Synthesis and structure–property relationships of bismaleimides containing oxyalkylene linkages*

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The synthesis and the effects of variation in structure on the resulting processing and final properties of a series of bismaleimides based on diamines containing flexible units of variable length or flexible units of fixed length with varying-length pendent groups is presented. Thermal analysis, parallel-plate rheometry and torsion impregnated-cloth analysis were utilized to characterize the processing, cure and final properties. It was found that, by appropriately choosing the size of main-chain and pendent aliphatic groups in bismaleimides containing oxyalkylene linkages, one can control the breadth of the cure window without adversely affecting either thermal stability or final glass transition temperatures.

(Keywords: bismaleimides; oxyalkylene; synthesis; dynamic mechanical analysis; parallel-plate rheometry; torsion impregnated cloth analysis)

INTRODUCTION

Bismaleimides (BMI) are thermally curable monomers or oligomers that produce thermoset resins with high thermal stability and low water susceptibility and can be used as matrix resins for advanced composites[1]. These monomers or oligomers cure through addition reactions to give highly crosslinked network polyimides having good physical and mechanical properties[2]. Owing to the low molecular weights, these monomers are inherently more processible by melt or solution processes than are linear polyimides. Bismaleimides do have problems with solvent retention, high curing temperature, brittleness and high T_g of the final polymer due to the high crosslink density obtained in the network polymers[3,4].

Recently, a series of diamines containing flexible units of varying length or flexible units of fixed length with pendent groups of varying length have been incorporated in polyimide systems[5]. It was considered desirable to utilize these diamines in bismaleimide structures in order to improve their processibility and resultant properties. The research reported here studies the synthesis and the effects of variation in structure on the resulting processing and final properties of bismaleimides based on the aforementioned diamines.

EXPERIMENTAL

Instrumentation and chemicals

Melting points were obtained on an Electrochemical capillary melting-point apparatus and are uncorrected. Nuclear magnetic resonance (n.m.r.) spectra were obtained using a Varian EM-360-A spectrometer (^1H) and an IBM AF-100 spectrometer (^1H and ^{13}C). All samples were run in deuterated chloroform or dimethylsulphoxide (DMSO) with tetramethylsilane (TMS) as an internal standard at a concentration of approximately 10% (w/v). Infra-red spectra (i.r.) were recorded with a Perkin–Elmer 1600 Series FTIR using KBr discs. Mass spectrometric analysis was performed on a Finnigan MAT INCOS 50 spectrometer with a solids probe inlet. Elemental analyses were performed by Midwest Micro Laboratories, Indianapolis, Indiana. Differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.) data were obtained with a Perkin–Elmer Series 7 thermal analysis system. All starting materials were purchased from Aldrich Chemical Co. and were used without further purification unless noted.

General procedure for the synthesis of amic acids

The appropriate dinitro compound (10.0 mmol) was dissolved in tetrahydrofuran (THF) (50 ml) and catalytically reduced using 10% Pd/C to the corresponding diamine. The solution containing the diamine was then filtered into a stirred solution of maleic anhydride (20.5 mmol) in tetrahydrofuran (100 ml). The mixture was stirred for 4 h at room temperature and at 50°C for 1 h. The solution was cooled to room temperature, the precipitate was collected and washed with fresh THF to remove excess maleic anhydride, and the bis(amic acid) obtained was vacuum dried.

1,2-Bis(4-maleamidophenoxy)ethane. A yellow powder was obtained in a 92% yield: m.p. 192–194°C. I.r. (KBr) cm^{-1}: 3296 (N–H), 3051 (aromatic C–H), 2945 (aliphatic C–H), 1714 (C=O), 1624 (C=O), 1244 (C–O–C). ^1H n.m.r. (DMSO-d_6) δ: 3.3–3.6 (b, 2H, NH), 4.29 (S, 4H,

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CH_2), 6.20–6.57 (m, 4H, CH=CH), 6.94–7.60 (d–d, 8H, aromatic), 10.40 (s, 2H, COOH). ^{13}C n.m.r. (DMSO-d_6) ppm: 66.50 (CH_2), 114.6 (Ar, CH), 121.21 (Ar, CH), 130.6 (Ar, C), 131.77 (CH), 131.89 (CH), 154.96 (C, Ar), 162.85 (C=O), 166.4 (C=O).

1,3-Bis(4-maleamidophenoxy)propane. A yellow powder was obtained in a 76% yield: m.p. 174–176°C. I.r. (KBr) cm^{-1}: 3287 (N–H), 3106 (aromatic C–H), 2960 (aliphatic C–H), 1700 (C=O), 1621 (C=O), 1243 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 2–2.3 (broad, 2H, CH_2), 3.3–3.6 (broad, 2H, NH), 3.9–4.3 (t, 4H, CH_2), 6.1–6.5 (m, 4H, CH=CH), 6.8–7.6 (d–d, 8H, aromatic), 10.4 (s, 2H, COOH). ^{13}C n.m.r. (DMSO-d_6) ppm: 28.65 (CH_2), 64.4 (CH_2), 114.78 (CH, Ar), 121.22 (Ar, CH), 130.61 (CH), 131.38 (C, Ar), 131.76 (CH), 155.07 (C, Ar), 162.85 (C=O), 166.41 (C=O).

