

Thermal Behavior and Cured Products of Fluorine-Containing Bismaleimides

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SYNOPSIS

Thermal behavior of fluorine-containing bismaleimides was investigated by differential scanning calorimetry and the effects of introducing fluorine groups on thermal behavior and properties of cured products were discussed. The melting point was lower and the polymerization temperature was higher with increasing fluorine content. This decrease in polymerization reactivity of fluorine-containing bismaleimide was explained by the stabilization energy of the double bond or the bismaleimide molecule itself as calculated by the MNDO or MM method. Thermal polymerization of the double bond was interpreted by an autocatalytic reaction mechanism in which the activated biradical product accelerated the radical propagation. It was found that the fluorine-containing cured product had good thermal stability and a low dielectric constant.

INTRODUCTION

Bismaleimide resins are good heat-resistant polymers. They are suitable for use in a wide range of composite materials since they contain unsaturated double bonds that can thermally polymerize without the formation of volatile by-products that cause voids; in this point, they differ from other conventional condensation-type polyimides. In particular, they have been utilized to make multilayer printed wiring boards for large-scale computers and fiber-reinforced plastics for aerospace industries.¹⁻³

Bis(4-maleimidophenyl) methane (BMI) is generally used as a component of bismaleimide resin compounds. However, BMI monomer has a relatively high melting point and a relatively low polymerization temperature and therefore does not flow easily in the uncured state. Moreover, the cured product is highly brittle. BMI is often used after improving it with additives or tougheners such as diamines, dithiols, and reactive elastomers. But introducing such additives causes a lowering of the

glass transition temperature and/or the thermal decomposition temperature of the cured products.

Recently, a new bismaleimide that has flexible ether groups and a long phenoxy chain within a monomer structure has begun to be used as a heat-resistant material instead of BMI.⁴⁻⁶ This bismaleimide monomer has a high molecular weight, which makes it possible to reduce the crosslinking density of the cured products. Consequently, this bismaleimide monomer by itself is expected to be suitable for making thermally stable composite materials because the cured product has good mechanical properties.⁷

Moreover, the introduction of fluorine-containing groups within a bismaleimide monomer structure was carried out for the purpose of good thermal stability and flame retardancy. The thermal polymerization reactivity of the unsaturated double bond in the maleimide ring is presumed to decrease due to introduction of fluorine-containing substituent groups that have an electron-withdrawing property.

In this article, the effects of the fluorine-containing groups on the melting point and the thermal polymerization reactivity of the bismaleimides were investigated by differential scanning calorimetry (DSC). Polymerization reactivity was interpreted by a molecular structure calculation. In addition,

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the thermal and electrical properties of the cured products were investigated.

EXPERIMENTAL

Materials

The bismaleimides used were commercially available. 2,2-Bis[4-(2-trifluoromethyl-4-maleimido-phenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (MF-12) and 2,2-bis[4-(4-maleimidophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane (MF-6) were purchased from Central Glass Co. Ltd. 2,2-Bis[4-(4-maleimidophenoxy)phenyl]propane (MF-0) was purchased from Mitsui Toatsu Chemicals, Inc. MF-6 and MF-12 were purified by recrystallization with chloroform-methanol mixed solvent. MF-0 was purified by recrystallization as described elsewhere.⁷

The cured products were obtained by heating at 170°C for 20 min and 250°C for 60 min. 2,5-Dimethyl-2,5-(*t*-butylperoxy)hexyne-3 was added as a radical initiator. The amount of the initiator was 0.5 wt % resin.

Apparatus

DSC was performed on a Rigaku Denki 8240 differential scanning calorimeter at a heating rate of 10 K min⁻¹ in the air. The sample weight was about 5 mg.

Thermal gravimetric analysis of cured resins was carried out in a Shinku-Riko TGD-7000RH model at a heating rate of 5°C min⁻¹ in the air. The sample weight was about 10 mg. The temperature at the maximum decomposition rate (the temperature at

the 50% weight loss) was defined as the thermal decomposition temperature.

