

Synthesis, Structure, Reactivity, and Thermal Properties of New Biphenylphosphine Oxide Bismaleimide Resins

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ABSTRACT: A new type of bismaleimide (BMI) resin was synthesized and confirmed by IR spectroscopy, elemental analysis, ¹H-NMR spectroscopy, and ¹³C-NMR spectroscopy. The reactivity was measured by differential scanning calorimetry. In addition, compositions of the synthesized BMI with three conventional BMIs (4,4'-bismaleimidodiphenylmethane, 4,4'-bismaleimidodiphenylether, 4,4'-bismaleimidodiphenylsulfone) were used for making a comparison of their reactivity and thermal properties. Through the eval-

uation of thermogravimetric analyses, the polymers obtained through the reactions between the newly synthesized BMI containing biphenylphosphine oxide and other BMIs also demonstrated excellent thermal properties in the high temperature region and a high char yield of up to 30–45%. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1–8, 2006

Key words: bismaleimide; char yield; flame retardancy; phosphorus; thermal properties

INTRODUCTION

Because of the rapid development of polymeric materials in various industrial fields in recent years,^{1,2} it is crucial to improve the thermal and flame resistances of polymeric materials. In general, polymers containing aromatic and/or heterocyclic ring structures such as polybenzothiazoles, polyoxadiazoles, polyquinoxalines, and polyimides are known to have excellent thermal stability.³ Bismaleimide (BMI) polymers, which have excellent processability and a good balance between thermal and mechanical properties, are an important class of polymers for applications in advance composites, electronics, and aerospace.^{4,5} In particular, BMI resins can be fabricated under epoxylike conditions and offer a performance temperature range between epoxies and polyimides. Therefore, various BMIs have been investigated and introduced to the commercial markets. These maleimides and capped prepolymers are cured into a highly crosslinked network by addition reactions without evolution of volatile by-products.

The incorporation of halogen and/or phosphorus into the polymer skeleton can improve flame resistance.⁶ Currently, the incorporation of halogen into polymers is not preferred for environmental reasons. To prevent this problem, polymers were modified by introducing phosphorus into the molecular structure, which improved the

flame properties.^{7,8} Krevelen proposed that the char residue from pyrolysis is linearly proportional to the oxygen index for a halogen-free polymer.⁹ According to our previous investigations,¹⁰ nonphosphorylated polymers give an approximate 0 char yield when pyrolyzed at a higher temperature in air. In contrast, the incorporation of phosphorus into polymer structures can produce adequate char yield during pyrolysis.

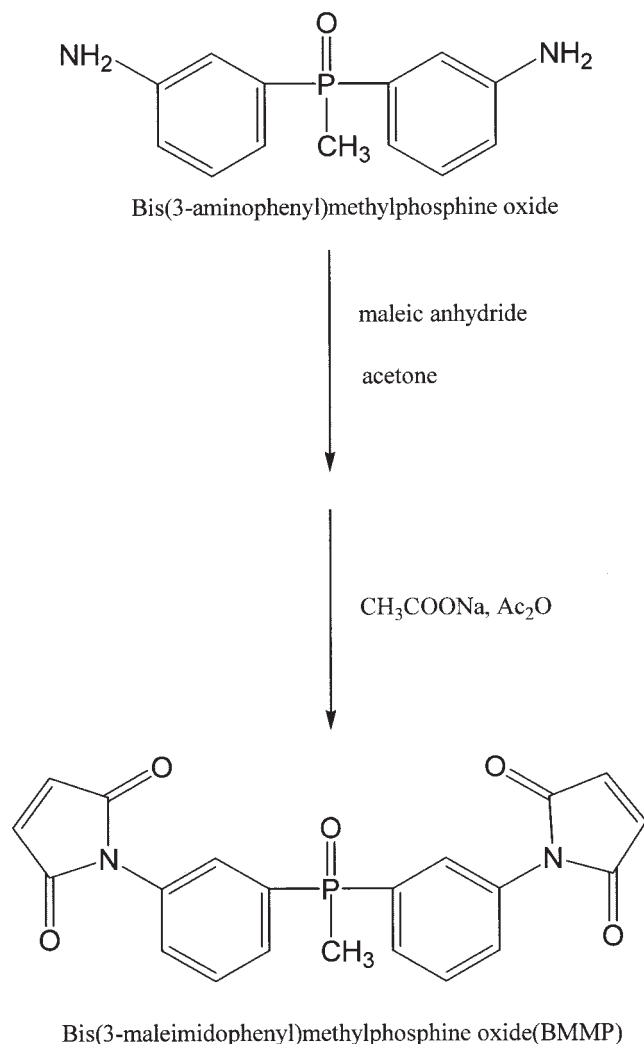
In the present work, a new type of BMI resin, bis(3-maleimidophenyl)methylphosphine oxide (BMMP), was prepared by the reaction of bis(3-aminophenyl)methylphosphine oxide with maleic anhydride followed by treatment with acetic anhydride, according to Scheme 1. The curing behaviors and thermal and flame properties of the new BMI polymers were studied. Moreover, compositions of the synthesized BMMP with three reactants, 4,4'-bismaleimidodiphenylmethane (BDM), 4,4'-bismaleimidodiphenylether (BDE), and 4,4'-bismaleimidodiphenylsulfone (BDS), were used for making a comparison of its reactivity and thermal properties. The reactivity was measured by differential scanning calorimetry (DSC). Through the evaluation of thermogravimetric analyses (TGA), the polymers obtained through the reactions between the new BMMP and the other BMIs also demonstrated excellent thermal properties and high char yield.

