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A comparative study of the relative reactivity of alkenyl-functionalized toughening modifiers for *bis*-maleimides

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Summary

A study of the copolymerization of HPLC-pure *bis*(4-maleimidophenyl)methane (DDM-BMI) with four alkenyl-functionalized aromatic comonomers using differential scanning calorimetry (DSC) and the effects of various catalysts on the reaction is presented. The added catalysts appeared to have little effect on the overall polymerization behaviour and the onset of reaction was largely governed by the fusion temperature of the DDM-BMI monomer. However, the maximum rate (during scanning at 10K/minute) was dependent on the structures of the alkenyl co-monomers.

A study of the relative reactivity of *ortho* disubstituted allyl and propenyl *bis*-phenols employing DSC and dilute solution Fourier transform infra-red (FT-IR) spectroscopy is also presented. Attempts are made to reconcile the reactivity with the nature and orientation of the substituents.

Introduction

Bis-maleimides (BMI's) can be thermally polymerized by a variety of free-radical or anionic means. The resulting polymers, while possessing high glass transition temperatures, thermo-oxidative stability, and low moisture absorption are handicapped by their inherent brittleness due to the high cross-link density of the polymer network (1). The kinetics associated with the bulk thermal polymerization of BMI's are complex (2,3) indicating a cure process that may involve a number of competing mechanisms. The effect of monomer purity on the thermal behaviour of BMI's and *bis*-citraconimides (BCI's) has already been noted (2-5). The HPLC-pure *bis*(4-maleimidophenyl)methane (DDM-BMI) monomer displays a sharp crystalline melt endotherm closely followed by an overlapping polymerization exotherm making resolution of the two transitions impossible. Moreover, a second, diffuse, high temperature exotherm is observed (which is absent in samples of lesser purity) for which a mechanism has been postulated (2,5) involving an intramolecular cycloaddition reaction of unreacted maleimido groups on the aromatic nucleus.

In an attempt to overcome the brittle nature of BMI resins, efforts have been made to copolymerize BMI's with a variety of compounds (1), particularly alkenyl-substituted aromatics bearing reactive allyl- or propenyl functional groups. Two separate reaction mechanisms have been proposed (1) to account for the co-reaction of the maleimide C=C bond with the alkenyl groups. It is believed (1,6,7) that the reactive maleimide C=C bond undergoes co-reaction with the allyl group *via* an 'ene' reaction to produce a propenyl-bridged intermediate (for which heteronuclear n.m.r. evidence has been advanced) (6). It is postulated (1) that the reaction proceeds with this intermediate undergoing a Diels-Alder reaction with another maleimide group and cross-linking occurs *via* further 'ene'/Diels-Alder steps whereas the propenyl group is thought (1) to react with the BMI *via* a series of Diels-Alder steps. In either case the resulting copolymers exhibit improved toughness characteristics compared with the BMI homopolymer (1). This work involved two discrete, but related studies: an investigation of the copolymerization of DDM-BMI with four alkenyl aromatic comonomers and the effects of various catalysts using DSC, and also a study of the relative reactivity of *ortho* disubstituted allyl and propenyl *bis*-phenols combining DSC and FT-IR techniques.

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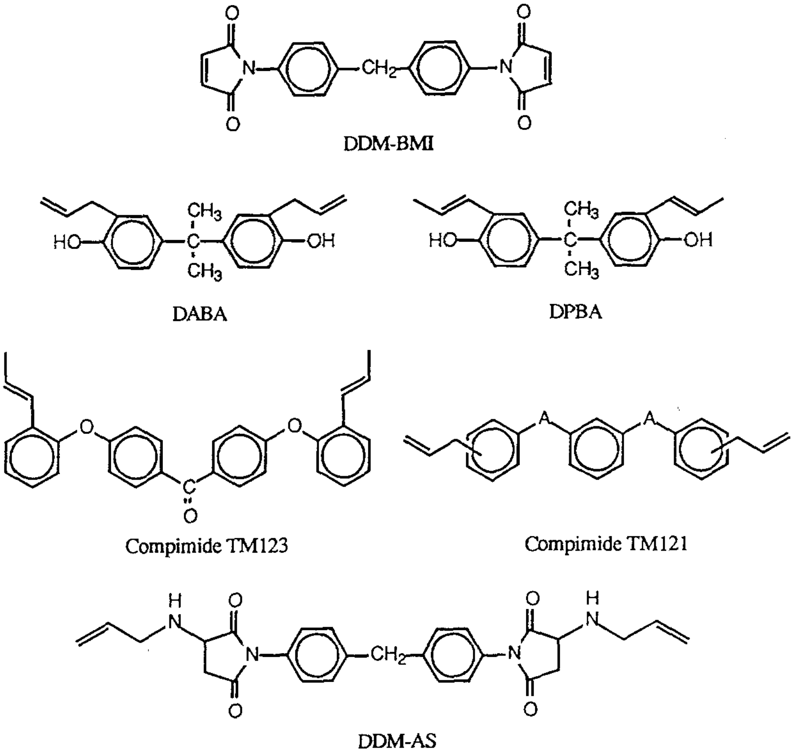

