Preparation and Characterization of Bismaleimide-Diamine Prepolymers and Their Thermal-Curing Behavior

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ABSTRACT: Various bismaleimide-diamine Michael addition type prepolymers were prepared through melt condensation and using acetone, dimethylformamide, and *m*-cresol as solvents in a molar ratio of 1 : 1. Structures of the prepolymers, such as terminal moieties and molecular weight of main chain, depended strongly on the preparation conditions used. More terminal double bonds were observed in the molecule of the prepolymer (sample 3) prepared in dimethylformamide solution without a catalyst. In contrast, the prepolymer produced in *m*-cresol solution had a polyaspartimide structure with a higher molecular weight. The differential scanning calorimetry and Fourier transform infrared spectra results demonstrated that the molecular structure of the prepolymer had a noticeable effect on their thermal-curing behavior. Thermal properties (T_g and T_d) of cured polymers were evaluated. The polyimide (sample 3b) from sample 3 exhibited the highest T_g and T_{d_1} , but still retained very good processing properties for film casting. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2471–2477, 1998

Key words: bismaleimide, diamine, prepolymer, Fourier transform infrared spectra, differential scanning colorimetry, thermal gravimetric analysis

INTRODUCTION

It is well known that bismaleimides (BMIs) are a type of thermosetting resin, with high temperature stability, hot-wet strength, and fatigue resistance.¹ BMI resins have been used widely in composite materials as matrices with good performances. The unsaturated end groups of BMI can be polymerized thermally without the formation of volatile byproducts, offering considerable advantages in processing over the conventional condensation type polyimides. They suffer, however, from brittleness resulting from their high crosslink density. Various attempts have been made to improve the impact and fracture toughness of polybismaleimide materials. One of the

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important modifications is the use of an other monomer, such as diamine (DA). The addition of DA to the double bond of BMI gives a prepolymer. Longer segments between crosslinking points would reduce the brittleness of the polyimides produced from prepolymers. Many studies of the copolymerization of BMI and DA, as well as the thermal and mechanical properties of cured polyimides, have been reported.²

Varma and colleagues³ reported the preparation of BMI-DA prepolymer in acetone solution with a molar ratio of 1 : 0.3-0.4 (BMI/DA). Although there was no information on the structure of the resulting adducts available, it seems to be rational that the prepolymer molecule was terminated by the double bond of maleimide (MI) ring, whereas a lot of BMI monomer remained in the reaction mixture. The crosslinking polyimide was formed through the polymerization of double bonds. However, using the molar ratio of 1 : 2

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(BMI/DA), an aromatic amine-terminated bisaspartimide was synthesized in dimethylacetamide solution,⁴ which can be polymerized through the formation of amide moiety. Meanwhile, in an mcresol solution, several linear polyaspartimides with high molecular weight were prepared in molar ratio of 1 : 1 (BMI/DA).⁵ Until recently, although many novel BMIs and DAs have been used in the preparation of prepolymers to get a modified structure,⁶ few studies have been concerned with the characterization and properties of the prepolymer in detail. Apparently, because prepolymers prepared under different conditions may have different molecular structures, curing behavior, and the corresponding thermal properties of cured polyimide, it would be of interest to investigate the dependences of the structure and curing behavior of the prepolymers on the conditions used in preparing the prepolymers. Optimized conditions of preparation would likely provide a prepolymer with terminated crosslinkable double bonds and a proper molecular weight of main chain, which can be made into films with good processing properties and better thermal properties of the subsequently cured polyimides.

EXPERIMENTAL

Materials

N,N'-Bismaleimido-4,4'-diphenylmethane (BM) was selected as a BMI monomer, which is commercially available. It was purified by recrystallization from methanol/chloroform and dried at 60°C in a vacuum. 4,4'-Diaminodiphenylmethane (DAM) as an aromatic diamine was recrystallized from ethanol and dried in nitrogen. The solvents were purified by the usual methods.

Prepolymers

Five BMI-DA type prepolymers were prepared as follows.

Sample 1

BM (0.02 mol) and DAM (0.02 mol) were charged into a flask. The mixture was stirred at 95° C for 30 min in nitrogen, followed by stirring at $110-120^{\circ}$ C for 1 h. The resulting bright red liquid was poured onto a shallow disk under nitrogen. After cooling to room temperature, it was ground to obtain a bright yellow powder.

