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PII: S0032-3861(98)00026-3

Polymer Vol. 39 No. 25, pp. 6541–6548, 1998

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Studies on polyimides. Part 1: Synthesis of model compounds and their reaction with hexamethylenetetramine

Marcus J. Caulfield, Mark G. Looney, Richard A. Pittard and David H. Solomon*
Polymer Science Group, Department of Chemical Engineering, University of Melbourne, Parkville, Victoria 3052, Australia
(Received 13 November 1997; revised 23 December 1997)

The synthesis of a series of *N*-(hydroxyphenyl) succinimides is described along with their reaction with HMTA. The succinimides serve as a model for the more complicated polyimide/HMTA systems. Both benzoxazine and benzylamine type intermediates have been identified as the initial major intermediates formed depending on the substitution pattern of the phenolic ring. The rate of reaction of HMTA with the *N*-(hydroxyphenyl) succinimide compounds was measured via ^{13}C nuclear magnetic resonance spectroscopy. It was found that the presence of the succinimide ring increases the reactivity to HMTA of the hydroxyphenyl compounds studied. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyimide; hexamethylenetetramine; phenol–formaldehyde resin)

INTRODUCTION

Polyimides are used in many specialized applications where they contribute excellent thermal and chemical stability to the system. These properties are related to the heterocyclic ring structure and minimal number of oxidizable hydrogens. Often the polyimide is used as a blend with phenol–formaldehyde resins. For example, poly(*N*-(4-hydroxyphenyl) maleimide) (**1**) has been used in composite formulations with phenol–formaldehyde resins, and shown to form miscible blends with improved thermal properties after being crosslinked with hexamethylenetetramine (HMTA) (**2**)[1–5]. The reaction between polyimides and HMTA has been noted but there are no studies directed towards an understanding of the chemical interactions between the polyimide/HMTA. In this paper we describe the first formed intermediates in the reaction of HMTA with appropriately substituted polyimide model compounds and report on the rate of formation of the intermediates by the use of nuclear magnetic resonance spectroscopy (n.m.r.).

EXPERIMENTAL

Materials

Succinic anhydride (**3**) (AR) (Aldrich) was used as received, aminophenols were either purchased from Aldrich or synthesized using standard literature procedures[6,7]. All were recrystallized from ethyl alcohol. 2,4,6-Trimethylphenol (TMP) (Aldrich) was recrystallized from pentane. 2,4-Xylenol (Aldrich, 99%) and *o*-cresol (Aldrich, 99%) were distilled at 4.5 mmHg before use. Hexamethylenetetramine (HMTA) (Aldrich, 99%) was dried under reduced pressure. All solvents were purified in the normal manner.

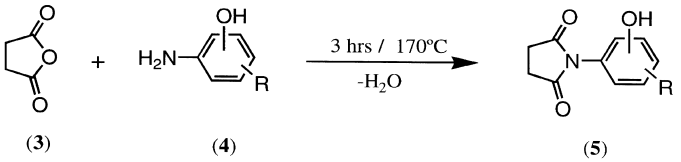
* To whom correspondence should be addressed

Instrumentation

Melting points (uncorrected) were determined using an Electrothermal melting point apparatus. Proton (^1H), carbon (^{13}C) and nitrogen (^{15}N) n.m.r. spectra were recorded on a Varian Unity spectrometer operating at 400, 100 and 40.5 MHz, respectively, using d_6-dimethylsulfoxide (DMSO) as a solvent, unless otherwise stated. For ^1H spectra, the residual central peak of d_6-DMSO (δ_H 2.49 ppm) was used as an internal reference, whilst the central peak d_6-DMSO (δ_C 39.5 ppm) was used as an internal reference for ^{13}C spectra. For ^{15}N spectra, the ^{15}N resonance of 98 at.% ^{15}N-labelled HMTA at δ_N 44.0 ppm was used as reference. Chemical shifts are quoted in ppm on the δ scale, followed by proton integration, multiplicity (br, broad; s, singlet; d, doublet; m, multiplet), coupling constant (s) in Hz, and possible assignment. Fourier transform infrared (i.r.) spectra were recorded on a Bio-Rad FTS-60A spectrophotometer. Samples were recorded in a potassium bromide disc and reported as absorption maxima, n_{max}, quoted in wave numbers (cm^{-1}) using the following abbreviations: br, broad; sh, shoulder; s, strong; m, medium; w, weak. Mass spectra (m.s.) were recorded at 70 eV, unless otherwise stated on a VG Micromass 7070F spectrometer and data expressed as *m/z* and relative intensity (% of base peak). Elemental analyses were carried out by Chemical & Micro Analytical Services Pty. Ltd and at the University of Tasmania. Liquid chromatography was performed using Merck TLC-grade silica gel, No. 7730.

*General procedure for synthesis of N-(hydroxyphenyl) succinimides (**6–13**)*

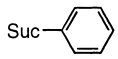
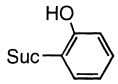
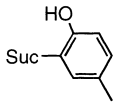
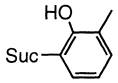
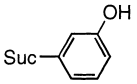
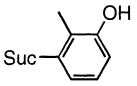
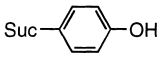
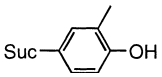
The *N*-(hydroxyphenyl) pyrrolidine-2,5-diones (**6–13**), more commonly referred to as succinimide compounds were synthesized by heating succinic anhydride (**3**) (1.1 equivalent) with the appropriate amino phenol (**4**) (1 equivalent) at 170°C for 3 h (*Scheme 1*). The subsequent cyclodehydration reaction afforded the desired *N*-(hydroxyphenyl) succinimides (**6–13**) (*Table 1*) in excellent yields after recrystallization from ethyl alcohol.



(**3**) (**4**) (**5**)

Scheme 1 Synthesis of *N*-(substituted phenyl) succinimides (**7–13**), where R = H or CH_3

Table 1 Substitution and percentage yields for compounds (**6–13**)

Structure[a]	Abbreviated name[b]	Number	Yield (%)
	**PSI**	(**6**)	77
	**2HPSI**	(**7**)	78
	**5M2HPSI**	(**8**)	86
	**3M2HPSI**	(**9**)	90
	**3HPSI**	(**10**)	90
	**2M3HPSI**	(**11**)	91
	**4HPSI**	(**12**)	81
	**3M4HPSI**	(**13**)	72

[a]Where Suc = a succinimide ring
[b]Where P = phenyl, H = hydroxy, M = methyl and SI = succinimide

*N-Phenyl-pyrrolidine-2,5-dione (PSI) (**6**)*

Yield 77% as white needles, m.p. 153–154°C (lit. m.p.[8] 154–155°C). ^{1}H n.m.r., δ (ppm): 2.78 (s, 4H, –CO–C**H$_2$**–C**H$_2$**–CO–); 7.22 (m, 2H, 2′-**H**, 6′-**H**); 7.36 (1H, m, 4′–**H**); 7.43 (m, 2H, 3′-**H**, 5′-**H**). ^{13}C n.m.r., δ (ppm): 28.9 (–CO–**C**H$_2$–**C**H$_2$–CO–); 127.5 (2′-**C**, 6′-**C**); 128.5 (4′-**C**); 129.2 (3′-**C**, 5′-**C**); 133.1 (1′-**C**–N–); 177.3 (2* **C**=O). I.r. (KBr) (cm^{-1}): 3471 br; 2938; and 1776 w; 1708; 1392; and 1189 s. M.s. 175 (M$^+$, 42%), 120 (27), 119 (71), 93 (50), 92 (31), 91 (65), 77 (46), 65 (28), 63 (69), 62 (41), 55 (41), 54 (100). Elemental analysis (%): calc. for $C_{10}H_9NO_2$: C, 68.6; H, 5.2; N, 8.0%. Found: C, 68.3; H, 5.2; N, 8.0%.

