Synthesis, Flame Retardancy, and Thermal Degradation Behaviors of Novel Organo-Phosphorus Compounds Derived from 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO)

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Abstract: A series of novel organo-phosphorus compounds was synthesized from 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) in an attempt to obtain high phosphorus (P) containing halogen-free flame retardant (FR). The success of synthesis was confirmed by ^{1}H and ^{31}P NMR spectra. The P content of FR varied from 12.95 to 19.22 wt%. Thermal stabilities of synthesized FRs and their flame retardancy for Acrylonitrile-Butadiene-Styrene copolymer (ABS) were investigated by thermal gravimetric analysis (TGA) and the classification of UL-94 V-0 rating, respectively. 27.5-30.0 wt% FR loadings gave the V-0 rating for the ABS/FR mixtures and no fume emission was observed. It was found that the flame retardancy strongly depends on the P content of FR and 5.03-5.30 wt% P is required in the formulation to exhibit self-extinguishing ability when phosphinate or phosphonate FRs are employed. The mode of flame retardancy action is also discussed.

Keywords: 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), organo-phosphorus, flame retardant, phosphorus content, acrylonitrile-butadiene-styrene copolymer (ABS).

Introduction

Today, polymers are widely used in very variety of applications. For a typical example, acrylonitrile-butadiene-styrene copolymer (ABS) is commonly utilized for appliances and consumer electronics, automobiles, tools, toys, and so on due to the balance of composition of co-monomer units and excellent appearance of its molded products. However, ABS is highly combustible, inherently easy to be decomposed when exposed to heat, and fails in the fire inhibition test like UL-94. Therefore, its poor flame resistance should be improved by incorporating the flame retardant (FR) in certain areas of applications.[1-4] Halogen-based flame retardants, especially aromatic bromine compounds, are the most widely used for that purpose. However, the generation of toxic, corrosive, and halogenated gases during virgin material processing and after-use waste incineration evoke environmental issues. Nowadays, EU forbids the use of polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs) in electric and electronic applications.

Great deal of efforts have been attempted to develop non-halogen flame retardants to substitute halogen ones.[5,6] Among many non-halogen chemicals proposed, organo-phosphorus compounds, which generate less toxic gases and smoke, are the materials to be taken into consideration as the first choice.[7-10] Triphenyl phosphate (TPP) and its analogues are widely known to be most effective flame retardants for many polymers.[11] But, because the evaporation temperatures of TPP and its analogues are quite lower than the processing temperatures of polymers in concern, they are not suitable to adopt for real applications. A considerable amount of TPP tends to evaporate during processing.[12] On the other hand, aromatic bisphosphates are thermally more stable than monophosphates and their evaporation temperatures are much higher compared to TPP. Phenyl diphosphate (PDP), resorcinol diphosphate (RDP), and tetra-2,6-dimethyl phenyl resorcinol diphosphate (DMP-RDP) are the typical examples of chemical species that are widely accepted in industries. However, they can not exhibit UL94 V-0 rating for highly combustible polymers like styrenic polymers because of their low P content.[13] The other chemical compound which attains great commercial success is 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). It is not employed as an addition type FR and normally incorporated into the backbones of epoxy resins or the amine hardeners *via* appropriate chemical reactions.[14-23] It is now well

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Table I. Structures and Characteristics of FRs Employed in this Study

FR	Generic Name	Abbreviated Name	P Content (wt%)	Yield (%)	Mp (°C)
	2-(6-oxido-6H-dibenz<c,e><1,2> oxaphosphorin-6-yl)methyl diphenyl phosphate	ODOPM-DP	12.95	96	105
	Bis-2-(6-oxido-6H-dibenz<c,e><1,2> oxaphosphorin-6-yl)methyl phenyl phosphonate	B-ODOPM-P	15.12	90	129
	Bis-2-(6-oxido-6H-dibenz<c,e><1,2> oxaphosphorin-6-yl)methyl methyl phosphonate	B-ODOPM-M	16.82	92	191
	2-(6-oxido-6H-dibenz<c,e><1,2> oxaphosphorin-6-yl)methyl diethyl phosphinate	ODOPM-DE	17.68	90	110
	2-(6-oxido-6H-dibenz<c,e><1,2>oxa phosphorin-6-yl)methyl methyl methyl phosphonate	ODOPM-MM	18.32	85	125
	2-(6-oxido-6H-dibenz<c,e><1,2> oxaphosphorin-6-yl)methyl dimethyl phosphinate	ODOPM-DM	19.22	93	150

