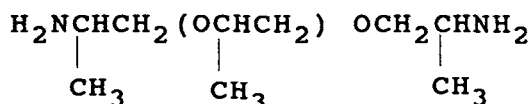


A Low-Temperature Thermosetting Bis-maleimide Resin

INTRODUCTION

A range of polyoxypropyleneamines are commercially available as the "Jeffamine" series. These are primarily used as curing agents, particularly for epoxy resins.^{1,2} The general formula of a particular class of these compounds (the "D" series) is given below:



The amine functionality is attached to a secondary carbon atom and is therefore sterically hindered, resulting in moderate reactivity that can have advantages in the handling of epoxy cure formulations. Although much work has been carried out on the behavior of Jeffamine/epoxy resins, far less attention has been given to Jeffamine/bis-maleimide resins although there is a patent in this area.³ Aliphatic and aromatic primary diamines generally react with bis-maleimides to give cross-linked products even when the reaction is carried out in solution at mild or ambient temperature. It was felt that the moderate reactivity of Jeffamines may allow for the convenient processing of bis-maleimide polymers in solution. A study of the polymer formed on reaction between a low molar mass Jeffamine (D-230) and a commercially available bis-maleimide is reported here.

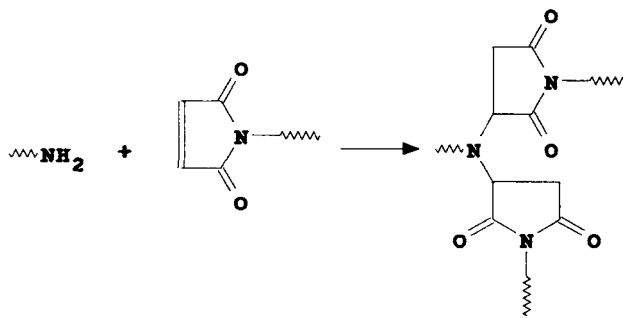
EXPERIMENTAL

Jeffamine D-230 (approximate molecular weight 230 g mol⁻¹) was obtained from FLUKA Chemicals. 1,1'-(Methylenedi-4,1-phenylene)bismaleimide (BM) was obtained from Aldrich Chemical Co. Both materials were used without further purification. The copolymerization of these two monomers was carried out by dissolving 10 mmol of each of the monomers in 100 mL of dichloromethane and refluxing the mixture for 2 h. The product was obtained as a yellow solid by precipitation into diethyl

ether (yield 2.4 g, 41%). The infrared spectrum of the product was obtained from a KBr disc sample and showed that the succinimide C—N—C stretch at 1180 cm⁻¹ had replaced the maleimide C—N—C stretch at 1137 cm⁻¹. The proton NMR spectrum of the product (recorded on a Jeol 90 MHz instrument, CDCl₃ solvent and TMS reference) was consistent with an addition product, but did show some residual unreacted maleimide protons. Gel permeation chromatography (tetrahydrofuran solvent, PLgel column, refractive index detector, and polystyrene standard calibration) gave a molecular mass (M_n) = 6309 (M_w/M_n = 1.21). The synthesis was repeated by carrying out the reaction at ambient temperature, and under these conditions, the product gave M_n = 5475 (M_w/M_n = 1.36). Differential scanning calorimetry (DSC) runs were carried out using a Mettler DSC 30 instrument with a heating/cooling rate of 5°C/min. Dynamic mechanical thermal analysis (DMTA) measurements were carried out using a Polymer Laboratories instrument (1 Hz, 4°C/min heating rate, single cantilever). Thermogravimetric analysis was carried out using a Stanton Redcroft TG 750 thermobalance (air atmosphere, heating rate 10°C/min).

