Novel Nitrogen–Phosphorus Flame Retardant Based on Phosphonamidate: Thermal Stability and Flame Retardancy

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1. INTRODUCTION

Recently, restrictions on the use of halogen flame retardants (FRs) have resulted in the development of eco-friendly FRs, and the phosphorus-containing FR is one of the well-known candidates. Among them, organophosphorus and phosphorus–nitrogen FRs appear to be very effective fire retardants and they produce less toxic moiety and smoke during combustion.

The mode of FR action works either in the condensed phase or the gas phase or in both phases through a physical and/or chemical mechanism. As a consequence, they intervene in the combustion during thermal degradation, ignition, or flame spread. The mechanism of phosphorus-containing FRs acts in the gas phase via active radicals such as PO\(^{\bullet}\), PO\(^{2\bullet}\), and HPO\(^{\bullet}\) playing a role as scavengers of H\(^{\bullet}\) and OH\(^{\bullet}\). The flame-retardant efficiency of these FRs is also contributed from residual char acting on condensed phase to protect material from flammable gases, oxygen, and heat.

Another recently studied new class of flame retardant which meets flammability and environment issues is nitrogen-phosphorus (P–N) containing compound. P–N FRs have higher thermal stability and produce less toxic smoke than phosphorus-based FRs. Lately, we reported some P–N FRs based on bisphosphonamidate which promote more residual char formation than the corresponding bisphosphate FRs and they exhibit outstanding fire retardancy for charrable polymers such as polycarbonate (PC) in the condensed phase. Besides, the P–N compound (DPPMP) providing a gas-phase action exhibited good flame retardancy for noncharrable polymers such as ethylene–vinylacetate (EVA) and acrylonitrile–butadiene–styrene (ABS). DPPMP exhibits good flame retardancy; however, it has a low phosphorus (P) content and a large loading is therefore required to obtain good flame retardancy for ABS and EVA (V-0 ranking).

As mentioned in the literature, the P content of FRs is one of the most critical factors governing their flame retardancy. Commercial aliphatic phosphates in general have a higher P content than the aromatic ones because of their smaller molecular weight. However, they are more sensitive to hydrolysis. For that reason, it is not easy to attain both good hydrostability and high P content. It is hypothesized that to overcome this disadvantage, both aliphatic moiety with a high P content and thermostable aromatic moiety would be combined in one structure of FRs.

Building on the above assumption, in this study, a novel P–N FR based on phosphonamidate containing aromatic
and aliphatic groups with both a good hydrostability and high P content, which exhibits good flame retardancy for nonchar-
rable polymers such as EVA and ABS in the gas phase, was
synthesized and compared with other FRs based on bisphosphoramidate and bisphosphate acting in the condensed
phase. Their FR behavior and thermal stability were also
studied.

2. RESULTS AND DISCUSSION

2.1. Synthesis of a Novel Phosphonamidate FR:
DMPMP. Scheme 1 shows the synthesis route of dimethyl
N,N′-1,3-phenylenebis(P-methylphosphonamidate (DMPMP)
via the two-step reaction. Methyl phosphonic dichloride
(MPDC) was not available from commercial sources and
therefore was synthesized in our laboratory following the
procedure published in the previous report. The 1H NMR
spectrum of MPDC showed a signal at 2.55 ppm which
corresponds to the protons of CH$_3$-$\text{P}$. An methyl methyl
phosphochloridate (MMPC) compound, an intermediate
reagent, was obtained by reacting methanol with MPDC, and
its subsequent reaction with 1,3-phenylene diamine gave the
final product, DMPMP, with high purity. The 1H and 31P
NMR spectra of DMPMP are shown in Figure 1 A,B,
respectively. The clear chemical shifts of the protons are
observed at 6.75 (s, 1H), 7.00 (m, 1H), and 7.61 (d, 2H)
which correspond to the protons of the aromatic phenyl group.
Besides, the clear chemical shifts of the protons are observed at
6.55 (d, 2H), 1.48 (d, 6H), and 3.55 (d, 6H) which
correspond to the protons of $N^-$-$\text{H}$, CH$_3$-$\text{P}$, and CH$_3$-$\text{O}$-
$\text{P}$, respectively. A single phosphorus compound with a single
peak at 29.463 ppm was also clearly con
irmed by the 31P
NMR spectrum.

