Novel maleimide functionalized oligomers:
1. Model compound studies

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The acid catalysed reaction of formaldehyde with activated aromatics (e.g. phenol) to form oligomers is well known. The feasibility of using this approach to prepare maleimide functionalized oligomers has been explored by undertaking model compound studies with *N*-(4-phenoxy)-phenylmaleimide (PPM), *N*-(2-methoxy)-phenylmaleimide (MPM) and *N*-phenylmaleimide (PM). Under common reaction conditions PPM readily forms a series of discrete methylene bridged oligomer structures, MPM reacts relatively slowly to give a dimer only whilst PM does not react. Thermal analysis of the cured PPM oligomers shows that they possess excellent thermal properties.

(Keywords: aromatic maleimides; formaldehyde; oligomerization; characterization; thermal analysis)

INTRODUCTION

Thermosetting resin compositions based on bismaleimides (BMIs) have been extensively studied as high performance composite matrices over the past 20 years. Such materials are ideally suited to high temperature applications due to their excellent thermal stability and high glass transition temperatures (T_g). Unfortunately, the highly crosslinked nature of cured BMIs makes them inherently brittle, thus limiting their utility. Much effort has been directed towards improving the toughness of BMIs without compromising other desirable properties[1-3]. The present investigation highlights the novel synthesis of alternative maleimide systems and forms part of a broader study to develop improved toughness matrices.

It is well known that oligomers can be prepared from the acid catalysed reaction of formaldehyde with activated aromatic hydrocarbons (e.g. phenol[7] and aniline), heterocyclic compounds (e.g. furan) and their substituted derivatives to afford polyaromatics adjoined predominantly by methylene bridges. Previously we have undertaken related studies of the reactions of unsubstituted aromatics with formaldehyde[4,5]. In particular, oligomers based on diphenyl ether, naphthalene, 4,4′-diphenoxybenzophenone and 4,4′-diphenoxydiphenylsulphone have been prepared. Functionalization of such oligomers is fairly straightforward and a methacrylate-functionalized oligomer based on diphenyl ether has found application in compositions for light-curable dental composites[4]. In this paper we describe the acid catalysed reactions of formaldehyde with some maleimide-functionalized aromatics. Maleimides are labile under the reaction conditions, strong aqueous mineral acids, which are normally employed in these condensations. In particular, the effect of compensating for the deactivating effect of the maleimido group in *N*-phenylmaleimide on the reaction by introducing active ether substituents as in *N*-(4-phenoxy)-phenylmaleimide and *N*-(2-methoxy)-phenylmaleimide was examined.

EXPERIMENTAL

N-phenylmaleimide (Aldrich) and *N*-(2-methoxy)-phenylmaleimide (Mitsui Toatsu) were used as supplied. *N*-(4-phenoxy)-phenylmaleimide (m.p. = 160°C) was prepared according to the method of Searle[6].

Oligomerization of N-*(4-phenoxy)-phenylmaleimide (PPM)*

Trifluoromethane sulphonic acid (0.2 ml) was added to a stirred solution of PPM (30 g, 0.113 mol) and paraformaldehyde (12 g, 0.40 mol) in 1,2-dichloroethane (300 ml). The reaction mixture was then refluxed for 2–3 h with any water formed being removed by azeotropic distillation. The resulting solution was cooled, washed with 5% w/v aqueous sodium carbonate solution, dried over magnesium sulphate, filtered and the solvent evaporated to yield a yellow powder (31 g) having a softening point (Kofler bar) of 55°C. Gel permeation chromatographic (g.p.c.) examination of the product revealed a number of peaks corresponding approximately to the molecular weights of unreacted PPM monomer, dimer (I), trimer (II), tetramer (III and IV) and higher oligomers. A 17 g portion of the mixture was separated into individual components by column chromatography using 230–400 mesh Kieselgel 60

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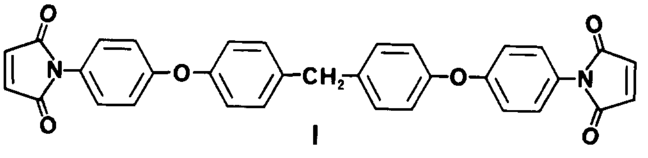

