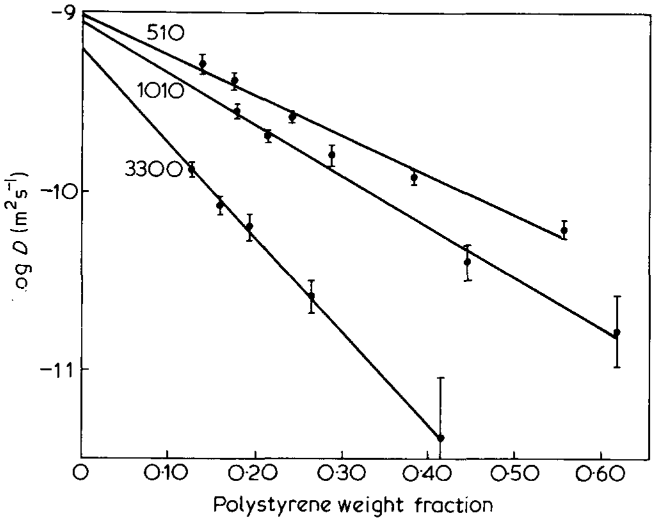

Figure 2 Concentration and molecular weight dependence of log*D* for short-chain polystyrenes in deuterochloroform

The negative $\partial D/\partial c$ behaviour observed in *Figure* 1 would indicate that for these short chains, the hydrodynamic forces dominate over the thermodynamic[7,8], and that the domination is inversely proportional to the molecular weights studied here, in a similar fashion to that observed by King *et al.*[7].

Assuming the chains can be approximated as hard spheres, the isotropic overall chain rotational correlation time, τ_r, can be estimated from the translational self-diffusion coefficients, D_t, through the classical relations $D_t = kT/6\pi\eta R$, $D_r = kT/8\pi\eta R^3$ and from $\tau_r = 1/6D_r$, such that

$$\tau_r = 0.22R^2/D_t \qquad (1)$$

where R, the radius of the sphere, has been estimated for these chains from the molecular weight and concentration-dependent radius of gyration relation of Jannink *et al.*[9]. At a polystyrene weight fraction of 0.20, $\tau_r = 3\times10^{-10}$ s, $9\pm1\times10^{-10}$ s, and $117\pm23\times10^{-10}$ s for molecular weights 510, 1010 and 3300, respectively. Lauprêtre *et al.*[10], through ${}^1HT$, and intrinsic viscosity data estimated τ_r for a short-chain polystyrene of molecular weight 600 to be 5×10^{-10} s at 25°C and 10% w/w polymer. From the data here, τ_r for a molecular weight 600 sample under similar conditons is estimated to be 3–4 $\times 10^{-10}$ s, which is in fair agreement with the above study.

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Differential scanning calorimetric study of the crystallization kinetics of polyglycolic acid at high undercooling

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The use of polyglycolic acid (PGA) as a synthetic absorbable suture material has led to extensive research into the structure and properties of this polymer and its development for other biomedical applications[1–8]. PGA is the simplest aliphatic polyester, and is usually produced in semi-crystalline form. The crystal structure of PGA was determined by X-ray diffraction; the dimensions of the orthorhombic unit cell are $a = 5.22$ Å, $b = 6.19$ Å, and c (the fibre axis) = 7.02 Å[9]. Two macromolecular chains in planar zig-zag conformation passing through the unit cell result in tight molecular packing and better hydrogen bonding[9]. Microscopy studies of the morphology of PGA crystallized at different temperatures have found that PGA crystallizes as spherulites, hedrites, and hedritic rosette depending on the crystallization conditions[10].

