ELSEVIER

Polymer 40 (1999) 1251–1260

polymer

Studies on polyimides: 2. Formation of high molecular weight poly(*N*-(hydroxyphenyl) maleimides)

Marcus J. Caulfield, David H. Solomon*

Polymer Science Group, Department of Chemical Engineering, University of Melbourne, Parkville, Victoria 3052, Australia

Received 10 February 1998; revised 25 March 1998; accepted 27 March 1998

Abstract

A series of *N*-(substituted phenyl) maleimides was synthesized and their free radical chain polymerization examined. Polymerization of the *N*-(hydroxyphenyl) maleimides in DMF gave typically very low molecular weight polymers. Masking the phenolic functionality with an acetoxy group gave marginally higher molecular weights. Protection using a tetrahydropyranyl (THP) substituent gave a similar polymerization pattern to acetoxy. However, the THP protected monomers had increased solubility in non-polar solvents such as benzene, and when polymerized in this solvent gave very much higher molecular weight polymers. The reactivity of the maleimide monomers was also found to be dependent on the substitution pattern of the phenyl ring, with substituents in the *ortho* position tending to lower the molecular weight of the polymer formed. The THP substituent was readily removed to yield poly(*N*-(hydroxyphenyl) maleimides). The polymers were found to exhibit excellent thermal stability.

Keywords: Polyimide; *N*-(substituted phenyl) pyrrolidone-2,5-diones; THP

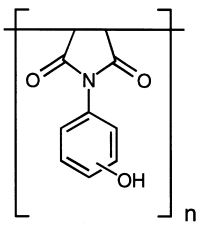
1. Introduction

The free radical chain polymerization of 1*H*-pyrrole-2,5-diones, more commonly referred to as maleimides, and the *N*-substituted derivatives has been extensively studied [1–5]. Despite the 1,2-disubstituted ethylene structure of the maleimide ring, both homo- and copolymerizations have been reported to occur with a variety of *N*-substituents and comonomers [6–8]. The resulting polymers generally exhibit both good thermal and chemical stability [9,10].

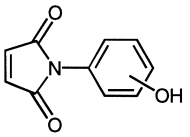
Poly(*N*-(hydroxyphenyl) maleimides) (**1**) have been extensively used either individually or in composite formulations with other phenolic resins in applications where good thermal properties are desirable [11–13]. However, the free radical polymerization of *N*-(hydroxyphenyl) maleimide (**2**) monomers gives polymers in relatively poor yields and low molecular weights. This has previously been attributed to the presence of the free phenolic substituent during the free radical polymerization [14]. However, there are reports in the literature concerning the free radical polymerization of monomers containing free phenolic groups which range from evidence of no effect [15,16] to observations of considerable problems associated with the phenolic group [15,17–19].

The choice of a solvent for the polymerizations of the maleimides is limited by the poor solubility of both monomeric and polymeric materials. Consequently, polar solvents are often used for the polymerizations, many of which are undesirable as solvents for free radical polymerization. It is therefore of interest to produce maleimide-based polymers of improved solubility in common solvents and of high molecular weight, both of which are highly desirable engineering properties for their use in industrial applications.

In this article, we describe the synthesis and controlled free radical chain polymerization of a series of novel *N*-(substituted phenyl) maleimides to form high molecular weight polymeric materials in inert solvents. The process is applicable generally to other phenolic monomers.



(**1**)



(**2**)

* Corresponding author.

0032-3861/98/$ - see front matter
PII S0032-3861(98)00258-4

2. Experimental

2.1. Materials

Maleic anhydride (AR), sodium acetate (99%), nickel(II) acetate tetrahydrate (98%), 3,4-dihydro-2*H*-pyran (97%) and acetic anhydride (98%) were obtained from Aldrich and used as received. Pyridinium *p*-toluenesulfonate (PPTS) was prepared as previously described [20]. The aminophenols (Aldrich) were recrystallized from ethyl alcohol. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from diethyl ether. *N*,*N*-Dimethylformamide (DMF) was dried over CaH_2. Solvents were purified by conventional methods.

2.2. Instrumentation

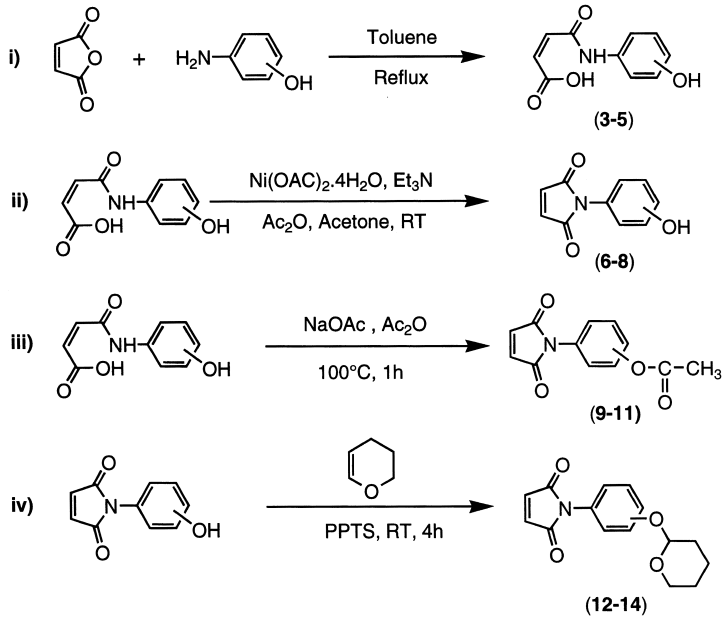
Melting points (uncorrected) were determined using an electrothermal melting point apparatus. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on a Varian Unity spectrometer operating at 400 and 100 MHz, respectively, using d_6-dimethylsulfoxide (DMSO) as a solvent, unless otherwise stated. For ^{1}H 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. 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 (IR) spectra were recorded on a Bio-Rad FTS-60A spectrophotometer. Samples were recorded in a potassium bromide disc and reported as absorption maxima, ν_{MAX}, quoted in cm^{-1} using the following abbreviations: br = broad, sh = shoulder, s = strong, m = medium, w = weak. Mass spectra (MS) 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 and Micro Analytical Services Pty. Ltd and at the University of Tasmania. Liquid chromatography was performed using Merck TLC grade silica gel, No. 7730. Thermal analysis was carried out on a TA Instruments modulated differential scanning calorimetry (MDSC) instrument, model 2920, at a heating rate of 15°C min^{-1} under a nitrogen atmosphere and on a Setaram thermal gravimetric analysis (TGA) instrument, model TAG 24, at a heating rate of 10°C min^{-1} under an argon atmosphere.

2.3. Monomer syntheses

2.3.1. Synthesis of *N*-(hydroxyphenyl) maleimide monomers (**6**–**8**)

The synthesis of the desired *N*-(hydroxyphenyl) maleimide compounds proceeded via a two step synthesis described in Scheme 1*i*. The *N*-(hydroxyphenyl) maleamic acids (**3**–**5**) were prepared in near quantitative yields (> 95%) from the appropriate substituted amino phenols and maleic anhydride according to the procedure described previously [13].

