

Studies of Silicon-Containing Bismaleimide Resins. Part I: Synthesis and Characteristics of Model Compounds and Polyaspartimides

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Abstract

A series of silicon-containing bismaleimide ((4,4'-bismaleimido phenoxy) silane, BMI) monomers has been synthesized by a two-step reaction for use as flame retardant or modifier of general resins. The synthesized BMI monomers are characterized by the ^1H -, ^{13}C - and ^{29}Si -NMR spectroscopy and element analysis. These BMI monomers were reacted with free radical initiator to prepare silicon-containing BMI polymers and also with various aromatic diamines to prepare a series of polyaspartimides as reactive flame-retardants by focused microwave irradiation. The polymerization degrees of polyaspartimides depend on the alkalinity and nucleophilicity of diamines as chain extenders. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) have been used to study the thermal properties of all the BMI resins such as the melting temperature, curing temperature, glass transition temperature (T_g) and thermal resistance. All the silicon-containing BMI resins, except BMI polymers, have a T_g in the range of 155–162°C and 5% weight loss temperatures ($T_{5\%}$) of 361–380°C and 358–377°C in air and nitrogen atmosphere, respectively. The higher heat resistance of cured BMI resin relative to BMI polymer is due to its higher cross-linking density. Since the re-cross-linking reactions of BMI polymers and polyaspartimides occur more easily in the oxidation environment, their thermal stabilities in air are higher than those in nitrogen gas. In addition, thermal decomposition properties of polyaspartimides depend on their structures and compositions of both diamine segments and BMI segments.

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Keywords

Silicon-containing bismaleimide resins, polyaspartimides, reactive flame-retardants, focused microwave irradiation

1. Introduction

Bismaleimide (BMI) resins are of particular interest because of their relatively low cost, high durability, high modulus and low flammability. These resins can provide a higher service temperature than the epoxy resins, while still maintaining epoxy-like processing property. As such, they are widely used as high heat-resistance mate-

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rials in the aerospace industry, in multilayer printed-circuit boards and in surface-mounting devices, as well as high-temperature adhesive agents and in many other applications. The double bond of BMI monomers, activated by the presence of carbonyl groups, is excessively electron-depleted. Besides the self-curing of BMI, its reaction with an olefinic compound can also be performed using ENE/Diels–Alder reactions to produce the cured resin [1, 2]. Also, it can form various linear polymers [3–5] through Michael-addition reactions. BMI, for example, undergoes the above nucleophilic addition with thiols or hydrogen sulfide to prepare polyimidothioether [6–8] or reacts with diamine to synthesize polyaspartimide [9–11]. The molecular design of polyaspartimide is intended mainly to extend the molecule chain length of BMI, to reduce the brittleness of traditional BMI resins, to retain its thermal stability, and to exhibit better solubility and processing than those of ordinary linear polyimide. In recent years, the applications of polyaspartimide have focused on biodegradable and absorbent gelling materials [12], phosphate-free detergents [13], thermotropic liquid crystalline [14], poly(amide aspartimide)s with high T_g and thermal stability [15], hybrid nanocomposites [16], etc. By the introduction of phosphorus or silicon, the BMI monomers can be applied as a reactive-type flame retardant to be added into resins to enhance their thermal stability and flame retardation [17–20].

At present, few systematic investigations on BMI modified by introducing Si as a reactive flame retardant have been performed. A series of silicon-containing bismaleimides had been prepared by Mikroyannidis and Melissaris [21] as a thermal stable resin *via* the Towney procedure [22]. Some soluble derivatives of those BMI had also been synthesized with bisfurans *via* the Diels–Alder reaction [23]. The properties of siloxane resins arise mainly from the physical and chemical characteristics of the Si–O bond. These backbone chains are sometimes considered to have an organic–inorganic nature as compared with general organic polymers. The siloxane unit is characterized by a lower intermolecular force, ease of rotation and the relatively long Si–O bond. These enable the siloxane molecules to be unusually flexible and to display properties which are fairly constant over a wide temperature range [24].

The main objective of this research was to synthesize a series of silicon-containing bismaleimide monomers by a two-step reaction for using as the application of reactive flame retardant. Nevertheless, to further upgrade BMI monomers as high-performance reactants, a processing problem remains to be considered [25]: BMI tends to recrystallize easily from the blend system during aging. As a result, the BMI-containing blend systems often showed an inconsistent property. To improve the above drawbacks and the brittleness caused by the extensive cross-linking that occurs during polymerization, another aim of this study was to polymerize three silicon-containing BMI monomers by a free-radical initiator for studying their actual thermal properties. At the same time, a Michael addition reaction was performed between BMI monomers and different structures of diamines to synthesize various Si-containing polyaspartimides for studying their unique properties. The

applications of all the BMI monomers and aspartimide oligomers as reactive flame-retardant in the blending systems of general resins will be discussed.

2. Experimental

2.1. Materials

4-Aminophenol, maleic anhydride and cuprous chloride were obtained from Lancaster. Triethyl amine (TEA) was obtained from Tedia. Dichlorodimethylsilane (DCMS), dichloro-diphenylsilane (DCPS) and phenylmethyl-dichloro-silane (PMCS) were obtained from Aldrich. Diaminodiphenyl ether (OA), diaminodiphenyl sulfone (SA), 1,3-phenylene diamine (3A), 1,4-phenylene diamine (4A) and 2,2'-bis(4-aminophenyl) hexafluoropropane (FA) were obtained from TCI. Tetrahydrofuran (THF) was distilled after dehydration with sodium. N,N-Dimethylformamide (DMF) was dried by CaH₂ overnight. The other solvents were purified by conventional methods.