The dielectric constants of cured resins were measured on a Yokogawa Hewlett-Packard 4192A model LF impedance analyzer at 25°C. The frequency was 1 MHz. The electrodes were formed on the both sides of the sample surfaces with silver paste. The diameter of the electrode was 40 mm. The accuracy in the dielectric constant was estimated to be ±2%.

The molecular structure calculation was carried out by the molecular mechanics (MM) and modified neglect of diatomic overlap (MNDO) methods. The MM method performs the valence geometry optimization to evaluate the energetics using the bond length and angle potentials of the constituent atoms.⁸ The stabilization of bismaleimide molecules were calculated by the MM method. MNDO is one of the semiempirical molecular orbital methods.⁹ The electron densities and the molecular orbital energies were obtained by the MNDO method.

RESULTS AND DISCUSSION

Melting Point

It is important to investigate thermal properties of thermosetting molding materials by DSC. The cured products are obtained by molding under a flow condition and the crosslinking reaction occurs above the polymerization temperature. This flow condition is between the melting point and the polymerization initial temperature.

The DSC curve of a typical bismaleimide under the isochronal heating process is shown in Figure 1. Endothermic behavior due to fusion of the solid state

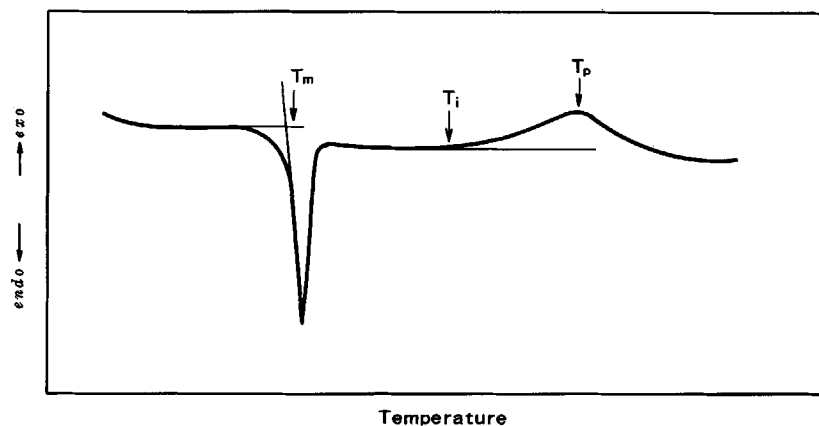


Figure 1 DSC curve of typical bismaleimide. T_m , melting point; T_i , polymerization initial temperature; T_p , polymerization peak temperature.

Table I Melting Behavior of Bismaleimides

Monomer	MW	FC (%)	T_m (°C)	Δh_f (J · g ⁻¹)	ΔH_f (kJ · mol ⁻¹)	ΔS_f (kJ · mol ⁻¹ K ⁻¹)
MF-0	571	0	142	65.3	37.3	90.5
MF-6	679	17	136	48.1	32.3	79.8
MF-12	815	28	112	32.2	26.2	68.2

MW, molecular weight; FC, fluorine content; T_m , melting point; Δh_f , specific heat of fusion; ΔH_f , molar heat of fusion; ΔS_f , molar entropy change of fusion.

is observed in the lowest temperature region. The melting point (T_m) is defined as the onset temperature of the endothermic peak. Next, thermal polymerization of double bonds occurs exothermally. The polymerization initial temperature (T_i) is the onset temperature of the exothermic peak. The polymerization reaction converges via the polymerization peak temperature (T_p), where the reaction rate reaches its maximum. Then the effect of introducing fluorine groups on the thermal behavior of bismaleimides was investigated.