EXPERIMENTAL

Reagents

Reagent grade sodium acetate, acetic anhydride, and maleic anhydride and gas chromatography grade ac-

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Scheme 1 The synthesis of bis(3-maleimidophenyl)methylphosphine oxide (BMMP).

etone were purchased from Merck and used without further purification. BDM was procured from TCI Co. and used as received. BDE, BDS, and bis(3-aminophenyl)methylphosphine oxide were prepared by methods described previously.^{10,11}

Synthesis of BMMP

Maleic anhydride (19.62 g, dissolved in acetone) was gradually added to a well-stirred solution of bis(3-aminophenyl)methylphosphine oxide (20.04 g, in fresh distilled acetone) in an ice bath over a period of 2 h. The solution was stirred for an additional 4 h at 10°C, and light-yellowish precipitates were collected when the acetone was removed. Cyclodehydration of the intermediate to maleimide was carried out by treating it with acetic anhydride (10.21 g) and sodium acetate (0.75 g) in acetone and refluxing for 12 h. After being cooled to room temperature, the acetone in the

reaction mixture was removed with a rotary evaporator under reduced pressure. The residue was extracted with CHCl₃ and purified by column chromatography. The light-yellowish solids were recrystallized from toluene, filtrated, and vacuum dried. The yield was 75% with a melting point at about 82°C.

Characterization and measurements

The melting points were determined by a Gallenkamp MPD350. The IR spectra were examined using a Perkin-Elmer model 842. The ¹H-NMR and ¹³C-NMR spectra were obtained with a Bruker AMX-400, in which the samples were dissolved in DMSO-*d*₆ with tetramethyl silane as an internal standard. The curing cycles and reactivity were measured by DSC on a Du Pont 910. The thermal resistances were evaluated by TGA with a Du Pont 951 at a heating rate of 20°C/min.

Preparation of tested samples

The thermal and flame properties of the BMIs were evaluated here by preparing seven polymers: BMMP homopolymer, BDM homopolymer, BDE homopolymer, BDS homopolymer, BMMP/BDM copolymer, BMMP/BDE copolymer, and BMMP/BDS copolymer. To obtain polymers with good thermal stability, BMMP/BDM, BMMP/BDE, and BMMP/BDS were polymerized with equal equivalent weight ratios. Curing cycles were determined by DSC thermograms.

RESULTS AND DISCUSSION

The newly synthesized BMI resins were obtained through the reaction of bis(3-aminophenyl)methylphosphine oxide with maleic anhydride and treatment by acetic anhydride, according to Scheme 1. The chemical structure of the new BMI resin, BMMP, was characterized by elemental analysis, IR spectroscopy, ¹H-NMR spectroscopy, and ¹³C-NMR spectroscopy.

Identification of BMMP

The elemental analysis data of BMMP listed in Table I are in good agreement with the calculated values. The IR spectrum of BMMP (Fig. 1) showing a peak at 1716 cm⁻¹ represents the absorption of C=O and C—N—C at 1383 cm⁻¹, P=O at 1167 cm⁻¹, P—CH₃ at 1300

TABLE I
Elemental Analysis Data of BMMP

Material	C (%)		H (%)		N (%)	
	Exptl	Calcd	Exptl	Calcd	Exptl	Calcd
BMMP	61.04	62.06	4.29	3.69	6.26	6.89