Research on the other semi-crystalline polymers, particularly linear polyethylene, has well established that the distinctive morphological features of a polymer are a consequence of the kinetic factors involved in the crystallization process[11–14]. Therefore, the different forms of PGA observed at different T_c must result from different crystallization mechanisms. Consequently, a thorough understanding of the kinetics of PGA crystallization is of both theoretical and practical interest, and helps in explaining both the fundamental mechanism involved in the formation of PGA's distinctive morphologies and their dependence on crystallization conditions. The practical value stems from the fact that many properties of semi-crystalline polymers, from the physical and mechanical to the thermodynamic, depend on their

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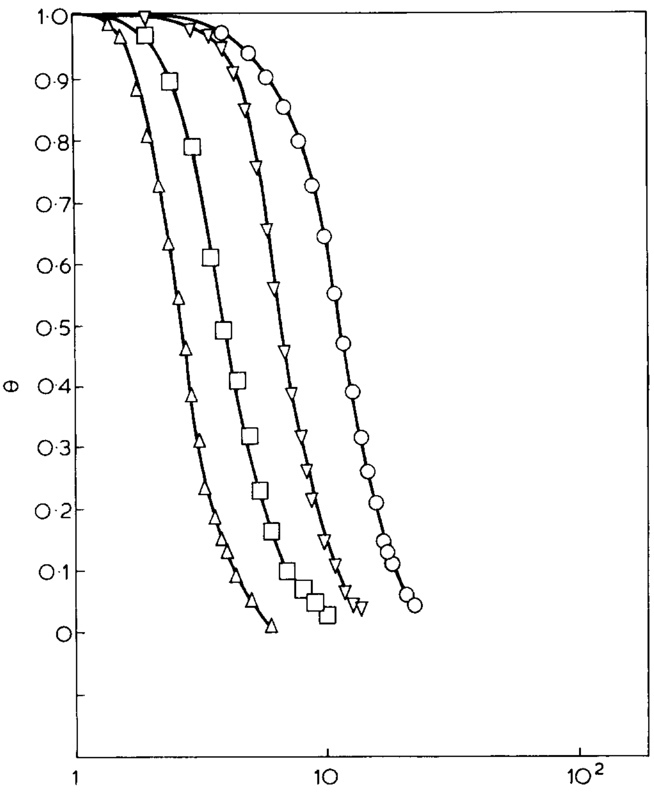

Figure 1 Avrami plots of θ, normalized fraction of untransformed PGA vs log t at indicated temperatures of crystallization. $\theta = 1 - [(1-\lambda)_t/(1-\lambda)_\infty]$; △, 474 K (201°C); □, 476 K (203°C); ▽, 478 K (205°C); ○, 480 K (207°C)

morphological structure[15–17]. An investigation of the crystallization mechanism responsible for the observed properties of PGA, particularly its biodegradability, is important in developing techniques by which the properties of such polymers may be designed specifically for certain applications. Published information on the crystallization kinetics of PGA is virtually nonexistent. A brief theoretical analysis of the crystallization kinetics of PGA at high undercooling and experimental findings will be presented.

The PGA used in this study was obtained in suture form from the American Cyanamid Company under the trade name Dexon^R. It is braided, and has been sterilized by ethylene oxide and packed in a sealed plastic bag. Its melting point is between 224–227°C. According to the manufacturer, the weight-average molecular weight ranges from 20 000 to about 145 000. The PGA suture was chopped into segments about 5 mm long and packed inside an aluminium sample pan designed for use in differential scanning calorimetry (d.s.c.). Seven to eight mg was used for each study. To ensure that samples absorbed no moisture, they were stored in a desiccator filled with P_2O_5 and anhydrous $CaSO_4$. A Perkin-Elmer DSC, model 1B, calibrated by the standard calibration kit provided by the manufacturer, was employed in this study.

Satisfactory kinetic data obtained by the d.s.c. in crystallization kinetic studies of polymers have been reported previously[18–19]. The d.s.c. possesses several advantages in such studies. It needs only minimal samples, and, more important, achieves a rapid thermal equilibrium, particularly at a high undercooling. The crystallization kinetics at high undercooling are of practical importance because fibres of PGA produced through melt-spinning are usually crystallized at high undercooling. Therefore, the use of d.s.c. gives the opportunity to obtain crystallization kinetic data at the crystallization temperature close to that of manufacturing.