DDM-BMI

DABA

DPBA

Compimide TM123

Compimide TM121

DDM-AS

Scheme 1 Monomers encountered in this work

The commercial aromatic modifiers employed in this study were 2,2'-*bis*(3-allyl-4-hydroxyphenyl)isopropylidene (DABA), Compimide TM121, and Compimide TM123. Both 2,2'-*bis*(3-propenyl-4-hydroxyphenyl)isopropylidene (DPBA), prepared using a synthetic procedure first reported by Bader (7), and a novel allyl-functionalized succinimide (DDM-AS) were prepared in-house (Scheme 1). Five catalysts were also used in the course of this work: 2-methylimidazole (2-MI) and diazobicyclo-2,2,2-octane (DABCO) are both basic catalysts shown (1) to accelerate the thermal homo- and copolymerization of BMI's, while Copper(II) acetylacetonate, Cu(Acac), Cobalt(III) acetylacetonate $Co_2(Acac)_3$, and Vanadium(III) acetylacetonate $V_2(Acac)_3$ are all transition metal complexes which are known to act as polymerization catalysts for certain resin systems (*e.g.*, cyanate esters) (8).

The second phase of the study involved the co-reaction of 'crude' (96 %) DDM-BMI with 2,2'-*bis*(3-allyl-4-hydroxyphenyl)isopropylidene (DABA) to mimic the behaviour of the commercial Matrimid 5292 resin and the analogous reaction with 2,2'-*bis*(3-propenyl-4-hydroxyphenyl)isopropylidene (DPBA) in order to determine the relative reactivities of these substituents to the maleimide group.

Experimental

Infrared spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer interfaced to a Perkin-Elmer 7300 computer; the monomer samples were presented either as thin films or KBr disks. Dilute solution FT-IR study spectra were obtained for solutions of the monomers in freshly-distilled Analar grade carbon tetrachloride at concentrations of approximately 10^{-3} to 10^{-5} mole/litre in a liquid cell of path length 1 mm. A 'blank' cell containing Analar carbon tetrachloride was scanned 1000 times before being subtracted from each sample to produce the final difference spectra.

Nuclear magnetic resonance (n.m.r.) spectra were recorded at 298 K using a Bruker AC-300 spectrometer operating at 300 MHz for ^{1}H and 30.4 MHz for ^{15}N. Samples were dissolved in d_6-acetone, and to those intended for ^{15}N analysis was added chromium(III) acetylacetonate (at an approximate concentration of 15 mg per 0.02 mole of nitrogen) (9) so as to eliminate nuclear Overhauser effects and reduce relaxation times. The ^{1}H chemical shifts are reported relative to tetramethylsilane and the ^{15}N to external nitromethane.

Differential scanning calorimetry was performed at 10 K/minute under nitrogen (50 cm^3/minute) using a Du Pont 910 calorimeter interfaced to a Du Pont 9900 computer/thermal analyzer. Samples (10 ± 1 mg) were run in open, uncoated aluminium pans, unless otherwise indicated. After conversion of the raw data to ASCII files using dedicated software, kinetic analysis was carried out using in-house programmes (10) on a Hewlett-Packard HP-86 computer.

The five commercial monomers featured in the present study were used as supplied. DDM-BMI (HPLC-pure) was blended, with 33 % and 50 % (w/w) of the desired modifier and 0.5 % (w/w) catalyst, by thorough mixing after fusion while quenching the sample to suppress reaction.