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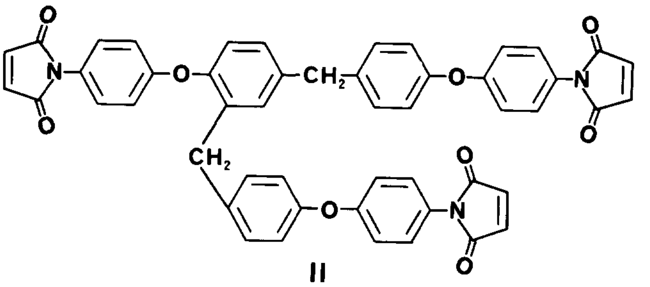

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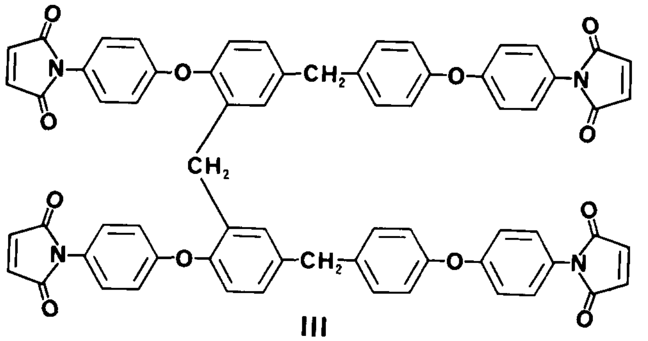

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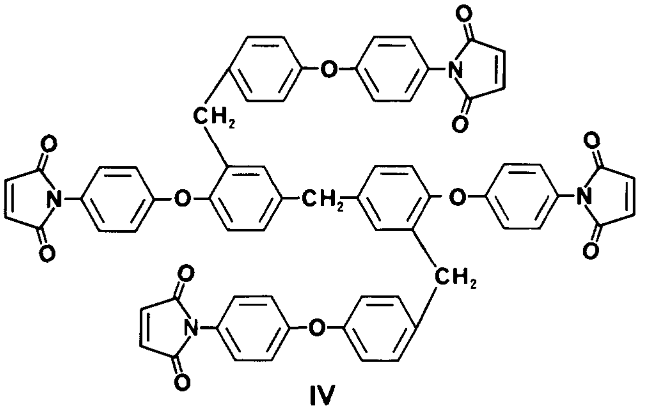


IV

(Merck 9385) as support and chloroform/hexane (gradually changing from chloroform/hexane (4:1) to pure chloroform) as eluent. Monomer and dimer of over 90% purity were obtained, but the trimer and tetramer fractions were somewhat impure. Repeated column chromatography on each of these fractions yielded relatively pure trimer (over 90%) and approximately 85% purity tetramer (as indicated by g.p.c.).

^{1}*H n.m.r.* (*CDCl*$_3$). Dimer, $\delta = 6.9$–7.3 (m, 16H, aromatics), 6.75 (s, 4H, maleimide), 3.84 (s, 2H, methylene); trimer, $\delta = 6.9$–7.3 (m, 23H, aromatics), 6.75 (s, 6H, maleimide), 3.84 (s, 4H, methylene); tetramer, aromatic and maleimide protons could not be separately integrated. However, the ratio of aromatic and maleimide protons ($\delta = 6.7$–7.3): methylene protons ($\delta = 3.8$) was 6.2:1 (theoretical ratio 6.33:1).

^{13}*C n.m.r.* (*CDCl*$_3$). Methylene bridge signals; dimer, $\delta = 40.8$ (4,4′-linkage); trimer, $\delta = 40.8$ (4,4′-linkage), 35.7 (2,4′-linkage) in a 1:1 ratio; tetramer, $\delta = 40.8$ (4,4′-linkage), 35.7 (2,4′-linkage), 30.9 (2,2′-linkage) in a 3.7:3.3:1 ratio, which corresponds to a mole ratio of 38:62 for isomers III:IV.

Oligomerization of N-*(2-methoxy)-phenylmaleimide (MPM)*

Trifluoromethane sulphonic acid (0.1 ml) was added to a stirred solution of MPM (2.0 g, 0.019 mol) and paraformaldehyde (1.0 g, 0.033 mol) in 1,2-dichloromethane (20 ml) and the above procedure repeated to give a pale yellow powder (2.1 g) having a softening point (Kofler bar) of 85–90°C. The compound gave a single peak by g.p.c.

^{1}*H n.m.r.* (*CDCl*$_3$). $\delta = 6.9$–7.5 (m, 6H, aromatics), 6.8 (s, 4H, maleimide), 3.85 (s, 2H, methylene), 3.65 (s, 6H, methoxy).

