

# *Bismaleimide and Bisazomethine High Temperature Polymers*

## Synopsis

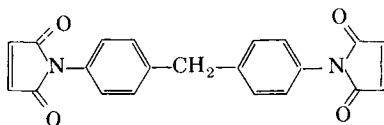
Conjugated aromatic bisazomethine, resulting from the reaction of terephthalaldehyde and aniline, has been found to react with bismaleimidodiphenylmethane to provide polymeric compositions with glass transition temperature higher than 300°C. These two materials form a low viscosity melt at ca. 150°C and the melt shows only a small viscosity increase when maintained at 120°C over a period of 8 h. Differential scanning calorimetry (DSC) of this composition shows that upon heating above 200°C, it cures rapidly to produce a thermally stable polymer. Thermal mechanical analysis (TMA) of the cured composition does not detect any softening up to 350°C. In the thermal gravimetric analysis (TGA), no weight loss is observed up to 400°C in air and the material leaves a rather large amount of residue (ca. 60%) even up to 600°C. Dynamic mechanical thermal analysis (DMTA) shows that the polymer maintains its high modulus with increasing temperature up to 250°C.

## INTRODUCTION

Low viscosity melt compositions that cure at elevated temperatures to produce polymers with high softening points and good thermal stability are very desirable for the development of easily processable high-performance polymers. Bismaleimides and aromatic bisazomethines are polar materials and it is reasonable to assume that they may form miscible melts at elevated temperatures. Upon further heating the azomethine double bonds may condense with the activated double bonds in bismaleimide to produce heterocyclic rings.<sup>1</sup> This heterocyclization has not been described in the literature for the synthesis of new polymers. Only polyamines containing some azomethines have been described to cure bismaleimides.<sup>2</sup> In this report we describe the reaction of a pure azomethine with bismaleimide to produce polymers with exceedingly high softening points and exceptional thermal stability.

## EXPERIMENTAL

Reagent-grade ethanol was used as a solvent. Terephthalaldehyde and aniline were obtained from Aldrich Chemical Company and were used without further purification. Commercial-grade 4,4'-bismaleimidodiphenylmethane (I) was obtained from Ciba-Giegy Corporation and was used as received. This material is a yellow crystalline powder and has greater than 85% of theoretical maleimide double-bond content; it melts at 150–160°C.



I

Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. Thermal decomposition of the polymers was studied in air with a DuPont 990A Thermal Gravimetric Analyzer and softening-point determination was attempted with a DuPont Model 943 Thermal Mechanical Analyzer by employing the penetration mode at a heating rate of 10°C/min. The cure temperature of this composition was estimated with a DuPont 910 Differential Scanning Calorimeter (DSC) at the heating rate of 5°C/min under argon.

TABLE I  
Melt Viscosity Measurements at 120°C

Time, h (at 120°C)	Viscosity, cps
0.25	780
2.0	810
4.0	860
6.0	890
8.0	910

The dynamic mechanical thermal behavior (tensile storage modulus,  $E'$ , and loss tangent,  $\tan \delta$ ) was examined on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) in the dual cantilever mode. The sample was subjected to oscillating deformation at 0.1, 1.0, and 10 Hz while the temperature was increased from 50°C to 250°C at 1°C/min.

### Preparation of *N,N'*-*p*-Phenylenedimethyldiylne Dianiline (II)

Terephthalaldehyde (26.8 g, 0.2 mol) was dissolved in 50 mL ethanol by heating at 60°C. Aniline (37.2 g, 0.4 mol) was added to the above solution; a yellow color appeared immediately and within a few minutes crystals started separating. The mixture was allowed to stay at room temperature overnight and the product was filtered. The yield was 28.7 g (56.8% of theoretical). Infrared spectrum of the product was recorded.

### Polymerization of Bismaleimide I with Bisazomethine II

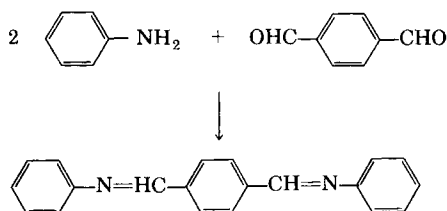
The bismaleimide (42.1 g) and the azomethine (14.2 g) were mixed in a beaker and the mixture was heated in an oil bath at 150°C. The mixture was stirred to obtain a homogeneous melt and it was cast between Mylar-lined glass plates. It was then placed in an oven at 150°C. The temperature was raised to 246°C over half an hour and the sample was heated at this temperature for 2 h. The sample was allowed to cool to room temperature in the oven; a small part of the sample was finely ground for infrared spectrum. The remaining sample was used for TMA, TGA, and DMTA studies.

### Viscosity Determination of the Melt

The bismaleimide (84.2 g) and the azomethine (28.4 g) were mixed in a beaker and the melt was obtained as outlined above. The melt was then placed in an oil bath at 120°C and allowed to equilibrate. Viscosity measurements were made using Brookfield rotating spindle viscometer and are listed in Table I. The melt was kept covered to avoid excessive exposure to air.

