

## Synthesis of a Novel Nitrogen-Phosphorus Flame Retardant Based on Phosphoramidate and Its Application to PC, PBT, EVA, and ABS

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**Abstract:** A novel nitrogen-phosphorus compound, diphenyl piperazine-1,4-diylbis(methylphosphinate)(DPPMP) was synthesized via a two step reaction and its flame retarding efficiency as a single component additive was investigated. The success of synthesis was confirmed by FTIR and  $^1\text{H}$  and  $^{31}\text{P}$  NMR analysis. The product was mixed with polycarbonate (PC), poly(butylene terephthalate) (PBT), ethylene-vinyl-acetate copolymer (EVA), and acrylonitrile-butadiene-styrene copolymer (ABS). The flame-retarding efficiency was evaluated using the limiting oxygen index (LOI) and the UL-94 vertical test methods. The addition of DPPMP enhanced the flame retardancy of the polymers and the V-0 ratings were obtained for the polymers examined in this study at a loading of 7-30 wt%. The gas-phase flame retardancy mode of action was suggested for this material from the thermogravimetry experiment results.

**Keywords:** flame-retardant, phosphorus-nitrogen compound, phosphoramidate, PC, PBT, EVA, ABS.

### Introduction

Flame retardants (FRs) based on organic phosphorus compounds are known to be one of the most promising candidates that can replace the halogen-based FRs.<sup>1</sup> The advantages of phosphorus containing flame retardants are environmental friendliness. There are too numerous literatures reporting the performances of phosphorus FRs to cite all of them. Recently, organic phosphorus compound have demonstrated good ability in flame retardancy and are believed to generate less toxic gas and smoke than halogen-containing compounds.<sup>2-10</sup>

Among many commercially available additive-type flame retardants (FR), which are employed without any co-agent such as a gas source or a char charmer, three materials, e.g. triphenyl phosphate (TPP), resorcinol bis(diphenyl phosphate) (RDP), and bisphenol A bis(diphenyl phosphate) (BDP) are mostly well known and widely used to polycarbonate (PC), PC/ABS blends, and polyesters. The performance of these phosphates strongly depends on the base polymer. They are very effective for charrable polymer such as PC but show no performance for non-charrable polymer such as Styrenics.<sup>11,12</sup> To obtain UL-94 V-0 rating with commercial phosphorus FRs for styrenic plastic including ABS and HIPS, the additional incorporation of halogen-based phosphorus such as aliphatic chloroethyl phosphonate or a char forming agent

along with phosphorus flame-retardants is inevitable.<sup>11,13-16</sup> Recently, Levchik and Weil<sup>11,14</sup> clearly stated in their review articles that the most effective flame retardants for HIPS and ABS are halogen containing compounds and it is difficult to find cost effective non-halogen alternatives for styrenic polymers containing no char-forming component.

On the other hand, nitrogen- and nitrogen-phosphorus compounds are known to evolve low toxic gases or vapors as well as low evolution of smoke during combustion and are better in the aspects of recyclability.<sup>17</sup> The nitrogen-phosphorus compounds of this category are nitrogen containing phosphorus compounds such as melamine or ammonium salts of phosphates or P-N compounds (phosphazene or phosphoramidate). The ammonium or melamine salts of phosphates have showed their fire retardancy performance when used as one of constituents in ternary intumescence system which is the mixture of several components. They played a role as a gas source and a catalyst in the char formation.<sup>18-23</sup> The fire retardant synergism was found for the binary mixture of melamine with triphenyl phosphate<sup>24</sup> or cyclic diphosphonate ester<sup>25</sup> and both gas and condensed phase effect were believed to contribute to the flame retardancy of poly(butylene terephthalate) (PBT). However, above systems are based on the mixture and thus the effective flame retarding mechanisms are not easily understood. Very recently, the novel intumescent system based on the phosphorus compound containing nitrogen was prepared by Gao *et al.*<sup>26</sup> in an attempt to develop single component intumes-

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cent FR. They reported that V-1 rating in UL-94 test was obtained at 20 wt% loading of this FR alone for PBT. Although this approach to obtain the effective intumescent system by employing a single component showed a limited success, no FR is able to render flame retardancy of V-0 rating for the moderately charrable polymer like PBT.

