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This is the Published version of the following publication

Baby, Alosly, Tretsiakova-McNally, Svetlana, Joseph, Paul, Zhang, Jianping and Arun, Malavika (2024) The Effects of Nitrogen-Containing Monomers on the Thermal Degradation and Combustion Attributes of Polystyrenes Chemically Modified With Phosphonate Groups. *Macromolecular Materials and Engineering*, 309 (6). ISSN 1438-7492

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The Effects of Nitrogen-Containing Monomers on the Thermal Degradation and Combustion Attributes of Polystyrenes Chemically Modified With Phosphonate Groups

Aloshy Baby,* Svetlana Tretsiakova-McNally,* Paul Joseph, Jianping Zhang, and Malavika Arun

In the present study, polystyrene (PS) is chemically modified with diethyl(acryloyloxymethyl)phosphonate (DEAMP) and an N-containing monomer, selected from different classes of compounds, via a *ter*-polymerization route; thus, exploring possible P–N synergistic effects on fire retardance of the base polymer. The successful incorporation of P and N monomeric units is confirmed by Fourier Transform Infrared (FT-IR), ¹H and ³¹P Nuclear Magnetic Resonance (NMR) spectroscopies. The thermal degradation and combustion attributes of modified polymeric materials are measured using standard techniques, including Thermo-Gravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), “bomb” calorimetry, and Pyrolysis Combustion Flow Calorimetry (PCFC). The thermal and combustion studies demonstrate that the thermal stability and combustion characteristics of styrenic polymers are significantly altered by the presence of even nominal amounts of P- and N-containing groups, and in certain cases, synergistic interactions of these groups are also evident. For instance, as revealed by TGA, the extent of char formation, under the oxidative atmosphere, in the prepared *ter*-polymers, is enhanced by 16–44%, when compared to the unmodified PS. The heat release rates and heat release capacities of *ter*-polymers, measured using the PCFC technique, are reduced by 18–50%, in comparison to the same parameters obtained for the unmodified counterpart.

1. Introduction

Polystyrene (PS) is a versatile and widely used polymer that finds extensive applications in various industries, ranging from packaging and construction to consumer goods.^[1,2] While its popularity is attributed to its lightweight and insulating properties, one significant challenge that is associated with PS is its relatively high flammability.^[2–4] This restricts the wider applicability of PS, especially as an insulation material for buildings and also limits the use of styrene-based polymers in the construction sector.^[3] In addition, the combustion of PS-based materials can often result in melt-flow and melt-dripping, thus, creating a secondary fire hazard and exacerbating the severity of real-life fire situations.^[2,4] In order to address these fire safety concerns, extensive research has been conducted in the field of fire-retardants (FRs) suitable for PS. Researchers have explored the use of various additives that can be blended with PS to enhance the fire retardancy of the

base polymer.^[5–10] However, the high loadings of additive FRs that are often required can lead to a deterioration in the mechanical properties of the products.^[2,3] The application of halogenated FRs, which in the past dominated the polymer industry, has been subsequently restricted in many countries due to the toxicity and bio-accumulation issues.^[2,11,12] Hence, the development of efficient FRs for PS not only addresses safety concerns but also aligns with broader sustainability goals set by the United Nations (UN). As regulations regarding fire safety become more stringent, the demand for newer types of fire-resistant materials continues to grow. It is also prudent to strike a balance between enhancing the fire retardance of PS, maintaining its cost-effectiveness and environmental sustainability.^[3]

As an alternative to halogenated FRs for PS, phosphorus (P) based compounds have gained interest, and different formulations have been developed by many research groups.^[13–17] As reported previously, several organophosphorus groups were found to be effective in reducing the ignition propensities and

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DOI: 10.1002/mame.202300432

suppressing the extents of combustion of PS-based polymers.^[3,16–19] In most of the previously reported studies, the organophosphorus compounds were incorporated into the PS chains via a *co*-polymerization technique.^[17,19–21] For example, as reported in ref. [19], the incorporation of unsaturated P monomer, diethyl(acryloyloxymethyl)phosphonate (DEAMP), into PS had led to a 14% decrease in the heat release capacity (HRC) and peak heat release rate (pHRR), measured through PCFC, at a low level of P loading (0.10 mol). In other studies, a similar unsaturated P monomer, diethyl(methacryloyloxymethyl)phosphonate (DEMMP), was introduced into PS, which increased the limiting oxygen index (LOI) of the corresponding *co*-polymer to 22.5% from 17.9% for PS.^[20,22] In our previous study, with a view to obtaining a better level of fire retardance for PS, a phosphorus compound in combination with a nitrogen-containing compound was introduced into the PS chains via *ter*-polymerization technique.^[19] It was also found that the thermal stability and combustion characteristics of PS were significantly altered by the presence of nominal amounts of P- and N-containing units in the polymeric chains. Further, it was identified that the covalently bound P and N compounds could exert a P–N synergistic interaction and lower the combustibility of PS.^[17–22] This aspect was further explored in the present study. The overall aim of this work was to determine the effect of the varied chemical environments of N atoms in the selected N-containing monomers on the P–N synergism by measuring the thermal and combustion characteristics of the modified polymers. For this purpose, the chemical modification of PS was carried out through *ter*-polymerization of styrene with DEAMP and a N-containing monomer of interest. The N-containing compounds were endowed with chemical functionalities, such as: cyclic imides, amides, substituted amides, and a nitrile. The various N-substituted monomers were employed to identify the effect of the substitution pattern (i.e., the number and the chemical nature of the substituents) on the extents of P–N synergism. For the present study, both unsubstituted and N-substituted imides and amides were chosen including maleimide (MI), N-methyl maleimide (MeMI), N-ethyl maleimide (EtMI), N-phenyl maleimide (PhMI), acrylamide (AM), N,N-dimethyl acrylamide (DMA), and N-isopropyl acrylamide (NIPAM). The nitrile monomer used in the present study was acrylonitrile (AN).

2. Experimental Section

2.1. Materials

All the chemicals, reagents, and solvents used in the present study were purchased from Merck (formerly Sigma–Aldrich, Gillingham, UK), except for ethyl acetate and methanol (obtained from Fischer Scientific, Loughborough, UK). The solid compounds were used as received. The various liquid monomers and reagents, and other solvents were dried by keeping them over molecular sieves (4 Å). Styrene (St), also purchased from Merck, containing 10–15 ppm of 4-*tert*-butylcatechol as an inhibitor, was purified with the aid of a proprietary inhibitor removal column and stored in a sealed vessel, in a freezer, to prevent possible thermal polymerization. Similarly, a measured amount of AN with 35–45 ppm of 4-methoxyphenol as an inhibitor, was first

passed through the inhibitor removal column, and then, stored in a sealed bottle, in a fridge at ≈ 5 °C, until further use. Further, other solvents and reagents were purified, if necessary, by standard literature precedents^[23] and were stored under sub-ambient temperatures in a refrigerator, or in a freezer, as applicable. The synthetic procedure for the P-containing monomer, DEAMP, was reported elsewhere.^[24] The chemical structures of DEAMP and N-containing monomers used in the present study are given in **Figure 1**.

2.2. Preparation of Styrenic Polymers

The detailed procedure for the preparation of the control sample, that is, homo-polymer, PS, was reported in the authors' previous study.^[19] The *ter*-polymerization of St with DEAMP and N-containing monomers (i.e., MI, MeMI, EtMI, PhMI, AM, DMA, NIPAM, and AN, as the case may be), was carried out in a dimethylformamide (DMF) solution, using azobisisobutyronitrile (AIBN) as the initiator, at 60 °C \pm 0.2 °C. The procedure for the preparation of *ter*-polymers was similar to that for the homo-polymer, except for the longer polymerization times, as 24 h were required for achieving sufficient degrees of conversion. The amount of St and DEAMP was kept constant for the *ter*-polymerization, that is, St 8.32 g and DEAMP 2.22 g, respectively. The amounts of N monomers in the polymerization feed and the corresponding yields obtained after polymerization are given in **Table 1**. The polymers formed in the DMF solution were separated through precipitation in an excess of methanol, collected by a vacuum filtration, and washed several times with the non-solvent (methanol) for removing the unreacted monomers. The polymers, after the initial drying in a vacuum oven, were further purified by precipitation from the solutions in dichloromethane (DCM) into methanol. After filtration, the obtained products were again dried in a vacuum oven at 50 °C \pm 1 °C for at least 16 h before further examinations. For the preparation of *ter*-polymers, the molar ratio of St/DEAMP/N-monomer in the feed was kept nominal and constant, that is, 0.80 mol/0.10 mol/0.10 mol, respectively.

