

Chain-Extended Bismaleimides. I. Preparation and Characterization of Maleimide-Terminated Resins

ZEKERİYA YERLİKAYA,¹ ZEKİ ÖKTEM,² and ERDAL BAYRAMLI^{1,*}

¹Department of Chemistry, Middle East Technical University, Ankara 06531, and ²Department of Chemistry, Abant İzzet Baysal University, Bolu 14100, Turkey

SYNOPSIS

Starting from aromatic diamines, a series of bismaleimides (BMIs) and maleimide-terminated structural resins were prepared in solution and characterized. Maleimide-terminated resins were prepared through Michael addition reaction with 3/2 molar ratio of bismaleimide and aromatic diamine as reactants. The structural analysis was performed by FTIR and ¹H-NMR spectroscopy. Thermal properties are investigated by TGA, DTA, and DSC. Number-average molecular-weights of the resins were determined by cryoscopy. The presence of methylene (—CH₂—) and ether (—O—) groups in the starting materials affect the reactivity and the degree of chain extension of the resins. From the viscosity measurements it was also found that thermal polymerization of BMIs could be taking place together with the Michael addition. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Aromatic bismaleimides (BMIs) are among the most successful intermediates for thermally resistant polymers. The BMIs can be self polymerized through their reactive maleic double bonds to give highly crosslinked brittle polyimides,^{1–6} which is their major disadvantage. This disadvantage has been overcome by introducing an appropriate chemical structure between two polymerizable maleimide groups.^{4,7–11} Another successful approach is the use of chain-extended high-molecular-weight prepolymers, which were prepared by the Michael addition reaction of BMIs and diamines.^{4,5,11–13} However, it is generally not desirable to use a high-molecular-weight polymer solution as a matrix precursor for fiber-reinforced composites, because at high solids content the solution is too viscous to handle; at low solids content there is usually insufficient resin pick up in one pass in the prepregging operation. Therefore, linear low-molecular-weight, amine-terminated bispartimides were prepared and cured via a ring-opening amidation reaction mechanism.¹⁴ The use of chain-extended prepolymers in place of BMIs is expected to reduce brittleness, because larger polymer segments would

be available for internal molecular motions after crosslinking.¹⁵

The BMIs are excellent candidates for carbon-fiber reinforced composite structures because of their high glass transition temperature (T_g), chemical, thermal, and oxidative stabilities, and the lack of volatile emissions during cure, in contrast to polyimides.

This article reports the synthesis of the most common BMIs, some combination of these BMIs and aromatic diamines into chain-extended low-molecular-weight forms that were terminated with maleimide groups at both ends, their spectroscopic characterization and thermal properties in detail. The chain extensions were carried out in *m*-cresol at 2:3 diamine to BMI molar ratio. A systematical approach was carried out to elucidate the effects of methylene (—CH₂—), ether (—O—), and the number of aromatic groups between linkages on the reactivity and the molecular weights of the resins. This information is helpful to produce BMIs with feasible processing conditions. It is hoped that the data obtained on solution polymerization can be extended to the melt polymerization techniques, which are more feasible as far as the industrial use is concerned.

In the next article that follows we report on the properties of cured maleimide-terminated resins with emphasis on their compatibility with various carbon fibers by means of acid-base surface

* To whom correspondence should be addressed.

energy determinations and interlaminar shear stress (ILSS) tests.

EXPERIMENTAL

Synthesis of Bismaleimides

All solvents and reagents were commercial and of analytical grade and used as received.

