Studies on a series of bis-arylimides containing four phenylene rings and their polymers: 3. Kinetic analysis of the thermal polymerizations

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A series of aryl bis-maleimides (BMIs) and bis-citraconimides (BCIs) were characterized by d.s.c. using both temperature scans and isothermal experiments. Impurities in the BMIs tend to increase the temperature at which thermal polymerization starts, while the converse is true for BCIs. This was attributed to the presence of an itaconimide impurity in the BCIs. In particular, the thermal polymerization kinetics of the compounds were investigated. Effects of structure and monomer purity on the thermal polymerization characteristics were identified.

(**Keywords: bis-maleimides; bis-citraconimides; differential scanning calorimetry; thermal polymerization; kinetics; purity**)

INTRODUCTION

Bis-maleimide (BMI) and to a lesser extent bis-citraconimide (BCI) monomers are increasingly being used in structural composite and adhesive applications where an enhancement in operational temperature is required relative to epoxy resins. In general the BMI and BCI systems are cured by thermal polymerization to produce a network by chain extension and crosslinking. The maleimide or citraconimide ring is susceptible to polymerization by a free radical or an anionic mechanism[1]. The polymerization rate may be enhanced by free radical initiators, or retarded by inhibitors such as hydroquinone. On the other hand basic compounds such as imidazoles are also effective accelerators[1] in the thermal polymerization, so that both radical and anionic mechnisms may be involved.

Bulk thermal polymerizations of this type show complex kinetics. The relative rates of free radical inhibition, transfer and termination are significant, and in the presence of air inhibiting peroxide species may be involved[2]. Further complications are reductions in molecular mobility due to increasing viscosity with conversion and leading ultimately to the formation of a glass where chemical reactions involving diffusion essentially stop.

A convenient way of monitoring the thermal polymerization is by d.s.c. in which the rate of evolution of heat due to reaction is measured[3]. This does not, however, give direct information on the concentration of chemical species. Kinetic models may be used to rationalize the data without necessarily revealing the exact chemical kinetic mechanism. This is of value for rationalizing relative reaction rates and temperature dependence of reactions, and it is of significance in the technological processing of resin and composites.

In this paper d.s.c. is applied to the kinetic study of four BMIs (structures IV, V, VI and VII in *Scheme 1*) and two BCIs (structures VIII and IX in *Scheme 1*). The general synthesis and thermal properties of these materials have been described elsewhere[4–6].

EXPERIMENTAL

The synthesis based on a method first reported by Searle[7] and purification by h.p.l.c. of the BMIs (IV–VII) and BCIs (VIII and IX) is outlined in our earlier publication[5]. Dynamic d.s.c. was performed at a range of heating rates (5, 10, 15 and 20 K min^{-1}) under nitrogen (40 cm^3 min^{-1}) using a Du Pont 910 calorimeter interfaced with a Du Pont 9900 computer/thermal analyser. Isothermal d.s.c. was carried out at four to five different temperatures over a 20 K range using a Perkin-Elmer DSC-7 calorimeter interfaced with a Perkin-Elmer 7300 computer. Monomer samples (10 ± 2 mg) were run in open aluminium pans. After conversion of the raw data to ASCII files using dedicated software, kinetic analysis was carried out using in-house programs[8] on a Hewlett-Packard HP-86 computer.

