Studies on Bismaleimides and Related Materials. 4.† Synthesis and Characterization of New Bismaleimides Based on Terphenyl, Tetraphenylketazine, and Bisphenol A: "Reactive Building Blocks" for Bismaleimides

P. N. Preston,*,‡ V. K. Shah,‡ S. W. Simpson,‡ I. Soutar,*,§ and N. J. Stewart⊥

Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, U.K., The Polymer Centre, School of Physics and Materials, University of Lancaster, Lancaster LA1 4YA, U.K., and BP Research Centre, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN, U.K.

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ABSTRACT: New bismaleimides (BMI's) have been synthesized in the Bisphenol A (**2e**, **2k**), terphenyl (**3e**, **3f**), and tetraphenylketazine (**4c**) series. In three monomers, an additional functionality has been introduced with respect to conventional bismaleimides [viz., allyl (for **2k**), *N*-maleimido (**3f**), and ketazine (**4c**)]; a new term, "reactive building block" BMI's, is introduced to describe such monomers. Cure profiles for new monomers have been determined by dynamic mechanical thermal analysis by supporting them on glass braids. Resins have been prepared on a multigram scale and have been studied by thermal gravimetric analysis for evaluation of thermal and thermooxidative stability.

1. Introduction

Thermally induced homopolymerization of bismaleimides (BMI's, **1**) gives rise to resins with good thermooxidative stability and low moisture absorption characteristics.[1] Unfortunately, high cross-link densities can often impart brittle characteristics, and efforts have been made to copolymerize the BMI with "reactive diluents" to overcome the problem; such toughening modifiers include Bisphenol A (**2a**) derived *o*-allylphenols (e.g., **2b** used in Ciba Geigy's Matrimide 5292 resin)[2] and propenylarenes.[3] More recently, it has been suggested[4] that compounds, e.g., azines, capable of participating in 1,3-dipolar cycloaddition reactions could be candidates for evaluation as reactive diluents. Other approaches include the synthesis of oligomeric materials with pendant maleimide groups based on *N*-(4-phenoxyphenyl)maleimide/formaldehyde condensation products[5] and on hydrocarbon systems.[6]

In this paper we describe results on the synthesis of a bismaleimide (**3e**) and a trismaleimide (TMI) (**3f**) based on terphenyl. We also introduce the general concept of "reactive building block" BMI monomers in which the key structural features (functionality) of "reactive diluents" are incorporated in the BMI linking group (X in structure **1**; Chart 1). We selected as targets for synthesis new BMI's incorporating allylic groups and also an azine functionality.

2. Experimental Section

2.1. Materials and Techniques. Terphenyl was purchased from Lancaster Synthesis, and 4,4′-(1-methylethylidene)bis[phenol] (commonly known as Bisphenol A) was purchased from Aldrich and used without further purification. Palladium on charcoal (5%) was also purchased from Lancaster Synthesis. *N*,*N*-Dimethylformamide (DMF) was purified by storing over potassium hydroxide pellets overnight and then distilled from calcium oxide. Acetone (99.9%; HPLC grade) was bought from Aldrich.

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‡ Heriot-Watt University.

§ University of Lancaster.

⊥ BP Research Centre.

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^{1}H NMR spectra were recorded at 200 MHz on a Bruker WP-200SY spectrometer. Spectral analyses of allylic derivatives **2** are labeled with respect to **2** and also **2A**. Infrared spectra were run as KBr disks on a Pye-Unicam SP3-100. Melting points were determined on a Gallenkamp electrothermal apparatus and are uncorrected. Elemental analyses were carried out at the University of Manchester Institute of Science and Technology. For most compounds prepared in this work, data from elemental analyses were in accord with proposed structures, but discrepancies on values for carbon analysis were obtained for bismaleimide derivatives **2e** (~1%) and **3e** (~2%) and the bismaleamic acid derivative **4a** (~1%). For each of these compounds, spectroscopic analyses were in accord with proposed structures. Fast atom bombardment (FAB) mass spectra were measured through the SERC service, University College of Swansea.

Preparation of 4,4′-(1-Methylethylidene)bis[2-nitrophenol] (2c). Concentrated nitric acid (45 mL, density 1.42) was added dropwise over 2 h to a stirred mixture of 4,4′-(1-methylethylidene)bis[phenol] (45.0 g, 0.20 mol), toluene (225 mL), and glacial acetic acid (150 mL) maintained at 0–5 °C. The mixture was stirred for a further 1 h and then gradually allowed to warm to room temperature. On cooling to 0 °C, the bright yellow title compound crystallized, and this crop was separated by filtration and washed with cold water (500 mL). The solid was then washed with cold methanol (100 mL) and cold diethyl ether (100 mL) (yield 18.0 g). The filtrate from above was extracted with toluene (300 mL), and the toluene layer was separated, washed with water (2 × 300 mL), and then dried (Na_2SO_4). Evaporation of the toluene under reduced pressure gave a residue that was recrystallized from butan-2-one/2-propanol (2:1) to give a second crop of the title compound (**2c**) (11.2 g; total yield 29.2 g, 46%), mp 133–135 °C (lit.[7] mp 133–135 °C). IR ν_{max} (KBr) (cm^{-1}) 3200 (OH str) 2969 (CH str), 1530, 1370 (NO_2 str).

Preparation of 4,4′-(1-Methylethylidene)bis[2-aminophenol] (2d). Palladium on activated carbon (5%, 600 mg) dispersed in ethanol (20 mL) was added in small portions over a 1-h period to 4,4′-(1-methylethylidene)bis[2-nitrophenol] (29.0 g, 0.09 mol) and hydrazine hydrate (98%, 120 mL) in ethanol (600 mL). After the initial exotherm had subsided, the mixture was heated under reflux for 2 h. The product was filtered through Celite, and the Celite was then washed with methylated spirit (200 mL). The combined filtrate was evaporated under reduced pressure to leave an oil which crystallized on trituration with cold methylated spirit (50 mL). This solid was separated by filtration, washed with cold water (50 mL) and finally cold diethyl ether (100 mL), and then dried to give the title compound (**2d**) (19.1 g, 81%), mp 277–279 °C (lit.[8] mp 271 °C). IR ν_{max} (KBr) (cm^{-1}) 3420, 3330 (NH str), 3200–2800 (OH str). ^{1}H NMR (DMSO-d_6) δ 1.5 [s, 6H,