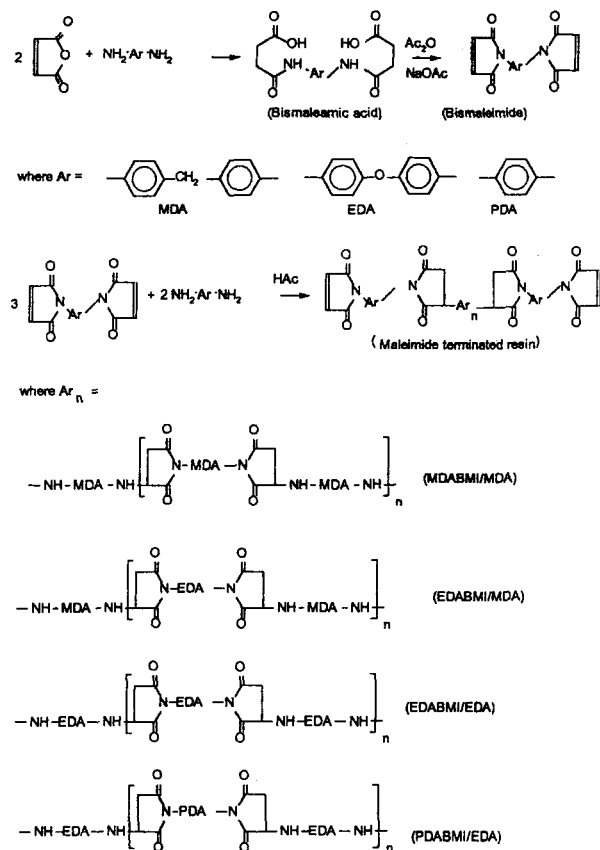
An amount of 1.0 mol of appropriate aromatic diamine, 4,4'-Diaminodiphenylmethane (MDA), 4,4'-Diaminodiphenylether (EDA), or *p*-Phenylenediamine (PDA), was dissolved in *N,N*-Dimethyl formamide (DMF), in a three-necked flask equipped with a magnetic stirring bar and fitted with a thermometer, a dropping funnel, and a reflux condenser with a CaCl₂ drying tube. Maleic anhydride (2.1 mol) as DMF solution, was added drop-wise over a period of 10 min at RT. The solution was maintained at 50°C for 2 h in a thermoregulated bath. Cyclization of amic acid^{7,16} was carried out by adding excess amount of fused sodium acetate and acetic anhydride mixture to the formed yellow solution. The temperature of the reaction mixture was maintained at 50°C for another 2 h, then the solution was poured into an ice bath. The precipitate was collected by filtration, repeatedly washed with cold water, and dried at 60°C in a vacuum oven (Scheme 1). MDABMI (I) and EDABMI (II) were purified by recrystallization from a methanol-chloroform (1:1 v/v) mixture.

Synthesis of Maleimide Terminated Resins

Chain extension of bismaleimides was performed by the Michael addition type reaction of a bismaleimide and an aromatic diamine in *m*-cresol. In a similar system as described above, the selected diamine (2.0 mol) as *m*-cresol solution, was added drop-wise to the *m*-cresol solution of bismaleimide (3.0 mol) at RT, containing a catalytical amount of glacial acetic acid. The reaction mixture was stirred in an oil bath at 100–105°C, until a viscous solution was obtained (6–96 h). The solution was then poured into ethanol and the precipitate was collected by filtration. The synthesized polymeric resins (Scheme 1) were washed repeatedly with ethanol and dried at 60°C in a vacuum oven.

Characterization

The IR spectra of the products were recorded in KBr pellets using a Nicolet-510 FTIR spectrophotometer. The ¹H-NMR spectra were recorded using a Bruker AC 80 NMR spectrometer. Proton NMR spectra were obtained using d-chloroform and DMSO-d₆ mixture as the solvent, and TMS as the internal standard.



Scheme 1 Route for bismaleimide synthesis and the structure of maleimide-terminated resins.

Thermal properties were determined by Perkin-Elmer type-4 DSC in nitrogen atmosphere and Netzch-429 TGA and DTA in air. Thermal analysis were performed at 10°C min⁻¹ heating rate.

Number-average molecular-weights, M_n , of maleimide-terminated resins were determined by cryoscopy. A well closed system, preventing the moisture absorption of dimethyl sulfoxide (DMSO) solutions of the resins, equipped with a Beckmann thermometer was used. Stirring of the solution was maintained by a magnetic stirring bar. Cryoscopic constant was determined by using purified azobenzene. Reproducible freezing points were obtained by melting and freezing the solution for several times. M_n values were calculated from the obtained linear $\Delta T/c$ vs. c curves.