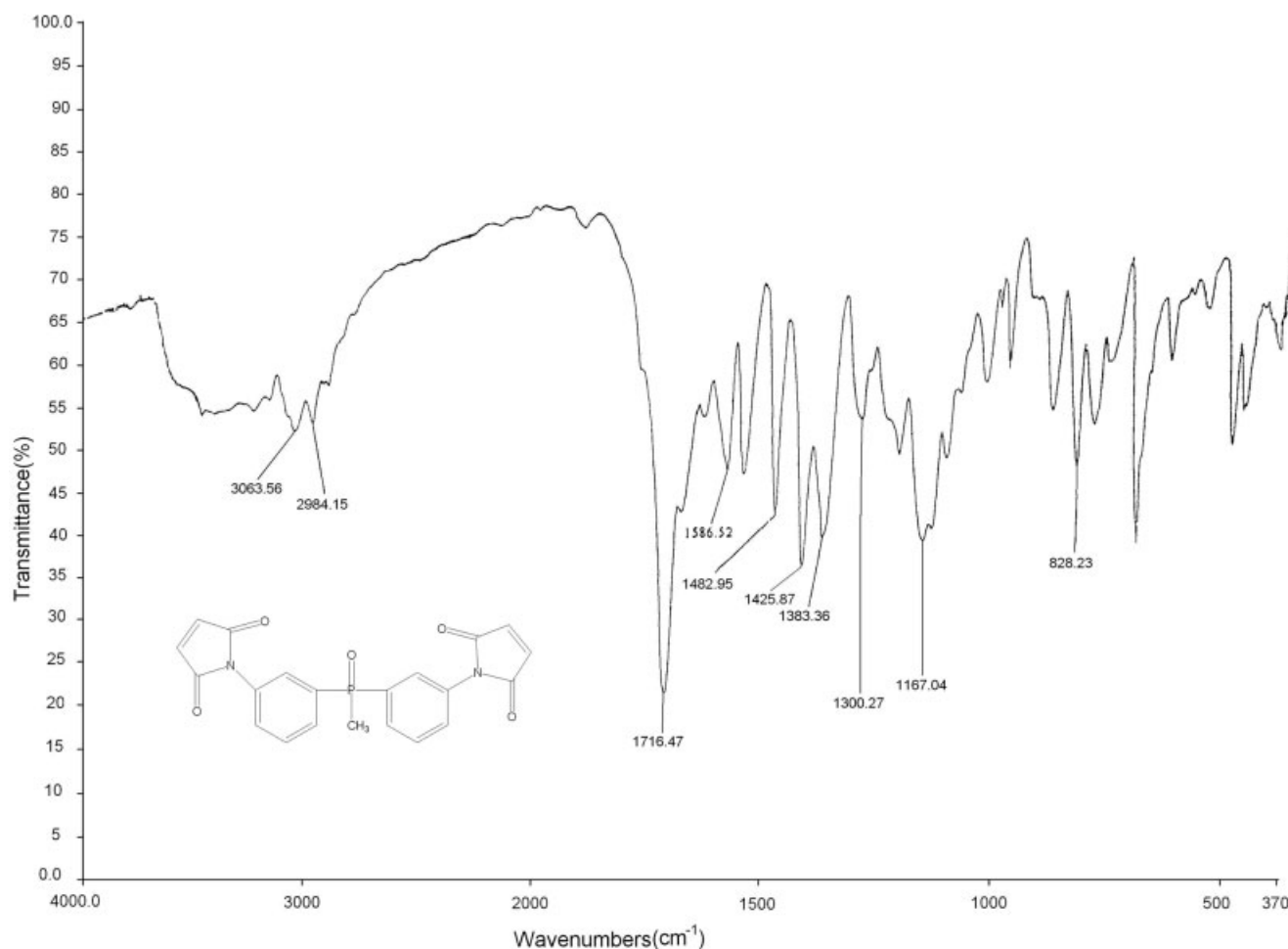


Figure 1 The IR spectrum of BMMP.

cm^{-1} , and $-\text{C}_6\text{H}_5$ at 1586 and 1482 cm^{-1} . The ^1H -NMR and ^{13}C -NMR spectra in $\text{DMSO-}d_6$ are given in Figures 2 and 3. The chemical shifts were characterized as follows: protons (H_i) and carbons (C_i) for the ethylene in BMMP at δ 7.20 (4H, s) and 134.97, respectively; H_a and carbons for the methyl at δ 2.09 (3H, d) and 16.23, respectively, for the carbonyl carbons at δ 169.90, and for the aromatic protons and carbons at δ 7.54–7.83 and 128.60–136.50, respectively. The chemical shifts of the characterized protons and carbons in BMMP are listed in Tables II and III. These are based on the assigned labels of protons and carbons in Figures 2 and 3.

Reactivity of BMMP

The polymerization reactions were studied by DSC. Significant caution was taken during the DSC study of the polymerization reaction to obtain homogeneous mixtures. The typical DSC thermograms in Figure 4 demonstrate the reactivity of self-polymerizations of BMMP/BDM/BDE/BDS. For all the BMIs that were

used, the exothermic starting temperature increased according to the order $\text{BMMP} < \text{BDM} < \text{BDE} < \text{BDS}$. A polymerization that exhibits a lower exothermic starting temperature under the same set of reaction conditions is more reactive. It is therefore reasonable to propose that BMMP is more reactive than BDM, BDE, and BDS for self-polymerization. The DSC thermograms in Figure 5 demonstrate the reactivity of BMMP toward the BMI agents (BDM/BDE/BDS). The lowest reactivity of BDS toward BMMP was compared with that of BDM and BDE. In the case of BDS, the electron-withdrawing group ($-\text{SO}_2-$) reduced the electron density of the amine nitrogen and subsequently reduced its nucleophilic attack on the double bond of the BMIs.