^{13}*C n.m.r.* (*CDCl*$_3$). Methylene bridge signal at $\delta = 39.3$ predominates (4,4′-linkage). Small signals (under 3 mol%) at 34.6 (2,4′-linkage) and 30.1 (2,2′-linkage) were noted.

Attempted oligomerization of N-*phenylmaleimide (PM)*

Trifluoromethane sulphonic acid (0.5 ml) and acetic acid (20 ml) were added to a solution of PM (2.0 g, 0.011 mol) and paraformaldehyde (1.0 g, 0.033 mol) in chloroform (40 ml) and the above procedure repeated. After 1 h of heating, g.p.c. analysis indicated that very little reaction had occurred. A further aliquot of paraformaldehyde (1.0 g, 0.033 mol) and trifluoromethane sulphonic acid (0.5 ml) in chloroform (5 ml) was added and the solution was refluxed for a further 3 h to yield, after work-up, mostly unreacted *N*-phenylmaleimide. The use of more forcing conditions (e.g. 98% sulphuric acid in place of trifluoromethane sulphonic acid) resulted in the loss of the maleimide ring.

RESULTS AND DISCUSSION

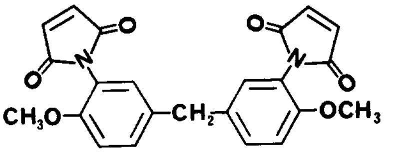
The preparation of oligomers by the conventional acid catalysed reaction of aqueous formaldehyde with the *N*-arylmaleimides employed in this work is not straightforward. Heterogeneous reaction mixtures are encountered, leading to concomitant problems in terms of unwanted side reactions and low yields. We have developed non-aqueous reaction conditions for a variety of activated aromatics using certain strong acid catalysts[5] and these were adopted in this work. At the onset, it was not obvious if deactivated aromatics, such as those with a maleimido substituent, would be sufficiently reactive to undergo electrophilic substitution under these conditions. Therefore, the aim of this work was to assess and attempt to overcome the deactivating effect of the maleimido group on a variety of aromatic molecules by introducing activating substituents, e.g. methoxy and phenoxy.

Attempted oligomerization of PM

All attempts to oligomerize PM were unsuccessful, even after repeating the reaction with a variety of temperatures, solvents and strong acid catalysts. Such efforts always resulted in either unreacted PM being recovered or the formation of gel and the disappearance of maleimide functionality, presumably the result of maleimide polymerization or miscellaneous side reactions such as ring opening. Kunugiza and Inoue[8] have described the preparation of a mixture of dimer, trimer and higher oligomers from the reaction of PM and paraformaldehyde in the presence of either HCl or H_2SO_4 and methanol as solvent. In our hands these conditions repeatedly afforded only intractable material and some unreacted PM.

Oligomerization of MPM and PPM

The presence of the activating methoxy substituent was sufficient to promote electrophilic attack on the aromatic ring of MPM. However, after 2 h reaction time, g.p.c. analysis indicated the formation of dimerized MPM only. The reaction was not usually carried out for longer periods since this tended to result in the formation of insoluble gel and the disappearance of the maleimide unsaturation, possibly the result of maleimide polymerization. Column chromatographic separation enabled relatively pure dimer to be obtained. ^{13}C n.m.r. spectroscopy analysis of this product revealed that structure V predominates, where the two MPM molecules are linked by a 4,4′-methylene bridge (relative to the methoxy substituent). There was some evidence for 2,4′- and 2,2′-linked structures, but these were at a very low concentration (under 3 mol%). So, although it is apparent that the presence of the methoxy substituent counteracts the deactivating effect of the maleimido group and enables electrophilic substitution on the ring to occur, the extent of reaction is rather limited. It may be that other factors, such as steric hindrance, are constraining further reaction.



V

The oligomerization of PPM proved to be more efficient. After about 3 h reaction time it was evident that a series of molecules varying in discrete molecular weight steps had formed and these corresponded to unreacted PPM, dimer, trimer and tetramer (plus higher oligomers), respectively (*Figure 1*), in the approximate ratio 12:20:38:30 mol% as determined by measurement of g.p.c. peak integrals. Obviously, longer reaction times would result in increased amounts of higher oligomers. These are, however, not easily characterized and so short conversions were used to obtain the optimum amount of lower oligomers for further study.