RESULTS AND DISCUSSION

Synthesis and Characterization of Bismaleimides

The bismaleimides MDABMI (I), EDABMI (II), and PDABMI (III) were prepared in 80–90% yield

by using a modification of the method described by Varma et al.⁷ The synthesis involved first the preparation of bisamic acid precursor by reacting maleic anhydride with the selected diamine in DMF. Cyclization of bisamic precursor was promoted by using fused sodium acetate^{7,17} and acetic anhydride.^{7,18} Synthesized BMIs were characterized by FTIR, and ¹H-NMR showed characteristic carbonyl absorption at $1715 \pm 5 \text{ cm}^{-1}$. The double frequency was appeared at $1590 \pm 2 \text{ cm}^{-1}$ as a small shoulder on the strong carbonyl absorption. The other prominent bands were observed as; for phenyl groups at $1610 \pm 10 \text{ cm}^{-1}$ and $1520 \pm 10 \text{ cm}^{-1}$, for C—N stretching at $1400 \pm 5 \text{ cm}^{-1}$, for C—N—C stretching at $1137 \pm 1 \text{ cm}^{-1}$ and for ether linkage stretching of EDABMI at 1245 cm^{-1} . The bands due to the protons of maleimido double bonds and aromatic rings were also observed at $3172 \pm 2 \text{ cm}^{-1}$ and $3100 \pm 10 \text{ cm}^{-1}$, respectively.

In the ¹H-NMR spectra of MDABMI (I) and PDABMI (III), signals due to the protons attached to maleimido double bonds appeared at 6.82 and 6.84 ppm. The CH₂ and aromatic protons of MDABMI (I) were appeared at 4.03 and 7.30 ppm, respectively. The aromatic proton absorption of PDABMI (III) was observed as separate doublets at 8.10 and 7.79 ppm. A complex pattern was observed for EDABMI (II), where the absorption of double bond protons was shifted to the aromatic region. The absorption at 7.34 and 7.21 ppm was attributed to phenyl protons, and the absorption at 7.14 ppm was attributed to the protons of maleimido double bonds. The ratio of integration of =C—H, CH₂, and aromatic protons agrees well with the calculated proton numbers. The obtained FTIR and ¹H-NMR spectra of BMIs are in accord with the literature values.^{5–8}

Synthesis and Characterization of Maleimide Terminated Resins

The procedure described by Crivello⁵ was followed for the chain extension of BMIs. In order to obtain maleimido groups at both ends, the molar ratio of BMI to diamine was taken as 3:2. The maleimide-terminated resins were prepared in 90–95% yield by allowing one of the BMI to react a selected diamine in *m*-cresol solution with 13–15% (w/w) solid concentration and containing a catalytic amount of glacial acetic acid. Reactions were carried at 100–105°C until an appreciable increase in solution viscosities observed. Increase in solution viscosities for the polymerization of EDABMI/MDA (V) and EDABMI/EDA (VI) required only 6 h, where for the polymerization of PDABMI/EDA (VII) was obtained

within 40 h. For the polymerization of MDABMI/MDA (IV), considerable increase in viscosity was observed at the end of 96 h. The BMI/diamine ratio (3:2) was taken so that low molecular weight polymeric resins with maleimido groups at both ends would be formed; therefore, the time for the increase of solution viscosities is taken as a measure of the progression of the reactions by indicating the reactivity of the systems, but not the formation of ultra-high molecular weight products.

