Effect of Barbituric Acid on the Self-Polymerization Reaction of Bismaleimides

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SYNOPSIS

Barbituric acid (BTA) was used as an initiator for the homopolymerization of bismaleimide (BMI). The reaction was controlled by the amount of barbituric acid and ended up with solvent-soluble oligomers. The effects of varying the amounts of BTA, as well as the reaction time, on BMI's self-polymerization reaction were investigated. The thus-formed oligomers were characterized by gel permeation chromatography (GPC), infrared spectra (IR), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC). The degree of reaction increased proportionally to the concentration of BTA or the length of the reaction time. Thus, solvent-soluble BMI oligomer can be controlled and obtained.

INTRODUCTION

Bismaleides (BMIs) can be cured by two kinds of mechanisms, namely, free radical polymerization and Michael addition polymerization:
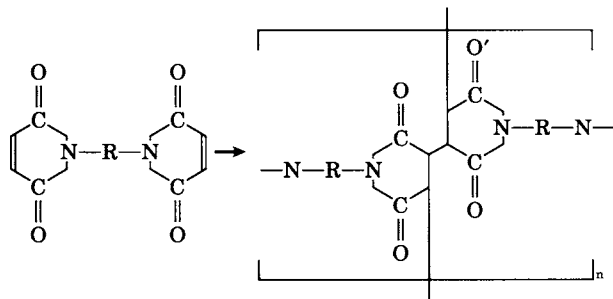
Free radical polymerization
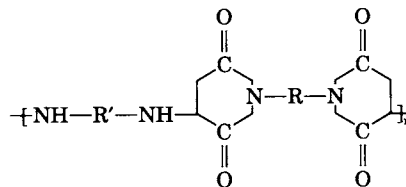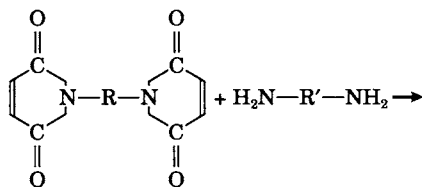
Michael addition polymerization

Free radical polymerization is usually initiated by heat or peroxides.[1,2] A BMI monomer has two carbon — carbon double bonds that tend to form crosslinking networks rapidly via free radical polymerization. Therefore, it is difficult for BMI monomer to form solvent-soluble oligomer first by free radical polymerization and then by final crosslinking with diamines by Michael addition. For the applications of high-temperature prepregs and structural laminates, BMI was usually reacted with diamines by Michael addition to form linear solvent-soluble polymers.[3,4] Final crosslinking networks of the resin system was produced through free radical polymerization.

In this investigation, barbituric acid (BTA), which is usually used as photoinitiator,[5-8] was used to react with bismaleimides thermally. Hence, the reactions were performed under temperatures that permitted the BTA to generate free radicals. Also, the reactions using different molar ratio of BMI/ BTA were studied.

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EXPERIMENTAL

Reagents

N,N'-bismaleimide-4,4'-diphenylmethane (BMI, Mitsui Toatsu Chemical) was used as the BMI component and was purified by recrystallization prior to use. BTA from Merck was used as received.

The solvent for synthesis of the oligomer was r-butyrolactone (Merck), which was dried with anhydrous calciumsulfate and fractionally distilled before use.

Preparation of Oligomer

Into a 250-mL three-necked flask fitted with a paddle stirrer, thermometer, and nitrogen inlet were added 0.1 mol BMI, the desired quantity of BTA, and 100 mL r-butyrolactone. The reaction temperature was controlled at 120 ± 4°C with an oil bath. Molar ratios of BMI/BTA used were as follows: 2/1, 4/1, 10/1, and 20/1. While reacting, samples were taken every hour. The samples were then precipitated in a large amount of methanol and the precipitates were collected by filtration and dried at vacuum at room temperature for more than 48 h.