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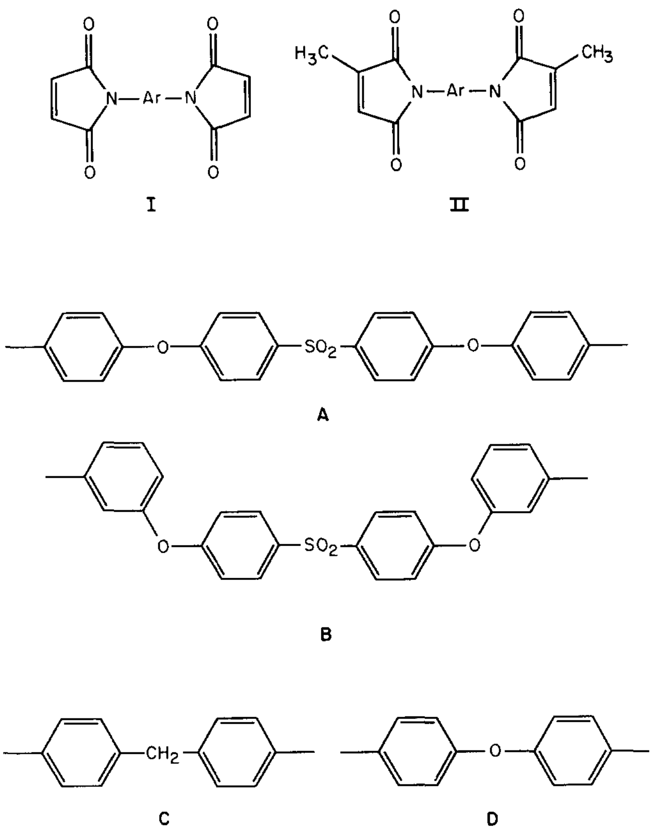

Scheme 1 IV = I, Ar = A; V = I, Ar = B; VI = I, Ar = C; VII = I, Ar = D; VIII = II, Ar = A; IX = II, Ar = B

RESULTS AND DISCUSSION

Significant differences were found in the thermal characteristics of BMIs and BCIs of different structure and level of purity[4–6]. Pure BMI V and BCI IX have fusion temperatures ~135°C below the melting points of the all-*para* compounds (IV and VIII). The overlapping of the fusion endotherm with the polymerization exotherm for the pure BMIs (IV, VI and VII) prevented the quantitative d.s.c. study of their melting and polymerization. However for the 96% pure materials (IV, VI and VII) discrete melting and polymerization processes were observed so that quantitative kinetic data for the polymerization could be obtained by d.s.c. A second diffuse exotherm was observed in the d.s.c. scans for all of the pure BMIs, after the exotherm due to the main thermal polymerization. This phenomenon was discussed[6] and it was attributed to an intramolecular reaction between unreacted maleimide groups and phenylene rings. For pure BMI (V) this second exotherm was 31 kJ mol^{-1}, ~50% of the value for the primary exotherm.

We have shown[6] that the average values for overall heat of polymerization (ΔH_0) from d.s.c. scans at different heating rates for BMI V were 64 kJ mol^{-1} for the 96.5% and 99.8% pure compounds. The corresponding value for BMI IV, 96.5% pure, was 49 kJ mol^{-1}. The 99.8% pure BCIs (VIII and IX) gave higher enthalpies of polymerization (86 ± 6 kJ mol^{-1}). The average values for polymerization enthalpy of the BMIs (IV, V, VI and VII) are 60 ± 7 kJ mol^{-1}, close to the value of 62.5 kJ mol^{-1} reported recently[9] for VI, but considerably less than twice that reported[10] for maleimide itself (89 kJ mol^{-1}) of maleic anhydride (60 kJ mol^{-1}). Thus, it appears that the thermal polymerization of BMIs in the bulk state does not proceed to completion. A similar conclusion is apparent from a recent study of the bulk polymerization of *N*-phenylmaleimide in the presence of peroxide initiators. The highest ΔH_0 was 80.4 kJ mol^{-1}, obtained with 1% (w/w) of t-butylperoctoate[11]. The same paper reports ΔH_0 for a series of BMIs with internal flexible oligomeric chains. The bulk polymerization of these compounds was studied by d.s.c. using 1% dicumyl peroxide as initiator, and ΔH_0 was found to be in the range 92–182 kJ mol^{-1}, with the highest values corresponding to the compounds of lower molecular weight.

For the monomers which displayed discrete melting and polymerization it was possible to obtain kinetic data from d.s.c. experiments. The thermal polymerization is a complex process involving large increases in viscosity and changes of state. For this reason the kinetics derived from d.s.c. must be treated as a phenomonological analysis. As a first approximation the analysis was based on the simple *n*th order model:

$$\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^n \qquad (1)$$

where n is the order of reaction and k is the apparent rate constant which is assumed to be of the Arrhenius form, $k = A\exp(-E/RT)$, where A is a constant, E is the apparent activation energy, T is the absolute temperature and α is the fractional conversion. Two methods were used for data analysis, based on logarithmic forms of equation (1):

$$\ln(\mathrm{d}\alpha/\mathrm{d}t) = \ln A - (E/R)T + n[\ln(1-\alpha)] \qquad (2)$$

In the first method an unweighted multiple linear regression (MLR) routine was used to find best-fit values for the independent variables $\ln A$, E/R and n.