All samples were heated to 250°C (~20°C above the melting point of PGA) for 25 min to ensure no trace of crystallinity remained. The melted samples were then rapidly cooled to the desired temperatures of crystallization (T_c), which ranged from 201 to 207°C. Studies at T_c greater than 207°C were not conducted by the d.s.c. due to the much longer time required for the completion of crystallization. Over the studied temperature range, it was found that an average of ~30 s was needed to establish the new thermal equilibrium. This duration depended on the weight of the samples and the degree of undercooling. Isothermal crystallization started when the new equilibrium was reached and continued until the crystallization was almost complete, as determined by the restoration of the baseline. The area under the crystallization curve at the desired time interval was measured by a polar planimeter, and the corresponding percentage of crystallinity at each desired time interval was calculated in the usual expression[18,20]. A value of 45.7 cal g^{-1} for the heat of fusion of 100% crystallized PGA was used for the crystallinity calculation[5]. Because the rate of secondary crystallization in the later (or tail) stage was extremely slow, the percentage of crystallinity at infinite time $(1-\lambda)_\infty$ was obtained by a previously successful extrapolation method[14,18,21,22].

The series of crystallization isotherms at different T_c's shown in *Figure* 1 were obtained by the usual form of

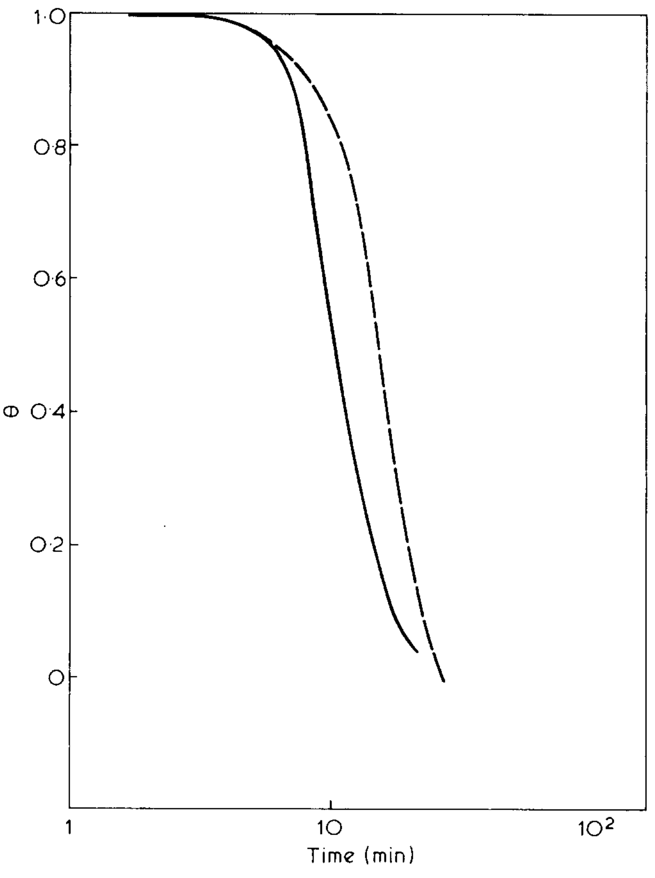

Figure 2 Superimposing (——), an experimental isotherm (T_c = 205°C) with (— — —) a theoretical Avrami isotherm of $n = 4$