accepted that DOPO generates less toxic gases and corrosive smoke. However, most studies have been focused on modifying the epoxy or amine backbone structures to improve thermal and flame retardant property. The P contents of thus obtained DOPO derivatives are also relatively low since inherent P content of DOPO is only 14.33 wt%. Therefore, neither DOPO nor its derivatives cannot pass UL-94 test, which is the most commonly employed test method for electric and electronic applications, for non-charrable and highly flammable polymers such as ABS and polyolefins.

In this work, a series of novel organo-phosphorus FRs was synthesized from DOPO. They contain higher P contents compared to DOPO and are expected to show better flame retardant performances for ABS. The minimum phosphorus (P) content which shows UL-94 rating in various ABS/FR mixtures was investigated to elucidate the relationship between chemical structure and FR performance. The chemical structures and abbreviation of synthesized FRs are presented in Table I.

Experimental

Materials. Paraformaldehyde, dimethyl methylphosphonate, diphenyl chlorophosphate, and phenylphosphonic dichloride of reagent grades were purchased from Aldrich. Xylene, dioxane, ethyl ether, triethylamine, thionyl chloride, methylene chloride, acetonitrile, hexane, methanol, chloroform, and pyridine were received from Samchun Chemical Company of Korea. 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) was obtained from Tokyo Kasei Kogyo Co. Ltd, Japan. Acrylonitrile-Butadiene-Styrene copolymer (ABS) of commercial grade was provided by the Cheil Industries, Korea.

2-(6-oxido-6H-dibenz <c,e><1,2> oxaphosphorin-6-yl) methanol (ODOPM), methylphosphonic dichloride, diethylphophinic chloride, dimethylphosphinic chloride, and methyl methylphosphonochloridate as the starting materials for synthesizing the target FRs were prepared in our laboratory by adopting the synthesis methods found in the literatures.[18,24-27]

Synthesis of Organo-Phosphorus Flame Retardants (FRs).
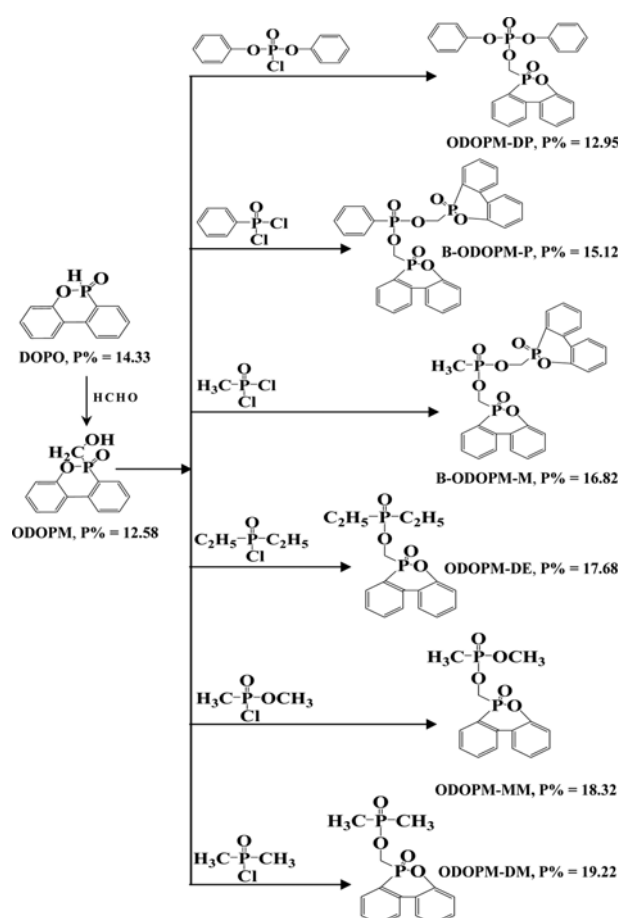
Scheme I. Synthesis scheme for organo-phosphorus FRs employed in this study.