The second method involves a linear regression of F upon $1/T$, where

$$F = \ln(\mathrm{d}\alpha/\mathrm{d}t) - n[\ln(1-\alpha)] \qquad (3)$$

to give $(-E/R)$ as the slope and $\ln A$ as the intercept of the regression line, for a given fixed value of the reaction order n.

A set of d.s.c. scans obtained at 20 K min^{-1} heating rate are shown in *Figure 1* as plots of heat flow against temperature. Linear baselines were assumed to define the main exothermic peak and the height of the peak relative to the baseline at a given temperature was taken as the exothermic heat flow associated with the polymerization reaction ($\mathrm{d}h/\mathrm{d}t$). The heat flow due to reaction at a given time and temperature was taken as $\mathrm{d}\alpha/\mathrm{d}t = (\mathrm{d}h/\mathrm{d}t)/\Delta H_0$. The enthalpy of reaction ΔH_0 was taken as the total peak area. The results of the MLR analysis of equation (2) for BMI IV (96%) are shown in *Figure 2* as a plot of estimated $\ln k$ against reciprocal absolute temperature.

Scan kinetics for given order n were obtained by linear regression of F upon $1/T$ over the fractional conversion range 5–50%. Typical values of $\ln k$ *versus* reciprocal absolute temperature for different values of n (= 1, 2 or 3) are shown in *Figure 3*. It is seen that the second-order plot is approximately linear over the range of conversion.

The results of the kinetic analyses of the d.s.c. scans at 20 K min^{-1} heating rate for the compounds studied are listed in *Table 1*. These are the MLR values for $\ln A$ and n, and also the linear regression values for $\ln A$ and E for an assumed reaction order n = 1 and 2, respectively. Structure V is the only highly pure BMI which showed a well-separated fusion endotherm and polymerization