The number-average molecular-weights, M_n , of the synthesized maleimide-terminated resins were determined by cryoscopy technique,¹⁹ with DMSO as the solvent. The moisture absorption of DMSO was prevented by using a well-closed, specially designed and constructed system. The reproducibility of the results were controlled by repeating the measurements for several times. Cryoscopic constant (K_f) was determined from the slope of the plot of $M\Delta T$ vs. c by using azobenzene as a standard:

$$K_f = M\Delta T/c \quad (1)$$

where M is the molecular weight of the azobenzene, ΔT is the freezing point depression, and c is the solute concentration per 100 g of the solvent. K_f is found to be equal to -133.7 (°C · g/mol). Also, ideality of the polymeric solutions were controlled by deviation from linearity of the $\Delta T/c$ vs. c curves. Number-average molecular-weights (M_n) of the resins are calculated from the intercept of the ΔT against c (Fig. 1):

$$M_n = K_f/(\Delta T/c)_{c=0} \quad (2)$$

Calculations were performed by linear curves with at least three points and a linear regression of 0.99. Results (Table I) showed that low molecular weight polymeric resins were obtained as expected. M_n of PDABMI/EDA could not be determined because of insufficient solubility of the resin in DMSO. Although the polymerization time was only 6 h in the preparation of the resins V and VI, the molecular weights of these resins were calculated to be larger than that of the resin IV. It can, therefore, be concluded that the reactivity or basicity of the starting BMIs and the diamines containing ether groups affect the degree of chain extension and polymerization time. It is interesting to note that faster reactions have higher M_n values.

An application of the theory of step-wise polymerization (for Michael addition) shows that, with 3:2 reactants ratio the limiting average degree of polymerization (X_n) (as extend of reaction; $p \rightarrow 1$)

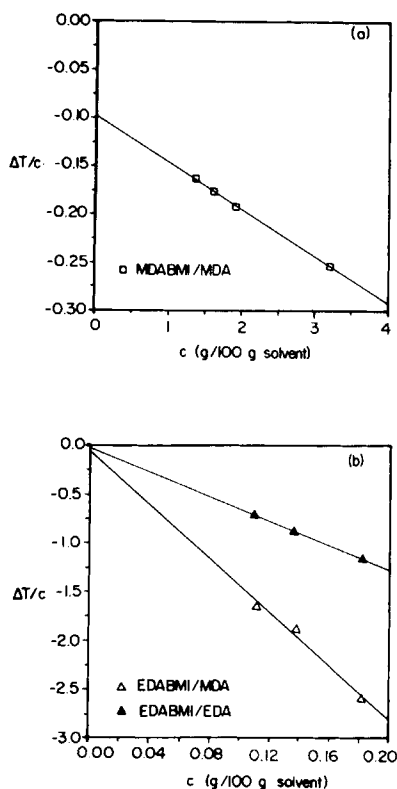


Figure 1 Freezing point depression-concentration curve of MDABMI/MDA (IV) (a), EDABMI/MDA (V) (b), and EDABMI/EDA (VI) (b).

is equal to 5 for the structures given in scheme 1. The n number in Table I correspond to $X_n - 1.5$ when the end groups are considered. The excessively large values of n for resins VI has led us to suspect that thermal polymerization of BMIs could be taking place together with the Michael addition. This postulate is tested in an experiment with a reaction mixture that lacks the diamine for resins IV precursors. Under the same experimental conditions, in *m*-cresol with glacial acetic acid, the flow time in Ubbelohde viscometer at 30°C increased 1.23 times after the 18 h reaction period. For resins V and VI precursor (EDABMI), interestingly, the flow time was unchanged for the reactants (without the diamine) before and after the 6 h reaction period. The BMIs are also investigated under microscope (crosspolarized filters) that has a hot-stage capable of 350°C maximum temperature. The iridescent colors in the interval 160–170°C for the MDABMI (I) and EDABMI (II) indicated that they show a thermotropic liquid crystalline behavior; therefore, the increase in viscosity can be taken as an indicator of thermal polymerization, but, lack of it cannot be interpreted as the absence of thermal polymerization

due to possible morphological changes in the solution. Investigation of the kinetics and the mechanism of BMI thermal polymerization is outside the scope of this study; nevertheless, it may account for the relatively large n values obtained for resins VI and resin V. In summary, it can be stated that ether linkages compared to methylene linkages increase the BMI reactivities, possibly due to the electron donating capability of the oxygen.