*N-(2′-Hydroxyphenyl)-pyrrolidine-2,5-dione (2HPSI) (**7**)*

Yield 78% as light brown needles, m.p. 176–178°C. ^{1}H n.m.r., δ (ppm): 2.77 (s, 4H, –CO–C**H$_2$**–C**H$_2$**–CO–); 6.86 (ddd, 1H, J = 7.6, 7.6 and 1.3 Hz, 5′-**H**); 6.93 (dd, 1H, J = 7.9 and 1.3 Hz, 3′-**H**); 7.03 (dd, 1H, J = 7.6 and 1.5 Hz, 6′-**H**); 7.25 (ddd, 1H, J = 7.6, 7.6 and 1.5 Hz, 4′-**H**); 9.72 (s, 1H, 2′-O**H**). ^{13}C n.m.r., δ (ppm): 28.6 (–CO–**C**H$_2$–**C**H$_2$–CO–); 116.6 (3′-**C**); 119.1 (5′-**C**); 119.8 (1′-**C**–N–); 129.6 (4′-**C**); 130.1 (6′-**C**); 153.4 (2′-**C**–OH); 176.9 (2* **C**=O). I.r. (KBr), (cm^{-1}): 3369 br; 1770 w; 1707; 1398; and 1191 s. M.s. 191 (M$^+$, 38%), 147 (25), 146 (44), 136 (30), 109 (67), 108 (32), 80 (36), 79 (46), 53 (100). Elemental analysis (%): calc. for $C_{10}H_9NO_4$: C, 62.8; H, 4.7; N, 6.8%. Found: C, 62.8; H, 4.7; N, 7.0%.

*N-(2′-Hydroxy-5′-methylphenyl)-pyrrolidine-2,5-dione (5M2HPSI) (**8**)*

Yield 86% as light brown needles, m.p. 229–230°C. ^{1}H n.m.r., δ (ppm): 2.20 (s, 3H, 5′-C–C**H$_3$**); 2.76 (s, 4H, –CO–C**H$_2$**–C**H$_2$**–CO–); 6.81 (d, 1H, J = 8.4 Hz, 3′-**H**); 6.82 (s, 1H, 6′-**H**); 7.05 (dd, 1H, J = 8.2 and 2.1 Hz, 4′-**H**); 9.39 (s, 1H, 2′-O**H**). ^{13}C n.m.r., δ (ppm): 19.8 (5′-C–**C**H$_3$); 28.6 (–CO–**C**H$_2$–**C**H$_2$–CO–); 116.4 (3′-**C**); 119.5 (1′-**C**–N); 127.8 (5′-**C**); 129.6 (4′-**C**); 130.5 (6′-**C**); 151.0 (2′-**C**–OH); 176.9 (2* **C**=O). I.r. (KBr), (cm^{-1}): 3180 br; 1779 w; 1689 s; 1519; and 1433 m. M.s. (CI, ammonia) 206 (MH$^+$, 100%), 205 (M$^+$, 24), 123 (12). Elemental analysis (%): calc. for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.4; N, 6.8%. Found: C, 64.3; H, 5.3; N, 6.8%.

*N-(2′-Hydroxy-3′-methylphenyl)-pyrrolidine-2,5-dione (3M2HPSI) (**9**)*

Yield 90% as light brown needles, m.p. 226–227°C. ^{1}H n.m.r., δ (ppm): 2.16 (s, 3H, 3′-C**H$_3$**); 2.73 (s, 4H, –CO–C**H$_2$**–C**H$_2$**–CO–); 6.75 (dd, 1H, J = 7.4 and 7.4 Hz, 5′-**H**); 6.82 (dd, 1H, J = 7.8 and 1.5 Hz, 6′-**H**); 7.13 (dd, 1H, J = 6.8 and 2.1 Hz, 4′-**H**); 9.07 (s, 1H, 2′-O**H**). ^{13}C n.m.r., δ (ppm): 16.2 (3′-C–**C**H$_3$); 28.8 (–CO–**C**H$_2$–**C**H$_2$–CO–); 118.7 (5′-**C**); 119.4 (1′-**C**–N); 125.8 (3′-**C**); 127.0 (6′-**C**); 131.1 (4′-**C**); 151.7 (2′-**C**–OH); 177.3 (2* **C**=O). I.r. (KBr), (cm^{-1}): 3283 br; 1698 s; 1483; 1394 m; and 1184 s. M.s. (CI, ammonia) 223 (MNH$_4^+$, 22%), 206 (MH$^+$, 100), 205

(M^+, 44), 190 (22), 187 (16). Elemental analysis (%): calc. for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.4; N, 6.8%. Found: C, 64.3; H, 5.6; N, 6.9%.

*N-(3′-Hydroxyphenyl)-pyrrolidine-2,5-dione (3HPSI) (**10**)*

Yield 91% as buff crystals, m.p. 193–194°C (lit. m.p.[9] 195°C). ^{1}H n.m.r., δ (ppm): 2.74 (s, 4H, –CO–C**H$_2$**–C**H$_2$**–CO–); 6.66 (m, 2H, 2′-**H** and 4′-**H** or 6′-**H**); 6.79 (dd, 1H, J = 7.6 and 2.0 Hz, 4′-**H** or 6′-**H**); 7.24 (ddd, 1H, J = 7.6, 7.6 and 2.0 Hz, 5′-**H**); 9.70 (s, 1H, 3′-O**H**). ^{13}C n.m.r., δ (ppm): 28.5 (–CO–**C**H$_2$–**C**H$_2$–CO–); 114.2 (2′-**C**); 115.1 (4′-**C**); 117.7 (6′-**C**), 129.5 (5′-**C**); 133.7 (1′-**C**–N–); 157.6 (3′-**C**–OH); 176.9 (2* **C**=O). I.r. (KBr), (cm^{-1}): 3377 br; 1774 w; 1697; 1398; and 1186 s. M.s. 191 (M^+, 100%), 136 (28), 135 (65), 109 (41), 55 (25), 53 (74), 50 (32). Elemental analysis (%): calc. for $C_{10}H_9NO_3$: C, 62.8; H, 4.7; N, 7.3%. Found: C, 62.9; H, 4.7; N, 7.2%.

