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Control of reactivity of novolac resins: the use of 3,4-dihydro-2*H*-pyran as a labile protecting group

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Abstract

The control of the reactivity of novolac resins towards common crosslinkers through the use of 3,4-dihydro-2*H*-pyran as a protecting group is reported. This thermally labile protecting group is shown to be effective for the control of the cure of the novolac resin system through the use of models and on the resins themselves. The option of controlling the temperature of cure of the resins through the manipulation of the pH of the reaction mixture is also reported. The control of the cure was measured by differential scanning calorimetry (DSC). The use of the protecting group as a means to manipulate the structure of the cured resins is discussed.

Keywords: Novolac; Hexamethylenetetramine; 3,4-Dihydro-2*H*-pyran

1. Introduction

Phenol–formaldehyde resins are one of the oldest totally synthetic polymers having first been discovered some 100 years ago [1]. They were first commercialised in 1909 by Baekeland [2] and have since been used in numerous applications, including refractory and composite materials, adhesives, thermal insulation and electrical industries [1,3,4].

Two classes of phenol–formaldehyde resins are obtained from the reaction of phenol with formaldehyde under either acidic or alkaline conditions, producing novolac or resole resins respectively. Novolac resins typically consist of 8–10 phenolic units, linked via methylene bridges. Resoles on the other hand, are typically low molecular weight prepolymers, consisting of 1–2 phenolic units [1,5]. This paper focuses on the chemistry of novolac resins.

Novolac resins are classified as thermoplastic polymers and a crosslinking agent must be added to the resin before a more rigid, insoluble and infusible polymeric network is formed. The most commonly used crosslinking agent is hexamethylenetetramine (HMTA). The chemistry of this curing or crosslinking reaction with various substituted phenols has been examined extensively [6–8].

The *ortho*- and *para*-unsubstituted phenolic positions of the novolac resin are considered as the reactive sites towards HMTA. Plausible reaction mechanisms have been proposed for their reaction with HMTA, leading to the formation of intermediates such as benzoxazines and benzylamines, culminating in methylene linkages between the phenolic chains [6,7,9,10].

Control of the reactivity of novolac resins towards crosslinking agents such as HMTA is highly desirable and much work has been focused on this goal [11]. By controlling the temperature at which crosslinking reactions occur, volatiles such as solvent and adsorbed water can be removed before a rigid network is formed. In addition, the shaping and fabrication of composite materials can be done at a higher temperature, therefore allowing volatiles to be removed. Finally, there is the possibility of altering the reaction pathways because of the different temperature profiles, leading to different network structures.

On the other hand, it is also highly desirable to exert some control over the viscosity of novolac resins. Lowering the viscosity will also be beneficial during the fabrication of composite materials. In this paper, we report on methods for controlling the reactivity and viscosity of novolac resins towards HMTA, and postulate on the formation of novel network structures.

2. Experimental

2.1. Materials

All starting materials were obtained from either Aldrich Chemical Company or Tokyo Kasei Organic Chemicals,

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and used as received. All solvents were purified in the normal manner [12].

2.2. Analysis

Melting points (uncorrected) were determined using an electrothermal melting point apparatus. Boiling points (bp) were determined on a Büchi boiling point apparatus at atmospheric pressure. 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 chloroform-*d* ($CDCl_3$) unless otherwise stated. Tetramethylsilane (TMS) (δ_H 0.0) was used as an internal reference for ^{1}H spectra and the chloroform central peak (δ_C 77.0) was used as an internal reference for ^{13}C spectra. Chemical shifts are quoted in ppm on the δ scale, followed by proton integration and multiplicity (br, broad; s, singlet; d, doublet; m, multiplet). Fourier transform infrared (IR) spectra were recorded on a Bio-Rad FTS-60A spectrophotometer. Samples were prepared in a KBr disc unless otherwise stated, and reported as absorption maxima, ν_{MAX}, quoted in cm^{-1}. Mass spectra (MS) were recorded at 70 eV, on a VG Micromass 7070F spectrometer and data expressed as *m/z*. Elemental analysis was carried out on a Carlo Erba 1108 CHNO-S analyzer at the University of Tasmania. Radial chromatography was conducted on a Harrison Research Chromatotron Model 7924T using plates prepared as per the manufacturer's instructions [13]. Thermal analysis was carried out on a TA Instruments modulated differential scanning calorimeter (MDSC) Model 2920, at a heating rate of 10°C min^{-1} under a nitrogen atmosphere.