RESULTS AND DISCUSSION

Reaction of the Jeffamine D-230 and BM in solution yields a linear, soluble polymer with a degree of polymerization of ca. 10. Attempts to generate a polymer from 1,6-hexanediamine and BM under the same conditions produced a gelatinous, cross-linked polymer. The reaction of primary, unhindered diamines with bis-maleimides in solvent has been thoroughly investigated.⁴ The usual mechanism is that of a Michael addition of the amine across the maleimide double bond to give a polyaspartimide:



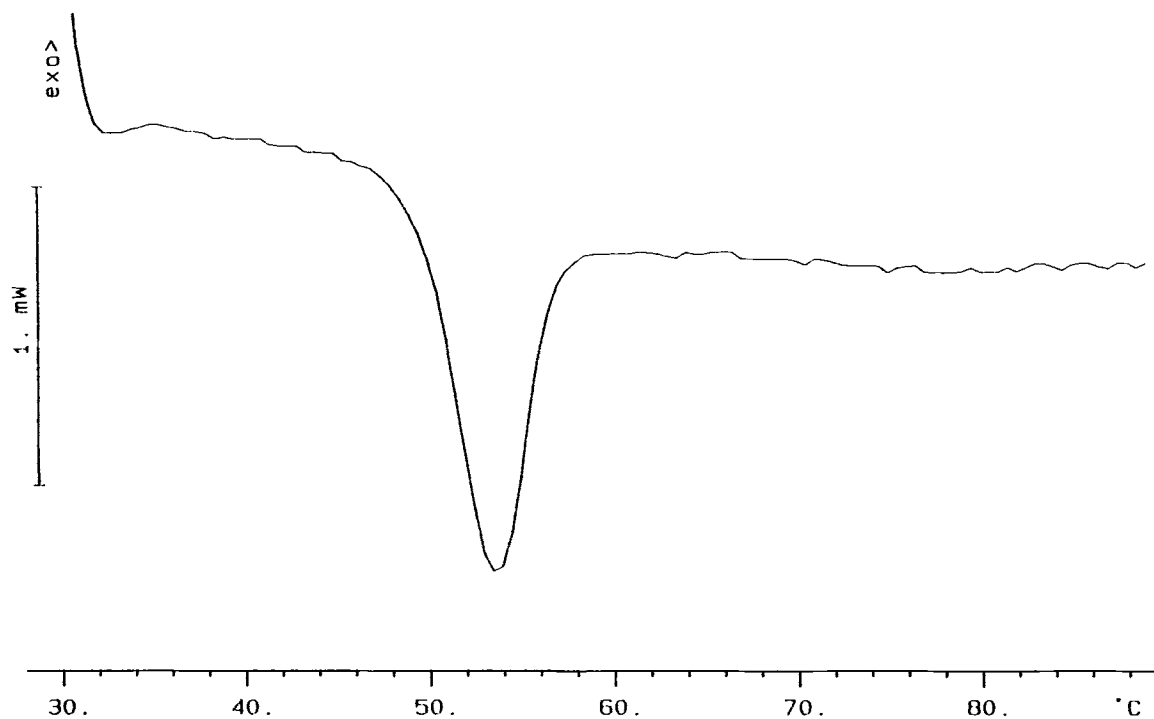


Figure 1 DSC trace of first heating cycle of polymer.