2.3.1.1. N-(2′-Hydroxyphenyl)-4-amino-4-oxobut-2-enoic acid (N-(2′-hydroxyphenyl) maleamic acid) (**3**). Yield 97% as a yellow powder, m.p. 183–184°C. ^{1}H NMR (DMSO), δ (ppm): 6.35 (1H, d, *J* 12.2 Hz, –CO–CH=C**H**CONH–); 6.68 (1H, d, *J* 12.2 Hz, –CO–C**H**=CH–CONH–); 6.80 (1H, ddd, *J* 8.2, 8.2 and 1.5 Hz, 5′-**H**); 6.91 (1H, dd, *J* 8.2 and 1.5 Hz, 3′-**H**); 7.01 (1H, ddd, *J* 8.2, 8.2 and 1.5 Hz,



Scheme 1. Synthesis of *N*-substituted functional maleimides.

4′-**H**); 7.79 (1H, dd, *J* 8.2 and 1.5 Hz, 6′-**H**); 9.89 (1H, s, 2′-O**H**); 9.96 (1H, s, –N**H**); 13.57 (1H, s, –CO–O**H**). ^{13}C NMR (DMSO), δ (ppm): 115.66 (3′-**C**); 118.96 (6′-**C**); 122.89 (5′-**C**); 125.16 (4′-**C**); 125.63 (1′-**C**–NH–); 131.13 (–CO–CH=**C**H–CONH–); 131.67 (–CO–**C**H=CH–CONH–); 148.46 (2′-**C**–OH); 163.47 (5-**C**=O); 166.83 (2-**C**=O). IR (KBr), ν (cm^{-1}): 3396 s; 3165 br; 1699; 1617; 1566; 1541; 1502; and 1458 s. MS 207 (M$^+$, 35%), 192 (29), 190 (20), 189 (23), 110 (100), 109 (31). Elemental analysis (%): calc. for $C_{10}H_9NO_4$: C, 58.0; H, 4.4; N, 6.8%. Found: C, 57.7; H, 4.2; N, 6.7%.

2.3.1.2. N-(3′-Hydroxyphenyl)-4-amino-4-oxobut-2-enoic acid (N-(3′-hydroxyphenyl) maleamic acid) (**4**). Yield 98% as yellow crystals, m.p. 191–192°C. ^{1}H NMR (DMSO), δ (ppm): 6.30 (1H, d, *J* 12.1 Hz, –CO–CH=C**H**–CONH–); 6.45 (1H, d, *J* 12.1 Hz, –CO–C**H**=CH–CONH–); 6.49 (1H, dd, *J* 8.0 and 2.2 Hz, 4′-**H**); 6.98 (1H, dd, *J* 8.0 and 2.2 Hz, 6′-**H**); 7.10 (1H, dd, *J* 8.0 and 8.0 Hz, 5′-**H**); 7.23 (1H, dd, *J* 2.2 and 2.2 Hz, 2′-**H**); 9.46 (1H, s, 3′-O**H**); 10.29 (1H, s, –N**H**); 13.15 (1H, s, –CO–O**H**). ^{13}C NMR (DMSO), δ (ppm): 106.8 (2′-**C**); 110.4 (4′-**C**); 111.2 (6′-**C**); 129.6 (5′-**C**); 130.6 (–CO–CH=**C**HCONH–), 131.8 (–CO–**C**H=CHCONH–); 139.6 (1′-**C**–NH–); 146.2 (3′-**C**–OH); 157.7 (5-**C**=O); 167.0 (2-**C**=O). IR (KBr), ν (cm^{-1}): 3310; and 3223 br; 1704; 1580; 1527; 1478; and 1292 s MS 207 (M$^+$, 7%), 109 (100), 80 (32), 52 (37). Elemental analysis (%): calc. for $C_{10}H_9NO_4$: C, 58.0; H, 4.4; N, 6.8%. Found: C, 57.8; H, 3.9; N, 6.4%.

2.3.1.3. N-(4′-Hydroxyphenyl)-4-amino-4-oxobut-2-enoic acid (N-(4′-hydroxyphenyl) maleamic acid) (**5**). Yield 93% as yellow plates, m.p. 207–208°C. ^{1}H NMR (DMSO), δ (ppm): 6.30 (1H, d, *J* 12.2 Hz, –CO–CH=C**H**–CONH–); 6.47 (1H, d, *J* 12.2 Hz, –CO–C**H**=CH–CONH–); 6.73 (2H, d, *J* 8.9 Hz, 3′-**H** and 5′-**H**); 7.42 (2H, d, *J* 8.9 Hz, 2′-**H** and 6′-**H**); 9.37 (1H, s, 4′-O**H**); 10.38 (1H, s, –N**H**); 13.69 (1H, s, –CO–O**H**). ^{13}C NMR (DMSO), δ (ppm): 115.3 (3′-**C** and 5′-**C**); 121.6 (2′-**C** and 6′-**C**); 129.8 (–CO–CH=**C**HCONH–); 131.3 (–CO–**C**H=CH–CONH–); 131.8 (1′-**C**–NH–); 154.2 (4′-**C**–OH); 162.8 (5-**C**=O); 166.5 (2-**C**=O). IR (KBr), ν (cm^{-1}): 3430; 3293; 3129; and 3072 br; 2828 w; 1699; 1545; 1506; and 1251 s. MS 207 (M$^+$, 1%), 109 (100), 80 (47). Elemental analysis (%): calc. for $C_{10}H_9NO_4$: C, 58.0; H, 4.4; N, 6.8%. Found: C, 58.0; H, 4.2; N, 6.8%.

2.3.2. General method for cyclodehydration

The desired *N*-(hydroxyphenyl) maleimide compounds (**6**–**8**) were isolated in good yields by using a modification of a method developed for bismaleimides [21]. The appropriate *N*-(hydroxyphenyl) maleamic acid (0.100 mol) together with acetic anhydride (0.100 mol), nickel(II) acetate tetrahydrate (0.040 mol) and triethylamine (0.025 mol) in acetone were stirred at room temperature for 72 h. The corresponding *N*-(hydroxyphenyl) maleimides (**6**–**8**) were isolated via liquid chromatography eluting with dichloromethane (DCM)/ethyl acetate (10:1) in yields between 40 and 80% (Scheme 1ii).

2.3.2.1. N-(2′-Hydroxyphenyl)-1H-pyrrole-2,5-dione (N-(2′-hydroxyphenyl) maleimide) (2HPMI) (**6**). Yield 41% as yellow needles, m.p. 133–134°C. ^{1}H NMR (DMSO), δ (ppm): 6.86 (1H, ddd, *J* 7.6, 7.6 and 1.2 Hz, 5′-**H**); 6.94 (1H, dd, *J* 7.8 and 1.2 Hz, 3′-**H**); 7.12 (1H, dd, *J* 7.8 and 1.7 Hz, 6′-**H**); 7.15 (2H, s, –CO–C**H**=C**H**–CO–); 7.26 (1H, ddd, *J* 7.8, 7.8 and 1.9 Hz, 4′-**H**); 9.83 (1H, s, 2′-O**H**). ^{13}C NMR (DMSO), δ (ppm): 116.7 (3′-**C**); 118.8 (1′-**C**–N–); 119.3 (5′-**C**); 130.4 (4′-**C**); 130.6 (6′-**C**); 135.5 (–CO–**C**H=**C**H–CO–); 154.2 (2′-**C**–OH); 170.4 (2 * **C**=O). IR (KBr), ν (cm^{-1}): 3404; and 3331 br; 3091; and 1768 w; 1698; 1600; 1413; and 1154 s. MS 189 (M$^+$, 89%), 145 (100), 144 (19), 108 (30), 82 (79), 52 (76), 50 (51). Elemental analysis (%): calc. for $C_{10}H_7NO_3$: C, 63.5; H, 3.7; N, 7.4%. Found: C, 63.5; H, 3.6; N, 7.5%.

