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The use of differential scanning calorimetry to study polymer crystallization kinetics

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A Tektronix-31 programmable calculator interfaced to a Perkin Elmer differential scanning calorimeter, model 2, substantially improves the accuracy of measuring the time-dependent development of the degree of crystallinity ($\times 10$) and hence improves the quality of the rate data. Storing energy flow data at preset time intervals directly into the memory of the calculator improves the accuracy of the measurement of time, and enables the evaluation of the onset of crystallization and the baseline of the calorimeter initially. This substantially improves the measurement of the degree of crystallinity developing with time by integrating the energy flow data over the time interval from the onset of crystallization. Polyethylene samples are studied since their rate constants have a marked temperature dependence which enables the accuracy of the analytical procedure to be assessed. Primary and secondary crystallization processes are separated.

Keywords Interface; differential scanning calorimetry; base-line corrections; microprocessor; crystallization; kinetics

INTRODUCTION

In previous publications^{1,2} the use of differential scanning calorimeters (d.s.c.) to measure isothermal crystallization rate parameters has been assessed and compared with conventional dilatometry³. In general it was concluded that whilst the apparent temperature control of the Perkin-Elmer d.s.c., model 2, was satisfactory, i.e. ± 0.025 K, its greater sensitivity than the d.s.c.-1B was not being used to its full potential since the thermal rate-time data were displayed on a 1-10 mV recorder with a limiting response of $\sim 1\%$. Interfacing the calorimeter to a digital millivoltmeter, and hence to a microprocessor, enables this increased sensitivity to be realized.

This report considers various experimental procedures which are available with this computer interface, which assists in the analysis of isothermal crystallization rate data.

EXPERIMENTAL

Polyethylene fractions, Marlex 60, supplied by Philips Petrochemical Co. Ltd., were used. Their molecular weight characteristics are listed in Table 1. Dilatometry has been described elsewhere³.

A Perkin-Elmer d.s.c., model 2, was used to study the crystallization behaviour of moulded polymer samples of 5-30 mg weighed to 0.01 mg, and sealed in aluminium pans under nitrogen. The d.s.c.-2 was interfaced to two computers—a Perkin-Elmer Scanning Autozero and

through a Perkin-Elmer microvoltmeter to a Tektronix-31 programmable calculator. The output from the calorimeter was also displayed on a 10 mV Recorder.

The scanning autozero stored the calorimeter baseline without a sample, as a function of temperature, and subsequently subtracted it from subsequent determinations with samples. It substantially improved the linearity of the corrected baseline of the calorimeter over a wide temperature range.

The Tektronix-31 programmable calculator stored the corrected calculator output—digitalized by the Perkin-Elmer interface at a programmed time interval. The data was stored as a composite number of temperature and energy flow rate. Up to 400 data points could be stored for each isothermal crystallization run at preset time intervals.

Isothermal temperatures of the d.s.c.-2 were calibrated from the melting characteristics of zone-refined stearic acid, m.pt. 343.2 K, and benzoic acid, m.pt. 395.2 K, and ultra pure indium, m.pt. 429.8 K, by extrapolating to zero

Table 1 Polyethylene characteristics

Serial number	\bar{M}_n	Molecular weight $\times 10^{-3}$ \bar{M}_w	D^*
A	19.0	142.0	7.4
B	25.0	41.0	1.6
C	32.0	99.0	3.1
D	78.0	165.0	2.1

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heating rate. The heat of fusion of indium was taken to be 28.45 J g^{-1} in calibrating the thermal response of the calorimeter.

RESULTS AND DISCUSSION

Analytical procedures

Isothermal crystallization was conventionally studied by quenching the molten sample to the crystallization temperature, T_c , and then following the rate of heat evolution with time until it became less than the thermal response of the sensors (Figure 1). The fractional crystallinity X_t , which developed up to time t was defined to be the fractional area under the rate-time curves above the baseline, i.e.

$$X_t = \int_0^t \frac{dH}{dt} dt / \int_0^{\infty} \frac{dH}{dt} dt \quad (1)$$

The crystallinity-time dependence was then analysed using the Avrami equation

$$-\ln(1 - X_t) = Zt^n \quad (2)$$

in which X_t is the weight fraction of crystallized material defined as in equation (1), Z a composite rate constant and n the Avrami exponent. Accordingly,

$$\log(-\ln(1 - X_t)) = \log Z + n \log t \quad (3)$$

and $\log(-\ln(1 - X_t))$ against $\log(t)$ plots are linear with slopes n . The rate constant, Z , was calculated from the half-life of the crystallization, $t_{1/2}$, and the average value of n , since

$$Z = \ln(2)/t_{1/2}^n \quad (4)$$

Such an analysis requires accurate determination of:

- experimental time (t) from the initial onset of crystallization, and
- accurate evaluation of X_t , involving determination of initial and final baseline, and construction of the baseline under the total crystallization isotherms.