Levchick *et al.*<sup>27</sup> prepared a series of aromatic-substituted and spiro-aromatic substituted phosphazenes and evaluated their flame retardancy on PBT. They reported that these additives increased the formation of thermally stable residues and acted as an effective charring promoter for PBT. Although the increase of LOI values was observed, no V-0 rating was gained at 20 wt% loading of FR. They also reported that, among various FRs studied, tris(phenylene-1,2-dioxy) tricyclophosphazene showed the best performance and a gas-phase mode of action was suggested for this material which other FRs worked predominately at condensed phase. Considering the another compounds based P-N structures, the derivatives of phosphoramidate derived from piperazine unit were also reported to exhibit fire retardancy of UL-94 V-0 at a phosphorus concentration of around 1.42 wt% for the PC/ABS blends.<sup>28,29</sup> However, the fire-retarding mechanism of these compounds was not discussed at all.

Summarizing the above discussions, the most of nitrogen-containing phosphorus compounds work either at intumescent system or at condensed phase. In those cases, the FR is consisted of a mixture of at least two components. Single FR is not likely to exhibit effective flame retardancy for non charrable polymer like ABS. To develop new nitrogen-containing phosphorus compound, working at gas phase, we incorporate piperazine unit with methylphosphonyl group in an attempt to retain high P and N contents. Moreover, the thermal stability and fire retarding behavior of this material are investigated and evaluated for a wide range of polymers from highly charrable (PC), moderately charrable (PBT), and two non charrable polymers (EVA and ABS).

## Experimental

**Materials.** Piperazine, phenol (C<sub>6</sub>H<sub>5</sub>OH), dimethyl methylphosphonate, ((CH<sub>3</sub>O)<sub>2</sub>P(O)CH<sub>3</sub>), and thionyl chloride (SOCl<sub>2</sub>) were purchased from Aldrich. Acetone, methylene chloride (MC), tetrahydrofuran (THF), toluene, pyridine, and triethylamine were purchased from Samchun Chemical Company, Korea. Polycarbonate (PC), poly(butylene terephthalate) (PBT), acrylonitrile-butadiene-styrene copolymer (ABS) of commercial grades were provided from the Cheil Industries, Korea. Ethylene-vinyl-acetate copolymer (EVA) which is a blend of EVA copolymer, LLDPE, and PE-g-MA (90:10:10) was provided from the LS-Cable Company, Korea.

**Synthesis.** We have synthesized one novel P-N FR whose structure is shown below together with its synthesis scheme and abbreviated which will be used afterwards.

### Synthesis of Phenyl Methyl Phosphonochloridate (PMPC)

**According to Literature<sup>30</sup>:** Firstly, methyl phosphonic dichloride (MPDC) was synthesized following the procedure found in the literature.<sup>31</sup> MPDC (133 g, 1.0 mole) was dissolved in dry toluene into a round-bottom flask equipped with a temperature controller, reflux condenser, and a stirrer, which was kept at 0 °C. The solutions of phenol (94 g, 1.0 mole) and triethylamine (101 g, 1.0 mole) in dry toluene were separately prepared and added dropwise with stirring. After addition, the mixture was then allowed to warm up to room temperature and refluxed for 8 h. Et<sub>3</sub>N·HCl was removed by filtering and evaporation of the filtrate gave the crude product, phenyl methyl phosphochloridate (90% yield). This product was used for the next reaction without further purification.

**Synthesis of Diphenyl Piperazine-1,4-Diylbis(methylphosphinate)(DPPMP):** To a solution of phenyl methyl phosphochloridate (171 g, 0.90 mole) in dry dichloromethane at 0 °C, The solutions of piperazine (38.3g, 0.445 mole) and triethylamine (91 g, 0.9 mole) in dry dichloromethane were separately prepared and was added dropwise with stirring. After addition, the mixture was then allowed to warm up to room temperature and refluxed for 6 h. The removal of solvent gave the mixture containing the target material. The mixture was dissolved in THF and precipitated in water, which gave crude product (70% yield). The crude product was further washed with acetone to give brown solid and water-insolubility (48% yield). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): δ = 1.549 (d, CH<sub>3</sub>), 3.03 (t, CH<sub>2</sub>-N), 7.17-7.32 (m, H-Ar). <sup>31</sup>P-NMR (CDCl<sub>3</sub>, ppm): δ = 36.04(s).

