Studies on a series of bisarylimides containing four phenylene rings and their polymers: 1. Synthesis and characterization of the monomers

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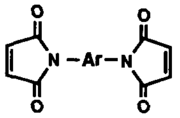
Two aryl bismaleimides and the corresponding biscitraconimides, in which the imide groups were attached to the ends of aromatic residues containing four phenylene rings, were prepared and then purified by preparative high-performance liquid chromatography. Rigorous purification in this way was found to have marked effects on the thermal polymerization characteristics of these compounds as determined by the differential scanning calorimetry technique. The polymerization of bis-4-maleimidophenylmethane and of bis-4-maleimidophenyl ether was also affected by rigorous purification. Samples of the corresponding two bisnadimides containing four phenylene rings were also prepared.

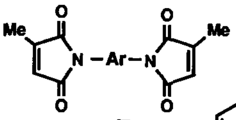
(Keywords: bismaleimides; biscitraconimides; bisnadimides; purification; polymerization; differential scanning calorimetry)

INTRODUCTION

Many aryl bismaleimides (structure **I**) have been prepared as monomers for crosslinked resin systems, and resins based on bis-4-maleimidophenylmethane (Ar = 4,4′-diphenylenemethane in **I**) are available commercially[1]. Most of these compounds have melting points greater than 150°C and close to the temperature at which thermal polymerization starts[2], so that typical d.s.c. scans for these monomers show a sharp melting endotherm quickly followed by a broad exothermic reaction peak due to polymerization and crosslinking. The close proximity of the melting and polymerization temperatures may lead to difficulties in using the d.s.c. technique[3] for investigating the kinetics of polymerization of these compounds and can cause problems in their use as monomers for composites[2]. Hence, we were interested to find bismaleimides with melting points below 100°C, which were expected to show a substantial temperature gap between melting and the start of polymerization. We also wanted to examine monomers containing a high proportion of phenylene to maleimide residues in the hope of obtaining crosslinked resins of improved thermal and oxidative stability.

Another way of increasing the temperature gap between melting and polymerization is to increase the temperature at which polymerization starts. Information on the polymerizability of arylcitraconimides is conflicting. Thus, it has been reported[4] that *N*-phenylcitraconimide does not polymerize in solution with free-radical initiators, but other workers report that biscitraconimides polymerize at temperatures lower than those found for the corresponding maleimides[5–8]. However, on general grounds citraconimides would be expected to polymerize less readily than the corresponding maleimides, and as the melting points of the two types of compound are similar, e.g. *N*-phenylmaleimide m.p. 91°C, and *N*-phenylcitraconimide m.p. 98°C, biscitraconimides (structure **II**) should show a larger temperature gap between melting and polymerization than the corresponding bismaleimides. The thermal curing of bisarylnadimides to crosslinked resins is a complex process (see for example ref. 9) in which polymerization is preceded by a reversed Diels–Alder reaction forming maleimide groups, which then act as key monomers in the subsequent polymerization[10]. Reversion of the Diels–Alder reaction requires temperatures in excess of 250°C so that with monomers of this type (structure **III**)


I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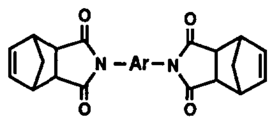
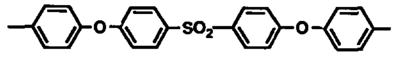

III

A


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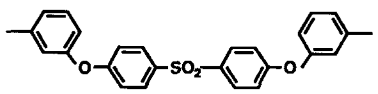

IV = I, Ar = A ; V = I, Ar = B ; VI = II, Ar = A ; VII = II, Ar = B
VIII = III, Ar = A ; IX = III, Ar = B.

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it should also be possible to select compounds showing a substantial gap between the melting and polymerization temperatures.

This paper reports the synthesis and characterization of two bismaleimides, structures **IV** and **V**, two biscitraconimides, **VI** and **VII**, and two bisnadimides, **VIII** and **IX**, in which the imide groups are attached to the ends of aromatic residues with the four-ring structures, A or B. Samples of the bismaleimides and the biscitraconimides were purified by preparative h.p.l.c. to obtain material for kinetic studies and it was found that this had marked effects on their thermal polymerization characteristics as indicated by d.s.c. measurements. Structures **IV**, **V** and **VIII** have been mentioned previously[11–13] but little analytical data were presented and no attempt at purification made.