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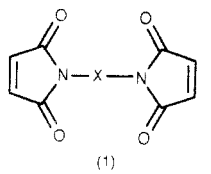
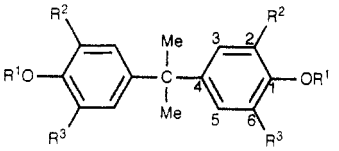
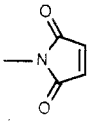
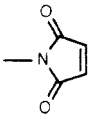
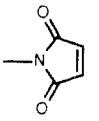
Chart 1

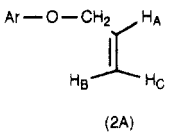


(1)

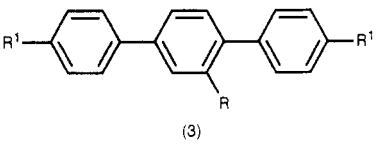


(2)

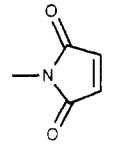
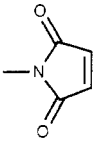
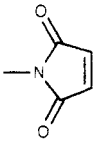
	R^1	R^2	R^3
a.	H	H	H
b.	H	H	$CH_2CH{=}CH_2$
c	H	NO_2	H
d.	H	NH_2	H
e.	$COCH_3$		H
f.	$CH_2CH{=}CH_2$	NO_2	H
g.	H	NO_2	$CH_2CH{=}CH_2$
h.	H	$NHCOCH_3$	H
i.	$CH_2CH{=}CH_2$	$NHCOCH_3$	H
j.	$CH_2CH{=}CH_2$	$NH_3^+Cl^-$	H
k.	$CH_2CH{=}CH_2$		H
l.	H		$CH_2CH{=}CH_2$

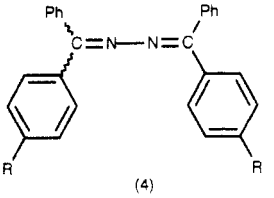


(2A)

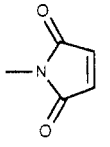


(3)

	R	R^1
a.	H	NO_2
b.	NO_2	NO_2
c.	H	NH_2
d.	NH_2	NH_2
e.	H	
f.		



(4)

	R
a.	NH_2
b.	$NHCOCH{=}CHCO_2H$
c.	

$C(CH_3)_2$], 4.4 (br s, 4H, NH_2), 6.2–6.5 (m, 6H, ArH), 8.6–8.8 (br s, 2H, OH).

Preparation of 4,4′-(1-Methylethylidene)bis[2-maleimido-*O*-acetylphenol] (2e). 4,4′-(1-Methylethylidene)bis[2-aminophenol] (**2d**) (2.58 g, 0.01 mol) in DMF (70 mL) was added to maleic anhydride (1.96 g, 0.02 mol) in DMF (30 mL) over 1 h at room temperature. The mixture was stirred at 35 °C for 2 h while maintained under an atmosphere of nitrogen. Anhydrous sodium acetate (0.45 g, 5.53 mmol) and potassium chloride (0.09 g, 1.21 mmol) were added, followed by acetic anhydride (10.2 g, 0.10 mol) in DMF (20 mL) over 0.5 h at room temperature; the mixture was then stirred for 6 h at 40–45 °C. The solvent was evaporated under reduced pressure to leave a brown oil that was extracted with ethyl acetate (250 mL). The ethyl acetate solution was washed with water (2 × 200 mL), dried (Na_2SO_4), and evaporated under reduced pressure to leave an oily residue. This was chromatographed [silica gel, methanol:chloroform (2:98) eluent] to give a fraction (R_f = 0.49) that was purified by reprecipitation from ethyl acetate solution by slow addition of the minimum amount of petroleum ether (bp 40–60 °C). Yield of **2e**: 1.2 g, 24%, mp 199–202 °C. Found: C, 63.6; H, 4.3; N, 5.4. $C_{27}H_{28}N_2O_8$ requires C, 64.54; H, 4.38; N, 5.58. IR ν_{max} (KBr) (cm^{-1}) 3100, 2980 (CH str), 1720 (C=O str). ^1H NMR ($CDCl_3$) δ 1.7 [s, 6H, $C(CH_3)_2$], 2.17 (s, 6H, $COCH_3$), 6.8 (s, 4H, CH=CH), 7.0–7.4 (m, 6H, ArH) (a minor impurity was evident from observation of a doublet resonance at δ 2.20).

Preparation of 4,4′-(1-Methylethylidene)bis[2-nitro-*O*-(2-propenyl)phenol] (2f).[9] 4,4′-(1-Methylethylidene)bis[2-nitrophenol] (**2c**) (13.32 g, 0.042 mol), anhydrous potassium carbonate (12.74 g, 0.092 mol), allyl bromide (11.16 g, 0.092 mol), and dry acetone (50 mL) were heated under reflux for 24 h. On cooling, the bright orange precipitate was filtered and the filtrate set aside. The solid was extracted with diethyl ether (5 × 250 mL), and the ether extract was combined with the acetone solution from above. The combined extract was evaporated under reduced pressure to leave a residue that was recrystallized from diethyl ether to give the bright orange title compound (**2f**) (two crops, total yield 14.0 g, 84%), mp 68–69 °C. Found: C, 63.0; H, 5.5; N, 7.2. $C_{21}H_{22}N_2O_6$ requires C, 63.32; H, 5.53; N, 7.04. IR ν_{max} (KBr) (cm^{-1}) 3060, 2960, 2920, 2860 (CH str), 1830, 1370 (NO_2 str), 1240 (CO str). ^1H NMR ($CDCl_3$) δ 1.7 [s, 6H, $C(CH_3)_2$], 4.66 (dt, 4H, J = 4.9 and 1.5 Hz, OCH_2), 5.31 (dq, 2H, $J_{H_A-H_C}$ = 10.5 Hz, $J_{H_C-CH_2} = J_{H_C-H_B}$ = 1.6 Hz, H_C), 5.46 (dq, 2H, $J_{H_B-H_A}$ = 17.2 Hz, $J_{H_B-CH_2} = J_{H_B-H_C}$ = 1.6 Hz, H_B), 6.01 (qt, 2H, $J_{H_A-H_B}$ = 17.7 Hz, $J_{H_A-H_C}$ = 10.5 Hz, $J_{H_A-CH_2}$ = 4.9 Hz, H_A), 6.99 (d, 2H, J = 8.8 Hz, H-6 and H-6′), 7.27 (2H, dd, J = 8.8 and 2.5 Hz, H-5 and H-5′), 7.73 (d, 2H, J = 2.5 Hz, H-3 and H-3′). m/z 398 (87%) [$M^{\cdot+}$].

