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Studies on polyimides: Part 3. Interactions between hexamethylenetetramine and models for polyimides and novolacs

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Abstract

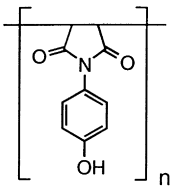
The interactions between hexamethylenetetramine (HMTA) and models for both poly(*N*-(hydroxyphenyl) maleimides) and phenol-formaldehyde resins have been examined. There is direct interaction between HMTA and the *N*-(hydroxyphenyl) succinimide and xylenols used as model compounds. When the model compounds both contain a free *ortho* position, four different benzoxazine derivatives are formed, that is, the succinimide–succinimide and xylenol–xylenol benzoxazines and the two 'mixed' systems. The rate of reaction of HMTA with the mixed system was measured via ^{13}C nuclear magnetic resonance spectroscopy (n.m.r.). The relative rates of formation of the benzoxazine derivatives are dependent on the substitution pattern of the phenolic rings. Control over the interactions between HMTA and the models was achieved via selective masking of the phenolic groups using the thermally labile tetrahydropyranyl (THP) group.

Keywords: Polyimide; Hexamethylenetetramine; Phenol-formaldehyde resin

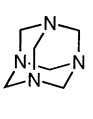
1. Introduction

In recent years there has been considerable work directed towards engineering high performance composite materials. One example is the use of poly(*N*-(hydroxyphenyl) maleimides) (**1**), which are blended with phenol-formaldehyde resins and after crosslinking with hexamethylenetetramine (HMTA) (**2**) to give composites with excellent thermal and chemical stability [1–6]. For example, it has been shown [1] that the incorporation of 50 wt% of poly(*N*-(hydroxyphenyl) maleimides) (HPMI) increases the *Tg* of a novolac from 90 to 175°C, and increased the thermal deflection temperature from 155 to 165°C for 20 wt% poly (HPMI). However, the chemistry of the crosslinking reaction is poorly understood.

We have previously reported [7] on the use of appropriately substituted *N*-(hydroxyphenyl) pyrrolidine-2,5-diones, herein referred to as *N*-(hydroxyphenyl) succinimides, with the generalized structure (**3**), to model polyimides in their reaction with HMTA. It was demonstrated that the model polyimides react in an analogous manner to the phenolic rings in phenol-formaldehyde resins, producing the same types of reactive intermediates. Further, the presence of the succinimide ring increases the reactivity of the phenolic ring towards HMTA, this was exemplified by the increased rate of HMTA consumption. However, in polyimide–phenol-formaldehyde resin blends, there are no reported studies on the chemistry of the process. In this paper, we describe our model studies on the possible interactions between HMTA, polyimides and phenol-formaldehyde resins. In addition, an approach to the control of the interactions by the use of thermally labile substituents is explored.



(1)



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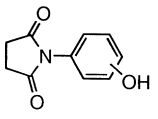

(3)

2. Experimental

2.1. Materials

Succinic anhydride (Aldrich, AR) was used as received, aminophenols were either purchased from Aldrich or synthesized using standard literature procedures [8,9]. All were recrystallized from ethyl alcohol. 2,4,6-Trimethylphenol (TMP) (Aldrich) was recrystallized from pentane. 2,4-Xylenol (Aldrich, 99%) and 2,6-Xylenol (Aldrich, 99%)

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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.

2.2. Instrumentation

Melting points (uncorrected) were determined using an electrothermal melting point apparatus. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance (n.m.r.) 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 (δH 2.49 ppm) was used as an internal reference, whilst the central peak d_6-DMSO (δC 39.5 ppm) was used as an internal reference for ^{13}C spectra. Chemical shifts are quoted in ppm on the d 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 (*FT*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, ν_{MAX}, quoted in wave numbers (cm^{-1}) using the following abbreviations: br = broad, sh = shoulder, s = strong, m = medium, w = weak. Liquid chromatography was performed using Merck TLC grade silica gel, No. 7730.

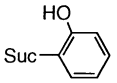
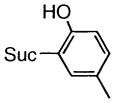
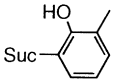
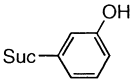
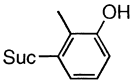
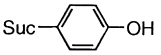
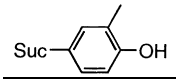
2.3. Synthesis of N-(hydroxyphenyl) succinimides (4–10)

The *N*-(hydroxyphenyl) succinimide compounds (**4**–**10**), were synthesized by heating succinic anhydride (1.1 equivalent) and the appropriate amino phenol (1 equivalent) at 170°C for 3 h (Scheme 1). The subsequent cyclodehydration reaction afforded the desired *N*-(hydroxyphenyl) succinimides in excellent yields after recrystallization from ethyl alcohol (Table 1). Full experimental details have been detailed in our previous paper [7].

2.4. Procedure for preparation of 'mixed' benzoxazine derivatives

A mixture of the *N*-(hydroxyphenyl)-succinimide (3.00 mmol), 2,4-xylenol (14) (3.00 mmol) and hexamethylenetetramine (**2**) (1.00 mmol) in 2,4,6-trimethylphenol (TMP) (21.00 mmol) was heated at 130°C for 3 h. The reaction mixture was purified by liquid chromatography eluting with dichloromethane/petroleum spirits (8:2) and dichloromethane/ethyl acetate (7:3) to afford the desired benzoxazine derivatives.