EXPERIMENTAL

Fusion temperatures were measured using a Koffler hot-stage microscope. Infra-red spectra were recorded with a Perkin–Elmer 1750 *F.T.*i.r. spectrometer interfaced with a Perkin–Elmer 7300 computer; the samples were presented as KBr discs. ^1H and ^{13}C n.m.r. spectra were obtained using a Bruker WH90 *F.T.*i.r. spectrometer. D.s.c. was performed at 10°C min^{-1} in nitrogen using a Du Pont 910 calorimeter interfaced with a Du Pont 9900 computer/thermal analyser. Analytical h.p.l.c. was performed using Waters equipment with a silica column and a u.v. detector running at 280 nm linked to a computing integrator. The liquid phase was h.p.l.c. grade methylene chloride containing 2% v/v h.p.l.c. grade tetrahydrofuran.

Purification of bisimides by preparative h.p.l.c.

This was performed using Waters equipment fitted with a silica column and a refractometer-type detector; the liquid phase was h.p.l.c. grade methylene chloride containing 2% v/v h.p.l.c. grade tetrahydrofuran. Samples of the crude imides, 1–10 g in 75 ml solvent, were loaded onto the column and then eluted in batches. Each batch was analysed by h.p.l.c. and only those with purity greater than 99% were combined to give the final product. This was washed with dilute ferrous sulphate solution and with water, then dried over sodium sulphate and the solvent removed by evaporation.

Bis-4-(4-maleimidophenoxy)phenylsulphone, IV

Maleic anhydride, 33 g, was added to a solution of bis-4-(4-aminophenoxy)phenylsulphone[14], 73 g, in 220 ml dimethylformamide, which was stirred under nitrogen. The reaction mixture was cooled and the addition controlled so that the temperature did not exceed 15°C. After stirring for 1 h at room temperature, 11 g anhydrous sodium acetate and 52 g acetic anhydride were added and the mixture stirred for 1 h at 55°C. The product, 93 g after washing and drying, was isolated by pouring the reaction mixture into methanol. A portion of this product, 10 g, was washed in succession with 100 ml portions of methanol, carbon tetrachloride, acetone and ether to give (after drying) 5.5 g of a yellow powder, which analysed correctly for C, H and N, but was only 96.5% pure by h.p.l.c. Purification by h.p.l.c. gave yellow crystals, 99.9% pure. Found: C, 64.61; H, 3.28; N, 4.67%. $C_{32}H_{20}N_2O_8S$ requires: C, 64.86; H, 3.40; N, 4.73%. δ_H (ppm from TMS): 8.3–6.9 (m, Ar–H), 7.20 (s, unsat. C–H).

Bis-4-(3-maleimidophenoxy)phenylsulphone, V

This was prepared from bis-4-(3-aminophenoxy)-phenylsulphone[15], 30 g, and maleic anhydride, 13.6 g, using the method described above for **IV**, but without washing with solvents. The yield of crude product (74.6% pure by h.p.l.c.) was 30 g. M.p. = 90–100°C (lit.[12] m.p. 90–100°C). Preparative h.p.l.c. gave material 99.8% pure, m.p. = 93–100°C. Found: C, 64.68; H, 3.41; N, 4.70%. $C_{32}H_{20}N_2O_8S$ requires: C, 64.86; H, 3.40; N, 4.73%. δ_H (ppm from TMS): 8.2–6.9 (m, Ar–H), 7.18 (s, unsat. C–H).

Bis-4-(4-citraconimidophenoxy)phenylsulphone, VI

Citraconic anhydride, 21.7 g, was added with stirring to a cooled solution of the bis-4-(4-aminophenoxy)-phenylsulphone, 41.8 g, in 50 ml toluene and 50 ml dimethylformamide at such a rate that the temperature did not exceed 15°C. After addition was complete the reaction mixture was stirred at room temperature for 1 h. Then 0.45 g *p*-toluenesulphonic acid was added and the mixture heated under reflux for 5 h, collecting the water evolved in a Dean and Stark trap. The product was poured into methanol and the solid obtained was washed and dried to give 42 g of a grey powder: m.p. = 151–155°C, 76.9% pure by h.p.l.c.. Preparative h.p.l.c. gave 99.8% pure material, m.p. = 190–193°C. Found: C, 65.59; H, 3.97; N, 4.22%. $C_{34}H_{24}N_2O_8S$ requires: C, 65.80; H, 3.90; N, 4.51%. δ_H (ppm from TMS): 8.2–7.1 (16 H, m, Ar–H), 6.81 (2 H, d, unsat. C–H), 2.08 (6H, d, 2 × Me).