Six different novel organo-phosphorus FRs shown in Table I were synthesized according to the synthesis scheme presented in Scheme I. The detailed synthesis methods are given below. ^{1}H and ^{31}P NMR were employed to prove the success of synthesis.

Measurements and Sample Preparation.

Spectroscopic Analysis: ^{1}H and ^{31}P NMR were performed on a Varian Unity Inova 500NB spectrometer by using CDCl$_3$ as a solvent and tetramethylsilane (TMS) as a reference. The chemical shift of ^{31}P NMR spectra are relative to the external standard of 85% H$_3$PO$_4$.

Thermogravimetric Analysis: TGA was performed on 2 to 10 mg samples under nitrogen and air atmospheres at a heating rate of 10 °C/min using TGA 2050 thermo-gravimetric analyzer.

Sample Preparation for UL-94 Test: Mixture of a synthesized flame retardant with ABS at the designated composition was processed in a Haake PolyDrive mixer with 60 rpm for 7 min at 230 °C for ABS. The compounded mixtures were compression molded at 220 °C for 7 min in a 30 bar press to obtain test bars.

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, 12.7 mm in width, and about 3.2 mm in thickness.

Results and Discussion

Synthesis of Novel Organo-Phosphorus Compounds Derived from DOPO. The detailed synthesis methods are given below. ^{1}H and ^{31}P NMR results presented in Figures 1-6 clearly confirm that the target FRs of high purities were synthesized successfully.

Synthesis of ODOPM-DP, B-ODOPM-P, B-ODOPM-M: General Procedures: A mixture of ODOPM and tri-ethylamin in dioxan was placed into a three-necked round-bottomed flask equipped with mechanical stirrer, a dropping funnel, and a condenser with a nitrogen inlet. The mixture was stirred and cooled to 0 °C. A solution of diphenyl chlorophosphate, phenylphosphonic dichloride, or methylphosphonic dichloride in dioxan was added dropwise for the synthesis of each FR. The reaction temperature was increased slowly to 120 °C and the reaction mixtures were refluxed at that temperature for another 6 h. The products were concentrated by removing the solvents and washed with water to obtain pure solid target FRs.

ODOPM-DP: 2-(6-Oxido-6H-dibenz <c,e><1,2> oxaphosphorin-6-yl)methyl diphenyl phosphate

^{1}H NMR (CDCl$_3$, ppm): δ=4.71-4.86 (m, 2H, P-O-**CH$_2$**), 6.90-8.01 (m, 18H, Ar-**H**) (Figure 1(A)). ^{31}P NMR (CDCl$_3$, ppm): two single peaks; δ=21.72, -17.22 (Figure 1(B)).

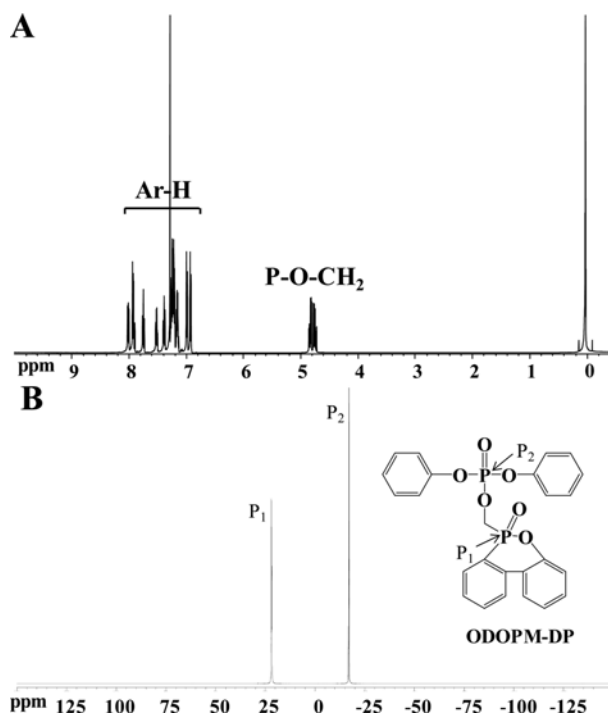**B-ODOPM-P: Bis-2-(6-oxido-6H-dibenz <c,e><1,2> oxaphosphorin-6-yl)methyl phenyl phosphonate**