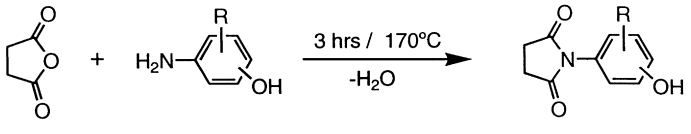
Table 1
Substitution of the *N*-(hydroxyphenol) succinimide model compounds (**4**–**10**)

Structure[a]	Abbreviated name[b]	Number
	2HPSI	**4**
	5M2HPSI	**5**
	3M2HPSI	**6**
	3HPSI	**7**
	2M3HPSI	**8**
	4HPSI	**9**
	3M4HPSI	**10**

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

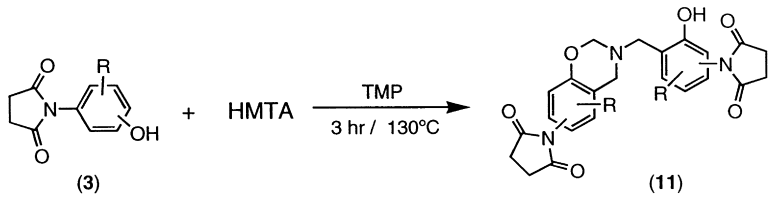
2.5. N-(hydroxyphenyl) succinimide/2,4-xylenol/HMTA n.m.r. reactions

A 3:3:2 mole ratio mixture of the appropriate *N*-(hydroxyphenyl) succinimide/2,4-xylenol and HMTA in 2,4,6-trimethylphenol (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, dissolved in d_6-DMSO (1.000 g) and the reaction mixture observed 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 (at approximately 81.8, 49 and 55 ppm) were monitored. The integrations were standardized relative to the ethylene resonances of the succinimide ring (28.7 ppm) whose intensity remains unchanged during the course of the reaction.



(**3**)

Scheme 1. Synthesis of *N*-(hydroxyphenyl) succinimides (**4**–**10**) where R = H or CH_3.



Scheme 2. Reaction of HMTA with *N*-(hydroxyphenyl) succinimides that contain a vacant *ortho* position, where R-H or CH_3.

2.6. Synthesis of THP masked phenolic derivatives

The tetrahydropyranylation of 5M2HPSI (**5**) and 2,4-xylenol (**14**) was carried out according to our previously reported method [10].

*2.7. N-[5′-methyl-(2′-[(tetrahydro-2H-pyran-2″-yl)oxy] phenyl]-pyrrolidine-2,5-dione (5M2THP-PSI) (***19***)*

Yield 88%. m.p. 144–145°C. ^{1}H n.m.r., δ (ppm): 1.44–1.70 (6H, overlapping m, 4″–H_2, 5″–H_2 and 6″–H_2); 2.25 (3H, s, 5′–CH_3); 2.81 (4H, s, –CO–CH_2–CH_2–CO–); 3.55 (2H, app. complex m, 3″–H_2); 5.43 (1H, app. s, 1″–H_2); 6.97 (1H, d, J 1.8 Hz, 6′–H); 7.10 (1H, d, J 8.5 Hz, 3′–H); 7.18 (1H, dd, J 8.6 and 1.8 Hz, 4′–H). ^{13}C n.m.r., δ (ppm): 17.91 (5″–C); 19.85 (5′–CH_3); 24.66 (4″–C); 28.44 and 28.46 (–CO–CH_2–CH_2–CO–); 29.62 (6″–C); 60.76 (3″–C); 95.50 (1″–C); 115.62 (3′–C); 121.84 (1′–C–N–); 129.56, 130.31, 130.33 and 149.61 (Ar–C); 176.48 (2*C=O). I.r. (KBr) (cm^{-1}): 2958; 2943 and 2883 m; 1710 s; 1512; 1438; 1293; 1269 and 1192 m.

2.8. 2,4-Dimethyl-1-tetrahydro-2H-pyran-2′-yl) oxyphenyl ***(20)***

Yield 55%. Colourless liquid. ^{1}H n.m.r., δ (ppm): 1.62–1.94 (6H, overlapping complex m, 4′–H_2, 5′–H_2 and 6′–H_2); 2.31 (6H, 2*CH_3); 3.70 (2H, app. complex m, 3′–H_2); 5.40–5.45 (1H, app. complex m, 1′–H_2); 6.97–7.03 (3H, Ar–H). ^{13}C n.m.r., δ (ppm): 16.15 (2–CH_3); 18.93 (5′–C); 20.45 (4–CH_3); 25.29 (4′–C); 30.55 (6′–C); 61.94 (3′–C); 96.27 (1′–C); 114.18, 126.95, 127.03, 130.42 and 131.34 (Ar–C); 152.84 (1–C). I.r. (NaCl plates) (cm^{-1}): 2943 and 2871 s; 1503; 1251; 1201; and 1132 s.

