Novel maleimide functionalized oligomers:
2. Co-oligomerization studies

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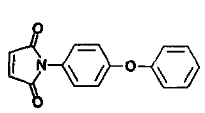
Novel maleimide functionalized oligomers have been prepared from the acid catalysed co-oligomerization of *N*-(4-phenoxy)-phenylmaleimide (PPM) with a series of activated aromatics (diphenyl ether (DPE), diphenylmethane (DPM) and dibenzofuran (DBF)) in the presence of formaldehyde. The resultant oligomers can be polymerized to form infinite networks possessing glass transition temperatures (T_g) in excess of 400°C. Cured co-oligomers containing a 55:45 mol% ratio of PPM and DPE exhibit an optimum combination of modulus, toughness and T_g which is comparable to commercially available BMI compositions.

(Keywords: aromatic maleimide; formaldehyde; oligomerization; characterization; tough; mechanical properties)

INTRODUCTION

Crosslinked networks derived from bismaleimides (BMIs) are well known for their good thermal stability and high glass transition temperatures (T_g). Unfortunately, the highly crosslinked nature of cured BMI networks makes them inherently brittle, thus limiting their utility as structural materials. In a previous paper[1] it was shown that *N*-(4-phenoxy)-phenylmaleimide (PPM) (*Structure I*) reacted readily with formaldehyde under acid catalysis without loss of maleimide functionality to form oligomeric structures displaying good high temperature properties. The aim of the present work was to co-oligomerize PPM with other activated aromatics, thus linking a variety of such aromatic molecules through methylene bridges. The maleimide functionalized oligomers thus formed would have the potential to cure to networks with lower crosslink densities than conventional BMI systems and would hopefully display a useful compromise between gaining improved toughness without substantial loss in the stiffness or T_g. Diphenyl ether (DPE), diphenylmethane (DPM) and dibenzofuran (DBF) are all capable of undergoing acid catalysed electrophilic substitution reactions with formaldehyde and were chosen as co-monomers.



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EXPERIMENTAL

Materials

PPM (m.p. = 160°C) was synthesized from 4-phenoxy aniline and maleic anhydride according to the method of Searle[2]. DPE (ICI), DPM (Aldrich) and DBF (Aldrich) were used as supplied. Typical syntheses of PPM/DPE, PPM/DPM and PPM/DBF co-oligomers are described as follows.

Preparation of PPM/DPE co-oligomers

A mixture of PPM (132.9 g, 0.50 mol), DPE (42.5 g, 0.25 mol), 1,3,5-trioxan (70 g) and trifluoromethane sulphonic acid (2 ml) was dissolved in 1,2-dichloroethane (800 ml) and heated to 60–70°C with stirring. A solution of DPE (42.5 g, 0.25 mol) in 1,2-dichloroethane (200 ml) was then added to the reaction mixture over a 3 h period. Any water formed was removed by azeotropic distillation. Further portions of trifluoromethane sulphonic acid (2 ml in 1,2-dichloroethane (100 ml)) were added after 1 h and 3 h. After a total reaction time of 5 h, gel permeation chromatography (g.p.c.) indicated that all the PPM and DPE had reacted to form oligomer and the reaction was stopped by the addition of an excess of 5% w/v aqueous sodium carbonate solution. The resultant mixture was washed with aqueous sodium carbonate solution, dried over magnesium sulphate, filtered and the co-oligomer precipitated by dropwise addition to hexane. After drying under vacuum, a pale yellow powder was obtained (190 g) which had a softening point of 70°C and $M_n = 1200$, $M_w = 4400$.

^{1}H n.m.r. ($CDCl_3$): broad signals at $\delta = 6.4$–7.4 (aromatics), 6.8 (maleimide) and 3.5–4.1 (methylene). Ratio of aromatic and maleimide protons to methylene protons was 4.6:1.

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^{13}C n.m.r. ($CDCl_3$): methylene linkage signals at $\delta = 40.2$ (4,4′-linkage), 35.3 (2,4′-linkage) and 30.4 (2,2′-linkage) in a ratio of 13:6:1 (20% error).