2.3. Characterization Techniques

The Fourier-Transform Infrared (FT-IR) spectroscopy, in the Attenuated Total Reflectance (ATR) mode, was carried out on finely powdered polymeric samples, using a Thermo Nicolet, Nexus Spectrometer (Nicolet, USA). The spectra were run (64 scans) over a wavenumber range of 4000 – 600 cm^{-1} and with a resolution of 4 cm^{-1} . ^1H and ^{31}P Nuclear Magnetic Resonance (NMR) spectra of the prepared polymers were recorded in deuterated solvents (CDCl_3 or d_6 -DMF, as the case may be) using a Bruker spectrometer (Bruker, Coventry, UK), operating at 600 MHz for protons. The ^1H NMR spectra of each polymer were used to calculate the degree of incorporation of P- and N- containing monomeric units, and subsequently, of the P and N loadings (wt%), as detailed in an earlier study.^[25]

Thermo-Gravimetric Analysis (TGA) runs were performed on the polymeric samples in the uniform powdered forms using a Mettler Toledo, TGA 2 (Leicester, UK) instrument, according to

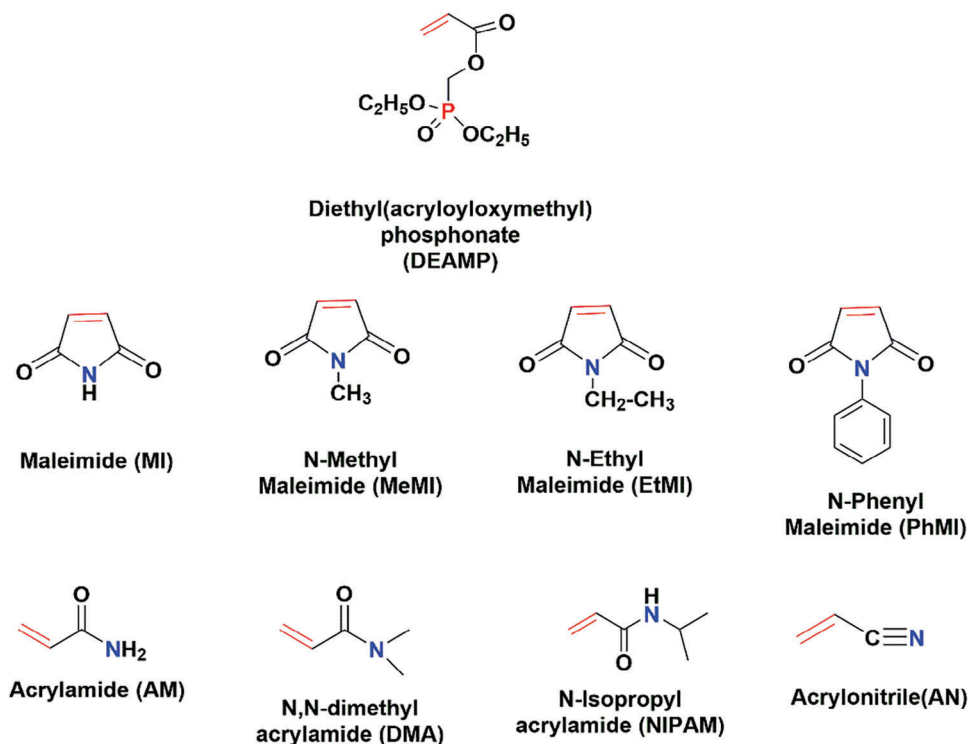


Figure 1. Chemical structures of DEAMP and N-containing monomers.

the procedure described in BS EN ISO 11358-1: 2014. The TGA runs were carried out on $\approx 8\text{--}9$ mg of sample, at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and flow rate of $50\text{ mL}\cdot\text{min}^{-1}$, under both nitrogen and air atmospheres, and in the temperature interval between $30\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$.

The TGA tests were also carried out at a heating rate of $60\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under the nitrogen atmosphere between $30\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ to enable a comparison with the results obtained from Pyrolysis Combustion Flow Calorimetry (PCFC) (i.e., at $60\text{ }^\circ\text{C}\cdot\text{min}^{-1}$). All samples were tested at least in duplicate to ensure the repeatability. The Differential Scanning Calorimetry (DSC) runs of polymeric materials were carried out using a Mettler Toledo DSC 1/700 instrument (Leicester, UK). A pinhole was made in the lid of the standard aluminium DSC crucible to release any excess pressure due to the formation of any gaseous

species during the runs. Each polymer sample, in a powdered form ($\approx 8\text{--}9$ mg), was heated from $30\text{ }^\circ\text{C}$ to $500\text{ }^\circ\text{C}$, under the nitrogen atmosphere, at a heating rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ and at a flow rate of $50\text{ mL}\cdot\text{min}^{-1}$.

The PCFC measurements of polymers were obtained using a Fire Testing Technology Ltd. (Gosport, UK) micro-scale combustion calorimeter according to the procedure described in ASTM D7309. For each run, an accurately weighed sample was first heated to $\approx 900\text{ }^\circ\text{C}$, at a heating rate of $1.0\text{ }^\circ\text{C}\cdot\text{s}^{-1}$, in a stream of nitrogen. The thermal degradation products were collected and then mixed with a stream of air prior to entering a combustion chamber maintained at $900\text{ }^\circ\text{C}$. All tests were run in triplicates, and the average values were reported.

The “bomb” calorimetric runs were performed, using a Parr 6200 calorimeter, to determine the heat of combustion in

Table 1. Characteristics of the modified styrenic polymers.

Polymer sample	Amount of N-monomer in the feed [g]	St/DEAMP/N-monomer ratio in polymer [mol%]	P content [wt%]	N content [wt%]	Yield [%]
PS	—	100/0.00/0.00	—	—	62.3
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -MI)	0.97	63.7/11.0/25.3	2.95	3.07	42.5
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -MeMI)	1.11	69.2/8.90/21.9	2.37	2.63	42.4
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -EtMI)	1.25	49.0/8.1/43.0	2.04	4.89	39.5
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -PhMI)	1.73	51.3/8.30/40.3	2.12	2.35	51.6
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -AM)	0.71	45.9/8.1/43.9	3.11	6.04	29.0
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -DMA)	0.99	86.9/11.1/2.00	2.93	0.24	42.7
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -NIPAM)	1.13	57.3/11.7/31.0	2.99	3.58	32.9
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -AN)	0.53	71.3/7.90/20.8	2.37	2.82	19.4