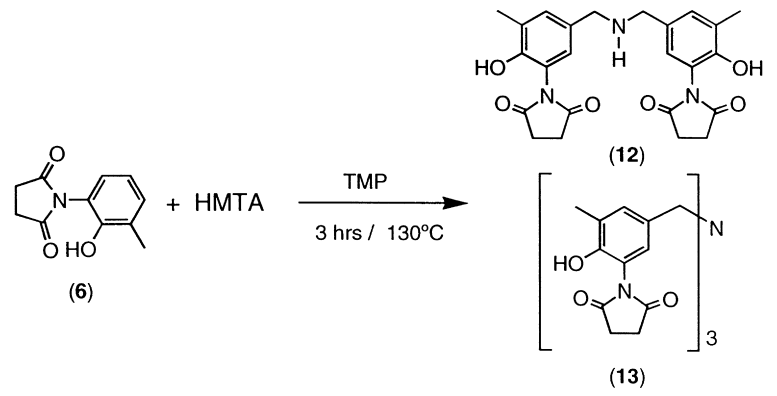
3. Results and discussion

The mechanism via which HMTA reacts with the phenolic ring of the model polyimide compounds depends on the substitution of the phenolic ring. Reaction occurs at the vacant positions either *ortho* or *para* to the hydroxyl substituent. For example, in the reaction of model polyimides which contain a vacant *ortho* position, relative to the hydroxyl group, the initial intermediates formed are benzoxazines type derivatives with the general structure (**11**) (Scheme 2).

For the model compounds which contain a vacant *para* position, 3M2HPSI (**6**), the initial products formed were a mixture of benzylamine type derivatives according to Scheme 3.

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. Similar reaction mechanisms have been demonstrated to occur during the reaction of model compounds for phenol-formaldehyde resins with HMTA [11–13].

Industrially, polyimides are blended with phenol-formaldehyde resins and then crosslinked with HMTA, resulting in an infusible, insoluble, three-dimensional polymeric network. Given the different rates of reaction between



Scheme 3. Reaction of 3M"HPSI (**6**) and HMTA in a mole ratio of 3:1 (phenolic:HMTA).

HMTA with either the phenol-formaldehyde models or the polyimide compounds individually, it was of interest to establish whether in the mixed systems a homogenous polymeric network is formed or whether one polymer forms a separate crosslinked phase within which the other is dispersed. It would be expected that the properties of the mixed system are dependent on the phase structure formed. One technique to examine such systems is by the use of high resolution solid state ^{13}C n.m.r. with cross polarization and magic angle spinning (CP/MAS NMR) [14–16]. However, due to the experimental limitations of the technique, the resonances observed for each of the carbon environments tend to be fairly broad, making the assignment of small changes in the chemical structure of the polymeric network difficult. Consequently, it was envisaged that by using monomeric model compounds the study of the chemistry could be simplified greatly.

3.1. Selection of suitable models for phenol-formaldehyde resin

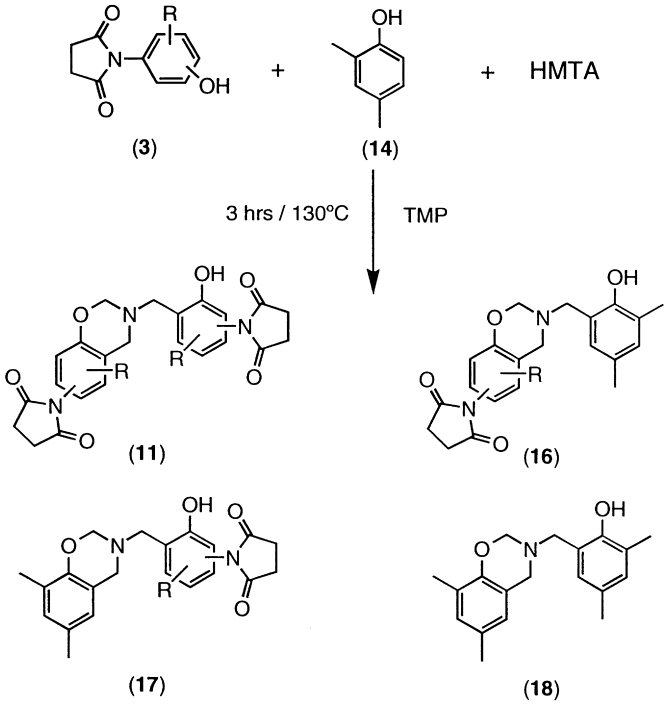
Previous studies [17,18,13] have used 2,4-xylenol (**14**) and 2,6-xylenol (**15**) as model compounds for the repeat units of phenol-formaldehyde resins, since they contain one reactive site, either *ortho* or *para* to the hydroxyl group and represent the two different internal phenolic units of a phenol-formaldehyde resin. When reacted with HMTA, 2,4-xylenol was found to form benzoxazine type derivatives and 2,6-xylenol forms benzylamine type derivatives. The reaction conditions used during this present study (i.e. TMP as solvent, 130°C) are somewhat different from those used by other workers, however, the reaction products are similar. The rate at which the *para* reaction occurs under the present conditions is very slow. Consequently, it was decided to focus attention on the interactions between HMTA and a mixture of the models which contain a vacant *ortho* position.