*N-(3′-Hydroxy-2′-methylphenyl)-pyrrolidine-2,5-dione (2M3HPSI) (**11**)*

Yield 80% as brown crystals, m.p. 201–202°C. ^{1}H n.m.r., δ (ppm): 1.83 (s, 3H, 2′-C**H$_3$**); 2.81 (m, 4H, –CO–C**H$_2$**–C**H$_2$**–CO–); 6.56 (d, 1H, J = 7.8 Hz, 6′-**H**); 6.86 (d, 1H, J = 8.1 Hz, 4′-**H**); 7.06 (dd, 1H, J = 8.1 and 7.9 Hz, 5′-**H**); 9.66 (s, 1H, 3′-O**H**). ^{13}C n.m.r., δ (ppm): 10.6 (2′-**C**H$_3$); 28.6 (–CO–**C**H$_2$–**C**H$_2$–CO–); 114.9 (4′-**C**); 118.9 (6′-**C**); 122.5 (2′-**C**); 126.2 (5′-**C**); 132.9 (1′-**C**–N–); 156.0 (3′-**C**–OH); 176.9 (2* **C**=O). I.r. (KBr), (cm^{-1}): 3305 br; 1771 w; 1694; 1473; 1279 m; and 1185 s. M.s. 205 (M^+, 100%), 187 (18), 160 (19), 146 (26). Elemental analysis (%): calc. for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.4; N, 6.8%. Found: C, 64.3; H, 5.6; N, 7.0%.

*N-(4′-Hydroxyphenyl)-pyrrolidine-2,5-dione (4HPSI) (**12**)*

Yield 81% as colourless needles, m.p. 284–285°C (lit. m.p.[10] 286–287°C). ^{1}H n.m.r., δ (ppm): 2.72 (s, 4H, –CO–C**H$_2$**–C**H$_2$**–CO–); 6.83 (d, 2H, J = 8.8 Hz, 3′-**H**, 5′-**H**); 7.02 (d, 2H, J = 8.8 Hz, 2′-**H**, 6′-**H**); 9.70 (s, 1H, 4′-O**H**). ^{13}C n.m.r., δ (ppm): 28.3 (–CO–**C**H$_2$–**C**H$_2$–CO–); 115.4 (3′-**C**, 5′-**C**); 123.8 (1′-**C**–N–); 128.3 (2′-**C**, 6′-**C**); 157.1 (4′-**C**–OH); 177.2 (2* **C**=O). I.r. (KBr), (cm^{-1}): 3266 br; 1772 w; 1691; 1522; 1205; and 1192 s. M.s. 191 (M^+, 43%), 135 (42), 109 (71), 108 (58), 107 (37), 79 (36), 53 (94), 51 (30), 50 (100). Elemental analysis (%): calc. for $C_{10}H_9NO_3$: C, 62.8; H, 4.7; N, 6.8%. Found: C, 62.9; H, 4.7; N, 7.0%.

*N-(4′-Hydroxy-3′-methylphenyl)-pyrrolidine-2,5-dione (3M4HPSI) (**13**)*

Yield 72% as colourless needles, m.p. 167–168°C. ^{1}H n.m.r., δ (ppm): 2.72 (s, 4H, –CO–C**H$_2$**–C**H$_2$**–CO–); 2.11 (s, 3H, 3′-C**H$_3$**); 6.82–6.83 (m, 2H, 5′-**H** and 6′-**H**); 6.89 (s, 1H, 2′-**H**); 9.61 (s, 1H, 4′-O**H**). ^{13}C n.m.r., δ (ppm): 15.9 (3′-**C**H$_3$); 28.3 (–CO–**C**H$_2$–**C**H$_2$–CO–); 114.5 (5′-**C**); 123.5 (3′-**C**); 124.3 (1′-**C**–N–); 125.5 (6′-**C**); 129.2 (2′-**C**); 155.2 (4′-**C**–OH); 176.3 (2* **C**=O). I.r. (KBr), (cm^{-1}): 3394; and 1696 s; 1509; 1274; 1234; 1183; and 1111 m. M.s. 205 (M^+, 100%), 149 (23), 123 (45), 122 (30). Elemental analysis (%): calc. for $C_{11}H_{11}NO_3$: C, 64.4; H, 5.4; N, 6.8%. Found: C, 64.6; H, 5.5; N, 6.8.

Synthesis of hexamethylenetetramine (HMTA) labelled with approx. 10% ^{13}C and 98% ^{15}N

The labelled HMTA (*Scheme 2*) was prepared by adding dropwise to frozen ammonia (1000 ml, 98 at.% ^{15}N), formaldehyde (12 ml of a 20 wt.% solution in water, 10 at.% ^{13}C). The reaction flask was sealed with a balloon, and the ammonia allowed to warm to room temperature with vigorous shaking. Excess natural abundance ammonia was then added, and the resulting aqueous solution reduced to yield ^{13}C- and ^{15}N-labeled hexamethylenetetramine as a white crystalline product (1.85 g, 96%), m.p. 283°C. ^{1}H n.m.r., δ (ppm): 4.73(s, 12H). ^{13}C n.m.r., δ (ppm): 74.85. I.r. (KBr), (cm^{-1}): 2950; 2871; 1457; and 1371 w; 1237; and 1006 s. M.s. 150 (M^+, 100%), 146 (49), 120 (41), 91 (58).

*General procedure for preparation of benzoxazine derivatives (**17–22**)*

A mixture of the *N*-(hydroxyphenyl)-succinimide (3.00 mmol) and hexamethylenetetramine (**2**) (1.00 mmol) in 2,4,6-trimethylphenol (**16**) (21.00 mmol) was heated at 130°C for 3 h. The reaction mixture was then purified by vacuum liquid chromatography eluting with dichloromethane/petroleum spirits (8:2) and dichloromethane/ethyl acetate (7:3) to afford the desired benzoxazine derivative.

*2′-[8-(Pyrrolidine-2,5-dione)-(4H-benzo-1,3-oxazin-3-yl) methyl]-6′-(pyrrolidine-2,5-dione)-phenol (2HPSI-benzoxazine derivative) (**17**)*

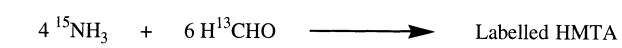
M.p. 162–164°C. ^{1}H n.m.r., δ (ppm): 2.87–2.90 (8H, app. s, 2* –CO–C**H$_2$**–C**H$_2$**–CO–), 3.99 (2H, s, 4-**H**), 4.07 (2H, s, 1-**H**), 4.85 (2H, s, 2-**H**), 6.83–6.95 (6H, app. m, Ar–**H**), 9.90 (1H, s, 2′-O**H**). ^{13}C n.m.r., δ (ppm): 28.61 (4* –CO–**C**H$_2$–**C**H$_2$–CO–); 48.66 (4-**C**); 54.38 (1-**C**); 80.79 (2-**C**); 119.54; 119.60 and 119.64 (Ar–**C**); 119.88 (4a-**C**); 121.24; 121.85; 127.73; 128.63; 128.90 and 130.62 (Ar–**C**); 148.39 (1′-**C**–OH); 152.87 (8a-**C**–O–); 175.90 and 176.25 (4* **C**=O). I.r. (KBr), (cm^{-1}): 3271 br; 1692 s; 1608; 1598; 1401; 1285; 1187 m. M.s.(LSIMS in mnba): 436 (MH^+, 65%), 435 (M + , 28), 424 (20), 245 (24), 231 (29), 204 (100), 176 (26). Elemental analysis (%): calc. for $C_{23}H_{21}N_3O_6$: C, 63.4; H, 4.9; N, 9.6%. Found: C, 63.4; H, 5.1; N, 9.8.