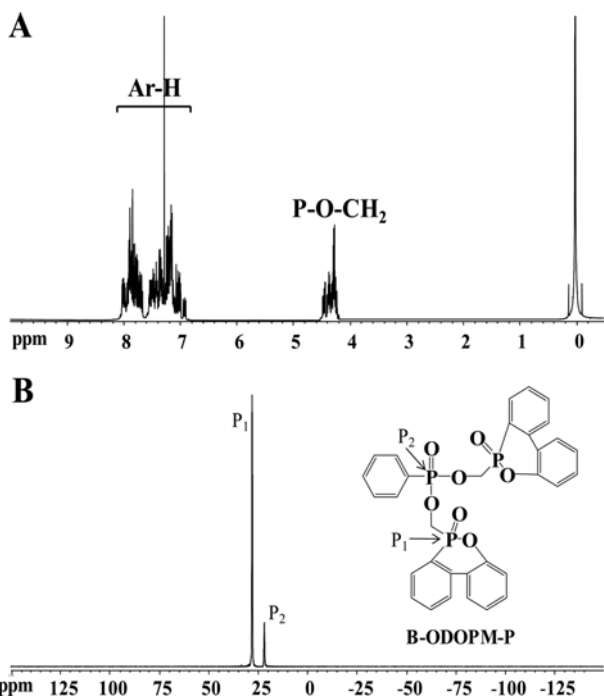**Figure 1.** ^{1}H (A) and ^{31}P NMR (B) spectra of ODOPM-DP.

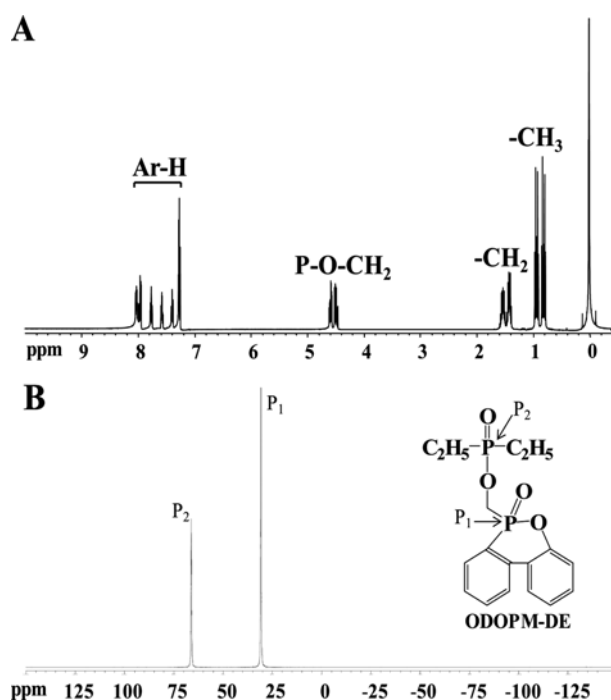**Figure 2.** ^{1}H (A) and ^{31}P NMR (B) spectra of B-ODOPM-P.

Figure 3. ^{1}H (A) and ^{31}P NMR (B) spectra of B-ODOPM-M.

Figure 4. ^{1}H (A) and ^{31}P NMR (B) spectra of ODOPM-DE.

Figure 5. ^{1}H (A) and ^{31}P NMR (B) spectra of ODOPM-MM.

^{1}H NMR (CDCl$_3$, ppm): δ=4.20-4.51 (m, 4H, P-O-C**H**$_2$), 6.90-8.05 (m, 21H, Ar-**H**) (Figure 2(A)). ^{31}P NMR (CDCl$_3$, ppm): two single peaks; δ=27.99, 21.89 (Figure 2(B)).