(**14**) (**15**)

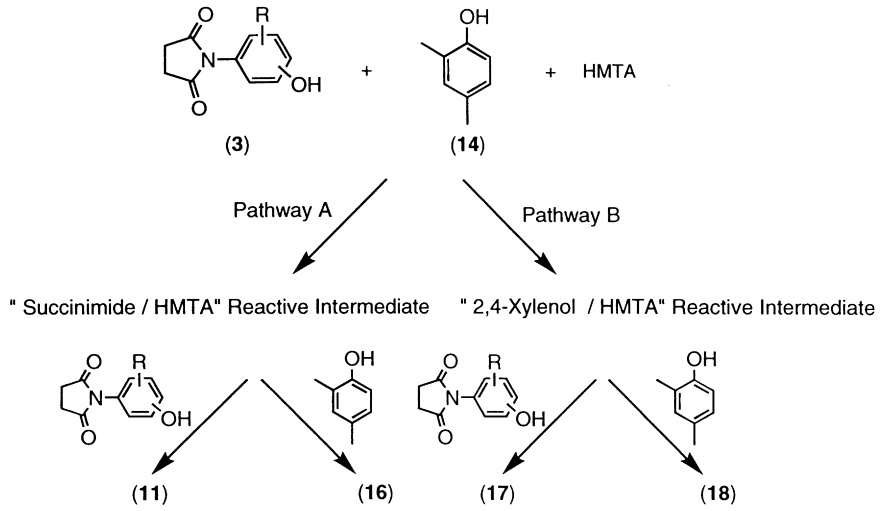
3.2. Reactivity of models for polyimide and phenol-formaldehyde resin towards HMTA

A mixed system where the *N*-(hydroxyphenyl) succinimides, which contain a vacant *ortho* position, and 2,4-xylenol can compete for reaction with HMTA was examined. The ratio of phenolic unit to HMTA was kept constant at 3:1, i.e. 3:3:2 (*N*-(hydroxyphenyl) succinimide/xylenol/HMTA). This ratio was chosen so that these results could be compared with reactions conducted on other phenolic systems in the literature and in published reports in our group [13]. A general example is shown in Scheme 4, with the interaction between HMTA, *N*-(hydroxyphenyl) succinimide (**3**) and 2,4-xylenol (**14**). After heating the reactants at 130°C for 3 h, four different benzoxazine species were observed in the ^{13}C n.m.r. of the crude reaction mixture.

However, the isolation and identification of the



Scheme 4. Generalized reaction between *N*-(hydroxyphenyl) succinimides/2,4-xylenol and HMTA in a mole ratio of 2:3:2, where R = H or CH_3.



Scheme 5. Proposed mechanism for the formation of benzoxazines derivatives (**11**) and (**16**).

benzoxazine derivatives was a long and tedious process. The benzoxazine derivatives (**11**) and (**18**) were isolated and fully characterized, however, due to the extreme difficulties in separating the 'mixed' benzoxazine species (**16**) and (**17**), they were characterized as a mixture of the two isomers. All spectroscopic data (i.e. n.m.r., M.S., *FT* i.r., etc.) supported the proposed structures. The structures of the 'mixed' benzoxazine derivatives and relative yields were identified from their ^{13}C n.m.r. resonances in the crude reaction mixture.

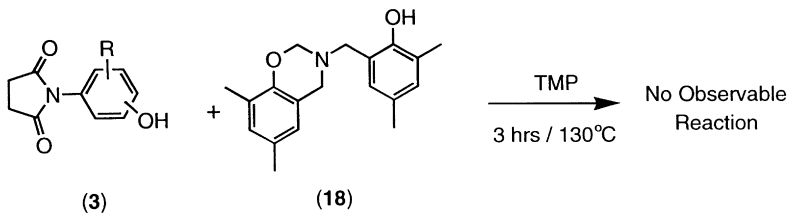
The benzoxazine derivatives of types (**11**) and (**18**) were identified as being derived from the interaction of HMTA with two succinimide or two 2,4-xylenol compounds together, respectively. The formation of such intermediates suggests that the presence of either the succinimide or xylenol compounds in the systems does not preclude the normal mechanism of the reactions between the phenolic rings and HMTA. The other two benzoxazine derivatives (**16**) and (**17**), represent the formation of 'mixed' benzoxazine species. These results are consistent with each of the phenolic units (from either the succinimide or xylenols) forming separately a reactive intermediate with HMTA. These intermediates can then react with the succinimide or xylenol to form the four benzoxazines observed. Thus, in pathway A (Scheme 5), the initial reactive intermediate is derived from a succinimide–HMTA interaction, and further reaction forms either (**11**) or (**16**). The formation of (**17**) and (**18**) would follow a similar proposed mechanism, the initial interaction occurs through the xylenol to form a xylenol–HMTA reactive intermediate, which either further reacts with a xylenol molecule to form (**18**) or can react with the phenolic ring of the succinimide compound to form (**17**) (Scheme 5, Pathway B).

Alternative mechanisms which involve interchange reactions between a first formed benzoxazine and the free xylenol or succinimide were tested (Scheme 6).