To confirm its successful synthesis, the Fourier transform
infrared (FT-IR) spectrum of DMPMP was analyzed
spectroscopically by employing FT-IR experiments presented
in Figure 2. From Figure 2, the adsorption signal of the
saturated carbon (sp$^3$) is observed at 2892–3018 cm$^{-1}$. The
peak at 961 cm$^{-1}$ corresponds to the vibration of the P═O
bonding. The peak at 3186 cm$^{-1}$ corresponds to the vibration/
stretching band of N═H. The peaks at 1045 and 1223 cm$^{-1}$
can be assigned to the stretching bands of P═O═C and P═O,
respectively. The shoulder at 1507 cm$^{-1}$ corresponds to the
vibration of the CH$_3$-$\text{P}$$(\text{O})$═O group. The results from 1H
NMR, 31P NMR, and FT-IR indicated that the high purity
DMPMP was successfully synthesized.

2.2. Thermal Degradation Properties. Figure 3 shows the
thermogravimetric analysis (TGA) curves in a nitrogen
atmosphere from 50–600 °C at a heating rate of 10 °C/min
for the single phosphate, two phosphoramidate, and single
novel phosphonamidate compounds employed in this study. In
Figure 3, it is observed that the thermal degradation properties
and yield of charred residue of the FR are highly dependent on
the type of pendent group attached to the center aromatic
compound, that is, resorcinol or 1,3-phenylene diamine. At 600
°C, resorcinol bis(diphenyl phosphate) (RDP) leaves less
charred residue (4.6 wt %) than N-RDP and 4N-RDP (32.3 and 50.4 wt %, respectively). P–N compounds have a tendency to leave more charred residue than P compounds with the corresponding structure. Considering the initial degradation temperature ($T_{d1}$), the $T_{d1}$ of N-RDP is higher than that of RDP. Therefore, P–N FRs exhibit greater thermal stability and leave more charred residue than the FRs having only phosphorus elements.

The other point we claim is that P–N FRs containing –NH– groups tendentially generate a nitrogen-rich residue because of the intermolecular coupling transesterification reaction. This has also been reported in the literature.20 This is also found in the case of DMPMP; while RDP contains no –NH– in its structure, no transesterification reaction is observed and less charred residue is found. However, DMPMP decomposed in one long step and left a less amount of charred residue (20.8 wt %) than N-RDP and 4N-RDP, which indicates that the gas phase mechanism is dominant for the DMPMP compound. We also speculate that CH$_3$–P(O)– is responsible for the decomposition step of DMPMP occurring at lower temperatures than the other P–N compounds.

Scheme 2 is proposed to present the decomposition with the mode of action being mainly in the gas phase and the intermolecular transesterification reaction of DMPMP in this study.

To better understand the char formation of these P–N FRs, the solid residues of these P–N FRs obtained at 600 °C were investigated by FT-IR. The thermal degradation of N-RDP, 4N-RDP, and DMPMP was performed under nitrogen in the TGA apparatus. After performing TGA at 600 °C, the residual char was taken out and analyzed by FT-IR measurement. The results are shown in Figure 4.

We previously reported that P–N-rich residual chars are formed through the interaction between the hydrogen atoms in the weak acid of P–NH–C and the phosphate groups of N-RDP and 4N-RDP.20 These results are compared with those of DMPMP in this study. The distinct absorption signal at 3186 cm$^{-1}$ which was characteristic to the stretching vibration of N–H disappeared, and the peak of the P–N–C bonding at 961 cm$^{-1}$ was shifted to a lower wavenumber (936 cm$^{-1}$). These certainly recommend that the residual char of DMPMP also undergoes intermolecular coupling by the transesterification of the secondary amine (–NH–) in phosphonamidate, and P–N-rich residual chars are also formed through the interaction between the hydrogen atoms in the weak acid of P–NH–C and phosphonate. Besides, the vibration band of saturated C–H appearing at 2892–3018 cm$^{-1}$ also decreases and gradually disappears. The peaks of P=O stretching appearing at 1223 cm$^{-1}$ become broadened and are shifted to higher wavenumbers (1196 cm$^{-1}$) at 600 °C. In addition, the peak of CH$_3$–P(O) appearing at 1507 cm$^{-1}$ disappears. All these results indicate that DMPMP also undergoes decomposition by eliminating hydrocarbons to generate the PO$^\cdot$ radical, thus giving it gas-phase action flame-retarding efficiency which was discussed above in the thermal degradation mechanism of DMPMP presented in Scheme 2.