B-ODOPM-M: Bis-2-(6-oxido-6H-dibenz <c,e><1,2> oxa-phosphorin-6-yl)methyl methyl phosphonate

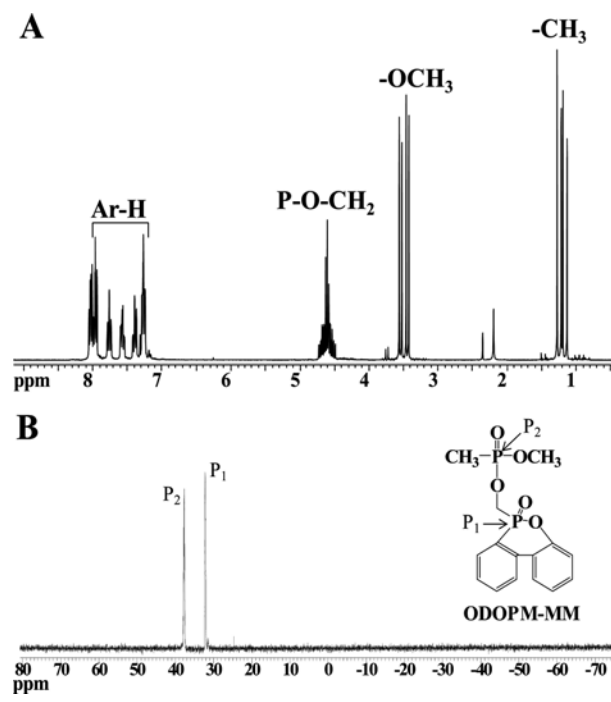^{1}H NMR (CDCl$_3$, ppm): δ=0.84-1.04 (m, 3H, P-C**H**$_3$), 4.19-

4.55 (m, 4H, P-O-C**H**$_2$), 7.18-8.10 (m, 16H, Ar-**H**) (Figure 3(A)). ^{31}P NMR (CDCl$_3$, ppm): two single peaks; δ=35.71, 28.89 (Figure 3(B)).

Synthesis of ODOPM-DE, ODOPM-MM, and ODOPM-DM: General Procedures: A mixture of ODOPM and tri-ethylamine in dioxane was placed into a three-necked round-
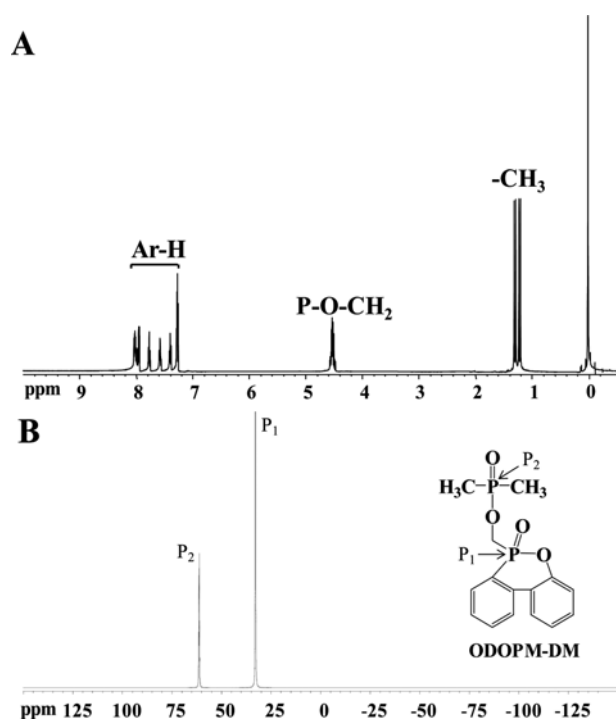
Figure 6. ^{1}H (A) and ^{31}P NMR (B) spectra of ODOPM-DM.

Figure 7. TGA thermograms of neat ABS and FRs under nitrogen.

bottomed flask equipped with mechanical stirrer, a dropping funnel, and a condenser with a nitrogen inlet. The mixture was stirred and cooled to 0 °C. A solution of diethylphosphinic chloride, methyl methylphosphonochloridate, or dimethyl-phosphinic chloride in dioxane was added dropwise for the synthesis of each FR. The reaction temperature was increased slowly to 80 °C and the reaction mixtures were refluxed at that temperature for another 6 h. After cooling and standing, the filtrate was collected by filtration and solvent was evaporated to obtain solid product. Target FRs of high purity were obtained after purification by a flash column chromatography.

