Synthesis and Characteristics of Phosphonate-Containing Maleimide Polymers

Wei-Jye SHU,[*,**] Li-Hsiang PERNG,[*,†] and Wei-Kuo CHIN[**]

[*]*Department of Chemical Engineering, Ta-Hwa Institute of Technology, Chiung-Lin,*
307 Hsinchu, Taiwan, Republic of China
[**]*Department of Chemical Engineering, National Tsing Hua University,*
300 Hsinchu, Taiwan, Republic of China

ABSTRACT: Phosphonate-containing *N*-phenyl maleimide monomers were synthesized by a two-step reaction. All maleimide polymers were synthesized by free radical polymerization in toluene solution using azobis(isobutyronitrile) (AIBN) as initiator. The structures of the maleimide monomers were identified by ^{1}H, ^{13}C, ^{31}P-NMR, and element analysis. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) were used to analyze the thermal properties of the polymers. The degree of polymerization in phosphonate-containing maleimide polymers should be affected by side chains. The introduction of phosphonate into a side chain of maleimide polymer may reduce the glass transition temperature (T_g) and thermal stability, but increase char yield of solid residue as an excellent flame retardant. T_g and thermal stability of the phosphonate-containing maleimide polymers depended on substitution of the phenyl ring in the side chain. Phosphonate-containing maleimide polymers with halogen or sulfur atom may combine the flame retarding mechanism of gas-phase and solid-phase to promote their flame retardancy.
     KEY WORDS   Phosphonate-Containing Maleimide Polymers / Flame Retardant /

The combustibility of organic polymers limits their application. Therefore, the development of organic polymers with flame retardancy has become an important study topic. Traditional flame retarding polymers are prepared from physical blending with flame retarding additives.[1,2] Flame retarding additives are always halogens. Halogen ions catch free radicals released during combustion and interrupt combustion reactions to get higher flame resistance. Nevertheless, such decomposition reactions release simultaneously smoke and toxic substances. The applications of halogen-containing flame retardants are limited due to more and more strict environment laws. In contrast, the development of non-halogen flame-retardants, such as the phosphorus-containing flame-retardants with the lower smoke density and toxicity will become the mainstream in the future. Like halogens, phosphorus-containing compositions evolved in gas phase catch free radicals released during combustion and interrupt combustion reactions. The thermal decomposition of phosphorus-containing polymer, mainly having a flame retarding ability in condensed phase,[3] produces condensation reactions and catalyzes the chain transfer of carbonization to form high char yield of solid residue. The char layer prevent heat transfer, brings down the burning temperature and inhibits the release of combustible gas to get a fine fireproof effect.[3,4] Due to restrictions in applications for some reasons such as processing or physical properties, studies of phosphorus-containing flame retardant have changed gradually from additive type to reactive type.

N-substituted maleimide monomers, such as *N*-phenylmaleimide (PM), *N*-hydroxyphenylmaleimide (HPM) and halogen-substituted *N*-hydroxyphenylmaleimide (XHPM), are usually designed to modify thermal stability and fire resistance of organic matrix materials.[5–8] All these monomers are homopolymerized or copolymerized with monomers such as styrene for the purpose of materials-modification. Copolymers, for example, of PM with styrene,[9–11] methyl methacrylate,[12–14] acrylonitrile[15] or vinyl acetate[16] have higher thermal stability and fire resistance. HPM polymer use is limited since the phenol group induces chain transfer during polymerization to lead lower polymerization. The introduction of substituted side groups in the HPM monomer[17] promote polymerization. Halogen-substituted XHPM polymers possess thermal stability from imide ring and flame retardancy from halides.[18–20] Studies on phosphorus-introduced flame retardant systems are few in the literature.[21] We designed *N*-phenylmaleimide polymers with different substituted phosphonate-containing side groups to study thermal stability and flame retarding properties.

[†]To whom correspondence should be addressed (Tel: +886-3-5923551, Fax: +886-3-5927310, E-mail: ceplh@thit.edu.tw (Li-Hsiang Perng)).

EXPERIMENTAL

Materials

4-Aminophenol, 3-aminophenol, 4-amino-2,6-dibromophenol, maleic anhydride, and cuprous (I) chloride were obtained from Lancaster. Acetic anhydride and triethylamine (TEA) were obtained from TEDIA. Diethyl chlorophosphonate (DECP), diphenylphosphoryl chloride (DPPC), and diethyl chlorothiophosphonate (DECTP) were obtained from Aldrich Chemicals. Cobalt acetate was obtained from Showa. All reagents were used as received. Tetrahydrofuran (THF) was distilled after dehydration with sodium. N,N-Dimethylformamide (DMF) was dried over CaH_2. Other solvents were purified by conventional methods.

Synthesis

N-Hydroxyphenylmaleimide.[22, 23] In a three-neck flask equipped with a teflon-stirrer and a thermometer and purged with nitrogen gas at a constant flow rate, 10 g (0.0917 mol) of 3-(or 4)-aminophenol were added gradually into the solution of maleic anhydride (11 g) in 50 mL of DMF and the mixture was stirred 2 h in a water bath to obtain a clear amic acid solution. A mixture of 5.5 g phosphorus pentaoxide, 2.5 g sulfuric acid and 50 mL DMF was then added dropwise to the amic acid solution, already raised temperature to 80°C, over a period of 1 h. After stirring for 6 h, the mixture was cooled and poured into 500 mL ice water to obtain the precipitate by filtering. The precipitate was washed several times with de-ionic water and recrystallized several times with isopropanol to obtain the *N*-phenylmaleimide monomer dried under reduced pressure.

