

# Studies of silicon-containing maleimide polymers: 1. Synthesis and characteristics of model compounds

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## Abstract

A series of the (*N*-maleimido phenoxy)silane monomers were synthesized by a two-step reaction for using as the application of flame retardant, functional modifier, or a photoresist material in deep-UV region. All of the monomers with maleimide ring were polymerized by radical polymerization in toluene solution using 2,2'-azobisisobutyronitrile (AIBN) as initiator so as to prepare homopolymers. The structures of the maleimide monomers were identified by <sup>1</sup>H, <sup>13</sup>C, <sup>29</sup>Si NMR and element analysis. The chemical structures of polymers were identified by Fourier transform infrared reflection (FT-IR) spectroscopy. The molecular weight distributions of polymers were measured by gel permeation chromatography (GPC) equipment. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used to analyze the thermal properties of the polymers. The degree of polymerization in silicon-containing maleimide polymers should be affected by side chains. The introduction of alkylsilane into a side chain of maleimide polymer may reduce the glass transition temperature (*T<sub>g</sub>*) and thermal stability, but increase char yield of solid residue as an excellent flame retardant.

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## 1. Introduction

The development of non-halogen flame-retardants, such as the phosphorus- or silicon-containing flame-retardants with the lower smoke density and toxicity has been widely valued in recent years. 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 [1], 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 [1,2]. In the applications of silicon-containing flame retardant, silicon-containing polymer, smoke-repressing silicon compounds, and the system with an organic silicate has been used. When the material burns, the derived silicon carbide can promote the carbonization effect and fire resistance. The combustible, smoke, or

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poison material released in the burning process can be repressed. The environmental rules are more and more rigorous at the present time, the P/Si type flame retardant has replaced the halogen-type and become the main current of the fire-resistance material.

*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 [3–6]. 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 [7–9], methyl methacrylate [10–12], acrylonitrile [13], or vinyl acetate [14] have higher thermal stability and fire resistance. The copolymers of silane-containing PM with styrene type monomers have also been studied as a photoresist material in deep-UV region [15–20]. 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 [21] promotes polymerization. Halogen-substituted XHPM polymers possess thermal stability from imide ring and flame retardancy from halides [22–24]. Our team has designed *N*-phenylmaleimide polymers with different substituted side groups to study thermal stability and flame retarding properties. We have developed a series of phosphonate-containing maleimide monomers which exhibit good flame resistance [25]. This research is mainly to synthesize a series of novel silicon-containing maleimide monomers for use as the application of flame retardant, functional modifier, or a photoresist material.

## 2. Experimental

### 2.1. Materials

4-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. Chloro-trimethylsilane, triphenylchloro-silane, *t*-butyl-dimethylchloro-silane, and chloro-triethylsilane were obtained from Aldrich. Cobalt acetate was obtained from Showa. All reagents were used as received. Tetrahydrofuran (THF) was distilled after dehydration with sodium. *N,N*-Dimethyl-formamide (DMF) was dried over CaH<sub>2</sub>. Other solvents were purified by conventional methods.

### 2.2. Synthesis

#### 2.2.1. *N*-Hydroxyphenylmaleimide (4HPMI) [26,27]

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 4-aminophenol were added gradually into the solution of maleic anhydride (11 g) in 50 mL of DMF and the mixture was stirred for 2 h in a water bath to obtain a clear amic acid solution. A mixture of 5.5 g phosphorus pentoxide, 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 one hour. 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.

#### 2.2.2. *N*-(2,6-Dibromo-4-hydroxyphenyl)maleimide (DBHPMI) [28]

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.

#### 2.2.3. Silicon-containing maleimide monomers [29]

A flask as above with ice bath was charged with 100 mL THF and added to a mixture of 0.016 mol *N*-hydroxyphenylmaleimide or DBHPMI, 3 mL TEA and 0.012 g Cu<sub>2</sub>Cl<sub>2</sub>. A solution of 0.0192 mol chloro-silane 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 silicon-containing *N*-phenyl maleimide monomer dried under reduced pressure.

