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A study of the polymerization behaviour of *N*-(4-phenoxy)-phenylmaleimide using DSC analysis

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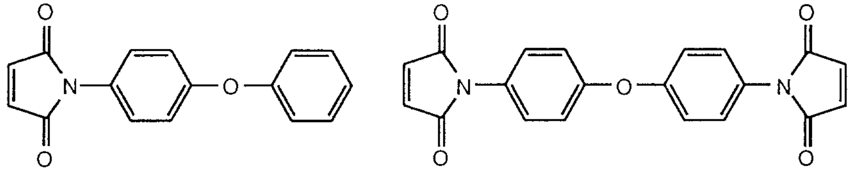
Summary

The thermal cure of a monofunctional maleimide *N*-(4-phenoxy)-phenylmaleimide (*1*) was examined using differential scanning calorimetry (DSC). The analogous *bis*-maleimide *bis*-(4-maleimidophenyl)ether (*2*) was also analyzed in the same manner for comparison. Polymerization kinetics derived from scanning DSC measurements showed an order of reaction varying between n = 1 and 2 for (*1*), compared to an order of reaction between n = 2 and 3 (by multiple linear regression analysis) for (*2*). The overall enthalpy of polymerization (ΔH_0) for *N*-(4-phenoxy)-phenylmaleimide (94kJ/mole) agrees well with that obtained for maleimide itself (89kJ/mole) using conventional calorimetric techniques indicating that polymerization appears complete within the timescale of the experiment. In contrast the analogous BMI displays a markedly lower overall polymerization enthalpy (*ca.* 66kJ/mole) indicating an apparent conversion of only 37%.

Introduction

Bis-maleimide (BMI) 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 systems are cured by thermal polymerization to produce a network by chain extension and crosslinking. The maleimide ring is susceptible to polymerization by a free-radical or an anionic mechanism(1), but a number of values for the overall enthalpy of polymerization have been reported in the literature(1) for difunctional BMI monomers which display a wide variation in magnitude.



(*1*) (*2*)

Scheme 1. Monomers used in this study

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To date *N*-phenylmaleimide has often been used as a model maleimide in thermal analysis. However, this monomer is quite volatile and data from DSC scans are often variable (even in sealed pans) indicating that some monomer is lost before polymerization occurs, resulting in a smaller ΔH_0 than anticipated. The preparation of *N*-(4-phenoxy)-phenylmaleimide (*1*) has recently been reported(2) as a precursor compound in connection with research into functionalized oligomers. It was apparent to us that this compound might be of considerable interest as a model maleimide suitable for thermal analysis (and in particular DSC analysis) and so a sample of the monomer was prepared and characterized(3) using single crystal *X*-ray crystallographic techniques.

Experimental

Materials

The syntheses of *N*-(4-phenoxy)-phenylmaleimide (*1*) and *bis*-(4-maleimidophenyl)ether (2) were based on a method first reported(4) by Searle and subsequently modified(5). The monomers were both recrystallized from methanol to microanalytical purity.

Equipment

Fusion temperatures were measured using a Gallenkamp melting point apparatus. Infra-red spectra were recorded with a Perkin-Elmer 1750 FT-IR spectrometer interfaced with a Perkin-Elmer 7300 computer; the samples were presented as KBr disks. ^{1}H nmr spectra were obtained at 298K using a Bruker AC300 FT nuclear magnetic resonance spectrometer operating at 300 MHz. DSC was performed at a range of heating rates (5, 10, 15 and 20K/minute) under nitrogen (40cm^3/minute) using a Du Pont 910 calorimeter interfaced with a Du Pont 9900 computer/thermal analyzer. Monomer samples (3±1 mg) were run in sealed aluminium pans. After conversion of the raw data to ASCII files using dedicated software, kinetic analysis was carried out using in-house programmes(6) on a Compaq 286 personal computer.

Results and Discussion

The data from the DSC experiments are shown in Table 1. In each case the monofunctional monomers produced reproducible thermal behaviour with a sharp endothermic peak at *ca.* 163°C due to crystalline melt and a diffuse polymerization exotherm spanning 250-375°C (which appears to contain at least two fundamental peaks within it). The average polymerization enthalpy (ΔH_0) from the dynamic data for (*1*) was 94kJ/mole, compared with 66kJ/mole for the analogous BMI (2).

