Studies of Fluorine-Containing Bismaleimide Resins. Part I: Synthesis and Characteristics of Model Compounds[1]

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Abstract—A series of fluorine-containing bismaleimide (FBMI) monomers are synthesized by a 2-step reaction for using as the applications of low-k materials. The synthesized FBMI monomers are characterized by the ^{1}H, ^{13}C, ^{19}F nuclear magnetic resonance (NMR) spectroscopy and element analysis. These FBMI monomers react with free radical initiator or self-cure to prepare FBMI-polymers. All the self-curing FBMI resins have the glass transition temperatures T_g in the range of 130–141°C and show the 5% weight loss temperatures $T_{5\%}$ of 280–322°C in nitrogen atmosphere. The higher heat resistance of self-curing FBMI resin relative to FBMI-homopolymer is due to its higher cross-linking density. The FBMI resins exhibit improved dielectric properties as compared with commercial bismaleimide (BMI) resins with the dielectric constants ε lower than 2.44 which is related to the low polarizability of the C−F bond and the large free volume of CF_3 groups in the polymers. Besides, the flame retardancy of all these FBMI resins could be enhanced via the introduction of Br-atom.

INTRODUCTION

The bismaleimide resins (BMI) 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 have been widely used as high heat-resistance materials in the aerospace industry, in multilayer printed-circuit boards (PCB), 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 low-k materials are generally defined as a material with dielectric constant ε bellow 3.9. The ε of commercial epoxies, for example, are about 3.3−3.5. It is well known that incorporation of fluorinated groups into polymer's structure could effectively improve the dielectric property for applications in PCB substrates and electronic packaging technology. The ε of polymer materials could be decreased sufficiently, which is related to the low polarizability of the carbon-fluorine (C−F) bond as well as the large molecular free volume in opposition to other atoms [12]. Besides, the hydrophobic and oleophobic nature of perfluorinated alkyl groups could reduce T_g of materials and further decrease the dielectric constants [13]. The incorporation of fluorinated substituents in the network structure of epoxies will improve the resins durability in moist environments and lower their moisture adsorption [14]. In investigation of fluorinated polymer materials, Sasaki [15] incorporated perfluorobutenyloxy groups into the chain of epoxy resins and found that dielectric constant of the materials decreased to 2.7−2.8.

The main objective of this research was to synthesize a series of novel F-containing bismaleimide monomers by a 2-step reaction. The applications of all the FBMI monomers as the low-k materials or modifier in the blending systems of general resins would then be discussed.

EXPERIMENTAL

Materials

4-Aminophenol, 4-amino-2,6-dibromophenol, maleic anhydride, and cuprous(I) chloride were obtained from Lancaster. Triethyl amine (TEA) and acetic anhydride were obtained from TEDIA.

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2,3-Dichloro-hexafluoro-2-butene (DCHFB) and 1,3-dichloro-tetrafluoro-acetone (DCTFA) 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-Dimethylformamide (DMF) was dried by CaH_2 over night. The other solvents were purified by conventional methods.

Synthesis

N-Hydroxyphenylmaleimide (4HPMI). The nitrogen gas through a nitrogen purge tube is injected into a three-neck flask equipped with a teflon stirrer and a thermometer [16, 17]. The reaction system is cooled with cold water to maintain the temperature below 15°C. This flask is first added into the solution of maleic anhydride (11 g) in 50 mL of DMF and again added dropwise into 4-aminophenol 10 g (0.0917 mol) to obtain the mixture, which is stirred about two hours in water bath below 15°C with nitrogen purge so as to obtain a clear amic acid solution. Then a mixture containing 5.5 g of phosphorus pentaoxide, 2.5 g of sulfuric acid and 50 mL of DMF is added dropwise into this amic acid solution during a period of one hour. The resulting mixture, after stirring at 80°C about 6 hours, is cooled and poured into 500 mL of ice water to obtain the precipitate, which is washed with de-ionic water and recrystallized with isopropanol, and further dried in vacuo to obtain a N-hydroxyphenyl maleimide.

N-(2,6-Dibromo-4-hydroxyphenyl)maleimide (DBHPMI). With the same type of flask as above, 10 g (0.0288 mol) 4-amino-2,6-dibromophenol are added gradually to a solution of maleic anhydride (3.5 g) in 50 mL THF and the mixture is stirred 5 h in a water bath to obtain a clear amic acid solution [18]. The mixture including stoichiometric amounts of acetic anhydride, 0.5 g cobalt acetate and 1.5 g TEA, is added dropwise to this solution of amic acid already raised temperature to 80°C. After stirring 5 hours, the mixture is distilled to remove THF and obtain the precipitate. The precipitate is 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.