4-(4-Citraconimidophenoxy)phenyl-4-(4-itaconimidophenoxy)phenylsulphone, X

This was separated from the crude product of the bis-citraconimide preparation by preparative h.p.l.c.; m.p. = 202–210°C, 99.1% pure. Found: C, 65.35; H, 4.22; N, 4.22%. $C_{34}H_{24}N_2O_8S$ requires: C, 65.80; H, 3.90; N, 4.51%.

Bis-4-(3-citraconimidophenoxy)phenylsulphone, VII

This was prepared from bis-4-(3-aminophenoxy)-phenylsulphone, 50 g, and citraconic anhydride, 26 g, using the method described above for **VI**, but removing some impurities by dissolving the crude product in methylene chloride, boiling with activated charcoal, and precipitating into methanol. The yield of dried material (81% pure) was 8 g. Preparative h.p.l.c. gave material 99.8% pure, m.p. 79–85°C. Found: C, 65.73; H, 3.90; N, 4.49%. $C_{34}H_{24}N_2O_8S$ requires: C, 65.80; H, 3.90; N, 4.51%. δ_H (ppm from TMS): 8.3–7.0 (16 H, m, Ar–H), 6.80 (2 H, d, unsat. C–H), 2.07 (6 H, s, 2 × Me).

Bis-4-(4-nadimidophenoxy)phenylsulphone, VIII

Nadic anhydride, 22.7 g, dissolved in 50 ml toluene plus 20 ml dimethylformamide was added with stirring to a solution of bis-4-(4-aminophenoxy)phenylsulphone in toluene, 55 ml, and dimethylformamide, 20 ml, at such a rate that the temperature did not exceed 30°C. *p*-Toluenesulphonic acid, 3 g, was added and the mixture heated to reflux for 20 h, removing water with a Dean and Stark trap, after which it was poured into methanol to isolate the imide. The yield was 49 g, purity 99.0%, m.p. 210–214°C (lit.[13] m.p. = 210–225°C). Calculated for $C_{42}H_{32}N_2O_8S$: C, 69.60; H, 4.45; N, 3.86%. Found: C, 69.85; H, 4.75; N, 3.85%. δ_H (ppm from TMS): 8.1–6.9 (16 H, m, Ar–H), 6.22 (4 H, s, unsat. C–H), 3.48 (4 H, s, bridgehead H), 3.32 (–, s, ring junction H), 1.60 (4 H, s, 2 × bridge CH_2).

Bis-4-(3-nadimidophenoxy)phenylsulphone, IX

The crude imide, 14.1 g, was prepared from bis-4-(3-aminophenoxy)phenylsulphone, 10.0 g, and nadic anhydride, 7.6 g, in the same way as described for **VIII**. Then, crude imide was dissolved in boiling chloroform, treated with activated charcoal, filtered and then recrystallized from this solution after addition of a little methanol. This gave the imide as a white powder, 97.2% pure, m.p. 210–215°C. Found: C, 69.49; H, 4.38; N, 3.74%. $C_{42}H_{32}N_2O_8S$ requires: C, 69.60; H, 4.45; N, 3.86%. δ_H (ppm from TMS): 8.2–6.8 (16 H, m, Ar–H), 6.20 (4 H, s, unsat. C–H), 3.45 (4 H, s, bridgehead H), 3.33 (–, s, ring junction H), 1.59 (4 H, s, 2 × bridge CH_2).

RESULTS

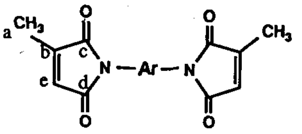
Monomer synthesis

The bismaleimides, **IV** and **V**, were prepared by a modification of Searle's[16] method in which the maleamic acids were obtained by treating the diamines with maleic anhydride, using dimethylformamide as the solvent, and then warming the amic acid solutions with sodium acetate and acetic anhydride to effect cyclization. Elemental analysis showed these products to be impure and purification could not be effected by recrystallization. Washing with poor solvents effected some purification of compound **IV** so that the results of elemental analysis now fell within acceptable limits, but analysis by h.p.l.c. showed this material to be only 96.5% pure; purification to 99.9% was effected by preparative h.p.l.c. The purity of crude **V** (75% pure by analytical h.p.l.c.) was not improved by solvent washing, but 99.8% pure material was obtained by preparative h.p.l.c.