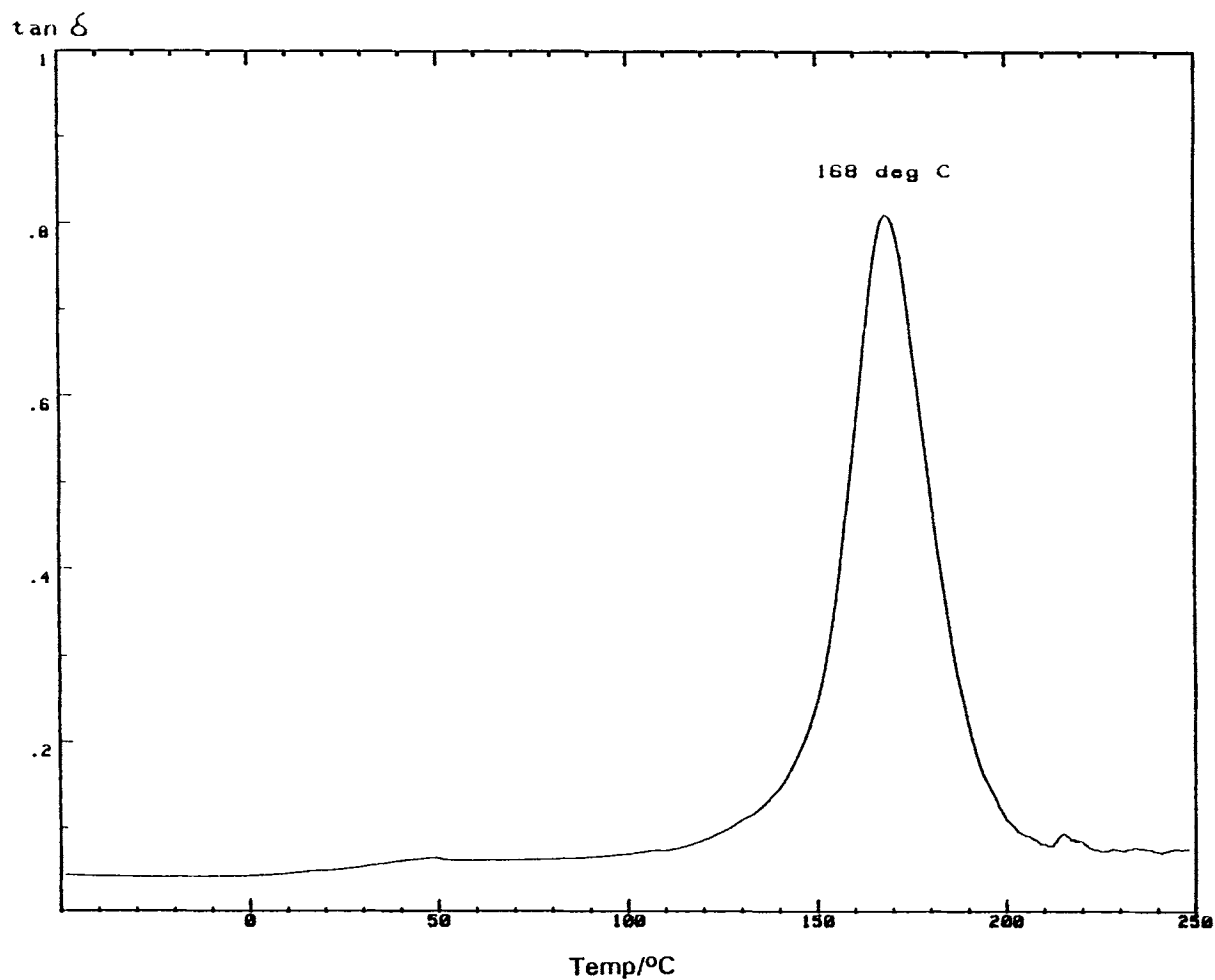


Figure 2 DMTA trace for thermally cross-linked polymer.