#### 2.2.4. Silicon-containing polymer [30]

A flask was charged with maleimide monomers, 2,2'-azobis(isobutyronitrile) (AIBN) (10 mmol/L) as initiator and toluene as solvent. The unsaturated monomers synthesized above were polymerized by free radicals at 70 °C for about 12 h to form a mixture containing *N*-phenyl maleimide polymers. The mixture was dis-

solved in dichloromethane and poured into methanol to precipitate the *N*-phenyl maleimide polymers dried under reduced pressure.

### 2.3. Instrumentation

$^{13}\text{C}$ ,  $^1\text{H}$ , and  $^{29}\text{Si}$  NMR spectra and elemental analysis (C, H, N) of all the *N*-phenylmaleimide 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 a Waters gel permeation chromatography (GPC, Waters 1515HPLC/2410RI-detector) at a flow rate of 1.0 mL/min with 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  $10^\circ\text{Cmin}^{-1}$  in  $\text{N}_2$ , and thermogravimetry

(TGA, TA-Instruments TGA 51) at a heating rate of  $20^\circ\text{Cmin}^{-1}$  in air or  $\text{N}_2$ , respectively. The temperature of DSC system was first calibrated using standard sample of indium and the TGA system by a general instrumental calibration. All the samples of above thermal analysis were taken about 5 mg. Melting points of all monomers were tested by DSC at a heating rate of  $10^\circ\text{Cmin}^{-1}$  in  $\text{N}_2$ .

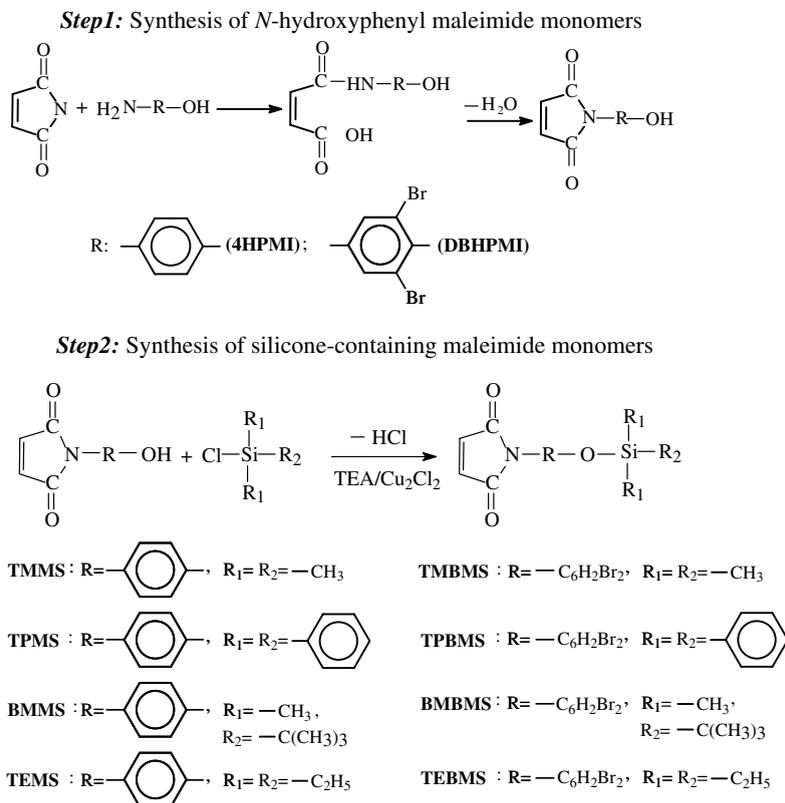
## 3. Results and discussion

Silicon-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 (Scheme 1). Silicon-containing maleimide monomers were then prepared by a condensation reaction in Step 2 (Scheme 1).