Preparation of PPM/DPM co-oligomers

A mixture of 1,3,5-trioxan (50 g), DPM (67.2 g, 0.40 mol) and trifluoromethane sulphonic acid (2 ml) was dissolved in 1,2-dichloroethane (400 ml) and heated to reflux with stirring. A solution of PPM (99 g, 0.40 mol) in 1,2-dichloroethane (600 ml) was then added steadily over $1\frac{1}{4}$ h. Any water formed was removed by azeotropic distillation. Further quantities of 1,3,5-trioxan (20 g and 5 g) and trifluoromethane sulphonic acid (1 ml and 0.5 ml) in 1,2-dichloroethane (100 ml) were added after 1 h and $1\frac{1}{2}$ h, respectively. After 3 h, g.p.c. analysis indicated that all the PPM and DPM monomer had reacted and the oligomerization was stopped by the addition of excess 5% w/v aqueous sodium carbonate solution. The resultant mixture was worked up as described for the PPM/DPE co-oligomers to yield a pale yellow powder (132 g) which had a softening point of 130°C and $M_n = 1500$, $M_w = 4900$.

Preparation of PPM/DBF co-oligomers

DBF (16.5 g, 0.098 mol), 1,3,5-trioxan (12 g) and trifluoromethane sulphonic acid (0.3 ml) were dissolved in 1,2-dichloroethane (150 ml) and heated to reflux with stirring. A solution of PPM (26.2 g, 0.098 mol) in 1,2-dichloroethane (200 ml) was then added steadily over 1 h, with any water formed being removed by azeotropic distillation. A further quantity of trifluoromethane sulphonic acid (0.2 ml) in 1,2-dichloroethane (100 ml) was added after $1\frac{1}{2}$ h. After 2 h the reaction was stopped by the addition of excess 5% w/v aqueous sodium carbonate solution. The resultant mixture was worked up as described for the PPM/DPE co-oligomers to yield a cream powder (32.5 g) which had a softening point of 150°C and $M_n = 1200$, $M_w = 3400$.

Curing and characterization of co-oligomers

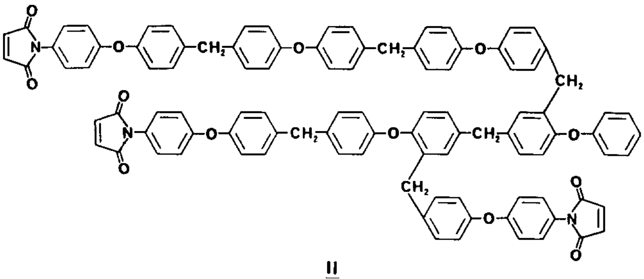
Neat resin castings were prepared by compression moulding portions of the maleimide co-oligomers in metal moulds (60 × 12.7 × 3 mm) for 30 min at 190°C, 30 min at 220°C, 2 h at 250°C under 200–800 psi pressure with heating and subsequent cooling at 2°C min^{-1}. After demoulding, the castings were post-cured freestanding in air at 250°C and, in some cases to enhance T_g values, 300°C for varying times. No apparent decomposition, other than slight darkening of the samples, seemed to occur at these elevated temperatures. The mechanical properties were determined at 25°C according to ASTM D790 (flexural strength and modulus), ASTM E399 (K_{1c}, plane strain fracture toughness) and Plati and Williams[3] (G_{1c}, critical strain energy release rate). Cured co-oligomer T_g values were measured by dynamic mechanical thermal analysis (d.m.t.a.) (Polymer Laboratories instrument operating in bending mode). Uncured co-oligomer molecular weights were determined by g.p.c. (Waters Associates instrument with model 510 pump and model 490 multiwavelength u.v. detector equipped with a 10^3 Å pore size ultrastyragel column) calibrated with polystyrene standards and using chloroform as solvent at 25°C. Softening points were measured by Kofler bar.

RESULTS AND DISCUSSION

Co-oligomer synthesis

The acid-catalysed oligomerization of PPM and its reaction with formaldehyde (derived from decomposition of paraformaldehyde or 1,3,5-trioxan) under non-aqueous conditions was discussed previously[1]. It was shown that the resultant oligomers consist of PPM molecules linked through methylene bridges at either the *para* or *ortho* positions on the phenoxide moiety of PPM. *Para* linkages are favoured presumably due to steric factors. ^{13}C n.m.r. analysis of a PPM/DPE (50:50 mol%) co-oligomer prepared in the present work also shows that reaction at the *para* positions occurs most frequently. The ratio of 4,4′:2,4′:2,2′ methylene linkages was estimated to be 13:6:1. A representative PPM/DPE co-oligomer structure consistent with this information is depicted (*Structure II*). The PPM/DPM and PPM/DBF co-oligomers would probably have similar types of structure with 4,4-methylene linkages predominating.