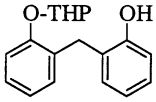
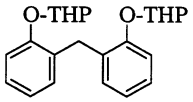
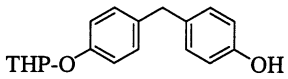
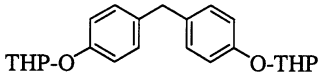
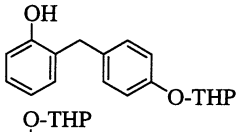
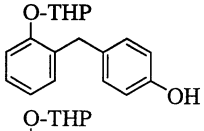
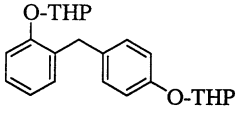
2.3. Synthesis

2.3.1. General method for preparation of DHP protected phenols

The mono-tetrahydropyranyl addition to the dihydroxydiphenyl methanes was carried out by adding to a stirred solution of the appropriate phenol (2.5 mmol) in a dichloromethane/diethyl ether solution ((1:1 mixture), 10 ml), pyridinium *p*-toluene sulphonate (PPTS) (0.30 mmol) and 3,4-dihydro-2*H*-pyran (DHP) (1.5 mmol). The solution was stirred for 3 h and the PPTS removed via an aqueous work up. The combined organic fractions were dried over $MgSO_4$ and the solvent removed under reduced pressure. The products were separated via radial chromatography eluting with petroleum spirits (40–60°C): diethyl ether (7:3). The purity of the products was checked via thin layer chromatography (TLC) using petroleum spirits (40–60°C)/diethyl ether (2:1).

The addition of two tetrahydropyranyl groups was conducted using a similar method except an excess of DHP was added. The various THP-protected compounds and their corresponding yields are presented in Table 1.

Table 1
Structure and percentage yield for compounds (**4**–**10**)

Structure[a]	Number	Yield (%)
	**4**	56
	**8**	6
	**5**	34
	**9**	18
	**6**	48
	**7**	21
	**10**	15

[a] THP = tetrahydropyranyl group.

2.3.2. 3,4-Dihydro-2H-pyran addition to 4,4′-dihydroxydiphenyl methane (2)

Addition of the tetrahydropyranyl group to 4,4′-dihydroxydiphenyl methane (**2**) yielded three compounds.

4,4′-Ditetrahydropyranloxydiphenyl methane (**9**) yield 18%, bp 220°C. ^{1}H NMR δ: 7.0 (m, 8 H), 5.37 (t, 2H), 3.91 (m, 2H), 3.85 (s, 2H), 3.59 (m, 2H), 2.0 (m, 2H), 1.85 (m, 4H), 1.65 (m, 6H). ^{13}C NMR δ: 156.3, 135.5, 130.2, 117.2, 97.0, 62.2, 40.7, 31.0, 25.9, 19.5. R_f 0.58. IR: 2943, 1508, 1235, 1038, 968, 921 cm^{-1}. MS: 368 (M^+), 284, 200 (100%), 107, 85. Elemental analysis (%): calc. for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 74.91; H, 7.73.

4-Hydroxyphenyl-4′-tetrahydropyranyloxyphenyl methane (**5**) yield 34%, bp 210°C. ^{1}H NMR δ: 7.06–6.92 (m, 6H), 6.69 (m, 2H), 5.37 (t, 1H), 3.92 (m, 1H), 3.80 (s, 2H), 3.58 (m, 1H), 1.95 (m, 1H), 1.80 (m, 2H), 1.60 (m, 3H). ^{13}C NMR δ: 155.3, 154.2, 135.1, 133.4, 129.8, 129.8, 116.7, 115.4, 96.8, 62.3, 40.3, 30.5, 25.3, 18.9. R_F 0.33. IR: 3366 (br, O–H), 2945, 1508, 1455, 1233, 970, 754 cm^{-1}. MS: 284 (M^+), 200 (100%), 107, 85. Elemental analysis (%): calc. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.96; H, 7.01.

Unchanged starting dimer (**2**) 44% was recovered. Reaction of 4,4′-dihydroxydiphenyl methane with excess DHP gave 4,4′-ditetrahydropyranyloxydiphenyl methane (**9**) 97% yield. Spectroscopic analysis agreed with that obtained above.