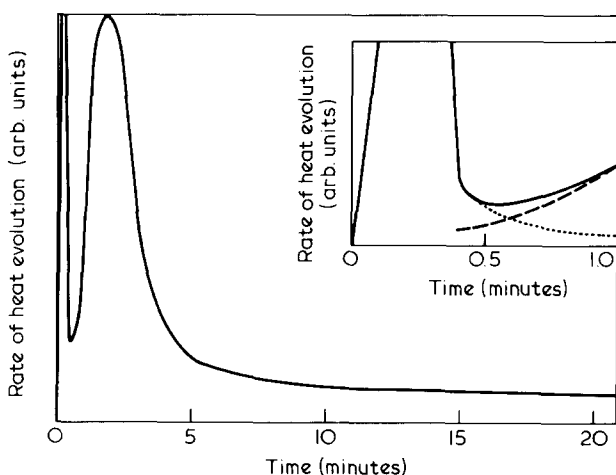


Figure 1 Typical crystallization isotherm, Sample B at 397 K as observed: Inset (· · · ·) cooling curve component; (---) crystallization component

Experimental time

On quenching, at 320 or 160 K min^{-1} , heat cannot be lost fast enough from the sample for the temperature to match the programmed cooling and the calorimeter does not reach the crystallization temperature as shown by the average temperature indicator until 20–40 seconds after programmed cooling is complete. Although thermal control of the calorimeter is apparently achieved, the sample within the calorimeter is at a higher temperature and continues to cool to the programmed temperature before crystallization develops. Accordingly, the calorimeter output indicates that the sample loses heat at a progressively slower rate until crystallization starts. Thereafter the heat is evolved at a progressively increasing rate up to a maximum. Following this, the output decreases until it returns to the calorimeter baseline and the crystallization is then apparently complete; see Figure 1.

Since there appears to be no induction period for the crystallization of polyethylene, the cooling exotherm overlaps the initial development of crystallization masking the baseline of the calorimeter and the time at which crystallization develops, i.e. t_0 .

To separate the two components of the exotherms, the initial cooling curves (cooling over 15 K) of solid and liquid samples were examined in isolation in the narrow temperature range in which crystallization/melting did not occur. All the cooling curves were superimposable and could be stored directly into the calculator for subsequent subtraction from the crystallization isotherm. In carrying out this procedure, the start of the crystallization was measured from the initial deflection of the corrected isotherm from the baseline. Cooling correction was necessary over a short time period and crystallization developed at 24 ± 2 seconds from the switching on of the (average temperature) indicator lamp.

All the corrected crystallization exotherms exhibited the general shape outlined in Figures 1 and 3.

Baseline corrections

There has been much debate about the form of the d.s.c. baselines before, during and after crystallization and several conflicting procedures have been adopted^{1,2,4,5} to correct for variations in the baseline during crystallization, see Figure 2. These have included, using the final baseline achieved as the baseline for the entire isotherm and back projecting to the forward edge of the crystallization isotherm^{1,2}, joining the minimum observed in the isotherms initially and finally⁴ varying the initial and final baselines in proportion to the degree of conversion.

The latter procedure adopts the convention that the baseline is proportional to the heat capacity of the sample, and while this is indeed the case in d.t.a. and non-isothermal d.s.c. measurements there is no justification in theory for it in isothermal d.s.c. Under these conditions the baseline is determined by the relative rate of heat loss from the reference and standard calorimeters incorporating the sample, and this will be temperature and sample size dependent.

