polymer communications

Studies on bismaleimides and related materials: 1. D.m.t.a. investigation of the reaction of bismaleimides with *m*-tolualdehyde azine and 3,5-dimethylpyridine *N*-oxide: an approach to the design of novel reactive diluents

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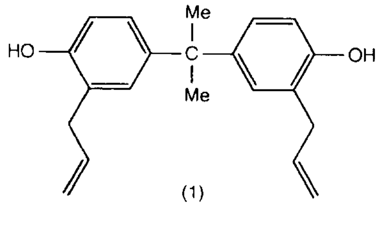
(Received 16 August 1993; revised 15 October 1993)

Dynamic mechanical thermal analysis (d.m.t.a.) profiles have been recorded for interaction of *m*-tolualdehyde azine and 3,5-dimethylpyridine *N*-oxide with the bismaleimide (BMI) derived from 3,3'-diaminobenzophenone. Additional chemical events for each system are recognized at temperatures below the conventional BMI curing region. Resins prepared from the BMI/azine and BMI/*N*-oxide systems have lower thermal stability than the neat resin but differences are moderate at low additive concentrations.

(Keywords: bismaleimide; azine; heteroaromatic *N*-oxide)

Introduction

Thermally induced polymerization of bismaleimides (BMIs) gives rise to polymers with good high temperature stability and low moisture absorption in wet environments[1,2]. Unfortunately, because BMI resins possess high crosslink densities, they are more brittle and often more difficult to process than conventional epoxy systems. The last few years have seen progress in the development of 'reactive diluents', which are compounds capable of copolymerizing with the BMI; examples include the use of *o*-allylphenols (see, for example, Ciba-Geigy's Matrimide 5292 comprising **1** and **2**)[3] and styrene derivatives[4]. The reactive diluent (**1**) probably functions by 'ene' reaction with the BMI followed by Diels–Alder reaction of the ensuing styrene derivative.



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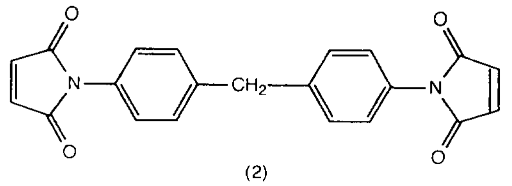

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We now describe a new approach to reactive diluent chemistry based on use of the classical 1,3-dipolar cycloaddition reaction[5]. In principle, a 1,3-dipolar species $(a=b^+-c^-)$ can react with a maleimide (**3**) to give a cycloadduct (**4**), and indeed, many such processes are documented[6]. Of course, thermal reactions of this type are reversible, so the ideal reactive diluent would function initially by 1,3-dipolar cycloaddition followed by a secondary process of thermal rearrangement of the cycloadduct (**4→5**). Below, we describe investigations on compounds from two classes that can function by 1,3-dipolar cycloaddition with BMIs: in one case, rearrangement (**4→5**) would not be expected, but in the other, thermal transformation of the cycloadduct can occur (*Scheme 1*).

Azines (**6**) were selected because they are known to react with dipolarophiles by a process of 'criss-cross cycloaddition'[7,8] and use of such reactions has been exploited in organic[9] and polymer[10–13] synthesis. Of relevance to this work is the melt oligomerization of benzaldazine (**6a**, 1 mol equiv) with a series of BMIs (**7**, 2 mol equiv) leading to oligomers (**8**) with a degree of polymerization, *n*, of around 5 (ref. 14).

Secondly, we chose a pyridine *N*-oxide derivative for investigation. Hisano and co-workers[15–17] studied the reaction of 3,5-dimethylpyridine *N*-oxide with N-substituted maleimides and discovered a process of 1,3-dipolar cycloaddition with ensuing thermal [1,5] sigmatropic rearrangement of the cycloadduct (see, for example, *Scheme 2*[17]).

