electrode have been measured with a static potentiometer in the dark and under irradiation with light[2] (Fig. 1). Anodic current which is proportional to the intensity of light begins to flow for wavelengths shorter than 415 nm, that is 3.0 eV, which corresponds to the band gap of TiO_2. The current reaches saturation at potentials positive relative to a saturated calomel electrode (SCE). These facts suggest that the anodic reaction is related to the formation of holes in the valence band by light excitation. Oxygen evolution was confirmed by several means of analytical measurements[3,4]. Oxygen evolution occurs at −0.5 V (SCE) in an aqueous electrolyte of *p*H 4.7; this is more negative than the standard potential. We have termed such behaviour "photosensitized electrolytic oxidation" (ref. 2). When halogen ions were introduced in the electrolyte, they were also oxidized through the suggested mechanism of photosensitized electrolytic oxidation. This also occurred with other types of n-type semiconductor such as ZnO and CdS (ref. 5). We believe therefore that the oxygen evolution reaction on the TiO_2 electrode under irradiation belongs to the first category described above.

We then constructed an electrochemical cell in which a TiO_2 electrode was connected with a platinum black electrode through an external load (Fig. 2). When the surface of the TiO_2 electrode was irradiated, current flowed from the platinum electrode to the TiO_2 electrode through the external circuit. The direction of the current reveals that the oxidation reaction (oxygen evolution) occurs at the TiO_2 electrode and reduction (hydrogen evolution) at the platinum black electrode.

We suggest that water can be decomposed by visible light into oxygen and hydrogen, without the application of any external voltage, according to the following schemes:

$$TiO_2 + 2\,h\nu \rightarrow 2\,e^- + 2\,p^+ \quad (1)$$
(excitation of TiO_2 by light)

$$2\,p^+ + H_2O \rightarrow \tfrac{1}{2}\,O_2 + 2\,H^+ \quad (2)$$
(at the TiO_2 electrode)

$$2\,e^- + 2\,H^+ \rightarrow H_2 \quad (3)$$
(at the platinum electrode)

The overall reaction is

$$H_2O + 2\,h\nu \rightarrow \tfrac{1}{2}\,O_2 + H_2 \quad (4)$$

The starting potential of the oxidation reaction at the TiO_2 electrode corresponds almost exactly to the flatband potential which is constant in the electrolyte solution of a given *p*H. To

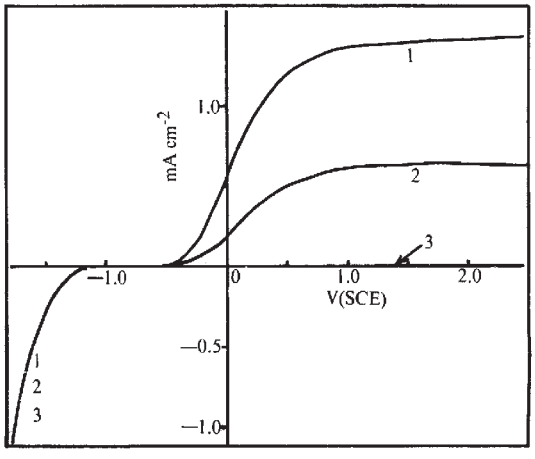

Fig. 1 Current–voltage curves for TiO_2 n-type semiconductor. A single crystal wafer of n-type TiO_2 (rutile) was used after treatment at 700° C at 10^{-4} ~10^{-5} torr for roughly 4 h to increase the conductivity of the crystal. This wafer was approximately 1.5 mm thick and the exposed (001) surface area was approximately 1.0 cm². Indium was evaporated on to one side of the surface to ensure ohmic contact and a copper lead wire was connected on the indium layer with silver paste. All other surfaces were sealed by epoxy resin.

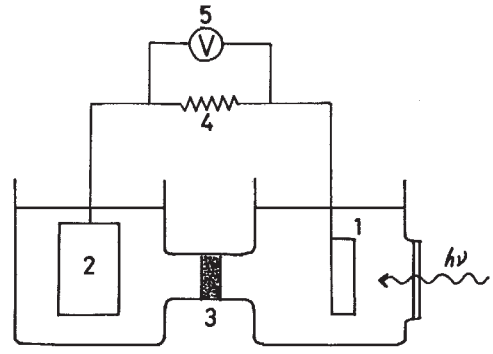

Fig. 2 Electrochemical cell in which the TiO_2 electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 cm².

increase the efficiency of the decomposition process, more reducible species, for example, dissolved oxygen or Fe^{3+} ions, must be added in the compartment of the platinum electrode. When Fe^{3+} ions were added, the current produced under irradiation increased. Currents of a few mA flowed when the TiO_2 electrode (surface area ~1 cm²) was irradiated by a 500 W xenon lamp; we estimate the quantum efficiency in this case to be approximately 0.1. The e.m.f. of the cell was measured to be up to 0.5 V.