Bis-4-(*N*-allylaminosuccinimidophenyl)methane (DDM-AS)

Two methods were employed to synthesize the monomer. Initially a method first reported by Crivello (11) and subsequently modified by Varma *et al.* (12) was used in which DDM-BMI (0.02 moles) and allylamine (0.05 moles) were refluxed together in an aprotic solvent (acetone) to undergo a Michael addition (13) to form the succinimide adduct. However, aspartimides prepared from similar syntheses involving solvents which become occluded in the resulting polymers have been shown (14,15) to have deleterious effects on the cured resin properties. Hence, a molten blend technique was adopted in which DDM-BMI (3.46 g, 0.02 moles) and allylamine (1.50 g, 0.026 moles) were gently fused in a boiling tube under nitrogen, at room temperature for 15 minutes and in the melt for 30 minutes using an oil bath. On cooling, the diallyl adduct, a pale amber solid, was finely ground prior to analysis and DSC characterization. Some homopolymerization of the BMI was apparent despite the precautions taken to avoid premature reaction. Moreover, allylamine being an aliphatic amine is markedly more basic than aromatic amines (*cf* allylamine pK_a *ca.* 9.5 and aniline pK_a *ca.* 4.6) (13) and may undergo a modification of the Gabriel amino-acid synthesis (16) with maleimide as that observed (13) for succinimides and primary aliphatic amines. M.p. 137-139°C. Found: C, 67.16; H, 5.93; N, 11.19 %. $C_{27}H_{22}N_4O_4$ requires: C, 68.63; H, 5.97; N, 11.86 %. ^{1}H n.m.r. (300 MHz, D_6-DMSO, ppm from TMS) 7.34-7.26 (d of d, Ar-H) 7.24-7.20 (d of d, Ar-H) 7.17 (s, $=C\underline{H}$ unreacted maleimide) 6.00-5.75 (m, allyl $-C\underline{H}=$) 5.22-5.05 (m, allyl $=C\underline{H}_2$) 4.03 (s, Ar-$C\underline{H}_2$-Ar) 3.60-3.45 (m, succinimide CH_2) 3.39 (d, allyl $-CH_2-$) 2.72 (s, $N\underline{H}$); ^{15}N n.m.r. (30.4 MHz, D_6-DMSO, ppm from $MeNO_2$) -340 (s, $\underline{N}H$) -217 (s, unreacted maleimide $>\underline{N}-$) -192 (s, succinimide $>\underline{N}-$); FT-IR (KBr disk) 3309(bs) 3069(w) 2918(m) 1708(vs) 1667(m) 1604(m) 1510(s) 1387(s) 1307(w) 1181(s) 1022(w) 995(w) 921(m) 826(m) 814(w) 789(w) 675(m).

Results

In each example of the prepolymer blends containing DDM-BMI/commercial modifier/catalyst, a similar DSC profile was observed. Hence only a single representative composite plot is shown (Figure 1) for each uncatalyzed prepolymer blend containing 50 % (w/w) DDM-BMI. In most cases a sharp crystalline melt endotherm representing the fusion of the BMI monomer was immediately followed by a polymerization exotherm spanning 100-200°C. The proximity of the melt endotherm and polymerization exotherm was such that in most cases the two were unable to be resolved and as a result kinetic analysis was not attempted. The results for the commercial blends studied are tabulated below (Table 1).

The temperature at which the exothermic heat flow in the calorimeter reaches a maximum is often taken as a measure of polymerization reactivity. This criterion must be used with care for with reactive monomers of high melting point the value of T_{max} is set by the monomer's melting point rather than by its reactivity. This is noted, but as one BMI was used consistently in all copolymerizations, the Tmax values were used to give an indication of the relative reactivities of each blend.

