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Technique for the study of diffusion of large molecules in polymers based on infrared microdensitometry

THE diffusion of small molecules (in the gaseous, vapour or liquid phases) through polymeric matrices has been the subject of much study[1], and the techniques for such studies are, by and large, well established. Similar studies in the case of large molecules (broadly speaking, those forming solids at room temperature) in polymers, including polymeric self-diffusion, have been more rare[2–5]. Existing techniques for measurements of the diffusion of large molecules in synthetic polymers rely mainly on radioactive labelling of the diffusants. Nuclear magnetic resonance (NMR) has been used[5], but is limited to measurements of diffusion in the melt, and also to relatively high diffusion rates[5]. Measurements involving radioactively labelled diffusants have two major shortcomings, in addition to the necessity of having to obtain the required labelled material: they fail with diffusants which are surface active with respect to the polymer[2], and they may involve significant interfacial resistance which the method does not reveal[2,3].

We have developed a simple technique for the measurement of the translational diffusion of large molecules in polymeric matrices, based on microdensitometry in the infrared. Essentially, a step function in the concentration of the diffusant is set up within the bulk matrix, and diffusion is allowed to occur at the required pressure and temperature. At some known time the diffusion is effectively terminated by quenching, and a thin slice through the composite centre is removed and scanned in the microdensitometer (Fig. 1).

To obtain a measure of the concentration of the diffusant it is necessary that it absorb at some infrared frequency unaffected by the bulk polymer, and the scanning of the thin section is, therefore, carried out at that frequency. A commercial double-beam infrared spectrometer has been adapted for the purpose, and is capable of achieving a resolution of better than 100 μm in lateral scan. Figure 2 shows the expected and observed concentration profiles for a typical run. The value of the diffusion coefficient D, is readily evaluated from the shape of the profile[6]. It is also possible to evaluate the concentration dependence of D, where it is significant. Interface resistance, if any, is revealed by discontinuities in the broadened concentration profile[6]. Values of D in the range 10^{-5}–10^{-10} cm^2 s^{-1} may be obtained in times of the order of 1–30 d, and the estimated errors are of the order of 15%.

We have studied the diffusion of various long-chain, n-alkyl amides in low density polyethylene at about the melting temperature. The dependence on temperature and chain length is summarised in Fig. 3. The discontinuity in the slope of the Arrhenius plot as the temperature is raised is probably the result of the breakdown of the crystalline lamellae in the polythene, which at temperatures below about 80 °C comprise some 60% of the polymer; this leads to a decrease in the tortuosity of the path taken by the amide chains in the amorphous polymer regions, over and above the usual temperature dependence.

The diffusional behaviour of longer molecules in polymeric matrices is being explored.

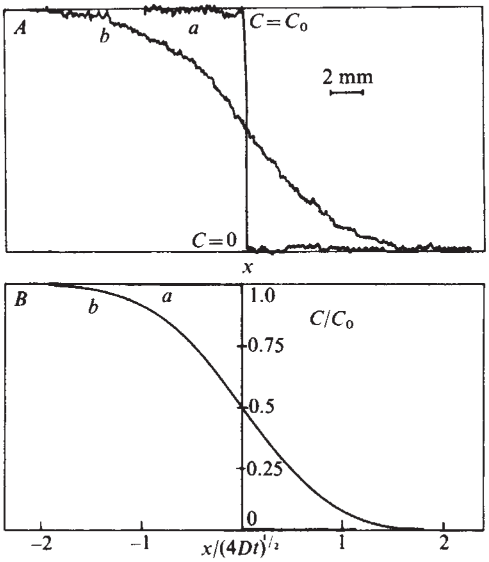

Fig. 2 Concentration profiles. *A*, observed profiles: *a*, $t \approx 0$ (initial step function; $t = 54$ s., $C_0 = 0.5\%$ stearamide in low density polythene (LDPE), weight ratio); *b*, after time $t (t = 5.22 \times 10^4$ s., $T = 130$ °C; C_0 as in (*a*)). Both profiles scanned at 1,660 cm^{-1}, an amide absorption frequency. *B*, calculated profiles[6].