To test these points, the same polymer sample melted and crystallized was cooled through 15 K to various preset temperatures over a wide range, 80 K, but under conditions where neither crystallization nor melting was

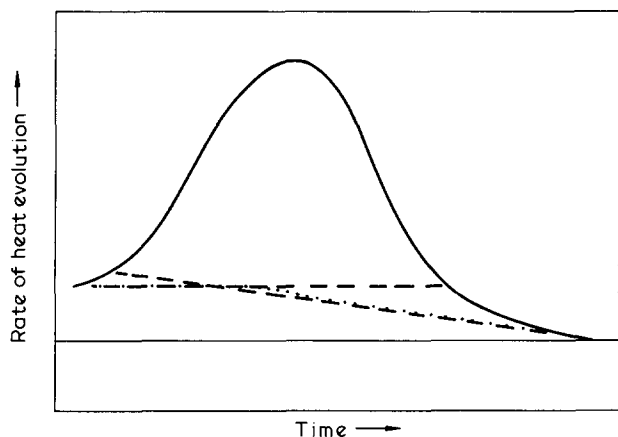


Figure 2 Isotherm Baseline corrections, as per ref 5. (---) Extrapolated; (····) estimated baseline

occurring, and the cooling curves measured. The final baseline achieved was observed to vary linearly with temperature, and solid and liquid polymers gave the same extrapolated baseline values in the temperature regions in which isothermal crystallizations were measured. The baseline during crystallization would then not vary with conversion.

Similar conclusions were also established in storing the cooling curves and then subtracting these directly from the total crystallization exotherms in that the corrected initial zero readings prior to the onset of crystallization were within experimental error identical to those finally achieved at the apparent end of crystallization.

Evaluation of the degree of crystallinity, X_t

The linear baseline simplified the evaluation of X_t (equation (1)) by integration. Simpson's rule was measured on 400 data points determined over a constant time interval chosen such that they covered the entire isotherm. An initial and final baseline was determined and the initial data corrected for cooling from data previously stored in the calculator.

This procedure clearly was a substantial improvement on those adopted previously^{1,2} and indeed in other publications concerned with the use of d.s.c. to measure specific heats^{6,7}, it was concluded that the above method of data acquisition reduced the variations in measurements to $\pm 0.2\%$, an improvement of $\times 10$. The increased number of data points, $\times 10-20$, also implies a further improvement in the quality of crystallization data so determined.

Primary crystallization

As outlined elsewhere², rate measurements were restricted by the sensitivity of the calorimeter, $0.14-8.5 \mu\text{J s}^{-1}$, sample size up to 30 mg, and the enthalpy of fusion, $100-200 \text{ J g}^{-1}$. Computer interfacing did not extend this range but improved the accuracy of the evaluation of X_t to lower values. This limited the range of crystallization measurement in polyethylene to 6-7 K.

The development of crystallinity with time at each temperature was determined, as outlined above, and was similar in all details to that observed by dilatometry (see Figure 1 of ref 1). However, as can be seen from Figure 3, the reproducibility of the crystallization plots is substantially improved. The crystallization isotherms are compared at $397.0 \pm 0.1 \text{ K}$. T_{max} varied linearly with

temperature over this short range, i.e. $1.25 \rightarrow 1.75 \text{ min}$. The isotherm at 397.0 K was repeated $\times 8$ and the maximum variation in T_{max} was no greater than 2 seconds. Attributing all this variation to temperature variations implies a maximum of 0.014 K.

Analysis of the crystallization-time dependence by equations (1-4) indicated two processes which can be separated on a time scale, see Figure 4. Rate constants, Z , and values of n were obtained from the primary process

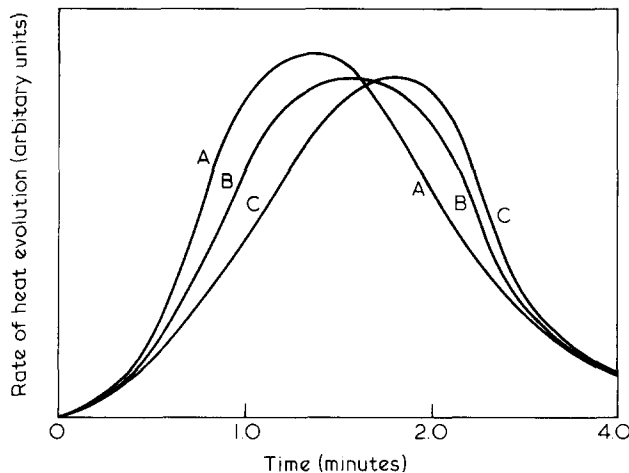


Figure 3 Temperature dependence of crystallization isotherms AA. 396.9 K, BB. 397.0 K, CC = 397.1 K, sample B