2.2. Synthesis

2.2.1. N-Hydroxyphenyl Maleimide [26]

A three-neck flask equipped with a Teflon stirrer and a thermometer is injected into nitrogen gas through a nitrogen purge tube and cooled with cold water to maintain its temperature below 15°C. This flask is first added into the solution of maleic anhydride (11 g) in 50 ml DMF and again added drop-wise into 4-aminophenol (10 g, 0.0917 mol) to obtain the mixture, which is stirred for about 2 h in a water bath below 15°C with nitrogen purge, so as to obtain a clear amic acid solution. Then a mixture containing 5.5 g phosphorus pentoxide, 2.5 g sulfuric acid and 50 ml DMF is added drop-wise into this amic acid solution over a period of 1 h. The resulting mixture, after stirring at 80°C for about 6 h, is cooled and poured into 500 ml ice water to obtain the precipitate, which is washed with de-ionized water, re-crystallized with isopropanol and further dried *in vacuo* to obtain N-hydroxyphenyl maleimide.

2.2.2. Silicon-Containing BMI Monomers [27]

A solution of 0.025 mol N-hydroxyphenyl maleimide, 3 ml TEA and 0.012 g Cu₂Cl₂ in 100 ml THF is put into the same type of flask setup as above with an ice bath and nitrogen purge at a fixed flow rate. A solution of 0.01 mol DCMS in 50 ml THF is added gradually to the above mixture during a period of 2 h. Then the reaction for this mixture is kept at 40°C for another 12 h. The resulting mixture is filtered to remove the precipitate of amine hydrochloride, and then distilled to remove THF solvent to obtain the product, which is again dissolved in 100 ml ethyl acetate and extracted by a 1% NaOH solution to obtain the organic layer. This organic solution dried by anhydrous magnesium sulfate is distilled under reduced pressure to obtain the precipitate, which is re-crystallized several times with n-hexane and then dried *in vacuo* to obtain the phosphonate-containing BMI monomer.

2.2.3. Silicon-Containing BMI Polymers [28]

The BMI monomer synthesized above, 2,2-azobisisobutyronitrile (AIBN) (10 mmol/l) as initiator and toluene as a solvent are added into a flask. The free radical polymerization of this mixture is carried out at 70°C for 10 h and then toluene is removed under reduced pressure to obtain a mixture, which is again dissolved in dichloromethane and precipitated by methyl alcohol several times to obtain the soluble BMI polymer. The resulting product after vacuum drying is weighed to obtain a yield of about 56–65%. In addition, the self-curing of BMI monomer synthesized above is also heated at 250°C for 2 h with nitrogen purge at a fixed flow rate to form the BMI cured resin.

2.2.4. Polyaspartimides [9, 29]

The same mol ratio of the BMI monomer (1 g) synthesized above with diamine is taken into a single-port flask with 30 ml *m*-cresol as solvent. Acetic acid (0.1 ml) is then added into this flask, held in a microwave cavity (Discover, CEM) for 30 min at 130°C and 250 W maximum power to produce a Michael addition reaction. Large amounts of methanol are poured into the obtained mucus to precipitate the polymer, which is then extracted several times with hot ethanol to remove the remaining solvent and non-reacting monomers to obtain the polyaspartimide.

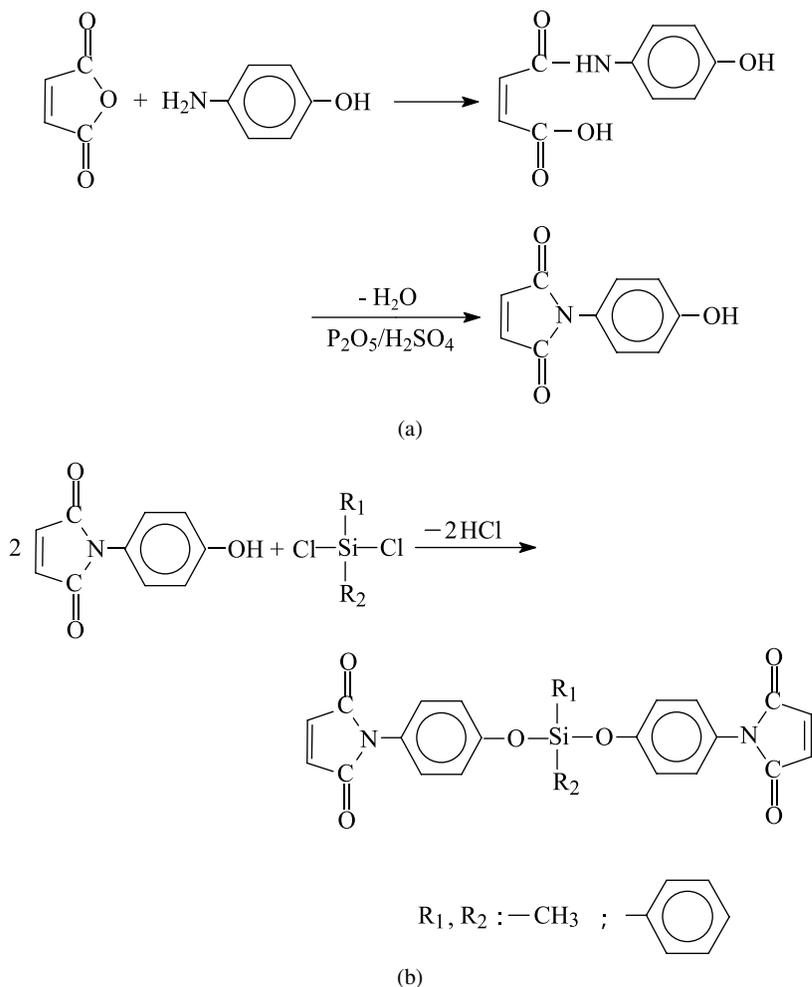
2.3. Instruments

The ¹H-, ¹³C- and ²⁹Si-NMR spectra of all the monomers synthesized above are analyzed by Bruker MSL Nuclear Magnetic Resonance Spectrometer. The elemental analysis (C, H, N) of these above monomers is performed using a Heraeus CHN-O Rapid Element Analyzer. The FT-IR spectra of all the monomers and polymers synthesized above are recorded on a Nicolet Omnic 3 Fourier Transform Infrared Reflection spectrophotometer. A Waters 510 Gel-Permeation Chromatography (GPC) system using standard samples of polystyrene with narrow molecular weight distribution calibrating is then used to analyze the molecular weight distributions of the phosphonate-containing polyaspartimides with a sample concentration of 0.5 wt% in THF as effluent flow at a flow rate of 1.0 ml/min. An Ubbelohde viscometer is used to measure the intrinsic viscosity of these soluble polymers. The melting temperature, curing temperature and glass transition temperature of these polymers are analyzed by differential scanning calorimetry (DSC) (TA Instruments DSC-Q10) at a heating rate of 10°C/min in N₂. The thermal decomposition of the silicon-containing BMI resins is analyzed by thermogravimetric analysis (TGA) (TA-Instruments TGA-Q50) at a heating rate of 20°C/min in N₂ or air.