1,4-Bis(4-maleamidophenoxy)butane. A yellow powder was obtained in a 97% yield: m.p. 205–207°C. I.r. (KBr) cm^{-1}: 3307 (N–H stretch), 3095 (aromatic C–H), 2942 (aliphatic C–H), 1695 (C=O), 1619 (C=O), 1237 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 1.6–1.9 (broad, 4H, $2CH_2$), 3.5–3.6 (broad, 2H, NH), 3.8–4.2 (t, 4H, CH_2), 6.1–6.5 (m, 4H, CH=CH), 6.8–7.6 (d–d, 8H, aromatic), 10.2–10.4 (s, 2H, COOH). ^{13}C n.m.r. (DMSO-d_6) ppm: 25.38 (CH_2), 67.31 (CH_2), 114.57 (CH, Ar), 121.22 (Ar, CH), 130.83 (CH), 131.27 (C, Ar), 131.75 (CH), 155.20 (C, Ar), 162.81 (C=O), 166.41 (C=O).

1,5-Bis(4-maleamidophenoxy)pentane. A yellow powder was obtained in a 94% yield: m.p. 190–191°C. I.r. (KBr) cm^{-1}: 3295 (N–H stretch), 3095 (aromatic C–H), 2942 (aliphatic C–H), 1705 (C=O), 1631 (C=O), 1243 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 1.5–1.9 (broad m, 6H, $3CH_2$), 3.5–3.7 (broad, 2H, NH), 3.8–4.1 (t, 4H, CH_2), 6.1–6.61 (m, 4H, CH=CH), 6.8–7.6 (d–d, 8H, aromatic), 10.2–10.4 (s, 2H, COOH). ^{13}C n.m.r. (DMSO-d_6) ppm: 22.16 (CH_2), 28.39 (CH_2), 67.55 (CH_2), 114.56 (CH, Ar), 121.24 (Ar, CH), 130.23 (CH), 131.21 (C, Ar), 131.61 (CH), 155.20 (C, Ar), 162.81 (C=O), 166.38 (C=O).

1,6-Bis(4-maleamidophenoxy)hexane. A yellow powder was obtained in a 64.1% yield: m.p. 198–199°C. I.r. (KBr) cm^{-1}: 3213 (N–H stretch), 3119 (aromatic C–H), 2942 (aliphatic C–H), 1713 (C=O), 1625 (C=O), 1243 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 1.4–1.7 (broad m, 4H, $2CH_2$), 2.4–4.4 (broad, 8H, $4CH_2$), 6.2–6.6 (m, 4H, CH=CH), 6.8–7.8 (d–d, 8H, aromatic), 10.3–10.4 (s, 2H, COOH). ^{13}C n.m.r. (DMSO-d_6) ppm: 25.23 (CH_2), 29.58 (CH_2), 67.54 (CH_2), 114.55 (CH, Ar), 121.22 (Ar. CH), 130.20 (C, Ar), 131.64 (CH), 131.77 (CH), 155.27 (C, Ar), 162.80 (C=O), 166.40 (C=O).

1,2-Bis(4-maleamidophenoxy)propane. A yellow powder was obtained in a 85% yield: m.p. 208–210°C. I.r. (KBr) cm^{-1}: 3284 (N–H stretch), 3088 (aromatic C–H). 2932 (aliphatic C–H), 1700 (C=O), 1628 (C=O), 1235 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 1.3–1.4 (d, 3H, CH_3), 3.3–3.6 (b, 2H, NH), 4.1–4.3 (d, 2H, CH_2), 4.5–4.8 (broad, 1H, CH), 6.1–6.5 (m, 4H, CH=CH), 6.8–7.6 (d–m, 8H, aromatic), 10.4 (s, 2H, COOH). ^{13}C n.m.r. (DMSO-d_6) ppm: 16.42 (CH_3), 70.76 (CH_2), 72.76 (CH), 114.78 (CH, Ar), 116 (CH, Ar), 121.32 (Ar, CH), 130.66 (CH), 131.58 (C, Ar), 131.68 (CH), 154.75 (C, Ar), 155.07 (C, Ar), 162.95 (C=O), 166.47 (C=O).

1,2-Bis(4-maleamidophenoxy)butane. A yellow powder was obtained in a 94% yield: m.p. 194–196°C. I.r. (KBr) cm^{-1}: 3280 (N–H stretch), 3084 (aromatic C–H), 2964 (aliphatic C–H), 1708 (C=O), 1626 (C=O), 1234 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 0.80–1.1 (t, 3H, CH_3), 1.5–2.2 (m, 2H, CH_2), 2.9–3.0 (b, 2H, NH), 4.3, 4.7 (broad, 1H, CH), 6.1–6.6 (m, 4H, CH=CH), 6.8–7.6 (d–m, 8H, aromatic), 10.41 (s, 2H, COOH).

1,2-Bis(4-maleamidophenoxy)pentane. A yellow powder was obtained in a 98% yield: m.p. 142–144°C. I.r. (KBr) cm^{-1}: 3277 (N–H stretch), 3075 (aromatic C–H), 2945 (aliphatic C–H), 1702 (C=O), 1625 (C=O), 1234 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 0.84, 1.27, 1.69 (broad, 13H, CH_3, CH_2), 4.11, 4.61 (broad, 3H, CH_2, CH), 6.17–6.55 (m, 4H, CH=CH), 6.75–7.58 (d–m, 8H, aromatic), 10.39 (s, 2H, COOH), 12.85 (broad, 1H, NH).