### 3.1. Characterization of monomers

#### 3.1.1. Trimethyl(4-(*N*-maleimido) phenoxy)silane (TMMS)

Yield 75% as a yellow powder with mp 188–189°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.11 (2H, s,



Scheme 1. Synthesis of silicon-containing maleimide monomers. Step 1: Synthesis of *N*-hydroxyphenyl maleimide monomers. Step 2: Synthesis of silicone-containing maleimide monomers.

–CO–CH=CH–CO–); 7.07 (2H, d, 2'-H, 6'-H); 6.82 (2H, d, 3'-H, 5'-H); 3.34 (9H, t, Si–CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 170.3 (2-C=O); 157.0 (4'-C–O–Si); 134.5 (–CO–CH=CH–CO–); 128.4 (3',5'-C); 122.5 (1'-C–N–); 115.4 (2',6'-C); 19.5 (Si–CH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ (ppm): 24.1. EA (%): C, 59.8; H, 5.8; O, 18.3; N, 5.3 (calcd.: C, 59.7; H, 5.7; O, 18.4; N, 5.4).

### 3.1.2. Triphenyl(4-(*N*-maleimido)phenoxy)silane (TPMS)

Yield 70% as a buff powder with mp 152–153 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.24 (2H, dd, 2''-H, 6''-H); 7.16 (2H, d, 2'-H, 6'-H); 7.11 (2H, s, –CO–CH=CH–CO–); 7.07 (1H, dd, 4''-H); 6.89 (2H, d, 3'-H, 5'-H); 6.82 (2H, dd, 3''-H, 5''-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 169.8 (2-C=O); 155.3 (4'-C–O–Si); 134.3 (2'',6''-C); 134.0 (–CO–CH=CH–CO–); 129.0 (1'',Si–C); 128.0 (3'',5''-C); 127.6 (4''-C); 123.8 (1'-C–N–); 116.2 (3',5'-C); 115.8 (2',6'-C). <sup>29</sup>Si NMR (d-CDCl<sub>3</sub>), δ (ppm): 3.1. EA (%): C, 75.0; H, 4.6; O, 10.7; N, 3.2 (calcd.: C, 75.2; H, 4.7; O, 10.7; N, 3.1).

### 3.1.3. *t*-Butyldimethyl(4-(*N*-maleimido)phenoxy)silane (BMBMS)

Yield 71% as a golden powder with mp 181–182 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.07 (2H, d, 2'-H, 6'-H); 6.82 (2H, d, 3'-H, 5'-H); 7.11 (2H, s, –CO–CH=CH–CO–); 3.01 (9H, t, C–CH<sub>3</sub>); 2.34 (6H, t, Si–CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 170.3 (2-C=O); 157.0 (4'-C–O–Si); 134.5 (–CO–CH=CH–CO–); 128.4 (3',5'-C); 122.5 (1'-C–N–); 115.4 (2',6'-C); 34.5 (–C–CH<sub>3</sub>); 31.2 (–C–CH<sub>3</sub>); 19.5 (Si–CH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ (ppm): –3.2. EA (%): C, 61.9; H, 7.3; O, 16.3; N, 4.6 (calcd.: C, 61.8; H, 7.2; O, 16.5; N, 4.8).

### 3.1.4. Triethyl(4-(*N*-maleimido)phenoxy)silane (TEMS)

Yield 72% as a soil powder with mp 182–183 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.05 (2H, d, 2'-H, 6'-H); 6.84 (2H, d, 3'-H, 5'-H); 7.12 (2H, s, –CO–CH=CH–CO–); 3.27 (6H, q, Si–CH<sub>2</sub>–); 2.34 (9H, t, Si–CH<sub>2</sub>–CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 170.6 (2-C=O); 157.2 (4'-C–O–Si); 134.1 (–CO–CH=CH–CO–); 128.3 (3',5'-C); 122.2 (1'-C–N–); 115.4 (2',6'-C); 22.5 (Si–CH<sub>2</sub>–); 21.3 (Si–CH<sub>2</sub>–CH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ (ppm): 20.1. EA (%): C, 63.5; H, 6.8; O, 15.9; N, 4.5 (calcd.: C, 63.3; H, 6.9; O, 15.8; N, 4.6).