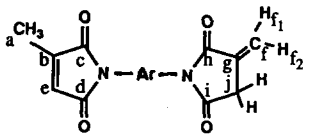
Table 1 Assignment of ^1H n.m.r. spectra of the biscitraconimide, **VI**, and the citraconimide/itaconimide, **X**

Chemical shift (ppm)	Multiplicity	Assignment	Integral
	Biscitraconimide, **VI**		
8.2–7.1	multiplet	Aromatic H	16 H
6.81	doublet	H_e	2 H
2.08	doublet	H_a	6 H
	Citraconimide/itaconimide, **X**		
8.2–7.0	multiplet	Aromatic H	16 H
6.50	multiplet	H_e and H_{f1}	2 H
5.77	triplet	H_{f2}	1 H
3.52	triplet	H_j	2 H
2.18	doublet	H_a	3 H

The biscitraconimides, **VI** and **VII**, were obtained by treating the diamines with citraconic anhydride, using a mixture of toluene and dimethylformamide as the solvent, and then heating to reflux in the presence of *p*-toluenesulphonic acid as catalyst to effect conversion of the amic acids to the imides. Purification of these compounds could not be effected by recrystallization or solvent treatment, but was achieved by preparative h.p.l.c., which gave samples of each monomer 99.8% pure. The crude product from which pure **VI** was isolated contained about 25% of an isomeric impurity, which was isolated by preparative h.p.l.c. (99.1% pure) and examined further. This material gave an *F.T.*i.r. spectrum very similar to that of **VI**, but showing significant differences in the region between 2900 and 3100 cm^{-1} associated with C–H bond vibrations. The isomer's ^1H n.m.r. spectrum (*Table 1*) was very similar to that of **VI** in the region for aromatic protons but showed additional resonance peaks in the aliphatic region indicating the presence of $-CH_2-$ and $=CH_2$ groups as in an itaconimide, together with peaks for the $-CH_3$ and $>C=CH-$ protons of the citraconimide ring, also shown in the spectrum of **VI**. Integration of this spectrum showed the presence of one methyl group as compared with the two methyl groups shown by integration of the spectrum from **VI**. Thus, the isomer appears to have the citraconimide/itaconimide structure **X**, and this was confirmed by ^{13}C n.m.r. measurements:



VI



X

These (*Table 2*) showed a doubling of the two resonances due to the carbonyl carbon atoms, indicating the presence of two different imide rings in **X**, as compared with the two carbonyl resonances due to the pair of identical imide rings in **VI**. The resonances due to aromatic carbons in **X** show a similar doubling due to the presence of different imide rings attached to the ends of the same aromatic residue found in **VI**. The spectrum of **X** shows signals assigned to the CH_3- and $>C=CH-$ carbon atoms of the citraconimide ring, also found in **VI**, together with resonances due to the $CH_2=C<$ and $-CH_2-$ carbons present in the itaconimide ring of **X**.

The bisnadimides, **VIII** and **IX**, were obtained by treating the diamines with nadic anhydride and then removing water by azeotropic distillation in the presence of *p*-toluenesulphonic acid to effect cyclodehydration. They were not subjected to rigorous purification.

D.s.c. measurements

These were used to investigate the effect of purity on the thermal polymerization characteristics of the bismaleimides and the biscitraconimides. The d.s.c. scan (see *Figure 1*) for the purest (99.9%) sample of the bismaleimide, **IV**, showed a sharp endothermic peak at 221°C, corresponding to the melting point observed at 220°C using a hot-stage microscope, accompanied and followed immediately by a narrow exothermic peak. Further investigation[17] showed that the product of such thermal treatment was an insoluble resin, so that the exothermic peak is due to polymerization. The two peaks could not be resolved, showing that polymerization starts as the imide melts, and the narrow shape of the exotherm shows that polymerization then occurs very rapidly. With the 96.5% pure monomer, obtained by washing crude product with acetone, the d.s.c. scan showed a sharp melting endotherm quickly followed by a broad polymerization exotherm indicating a rate of cure much lower than that found for the pure monomer. Samples of

Table 2 Assignment of ^{13}C n.m.r. spectra for the biscitraconimide, **VI**, and the citraconimide/itaconimide, **X**