### 2.3. Flame-Retardant Performances

The flame-retarding performances of the FRs used in this work were investigated on noncharrable polymers, that is, ABS and EVA. The amounts of the FRs added to ABS and EVA were 20–30 and 10–20 wt %, respectively. Tables 1 and 2 show the UL-94V results for ABS and EVA formulations, respectively.

| FR | P (%) in FR | ABS/FR (wt/wt) | P (%) in formulation | UL-94V |
|----|------------|----------------|---------------------|--------|
| RDP | 10.78 | 100/0 | 0.00 | NC |
| N-RDP | 10.82 | 70/30 | 3.23 | NC |
| 4N-RDP | 10.86 | 70/30 | 3.25 | NC |
| DMPMP | 21.20 | 80/20 | 4.24 | V-0 |

In Tables 1 and 2, the UL-94V tests are evaluated for these formulations. The mixtures containing RDP, N-RDP, or 4N-RDP give no-rating and V-2 in the UL-94V results for ABS and EVA, respectively. In contrast, the mixtures containing DMPMP give a UL-94 V-0 ranking for both ABS and EVA, even though the P content in the formulations of these
mixtures is not very different. This means that the fire-retardant efficiency strongly depends on the structure and fire-retarding mechanism of the FR. The UL-94V results demonstrate more clearly the effect of the structure of the FR on its fire-retarding ability. The flame-retarding behavior of DMPMP was again seen to function by the gas-phase mode of action. Moreover, we proposed that the minimum P content of 4–5 wt % is required to get effective gas phase acting flame retardancy in a mixture for a noncharrable polymer such as ABS.28 This can be reasserted for DMPMP, which is a gas phase acting FR and shows a V-0 rating for ABS at 4.24 wt % of P in the formulation. In addition, we proposed DPPMP as a promising P–N FR27 which gives a V-0 ranking at a 30 wt % FR loading for ABS in the gas-phase mode of action. DMPMP with a higher P content in its structure than DPPMP gives a V-0 rating at a lower FR loading for ABS (20 wt %) in the gas-phase mode of action. This indicates that one of the most crucial factors governing the flame retardancy of FRs is the P content. All these results suggest that the fire-retarding efficiency of the FR significantly depends on two significant factors, its structure and P content.

The abovementioned discussion was further confirmed by TGA of the formulations, and the results are given in Figures 5 and 6.

The TGA results in Figures 5 and 6 indicate that the amount of the residual char of the mixture containing FRs is directly proportional to the char formation of FR trends in the abovementioned discussion. The TGA curves of the mixtures of different FRs with ABS in Figure 5 show that the T_d of the mixtures is lower than that of ABS, indicating that the presence of the FRs decreases T_d and leads to the destabilization of the ABS matrix below 450 °C.

It is widely known that the flame retardancy of phosphate compounds such as RDP is inefficient for highly flammable polymers such as ABS when blended with a single FR system,29 and we previously reported that P–N FRs based on phosphoramidate easily operate in the condensed phase mode of action.30 In this study, N-RDP and 4N-RDP were incorporated into ABS for no rating in UL-94 results because of the condensed phase mode of action leaving a remarkable amount of charred residue (12 wt % in the formulation with ABS for N-RDP and 15.9 wt % in the formulation with ABS for 4N-RDP). Otherwise, the TGA results of the ABS/DMPMP mixture show 6.0 wt % charred residue, which is proportional to the char-yielding behavior of DMPMP, and a V-0 rating is observed for this mixture, suggesting that the gas-phase action dominates over the condensed phase one. Furthermore, the TGA curve of ABS/DMPMP mixture shows a lower initial decomposition temperature than neat ABS. This is owing to the decomposition of DMPMP and/or the products from DMPMP and ABS interaction during thermal degradation. To support for the effect of DMPMP on the thermal decomposition behavior of ABS or EVA, the comparison between calculated and experimentally determined TGA curves was studied (Figure 7). These TGA curves should be different if there is interaction between the FR and polymeric material. However, there are almost no differences between the two calculated and experimental TGA curves. The reason is probably that DMPMP with low loading evaporates almost completely during thermal decomposition.