Table 1. Thermal Behaviour of Maleimide Monomers

Sample	Scan Rate K/min	T_m[a] (°C)	T_o[b] (°C)	T_{exo}[c] (°C)	ΔH_o[d] J/g	kJ/mole
(*1*)	20	165.7	256.6	334.3	348.1	92.2
	15	165.1	237.2	337.2	384.4	101.9
	10	163.3	257.5	328.9	334.5	88.6
	5	162.7	222.1	308.6	357.9	94.8
(*2*)	10	163.8	180	244.9	183.1	65.9

[a] crystalline melting endotherm.

[b] onset of polymerization exotherm.

[c] maximum of exothermic peak.

[d] overall polymerization exotherm.

We have already shown(7-9) that the average values for overall heat of polymerization (ΔH_o) from DSC scans at different heating rates for a range of (BMIs) were 60±7 kJ/mole, close to the value of 62.5 kJ/mole reported recently(10) for *bis*-4-(3-maleimidophenoxy)phenylsulphone, but considerably less than twice that reported(11) for maleimide itself (89 kJ/mole) or maleic anhydride (60 kJ/mole). We concluded that it appeared that the thermal polymerization of BMIs in the bulk state did not appear to proceed to conclusion - a finding in common with that from a study of the bulk polymerization of *N*-phenylmaleimide in the presence of peroxide initiators(12). In this study the highest ΔH_o was 80.4 kJ/mole, obtained with 1% (w/w) of *tert*-butylperoctoate(12). This is also in line with the behaviour observed(13) in infra-red spectra of aliphatic BMIs where conversion was below 40% at 200°C and for Kerimid 601 polymerizations(14) 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 crosslinked, glassy matrix, in which translational movement of unsaturated imide groups is restricted, occurs to such an extent that polymerization cannot proceed to completion within the timescale of the experiment.

Kinetic Analysis

The thermal polymerization is a complex process(1,7) involving large increases in viscosity and changes of state. For this reason the kinetics derived from DSC must be treated as a phenomenological analysis. As a first approximation the analysis was based on the simple n'th order model:

$$d\alpha/dt = k(1-\alpha)^n \tag{1}$$

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

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

In the first method an unweighted multiple linear regression routine was used to find best-fit values for the independent variables lnA, E/R and n.

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

$$F = \ln (d\alpha/dt) - n[\ln(1-\alpha)] \tag{3}$$

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

A DSC scan obtained at a heating rate of 10K/minute is shown in Figure 1 as a plot 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 (dh/dt). The heat flow due to reaction at a given time and temperature was taken as $d\alpha/dt = (dh/dt)/\Delta H_0$. The enthalpy of reaction ΔH_0 was taken as the total peak area.

Scan kinetics for a given order n were obtained by linear regression of F upon 1/T (K) over several fractional conversion ranges (*e.g.*, 5-50%). Typical values of $\log_e k$ *vs.* $10^3/T$ for different values of n = 1 or 2 are shown in Table 2 for monomers (*1*) and (*2*).

Multi-linear regression (MLR) analysis over the range 5-90% conversion gives an average value of n = 1.1 for the thermal cure of (*1*), while this rises to n = 2.1 over the rage 5-50%. A fixed first order plot for (*1*) is approximately linear over an apparent 5-50% conversion range, while a second order plot of the same monomer appears to be an excellent fit up to 50% conversion. Beyond this point deviation occurs fairly dramatically and this deviation is most likely due to diffusion control (viscosity). Figure 2 depicts the kinetic plot for different fixed orders of reaction (n = 1, 2 and 3). It can clearly be seen that the second order plot best fits the data over the apparent conversion range 5-50%.

Table 2. Kinetics of Thermal Polymerization from DSC Data

Sample	Scan Rate K/min	n[a]	lnA[b]	E[c] kJ/mole	L Reg Range[d] (%)
(*1*)	10	1	15.2	101.9	5-40
		1	15.0	100.9	5-50
		1	16.2	106.8	5-95
		1.1[e]	17.4	111.6	5-90
		2.1[e]	27.7	159.8	5-50
	20	1	18.1	114.8	5-50
		2	26.6	154.9	5-50
(2)[f]	10	1	16.6	96.0	5-50
		2	25.4	132.3	5-50
		2.8	32.3	160.9	5-50

Note: all regression correlation coefficients were greater than 0.99

[a] n is the order of reaction

[b] A is a constant (from the Arrhenius equation)

[c] E is the apparent activation energy.

[d] Linear regression range over which data quoted applies.

[e] Multi-linear regression analysis·

[f] 96% pure (by HPLC analysis).