The melting behavior of bismaleimides is described in Table I. The melting point of bismaleimide is lowered by introducing fluorine groups. In general, the melting point tends to be high with increasing molecular weight because the cohesive energy between molecules in the crystal state is large. Although the molecular weights of fluorine-containing bismaleimides are large, their melting points are relatively low compared with that of MF-0. This is considered due to a low packing density of molecules in the crystal state and weak intermolecular interaction for fluorine-containing bismaleimides. The heat of fusion obtained from the endothermic peak area is lowered by introducing fluorine groups. The molar heat of fusion of MF-12 is about 30% lower than that of MF-0. It is suggested that the fluorine-containing bismaleimides have a crystal structure with low molecular density since the intermolecular interaction is relatively weak.

Similarly, the molar entropy change of fusion tends to be small with introducing fluorine content. It is considered to reflect the small entropy change between the crystal and liquid states since the orderliness of the crystal state is low in the case of fluorine-containing bismaleimides. Then intermolecular interactions in the crystal state are weakened and the melting points are lowered by increasing the fluorine content of the bismaleimide structure.

Polymerization Reaction

The polymerization reactions of bismaleimides are tabulated in Table II. The higher the fluorine content, the lower the reactivity and the higher the polymerization initial temperature. The polymerization peak temperature also tends to be high in the cases of fluorine-containing bismaleimides. The fluorine-containing monomer has a large temperature range between its melting point and polymerization initial temperature, at which the material has good fluidity for moldability. Therefore, the fluorine-containing bismaleimides have good moldability.

The molar heats of polymerization of fluorine-containing bismaleimides are relatively high compared with MF-0. The molar heat of polymerization is represented by the following equation¹⁰:

$$H_p = D\sigma - D\pi. \quad (1)$$

Table II Polymerization Reaction of Bismaleimides

Monomer	T_i (°C)	T_p (°C)	ΔT	Δh_p (J · g ⁻¹)	ΔH_p (kJ · mol ⁻¹)	k (min ⁻¹)	n	m
MF-0	230	270	88	99.2	56.6	0.46	1.06	0.87
MF-6	254	281	118	102.2	69.4	0.79	0.99	0.88
MF-12	270	323	158	81.6	66.5	0.73	0.89	0.83

T_i , polymerization initial temperature; T_p , polymerization peak temperature; ΔT , $T_i - T_m$; Δh_p , specific heat of polymerization; ΔH_p , molar heat of polymerization; k , rate constant; n , reaction order relating to concentration of reactant; m , autocatalytic reaction order.

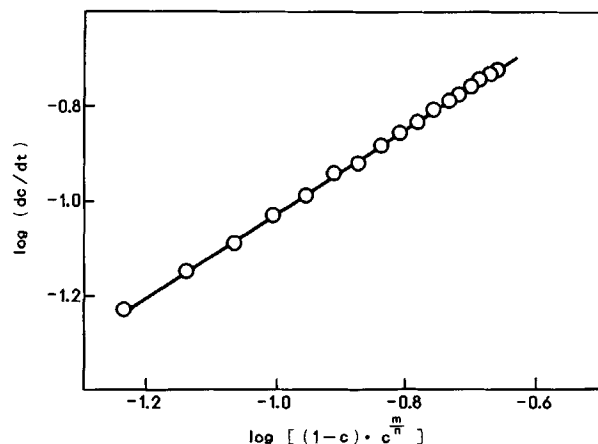


Figure 2 Autocatalytic reaction of thermal polymerization.

Here, H_p is the heat of polymerization and D_σ and D_π are the bond dissociation energies of σ -bond and π -bond, respectively. The molar heat of polymerization is the enthalpy change from the double bond to the single bond. This molar heat of polymerization is reported as $70 + 20 \text{ kJ mol}^{-1}$ in the case of most vinyl monomers.¹¹ The molar heats of polymerization of bismaleimides are similar to most of those for vinyl monomers.