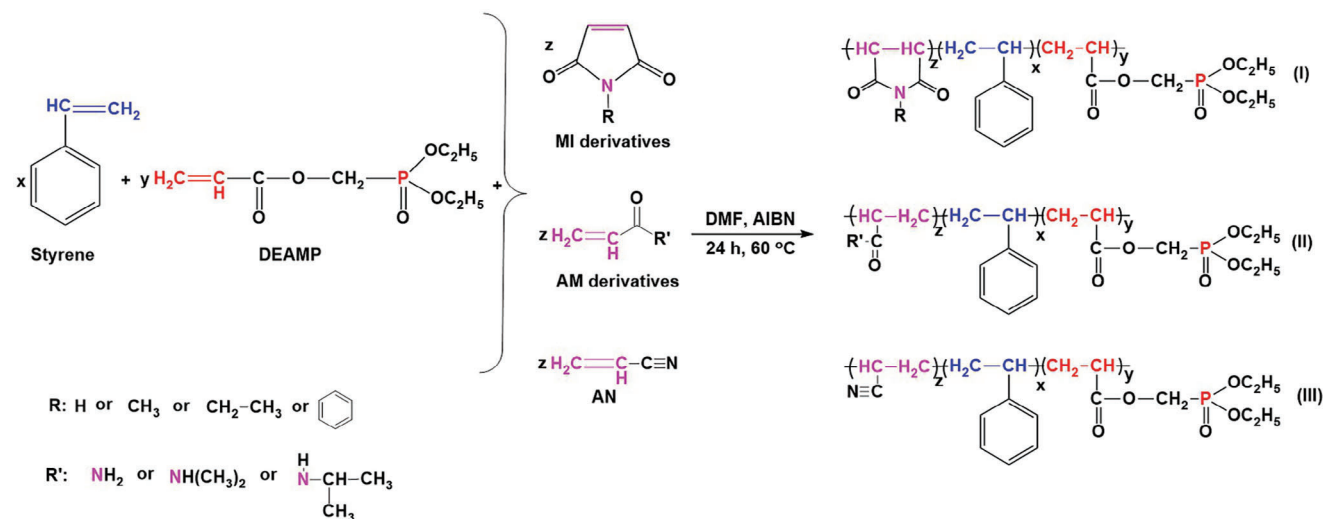


Figure 2. The schematic diagram of the routes of *ter*-polymerization of St, DEAMP, and N-containing monomers.

accordance with BS EN ISO 18125:2017. The measurements were conducted on the dry polymer sample, in the form of a pellet weighing ≈ 0.5 g. The “bomb” was filled with oxygen up to a pressure of 31 bars, and the sample was consequently ignited. For each sample, triplicate runs were done for better accuracy, and average values were reported in this paper.

3. Results and Discussion

A schematic representation of the polymerization routes for preparing styrenic *ter*-polymers is given in **Figure 2**. The *ter*-polymerization of St using DEAMP and an N-containing monomer in question was carried out in the DMF solvent over 24 h, at 60 °C. Generally, the products from *ter*-polymerization route were white powders irrespective of the monomers used. The scheme (I) in **Figure 2** represents the *ter*-polymerization of St with DEAMP and maleimide derivatives; while, the scheme (II) represents the *ter*-polymerization of St with DEAMP and acrylamide derivatives. Similarly, scheme III shows the *ter*-polymerization of St, using DEAMP and AN monomers.

3.1. Structural Characterization of Polymers

The chemical structures of styrenic polymers modified with DEAMP and different N-bearing monomers were confirmed by the results of FT-IR and NMR spectral analyses. The FT-IR (ATR) spectra of styrenic *ter*-polymers are given in **Figures S1 and S2**, Supporting Information. In the case of the modified polymers, the peaks characteristic for the base PS matrix, at 2840–3062 cm^{-1} , as well as the additional signals owing to the presence of C=O (1740–1660 cm^{-1}), P=O (1250–1254 cm^{-1}), P–O–C (1020–1025 cm^{-1}), and C–N (1342–1380 cm^{-1}) bonds, were observed in the FT-IR spectra.^[26–29] These features indicate the incorporation of both DEAMP and a chosen N-containing monomer into the polymeric chains of PS. Further, the chemical structures and constitutions of the *ter*-polymers

were confirmed from the ¹H-NMR and ³¹P-NMR spectra, given in **Figures S3–S10**, Supporting Information. The modified polymers showed ³¹P NMR signals within a range of 19 ppm (**Figures S3–S10**, Supporting Information). The P and N contents in *ter*-polymers, shown in **Table 1**, were determined from the corresponding ¹H-NMR spectra of the *ter*-polymers. It is relevant to note that the P and N contents within the product polymer mainly depend on the relative reactivities of P and N monomers with St and degrees of conversion, which could vary substantially, depending on the chemical structure of the monomers. Hence, the mole fraction of P/N monomeric units within the modified polymers could not be controlled with any amount of precision. However, it can be noted that the P content within the modified system was almost in the same range (i.e., 2–3 wt%); while, there was a difference in the N contents depending on their reactivity.

3.2. Thermo-Gravimetric Analysis

The thermal degradation studies of styrenic *ter*-polymers containing DEAMP and MI or its derivatives were carried out under the nitrogen atmosphere, and the corresponding data is given in **Table 2**. **Figure 3a** represents the thermograms (TGs) of PS and styrenic polymers modified with DEAMP and MI derivatives. The unmodified PS underwent its thermal degradation in a single stage, leaving almost no char residue at the end of the run (i.e., at 800 °C). It is also evident from the TG profiles that the *ter*-polymers containing DEAMP and an N-substituted MI (i.e., MeMI, or EtMI, or PhMI) monomers exhibited a three-step degradation. Meanwhile, *ter*-polymer with unsubstituted MI (poly(*S-ter*-DEAMP-*ter*-MI)) showed a two-step pyrolysis pattern (**Figure 3a**). From the TG curves (**Figure 3a**), it is evident that the thermal decomposition of all styrenic *ter*-polymers began earlier ($T_{\text{onset-1}} = 127\text{--}162$ °C) than the unmodified PS (**Table 2**). It can be expected that the onset of thermal degradation at lower temperatures observed for the *ter*-polymers could be due to the initial cracking of the pendant P-containing groups, which could possibly be influenced by the MI groups incorporated into the styrene

Table 2. TGA data for PS and obtained *ter*-polymers under the nitrogen and air atmospheres.

Polymer Sample	$T_{\text{onset-1}}$ [°C]	$T_{\text{onset-2}}$ [°C]	$T_{\text{onset-3}}$ [°C]	T_{max} [°C]	CR [wt%]
	N ₂ /air	N ₂ /air	N ₂ /air	N ₂ /air	N ₂ /air
PS	–/–	–/–	399/318	449/402	0.70/0.30
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -MI)	147/140	–/–	343/333	410/393	25.0/44.1
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -MeMI)	127/119	293/286	329/321	387/363	9.10/15.8
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -EtMI)	162/105	291/276	345/319	386/365	8.30/16.8
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -PhMI)	145/110	303/286	334/328	382/381	10.5/23.0
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -AM)	–/185	297/303	327/346	382/352	9.20/22.5
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -DMA)	–/140	304/322	340/352	388/416	7.80/20.5
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -NIPAM)	–/114	292/279	333/312	383/357	9.00/19.8
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -AN)	–/–	300/279	329/320	384/357	8.50/21.5
Average standard deviation	±0.9/±0.2	±0.8/±0.5	±0.9/±0.8	±1.0/±0.4	±0.5/±0.5

$T_{\text{onset-1}}$: first step degradation temperature of styrenic *ter*-polymers, $T_{\text{onset-2}}$: second step degradation temperature of styrenic *ter*-polymers, $T_{\text{onset-3}}$: main chain degradation temperature of polymers, T_{max} : temperature of a maximum rate of degradation, and CR: char residue at 500 °C.

backbone.^[19] Further, the *ter*-polymers of styrene with DEAMP and one of the N-substituted maleimides, MeMI, EtMI, or PhMI, demonstrated a temperature range corresponding to the second mass loss ($T_{\text{onset-2}}$), at ≈291–303 °C. The degradation steps corresponding to $T_{\text{onset-1}}$ and $T_{\text{onset-2}}$ of the abovementioned *ter*-polymers were also visible in the DTG curves (Figure S11a, Supporting Information). The second step of thermal degradation could be due to the release of ethylene molecules from the incorporated phosphonate moieties via *cis*-elimination reactions.^[26,30] In fact, the $T_{\text{onset-2}}$ of poly(S-*ter*-DEAMP-*ter*-MI) was not easily identifiable in the TG curve, whereas the same degradation step was visible in its DTG curve (Figure S11a, Supporting Information) as a small peak at a temperature of 308 °C.