### 3.1.5. Trimethyl(2,6-dibromo-4-(*N*-maleimido)phenoxy)silane (TMBMS)

Yield 72% as a dark purple powder with mp 159–160 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.56 (2H, s, –CO–CH=CH–CO–); 7.16 (2H, d, 2'-H, 6'-H); 3.33 (9H, t, Si–CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 170.3 (2-C=O); 151.1 (4'-C–O–Si); 134.9 (–CO–CH=CH–CO–); 131.4 (3',5'-C); 110.5 (1'-C–N–); 115.4 (2',6'-C); 20.1 (Si–CH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ (ppm): –11.1. EA (%): C,

37.4; H, 3.2; O, 11.3; N, 3.4 (calcd.: C, 37.2; H, 3.1; O, 11.5; N, 3.3).

### 3.1.6. Triphenyl(2,6-dibromo-4-(*N*-maleimido)phenoxy)silane (TPBMS)

Yield 58% as a olivine powder with mp 158–159 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.23 (2H, dd, 2''-H, 6''-H); 7.21 (2H, d, 2'-H, 6'-H); 7.12 (2H, s, –CO–CH=CH–CO–); 7.07 (1H, dd, 4''-H); 6.82 (2H, dd, 3''-H, 5''-H). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 169.8 (2-C=O); 151.3 (4'-C–O–Si); 134.3 (2'',6''-C); 134.0 (–CO–CH=CH–CO–); 133.5 (1'',Si–C); 128.0 (3'',5''-C); 127.6 (4''-C); 137.9 (1'-C–N–); 116.4 (3',5'-C); 116.1 (2',6'-C). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ (ppm): –12.7. EA (%): C, 55.7; H, 3.2; O, 7.8; N, 2.2 (calcd.: C, 55.5; H, 3.1; O, 7.9; N, 2.3).

### 3.1.7. *t*-Butyl dimethyl(2,6-dibromo-4-(*N*-maleimido)phenoxy)silane (BMBMS)

Yield 65% as a light brown powder with mp 166–167 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.11 (2H, s, –CO–CH=CH–CO–); 6.87 (2H, d, 2'-H, 6'-H); 3.01 (9H, s, C–CH<sub>3</sub>); 2.34 (6H, t, Si–CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 170.3 (2-C=O); 149.7 (4'-C–O–Si); 141.5 (1'-C–N–); 134.5 (–CO–CH=CH–CO–); 121.4 (2',6'-C); 118.4 (3',5'-C); 34.5 (–C–CH<sub>3</sub>); 31.2 (–C–CH<sub>3</sub>); 19.5 (Si–CH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ (ppm): –9.2. EA (%): C, 40.3; H, 4.1; O, 10.5; N, 3.0 (calcd.: C, 40.1; H, 4.2; O, 10.7; N, 3.1).

### 3.1.8. Triethyl(2,6-dibromo-4-(*N*-maleimido)phenoxy)silane (TEBMS)

Yield 64% as a soil powder with mp 157–158 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ (ppm): 7.12 (2H, s, –CO–CH=CH–CO–); 7.08 (2H, d, 2'-H, 6'-H); 3.27 (6H, q, Si–CH<sub>2</sub>–); 2.34 (3H, t, Si–CH<sub>2</sub>–CH<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>), δ (ppm): 170.3 (2-C=O); 149.7 (4'-C–O–Si); 141.5 (1'-C–N–); 134.5 (–CO–CH=CH–CO–); 121.4 (2',6'-C); 118.4 (3',5'-C); 22.5 (Si–CH<sub>2</sub>–); 21.3 (Si–CH<sub>2</sub>–CH<sub>3</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ (ppm): –25.2. EA (%): C, 41.5; H, 4.2; O, 10.2; N, 2.9 (calcd.: C, 41.7; H, 4.1; O, 10.4; N, 3.0).