Apparata

The BTA's electron spin resonance (ESR) spectra at different temperatures were taken using a Bruker ER 200D 10/12 ESR spectrometer. Infrared (IR) spectra were recorded on a Nicolet FT-IR spectrophotometer with KBr pellets at room temperature. The chromatograms were recorded on a Merck gel permeation chromatography (GPC) (column number SP-4 and SP-40) and refractive index detector. DMF was used as eluent with a flow rate of 0.5 mL/min. Thermogravimetric analysis (TGA) was carried out on a 951 TGA module at a heating rate of 20°C/min in a nitrogen atmosphere (flow rate: 20 mL/min). Differential scaning calorimetry (DSC) was done using a 910 DSC module at a heating rate of 10°C/min in a nitrogen atmosphere (flow rate: 20 mL/min). Sample sizes of 10 ± 2 mg were used.

RESULTS AND DISCUSSION

Reaction Pathway

The BTA's ESR spectra at different temperatures (Fig. 1) reveal that the number of free radicals generated increased with temperature. The radical might be formed by hydrogen abstraction from C5,
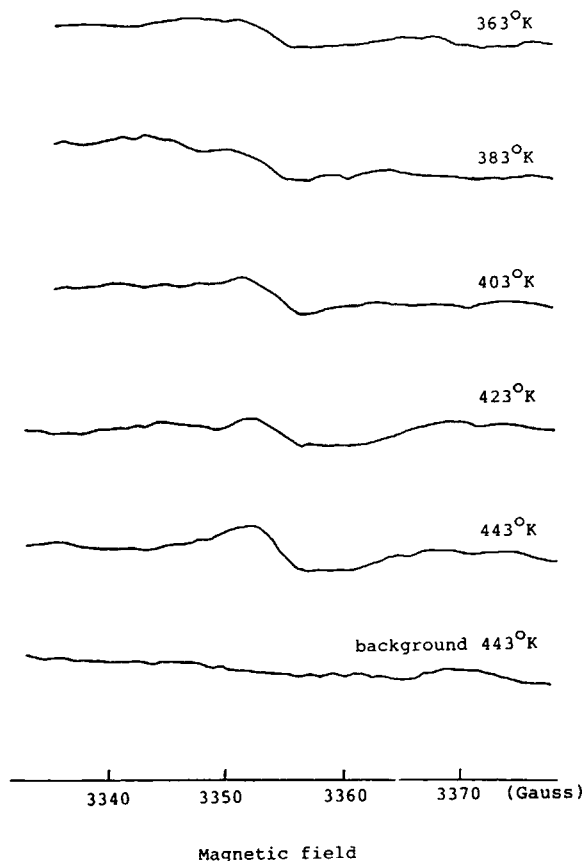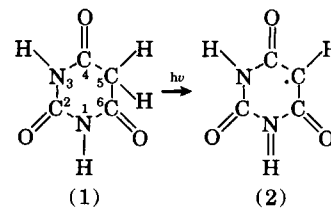
Figure 1 First-derivative ESR spectra observed in BTA at different temperatures. Microwave frequency = 9.40 Hz.

and a pair of radicals could be formed by two such abstractions in neighboring molecules, according to a mechanism proposed by Melo[9] in a photo-induced reaction:

The IR spectra of different BMI and BTA compositions are shown in Figure 2. The single C — C bond with an absorption peak at 1,185 cm^{-1} was observed after the first 30 min of reaction of BMI and BTA at 120°C. This finding indicates that the carbon — carbon double bond of the BMI resin had reacted. The BTA also reacted with BMI as the 3187 cm^{-1} absorption peak disappeared. Thus, the BMI reaction pathway may well be as follows:
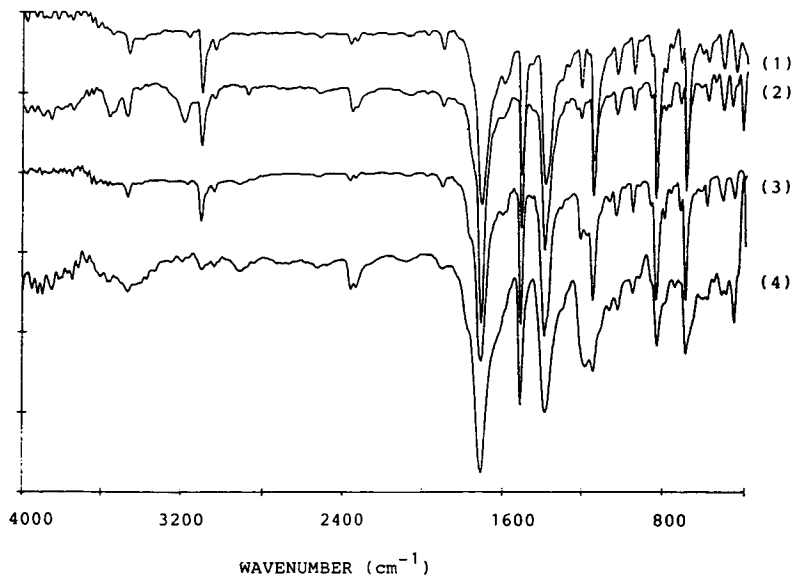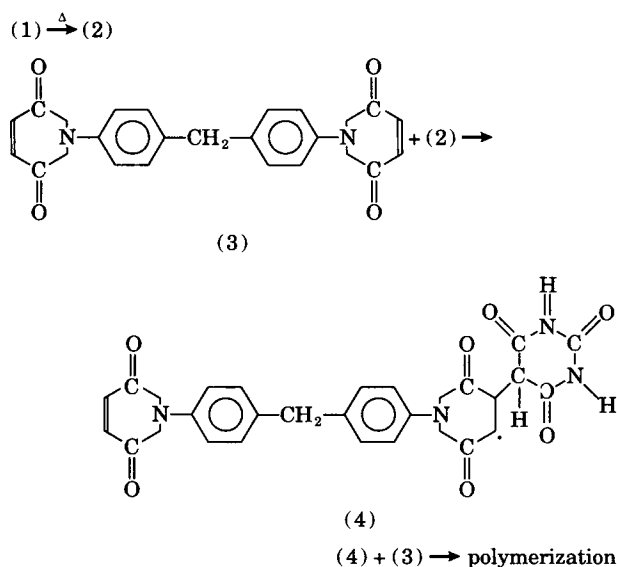
Figure 2   IR spectra of (1) uncured pure BMI monomer, (2) uncured BMI/BTA = 10/1 resin system, (3) BMI/BTA = 10/1 resin system reacted for 30 min at 120°C, (4) the precipitated sample from (3) cured for 4 h at 220°C under N_2 atmosphere.

(1) $\xrightarrow{\Delta}$ (2)

(3)

(4)

(4) + (3) → polymerization

Molecular Weight Distribution of the Oligomers

The GPC results for the case of BMI/BTA mole ratio equal to 10/1 (Fig. 3) show that molecular weight increased with reaction time. Through pre-polymer molecular fraction analysis of the four sets of data, it was determined that both monomers and oligomers, composed of eight monomer units in average by theoretical calculation, were the major components of each reaction.

Figure 4 presents the relative percentage change between monomers and oligomers for BMI/BTA

mole ratios equal to 4/1 and 10/1. Tables I and II list the percentage change of monomers in different BMI/BTA mol ratios and reaction times, respectively. As shown in Table I, even for molar ratio of BTA/BMI as low as 1/20 nearly one half of the monomers were consumed in 1 h at 120°C. This is more than the amount consumed through the reaction with BTA by Michael addition alone. Furthermore, when the BMI/BTA mol ratio was 2/1, the reaction was so rapid that the resin system gelled within 45 min. Moreover, the trend shown in Table II indicated that the monomers still continue to react when the reaction time was more than 24 h at 120°C.