*2′-[6-Methyl-8-(pyrrolidine-2,5-dione)-(4H-benzo-1,3-oxazin-3-yl)methyl]-4′-methyl-6′-(pyrrolidine-2,5-dione)-phenol (5M2HPSI-benzoxazine derivative) (**18**)*

M.p. 196–197°C. ^{1}H n.m.r. ($CDCl_3$), δ (ppm): 2.23 and 2.26 (2* s, 6H, 2* Ar–C**H$_3$**), 2.87 and 2.88 (2* s, 8H, 2* –CO–C**H$_2$**–C**H$_2$**–CO–); 3.99 (s, 2H, 4-**H**); 4.06 (s, 2H, 1-**H**); 4.82 (s, 2H, 2-**H**); 6.82–6.87 (app. m, 4H, Ar–**H**); 9.80 (s, 1H, 1′-O**H**). ^{13}C n.m.r. ($CDCl_3$), δ (ppm): 20.23; 20.41 (2* Ar–**C**H$_3$); 28.51 (2* –CO–**C**H$_2$–**C**H$_2$–CO–); 48.37 (4-**C**); 54.30 (1-**C**); 80.83 (2-**C**); 119.10 and 119.13 (Ar–**C**); 119.18 (4a-**C**); 121.52; 127.97 and 128.63 (Ar–**C**); 129.21 (5′-**C**–CH$_3$); 129.31 (Ar–**C**); 130.76 (6-**C**–CH$_3$); 131.22 (Ar–**C**); 146.03 (1′-**C**–OH); 150.38 (8a-**C**–O–); 175.97 and 176.30 (4* **C**=O). I.r. (KBr), (cm^{-1}): 3401 br; 1708 s; 1493; 1232; and 1181 m. M.s. (LSIMS) 464 (MH^+, 89%), 463 (M^+, 51), 308 (23), 259 (20), 247 (23), 246 (33), 218 (100), 217 (21), 192 (46), 176 (22), 156 (22), 155 (99). Elemental analysis (%): calc. for $C_{25}H_{25}N_3O_6$: C, 64.8; H, 5.4; N, 9.1%. Found: C, 64.7; H, 5.4; N, 9.1%.

*2′-[7-(Pyrrolidine-2,5-dione)-(4H-benzo-1,3-oxazin-3-yl) methyl]-5′-(pyrrolidine-2,5-dione)-phenol (3HPSI-benzoxazine derivative) (**19**)*

M.p. 153–154°C. ^{1}H n.m.r., ($CDCl_3$) d (ppm): 2.75 (s, 8H, –CO–C**H$_2$**–C**H$_2$**–CO–); 3.87 (s, 2H, –N–C**H$_2$**–



Scheme 2 Synthesis of ^{13}C and ^{15}N isotopically enriched HMTA

Benzox.); 3.97 (s, 2H, –N–C**H**$_2$–Ph–); 4.94 (s, 2H, –O–C**H**$_2$–N–); 6.66–6.74 (m, 4H, Ar–**H**); 7.11 (d, 1H, $J = 8.1$ Hz, Ar–**H**); 7.34 (d, 1H, $J = 8.1$ Hz, Ar–**H**); 9.78 (s, 1H, 1′-O**H**). ^{13}C n.m.r. ($CDCl_3$), δ (ppm): 28.40 (2 * –CO–**C**H$_2$–**C**H$_2$–CO–); 48.69 (4-**C**); 54.42 (1-**C**); 80.76 (2-**C**); 114.96; 115.21; 117.72; 118.99 and 119.57 (Ar–**C**); 121.12 (4a-**C**); 128.44; 130.01; 131.54 and 132.82 (Ar–**C**); 153.54 (1′-**C**–OH); 158.19 (8a-**C**–O–); 176.07 and 176.10 (4* **C**=O). I.r. (KBr), (cm^{-1}): 3360 br; 2936 w; 1708 s; 1492; 1391; 1231; and 1179 m. M.s. (CI, ammonia desorption) 436 (MH^+, 46%), 435 (M^+, 18), 233 (100), 232 (49), 231 (37), 204 (58). Elemental analysis (%): calc. for $C_{23}H_{21}N_3O_6$: C, 63.5; H, 4.9; N, 9.6%. Found: C, 63.8; H, 5.0; N, 9.8%

*2′-[7-(Pyrrolidine-2,5-dione)-(8-methyl-4H-benzo-1,3-oxazin-3-yl)methyl]-6′-methyl-5′-(pyrrolidine-2,5-dione)-phenol (2M3HPSI-benzoxazine derivative) (**20**)*

M.p. 189–190°C. ^{1}H n.m.r. ($CDCl_3$), δ (ppm): 1.98; 2.01 (s, 6H, 2* Ar–C**H**$_3$); 2.94 (s, 8H, 2* –CO–C**H**$_2$–C**H**$_2$–CO–); 4.07 (s, 2H, 4-**H**); 4.11 (s, 2H, 1-**H**); 4.95 (s, 2H, 2-**H**); 6.58 (d, 1H, $J = 7.9$ Hz, Ar–**H**); 6.68 (d, 1H, $J = 8$ Hz, Ar–**H**); 6.91 (d, 1H, $J = 8.1$ Hz, Ar–**H**); 6.94 (d, 1H, $J = 8$ Hz, Ar–**H**); 10.09 (s, 1H, 1′-C–O**H**). ^{13}C n.m.r. ($CDCl_3$), δ (ppm): 10.51 and 10.64 (2* Ar–**C**H$_3$); 28.56 (2* –CO–**C**H$_2$–**C**H$_2$–CO–); 48.80 (4-**C**); 54.43 (1-**C**); 80.67 (2-**C**); 118.47; 119.33; 120.23; 121.11 and 123.46 (Ar–**C**); 124.29 (4a-**C**); 125.62; 125.62; 127.21; 130.42 and 131.73 (Ar–**C**); 151.99 (1′-**C**–OH); 156.69 (8a-**C**–O–C); 176.21 and 176.25 (4* **C**=O). I.r. (KBr), (cm^{-1}): 3472 br; 2928; and 2856 w; 1711 s; 1390; and 1183 m. M.s. (LSIMS) 464 (MH^+, 19%), 463 (M^+, 15), 307 (14), 246 (16), 218 (34), 155 (29), 154 (100). Elemental analysis (%): calc. for $C_{25}H_{25}N_3O_6$: C, 64.8; H, 5.4; N, 9.1%. Found: C, 64.7; H, 5.4; N, 9.1%.