Biscitraconimide, VI		Citraconimide/itaconimide, X	
Chemical shift (ppm)	Assignment	Chemical shift (ppm)	Assignment
		172.7	C_h
170.5	C_d	170.5	C_d
169.4	C_c	169.4	C_c
		168.4	C_i
161.4		161.4, 161.2	
154.2		154.2, 155.1	
145.9		145.9, 145.9	
136.0	Aromatic carbons	135.9, 136.2	Aromatic carbons
129.8		129.9, 129.8	
127.7		127.2, 128.2	
120.6		120.6, 120.5	
118.2		118.2, 118.5	
		132.8	C_g
128.4	C_e	128.2	C_e
		122.0	C_f
120.1	C_b	120.5	C_b
		33.9	C_j
11.1	C_a	11.2	C_a

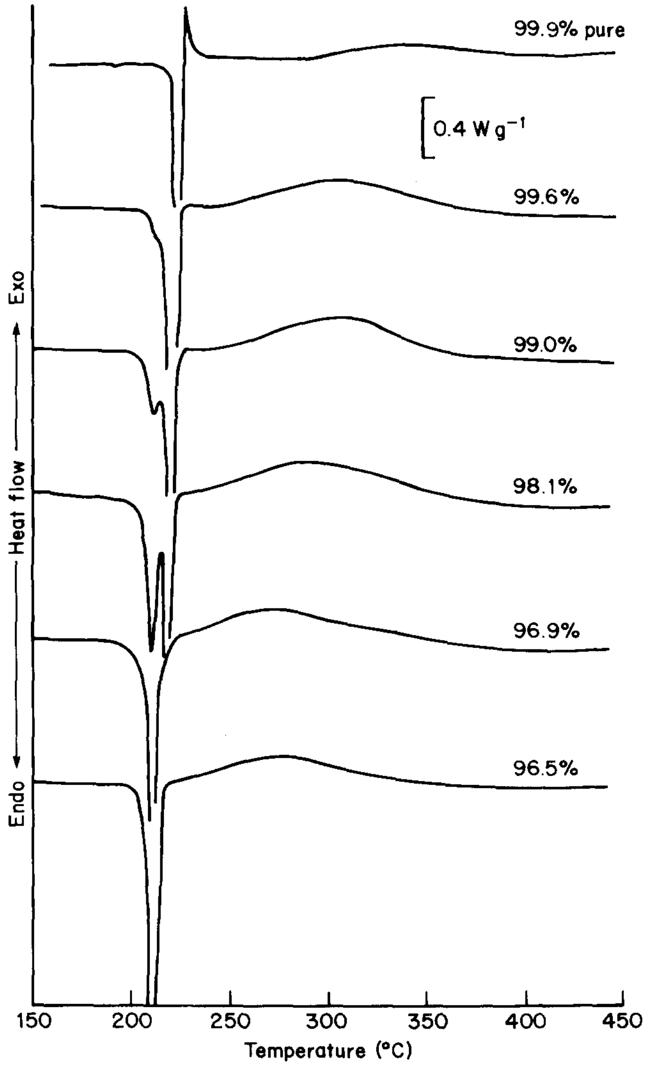


Figure 1 D.s.c. scans for the bismaleimide, **IV**

intermediate purity obtained by powder blending selected quantities of pure monomer with 96.5% pure material gave scans similar in shape to that obtained with the 96.5% material, showing that small quantities of impurities can have a marked effect on the rate of polymerization. These blends showed two adjacent melting endotherms due to inadequate mixing. The marked effect of only 0.3% impurity leading to a broad polymerization exotherm indicates the presence of a powerful inhibitor in the crude monomer.

The d.s.c. scans in *Figure 2* show the effects of impurities on the thermal polymerization of the bismaleimide, **V**. Monomer isolated by preparative h.p.l.c. (99.8% pure) showed a small, rather diffuse endotherm at 83°C, about 10°C below the fusion temperature measured on a hot-stage microscope, followed by a polymerization exotherm running from about 125 to 200°C. Crude, 74.6% pure, monomer isolated directly from the preparation, although molten below 100°C, required a temperature close to 220°C to initiate polymerization. D.s.c. scans for samples of intermediate purity, obtained by dissolving selected quantities of pure and crude material in acetone and then removing this by evaporation, showed that although the behaviour of **V** was not quite so sensitive to impurities as **IV**, decrease in purity leads to an increase in the temperature at which polymerization starts in the d.s.c. experiment and it is clear that the crude material from the monomer preparation contains a polymerization inhibitor.