The above results prove that BTA can easily initiate BMI to go through self-polymerization. With BMI/BTA ratios lower than 20/1, an oligomer composed of roughly eight monomer units can be formed easily. Molecular weights of more than 3,000 could not be achieved easily as chain transfer and termination reactions become more important when molecular weight increases. The reacted system was very stable and minor molecular weight increase was observed. In other words, the mobility of free radicals limits further increase of molecular weight. With high BTA concentrations, such as BMI/BTA less than or equal to 2/1, the reactions would be so vigorous that they could cause gelation very soon at 120°C.

In free radical polymerization, the reaction rate is strongly influenced by temperature. Reactions at temperatures exceeding 140°C resulted in fast ge-
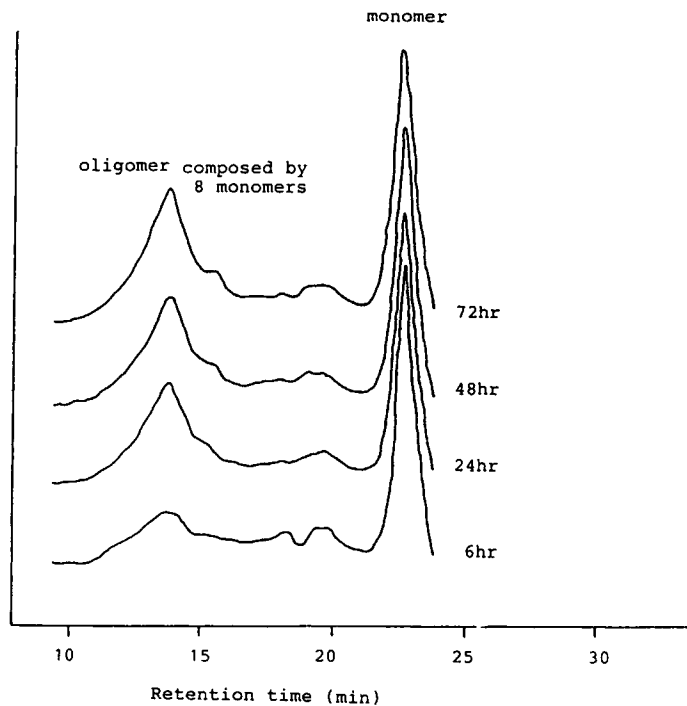
Figure 3   GPC analysis of BMI/BTA = 10/1 with different reaction times.
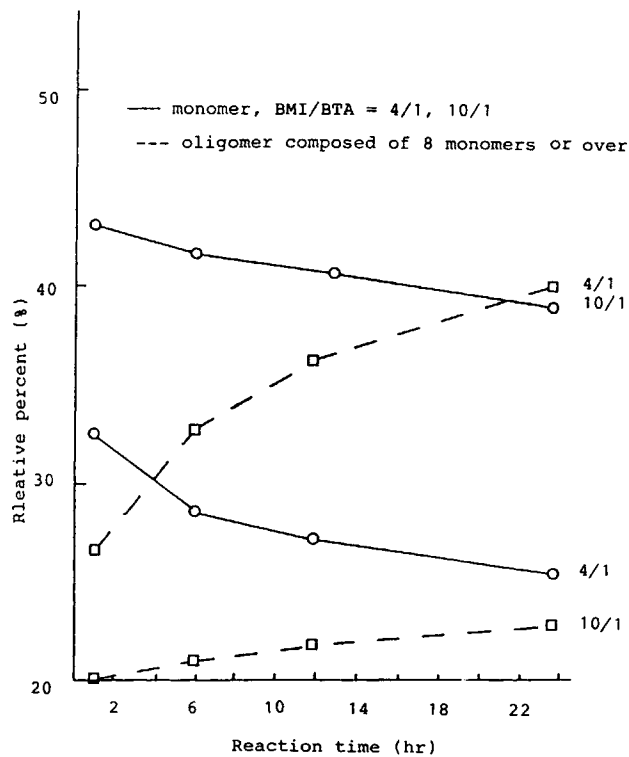

Figure 4   Relative percentage change in monomers and oligomers for the total molecular distribution measured by GPC.