Preparation of 4,4′-(1-Methylethylidene)bis[2-nitro-6-(2-propenyl)phenol] (2g). 4,4′-(1-Methylethylidene)bis[2-nitro-*O*-(2-propenyl)phenol] (**2f**)[9] (12.9 g, 0.032 mol) and diphenyl ether (30 mL) were heated on a sand bath at 200 °C for 4 h under an atmosphere of nitrogen. The product was cooled and the viscous dark brown oil was chromatographed (silica gel, ethyl acetate: petroleum ether (bp 40–60 °C) (2:98) eluent). The resulting yellow oil was triturated with cold methylated spirit (*ca.* 5 mL) to give

the yellow title compound (4.64 g, 36%), mp 68.5–69 °C. Found: C, 63.4; H, 5.4; N, 6.9. $C_{21}H_{22}N_2O_6$ requires C, 63.32; H, 5.53; N, 7.04. IR ν_{max} (KBr) (cm^{-1}) 3415 (OH str), 3170, 2968 (CH str), 1537, 1327 (NO_2 str). ^1H NMR ($CDCl_3$ δ 1.7 [s, 6H, $C(CH_3)_2$], 3.40 (d, 4H, J = 6.5 Hz, $CH_2CH{=}CH_2$), 4.93–5.10 (m, 4H, $CH_2CH{=}CH_2$), 5.76–6.01 (m, 2H, $CH_2CH{=}CH_2$), 7.17 (d, 2H, J = 2.1 Hz, H-5,5'), 7.91 (d, 2H, J = 2.4 Hz, H-3,3'). m/z 398 (23%) [$M^{\bullet+}$].

Preparation of 4,4'-(1-Methylethylidene)bis[2-acetamidophenol] (2h). 4,4'-(1-Methylethylidene)bis[2-aminophenol] (**2d**) (5.16 g, 0.02 mol), water (60 mL), and acetic anhydride (5.19 g, 0.05 mol) were heated on a boiling water bath for 45 min with occasional shaking. After the mixture was cooled to room temperature, the pale gray precipitate was separated by filtration, washed with water (100 mL), and dried to give the pure title compound (6.28 g, 92%), mp 277–280 °C. Found: C, 66.4; H, 6.3; N, 8.2. $C_{19}H_{22}N_2O_4$ requires C, 66.67; H, 6.43; N, 8.19. IR ν_{max} (KBr) (cm^{-1}) 3400 (NH str), 3300–2500 (OH str), 1660 (C=O str). ^1H NMR (DMSO-d_6) δ 1.5 [s, 6H $C(CH_3)_2$], 2.1 (s, 6H, $COCH_3$), 6.4–6.8 (m, 4H, ArH), 7.3–7.5 (m, 2H, ArH), 9.4 (s, 2H, NH), 9.5–9.6 (br s, 2H, OH).

Preparation of 4,4'-(1-Methylethylidene)bis[2-acetamido-*O*-(2-propenyl)phenol] (2i). 4,4'-(1-Methylethylidene)bis[2-acetamidophenol] (**2h**) (6.17 g, 0.018 mol), anhydrous potassium carbonate (5.49 g, 0.04 mol), allyl bromide (4.80 g, 0.04 mol), and dry acetone (170 mL) were heated under reflux for 24 h. The mixture was cooled and the solvent evaporated under reduced pressure to leave a solid cream residue that was extracted by digesting with diethyl ether (5 × 200 mL). Diethyl ether was evaporated under reduced pressure and the solid residue was chromatographed [silica gel, ethyl acetate:petroleum ether, bp 40–60 °C (1:1) eluent] to give a cream oil. This oil was dissolved in ethyl acetate (10 mL), and petroleum ether (bp 40–60 °C) was added slowly to precipitate the title compound (6.81 g, 89%), mp 109–110 °C. Found: C, 71.2; H, 7.0; N, 6.6. $C_{25}H_{30}N_2O_4$ requires C, 71.09; H, 7.11; N, 6.63. IR ν_{max} (cm^{-1}) 3303 (NH str), 3010, 2966 (CH str), 1683 (C=O str). ^1H NMR ($CDCl_3$) δ 1.6 [s, 6H, $C(CH_3)_2$], 2.1 (s, 6H, $COCH_3$), 4.5 (dt, 4H, J = 5.4 and 1.4 Hz, OCH_2), 5.28 (dq, 2H, $J_{H_A-H_C}$ = 10.7 Hz, $J_{H_C-H_B}$ = $J_{H_C-CH_2}$ = 1.4 Hz, H_C), 5.37 (dq, 2H, $J_{H_B-H_A}$ = 17.5 Hz, $J_{H_B-CH_2}$ = $J_{H_B-H_C}$ = 1.5 Hz, H_B), 6.04 (qt, 2H, $J_{H_A-H_B}$ = 17.3 Hz, J_{HA-H_C} = 10.6 Hz, $J_{H_A-CH_2}$ = 5.2 Hz, H_A), 6.68–6.86 (m, 4H, ArH), 7.65–7.76 (br s, 2H, NH), 8.34 (d, 2H, J = 2.2 Hz, H-3 and H-3').

Preparation of 4,4'-(1-Methylethylidene)bis[2-amino-*O*-(2-propenyl)phenol] Dihydrochloride (2j). 4,4'-(1-Methylethylidene)bis[2-acetamido-*O*-(2-propenyl)phenol] (**2i**) (4.22 g, 0.01 mol) and 6 M hydrochloric acid (4 mL) were heated under an atmosphere of nitrogen for 3 h. The mixture was cooled and evaporated under reduced pressure to leave the title compound as a beige solid. This was dried over phosphorus pentoxide in a vacuum desiccator for 10 days, and the product (**2j**) (4.11 g, 100%) was used without further purification to analytical standard.