Reagent grade (95% pure from Aldrich Chemical Co.) bis-4-maleimidophenylmethane gave a d.s.c. scan (*Figure 3*) showing a melting endotherm quickly followed by a polymerization exotherm running from about 160 to 260°C. Purification by passing a solution through an alumina column followed by recrystallization produced 100% pure material which gave a d.s.c. scan similar in shape to that obtained using pure **IV** and in which the melting endotherm and the polymerization exotherm

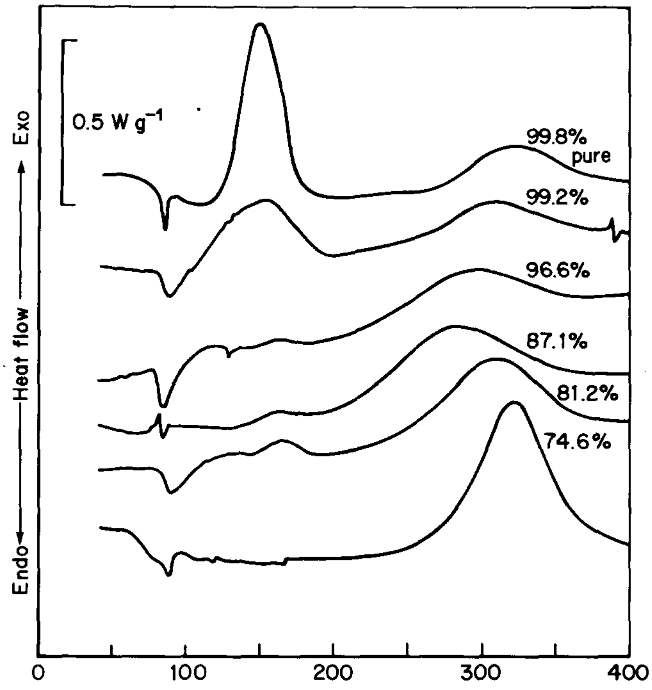


Figure 2 D.s.c. scans for the bismaleimide, V

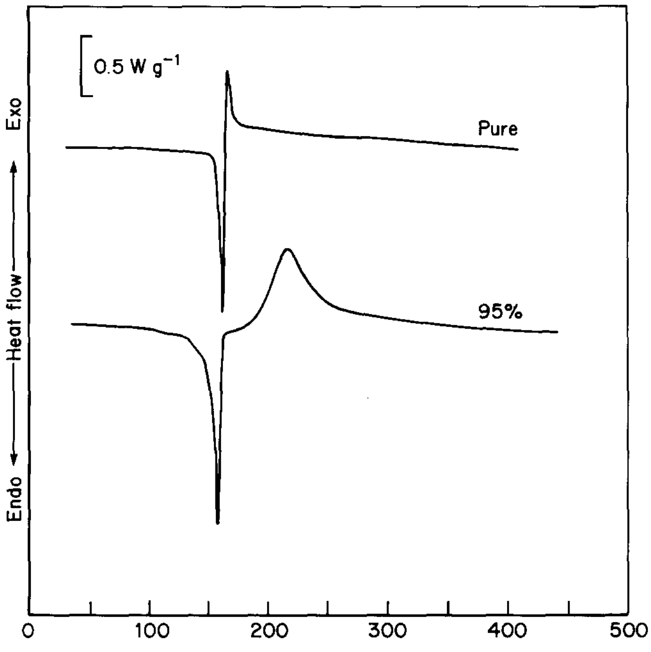


Figure 3 D.s.c. scans for bis-4-maleimidophenylmethane

could not be resolved due to rapid polymerization on melting. Similar results were obtained using bis-4-maleimidophenyl ether obtained by Searle's method and purified using an alumina column. The crude monomer showed a melting endotherm at about 170°C followed by a broad polymerization exotherm peaking at 240°C, but with the pure monomer the melting endotherm at 180°C was not resolved from the sharp polymerization exotherm.

The d.s.c. scans in *Figure 4* show the effects of purification by preparative h.p.l.c. (which gave samples of each compound 99.8% pure) on the thermal behaviour of the biscitraconimides, **VI** and **VII**. The scan for purified **VI** showed a sharp melting endotherm at 190°C followed by a broad polymerization exotherm running from about 275 to 425°C. Crude **VI**, 76.9% pure, gave a diffuse fusion endotherm at about 160°C followed immediately by a polymerization exotherm running up to about 350°C. Thus, here the crude monomer polymerizes over a temperature range considerably lower than found for the pure material. In contrast, the scan for pure **VII** was very similar to that for the crude (81.0% pure) material; both showed a diffuse liquefaction endotherm at about 75°C followed by a broad polymerization exotherm running from 250 to 425°C, similar to that found for the pure sample of **VI**.