Sample 2

It was prepared by refluxing BM and DAM in a molar ratio of 1:1 in acetone for 6-8 h, until a homogeneous solution was obtained. Acetone was removed by a rotary evaporator. The resulting prepolymer was obtained as shining powder by further removal of acetone residue under reduced pressure.

Sample 3

To a continuously stirred solution of BM (0.015 mol) in dimethylformamide (DMF) in nitrogen was added DAM (0.015 mol). The reacted mixture was immersed in an oil bath maintained at $100-110^{\circ}$ C for 24 h. The resulting brown solution was poured over crushed ice, the obtained yellow solid was filtered and washed with cold water, and then dried under reduced pressure.

Sample 4

The procedure for preparing sample 4 was similar to that for sample 3, but using glacial acetic acid (1.5 mL) as a catalyst.

Sample 5

To a solution of BM (0.01 mol) and DAM (0.01 mol) in fresh *m*-cresol (20 mL), glacial acetic acid (0.1 mL) was added. The flask with the reaction mixture was immersed in an oil bath maintained at $100-110^{\circ}$ C for 24 h. The resulting dark brown solution was poured into methanol to give a yellow solid, which was then dried in a vacuum.

Film Casting

The 15% solution of prepolymer samples 1–5 in DMF was cast on a glass slide. The solvent was evaporated overnight in a convection oven at 60°C. Then, thermally treated samples were made by gradually increasing the temperature as follows: 150°C for 2 h and 200°C for 2 h, giving samples 1a–5a; then 250°C for 2 h and finally cured at 280°C for 30 min, giving samples 1b–5b, respectively. After heat treatment, the slide was cooled to room temperature. The film was removed from the glass slide by soaking it in cold water, then dried in vacuum. The thickness of the cured film was ~ 0.1–0.2 μ m.

Measurements

¹H NMR spectra were collected on a Varian XL-200 NMR spectrometer. The Fourier transform infrared (FT-IR) spectra were recorded on a PE FT-IR 1760 spectrometer. Thermal analyses were performed by using PE DSC-7 series, and thermal gravimetric analysis (TGA) measurements were under the heating rate of 20° C min⁻¹.

RESULTS AND DISCUSSION

Characterization of the Prepolymer

The prepolymer samples **1–5** were synthesized under different reaction conditions, including the solvents used and the reaction temperature, or in the thermal melt state (described in the Experimental section) with the addition of DAM to BM. Considering the requirement for the prepolymer with terminated crosslinkable double bond and proper molecular weight of the main chain, the molar ratio of BM/DAM was chosen as 1:1. The FT-IR spectra of samples 1-5 are shown in Figure 1. According to the assignment of bands reported by Ciulio and colleagues,⁷ a strong band at ~ 3100 cm⁻¹ is associated with $\nu_{=C-H}$ of the MI ring and a very strong band at 1150 cm^{-1} with $\nu_{\rm C-N-C}$ of the MI ring. Other identified bands of the MI ring are at $\sim 830 \text{ cm}^{-1}$ and $\sim 690 \text{ cm}^{-1}$. The band at 1150 cm^{-1} could be used for monitoring the polyaddition reaction process. On the other hand, the bands at 2900 cm^{-1} and 2850 $\rm cm^{-1}$ ($\nu_{_\rm CH2_}$) and 1180 $\rm cm^{-1}$ ($\nu_{\rm C_N_C}$) are due to the formation of succinimide (SI) rings during the polyaddition reaction. (Scheme 1) The ratio of the band at 1180 cm^{-1} to the band at 1150 cm^{-1} expresses the relative proportion of the SI ring to the MI ring (SI/MI) in identical prepolymer molecules that can be used to characterize the molecular structure of the prepolymers. For sample 3, prepared from a DMF solution without a catalyst, the band at 1150 cm⁻¹ is much stronger than that at 1180 cm⁻¹ (i.e., SI/MI is very small). Sample 3 should have more terminated crosslinkable double bonds and a corresponding small chain length of the prepolymer molecule. In contrast, for sample 2, prepared in acetone solution, the band at 1180 cm^{-1} is stronger than that at 1150 cm^{-1} . In the FT-IR spectrum of sample 5, the band at 1150 cm^{-1} is hardly observed, indicating a very big SI/MI and lack of terminated double bond in the prepolymer with a relatively high molecular weight. In the case of samples 1 and 4, the bands at 1150 and 1180 cm^{-1} are almost equal. Therefore, the FT-IR spectra of the prepolymers can be used to evaluate the extents of chain propagation



Figure 1 FT-IR spectra of prepolymers.