(i) *N-(3-Hydroxyphenyl)maleimide* (**3HPMI**). Yield 64% as straw yellow powder, mp 137–138°C. ^{1}H NMR(DMSO), δ(ppm): 6.73(2 H, m, 2′–**H**, and 4′–**H** or 6′–**H**); 6.88 (1 H, dd, $J = 8.2$ and 2.4 Hz, 4′–**H** or 6′–**H**); 7.13 (2 H, s, –CO–C**H**=C**H**–CO–); 7.24 (1 H, dd, $J = 8.2$ and 8.2 Hz, 5′–**H**); 4.05 (1 H, s, 3′–**OH**). ^{13}C NMR (DMSO), δ (ppm): 113.8 (2′–**C**); 114.7 (4′–**C**); 117.2 (6′–**C**); 129.5 (5′–**C**); 132.4 (1′–**C**–N–); 134.6 (–CO–C**H**=C**H**–CO–); 157.6 (3′–**C**–OH); 169.9 (2–**C**=O). EA(%): C, 63.0; H, 3.9; N, 7.0 (calc.: C, 63.5; H, 3.7; N, 7.4).

(ii) *N-(4-Hydroxyphenyl)maleimide* (**4HPMI**). Yield 71% as orange needles, mp 185–186°C. ^{1}H NMR (*d*-chloroform), δ (ppm): 7.38 (2 H,d, 2′–**H**, 6′–**H**); 7.19 (2 H, d, 3′–**H**, 5′–**H**); 6.83 (2 H, s, –CO–C**H**=C**H**–CO–); 3.70 (1 H, 4′–**OH**). ^{13}C NMR (*d*-chloroform), δ (ppm): 122.5 (3′–**C**, 5′–**C**); 126.6 (1′–**C**–N–); 128.5 (2′–**C**, 6′–**C**); 134.5 (–CO–C**H**=C**H**–CO–); 150.1 (4′–

C–OH); 168.4 (2–**C**=O). EA(%): C, 63.1; H, 3.8; N, 7.1 (calc.: C, 63.5; H, 3.7; N, 7.4).

N-(2,6-Dibromo-4-hydroxyphenyl)maleimide (**DBHPMI**).[24] With the same type of flask as above, 10 g (0.0288 mol) 4-amino-2,6-dibromophenol were added gradually to a solution of maleic anhydride (3.5 g) in 50 mL THF and the mixture was stirred 5 h in a water bath to obtain a clear amic acid solution. The mixture including stoichiometric amounts of acetic anhydride, 0.5 g cobalt acetate and 1.5 g TEA, was added dropwise to this solution of amic acid already raised temperature to 80°C. After stirring 5 h, the mixture was distilled to remove THF and obtain the precipitate. The precipitate was washed several times with de-ionic water to reach a neutral state and recrystallized several times with ethyl acetate/*n*-hexane to obtain the bromine-containing *N*-phenyl maleimide monomer dried under reduced pressure.

Yield 60% as fine golden yellow needles, mp 202–203°C. ^{1}H NMR (*d*- chloroform), δ (ppm): 6.84 (2 H, s, –CO–C**H**=C**H**–CO–); 6.65 (2 H, s, 2′–**H**, 6′–**H**); 3.64 (1 H, 4′–**OH**). ^{13}C NMR (*d*-chloroform), δ (ppm): 115.5 (3′–**C**, 5′–**C**); 122.6 (1′–**C**–N–); 128.5 (2′–**C**,6′–**C**); 134.5 (–CO–C**H**=C**H**–CO–); 157.1 (4′–**C**–OH); 170.4 (2–**C**=O). EA (%): C, 34.0; H, 1.5; N, 4.2 (calc.: C, 34.6; H, 1.4; N, 4.0).

Phosphonate-containing Monomers.[25] The flask as above with ice bath was charged with 100 mL THF and added to a mixture of 0.016 mol *N*-hydroxyphenylmaleimide, 3 mL TEA and 0.012 g Cu_2Cl_2. A solution of 0.0192 mol chlorophosphonate (such as diethyl chlorophosphonate, DECP 3.3 g) in 50 mL THF was added gradually to the mixture during 2 h. The reaction was kept at room temperature for 12 h. The mixture was filtered to remove the precipitate of amine hydrochloride and distilled to remove THF to obtain the precipitate. The precipitate was dissolved in 100 mL ethyl acetate and extracted by 1% NaOH solution to obtain the organic layer. The organic layer was isolated and dried with anhydrous magnesium sulfate. The organic layer was recrystallized with *n*-hexane to obtain the phosphonate-containing *N*-phenyl maleimide monomer dried under reduced pressure.