## 3.2. Properties of maleimide-series monomers

All the maleimide-series monomers exhibited high melting point around 152–189 °C. This might be related to the structure of imide and phenyl rings. In <sup>29</sup>Si NMR spectra, the chemical shift (δ) of Br-containing monomers moved downfield compared with those of Br-free maleimide monomers. The chemical shift of TMMS, for example, was 24.1 ppm and that of TMBMS was –11.1 ppm. This was probably due to the fact that bromine atoms possess higher electro-negativity to cause the lower electron density and higher de-shielding effect around silicon atoms. Fig. 1 is the comparative FT-IR

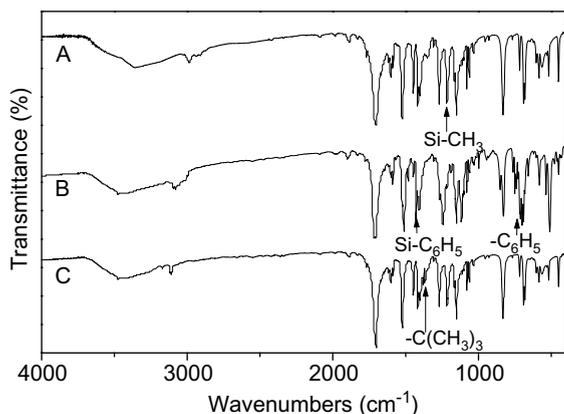


Fig. 1. FT-IR spectra of TMMS monomer (A), TPMS monomer (B), and BMMS monomer (C).

spectra of Br-free maleimide monomers. It can be seen a Si-CH<sub>3</sub> characteristic absorption peak at 1210 cm<sup>-1</sup> from TMMS, a Si-C<sub>6</sub>H<sub>5</sub> peak at 1430 cm<sup>-1</sup> and mono-substitution of benzene at 700 cm<sup>-1</sup> and 750 cm<sup>-1</sup> from TPMS, and a furcating peak of -C(CH<sub>3</sub>)<sub>3</sub> at 1350 cm<sup>-1</sup> from BMMS.

### 3.3. Properties of maleimide polymers

Variance of chemical structure during the synthesis reaction was identified by FT-IR, such as TMMS system shown in Fig. 2. FT-IR spectra of 4HPMI monomer revealed absorption bands  $\nu$  (cm<sup>-1</sup>): 3483 (-OH); 1706 (C=O); 1597, 1520 (C=C from benzene); 831 (di-substitution of benzene); 1414 (C-N-C) and 692 (C=C from maleimide ring). TMMS monomer revealed absorption bands  $\nu$  (cm<sup>-1</sup>): 1210 (Si-CH<sub>3</sub>) and 1080 (-Si-O). Absorption band of the hydroxyl group (3483 cm<sup>-1</sup>) disappeared completely in the spectra of TMMS monomer.

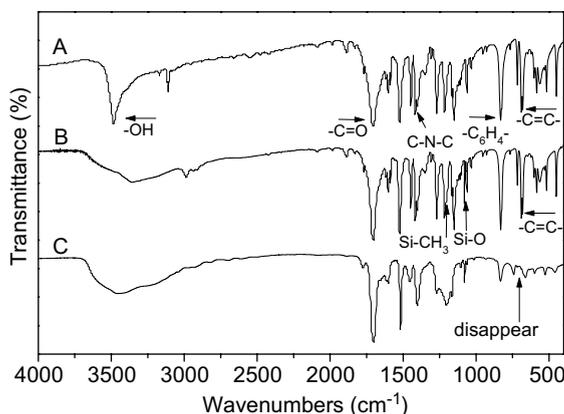


Fig. 2. FT-IR spectra of 4HPMI monomer (A), TMMS monomer (B), and TMMS polymer (C).