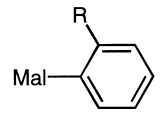
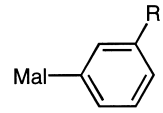
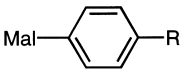
2.3.2.2. N-(3′-Hydroxyphenyl)-1H-pyrrole-2,5-dione (N-(3′-hydroxyphenyl) maleimide) (3HPMI) (**7**). Yield 56% as a yellow powder, m.p. 136–137°C (lit. m.p. [22] 135°C). ^{1}H NMR (DMSO), δ (ppm): 6.73 (2H, m, 2′-**H** and 4′-**H** or 6′-**H**); 6.88 (1H, dd, *J* 8.2 and 2.4 Hz, 4′-**H** or 6′-**H**); 7.13 (s, 2H, –CO–C**H**=C**H**–CO–); 7.24 (1H, dd, *J* 8.2 and 8.2 Hz, 5′-**H**); 9.71 (1H, s, 3′-O**H**). ^{13}C NMR (DMSO), δ (ppm): 113.8 (2′-**C**); 114.7 (4′-**C**); 117.2 (6′-**C**); 129.5 (5′-**C**); 132.4 (1′-**C**–N–); 134.6 (–CO–**C**H=**C**H–CO–); 157.6 (3′-**C**); 169.9 (2 * **C**=O). IR (KBr), ν (cm^{-1}): 3300 br; 3091 w; 1698; 1600; 1415; and 1154 s. MS 189 (M$^+$, 100%), 133 (28), 119 (23), 52 (35), 50 (20). Elemental analysis (%): calc. for $C_{10}H_7NO_3$: C, 63.5; H, 3.7; N, 7.4%. Found: C, 63.4; H, 3.6; N, 7.3%.

2.3.2.3. N-(4′-Hydroxyphenyl)-1H-pyrrole-2,5-dione (N-(4′-hydroxyphenyl) maleimide) (4HPMI) (**8**). Yield 62% as fine orange needles, m.p. 184–185°C (lit. m.p. [21] 182–184°C). ^{1}H NMR (DMSO), δ (ppm): 6.83 (2H, d, *J* 8.8 Hz, 2′-**H**, 6′-**H**); 7.09 (2H, d, *J* 8.8 Hz, 3′-**H**, 5′-**H**); 7.13 (2H, s, –CO–C**H**=C**H**–CO–); 9.64 (1H, s, 4′-O**H**). ^{13}C NMR (DMSO), δ (ppm): 115.5 (3′-**C**, 5′-**C**); 122.6 (1′-**C**–N–); 128.5 (2′-**C**, 6′-**C**); 134.5 (–CO–**C**H=**C**H–CO–); 157.1 (4′-**C**–OH); 170.4 (2 * **C**=O). IR (KBr), ν (cm^{-1}): 3483 br; 3110; and 1770 w; 1704; 1522; and 1150 s. MS 189 (M$^+$, 100%), 119 (28), 52 (29), 50 (22). Elemental analysis (%): calc. for $C_{10}H_7NO_3$: C, 63.5; H, 3.7; N, 7.4%. Found: C, 63.5; H, 3.8; N, 7.5%.

*2.3.3. Synthesis of N-(acetoxyphenyl) maleimides (**9**–**11**)*

The *N*-(acetoxyphenyl) maleimides (**9**–**11**) were prepared according to the procedure described previously [23], and used after purification via liquid chromatography (Scheme 1iii, Table 1).

Table 1
Substitution and percentage yields for compounds **6**–**14**

Structure[a]	Hydroxy-	Acetoxy-	THP-oxy-
	41 (**6**)	78 (**9**)	86 (**12**)
	56 (**7**)	74 (**10**)	72 (**13**)
	62 (**8**)	76 (**11**)	85 (**14**)

2.3.3.1. N-(2′-Acetoxyphenyl)-1H-pyrrole-2,5-dione (N-(2′-acetoxyphenyl) maleimide) (2APMI) (**9**). Yield 78% as a light yellow solid, m.p. 103–104°C. ^{1}H NMR (DMSO), δ (ppm): 2.12 (3H, s, 8′-C**H**$_3$); 7.22 (s, 2H, –CO–C**H**=C**H**–CO–); 7.34 (1H, d, *J* 7.9 Hz, 3′-$_H$), 7.37–7.42 (2H, app. overlapping m, 5′-**H** and 6′-**H**); 7.50 (1H, dd, *J* 7.8 and 2.5 Hz, 4′-**H**). ^{13}C (DMSO), δ (ppm): 20.51 (–CO–**C**H$_3$); 123.66 (1′-**C**–N–); 123.77 (3′-**C**); 126.20 (5′-**C**); 129.68 (4′-**C**); 129.92 (6′-**C**); 135.00 (–CO–**C**H=**C**H–CO–); 146.34 (2′-**C**–OAc); 167.88 (–**C**O–CH$_3$); 169.16 (2 * **C**=O). IR (KBr), ν (cm^{-1}): 3100 w; 1756; 1715; and 1505 s; 1399; and 1157 m. MS 231 (M$^+$, 5%), 189 (100), 145 (60), 82 (31), 52 (34). Elemental analysis (%): calc. for $C_{12}H_9NO_4$: C, 62.3; H, 3.9; N, 6.1%. Found: C, 62.3; H, 4.0; N, 6.1%.

2.3.3.2. N-(3′-Acetoxyphenyl)-1H-pyrrole-2,5-dione (N-(3′-acetoxyphenyl) maleimide) (3APMI) (**10**). Yield 74% as a yellow oil which crystallized overnight, m.p. 43–45°C. ^{1}H NMR (DMSO), δ (ppm): 2.29 (3H, s, –CO–C**H**$_3$); 7.15–7.19 (2H, app. overlapping m, 2′-**H** and 4′-**H**); 7.20 (2H, s, –CO–C**H**=C**H**–CO–); 7.26 (1H, d, *J* 8.2 Hz, 6′-**H**); 7.53 (1H, dd, *J* 8.2 and 8.2 Hz, 5′-**H**). ^{13}C NMR (DMSO), δ (ppm): 20.8 (–CO–C**H**$_3$); 120.2 (6′-**C**); 121.3 (4′-**C**); 124.0 (2′-**C**); 129.6 (5′-**C**); 132.5 (1′-**C**–N–); 134.8 (–CO–**C**H=**C**H–CO–); 150.5 (3′-C); 169.1 (–**C**O–CH$_3$); 169.7 (2 * **C**=O). IR (KBr), ν (cm^{-1}): 3305 br; 1763 w; 1718; 1492; 1213; and 1150 s. MS 231 (M$^+$, 7%), 190 (12), 189 (100), 161 (5), 145 (5), 133 (6), 43 (9). Elemental analysis (%): calc. for $^{12}C^{1}_{12}H^{14}_{9}N^{16}O_4$: *C, 62.3; H, 3.9; N, 6.1%. Found: C, 62.3; H, 3.8; N, 6.0%.*