## RESULTS AND DISCUSSION

In the preparation of bisazomethine II, aniline reacts with terephthalaldehyde to produce the conjugated structure shown below.



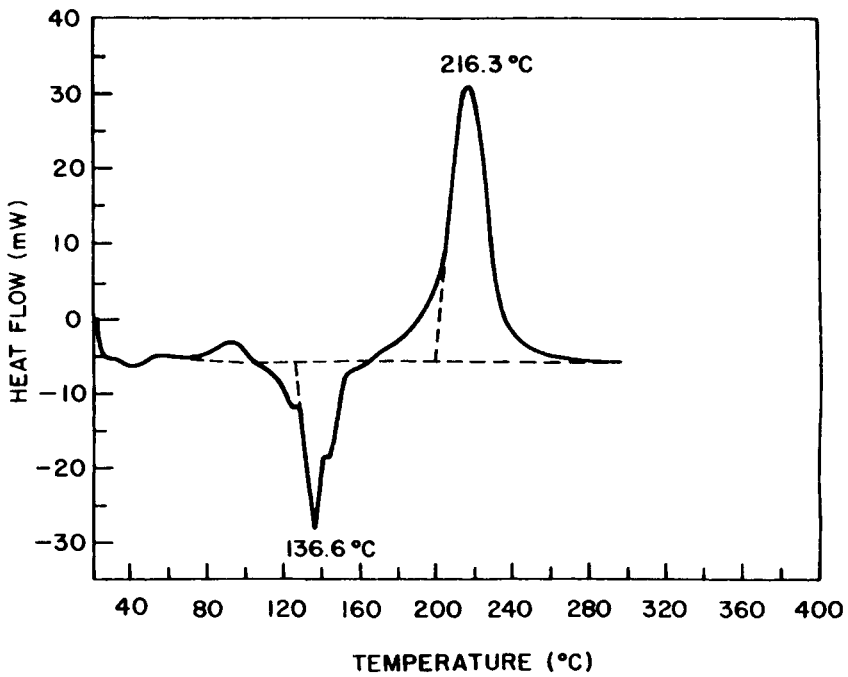


Fig. 1. Differential scanning calorimetry of the uncured mixture of bismaleimide I and bisazomethine II.

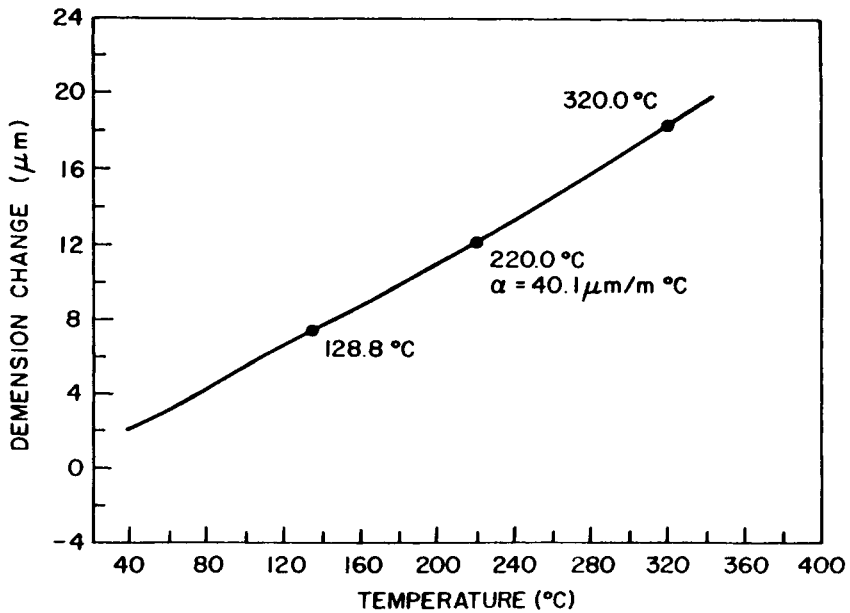


Fig. 2. Thermal mechanical analysis of the cured composition.