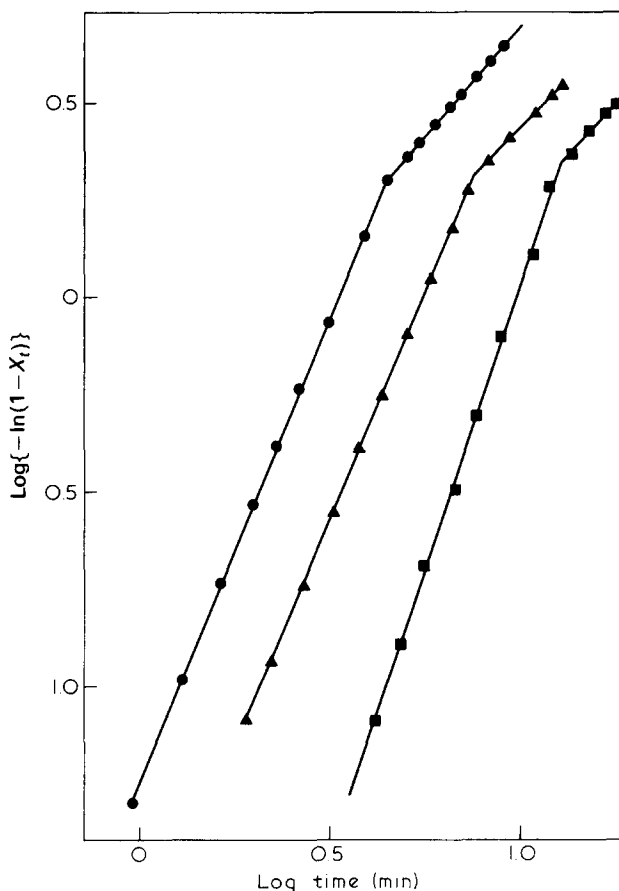


Figure 4 Analysis of crystallization isotherms by equation (3), sample B: ●, 398.5 K; ▲, 399.5 K; ■, 400.8 K

assuming that it proceeded independently of the secondary process, see Table 2. As observed previously, the n values listed for sample B are consistently lower measured by d.s.c. than by dilatometry, although the two determine very similar $t_{1/2}$ values. The n values are consistently less than 3 and between 2.1 and 3.0, but considered to be due to crystallization of heterogeneously nucleated spherulites.

No variations in rate with sample size was observed.

As outlined by Mandelkern⁸ plots of $\ln Z$ vs. $T_c^{a-1}/(T_m^0 - T_c)^a$ for the correct value of a should be linear with slope equal to $4\sigma_e\sigma_u/R\Delta H^a$, where σ_e and σ_u are the interfacial free energies per unit area of the end and side surfaces of the nucleus, ΔH is the enthalpy of fusion and R the gas constant. Figure 5 shows the best fit to be given by $a = 1$, which suggests that crystal growth proceeds by two-dimensional secondary nuclei, whilst making the approximation⁹ $\sigma_u = 0.1 \Delta H$ a value of 18 kJ mol^{-1} for σ_e is obtained.

Table 2 Primary crystallization parameters for sample B

Method	Crystallization temperature (K)	n	$t_{1/2}$ (min)	Z_1 (min^{-n})
D.s.c.-2	397.5	2.7	1.8	1.4×10^{-1}
	398.5	2.4	2.7	6.4×10^{-2}
	399.5	2.5	3.9	2.3×10^{-3}
	400.5	3.2	7.8	9.7×10^{-4}
	401.0	2.7	15.5	4.2×10^{-4}
	402.0	2.7	37.0	4.0×10^{-5}
	402.5	2.9	77.0	2.3×10^{-6}
Dilatometry	403.0	2.8	184.0	3.2×10^{-7}
	400.5	2.8	9.5	1.3×10^{-3}
	401.5	3.2	36.0	7.3×10^{-6}
	402.0	3.2	77.0	6.4×10^{-7}
	402.5	3.3	187.0	2.2×10^{-8}