When the temperature reached the 330–360 °C range, the modified polymers seemed to undergo the main chain degradation (Table 2). Another important feature is the one related to the char formation propensities of the *ter*-polymers. It was observed that, at 500 °C, under nitrogen atmosphere, poly(S-*ter*-DEAMP-*ter*-MI) showed an increase of 25.0 wt% in the char formation, as opposed to 0.5 wt% measured for the control sample. Nevertheless, the use of N-substituted maleimides as N-monomers lowered the amounts of char formed by the corresponding *ter*-polymers (Table 2). Meanwhile, the presence of N-phenyl sub-

stituent within maleimide slightly enhanced the char residue formation to 10.5 wt%, which could be due to the presence of the aromatic ring in PhMI. The char residues formed at 500 °C were further found to be reduced as the temperature increased to 800 °C. It can be assumed here that the significant increase in the amount of char residue was due to the possible synergistic action between the P- and N- containing moieties. Among the *ter*-polymers, the P–N synergism was found to be more prominent for poly(S-*ter*-DEAMP-*ter*-MI), which was manifested by a 22.2 wt% increase in the char residue at 800 °C in the inert atmosphere. At the same time, the P–N synergistic effect was less pronounced when an N-substituted MI was used as the N-containing monomer, together with DEAMP, during polymerization reaction. Among the styrenic *ter*-polymers with alkyl substituted MI groups, it was not straightforward to identify which one exhibited the enhanced P–N synergistic action. Indeed, poly(S-*ter*-DEAMP-*ter*-MeMI) showed enhanced char formation, whereas poly(S-*ter*-DEAMP-*ter*-EtMI) had higher main chain degradation temperatures. The alkyl substitution of H atoms in the N–H group of MI seemed to result in a slightly decreased interaction of the pendant N-containing moieties with the P-monomer units in the polymeric chains. At the same time, the presence of phenyl (Ph) groups within MI units appeared to boost the P–N synergistic

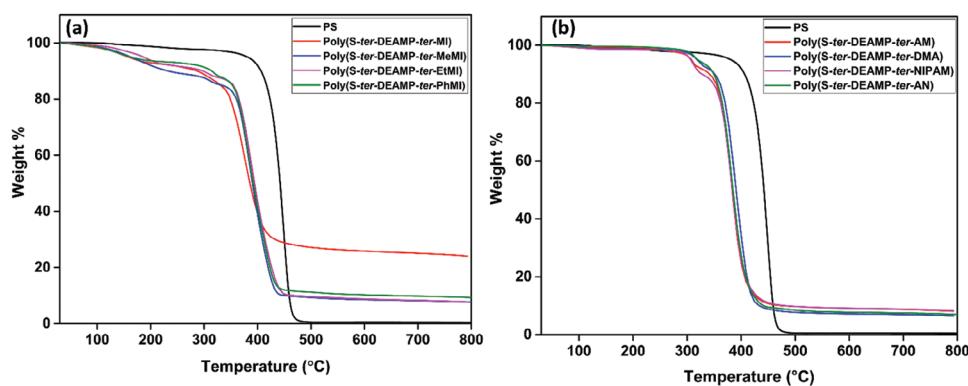


Figure 3. TG curves obtained at a heating rate of 10 °C·min^{−1} for a) PS and styrenic *ter*-polymers containing DEAMP and MI-derived monomers and b) PS and styrenic *ter*-polymers containing DEAMP, AM-derivatives, or AN under the nitrogen atmosphere.

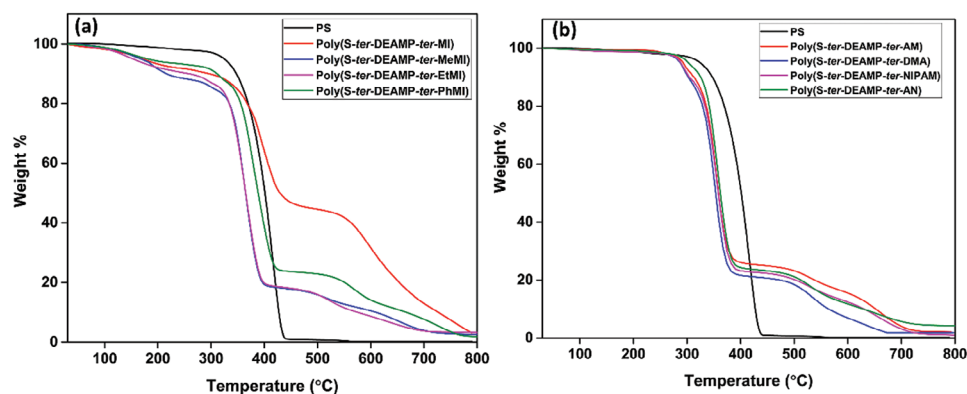


Figure 4. TG curves obtained at a heating rate of 10-min^{-1} for a) PS and *ter*-polymers containing DEAMP and MI-derived monomers and b) PS and styrenic *ter*-polymers containing DEAMP, AM-derivatives, or AN under the air atmosphere.

interactions compared to those of the polymers with alkyl substituted MIs (Me-MI or Et-MI).

Figure 3b presents the TG curves of styrenic *ter*-polymers containing DEAMP, AM or its derivatives, or acrylonitrile (AN) used as N-monomers under the nitrogen atmosphere. The corresponding DTG curves of *ter*-polymers are given in Figure S11b, Supporting Information. It can be seen that the thermal degradation of these *ter*-polymers was characterized by a two-step mass loss process. It is also interesting to note that the $T_{\text{onset-1}}$ observed in the TGA curves of the *ter*-polymers with MI-based units was absent in the case of the *ter*-polymers with AM derivatives or AN units. This could imply that both sets of DEAMP containing styrenic *ter*-polymers with MI and AM/AN units followed different pyrolytic routes during their thermal degradation. However, the $T_{\text{onset-2}}$ appeared to be in the same temperature range (293–304 °C) as that of N-substituted MI and DEAMP containing *ter*-polymers (Table 2). Meanwhile, the alkyl substitution of hydrogen atoms within the amide moieties slightly lowered the $T_{\text{onset-2}}$ of the corresponding *ter*-polymers (Table 2). The lower degradation temperature of *ter*-polymers could be due to the interaction of N-containing moieties with the DEAMP units in the PS chains. The char residue formation by the *ter*-polymers was also found to be increased by the presence of DEAMP and AM monomers that were covalently attached to the polymeric chains. The extent of char formation, at 500 °C, increased from 0.7 wt% for PS to 7.8–9.2 wt% for modified polymers. Among these *ter*-polymers, the P–N synergism, gauged mainly by the charring ability, was revealed more in the polymers containing unsubstituted amide groups rather than alkyl substituted amide units.

The TG curves of styrenic *ter*-polymers containing DEAMP and MI-derived monomers under the air atmosphere are given in Figure 4a. The evaluated data are detailed in Table 2. The TG data obtained in the air showed that the onset of mass loss of all the polymers started at temperatures 20–80 °C lower than those recorded under the inert atmosphere (Figure 4a and Table 2). This is expected as the presence of oxygen can generally trigger an earlier thermal-oxidative degradation of the polymers.^[30] It is also interesting to note that the TG residues formed at 500 °C by the *ter*-polymers in the oxidative atmosphere were 10–20% higher than those obtained in the inert atmosphere. For example, poly(S-*ter*-DEAMP-*ter*-MI) had a nearly 20% increase in char

residues in the oxidative atmosphere (44.0 wt%) rather than under the inert one (25.0 wt%). Indeed, char residue formation of *ter*-polymers during thermal degradation was lowered in the presence of alkyl and phenyl groups inside the MI units (Table 2). Evidently, the substitution of H atoms within the MI units with relatively large and bulky phenyl groups, as compared to methyl and ethyl substituents, exhibited higher char yields than *ter*-polymers containing MeMI and EtMI. Thus, it can be suggested here that the presence of aromatic side groups (Ph) stabilized the char and improved P–N synergistic interactions.