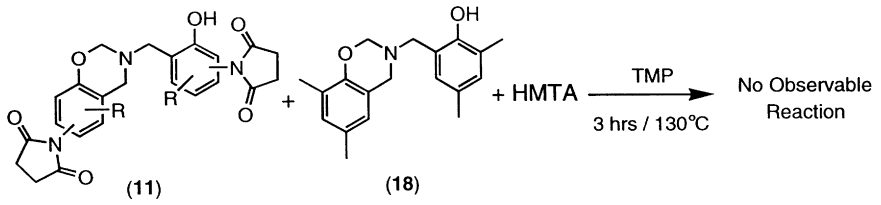
The resulting crude reaction mixture was observed directly via ^{13}C n.m.r. spectroscopy. The characteristic resonances of the benzoxazine derivative were unchanged from their position in the starting materials, suggesting that the benzoxazine does not readily decompose under the present reaction conditions. Further, there was no evidence of the formation of the 'mixed' benzoxazine derivatives. This lends support to the theory whereby the mixed benzoxazines are formed directly and not from an interchange process.

To further investigate other pathways for the formation of the 'mixed' benzoxazines, a mixture of the benzoxazine derivatives (**11**) and (**18**) was heated in the presence of HMTA at 130°C for 3 h (Scheme 7). This system more accurately represents the conditions for the interaction between the *N*-(hydroxyphenyl) succinimides, 2,4-xylenol and HMTA, where there is an excess of HMTA.

The ^{13}C n.m.r. of the crude reaction mixture showed little evidence of the breakdown of either of the benzoxazine



Scheme 6. 2,4-Xylenol benzoxazine derivative (**18**) and *N*-(hydroxyphenyl) succinimides (**3**) in a 1:1 mole ratio, where R = H or CH_3.



Scheme 7. Reaction of benzoxazine derivatives (**11**) and (**18**) with HMTA at 130°C, where R = H or CH_3.

derivatives and no formation of either of the 'mixed' benzoxazine derivatives. Therefore, under the present reaction conditions, the mixed benzoxazine derivatives are probably derived from interaction between HMTA, a *N*-(hydroxyphenyl) succinimide and a 2,4-xylenol molecule. It would be reasonable to assume that a similar reaction mechanism occurs in the composite system where the poly(*N*-(hydroxyphenyl) maleimides) and the phenol-formaldehyde resin could interact with HMTA forming an interconnected three-dimensional network.

3.3. Kinetics of reaction between HMTA and model's for polyimides and phenol-formaldehyde resins

The relative reactivity of the xylenol and *N*-(hydroxyphenyl) succinimide compounds towards HMTA in the

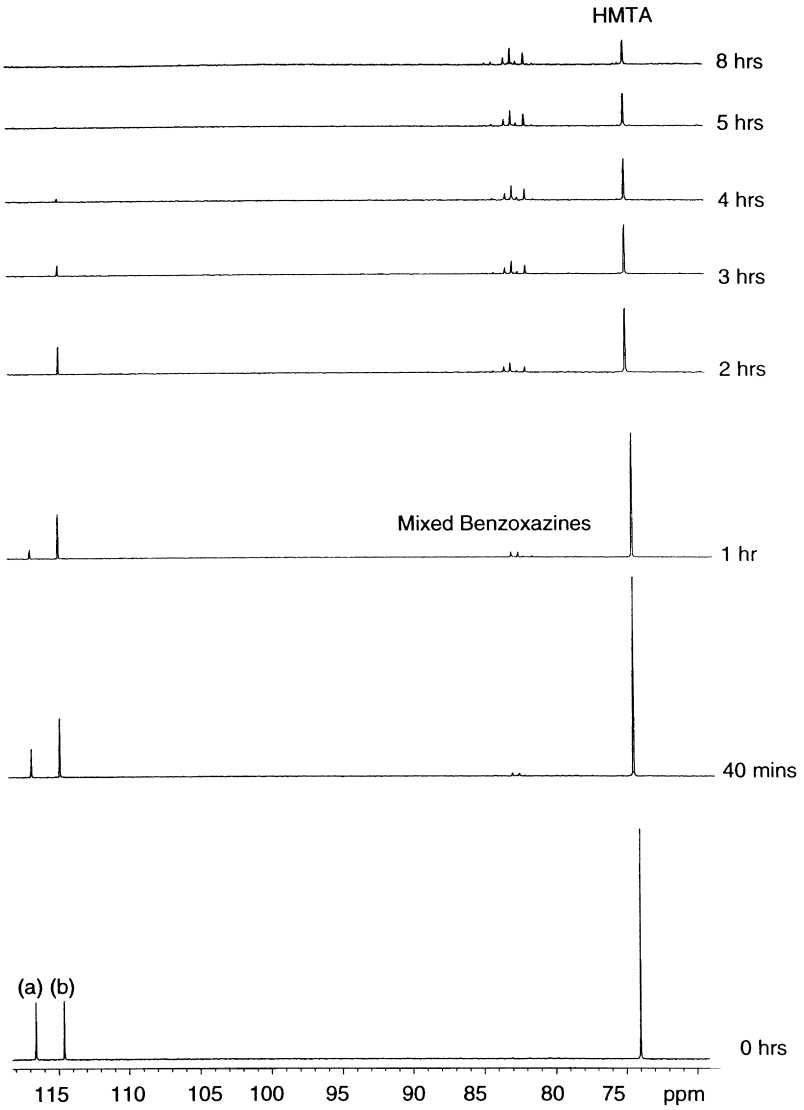


Fig. 1. ^{13}C n.m.r. spectra of interaction between 5M2HPSI (**5**)/2,4-xylenol (**14**) and HMTA, where (a) and (b) are the *ortho* reactive position sites for 5M2HPSI and 2,4-xylenol, respectively.