1,2-Bis(4-maleamidophenoxy)hexane. A yellow powder was obtained in a 97% yield: m.p. 151–153°C. I.r. (KBr) cm^{-1}: 3281 (N–H stretch), 3091 (aromatic C–H), 2954 (aliphatic C–H), 1706 (C=O), 1627 (C=O), 1236 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 0.8–2.2 (broad m, 9H, $CH_2CH_2CH_2CH_3$), 3.3–3.6 (b, 2H, NH), 4.1–4.3 (d, 2H, CH_2), 4.5–4.9 (broad, 1H, CH), 6.1–6.5 (m, 4H, CH=CH), 6.8–7.6 (d–m, 8H, aromatic), 10.4 (s, 2H, COOH).

General procedure for the preparation of bismaleimides

In a 100 ml round-bottomed flask was placed acetic anhydride (40 ml) and sodium acetate (24 mmol). The solution was stirred and the temperature was raised to 50–55°C. To the preheated solution, 17.0 mmol of the appropriate bis(amic acid) was added slowly. The temperature was then raised to 80–90°C and allowed to stir for 8 h. The solution was cooled to room temperature with constant stirring. The contents of the flask were poured into 250 ml of ice–water and stirred for 1 h. The precipitate was filtered and once again stirred in 250 ml of ice-cold sodium bicarbonate for 0.5 h. The solids were filtered, dissolved in methylene chloride and washed with dilute base solution. The organic layer was dried with anhydrous magnesium sulphate and the solvent evaporated to give a yellow solid, which was later dried in vacuum.

1,2-Bis(4-maleimidophenoxy)ethane. A pale yellow powder was obtained in a 88% yield: m.p. 215–217°C. I.r. (KBr) cm^{-1}: 3095 (aromatic C–H), 2942 (aliphatic C–H), 1707 (C=O), 1396 (C–N stretch, tertiary amine), 1249 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 4.1–4.3 (s, 4H, CH_2), 6.6–7.2 (m, 8H, CH=CH and aromatic). ^{13}C n.m.r. (DMSO-d_6) ppm: 66.58 (CH_2), 114.73 (Ar, CH), 124.31 (CH), 128.21 (Ar, CH), 134.48 (Ar, C), 157.61 (Ar, C), 170.03 (C=O). M.s. m/z (relative intensity): 404 (M^+, 72.26). Analysis calculated for $C_{22}H_{16}N_2O_6$, C 65.35, H 3.99; found, C 65.00, H 3.90.

1,3-Bis(4-maleimidophenoxy)propane. A yellow powder was obtained in a 72% yield: m.p. 130–132°C. I.r. (KBr) cm^{-1}: 3106 (aromatic C–H), 2921 (aliphatic C–H), 1714 (C=O), 1398 (C–N stretch, tertiary amine), 1245 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 2.1–2.4 (m, 2H, CH_2), 3.9–4.4 (t, 4H, CH_2), 6.7–6.8 (s, 4H, CH=CH), 6.9–7.4 (m, 8H, aromatic). ^{13}C n.m.r. ($CDCl_3$) ppm: 29.1 (CH_2), 64.64 (CH_2), 115.04 (Ar, CH), 123.95 (CH), 127.53 (Ar, CH), 134.05 (Ar, C), 158.36 (Ar, C), 169.70 (C=O). M.s. *m/z* (relative intensity): 418 (M^+, 58.47), 229 (100). Analysis calculated for $C_{23}H_{18}N_2O_6$, C 66.03, H 4.34; found, C 65.09, H 4.6.

1,4-Bis(4-maleimidophenoxy)butane. A yellow powder was obtained in a 82% yield: m.p. 169–170°C. I.r. (KBr) cm^{-1}: 3095 (aromatic C–H), 2960 (aliphatic C–H), 1717 (C=O), 1395 (C–N stretch, tertiary amine), 1249 (C–O–C). ^{1}H n.m.r. ($CDCl_3$) δ: 1.9–2.4 (broad m, 4H, CH_2), 3.9–4.3 (broad, 4H, CH_2), 6.7–6.8 (s, 4H, CH=CH), 6.9–7.3 (m, 8H, aromatic). ^{13}C n.m.r. ($CDCl_3$) ppm: 25.85 (CH_2), 67.69 (CH_2), 115.05 (Ar, CH), 123.79 (CH), 127.57 (Ar, CH), 134.11 (Ar, C), 158.87 (Ar, C), 169.76 (C=O). M.s. *m/z* (relative intensity): 432 (M^+, 8.52), 202 (100). Analysis calculated for $C_{24}H_{20}N_2O_6$, C 66.66, H 4.66; found, C 64.73, H 4.33.