2.3.3. 3,4-Dihydro-2H-pyran addition to 2,4′-dihydroxydiphenylmethane (3)

The ditetrahydropyranyl group addition to 2,4′-dihydroxydiphenylmethane (**3**) yielded four compounds: 2,4′-Ditetrahydropyranyloxydiphenyl methane (**10**) yield 14%, bp 200°C. ^{1}H NMR δ: 7.2 (m, 5H), 7.0 (m, 3H), 5.47 (t, 1H), 5.42 (t, 1H), 4.0 (s, 2H), 3.95 (m, 1H), 3.8 (m, 1H), 3.6 (m, 2H), 2.0 (m, 2H), 1.9 (m, 4H), 1.65 (m, 6H). ^{13}C NMR δ: 155.3, 154.8, 134.4, 130.5, 130.4, 129.7, 127.4, 121.3, 116.4, 114.2, 96.6, 95.9, 62.0, 61.7, 35.7, 35.7, 30.5, 30.5, 25.3, 18.9, 18.7. R_f 0.91. IR: 2943, 1509, 1236, 1037, 968, 921, 753 cm^{-1}. MS: 369 (M + H$^+$), 367, 285, 200 (100%). Elemental analysis (%): calc. for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 74.84; H, 7.60.

2-Hydroxyphenyl-4′-tetrahydropyranyloxyphenyl methane (**6**) yield 44%. ^{1}H NMR δ: 7.1–6.7 (m, 8 H), 5.5 (br, OH), 5.46 (t, 1H), 4.0 (m, 1H), 4.0 (s, 2H), 3.7 (m, 1H), 2.1 (m, 1H), 1.9 (m, 2H), 1.7 (m, 3H). ^{13}C NMR δ: 155.4, 154.0, 133.5, 130.8, 129.8, 127.7, 127.6, 120.6, 116.7, 115.6, 96.6, 62.2, 35.40, 30.5, 25.3, 18.9. R_f 0.65. IR: 3360 (br, O–H), 2946, 1508, 1455, 1233, 970, 754 cm^{-1}. Elemental analysis (%): calc. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.98; H, 7.18.

4-Hydroxyphenyl-2′-tetrahydropyranyloxyphenyl methane (**7**) yield 21%. R_F 0.56. This was seen to be a mixture of the above dimer and the required product. All attempts to separate this mixture failed, and it was noted that this compound underwent rapid equilibration to form a mixture with the above dimer (**6**) in the presence of acid. This equilibration is of interest to us and will be reported in subsequent papers. The 4-hydroxyphenyl-2′-tetrahydropyranyloxyphenyl methane (**7**) was therefore not obtained in a pure form.

Unchanged starting material (**3**) recovered yield 16%. R_f 0.33.

Reaction of 2,4′-dihydroxydiphenylmethane with an excess of DHP gave 2,4′-ditetrahydro-pyranyloxyphenylmethane (**10**) in 88% yield. Spectroscopic analysis agreed with those obtained above.

2.3.4. 3,4-Dihydro-2H-pyran addition to 2,2′-dihydroxydiphenyl methane (1)

The tetrahydropyranyl group addition to 2,2′-dihydroxdiphenyl methane (**1**) yielded three compounds: 2,2′-ditetrahydropyranyloxydiphenyl methane (**8**) yield 6%, mp 89–92°C. ^{1}H NMR δ: 7.1 (m, 6H), 6.9 (m, 2H), 5.4 (m, 2H), 4.1 (s, 2H), 3.8 (m, 2H), 3.6 (m, 2H), 1.9 (m, 2H), 1.8 (m, 4H), 1.6 (m, 6H). ^{13}C NMR δ: 155.1, 130.7, 130.6, 127.3, 121.3, 114.3, 96.3, 62.0, 62.0, 30.7, 25.5, 18.9, 18.9. R_f 0.66. IR: 2946, 1489, 1454, 1233, 1123, 1020, 762 cm^{-1}. MS: 369 (M + H$^+$), 285, 200 (100%), 175, 107, 85. Elemental analysis (%): calc. for $C_{23}H_{28}O_4$: C, 74.97; H, 7.66. Found: C, 74.93; H, 7.65.