The maleimide-terminated resins were further characterized by FTIR and ¹H-NMR. The FTIR spectra of the resins (Fig. 2) showed broadening and overlapping of some of the characteristic absorption bands. The formation of polymeric chain was observed by the formation of broad N—H absorption between 3200–3650 cm⁻¹. The characteristic carbonyl absorption band of imides observed at 1720 cm⁻¹. The expected double bond frequency of the maleimido end groups was overshadowed by the strong aromatic and carbonyl absorptions. The bands due to phenyl groups and C—N stretching were observed at 1510 ± 5 cm⁻¹ and 1390 ± 5 cm⁻¹, respectively. The other expected bands due to =C—H, CH₂, and aromatic C—H, although mostly overshadowed by the broad N—H absorption, could be observed as weak absorption bands between 2845–3130 cm⁻¹.

In the ¹H-NMR spectra of MDABMI/MDA (IV) and EDABMI/MDA (V), aromatic protons were observed between 6.66 and 7.47 ppm. The aromatic proton absorption of EDABMI/EDA (VI) was observed as broad two separate peaks at 7.21 and 6.73 ppm (Fig. 3). The polymerization of BMIs and diamine was observed by the formation of imino protons (—NH—), and methine protons were (adjacent to imino groups) absorptions at 5.92 and 4.71 ppm, respectively. The same absorptions were reported by Kumar¹⁴ to be observed at 5.60 and 4.80 ppm for the resin IV, which was terminated with amino end groups. Although the absorption of protons of expected maleimido end groups were mostly overshadowed by the strong aromatic proton absorption, the weak absorption at 6.56 ± 1 ppm has been assigned to the protons of maleimido end groups. The —CH₂— protons were observed at 4.03 and 3.66 ± 2