Thermal and flame properties

To compare the thermal and flame properties of these cured polymers, they were divided into two groups: nonphosphorylated polymers: BDM, BDE, and BDS homopolymers; and phosphorylated polymers:

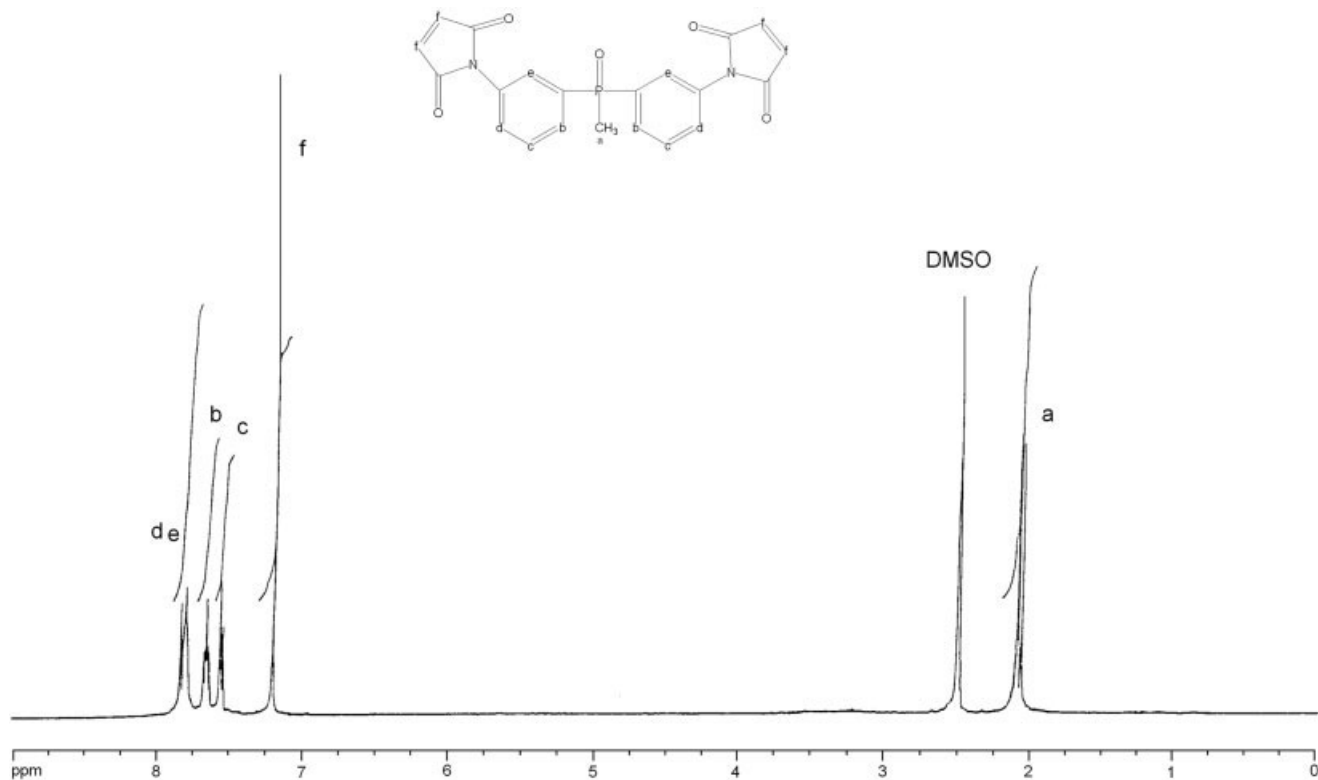


Figure 2 The ^1H -NMR spectrum of BMMP.