For TMMS polymer, absorption of C=C within maleimide ring disappeared completely for the reason of polymerization to be finished.

GPC data of polymers prepared from various maleimide monomers are shown in Table 1. The chromatographic curves of Br-free polymers are shown in Fig. 3. The polydispersity index ( $\overline{M}_w/\overline{M}_n$ ) of all these polymers are close to about 2.5. The polymer with a bigger side group, such as TPMS, might exhibit a broader chromatographic peak. The molecular weights of polymers derived from the silicon-containing maleimide monomer were higher than general *N*-hydroxyphenylmaleimide homopolymer since the silane units of the maleimide polymers masked the phenol group. In addition, steric hindrance and chain transfer caused by silane side chains should also be the reason of reducing polymerization efficiency. The degree of polymerization ( $\overline{DP}$ ) of TPMS polymer, for example, was lower for its higher phenyl density in side chains. The  $\overline{DP}$  of Br-containing polymers were lower than the halogen-free systems for steric hindrance induced by bromine atoms.

Glass transition temperatures ( $T_g$ ) of various *N*-phenyl maleimide polymers analyzed by DSC are listed in Table 2.  $T_g$ s of all the silane-containing maleimide polymers were among 160–180 °C. The DSC curves of Br-free polymers are shown in Fig. 4. The polymer of TPMS possessed the highest  $T_g$  indicating its rigid phenyl ring of silane side chain to reduce molecular mobility.

Thermal properties of all maleimide polymers measured by TGA in N<sub>2</sub> or air as shown in Figs. 5–8 are also listed in Table 2. As seen in Fig. 5 and Table 2,  $T_{5\%}$  of all the polymers derived from the halogen-free maleimide monomers was higher than 367 °C when were heated under nitrogen gas, especially for that of TPMS around 385 °C. Decomposition reactions should be initialized mainly by scission of silane side chains because of owning lower bond energy [31], and further produced scission of the maleimide main-chain along with carbonization to form char yield of solid residue. Thermal stability of all the maleimide polymers in N<sub>2</sub> was higher than that in air because of the oxidization reaction. When all halogen-free maleimide polymers were heated in air, decomposition, as shown in Fig. 6, changed from one-stage to two-stage. The decomposition of the second stage should be the oxidized combustion reaction under the high temperature. The char yield of the silicon-containing maleimide polymer pyrolyzed in air was generally increased with increasing the silicon content. This might due to the high oxidation resistance of silicon-containing solid residue, such as silicon oxide or silicon-carbon alloy [32]. Besides, maximum rates of weight loss of these polymers were decreased and the pyrolysis curves moved to higher temperature as the silicon content was increased. The results of higher char yield and lower weight loss rates during pyrolysis of silicon-containing system showed that the introduction

Table 1  
GPC data of polymers prepared from maleimide monomers

Monomer	Yield	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	DP
TMMS	75	15,995	6582	2.43	25.2
TPMS	70	22,442	8501	2.64	19.0
BMMS	71	17,370	7004	2.48	23.1
TEMS	72	17,115	6792	2.52	22.4
TMBMS	70	23,638	9939	2.53	22.3
TPBMS	58	29,727	11,051	2.69	18.2
BMBMS	65	24,488	9492	2.58	20.5
TEBMS	64	24,262	9121	2.66	19.7