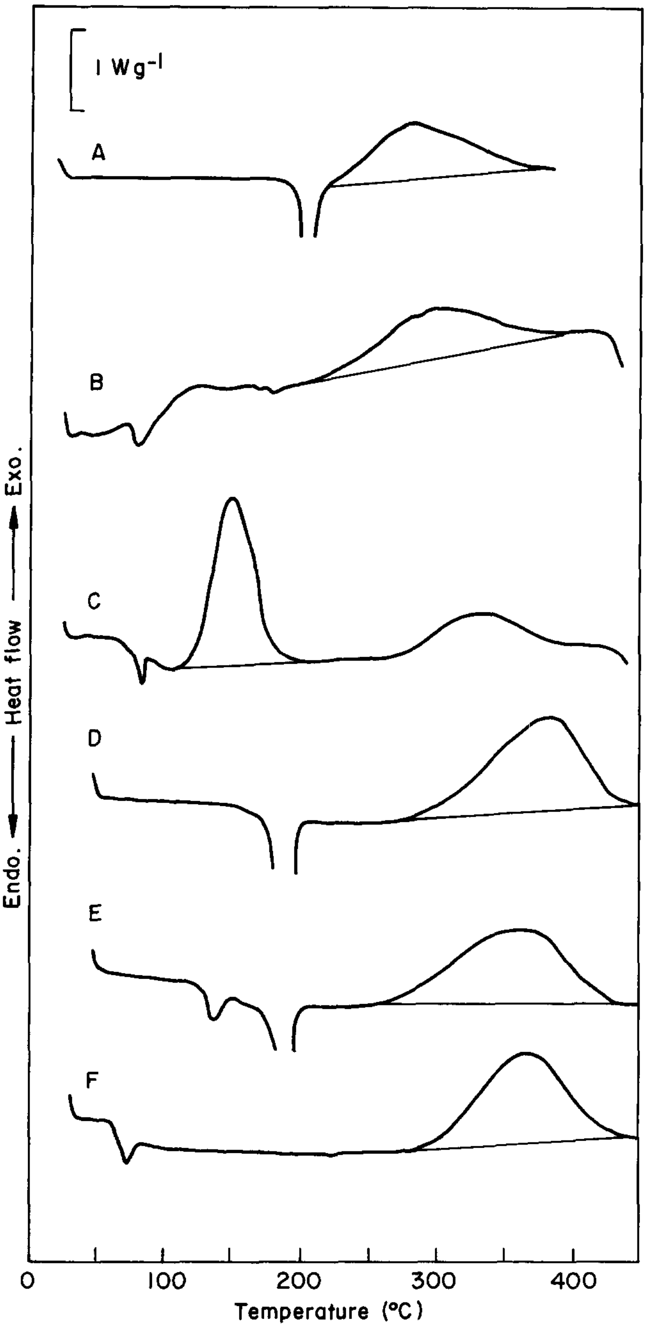

Figure 1 Scanning d.s.c. thermograms of monomers (20 K min^{-1}, under nitrogen) showing analysis limits: (A) IV, 96%; (B) V, 96%; (C) V, pure; (D) VIII, pure; (E) VIII, pure (+2% hydroquinone); (F) IX, pure

exotherm, so that the kinetics could be determined by d.s.c. Although dynamic d.s.c. is often used for kinetic analysis it is complicated by the dependence of rate on two simultaneously changing variables (conversion and temperature). On the other hand analysis of isothermal data is simple and involves fewer theoretical assumptions.

Isothermal data were also obtained over a 20 K temperature range for BMIs IV and V and BCIs VII and IX. The hydroquinone-doped BCI VIII was only run isothermally at 385°C. These isothermal data are presented in the form of 'master plots' showing the dependence of fractional conversion on reduced time, taken as the ratio of real time to half-life, $t/t_{1/2}$, where $t_{1/2}$ is the elapsed time at 50% conversion. For a given monomer and a kinetic mechanism in which the overall rate follows an Arrhenius type of temperature dependence, the plots of conversion against reduced time should all lie on the same curve, and the shape of the curve is characteristic of the kinetic function.

The isothermal results are summarized in *Table 2*. The BMI (IV, 96%) in *Figure 4* shows a very good fit to a second-order reaction. The data for the BMI (V, 96%) in *Figure 5* indicate an initial region of approximately first-order dependence up to ~20% conversion, followed by an apparent reaction order of ~1.5 up to ~60% conversion. A pure BCI (VIII) doped with 2% hydroquinone, indicates in *Figure 6* an approximate second-order fit at low conversion, increasing to third-order at fractional conversions about 30%. In contrast the same undoped pure BCI (*Figure 7*) appears to show a lower kinetic order of ~1.5. Finally, *Figure 8* shows the data for the *meta*-linked BCI (IX, pure) and this presents a convincing fit to first-order kinetics.

We have shown[5,6] that with BCIs VIII and IX the situation is more complex as impurities reduced the polymerization temperature for VIII, but had little effect on IX. The effect on VIII was so great that polymerization started immediately after melting, at a temperature below that found for impure samples of the corresponding BMI (IV). This difference of relative reactivity may be

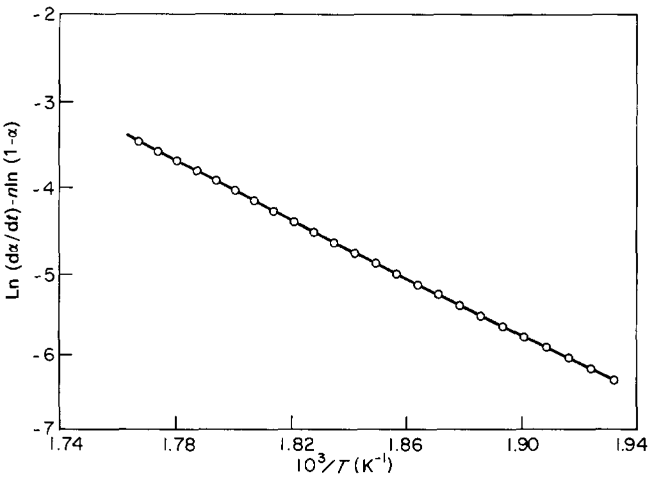

Figure 2 Multiple linear regression plot for reaction order $n = 2.6$ of monomer IV (96%); $\alpha = 5$–50%