BMMP homopolymer and BMMP/BDM, BMMP/BDE, and BMMP/BDS polymers. From the polymer decomposition temperatures and temperatures of some characteristic weight losses, which are shown in Figures 6–9, we can compare the thermal properties of these cured polymers. From TGA cures, we found that poly(BMMP) exhibited excellent thermal stability at high temperature; as seen in Figure 6, the curves of

nonphosphorylated polymers was crossed by the poly(BMMP) curve near the range of 470–510°C. In Figure 7 we also find that the high temperature thermal stability of polymers was increased when the BDM, BDE, and BDS were copolymerized with BMMP. Moreover, note also in these figures that the BMI polymers containing phosphorus oxide have a lower thermal degradation rate than conventional BMI poly-

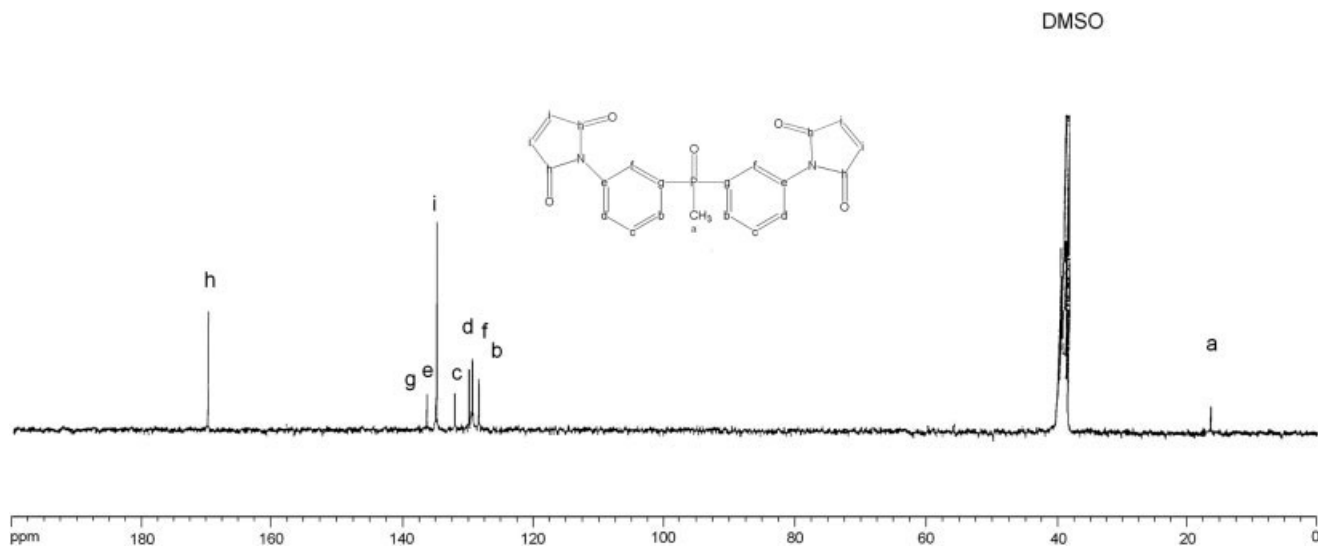


Figure 3 The ^{13}C -NMR spectrum of BMMP.

TABLE II
¹H-NMR Data of BMMP

	Type of proton					
	a	b	c	d	e	f
Chemical shifts (ppm)	2.09	7.66	7.54	7.83	7.76	7.20
	3H, d	2H, d	2H, t	2H, d	2H, s	4H, s

mers. In addition, the relatively low temperature of a 1% weight loss of poly(BMMP) (Figs. 6, 8) possibly resulted from the fact that the phosphorus in these phosphorylated polymers became phosphoric acid on pyrolysis, which catalyzed the dehydration of these polymers at a lower temperature. The phenomenon of the degradation of the phosphine oxide group at a relatively low temperature played an important role in enhancing the flame retardancy. The oxidized degradation of the phosphine oxide group formed a protective layer on the polymer surface and served as a barrier against heat and oxygen diffusion, which in-

creased both the thermal stability and flame retardancy of the polymers.

The char yield of these cured polymers in nitrogen and air environments are shown in Tables IV and V. We found that the phosphorous-containing polymers, poly(BMMP), poly(BMMP/BDM), poly(BMMP/BDE), and poly(BMMP/BDS), have a higher char yield than that of the nonphosphorylated polymers, BDM, BDE, and BDS. The char yield was increased from 30 to above 45% when copolymerized with BMMP. Therefore, the phosphorous-containing polymers were confirmed to be more flame resistant than the nonphosphorylated polymers.

CONCLUSIONS

A new BMI resin was obtained through the reaction of bis(3-aminophenyl)methylphosphine oxide with maleic anhydride. The structure of the new BMI resin, BMMP, was confirmed through elemental analysis, IR,

TABLE III
¹³C-NMR Data of BMMP

	Type of carbon									
	a	b	c	d	e	f	g	h	i	
Chemical shifts (ppm)	16.23	128.60	132.20	130.11	135.19	129.48	136.50	169.90	134.97	

TABLE IV
TGA Data of Bismaleimide Polymers in Nitrogen Environment

Materials	PDT ^a (°C)	Temperature (°C) at characteristic weight loss					Residue (%) at 650°C
		10%	20%	30%	40%	50%	
Poly(BMMP)	400.4	418.2	457.6	508.3	—	—	64.2
Poly(BDM)	432.9	485.5	496.4	506.4	554.8	—	51.7
Poly(BDE)	383.6	462.4	481.2	494.0	543.7	652.0	50.1
Poly(BDS)	448.9	462.1	462.6	463.1	471.2	474.2	30.5
Poly(BMMP/BDM)	444.8	454.2	477.7	580.3	—	—	68.4
Poly(BMMP/BDE)	437.6	451.0	482.5	524.3	609.9	—	58.6
Poly(BMMP/BDS)	432.6	439.4	450.8	517.6	—	—	62.2

^aPDT, initial decomposition temperature of polymer.