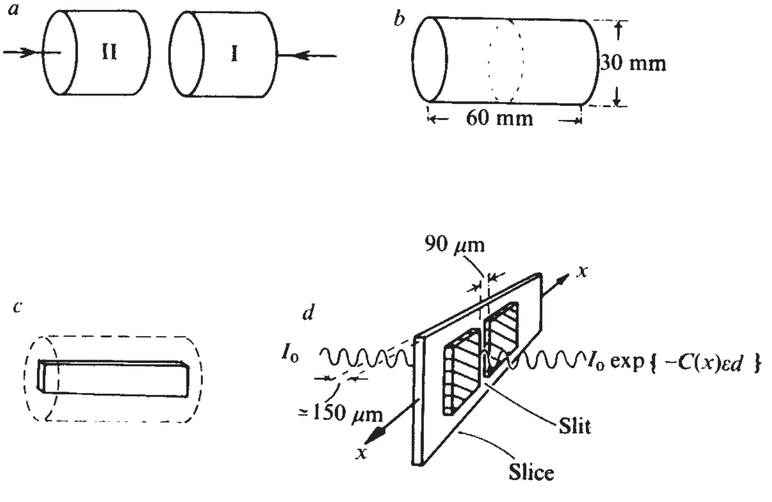

Fig. 1 Outline of experimental procedure: *a*, Specimen I—pure polymer and specimen II—polymer + diffusant, dispersed uniformly (about 0.1—1 % w/w); *b*, specimen I and II joined together; *c*, slice removed from centre of composite; *d*, slice scanned in x direction for concentration profile. ε, Extinction coefficient of the diffusant at the chosen infrared wavelength, and the concentration $C(x)$ as x varies is recorded directly (Fig. 2) using a linear–log convertor.

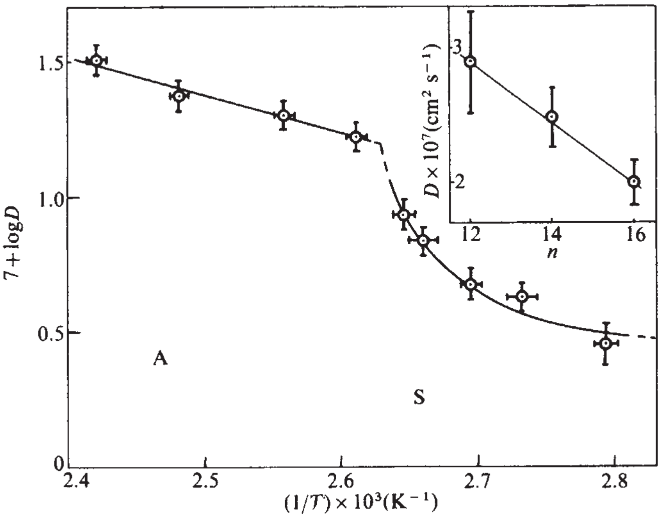

Fig. 3 Variation of the diffusion constant, *D*, of stearamide in LDPE as a function of temperature, *T*, about the melting region of the polymer: A, amorphous regime; S, semicrystalline regime. Inset, Diffusion constants, *D*, of $CH_3(CH_2)_nCONH_2$ in LDPE as a function of *n*, at 118 °C. *D* decreases as diffusant length increases.

We thank ICI Plastics Division (Welwyn) for preparing the materials, and one of us (J.K.) thanks Dow Corning Chemicals for a maintenance grant. We are also grateful to Professor D. Tabor for encouragement.

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Received July 22; accepted August 22, 1975.

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Palaeotemperatures from tree rings and the D/H ratio of cellulose as a biochemical thermometer

DENDROCHRONOLOGY can provide sequences of tree rings from various parts of the world. The wood making up these rings can be accurately dated to ±1 yr. Samples can be obtained going back a considerable time, for example wood from *Pinus aristata* (Bristle Cone Pine) trees can be obtained which goes back beyond 9,000 yr BP. If the isotopic ratios of the elements in the individual constituents in the wood contain a record of past climate, it may enable a curve of a climatic variable like temperature to be determined on a time base accurate to ±1 yr.