Experimental

Materials. Azine derivatives (**6b**[18] and **6c**[19]) and 3,5-lutidine *N*-oxide (**9**)[20] were prepared by literature procedures; they were characterized as follows.

m-Tolualdehyde azine (**6b**) (yield, 89%), m.p. 75–77°C (lit[18] 71–72°C). ν_{max} (KBr) 2950 (CH stretch), 1620 (C=N

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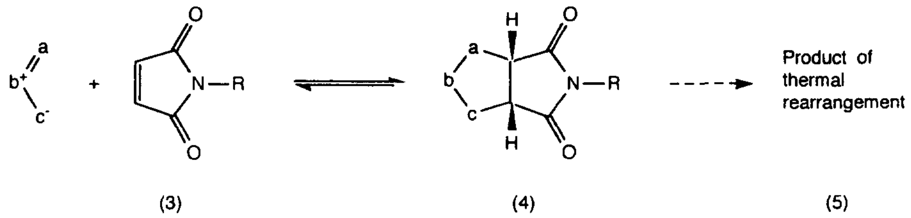
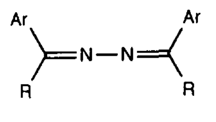


Scheme 1



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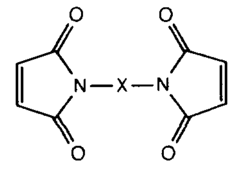
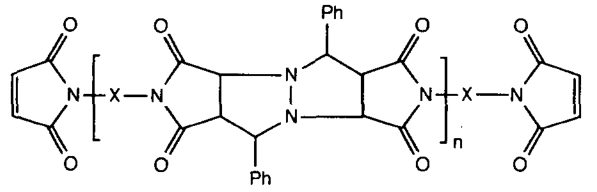


(7)

	Ar	R
a,	Ph	H
b,	m-MeC$_6$H$_4$	H
c,	Ph	Et

X = eg o-, m-, and p- Phenylene



(8)

stretch)cm^{-1}. δ_H (CDCl$_3$) 2.4 (s, 6H, CH$_3$), 7.25–7.4 (m, 4H, Ar–H), 7.5–7.8 (m, 4H, Ar–H), 8.65 (s, 2H, =CH).

Propiophenone azine (**6c**) (yield, 53%), m.p. 67–70°C (lit[19] 68°C). ν_{max} (KBr) 2960, 2930, 2860 (CH stretch), 1580 (C=N stretch)cm^{-1}. δ_H (CDCl$_3$) 1.15 (t, 6H, CH$_3$, $J=8$ Hz), 2.90 (q, 4H, CH$_2$, $J=8$ Hz), 7.4–7.6 (m, 6H, Ar–H), 7.8–8.0 (m, 4H, Ar–H).

3,5-Lutidine *N*-oxide (yield, 46%), m.p. 103–105°C (lit[20] 101–102°C). δ_H (CDCl$_3$) 2.12 (d, 6H, 2×CH$_3$, $J<1$ Hz), 6.82–6.92 (m, H-4), 7.80–7.92 (m, 2H, H-2 and H-6). *m/z* (EI) 123 ($M^{+\bullet}$).

Bismaleimide derivative (**13**). This compound was prepared from 3,3′-diaminobenzophenone[21] by a standard method[22]; full data for characterization are given in part 3 of this series[23].

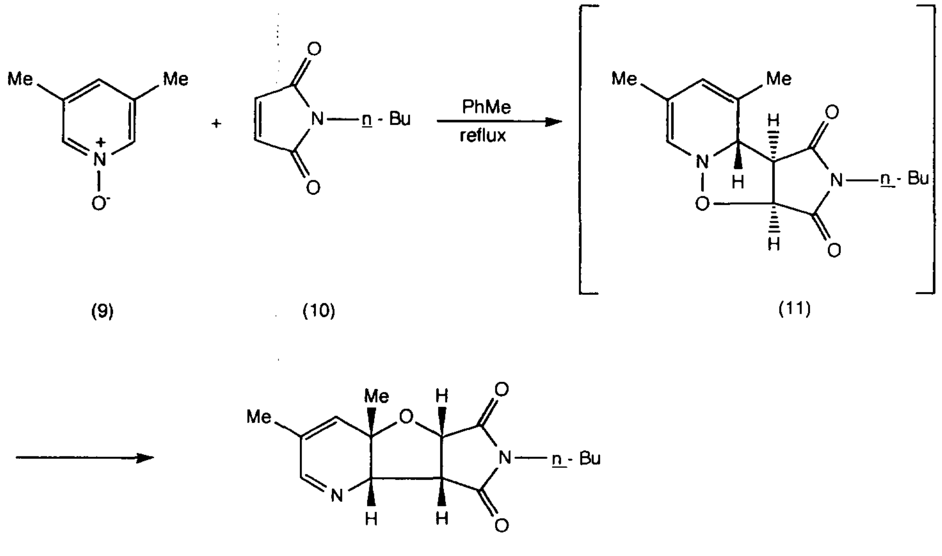
N,N,-Dimethylformamide (DMF) was purified by storing over potassium hydroxide pellets overnight and then distilling from calcium oxide.