Conclusion

The DSC analysis for the thermally initiated polymerization of *N*-(4-phenoxy)-phenylmaleimide yields an overall polymerization enthalpy (ΔH_0) of 94kJ/mole. This in turn indicates that most of those enthalpies quoted in the literature for BMIs relate to incomplete polymerizations (which can be as low as 26% for (2)(1). Second order kinetics were observed up until an apparent conversion of 50%. The reproducibility of these data commend *N*-(4-phenoxy)-phenylmaleimide as a suitable model maleimide in thermal analysis. The present data

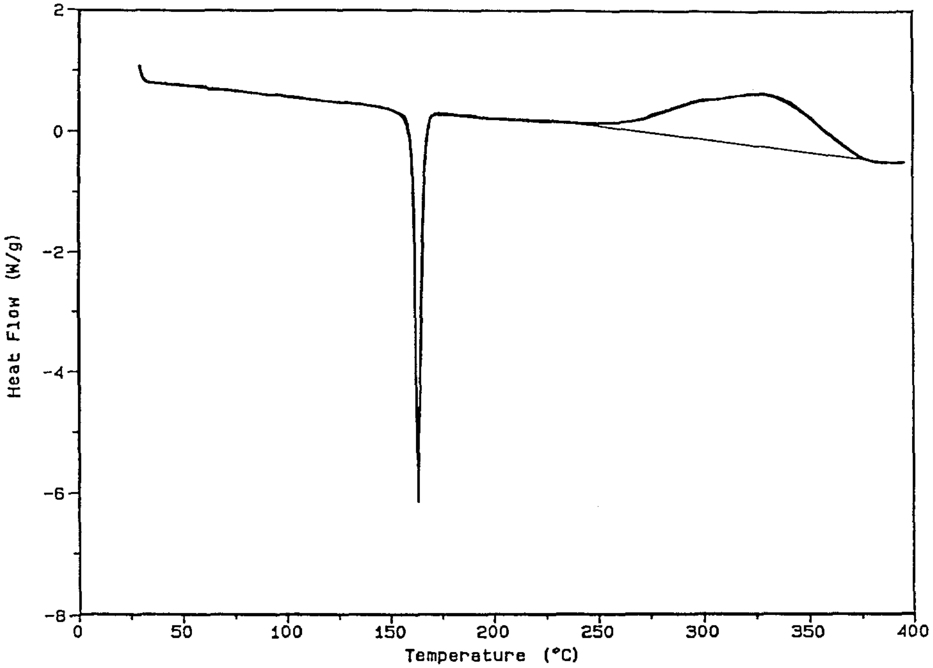

Figure 1. Scanning DSC thermogram (10K per minute, under nitrogen) for *N*-(4-phenoxy)phenylmaleimide showing analysis limits.

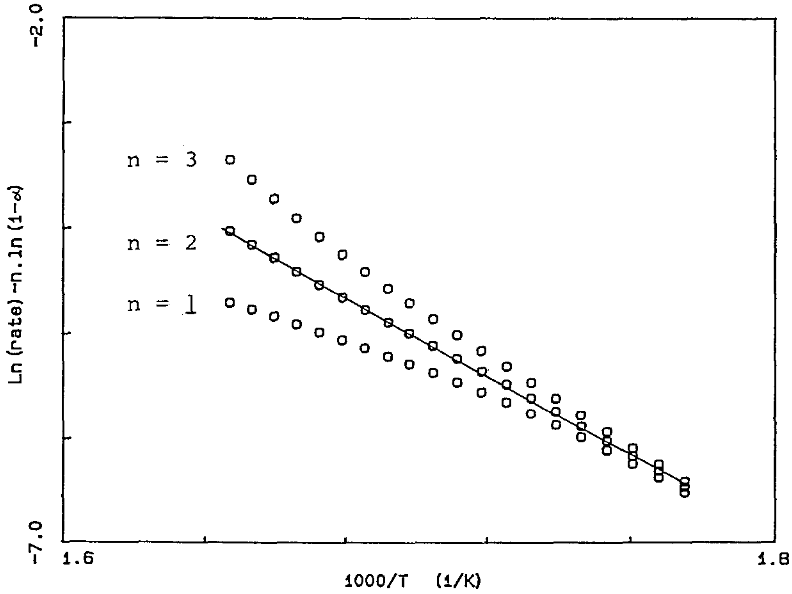

Figure 2. Linear regression plots for fixed values of reaction order (n = 1, n = 2 and n = 3) for *N*-(4-phenoxy)-phenylmaleimide; α = 5 - 50%.

indicate that reaction of maleimide groups in BMIs does not go to completion, presumably due to early vitrification of the network prior to thermo-oxidative degradation at higher cure temperatures.

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