(i) *Diethyl (3-(N-maleimido) phenyl) phosphonate* (**3MIP**). Yield 78% as a dark brown liquid, ^{1}H NMR (*d*-chloroform), δ (ppm): 7.38 (1 H,d, 2′–**H**); 7.14 (1 H,d, 6′–**H**); 7.29 (2 H, d, 4′–**H**,5′–**H**); 6.83 (2 H, s, –CO–C**H**=C**H**–CO–); 3.87 (2 H, q, O–C**H₂**–CH₃); 1.65 (3 H, t, O–CH₂–C**H₃**). ^{13}C NMR (*d*-chloroform), δ (ppm): 151.5 (3′–**C**–O–P), 130.5 (5′–**C**); 132.4 (1′–**C**–N–); 117.5 (2′–**C**); 122.6 (6′–**C**); 134.5 (–CO–C**H**=C**H**–CO–); 119.1 (4′–**C**); 169.4 (2–**C**=O); 65.3 (O–**C**H₂–CH₃); 16.5 (O–CH₂–**C**H₃). ^{31}P NMR (*d*-

chloroform), δ (ppm): −6.9. EA (%): C, 51.9; H, 5.0; O, 29.1; N, 4.1 (calc.: C, 51.7; H, 4.9; O, 29.5; N, 4.3).

(ii)*Diethyl (4-(N-maleimido) phenyl) phosphonate* (**4MIP**). Yield 85% as a dark brown liquid. ^{1}H NMR(*d*-chloroform), δ (ppm): 7.41 (2 H, d, 2′–**H**, 6′–**H**); 7.34 (2 H, d, 3′–**H**, 5′–**H**); 6.84 (2 H, s, –CO–**CH**=**CH**–CO–); 3.89 (2 H, q, O–**CH₂**–CH₃); 1.67 (3 H, t, O–CH₂–**CH₃**). ^{13}C NMR (*d*-chloroform), δ (ppm): 128.5 (3′–**C**, 5′–**C**); 129.4 (1′–**C**–N–); 120.5 (2′–**C**, 6′–**C**); 133.5 (–CO–**CH**=**CH**–CO–); 151.1 (4′–**C**–O–P); 168.4 (2–**C**=O); 67.3 (O–**CH₂**–CH₃); 16.5 (O–CH₂–**CH₃**). ^{31}P NMR (*d*-chloroform), δ (ppm): −6.8. EA (%): C, 52.1; H, 5.1; O, 29.0; N, 4.2 (calc.: C, 51.7; H, 4.9; O, 29.5; N, 4.3).

(iii) *Diethyl (2,6-dibromo-4-(N-maleimido) phenyl)-phosphonate* (**BrMIP**). Yield 70% as bottle green powder, mp 156–157°C. ^{1}H NMR (*d*-chloroform), δ (ppm): 7.78 (2 H, s, 2′–**H**, 6′–**H**); 6.85 (2 H, s, –CO– **CH**=**CH**–CO–); 4.45 (2 H, q, O–**CH₂**–CH₃); 1.43 (3 H, t, O–CH₂–**CH₃**). ^{13}C NMR (*d*-chloroform), δ (ppm): 117.5 (3′–**C**, 5′–**C**); 151.4 (1′–**C**–N–); 131.5 (2′–**C**, 6′–**C**); 137.5 (–CO–**CH**=**CH**–CO–); 148.1(4′–**C**–O–P); 168.4 (2–**C**=O); 66.3 (O–**CH₂**–CH₃); 17.5 (O–CH₂–**CH₃**). ^{31}P NMR (*d*-chloroform), δ (ppm): −8.4. EA (%): C, 35.1; H, 2.6; O, 19.6; N, 2.7 (calc.: C, 34.8; H, 2.9; O, 19.9; N, 2.9).

(iv) *Diethyl (4-(N-maleimido) phenyl) thiophosphonate* (**4MTP**). Yield 68% as a dark brown liquid. ^{1}H NMR (*d*-chloroform), δ (ppm): 7.40 (2 H, d, 2′– **H**, 6′–**H**); 7.31 (2 H, d, 3′–**H**, 5′–**H**); 6.87 (2 H, s, –CO–**CH**=**CH**–CO–); 4.25 (2 H, q, O–**CH₂**–CH₃); 1.41 (3 H,t, O–CH₂–**CH₃**). ^{13}C NMR (*d*-chloroform), δ (ppm): 127.1 (3′–**C**, 5′–**C**); 128.1 (1′–**C**–N–); 121.8 (2′–**C**, 6′–**C**); 134.5 (–CO–**CH**=**CH**–CO–); 150.1 (4′–**C**–O–P); 169.2 (2–**C**=O); 65.3 (O–**CH₂**–CH₃); 16.1 (O–CH₂–**CH₃**). ^{31}P NMR (*d*-chloroform), δ (ppm): −6.7. EA(%): C, 49.2; H, 4.9; O, 23.0; N, 3.9 (calc.: C, 49.3; H, 4.7; O, 23.5; N, 4.1).

(v) *Diphenyl (4-(N-maleimido) phenyl) phosphonate* (**PhMIP**). Yield 72% as a dark red liquid. ^{1}H NMR (*d*-chloroform), δ(ppm) 7.38 (2 H, d, 2′–**H**, 6′–**H**); 7.25 (2 H, d, 3′–**H**, 5′–**H**); 6.82 (2 H, s, –CO–**CH**=**CH**–CO–); 7.25 (2 H, d, 2″–**H**, 6″–**H**); 7.24 (2 H, d, 3″–**H**, 5″–**H**); 7.21 (1 H, d, 4″–**H**). ^{13}C NMR (*d*-chloroform), δ(ppm): 129.1 (1′–**C**–N–); 121.5 (2′–**C**, 6′–**C**); 120.5 (2″–**C**, 6″–**C**); 126.0 (3′–**C**, 5′–**C**); 130.4 (3″–**C**, 5″–**C**); 134.5 (–CO–**CH**=**CH**–CO–); 150.7 (4′–**C**–O–P); 169.4 (2–**C**=O); 149.7 (1″–**P**–O–**C**); 127.7 (4″–**C**). ^{31}P NMR (*d*-chloroform), δ (ppm): −6.5. EA (%): C, 51.3; H, 4.6; O, 29.2; N, 4.1 (calc.: C, 51.7; H, 4.9; O, 29.5; N, 4.3).