Polymerizations. For dynamic mechanical thermal analysis (d.m.t.a.) studies monomers were dissolved in DMF and impregnated on glass braid (Vidatape C, 13 mm × 0.09 mm; Jones Stroud Insulations). Braids were then dried in air at 25°C for 24 h. Cure cycles for preparing resins on a quantitative basis are given in the footnote to *Table 1*.

Polymer characterization. D.m.t.a. studies were conducted on a Polymer Laboratories d.m.t.a. unit using a test frequency of 10 Hz and a heating rate of 5°C min^{-1}. The thermal stability of the cured resins was measured using a Perkin–Elmer TGA-7 and heating rate of 20°C min^{-1}.

Results and discussion

The desirable features we sought from d.m.t.a. were evidence from the profiles of lowering of BMI softening/melting temperature, of interaction of the BMI with the



Scheme 2

Table 1 Effect of additives (**6c**) and (**9**) on the thermal stability of cured resins derived from bismaleimide (**13**)[a] (heating rate 20°C min^{-1})

Additive (wt%)	Thermal gravimetric analysis: Temp. (°C) for 5% weight loss	Temp. (°C) for 10% weight loss	Residue at 1000 K (%)
None	443	454	60
6c (10)	372	409	60
6c (20)	359	382	57
6c (30)	354	375	57
6c (40)	350	371	53
9 (10)	377	414	57
9 (20)	344	372	58
9 (30)	339	368	59
9 (40)	350	380	62

[a] Cure cycles were, sequentially, for **13** and **13**+**6c**: 1 h at 180C, 2 h at 200°C and 6 h at 300°C; and for **13**+**9**: 4 h at 110°C, 2 h at 200°C and 6 h at 250°C

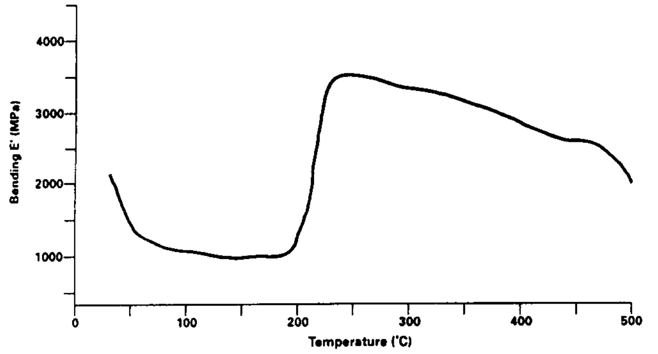


Figure 1 Curing profile of Ciba Geigy's BMI resin 'Matrimide 5292', as revealed by d.m.t.a. of a glass-braid supported matrix

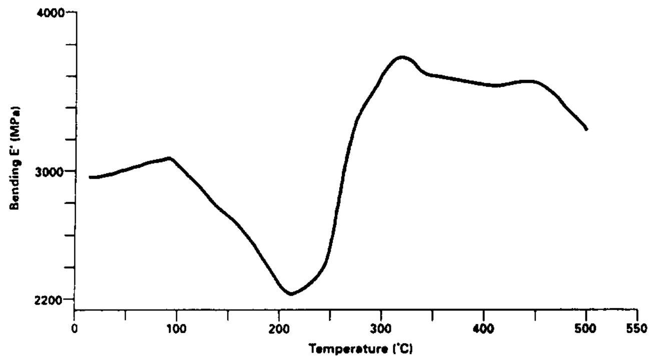
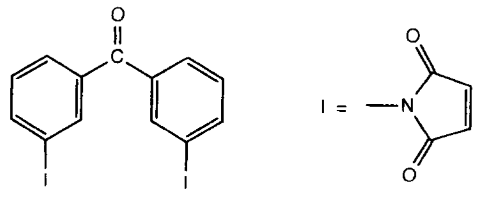


Figure 2 Curing profile of BMI (**13**)-impregnated glass braid as revealed by d.m.t.a.

reactive diluent, and finally of a conventional BMI cure onset temperature.