3. Results and Discussion

Three soluble silicon-containing BMI monomers have been synthesized through a two-step process as shown in Scheme 1.

The first step is the synthesis of *N*-hydroxyphenyl maleimide *via* an imide reaction [26, 27] and the second step is the synthesis of silicon-containing BMI



Scheme 1. Synthesis of Si-containing BMI monomers. (a) Step 1: Synthesis of N-hydroxyphenyl maleimide monomer. (b) Step 2: Synthesis of Si-containing BMI monomers.

monomers *via* a condensation reaction [28]. The monomer structures so obtained are shown in Fig. 1.

3.1. Structure Identification of BMI Monomers

3.1.1. *N*-(4'-hydroxyphenyl)maleimide (4HPMI)

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

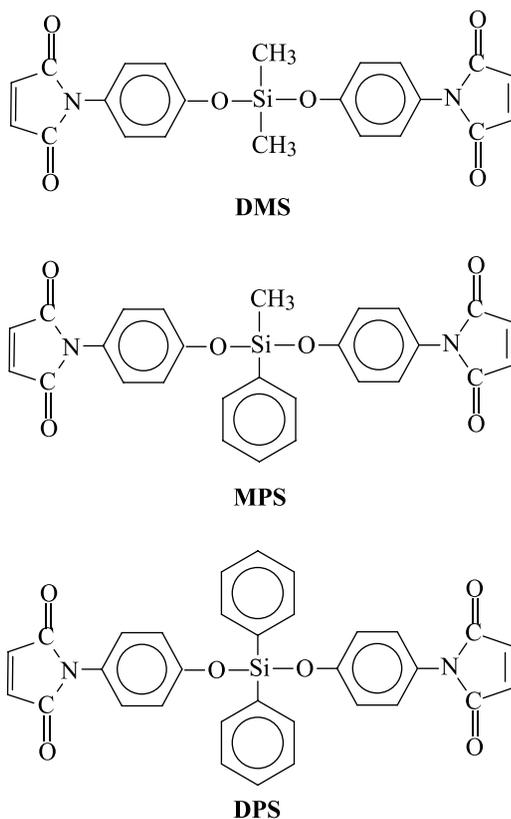


Figure 1. Chemical structure of silicon-containing BMI monomers.

3.1.2. Dimethyl(4,4'-bismaleimido phenoxy)silane (DMS)

Yield 90% as a yellow powder, mp 170°C, curing temp. 243°C. ¹H-NMR (d-chloroform) (δ, ppm): 7.18 (4H, s, 2'-H, 6'-H); 6.83 (4H, s, 3'-H, 5'-H); 6.81 (4H, s, -CO-CH=CH-CO-); 0.39 (6H, s, Si-CH₃). ¹³C-NMR (d-chloroform) (δ, ppm): 169.8 (2-C=O); 155.4 (4'-C-O-Si); 134.7 (-CO-CH=CH-CO-); 127.8 (3'-C, 5'-C); 120.3 (1'-C-N-); 116.0 (2'-C, 6'-C); 0.4 (Si-CH₃). ²⁹Si-NMR (d-chloroform) (δ, ppm): -7.4. EA (%): C, 60.1; H, 4.2; O, 22.0; N, 6.4 (calc.: C, 60.8; H, 4.1; O, 22.1; N, 6.5).

3.1.3. Methylphenyl(4,4'-bismaleimido phenoxy)silane (MPS)

Yield 86% as a golden powder, mp 171°C, curing temp. 244°C. ¹H-NMR (d-chloroform) (δ, ppm): 7.75 (2H, q, 2''-H, 6''-H); 7.42 (2H, q, 3''-H, 5''-H); 7.52 (1H, t, 4''-H); 7.15 (4H, s, 2'-H, 6'-H); 6.86 (4H, s, 3'-H, 5'-H); 6.81 (4H, s, -CO-CH=CH-CO-); 0.09 (3H, s, Si-CH₃). ¹³C-NMR (d-chloroform) (δ, ppm): 169.8 (2-C=O); 155.4 (4'-C-O-Si); 134.2 (-CO-CH=CH-CO-); 131.2 (1''-C-Si); 134.9 (2''-C, 6''-C); 130.5 (4''-C); 127.8 (3''-C, 5''-C); 123.7 (1'-C-N-); 120.3 (3'-C, 5'-C); 116.0 (2'-C, 6'-C); 0.4 (Si-CH₃). ²⁹Si-NMR (d-chloroform)

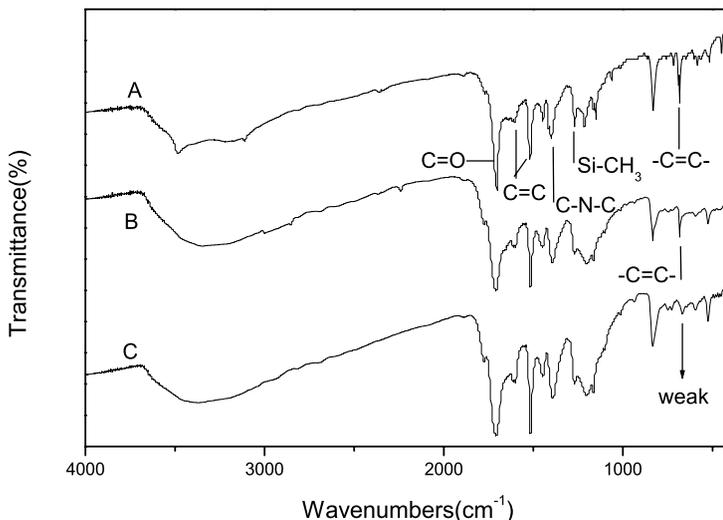


Figure 2. FT-IR spectra of DMS monomer (A), polymer (B) and cured resin (C).