Phosphonate-Containing Polymer.[26] A flask was charged with maleimide monomers, 2,2′-azobis-

isobutyronitrile (AIBN) (10 mmol L⁻¹) as initiator and toluene as solvent. The unsaturated monomers were polymerized by free radicals at 70°C for 12 h to form a mixture containing *N*-phenyl maleimide polymers. The mixture was dissolved in dichloromethane and poured into methanol to precipitate the *N*-phenyl maleimide polymers dried under reduced pressure.

Instrumentation

^{13}C, ^{1}H, and ^{31}P NMR spectra and elemental analysis (C, H, N) of all the *N*-phenyl maleimide monomers were measured by the Bruker MSL NMR Spectrometer and Heraeus CHN–O Rapid Analyzer, respectively. Infrared reflection (IR) spectra of all imide monomers and polymers were obtained by a Nicolet Omnic 3 Fourier Transform Infrared Reflection (FT-IR) spectroscopy. The molecular weight distribution of the maleimide polymers was measured by Waters 510 Gel Permeation Chromatography (GPC) at a flow rate of 1.0 mLmin⁻¹ at a sample concentration of 0.5 wt% in THF as effluent flow. The GPC system was first calibrated using standard samples of polystyrene with narrow distribution of molecular weight. The thermal properties of the organic compounds synthesized were investigated by a differential scan calorimeter (DSC, TA-Instruments DSC 10) at a heating rate of 10°C min⁻¹ in N₂, and thermogravimetry (TG, TA-Instruments TGA 51) at a heating rate of 20°C min⁻¹ in air or N₂, respectively. Melting points of all monomers were tested by DSC at a heating rate of 10°C min⁻¹ in N₂.

RESULTS AND DISCUSSION

Phosphonate-containing maleimide monomers were synthesized by a two-step reaction as shown in scheme 1. *N*-Hydroxyphenylmaleimide monomers were synthesized through imidized reactions in Step 1.[22-24] Phosphonate-containing maleimide monomers were then prepared by a condensation reaction in Step 2.[25]

Properties of Maleimide-Series Monomers

Melting points of all *N*-hydroxyphenylmaleimide monomers were found to be in the order: DBHPMI> 4HPMI> 3HPMI and affected by the regularity of molecular arrangement and high polarity of bromine.

In ^{31}P NMR spectra, the chemical shift (δ) of BrMIP moved downfield (−8.4 ppm) compared with those of 3MIP and 4MIP. This was probably due to the fact that bromine atoms of BrMIP possess higher electronegativity to cause the lower electron density and higher de-shielding effect around phosphorous atoms. For the same reason, 4MTP exhibited higher δ than

Step1: Synthesis of *N*-hydroxyphenyl maleimide monomers
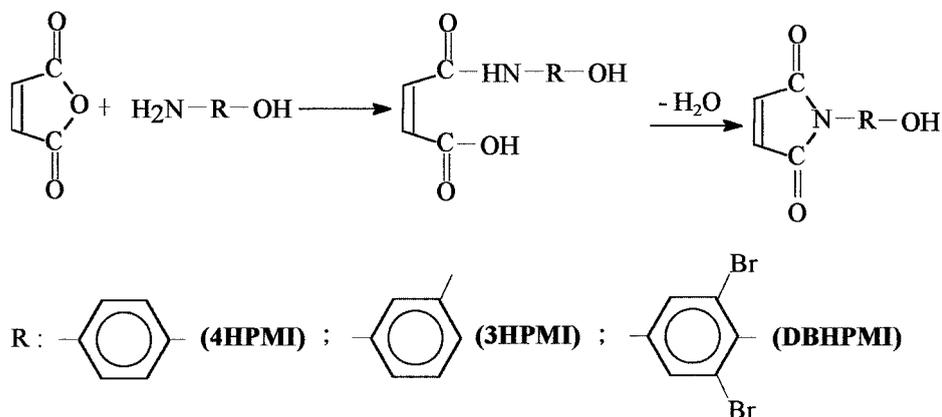
Step2: Synthesis of phosphonate-containing maleimide monomers
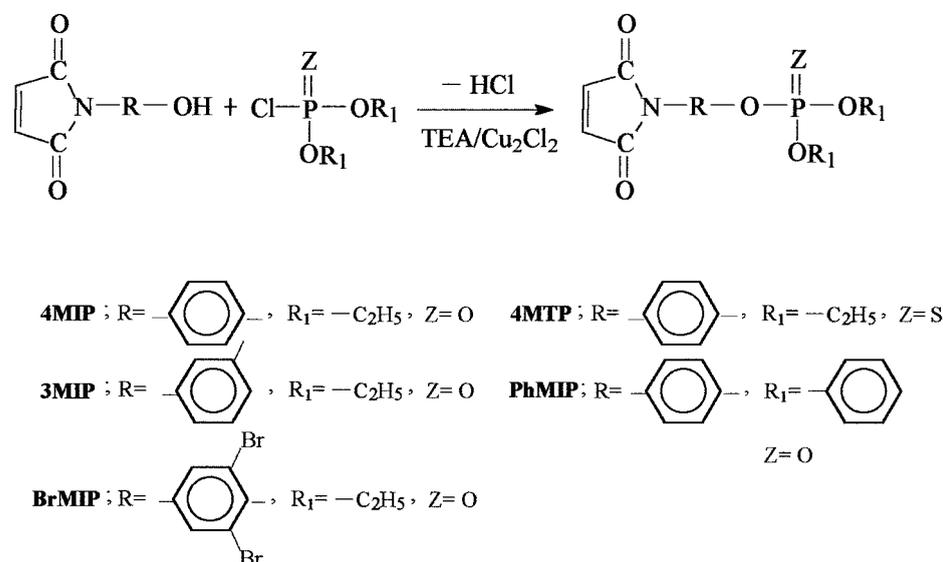
Scheme 1.

