Studies on a series of *bis*-arylimides containing four phenylene rings and their polymers: 2. Polymerization of monomers and thermal analysis of the polymers

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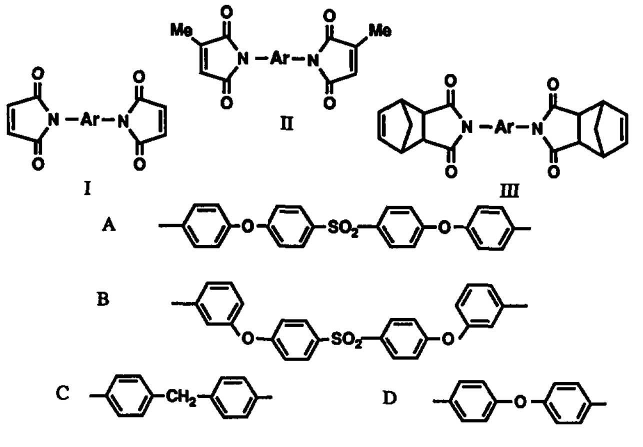
Examination by d.s.c. of the thermal cure of two aryl *bis*-maleimides and the corresponding pair of citraconimides, in which the imide groups are attached to the ends of aromatic residues containing four phenylene rings, indicates that the pure *bis*-maleimides polymerize at lower temperatures than the corresponding citraconimides. A second reaction occurs after polymerization of the pure *bis*-maleimides has stopped; this appears from *FT*i.r. to involve residual maleimido groups; pure samples of *bis*-4-maleimidophenylmethane and *bis*-4-maleimidophenyl ether also showed this effect. Weight reduction commensurate with evolution of about 1.2 moles of cyclopentadiene occurred on curing the corresponding two *bis*-nadimides containing four phenylene rings at atmospheric pressure, the extent of this loss being independent of temperature in the range 250–350°C. Resins from the *bis*-maleimides containing four phenylene rings showed thermal/oxidative stability, measured by t.g.a., similar to that found for resins from *bis*-4-maleimidophenylmethane and *bis*-4-maleimidophenyl ether; resins from the *bis*-maleimides were rather more stable than those from the corresponding *bis*-citraconimides and *bis*-nadimides.

(Keywords: *bis*-maleimides; *bis*-citraconimides; *bis*-nadimides; polymerization; thermo-oxidative stability; differential scanning calorimetry; phenylene groups; thermal stability; thermogravimetric analysis)

INTRODUCTION



IV = I,Ar = A ; V = I,Ar = B ; VI = I,Ar = C ; VII = I,Ar = D
VIII = II,Ar = A ; IX = II,Ar = B ; X = III,Ar = A ; XI = III,Ar = B

Addition cured polyimides prepared by thermal polymerization of unsaturated *bis*-imides with the general structures I to III have been examined widely as potential replacements for epoxy resins[1–4]. These polyimides are highly cross-linked so that the preferred techniques for investigating polymerization of the monomers are based on differential scanning calorimetry (d.s.c.) and Fourier transform infra-red analysis (*FT*i.r.). Typical d.s.c. scans for the *bis*-maleimides, I, and *bis*-citraconimides, II, show a melting endotherm followed by an exotherm due to the polymerization. *Bis*-maleimides, with melting points greater than 150°C, start to polymerize on fusion and if polymerization is fast at this temperature the melting endotherm cannot be resolved from the polymerization exotherm which appears as a sharp peak on the scan (see for example the scan for compound IV in *Figure 2*). The temperature at which the exothermic heat flow in the calorimeter reaches a maximum, T_{max}, during the polymerization is often taken as a measure of polymerization reactivity; the lower T_{max} the higher the 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. Several authors [2,5–8] report T_{max} values for *bis*-maleimides greater than those found for the corresponding (Ar the same in I and II) *bis*-citraconimides, indicating that the citraconimides are the more reactive. This is surprising since methyl-substituted vinyl monomers usually polymerize by free radical mechanisms less readily than their unsubstituted analogues[9]. In making comparisons of reactivity it is also important to use monomers of high purity, as we have shown[10] that impurities can have very large effects on

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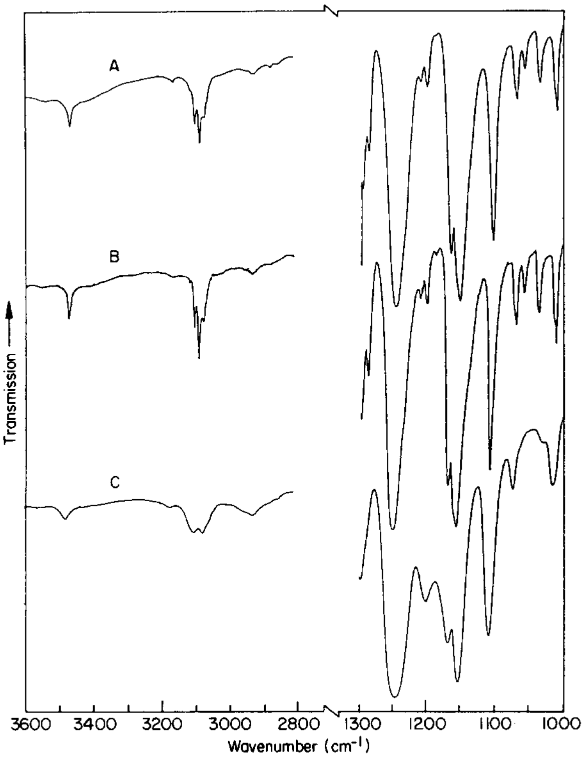


Figure 1 Partial *FT*i.r. spectra for compound IV: A, monomer; B, after heating to 275°C at 10 K min^{-1}; C, after heating to 400°C at 10 K min^{-1} (before and after the second d.s.c. exotherm)

the thermal polymerization of *bis*-maleimides and *bis*-citraconimides.

In a previous paper[10] we described the preparation of purified samples of the *bis*-imides IV to XI and the effects of rigorous purification on the thermal polymerization of the *bis*-maleimides and *bis*-citraconimides. This paper reports a detailed investigation of the thermal polymerization of these *bis*-imides using mainly d.s.c. and *FT*i.r. techniques. Thermal polymerization of the *bis*-nadimides, X and XI, was examined by d.s.c. and by thermogravimetric analysis (t.g.a.). The thermal and oxidative stability of the resins prepared was also examined by t.g.a.