(δ , ppm): -19.3 . EA (%): C, 65.5; H, 3.9; O, 19.4; N, 5.5 (calc.: C, 65.3; H, 4.0; O, 19.4; N, 5.6).

3.1.4. Diphenyl(4,4'-bismaleimido phenoxy)silane (DPS)

Yield 82% as a yellow powder, mp 174°C , curing temp. 252°C . $^1\text{H-NMR}$ (d-chloroform) (δ , ppm): 7.75 (4H, q, 2''-H, 6''-H); 7.41 (4H, q, 3''-H, 5''-H); 7.45 (2H, t, 4''-H); 7.05 (4H, s, 2'-H, 6'-H); 6.87 (4H, s, 3'-H, 5'-H); 6.81 (4H, s, -CO-CH=CH-CO-). $^{13}\text{C-NMR}$ (d-chloroform) (δ , ppm): 169.8 (2-C=O); 155.4 (4'-C-O-Si); 134.3 (-CO-CH=CH-CO-); 134.9 (1'-C-Si-); 134.1 (2''-C, 6''-C); 131.2 (4''-C); 128.2 (3''-C, 5''-C); 125.3 (1'-C-N-); 120.3 (3'-C, 5'-C); 115.9 (2'-C, 6'-C). $^{29}\text{Si-NMR}$ (d-chloroform) (δ , ppm): -37.9 . EA (%): C, 68.5; H, 3.7; O, 17.1; N, 5.1 (calc.: C, 68.8; H, 3.9; O, 17.2; N, 5.0).

3.2. Characteristics of BMIs

Figures 2 and 3 show the FT-IR spectra of DMS and DPS monomers, polymers and cured resins, respectively. The characteristic absorption peaks of the above BMI monomers can be seen from the FT-IR spectra, such as the ones at ν (cm^{-1}): 1710 (C=O); 1600, 1520 (C=C from benzene); 831 (disubstitution of benzene); 1400 (C-N-C); 690 (C=C from maleimide ring); 1090 (Si-O-C); 1390 (Si-CH₃) and 1395 (Si-Ph). The above BMI polymers can be identified from the FT-IR spectra, in which their C=C characteristic absorption peak at 690 cm^{-1} has been attenuated by the free radical polymerization reaction but their non-polymerized C=C bond from maleimide ring still exists. The result of these polymers still existing some unsaturated double bond reflects the fact that their free-radical polymerization due to hindrance from imide and benzene ring, or a comb-like structure themselves, inhibits the completion of the reaction of the double bond.

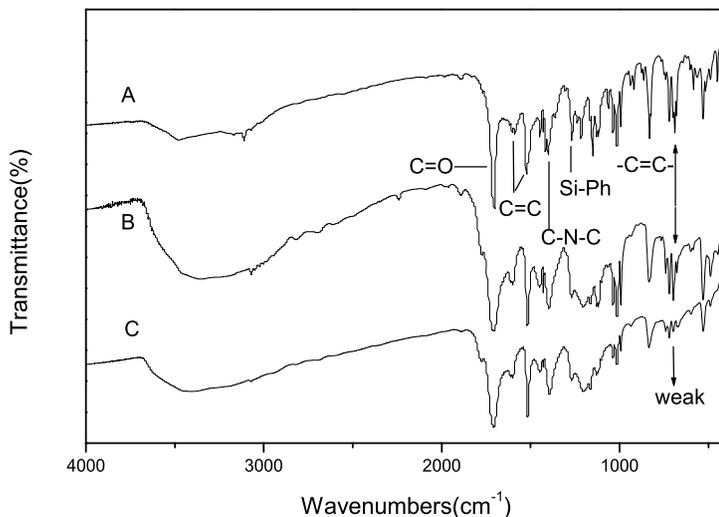


Figure 3. FT-IR spectra of DPS monomer (A), polymer (B) and cured resin (C).

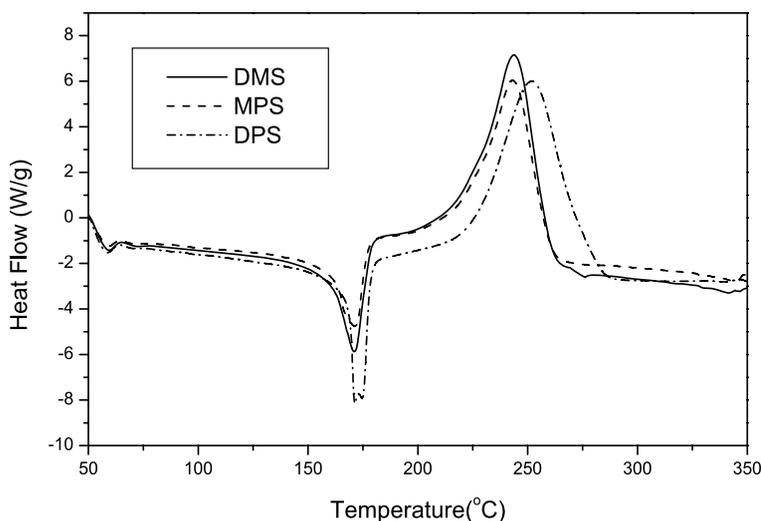


Figure 4. DSC curves of BMI monomers in nitrogen gas.