2-Hydroxyphenyl-2′-tetrahydropyranyloxyphenyl methane (**4**) yield 56%, bp 167°C. ^{1}H NMR δ: 8.1 (br, OH), 7.2–6.7 (m, 8 H), 5.4 (m, 1H), 3.9 (d, 2H), 3.8 (m, 1H), 3.5 (m, 1H), 2.0–1.4 (m, 6H). ^{13}C NMR δ: 154.1, 130.5, 130.4, 129.1, 127.7, 127.5, 126.7, 122.4, 120.2, 115.8, 115.1, 97.4, 62.4, 30.4, 30.2, 24.9, 18.9. R_F 0.51. IR: 3392 (br, O–H), 2945, 1491, 1454, 1236, 1023, 969, 754 cm^{-1}. MS: 284 (M$^+$), 200 (100%), 107, 85. Elemental analysis (%): calc. for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.97; H, 7.04.

Unchanged dimer (**1**) recovery 36%. R_F 0.42.

Reaction of 2,2′-dihydroxydiphenyl methane (**1**) with excess DHP yielded 2,2′-ditetrahydropyranyloxydiphenyl methane (**8**) in yield of 93%. All spectroscopic analysis agreed with that obtained above.

2.4. General method for reaction of DHP with novolac resins

For the purpose of this study a conventional novolac resin was chosen, which is characterised by a statistical distribution of *ortho* and *para* linkages between phenol units. Varying the amount of tetrahydropyranyl groups added reduced the percentage of hydroxyl groups in the novolac resin. For the calculation of the required amount of DHP for 30, 50 and 100% protection, a value of 10 phenolic repeat units per molecule was used. This was experimentally determined by measuring the ratio of methylene linkages to phenolic resonances via ^{13}C NMR. The DHP was then added in 30, 50 and 100% equivalents by weight. Stirring an acetone solution of the required amount of novolac resin, 3,4-dihydro-2*H*-pyran (DHP) and pyridinium *p*-toluenesulphonate (PPTS) at room temperature for 24 h performed the addition of the tetrahydropyranyl group. The PPTS was removed via an aqueous wash and the combined organic layers dried over $MgSO_4$. Removal of the solvent under reduced pressure yielded a dark brown viscous oil.

2.4.1. 30% Protected novolac

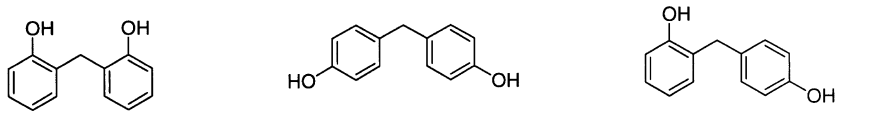
Resin (4.0 g, 4.0 mmol), PPTS (0.20 g, 0.69 mmol) with DHP (1.3 ml, 17 mmol) yielded a product with ^{1}H NMR δ (Acetone-d_6): 6.4–7.2, 4.9, 4.8, 2.8–4.0, 1.3–1.8. IR: 3347 (br, O–H), 2946, 2869, 1700, 1611, 1511, 1441, 1363, 1233, 1109, 1021, 967 cm^{-1}.

2.4.2. 50% Protected novolac

Resin (4.0 g, 4.0 mmol), PPTS (0.20 g, 0.69 mmol) with DHP (2.2 ml, 28 mmol) yielded a product with ^{1}H NMR δ (Acetone-d_6): 6.5–7.2, 5.2–5.3, 4.9, 4.8, 2.6–4.2, 1.3–1.9. IR: 3392 (br, O–H), 2945, 2871, 1702, 1510, 1233, 1125, 1073, 1032, 1022, 967 cm^{-1}.

2.4.3. Attempted formation of 100% protected novolac

Resin (4.0 g, 4.0 mmol), PPTS (0.20 g, 0.69 mmol) with DHP (4.4 ml, 57 mmol) yielded a product with ^{1}H NMR δ (Acetone-d_6): 6.6–7.2, 5.1–5.4, 4.9, 4.8, 2.6–4.2, 1.3–1.9. IR: 3395 (br, O–H), 2944, 2871, 1711, 1507, 1236, 1202, 1125, 1036, 1022, 968, 920 cm^{-1}.



(**1**) 2,2'-dihydroxydiphenyl methane (**2**) 4,4'-dihydroxydiphenyl methane (**3**) 2,4'-dihydroxydiphenylmethane

Fig. 1. Phenolic dimers used as models for novolac resins.