These results suggest that P–N FRs based on phosphonamidate with the CH_3–P(O)– group in their structures tend to function by the gas-phase mode of action in their flame-retarding mechanism more than the condensed phase mode of action (Figure 8).

### Table 2. UL-94V Results for EVA with and without FRs

| FR          | P (%) in FR | EVA/FR (wt/wt) | P (%) in formulation | UL-94V dripping |
|-------------|-------------|----------------|----------------------|-----------------|
| RDP         | 10.78       | 80/20          | 2.12                 | V-2             |
| N-RDP       | 10.82       | 80/20          | 2.16                 | V-2             |
| 4N-RDP      | 10.86       | 80/20          | 2.17                 | V-2             |
| DMPMP       | 21.20       | 90/10          | 2.12                 | V-0             |
| RDP         | 10.86       | 80/20          | 2.12                 | V-2             |
| N-RDP       | 10.82       | 80/20          | 2.16                 | V-2             |
| 4N-RDP      | 10.86       | 80/20          | 2.17                 | V-2             |
| DMPMP       | 21.20       | 90/10          | 2.12                 | V-0             |
| MP          | 17.21       | 80/20          | 2.21                 | V-0             |
| MP          | 17.21       | 80/20          | 2.21                 | V-0             |
| MP          | 17.21       | 80/20          | 2.21                 | V-0             |
| MP          | 17.21       | 80/20          | 2.21                 | V-0             |

**Figure 5.** TGA curves of the mixtures of FRs with ABS (in nitrogen, 10 °C/min).

**Figure 6.** TGA curves of the mixtures of FRs with EVA (in nitrogen, 10 °C/min).

3. CONCLUSIONS

In order to look into factors influencing the fire retardant performances of P–N FRs which would make them efficient for noncharrable polymers such as ABS and EVA and operate in the gas-phase mode of action, a novel P–N FR (DMPMP) based on phosphonamidate was synthesized and its FR performances and thermal decomposition were compared with those of P–N FRs based on phosphoramidates and RDP which function in the condensed phase mode of action. From

<references>
1. ACS Omega 2019, 4, 17791–17797
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the TGA and FT-IR results, it was clearly observed that P–N FRs containing −\(\text{NH}−\) groups tendentially generate a nitrogen-rich residue because of the intermolecular coupling transesterification reaction and act either in the gas phase or the condensed phase. When DMPMP was added to polymers, V-0 ratings were achieved at a low loading (20 wt % DMPMP for ABS and 10 wt % DMPMP for EVA), indicating that DMPMP is an efficient and promising FR. These results demonstrated our above assumption. Moreover, another additional advantage of DMPMP is that it is a water-insoluble solid. A gas phase is believed to be at the main FR mechanism for DMPMP and the pendant group \(\text{CH}_3−\text{P(}\text{O})\) in this structure may be responsible for this action.

4. EXPERIMENTAL SECTION

4.1. Materials. Aniline, piperazine, resorcinol, diphenyl chlorophosphate, dimethyl methyl phosphonate, methanol, and 1,3-phenylene diamine were purchased from Aldrich, Germany. Thionyl chloride, triethylamine, chloroform, and tetrahydrofuran (THF) were purchased from Samchun Chemical Company, Korea. Polycarbonate (PC), ABS, and RDP of commercial grades were provided by Cheil Industries, Korea. EVA which is a blend of EVA copolymer, LLDPE, and PE-\(\text{g}\)-MA (80:10:10) was provided by the LS-Cable Company, Korea.

4.2. Synthesis. 4.2.1. Synthesis of Phosphoramidate FRs. Two phosphoramidates were synthesized according to the procedure presented in the previous report.\(^{20}\) The chemical structures, full names, and abbreviations of two FRs used in this work are shown in Table 3.