The curves of two BMI monomers measured by DSC at a heating rate of $10^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere are shown in Fig. 4. There are similar melting endothermic peaks around $170\text{--}174^{\circ}\text{C}$ and a curing exothermic peak in the range of $243\text{--}252^{\circ}\text{C}$ for these monomers. The melting point of DPS is higher than that of DMS and MPS due to the higher density of the benzene ring of the former relative to the latter. The general commercial BMI resin always has a melting temperature too close to its exothermic curing temperature leading to a narrower processing window [30] and its viscosity will increase rapidly to obstruct its evolution of blebs.

Table 1.

Molecular weights and thermal properties of silicon-containing BMI polymers and cured resins

Monomer	Yield (wt%)	M_w^a	M_n^a	T_g (°C)	$T_{5\%}$ (°C) ^c		Char at 800°C (wt%) ^c	
					N ₂	Air	N ₂	Air
DMS (polymer)	65	27 975	6364	140	292	292	39.2	4.9
DMS (cured) ^d	–	–	–	155	377	380	49.7	5.9
MPS (polymer)	62	25 243	6105	142	294	291	38.9	4.4
MPS (cured) ^d	–	–	–	158	365	367	46.4	5.3
DPS (polymer)	56	21 453	5889	145	296	280	36.3	4.0
DPS (cured) ^d	–	–	–	162	358	361	46.0	5.2

^a Determined by GPC with a concentration of 0.5 wt% sample in THF.^b Determined by DSC at a heating rate of 10°C/min in N₂.^c The $T_{5\%}$ and char at 800°C represent the onset temperature of 5% weight loss and yield of solid residue, respectively, analyzed by TGA at a heating rate of 20°C/min in N₂ or air.^d Self-curing at 250°C for 2 h.

In contrast, the margin between the melting temperature and the initial polymerization temperature of these Si-containing BMI monomers is relatively larger, thus allowing a bigger processing window for a better fusing fluidity and processing. Therefore, the self-curing of these BMI monomers is easier. Comparing the T_g of the above polymers or cured resins in the range of 140–155°C, 142–158°C or 145–162°C, respectively, as given in Table 1, that of the DPSs is higher than the MPS or DMSs, due to the high density of benzene ring.

The thermal decomposition properties of TGA curves of the three BMI polymers and cured resins measured in nitrogen and air atmosphere, respectively, as shown in Figs 5 and 6 are also listed in Table 1. The decomposition for the cured BMI resin is a one-stage and two-stage process in nitrogen and air atmosphere, respectively, while for the BMI polymer, it is a two-stage and three-stage process in nitrogen and air atmosphere, respectively. These results indicate that the higher the cross-linking extent of the BMI resin is, the higher its thermal stability is. Therefore, as the BMI polymer is heated in nitrogen, its first stage should be initialized from scission of its silane linkage because of its weaker bond energy. Then, its second-stage should produce the random chain scission and carbonization reactions of its five-membered ring and imide chain. Besides, its third-stage in air ought to produce the combustion reaction of carbonization under oxidation environment at high temperature. Thus, the decomposition of first two stages for this polymer in air is still similar to that in nitrogen, indicating that its dominant degradation mechanisms in first two stages remain unchanged in the oxidation environment. As can be seen in Table 1, the $T_{5\%}$ of DPS polymer (297°C) in nitrogen is higher than that of DMS (292°C), similar to the results for T_g of these polymers. In air, the $T_{5\%}$ of the DMS polymer (292°C) is higher than that of DPS (280°C). The former relative to the latter, due to its higher reactivity of the residual C=C bonds in the oxidation environment, produces rela-

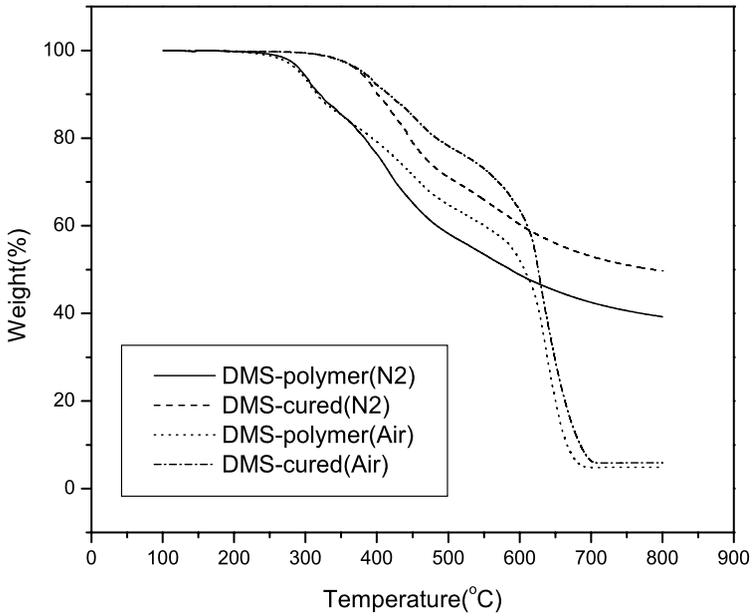


Figure 5. TGA curves of DMS polymer and cured resin.