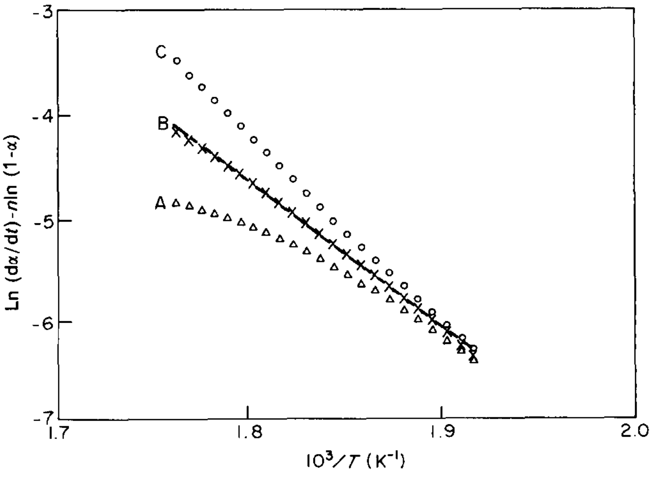

Figure 3 Linear regression plots for fixed values of reaction order (A) $n = 1$, (B) $n = 2$ and (C) $n = 3$ for monomer IV (96%); $\alpha = 5$–50%

Table 1 Kinetics of polymerization from d.s.c. scans (20 K min^{-1}, 5–50% conversion)

	Multiple linear regression				Fixed order			
Material	*n*	ln *A*	*E*	Corr. coeff.	*n*	ln *A*	*E*	Corr. coeff.
IV (96%)[a]	2.6	25.9	140.3	0.99994	1	13.2	84.6	0.99005
					2	20.9	118.6	0.99921
V (96%)	1.4	95.4	96.0	0.97160	1	12.8	84.7	0.98258
					2	19.0	111.7	0.99106
V (pure)[b]	2.5	48.7	185.1	0.99991	1	30.4	122.8	0.99201
					2	42.6	164.4	0.99948
VI (96%)[c]	2.5	54.4	235.4	0.99945	1	34.7	159.1	0.99187
					2	48.0	210.7	0.99937
VII (96%)[c]	2.8	32.3	160.9	0.99991	1	16.6	96.0	0.98860
					2	25.4	132.3	0.99880
VIII (doped)[d]	1.9	17.8	115.7	0.99979	1	11.7	86.5	0.99670
					2	18.3	118.0	0.99994
VIII (pure)	1.4	17.9	121.7	0.99849	1	14.9	106.6	0.99864
					2	21.9	141.9	0.99893
IX (pure)	1.8	24.5	151.8	0.99981	1	16.7	113.9	0.99781
					2	26.4	161.7	0.99991

[a] Not rigorously pure (~96% pure by h.p.l.c.)
[b] Pure (by h.p.l.c.)
[c] Heating rate of 10 K min^{-1}
[d] Pure + 2% hydroquinone

Table 2 D.s.c. isothermal kinetics (5–50% conversion)

Material	Temperature (°C)	*n*	*E* (kJ mol^{-1})
VI (96%)	270–290	2	66.3
V (96%)	300–320	1.5	78.6
V (pure)	130–145	1–2	21.2
VIII (pure) + 2% hydroquinone	385	2–3	–
VIII (pure)	375–395	1.5	147.1
IX (pure)	375–395	1	143.5