1,5-Bis(4-maleimidophenoxy)pentane. A yellow powder was obtained in a 79% yield: m.p. 98–100°C. I.r. (KBr) cm^{-1}: 3095 (aromatic C–H), 2942 (aliphatic C–H), 1707 (C=O), 1396 (C–N stretch, tertiary amine), 1249 (C–O–C). ^{1}H n.m.r. ($CDCl_3$) δ: 1.6–2.40 (broad m, 6H, CH_2), 3.7–4.1 (t, 4H, CH_2), 6.7–6.8 (s, 4H, CH=CH), 6.8–7.2 (m, 8H, aromatic). ^{13}C n.m.r. ($CDCl_3$) ppm: 22.63 (CH_2), 28.85 (CH_2), 67.99 (CH_2), 115.03 (Ar, CH), 123.71 (CH), 127.53 (Ar, CH), 134.08 (Ar, C), 158.64 (Ar, C), 169.74 (C=O). M.s. *m/z* (relative intensity): 446 (M^+, 14.42), 189 (100). Analysis calculated for $C_{25}H_{22}N_2O_6$, C 67.26, H 4.97; found, C 65.87, H 5.06.

1,6-Bis(4-maleimidophenoxy)hexane. A yellow powder was obtained in a 92% yield: m.p. 151–153°C. I.r. (KBr) cm^{-1}: 3072 (aromatic C–H), 2942 (aliphatic C–H), 1707 (C=O), 1396 (C–N stretch, tertiary amine), 1249 (C–O–C). ^{1}H n.m.r. ($CDCl_3$) δ: 1.2–1.90 (broad m, 8H, CH_2), 3.7–4.0 (t, 4H, CH_2), 6.7–6.8 (s, 4H, CH=CH), 6.8–7.3 (m, 8H, aromatic). ^{13}C n.m.r. ($CDCl_3$) ppm: 25.75 (CH_2), 29.06 (CH_2), 66.06 (CH_2), 115.03 (Ar, CH), 123.65 (CH), 127.52 (Ar, CH), 134.05 (Ar, C), 158.02 (Ar), 158.68 (Ar, C), 169.76 (C=O). M.s. *m/z* (relative intensity): 460 (M^+, 14.45), 189 (100). Analysis calculated for $C_{26}H_{24}N_2O_6$, C 67.82, H 5.25; found, C 67.03, H 5.17.

1,2Bis(4-maleimidophenoxy)propane. A yellow powder was obtained in a 81% yield: m.p. 198–200°C. I.r. (KBr) cm^{-1}: 3088 (aromatic C–H), 2932 (aliphatic C–H), 1711 (C=O), 1398 (C–N stretch, tertiary amine), 1235 (C–O–C). ^{1}H n.m.r. ($CDCl_3$) δ: 1.1–1.4 (d, 3H, CH_3), 3.7–4.0 (d, 2H, CH_2), 4.4–4.8 (broad, 1H, CH), 6.6–6.80 (s, 4H, CH=CH), 6.8–7.3 (m, 8H, aromatic). ^{13}C n.m.r. ($CDCl_3$) ppm: 17.02 (CH_3), 71.17 (CH_2), 72.61 (CH), 115.26 (Ar, CH), 116.57 (Ar, CH), 124.29 (CH), 127.59 (Ar, CH), 134.12 (Ar, C), 157.40 (Ar, C), 158.22 (Ar, C), 169.69 (C=O). M.s. *m/z* (relative intensity): 418 (M^+, 55.30), 188 (100). Analysis calculated for $C_{23}H_{18}N_2O_6$, C 66.03, H 4.34; found, C 65.55, H 4.39.

1,2-Bis(4-maleimidophenoxy)butane. A yellow powder was obtained in a 68% yield: m.p. 53–54°C. I.r. (KBr) cm^{-1}: 3107 (aromatic C–H), 2966 (aliphatic C–H), 1713 (C=O), 1396 (C–N stretch, tertiary amine), 1243 (C–O–C). ^{1}H n.m.r. ($CDCl_3$) δ: 0.8–1.2 (t, 3H, CH_3), 1.15–2.1 (m, 2H, CH_2), 4.1–4.3 (d, 2H, CH_2), 4.4–4.8 (m, 1H, CH), 6.80–6.90 (s, 4H, CH=CH), 6.9–7.4 (m, 8H, aromatic). ^{13}C n.m.r. (DMSO-d_6) ppm: 9.75 (CH_3), 25.07 (CH_2), 70.37 (CH_2), 78.81 (CH), 115.7 (Ar, CH), 117.14 (Ar, CH), 125.88 (CH), 128.85 (Ar, C), 125.17 (Ar, CH), 135.17 (Ar, CH), 157.90 (Ar, C), 170.65 (C=O). M.s. *m/z* (relative intensity): 432 (M^+, 22.63), 189 (100). Analysis calculated for $C_{24}H_{20}N_2O_6$, C 66.66, H 4.66; found, C 66.03, H 4.88.