*2′-[6-(Pyrrolidine-2,5-dione)-(8-methyl-4H-benzo-1,3-oxazin-3-yl)methyl]-4′-(pyrrolidine-2,5-dione)-phenol (4HPSI-benzoxazine derivative) (**21**)*

M.p. 149–151°C. ^{1}H n.m.r. (DMSO), δ (ppm): 2.80 (8H, app. s, 2* –CO–C**H**$_2$–C**H**$_2$–CO–); 3.85 (2H, s, 4-**H**); 4.00 (2H, s, 1-**H**); 4.88 (2H, s, 2-**H**); 6.88–7.33 (6H, app. m, Ar–**H**); 9.37 (1H, s, 1′-C–O**H**). ^{13}C n.m.r. (DMSO), δ (ppm): 28.52 and 28.80 (2* –CO–**C**H$_2$–**C**H$_2$–CO–); 48.79 (–N–**C**H$_2$–Benzox.); 49.70 (–N–**C**H$_2$–Ph); 82.75 (O–**C**H$_2$–N–); 118.85; 119.71; 119.74; 119.95; 121.35; 125.78; 127.56; 128.30; 128.52 and 129.78 (Ar–**C**); 149.53 (1′-**C**–OH); 151.83 (8a-**C**–O); 176.55 and 177.23 (4* **C**=O). I.r. (KBr), (cm^{-1}): 3472 br; 2941 w; 1714 s; 1474; 1390 and 1185 m. M.s. (LSIMS in mnba) 436 (MH^+, 90%), 435 (M^+, 35), 424 (12), 341 (19), 245 (29), 231 (31), 219 (15), 204 (100), 176 (28). Elemental analysis (%): calc. for $C_{23}H_{21}N_3O_6$: C, 63.5; H, 4.9; N, 9.6%.; Found: 63.1; H, 5.4; N, 8.5.

*2′-[6-(Pyrrolidine-2,5-dione)-(8-methyl-4H-benzo-1,3-oxazin-3-yl)methyl]-6′-methyl-4′-(pyrrolidine-2,5-dione)-phenol (3M4HPSI-benzoxazine derivative) (**22**)*

M.p. 186–187°C. ^{1}H n.m.r. ($CDCl_3$), δ (ppm): 2.19 (s, 3H, Ar–C**H**$_3$); 2.23 (s, 3H, Ar–C**H**$_3$); 2.80; 2.81 (s, 8H, 2* –CO–C**H**$_2$–C**H**$_2$–CO–); 4.01 (s, 1H, 4-**H**); 4.03 (s, 1H, 1-**H**); 4.90 (s, 1H, 2-**H**); 6.65 (d, 1H, $J = 2.3$ Hz, Ar–**H**); 6.69 (d, 1H, $J = 2.4$ Hz, Ar–**H**); 6.88 (d, 1H, $J = 2.2$ Hz, Ar–**H**); 6.95 (d, 1H, $J = 2.3$ Hz, Ar–**H**); 10.09 (s, 1H, 1′-C–O**H**). ^{13}C n.m.r. ($CDCl_3$), δ (ppm): 15.45 and 15.60 (2* Ar–**C**H$_3$); 28.16 and 28.18 (2* –CO–**C**H$_2$–**C**H$_2$–CO–); 48.72 (4-**C**); 54.43 (1-**C**); 80.67 (2-**C**); 118.37 (Ar–**C**); 120.27 (4a-**C**); 122.68; 123.34; 124.20; 125.08; 126.39; 127.16; 127.29 and 128.44 (Ar–**C**); 151.36 (1′-**C**–OH); 155.91 (8a-**C**); 176.45 and 176.55 (4* **C**=O). I.r. (KBr), (cm^{-1}): 3436 br; 2927 w; 1708 s; 1486; 1399; and 1182 m. M.s. (LSIMS in mnba) 464 (MH^+, 55%), 463 (M^+, 48), 307 (18), 247 (31), 245 (45), 245 (37), 219 (19); 218 (100); 217 (47). Elemental analysis (%): calc. for $C_{25}H_{25}N_3O_6$: C, 64.8; H, 5.4; N, 9.1%. Found: C, 64.9; H, 5.5; N, 9.4%.

General procedure for N-(hydroxyphenyl) succinimide/HMTA kinetic experiments

A 3:1 mole ratio mixture of the appropriate phenolic compound and HMTA (**2**) in 2,4-6-trimethylphenol (**16**) (TMP) was heated at 130°C for 8 h. Samples (0.300 g each) were taken at 20 min intervals for the first 3 h, then every hour for 4 h. The reaction mixture was then dissolved in d_6-DMSO (1.000 g) and examined directly by ^{13}C n.m.r. spectroscopy. In order to minimize the nuclear Overhauser effect (NOE) on the comparison of different samples, each sample was made up to the same concentration and accumulated under similar conditions, i.e. relaxation delay, temperature, accumulation time, etc. The resulting spectra were integrated and the reduction of the HMTA (74.0 ppm) resonance and the increase of the methylene resonance of the benzoxazine (81.8, 49 and 55 ppm) were monitored. The integrations were standardized relative to the ethylene resonances of the succinimide ring (28.7 ppm). In other systems (see below) which contain 2,4-xylenol, the *ortho* methyl group was used as an internal standard. The intensity of the ethylene and *ortho* methyl integrations remain unchanged during the course of the reaction.

The rates of the *N*-(hydroxyphenyl) succinimide reactions were compared to the reactions involving HMTA with 2,4-xylenol (**14**) and *o*-cresol (**15**) individually under similar conditions used for the model compounds.

2,4-Xylenol has been used successfully by numerous workers, including members from our group[11,12] to model one type of internal phenolic unit of a phenol–formaldehyde resin. *o*-Cresol was used as it represents a phenolic ring with both a free *ortho* and *para* site on the same molecule, which closely represents the substitution of model compounds (**7**) and (**11**) which model an end group.

RESULTS AND DISCUSSION

Studies on the reaction between polyimides and HMTA are difficult due to the complexity of the system, it was useful to use a model compound approach to elucidate the chemistry involved.

Selection of a suitable model polyimide compound system

The polymeric backbone of poly(*N*-(hydroxyphenyl) maleimides) consists of a five-membered heterocyclic ring system. An appropriate choice for a model compound system was considered to be *N*-(substituted phenyl) pyrrolidine-2,5-diones, herein referred to as *N*-(substituted phenyl) succinimide compounds, with the general structure (**5**). The succinimide ring is structurally similar to the repeat unit of the polymer, and the reactivity of the model compounds towards HMTA was expected to be similar or at least be a guide to the reactions of the polymeric system.

