributes.

**Keywords:** Polystyrene, reactive modification, thermal stability, P-N synergism, fire retardance.

### Introduction

The relative high flammability of polystyrene (PS) often restricts its wider applicability as an insulation material in the building and construction sectors [1]. In a previous study by the authors [2], several organic phosphonates were found to be effective in inhibiting the ignition propensities and suppressing the combustion of styrene-based polymers. These effects were thought to arise from both gaseous- and condensed-phase inhibitory actions of the P-bearing groups [3]. With a view to further improve the fire retardance of PS, we tried to chemically bind both phosphorus- and nitrogen-containing groups, *via* a ter-polymerization route, thus exploring possible P-N synergism [3]. The present paper specifically reports on the reactive modification of styrenic polymers with diethyl(acryloyloxymethyl) phosphonate (DEAMP), or diethyl-p-vinylbezy phosphonate (DEpVBP), along with a N-containing compound, where N atom is in different chemical environments. Furthermore, the influence of the chemical environments of P and N atoms within the FR groups on the thermal behaviors and combustion characteristics of the modified polymers is discussed.

### Experimental

The chemical structures of P- and N- containing monomers used in this study are given in Figure 1. These included: DEAMP and DEpVBP as P-containing monomers; maleimide (MI), N-methylmaleimide (MeMI), N-ethylmaleimide (EtMI), acrylamide (AM), N,N-dimethyl acrylamide (DMA) and N-isopropyl acrylamide (NIPAM), as N-bearing unsaturated compounds. The unmodified PS (used as a control sample) and the ter-polymers of styrene (St), with the above-mentioned monomers were prepared through free-radical polymerization reactions as reported previously [2]. The thermo-gravimetric analyses (TGA) were carried out on *ca.* 10 mg samples, on a Mettler Toledo TGA 2 instrument in a 25 - 800 °C temperature range, under both nitrogen and air atmospheres, and at a heating rate of 10°C·min<sup>-1</sup>. The heat of combustion,  $\Delta H_{\text{comb}}$ , (average of duplicate runs) was obtained using a Parr 6200 oxygen bomb calorimeter, and the Pyrolysis Combustion Flow Calorimetric (PCFC) measurements were conducted using a micro-scale combustion calorimeter (Fire Testing Technology Ltd.).

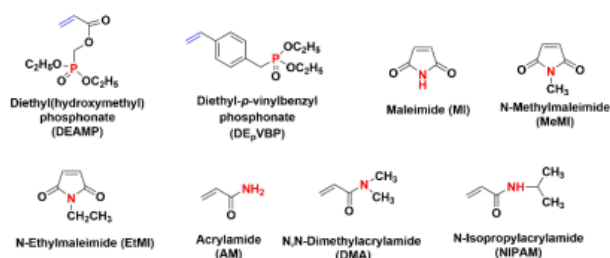


FIGURE 1. Chemical structures of P- and N- containing monomers.

## Results and Discussion

Table 1 summaries relevant parameters measured using TGA, ‘bomb’ calorimetry and PCFC for styrenic polymers incorporating the P- (i.e., DEAMP) and different types of N-monomers. The results of DEpVBP containing materials were not included for brevity. Here, we examined the effects of two chemical environments of the N atom (i.e., as an imide and an amides) with a view to identifying the P-N synergism, if present, and also the resultant thermal stability of the ter-polymers. It is evident from Table 1 that the ter-polymerisation of St with P- and N- compounds resulted in increased levels of char formation, and lower  $\Delta H_{\text{comb}}$  and reduced heat release capacity (HRC). However, the ter-polymers with built-in imide units, e.g., MI, MeMI and EtMI, exhibited a comparatively better performance than the ter-polymers with amide groups (AM, DMA, and NIPAM). For example, the HRC values for the ter-polymer with DEAMP and MI were reduced by almost 50%, whereas in the case of the ter-polymers with DEAMP and NIPAM the HRC was dropped only by 20%. These results revealed that the presence of cyclic imides, along with P-moieties, in the polymeric chains of PS tends to enhance its fire retardance to a greater degree as compared to amides. Furthermore, the alkyl substitutions of N atoms in the N-monomers showed a positive effect on the thermal stability of the modified PS. These results also indicated the beneficial effects of P- and N- containing monomeric units on the fire retardance of PS, and therefore warrant further investigation.

TABLE 1. The char residues, heats of combustion, and PCFC data of modified PS polymers

Sample	Char residue <sup>a</sup> (wt %)	Char residue <sup>b</sup> (wt %)	$\Delta H_{\text{comb}}$ (kJ/g)	HRC (J/g·K)	EHC (kJ/g)
PS	0.5	0.4	40.4	753.0	36.4
Poly(St-ter-DEAMP-ter-MI)	24.3	3.6	31.3	341.0	25.8
Poly(St-ter-DEAMP-ter-MeMI)	6.9	2.6	31.7	431.6	27.3
Poly(St-ter-DEAMP-ter-EtMI)	7.5	3.1	31.5	440.3	31.4
Poly(St-ter-DEAMP-ter-AM)	8.2	2.8	33.9	617.7	34.1
Poly(St-ter-DEAMP-ter-DMA)	6.4	3.4	35.3	621.0	36.2
Poly(St-ter-DEAMP-ter-NIPAM)	7.7	1.2	35.4	590.3	34.4

Char residue<sup>a</sup>: char formed at 800°C under N<sub>2</sub>, Char residue<sup>b</sup>: char formed at 800°C under air,  $\Delta H_{\text{comb}}$ : Heat of combustion, HRC: Heat Release Capacity, EHC: Effective Heat of Combustion.

**Acknowledgement:** AB is grateful for the provision of the overseas PhD studentship from Ulster University, UK. This research was supported by the Royal Society of Chemistry (ID R19-3521).

## References:

- 1 A. Baby, S. Tretsiakova-McNally, M. Arun, P. Joseph, J. Zhang, Reactive and Additive Modifications of Styrenic Polymers with Phosphorus-Containing Compounds and Their Effects on Fire Retardance, *Molecules* 2020; 25: 1–36.
- 2 A. Baby, S. Tretsiakova, M. Paul, J. Malavika, A. Jianping, Z. Doris, The influence of phosphorus and nitrogen - containing groups on the thermal stability and combustion characteristics of styrenic polymers, *J. Therm. Anal. Calorim* 2022:1-13.
- 3 S. Tretsiakova-mcnally, A. Baby, P. Joseph, D. Pospiech, E. Schierz, A. Lederer, M. Arun, G. Fontaine, Gaseous- and Condensed-Phase Activities of Some Reactive P- and N-Containing Fire Retardants in Polystyrenes, *Molecules* 2023; 28:1–18.