ODOPM-DE: 2-(6-Oxido-6H-dibenz <c,e><1,2> oxa-phosphorin-6-yl)methyl diethyl phosphinate

^{1}H NMR (CDCl$_3$, ppm): δ=0.78-0.97 (m, 6H, P-CH$_2$-**CH$_3$**), 1.39-1.58 (m, 4H, P-C**H$_2$**- CH$_3$), 4.46-4.61 (m, 2H, P-O-**CH$_2$**), 7.25-8.04 (m, 8H, Ar-**H**) (Figure 4(A)). ^{31}P NMR (CDCl$_3$, ppm): two single peaks; δ=65.99, 30.64 (Figure 4(B)).

ODOPM-MM: 2-(6-Oxide-6H-dibenz <c,e><1,2> oxa-phosphorin-6-yl)methyl methyl methyl phosphonate

^{1}H NMR (CDCl$_3$, ppm): δ=1.12-1.28 (q, 3H, P-**CH$_3$**), 3.42-3.58 (q, 3H, P-O-**CH$_3$**), 4.50-4.72 (m, 2H, P-O-**CH$_2$**), 7.24-8.08 (m, 8H, Ar-**H**) (Figure 5(A)). ^{31}P NMR (CDCl$_3$, ppm): two single peaks; δ=37.58, 32.09 (Figure 5(B)).

ODOPM-DM: 2-(6-Oxide-6H-dibenz <c,e><1,2> oxa-phosphorin-6-yl)methyl dimethyl phosphinate

^{1}H NMR (CDCl$_3$, ppm): δ=1.20-1.32 (m, 6H, P-**CH$_3$**), 4.50-4.55 (m, 2H, P-O-**CH$_2$**), 7.26-8.04 (m, 8H, Ar-**H**) (Figure 6(A)). ^{31}P NMR (CDCl$_3$, ppm): two single peaks; δ=61.17, 32.76 (Figure 6(B)).
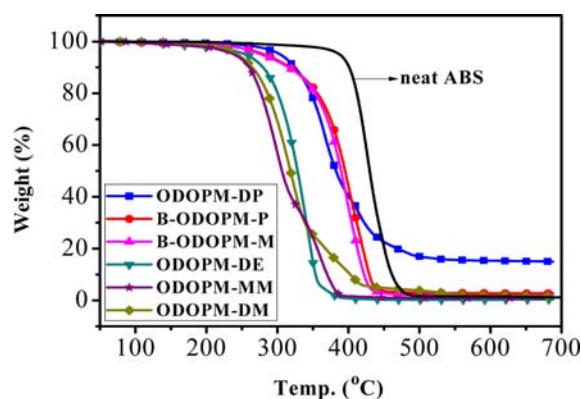
Thermal Properties. The TGA results for neat DOPO derivatives synthesized in this study and ABS are shown in Figure 7. Among six FRs synthesized, five FRs excluding ODOPM-DP have initial degradation temperatures (T_{onset}) quite lower than that of neat ABS and show a one-step thermal degradation with no charred residue after 600 °C. It is very interesting to notice that ODOPM-DP leaving considerable amount of charred residue is phosphate and contains all aromatic moieties and no chars are formed for other phosphonate and phosphinate compounds. Note that even B-ODOPM-P surrounded by all aromatic moieties does not leave little charred residue. We reported very recently that the same trends are found for different FRs derived from DOPO.[28] And other research works have also reported the similar results.[29-31] From the results shown in Figure 7, it is postulated that main flame retardant action is based on the gas phase and very little contribution from the condensed phase is expected for five FRs. In the case of ODOPM-DP, considerable degree of condensed phase action may be possible.