TABLE V
TGA Data of Bismaleimide Polymers in Air Environment

Materials	PDT (°C)	Temperature (°C) at characteristic weight loss					Residue (%) at 650°C
		10%	20%	30%	40%	50%	
Poly(BMMP)	384.2	414.3	451.8	502.8	590.7	678.9	53.3
Poly(BDM)	332.0	468.8	493.6	508.4	559.6	585.8	6.1
Poly(BDE)	308.3	439.7	480.0	496.3	550.6	576.7	1.4
Poly(BDS)	448.9	465.5	470.6	484.9	547.7	595.9	16.5
Poly(BMMP/BDM)	441.1	452.4	477.6	523.5	562.0	657.4	50.9
Poly(BMMP/BDE)	417.5	446.0	472.7	518.2	519.5	521.2	31.3
Poly(BMMP/BDS)	427.6	435.2	445.5	509.7	586.8	638.5	46.9

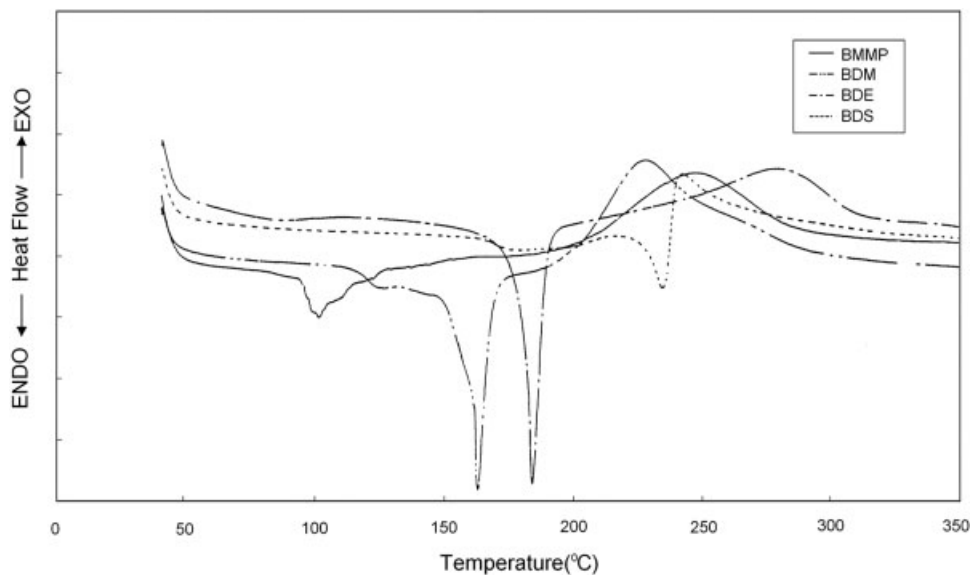


Figure 4 DSC thermograms of four compositions: BMMP, BDM, BDE, and BDS (heating rate = 10°C/min).