Fluorine-containing bismaleimide monomers. The dissolution of 0.025 mole of N-hydroxyphenylmaleimide, 3 mL of triethylamine and 0.012 g of Cu_2Cl_2 in 100 mL of THF is put into the same type of flask setup as above with an ice bath and nitrogen purge at a fixed flow rate [19]. The solution of 0.01 mole of dichloride (DCHFB or DCTFA) in 50 mL of THF is added gradually to the above mixture during a period of 2 hours. 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 of 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 recrystallized several times with n-hexane and then dried in vacuum to obtain the fluorine-containing bismaleimide monomer.

Fluorine-containing bismaleimide polymers. The bismaleimide monomer synthesized above, 2,2-azobisisobutyronitrile (AIBN) (10 mmol/L) as initiator, and toluene as a solvent are added into a single-port flask [20]. The free radical polymerization of this mixture is held in a microwave cavity (Discover, CEM) for 60 min at 100°C and maximum-power of 250 W. 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 FBMI-homopolymer. The resulting product after drying in vacuum is weighed to obtain a yield of about 58−65%. In addition, the FBMI monomer synthesized above is also heated at 200°C for two hours with nitrogen purge at a fixed flow rate to form the FBMI self-curing resin.

Instrumentation

The ^1H, ^{13}C, ^{19}F NMR spectra of all the monomers synthesized above are analyzed by Bruker MSL Nuclear Magnetic Resonance Spectrometer. The element analyses (C, H, N) of these above monomers are performed by a Heraeus CHN−O Rapid element Analyzer. The FTIR spectra of all the monomers and polymers synthesized above are analyzed by a Nicolet Omnic 3 Fourier Transform Infrared Reflection spectrophotometer. A Waters 510 Gel Permeation Chromatography (GPC) system after using standard samples of polystyrene with narrow molecular weight distribution calibrating is then used to analyze the molecular weight distributions of the fluorine-containing bismaleimide polymers with a sample concentration of 0.5 wt % in THF as effluent flow at a flow rate of 1.0 mL/min. The melting temperature, curing temperature and glass transition temperature of these polymers are analyzed by DSC (TA-Instruments DSC-Q10) at a heating rate of 10 grad/min in N2. The thermal decomposition of the FBMI resins is analyzed by TGA (TA-Instruments TGA-Q50) at a heating rate of 20 grad/min in N_2 or air. The electrical properties are measured on a Precision Component Analyzer (Wayne Kerr 6440B). All the polymers were heated to the form of thin film with the thickness about 50 μm on copper sheet and then tested by a special cell arrangement at 500 MHz.
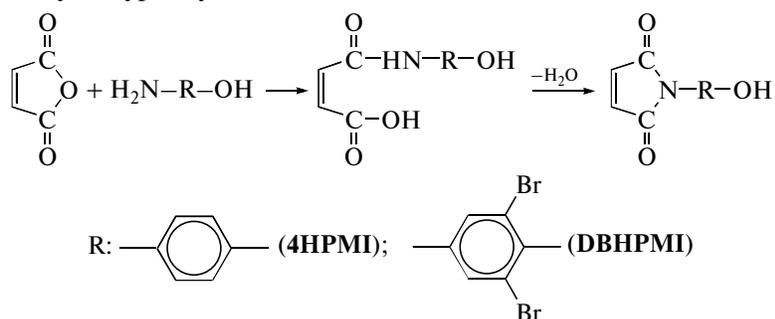
RESULTS AND DISCUSSION