4MIP due to the lower electro-negativity of sulfur atoms compared to oxygen atoms. Phosphorous atom in PhMIP appeared upfield (−6.5 ppm) compared with that in 4MIP (−6.8 ppm) because the phenoxy group of the former exerted more shielding effect around phosphorous atoms than the alkoxy group[27, 28] of the latter.

Properties of Maleimide Polymers

GPC data of polymers prepared from various maleimide monomers are shown in Table I. The yield, degree of polymerization (DP) and molecular weight of the polymers derived from the phenol-type monomers were relatively low. This should be due to the presence of free phenolic substituents during free radical polymerization.[29] The yield and molecular weight of polymer derived from the phosphonate-containing maleimide monomer were low. Although the phosphonate units of the maleimide polymers masked the phenol group, steric hindrance and chain transfer caused by

phosphonate ester side-chains should be the reason of reducing polymerization efficiency.

Variance of chemical structure during the synthesis reaction was identified by FT-IR and ^{1}H NMR spectra, such as 4MIP system shown in Figures 1 and 2, respectively. FT-IR spectra of 4HPMI monomer revealed absorption bands v (cm^{-1}): 3483 (–OH); 1706 (C=O); 1597, 1520 (C=C from benzene); 831 (disubstitution of benzene); 1414 (C–N–C) and 692 (C=C from maleimide ring) as shown in Figure 1. Absorption band of the hydroxyl group (3483 cm^{-1}) disappeared completely in the spectra of 4MIP monomer and there was a prominent absorption band in 1227–1232 cm^{-1} due to the double bond of P=O. For 4MIP polymer, absorption of C= C within maleimide ring disappeared completely for the reason of polymerization to be finished. The above result was identified by ^{1}H NMR spectra as shown in Figure 2. The absorption peak of unsaturated bond of maleimide ring disappeared com-

Table I. GPC data of polymers[a] prepared from maleimide monomers

Monomer	Yield/wt%	M_w	M_n	M_w/M_n	DP
3HPMI	52	4501	3126	1.44	16.9
4HPMI	60	5870	3494	1.68	18.5
DBHPMI	63	13051	6942	1.88	20.0
3MIP	56	8683	5566	1.56	17.1
4MIP	65	19830	7996	2.48	24.6
BrMIP	68	26289	9958	2.64	20.6
4MTP	67	19319	7458	2.59	21.9
PhMIP	60	19349	7588	2.55	18.0

[a]All polymers were synthesized at 70°C for 12 h with initiator AIBN (10 mmol L^{-1}) in toluene.
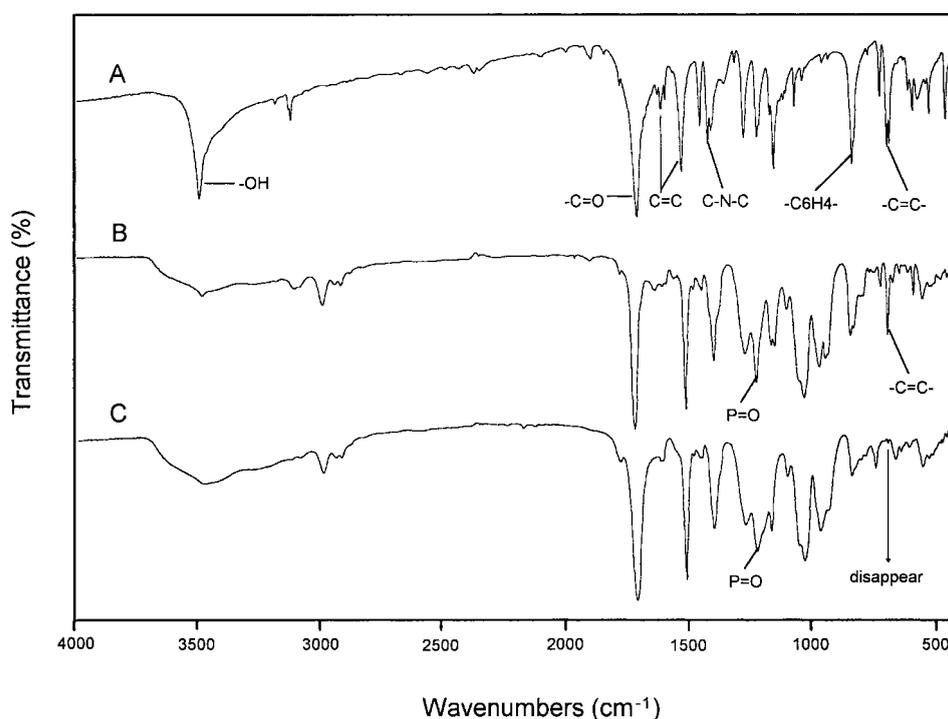
Figure 1. FT-IR spectra of 4HPMI monomer (A), 4PMIP monomer (B), and 4PMIP polymer(C).

pletely from downfield (6.84 ppm) to upfield (2.8 ppm) since its electron density around proton changed after polymerization.