The thermal decompositions of ABS/FR mixtures are presented in Figure 8 and the thermal stability parameters therein are summarized in Table II. It can be seen that, in nitrogen atmosphere, the ABS/FR mixtures display a major mass loss *via* a single-step decomposition of approximately 90-98% from 376 to 495 °C (Figure 8(A)). In air atmosphere, more complicated behaviors are observed (Figure 8(B)). Followed by major weight losses (approximately 70-85%) at 371-450 °C, continued mass decreases at a reduced rate are observed at 450-550 °C. The second step degradation is believed to be related to the residual char formation during oxidative degradation. The continued mass losses beyond 550 °C belong to furthermore decomposition of the char layer. In addition, TGA results clearly show that the ABS/FR mixtures possess lower thermal stability than neat ABS at the early stage of decomposition, suggesting that the P containing volatiles are generated from the decomposition of FR and accelerate the thermal degradation of ABS. However, at the later stage of degradation, more complicated interactive reactions between FR generated in the earlier stage of degradation and decom-
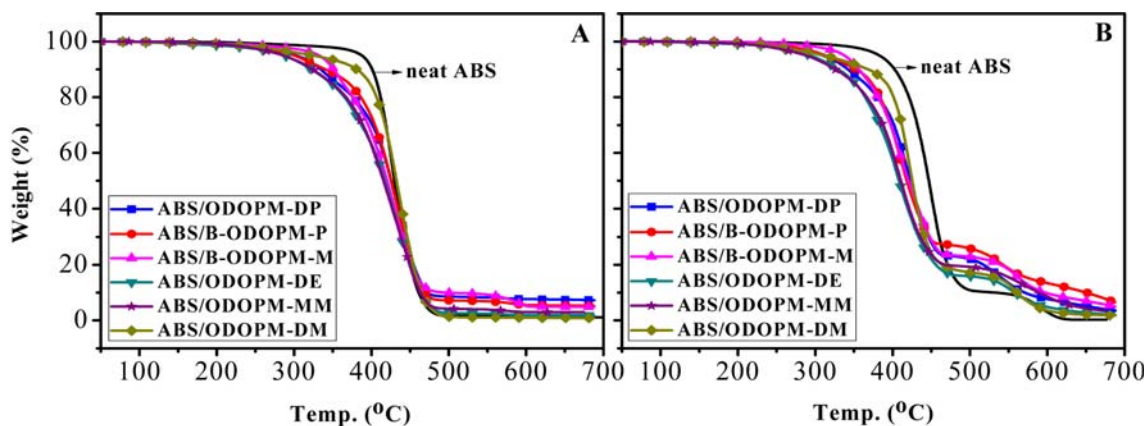
Figure 8. TGA thermograms of neat ABS and 72.5/27.5 (wt/wt) ABS/FR mixtures for two FRs, ODOPM-MM and ODOPM-DM, and 70/30 (wt/wt) mixtures for the rest four FRs under nitrogen (A) and air (B).

Table II. Summary of Thermal Stability Parameters for TGA Results Presented in Figure 8

Samples	T_{onset} (ºC)		T_{max} (ºC)		Residue at 500 ºC (%)		Residue at 650 ºC (%)	
	N₂	Air	N₂	Air	N₂	Air	N₂	Air
Neat ABS	403	409	490	494	1.69	10.7	1.34	0.0
70/30 ABS/ODOPM-DP	376	371	481	464	8.64	22.1	7.45	5.5
70/30 ABS/B-ODOPM-P	385	361	482	459	7.24	26.0	5.48	10.2
70/30 ABS/B-ODOPM-M	372	366	485	463	9.97	22.8	4.92	7.0
70/30 ABS/ODOPM-DE	365	361	491	476	2.61	15.8	1.90	2.8
72.5/27.5 ABS/ODOPM-MM	367	362	485	468	4.30	19.1	2.95	4.8
72.5/27.5 ABS/ODOPM-DM	401	398	495	474	1.34	17.2	0.99	2.1

Table III. UL-94 Results for Neat ABS and for the Mixtures of ABS with Various Organo-Phosphorus FRs

Sample	P% in FR (wt%)	P% in the Mixture	UL-94 Results Burning Time		UL-94 Rating	Fume
			First	Second		
Neat ABS	-	0	>60	-No rating	+	
ABS/ODOPM-DP (30 wt%)	12.95	3.89	23	>60	No rating	Scarcely
ABS/B-ODOPM-P (30 wt%)	15.12	4.54	15	>60	No rating	Scarcely
ABS/B-ODOPM-M (30 wt%)	16.82	5.05	0	1.5	V-0	-
ABS/ODOPM-DE (30 wt%)	17.68	5.30	0	0.9	V-0	-
ABS/ODOPM-MM (27.5 wt%)	18.32	5.03	0	1.8	V-0	-
ABS/ODOPM-DM (27.5 wt%)	19.22	5.29	0	1.2	V-0	-

posed ABS are possible and contribute significantly to the formation of the residual chars which would prevent further degradation. But, no direct correlation between the FR structure and the extent of charring is found. For an example, the greatest charred residue is observed for the mixture with B-ODOPM-P whilst the highest charring amount is found for ODOPM-DP in the neat FR cases.