It is possible that the hydrogen evolution reaction shifts towards more positive potential than normal when suitable p-type semiconductor electrodes are irradiated, in the same way that photosensitized oxygen evolution occurs with n-type semiconductor electrodes. If such a p-type semiconductor electrode is used instead of the platinum electrode, electrochemical photolysis of water may occur more effectively.

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BIOLOGICAL SCIENCES

One and Two-dimensional Structure of Alpha-Helix and Beta-Sheet Forms of Poly(L-Alanine) shown by Specific Heat Measurements at Low Temperatures (1.5–20 K)

HOMOPOLYPEPTIDES provide good model systems for various aspects of proteins[1,2]. Recent advances in high polymer and solid state physics have enabled the vibrational aspects of the simpler homopolypeptides to be treated as normal—but complicated—polymers by the theoretical techniques of lattice dynamics based on the experimental methods of neutron, infrared and Raman spectroscopy. Basically, however, these latter methods examine the optical vibrational modes of a system, that is, those modes which are of energy higher than, for example, 70 cm^{-1}. The important lower-energy modes are

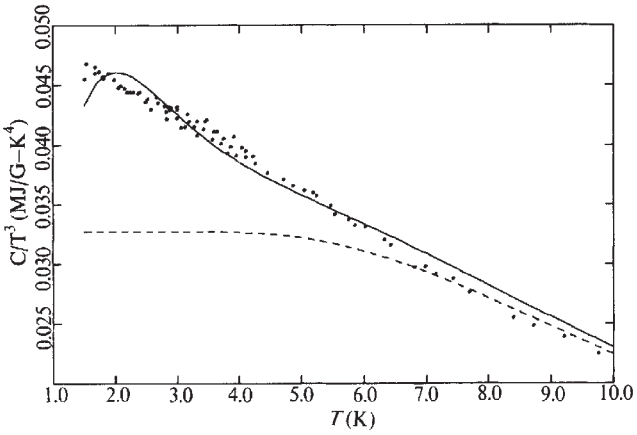

Fig. 1 Poly(L-alanine) in alpha-helix form: specific heat divided by cube of temperature versus temperature: ●, experimental points; ——, fitted to a Tarasov one and three-dimensional model, with an independent set of vibrators (Einstein mode). Compare - - -, a fit to the one and three-dimensional model only.

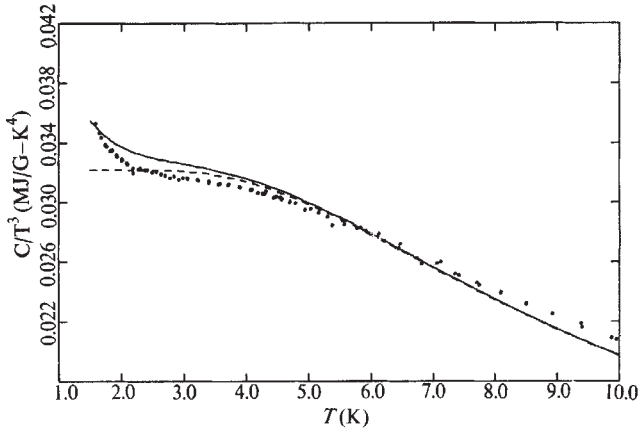

Fig. 2 Poly(L-alanine) in beta-sheet form: specific heat divided by cube of temperature versus temperature: ●, experimental points; ——, fitted to a Tarasov one and two-dimensional model, with an independent set of vibrators (Einstein mode). Compare - - -, a fit to the two and three-dimensional model only.

well examined by specific heat measurements, which do not require single crystal samples, at low temperatures (for example, 1–20 K, where only the acoustic modes are excited thermally to any appreciable extent—1 K ~ 0.7 cm^{-1}). The low temperature measurements presented here are the first made on a polypeptide in alpha and beta-conformation, and clearly show the one-dimensional nature of the α-helix and the two-dimensional nature of the β-sheet structure. Quantitatively, these measurements also provide tests of theories of published vibrational models of homopolypeptides, and will give hydrogen bond strengths.

At sufficiently low temperatures, the specific heat, C, of any one-dimensional non-metallic solid is proportional[3] to temperature T^1 (measured in K from absolute zero), for a two-dimensional solid $C \propto T^2$, and for a three-dimensional solid $C \propto T^3$. The constants of proportionality depend on the interatomic forces, and are usually expressed as Debye "effective temperatures" θ_1, θ_2, θ_3 respectively. For simplicity, we use the Tarasov model[4,5].