3. Results and discussion

The reactivity of novolac resins towards crosslinking agents can be controlled using a variety of methods, including pH, concentration of crosslinker, temperature and type of crosslinker. In this paper, we examine chemical modification of the structure of the novolac resins as a tool for controlling the reactivity of the novolac resin and thus its final crosslinked structure.

3.1. Compounds which model the functionality of novolac resins

The curing reactions between novolac resins and crosslinking agents such as HMTA are often very complicated. The cured resins are inevitably highly crosslinked materials that do not melt or dissolve, hampering the elucidation of significant structural information. We therefore chose to examine compounds that model the functional groups in a novolac resin then apply these results to a novolac resin system.

The phenolic dimers (**1**), (**2**), and (**3**) (Fig. 1) were chosen as they are representative of the different types of functional groups present in a novolac resin.

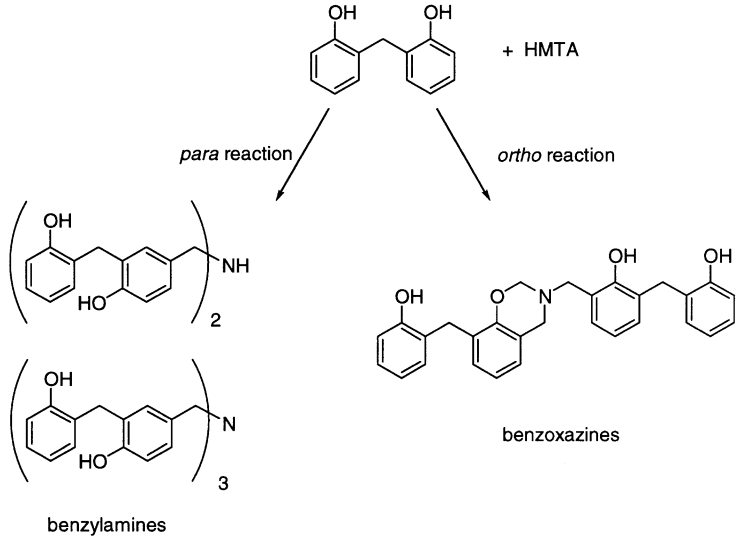
We have previously described the reactivity of these compounds towards HMTA, and found that the reaction requires a free phenolic group and the nature of the initially formed intermediates depends on the point of reaction. Reaction at free *ortho* positions relative to the phenolic group, tends to form benzoxazine compounds, and free *para* positions form benzylamines [7,14–16]. This is exemplified by the reaction of 2,2′-dihydroxyldiphenyl methane with HMTA (Scheme 1).

It was therefore envisaged that masking or protecting the phenolic functionality could manipulate its reactivity towards HMTA.

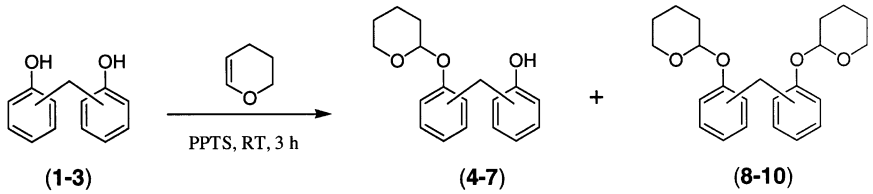
3.2. Choice of protecting group for novolac resins

Traditional methods for protecting hydroxyl or phenolic groups, such as acetylation or methylation were investigated, but for the purposes of this study were found to be unsuitable for a variety of reasons (stability, reversibility, etc). An alternative protecting group is the versatile tetrahydropyranyl group (THP), which has previously been used to mask phenolic groups during organic synthesis [17–19].

The tetrahydropyranyl group can be removed either chemically or thermally at temperatures above 150°C. Therefore a proportion of the phenolic groups can be masked, limiting the reactivity of the novolac resin, and when necessary the protecting group removed allowing further crosslinking reactions to occur. To investigate this, the addition of a tetrahydropyranyl group to the phenolic dimers (**1**–**3**) was conducted using standard synthetic methodology, yielding a series of novel mono and di-THP protected dimers (**4**–**10**), according to Scheme 2.



Scheme 1. Some of the proposed products from reaction of 2,2′-dihydroxyphenyl methane (**2**) with HMTA.