2.3.3.3. N-(4′-Acetoxyphenyl)-1H-pyrrole-2,5-dione (N-(4′-acetoxyphenyl) maleimide) (4APMI) (**11**). Yield 76% as pale yellow needles, m.p. 160–161°C (lit. m.p. [24] 160–161°C). ^{1}H NMR (DMSO), δ (ppm): 2.30 (3H, s, –CO–C**H**$_3$); 7.20 (2H, s, –CO–C**H**=C**H**–CO–); 7.25 (2H, d, *J* 8.8 Hz, 2′-**H** and 6′-**H**); 7.38 (2H, d, *J* 8.8 Hz, 3′-**H** and 5′-**H**). ^{13}C NMR (DMSO), δ (ppm): 20.8 (–CO–C**H**$_3$); 122.3 (3′-**C** and 5′-**C**); 127.9 (2′-**C** and 6′-**C**); 129.0 (1′-**C**–N–); 134.7 (–CO–**C**H=**C**H–CO–); 149.6 (4′-**C**–OAc); 169.2 (–**C**O–CH$_3$); 169.9 (2 * **C**=O). IR (KBr), ν (cm^{-1}): 3036 w; 1750; 1710; and 1509 s; 1153 m. MS 231 (M$^+$, 4%), 189 (100), 119 (23), 52 (16). Elemental analysis (%): calc. for $C_{12}H_9NO_4$: C, 62.3; H, 3.9; N, 6.1%. Found: C, 61.7; H, 3.7; N, 5.7%.

2.3.4. Synthesis of N-(tetrahydropyranyl oxyphenyl) maleimides (**12**–**14**)[25]

The tetrahydropyranylation of the *N*-(hydroxyphenyl) maleimides (**6**–**8**) was carried out by stirring a solution of the appropriate *N*-(hydroxyphenyl) maleimide (1.0 mmol), 3,4-dihydro-2*H*-pyran (DHP) (1.5 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (0.1 mmol) in DCM at room temperature for 4 h. The PPTS was removed via an aqueous wash and after evaporation of the solvent, the crude mixture was recrystallized from ethyl alcohol to yield the desired *N*-(tetrahydropyranyl oxyphenyl) maleimides (**12**–**14**) in excellent yields (Scheme 1iv).

2.3.4.1. N-[2′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl]-1H-pyrrole-2,5-dione (N-[2′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl] maleimide) (2THP-PMI) (**12**). Yield 86%, m.p. 125–126°C. ^{1}H NMR (DMSO), δ (ppm): 1.40–1.70 (6H, overlapping complex m, 4″-**H**$_2$, 5″-**H**$_2$ and 6″-**H**$_2$); 3.55 (2H, app. m, 3″-**H**$_2$); 5.55 (1H, app. m, 1″-**H**$_2$); 7.05 (1H, dd, *J* 7.6 Hz, 5′-**H**); 7.21 (1H, d, *J* 8.0 Hz, 3′-**H**); 7.23–7.24 (2H, 2 app. s, –CO–C**H**=C**H**–CO–); 7.26 (1H, dd, *J* 1.6 and 7.6 Hz, 6′-**H**); 7.40 (1H, ddd, *J* 1.6 and 7.6 Hz, 4′-**H**). ^{13}C NMR (DMSO), δ (ppm): 17.64 (5″-**C**); 24.57 (4″-**C**); 29.45 (6″-**C**); 60.63 (3″-**C**); 94.85 (1″-**C**); 115.19 (3′-**C**); 120.58 (1′-**C**–N–); 121.16 (5′-**C**); 130.20 (4′-**C**); 130.32 (6′-**C**); 134.89 and 135.03 (–CO–**C**H=**C**H–CO–); 152.21 (2′-**C**); 169.99 and 170.05 (2 * **C**=O). IR (KBr), ν (cm^{-1}): 2965; and 2943 w; 1709 s; 1599; 1506; 1459; 1397; 1297; and 1249 m. MS 273 (M$^+$, 1%), 215 (1), 189 (95), 145 (14), 85 (100), 84 (19), 67 (22), 57 (25), 43 (21). Elemental analysis (%): calc. for $C_{15}H_{15}NO_4$: C, 65.9; H, 5.5; N, 5.1%. Found: C, 65.9; H, 5.7; N, 5.0%.

2.3.4.2. N-[3′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl]-1H-pyrrole-2,5-dione (N-[3′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl] maleimide) (3THP-PMI) (**13**). Yield 72%, isolated as an orange oil. ^{1}H NMR (DMSO), δ (ppm): 1.50–1.90 (6H, overlapping complex m, 4″-**H**$_2$, 5″-**H**$_2$ and 6″-**H**$_2$); 3.33–3.78 (2H, app. complex m, 3″-**H**$_2$); 5.47 (1H, app. s, 1″-**H**$_2$); 6.94 (1H, dd, *J* 7.7 and 1.9 Hz, 4′-**H**); 6.99 (1H, d, *J* 2.3 Hz, 2′-**H**); 7.06 (1H, dd, *J* 8.4 and 2.4 Hz, 6′-**H**); 7.16 (2H, s, –CO–C**H**=C**H**–CO–); 7.34 (1H, dd, *J* 8.4 Hz, 5′-**H**). ^{13}C NMR (DMSO), δ (ppm): 18.55 (5″-**C**); 24.67 (4″-**C**); 29.79 (6″-**C**); 61.58 (3″-**C**); 95.90 (1″-**C**); 115.21 (4′-**C**); 115.62 (2′-**C**); 119.94 (6′-**C**); 129.55 (5′-**C**); 132.50 (1′-**C**–N–); 134.68 (–CO–**C**H=**C**H–CO–); 156.75 (3′-C–O); 169.87 (2 * **C**=O). IR (KBr), ν (cm^{-1}): 2964 and 2943 w; 1709 s; 1600; 1505; 1459; 1397; 1297; 1249; 1203; 1154 and 1120 w. MS 273 (M$^+$, 1%), 215 (1), 189 (95), 145

(14), 85 (100), 84 (34), 67 (28), 57 (24), 43 (18), 41 (15). Elemental analysis (%): calc. for $C_{15}H_{15}NO_4$: C, 65.9; H, 5.5; N, 5.1%. Found: C, 65.7; H, 5.7; N, 5.2%.

2.3.4.3. N-[4′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl]-1H-pyrrole-2,5-dione (N-[4′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl] maleimide) (4THP-PMI) (**14**). Yield 85%, m.p. 120–121°C. ^{1}H NMR (DMSO), δ (ppm): 1.50–1.90 (6H, overlapping complex m, 4″-**H**$_2$, 5″-**H**$_2$ and 6″-**H**$_2$); 3.65 (2H, app. complex m, 3″-**H**$_2$); 5.51 (1H, dd, *J* 3.3 Hz, 1″-**H**$_2$); 7.11 (2H, d, *J* 6.9 Hz, 3-**H** and 5-**H**); 7.15 (2H, s, –CO–C**H**=C**H**–CO–); 7.22 (2H, d, *J* 6.9 Hz, 2-H and 6-H). ^{13}C NMR (DMSO), δ (ppm): 18.54 (5″-**C**); 24.68 (4″-**C**); 29.75 (6″-**C**); 61.55 (3″-**C**); 95.77 (1″-**C**); 116.64 (3′-**C** and 5′-**C**); 124.91 (1′-**C**–N–); 128.19 (2′-**C** and 6′-**C**); 134.59 (–CO–**C**H=**C**H–CO–); 155.86 (4′-**C**); 170.16 (2 * C=O). IR (KBr), ν (cm^{-1}): 3094; 2943 and 2876 w; 1715 and 1510 s; 1399; 1291; 1239; 1202; 1173; 1153 and 1119 m. MS 273 (M^+, 7%), 215 (15), 189 (100), 85 (35), 67 (9), 57 (10), 43 (10). Elemental analysis (%): calc. for $C_{15}H_{15}NO_4$: C, 65.9; H, 5.5; N, 5.1%. Found: C, 65.8; H, 5.7; N, 5.2%.