1,2-Bis(4-maleimidophenoxy)pentane. A yellow powder was obtained in a 71% yield: m.p. 48–49°C. I.r. (KBr) cm^{-1}: 3095 (aromatic C–H), 2954 (aliphatic C–H), 1713 (C=O), 1396 (C–N stretch, tertiary amine), 1237 (C–O–C). ^{1}H n.m.r. (DMSO-d_6) δ: 0.8–2.1 (broad m, 7H, $CH_2CH_2CH_3$), 4.1–4.3 (d, 2H, CH_2), 4.8–5.2 (broad, 1H, CH), 6.80–7.0 (s, 4H, CH=CH), 7.0–7.8 (m, 8H, aromatic). ^{13}C n.m.r. (DMSO-d_6) ppm: 14.31 (CH_3), 19.11 (CH_2), 34.32 (CH_2), 70.74 (CH_2), 77.74 (CH), 115.71 (Ar, CH), 117.10 (Ar, CH), 125.86 (CH), 128.44 (Ar, C), 128.44 (Ar, C), 128.89 (Ar, C), 135.16 (CH), 159.10 (Ar, C), 169.76 (C=O). M.s. *m/z* (relative intensity): 446 (M^+, 15.62), 189 (100). Analysis calculated for $C_{25}H_{22}N_2O_6$, C 67.26, H 4.97; found, C 66.51, H 5.28.

1,2-Bis(4-maleimidophenoxy)hexane. A yellow powder was obtained in a 65.1% yield: m.p. 46–47°C. I.r. (KBr) cm^{-1}: 3095 (aromatic C–H), 2942 (aliphatic C–H), 1713 (C=O), 1390 (C–N stretch, tertiary amine), 1237 (C–O–C). ^{1}H n.m.r. (DMSO) δ: 0.96–2.2 (broad m, 9H, $CH_2CH_2CH_2CH_3$), 4.2–4.4 (d, 2H, CH_2), 4.8–5.2 (broad, 1H, CH), 6.90–7.0 (s, 4H, CH=CH), 7.0–7.6 (m, 8H, aromatic). ^{13}C n.m.r. (DMSO) ppm: 14.23 (CH_3), 23.35 (CH_2), 27.48 (CH_2), 32.09 (CH_2), 70.75 (CH_2), 77.82 (CH), 115.71 (Ar, CH), 117.11 (Ar, CH), 125.88 (CH), 128.43 (Ar, C), 128.85 (Ar, C), 135.17 (CH), 144.43 (Ar, CH), 158.97 (Ar, C), 159.13 (Ar, C), 170.66 (C=O). M.s. *m/z* (relative intensity): 460 (M^+, 15.33), 189 (100). Analysis calculated for $C_{26}H_{24}N_2O_6$, C 67.82, H 5.25; found, C 66.41, H 5.65.

Dynamic mechanical analysis

A Rheometrics model RMS-7200 spectrometer was used for the parallel-plate rheology and torsion impregnated-cloth analysis (t.i.c.a.) studies. Temperature scans were run at 3°C min^{-1} in a nitrogen atmosphere. Scans were run using a frequency of 1 Hz, with a strain amplitude of 0.3 V applied to the sample.

For parallel-plate experiments, approximately 0.5 to 1.0 g of resin was pressed into a 25 mm disc. The height between the two plates was always maintained between 1 and 2 mm. The starting temperatures for the scans were fixed based on melting points obtained from d.s.c. The temperature scans were started at a temperature at least 25°C below the melting point in order to see the whole cure window. Once the test chamber was equilibrated at the starting temperature, the resin specimen was placed in the chamber and the temperature scan was started after 1 min. The parallel-plate rheometer consists of fixtures with two parallel 25 mm circular plates. The resin disc is placed between the plates and the plates are then brought together and the scan is started.

T.i.c.a. specimens were prepared by dissolving approximately 0.75 to 1.0 g of resin in 25–30 ml of solvent ($CHCl_3$). Once the resin was completely dissolved, it was poured evenly over a 3 inch by 3 inch (76 mm × 76 mm) piece of fibre glass cloth and the solvent was allowed to evaporate, after which remaining solvent was removed by drying in a fume hood at room temperature for one week. The cloth is then cut in half and each half folded in thirds such that two 0.5 inch by 3 inch (13 mm × 76 mm) cloth bars are formed. The two cloth pieces are mounted together into a sample holder and mounted into the instrument in the same fixture used to test 0.5 inch wide bar specimens.

RESULTS AND DISCUSSION

Monomers

The syntheses of the bismaleimides are shown in *Figure 1* and were accomplished as described in the 'Experimental' section. It should be noted that these bismaleimides, being tetrafunctional, form crosslinked polymers whose molecular weight between crosslinks, M_c, is expected to be the molecular weight of the respective monomer. Further, bismaleimides **1–5** have increasing chain length between crosslinks, while bismaleimides **6–9** have the same chain length between crosslinks as bismaleimide **1** but with increasing pendent-group length and hence increasing M_c. It is therefore of interest to examine the effect of these two factors on processing and properties.

Thermal properties

D.s.c. analyses of bismaleimides **1–9** were determined from 30°C to about 400°C under a nitrogen atmosphere at a rate of 40°C min^{-1}. All d.s.c. curves exhibited a clear sharp endotherm associated with the melting points of these bismaleimides (*Table 1*). As expected, the packing tends to decrease for bismaleimides having pendent groups resulting in lower melting points when compared with the linear structural isomers. Also for the linear bismaleimides the melt temperatures follow an odd–even chain-length effect. An even number of carbons on the main chain apparently results in better packing, and hence higher melting temperatures are observed for these compounds. Such an effect is not observed for the pendants. In general for the pendants, the greater the size of the pendent groups, the lower were the melt temperatures. Cure reactions of the above bismaleimides were observed as exothermic peaks above 250°C.