The thermal polymerization reaction is regarded as an autocatalytic reaction in which the product is the activated biradical state. The general autocatalytic reaction is represented by the following equation:

$$v = dc/dt = k(1 - c)^n c^m. \quad (2)$$

Here, v is the reaction rate, c is the concentration of product, k is the rate constant, n is the reaction order relating to the concentration of reactant, and m is the autocatalytic reaction order. The exothermic behavior can be treated as an autocatalytic re-

action using eq. (2) as shown in Figure 2. The k , n , and m obtained from Figure 2 are listed in Table II. As the values for each parameter are almost the same, independent of the bismaleimide structure, it is considered the thermal polymerization of all bismaleimides must follow a similar reaction mechanism.

Since n is almost 1, formation of activated biradical product is regarded as a first-order reaction: One molecule is excited separately and there are no intermolecular interactions during the activation process. The value of m is also about 1, independent of fluorine content. It is confirmed that the activated biradical product acts as a catalyst in the radical chain reaction, which involves the thermal polymerization of double bonds. The values of k tend to be somewhat high with increasing fluorine content. It is presumed the high reaction rate constant is due to the high polymerization temperature in the case of fluorine-containing bismaleimides.

Electron Density and Stabilization Energy

Fluorine-containing bismaleimides have low reactivity and high polymerization temperature. It is assumed that the electron density of the double bond is reduced by the electron-withdrawing substituent groups, i.e., the fluorine groups. The electron densities of double bonds in the maleimide rings were calculated by the MNDO method. The results are listed in Table III. The electron-withdrawing effect of the fluorine group is only effective in its neighboring atoms. The electron density of the double bond, which is far removed from the fluorine substituent group, does not change in the cases of MF-6 and MF-12.

On the other hand, the difference in HOMO and LUMO ($\Delta\epsilon$) is dependent on the fluorine content as shown in Table III. The $\Delta\epsilon$ values of fluorine-containing bismaleimides are higher than that of

Table III Molecular Structure Calculation of Bismaleimides

Monomer	ρ	HOMO (eV)	LUMO (eV)	$\Delta\epsilon$ (eV)	D_d (kJ · mol ⁻¹)	D_d/RT_i	E (eV)
MF-0	0.04	-8.95	-1.15	7.80	816	195	-2.82
MF-6	0.04	-9.39	-1.25	8.14	849	194	-3.61
MF-12	0.04	-9.67	-1.47	8.20	855	189	-3.66

ρ , electron density on double bond; HOMO, energy level of high occupied molecular orbital; LUMO, energy level of low unoccupied molecular orbital; $\Delta\epsilon$, LUMO - HOMO; D_d , bond dissociation energy of double bond; D_d/RT_i , Boltzmann factor; E , stabilization energy.

MF-0. This Δe relates to the ease of excitation on intramolecular sites: The molecule is excited by formation of a biradical structure produced when one electron transfers from HOMO to LUMO. The polymerization onset temperature is related to Δe as shown in Figure 3. It is reported that Δe is also related to the experimental bond dissociation energy of the double bond (D_d).¹⁰

$$D_d = 23.0 \cdot \Delta e + 14.9. \quad (3)$$

The results of D_d and D_d/RT_i obtained from Δe by using eq. (3) are listed in Table III. The Boltzmann factors, D_d/RT_i of all bismaleimides, are almost the same. It is considered that reactivity of the double bond can be estimated with Δe . Then, the activation energy of the polymerization reaction is approximated by the stabilization energy of the double bonds.

Similarly, stabilization of the molecule itself is closely related with the polymerization reactivity of the bismaleimides. The stabilization energies (E) of the bismaleimides were calculated by the MM method and are listed in Table III. Bismaleimide monomers become stabler with increasing fluorine content. The fluorine-containing bismaleimides have low reactivity so they are not excited easily. The relationship of polymerization temperature and molecular stabilization energy is shown in Figure 4.