Glass transition temperatures (T_g) of various N-phenyl maleimide polymers analyzed by DSC are listed in Table II. Phenol-type polymers possessed higher T_g than the phosphonate-type polymers for the reason that the phenol groups of the former formed hydrogen bonds[30, 31] to reduce mobility of side chains. T_g of DBHPMI polymer was lower than that of the others containing phenol-type side chain since interaction of hydrogen bond of the former was lower than that of the latter. T_g of all the phosphonate-containing maleimide polymers among 168–190°C was lower than that of all the phenol-type maleimide polymers because of the higher molecular mobility of phosphonate ester side chain. Thus, T_g of the phosphonate-containing polymers was of the order: PhMIP > 4MIP > BrMIP >

3MIP > 4MTP. PhMIP possessed the highest T_g indicating its rigid phenyl ring of phosphonate ester side chain to reduce molecular mobility.

Thermal properties of all maleimide polymers measured by TG in N$_2$ or air as shown in Figures 3–5 are listed in Tables II and III. As seen in Figure 3, $T_{5\%}$ of all the polymers derived from the phenol-type maleimide monomers was higher than 320°C when were heated under nitrogen gas, especially for that of 4HPMI around 382°C. Decomposition reactions should be directly initialized by scission of maleimide main-chains so as to appear only a one-stage pyrolysis. There was a two-stage decomposition during the scission of each phosphorus-containing polymer, except PhMIP, under nitrogen atmosphere. Maximum rates of weight loss of two stages for 4MIP (as shown in Figure 3) occurred at 279°C and 430°C, respectively. As shown in Table II, $T_{5\%}$ of all the polymers with a phosphonate-containing
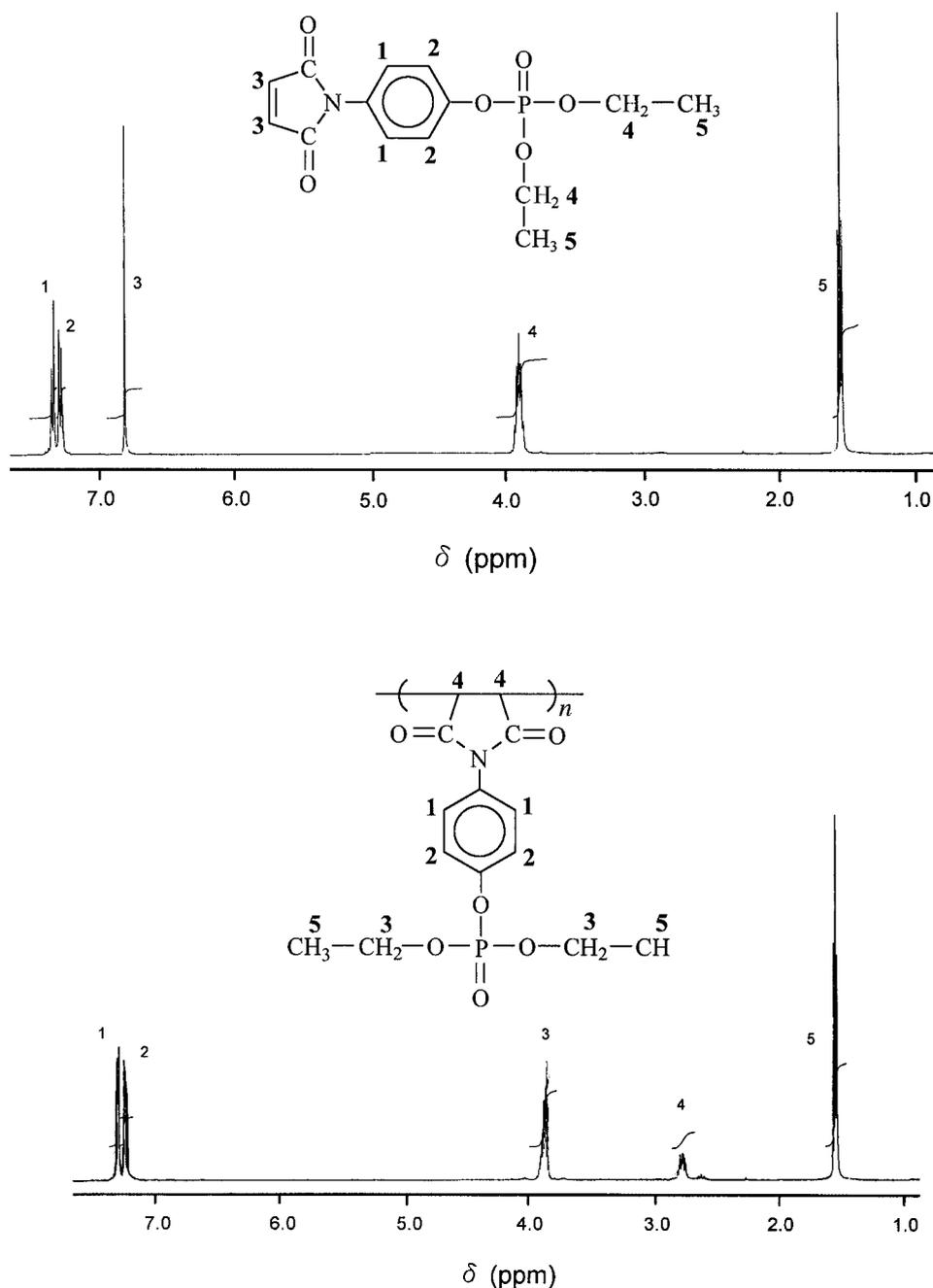
Figure 2. ^{1}H NMR spectra of Diethyl (4-(N-maleimido)phenyl) phosphonate (4MIP) monomer and polymer.