2.4. Polymerization procedure

A 10 cm^3 decomposition flask was charged with the required maleimide monomer (353 mmol l^{-1}), 2,2′-azobisisobutyronitrile (AIBN) (60 mmol L^{-1}) in the appropriate solvent (either DMF or benzene). The reaction mixture was degassed via three freeze–pump–thaw cycles and the polymerization carried out at 70°C for 6 h. The solvent was removed under reduced pressure and the polymerization mixture dissolved in acetone or tetrahydrofuran (THF) and precipitated into water or methyl alcohol depending on the monomer. The polymer thus obtained was purified further by reprecipitation from acetone or THF into water or methyl alcohol. The yield was determined gravimetrically.

2.4.1. Poly(N-[2′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl]-1H-pyrrole-2,5-dione) (P(2THP-PMI)) (**15**)

Yield 58% as an off-white powder. M_n 17 870; M_w 40 230; PD 2.25; DP 65.43. ^{1}H NMR (DMSO), δ (ppm): 1.43–2.00 (10 H, broad multiplet, 4″-**H**$_2$, 5″-**H**$_2$ and 6″-**H**$_2$ and –CO–C**H**–C**H**–CO–); 3.50–4.20 (2 H, broad multiplet, 3″-**H**$_2$); 5.30–5.50 (1 H, broad singlet, 1″-**H**); 6.40–7.20 (4H, broad multiplet, Ar–**H**). IR (KBr), ν (cm^{-1}): 3470 w; 2944 m; 1715 s; 1601; 1503; 1460; 1392; 1378; 1289; 1248 m.

2.4.2. Poly(N-[3′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl]-1H-pyrrole-2,5-dione) (P(3THP-PMI)) (**16**)

Yield 58% as an off-white powder. M_n 15 290; M_w 33 850; PD 2.21; DP 55.98. ^{1}H NMR (DMSO), δ (ppm): 1.30–2.00 (10 H, broad multiplet, 4″-**H**$_2$, 5″-**H**$_2$ and 6″-**H**$_2$, and –CO–C**H**–C**H**–CO–); 3.30–3.90 (2 H, broad multiplet, 3″-**H**$_2$); 5.20–5.40 (1 H, broad singlet, 1″-**H**); 6.40–7.40 (4H, broad multiplet, Ar–**H**). IR (KBr), ν (cm^{-1}): 3470 w; 2944 m; 1707 s; 1604; 1492; 1391; 1248; 1202 and 1184 m.

2.4.3. Poly(N-[4′-[(tetrahydro-2H-pyran-2″-yl)oxy]phenyl]-1H-pyrrole-2,5-dione) (P(4THP-PMI)) (**17**)

Yield 82% as an off-white powder. M_n 40 000; M_w 77 600; PD 1.93; DP 146.50. ^{1}H NMR (DMSO), δ (ppm): 1.50–2.10 (10 H, broad multiplet, 4″-**H**$_2$, 5″**H**$_2$ and 6″-**H**$_2$, and –CO–C**H**–C**H**–CO–); 3.50–4.10 (2 H, broad multiplet, 3″-**H**$_2$); 5.20–5.40 (1 H, broad singlet, 1″-**H**); 6.40–7.30 (4H, broad multiplet, Ar–**H**). IR (KBr), ν (cm^{-1}): 3468 w; 2944 m; 1706 and 1512 s; 1396; 1242; 1203; 1182; 1169 and 1113 m.

2.5. Molecular weight determination

Number and weight average molecular weights (M_n and M_w) and polydispersity (M_w/M_n) were determined by gel permeation chromatography (GPC) in THF, where the molecular weight was calibrated with polystyrene standards. In reporting the properties of the polymers formed, the degree of polymerization (DP) is also used as it allows for the ready comparison of monomers with differing molecular weights.

$$\mathrm{DP} = \frac{M_n}{\text{Molecular weight of monomer}}$$

3. Results and discussion

The free radical polymerization of the *N*-(hydroxyphenyl) maleimides was initially investigated to determine substituent effects and the effect of the free phenolic group.

3.1. Polymerization of N-(hydroxyphenyl) maleimide compounds (**6**–**8**)

Earlier investigations on free radical initiated polymerizations involving *N*-(hydroxyphenyl) maleimides have been carried out as the free phenol in DMF, at quite high initiator concentrations (upwards of 20 mol%). In order to gauge the influence of the substitution of the phenolic ring on the polymerizations, the same reaction conditions were used for the *ortho*, *meta* and *para* derivatives (Table 2).

The observed molecular weights tended to be very low, corresponding to only 3–5 monomer units. The DP for the polymer derived from the monomer that contains the substituent *ortho* to the maleimide ring tended to be lower than either the *meta* or *para* derivatives. One possible explanation for this phenomenon is related to the proximity of the free phenolic group to the propagating radical in the *ortho* derivative. This could lead to an intramolecular hydrogen abstraction from the phenolic group by the propagating radical, causing the termination of the propagating

Table 2
Free radical polymerization of *N*-(substituted phenyl) maleimide monomers[a]

Monomer	[AIBN][b]	Yield (%)	M_w ($\times 10^3$)	M_n ($\times 10^3$)	M_w/M_n	DP
2HPMI (**6**)	60	23	1.04	0.82	1.26	4.34
3HPMI (**7**)	60	41	2.10	1.48	1.42	7.83
4HPMI (**8**)	60	54	2.49	1.50	1.66	7.94
2APMI (**9**)	60	42	2.09	1.35	1.55	5.84
3APMI (**10**)	60	46	2.43	1.63	1.49	7.06
4APMI (**11**)	60	64	4.25	1.80	2.36	7.79
2THP-PMI (**12**)	60	65	19.94	5.90	3.04	21.60
	6	58	40.23	17.87	2.25	65.43
3THP-PMI (**13**)	60	76	31.60	5.99	5.27	21.93
	6	58	33.85	15.29	2.21	55.98
4THP-PMI (**14**)	60	79	62.00	22.20	2.81	81.28
	6	82	77.60	40.00	1.93	146.50

[a][Monomer] = 353 mmol l^{-1} at 70°C for 6 h
[b]mmol l^{-1}

carbon-centred radical and the formation of an oxygen-centred radical. Reinitiation of the resulting oxygen-centred radical could be relatively slow (retardation) or non-existent (inhibition). The *meta* and *para* derivatives are not as likely to undergo such an intramolecular hydrogen abstraction but are more inclined to an intermolecular reaction because of the relative position of the phenolic substituent and the radical centre. A similar mechanism for the inhibition of the free radical polymerization of *ortho*-hydroxystyrene has previously been proposed [16].