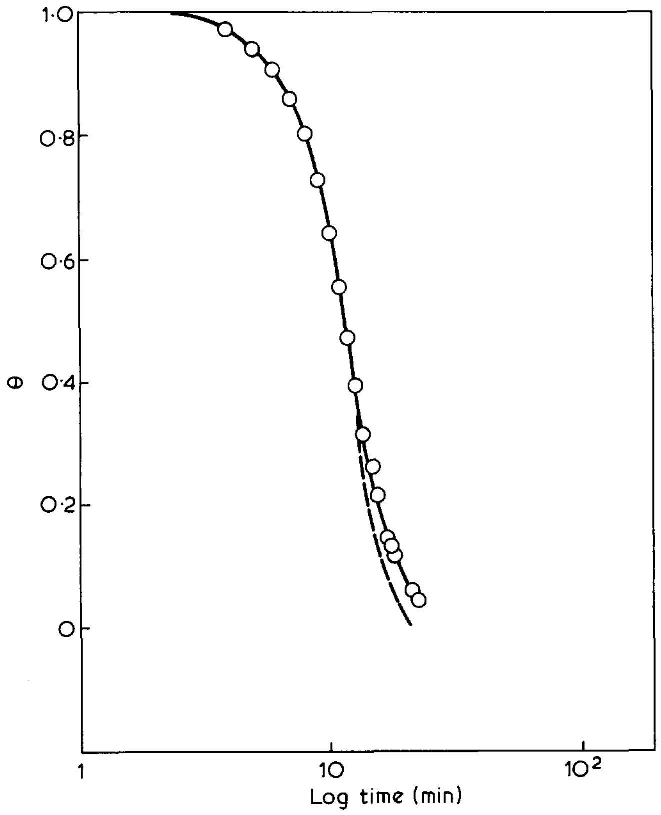

Figure 3 Superimposing (——), an experimental isotherm (T_c = 207°C) with (— — —), a theoretical Avrami isotherm of n = 4

Avrami's equation, $\ln\theta = Kt^n$, θ was calculated from the equation: $1-\theta=(1-\lambda)_t/(1-\lambda)_\infty$. This figure exhibits the characteristics of a crystallization isotherm: an induction period, an accelerated stage, and a slowly tailed period. The half time (when $\theta=0.5$) increased from 2.7 min at $T_c=201$°C to 11 min at $T_c=207$°C. At higher T_c, a further increase in half time would occur. Within the studied temperature range, the isotherms are closely arranged along the time scale. Should crystallization occur at even higher T_c, the dependence of the rate of crystallization on temperature should be even stronger.

The agreement of the experimental isotherms with the theory was analysed further by shifting the experimental isotherm along the time axis, and superimposing it with theoretical isotherms, e.g. $n=4,3,2$ until the best fit was reached. By this method, one can determine the Avrami time exponent n. *Figures* 2 and 3 show these superimpositions at $T_c=205$ and 207°C respectively. It was found that the experimental isotherms followed the theoretical $n=4$ isotherms up to a certain relative degree of transformation. The extent of adherence to the theoretical isotherms depended on the crystallization temperature, and became better as the T_c increased. For example, at $T_c=207$°C, the agreement between theoretical and experimental isotherms was up to 63% relative to the degree of transformation. However, at $T_c=205$°C, the extent of adherence was less than 10%. Those experimental isotherms of T_c lower than 205°C did not correspond to the theoretical isotherms $n=4$ or 3 or 2 over the entire range of transformation. These experimental isotherms showed a faster relative degree of transformation than the theoretical $n=4$ isotherm, especially at the initial stage of crystallization. This suggests that at T_c lower than 205°C the crystallization of PGA may start before the sample can reach the desired thermal equilibrium on the sample holder of the d.s.c.

This dependence on temperature of the adherence of the experimental isotherms to the theoretical ones has also been reported in the polyethylene system[21]. A twofold general conclusion follows. The experimental isotherms of PGA do not adhere to the theoretical Avrami isotherms throughout the whole crystallization transformation; better adherence could be achieved at higher T_c. More useful information could be obtained by examining the effect of the molecular weight of PGA on its crystallization kinetics. This investigation will be the subject of a separate study.

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