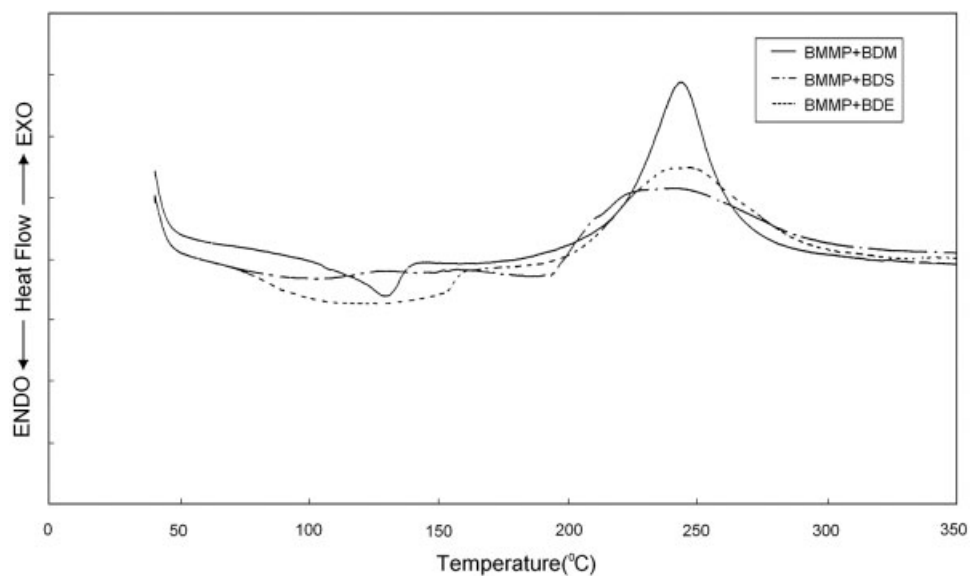


Figure 5 DSC thermograms of three compositions: BMMP/BDM, BMMP/BDE, and BMMP/BDS (heating rate = 10°C/min).

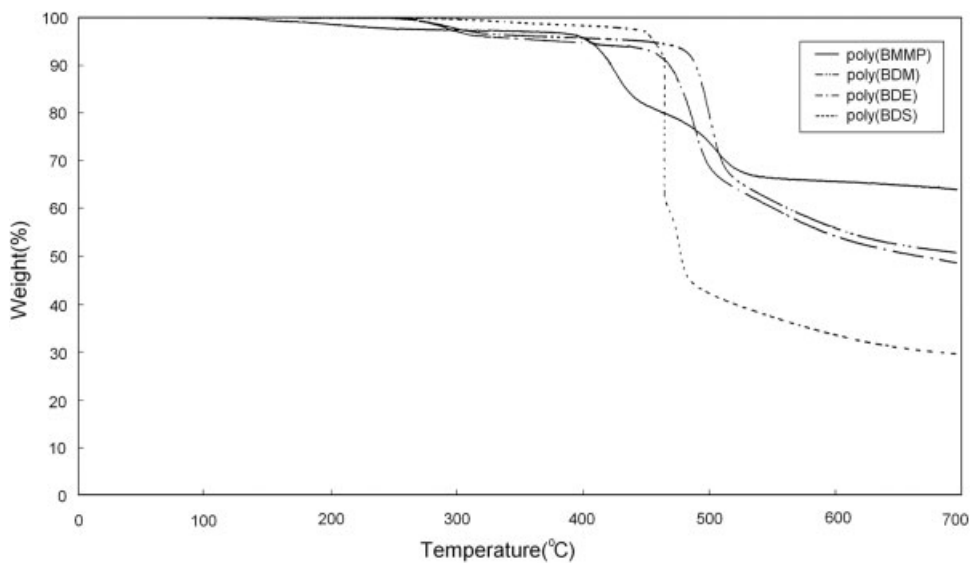


Figure 6 TGA thermograms of poly(BMMP), poly(BDM), poly(BDE), and poly(BDS) in a nitrogen environment (heating rate = 20°C/min).

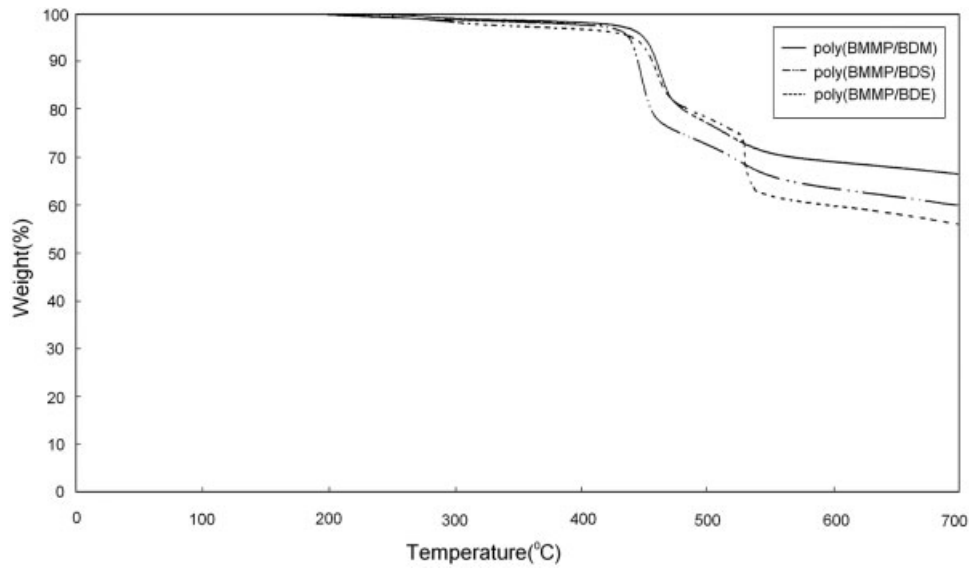


Figure 7 TGA thermograms of poly(BMMP), poly(BDM), poly(BDE), and poly(BDS) in an air environment (heating rate = 20°C/min).