RESULTS

Polymerization of the bis-*maleimides IV to VII*

Samples of the pure *bis*-maleimides IV and V polymerized when heated to 220°C for 10 min. The polymers were completely insoluble in boiling dimethyl formamide, analysed correctly for C, H and N, and gave *FT*i.r. spectra almost the same as those for the corresponding monomers (see *Figure 1* for spectra from IV). However, they showed slight absorptions at 2925 cm^{-1} consistent with the appearance of saturated C–H on polymerization. Examination of the d.s.c. scan for IV (*Figure 2*) shows a sharp exothermic peak, corresponding to this polymerization, superimposed on the melting endotherm. Polymerization appears complete by about 240°C, but a second, much more diffuse exotherm starts at about 275°C and continues up to 375°C. The second *bis*-maleimide, V, shows similar behaviour at four different scanning rates (*Figure 3*), but as it fuses at a much lower temperature the small fusion endotherm (at about 90°C) is resolved from the exotherm due to polymerization. The lower fusion temperature of

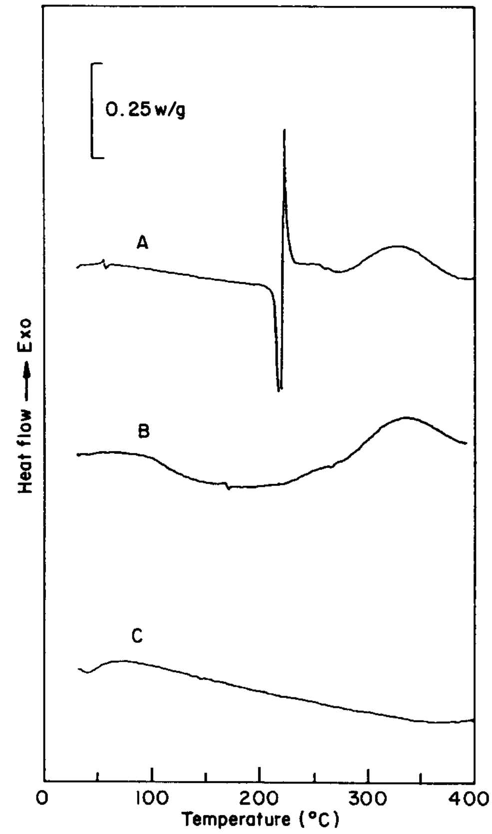


Figure 2 D.s.c. scans at 10 K min^{-1} for compound IV: A, first scan on monomer; B, rescan after quenching from 275°C; C, rescan after quenching from 400°C

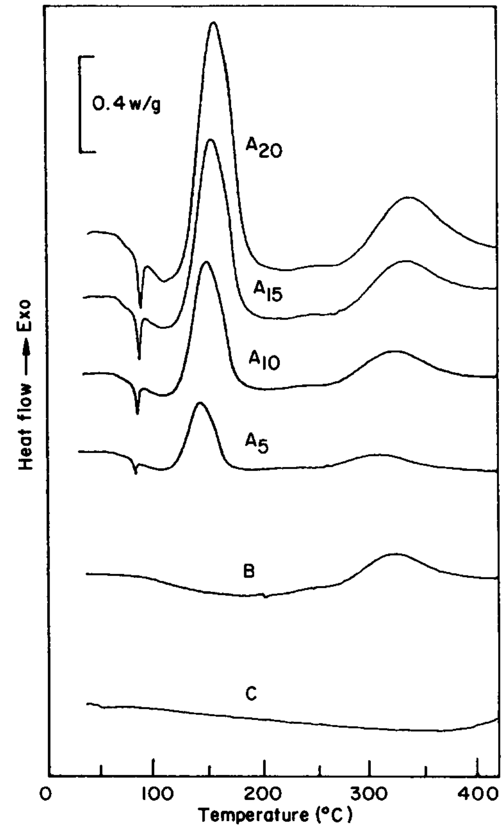


Figure 3 D.s.c. scans for compound V: A, scans on monomer at heating rates denoted by subscripts in K min^{-1}; B, rescan at 10 K min^{-1} after quenching from 250°C; C, rescan at 10 K min^{-1} after quenching from 400°C

Table 1 Enthalpy of polymerization, ΔH, for the *bis*-maleimides IV and V by scanning d.s.c.

Rate of scan ($\mathrm{K\,min^{-1}}$)	ΔH ($\mathrm{kJ\,mol^{-1}}$)		
	V (99.8%)	V (96.5%)	IV (96.5%)
20	68	57	51
15	63	72	44
10	63	70	51
5	57	65	–
Average	63	66	50

V allows polymerization to start at a lower temperature than is possible for IV (which melts at 220°C) so that polymerization proceeds less rapidly and more diffuse polymerization peaks are obtained. Polymerization stops at about 200°C and there is then a substantial gap before the second process starts at about 260°C continuing up to 375°C. These data were confirmed by rescanning experiments in which samples of IV and V were taken up to 250°C, at $10\,\mathrm{K\,min^{-1}}$, quenched, and then rescanned to 400°C (*Figures 2* and *3*). The rescans do not show the fusion and polymerization processes, confirming that these were completed in the scans to 250°C, but the second exotherms show up exactly as expected. Further rescans (*Figures 2* and *3*) showed no processes until thermal decomposition started at about 400°C, indicating that the glass transition temperatures, T_gs, of these resins are above their decomposition temperatures.

Thermogravimetric analysis performed on polymers, made by heating samples of the pure monomers until the polymerization was complete but before the second exothermic process had started (see Experimental section for details), showed that there was no loss in weight until after the second process had been completed. *FT*i.r. spectra (see for example *Figure 1*) on the products obtained by heating, to complete the second process but avoid thermal decomposition, showed a significant increase in absorption at $2925\,\mathrm{cm^{-1}}$, attributed to saturated C–H, and small changes in the shape of the band at about $3100\,\mathrm{cm^{-1}}$, assigned to unsaturated and aromatic C–H bonds. Absorption between 1190 and $1200\,\mathrm{cm^{-1}}$ increased giving a broad band in this region, which is associated with the C–N–C vibrations in succinimides[11], indicating the appearance of succinimide rings different in structure from those introduced via the polymerizations.