Column chromatographic separation enabled fairly pure samples of dimer, trimer and tetramer to be isolated. These were analysed by ^{1}H and ^{13}C n.m.r. spectroscopy and their spectra found to be consistent with structures I (dimer), II (trimer) and III/IV (38/62 mol%) (mixture of tetramer isomers). No evidence was found for methylene bridging via the aromatic ring attached to maleimide, presumably due to deactivation. However, the ring distant from the maleimido group is sufficiently activated by the ether oxygen to participate in the reaction.

Structural analysis of the products and monitoring of the reaction by g.p.c. allows speculation on the nature of the oligomerization process (*Scheme 1*). It appears that the initial step is the dimerization of PPM by formation of a 4,4′-methylene linkage. No evidence for a 2,4′- or 2,2′-link was obtained, suggesting some steric influence (control) from the phenylmaleimide group of PPM. Trimer is formed by the addition of a PPM molecule principally through a 2,4′-methylene linkage, the 2,2′-link does not appear to be favoured. There are two approaches to forming tetramer; either (a) linking two dimer molecules by a 2,2′-linkage (III) or (b) adding a PPM molecule to trimer via a 2,4′-linkage (IV), with the latter process occurring slightly more frequently. Further oligomer formation could occur by a variety of processes involving all species present in the reaction mixture, e.g. addition of monomer to tetramer, dimer to trimer, tetramer to tetramer, etc. Certainly it is apparent that maleimide functionalized aromatic oligomers of known structure can be synthesized by this approach.

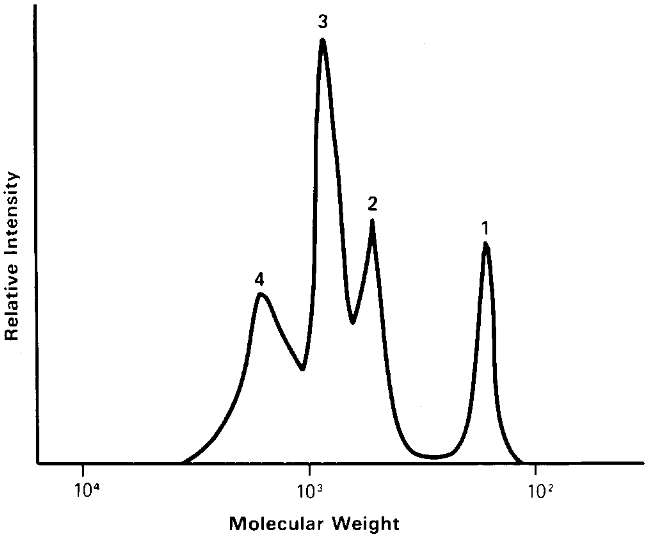


Figure 1 G.p.c. trace of PPM oligomer mixture (chloroform solution, calibrated with polystyrene standards): (1) PPM monomer; (2) dimer; (3) trimer; (4) tetramer plus higher oligomers