Reactivity of model polyimide compounds towards HMTA

The reactivity of the succinimide ring towards HMTA was first examined by heating HMTA with *N*-phenyl

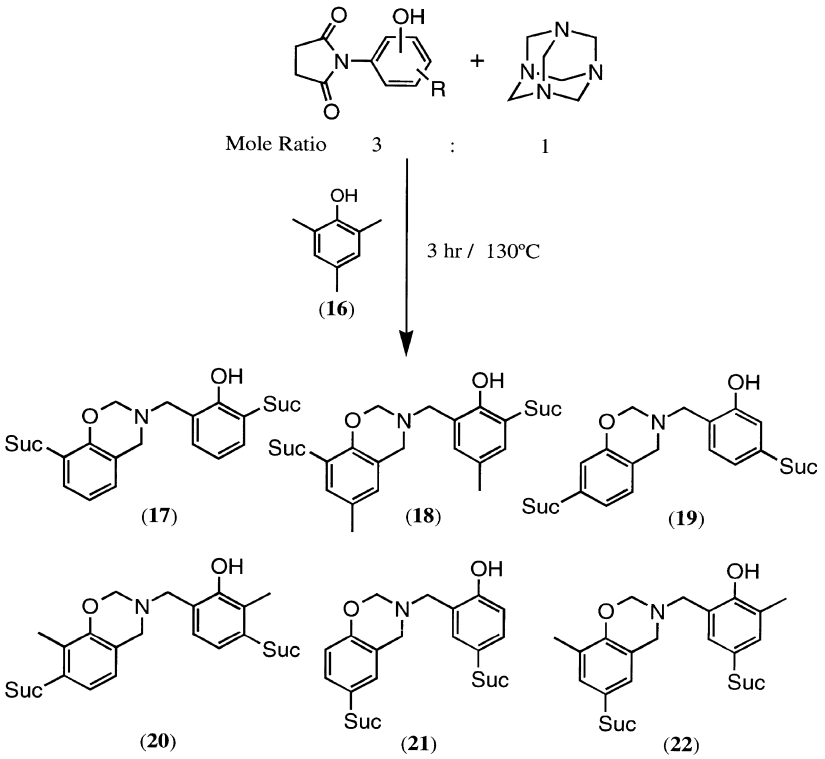
succinimide (**6**). The only species observed were unchanged starting materials, which suggests that the five-membered succinimide ring does not directly react with HMTA, nor does it sufficiently activate the aromatic ring towards reaction with HMTA. The reactivity of the phenolic ring towards HMTA in the polymeric system was therefore attributed to the presence of a hydroxyl substituent. In order to study the effect of the succinimide ring on the reactivity of the phenolic ring, a series of novel *N*-(hydroxyphenyl) succinimide compounds was synthesized.

The *N*-(hydroxyphenyl) succinimides (**7–13**) (*Table 1*) were targeted as models because they represent a range of substitution patterns used in practice or they were of interest in relation to mechanistic studies. Based on previous work[13], the reactive sites of a phenolic ring are either positioned *ortho* or *para* to the hydroxyl group. Therefore the number of reactive sites *ortho* or *para* to the phenolic hydroxyl group was controlled by either the position of the succinimide ring or by the addition of a methyl substituent. For example with 5M2HPSI (**8**), the hydroxyl group is *ortho* relative to the succinimide ring, and the methyl group is *para* disposed relative to the hydroxyl substituent. This compound has only one available site for reaction, that *ortho* to the hydroxyl group, therefore limiting the number of possible reaction products.

Heating a solid mixture of an *N*-(hydroxyphenyl) succinimide and HMTA in a mole ratio of 3:1 progressively up to a temperature of 205°C resulted in little reaction and the lack of reactivity observed for the *N*-(hydroxyphenyl) succinimide/HMTA system was attributed to the inhomogeneity of the reaction mixture. Therefore a solvent system was sought which would dissolve both reactants at a lower temperature than that required for the neat reaction. Various solvents were examined with 2,4,6-trimethylphenol (TMP) (**16**) being selected since it can dissolve both reactants at 130°C and was found to not directly react with HMTA. The model polyimide compounds (**7–13**) were individually subjected to the reaction conditions described in *Scheme 3*. Isolation of the reaction products was achieved via standard chromatographic techniques.

The major products formed initially were intermediates (**17–22**) from the model compounds (**7–13**), with the exception of 3M2HPSI (**9**). They were isolated and found to have the same general structure. Analysis of these compounds (**17–22**) with ^{13}C n.m.r. show resonances which are characteristic of benzoxazine type species. All other spectroscopic evidence supports the proposed benzoxazine structures.

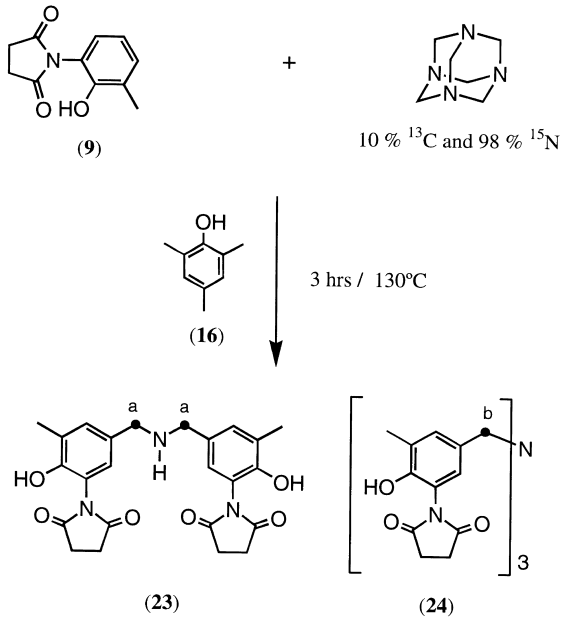
N-(3-Methyl-2-hydroxyphenyl) succinimide (3M2HPSI) (**9**) has only a vacant *para* reactive site; this precludes the formation of benzoxazine type intermediates. The reaction mixture formed was not homogeneous, and attempts to form a homogenous solution were unsuccessful even at high TMP concentrations. Nevertheless, it was anticipated that useful information could be gained by examining the reaction between HMTA and (**9**) using the previously described conditions (*Scheme 3*). To facilitate in the unambiguous identification of the reactive intermediates, which because of the solubility problems are formed in trace quantities, labelled HMTA was used. The utility of using isotopically enriched compounds has long since been recognised[14–16], it allows the detection of trace amounts of compounds which would otherwise not be observed using standard n.m.r. techniques. Isotopically enriching both the ^{13}C and ^{15}N of HMTA allows the correlation of the resonances observed in the ^{13}C n.m.r. spectrum with those in the ^{15}N spectra, therefore allowing for the identification of the intermediates. The reaction products observed were identified as a mixture of di- and tri-benzylamines (**23–24**), by both the characteristic ^{13}C n.m.r. resonances at δ 51.29 (a), and 55.2 (b) ppm of the bridging methylene carbon and the ^{15}N n.m.r. signals of the amine nitrogen at δ 46.6 and 53.9 ppm for



Scheme 3 Conditions for reaction of HMTA with *N*-(hydroxyphenyl) succinimides, where Suc = succinimide ring and R = H or CH_3

compounds (**23**) and (**24**), respectively. The major product was the tri-benzylamine derivative (**24**) (*Scheme 4*).