Flame Retardancies. Table III shows the UL-94V test results for neat ABS and for the mixtures of ABS with various FRs.

ODOPM-DP whose thermal degradation and amount of charred residue are the greatest among six FRs shows no rating even at 30 wt% loading. It is well known that the phosphate type FRs act dominantly in the condensed phase. Since ODOPM-DP leaves the considerable amount of charred residue, it is assumed that ODOPM-DP works in both condensed and gas phases. However, the P content of ODOPM-DP is rather low and then the flame inhibition ability of ODOPM-DP in the gas phase is not enough to extinguish the flame. Furthermore, the for-

mation of char layer during the degradation of ODOPM-DP, as clearly indicated from the TGA results shown in Figure 8, is probably not sufficient enough to make an effective insulating protective layer which will prevent the transfer of combustible gases to the surface of combusting flame.

The other five FRs, B-ODOPM-P, B-ODOPM-M, ODOPM-DE, ODOPM-MM, and ODOPM-DM, that do not leave any charred residues and decompose completely before the decomposition of ABS exhibit better flame retardancy for ABS. B-ODOPM-M and ODOPM-DE show the V-0 rating at 30 wt% FR loading. And lesser amount (27.5 wt%) of FR loading is enough to give the V-0 rating for ODOPM-MM and ODOPM-DM containing mixtures. These results clearly indicate that the main action of flame retardancy of these FRs should be based on the gas phase. DOPO is known to release the stable dibenzofuran under thermal decomposition and then, phosphorus-containing PO radical is formed.[32-37] Schafer *et al.*[32] reported from the study on the flame-retardancy of DOPO containing epoxy resin that the significant amounts of PO radicals are released from the DOPO. The generated PO radicals are the active species during the combustion process and interact with H and OH radicals existing in the gaseous phase of the fire. It should be noted that, in addition to DOPO group, FRs employed in this work also contain other phosphorus groups such as $P(O)-C_6H_5$, $P(O)-CH_3$, and $P(O)-C_2H_5$ that would produce P-bearing species like $^\bullet PO$, $^\bullet HOPO$, $^\bullet HOPO_2$, and $^\bullet PO_2$ in the vapor phase and promote to the recombination with $^\bullet H$ and $^\bullet OH$.[38-41]

In our previous studies,[27,28,42-44] it was asserted that the flame retardancy and consequent inhibition efficiency mainly depends on the P content of FR. Results shown in Table III clearly indicate that, with increasing the P content of FR, the lower FR loading is needed and that the minimum P content in the mixture which gives V-0 rating is about 5 wt%. This finding strongly supports our assertion that the P content in FR is the most important factor governing the flame retardancy and the chemical structure of FR is also important.

Conclusions

In an attempt to investigate the factors governing the flame retarding performances of organo-phosphorus FR, various novel FRs derived from DOPO were synthesized successfully and their flame retardancy for the mixtures with highly combustible polymer, ABS, was investigated by UL-94V test. V-0 rating can be obtained at 30 wt% FR loadings for B-ODOPM-M or ODOPM-DE and 27.5 wt% FR loading for ODOPM-MM or ODOPM-DM. Those four FR species leave no charred residue when decomposed alone and very little residue for the mixture with ABS. No rating can be achieved even at 30 wt% FR loading for ODOPM-DP which leaves considerable amount of charred residue and great deal of contribution is expected from the condensed phase action. Therefore, it is concluded that the P content in FR is very

crucial factor governing the flame retardancy. Most important finding is that at least 5 % of P content is needed in the formulation to achieve UL-94 V-0 rating for highly flammable polymer such as ABS. The second finding to note is that the nature of chemical structure is also important.

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