**Table I   BMI Monomer Residue after 1 h
Reaction at 120°C Resulting from
GPC Chromatograms**

BMI/BTA	% of Monomer Residue
2/1	a
4/1	32.4
10/1	43.1
20/1	54.9

a After 45 min, the resin system turns into gelation.

**Table II   BMI Monomer Residue for Various
Reaction Times at 120°C (BMI/BTA = 10/1)
Resulting from GPC Chromatograms**

Reaction Time (h)	% of Monomer Residue
1	43.1
6	41.8
24	39.0
48	37.3
72	35.9

lation even at low BTA concentration, such as the case with BMI/BTA mol ratio equal to 10/1 for 30 min.

If the BMI undergoes self-polymerization, as it did when peroxide was used as an initiator or when heated above 160°C,[10] it crosslinks easily. Hence, the BMI system can hardly form a homogeneous solution when it performed free radical polymerization in the usual way. On the contrary, by using BTA as an initiator for the BMI reaction a solvent-soluble resin system with molecular weight about 3000, in other words, a controllable polymer resin system, can be obtained.

TGA Results

The thermal stabilities of the various resins were evaluated by TGA under nitrogen atmosphere. As shown in Figure 5, the higher the BTA amount the lower the decomposition temperature. Moreover, the

TGA curves become independent of reaction time for samples with the same BMI/BTA ratio reacted for more than 1 h. In addition, when compared to a pure BTA decomposition curve, the BMI/BTA resin systems did not decompose at the BTA's first thermal decomposition temperature (T_d), but decomposed near the BTA's secondary T_d. This result shows that the BTA chemically bonded with the BMI and that it might have reacted completely with the BMI within the first hour.

Curing Behavior of the Oligomers

To investigate the curing behavior, thermal scans of the oligomers were performed using DSC under nitrogen atmosphere. The DSC curves for different mol ratios of BMI/BTA after reaction for 1 h and different reaction times at fixed BMI/BTA mol ratios are shown in Figures 6 and 7, respectively. At higher BTA concentrations, such as BMI/BTA equal to 4/1 (Fig. 6), the curve has two exotherm
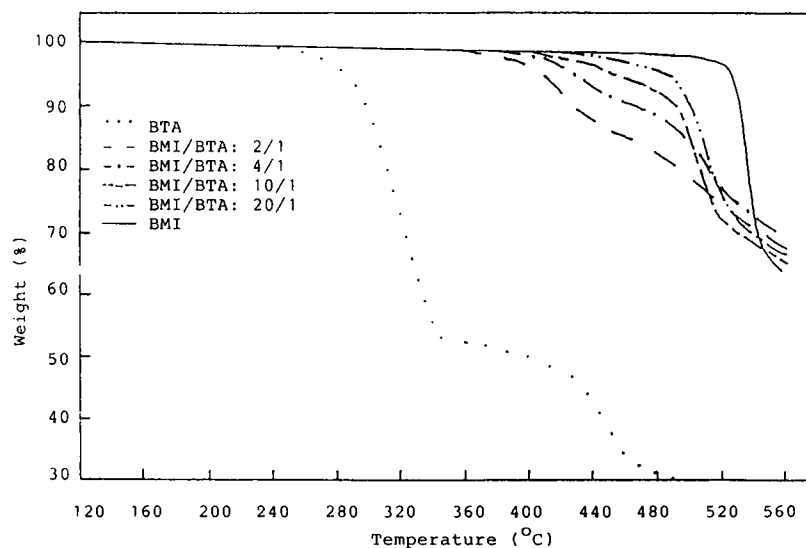