(SI/MI) through BM/DMA addition, increasing as the following order: samples 5 > 2 > 1, 4 > 3. Sample 3 has more crosslinkable terminated double bonds and the proper molecular weight suitable for casting film.

The ¹H NMR spectra of samples **1–5** are shown in Figure 2, where the multiplet at 7.3 ppm is assigned to phenyl protons of BM, and the AA'BB' quartet at 6.80 and 7.11 ppm is assigned to the phenyl protons of DMA. The broad D_2O -



Figure 2 ¹H NMR spectra of prepolymers.

exchangeable signal at 6.0 ppm is due to the amino proton (---NH---) of aspartimide moiety and the multiplet at 2.7, 3.3, and 4.8 ppm to the protons of the SI ring. From this, it can be deduced that the prepolymers have the polyaspartimide structure (Scheme 1) in along the molecule backbone. Absorption at ~ 7.2 ppm, observed in samples 1-4, verifies the presence of the olefin proton of the terminated MI ring. For sample 5, the disappearance of the signal at ~ 7.2 ppm clearly indicates a lack of the terminated double bond of the MI ring in the prepolymer, confirming a molecular backbone of polyaspartimide with high molecule weight. The observed D₂O-exchangeable signal at 9.9 ppm in ¹H NMR of sample 5 is interpreted as due to the formation of amide groups (-CONH-) (Scheme 2). Moreover, the





additional band at 1640 cm⁻¹ (only in the FT-IR spectrum of sample **5**), assigned to the carbonyl group of amide moiety, also provides evidence to the formation of the amide groups. It implies that, in some cases, a little crosslinking through the formation of amide group⁵ has occurred in the prepolymer stage. In ¹H NMR of sample **2**, an absorption was observed at 1.75 ppm, which could be assigned to methyl groups of acetone imide, stemming from the reaction of acetone solvent with amino groups.

In summary, the molecular structure of the BM/DMA prepolymers, based on the extents of chain propagation of BM/DMA addition polymerization, depends strongly on the reaction conditions during preparation, such as the solvents used, the catalyst, and reaction temperature despite using the same initial monomer and a molar ratio of 1 : 1 for BM/DMA.



Scheme 2



Figure 3 DSC traces of prepolymers.

Curing Behaviors

Thermal scans of samples 1-5 were performed using a differential scanning calorimeter (Fig. 3). Differential scanning calorimetry (DSC) traces show very noticeable effects of the molecular structure of the prepolymers (prepared under various reaction conditions) on curing behavior. The DSC scan for the BM monomer is presented for reference; in this case, homopolymerization was completed by \sim 170°C and a second much more diffuse exotherm starts at $\sim 220^\circ C$ and continues up to 330°C. In DSC scans for sample 1, a small crystalline melt endotherm was observed, representing the fusion of the prepolymer. In addition, a very broad polymerization exotherm spanning 175–335°C was observed. Samples 2-5 did not show melting endotherms. Sample 2, prepared in acetone solution, exhibited only a diffuse exotherm at lower temperatures, from 100 to 200°C, which mainly represents additional polymerization of DMA to BM. Samples 3 and 4, prepared in DMF solution with or without a catalyst, show similar DSC traces. There is no diffuse exotherm at a lower temperature, but a broad exotherm at a higher temperature (200–250°C), resulting from the polymerization of the double bond of the MI ring. Measurement of the enthalpy of polymerization by DSC yields values for ΔH of 250 J g^{-1} for sample **3** and 99 J g^{-1} for sample **4.** Therefore, it can be concluded that prepolymer 3 might be relatively more reactive than prepolymer 4. namely that there is more terminated MI ring in the molecule of prepolymer **3**. For prepolymer **5**, a very small and very diffuse exotherm at $\sim 225^{\circ}\text{C}$ was observed. This type of prepolymer has a less terminated reactive group for crosslinking, because of the polyaspartimide backbone structure of relatively high molecular weight. These results demonstrate different thermal-curing behaviors between prepolymer samples **1–5**.