The bisnadimide monomers, **VIII** (99.0% pure) and **IX** (97.2% pure), gave very similar d.s.c. scans in which sharp melting endotherms, both close to 210°C, were followed by broad endotherms attributed to the retro Diels–Alder reaction and then the polymerization exotherms starting at about 300°C.

DISCUSSION

Synthesis of biscitraconimides

Itaconic and citraconic anhydrides are interconvertible[18] and dehydration of bisitaconamic acids can give

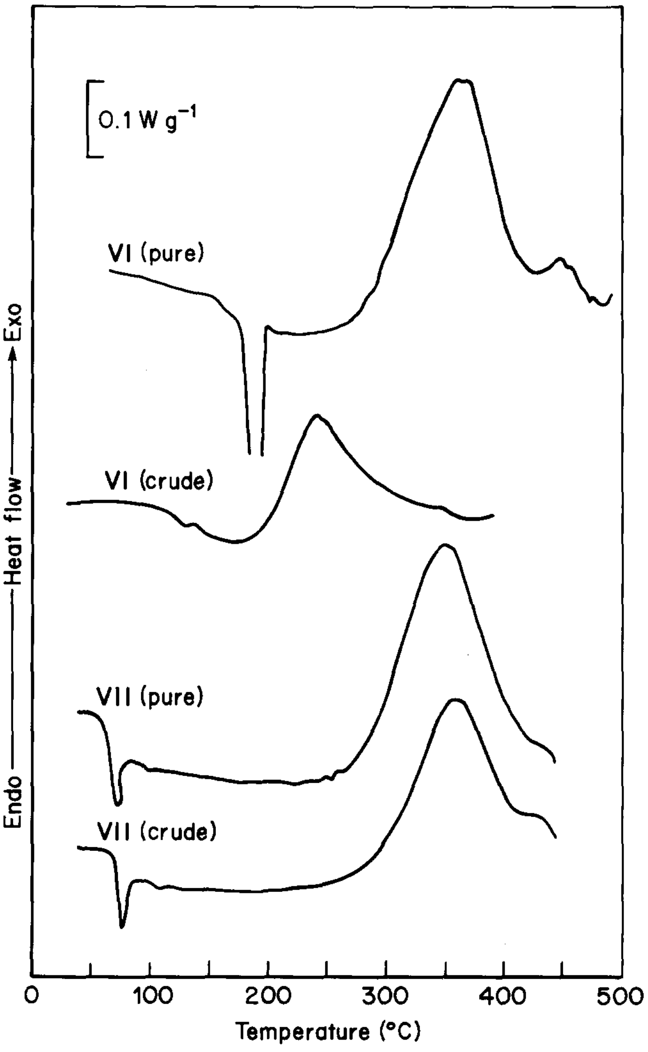


Figure 4 D.s.c. scans for the biscitraconimides, VI and VII

biscitraconimides[19], so that the formation of a citraconimide/itaconimide such as **X** during the synthesis of a biscitraconimide is not surprising, although it appears not to have been reported previously.

Fusion and polymerization of the monomers

The all *para* substituted bismaleimide, **IV**, and the corresponding biscitraconimide, **VI**, both show sharp d.s.c. melting endotherms at temperatures close to the melting points recorded using a hot-stage microscope. In contrast, the *meta*, *para* substituted isomers, **V** and **VII**, show much smaller and more diffuse endotherms at temperatures about 10°C below their fusion temperatures measured by microscopy. Thus, **V** and **VII** are much less crystalline than **IV** and **VI** and provide melts about 135°C below the melting points of the all *para* compounds. This effect of *meta* substitution has been observed previously in other bismaleimides, e.g. bis-*p*-maleimidobenzene m.p. = 346–350°C with m.p. = 202°C for the *meta* isomer[20], and m.p. = 246–250°C for bis-*p*-maleimidophenylsulphone compared with m.p. = 203–205°C for the *meta* isomer[21]. The low fusion temperature of **V** provides a substantial temperature gap between melting and polymerization leading to d.s.c. scans for the pure monomer with which polymerization could be studied without interference from melting. This contrasts with the situation for pure **IV** where fusion occurs at a much higher temperature so that melting and polymerization are simultaneous and in the d.s.c. scans the peaks for these processes cannot be resolved. The high temperatures required to initiate polymerization of the pure biscitraconimides, **VI** and **VII**, lead to substantial temperature gaps between fusion and polymerization, especially with **VII** due to the low fusion temperature of this compound. Both of the bisnadimides, **VIII** and **IX**, show substantial gaps between fusion and polymerization as the temperatures required for the reverse Diels–Alder reaction are well above the melting points of these compounds.