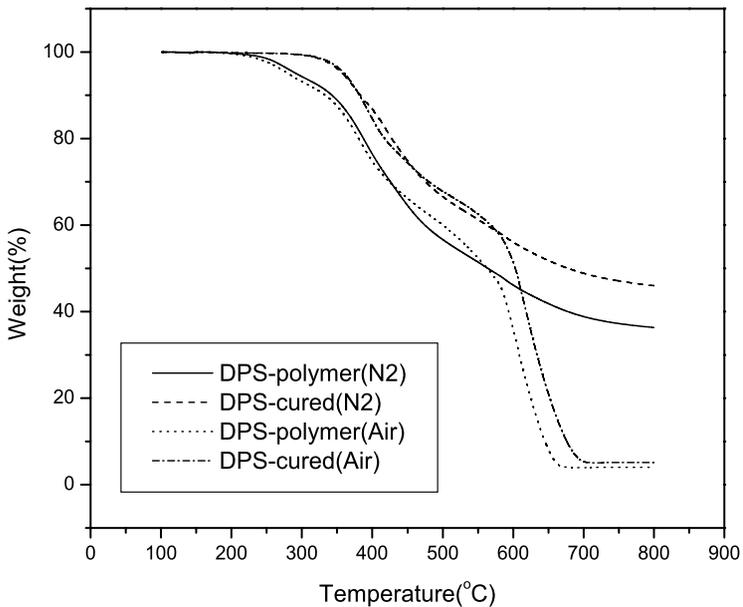
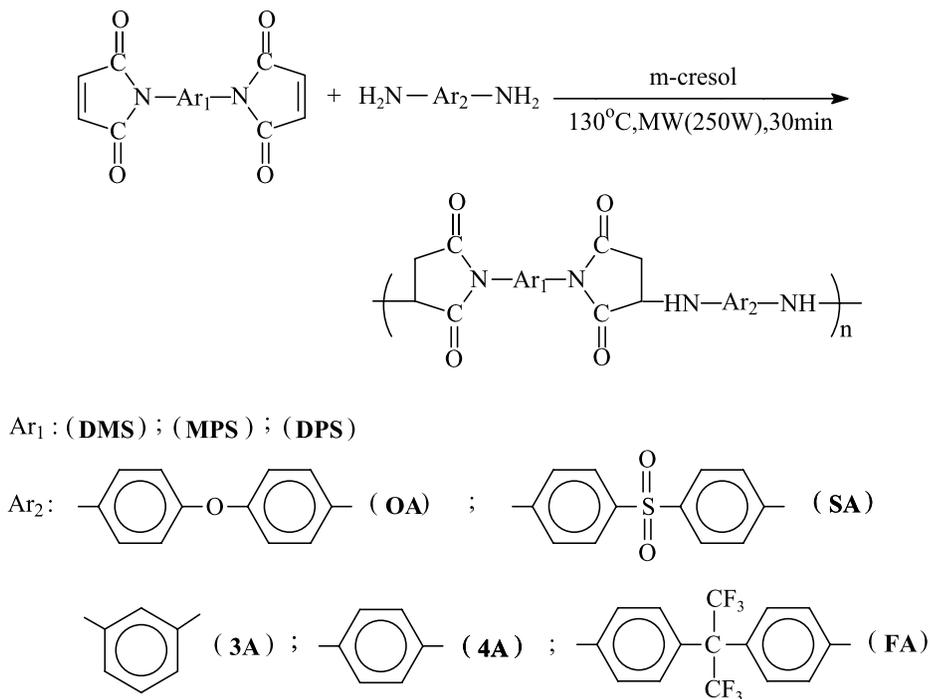


Figure 6. TGA curves of DPS polymer and cured resin.

tively more re-cross-linking reactions during thermal process to increase its thermal stability. In air, the decomposition of DMS polymer, relative to DPS, because of its higher silicon content, shows higher flame retardancy. The $T_{5\%}$ and char yields at



Scheme 2. Synthesis of polyaspartimides.

800°C of DMS cured resin are around 377°C, 49.7% and 380°C, 5.9% in nitrogen and air atmosphere, respectively. As mentioned above, since the cross-linking density of DMS cured resin is higher than that of MPS or DPS, the $T_{5\%}$ and char yield of the former are higher than those of the others.

3.3. Characteristics of Polyaspartimides

Polyaspartimides have been synthesized by focused microwave irradiation through a Michael addition reaction of the silicon-containing BMI monomer with various aromatic diamines [9, 30], which is illustrated in Scheme 2.

Using acetic acid as a catalyst, a Michael addition reaction of BMI monomer with various aromatic diamines would always be maintained for 72 h at least [11]. In this study we selected a focused microwave irradiation method to obtain a viscous co-polymer solution within only about 25–30 min. After purification, the co-polymer obtained above forms a powder of dark brown color with average yield of about 52–70%, as listed in Table 2. The above compounds can only be dissolved in phenol-like and amide-like polar solvents.

Figure 7 shows the FT-IR spectra of DMS monomer before and after addition reaction with OA and FA. It is obvious that its –NH bending is produced at 1640 cm^{-1} and its C=C characteristic absorption peak at 690 cm^{-1} is attenuated by Michael addition reaction.

Table 2.

Molecular weights and properties of polyaspartimides prepared from reacting BMI monomers with various diamines

Compound	Yield (wt%)	$[\eta]^a$ (dl/g)	T_g^b ($^{\circ}\text{C}$)	M_w^c	M_n^c	M_w/M_n	DP
DMS-OA	62	0.67	122	6237	13 222	2.12	9.9
DMS-SA	67	0.57	137	5695	11 561	2.03	8.4
DMS-3A	57	0.56	144	5434	13 042	2.40	10.1
DMS-4A	68	0.65	150	6133	13 799	2.25	11.4
DMS-FA	55	0.53	134	5945	13 555	2.28	8.1
MPS-OA	63	0.67	114	6643	14 017	2.11	9.6
MPS-SA	68	0.61	129	6743	13 351	1.98	9.1
MPS-3A	60	0.63	139	6120	14 810	2.42	10.2
MPS-4A	70	0.72	146	6960	15 382	2.21	11.6
MPS-FA	58	0.60	127	6368	14 264	2.24	8.0
DPS-OA	60	0.62	130	7163	15 042	2.10	9.5
DPS-SA	66	0.52	146	7539	14 701	1.95	9.4
DPS-3A	54	0.51	149	6885	16 937	2.46	10.4
DPS-4A	69	0.56	156	7878	16 859	2.14	11.9
DPS-FA	52	0.51	139	6692	14 589	2.18	7.8

^a Intrinsic viscosities measured in DMF at 30 $^{\circ}\text{C}$.

^b Determined by DSC at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in N_2 .

^c Distribution of molecular weight is determined by GPC with a concentration of 0.5 wt% sample in THF as a solvent.