One might expect the biochemical pathways leading from CO_2 and water to the compounds that make up the wood to have isotopic effects. The question is whether the isotopic effects have significant temperature coefficients. If they do, one would have in effect a "biochemical thermometer". Here we report the existence of such a biochemical thermometer.

To study how the isotopic composition of the constituents of wood varies with temperature we have studied wood laid down during the course of one year by a *Pinus radiata* (Monterey Pine) tree growing in Hamilton, New Zealand. This particular system was chosen because at this location *P. radiata* grows throughout the year[1,2]. Wide rings (2 cm) are laid down which enables different parts of the ring, and therefore wood laid down at different temperatures, to be sampled.

The isotopic composition of the atmospheric precipitation varies only slightly between winter and summer (about 20‰) in deuterium content[3] so that any temperature effects are not masked by changing isotopic composition of the atmospheric precipitation during the year. During the year in Hamilton both the monthly mean maximum daily temperature and the monthly mean daily temperature vary through a cycle with an amplitude of 10 °C. Thus the method enables even small temperature-induced isotopic effects to be detected.

In Fig. 1 we present a plot of the deuterium/hydrogen (D/H) ratio of the C–H hydrogens of cellulose across two rings laid down during the period 1919–20 by a *P. radiata* tree growing in Hamilton, New Zealand. Cellulose was prepared by the standard techniques of wood chemistry (see for example ref. 4). Before the cellulose was combusted the exchangeable hydrogens on the hydroxyl groups were brought to a standard D/H by equilibration with water of known D/H (7 d, 95 °C). The results are reported in per mille deviation from standard mean ocean water[5]. The system is at least 30‰ depleted in the summer as compared with the winter and seems to record the annual temperature cycle. It should be noted that the isotopic composition of the cellulose varies in the opposite direction to the isotopic composition of the atmospheric precipitation, which is more depleted in deuterium in the winter and less depleted in the summer. Thus the effect could not be the result of the changing of the isotopic composition of the precipitation. Similarly the results could not reflect changes in the isotopic composition of cell sap since cell sap would, if anything,

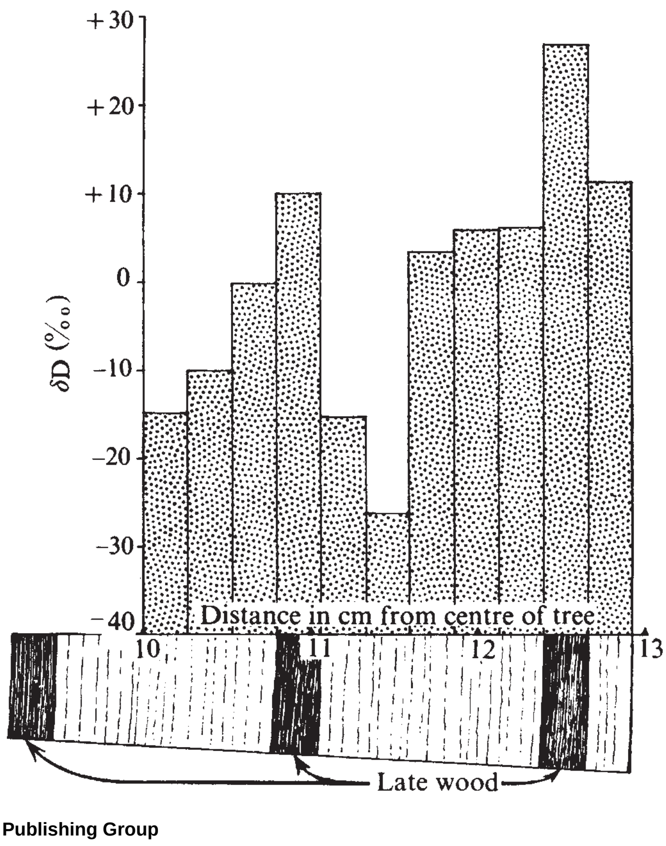

Fig. 1 Variation in isotopic ratio of the C–H hydrogens in cellulose across tree rings.