### Spectroscopic Analysis.

**FTIR Spectrophotometry:** The FTIR spectra were recorded on Nicolet 300 using KBr pellets. <sup>1</sup>H- and <sup>31</sup>P-NMR were performed on a Varian Unity Inova 500 NB spectrometer by using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as a reference. The chemical shift of <sup>31</sup>P-NMR spectra are relative to the external standard of 85% H<sub>3</sub>PO<sub>4</sub>.

**Thermal Analysis.** Differential scanning calorimetry (DSC, TA 2910 instrument) was carried out of 10 mg samples under nitrogen gas at a heating rate of 10 °C/min.

Thermogravimetric analysis (TGA) was obtained from 2 to 10 mg samples under nitrogen and air atmospheres at a heating rate of 20 °C/min using a TGA 2050 thermogravimetric analyzer.

**Limiting Oxygen Index (LOI).** LOI value was measured by a Fire Testing Technology Instrument at a flow rate of 10.6 L/min with test specimen bars of 127 mm in length, 6.5 mm in width, and about maximum up to 3.2 mm in thickness.

**UL-94 Measurement.** Fire retardancy performance was evaluated according to the testing procedure of FMVSS 302/ZSO 3975 with test specimen bars of 127 mm in length, 13.0 mm in width, and about maximum up to 3.2 mm in thickness.

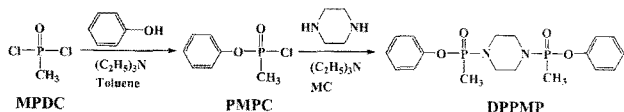
**Sample Preparation for LOI and UL-94 Test.** Mixture of a synthesized flame retardant and a polymer at the desig-

nated composition was processed in a Haake PolyDrive mixer with 60 rpm for 7 min at 230 °C for PC and ABS, 60 rpm for 10 min at 230 °C for PBT, and 40 rpm for 10 min at 170 °C for EVA.

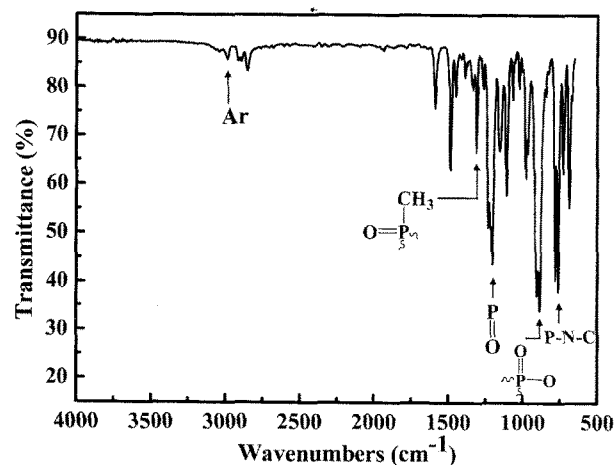
## Results and Discussion

**Synthesis of DPPMP.** DPPMP was synthesized via two-step reaction presented in Scheme I. Starting MPDC was not available from commercial sources and thus made by us according to the procedure described in the literature.<sup>31</sup> <sup>1</sup>H-NMR of MPDC showed clear peak at 2.55 ppm which was assigned to the protons of CH<sub>3</sub>-P. The intermediate, PMPC was obtained by reacting MPDC with phenol and consequential reaction of PMPC with piperazine gave the final product, DPPMP with high purity. The total yield from the starting MPDC was about 60%. Figure 1 shows the FTIR spectra of DPPMP. In Figure 1, the absorption band of saturation carbon (sp<sup>3</sup>) is observed at 2930-2984 cm<sup>-1</sup>. The peaks at 3050 and 1591 cm<sup>-1</sup> correspond to the vibration of aromatic phenyl. The peaks at 2852 and 760 cm<sup>-1</sup> correspond to the vibration of tertiary amine, P-N-C. The peaks at 1202 and 1107 cm<sup>-1</sup> can be contributed to the stretching band of P=O and P-O-C, respectively. The shoulders at 1312 cm<sup>-1</sup> and 887 cm<sup>-1</sup> were corresponded to the vibration of CH<sub>3</sub>-P(O)- group.