For the model compounds which contain both an *ortho*- and *para*-reactive site relative to the hydroxyl group, compounds (**5**), (**8**) and (**9**), a more complicated product distribution is observed. The initial major intermediates are derived from reaction at the *ortho* position to form the benzoxazine type species (**17**, **19** and **20**). Once the majority of the *ortho*-reactive sites have reacted and there is still an excess of HMTA in the system, reaction at the *para* position occurs to form benzylamine-type species as indicated by the characteristic ^{13}C and ^{15}N n.m.r. signals in the crude reaction mixture. Therefore reaction at the *ortho* position dominates the reaction pathway when there are free *ortho*- and *para*-reactive sites, and reaction at the *para* position occurs latter when most of the *ortho* sites have been consumed.



Scheme 4 Reaction of labelled HMTA with 3M2HPSI (**9**)

We have previously reported that both benzoxazines and benzylamines are the initial intermediates during the reaction between HMTA with phenol–formaldehyde resins[17–19]. These reactive intermediates have been shown to decompose to form methylene linkages. Their formation during the reaction of HMTA with *N*-(hydroxyphenyl) succinimide compounds suggests that the phenolic ring of the succinimides reacts in an analogous manner to that in a phenolic resin. The succinimide ring appears to have little effect on the structure of the polymerization intermediates.

Substituent effects on the kinetics of reaction between HMTA and the model polyimides

The effect of the succinimide ring on the rate of reaction of HMTA with the phenolic ring is of interest. In order to clarify this point, a series of n.m.r. experiments was carried out in which the rate of consumption of HMTA was determined over a period of 8 h by measurement of the chemical shift at approximately 74 ppm (*Figure 1*).

From *Figure 1*, it is observed that with the loss of the resonances associated with the *ortho* position relative to the hydroxyl group at approximately 113 ppm there is a concurrent appearance of resonances associated with the methylene linkage of the benzoxazine at approximately 48, 54 and 81 ppm. This is consistent with the reaction of the phenolic ring of the model polyimide with HMTA to form the benzoxazine product. The time for half of the available HMTA to be consumed, $t_{1/2}$ values was calculated from the spectral data for each of the model compounds (**7–13**) (*Table 2*). In addition, the $t_{1/2}$ values for 2,4-xylenol (**14**), which contains one free *ortho* position, and *o*-cresol (**15**), which contains both an *ortho* and a *para* position free were measured. These two models have previously been used in our earlier study to model the internal and end groups of phenol–formaldehyde resin, respectively[11]. Their use in this study is to illustrate the variation in reactivity of the phenolic ring of the *N*-(hydroxyphenyl) succinimides compared to a phenolic ring without a succinimide ring substituent. (Please note that the measured $t_{1/2}$ value for the reaction of HMTA with 2,4-xylenol is considerably longer than we have previously reported for the neat reaction[11] because in the present study the reactions were conducted in

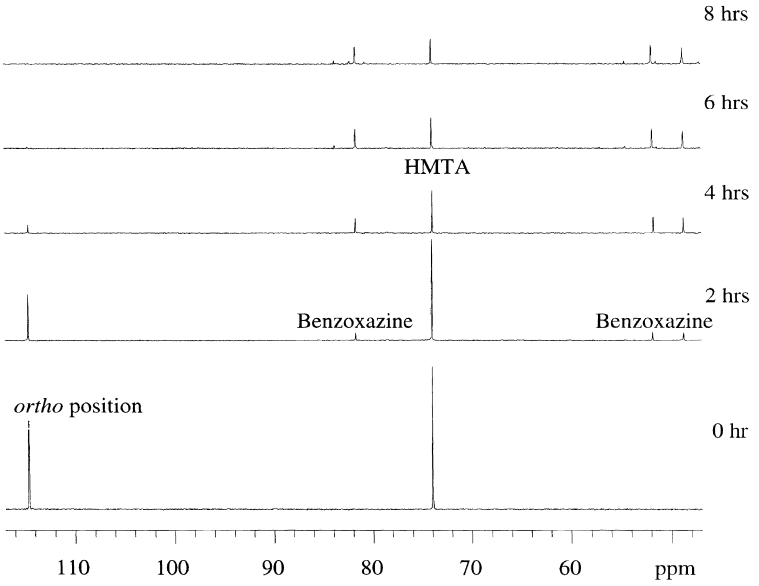


Figure 1 ^{13}C n.m.r. spectra of 3M4HPSI (**13**) and HMTA in 3:1 mole ratio at 130°C

Table 2 Measured $t_{1/2}$ values for reaction of HMTA with phenolic compounds at 130°C

Compound	$t_{1/2}$ HMTA	Major product
2HPSI (**7**)	30 min	Benzoxazine[a]
5M2HPSI (**8**)	50 min	Benzoxazine
3M2HPSI (**9**)	Inhomogeneous	Benzylamines[b]
3HPSI (**10**)	1 h 55 min	Benzoxazine[a]
2M3HPSI (**11**)	2 h 30 min	Benzoxazine[a]
4HPSI (**12**)	Inhomogeneous	Benzoxazine[b]
3M4HPSI (**13**)	2 h 40 min	Benzoxazine
2,4-Xylenol (**14**)	4 h	Benzoxazine
***o*-Cresol** (**15**)	3 h 25 min	Benzoxazine[a]

[a]Benzylamine type products observed after *ortho*-reactive sites consumed
[b]Inhomogeneous reaction mixture, therefore $t_{1/2}$ not able to be measured

solution state using a solvent to overcome solubility problems.) Our reaction conditions allow us to compare the relative reactivity of HMTA towards the *N*-(hydroxyphenyl) succinimides but not to deduce more accurate kinetic data.

Examining the $t_{1/2}$ values (*Table 2*), the rate of consumption of HMTA is influenced by the presence and relative position of the five-membered succinimide ring, with the $t_{1/2}$ values for the models containing a succinimide ring being significantly shorter than that for the phenol–formaldehyde models (**14**) and (**15**). The most dramatic change in the rate of reaction observed was for 5M2HPSI (**8**), which has a vacant *ortho* position and whose measured $t_{1/2}$ value of 50 min is considerably shorter than that of the phenol model, 2,4-xylenol (**14**), which is 4 h. Both (**8**) and (**14**) are 2,4-substituted phenols, with the difference in substitution between the two compounds being the presence of the succinimide ring which is *ortho* to the hydroxyl substituent in compound (**8**) instead of a methyl substituent in 2,4-xylenol.

The effect of the succinimide ring on the reactivity of 3M4HPSI (**13**) towards HMTA is less pronounced. Compound (**13**) has the same 2,4-substitution pattern as both (**8**) and (**14**), but the succinimide ring is positioned *para* to the hydroxyl moiety. This change in the position of the succinimide ring reduces the relative rate of HMTA consumption compared to when the succinimide ring is *ortho* to the hydroxyl moiety, although (**13**) has a $t_{1/2}$ value 80 min shorter than the xylenol (**14**).