A typical co-oligomer g.p.c. trace is shown in *Figure 1*. The trace shows a fairly broad peak made up of a variety of oligomer structures ranging from low molecular weight products (e.g. dimers, trimers, tetramers etc.) up to polymeric structures with significant molecular weights. The oligomerization reactions were terminated when residual monomers became undetectable by g.p.c. Careful sequential addition of monomers and control of monomer ratios was found necessary to avoid formation of crosslinked high molecular weight products prior to complete monomer incorporation and to obtain



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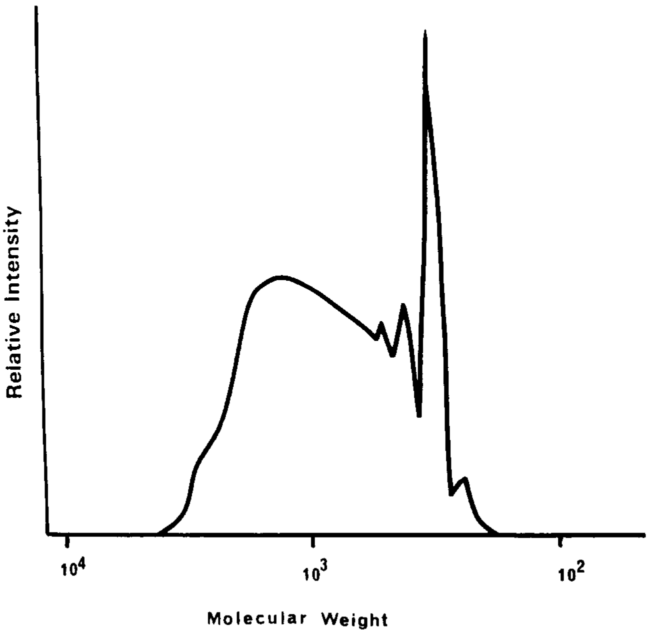

Figure 1 Typical co-oligomer g.p.c. trace (DPE8, *Table 1*)

the optimum yield of co-oligomer. The experimental procedures detailed in this paper represent a significant amount of optimization work and describe the most favourable conditions to achieve full monomer incorporation into low molecular weight oligomers. However, once optimized, the oligomerizations have been found to give acceptable reproducibility.

The main difference between the three types of co-oligomerization is that DPE, DPM and DBF have different reaction rates in electrophilic substitutions and, more significantly, have different reactivities when compared to PPM. Optimization of the co-oligomerization of DPE, DPM and DBF, each with PPM, was preceded by a rough determination of their relative homopolymerization rates with formaldehyde under a standard condition giving the following relative rates of reaction with formaldehyde: DPE $\gg$ PPM > DBF > DPM. Thus to ensure efficient incorporation of all monomer types into oligomer, DPE was added to the PPM/formaldehyde/acid mixture over several hours whilst the opposite sequence was carried out for PPM/DPM and PPM/DBF co-oligomer syntheses.

Table 1 details the characterization data for a number of co-oligomers. A fairly wide range of oligomers was synthesized, varying in molecular weight and composition. The variation in M_n, M_w and M_w/M_n reflects the difficulty in obtaining good reproducibility between co-oligomer batches. All PPM/DPE and PPM/DPM co-oligomers have softening points ranging from about 70 to 135°C. PPM/DBF co-oligomers tend to have fairly high softening points (about 150°C), as expected, and this is attributed to the comparatively rigid DBF structure relative to DPE and DPM, which possess flexible ether or methylene linkages.

A broad range of PPM/DPE co-oligomer compositions were synthesized (i.e. 100:0 to 25:75 mol% PPM:DPE) to find the optimum combination of properties such as T_g and mechanical properties for the cured systems. *Table 2* reveals the change in T_g with varying PPM content as measured by d.m.t.a. Comparing T_g values for co-oligomers post-cured under identical conditions (i.e. post-cure A – 250°C for 16 h followed by 300°C for 4 h) shows that the T_g of each co-oligomer containing over 55 mol% PPM (DPE1, DPE2 and DPE3) is at least 415°C and is in fact indistinguishable from the co-oligomer decomposition temperature. Co-oligomers containing less than 55 mol% PPM content (DPE9, DPE10 and DPE11) have two d.m.t.a. transitions. The lower is attributed to the T_g; the higher transition is the onset of decomposition. Typical d.m.t.a. traces illustrating this behaviour are shown in *Figure 2* (for DPE2, 67:33 PPM:DPE and DPE9, 50:50 PPM:DPE). In general, the cured co-oligomer T_g decreases with