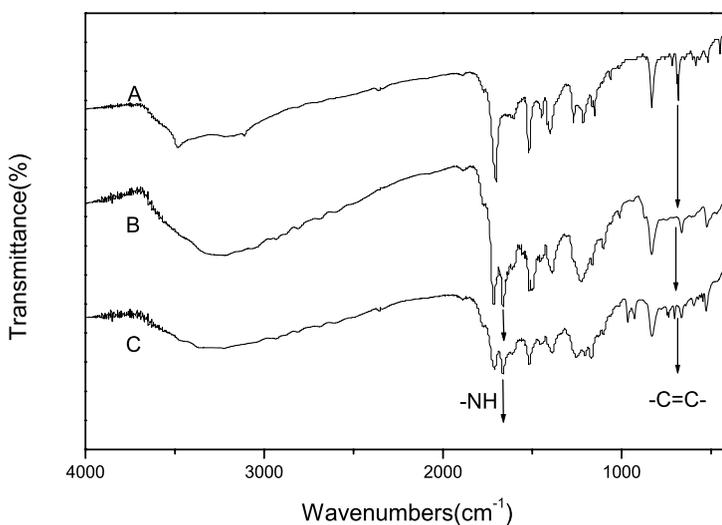


Figure 7. FT-IR spectra of DMS monomer (A), DMS-OA polyaspartimide (B) and DMS-FA polyaspartimide (C).

The basic properties of various polyaspartimides are given in Table 2. Their intrinsic viscosity in the range of 0.51–0.72 dl/g is affected mainly by the structure of chain extender. For example, as comparing the diphenyldiamine series polymers, the electron-withdrawing group $-\text{SO}_2$ and $-\text{CF}_3$ within their chain extenders SA and FA have reduced the alkalinity and nucleophilicity of diamines, leading to reduce their polymerization degree and intrinsic viscosity. Also, when comparing the phenylene diamine series polymers, because of the lower activity of the *meta*-amino position of polymer **3A** relative to the *para*-position of **4A**, the polymerization degree and intrinsic viscosity of the former are lower than those of the latter. The T_g values of various polyaspartimides measured by DSC are also listed in Table 2. The T_g values of the DPS-series are higher than the other series. The results are similar to those of the BMI cured resins and polymers. For the above three polymers, their T_g values for the same BMI-segment are apparently determined by the mobility or chain flexibility of their diamine segments in the order **4A** > **3A** > SA > FA > OA.

Figures 8 and 9 show the TGA curves of the DPS-series polyaspartimides measured in nitrogen and air, respectively, while their thermal decomposition properties are listed in Table 3. As seen in Figs 8 and 9, except the FA-segment of polyaspartimide in air, thermal decomposition processes for the DPS-series polyaspartimides are similar to those for the BMI polymers, which proceed through a two-stage and three-stage cracking under nitrogen and air atmosphere, respectively. Therefore, the decomposition of the first stage for polyaspartimides in nitrogen atmosphere should be first initialized by scission of the silane or HN–C (secondary amine) linkage

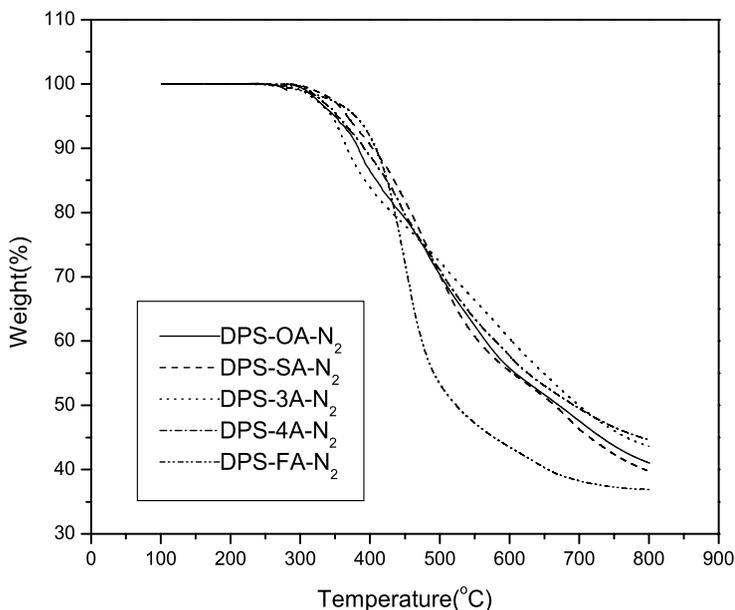


Figure 8. TGA curves of DPS-series polyaspartimides in nitrogen gas.

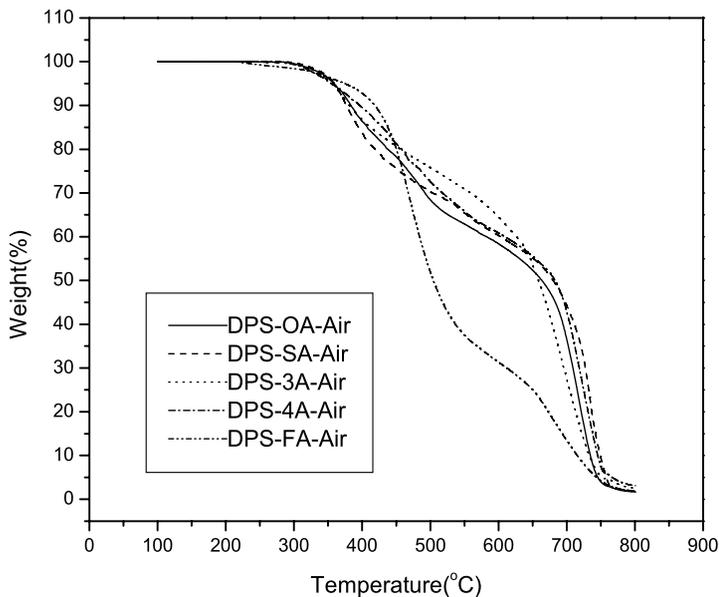


Figure 9. TGA curves of DPS-series polyaspartimides in air.

Table 3.