Our poly(L-alanine) (PLA) was polymerized by the N-carboxyanhydride method[6] by Dr Masanao Oya into predominantly α and β forms[7].

Details of the sample characterization and of the specific heat apparatus and methods are given elsewhere[8,9].

The results above 10 K are easily fitted to the Tarasov two-parameter models, showing definite one and three-dimensional (α) or two and three-dimensional (β) molecular contributions to the specific heat. (The gram-molecular weight of the vibrating unit was taken as 71.08.) Figs. 1 and 2 show the results below 10 K, conveniently scaled. For both forms the experimental data rise markedly above the Tarasov fits extended to lower temperatures (dashed lines) (α: $\theta_1 = 321$ K, $\theta_3 = 51$ K; β: $\theta_2 = 156$ K, $\theta_3 = 34.9$ K), giving evidence for another contribution to the specific heat. Specific heat bumps have been observed in other polymers and glasses[8,9]. We, too, assume empirically that the solid contains a small mole-fraction f of Einstein oscillators[3] with characteristic temperature θ_E. The corresponding fits (that is, α, one and three-dimensional Tarasov model, plus a set of independent oscillators; β, one and two-dimensional Tarasov model, plus a set of independent oscillators) are quite good (standard deviations: α 4.2%, β 3.1%) with parameters for the α-form $\theta_1 = 321$ K (1.9%), $\theta_3 = 51$ K (3.6%), $\theta_E = 9.95$ K (0.5%), $f = 0.001\,75$ (0.1%), and for the β-form $\theta_2 = 156$ K (6.6%), $\theta_3 = 34.9$ K (0.3%), $\theta_E = 2.5$ K (0.01%) and $f = 0.000\,040$ (0.05%). The numbers (x%) are the change in the s.d. of the total specific heat fit when the parameter value is increased by 5% from the values quoted. Note that the fit is relatively insensitive to the value of f.

The origin of the Einstein modes is not clear[8,9]. It has been suggested[10] that a tunnelling state due to the rotation of an (impurity) hydroxyl group would have an energy splitting of about 10^{-4} eV, and so could be an explanation for the specific heat bump observed in PLA.

A priori calculations, via lattice dynamics, have been made on PLA in the α[11–13] and β[14] conformations, but the published data have not yet been presented with sufficient resolution for comparison with our results. Thus, we hope that theorists will be encouraged to make the necessary relatively small extensions to their elaborate computer calculations.

These measurements will be valuable in the basic thermodynamics of polypeptides[15], and in theories of enzyme action, where the low-frequency modes of vibration may well be important. This method might also be a feasible way of estimating the proportion of α to β structure present in an enzyme.

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Note added in proof. Reasonable agreement has been found between our α-PLA data and those calculated from the frequency distribution of ref. 11 (B. Fanconi, private communication). The specific heat of α-PLA has been measured (1.3–4.3 K) also by P. Delhaes, M. Daurel and E. Dupart (*CR Acad. Sci.*, **274**, 308; 1972).

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Performance of Composite Foetal Hearts

WE wished to study the interactions between pieces of foetal heart tissue of different origins, to see if they could influence the healing of myocardial infarctions, or the pacing of the ventricles in heart block. We had established a baseline for the performance of intact foetal hearts and slabs of foetal heart tissue in culture, and related it to the stage of development in rat, mouse, cat, rabbit and man, showing that less developed foetal hearts live longer, and beat better than older foetal hearts[1]. We extended this technique to examine the effects of parts of foetal hearts on each other, because it gives consistent results, uncomplicated by rejection, other than that originating in the cells concerned. We used hearts of litter mates, hearts from different species, at different stages of development, and across the species barrier. As controls we used hearts sectioned and re-assembled.

Hearts were cut vertically into two along the atrial and ventricular septa and cultured with the cut surfaces touching in as nearly normal position as possible. They were put on stainless steel wire mesh—bridge-shaped grids—with a mesh size of 0.1 mm, and were arranged so that the lower surfaces of the hearts just touched the culture medium (Burroughs Wellcome 199 plus 35% colostrum-deprived calf serum, plus 50 μg/ml. insulin, plus 0.1 μg/ml. cortisol). The cultures were incubated at 37° C, in 95% oxygen and 5% carbon dioxide, as described before[1].