The reactivity of the *N*-(hydroxyphenyl) succinimide compounds that have both a vacant *ortho* and *para* position relative to the hydroxyl group, compounds (**7**) and (**11**), were compared to *o*-cresol (**15**). The $t_{1/2}$ value for *o*-cresol was 3 h and 25 min (*Table 2*). The measured $t_{1/2}$ value for 2HPSI (**7**) of 30 min was the fastest of any of the model compounds investigated. The plot of percentage initial HMTA against time gives us some insights into the reaction mechanism (*Figure 2*), this is also compared to the reaction of 5M2HPSI (**8**) and HMTA.

From the shape of the curves in *Figure 2*, we can relate the changes in the rate of HMTA consumption to the possible reaction mechanisms. Initially for the reaction of both 2HPSI (**7**) and 5M2HPSI (**8**) with HMTA, the rate of HMTA consumption is high corresponding to the reaction to form benzoxazine type intermediates. For the reaction of 2HPSI (**7**), after approximately 40 min, the *ortho*-reactive sites have reacted, and the reaction mechanism is then dominated by reaction at the *para* position to form benzylamine intermediates. At this point, resonances associated with benzylamine-type intermediates are apparent in the ^{13}C n.m.r. spectrum. This reaction proceeds at a slower rate, as evidenced by the reduced rate of HMTA consumption. The reaction of 5M2HPSI (**8**) with HMTA is initially quite fast and after approximately 1 h, the *ortho*-reactive sites have reacted to form benzoxazine derivatives. Flattening off of the HMTA consumption is consistent with no further reaction occurring, this is because the *para*-reactive site in (**8**) is blocked by a methyl substituent.

A similar reaction profile is observed for reaction between HMTA and 2M3HPSI (**11**), although the relative rate of reaction is slower. Nevertheless the $t_{1/2}$ value is over 1 h shorter than *o*-cresol.

Analysis of kinetic results

All the succinimide derivatives examined in this study were found to be more reactive towards HMTA than the phenolic rings without a succinimide ring attached. The increased rate of reaction between HMTA and the *N*-(hydroxyphenyl) succinimide compounds is most pronounced in the reaction where the succinimide ring is *ortho* disposed relative to the phenolic hydroxyl and where there is a free position *ortho* to phenol. The origins for the increased rate of reaction are unclear, but it is possible it is associated with the increased amount of intramolecular bonding between the phenolic hydroxyl and the carbonyl of the succinimide ring. The intramolecular bonding would be most effective in the models where the distance between the hydroxyl group and the carbonyl group is closest. From models and basic molecular modelling, the distance between the carbonyl oxygen and the hydrogen of the hydroxyl group of the *ortho*-substituted derivative is

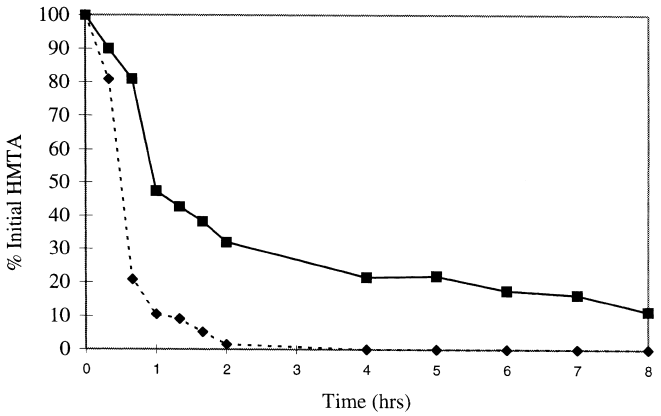


Figure 2 Plot of percentage initial HMTA against time for 5M2HPSI (**8**) (■) and 2HPSI (**7**) (♦)

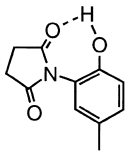


Figure 3 Proposed intramolecular bonding for 5M2HPSI (**8**)

approximately 1.8 Å; this distance is very favourable for the formation of strong hydrogen bonding (*Figure 3*).

Although a seven-membered ring is formed, the proximity of the carbonyl to the phenolic hydroxyl would appear to ensure strong intramolecular bonding does occur. The possibility of effective intramolecular bonding is unlikely for the *meta* and *para* succinimide derivatives as the carbonyl group is not as favourably positioned with respect to the hydroxyl group. The strength of the possible intramolecular bonding correlates well with the observed rates of reaction of the succinimide derivatives and HMTA; with the compounds with the strongest intramolecular bonding, i.e. the *ortho* derivatives, being by far the most reactive of the succinimide derivative investigated.

In order to explain these observations in terms of the effect of the succinimide ring on the reactivity of the phenolic ring, it is informative to refer to the formation of the benzoxazine intermediates from phenols. It has been suggested in the literature[11,20–22] that the reaction between HMTA and 2,4-xylenol proceeds via a two-step process to form benzoxazine intermediates. The initial step involves rapid intermolecular hydrogen bonding between HMTA and xylenol to form a complex. This complex then decomposes in the rate-determining step to form benzoxazine.

We suggest that the *N*-(hydroxyphenyl) succinimide compounds react in analogous manner to xylenol, forming the same kind of intermolecular bonded phenol/HMTA complex. This could be the result of the intramolecular bonding which could have possible ramifications on the stability of the intermolecular bonded complex and/or on the characteristics of the phenolic hydroxyl.

CONCLUSIONS

The mechanistic pathway taken during the reaction of the *N*-(hydroxyphenyl) succinimides (**7–13**) with HMTA is dependent on the substitution of the phenolic ring. With compounds containing a free *ortho* position, the initial intermediates are benzoxazine type species. When there is only a free *para* position, benzylamines are the initial intermediates, with both di- and tri-benzylamines observed. In systems which contain both an *ortho* and *para* position vacant in the one molecule, reaction initially occurs at the *ortho* position to form benzoxazine-type species, then reaction at the *para* position occurs to form the benzylamine type products. The five-membered succinimide ring does not change the nature of the intermediates observed, although it has a marked effect on the rate of their formation. *N*-(Hydroxyphenyl) succinimides which have the succinimide ring *ortho* disposed relative to the hydroxyl substituent and which have a free *ortho* position were found to react more than 4 times faster than the corresponding phenolic compound without a succinimide ring. This increase in reactivity is thought to stem from the effects of a competition between intermolecular bonding between the hydroxyl group of the phenolic ring and the nitrogen of HMTA and intramolecular molecular bonding between the hydroxyl moiety and the carbonyl of the succinimide ring. The effects of intramolecular bonding would be most pronounced in the models which contain the succinimide ring *ortho* disposed relative to the hydroxyl group, which is reflected in the increased relative reactivity of those models towards HMTA compared to the models with the succinimide ring *meta* and *para* disposed.

ACKNOWLEDGEMENTS

The authors wish to thank Xiaoqing Zhang and Greg Qiao for their productive discussions. We also acknowledge Comalco Aluminium Limited and the Australian Research Council for financial assistance.

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