Thermal decomposition properties of polyaspartimides prepared from reacting bismaleimide monomers with various diamines

Compound	Si (wt%) ^a	F (wt%) ^a	$T_{5\%}$ (°C) ^b		Char at 800°C (wt%) ^b	
			N ₂	Air	N ₂	Air
DMS-OA	4.44	0	345	354	38.2	1.2
DMS-SA	4.13	0	360	366	35.1	1.0
DMS-3A	5.20	0	341	350	42.9	1.7
DMS-4A	5.20	0	343	351	43.5	1.9
DMS-FA	3.81	15.5	356	363	34.4	0.9
MPS-OA	4.05	0	347	355	37.3	1.5
MPS-SA	3.78	0	363	370	34.5	1.2
MPS-3A	4.67	0	344	351	41.2	2.3
MPS-4A	4.67	0	346	354	42.3	2.5
MPS-FA	3.52	14.3	360	368	34.0	1.1
DPS-OA	3.71	0	352	359	41.1	1.6
DPS-SA	3.49	0	367	375	39.2	2.0
DPS-3A	4.23	0	348	355	43.3	2.5
DPS-4A	4.23	0	350	356	44.1	3.1
DPS-FA	3.26	13.3	364	371	36.9	1.4

^a The theoretical Si/F weight ratio of composition in the oligomer.

^b The thermal decomposition properties are analyzed by TGA at a heating rate of 20°C/min in N₂ or air.

with the weaker bonding and then, after the first stage, it is similar to those for BMI polymers. In air atmosphere, the decomposition of the first two stages for polyaspartimides is still similar to those in nitrogen. However, comparing the $T_{5\%}$ in nitrogen and in air atmosphere, respectively, as listed in Table 3, their reaction of residue double bond with amine-terminated chain or themselves during the first two stages should be catalyzed by the oxidation environment to produce the re-polymerization reaction, leading to an increase in their thermal stability. These results also indicate that their decomposition and re-polymerization of first two stages can proceed simultaneously in the oxidation environment. Only in the third stage, their decomposition of high temperature is governed mainly by thermal oxidation. In addition, the $T_{5\%}$ values of these above polymers are also affected by their thermal stability of diamines. For example, because of the higher thermal stability of SO_2 and CF_3 groups of SA- and FA-segment polymers relative to the others, the $T_{5\%}$ values of the former two are 367°C and 364°C in nitrogen atmosphere, and 375°C and 371°C in air atmosphere, respectively, higher than those of the others. The carbonized char yield at 800°C for 4A-segment polyaspartimide, due to the higher silicon content, is the highest of all the polymers and is about 44.1% and 3.1% in nitrogen and air atmosphere, respectively. While for the FA-segment polyaspartimide it is the lowest compared to all the others, because of both its lower silicon content and larger proportion of fluorine release, and is about 36.9% and 1.4% in nitrogen and air atmosphere, respectively. The results of the FA-segment polyaspartimide decomposed in air to form lower char yield of solid residue relative to the others indicate that the fluorine-content inhibits its carbonization reaction in the oxidation environment [31] and rapidly reduces its char yield. In addition, the introduction of FA into this polymer can apparently increase its thermal stability in air, leading to a change in its decomposition process from three stages to two stages.

The thermal decomposition properties of the DMS and MPS-series polyaspartimides measured by TGA in nitrogen and air atmosphere, respectively, are also listed in Table 3. Comparing the decomposition of the DMS or MPS-series with the DPS-series polyaspartimides in nitrogen or in air, thermal stability and char yield of the former are lower than those of the latter. A higher phenyl density for the DPS-series relative to the DMS or MPS-series polyaspartimides can simultaneously enhance their thermal stability and char yield of carbonization, which is dissimilar to the results for the BMI self-cured resins and polymers. Therefore, thermal decomposition for these polyaspartimides apparently depends on their structure and composition of diamine-segments and BMI-segments. Thus, the $T_{5\%}$ values of the DMS-series polyaspartimides are in the range of $341\text{--}360^\circ\text{C}$ and $350\text{--}366^\circ\text{C}$ in nitrogen and air atmosphere, respectively. From comparing the above results of the three polyaspartimide series, as seen in Table 3, the decomposition for SA-segment polyaspartimides, whether in DMS, MPS or DPS-series, may decompose easily and release large amounts of SO_2 gas leading to inhibit its re-cross-linking reaction catalyzed by oxidation. The results of char yields at 800°C for DMS-series polyaspartimides around 34.4–43.5% and 0.9–1.9% in nitrogen and air atmosphere,

respectively, indicate that they are more easily oxidized than the other series. These facts confirm that the thermal stability and flame retardancy of polyaspartimides are mainly affected by their structure and compositions of amine-segments and BMI-segments.

4. Conclusions

The synthesis of three silicon-containing BMI monomers by a two-step process has been performed with imide and condensation reactions. The margin between fusing temperature and initial self-curing temperature for DMS monomer is relatively larger than that for MPS and DPS, indicating that the former produces a larger processing window relative to the others. This result makes the higher self-curing degree of the former and increases its thermal stability and flame retardancy. The T_g of the DPS cured resin with high phenyl density is higher than that of the others. The DMS polymer relative to the MPS or DPS one, as catalyzed by oxygen in air, can produce more easily the re-cross-linking reaction to promote its thermal stability and flame retardancy. Besides, because of the higher silicon content of the DMS relative to the MPS or DPS, char yield of the former, whether in soluble polymer or cured resin, is higher than that of the others. The silane-containing polyaspartimides have been synthesized by the silicon-containing BMI monomers reacting with diamines as chain extender agent. The polymerization degree of polyaspartimides synthesized depends on the alkalinity and nucleophilicity of diamines. Besides, the thermal stability and flame retardancy of the DPS-series, due to the high phenyl density, are higher than those of the other series. Thermal decomposition of polyaspartimides, depends on their re-crosslinking reaction catalyzed by the oxidization environment. The properties of the silane-containing polyaspartimides or BMI polymers depend on their structures and compositions, which make them suitable to be used as a superior flame retardant.

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