Four series of experiments were done and each examined one set of variables. The beating rates of the two halves were recorded after 12, 19 and 24 h and thereafter every 24 h. The time taken for the beating of the half hearts to synchronize was noted, and then a sample of joined hearts from each series was placed in 10% formal saline and examined histologically. The hearts were serially sectioned at 7 μm, and stained with Erhlich's haematoxylin and eosin, or Verhoeff's elastic stain and Van Gieson stain.

The control hearts (group 1) consisted of mouse and rat hearts sectioned and rejoined at various stages of development.

Mouse hearts were three 12-day (55% term), ten 13-day (59% term), three 15-day (68% term), three 16-day (73% term), and thirteen 17.5-day (80% term) hearts. Two 16-day foetal rat hearts (68% term) were included together with the 15-day mouse hearts, to serve as a control for group 3 (described later).

Mouse and rat hearts from different foetuses in the same litter, sectioned and cultured in apposition, at various stages of development constituted group 2. The mouse litter mate hearts were three 12-day (55% term), four 15-day (68% term), six 16-day (73% term) and seventeen 19.5-day (88% term). The rat litter mate hearts were four 16-day (68% term).

Six hearts from different species at the same stage of development, cultured in apposition, constituted group 3. These were 15-day (68% term) mouse hearts and 16-day (also 68% term) rat hearts.

Group 4 consisted of five hearts at different stages of development from cat foetuses at 21 days (33% term) and mouse foetuses at 18 days (82% term).

All composite hearts except the mouse/cat chimeras, which became contaminated, were beating synchronously after 144 h. Less developed hearts synchronized earlier than more fully developed foetal hearts. In all cultures, the beating rate assumed by the composite organ was the rate of the faster half-heart.

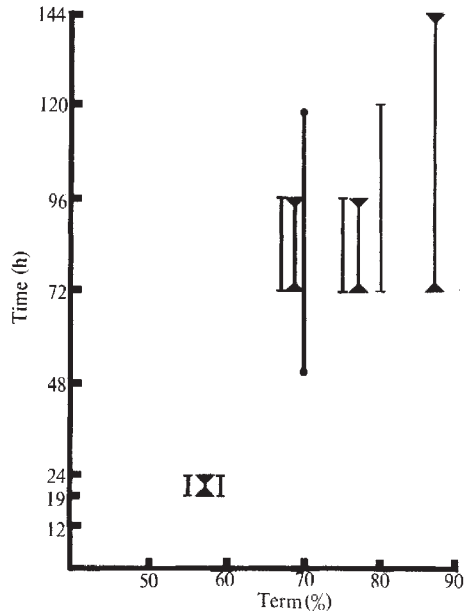

Fig. 1 Relation of heart maturity to synchronized beating. Observed time of onset of synchronized beating and the time when all the hearts in the series were beating synchronously related to the percentage of full term development. Since we only removed the hearts from the incubator at set intervals to observe the beating, the actual time of onset is not recorded. ——, Rejoined heart; ▶——◀ composite heart, same species; ●——●, composite heart, different species.

There was no significant difference in performance between composite hearts made from halves of the same or different species, or noticeable difference from the survival and performance of intact hearts at comparable stages of development.

The record of beating performance is of necessity incomplete, because it was only possible to examine the cultures by removing them from their optimal environment in the incubator, with consequent damage. Thus our results relate to discrete observations at 12, 19, 24, 48, 72, 96, 120 and 144 h. We used alternate observations as an opportunity to change the culture medium.

All hearts were firmly adherent at the time of fixing. They were mostly taken for section as soon as the whole batch was beating synchronously. Some were left for comparison with intact hearts. The young hearts achieved synchronization sooner than the more mature hearts. They also had less collagen in the junctional area, even when cultured for longer periods, comparable with the time taken for the more mature hearts to achieve synchrony. In all composite hearts, collagen never forms an unbroken barrier across the join. Heart muscle is continuous with the muscle on the other side. No collagen was deposited in the junctional area in hearts whose components were younger than 60% of term. The cells in the junctional areas tended to align themselves to lie along the junctions, so that the line of union was obvious. We could see no evidence of tissue conflict in the junctional areas, but in the more mature hearts the presence of collagen suggests the formation of scar tissue rather than muscle fusion.

When the fusion of foetal gonad and lung tissues from widely different species was demonstrated[4–6], the connecting and epithelial tissues migrated and fused intimately, and we hoped for a similar result. Certainly with the young foetal hearts the muscle cells joined and there was no evidence of collagen formation; with the older hearts, however, some collagen was formed. One possible reason for this is mechanical; the older hearts are firmer than the younger hearts. When they are cut in half, they do not flatten and spread out as do the younger hearts and each beat moves the whole mass of muscle more violently, and prevents the cut surfaces staying in close contact. Another reason may be that the cells in the older hearts are