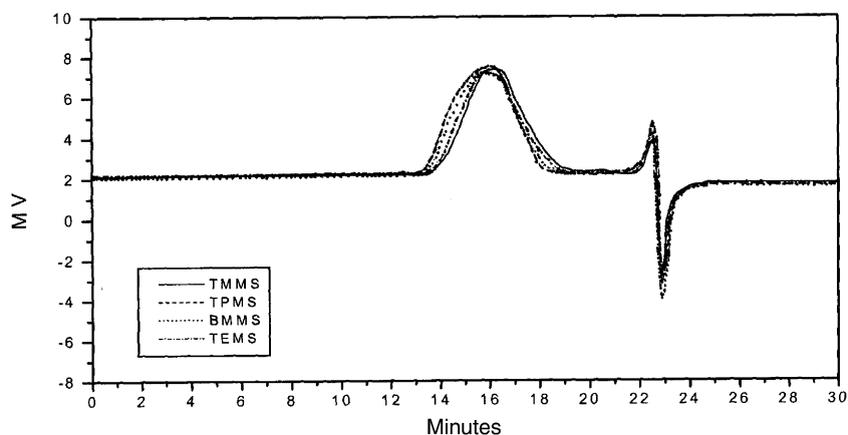


Fig. 3. The chromatographic curves (from GPC) of Br-free polymers.

Table 2  
Thermal properties of polymers prepared from maleimide monomers

Monomer	Si (%) <sup>a</sup>	Br (%) <sup>a</sup>	$T_g$ <sup>b</sup>	$T_{5\%}$ (°C) <sup>c</sup>		Char at 800°C <sup>c</sup>	
				N <sub>2</sub>	Air	N <sub>2</sub>	Air
TMMS	10.8	—	172	384	354	31.3	12.0
TPMS	6.3	—	183	385	380	22.9	2.8
BMMS	9.6	—	169	367	351	25.5	6.9
TEMS	9.3	—	165	377	372	26.6	5.4
TMBMS	6.7	38.2	167	256	249	33.0	7.3
TPBMS	4.6	26.5	179	247	233	17.8	3.8
BMBMS	6.3	35.6	164	241	235	25.0	4.3
TEBMS	6.1	34.7	160	236	230	24.3	4.6

<sup>a</sup> To be the theoretical calculation weight ratio of Si/Br composition in polymer.

<sup>b</sup>  $T_g$  represents the glass transition temperature analyzed by DSC at a heating rate of 10°Cmin<sup>-1</sup> in N<sub>2</sub>.

<sup>c</sup> Thermal properties analyzed by TGA at a heating rate of 20°Cmin<sup>-1</sup> in N<sub>2</sub> or in air.

of silane side chain into polymers improved flame retardancy.

As same as the non-bromide polymers mentioned above, the scission of Br-containing polymer in N<sub>2</sub> was a one-stage and in air a two-stage decomposition process as shown in Figs. 7 and 8. Since this maleimide polymer with two bromine atoms exhibited poor thermal stabil-

ity,  $T_{5\%}$  about 230–256°C was lower than that of non-bromide polymers. By introducing silicon in bromine-containing maleimide polymer, char yield via flame retardancy increased. Especially in air, synergy effect of Si/Br promoted flame retardancy to get higher char yield of solid residue. Since the bromine-containing polymers possessed lower silicon content, they exhibited

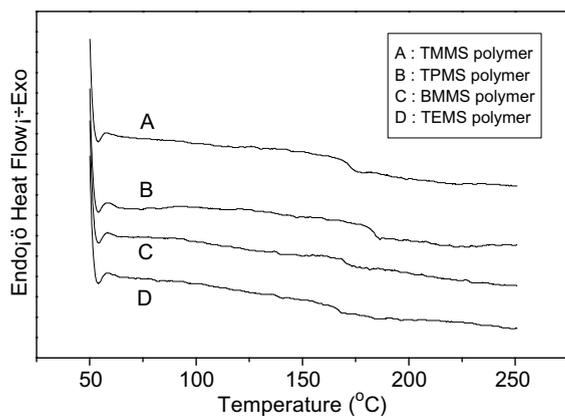


Fig. 4. The DSC curves of Br-free polymers.