Preparation of 4,4'-(1-Methylethylidene)bis[2-(*N*-maleimido)-*O*-(2-propenyl)phenol] (2k). Dry nitrogen gas was bubbled through a solution of 4,4'-(1-methylethylidene)bis[2-amino-*O*-(2-propenyl)phenol] dihydrochloride (**2j**) (4.11 g, 0.01 mol) in DMF (75 mL) and triethylamine (2.23 g, 0.022 mol) for 15 min. This was then added over 30 min to a solution of maleic anhydride (1.96 g, 0.02 mol) in DMF (20 mL). The mixture was stirred at 35 °C for 6 h under an atmosphere of nitrogen. The product was cooled and the solvent was evaporated under reduced pressure to leave a brown oil. This oil was dissolved in ethyl acetate (500 mL), and the extract was washed with water (2 × 75 mL), dried (Na_2SO_4), and evaporated under reduced pressure. The residual oil was dissolved in DMF (50 mL), and sodium carbonate (0.53 g, 5 mmol) was added; acetic anhydride (3.26 g, 0.032 mol) in DMF (10 mL) was then added dropwise over 30 min, and the mixture was stirred at 40–45 °C for 6 h under an atmosphere of nitrogen. The product was cooled and the solvent was evaporated under reduced pressure to leave a brown oil. The oil was extracted into ethyl acetate (250 mL), the solution was washed with water (2 × 75 mL) and then dried (Na_2SO_4), and the solvent was evaporated under reduced pressure. The residual dark yellow-brown solid was chromatographed [silica gel, ethyl acetate:petroleum ether (bp 40–60 °C) (30:70) eluent] to give the title compound (R_f = 0.19) as a yellow solid (1.70 g, 34%), mp 121.5–123.5 °C. Found: C, 69.9; H, 5.3; N, 5.6. $C_{29}H_{26}N_2O_6$ requires C, 69.88; H, 5.22; N, 5.62. IR ν_{max} (KBr) (cm^{-1}) 3092, 2969 (CH str), 1771 (sh), 1717 (C=O str). m/z (FAB) 499 (M + H)$^{\bullet+}$. ^1H NMR ($CDCl_3$) δ 1.6 [s, 6H, $C(CH_3)_2$], 4.48 (dt, 4H, J = 4.9 and 1.6 Hz, OCH_2), 5.18 (dq, 2H, $J_{H_A-H_C}$ = 10.5 Hz, $J_{H_C-CH_2}$ = $J_{H_C-H_B}$ = 1.5 Hz, H_C), 5.26 (dq, 2H, $J_{H_B-H_C}$ = 17.3 Hz, $J_{H_B-CH_2}$ = $J_{H_B-H_C}$ = 1.6 Hz, H_B), 5.89 (qt, 2H, $J_{H_A-H_B}$ = 17.4 Hz, $J_{H_A-H_C}$ = 10.3 Hz, $J_{H_A-CH_2}$ = 4.9 Hz, H_A), 6.80 (s, 4H, COCH=CHCO), 6.87 (d, 2H, J = 8.7 Hz, H-6 and H-6'), 7.07 (d, 2H, J = 2.4 Hz, H-3 and H-3'), 7.17 (dd, 2H, J = 8.7 and 2.5 Hz, H-5 and H-5').

Preparation of 4,4''-Dinitroterphenyl (3a). A mixture of fuming nitric acid (75 mL, density 1.5) and glacial acetic acid (50 mL) was added dropwise over 15 min to a solution of *p*-terphenyl (10.0 g, 0.434 mol) in glacial acetic acid (500 mL) held under reflux. After heating under reflux for a further 1.5 h, the product was cooled to precipitate pale yellow crystalline 4,4''-dinitroterphenyl (**3a**). This was recrystallized from pyridine to give a pure product (4.7 g, 34%), mp 282–285 °C (lit.[10] mp 274–275 °C). IR ν_{max} (KBr) (cm^{-1}) 1520, 1340 (NO_2 str).

Preparation of 2',4,4''-Trinitroterphenyl (3b). A mixture of fuming nitric acid (150 mL, density 1.5) and glacial acetic acid (100 mL) was added dropwise over 15 min to a solution of *p*-terphenyl (20.0 g, 0.086 mol) in glacial acetic acid (1 L) held under reflux. After heating under reflux for a further 7 days, the product was cooled in ice to precipitate a yellow solid. After filtration, the filtrate was added to ice water to precipitate more of the yellow solid. The combined precipitates were crystallized three times from ethyl acetate to give 2',4,4''-trinitroterphenyl (**3b**) (6.4 g, 20%), mp 206–208 °C. Found: C, 59.3; H, 2.7; N, 11.3. $C_{18}H_{11}N_3O_6$ requires C, 59.17; H, 3.01; N, 11.51. IR ν_{max} (KBr) (cm^{-1}) 1520, 1350 (NO_2 str). ^1H NMR (DMSO-d_6) δ 7.6–7.9 (m, 3H), 8.0–8.6 (m, 8H).

Preparation of 4,4''-Diaminoterphenyl (3c). Stannous chloride dihydrate (50.0 g, 0.22 mol) in concentrated hydrochloric acid (50 mL) was added dropwise over 15 min to a solution of 4,4''-dinitroterphenyl (**3a**) [10.0 g, 0.031 mol] in glacial acetic acid (1.5 L) held under reflux. The mixture was heated for a further 15 min under reflux, cooled, and filtered. The gray solid was boiled with aqueous sodium hydroxide (100 mL, 20%) to liberate an orange solid, which was filtered, washed with water (500 mL), and then recrystallized from pyridine to give the title compound (**3c**) (4.2 g, 52%), mp 248–253 °C (lit.[11] mp 242 °C). IR ν_{max} (KBr) (cm^{-1}) 3490, 3420 (NH str). ^1H NMR (DMSO-d_6) δ 5.2 (br, 4H, exch NH_2), 6.65 (d, 4H, J = 10 Hz, ArH), 7.38 (d, 4H, J = 10 Hz, ArH) (A_2B_2 system), 7.4 (s, 4H, ArH). m/z 260 ($M^{\bullet+}$).