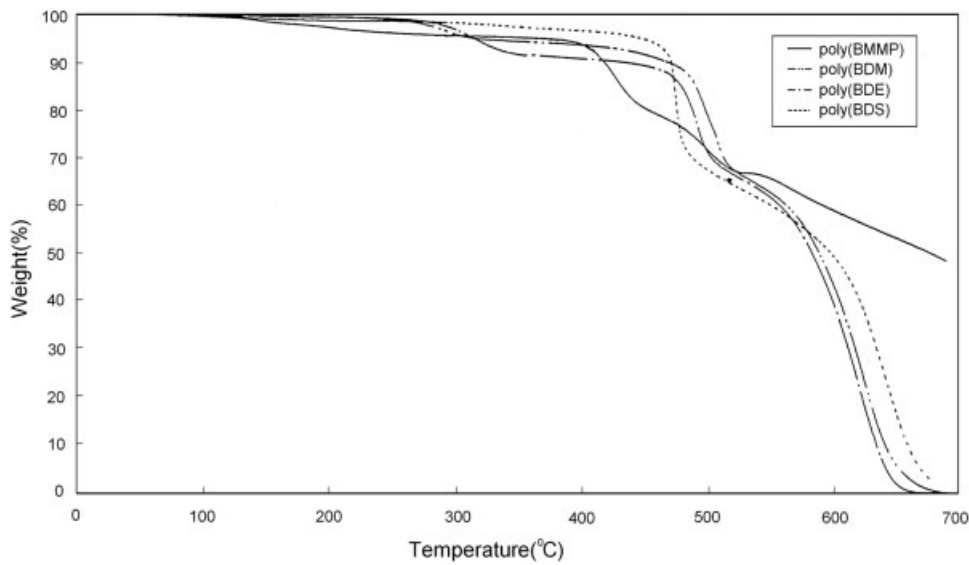


Figure 8 TGA thermograms of poly(BMMP/BDM), poly(BMMP/BDE), and poly(BMMP/BDS) in a nitrogen environment (heating rate = 20°C/min).

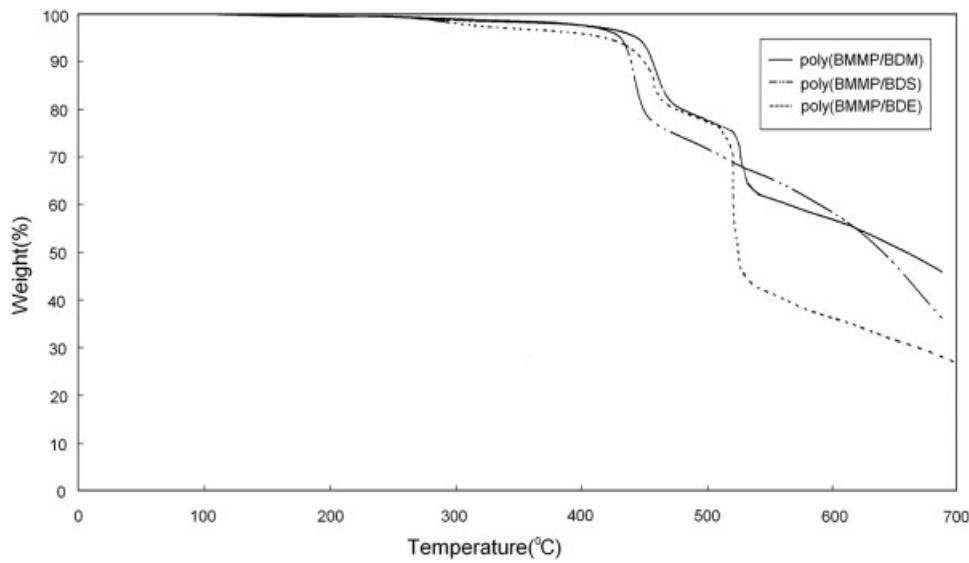


Figure 9 TGA thermograms of poly(BMMP/BDM), poly(BMMP/BDE), and poly(BMMP/BDS) in an air environment (heating rate = 20°C/min).

^1H -NMR, and ^{13}C -NMR characterizations. The synthesized BMMP and conventional BMIs BDM, BDE, and BDS cured by self-polymerization showed exothermic starting temperature increases according to the order $\text{BMMP} < \text{BDM} < \text{BDE} < \text{BDS}$. The synthesized BMMP homopolymers (BMMP/BDM, BMMP/BDE, and BMMP/BDS) showed a slower thermal degradation rate than conventional BDM, BDE, and BDS homopolymers. The flame retardancy of the BMI was confirmed in this study as capable of being significantly improved through introduction of phosphorus into the polymer structure. The BMMP-containing polymers had a higher char yield when undergoing pyrolysis.

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