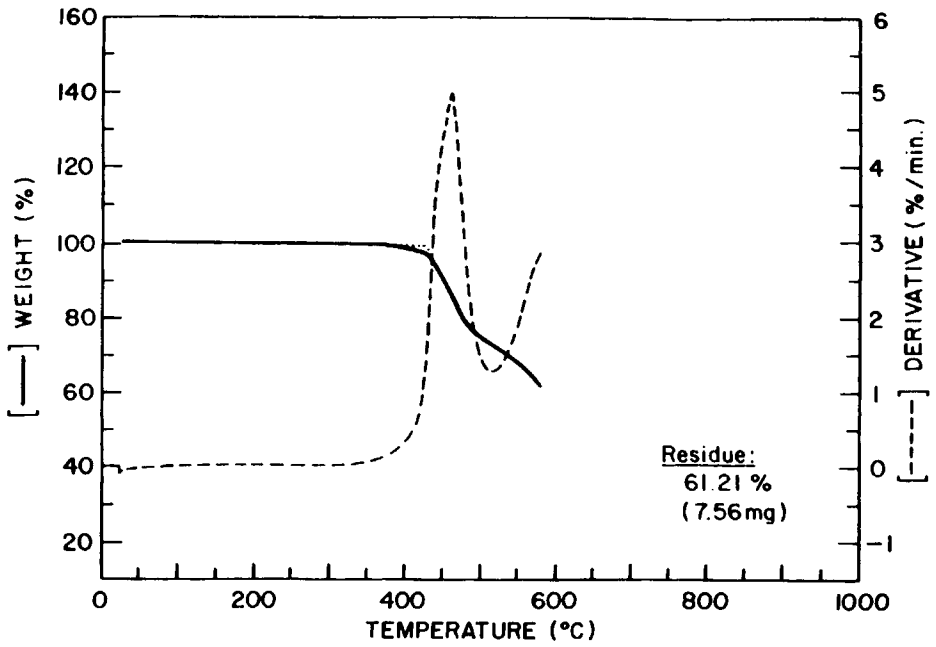


Fig. 3. Thermal gravimetric analysis of the cured composition in air.

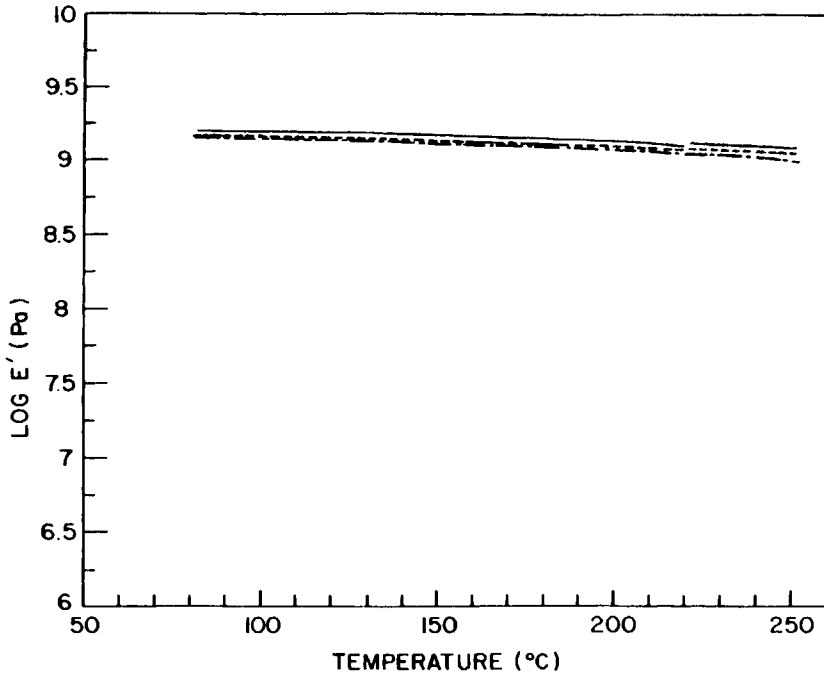


Fig. 4. Dynamic mechanical thermal analysis of the polymer resulting from bismaleimide I and bisazomethine II.

The melting point (159–160°C) and the infrared spectrum support the conjugated structure shown above.<sup>3</sup>

When the mixture of bismaleimide I and the azomethine II was heated at 150°C it formed a low viscosity melt. When the melt is allowed to stay at 120°C, the viscosity increase is rather small (Table I). This indicates that very little reaction between I and II may be going on. When the melt was cooled to room temperature soon after it was formed, it produced a light yellow mixture of crystals. The differential scanning calorimetric analysis (Fig. 1) of the crystalline mixture displays an endotherm at 136.6°C, which is probably due to melting of the crystals; the exotherm at 216.3°C is attributed to the copolymerization of I and II. When the mixture was heated at 246°C for 2 h, its infrared spectrum showed complete disappearance of the vinyl group absorptions present in the spectra of I and II. Thermal mechanical analysis (Fig. 2) of the cured composition (5 h at 246°C) does not exhibit any softening up to 350°C. Thermal gravimetric analysis (Fig. 3) of this composition, cured for 5 h at 246°C, displays thermal stability in air up to 400°C and furthermore the polymer leaves a rather large residue (61% up to 580°C). Dynamic mechanical thermal analysis (Fig. 4) indicates that the glass transition temperature is well in excess of 250°C, confirming the TMA results. The polymer retains its high modulus with increasing temperature at least up to 250°C. The DMTA at higher temperature needs to be studied. Nuclear magnetic resonance studies are in progress to understand the copolymerization mechanism of bismaleimides and bisazomethines.

## CONCLUSIONS

Bisamleimidodiphenylmethane and *NN'*-(*p*-phenylenedimethylidyne) dianiline from a low viscosity melt at 150°C. The melt displays only a modest increase in viscosity when maintained at 120°C for 8 h. This mixture copolymerizes upon heating above 200°C (DSC) to produce a hard crosslinked polymer. The polymer is thermally stable (TGA) up to 400°C in air and leaves a large residue up to 580°C. It displays high modulus (DMTA) and shows no softening up to 350°C (TMA). The polymer is potentially suitable for high temperature composites applications.

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## References

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