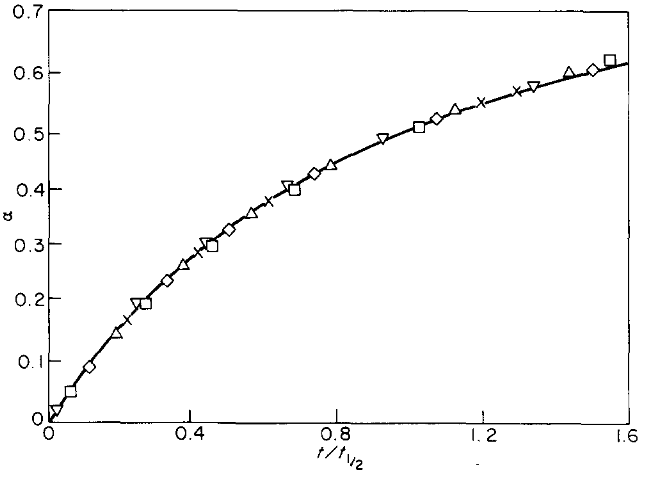

Figure 4 Fractional conversion as a function of reduced time for monomer IV (96%). The solid line represents a second-order reaction. Temperature: (□) 270°C; (◇) 275°C; (△) 280°C; (×) 285°C; (▽) 290°C

relevant to earlier reports[12,13–16] that the polymerization of BCIs starts at lower temperatures than those found for the corresponding BMIs. Bis-itaconimides are known[17] to polymerize readily on melting, so that the enhanced reactivity of crude VIII over that of the pure compound may be due to the presence of the

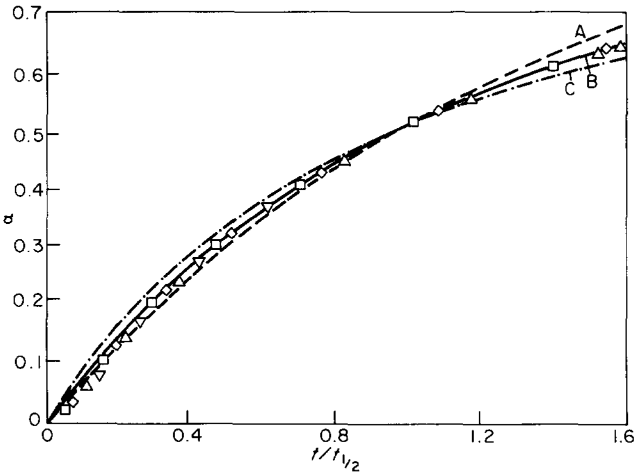

Figure 5 Fractional conversion as a function of reduced time for monomer V (96%). Calculated lines denote (A) $n = 1$, (B) $n = 1.5$ and (C) $n = 2$. Temperature: (□) 270°C; (◇) 275°C; (△) 280°C

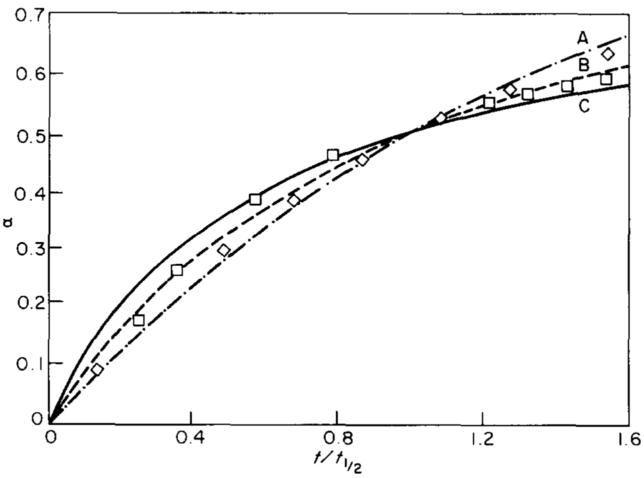

Figure 6 Fractional conversion as a function of reduced time at 285°C for pure monomer VIII (◇) and pure VIII doped with 2% hydroquinone (□). Calculated lines denote (A) $n = 1$, (B) $n = 2$ and (C) $n = 3$