Further, under the oxidative atmosphere, the *ter*-polymers exhibited a third decomposition step at a temperature above 500 °C (as appeared in the TG [Figure 4a] and DTG [Figure S12a, Supporting Information] curves of the *ter*-polymers). It is to be assumed here that the solid residue formed at 500 °C and underwent secondary oxidation reaction(s) as the temperature increased to 800 °C. The oxidation of the char residue was also clearly visible from the DTG curves (Figure S12a, Supporting Information), during the 500–800 °C temperature interval. Meanwhile, the relatively high amounts of char residue formed by the *ter*-polymers under the oxidative atmosphere at 500 °C were reduced nearly to 3 wt%, at 800 °C (Figure 4a). Thus, in the oxidative atmosphere, it can be seen that the *ter*-polymers of styrene containing DEAMP and MI-derived monomers exhibited excellent char forming abilities, especially at 500 °C. Nevertheless, the P–N synergistic interaction seemed to be stronger when the unsubstituted MI was used, whereas the presence of N-substituted MI units in the polymeric chains lowered the extent of synergistic effects between P- and N-containing moieties during the thermal degradation of the *ter*-polymers.

Figure 4b presents the TG curves of PS and *ter*-polymers containing DEAMP, AM, or its N-substituted derivatives, or AN, monomers under the air atmosphere. As observed in the case of *ter*-polymers containing DEAMP and MI derivatives, the degradation temperature of the *ter*-polymers was lower than that recorded under the inert atmosphere (Table 2). In the oxidative atmosphere, the most important finding is related to the formation of char residues. It can be also noted that, for the modified polymers, there was an increase in the char formation by 10–13 wt% at 500 °C, compared to the values measured under the inert atmosphere (Table 2). This increase in char yield was observed in the case of all *ter*-polymers irrespective of the chemical nature of

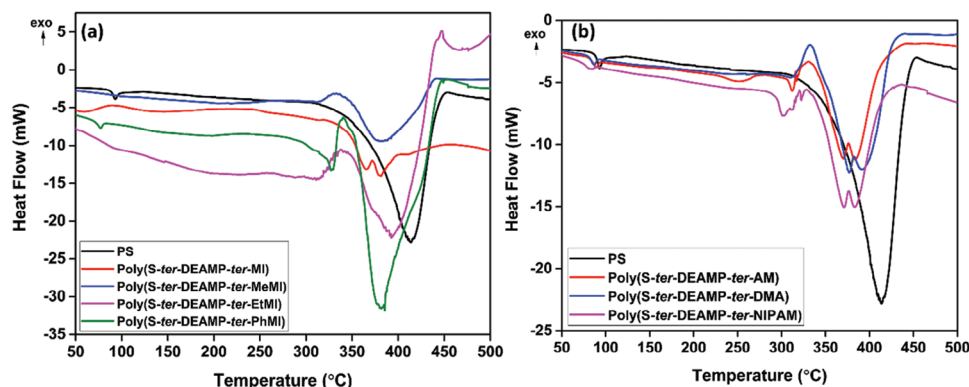


Figure 5. DSC curves obtained under the nitrogen atmosphere at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ for PS and styrenic *ter*-polymers containing: a) DEAMP and MI-derived monomers; b) DEAMP with AM-derived monomers.

N-containing monomers. For instance, *ter*-polymer with amide moieties exhibited an increase of 10.8–13.3% and polymer with nitrile units (poly[S-*ter*-DEAMP-*ter*-AN]) showed an increase of 12.4% in the char yield under the oxidative rather than under the inert atmosphere. However, the residue formed at $500\text{ }^{\circ}\text{C}$ underwent further oxidation to nearly 1.2–4.4 wt% as the temperature increased to $800\text{ }^{\circ}\text{C}$ (visible in the corresponding DTG curves, Figure S12b, Supporting Information).

3.3. Differential Scanning Calorimetry

The DSC plots obtained for PS and styrenic *ter*-polymers under the nitrogen atmosphere are given in Figure 5. The unmodified PS underwent a single stage endothermic decomposition in a temperature range of $300\text{--}452\text{ }^{\circ}\text{C}$.^[30] As opposed to PS, the *ter*-polymers with built-in DEAMP and phenyl substituted MI units (Figure 5a) exhibited a smaller endotherm in a temperature range of $290\text{--}330\text{ }^{\circ}\text{C}$. It was proposed in ref. [30] that the initial endothermic decomposition ($\approx 300\text{ }^{\circ}\text{C}$) could be possibly associated with the release of ethylene molecules from the ethyl groups of the “side arms” of the phosphonate groups. However, the endothermic effect preceding the main decomposition step was not clearly identifiable in the DSC curves of other maleimide-containing *ter*-polymers, which could be due to the overlapping with the main chain decomposition. The endothermic peak was observed in the temperature range of $320\text{--}350\text{ }^{\circ}\text{C}$, which could be attributed to the main chain decomposition of the *ter*-polymers. In the case of styrenic *ter*-polymers containing the monomeric units of DEAMP, AM, or an N-substituted acrylamide, the DSC curves demonstrated an endothermic decomposition step in a narrow temperature interval of $290\text{--}330\text{ }^{\circ}\text{C}$ first, followed by the endothermic peak of the main chain decomposition in a wider temperature range of $340\text{--}440\text{ }^{\circ}\text{C}$ (Figure 5b). It could also be seen that the main endothermic peak of *ter*-polymers centered around $370\text{--}390\text{ }^{\circ}\text{C}$ were split into two “shoulders”. Evidently, when compared to the unmodified PS, the main chain decomposition pattern of these *ter*-polymers was altered, presumably owing to the incorporation of DEAMP and maleimide/amide monomeric units.

It could be observed that the reactive modification of PS with DEAMP and N monomers considerably reduced the heat of py-

rolysis (ΔH_{pyro}) values, as given in Table S1, (Supporting Information). When compared to neat PS, the use of MI along with DEAMP for the modification of PS chains resulted in a sharp decrease of the ΔH_{pyro} , from 717 to 190 J g^{-1} .^[19] This drop in the values of ΔH_{pyro} implies a strong impact of P and N monomeric units on the polymer chains during their decomposition. Moreover, when compared to poly(S-*ter*-DEAMP-*ter*-MI), the N-methyl substitution in the MI units increased the ΔH_{pyro} value to 413 J g^{-1} . Meanwhile, *ter*-polymers containing N-ethyl and phenyl substituted MI units had higher ΔH_{pyro} than that of unmodified PS (Table S1, Supporting Information). In the case of poly(S-*ter*-DEAMP-*ter*-AM), a 50% reduction of the ΔH_{pyro} value (358 J g^{-1}) was achieved compared to that of PS. Moreover, using mono- or di-substituted acrylamide as an N-containing monomer increased the ΔH_{pyro} of poly(S-*ter*-DEAMP-*ter*-NIPAM) to 369 J g^{-1} when compared to the *ter*-polymer containing unsubstituted AM (Table S1, Supporting Information).

Thus, a good correlation between the DSC and TGA results revealed that poly(S-*ter*-DEAMP-*ter*-MI) and poly(S-*ter*-DEAMP-*ter*-AM), forming higher char residues at $500\text{ }^{\circ}\text{C}$, had the lower ΔH_{pyro} values. The remarkable increase in the char residue of *ter*-polymers could be due to the synergistic action between the incorporated P- and N- containing units. Hence, it can be also assumed that the P–N synergistic interactions occurring in the *ter*-polymers, where N atoms were bonded to H atoms (non-substituted), could have resulted in the lower ΔH_{pyro} values, compared to the *ter*-polymers containing substituted MI and AM units. Meanwhile, using the substituted functions of MIs and AMs as the N monomers lowered the char residue formation at $500\text{ }^{\circ}\text{C}$; whilst, increasing the ΔH_{pyro} values, which grew even further as the number of substituents at N increased. This reflects that the P–N synergistic action within the *ter*-polymers diminished when the N-substitution increased.