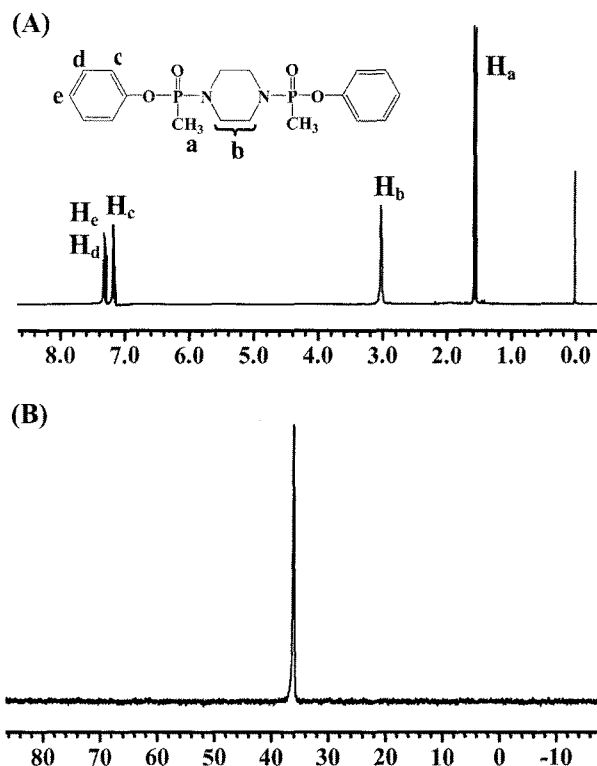
Figure 2(A, B) shows the <sup>1</sup>H-NMR and <sup>31</sup>P-NMR spectra of DPPMP compound. The clear chemical shifts of protons are observed at 7.17-7.31 (m, 10H), 3.03 (s, 4H), and 1.55 (d, 6H) which correspond to protons of aromatic phenyl, -CH<sub>2</sub>-N, and CH<sub>3</sub>-P(O)-. <sup>31</sup>P-NMR spectrum also shows the



**Scheme I.** Synthesis of diphenyl piperazine-1,4 diylbis(methylphosphinate) (DPPMP).



**Figure 1.** FTIR of DPPMP.



**Figure 2.** <sup>1</sup>H-NMR (A) and <sup>31</sup>P-NMR (B) spectra of DPPMP.

presence of single phosphorus compound. From these two results along with FTIR data, we confirm the successful synthesis of high purity DPPMP.

**Thermal Properties of DPPMP.** Figure 3(A, B) shows the DSC and TGA curves of DPPMP. The clear melting of DPPMP is observed at 172 °C from DSC (heating rate 10 °C. min), indicating that the purity of compound is very high. TGA results show that there is one step decomposition and no or very little residues are remaining, which suggests the gas-phase mode of action for this compound. Most of P-N compounds leave considerable amount of charred residues after combustion. In an extreme case, phosphorus oxynitride (PON)<sub>m</sub> was reported to start to decompose above 450 °C and leaves about 90% of solid residue at 600 °C when TGA experiments were performed in an inert atmosphere.<sup>27</sup> We speculate that CH<sub>3</sub>-P(O)- is responsible for the complete decomposition of DPPMP at relatively lower temperatures differently from other P-N compounds.

**Flame-Retardant Performance of DPPMP.** To evaluate the flame-retardant performance of DPPMP, four different polymers are selected covering a wide range of charring degree (PC for high-charring, PBT for moderately-charring, and EVA and ABS for non-charring). The compositions and LOI values for various compounds are listed in Table I. It should be noted that the LOI values of neat polymers varies with charring tendency. PC shows the highest value and ABS shows the lowest value. With addition of DPPMP, the