A series of soluble F-containing bismaleimide monomers have been synthesized through a 2-step
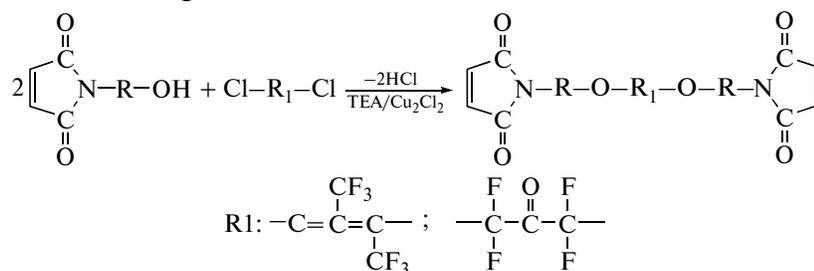
process as shown in Scheme 1. The first step is the synthesis of *N*-hydroxyphenyl maleimide via imide-reaction [16−18], and the second step is the synthesis of F-containing bismaleimide monomers via condensation reaction [19]. The monomer structures so obtained are shown as Scheme 2.
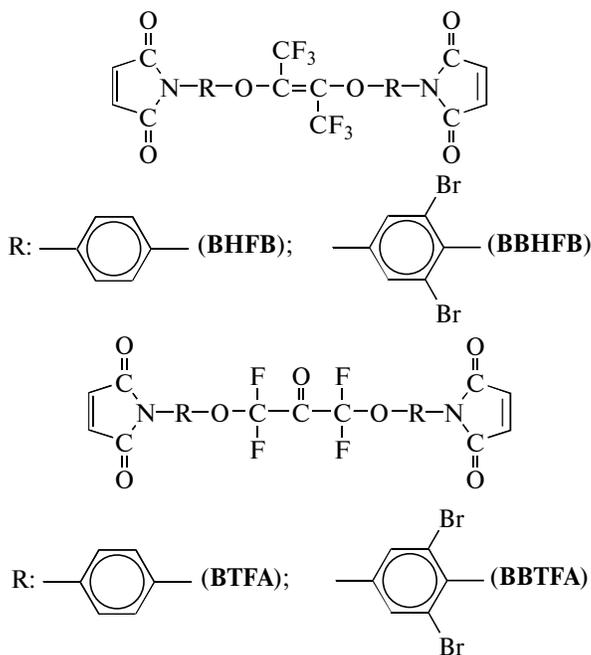
Step 1: Synthesis of *N*-hydroxyphenyl maleimide monomer

R: ⟨phenyl⟩ **(4HPMI)**; ⟨dibromophenyl⟩ **(DBHPMI)**

Step 2: Synthesis of F-containing bismaleimide monomers

$$R1: \ -C=C=C- \ ; \ -\overset{F}{\underset{F}{C}}-\overset{O}{\underset{}{C}}-\overset{F}{\underset{F}{C}}-$$

Scheme 1.

R: ⟨phenyl⟩ **(BHFB)**; ⟨dibromophenyl⟩ **(BBHFB)**

R: ⟨phenyl⟩ **(BTFA)**; ⟨dibromophenyl⟩ **(BBTFA)**

Scheme 2.

Structure Identification of Bismaleimide Monomers

(4,4'-Bismaleimidophenoxy)hexafluorobutene (BHFB). Yield 78% as a brown powder, m. p. 161°C,

curing temp. 190°C. ^{1}H NMR (*d*-DMSO, δ_H, ppm): 7.11 (4H, s, −CO−**CH**=**CH**−CO−), 7.07 (4H, d, *J* = 8.2 Hz, 2'−**H**, 6'−**H**), 6.83 (4H, d, *J* = 8.2 Hz, 3'−**H**, 5'−**H**). ^{13}C NMR (*d*-DMSO, δ_C, ppm)—170.3
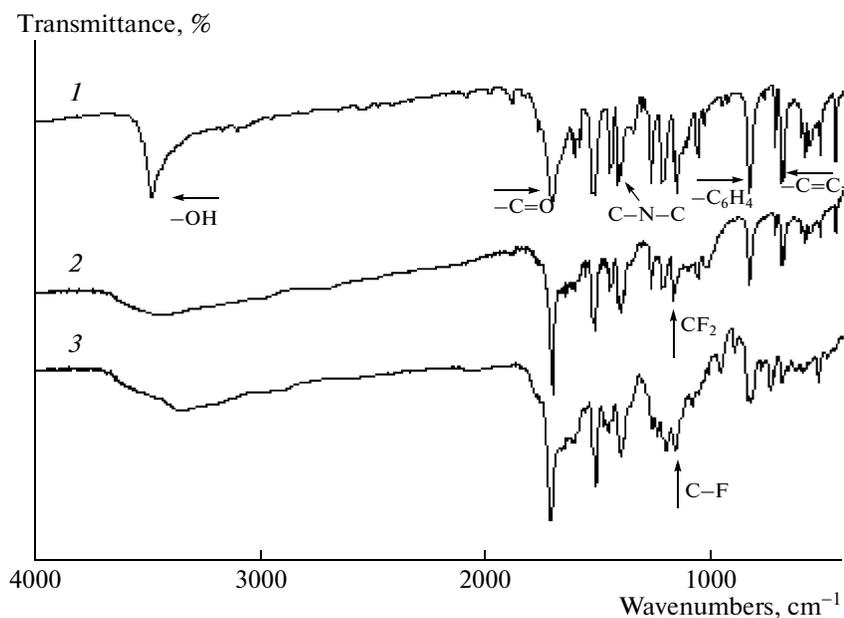
Fig. 1. FTIR spectra of (*1*) HPMI, (*2*) BHFB, and (*3*) BTFA monomers.