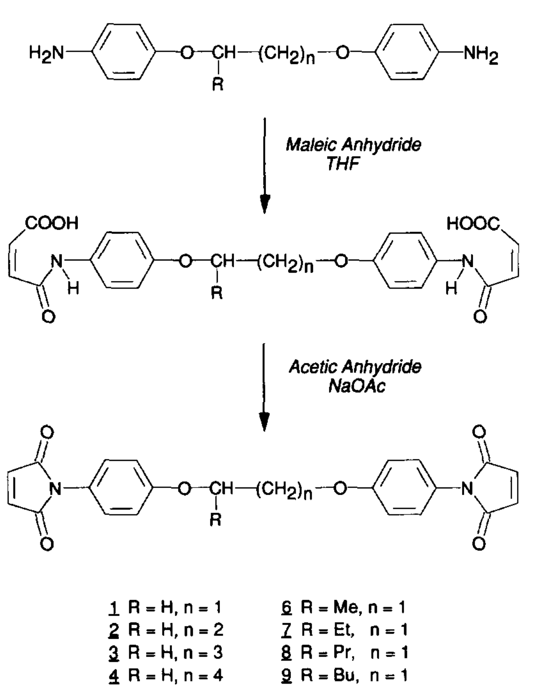

Figure 1 Synthetic scheme for bismaleimides 1–9

Table 1 Thermal properties of bismaleimides

	Transition temperature (°C)				
Structure	Initial melt	Minimum viscosity	Gel point	T_{vitrif}	$T_{g\infty}$
1	215	230	235	270	–
2	122	138	155	240	395
3	150	190	205	280	390
4	50	165	210	300	375
5	140	184	190	300	385
6	180	195	190	270	340
7	30	110	175	250	370
8	25	90	152	250	390
9	20	88	155	275	370

Thermogravimetric analyses of the bismaleimides were determined from 30 to 900°C at a rate of 40°C min^{-1} in both air and nitrogen. All the bismaleimides exhibited a two–step weight loss corresponding to degradation of the bismaleimides, with the first step believed to be the aliphatic portion of the molecule. All the bismaleimides showed onsets of degradation at approximately 450°C, although the weight loss of the first step increased with aliphatic content of the repeat unit, as expected. Thus increasing the number of aliphatic chain or pendent atoms does not appear to lower the thermal stability, the onset of degradation being determined by the presence of at least two aliphatic chain carbons.

Parallel-plate viscosity

Parallel-plate viscosity measurements of the bismaleimides **1–9** were determined under nitrogen at a rate of 3°C min^{-1}. The temperature range was fixed from the melt temperature obtained from the d.s.c. analysis.

All the viscosity runs obtained by parallel-plate measurements show a clear U-shaped curve as expected for a crosslinking system. The sample below its melting point is solid and, as the temperature is raised, begins to soften, which results in the lowering of viscosity. The fall in viscosity occurs until all the solid compound has melted. As the temperature is further increased, the viscosity of the melted compound falls until the material starts reacting, where two effects control the viscosity: (1) the kinetic effect, which tends to raise the viscosity, and (2) the temperature effect, which tends to decrease the viscosity. These effects result in a minimum viscosity and, as the crosslinking reaction proceeds, the viscosity starts to rise. The rise in viscosity occurs until the crosslinking reaction is completed. This whole pattern results in a U-shaped curve, which is the cure window. Viscosity–temperature curves are shown for straight-chain monomers (**1–5**) in *Figure 2* and for branched-chain monomers (**6–9**) in *Figure 3*.

The initial melting of the sample, taken as the onset of a drop of the viscosity curve, tends to follow the same pattern observed in the d.s.c. analysis but at a lower temperature owing to the different heating rates used in the respective experiments. The minimum-viscosity temperature was taken as the temperature at which the viscosity was at its lowest. The gel point, the temperature