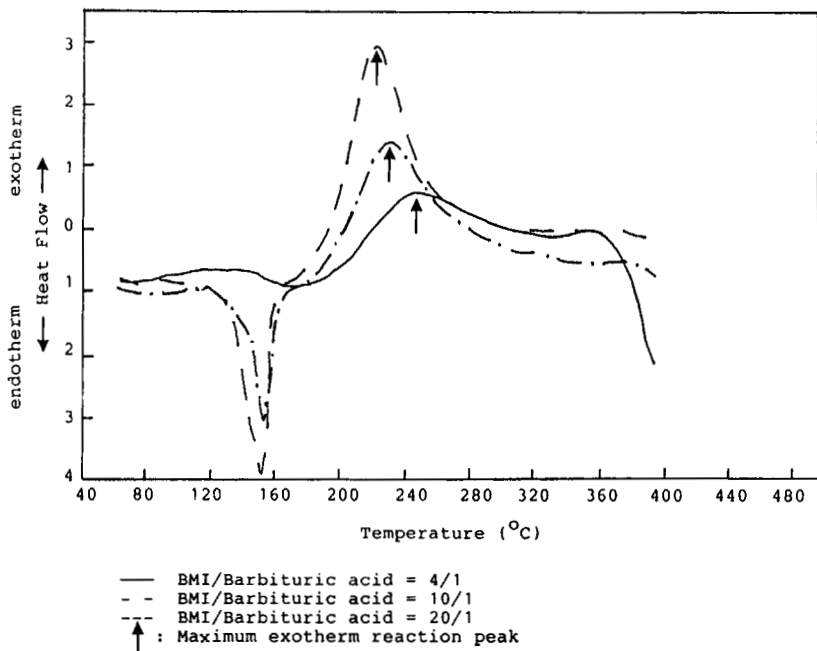**Figure 5**   TGA of resins with various compositions. Heating rate, 20°C/min in N_2.

Figure 6 DSC curves of oligomers reacted for 1 h at 120°C. Condition, atmosphere N_2, heating rate 10°C/min; N_2 flow, 20 cm^3/min; weight, 10 mg.

peaks. The first was believed to be due to a thermally induced polymerization reaction. The second exotherm, due to a higher BTA concentration, caused
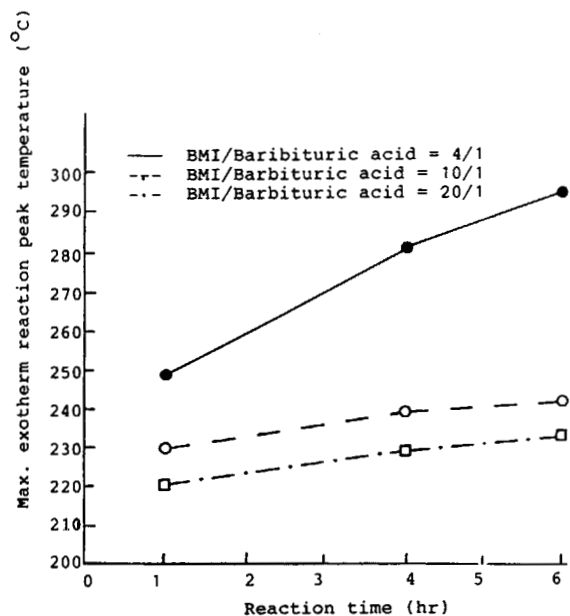

Figure 7 Shift of maximum exotherm reaction peak temperature for different molar ratios and reaction times.

pyrolysis. Moreover, as the degree of reaction increased (as a result of increased the reaction time or the amount of BTA), the maximum exotherm reaction peak shifted to higher temperatures. This shift reflects lower reactivity that, in turn, is caused by restricted motion of longer molecules produced at higher degree of reaction. For samples with lower degrees of reaction, such as BMI/BTA mol ratio = 10/1 or 20/1 in Figure 6, melting still occurred. In other words, with lower degrees of reaction, enough BMI monomers still existed to cause melting behavior. These phenomena indicates that the consumption of BMI monomers increase with BTA concentration and reaction time. These results confirmed the key GPC finding that BTA can initiate BMI polymerization.

CONCLUSIONS

It was found that BTA is an effective free radical initiator for BMI self-polymerization reactions. In addition, the molecular weight distribution of the BMI resin system can be controlled by the amount of BTA and reaction temperature. These findings should be useful for practical applications of BMI resin. Still, the detailed mechanism of the reaction

in BMI/BTA resin system is not well understood and requires further elucidation.

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