The d.s.c. scans for impure samples of IV and V (see Figures 1 and 2 of ref. 10) do not show a second exothermic process, although this could be because the peaks are covered by those due to the polymerization exotherms which are more diffuse and occur at higher temperatures than the corresponding peaks found in the scans for the pure monomers. However, measurement of the enthalpy of polymerization for pure (99.8%) and impure (96.5%) samples of V give average values for ΔH (see *Table 1*) of 63 ± 6 and $66 \pm 8\,\mathrm{kJ\,mol^{-1}}$ respectively, which are the same within experimental error. The area of the second exotherms in the scans for pure V gave values for ΔH of 33, 29, 31 and $30\,\mathrm{kJ\,mol^{-1}}$ at scanning rates of 20, 15, 10 and $5\,\mathrm{K\,min^{-1}}$ respectively, giving an average value of $\Delta H = 31\,\mathrm{kJ\,mol^{-1}}$. This is much too large to be hidden within the single exothermic peak found for the impure monomer samples. It was not possible to measure ΔH for pure samples of the *bis*-maleimide IV because with this material, the melting endotherm and the polymerization exotherm were not resolved, see *Figure 2*. However, impure (96.5%) IV polymerized much less readily than the pure monomer[10], so that with impure monomer ΔH could be measured, and the average value found (see *Table 1*) was $50 \pm 6\,\mathrm{kJ\,mol^{-1}}$. The area of the second exothermic peak found in scans for pure IV corresponded to a value for ΔH of about $15\,\mathrm{kJ\,mol^{-1}}$ which, as with the *bis*-maleimide V, appears too large to be included in the ΔH found for polymerization of the impure material. Thus, the reaction producing the second exotherm using pure samples of IV and V did not occur to a detectable extent in our d.s.c. experiments.

Carefully purified samples of *bis*-4-maleimidophenylmethane, VI, and of *bis*-4-maleimidophenyl ether, VII, both more than 99.9% pure, gave d.s.c. scans (*Figures 4* and *5*) in which the melting endotherms were not resolved from the polymerization exotherms. In both scans the polymerization exotherms appeared complete at 200°C, but were followed by small second exotherms running from about 250 to 350°C (*Figures 4* and *5*). The areas of the second exotherms corresponded to a value of $\Delta H = 12 \pm 4\,\mathrm{kJ\,mol^{-1}}$ for VI and $\Delta H = 30 \pm 7\,\mathrm{kJ\,mol^{-1}}$ for VII. These compare with those found for the polymerization exotherms where values of $\Delta H =$

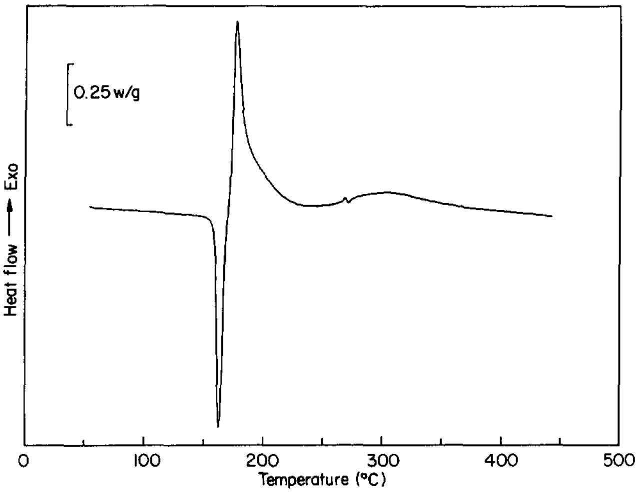


Figure 4 D.s.c. scan at $10\,\mathrm{K\,min^{-1}}$ on compound VI

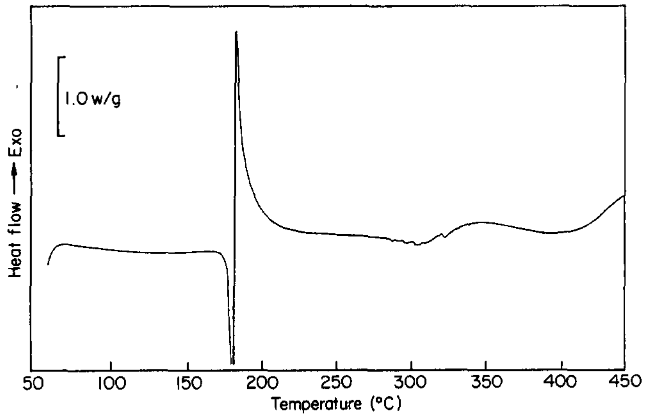


Figure 5 D.s.c. scan at $10\,\mathrm{K\,min^{-1}}$ on compound VII

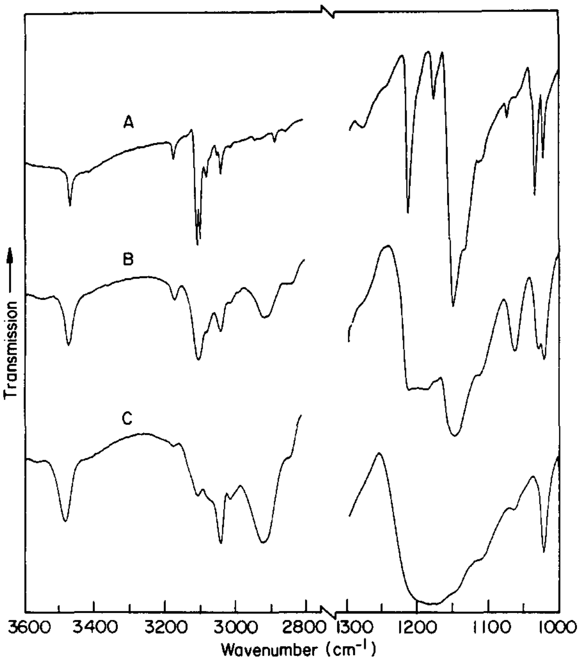


Figure 6 Partial *FT*i.r. spectra for compound VI: A, monomer; B, after heating to 230°C at 10 K min^{-1}; C, after heating to 400°C at 10 K min^{-1}