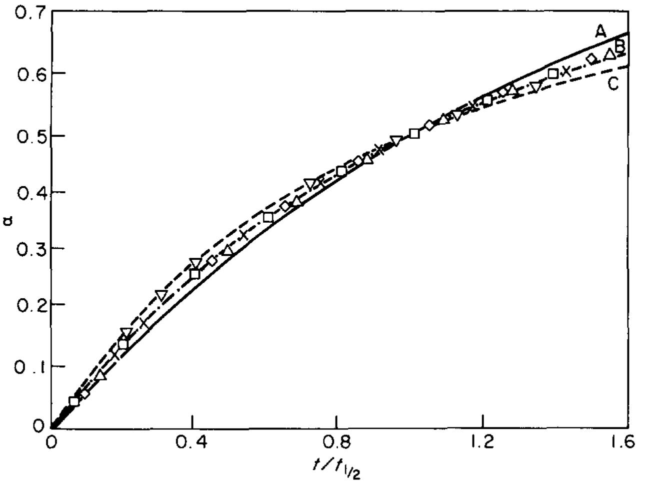

Figure 7 Fractional conversion as a function of reduced time for pure monomer VIII. Calculated lines denote (A) $n = 1$, (B) $n = 1.5$ and (C) $n = 2$. Temperature: (□) 270°C; (◇) 275°C; (△) 280°C; (×) 285°C; (▽) 290°C

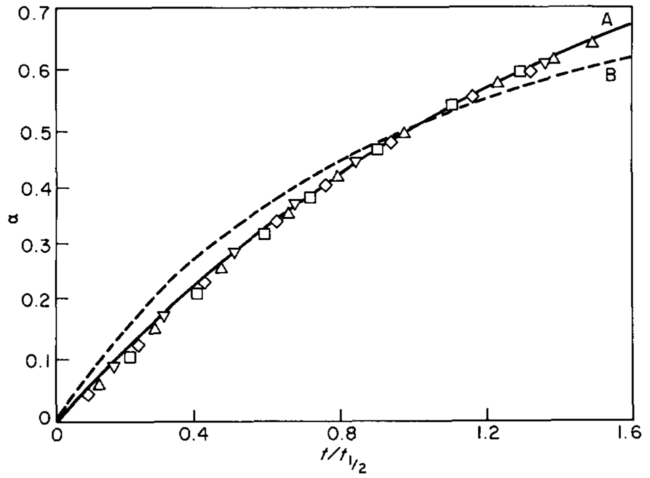

Figure 8 Fractional conversion as a function of reduced time for pure monomer IX. Calculated lines denote (A) $n = 1$ and (B) $n = 2$. Temperature: (□) 270°C; (◇) 275°C; (△) 280°C; (▽) 290°C

itaconimide–citraconimide as a major impurity in crude VIII[4,5].

The temperature dependences of the isothermal reactions are depicted in the form of logarithmic plots of conversion rate against reciprocal absolute temperature, for a constant overall conversion level of 50%. These experimental data are illustrated in *Figure 9*. The isothermal data indicate large differences in apparent activation energies which depend on both sample purity and structure. In order to compare the results of the dynamic data in a similar format to the isothermal Arrhenius plots, the dynamic data are mapped in the form of linear plots of $\ln(d\alpha/dt)_{\alpha=0.5}$ against reciprocal absolute temperature in *Figure 10*. The lines for dynamic data are calculated from the tabulated MLR parameters, and they illustrate several features of the reactions. The lines in the figure for the BCIs are grouped together in a higher temperature range relative to the BMIs. This indicates the general lower reactivity of the BCIs. The melting point for BMI V (93–100°C) is well below the temperature at which polymerization starts so that the two phenomena are clearly resolved and the retardation of polymerization due to impurities is shown unequivocably in the wide temperature difference between the lines (V, 96% and pure) in *Figure 10*. With the other BMIs the high melting points force the polymerization to occur at higher temperatures. This is illustrated in *Figure 10* where the intersection of the horizontal line $[\ln(d\alpha/dt)_{\alpha=0.5} = -7$, the fixed logarithmic conversion rate] with the linear plots at 50% conversion denotes the corresponding temperatures (T'), and also in *Table 3* by the monomer melting temperatures, T_m (d.s.c. peak). The 96% pure BMIs compounds (IV and V) are of comparable reactivity and of lower reactivity than compounds VI and VII. This is not unexpected due to the lower concentration of maleimide groups in these compounds. The higher