3.4. Combustion Studies of Styrenic *Ter*-Polymers Containing DEAMP and Different N-Monomers

The detailed data of the measured combustion parameters using PCFC are given in Table 3. Among the various combustion parameters, the HRC served as a reliable indicator of a polymer flammability.^[24,25] Clearly, the incorporation of DEAMP units

Table 3. PCFC data of PS and modified styrenic polymers.

Sample	HRC [$\text{J g}^{-1}\cdot\text{K}^{-1}$]	pHRR [W g^{-1}]	THR [kJ g^{-1}]	Temp to pHRR [$^{\circ}\text{C}$]	EHC [kJ g^{-1}]	CR [wt%]	ΔH_{comb} [kJ g^{-1}]
PS	753	751	36	434	36.4	0.00	40.4
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -MI)	340	339	21	392	25.7	15.9	31.3
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -MeMI)	431	432	26	415	27.3	4.60	31.7
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -EtMI)	440	439	29	420	31.4	5.70	31.5
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -PhMI)	455	455	29	403	31.2	5.70	33.3
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -AM)	617	620	32	405	34.1	4.90	33.9
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -DMA)	621	621	33	411	36.2	6.90	35.3
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -NIPAM)	628	628	32	405	33.9	4.50	35.4
Poly(S- <i>ter</i> -DEAMP- <i>ter</i> -AN)	597	598	33	409	35.1	4.90	36.9
Average standard deviation	± 6.8	± 7.0	± 0.3	± 0.7	± 0.5	± 1.0	± 0.3

HRC: heat release capacity, pHRR: peak heat release rate, THR: total heat release, EHC: effective heat of combustion, CR: char residue.

along with N moieties into PS chains resulted in a decrease of heat release capacity (HRC). As shown in Table 3, among the N monomers used, the incorporation of MI units resulted in an almost 50% reduction of HRC compared to that of PS. Meanwhile, in the case of the *ter*-polymers containing N-methyl and N-ethyl substituted cyclic imides, the HRC values reduced by 43% and 41%, respectively, when compared to the unmodified PS. This confirms that the incorporated MI units interacted with the chemically bound phosphonate moieties, and thereby, brought down the HRC values. The lower HRC values of styrenic *ter*-polymers containing DEAMP and MI (unsubstituted and substituted) revealed their reduced flammability and combustibility. Similarly, the peak heat release rate (pHRR) of these *ter*-polymers was also dramatically decreased (Table 3). When compared to the *ter*-polymer containing unsubstituted MI units, the pHRR and HRC values were slightly elevated for the *ter*-polymers with alkyl and phenyl substituents within the MI units; however, they remained well below the values obtained for the control sample of PS. It can be viewed that the decrease in the HRC and pHRR values of these *ter*-polymers is linked to the P–N synergistic action between DEAMP and MIs.^[31] The curves of the heat release rate (HRR) versus temperature for PS and styrenic *ter*-polymers containing DEAMP and MI-derived monomers are shown in Figure 6a. The reduction in the HRR is evident from Figure 6a. Indeed, much smaller peaks were observed between

300 °C and 360 °C, which corresponded well to the “shoulders” registered on the TG traces ($T_{\text{onset-2}}$: Table 2) and DTG curves of these *ter*-polymers.

The incorporation of DEAMP and the MI units contributed to the reduction of the total heat release (THR) to 22 kJ g^{-1} , from 36 kJ g^{-1} for PS. Similar to other combustion parameters, the THR value was slightly higher when polymeric chains had the substituents within the MI units but always remained lower than that of PS (Table 3). Another combustion parameter is the effective heat of combustion (EHC). When compared to the control sample of PS, the use of MI moieties along with DEAMP reduced the EHC by 29% for poly(S-*ter*-DEAMP-*ter*-MI). Meanwhile, there was a reduction of 25% in EHC for poly(S-*ter*-DEAMP-*ter*-MeMI) and 13% for poly(S-*ter*-DEAMP-*ter*-EtMI). Hence, it can be stated that the combustion inhibitory efficiency of P-containing FRs was enhanced by the presence of MI-containing groups; the unsubstituted MI units had better combustion inhibitory effects compared to the alkyl- and phenyl-substituted MI units. Generally, it is considered that the lower EHC was associated with the gaseous-phase fire retarding effect of P-containing fire retardants during combustion.^[32] From Table 3, it is evident that the char formation of these *ter*-polymers increased by 4.6–15.9 wt%.

Figure 6b presents the curves of HRR versus temperature for PS and styrenic *ter*-polymers containing DEAMP and either an amide-based monomer or AN. It is clear from Figure 6b that the

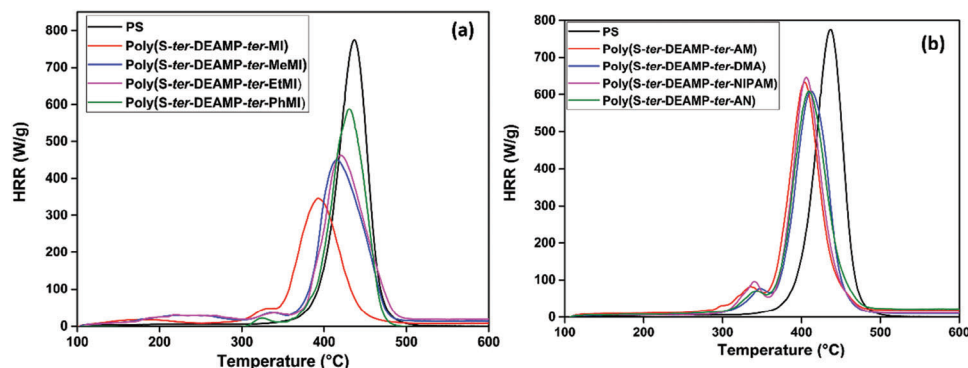


Figure 6. HRR versus temperature curves of PS and styrenic *ter*-polymers containing: a) DEAMP and the MI-derived monomer; b) DEAMP and the AM-derived, or AN, monomer.

styrenic *ter*-polymers with the built-in amide moieties were characterized by the reduced HRR values. However, when compared to the modification using MI and its derivatives, the decrease in the values of combustion parameters for the *ter*-polymers with acrylamides was more modest. For example, the *ter*-polymer, poly(*S-ter*-DEAMP-*ter*-AM), had the HRC values reduced by 18%, to 617.7 from 753.3 J g⁻¹·K⁻¹ for PS, compared to a 50% reduction for poly(*S-ter*-DEAMP-*ter*-MI). A similar trend was observed in the case of pHRR values of styrenic *ter*-polymers containing amide moieties. The substitution at the N atom within the acrylamide led to an increase in the combustion parameters of the corresponding *ter*-polymers, compared to those obtained for the *ter*-polymer with unsubstituted acrylamide units; while, remaining lower than characteristics of unmodified PS (Table 3). Evidently, the EHC value was reduced following the incorporation of both amide and DEAMP units into the polymeric chain (Table 3). Meanwhile, the *ter*-polymerization of St with DEAMP and AN also positively influenced the combustion behavior of PS. The HRC and pHRR values of poly(*S-ter*-DEAMP-*ter*-AN) were reduced by 21% when compared to those of PS.

The HRC values and the char residues obtained at 800 °C, under the nitrogen atmosphere from TGA of *ter*-polymers were plotted (Figure S13, Supporting Information). As seen from Figure S13, Supporting Information, the unmodified PS left behind an almost zero amount of residue but was characterized by the highest value of HRC. Meanwhile, in the case of the modified polymers with DEAMP and N-units, the HRCs of polymers were found to be reduced; while, the char yields, were enhanced. For example, as the char formation by poly(*S-ter*-DEAMP-*ter*-MI) was increased to 20 wt% from 0.3 wt% for PS, the HRC was reduced considerably, by more than 50% (to 340 J g⁻¹·K⁻¹) compared to PS (753 J g⁻¹·K⁻¹). A similar trend was observed for other *ter*-polymers. Hence, the reduction of the HRC of the modified polymers was related to the char formation capability of the *ter*-polymer in question.