side chain appeared to be lower than that with phenol-type side chain, indicating that the side chain of the former was a more flexible chain segment than that of the latter. The results of thermal decomposition of the phosphonate-containing polymers showed that decomposition reaction should be initialized mainly by scission of phosphonate ester side chains because of owning lower bond energy, and further produced scission of the maleimide main-chain[25] along with carbonization to form high char yield of solid residue. Thus, the thermal stability of all the maleimide polymers in N$_2$ was higher than that in air because of the oxidization reaction. When all phenol-type maleimide polymers were heated in air, decomposition, as listed in Ta-
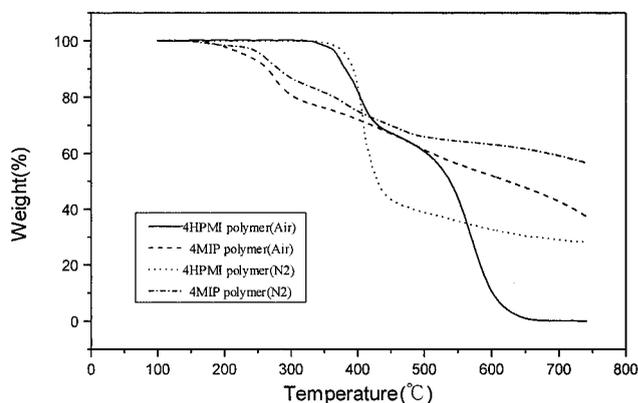

Figure 3. TG curves of polymers derived from 4HPMI and 4PMIP.

**Table II.** Thermal properties of polymers prepared from maleimide monomers

Monomer	P/%	Br/%	$T_g{}^a$/°C	$T_{5\%}{}^b$/°C		Char at 700°C[b] /wt%	
				Air	N_2	Air	N_2
3HPMI	0	0	222	371	370	0.0	25.3
4HPMI	0	0	242	369	382	0.0	29.1
DBHPMI	0	46.1	183	313	320	8.8	26.6
3MIP	9.54	0	170	264	267	44.5	58.5
4MIP	9.54	0	184	232	256	42.7	59.2
BrMIP	6.42	33.1	174	266	270	33.4	30.9
4MTP	9.09	0	168	257	258	42.7	55.6
PhMIP	7.36	0	190	325	328	43.4	46.1

[a] T_g represents the glass transition temperature analyzed by DSC at a heating rate of 10°C min^{-1} in N_2. [b] Thermal properties analyzed by TGA at a heating rate of 20°C min^{-1} in N_2 or in air.

Table III. Thermal properties of polymers prepared from maleimide monomers[a]

Monomer	Stage1				Stage2				Stage3			
	Air		N_2		Air		N_2		Air		N_2	
	T_1	V_1	T_1	V_1	T_2	V_2	T_2	V_2	T_3	V_3	T_3	V_3
3HPMI	412	0.262	406	0.330	450	0.172	–	–	–	–	–	–
4HPMI	405	0.197	408	0.670	549	0.210	–	–	–	–	–	–
DBHPMI	330	0.186	362	0.199	542	0.168	–	–	–	–	–	–
3MIP	267	0.152	279	0.125	379	0.059	412	0.046	547	0.049	–	–
4MIP	273	0.115	279	0.093	480	0.042	430	0.048	710	0.041	–	–
BrMIP	290	0.107	286	0.078	344	0.040	352	0.024	465	0.047	–	–
4MTP	275	0.143	287	0.147	394	0.056	410	0.056	706	0.083	–	–
PhMIP	386	0.123	439	0.130	710	0.037	–	–	–	–	–	–

[a] Thermal properties are analyzed by TGA at a heating rate of 20°C min^{-1} in N_2 or in air. T_i: Temperature (°C) of the maximum weight loss rate at stage i. V_i: Maximum weight loss rate (wt% °C^{-1}) at stage i.
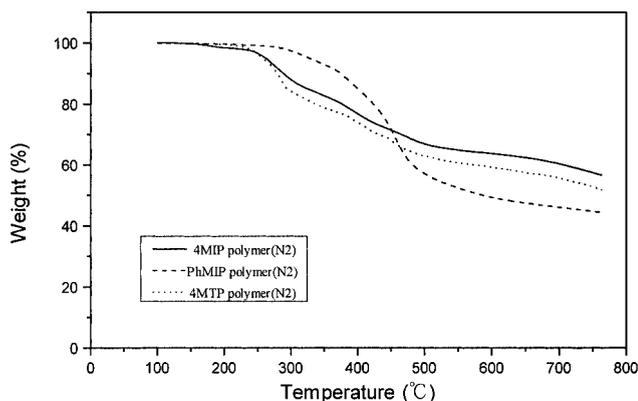
Figure 4. TG curves of 4MIP, PhMIP, and 4MTP polymers in N_2.
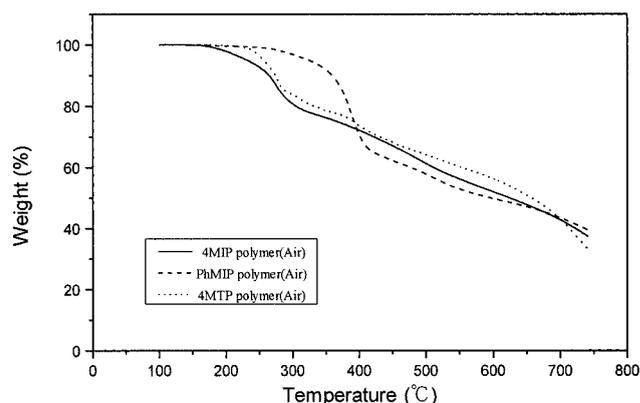
Figure 5. TG curves of 4MIP, PhMIP, and 4MTP polymers in air.