Table 2
Measured $t_{1/2}$ values for the reaction of model polyimides/2,4-xylenol/HMTA in a 3:3:2 mole ratio at 130°C

Compound	$t_{1/2}$ HMTA	Major product
2HPSI (**4**)	1 h 3 min	Benzoxazine
5M2HPSI (**5**)	1 h 30 min	Benzoxazine
3M2HPSI (**6**)	Inhomogeneous	Benzylamine[a]
3HPSI (**7**)	2 h 50 min	Benzoxazine
2M3HPSI (**8**)	3 h	Benzoxazine
4HPSI (**9**)	Inhomogeneous	Benzoxazine[a]
3M4HPSI (**10**)	4 h 30 min	Benzoxazine

[a]Inhomogeneous reaction mixture, therefore $t_{1/2}$ value not measured.

individual cases has previously been shown to vary considerably. The presence of the succinimide ring was shown to increase the reactivity of the phenolic ring towards HMTA in all the model polyimide compounds investigated. In addition, it was shown that the relative substitution of the phenolic ring affected the reactivity of the model polyimides. The model polyimides which contain the succinimide ring *ortho* disposed relative to the hydroxyl substituent generally reacted faster than either the *meta* or *para* derivatives.

The increased reactivity of the *N*-(hydroxyphenyl) succinimides towards HMTA, and its effects on the interaction with 2,4-xylenol were of interest. This could have ramifications on the structure of the composite material, if there was preferential incorporation of one component. Thus a series of NMR experiments was carried out where the rate of HMTA consumption was measured over a period of 8 h (Fig. 1).

From the ^{13}C NMR spectra in Fig. 1, it was observed that the intensity of the HMTA resonance (at approximately 74 ppm) decreases concurrently with the increase in the resonances associated with the four different types of benzoxazine derivatives (centered around approximately 81 ppm). The intensity of the *ortho* reactive site on the *N*-(hydroxyphenyl) succinimide decreases at a greater rate than that of 2,4-xylenol, which is consistent with the greater reactivity of the phenolic ring of the succinimide derivative.

The time for half of the available HMTA to be consumed, the $t_{1/2}$ value, was calculated from the spectral data for the interaction of each of the model compounds (**4**–**10**) and 2,4-xylenol with HMTA. Our reaction conditions allow for the comparison of the relative reactivity of HMTA towards the *N*-(hydroxyphenyl) succinimides and 2,4-xylenol systems but not to deduce more accurate kinetic data (Table 2).

The reactivity towards HMTA of the phenolic ring of the *N*-(hydroxyphenyl) succinimide and of the 2,4-xylenol system followed a similar trend to that observed for the system without the addition of 2,4-xylenol. The models which contain a vacant *ortho* site relative to the hydroxyl substituent are considerably more reactive towards HMTA than either the *meta* or *para* derivatives. This is most evident for the reaction of 2HPSI, 2,4-xylenol and HMTA system, where HMTA is consumed up to four times faster than the reaction between 3M4HPSI, 2,4-xylenol and HMTA. As noted earlier in systems which contain a vacant *para* position relative to the hydroxyl substituent further reaction occurs to form benzylamine type intermediates. This possibility of competing reaction pathways complicates the study of the reaction mechanism. However, it can be stated that the interaction between HMTA and the phenolic rings of both the *N*-(hydroxyphenyl) succinimide and 2,4-xylenol does occur. Further, the reactivity of the polyimide models depends on the substitution of the phenolic ring. The models which contain the succinimide ring *ortho* disposed relative to the hydroxyl substituent are considerably more reactive than either the *meta* or *para* disposed models.

To determine whether the increased reactivity of the phenolic ring of the polyimide models towards HMTA has any effect on the formation of the mixed benzoxazines, the rate of formation of the benzoxazine derivatives was monitored over the course of 8 h using their ^{13}C n.m.r. resonances.

3.4. Relative rates of formation of the benzoxazine derivatives

The interactions between HMTA and each of the *N*-(hydroxyphenyl) succinimides containing a vacant *ortho* position and 2,4-xylenol produces four types of benzoxazine derivatives. The rate at which each benzoxazine is produced is dependent on several factors. The first is the relative reactivity of the *N*-(hydroxyphenyl) succinimide. It was previously mentioned that the reaction between *ortho* substituted succinimides and HMTA occurred at a greatly increased rate compared to that of 2,4-xylenol and HMTA. Therefore, during the initial stages of the reaction, the benzoxazine derivatives are primarily derived from the reactions which contain the faster reacting species, i.e. the *N*-(hydroxyphenyl) succinimide derivatives, producing compounds such as (**11**) and (**16**). For example, during the reaction of 5M2HPSI (**5**), 2,4-xylenol and HMTA, the phenolic ring of the succinimide compound reacts more than four times faster than 2,4-xylenol, and consequently there is a higher proportion of *N*-(hydroxyphenyl) succinimide derived benzoxazines. The second controlling factor is the concentration of the reactants in the system. As the concentration of 5M2HPSI (**5**) in the system decreases, the probability of two *N*-(hydroxyphenyl) succinimide compounds interacting to form benzoxazine derivatives diminishes, and reactions involving 2,4-xylenol begin to dominate. This is evidenced by the increase in the benzoxazine derivative of