The heat of combustion (ΔH_{comb}) values, measured with the aid of an adiabatic “bomb” calorimeter, for PS and styrenic *ter*-polymers are also given in Table 3. As compared to the neat PS, the ΔH_{comb} values of all modified polymers were reduced, which proves the combustion inhibitory effects of the incorporated DEAMP and N monomeric units.

Thus, by correlating TGA, DSC, PCFC, and “bomb” calorimetry results, it is evident that those *ter*-polymers forming higher char residues had lower combustion attributes such as HRC, pHRR, THR, EHC, and ΔH_{comb} . For instance, among the two different sets of *ter*-polymers (i.e., *ter*-polymers containing derivatives of maleimide and acrylamide), poly(*S-ter*-DEAMP-*ter*-MI) and poly(*S-ter*-DEAMP-*ter*-AM) had higher char residues, especially at 500 °C, and lower combustion parameters such as HRC, pHRR, and ΔH_{comb} ; and hence, exhibited the improved combustion inhibitory action. It can be assumed that the remarkable enhancement in the char residue and combustion inhibition could be due to the synergistic interaction between the incorporated DEAMP and N monomers. Meanwhile, the combustion parameters of polymers increased with the substitution of H atoms bonded to the N atoms within maleimide and acrylamide units. This implies that the presence of N–H bonds could be essential to exert significant synergistic interaction.

3.5. A Comparison of the P–N Synergistic Influence on DEAMP Containing *Ter*-Polymers

The results presented in previous sections clearly indicated that there is an interaction between the PS matrix and the modifying groups. From the thermal and calorimetric testing results detailed in this study, it is obvious that combustion inhibition had been significantly increased by the incorporation of P- and N-containing groups, possibly by exerting some P–N synergistic effects. Hence, in order to evaluate the degree of fire retardance enhancement and the dependence of a P–N influence on different chemical environments of P and N atoms, some generalizations of the relevant parameters obtained from TGA (at 60 °C·min⁻¹, under the nitrogen atmosphere), PCFC, and “bomb” calorimetry were carried out. Figure 7a represents the plots of the char residues obtained through TGA (under the nitrogen atmosphere) and PCFC for the neat PS and for styrenic polymers containing DEAMP and N-monomeric units. Meanwhile, Figure 7b represents the plots of EHC and ΔH_{comb} obtained through PCFC and “bomb” calorimetry of PS and styrenic polymers containing DEAMP and N-monomer units. For convenience, PS and modified polymers are labeled as sample numbers in the X-axis of Figure 7a,b and as follows: 1-PS, 2-Poly(*S-ter*-DEAMP-*ter*-MI), 3-Poly(*S-ter*-DEAMP-*ter*-MeMI), 4-Poly(*S-ter*-DEAMP-*ter*-EtMI), 5-Poly(*S-ter*-DEAMP-*ter*-PhMI), 6-Poly(*S-ter*-DEAMP-*ter*-AM), 7-Poly(*S-ter*-DEAMP-*ter*-DMA), 8-Poly(*S-ter*-DEAMP-*ter*-NIPAM), and 9-Poly(*S-ter*-DEAMP-*ter*-AN).

From Figure 7a, it can be noted that the neat PS yielded a near zero char residue in both TGA and PCFC tests. However, the char residue was increased following the modification of PS with P-(DEAMP) and N-groups, indicating the effect of P–N synergistic actions. The enhanced char yield was potentially linked to the synergistic action of nitrogen and phosphorus bearing groups, resulting in the formation of various P–N intermediates during thermal decomposition. It can be seen that the *ter*-polymer containing cyclic imide, MI (i.e., poly(*S-ter*-DEAMP-*ter*-MI)), increased the char yield by 23% (TGA) and by 16% (PCFC); while, in the case of *ter*-polymer containing amide AM (i.e., poly(*S-ter*-DEAMP-*ter*-AM)), the char residue was enhanced by only 8% (TGA) and 5% (PCFC). It is also relevant to note that the P and N content calculated from ¹H NMR spectra (as given in Table 2) was higher for poly(*S-ter*-DEAMP-*ter*-AM) (i.e., P/N content: 3.11/6.04 wt%) than for poly(*S-ter*-DEAMP-*ter*-MI) (i.e., P/N content: 2.95/3.07 wt%). The variations in the P and N contents within the modified polymer could be due to the reactivity difference of selected monomers, which was expected to depend on the chemical nature of monomers. Despite the lower P and N contents, poly(*S-ter*-DEAMP-*ter*-MI) exhibited higher char formation than the styrenic *ter*-polymer containing AM units. This implies that the P–N synergism could be more prominent in the *ter*-polymers containing N monomer as a cyclic imide rather than amide. Meanwhile, it can be assumed that the substitution (the size and the number of substituents) within the imide and amide moieties influenced the reactivity and interactions with P groups. Evidently, the alkyl and phenyl substitutions of maleimide units led to a drastic reduction in the char yield of the corresponding *ter*-polymer as opposed to unsubstituted units (Figure 7a). The lower char yield of those polymers could be linked to their lower

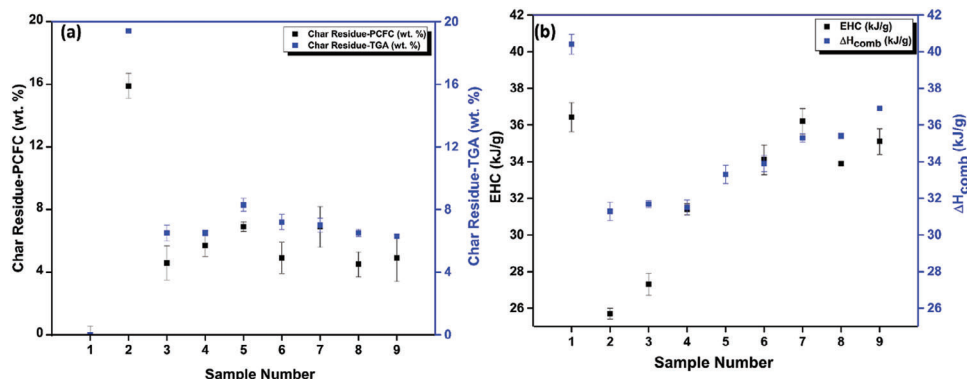


Figure 7. a) Plots of char residue obtained through TGA and PCFC; b) plots of EHC and ΔH_{comb} for PS and styrenic polymers containing DEAMP and different N-monomer units. Sample number as follows: 1-PS, 2-Poly(S-*ter*-DEAMP-*ter*-MI), 3-Poly(S-*ter*-DEAMP-*ter*-MeMI), 4-Poly(S-*ter*-DEAMP-*ter*-EtMI), 5-Poly(S-*ter*-DEAMP-*ter*-PhMI), 6-Poly(S-*ter*-DEAMP-*ter*-AM), 7-Poly(S-*ter*-DEAMP-*ter*-DMA), 8-Poly(S-*ter*-DEAMP-*ter*-NIPAM), and 9-Poly(S-*ter*-DEAMP-*ter*-AN).