(2−C=O), 162.2 (4'=C−O−), 134.5 (−CO−CH=CH−CO−), 128.3 (q, *J* = 29.2 Hz, CF$_3$**C**=C**C**F$_3$), 122.5 (1'−**C**−N−), 120.9 (4'−**C**−O−), 116.4 (2'−**C**, 6'−**C**), 115.0 (3'−**C**, 5'−**C**), 112.9 (q, *J* = 293.2 Hz, **C**F$_3$C=C**C**F$_3$). ^{19}F NMR (*d*-DMSO, δ$_F$, ppm): −114.3 (CF$_3$). EA, %: C 53.6, H 2.3, O 17.2, N 5.1 (calc., %: C 53.5, H 2.2, O 17.8, N 5.2).

(4,4'-Bismaleimidophenoxy)tetrafluoroacetone (BTFA). Yield 76% as a dark brown powder, m.p. 152°C, curing temp. 180°C. ^{1}H NMR (*d*-DMSO, δ$_H$, ppm): 7.13 (4H, s, −CO−**CH**=**CH**−CO−), 7.05 (4H, d, *J* = 8.0 Hz, 2'−**H**, 6'−**H**), 6.86 (4H, d, *J* = 8.0 Hz, 3'−**H**, 5'−**H**). ^{13}C NMR (*d*-DMSO, δ$_C$, ppm): 182.9 (quintet, *J* = 28.3Hz, −CF$_2$**C**OCF$_2$−), 171.1 (2−**C**=O), 158.2 (4'−**C**−O−), 134.2 (−CO−**C**H=**C**H−CO−), 122.7 (1'−**C**−N−), 119.4 (2'−**C**, 6'−**C**), 116.4 (3'−**C**, 5'−**C**), 119.5 (t, *J* = 294.3 Hz, −**C**F$_2$−). ^{19}F NMR (*d*-DMSO, δ$_F$, ppm): −63.4 (C−F). EA, %: C 54.9, H 2.2, O 22.0, N 5.4 (calc., %: C 54.8, H 2.4, O 22.2, N 5.6).

Bis(2,6-dibromo-1-(*N*-maleimido)phenyl)hexafluorobutene (BBHFB). Yield 70% as a brown powder, m.p. 159°C, curing temp. 195°C. ^{1}H NMR (*d*-DMSO, δ$_H$, ppm): 7.50 (4H, s, −CO−**CH**=**CH**−CO−), 7.15 (4H, s, 2'−**H**, 6'−**H**). ^{13}C NMR (*d*-DMSO, ppm)—171.5 (2−**C**=O), 159.1 (4'=C−O−), 134.7 (−CO−**C**H=**C**H−CO−), 129.3 (q, *J* = 30.2 Hz, CF$_3$**C**=C**C**F$_3$), 124.5 (1'−**C**−N−), 122.8 (4'−**C**−O−), 115.5 (2'−**C**, 6'−**C**), 112.9 (3'−**C**, 5'−**C**), 113.9 (q, *J* = 293.2 Hz, **C**F$_3$C=C**C**F$_3$). ^{19}F NMR (*d*-DMSO, δ$_F$, ppm): −128.2 (CF$_3$). EA, %: C 33.8, H 1.0, O 11.3, N 3.2 (calc., %: C 33.7, H 0.9, O 11.2, N 3.3).