Preparation of 2',4,4''-Triaminoterphenyl (3d). A slurry of palladium on charcoal (5%, 800 mg) in ethanol (10 mL) was added in small portions over 30 min to a mixture of 2',4,4''-trinitroterphenyl (**3b**) (2.4 g, 6.58 mmol), hydrazine hydrate (20 mL, 98%), and ethanol (75 mL). The mixture was warmed slowly to reflux temperature and held under reflux for 2 h. The product was filtered while hot through Celite, and the Celite was then washed with hot methylated spirit (2 × 75 mL). The solvent was evaporated under reduced pressure, the residual solid was dissolved in the minimum amount of hot ethanol, and the solution was added to twice the volume of water. The white precipitate was filtered, washed with water (2 × 100 mL), and then dried. It was finally washed with cold petroleum ether (bp 40–60 °C) and dried to give the pure title compound (**3d**) (1.5 g, 83%), mp 176–177 °C. Found: C, 78.3; H, 6.2; N, 15.5. $C_{18}H_{17}N_3$ requires C, 78.54; H, 6.18; N, 15.28. IR ν_{max} (KBr) (cm^{-1}) 3380, 3310 (NH str). ^1H NMR (DMSO-d_6) δ 4.8 (br, 2H, NH_2), 5.1 (br, 4H, NH_2), 7.13–7.85 (m, 11H, ArH). m/z 275 ($M^{\bullet+}$).

Preparation of 4,4''-Bismaleimidoterphenyl (3e). 4,4''-Diaminoterphenyl (3.0 g, 11.5 mmol) in (DMF) (50 mL) was added dropwise over 45 min into a solution of maleic anhydride (2.26 g, 0.0023 mol) in DMF (20 mL) at room temperature under an atmosphere of nitrogen; the mixture was then stirred at 35 °C for 2.5 h. Anhydrous sodium carbonate (0.53 g) was added followed by acetic anhydride (3.75 g, 3.2 mol equiv with respect to the bismaleamic acid) in DMF (10 mL) over 30 min at room temperature. The mixture was then stirred for 3 h at 40 °C, cooled, and added slowly to ice water (400 mL) to precipitate a brownish-yellow solid. This was washed with water (800 mL),

then dried, and washed finally with diethyl ether (100 mL) to give the title compound (**3e**) (8.52 g, 88%), mp > 360 °C. Found: C, 72.1; H, 3.7; N, 6.7. $C_{26}H_{16}N_2O_4$ requires C, 74.29; H, 3.81; N, 6.67. IR ν_{max} (KBr) (cm^{-1}) 3060 (CH str), 1700 (C=O str). *m/z* (FAB) 421 $(M + H)^{\bullet+}$

Preparationof2′,4,4″-Trismaleimidoterphenyl(3f). 2′,4,4″-Triaminoterphenyl (1.44 g, 5.24 mmol) in DMF (50 mL) was added dropwise over 30 min to a solution of maleic anhydride (1.54 g, 15.7 mmol) in DMF (10 mL) at room temperature. The mixture was stirred at 35 °C for 3 h and then cooled to room temperature. Anhydrous sodium carbonate (0.45 g) was added followed by acetic anhydride (1.71 g, 4.8 mol equiv with respect to the trismaleamic acid) in DMF (15 mL) over 30 min at room temperature. The mixture was stirred for 3 h at 40 °C, then cooled, and added slowly to ice water (300 mL). The precipitate was separated by filtration, washed with water (600 mL), and then air-dried. The solid was finally washed with cold petroleum ether (100 mL) (bp 40–60 °C) to give the title compound (2.68 g, 96%), mp 180–190 °C. Found: C, 69.6; H, 3.4; N, 8.1. $C_{30}H_{17}N_3O_6$ requires C, 69.90; H, 3.30; N, 8.16. IR ν_{max} (KBr) (cm^{-1}) 1700 (C=O str). ^1H NMR (DMSO-d_6) δ 7.0–7.2 (m, 6H, COCH=CHCO), 7.3–7.8 (m, 11H, ArH). *m/z* (FAB) 516 $(M + H)^{\bullet+}$.

Preparation of the Bismaleamic Acid (4b) from 4,4′-Diaminotetraphenylketazine (4a). 4,4′-Diaminotetraphenylketazine (**4a**) was prepared in 42% by a literature procedure:[12] mp 235–237 °C (lit.[12] mp 225–226 °C). IR ν_{max} (KBr) (cm^{-1}) 3440, 3360 (NH str), 1620 (CN str). ^1H NMR ($CDCl_3$) δ 3.5–3.9 (br, 4H, NH_2), 6.3–6.7 (m, 4H, ArH), 7.0–7.6 (m, 14H, ArH).

4,4′-Diaminotetraphenylketazine (2.0 g, 5.13 mmol) in DMF (10 mL) was added dropwise over 30 min to a stirred solution of maleic anhydride (1.01 g, 10 mmol) at room temperature under an atmosphere of nitrogen. After 6 h of stirring at 35 °C, the product was cooled and evaporated to dryness under reduced pressure. The solid residue was triturated with ethyl acetate (3 × 75 mL) to give an orange solid which was filtered and washed with cold petroleum ether (bp 40–60 °C) (150 mL). The final air-dried product (**4b**) (2.17 g, 73%) had mp 209–211 °C. Found: C, 70.6; H, 4.7; N, 9.6. $C_{34}H_{26}N_4O_6$ requires C, 69.62; H, 4.44; N, 9.56. IR ν_{max} (KBr) (cm^{-1}) 3360 (NH str), 3060 (CH str), 3300–2500 (OH str), 1710 (C=O str). ^1H NMR [$(CD_3)_2CO$] δ 6.52 (dd, 2H, J = 12.8 Hz, COCH=CHCO$_2$H), 6.54 (dd, 2H, J = 12.7 Hz, COCH=CHCO$_2$H), 7.01 and 7.04 (singlets assigned to COCH=CHCO from formation of **4c**), 7.1–7.8 (m, 18H, ArH). *m/z* (FAB) 587 $(M + H)^{\bullet+}$.

Preparation of 4,4′-Bismaleimidotetraphenylketazine (4c). Anhydrous sodium acetate (0.354 g, 4.3 mmol) and potassium chloride (0.071 g, 0.95 mmol) were added to a solution of the bismaleamic acid derived from 4,4′-diaminotetraphenylketazine (**4b**) (3.54 g, 6.04 mmol) in DMF (50 mL) at room temperature under an atmosphere of nitrogen. Acetic anhydride (1.97 g, 19 mmol) in DMF (10 mL) was then added dropwise over 15 min, and the mixture was stirred and heated at 40 °C for 3 h. The product was cooled and evaporated to dryness under reduced pressure. The residual solid was extracted into ethyl acetate (250 mL), and the extract was washed with saturated sodium hydrogen carbonate (100 mL) and then water (2 × 200 mL) and dried (Na_2SO_4). The solvent was then evaporated under reduced pressure to leave a yellow solid that was purified by reprecipitation from ethyl acetate (20 mL) with petroleum ether (ca. 200 mL). The title compound (**4c**) (2.86 g, 88%) had mp >360 °C. Found: C, 73.9; H, 4.2; N, 9.9. $C_{34}H_{22}N_4O_4$ requires C, 74.18; H, 4.00; N, 10.18. IR ν_{max} (KBr) (cm^{-1}) 1700. ^1H NMR ($CDCl_3$) δ 6.85 and 6.88 (singlets, 4H, COCH=CHCO), 7.2–7.7 (m, 18H, ArH). *m/z* (FAB) 551 $(M + H)^{\bullet+}$.