Evidence of early softening and conventional cure are observed in this work in the d.m.t.a. profile of Matrimide 5292 (*Figure 1*) at around 50 and 200°C, respectively. The conventional d.m.t.a. profile of BMI (**13**) (*Figure 2*) is gradually modified by increasing the molar ratio of *m*-tolualdehyde azine (**6b**) additive. *Figures 3a–e* were recorded from azine: BMI ratios of 1.00:6.38, 1.00:3.19, 1.00:2.13, 1.00:1.60 and 1.00:1.38, respectively. The temperature for onset of softening is lowered (see *Figure 3a*) and there is evidence for a low temperature process (~140°C) followed by a softening (~160°C) before the conventional onset of BMI curing (~220°C) (see *Figure 3c*). As the mole ratio of reactants approaches 1:1 (see *Figure 3d*) the low temperature process becomes dominant. A probably explanation for the profiles (*Figures 2* and *3*) is that criss-cross cycloaddition occurs at around 125°C causing chain extension, with a concomitant rise in storage modulus. The process observed near 200°C will represent a combination of events including the conventional BMI cure, in addition to the cure of cycloadducts from criss-cross cycloaddition.



(13)

The behaviour of lutidine *N*-oxide (**9**) with BMI (**13**) is less marked at low concentration of additive (*N*-oxide: BMI ratio, 1:3.30) (see *Figure 4a*), but increasing the additive concentration (*N*-oxide:BMI mole ratios, 1:1.10 and 1:0.82) provides d.m.t.a. profiles very similar in type (see, for example, *Figure 4b*) to the BMI/azine system (see *Figure 3d*).

It is known[15–17] that the maleimide/lutidine *N*-oxide reaction occurs at a reasonable rate in toluene under reflux (~110°C). The rise in storage modulus around 100–120°C can be ascribed to the maleimide/*N*-oxide interaction with concomitant rearrangement (cf. **11**→**12**); the curing region with onset at around 200°C can be rationalized in terms of a combination of BMI homopolymerization and BMI–*N*-oxide copolymerization.

The influence of lutidine *N*-oxide (**9**) and azine (**6c**) additives upon the thermal stability of cured resins was assessed in a quantitative manner from thermal gravimetric analysis. As would be anticipated, systems cured in the presence of reactive diluents suffer a deterioration, dependent upon concentration of additive, in thermal stability compared to that of the corresponding unmodified BMI resin. At low concentrations of additive (0.3 mol equiv) the impairment of thermal performance is moderate; for example, the neat resin based upon BMI (**13**) exhibits a temperature at which 10% weight loss is apparent (at a heating rate of 20°C min^{-1}) of 454°C compared to 409 and 414°C for formulations containing the azine (**6c**) and lutidine *N*-oxide, respectively (cf. *Table 1*).

Summary

The melting/curing profiles of BMI (**13**) have been recorded for homopolymerization and also in the presence of azine (**6b**) and *N*-oxide (**9**) additives. Processes with onset temperatures below the conventional BMI cure region can be tentatively ascribed to 1,3-dipolar cycloaddition reactions. The potential of 1,3-dipolar species (e.g. **6**, **9**) for use as BMI reactive diluents can be envisaged.

Acknowledgements

The work reported stemmed from a tripartite research programme between Heriot-Watt University, Lancaster University and BP plc. The permission of BP plc to publish this manuscript is gratefully acknowledged.