Bis(2,6-dibromo-1-(*N*-maleimido)phenyl)tetrafluoroacetone (BBTFA). Yield 71% as a dark brown powder, m.p. 150°C, curing temp. 185°C. ^{1}H NMR (*d*-DMSO, δ$_H$, ppm): 7.49 (4H, s, −CO−**CH**=**CH**−CO−), 7.21 (4H, s, 2'−**H**, 6'−**H**). ^{13}C NMR (*d*-DMSO, δ$_C$, ppm)—180.6 (quintet, *J* = 30.1Hz, −CF$_2$**C**OCF$_2$−), 173.2 (2−**C**=O), 162.2 (4'=C−O−), 136.3 (−CO−**C**H=**C**H−CO−), 124.2 (1'−**C**−N−), 121.3 (2'−**C**, 6'−**C**), 118.9 (3'−**C**, 5'−**C**)—116.4 (t, *J* = 294.3Hz, −**C**F$_2$−). ^{19}F NMR (*d*-DMSO, δ$_F$, ppm): −71.7 (C−F). EA, %: C 35.7, H 1.0, O 13.1, N 3.2 (calc., %: C 35.5, H 0.9, O 13.3, N 3.3).

Characteristics of Bismaleimides

According to the analysis of NMR, all monomers show the maleimide proton signals at δ$_H$ 7.1−7.5 (s). The aromatic proton signals at δ$_H$ 6.8 (d) represent the para-substituted benzene moiety in BHFB and BTFA, while the signals at δ$_H$ 7.1−7.2 (s) represent 1,3,4,5-substituted benzene moiety in BBHFB and BBTFA. The carbon signals δ$_H$ 128−129 (q) and 112−114 (q) represent **C**F$_3$C=C**C**F$_3$ moiety in BHFB and BBHFB. The carbon signals δ$_C$ 180−182 (quintet) and δ$_C$ 116−119 (t) exhibit CF$_2$**C**OCF$_2$ moiety in BTFA and BBTFA. The fluoride signals in ^{19}F NMR spectrum were corresponding to the above statements.

Figure 1 shows the FTIR spectra of HPMI, BHFB, and BTFA monomers. The characteristic absorption peaks of the above monomers can be seen from the FTIR spectra such as ν (cm^{-1}): 1713 (C=O); 1597, 1520 (C=C from benzene); 831 (disubstitution of benzene); 1400 (C−N−C) 697 (C=C from maleimide
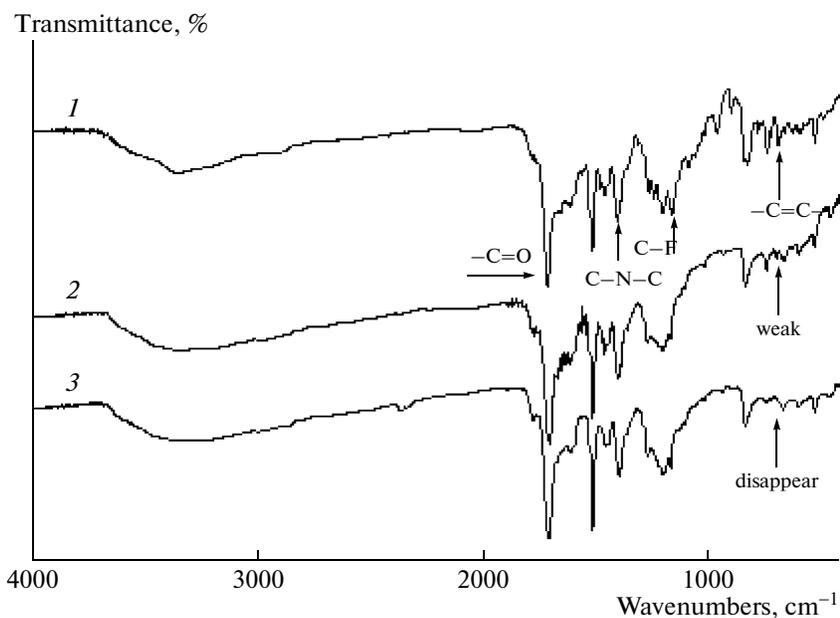
Transmittance, %