Impurities in the bismaleimides **IV** and **V** increase the temperature at which thermal polymerization starts, increasing the temperature gap between fusion and the start of polymerization. This effect was also found with bis-4-maleimidophenylmethane and with bis-4-maleimidophenyl ether, so that it could be of general concern. A significant gap between fusion and polymerization temperatures is important in some applications of bismaleimides and our data show that the use of impure monomers can be advantageous in this context, as well as being less expensive. With the biscitraconimides, **VI** and **VII**, the situation is more complex as impurities reduced the polymerization temperature for **VI** but had little effect with **VII**. The effect on **VI** was so great that polymerization started immediately after melting, at a temperature below that found for impure samples of the corresponding bismaleimide, **IV**. This inversion of the relative reactivity by impurities may be relevant to earlier reports[5–8,22] that the thermal polymerization of biscitraconimides starts at lower temperatures than those found for the corresponding bismaleimides. Bisitaconimides are known[19] to polymerize readily on melting, so that the presence of the itaconimide/citraconimide, **X**, as a major impurity in crude **IV** may cause the enhanced reactivity of crude **VI** over that for the pure compound.

ACKNOWLEDGEMENTS

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REFERENCES

1 Critchley, J. P., Knight, G. J. and Wright, W. W. 'Heat-Resistant Polymers', Plenum Press, London, 1983, p. 219

2 Stenzenberger, H. D. *Appl. Polym. Symp.* 1973, **22**, 77

3 Barton, J. M. *Adv. Polym. Sci.* 1985, **72**, 112

4 Pyriadi, T. M. and Mutar, E. H. *J. Polym. Sci., Polym. Chem. Edn.* 1980, **18**, 2535

5 Mikroyannidis, J. A. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 1717

6 Varma, I. K., Fohlen, G. M. and Parker, J. A. *J. Polym. Sci., Polym. Chem. Edn.* 1982, **20**, 283

7 Varma, I. K. *et al. Contemp. Topics Polym. Sci.* 1984, **4**, 115

8 Nair, C. P. R. *et al. J. Polym. Sci. (A) Polym. Chem.* 1986, **24**, 1109

9 Hay, J. N. *et al. Polymer* 1989, **30**, 1032

10 Burns, E. A. *et al.* 'Thermally stable laminating resins', TRW-11926-6013-RO-00, NASA CR-72633, TRW Systems Group, 1970

11 Kwiatowski, G. T. *et al. J. Polym. Sci., Polym. Chem. Edn.* 1975, **13**, 961

12 Domeier, L. A. and Gardner, H. C. Eur. Pat. Appl. 0148534, 1985

13 Sheppard, C. H. *et al.* 'Graphite reinforced thermoplastic composites', Final report (D180-26067-1) to US Dept Navy, Contract N00019-79-C-0203, Boeing Aerospace Co., 1980

14 Kwiatkowski, G. T. *et al. J. Polym. Sci., Polym. Chem. Edn.* 1974, **12**, 565

15 Schramm, J. *Liebigs Annalen Chem.* 1970, **740**, 169

16 'Organic Syntheses', Collect. Vol. 5 (Ed. H. E. Baumgarten), Wiley, New York, 1973, p. 944

17 Part 2 of this series (to be submitted)

18 'Organic Syntheses', Collect. Vol. 2 (Ed. A. H. Blatt), Wiley, New York, 1943, pp. 140 and 370

19 Hartford, S. L., Subramian, S. and Parker, J. A. *J. Polym. Sci., Polym. Chem. Edn.* 1978, **16**, 137

20 Kovacic, P. *J. Am. Chem. Soc.* 1959, **81**, 1187

21 Ninan, K. N. Krishnan, K. and Mathew, J. *J. Appl. Polym. Sci.* 1986, **32**, 6033

22 Parker, J. A. *et al. SAMPE J.* 1985, July/August, 11