2.2. Polymer Synthesis and Characterization. For DMTA studies monomers were dissolved in an appropriate solvent: **2e** and **2k** were dissolved in dichloromethane while **3e**, **3f**, and **4c** were dissolved in DMF (**3e** also required heating to 40 °C to obtain a homogeneous solution). The solutions were then used to impregnate glass braid (Vidatape C, 13 × 0.09 mm) (Jones Stroud Insulations). Braids were then dried in air at 25 °C for 24 h.

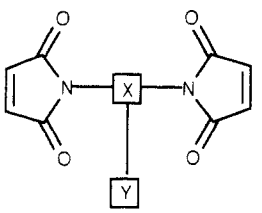
DMTA studies were conducted on a Polymer Laboratories DMTA unit using a test frequency of 10 Hz and a heating rate of 5 °C/min.

Cure cycles for the quantitative preparation of resins were 1 h at 180 °C, 2 h at 200 °C, and 6 h at 250 °C; and also 1 h at 180 °C, 2 h at 200 °C, 2 h at 250 °C, and 6 h at 300 °C.

The thermal and thermooxidative stabilities of the cured resins were measured using a Perkin-Elmer TGA-7 or TGA-2 machine with heating rates of 20 °C/min.

3. Results and Discussion

3.1. Synthesis. The synthetic chemistry and polymer characterization ensuing from bismaleimides are dominated by compounds **1** where two maleimide rings are joined by a variety of linking groups (X). In this work we describe the synthesis and polymerization of compounds **5** in which an additional reactive functional group is incorporated (see Y in structure **5**); a sensible terminology



(5)

Y

a. allyl - containing function

b. N - maleimido

c. azine - containing function

for such linkages (X–Y) is "reactive building blocks". An obvious class of such monomers would arise where Y is an *N*-maleimido group (see **5b** and cf. ref 5); a second class would incorporate in Y one or more reactive functionalities known to impart "reative diluent" properties to BMI comonomers [see, e.g., **5a** and (potentially)[4] **5c**]. In this paper we describe the synthesis of novel "reactive building blocks" in three categories: a trismaleimide based on terphenyl (cf. **3**), an allyl-containing BMI based on Bisphenol A (cf. **2**), and a BMI incorporating the ketazine framework (cf. **4**); in two of the groups studied (**2** and **3**), we have also synthesized, for comparison, BMI monomers that closely resemble the target "reactive building block" derivatives.

A first synthetic target was a reactive building block containing the allyl group to mimic, in part, Ciba-Geigy's Matrimide 5292 (see earlier and note structure **21** for a target based on Bisphenol A). Since thermally induced polymerization of the maleimido groups and Claisen rearrangement of allyl ethers would be expected to occur simultaneously, it was realized that the *O,O′*-diallyl bisphenol derivative **2k** would be a meaningful target. It was felt that a useful comparator BMI would be the bisphenol (**2**, R^2 = *N*-maleimido, $R^1 = R^3$ = H), but, in reality, the diester **2e** was isolated and purified and used for resin synthesis and characterization.

Nitration of Bisphenol A (concentrated HNO_3, glacial AcOH) gave the dinitro compound **2c** in moderate yield (46%), and reduction ($N_2H_4{\cdot}H_2O$/Pd-charcoal) gave the diamine **2d** in high yield. It is known[9] that *o*-aminophenols are air-sensitive, so imidization of the diamine **2d** was conducted under an atmosphere of nitrogen; the use of acetic anhydride as a cyclizing agent for the intermediate bismaleamic acid caused concomitant acetylation of the product, with the result that the diester **2** was actually isolated and used for resin synthesis. Our initial approach to synthesis of the bisallyl bismaleimide **2k** was through

Table 1. Cross-Linking Onset Temperatures of Bismaleimide Derivatives from DMTA

monomer	cure onset temp (°C)	monomer	cure onset temp (°C)
2e	271	**3f**	228
2k	206	**4c**	256
3e	282		

the bis allyl ether **2f**, which was easily prepared from dinitro-Bisphenol A (**2c**) and allyl bromide in the presence of anhydrous potassium carbonate. Claisen rearrangement of this diallyl ether (**2f**) gave the *O,O'*-diallyl-Bisphenol A derivative (**2g**) in modest yield (36%) but, regrettably, attempted reduction (N_2H_4·H_2O/Pd-charcoal) of the nitro groups caused concomitant reduction of the allyl groups, and the product di-*n*-propyl derivative (**2**, R^1 = H; R^2 = NO_2; R^3 = *n*-C_3H_7) could not be obtained analytically pure despite its desirability as a synthetic intermediate to a target comparator BMI (viz., **2**, R^1 = H; R^2 = *n*-C_3H_7; R^3 = *N*-maleimido).

The alternative approach was successful: 2,2'-diamino-Bisphenol A (**2d**) was protected as the *N,N'*-diacetylamino derivative (**2h**), and this was converted into the bisallyl ether (**2i**, 89%). The problematic[9] air sensitivity of *o*-aminophenols was circumvented by handling and isolation of the requisite diamine (**2**, R^1 = $CH_2CH{=}CH_2$, R^2 = NH_2, R^3 = H) as the dihydrochloride (**2j**). The free base of **2j** was generated in situ under an atmosphere of nitrogen and was routinely imidized to give the target "reactive building block" BMI (**2k**), albeit in modest yield (34%). An attempt was made to adduce spectral evidence that the bisallyl ether (**2k**) underwent the Claisen rearrangement (**2k** → **2e**; cf. **2f** → **2g**). Thus **2k** was heated in diphenyl ether at 200 °C for 3 h; a highly insoluble, intractable yellow-orange solid was isolated which could not be studied by NMR spectroscopy in solution. Infrared spectra (KBr disk and Nujol mull) showed a very weak, broad absorption (~3400–3250 cm^{-1}) which could be ascribed to OH stretching frequency.