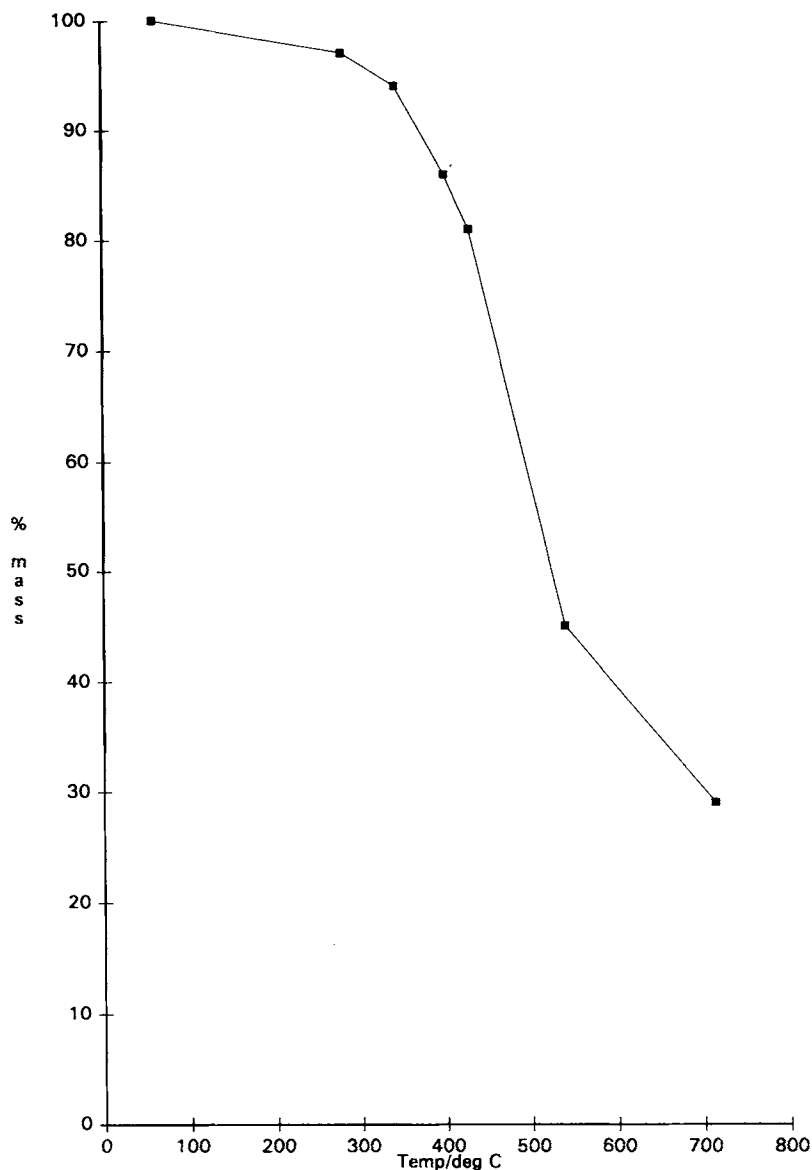


Figure 3 TGA trace for thermally cross-linked polymer in air.

Since there is a secondary amino site available for further reaction, branching and cross-linking takes place readily to give an insoluble product. Secondary diamines generally give soluble polymers.⁵ The observation that the polymer formed in this work is soluble in dichloromethane suggests that cross-linking is inhibited by virtue of the sterically hindered secondary amine in the Jeffamine unit. A small amount of the solid polymer was heated on a microscope slide to ca. 60°C. The polymer underwent softening and changed into a blood-red resin. On cooling, the solid material was found to swell in dichloromethane but was no longer soluble in this solvent (solvent left in contact with the heat-treated solid showed no trace of red coloration).

DSC analysis of the polymer (prior to heat treatment) shows a melting transition at 53–54°C (Fig. 1), which

roughly corresponds to the heating experiment mentioned above. The enthalpy of melting was 8.3 J g^{-1} (determined by the area under the melting curve). The second heating cycle shows no endotherm, but a well-defined glass transition at 67°C is observed. Given that the density of cross-links may be very small, and so a curing exotherm may be obscured by the melting endotherm, this would seem to suggest that cross-linking occurs on melting below 60°C. A sample of the cured polymer was prepared and analyzed by DMTA, giving a loss tangent ($\tan \delta$) peak at 168°C (Fig. 2). The cured polymer shows good thermal stability up to 300°C in air as determined by thermogravimetric analysis (Fig. 3).

This low-temperature thermosetting polymer may have potential applications in the field of high solids surface coatings, since as a low molecular weight polymer, it could

be cast on a surface in high concentrations without serious rheological problems and thermally cured under mild conditions.

We would like to express thanks to Mr. B. O'Donnell of the University of Newcastle upon Tyne for the DMTA measurement.

REFERENCES

1. L. G. Meyer, U.S. Pat. 4,122,069 (1978).
2. N. H. Reinberg, U.S. Pat. 3,316,185 (1967).
3. D. L. Alexander and G. P. Speranza, U.S. Pat. 4,826,995 (1990).

4. J. V. Crivello, *J. Polym. Sci. Polym. Chem. Ed.*, **11**, 1185 (1973).
5. J. E. White and D. A. Snider, *J. Appl. Polym. Sci.*, **29**, 891 (1984).

L. R. DIX
M. A. SIMPSON
L. N. LY

Department of Chemical & Life Sciences
University of Northumbria at Newcastle
Newcastle upon Tyne NE1 8ST
United Kingdom

Received August 26, 1992

Accepted September 16, 1992