Table 1 D.s.c. analysis[a] of uncured PPM oligomers

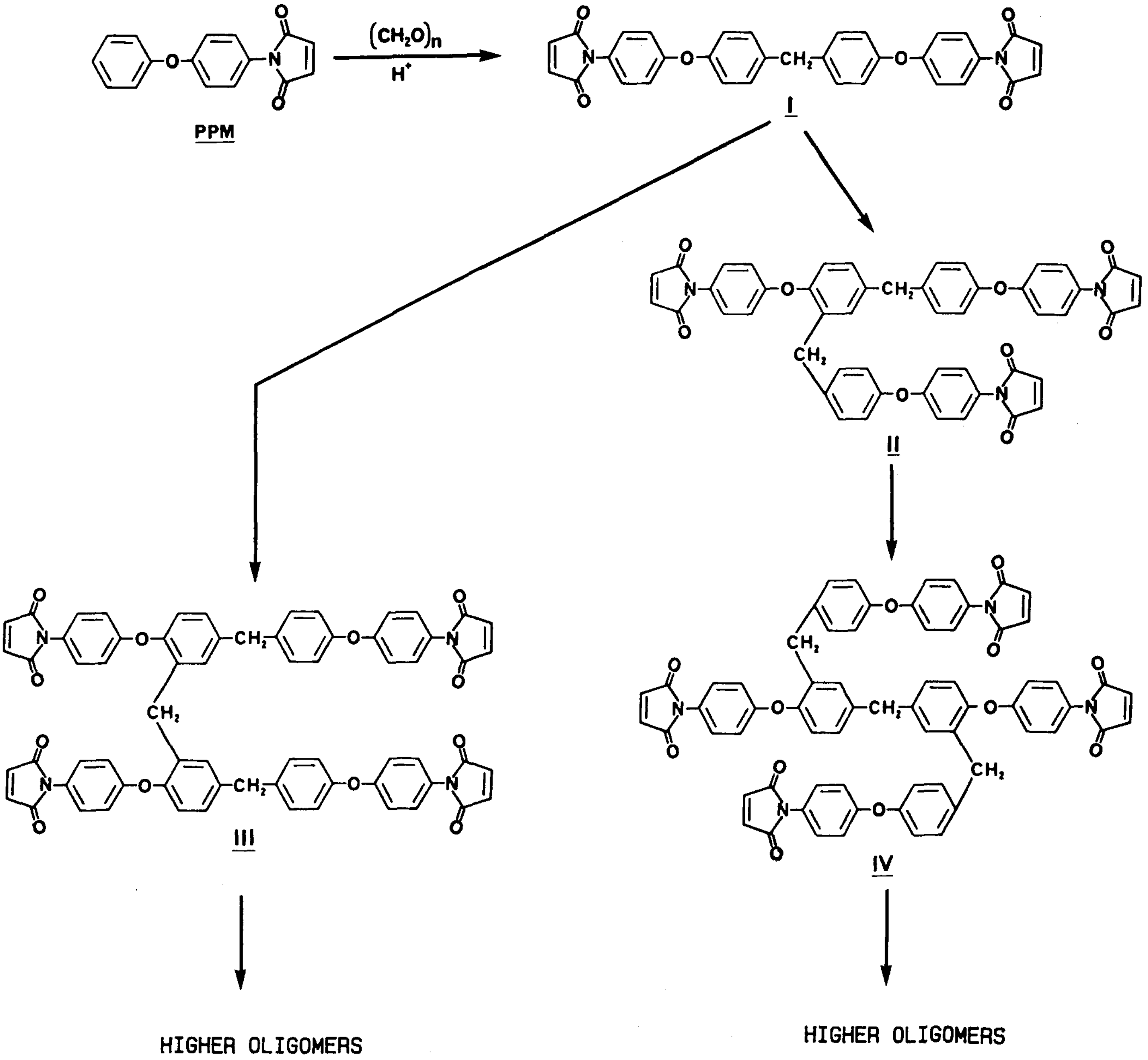
Sample	m.p. (°C)	T_g (°C)	Onset of cure exotherm (°C)	Cure exotherm peak maximum (°C)
Dimer (I)	203	–	240	284
Trimer (II)	–	88	220	274
Tetramer (III/IV)	–	95	236	285

[a] Heating at 20 K min^{-1} under N_2

Thermal analysis of PPM oligomers

The results of differential scanning calorimetry (d.s.c.) on uncured PPM dimer, trimer and tetramer are summarized in *Table 1*. The dimer (I) exhibits a crystalline melting endotherm at 203°C whereas the amorphous trimer (II) and tetramer (mixture of III and IV) display glass transitions at 88°C and 95°C, respectively. All samples exhibited similar cure exotherms with about the same peak maximum at 274–285°C.

Samples cured in air at 250°C for 16 h followed by 300°C for 2 h with heating and cooling being carried out at 2 K min^{-1} show excellent thermal properties. No glass transitions were observed below 400°C by either dynamic mechanical thermal analysis (d.m.t.a.) or thermomechanical analysis (t.m.a.) (heating at 10 K min^{-1} in air) for any of the cured PPM oligomers. The samples begin to decompose when heated above 400°C. Thermo-



Scheme 1 Formation of oligomers based on PPM

gravimetric analysis (t.g.a.) (heating at 10 K min^{-1} in nitrogen) revealed that the cured PPM oligomers have a weight loss of only 1.65–1.90% w/w over the range 30–480°C. This thermal performance compares favourably with other maleimide systems[1].

CONCLUSIONS

Work on model compounds has indicated the types of maleimide functionalized aromatics capable of forming oligomers by the acid catalysed reaction with formaldehyde. The work has also revealed conditions whereby oligomers can be successfully prepared without the occurrence of side reactions involving the relatively labile maleimide group. PPM readily oligomerizes to form a variety of well defined dimer, trimer and tetramer structures linked through various combinations of methylene bridges. MPM is not as reactive as PPM and tends only to form 4,4'-linked dimer. PM reacted only under forcing conditions to give products arising from degradation of the maleimide group. Thermal analysis indicates that the cured PPM oligomers exhibit a promising combination of high T_g and good thermal stability.

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