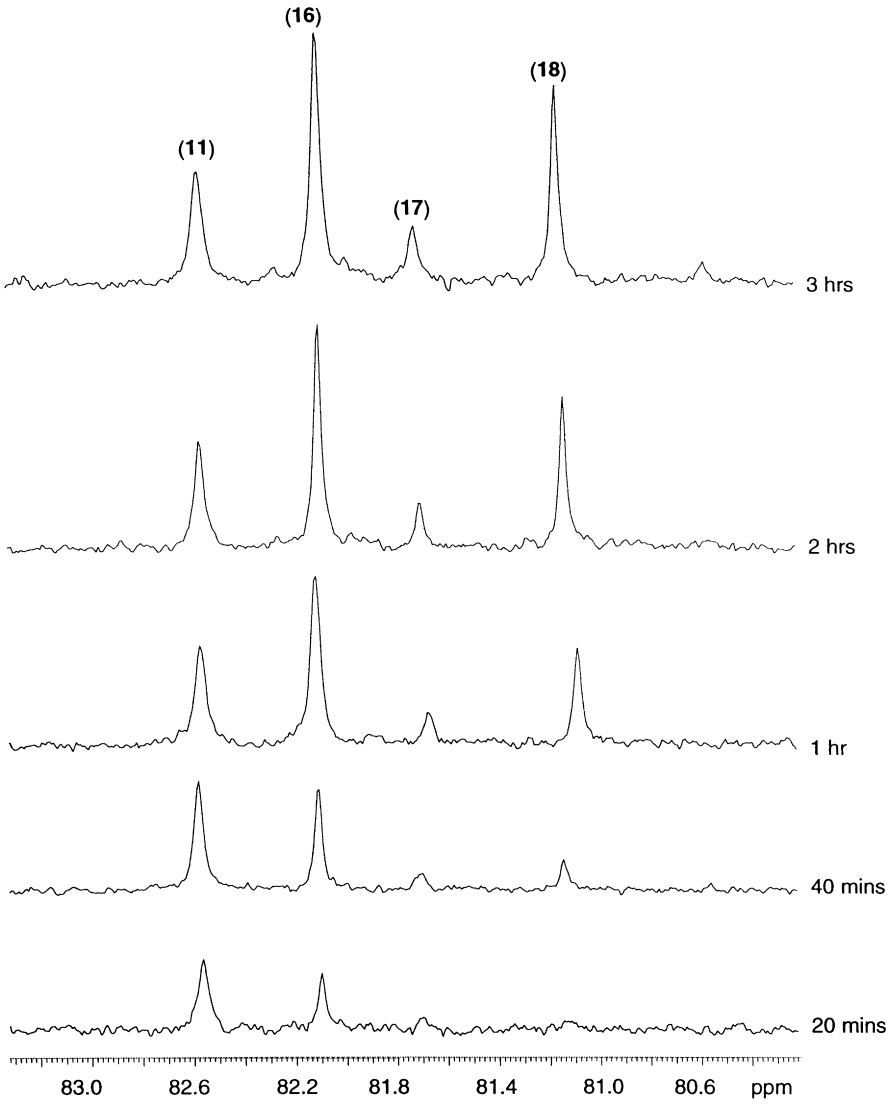


Fig. 2. ^{13}C n.m.r. spectra of interactions between 5M2HPSI (%)/2,4-xylenol (**14**) and HMTA.

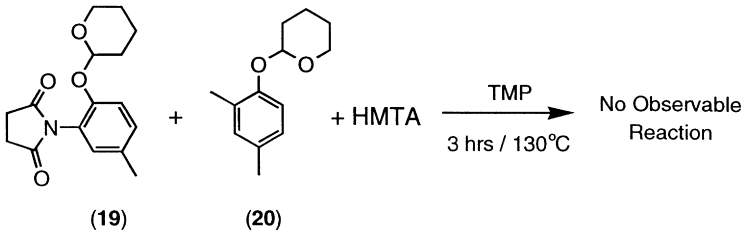
the type (**18**) in the later stages of the reaction, which is derived from the interaction of two 2,4-xylenol species.

The reaction to form the benzoxazine species of type (**17**), is not as prevalent in this system, as it involves the initial formation of a '2,4-xylenol-HMTA' reactive intermediate and then interaction with an *N*-(hydroxyphenyl) succinimide species. The difference in reactivity between these two species is significant and the concentration of the '2,4-xylenol-HMTA' reactive intermediate in the system would be quite low. Therefore, the possibility of it interacting with a free *N*-(hydroxyphenyl) succinimide species is unlikely before all the reactive succinimide species have been consumed.

The concentration of the normal 2,4-xylenol benzoxazine derivative (**18**) continues to increase during the course of the 8 h until all the free 2,4-xylenol has reacted. Under the present reaction conditions, there is no evidence of the breakdown of any of the benzoxazine derivatives formed over the 8 h. The increase in concentration of the four types of benzoxazine derivatives is demonstrated in the series of ^{13}C n.m.r. spectra shown in Fig. 2. The resonances are labelled with the corresponding benzoxazine derivatives from which they are derived.