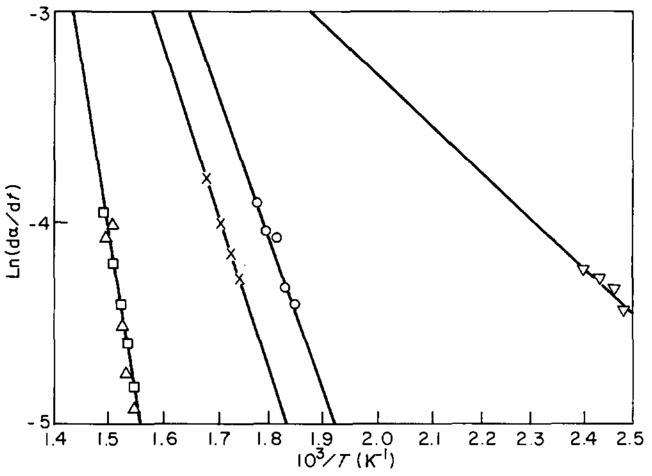

Figure 9 Logarithmic conversion rate as a function of reciprocal temperature at 50% conversion: (▽) pure V; (○) 96% IV; (×) 96% V; (□) pure VIII; (△) pure IX

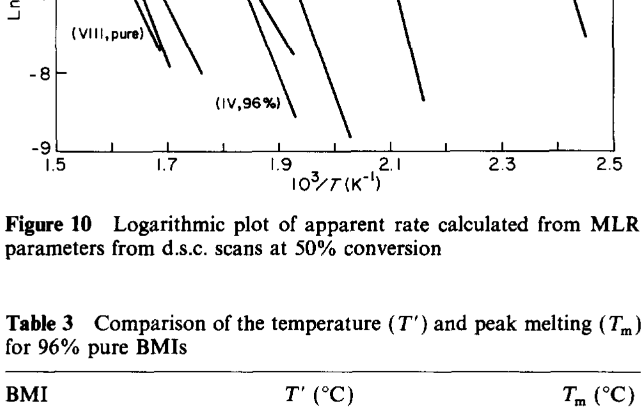

Figure 10 Logarithmic plot of apparent rate calculated from MLR parameters from d.s.c. scans at 50% conversion

Table 3 Comparison of the temperature (T') and peak melting (T_m) for 96% pure BMIs

BMI	T' (°C)	T_m (°C)
VI	201	160
VII	244	175
IV	269	209
V	270	90–100

melting points of BMIs IV, VI and VII forces the polymerization of these compounds to higher temperatures than that shown by the lower melting compound (V). However, this does not invalidate the general conclusion drawn on reactivity as *Figure 10* refers to apparent rate at 50% conversion and the temperatures corresponding to this conversion bear no consistent relationship to the melting points of the monomers as shown in *Table 3*. In particular for BMI V a high value of T' is observed, coupled with the lowest melting point.

The d.s.c. kinetic data enable the determination of relative reactivities and temperature dependences of the thermal polymerizations. The kinetic data should be regarded as a first approximation as the reactions are complex and concentrations of species are not directly determined. There are significant differences between apparent activition energies obtained for temperature scanning and isothermal experiments. The isothermal technique typically covers a limited temperature window of ~20–30 K, dependent on the reaction activiation energy and instrumental factors (i.e. sensitivity, signal-to-noise ratio and stability). Conversely, a temperature scan will cover a much wider temperature range in excess of 100 K. Over such a wide temperature range the systems are undergoing large viscosity increases and changes in state from liquid through gel to glass. In this process changes in reaction mechanism are likely, and the kinetics derived from a temperature scan represent an 'average' set of kinetic parameters.

In conclusion, the high temperatures required to effect polymerization of the pure BCIs lead to substantial temperature gaps between fusion and polymerization. For BMIs IV, VI and VII, polymerization occurs on melting, but impurities decrease reactivity and produce a temperature gap between melting and thermal polymerization. The markedly lower melting point of V also leads to a signifcant gap between melting and polymerization. With BCIs VIII and IX the situation is more complex as impurities reduced the polymerization temperature for VIII, but had little effect on IX.

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