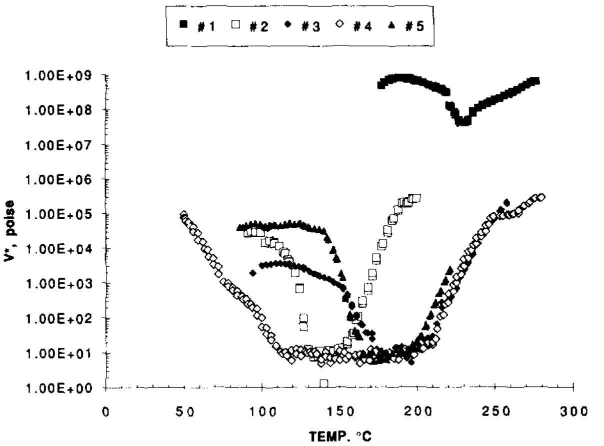

Figure 2 Parallel-plate viscosity for straight-chain bismaleimides **1–5**

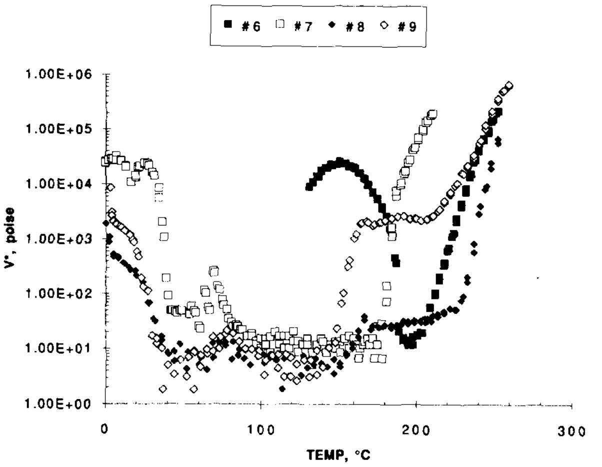

Figure 3 Parallel-plate viscosity for branched-chain bismaleimides **6–9**

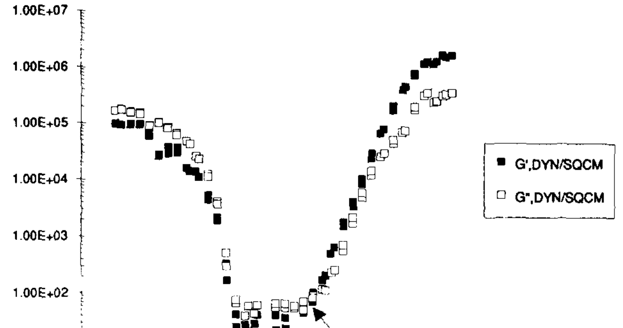

Figure 4 Prediction of gel point by parallel-plate rheometry

at which an infinite network starts to form, tends to follow the final-viscosity temperature very closely. The point at which the storage modulus G' rises above the loss modulus G'' was taken as the gel-point temperature, as was suggested by Tung and Dynes[6]. While this has been shown to be not precisely the gel point in some cases[7], it was felt that it was sufficiently accurate for our purposes. A typical plot of G' and G'' *versus* temperature is shown in *Figure 4* where the arrow depicts the estimated gel point. The values for initial melt, minimum viscosity and gel point for all the BMIs are given in *Table 1*.

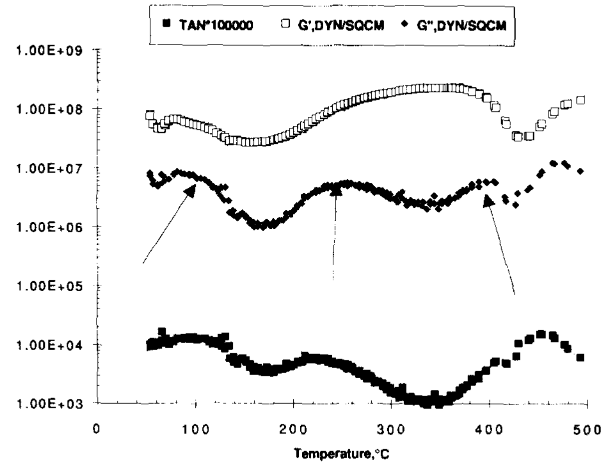

Figure 5 T.i.c.a. plot for BMI **2**

Torsion impregnated-cloth analysis

Dynamic mechanical analysis methods such as torsion impregnated-cloth analysis (t.i.c.a.)[8] can detect small polymer transitions or reactions not observed by other techniques (e.g. d.s.c.) and, since they are carried out with monomer impregnated on a glass cloth substrate, can follow the whole cure reaction from initial softening through cure to final softening of the fully cured polymer. The t.i.c.a. temperature scan provides a thermal profile of the storage (elastic) G' and loss (viscous) G'' moduli, and $\tan\delta$ (G'/G''). Analysis of the G'' curve gives information such as T_{g0}, the glass transition temperature of the uncured resin, T_{vitrif}, the vitrification temperature, and $T_{g\infty}$, the maximum glass transition temperature of the cured material. It should be noted that, since the t.i.c.a. runs are conducted with the resin impregnated on glass cloth, the moduli are the composite moduli and, as such, cannot be used to obtain the absolute modulus of the polymer. Differences, however, have been shown to be attributed to changes in mechanical behaviour of the polymer since the glass undergoes no significant changes in the temperature range of interest.

T.i.c.a. runs of the bismaleimides **1–9** were obtained under nitrogen atmosphere. The starting temperature for t.i.c.a. analysis was fixed from the parallel-plate measurements and the upper temperature was fixed at 450°C, which is the instrument's maximum range. *Figure 5* illustrates the technique for bismaleimide **2**, where the three arrows show T_{g0}, T_{vitrif} and $T_{g\infty}$, respectively. After the temperature is raised until the sample is in a liquid state, the modulus drops to a minimum. As the temperature is further raised, the crosslinking reaction sets in and starts converting the material from a liquid state to a solid state, resulting in increasing moduli. This portion of the curve is similar to the pattern of curves observed in parallel-plate measurements.