Table I Cryoscopy Results of the Resins

Resin	M_n	n
MDABMI/MDA (IV)	1350	0.80
EDABMI/MDA (V)	3050	3.80
EDABMI/EDA (VI)	6850	10.5

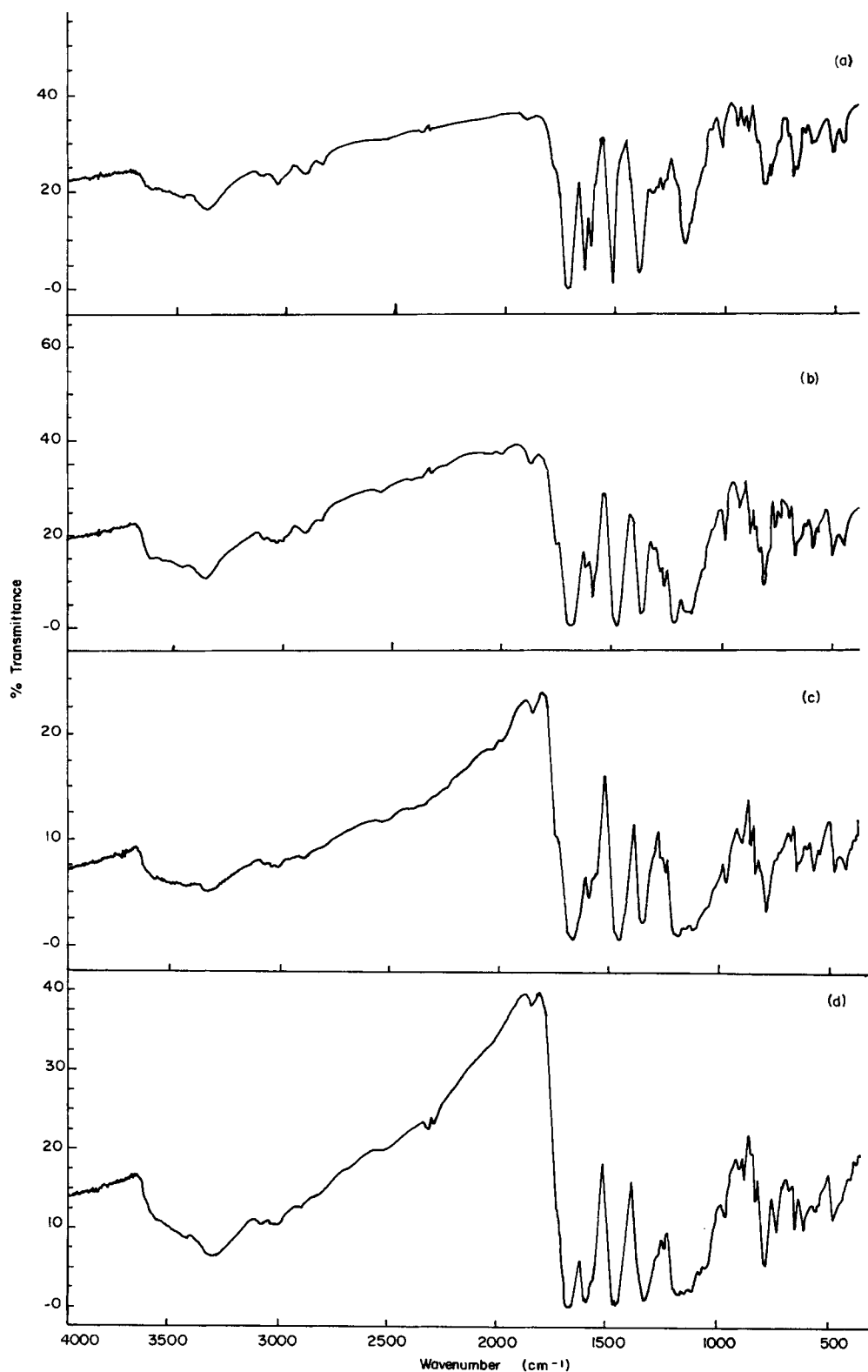


Figure 2 FTIR spectra of MDABMI/MDA (IV) (a), EDABMI/MDA (V) (b), EDABMI/EDA (VI) (c), and PDABMI/EDA (VII) (d).

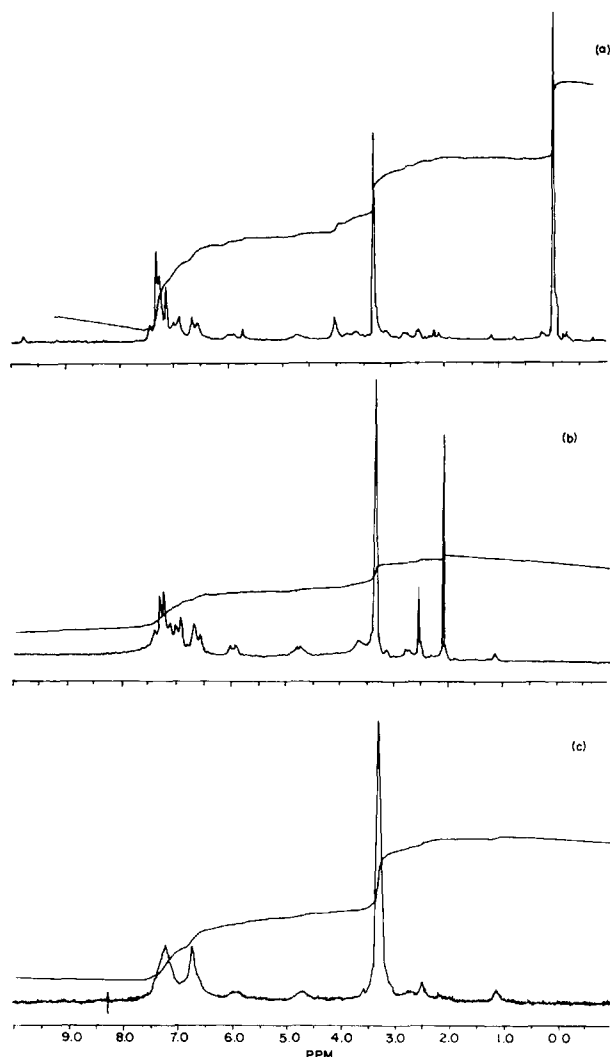


Figure 3 $^1\text{H-NMR}$ Spectra of MDABMI/MDA (IV) (a), EDABMI/MDA (V) (b), and EDABMI/EDA (VI) (c).