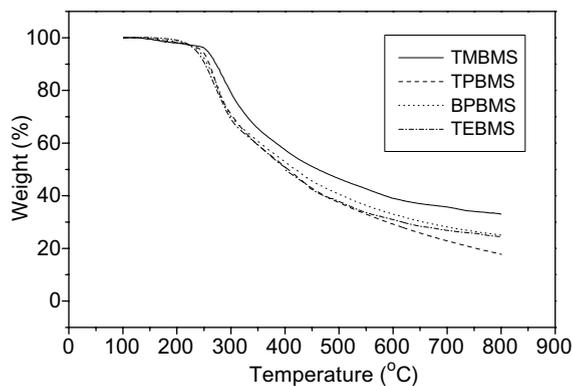
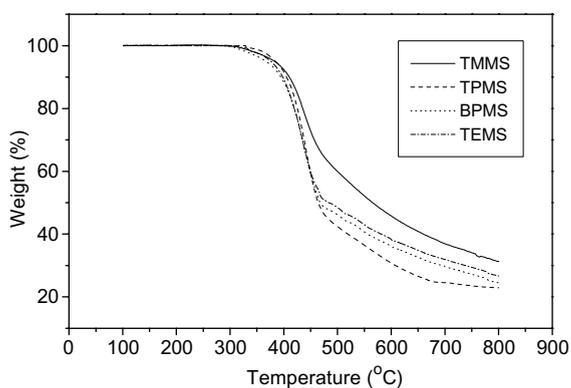
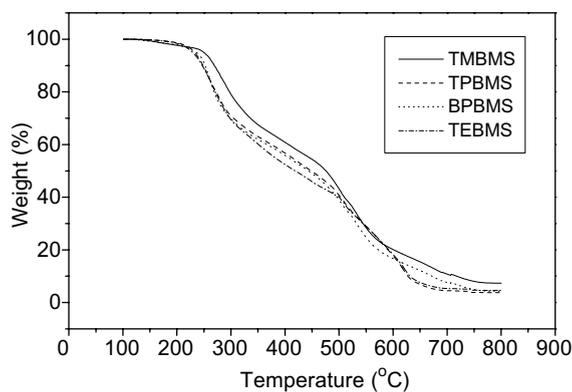
Fig. 7. TGA traces of Br-containing polymers in N<sub>2</sub>.Fig. 5. TGA traces of halogen-free polymers in N<sub>2</sub>.

Fig. 8. TGA traces of Br-containing polymers in air.

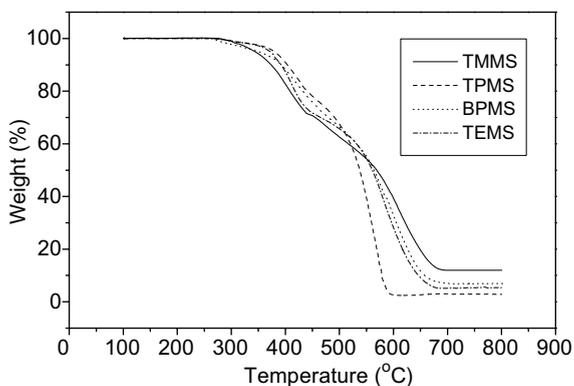


Fig. 6. TGA traces of halogen-free polymers in air.

lower char yields compared with the non-bromide system as listed in Table 2. But considering char yield per silicon content, they obtained higher char yield of solid residue than the non-bromide system.

#### 4. Conclusions

A series of silicon-containing *N*-phenyl maleimide monomers were synthesized by a two-step reaction. Homopolymers were successfully prepared from all of the monomers by radical polymerization in toluene solution. Polymerization and glass transition temperature of the resulting maleimide polymer depended on side chains. The introduction of alkylsilane into the side chains of maleimide polymers could improve their flame retardant. These polymers with halogen or silicon atom promoted flame retardancy also due to the synergy effect of Si/Br. All of the novel silicon-containing maleimide monomers or polymers could be used as the application of flame retardant, functional modifier, or a photoresist material.

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