3.2. Synthesis of the N-(acetoxyphenyl) maleimides (**9**–**11**) *and their polymerization*

The acetoxy substituent has been used by several workers to mask or protect the phenolic functionality of *N*-(hydroxyphenyl) maleimides before free radical polymerization [13,14]. The *N*-(acetoxyphenyl) maleimides (**9**–**11**) were synthesized directly from the corresponding maleamic acids using conventional synthetic methodology in good yields (Scheme 1iii). The polymerization of the *N*-(acetoxyphenyl) maleimides was carried out under similar reaction conditions to that used for the *N*-(hydroxyphenyl) maleimides, i.e. in DMF and at high initiator concentrations (Table 2).

The resulting polymers were generally produced in slightly higher yields; however, the degree of polymerization was not significantly affected. In addition, a reduction in the initiator concentration (AIBN) was also found to have a minimal effect on the observed DP. This is contrary to the normal effects of such a reduction in AIBN concentration in a conventional free radical polymerization; the DP should be increased. This result suggests that in addition to the presence of the phenolic group, other factors are contributing to the lack of reactivity of the maleimide monomers.

It has previously been noted that the reactivity of *N*-alkyl maleimides and styrene during free radical polymerizations is affected by the reaction solvent [26–29]. This could explain the lack of reactivity of the acetoxy maleimide derivatives whereby even after the removal of the phenolic group, the solvent could still become involved in the reaction. Hence, the polymerizations were attempted in the inert, non-polar solvent benzene [30]. However, the 2APMI (**9**) monomer was the only one which was found to be soluble and the resulting polymeric material precipitated out of solution after 30 min.

Therefore, the acetoxy group is only a partial solution to the problems associated with the polymerization of the phenolic-based maleimides. It does mask the phenolic group, but does not significantly improve the solubility of either the monomeric or polymeric materials in inert solvents, both of which are desirable factors in controlling the polymerizations.

3.3. Synthesis and free radical polymerization of N-(tetrahydropyran oxyphenyl) maleimides

The *t*-butyloxycarbonyl (*t*-BOC) group has previously been used to mask the phenolic functionality of both *N*-(hydroxyphenyl) maleimides [31,32] and hydroxystyrene [18] before their free radical polymerization. The *t*-BOC protected *N*-(substituted phenyl) maleimide monomers were noted to be sparingly soluble in non-polar solvents and dioxane was used during the free radical polymerization. The resulting polymers were of higher molecular weight than the polymerization of the free phenolic derivatives in DMF. It has also previously been noted that dioxane can effect both the yield and molecular weight of the polymers formed [33–35]. In light of the limitations of dioxane and the poor solubility of the monomers and polymers in inert solvents, the *t*-BOC group was deemed an unsuitable protecting group and an alternative protecting group was sought.

The tetrahydro-2*H*-pyranyl (THP) group is a versatile protecting group which has been used previously during organic syntheses [36,20] and to mask acid functionalities during polymerization reactions [37].

Typically alcohols, phenols, acids, etc., are converted to their tetrahydropyranyl ether derivatives under acid catalyzed conditions and are chemically stable under a variety of reaction conditions. The tetrahydropyranyl group can be removed chemically using acidic media or thermally at temperatures above 150°C to yield the free phenolic substituent. The *N*-(hydroxyphenyl) maleimides were protected using standard synthetic methodology to yield a series of *N*-(tetrahydropyranyl oxyphenyl) maleimides (**12**–**14**), according to Scheme 1iv, in high yields.

Initially, the polymerizations were conducted in DMF using the conditions used previously. The resulting polymers had very similar DPs as those observed for both the polymerization of the free phenolic and acetoxy-masked maleimide derivatives. This reaffirmed our theory that the controlling factor in the polymerizations was the effect of the solvent. The reactions were therefore attempted in benzene. The THP-masked maleimide monomers (**12**–**14**) were all soluble in benzene and their polymerizations using AIBN as an initiator at 70°C for 6 h proceeded in a homogeneous manner (Table 2).

The resulting polymers were all substantially higher in molecular weight than those derived from the polymerizations conducted in DMF. The DPs observed were greatly increased compared to the reactions involving both the free phenolic or the acetoxy-protected monomers. The greatest increase in reactivity was observed for the reaction of the monomer containing the THP group *para* disposed relative to the maleimide ring where a 10-fold increase in the DP was observed. The DPs observed for the polymerization of the *ortho* and *meta* substituted derivatives were similarly increased compared to the polymerization of the free phenolic derivatives but not to the same extent. The THP group is considerably larger than either the hydroxyl or the acetoxy group and consequently any problems associated with steric hindrance would be most pronounced in the *ortho* case. However, the degree of steric interaction is also expected to be quite high for the case of the *meta* derivative due to the size of the THP group, which is evidenced by the similarity in reactivity of the *ortho* and *meta* derivative. The effect of the substitution pattern of the phenyl ring on the polymerization was compared to the unsubstituted derivative *N*-phenyl maleimide. The reaction carried out in DMF produced relatively low DPs and in benzene non-homogenous reaction mixtures formed; therefore, no comparisons could be made due to the apparent overwhelming effect of DMF.

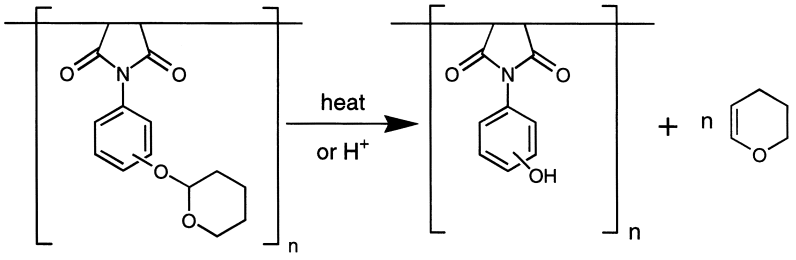
The concentration of AIBN in the systems during the polymerization of the *N*-(THP-oxyphenyl) maleimides also had a marked effect on the observed molecular weights of the polymers (Table 2).

The observed DPs for all of the *N*-(THP-oxyphenyl) maleimide derivatives were greatly increased, producing for the first time very high molecular weight phenolic-based polymaleimides, which are soluble in a wide range of solvents. The system is now reacting in the normal manner expected for a conventional free radical polymerization with regards to changes in the initiator concentration. The fact that this behaviour is observed for reactions carried out in benzene and not in DMF highlights the chain transfer effect of the DMF on the propagating radical. The relatively high concentration of DMF in the previously reported polymerizations means that it has a controlling influence on the course of the polymerizations. Thus previous work was complicated by the presence of the free phenol, the use of chain transfer type solvents and the high levels of initiator used. The use of the tetrahydropyranyl derivatives addresses all these issues; not only does it mask the phenolic functionality, but, perhaps even more importantly, it markedly improves the solubility of the *N*-substituted maleimide monomers and polymers in non-polar solvents. Thus it eliminates the need to use solvents such as DMF or dioxane, which we have clearly shown to act as chain transfer agents in these systems. Whilst chain transfer to DMF has been noted in other systems, e.g. styrene, the effects on molecular weight are not as great as shown here for the maleimide-derived radicals. Previous methods of masking the hydroxyl substituent have not addressed all these issues.