As the temperature is raised further, the kinetically controlled cure reaction proceeds at a faster rate until the glass transition temperature of the curing material overtakes the cure temperature. This point is T_{vitrif}, the vitrification temperature. A maximum in G'' and $\tan\delta$ is observed while G' continues rising. This maximum is expected since the material undergoes a transition from a rubbery state to a glassy state. This occurs at about 240°C for this monomer, which is, as expected, much higher than the gel-point temperature of about

155°C observed for the same system from parallel-plate measurements. Even after the vitrification temperature the cure reaction continues (albeit at a slower rate), which is seen by a continuing rise in G', but changes from a kinetically controlled process to a diffusion-controlled process until it flattens out, indicating the end of the cure reaction. At higher temperatures the material starts to soften and hence undergoes a transition from the glassy state to a rubbery state, and hence once again a rise in the G'' curve is observed. The temperature at which a maximum in G'' occurs is taken as the $T_{g\infty}$, the glass temperature of the completely cured material. In this bismaleimide this temperature is approximately 395°C. A similar pattern was observed for the other bismaleimides **1** and **3–9**. Results for these transitions sre shown in *Table 1*.

Vitrification temperatures were found to increase with the size of the monomer for bismaleimides **1–5**, except for bismaleimide **1**, which is highly crystalline and its melting point falls very close to the cure reaction temperature. As the size increases from bismaleimide **2** to bismaleimide **5**, the reactant concentration and the mobility of the unreacted monomers decrease, resulting in an increase in the vitrification temperature. The same effect was observed for the gel point in parallel-plate measurements.

The $T_{g\infty}$ for bismaleimides **2–5** are around 375–390°C, with a slight decrease with chain length. This temperature was not observed for bismaleimide **1**. Bismaleimide **8** shows a $T_{g\infty}$ at around 340°C, much less than the ones observed for the other compounds. The $T_{g\infty}$ for the branched bismaleimides tend to increase with the increase in size of the pendent groups, except for bismaleimide **9**, where it decreases. The pendent groups present in these compounds were expected to act as plasticizing agents and thus were expected to decrease the $T_{g\infty}$. The increase in $T_{g\infty}$ can be explained by the fact that, for branched compounds, the chain length between crosslinks remains the same and they differ only by the size of the pendent groups. These pendent groups, until the propyl group, may fit within the free volume available in the network, thus raising the $T_{g\infty}$. The decrease in $T_{g\infty}$ for bismaleimide **9** might be due to the plasticizing effect of the larger butyl group.

It is instructive to compare the two series of bismaleimides, straight-chain and pendent-chain, as a function of the number of aliphatic carbons, thereby comparing pairs of monomers with the same molecular weight but different topologies. This is illustrated in *Figure 6*, where n goes from 0 to 4 corresponding to the total number of aliphatic carbons given by $n+2$. The results from *Table 1* have been plotted in *Figure 7* as a function of number of aliphatic carbons to demonstrate this effect. The odd–even effect is very pronounced for the straight-chain monomers for initial melt and minimum viscosity, and even has an effect on gel point. There is no comparable effect for the branched-chain monomers. Vitrification and final T_g do not vary much with number of aliphatic carbons, although whatever trend appears seems to be reversed for the branched chains over the straight chains.

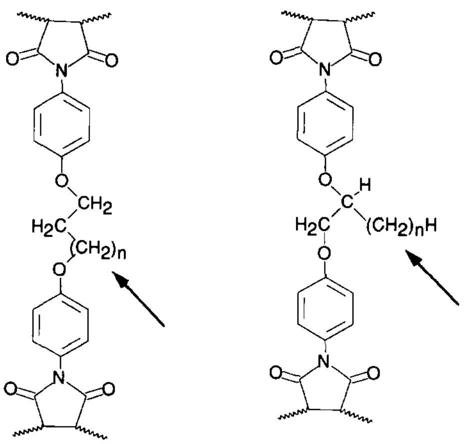

Figure 6 Comparison of straight-chain and branched-chain structures

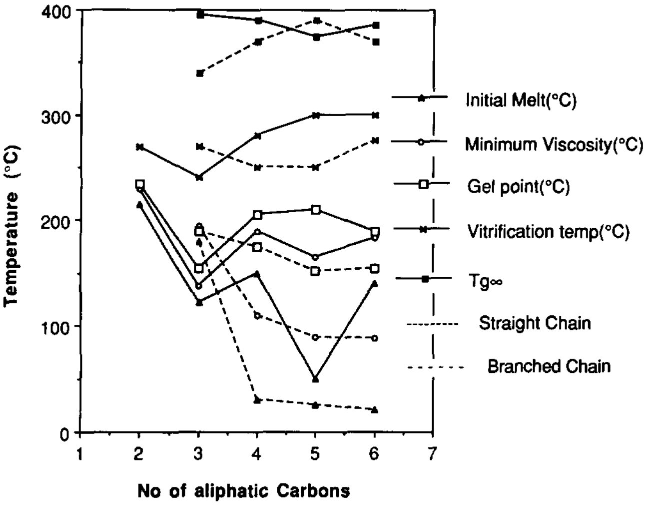

Figure 7 Combined thermal properties of bismaleimides

CONCLUSIONS

A combination of thermal analysis techniques provides a good estimate of processing and final properties of thermoset resins.

Final T_g, thermal stability and modulus of oxyalkylene-substituted BMIs appear to be relatively insensitive to the number of aliphatic carbon atoms in the chain.

The breadth of the cure window (temperature difference between initial melt and gel point) for this series of BMIs can be controlled through size of main-chain and pendent groups.

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