62 ± 5 kJ mol^{-1} and $\Delta H = 61 \pm 6$ kJ mol^{-1} were obtained for VI and VII respectively from d.s.c. measurements on impure samples of the two monomers. As with the longer chain *bis*-imides IV and V, no sign of a second exotherm was observed in scans run on the impure monomer samples before thermal decomposition started at about 400°C. Examination of *FT*i.r. spectra for polymer samples made from pure VI, before and after heating through the temperature span of the second exotherm, showed significant differences, see *Figure 6*. The *FT*i.r. spectrum of VI has been analysed in detail[11] with the doublet at 3109 and 3098 cm^{-1} being assigned to the maleimide =C–H, and the singlets at 3038 and 2920 cm^{-1} to aromatic C–H and alicyclic $>CH_2$ respectively. These bands were also observed for the prepolymer (Kerimid 601) from 2.5 mole of the *bis*-maleimide and 1.0 mole of *bis*-aminophenyl methane. The doublet at 3110 and the singlet at 3038 cm^{-1} show clearly in our spectrum from VI, but the band at 2920 cm^{-1} is very weak.

Polymer isolated at the end of the polymerization exotherm showed reduced absorption at 3110 cm^{-1} and significant absorption at 2920 cm^{-1}, as would be expected from the decrease in maleimide =C–H and the increase in saturated alicyclic >C–H due to polymerization. The spectrum from polymer heated to completion of the second exotherm showed further reduction in maleimide =C–H and a marked increase in the absorption at 2920 cm^{-1} associated with saturated >C–H bonds. Reactions occurring during the first (polymerization) and the second exotherms both reduce the concentration of maleimide groups present, but even at the end of the second exotherm the sample shows absorption at 3110 cm^{-1}, indicating that some carbon-to-carbon double bonds have not reacted. Monomeric VI shows a strong absorption at 1150 cm^{-1} assigned by Di Giulio *et al.*[11] to C–N–C bonds in maleimide rings. There is still absorption at this frequency in both polymer samples, but this is now accompanied by absorptions at higher frequencies, found by Di Giulio *et al.* for succinimides, aspartimides and the Kerimid prepolymer. Thus a broad band appears running from 1150 to beyond 1200 cm^{-1} which is particularly marked for polymer heated until the second exothermic process is complete. Spectra from *bis*-4-maleimidophenyl ether showed similar changes on polymerization and on heating to the end of the second exotherm (*Figure 7*), the appearance of a strong band at 1200 cm^{-1} at the end of the second exotherm became very noticeable.

Polymerization of the bis-*citraconimides VIII and IX*

Pure samples of VIII set to a glass on heating to 300°C for 2 h but the resins so obtained remained soluble in dimethyl formamide. Heating for 4 h at 335°C was required to obtain a resin that was completely insoluble. Elemental analysis gave values for carbon which were about 1% below those expected, indicating that the rigorous conditions required to produce an insoluble resin lead to some decomposition. The isomeric *bis*-citraconimide, IX, behaved in a similar fashion and gave an insoluble resin on heating to 335°C for 4 h. In line with this, both pure monomers gave d.s.c. scans showing diffuse exotherms running from about 250 to 400°C. Rescans on samples scanned previously to 400°C showed clear changes of slope typical of a glass transition (*Figure 8*); these were reproducible on further rescans and gave $T_g = 238$°C (taken as the onset temperature) for polymer from the all *para*-monomer, VIII, and

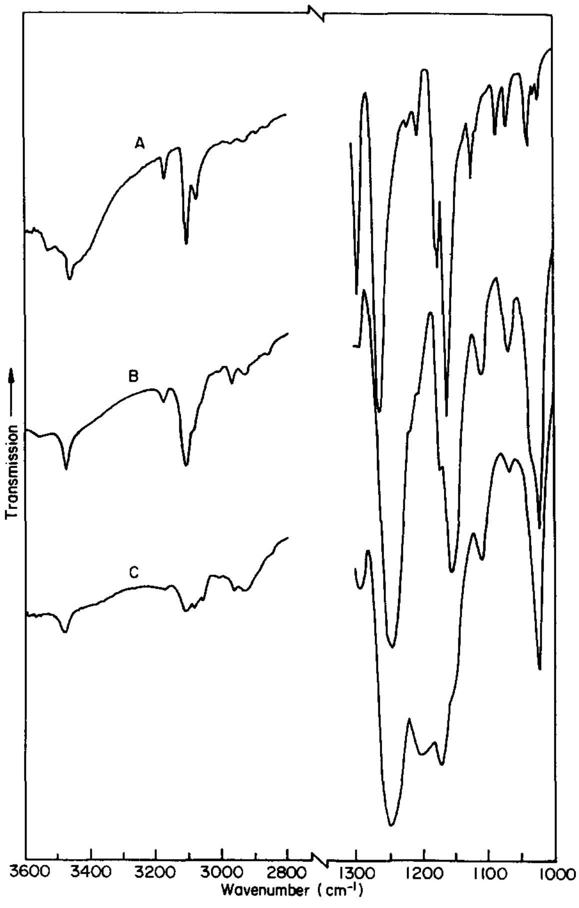


Figure 7 Partial *FT*i.r. spectra for compound VII: A, monomer; B, after heating to 230°C at 10 K min^{-1}; C, after heating to 400°C at 10 K min^{-1}

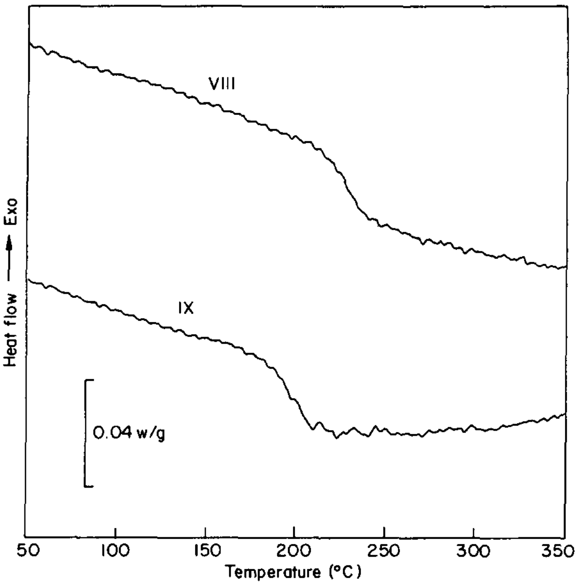


Figure 8 Rescans on compounds VIII and IX after previous scans to 400°C at 10 K min^{-1}

Table 2 Enthalpy of polymerization, ΔH, for the *bis*-citraconimides VIII and IX by scanning d.s.c.