Fig. 2. FTIR spectra of (*1*) BTFA monomer, (*2*) homopolymer, and (*3*) self-curing resin.
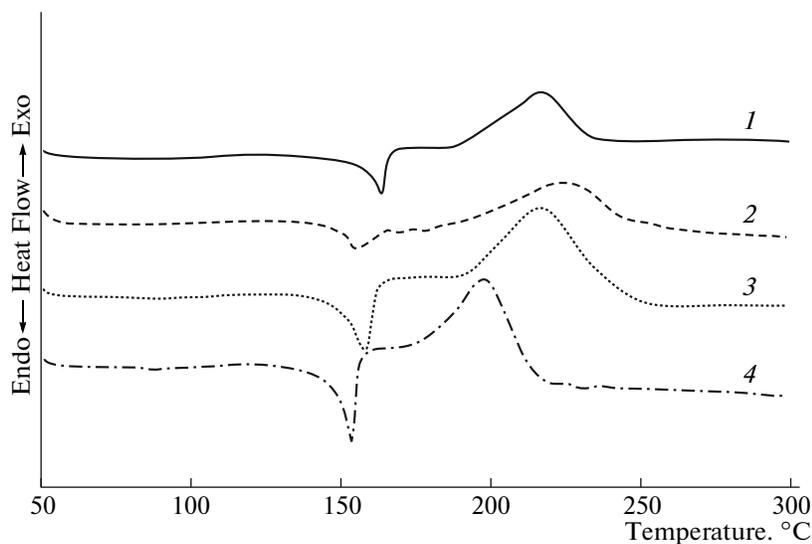

Fig. 3. DSC curves of FBMI monomers: (*1*) BHFB, (*2*) BTFA, (*3*) BBHFB, and (*4*) BBTFA.

ring), 1180 (CF_3 of BHFB); 1200 (C−F of BTFA) and 3450 (−OH from HPMI only) etc.

Figure 2 shows the FTIR spectra of BTFA monomer, homopolymer, and self-curing resin, respectively. These FBMI resins can be identified from the FTIR spectra, which their C=C characteristic absorption peaks at position 690 cm^{-1} have 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 their completed reaction of double bond.

The curves of FBMI monomers measured by DSC at a heating rate of 10 grad/min in nitrogen atmosphere are shown in Fig. 3. There are similar melting endothermic peaks around 150−161°C and curing exothermic peak in the range of 190−250°C for these monomers. The general commercial BMI-resin always has a melting temperature too close to its exo-

Table 1. Molecular weights and thermal properties of FBMI homopolymers and self-curing resins

Monomer	Yield, wt %	M_w^a	M_n^a	T_g, °C[b]	$T_{5\%}$, °C[b]		Char at 800°C, wt %[c]	
					N$_2$	Air	N$_2$	Air
BHFB (polym.)	65	1.77×10^4	7.58×10^3	124	289	282	30.5	1.7
BHFB (cyred)[d]	–	–	–	137	328	308	37.4	2.7
BTFA (polym.)	60	2.41×10^4	9.50×10^3	121	272	278	31.5	2.2
BTFA (cyred)[d]	–	–	–	130	280	284	35.9	3.8
BBHFB (polym.)	62	2.11×10^4	8.63×10^3	130	314	320	31.2	3.4
BBHFB (cyred)[d]	–	–	–	141	322	328	40.0	4.2
BBTFA (polym.)	58	2.80×10^4	1.08×10^4	126	309	315	34.8	4.5
BBTFA (cyred)[d]	–	–	–	134	315	322	41.3	5.7

[a] Distribution of molecular weight is tested by GPC with a concentration of 0.5 wt% sample in THF.

[b] The glass transition temperature T_g is analyzed by DSC at a heating rate of 10 grad/min in N$_2$.

[c] The $T_{5\%}$ and char at 800°C represents the onset temperature of 5% weight loss and yield of solid residue, respectively analyzed by TGA at a heating rate of 20 grad/min in N$_2$ or air.

[d] Self-curing at 200°C for 2 hrs.

thermic curing temperature leading to lower its processing window [21] and its viscosity will increase rapidly to obstruct its evolution of bubbles. In the contrast, the margin between the melting temperature and the initial polymerization temperature of these F-containing BMI monomers are relatively larger, thus allowing a bigger processing window for a better fusing fluidity and processing. Therefore, the self-curing of these BMI monomers is more easily.