Terphenyl was converted by a known[10] procedure into the dinitro derivative (**3a**; fuming HNO_3/glacial AcOH, reflux for 1.5 h), and, by extending the reflux time to 7 days, we were able to synthesize the trinitroterphenyl **3b**, albeit in low yield (20%). Reduction of **3a** and **3b** was achieved by stannous chloride/HCl and hydrazine hydrate/Pd-charcoal, respectively; imidization of **3a** and **3b** was carried out routinely to give high yields of the comparator BMI (**3e**) and the trismaleimide (TMI) (**3f**), respectively, in high yields.

A BMI (**4c**) in the ketazine series was selected as a target in view of the known reactivity of such substrates in criss-cross cycloaddition.[13] In this work the known diamine **4a**[12] was converted into the "reactive building block" BMI **4c** through an isolable bismaleamic acid **4b**. It was clear from the ^1H NMR spectra of the latter (**4b**) and of the BMI derivative (**4c**) that mixtures of *E* and *Z* isomers were present (ratio ca. 0.7:1; see Experimental Section) but no attempt was made to separate them. No success was achieved in attempts to prepare a comparator BMI based on 1,1,4,4-tetraphenylbutane because of the inherent difficulty in obtaining the requisite 4,4''-dinitro derivative from a complex nitration product.

3.2. Polymer Characterization. Cure profiles were established by DMTA, over the temperature range 40–450 °C for each of the key monomers **2e**, **2k**, **3e**, **3f**, and **4c**. In the following discussion, comparisons are drawn between the "reactive building block" BMI's (**2k** and **3f**) and the respective model compounds (**2e** and **3e**); a suitable model for the azine-derived BMI (**4c**) was not available.

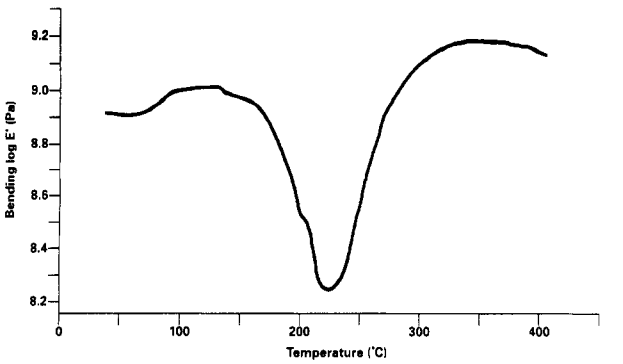


Figure 1. Cure profile from DMTA of bismaleimide **6**.

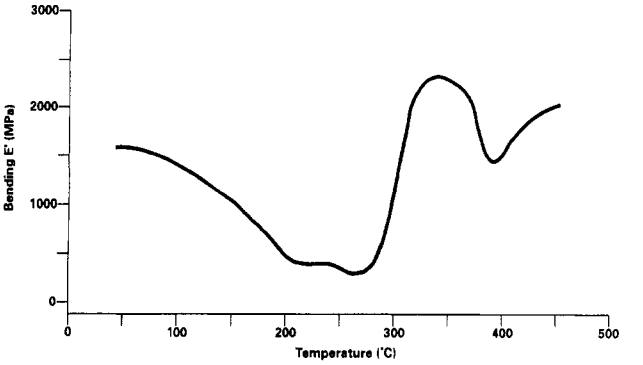
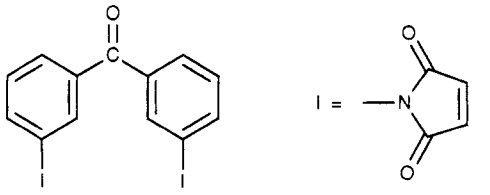
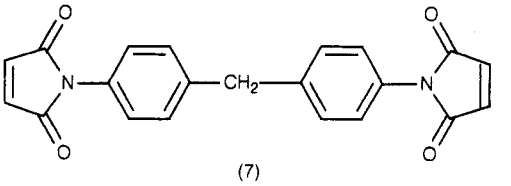


Figure 2. Cure profile from DMTA of bismaleimide **2e**.

It is instructive as a reference to consider a typical DMTA profile, as exemplified for curing of the benzophenone-based BMI (**6**) illustrated in Figure 1.[4] This shows



(6)



(7)

a softening region followed almost immediately by cross-linking (sharp rise in *E'*). The "model compound" **2e** derived from bisphenol A shows a similar softening/curing profile (Figure 2). In contrast, the functionalized BMI **2k** shows a very low temperature softening region followed by a rapid onset of curing at a temperature (ca. 235 °C) lowered compared to the model compound (**2e**, ca. 270 °C; see Table 1 and Figure 3). The early softening region observed for **2k** can be ascribed to the production of monomer mixtures, with associated melting point depression, through conversion by Claisen rearrangement (see **2k** → **2l**). The similarity of the profile for **2k** to that observed[4] for the Matrimide 5292 resin system (Figure 4) is evident and provides encouragement for scale up and process development work on **2k** and related "reactive building block" BMI's.

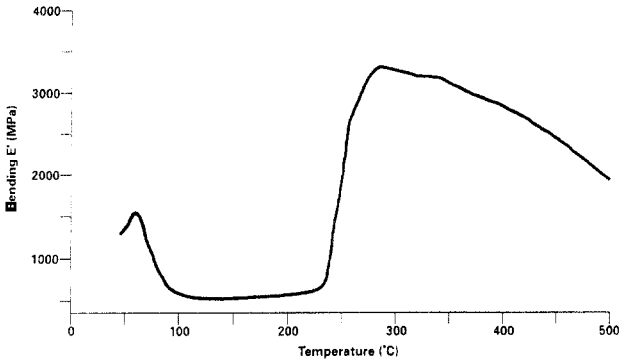


Figure 3. Cure profile from DMTA of bismaleimide **2k**.