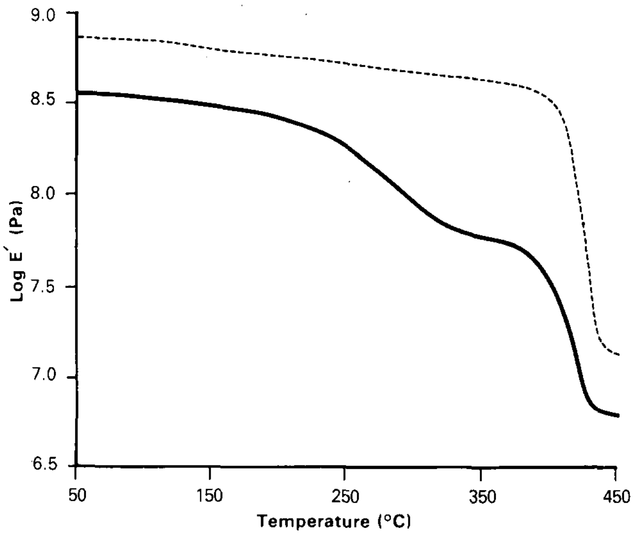

Figure 2 Typical d.m.t.a. traces for PPM/DPE co-oligomers (post-cured for 16 h at 250°C, 4 h at 300°C). – – –, DPE2, 67:33 mol% PPM:DPE; ——, DPE9, 50:50 mol% PPM:DPE

Table 1 Characterization data for a range of co-oligomers

Sample no.	Type	Composition PPM : comonomer (mol%)	M_n[a]	M_w[a]	M_w/M_n[a]	Softening point[b] (°C)
DPE1	PPM/DPE	100:0	960	3200	3.3	125
DPE2	PPM/DPE	67:33	1130	4000	3.5	85
DPE3	PPM/DPE	55:45	1600	9000	5.7	–
DPE4	PPM/DPE	55:45	800	3600	4.4	120
DPE5	PPM/DPE	52:48	1700	10 100	5.8	130
DPE6	PPM/DPE	52:48	2300	18 200	8.0	130
DPE7	PPM/DPE	52:48	2800	26 900	9.6	135
DPE8	PPM/DPE	50:50	1200	4400	3.7	70
DPE9	PPM/DPE	50:50	1800	5300	2.9	95
DPE10	PPM/DPE	33:67	1300	5300	4.0	85
DPE11	PPM/DPE	25:75	860	8300	9.7	75
DBF1	PPM/DBF	50:50	1200	3400	2.8	150
DPM1	PPM/DPM	60:40	900	2400	2.6	130
DPM2	PPM/DPM	55:45	1200	8200	6.8	105
DPM3	PPM/DPM	52:48	1500	4300	2.9	–
DPM4	PPM/DPM	50:50	1500	4900	3.3	130
DPM5	PPM/DPM	40:60	1300	5700	4.4	130

[a] Measured by g.p.c. calibrated with polystyrene standards
[b] Measured by Kofler bar

Table 2 Mechanical and thermal properties of cured PPM/DPE co-oligomers

Sample no.	Composition PPM/DPE (mol%)	Post-cure schedule[a]	M_n[b]	K_{1c} (MN $m^{-3/2}$)	G_{1c} (kJ m^{-2})	Flexural modulus (GPa)	d.m.t.a. transitions[c] (°C)
DPE1	100:0	A	960	–	–	–	420
DPE2	67:33	A	1130	–	–	–	415
DPE3	55:45	A	1600	0.40	0.10	3.3	435
DPE3	55:45	B	1600	0.37	0.08	3.5	435
DPE3	55:45	C	1600	0.36	0.09	3.2	440
DPE4	55:45	D	800	0.36	0.35	3.2	250/380
DPE5	52:48	B	1700	0.48	0.17	3.2	388
DPE6	52:48	B	2300	0.49	0.20	3.1	365
DPE7	52:48	B	2800	0.38	0.12	3.1	364
DPE9	50:50	A	1800	0.55	0.19	3.1	215/395
DPE10	33:67	A	1300	–	–	–	165/385
DPE11	25:75	A	860	–	–	–	135/360

[a] Samples post-cured according to:
A – 16 h at 250°C; 4 h at 300°C
B – 4 h at 250°C; 4 h at 300°C
C – 16 h at 250°C; 4 h at 300°C; 2 h at 350°C
D – 6 h at 240°C

[b] Data from *Table 1*

[c] Determined from d.m.t.a. by drawing tangents to the modulus/temperature graph