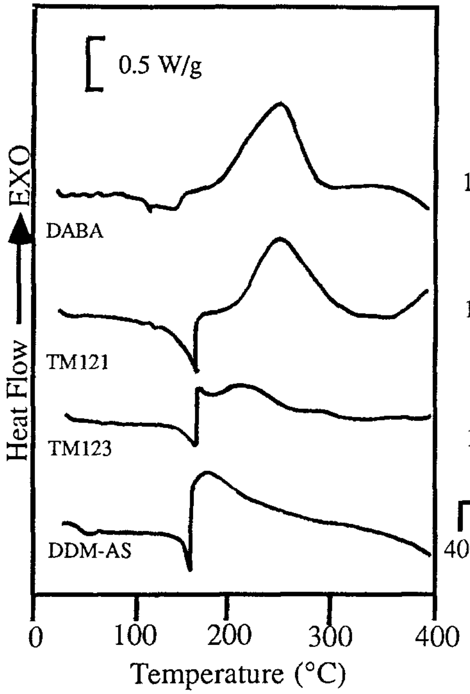

Fig. 1. Scanning DSC (10 K/min, Nitrogen)
DDM-BMI/alkenyl modifiers (50 % w/w)

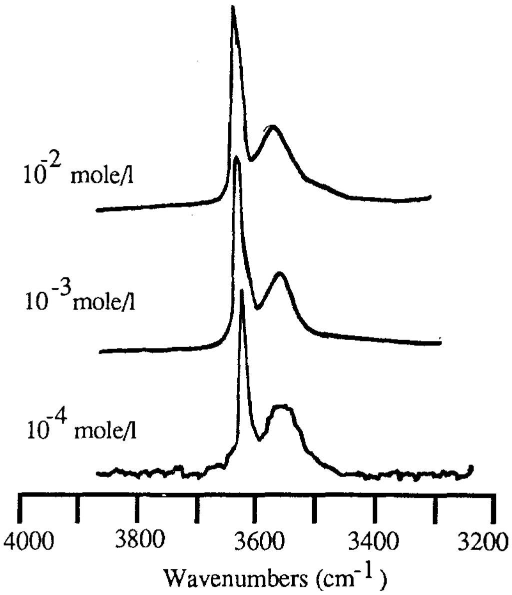

Fig. 3. FT-IR spectra of DABA (in CCl_4)

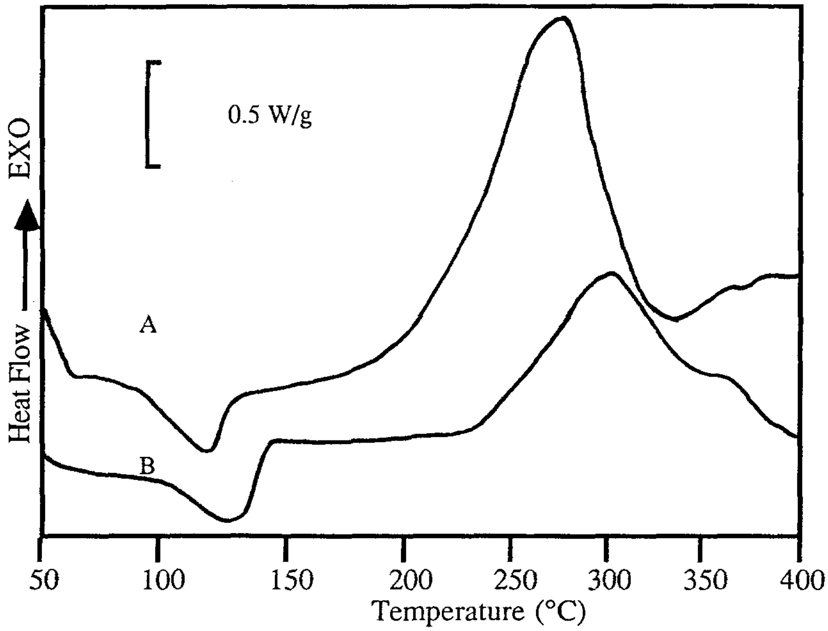

Fig. 2. Scanning DSC (10 K/min, Nitrogen)
DDM-BMI/DABA (A) and DDM-BMI/DPBA (B) (Molar ratio 1/0.87)

Table 1: Thermal behaviour of commercial modifier/DDM-BMI (50/50 w/w) prepolymer blends (10 K/minute, under nitrogen)

Catalyst	**Modifier** DABA	TM121	TM123	DDM-AS
-	164/250	184/248	168/215	169/181
2-MI	163/229	171/231	162/204	169/175
DABCO	162/250	174/241	162/202	169/177
Cu(Acac)	163/230	173/249	164/222	169/175
$V_2(Acac)_3$	163/254	165/248	165/219	169/182
$Co_2(Acac)_3$	167/251	179/249	170/220	169/176