Rate of scan ($K\ min^{-1}$)	ΔH ($kJ\ mol^{-1}$)	
	VIII (99.8%)	IX (99.8%)
20	88	81
15	81	92
10	82	85
5	92	86
Average	86	86

$T_g = 224°C$ for that from the *meta-para*-isomer, IX. Area measurements on the first scans at four different rates (*Table 2*) gave an average value of $\Delta H = 86 \pm 6$ kJ mol^{-1} for both monomers.

Polymerization of the bis-*nadimides X and XI*

Samples of these monomers melted at about 215°C and solidified to resins insoluble in boiling dimethyl formamide after heating at 330°C for 3 h. Microanalysis of these polymers gave carbon values about 4% below that required (and found) for the monomers. This is as expected because it is known that some of the cyclopentadiene produced by the reversed Diels–Alder reaction, which precedes polymerization, is lost by vaporization[12]. D.s.c. scans for the *bis*-nadimides (*Figure 9* gives curves for X; XI gave very similar results) showed fairly sharp endothermic peaks at the melting temperature followed by a diffuse endotherm. This is probably associated with evolution of some of the cyclopentadiene produced by the reversed Diels–Alder reaction. This process runs into an exothermic peak starting at about 300°C with a maximum at about 350°C. Rescans showed no significant discontinuities. Scans run at 400 psi (*Figure 9*) were similar in shape except that the diffuse endotherm was replaced by a plateau, presumably because the loss of cyclopentadiene by vaporization was reduced.

The processes occurring on heating samples of X and XI were investigated further by t.g.a., heating at 10 K min^{-1} under nitrogen. A plot of sample weight against temperature for XI is given in *Figure 10*; almost identical plots were obtained for X. There was a small (~1%) loss in weight at about 5°C above the melting point, probably due to vaporization of residual solvent. This was followed by a more extensive loss which continued up to 390°C, when a plateau was reached, continuing to about 450°C, where thermal decomposition started. The loss in weight between 250 and 390°C corresponds to about 10% of the sample's initial weight and the rate of weight loss reaches a maximum at 330°C. This is close to the maximum observed at 350°C, for the polymerization exotherm in the d.s.c. scan for this compound. Thus, it appears that evolution of cyclopentadiene and polymerization occur concurrently. The effect of temperature on the magnitude and on the rate of weight loss at atmospheric pressure was examined further. Samples were heated at 10 K min^{-1} to a

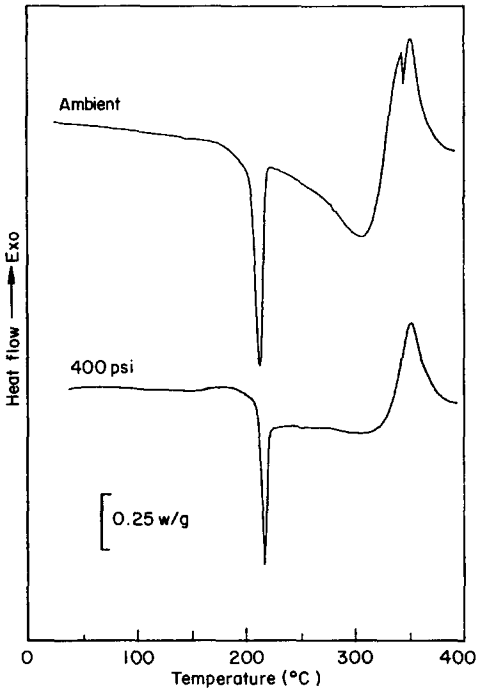


Figure 9 D.s.c. scans for compound X at ambient pressure and 400 psi at 10 K min^{-1}

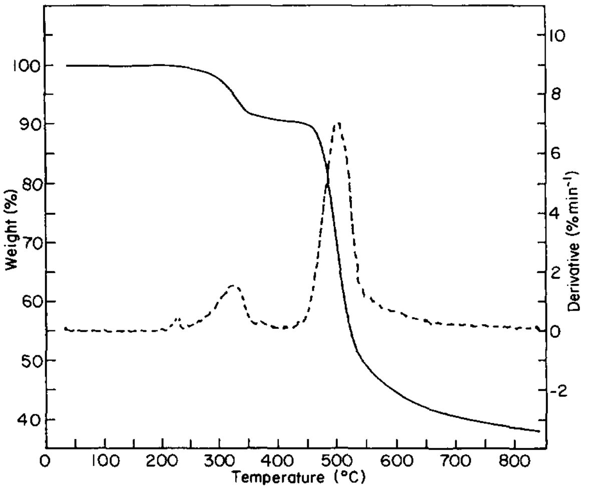


Figure 10 Thermogravimetry of compound XI at 10 K min^{-1} under nitrogen. ———, Weight (%); – – –, first derivative (% min^{-1})

predetermined temperature, T_i, and then held at this temperature until there was no further loss in weight. In this way curves such as those in *Figure 11* were obtained, confirming that the loss in weight reached a constant value, which appears from the data listed in *Table 3* to be independent of temperature in the range 250–350°C.