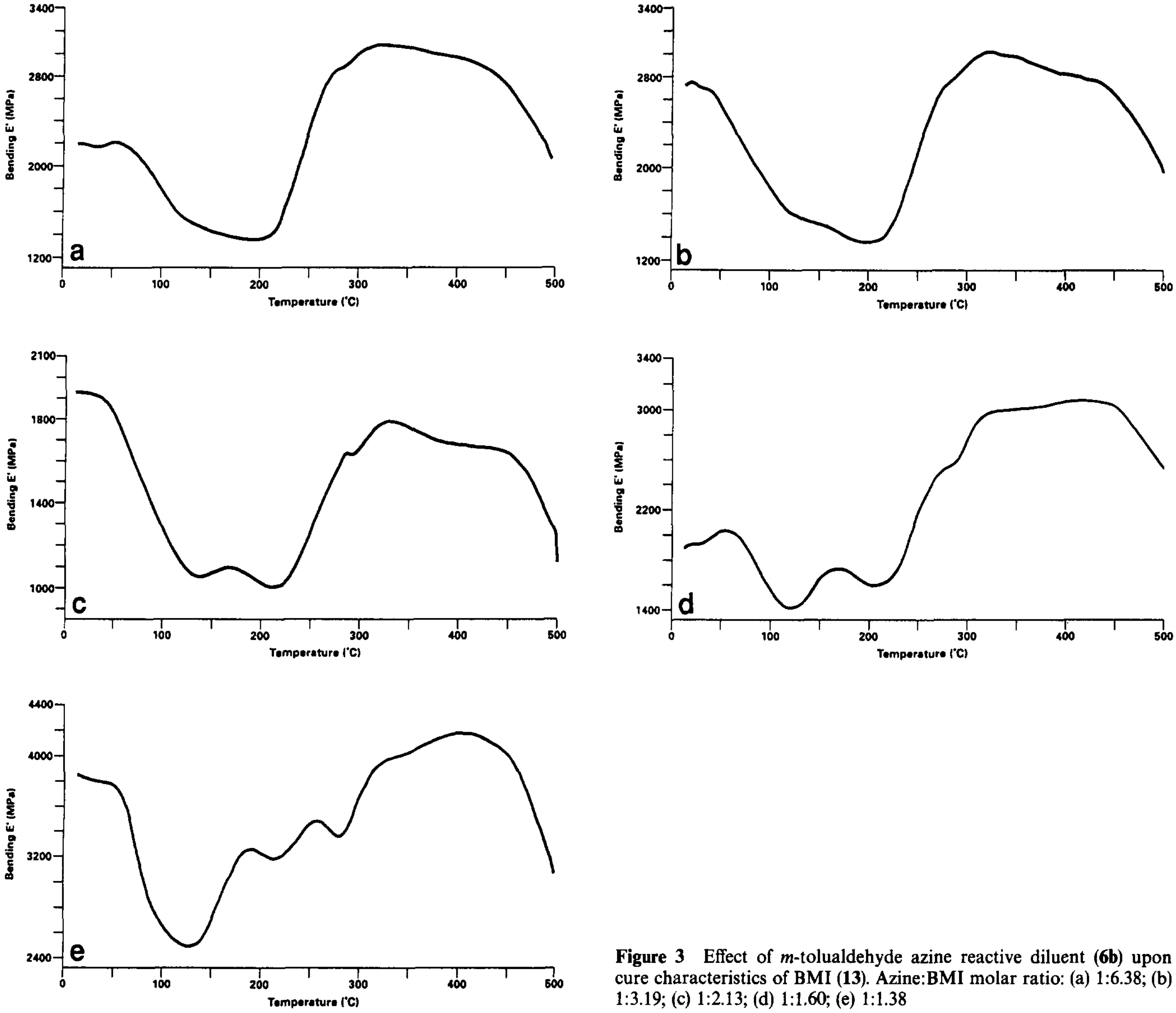


Figure 3 Effect of *m*-tolualdehyde azine reactive diluent (**6b**) upon cure characteristics of BMI (**13**). Azine:BMI molar ratio: (a) 1:6.38; (b) 1:3.19; (c) 1:2.13; (d) 1:1.60; (e) 1:1.38

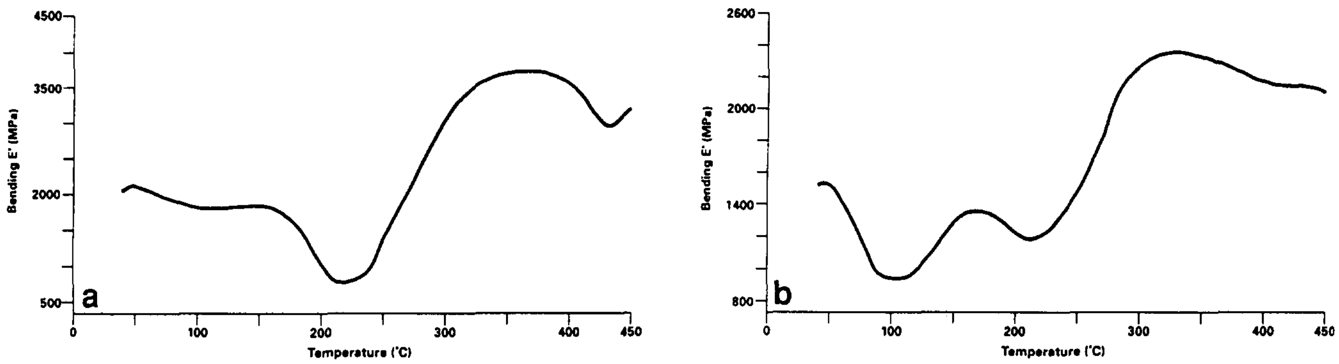


Figure 4 Effect of lutidine *N*-oxide reactive diluent (**9**) upon cure characteristics of BMI (**13**). Additive:BMI molar ratio: (a) 1:3.30; (b) 1:0.82

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