Note: Results quoted as T_{onset}/T_{max} (°C)

As the data demonstrate, the structure of the copolymer largely governs the reactivity of the prepolymer blend rather than the nature of the catalyst used. The only catalyst that appeared to reduce the value of T_{max} was 2-methylimidazole (2-MI), a small reduction of approximately 10°C was observed in each case. The remaining catalysts failed to demonstrate a consistent enhancement in the reactivity, but did show some beneficial effects on individual systems.
The structure of the copolymer had a more marked effect on the T_{max} values. Regardless of catalyst, the propenyl-substituted Compimide TM123 consistently displayed a T_{max} value some 30°C below those observed for the allyl-substituted modifiers (Figure 1). These findings agree with data that have been noted previously (17,18) in analyses carried out by the manufacturers of these and similar resin systems and will be discussed later.

Comparative reactivities of alkenyl *bis*-phenols

The commercial Matrimid 5292 resin system comprises DDM-BMI and DABA in a molar ratio of 1:0.87 (19,20). Thermal analysis of the prepolymer blend by dynamic DSC has revealed (19) the presence of two exotherms. This finding has been used (in conjunction with heteronuclear n.m.r. evidence) (20) to substantiate the mechanism proposed for the copolymerization: it is suggested that the first exotherm is due to the 'ene' reaction while the larger high temperature exotherm is due to the Diels-Alder step and further cross-linking reactions. During this study the DSC data only showed two discrete exotherms at the lowest heating rate (5 K/minute), but the position of the peak maxima (T_{max}, 272°C at 20 K/minute) do correlate with those reported in the literature (19). The analogous propenyl-substituted *bis*-phenol (DPBA) was also blended with DDM-BMI in an identical manner and to the same stoichiometry as the Matrimid 5292 blend. Analysis of this blend by dynamic DSC revealed a single broad exotherm (T_{max}, 299°C) with a shoulder attributed to the onset of thermal degradation. The DSC thermograms (20 K/minute) of both blends are shown as a composite plot (Figure 2) and the difference in reactivity between them may be plainly seen. The allyl-containing blend appears to commence polymerization at 158°C (70°C below that of the propenyl analogue) and exhibits a T_{max} of the second, higher temperature peak some 20°C below that of the propenyl analogue.

Dilute solution FT-IR Results of alkenyl *bis*-phenols

At a concentration of 1 x 10^{-2} mole/litre DABA displays three bands over the range 3800-3200 cm^{-1} (Figure 3): a sharp band at 3600 cm^{-1} due to 'free' (unassociated) O-H stretch, a broader band at 3650 cm^{-1} assigned (21,13) to intramolecularly-bonded O-H stretch, and a very diffuse band appearing as a shoulder at 3450 cm^{-1} assigned to intermolecularly-bonded O-H stretch. As the concentration is reduced ten-fold to 10^{-3} mole/litre the intermolecular O-H stretching band becomes virtually indistinguishable (while the remaining bands are unchanged in intensity). After a further ten-fold dilution (10^{-4} mole/litre) the profile of the spectrum consists of two bands representing free O-H and intramolecularly-bonded O-H stretch.

Similar experiments undertaken (14) with the di-*n*-propyl analogue, 2,2'-*bis*(3-*n*-propyl-4-hydroxyphenyl)isopropylidene are quite different. In this case the absence of a π-system adjacent to the hydroxyl group makes it impossible for such an intramolecular association to occur. Hence, at the highest concentration (1 x 10^{-2} mole/litre) the di-*n*-propyl analogue displays only two bands: a sharp band at 3600 cm^{-1} due to free O-H and an almost indistinguishable band at 3500 cm^{-1} due to intermolecular association. After a ten-fold dilution the spectrum consists solely of a band due to free O-H stretch. These experiments were repeated (13) with the analogous compounds containing the hexafluoroisopropylidene linkage and similar results were obtained. In this case the intermolecular associations are much stronger, resulting in more intense signals