The thermal decomposition properties of TGA curves of FBMI homopolymers and self-curing resins measured in nitrogen and air atmosphere, respectively are listed in Table 1. The TGA curves of BTFA resins measured in nitrogen and air atmosphere are shown in Fig. 4. The decomposition for the FBMI resins is a one-stage and two-stage process in nitrogen and air atmosphere, respectively. The second-stage in air ought to produce the combustion reaction of carbonization under oxidation environment of high temperature. Besides, the $T_{5\%}$ of self-curing resins is higher than that of homopolymer. These results indicate that the higher the crosslinking extent of the FBMI resin is, the higher its thermal stability is. As the data given in Table 1, the $T_{5\%}$ of BHFB homopolymer (289°C) in
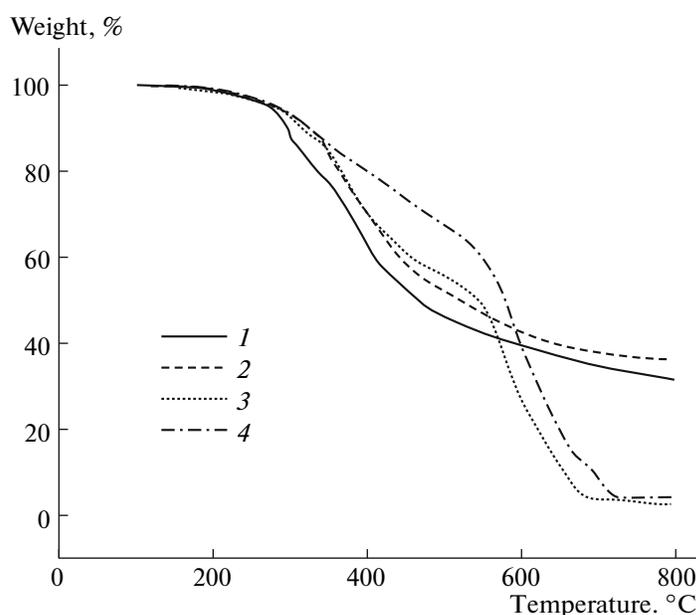
Fig. 4. TGA curves of BTFA homopolymers and self-curing resins: (*1*) BTFA-polymer (N$_2$), (*2*) BTFA-cured (N$_2$), (*3*) BTFA-polymer (air), and (*4*) BTFA-cured (air).

nitrogen is higher than that of the BTFA one (272°C), similar to the results of T_g of these polymers. This may due to the higher crosslinking density of BHFB resins induced by their butene structure.

The TGA curves of Br-containing FBMI cured resins measured in nitrogen and air atmosphere are shown in Fig. 5. The decomposition for the cured FBMI resin is also a one-stage and two-stage process in nitrogen and air atmosphere, respectively. As the FBMI resin was heated in nitrogen or air, its first-stage should be initialized from scission of its halogen linkage because of its weaker bond energy and then, followed by the random chain scission and carbonization reactions of its five-membered ring and imide chain. Besides, its second-stage in air ought to produce the combustion reaction of carbonization under oxidation environment of high temperature. As the data given in Table 1, the flame retardancy of all these FBMI resins could be enhanced via the introduction of Br-atom. The char yield of FBMI resins is increased with increasing the Br content in N_2. Although the char yield of the FBMI resins pyrolyzed in air isn't obviously increased with increasing the Br content, the maximum rates of weight loss of these polymers are decreased and the pyrolysis curves moved to higher temperature as the Br content was increased. The results of lower weight loss rates during pyrolysis of Br-containing system still showed that the introduction of Br-atom improved flame retardancy. The char yields at 800°C of BBTFA cured resin, for examples, are around 41.3 and 5.7% in nitrogen and air atmosphere, respectively.

Solubility Properties

The solubility of synthesized FBMI monomers and homopolymers was tested in various organic solvents and the results are summarized in Table 2. The solubility behavior of the FBMI resins depended on their
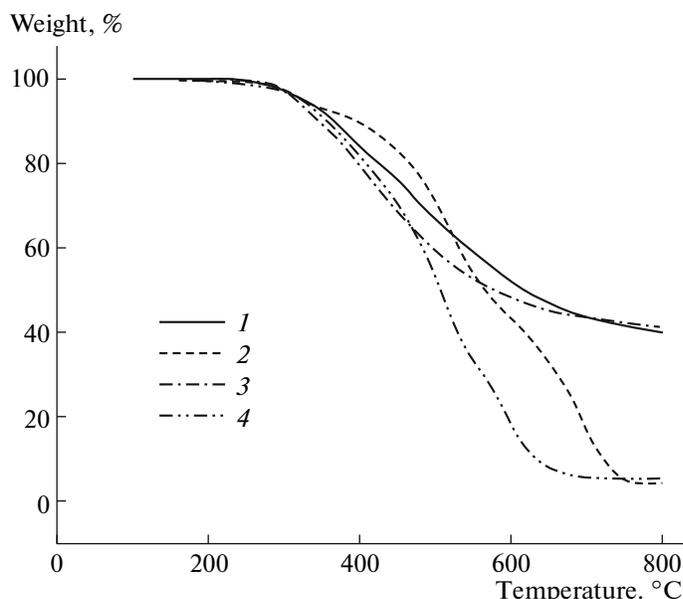