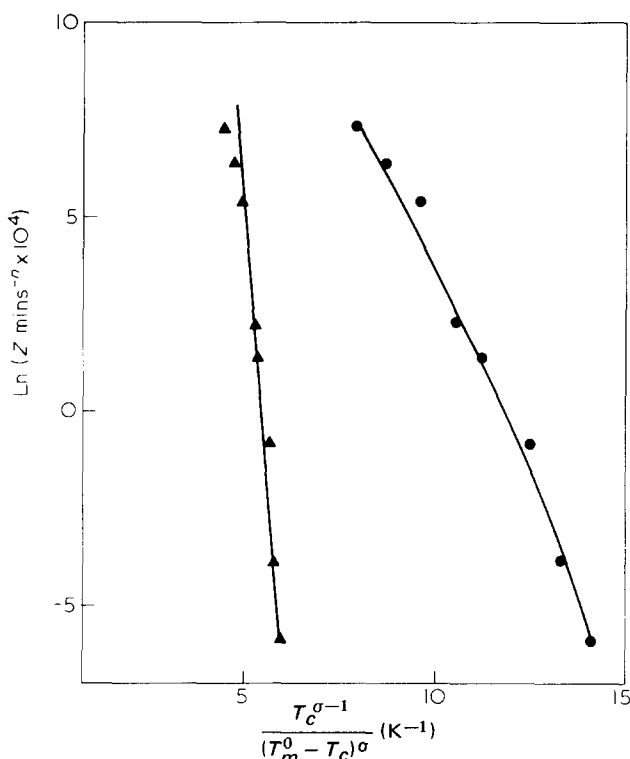


Figure 5 Evaluation of σ_e for sample B. $a = 1$ ($\times 10^2$); $a = 2$ ($\times 10$)

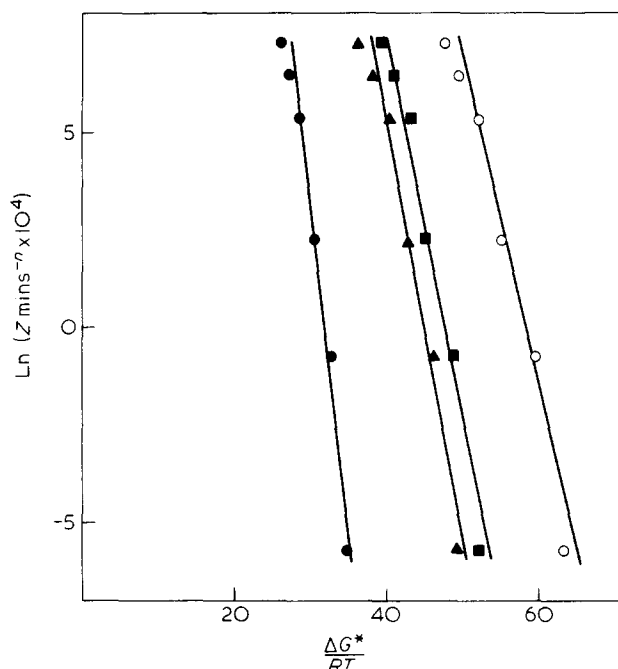


Figure 6 Evaluation of σ_e for sample B: 10 kJ mol^{-1} , slope 1.66; 15 kJ mol^{-1} , slope 1.03; 16 kJ mol^{-1} , slope 1.00; 20 kJ mol^{-1} , slope 0.84

The above analysis of the crystallization rate constants has made no allowance for polydispersity, but an alternative method for polydisperse samples has been proposed by Booth *et al.*⁹

It can be shown that

$$\ln Z = \text{constant} - \Delta G^*/RT_c \quad (5)$$

where ΔG^* is the free energy of formation of a nucleus of critical size and T_c is the crystallization temperature, and

$$\Delta G^*/RT_c = (0.4\sigma_e - 0.4RT_c \ln(I)) / (R(T_m^0 - T_c) - R^2T_c^2/8\bar{X}_n) \quad (6)$$

where \bar{X}_n is the number average chain length and I the probability that a sequence of chain units of length necessary to form a monolayer nucleus of the critical thickness, chosen so that chain folding is possible, does not contain a chain end. A value of I was calculated for each sample and hence from equation (6) $\Delta G^*/RT_c$ could then be calculated for various values of σ_e until the plot of $\ln(Z)$ vs. $\Delta G/RT$ had a slope of unity (Figure 6). This gave a value of σ_e of 16 kJ mol^{-1} . This value is similar to that observed from melting point studies¹⁰.