Where the *N*-(hydroxyphenyl) succinimide derivatives contain a vacant *ortho* position and react with HMTA at a similar rate to 2,4-xylenol, such as 3M4HPSI (**10**), the four benzoxazine derivatives are formed at approximately the same rate. This suggests that formation of the first reactive intermediates, as outlined in Scheme 5, occur at similar rates, and the possibility of these species reacting with the phenolic ring of a 2,4-xylenol molecule or a succinimide species is approximately equal.

The previous two systems outlined above both contain one reactive position, *ortho* to the hydroxyl group. For the systems where there is more than one reactive position on the phenolic ring, the number of possible reaction mechanisms is greater. The normal reaction through the *ortho* position to form the four benzoxazine derivatives can occur, but



Scheme 8. Reaction ot THP-masked phenolic compounds with HMTA.

in some systems, reaction can also occur through the *para* position. It has been noted, that 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 later when most of the *ortho* sites have been consumed. These difficulties make the interpretation of the relative growth of the different reaction products difficult. This exemplifies the difficulties encountered even using a model compound approach for examining the interaction between the polyimides, phenol-formaldehyde resins and HMTA.

3.5. Control of interactions between HMTA and both models for polyimides and phenol-formaldehyde resins

Interactions between the HMTA and the models for the polyimides and phenol-formaldehyde resins have been established. It was shown that there is a predominance of the more reactive phenolic ring in the benzoxazine derivatives formed. If this was generally applicable to the polymeric systems, we might expect there to be a higher level of crosslinking between the polyimides in the composite materials. Control over the level of crosslinking reactions that occur in composite materials is a desirable engineering characteristic. In our previous work on the synthesis of high molecular weight poly(*N*-(hydroxyphenyl) maleimides) [10,19], a tetrahydropyranyl (THP) group was used to mask the phenolic group during the free radical chain polymerization. The THP group effectively masks the reactivity of the hydroxyl group, and can be easily removed thermally. It was therefore envisaged that by masking the hydroxyl group of the model polyimides, their reactivity towards HMTA could be modified. To this end, the most reactive of the *N*-(hydroxyphenyl) succinimides, 5M2HPSI (**5**) and 2,4-xylenol (**14**) were masked with THP and their reactivity towards HMTA gauged, as outlined in Scheme 8.

The ^{13}C n.m.r. of the reaction mixture showed no evidence of any interaction between HMTA or either of the THP-masked phenolics. In the reaction of HMTA with 5M2HPSI (**5**) and (**20**), the only products observed are those derived from the reaction of 5M2HPSI to form the corresponding benzoxazine derivative. Further, in the reaction of HMTA with 2,4-xylenol (**14**) in the presence of the THP-masked succinimide derivative (**19**), the only product observed is the benzoxazine derived from xylenol (**18**). We can therefore control which phenolic ring interacts with HMTA in the system, and by varying the temperature of the system, the onset of the reaction with HMTA can be controlled.

Industrially, the reaction temperature at which the crosslinking reactions of phenol-formaldehyde resins and HMTA occur is varied along a ramped temperature cycle [16]. By selective masking using the THP derivative of either the phenol-formaldehyde resin or poly(*N*-(hydroxyphenyl) maleimides), the temperature at which reaction with HMTA occurs can be controlled. The THP masked polymeric material will not interact with HMTA, therefore in a composite blend, only the component with the free phenolic group will interact with HMTA. The possibility of the formation of an interpenetrating polymeric network is a consequence of the relative inertness of one of the polymeric materials in the blend towards HMTA. Two phases could be formed in the blend, whereby one polymer interacts with HMTA to form a crosslinked network, and the second does not undergo any crosslinking reactions. Possible changes in the physical properties of such a composite could be beneficial, and work is currently being conducted to more closely examine these systems. Further articles in this series will discuss the implications of the selective masking of the phenolic groups using THP groups.

4. Conclusions

N-(Hydroxyphenyl) succinimide and xylenol compounds have successfully been used to model both poly(*N*-(hydroxyphenyl) maleimides) and phenol-formaldehyde resins in their reaction with HMTA. Interactions between HMTA and *N*-(hydroxyphenyl) succinimides and 2,4-xylenol compounds to form four benzoxazine derivatives were noted. The relative rates of reaction were examined using ^{13}C n.m.r. techniques, and found to be dependent on the substitution pattern of the phenolic ring of the succinimide ring. The *N*-(hydroxyphenyl) succinimides which contain the hydroxyl group *ortho* to the succinimide ring, reacted faster than either the *meta* or *para* derivatives. This is evident in the disproportionately high concentration of benzoxazine derivatives derived from the succinimide compounds in the initial stages of the reaction. As the concentration of

unchanged succinimide compounds in the system decreases over time, the relative proportion of xylenol derived benzoxazine derivatives increases. Control over the relative rates of reaction of the succinimide and xylenol compounds was achieved by selective masking of the phenolic substituent with the thermally labile THP group. Masking the phenolic group with a THP group, stops all reactive interactions between HMTA and the phenyl ring. The THP group can be thermally removed at a specific temperature, unmasking the phenolic group and allowing reaction with HMTA to occur.

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