The FT-IR spectra of the samples **1a–5a** and 1b-5b, obtained after thermal treatment of the prepolymers (samples 1-5), are shown in Figure 4. Very clear bands at $\sim 1180 \text{ cm}^{-1}$ are observed. At the same time, the bands at \sim 1150, \sim 830, and $\sim 690 \text{ cm}^{-1}$ in samples **1a**, **2a**, and **4a**, due to the MI ring, disappeared, thus indicating that the C=C bond of the MI ring has completely reacted. However, in sample **3a**, these bands are still present, indicating some terminated MI ring remained. Only after further thermal treatment (up to 280°C) did the bands for double bonds in the FT-IR spectrum of sample **3b** become very small. This means that, in the thermal-curing course of sample 3, chain propagation and crosslinking are mainly through the polymerization of the double bond of MI. On the other hand, an additional band at 1640 cm^{-1} in the spectra of samples 1a, 4a. and 5a was observed. It is ascribed to the formation of the amide group, leading to crosslinking. Whereas, for the FT-IR spectra of samples **2a** and **3a**, the band at 1640 cm^{-1} is very small (showing a shoulder), indicating that a lesser reaction of amino groups with SI rings occurred. It is also deduced from the infrared (IR) spectra of samples 1a-5a that prepolymers with different molecule structures (samples 1-5) exhibit different curing behavior at the first thermal curing stage (heating at 150°C for 2 h and 200°C for 2 h). However, in the IR spectra of samples 1b-5b, the decrease in the bands at 2920, 2840, and $\sim 1180 \text{ cm}^{-1}$, accompanying an increase in the band at 1640 cm^{-1} , demonstrate that—for all of the samples-crosslinking through the formation of amide groups would continue by increasing treatment temperature. All of the results of the DSC and FT-IR spectra presents evidence for the step thermal-curing behavior of the prepolymers, either through double bond polymerization or formation of amide groups.

The glass transition temperatures of samples **1b–5b** were determined by DSC (Table I). Among the five samples, samples **1b** and **5b** from corresponding prepolymer samples **1** and **5**, prepared in the melt state and in *m*-cresol solution, have relatively low T_g 's (243°C and 242°C, respectively). It is suggested that the lower T_g can be ascribed to less terminated double bond moieties (larger SI/MI) in prepolymers **1** and **5**. The more terminated double bonds (smaller SI/MI) of pre-



Figure 4 FT-IR spectra of cured samples.

polymer 3 lead to the highest $T_g~(\rm 276^{\circ}C)$ for sample 3b.

Thermal stability of cured samples **1b–5b** was evaluated from TGA. Figure 5 shows TGA curves

Table I DSC and TGA Results of Polyimides

Polyimides	T_{g} (°C)	Thermal Decomposition (N_2)			
		$T_{d_1} (°C)$	$\begin{array}{c} T_{d_2} \\ (^{\circ}\mathrm{C}) \end{array}$	$Y_{c_1} \ (\%)$	$Y_{c_2} \ (\%)$
Sample 1b	244	379	605	68	4
Sample 2b	265	370	603	71	19
Sample 3b	276	440	675	69	33
Sample 4b	258	362	693	71	37
Sample 5b	243	370	631	67	21

of the five samples. Cured polyimides degrade in nitrogen by a two-step process; the first step occurs between 350° C and 400° C, with a 10-20%weight loss, except for sample 3b (< 10%). The second step begins at ~ 600 °C, and 67–71% residue is obtained at 800°C. The extrapolated temperature for the beginning of weight loss (\boldsymbol{T}_{d_1} and $T_{d_2}),$ the percentage char yield at 600°C (Y_{c_1}) and 800°C (Y_{c_2}) for samples **1b–5b** are given in Table I. From Table I, it is observed that thermal stability and char yield of the five samples are not very different, because of their similar polyimide backbone structures. Among the five samples, sample **3b** has the highest T_{d_1} (440°C) for its first degradation step, owing to the more terminated MI ring moieties.



Figure 5 TGA curves of cured samples.

CONCLUSIONS

Various BMI-DA Michael addition type prepolymers were prepared through melt condensation using acetone, DMF, and *m*-cresol as solvents at a molar ratio of 1 : 1. The structures of the prepolymers, such as terminal moieties and molecular weight of their main chain-based on the extent of the chain propagation through addition reaction of BM to DMA-depended strongly on the preparation conditions used. Prepolymer sample **3.** prepared in a DMF solution without a catalyst. had more terminated double bonds with the proper molecular weight. In contrast, prepolymer sample 5, produced in an *m*-cresol solution, had a polyaspartimide structure with a higher molecular weight. Meanwhile, it was found that the molecular structure of the prepolymer had noticeable effects on its thermal-curing behavior. Thermal properties $(T_g \text{ and } T_g)$ of the cured polyimides were evaluated. Polyimide sample **3b** from prepolymer sample 3 exhibited the highest T_{g}

and T_{d_1} , but still retained very good processing properties for film casting.

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