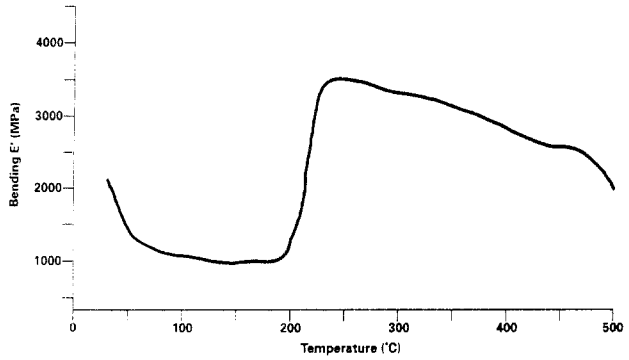


Figure 4. Cure profile from DMTA of Matrimide 5292 system **2b** + 7.

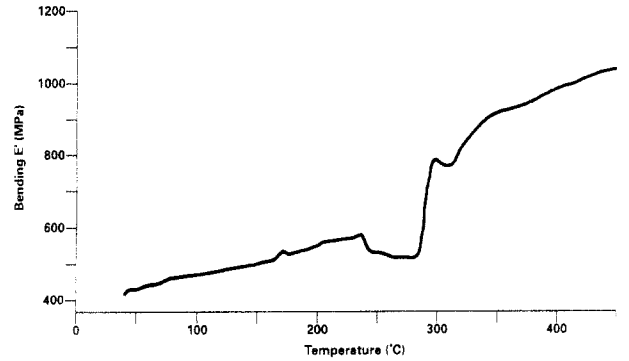


Figure 5. Cure profile from DMTA of bismaleimide **3e**.

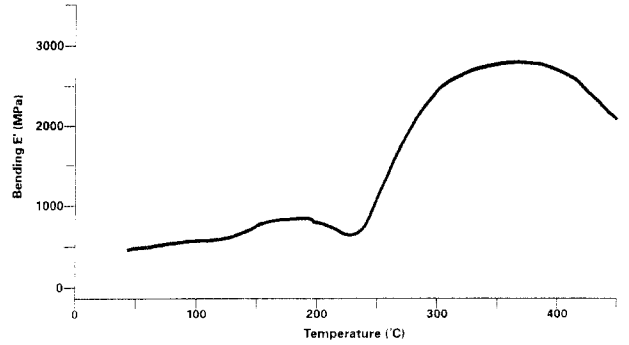


Figure 6. Cure profile from DMTA of trismaleimide **3f**.

Comparison of the terphenyl-derived trismaleimide **3f** and the model BMI **3e** is less clear-cut because of the large melting point differences between them (**3e**, >360 °C; **3f**, 180–190 °C). As would be expected, the BMI **3e** does not show a softening region, and presumably curing occurs in the solid state, with onset ca. 280 °C. Encouragingly, the cure onset temperature for the reactive building block BMI (**3f**, ca. 230 °C) is reduced by comparison with the model compound (**3e**, ca. 280 °C) (see Figures 5 and 6).

A comparator BMI for the azine-functionalized BMI **4c** could not be synthesized, but an interesting feature is

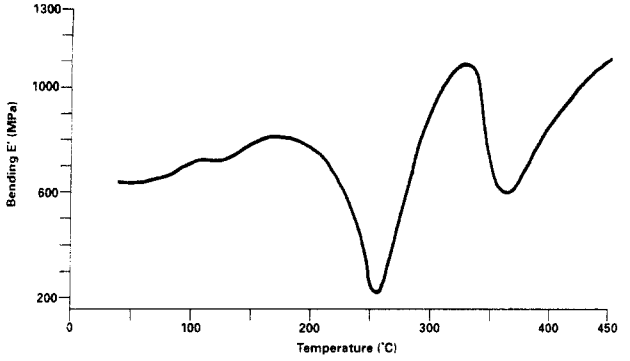


Figure 7. Cure profile from DMTA of bismaleimide **4c**.

Table 2. Thermal and Thermooxidative Stability of Bismaleimide Resins from Thermal Gravimetric Analysis[a]

	air			nitrogen		
monomer structure	temp (°C) for 5% wt loss	temp (°C) for 10% wt loss	% residue at 1000 K	temp (°C) for 5% wt loss	temp (°C) for 10% wt loss	% residue at 1000 K
2e	382 (420)	393 (430)	28 (5)	384 (419)	393 (436)	41 (45)
2k	417 (430)	446 (456)	27 (14)	421 (443)	446 (491)	47 (48)
3e	394 (433)	423 (460)	0 (0)	440 (465)	477 (508)	58 (63)
3f	443 (441)	476 (495)	27 (6)	466 (448)	488 (480)	65 (62)
4c	360 (359)	366 (402)	0 (10)	357 (429)	400 (492)	33 (64)

[a] See Experimental Section for low- and high-temperature cure regimes. Data from the high-temperature cure regime are given in parentheses.

evident in the DMTA trace (Figure 7). The initial cure profile features (softening/curing) are conventional (cf. Figure 1), but a secondary softening/curing process is observed at higher temperature (cure onset ca. 365 °C); a similar feature is observed in the DMTA investigation of the Bisphenol A derived BMI **2e** (cure onset ca. 400 °C; see Figure 2). It is likely that these effects arise from resin glass transitions followed by secondary cure processes, but further work is required to establish the nature of these events.

Cured resins were prepared for subsequent analysis of thermal stability from each of the BMI monomers using the cure cycle employed for production of Matrimide 5292 resin, 1 h at 180 °C, 2 h at 200 °C, and 6 h at 250 °C. However, because the cure onset, as established by DMTA, for compounds **2e**, **3f**, and **4c** occurs at temperatures greater than 250 °C (see Table 1), each of the five monomers was also subjected to a higher temperature cure regime, i.e., 1 h at 180 °C, 2 h at 200 °C, 2 h at 250 °C, and 6 h at 300 °C; by this means, an attempt was made to establish maximum cross-linked density in the cured resins. The materials obtained under the two different cure cycles were evaluated by TGA for thermal and thermooxidative stabilities (see Table 2). Superior thermal and thermooxidative stabilities were achieved in all cases, as a result of the higher temperature cure cycle.

4. Summary

Novel bismaleimides have been synthesized in which an additional reactive functional group is incorporated; we describe such monomers as "reactive building block" BMI's. In the examples described, the reactive functionalities are an allylic group (**2k**), an additional maleimido ring (**3f**), and a ketazine moiety (**4c**). Important characteristics of **2k** and **3f** are the relatively low onset of curing temperatures compared to model compounds **2e** and **3e**, respectively; an additional softening/curing region is apparent in the DMTA profile of **4c** but the detailed chemical nature of this event has not been determined.

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