Scheme 2. Synthesis of THP-protected dimers.

3.3. Effect of THP protection on reactivity of dimers towards HMTA

The reactivity of the protected and unprotected dimers towards HMTA was examined using differential scanning calorimetry (DSC). DSC analysis allows reactions to be monitored as a function of increasing temperature. The utility of this technique is exemplified by the DSC thermograms for the reaction of both the free phenolic dimer (**1**) Fig. 2(A) and the corresponding diprotected dimer (**8**), Fig. 2(B) with HMTA.

The thermogram for the reaction of (**1**) with HMTA (Fig. 2(A)) reveals an endothermic event between 115–120°C, corresponding to the melting point of the dimer and a significant exothermic event at 130°C, which is consistent with the onset of reaction. The reaction products were identified as both benzylamine and benzoxazine type species by their characteristic ^{13}C NMR. These results compare favourably with the data previously collected on the reactivity of the dimer compounds [20].

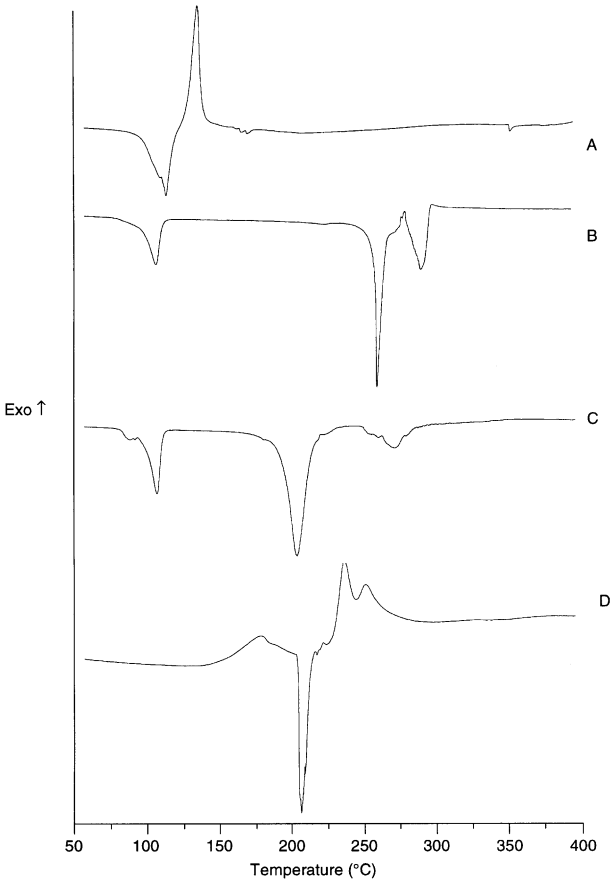


Fig. 2. (A) DSC trace of 2,2′-dihydroxydiphenyl methane (**1**) with HMTA 10% w/w. (B) DSC of 2,2′-ditetrahydropyranyloxydiphenyl methane (**8**) with HMTA 10% w/w. (C) DSC trace of 2,2′-ditetrahydropyranyloxydiphenyl methane (**8**). (D) DSC trace of 2-hydroxyphenyl-2′-tetrahydropyranyloxyphenyl methane (**4**) with HMTA 10%.

In contrast, the DSC thermogram for 2,2′-ditetrahydropyranyloxydiphenyl methane (**8**) (Fig. 2(B)) reaction with HMTA shows several important differences. Besides an endothermic melting peak at approximately 105–110°C, there are no further peaks until the endothermic THP deprotection reaction at approximately 260°C. This is immediately followed by an exothermic event that is related to the free phenolic dimers interaction with HMTA. The third endothermic peak occurring at approximately 280°C is due to the sublimation of excess HMTA from the system. This demonstrates that there is no reactive interaction between the THP-masked dimer and HMTA until the protecting group is removed. Then the interactions between the free phenolic group and HMTA occur normally, albeit at a greatly increased rate due to the increased temperature. This means that both the formation of the first formed intermediates occurs quicker and their subsequent decomposition to form methylene linkages can occur more readily.

Similar reaction profiles were observed for the other di-protected dimers, (**9** and **10**) with HMTA, where interaction only occurred after the thermal removal of the THP group.