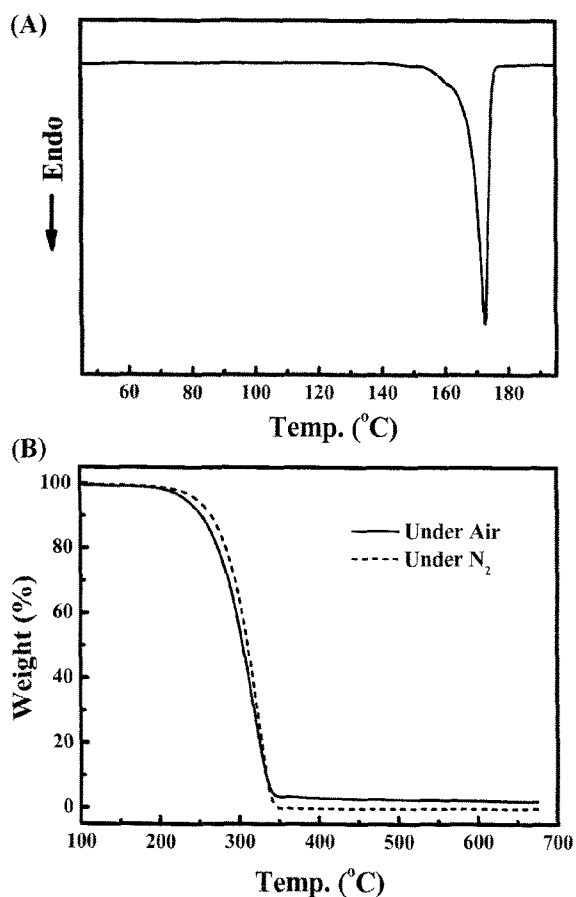


Figure 3. DSC (A) and TGA (B) thermograms of DPPMP.

Table I. Results for Mixtures of DPPMP with Various Polymers

Polymer	FR (wt%)	LOI	UL-94 Rating	Dripping	AFT <sup>a</sup>
PC	0	29.6	V-2	Yes	5/25
	5.0	31.4	V-2	No/Yes	0/4
	7.0	33.0	V-0	No	0/0
PBT	0	21.8	NC	Yes	Burns
	10	24.8	V-2	No/Yes	1/5
	15	27.0	V-2/V-0 <sup>c</sup>	No/Yes	0/0
EVA	0	18.7	NC	Yes	Burns
	10	22.8	V-2	No/Yes <sup>b</sup>	0/10
	20	24.0	V-2	No/Yes	0/5
	30	25.0	V-0	No	0/1
ABS	0	18.4	NC	No	Burns
	20	21.3	V-2	No	0/40
	30	23.2	V-0	No	0/0

<sup>a</sup>Average flaming time after the first and the second ignition. <sup>b</sup>No/Yes represents the responses of the first/second flame application. <sup>c</sup>Dripping occurs (can be classified as V-2) but no burning of cotton (can be classified as V-0) according to ref 27.

LOI value increases but the effect is most profound for PC ( $\Delta 3.4$  at 7 wt% loading) and worst for ABS ( $\Delta 5.2$  at 30 wt% loading). These results clearly indicate that PC can be flame-retarded most easily and PBT, EVA, and ABS are the most difficult polymers to be flame-retarded.

UL-94 test results are also given in Table I. V-0 rating was obtained at 7, 15, 30, 30 wt% loading for PC, PBT, EVA, and ABS, respectively, which has the exactly same order as that observed in the LOI experiments discussed before.

From these results, it becomes manifest that DPPMP is an effective additive-type flame retardant applicable to a wide range of polymers. At this juncture, it should be mentioned that DPPMP is water insoluble, which is one of the required properties of a promising flame retardant.

Finally, the mode of action of this compound will be discussed. Figures 4-7 show the thermogravimetry curves of neat polymer and polymer with designated loading of DPPMP taken under nitrogen. Firstly, it should be noticed that there is a different correlation between the amount of charred residue and LOI depending on neat polymers. The highest residue is observed for PC which shows the highest LOI while the lowest residue for ABS which has the

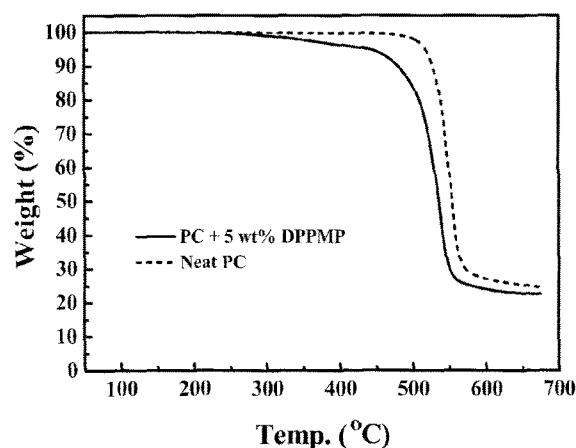


Figure 4. TGA thermograms of PC and PC with 5 wt% of DPPMP.