It is insufficient to discuss reactivity using only the stabilization energy of reactant. It must be estimated with the activation energy of the excitation process, which is the difference in stabilization en-

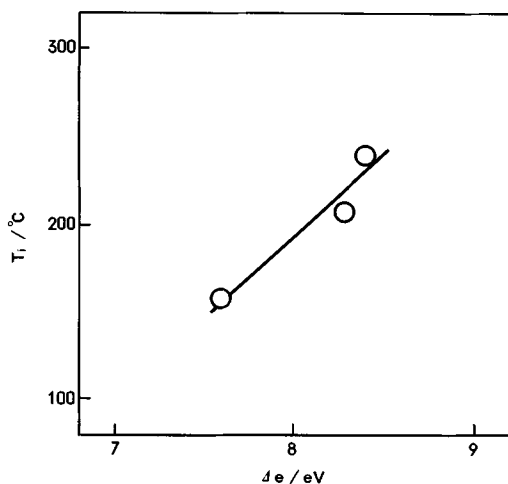


Figure 3 Relationship of polymerization temperature and activation energy.

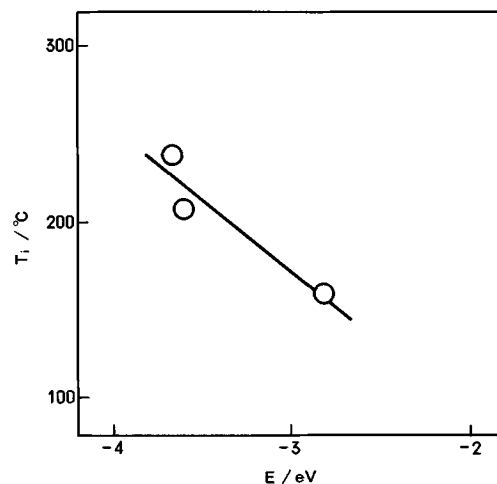


Figure 4 Relationship of polymerization temperature and molar stabilization energy.

ergy between the reactant and the activated species (biradical state). The calculation of stabilization energy of biradical state can be performed in principle, but it is enormously time consuming and is not practical.

Properties of Cured Resins

It is expected that cured resins obtained from fluorine-containing bismaleimides have good thermal stability and good electrical properties. The thermal decomposition temperatures in air of cured resins are listed in Table IV. Here, the decomposition temperature is defined as the maximum decomposition rate temperature, which is the decomposition temperature at a 50% weight loss. The decomposition temperature is higher with increasing fluorine content. This excellent thermal stability of fluorine-containing bismaleimides is due to the increased bond dissociation energy and the high oxidized state

Table IV Properties of Cured Products

Monomer	T_d (°C)	ϵ_{obs}	ϵ_{calc}
MF-0	546	3.2	3.1
MF-6	565	3.0	3.0
MF-12	577	2.8	2.8

T_d , decomposition temperature at a 50% weight loss; ϵ_{obs} , experimental dielectric constant measured at 1 MHz; ϵ_{calc} , dielectric constant calculated by Clausius-Mossotti equation.

due to the electron-withdrawing fluorine substituent groups.

Dielectric constants can be calculated to a certain extent from a sum of the bond or constituent group contributions to the related molecular quantities of molar polarization and molar volume. The relationship employed in this calculation is based on the Clausius–Mossotti relation.¹² Dielectric constants are proportional to the polarization density, which is defined as the ratio of molar polarization to molar volume. The molar polarization of the trifluoromethyl group is almost equal and its molar volume is about twice as large as for a methyl group.¹³ Therefore, the polarization density of the trifluoromethyl group is lower than the methyl group. The dielectric constant of cured resin with trifluoromethyl groups introduced instead of methyl groups is expected to be reduced. The dielectric constant of cured resins at 1 MHz and the values calculated by using with Clausius–Mossotti equation are listed in Table IV. The experimental values are in reasonable agreement with the calculated ones. It was found that cured resin obtained from bismaleimide with introduced trifluoromethyl groups instead of methyl groups, such as MF-6 and MF-12, has good thermal and electrical properties, i.e., high decomposition temperature and a low dielectric constant.

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