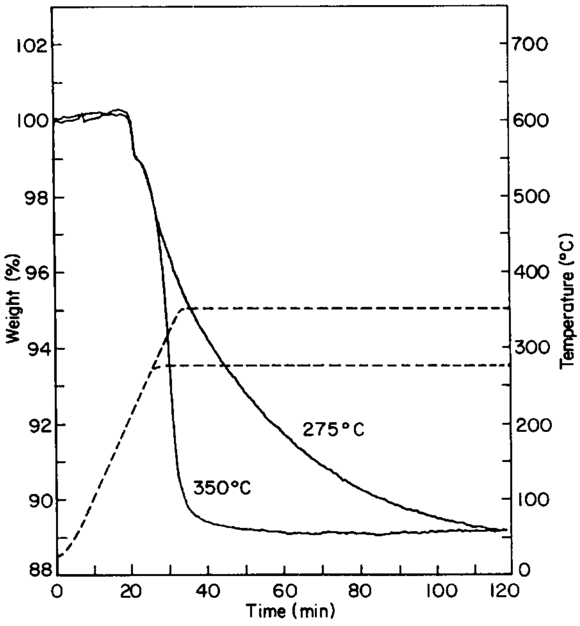


Figure 11 Thermogravimetry of compound X at 275°C and 350°C under nitrogen, after initial ramp at 10 K min^{-1}. ———, Weight (%); ---, temperature (°C)

Table 3 Effect of cure temperature on weight loss for the *bis*-nadimides X and XI

	Bis-nadimide X		*Bis*-nadimide XI	
Cure temp. (°C)	Final weight, W_f (%)	Time to W_f (min)	Final weight, W_f (%)	Time to W_f (min)
350	89	122	86	123
325	90	120	87	121
300	89	148	92	148
275	88	266	89	266
250	86	623	89	395

As would be expected, the time taken to reach constant weight loss decreased as T_i was increased.

Thermal and oxidative stability of the polymers

Stabilities were measured by t.g.a. using powdered samples of resin polymerized under nitrogen. Temperature programmes specific to each monomer were used (for details see Experimental section) and designed so as to effect polymerization without causing decomposition. Samples were examined in nitrogen and in air using a heating rate of 2 K min^{-1}. Data showing the temperatures at which the loss in weight reached specified levels are given in *Tables 4* and *5*.

DISCUSSION

Polymerization of the bis-*maleimides and the* bis-*citraconimides*

N-substituted maleimides undergo radical-initiated polymerization in solution[13] and molten *N*-phenylmaleimide is polymerized thermally[14], as are a wide range of aryl-*bis*-maleimides[1]. Aryl-citraconimides appear more difficult to polymerize; Mutar and Piriadi[15] failed to initiate polymerization of *N*-phenylcitraconimide with azodiisobutyronitrile at 100°C. We could not obtain polymer by heating this monomer, although under comparable conditions, *N*-phenylmaleimide polymerized readily[14]. However, there are several reports[2,5–8] from which it appears that *bis*-citraconimides polymerize thermally at temperatures lower than those found for the corresponding *bis*-maleimides. Our data for carefully purified samples of the *bis*-citraconimides VIII and IX show that these monomers do polymerize thermally to cross-linked resins, but the temperatures required are much higher than those needed to polymerize the corresponding *bis*-maleimides (see *Figure 12*). It also appears that polymers from the two *bis*-citraconimides are less highly cross-linked than those from the corresponding maleimides, because they show T_gs below 250°C. However, no glass transitions could be detected by d.s.c. before the *bis*-maleimide resins started to decompose above 400°C. Thus, polymerization of the *bis*-citraconimides is less extensive than for the corresponding maleimides. This is in line with previous findings for other pairs of imides where the lower glass transitions of the *bis*-citraconimide polymers, as

Table 4 Temperatures (°C) at which weight loss reached the levels specified on heating in nitrogen at 2 K min^{-1} measured by t.g.a.

	Weight loss (%)						
Polymer of	1	5	10	20	30	50	70
Bis-4-maleimidophenyl methane, VI	425	460	470	480	520	960	>960
Bis-4-maleimidophenyl ether, VII	430	460	465	470	490	720	>960
Bis-maleimide, IV	430	460	470	480	510	650	900
Bis-maleimide IV (96%)	420	430	440	450	490	630	840
Bis-maleimide V	420	440	440	450	480	650	>940
Bis-maleimide V (96%)	375	390	400	420	475	590	750
Bis-citraconimide VIII	405	440	450	470	480	550	>940
Bis-citraconimide IX	380	440	450	470	480	550	>940
Bis-nadimide X	415	430	450	460	470	540	>940
Bis-nadimide XI	405	430	450	460	470	560	>940

Table 5 Temperatures (°C) at which weight loss reached the levels specified on heating in air at 2 K min^{-1} measured by t.g.a.

Polymer of	Weight loss (%)							
	1	5	10	20	30	50	70	90
Bis-maleimide, IV	370	410	420	459	460	490	500	520
Bis-maleimide, V	350	410	430	460	490	500	510	540
Bis-citraconimide, VIII	350	420	450	470	500	540	560	570
Bis-citraconimide, IX	360	420	450	460	500	540	550	560
Bis-nadimide, X	350	410	450	460	500	530	550	560
Bis-nadimide, XI	350	410	450	460	490	510	540	550

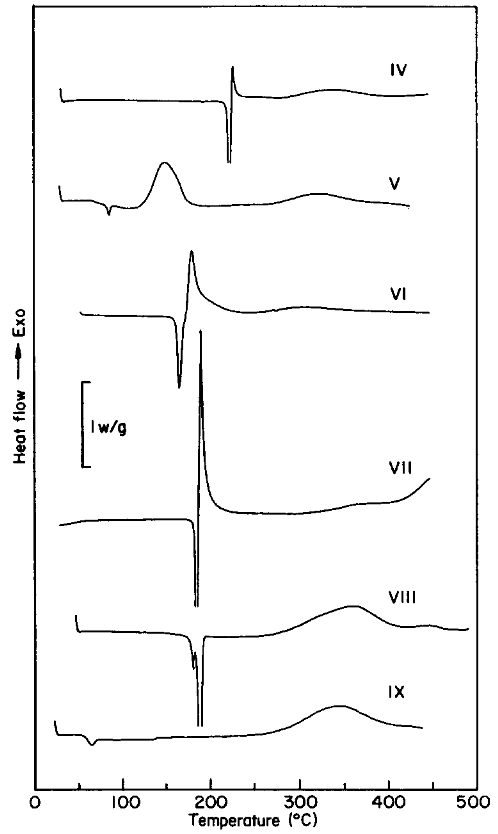


Figure 12 D.s.c. scans at 10 K min^{-1} on the pure monomers

compared with those from the corresponding *bis*-maleimides, have been attributed to a lower level of cross-linking[2]. It could be that the anomaly apparent here is due to the presence of impurities. We have shown[10] that careful purification can reduce the temperature required to initiate thermal polymerization of the *bis*-maleimides IV–VII.