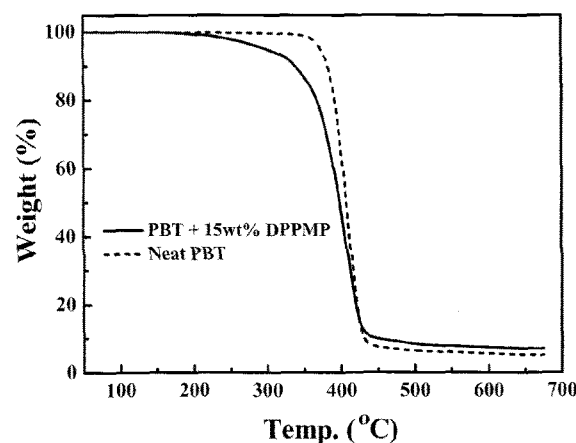


Figure 5. TGA thermograms of PBT and PBT with 15 wt% of DPPMP.

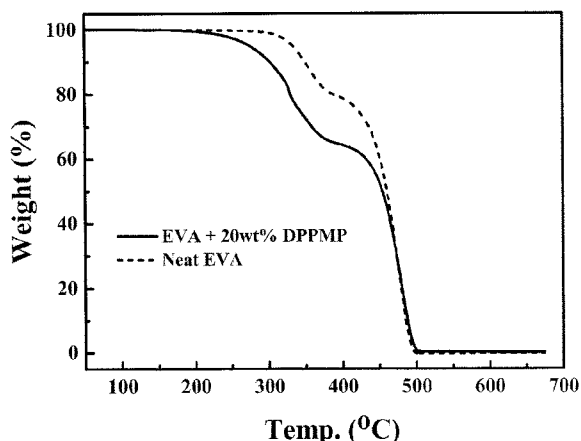


Figure 6. TGA thermograms of EVA and EVA with 20 wt% of DPPMP.

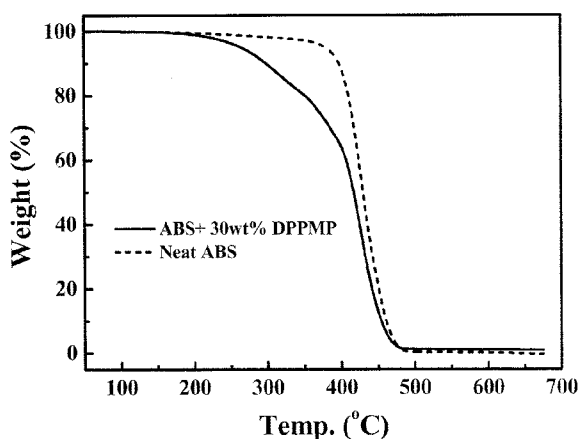


Figure 7. TGA thermograms of ABS, ABS with 30 wt% of DPPMP.

lowest LOI. Next thing to be noticed is that there is no or very little change in the amount of residue with the addition of DPPMP for all the compositions investigated in this study. The amount of residue becomes even less for the mixtures of PC (Figure 4). However, V-0 rating is obtained for this composition. These evidences indicate that the gas-phase mode of action is responsible for DPPMP. The similar findings were observed by us for the bicyclic phosphonates.<sup>32</sup>

## Conclusions

A novel phosphorus-nitrogen compound based on phosphoramidate, DPPMP was synthesized and tested as a single component fire-retardant additive for PC, PBT, EVA, and ABS. In thermogravimetry experiments DPPMP showed one step degradation and left very little residue above 340 °C. When this compound was added to polymers, the LOI values were increased and even UL-94 V-0 ratings were obtained at reasonable amount of loading, indicating

that DPPMP can be an efficient additive-type flame retardant. Moreover, this material is water insoluble. And no or little change in the amount of charred residue was observed with the addition of DPPMP. A gas-phase flame-retarding mode of action is believed to work for this compound and the presence of  $\text{CH}_3\text{-P(O)-}$  unit may be responsible for this action.

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