P and N contents compared to *ter*-polymer containing unsubstituted units (Table 2). Apparently, poly(S-*ter*-DEAMP-*ter*-PhMI) had lower P and N content (P/N content: 2.12/2.35 wt%) than the polymer containing alkyl substituted maleimide units (P/N content: 2.37/2.63 wt%) (Table 2). However, poly(S-*ter*-DEAMP-*ter*-PhMI) had exhibited better char formation than the *ter*-polymers with alkyl substituted maleimide units (Figure 7a). This implies that the phenyl groups inside the MI monomeric had a slightly better synergistic interaction with DEAMP compared to polymer with alkyl substituted MI units. Further, amide containing *ter*-polymers also decreased the char yield after the substitution of NH_2 in acrylamide side group. In addition, the *ter*-polymer containing AN promoted charring to 7.9% (TGA) and 6.3% (PCFC). In this case, the synergistic interaction between DEAMP and AN unit was found to be limited compared to the other prepared *ter*-polymers. However, the charring by poly(S-*ter*-DEAMP-*ter*-AN) was more efficient than by neat PS.

As it can be seen from Figure 7b, the ΔH_{comb} values obtained from “bomb” calorimetry (i.e., in the case of complete combustion) were higher than the corresponding EHC values calculated from PCFC (i.e., the case of incomplete and forced non-flaming combustion) for most of the modified polymers, except for poly(S-*ter*-DEAMP-*ter*-AM) and poly(S-*ter*-DEAMP-*ter*-DMA). As mentioned above, although poly(S-*ter*-DEAMP-*ter*-MI) had lower P and N content than that of poly(S-*ter*-DEAMP-*ter*-AM), the incorporation of MI lowered the EHC by 29% and ΔH_{comb} by 23% when compared to similar values of PS. Meanwhile, for the *ter*-polymer containing AM (poly(S-*ter*-DEAMP-*ter*-AM), the EHC was lowered by 6% and ΔH_{comb} by 16%. This indicates that the chemical environment of N atoms influenced the synergistic interaction with DEAMP monomer. However, the substitutions within the imide and amide monomers increased the heat of combustion of corresponding *ter*-polymers (Figure 7b). Generally, the values of EHC and ΔH_{comb} were primarily related to the gaseous-phase activity of a FR.^[19] Hence, it can be stated that the reactively modified polymers underwent their fire retarding action via condensed- and gaseous-phase activities and the P–N synergistic effect was more pronounced in the *ter*-polymers containing maleimide as an N monomer. The results also showed that the presence of unsubstituted H atoms bound to N atoms

within MI and AM units was essential for exerting higher synergism and lower combustibility, possibly due to the hydrogen bonding between the incorporated DEAMP and MI/AM units.

Figure 8 represents a comparison of the HRC and EHC values measured on the samples of PS, *co*-polymers containing either DEAMP or MI units (reported previously^[19]), and the *ter*-polymer, poly(S-*ter*-DEAMP-*ter*-MI). It is clear from Figure 8 that the incorporation of only DEAMP into the polymeric chains reduced the HRC and EHC moderately. Meanwhile, the use of MI alone for the modification of PS resulted in the increased HRC and slightly lowered EHC value when compared to those of PS. Interestingly, the simultaneous incorporation of DEAMP and MI into the polymeric chains had dramatically lowered both the HRC and EHC values (nearly a 50% reduction was observed) as compared to PS and the corresponding *co*-polymers. It is relevant to note that the P and N contents in the *co*-polymers^[19] were comparable with those of poly(S-*ter*-DEAMP-*ter*-MI). For example, poly(S-*co*-DEAMP) contained 3.07% P and poly(S-*co*-MI) contained 3.72%

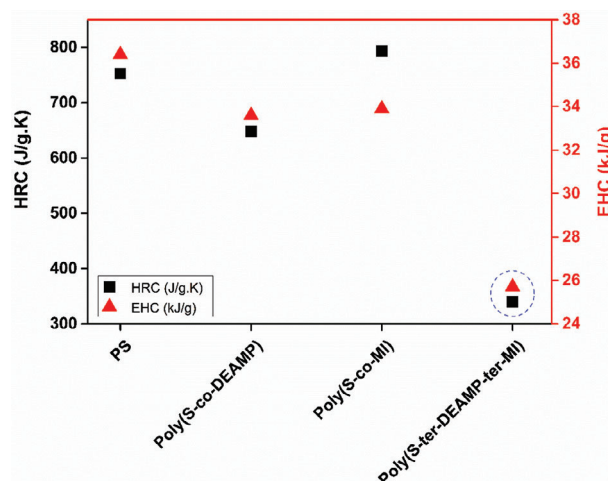


Figure 8. A comparison of the heat release capacity (HRC) and effective heat of combustion (EHC), measured using PCFC, for the unmodified PS, *co*-polymers, poly(S-*co*-DEAMP), and poly(S-*co*-MI),^[19] and the *ter*-polymer, poly(S-*ter*-DEAMP-*ter*-MI).

N; while, the *ter*-polymer, poly(*S-ter*-DEAMP-*ter*-MI) had 2.95% of P and 3.07% of N. These changes in combustion parameters prove the positive influence of N-containing compounds (i.e., a P–N synergism), when integrated along with DEAMP, in reducing combustion characteristics of styrenic polymers. Apparently, the results also showed that the *ter*-polymerization of St with DEAMP, and N monomers would be an upcoming and promising route for imparting fire retardancy for PS via exerting P–N synergism.

4. Conclusion

This study explored the influence of phosphonate units, DEAMP, incorporated into the polymeric chains of PS in combination with a N-containing monomer (from the class of cyclic imides, amides, or acrylonitrile) on thermal and combustion characteristics of *ter*-polymers. The successful incorporation of these monomeric units (P and N) was confirmed by the FT-IR, ¹H, and ³¹P NMR analyses. The TGA results of the *ter*-polymers indicated the influence of synergistic interactions between P- and N- containing groups on the thermal degradation patterns and combustion attributes of styrene-based polymers. It was also established that chemical incorporation of P- and N-groups resulted in an increase of charring ability and lowered the mass loss rate of the modified polymeric products. However, the thermal degradation of all modified polymers commenced at a lower temperature than that of the unmodified PS. Most importantly, the reactive modification of PS had increased its char-forming ability, indicating a condensed phase fire retardant activity.^[18] Interestingly, at 500 °C, the modified polymers demonstrated a 10–20% increase in residue formation under the oxidative atmosphere than that under the inert atmosphere.

Among the N-containing monomers used, the cyclic imides, along with DEAMP, were found to be more effective in reducing the combustibility of PS than amides. The *ter*-polymer, poly(*S-ter*-DEAMP-*ter*-MI), demonstrated almost a 50% reduction in the pHRR and HRC values, whereas poly(*S-ter*-DEAMP-*ter*-AM) had an 18% reduction in the pHRR and HRC values. In addition, the *ter*-polymers displayed the lower heats of combustion as opposed to the neat PS, indicating the gaseous phase fire retardant activity of incorporated monomers.^[18] A comparison of thermal and calorimetric characteristics of the modified styrenic polymers also revealed that the extent of the synergistic interactions between P and N strongly depends on the chemical environments of N atoms. Among the N monomers used in this study, unsubstituted MI monomeric units were found to be more capable of exerting P–N synergistic interaction, and thereby, of lowering the combustion parameters of PS. It is relevant to state that the substitution of H atoms bound to N atoms within the N monomeric moieties (for example, *N*-alkyl and *N*-phenyl substitution inside maleimide units or *N,N*-dimethyl and *N*-isopropyl substitution within amide units) did not result in any enhancements in the degree of the P–N synergism. This could imply that the presence of unsubstituted H atoms bound to N atoms within MI and AM units is essential for exerting higher synergism and lower combustibility. Evidently, from the results obtained, the *ter*-polymerization of styrene using P and N monomers can be considered as a promising technique for developing fire retarded PS. The physio–chemical processes, including the modes of action in

the condensed and vapor phases of these modifying groups dictating the FR effect, will be published separately.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

A.B. is grateful for the provision of the overseas Ph.D. studentship from the Ulster University, UK. This research was supported by the Royal Society of Chemistry (ID R19-3521).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

combustion characteristics, phosphorus-containing fire retardants, P–N synergism, reactive modification, styrenic polymers, thermal stability

Received: November 29, 2023

Revised: February 5, 2024

Published online: March 12, 2024

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