Secondary crystallization

There was a break in the time dependence of the crystallization isotherms at about 90–95% conversion, and this was attributed to the onset of a secondary process which predominated at the termination of the primary stage of spherulitic crystallization.

The analysis of the secondary process represents a problem since its exact mechanism is still unknown. Crystallization of interlamellar amorphous regions, lamella thickening, crystal perfecting and volume relaxation of voids have been variously invoked.

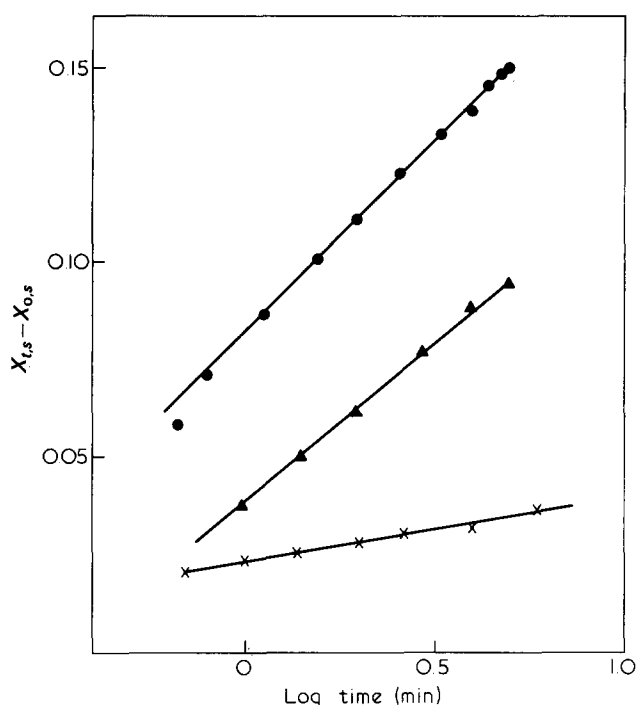


Figure 7 Logarithmic time dependence of secondary crystallization sample B: ●, 398.5 K; ▲, 399.5 K; X, 400.5 K

It has been described empirically by the relationship¹¹,

$$X_{t,s} - X_{0,s} = A + B \log(t - t_i) \quad (7)$$

in which $X_{t,s}$ and $X_{0,s}$ are the degrees of crystallinity developed at times t , and at the onset of the secondary process respectively. A and B are constants. This relationship was derived by analogy to volume relaxation of glassy polymers. The constant, A , contains a contribution from the relaxation time, τ , i.e. $A = -\ln(\tau)$, but its exact evaluation is limited by errors in selecting $X_{0,s}$ corresponding to t_i . Accordingly, rate parameters are not considered significant.

In these studies the higher sensitivities of the calorimeter were exploited by separate measurements on the development of the secondary process. The sensitivity of the calorimeter was increased towards the end of the primary process and the crystallization rate followed to the limiting baseline. Similar studies have been made by dilatometry.

Table 3 Secondary crystallization parameters

Sample No.	Method	Crystallization temperature (K)	n	Z_2^* (min ⁻¹)
B	Interfaced d.s.c.	398.5	1.0	0.130
		399.5	1.0	0.074
		400.5	1.0	0.046
C	Interfaced d.s.c.	399.5	1.0	0.104
		400.5	1.0	0.025
B	D.s.c.-2 ¹	397.5	0.8	0.270
		398.8	1.0	0.130
		399.8	1.1	0.080
C	D.s.c.-2 ¹	399.5	1.0	0.120
		400.5	1.0	0.160
B	Dilatometry	400.5	1.0	0.020
		401.5	1.0	0.007
C	Dilatometry	400.5	1.0	0.0048
		401.5	1.0	0.0021
		402.0	1.0	0.0014

Assuming that secondary crystallization involves the conversion of interlamellar regions, an Avrami rate equation, i.e. equation (2), with rate parameters, Z , and $n_2 = 1$ (for one dimensional growth) was to be expected. Z_2 and n_2 were determined over this terminal region, see Table 3, and compared with those determined separately by dilatometry. While the n_2 values were not significantly different from 1.0, the Z_2 values were substantially larger than those observed dilatometrically. These differences in the two techniques has been observed previously² and attributed to the nature of volume relaxation in a pseudo-solid material.

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