Fig. 5. TGA curves of Br-containing FBMI self-curing resins: (*1*) BBHFB (N_2), (*2*) BBHFB (air), (*3*) BBTFA (N_2), and (*4*) BBTFA (air).

chain packing density and intermolecular interactions. Thus, the FBMI with more flexible C–F chain such BTFA series generally displayed a higher solubility than those with more rigid components such as BHFB series. In aprotic polar solvents, such as N-methyl-2-pyrolidone (NMP), DMF, N,N-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO), they showed good solubility and even in less polar solvents, like m-cresol, THF, and methylene chloride (MC), they were soluble. This might be due to the presence of the flexible C–F ester structure and the bulky CF_3 group, which further hindered dense chain packing and reduced chain-chain interactions.

Table 2. Solubility of FBMI monomers and homopolymers

Monomer/polymer	Solvents[a]							
	NMP	DMF	DMAc	DMSO	m-Cresol	THF	MC	Acetone
BHFB (mono.)	++	++	++	++	+	+	+	+
BHFB (polym.)	++	++	++	+	+	+	+	+
BTFA (mono.)	+++	+++	+++	+++	++	++	++	++
BTFA (polym.)	+++	+++	+++	+++	++	++	++	++
BBHFB (mono.)	++	++	++	++	+	+	+	+
BBHFB (polym.)	++	++	++	++	+	+	+	+
BBTFA (mono.)	++	+++	++	++	++	++	++	++
BBTFA (polym.)	++	++	++	++	++	++	+	++

[a]Solubility was determined with 10mg of sample in 1 mL of solvent. +++: soluble at room temperature; ++: soluble on heating at 100°C; +: partial soluble on heating.

Table 3. Dielectric constants of FBMI homopolymers and self-curing resins

Monomer	F, wt %[a]	Br, wt %[a]	ε^{b}
BHFB (polym.)	21.2	0	2.23
BHFB (cured)	21.2	0	2.20
BTFA (polym.)	14.4	0	2.30
BTFA (cured)	14.4	0	2.27
BBHFB (polym.)	13.3	37.5	2.41
BBHFB (cured)	13.3	37.5	2.37
BBTFA (polym.)	9.1	37.9	2.44
BBTFA (cured)	9.1	37.9	2.42

[a] To be the theoretical calculation values of F/Br composition ratio.
[b] Dielectric constants of FBMI blends (at 500 MHz).

Electrical and Dielectric Properties

The electrical properties of the FBMI resins were studied by measuring the dielectric constant ε. The ε for the FBMI resins were measured by a dielectric spectrometer at 500 MHz and ambient temperature. The dielectric constants of FBMI resins are listed in Table 3. The ε of these resins decreases with the increase of the fluorine content. All the ε's of FBMI resins are lower than 2.44. The ε of BHFB cured resin is lowered even to 2.20. The decreased dielectric constants of the fluorinated resins can be interpreted by the low polarizability of the C−F bond and the large free volume of CF_3 groups. These results suggested that the C−F bond or CF_3 groups in the network structure of FBMI resins play an important role in their electrical and dielectric performances.

CONCLUSIONS

The synthesis of a series of soluble F-containing bismaleimide monomers by a 2-step process has been performed with imide and condensation reactions. The temperature margin between fusing temperature and initial self-curing temperature for FBMI monomer is relatively larger than that for the commercial BMI-resin, indicating that these FBMI produce a larger processing window. This result makes the higher self-curing degree and increases the thermal stability. The higher heat resistance of FBMI self-curing resin relative to FBMI-homopolymer is due to its higher cross-linking density. The T_g and the thermal stability of the BHFB series resin with butene structure is higher than those of the others. The FBMI resins exhibit improved dielectric properties as compared with commercial bismaleimide resins with the ε lower than 2.44. Besides, the flame retardancy of all these FBMI resins could be enhanced via the introduction of Br-atom. All the novel F-containing bismaleimide monomers can be applied as the low-*k* materials or modifier in the blending systems of general resins.

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