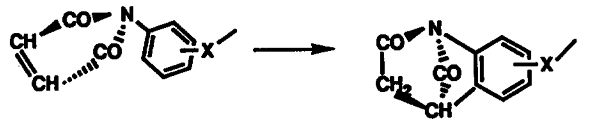
A comparative examination of *bis*-4-maleimidophenylmethane, VI, and *bis*-4-citraconimidophenylmethane by d.s.c. showed peaks for the polymerization exotherms of these compounds at 260 and 240°C respectively[2], so that in this study the citraconimide polymerized at the lower temperature. However, our pure sample of VI polymerized rapidly on melting at 160°C so that the peak of the polymerization exotherm on the d.s.c. scan (see *Figure 4*) occurred well below 200°C. Thus, carefully purified VI does polymerize at a lower temperature than a sample of the corresponding *bis*-citraconimide examined by other workers[2], but the effect of purification on polymerization of the *bis*-citraconimide remains to be resolved. The higher temperatures required to effect thermal polymerization of the *bis*-citraconimides VIII and IX, as compared with the corresponding *bis*-maleimides, is not unexpected. It is believed[16] that the low tendency of many 1,2-disubstituted ethylenes to polymerize by free radical mechanisms is because the approach of monomer molecules to the propagating radical is subject to steric hindrance. Hence, substitution of methyl for hydrogen at the reactive centre can only make polymerization more difficult.

The glass transition temperatures, $T_g = 238$ and 224°C, recorded for the resins from the *bis*-citraconimide monomers VIII and IX respectively are much as would be expected. They can be regarded as substantially cross-linked versions of poly(aryl ether sulphone)s with the repeat units *A* and *B* respectively. The polymer of *A*, Victrex PES, has $T_g = 225$°C and it is known that introduction of *meta-para* linked repeat units, as in *B*, reduces T_g[17]. D.s.c. scans for resins from the corresponding *bis*-maleimides IV and V did not indicate the presence of glass transitions before exothermic decomposition started at about 400°C. This is not unexpected as the resin from *bis*-4-maleimidophenylmethane, VI, has $T_g = 390$–400°C[2,18], and the aromatic residues between the maleimide groups in these monomers (structures *A* and *B*) are much more polar than that in VI (structure *C*). Kwiatkowski *et al.*[19] have reported that a cured resin from IV had $T_g > 330$°C.

The average values of $\Delta H = 60 \pm 7$ kJ mol^{-1} obtained for polymerization of the *bis*-maleimides IV–VII are close to that reported recently[18] for VI ($\Delta H = 62.5$ kJ mol^{-1}), but considerably less than twice those reported[20] for maleimide itself ($\Delta H = 89$ kJ mol^{-1}) or maleic anhydride ($\Delta H = 60$ kJ mol^{-1}). It therefore appears that thermal polymerization of these *bis*-maleimides does not go to completion. The *FT*i.r. spectrum for polymer obtained by heating *bis*-4-maleimidophenylmethane, VI, until the end of the polymerization exotherm showed substantial absorption at 3110 cm^{-1} (see *Figure 5*) also indicating that polymerization does not go to completion. This is in line with the behaviour observed[21] for aliphatic *bis*-maleimides, where conversion was below 40% at 200°C, and for Kerimid, *bis*-4-maleimidophenylmethane/*bis*-4-aminophenylmethane (molar ratio 2.5/1) polymerizations[11] where the residual concentration of maleimide double bonds dropped to a constant level, dependent on polymerization temperature, which was about 25% at 240°C. Cure to complete reaction for all these materials is not possible because conversion of liquefied monomer to a highly cross-linked matrix, which may have T_g

substantially greater than the polymerization temperature, restricts translational movement of unsaturated imide groups. This occurs to such an extent that polymerization cannot proceed to completion within the time scale of the experiments.

The second exotherm observed with pure samples of the four *bis*-maleimides indicates an apparent second reaction which does not require translational movement of maleimide groups. Comparison of the *FT*i.r. spectra for polymer from *bis*-4-maleimidophenylmethane isolated at the end of the polymerization exotherm with that from polymer at the end of the second exotherm (*Figure 6*) shows that during the second reaction the concentration of maleimide is reduced and that of the alicyclic CH_2 groups increases. Similar, but less well defined, changes were observed with *bis*-maleimides IV, VI and VII. All four compounds showed spectral changes between 1150 and 1200 cm^{-1} (*Figures 1, 6* and *7*) which suggest that the reactions occurring during the second exotherms give rise to succinimide rings different from those formed during the polymerization. A possible reaction consistent with these data involves intramolecular attack of maleimide groups on the phenylene rings to which they are attached to give a bridged ring structure as indicated below.



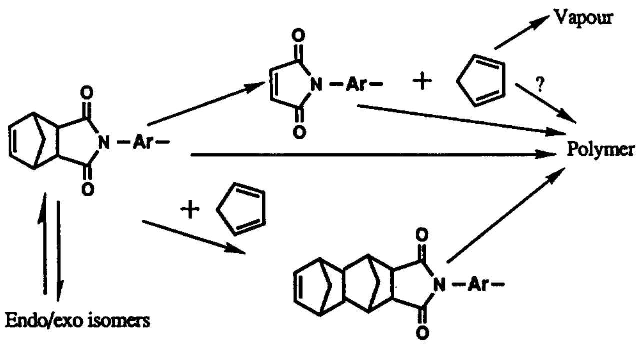
X = O or CH_2

With impure monomer samples the second reaction does not occur, presumably because the inhibitors, which increase the temperatures at which polymerization starts, also raise the temperature required to start the second reaction to that where thermal decomposition becomes predominant.

Average enthalpy values obtained for the *bis*-citraconimides VIII and IX ($\Delta H = 86$ kJ mol^{-1}) were greater than those found for the *bis*-maleimides. This is surprising since the relatively low glass transition temperatures found for the citraconimides indicate a lower degree of polymerization. However, the high temperatures required to effect polymerization of the citraconimides lead to some decomposition, as indicated by the low carbon analyses found for these polymers, and this could inflate the ΔH values recorded for these polymerizations.