Discussion

The DSC data involving the copolymerization of HPLC-pure DDM-BMI with a series of commercial aromatic modifiers each bearing a single reactive functional group demonstrated that those compounds functionalized with a propenyl group were more reactive than analogous allylic compounds. Little evidence appears to have been put forward to explain the generally held belief (17,18) that the propenyl compounds display enhanced reactivity over the allylic analogues. If the discussion centred simply on a question of steric requirements then this general result would be surprising. Methyl substituted vinyl monomers usually polymerize by free radical mechanisms less readily than their substituted analogues (22). However, it is known (23) that the allyl residue readily forms a resonance-stabilized radical and this may be responsible for the relatively greater reactivity of the propenyl group during a free radical polymerization. Zahir *et al.* (20) presented torsional braid analysis (TBA) data for model mixtures of a BMI and 2,6-diallylphenol and 2,6-dipropenylphenol at 150°C and adiabatic calorimeter data for the reaction of *N*-phenylmaleimide with 2-allylphenol and 2-propenylphenol. The data demonstrated that the *o*-propenyl phenols apparently reacted at lower temperature than the corresponding *o*-allyl phenols with the maleimide functional group. However, this study was performed on a mixture of propenyl isomers (24) and this may have relevance in a reaction which proceeds *via* a Diels-Alder mechanism. Preliminary work has been carried out involving 2-propenylphenol in the form of an unresolved mixture of *trans* and *cis* isomers (in the ratio 4:1 - used as supplied by Aldrich Chemical Co., 98 % pure) and the single *trans* isomer (separated using column chromatography, silica gel, chloroform, > 98 % by ^1H n.m.r.). Initial results suggest that there is indeed a marked difference in the reactivity of a (50 % w/w) blend of DDM-BMI with 2-propenylphenol (as a mixture of isomers and also as the single *trans* isomer). Further work, directed at addressing the relative reactivities of substituted phenols, is currently in hand.

In contrast to the alkenyl-aromatics, the DSC results for the *o*-alkenyl *bis*-phenols indicate that the allyl-substituted monomers are markedly more reactive than their propenyl analogues. This apparent reversal in reactivity was unexpected as the only difference in these materials is the presence of a hydroxyl group *ortho* to the reactive centre. Hence, it was decided to investigate this aspect further using FT-IR.

Tentative suggestions that O-H groups associate with π-clouds can be found in the literature from about 1950 onwards (21). Baker and Shulgin (25,26) studied *o*-allylphenol and compounds with more heavily substituted C=C double bonds. In *o*-allylphenol the associated form absorbs 63 cm^{-1} below the value for the unassociated, but the interaction is weaker in 2-propenylphenol in which the O-H...π-cloud separation is increased. The results obtained in the course of this work with analogous *bis*-phenols indicate the presence of similar O-H...π-cloud association in the alkenyl-*bis*-phenols.

The FT-IR data suggest that, in common with phenols, the *o*-allyl *bis*-phenols display intramolecular hydrogen-bonding between the adjacent phenol and π-cloud of the alkenyl group. It is reasonable to expect (in view of the data from 2-propenylphenols) that the propenyl analogue should experience a similar association. If, as Baker and Shulgin (25,26) suggest, this association is weaker in propenyl derivatives than in allyl compounds (infering that the propenyl group would be more available for reaction) then another factor must be considered. By orientating the C=C double bond towards the hydroxyl group to associate, the methyl group is turned outwards, thus hindering the approach of any co-monomer (*e.g.*, a BMI) to undergo reaction with the C=C double bond. In contrast, the allyl group (while being more strongly bound than the propenyl group) is still held by a relatively weak interaction. Moreover, the steric hindrance is markedly reduced, the approach of the BMI being obstructed by two vinylic hydrogen atoms.

The relative reactivities of these functionalized monomers are of technological interest as they form the basis of a rapidly expanding family of commercial resin systems (1). The evidence presented here suggests that the propenyl-functionalized aromatic co-monomers do react more readily than the allylic analogues, but that the effect of catalysis upon the copolymerization reaction is minimal. In the copolymerization with BMI's the thermal behaviour is dominated by the fusion of the BMI monomer. In contrast with literature data from TBA and adiabatic calorimetric experiments, the DSC measurements appear to suggest that the *o*-allyl *bis*-phenols are more reactive than the analogous *o*-propenyl *bis*-phenols. FT-IR spectra obtained from very dilute solutions support the suggestion that the π-cloud from alkenyl substituents associates with the adjacent hydroxyl group in an intramolecular hydrogen-bond.

Acknowledgements

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