N-RDP was synthesized by adding a mixture of 1.0 mol 1,3-phenylene diamine and 2.0 mol triethylamine dissolved in THF to a round-bottom flask equipped with a temperature controller, a reflux condenser, and a mechanical stirrer containing 2.0 mol diphenyl chlorophosphate at 0 °C. The mixture was then allowed to warm up to room temperature and it was further refluxed for 4–8 h. The \(\text{Et}_3\text{N} \cdot \text{HCl}\) salt was removed by filtering, and the filtrate was evaporated to give a crude product, which was purified by washing three times with distilled water. The success of the synthesis was confirmed by \(^1\text{H}\) and \(^{31}\text{P}\) NMR analysis. \(^1\text{H}\) NMR (CDCl\(_3, \delta\)): 7.20–7.10 (m, \(\text{H}−\text{Ar}\)), 6.75–6.74 (\(\text{HN}−\text{Ar}\)); \(^{31}\text{P}\) NMR (CDCl\(_3, \delta\)): 30.5 (s).

4N-RDP was synthesized in two steps. The starting material \(m\)-phenylene phosphorodichloridate (\(m\)PPDC) was synthesized in our laboratory following the procedure published in the previous report.\(^{20}\) A mixture of aniline (1.5 mol) and triethylamine (1.6 mol) in dry THF was placed in a round-bottom flask equipped with a temperature controller, a reflux condenser, and a mechanical stirrer. The reaction was maintained at 0 °C. A solution of \(m\)PPDC (0.37 mol) in THF was added dropwise to the flask over a period of 1 h. The mixture was further refluxed for 3 h. The precipitated \(\text{Et}_3\text{N} \cdot \text{HCl}\) salt was filtered off. The solvent was evaporated under reduced pressure, and the crude product was precipitated in water, filtered, and dried under vacuum overnight to give the final product. \(^1\text{H}\) NMR (CDCl\(_3, \delta\)): 6.90–6.85, 7.30–7.10 (m, \(\text{H}−\text{Ar}\)), 8.45 (m, \(\text{NH}−\text{Ar}\)); \(^{31}\text{P}\) NMR (CDCl\(_3, \delta\)): \(\delta = 1.56 \text{ (s)}\).

4.2.2. Synthesis of a Novel Phosphonamidate FR: DMPMP. We synthesized a novel P−N FR whose structure is presented in Scheme 1. First, MPDC was synthesized by following the procedure published in the previous report.\(^{27}\) MPDC (133 g, 1.0 mol) was dissolved in diethyl ether (ether)
in a round-bottom flask equipped with a temperature controller, reflux condenser, and a stirrer, which was maintained at 0–5 °C. Solutions of methanol (32.0 g, 1.0 mol) and triethylamine (101 g, 1.0 mol) in ether were separately prepared and added dropwise with stirring. The mixture was then allowed to warm up to room temperature and refluxed for 4 h at 30 °C. After the reaction, filtering and evaporating the filtrate gave the crude product, MMPC (80% yield). This product was used for the next reaction without further purification.

Solutions of 1,3-phenylene diamine (54.0 g, 0.5 mol) and triethylamine (101 g, 1.0 mol) in dry THF were separately prepared and added dropwise with stirring to a solution of MMPC (128.5 g, 1.0 mol) in dry THF at 0–5 °C. After their addition, the mixture was allowed to warm up to room temperature and refluxed for 6 h. The target material was insoluble in THF and was subjected to filtration and washed with distilled water to give the pure product (70% yield).

4.3. Measurements and Sample Preparation.

4.3.1. Spectroscopic Analysis. The FT-IR spectra were obtained using a Nicolet 300 with KBr pellets. 1H and 31P NMR spectra were analyzed on a Varian Unity Inova 500NB spectrometer using CDC13 or DMSO as the solvent and tetramethylsilane as a reference. The chemical shifts of the 31P NMR spectra are relative to the spectrum of 85% H3PO4 as an external standard.

4.3.2. Thermal Analysis. TGA was carried out on a TGA 2050 instrument by heating from room temperature to 650 °C at a heating rate of 10 °C/min in a nitrogen atmosphere. Differential scanning calorimetry was carried out on a TA2910 instrument under a nitrogen atmosphere at a heating rate of 10 °C/min.

4.3.3. UL-94 Preparation and Measurement. A mixture of the synthesized FR with the polymer with the designated composition was processed in a HAAKE PolyDrive mixer at 60 °C. The synthesized FR with the polymer with the designated composition was processed in a HAAKE PolyDrive mixer at 60 °C. The mixtures were then allowed to warm up to room temperature and reflushed for 4 h at 30 °C. After the reaction, filtering and evaporating the filtrate gave the crude product, MMPC (80% yield).

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