*3.4. Thermal properties and deprotection studies of poly(N-(tetrahydropyranyl oxyphenyl) maleimides (***12**–**14**)

Deprotection of the polymers can be accomplished either chemically under acidic conditions [20] or thermally at elevated temperatures according to Scheme 2.

The thermal deprotection of the poly(*N*-(tetrahydropyranyl oxyphenyl) maleimides) was followed by the Fourier transform infrared (FTIR) spectral changes of a sample of the polymer heated to 300°C (Fig. 1). The



Scheme 2. Deprotection of poly(*N*-(THP-oxyphenyl) maleimides) **15**–**17.**

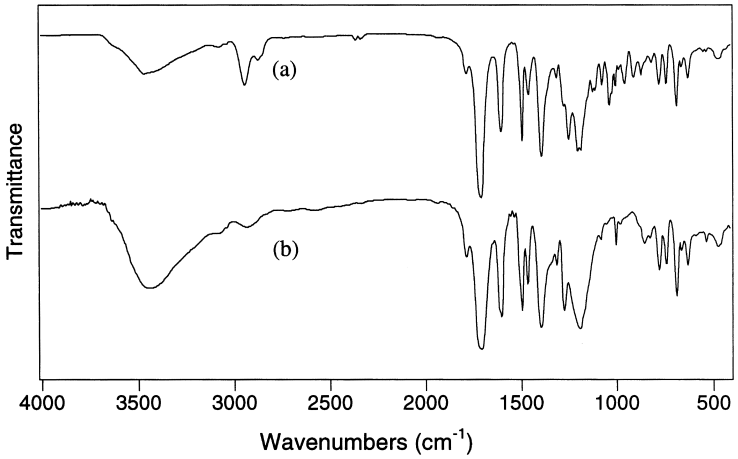


Fig. 1. FTIR spectra of poly(*N*-(2THP-oxyphenyl) maleimide) (**15**) before (a) and after (b) thermal deprotection of THP group at 300°C.

protected polymer has a series of absorption bands at approximately 2950 cm^{-1}, which is characteristic of the tetrahydropyranyl group and no strong hydroxyl band. The FTIR spectra of the deprotected polymer shows a strong broad absorption band at 3470 cm^{-1}, which is characteristic of a hydroxyl group and the bands associated with the THP group are gone. The spectral data (i.e. FTIR, NMR, etc.) of the deprotected polymer were found to be comparable to that of authentic poly(*N*-(hydroxy phenyl) maleimides) prepared by previous methods. Similarly, a sample of poly(*N*-(THP-oxyphenyl) maleimide) was deprotected in the bulk using HCl. The spectral data were similar to the polymers deprotected by heat treatment.

The thermal properties of the poly(*N*-(tetrahydropyranyl oxyphenyl) maleimides) (**15**–**17**) were examined using differential scanning calorimetry (DSC). Two consecutive measurements were taken for each sample which gave information about the deprotection reaction and the thermal properties of the deprotected polymers. The first run was heated at a rate of 15°C min^{-1} up to 325°C. The resulting thermograms reveal an endothermic event between 220 and

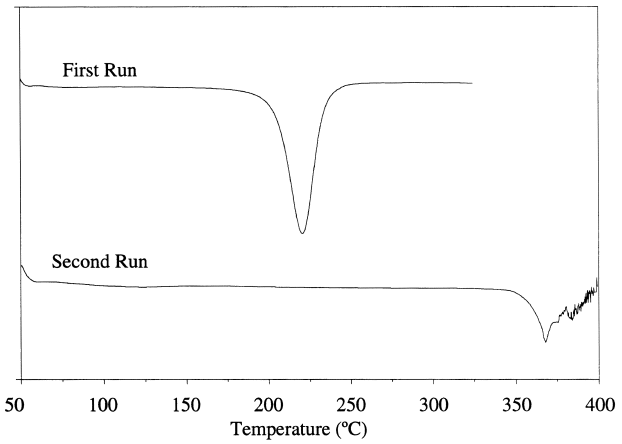


Fig. 2. DSC analysis of poly(*N*-(2THP-oxyphenyl) maleimide) (**15**) in a nitrogen stream at a heating rate of 15°C min^{-1}: first run, deprotection of THP group up to 325°C; second run, deprotected polymer up to 400°C.

240°C (thermal deprotection temperature, T_{dp}), depending on the substitution of the phenyl ring, corresponding to the deprotection of the THP group. The samples were allowed to cool to room temperature and a second run at a heating rate of 15°C min^{-1} up to 400°C was performed as shown in Fig. 2 for poly(*N*-(2THP-oxyphenyl) maleimide) (**15**), to measure the glass transition (T_g) of the deprotected polymer.

Attempts to measure T_g of the deprotected polymer thus formed were unsuccessful. Similar difficulties have been observed by other workers [31,32] attempting to measure T_g for poly(*N*-(4-*t*-butyloxycarbonyl phenyl) maleimide) (DP of 87), where after deprotection, there was no observable T_g. Previous workers have measured the thermal properties of relatively low molecular weight poly(*N*-(4-hydroxyphenyl) maleimide) (DP of 20) and found T_g to be 255°C [38]. The absence of a clear T_g could be associated with the notion that the size of the polymeric chains is reflected in the thermal stability of the polymer, i.e. the larger the chains the higher the T_g [13,39]. Our methodology produces polymeric materials of very high molecular weight, therefore we would expect to observe much higher T_g values than anything previously observed for lower molecular weight polymaleimides and is therefore not easily determined.

The thermal stability of the polymers was further investigated by thermal gravimetric analysis (TGA). All the poly(*N*-(THP-phenyl) maleimides) (**15**–**17**) were found to be stable up to around 200°C, depending on the substitution of the phenyl ring, but above 200°C they undergo thermal deprotection of the THP group by releasing dihydropyran (DHP), as shown in Fig. 3 for poly(2THP-PMI) (**15**).

The percentage weight loss from the TGA thermogram was estimated to be approximately 28%, which is in close agreement with the theoretically calculated percentage weight due to the evolution of DHP of approximately 30%. The results for the other two polymers were also in close agreement with the theoretical weight loss. Possible deviations could be the result of some retention of the DHP in the polymeric material or the occurrence of side reactions

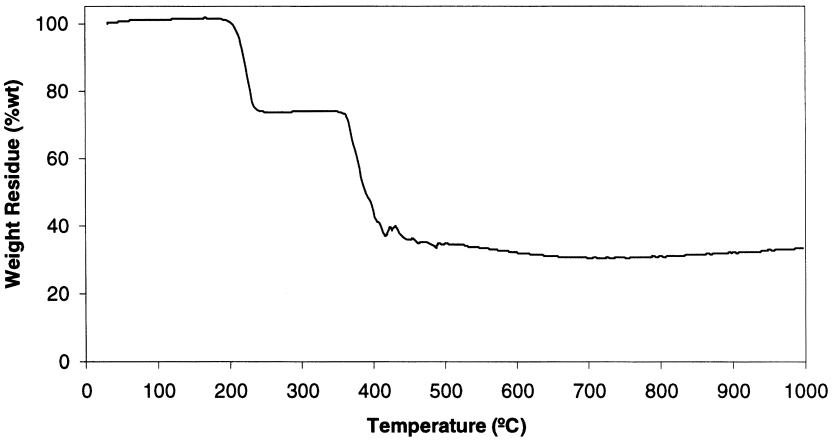


Fig. 3. Thermal gravimetric analysis (TGA) of poly(*N*-(2THP-oxyphenyl) maleimide) (**15**) at a heating rate of 10°C min^{-1}.

with the DHP group at the elevated temperatures used. Continued heating eventually leads to the decomposition of the main chain of the polymers at around 380°C. The temperature at which the polymer starts to decompose was defined as the onset of thermal decomposition temperature (T_{dec}) and was determined for each of the polymers (**15**–**17**). The results of the thermal analysis for each of the polymers are summarized in Table 3.