ppm for the BMIs and diamine units of the resins, respectively. The absorption of methylene protons of the maleimido groups in the chain was observed as separate and weak absorptions between the absorption of H_2O at 3.40 ppm and that of DMSO at 2.1 ppm. Also, the ratio of integration heights confirm the structure of synthesized maleimide terminated resins. In these spectra, the high-order split-

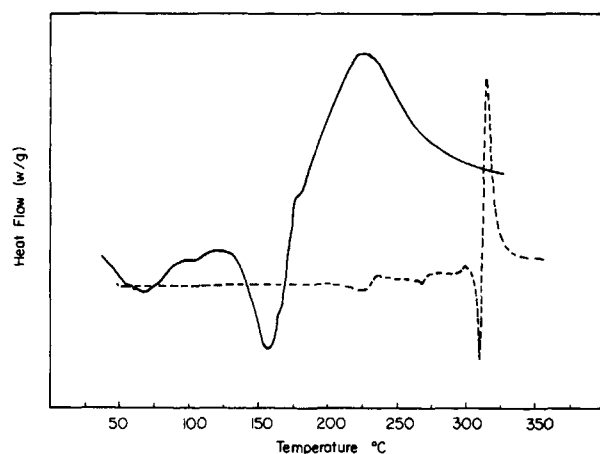


Figure 4 DSC traces of EDABMI (II) (—) and PDABMI (III) (-----).

ting due to isomerism¹⁴ could not be observed for the resin EDABMI/EDA (VI), because this resin polymerized up to relatively higher molecular weight than the others. Characterization of the resin VII (PDABMI/EDA) by $^1\text{H-NMR}$ could not be carried because of insufficient solubility of this resin in DMSO-d_6 .

Thermal Properties of Bismaleimides

Thermal scans of BMIs were performed by DSC in and N_2 atmosphere. From the obtained DSC traces, exothermic peak temperature (T_{exo}), onset temperature for curing reaction (T_1), and temperature for completion of curing reaction (T_2) were determined and are given in Table II. A sharp endotherm associated with melting of BMIs was observed for MDABMI (I) and PDABMI (III). Opposing to Varma et al.,⁷ a broad endotherm was observed before the appearance of a broad exothermic transition for EDABMI (II) (Fig. 4). In the DSC traces of PDABMI (III), the sharp endotherm of melting was followed by a sharp exothermic transition as soon as the PDABMI (III) melted, without any sign of decomposition (Fig. 4). Results obtained from the DSC analysis are mostly in accordance with the given literature values,^{7-9,12} except the T_m of

Table II Results of TGA, DTA, and DSC Analysis of Bismaleimides (Values are in $^{\circ}\text{C}$)

Bismaleimide	T_m	T_1	T_{exo}	T_2	T_d	T_{max}	$T_{10\%}$
MDABMI (I)	156	215	266	300	480	590	490
EDABMI (II)	158	178	229	275	430	580	450
PDABMI (III)	310	310	314	325	360	465	380

PDABMI (III) where the reported value⁵ is to be between 346–350°C.

TGA and DTA of uncured BMIs were studied by heating the samples in air at a rate of 10°C · min⁻¹. From the obtained TGA traces, initial decomposition temperature (T_d) and temperature of 10% weight loss ($T_{10\%}$), and from the DTA traces, temperature of maximum rate of decomposition (T_{max}) were calculated and are given in Table II.

Thermal Analysis of Maleimide-Terminated Resins

TGA and DTA of maleimide-terminated uncured resins were also studied by heating the samples in air at a rate of 10°C · min⁻¹. The thermogravimetry curves were characterized as the TGA and DTA traces of BMIs by T_d , $T_{10\%}$, and T_{max} . A two-step decomposition was only observed for uncured MDABMI/MDA (IV). These resins showed initial decomposition at 350–360°C, and the rate of decomposition is slower for the resins IV and VI with 10% weight loss up to 440 and 430°C, respectively. The first stage decomposition was accounted for a 20% weight loss up to 532°C. The reason for the early weight loss compared to BMIs may be due to the loss of diamine via reverse Michael addition reaction. T_g of uncured resins were determined by DSC. The results of DSC, TGA, and DTA are given in Table III.