3.4. Reactivity of the mono-THP protected phenolic dimers and control of end group structure

The ability to delay the reaction of the dimer with HMTA by protection with a THP group provides a mechanism for significant control of the resin chain structure. By masking one of the phenolic groups of the dimer with THP and leaving the other free to react, the reaction can only proceed from one side of the dimer, placing the protected group at the end of the chain.

To observe this the mono-THP protected dimer was reacted with HMTA at levels of 2.5, 5 and 10% w/w. The reaction was conducted isothermally at 150°C, this being the temperature of cure for the unprotected dimer but well below the observed temperature of THP deprotection. The mono-THP protected compounds were seen to cure, and the products were readily soluble in chloroform. NMR of

the compounds showed characteristic peaks for cure with the THP group still intact. The analogous reaction of the unprotected dimers with the same quantities of HMTA was also conducted, the products of these reactions were found to be insoluble in chloroform and acetone, this was observed for all concentrations of HMTA. Thus the presence of the protecting group limits the cure to the single unprotected ring resulting in the formation of lower molecular weight compounds. The NMR of mono-THP protected dimer with 2.5% HMTA w/w did not contain any residual HMTA after cure at 150°C therefore upon deprotection of the THP group free phenolic groups would remain.

The NMR of the mono-THP protected compounds with 5 and 10% HMTA w/w showed the presence of residual HMTA in the system leaving the dimers open to further cure on deprotection.

3.5. Secondary cure of mono-THP protected dimers

As noted above the reactions with 5% w/w or greater HMTA with mono-THP protected dimer showed residual HMTA after the primary cure of the unprotected ring. This would leave the protected ring free to undergo further cure on thermal removal of the THP group. This is shown in the DSC trace for the reaction of 2-hydroxyphenyl-2′-tetrahydro-pyranyloxyphenyl methane (**4**) containing HMTA 10% w/w, Fig. 2(D).

The mono-THP protected dimer (**4**) is an oil at room temperature therefore the first observed peak is the exothermic event at approximately 175°C, which is the interaction of the free phenolic moiety with HMTA as discussed above. As the temperature is increased, the THP group is thermally removed at approximately 210°C, followed immediately by reaction of the remaining HMTA in the system. These reactions are complicated due to the elevated temperatures involved. For the other mono-THP protected dimers (**5**), (**6**) and (**7**), similar trends were observed where normal interactions occur between the free phenolic groups and HMTA. When the temperature is increased past the thermal THP-deprotection point, further reaction occurs between the newly formed free phenolic and HMTA.

It should be noted that the temperature for the THP-deprotection reaction in this system is considerably lower than those observed for the di-THP protected monomers. This difference offers another way via which the reactivity of the THP-protected compounds can be controlled. The factors controlling the THP deprotection reaction are discussed in Section 3.6.

3.6. Factors controlling the deprotection of the THP-masked dimers

The deprotection temperature of 2,2′-ditetrahydropyranyloxydiphenyl methane (**8**) by itself was shown to occur at 200°C (Fig. 2(C)). This is considerably lower than that observed for the same compound in the presence of HMTA (Fig. 2(B)). A possible explanation for this change in deprotection temperature is that the deprotection reaction is catalysed by acid. HMTA is basic [21] and would therefore have the effect of increasing the required temperature of tetrahydropyranyl ether degradation. To confirm this a series of reactions was conducted in the DSC where the 2,2′-ditetrahydropyranyloxydiphenyl methane (**8**) was heated with either an acid (PPTS) or a base (sodium acetate) and the effect on the deprotection temperature noted. It was observed that in the presence of the PPTS the temperature of deprotection was lowered, while in the presence of sodium acetate deprotection temperatures comparable to those observed with HMTA were seen. These results support the hypothesis that the deprotection temperature depends on the pH of the reaction conditions. As both the protection and deprotection reactions are catalysed by acid, any addition of acid would increase the rate while any addition of base would decrease the rate of reaction. The change in pH will also have an effect on the reactivity of HMTA towards the hydroxyl groups. This would provide a further method for control of the temperature of reaction with HMTA.

3.7. Application of THP protection methodology to novolac resins

The applicability of our newly developed THP protection methodology as a means of controlling the reactivity of novolac resins was investigated by examining a commercially available novolac resin on protection. The conventional resin used had an average chain-length of 8–10 units, comprising 25% *ortho–ortho′*, 22% *para–para′* and 53% *ortho–para′* methylene linkages [6]. The level of THP-protection of the novolac resins was varied between 30, 50 and up to approximately 100% by weight.