Polymerization of the bis-*nadimides X and XI*

It is accepted[12] that in the thermal polymerization of *N*-arylnadimide groups, the rate determining steps involve reversed Diels–Alder reactions to produce *N*-arylmaleimide residues which then act as key monomers in the polymerization. The fate of the cyclopentadiene produced remains unclear, but it is known that some is lost from the system by evaporation while the remainder is incorporated into the resin, although the structures so produced in the resin remain ill-defined[22]:



In our experiments with the *bis*-nadimides X and XI the average loss in weight during the polymerizations (see *Table 3*) was 11.5%, which corresponds to the loss of 1.2 moles cyclopentadiene per mole of *bis*-nadimide employed. Elemental analysis of the polymers (see Experimental section) gave C, H and N contents close to those expected if all the weight lost was due to evolution of cyclopentadiene. The loss of cyclopentadiene appeared independent of the polymerization temperature within the range investigated (250–350°C), although the rate at which cyclopentadiene was evolved increased rapidly with temperature. This is consistent with a mechanism in which cyclopentadiene produced by the reversed Diels–Alder reaction reacts further on collision, so that the partition between reaction and evaporation is not much affected by temperature.

Thermal and oxidative stability of the polymers by thermogravimetric analysis

On heating samples at 2 K min^{-1} in an atmosphere of nitrogen, no major differences in thermal stability were found between resins from the *bis*-maleimides IV to VII, so that our hopes of obtaining a significant improvement by increasing the proportion of aromatic rings in the monomers were not realized (for details see *Table 4*). There is some indication from the data in *Table 4* that polymers from impure samples of IV and V are less stable than polymers from the corresponding pure monomers. Resins from the *bis*-citraconimides VIII and IX were rather less stable than the corresponding *bis*-maleimides, IV and V, but comparable in stability to the *bis*-nadimide resins from monomers X and XI. All the resins showed comparable stabilities on heating in air (*Table 5*) giving less than 10% char at 600°C.

EXPERIMENTAL

Apparatus

Infra-red spectra were recorded using a Perkin-Elmer model 1750 *FT*i.r. spectrometer interfaced with a Perkin-Elmer 7300 computer. The samples were presented as KBr discs.

D.s.c. was performed using a Du Pont 910 calorimeter interfaced with a Du Pont 9900 computer/thermal analyser.

Thermogravimetric analysis was carried out using a Du Pont 951 thermogravimetric analyser interfaced with either a Du Pont 1090 thermal analyser or a Du Pont 9900 computer/thermal analyser.

Preparation and elemental analysis of the polymers

Samples for t.g.a. examination and elemental analysis were obtained by heating the pure monomers under nitrogen in aluminium open-top pans in the d.s.c. calorimeter. The heating programmes involved a 10 K min^{-1} scan to 230, 170, 230, 230, 385, 385, 350 or 350°C for the imides IV, V, VI, VII, VIII, IX, X and XI respectively, followed by 15 min at the selected temperature. The samples were then quenched and removed from the pans by bending the pans in clean plastic bags to collect the resin fragments; these were then finely ground.

Polymers from IV and V. Found for IV: C, 64.70; H, 3.23; N, 4.53%. Found for V: C, 64.93; H, 3.49; N, 4.53%. $C_{32}H_{20}N_2O_8S$ requires: C, 64.86; H, 3.40; N, 4.73%.

Polymers from VIII and IX. Found for VIII: C, 64.36; H, 3.81; N, 4.33%. Found for IX: C, 65.05; H, 3.90; N, 4.49%. $C_{34}H_{24}N_2O_8S$ requires: C, 65.80; H, 3.90; N, 4.51%.

Polymers from X and XI. Found for X: C, 65.53; H, 4.06; N, 3.85%. Found for XI: C, 65.83; H, 4.26; N, 4.13%. $C_{42}H_{32}N_2O_8S$ requires C, 69.60; H, 4.45; N, 3.86%. Assuming 1.2 moles cyclopentadiene lost per mole monomers employed the analysis expected is: C, 66.83; H, 4.05; N, 4.34%.

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REFERENCES

1 Stenzenberger, H. in 'Structural Adhesives: Developments in Resins and Primers' (Ed. A. J. Kinloch), Elsevier, London, 1986, Ch. 3

2 Parker, J. A., Heimbuch, A. H., Hsu, M. S. and Chen, T. S. *SAMPE J.* 1985, **21**, 11

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

4 Landman, D. in 'Developments in Reinforced Plastics', (Ed. G. Pritchard), Vol. 5, Applied Science Publishers, London, 1986, Ch. 2, p. 39

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., Fohlen, G. M., Hsu, M.-t. and Parker, J. A. *Contemp. Topics Polym. Sci.* 1984, **4**, 115

8 Nair, C. P. R., Sebastian, T. V., Nema, S. K. and Rao, K. V. C. *J. Polym. Sci., Part A, Polym. Chem.* 1986, **24**, 1109

9 Lenz, R. W. 'Organic Chemistry of Synthetic High Polymers', Interscience, NY, 1967, p. 325

10 Barton, J. M., Hamerton, I., Rose, J. B. and Warner, D. *Polymer* 1991, **32**, 358

11 Di Giulio, C., Gautier, M. and Jasse, B. *J. Appl. Polym. Sci.* 1984, **28**, 1771

12 Hay, J. N., Boyle, J. D., Parker, S. F. and Wilson, D. *Polymer* 1989, **30**, 1032

13 Cubbon, R. C. *Polymer* 1965, **6**, 419

14 Warner, D. PhD Thesis, University of Surrey, March 1988

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

16 Odian, G. 'Principles of Polymerisation', 2nd Edn, John Wiley, NY, 1981, p. 267

17 Attwood, T. E., King, T., Leslie, V. J. and Rose, J. B. *Polymer* 1977, **18**, 369

18 Pascal, T., Mercia, R. and Silion, B. *Polymer* 1989, **30**, 739

19 Kwiatkowski, G. T., Robenson, L. M. Brode, G. L. and Bedwin, A. W. *J. Polym. Sci., Polym. Chem. Edn* 1975, **13**, 961

20 Busfield, W. K. in 'Polymer Handbook', 3rd Edn (Eds J. Brandrup and E. H. Immergut), John Wiley, NY, 1989, pp. 11-295

21 Hummel, D. O., Heinen, K. U., Stenzenberger, H. D. and Siesler, H. *J. Appl. Polym. Sci.* 1974, **18**, 2015

22 Lauver, R. W. in 'High Temperature Polymer Matrix Composites' (Ed. T. T. Serafini), Noyes Data Corp., Park Ridge, 1987, p. 136