Examining the overall trends in the thermal stability of the polymeric materials, from Table 3, we observe that the *para* derivative is the most thermally stable of the three substitution patterns. This is evident in both the temperature at which thermal deprotection of the THP group occurs (T_{dp}) and by the onset of the decomposition of the polymeric backbone (T_{dec}). The T_{dp} values for the *ortho* and *meta* derivatives are lower than that observed for the *para* derivative (**17**). This is probably related to there being more steric interaction between the THP group and the maleimide ring in the *ortho* and *meta* derivatives, whereas in the *para* case the THP group is unhindered by such interactions.

The temperature at which the thermal decomposition of the main polymeric backbone of the poly(*N*-(hydroxyphenyl) maleimides) occurs is also dependent on the substitution pattern of the phenolic ring. The highest T_{dec} values are associated with the polymers with the substituents in the *para* position relative to the maleimide ring. For example, a difference of over 20°C is observed between T_{dec} of P(2THP-PMI) (**15**) and P(4THP-PMI) (**17**).

Table 3
Thermal properties of the poly(*N*-(THP-oxyphenyl) maleimides) (**15**–**17**)

Polymer	Weight loss (wt%)[a]	T_{dp} (°C)[b]	T_{dec} (°C)[c]
P(2THP-PMI) (**15**)	27.9	220	361
P(3THP-PMI) (**16**)	25.7	219	360
P(4THP-PMI) (**17**)	25.8	248	382

[a]Measured in wt% by TGA after deprotection of THP group
[b]T_{dp} is the deprotection temperature measured in the first DSC run
[c]T_{dec} is the onset decomposition temperature

4. Conclusions

New methodology has been developed for the synthesis in high yields of *N*-(hydroxyphenyl) maleimides of differing substitution patterns. Polymerization in DMF typically gave low DPs, which was attributed to the presence of the free phenolic group and chain transfer to the solvent. Protection of the phenolic group with an acetoxy group marginally improved the observed DPs, but the effects of the solvent were still controlling the polymerizations. Protection of the phenolic group with a tetrahydropyranyl (THP) protecting group, masks the phenolic functionality and markedly improves the solubility of the monomeric and polymeric materials in inert non-polar solvents. The free radical polymerization of the THP protected maleimide derivatives produced high molecular weight polymers and upon deprotection produced, for the first time, high molecular weight poly(*N*-(hydroxyphenyl) maleimides). All polymers exhibited excellent thermal stability.

Acknowledgements

The authors wish to express their appreciation to Stuart Bateman, Jamie Munton and Mark Looney for their productive discussions. We also acknowledge Comalco Aluminium Limited and the Australian Research Council for financial assistance.

References

[1] Ostu T, Matsumoto A, Kubota T, Mori S. Polym Bull 1990;23:43.
[2] Iwatsuki S, Kubo M, Wakita M, Matsui Y, Kanoh H. Macromolecules 1991;24:5009.
[3] Matsumoto A, Oki Y, Otsu T. Eur Polym J 1993;29:1225.
[4] Oishi T, Yamaski H, Fujimoto M. Polym J 1991;23:795.
[5] Sato T, Masaki K, Kondo K, Seno M, Tanaka H. Polym Bull 1995;35:345.
[6] Olson KG, Butler GB. Macromolecules 1984;17:2480.

[7] Brown IM, Sandreczki TC. Macromolecules 1990;23:94.
[8] Brown IM, Sandreczki TC. Macromolecules 1990;23:4918.
[9] Takeoshi T. Advances in polymer science 94. Berlin: Springer-Verlag, 1994:1.
[10] Park JO, Jang SH. J Polym Sci, Polym Chem Ed 1992;30:723.
[11] Matsumoto A, Hasegawa K, Fukuda A, Otsuki K. J Appl Polym Sci 1991;43:365.
[12] Matsumoto A, Hasegawa K, Fukuda A. Polym Int 1993;31:275.
[13] Turner RS, Arcus RA, Houle CG, Schleigh WR. Polym Eng Sci 1986;26:1096.
[14] Chiang W-Y, Lu J-Y. J Appl Polym Sci 1993;50:1007.
[15] Bailey D, Tirrell D, Vogl O. J Polym Sci, Polym Chem Ed 1976;14:2725.
[16] Kato M. J Polym Sci, Polym Chem Ed 1969;7:2175.
[17] Moad G, Solomon DH. The chemistry of free radical polymerization, 1995:263.
[18] Fréchet JMJ, Eichler E, Ito H, Willson CG. Polymer 1983;24:995.
[19] Kurland JJ. J Polym Sci, Polym Chem Ed 1980;18:1139.
[20] Miyashita N, Yoshikoshi A, Grieco PA. J Org Chem 1977;42:3772.
[21] White JE, Scaia MD, Snider DA. J Appl Polym Sci 1984;29:891.
[22] Marks MJ, Scott DC, Guibeaux BR, Bales SE. J Polym Sci, Polym Chem Ed 1997;35:385.
[23] Chiang W-Y, Lu J-Y. Eur Polym J 1993;29:837.
[24] Chiang W-Y, Lu J-Y. J Polym Sci, Polym Chem Ed 1991;29:399.
[25] Vogel A, Furniss B, Hannaford, ? Vogel's textbook of practical organic chemistry. New York: Longman, 1989:552.
[26] Matsumoto A, Kubota T, Ostu T. Macromolecules 1990;23:4508.
[27] Oishi T, Iwahara M, Fujimoto M. Polym J 1991;23:1409.
[28] George MH. J Polym Sci, Part A 1964;2:3169.
[29] George MH, Ward JR. J Polym Sci, Polym Chem Ed 1973;11:377.
[30] Barson AC. In: Allen G, editor. Comprehensive polymer science, vol. 3. Oxford: Pergamon Press, 1988:171.
[31] Ahn K-D, Lee Y-H, Koo D-I. Polymer 1992;33:4851.
[32] Ahn K-D, Koo D-I, Willson CG. Polymer 1995;36:2621.
[33] Doi T, Akimoto A, Matsumoto A, Oki Y, Otsu T. J Polym Sci, Polym Chem Ed 1996;34:2499.
[34] Doi T, Akimoto A, Matsumoto A, Otsu T. J Polym Sci, Polym Chem Ed 1996;34:367.
[35] Oishi T, Kagawa K, Fujimoto M. J Polym Sci, Polym Chem Ed 1995;33:1341.
[36] Ma S, Venanzi L. Tetrahedron Lett 1993;34:8071.
[37] Kearns JE, McLean CD, Solomon DH. J Macromol Sci Chem 1974;A8 (4):673.
[38] Matsumoto A, Hasegawa K, Fukuda A, Otsuki K. J Appl Polym Sci 1992;44:205.
[39] Fox TG, Flory PJ. J Polym Sci 1954;14:315.