Table 3 Mechanical and thermal properties of cured PPM/DPM and PPM/DBF co-oligomers

Sample no.[a]	Composition PPM/comonomer (mol %)	M_n[b]	K_{1c} (MN $m^{-3/2}$)	G_{1c} (kJ m^{-2})	Flexural modulus (GPa)	d.m.t.a. transitions[c] (°C)
DPM1	60:40	900	0.47	0.18	3.7	230/ND[d]
DPM2	55:45	1200	0.38	0.16	3.4	195/385
DPM3	52:48	1500	0.63	0.26	3.5	227/ND
DPM4	50:50	1500	0.49	0.18	3.8	199/400
DPM5	40:60	1300	0.44	0.16	3.4	205/390
DBF1	50:50	1200	–	–	3.9	325/405

[a] Samples were post-cured 6 h at 240°C

[b] Data from *Table 1*

[c] Determined by drawing tangents to the d.m.t.a. modulus/temperature curve

[d] Not determined

reducing PPM content, presumably due to a concomitant reduction in crosslink density.

Similarly, two d.m.t.a. transitions were observed with the other co-oligomers over the composition range studied (*Table 3*). For cured PPM/DPM co-oligomers the major transition ranging from 195–230°C is attributed to the T_g whilst a minor transition at 385–405°C is probably due to the onset of decomposition. As expected, the PPM/DBF co-oligomers tend to have a higher T_g (325°C for DBF1) compared to the corresponding PPM/DPE and PPM/DPM co-oligomers (e.g. 199°C for DPM4 and 215°C for DPE9) due to the increased rigidity of the DBF molecule compared to DPE or DPM.

Mechanical properties

Some mechanical properties for the cured PPM/DPE co-oligomers are detailed in *Table 2*. This summarizes the effect of varying co-oligomer M_n, composition and post-cure temperature. The series DPE5 to DPE7 shows that there is very little change in flexural modulus, K_{1c} or G_{1c} when the oligomer M_n is varied from 1700 to 2800. Any differences in properties are within experimental error. More significant effects are noted on changing co-oligomer composition, i.e. increasing the PPM content from 50 to 55 mol% has the expected effect of increasing flexural modulus, reducing toughness and increasing T_g.

The post-cure schedule employed seems to have an important effect on cured resin G_{1c} and T_g. DPE4 was post-cured at 240°C, which is a conventional maleimide post-cure temperature (post-cure D, *Table 2*). The comparative oligomer DPE3 was post-cured sequentially at 250, 300 (post-cures A and B) and 350°C (post-cure C). Thus, whilst the flexural modulus and G_{1c} in all cases was similar, G_{1c} for DPE4 was approximately $3\frac{1}{2}$ times larger than the samples post-cured at higher temperatures and, although the T_g is reduced to 250°C, the onset of decomposition remains high (380°C). The combination of modulus, G_{1c} and T_g exhibited by DPE4 compares favourably with current commercially available BMI compositions based on 4,4′-bismaleimidodiphenyl methane[4].

Table 3 shows some mechanical properties for the

PPM/DPM and PPM/DBF co-oligomers. These were all post-cured at 240°C. PPM contents of the PPM/DPM co-oligomers were varied from 40 to 60 mol% but little variation in properties between samples was noted. Whilst the K_{1c} and G_{1c} values are comparable with commercial BMI systems, the T_g values tend to be rather low (195–230°C) compared to a typical T_g range of 250–300°C for commercial BMIs.

Co-oligomers containing DBF tend to have relatively high softening points (e.g. 150°C for DBF1) and rather high molten resin viscosities. As a result, the quality of moulded resin samples was poor and so K_{1c} and G_{1c} values were not determined for these systems. However, as expected, they demonstrate the highest values for flexural modulus amongst samples post-cured at 240°C due to the rigidity of the DBF monomer units.

CONCLUSIONS

Co-oligomers of PPM with other activated aromatics can be successfully prepared under controlled non-aqueous acid catalysed reaction conditions. The resultant co-oligomers can be cured to networks possessing T_g values in excess of 400°C, depending on co-oligomer type and post-cure temperature employed. Cured DPM co-oligomers tend to have lower T_g values than comparable DPE systems, whilst oligomers containing DBF have very high T_g but are difficult to process. Co-oligomers containing a 55:45 mol% ratio of PPM to DPE possess the optimum combination of modulus, toughness and T_g, which are comparable to commercially available BMI compositions.

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