Interestingly, there is an observable reduction in the viscosity of the THP-protected novolac resin. It is well known that the viscosity of the dissolved unprotected novolac resin in solvents is generally very high [22]. This high viscosity is believed to be primarily due to extensive intermolecular hydrogen bonding that occurs between the novolac chains. The protection of a significant proportion of phenolic groups with the THP-group disrupts the intermolecular hydrogen bonds, reducing the observed viscosity.

The reactivity of the protected novolacs towards 10% wt HMTA was examined by DSC analysis, as shown in Fig. 3.

The DSC thermograms for the THP-novolac systems (Fig. 3) show that there is a common endothermic THP-deprotection event at approximately 200°C for each of the novolacs. The 30% THP-protected novolac has a large exothermic crosslinking event at between 140–160°C, consistent with the unprotected phenolic ring reacting with HMTA. For the higher levels of phenolic THP-protection, 50 and 100%, there is a lowering of the intensity of this first peak. Interestingly there is a small exothermic peak at 175–180°C for the nominally 100% THP-protected novolac. Protection of 100% of the phenolic groups was not

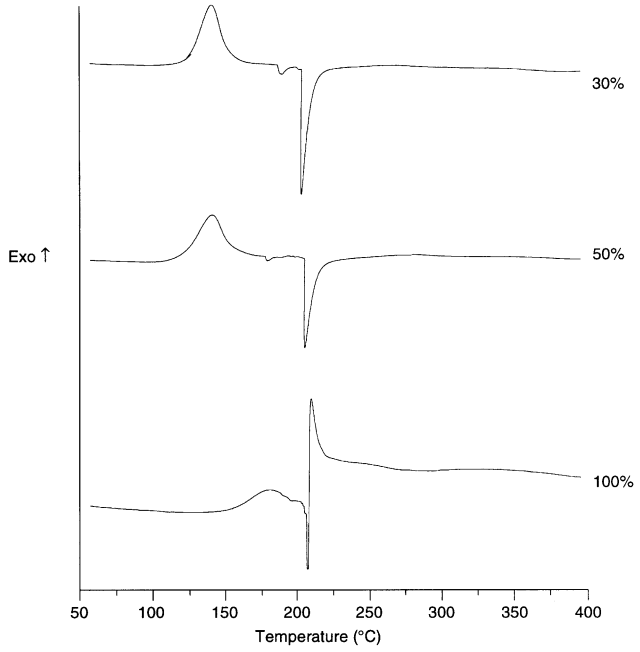


Fig. 3. DSC trace for protected Novolac with 10% HMTA w/w. Percentage THP protection as shown.

achieved, indicating that some of the phenolic groups are not accessible to the protecting agent under our reaction conditions. Even under reaction conditions where a vast excess of DHP was added, less than 100% THP protection was achieved. However, the level of initial cure observed is small compared to that seen in the 30 and 50% protected compounds.

The absence of a post deprotection exothermic cure peak requires comment. The prior crosslinking of the novolac may have the effect of using the available HMTA or of making the newly liberated phenolic groups inaccessible for further cure. This would explain the absence of the cure peak at the higher temperatures that would be expected from comparison with the dimer results. Confirmation of this is seen in the DSC of the novolac resin with attempted 100% protection (Fig. 3), where the post deprotection cure peak is observed. The greater level of protection would result in less initial crosslinking and more available HMTA for post deprotection cure.

The results seen for the novolac resins confirm the use of our models as a way of predicting the chemistry of the tetrahydropyranyl ethers in the more complex resin systems.

4. Conclusions

The use of a chemical protecting group provides a method for control of the cure onset temperature of novolac resins. The use of the THP group has provided a convenient method for the protection of the resins and has the advantage of being able to be removed thermally. This has been shown to increase the temperature of reaction with HMTA by preventing reaction with the phenolic groups required for cure until the thermal decomposition of the tetrahydropyranyl ether. As this is at a temperature higher than that required for reaction with HMTA the novolac is then free to cure. It can also be seen that this has a localised effect leaving the unprotected phenolic groups free to react at the normal cure temperature. The combination of these two factors alters the properties of the final crosslinked product. The effect on the carbon structure upon pyrolysis will be discussed in a following publication.

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