bles II–III, changed from one-stage to two-stage, and for the phosphonate-containing system, except PhMIP, from two-stage to three-stage. The decomposition of third stage for the phosphonate-containing polymers should be the oxidized combustion reaction under the high temperature. The decomposition of the first two stages for the resulting phosphonate-containing polymers in air was similar to those in N_2, indicating that the oxidation environment would not change the decomposition process[32] of the first two stages. The char yield of the phosphonate-containing maleimide polymer pyrolyzed in air could reach above 33 wt% at 700°C

due to the high oxidation resistance of phosphonate-containing solid residue. In Table III, maximum rates of weight loss of phosphonate-containing polymers in different environments were lower than those of the non-phosphide system. The results of higher char yield and lower weight loss rates during pyrolysis of phosphonate-containing system relative to those of non-phosphide system showed that the introduction of phosphonate into polymers increases flame retardancy.

The scission of DBHPMI in N_2 was a one-stage decomposition process as shown in Table III. Since this maleimide polymer with two bromine atoms ex-

hibited poor thermal stability. $T_{5\%}$ about 320°C was lower than that of 3- or 4-HPMI. The DBHPMI polymer due to flame retarding mechanism leaded to some char yield of carbonization about 8.8% at 700°C in air. Scission of BrMIP in N_2 was a two-stage decomposition process with $T_{5\%}$ about 270°C, indicating that the decomposition of first stage is initialized by scission of the phosphonate ester side chain or bromine-containing chain due to lower bond energy. The decomposition of second stage was similar to that of 3- or 4-MIP systems. By introducing phosphorus in bromine-containing maleimide polymer, char yield *via* flame retardancy increased. Especially in air, synergy effect of P/Br in BrMIP promoted flame retardancy to get higher char yield of solid residue. Since the bromine-containing polymers possessed lower phosphorus, they exhibited lower char yields compared with the non-bromide system as listed in Table II. But considering char yield per phosphorous content, BrMIP due to the synergy effect of P/Br, especially in air, gave higher char yield of solid residue than the 3- or 4-MIP. The introduction of P/Br into maleimide polymer compared with the DBHPMI reduced $T_{5\%}$ about 50°C. But this was still higher than 3MIP, 4MIP or 4MTP. This appeared that thermal stability of BrMIP due to its synergy effect of P/Br was highest of all the others, except PhMIP.

TG curves of 4MIP, PhMIP, and 4MTP polymers are shown in Figures 4 and 5. Since 4MIP and 4MTP possessed similar component and structure except the O/S atoms, the decomposition processes among them were also similar whatever in N_2 or in air. $T_{5\%}$ of the latter was higher than that of the former whatever in N_2 or in air. This shows that the introduction of sulfur/phosphorus atoms into the maleimide polymer lead to better thermal stability. Moreover, even though 4MTP possessed lower phosphorus content, char yield in air was nearby equal to that of 4MIP polymer, was probably due to capability for sulfur to catch hydrogen and oxygen radicals to bring out volatile of hydrogen sulfide and sulfur dioxide.[33] As shown in Figure 4, the decomposition of PhMIP in N_2 was a one-stage reaction with the highest $T_{5\%}$ about 328°C because of lower molecular mobility of rigid phenyl ring within side chain. The decomposition of PhMIP was dissimilar to that of the other two. The decomposition of PhMIP in air was a two-stage reaction with high $T_{5\%}$ and char yield of solid residue at 325°C and 43.4%, respectively. The rigid phenyl ring of phosphonate ester side chain in PhMIP, compared with the other two, may thus increase thermal stability leading to change in decomposition from a two-step to a one-step and, considering char yield per phosphorous content, promoted flame re-

tardancy.

CONCLUSION

Phosphonate-containing *N*-phenyl maleimide monomers were synthesized by a two-step reaction. Polymerization and glass transition temperature of the resulting maleimide polymer depended on side chains. The introduction of phosphonate into the side chains of maleimide polymer changed the thermal decomposition mechanism, which was initialized by scission of phosphonate ester side chain and produced scission of the maleimide main-chain along with carbonization to form high char yield of solid residue and became an excellent flame retardant. The compositions and structures of phosphonate-containing side chains in maleimide polymers affect decomposition, but not decomposition mechanisms. These polymers with halogen or sulfur atom promoted flame retardancy due to the synergy effect of P/Br or P/S.

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