CONCLUSION

Maleimide-capped chain-extended forms of BMIs are synthesized with combinations of ether and methylene linkages on the main body and the extended part of the resin. The ether moiety increased the rate of formation and the average molecular weight of the resin. The resin with only phenyl group between maleimide groups showed the least solubility in polar solvents and high T_m , as expected from the resulting rigid structure. The cryoscopy and the relative viscosity data indicates that during chain extension, certain amount of thermal polymerization of the BMIs also take place, which in general, decrease the processibility of the resin. This point warrants further study to elucidate the exact nature and mean of reducing this effect. TGA and DTA data showed that BMIs have excellent thermal stability up to 480°C. In comparison, maleimide-terminated resins showed an early weight loss, perhaps due to loss of diamine via reverse Michael addition process. The thermal stability of uncured resins up to 360°C are still acceptable values.

Table III Results of TGA, DTA, and DSC Analysis of Uncured Maleimide-Terminated Resins (Values are in °C)

Resin	T_d	T_{max}	$T_{10\%}$	T_g
MDABMI/MDA (IV)	350	560	440	185
EDABMI/MDA (V)	357	557	370	219
EDABMI/EDA (VI)	360	560	430	220
PDABMI/EDA (VII)	355	560	400	197

This study is supported by a Turkish Planning Organisation (DPT) and Turkish Research Council (TUBITAK) joint grant with No. DPT/TBAG-4.

REFERENCES

- I. K. Varma and D. S. Varma, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1419 (1984).
- J. V. Crivello, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 159 (1974).
- J. E. White and M. D. Scaia, *Polymer*, **25**, 850 (1984).
- J. E. White, M. D. Scaia, and D. A. Snider, *J. Appl. Polym. Sci.*, **29**, 891 (1984).
- J. V. Crivello, *J. Polym. Sci., Polym. Chem. Ed.*, **11**, 1185 (1973).
- C. Di Giulio, M. Gautier, and B. Jasse, *J. Appl. Polym. Sci.*, **29**, 1771 (1984).
- I. K. Varma and S. Sharma, *Polymer*, **26**, 1561 (1985).
- S. Takeda, H. Akiyama, and H. Kakiuchi, *J. Appl. Polym. Sci.*, **35**, 1341 (1988).
- T. Pascal, R. Mercier, and R. Sillion, *Polymer*, **30**, 739 (1989).
- M. Suzuki, A. Nagoi, M. Suzuki, and A. Takahashi, *J. Appl. Polym. Sci.*, **44**, 1807 (1992).
- H. Winter, H. A. M. Mostert, and M. G. V. Tholen, *J. Appl. Polym. Sci.*, **45**, 451 (1992).
- V. L. Bell and P. R. Young, *J. Polym. Sci., Polym. Chem. Ed.*, **24**, 2647 (1986).
- T. M. Donnellan and D. Roylance, *Polym. Eng. Sci.*, **32**, 409 (1992).
- D. Kumar, G. M. Fohlen, and J. A. Parker, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 245 (1983).
- T. M. Donnellan and D. Roylance, *Polym. Eng. Sci.*, **32**, 415 (1992).
- N. E. Searle, U.S. Pat., 2 44 536; *Chem. Abstr.*, **42**, 7340 (1948).
- J. E. White, *Ind. Eng. Chem. Prod. Res. Dev.*, **25**, 395 (1986).
- S. J. Shaw, *Mater. Sci. Technol.*, **3**(8), 589 (1987).
- E. J. Newitt and V. Kokle, *J. Polym. Sci., Part A-2*, **4**, 705 (1966).

Received January 19, 1995

Accepted July 13, 1995