We feel this work demonstrates the care needed when ascribing products to a catalytic reaction.

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Nuclear Magnetic Resonance in 'Monocrystalline' Polyoxymethylene

GENERAL equations have been derived for the second moment of a nuclear magnetic resonance line in an oriented polymer[1] on the basis of the Van Vleck formula[2]. These equations were verified for 'monocrystalline' polyoxymethylene obtained from a trioxane monocrystal by solid-phase radiation-induced polymerization.

Monocrystals of polyoxymethylene, 5–6 mm, were placed into a thin-walled glass ampoule in a way that their axes were normal to that of the ampoule. Nuclear magnetic resonance spectra were obtained at 77° K at various angles, θ', between the crystal axis and the magnetic field. A polycrystalline sample—small crystals disorderly packed into an ampoule—was prepared along with the monocrystals. The second moment value for the nuclear magnetic resonance line $\Delta H_2^2 = 18.5 \pm 0.5$ G^2 was determined for this sample. The ΔH_2^2 value was calculated theoretically for a known polyformaldehyde structure[3] and appeared to be 19·9 G^2. The discrepancy of 1·5 G^2 is somewhat in excess over the experimental error and may be considered as due to deviation of the C–H separation in the CH$_2$-group from the value of 1·09 Å

that was taken for calculation, or of the H–C–H angle from the tetrahedric form, or else to conservation of a certain degree of molecular motion in the polymer at the liquid nitrogen temperature. The ΔH_2^2 value as a function of θ' is shown in Fig. 1 for 'monocrystalline' samples. It was ascertained by X-ray analysis[4] that polyoxymethylene 'monocrystals' obtained by radiation-induced polymerization consist in reality of crystallites of a dual orientation: the crystallite axes either coinciding with that of the macroscopic crystal, or inclined to it at an angle of 76° 7'. The theoretical ΔH_2^2–θ' function was calculated for this structure, allowance being made for contributions from intra- and inter-molecular proton interaction. For proton separations greater than 5 Å, summation in the Van Vleck formula was replaced by integration. It will be seen from Fig. 1 that the calculated ΔH_2^2 values are essentially close to experimental ones. Yet they are somewhat higher than the latter: by 0·5 G^2 at $\theta' = 0$ and by 2 G^2 at $\theta' \geqslant 45°$. As with the polycrystalline sample, the discrepancy may be partially due to inaccuracy of calculation. But molecular motion seems to be the main reason for it. Increase in the difference between theoretical and experimental ΔH_2^2 values with increasing θ' might be an indication of a non-isotropic nature of molecular motion resulting in a certain narrowing of the nuclear magnetic resonance line.

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Thermal Helix-coil Transition in Poly-γ-benzyl-L-glutamate

THE thermally induced transition of solvated poly-γ-benzyl-L-glutamate (PBG) molecules from a helical to a random coil configuration has been the subject of recent investigations[1-3]. Similar transitions, brought about by temperature or by other changes, occur in several poly-amino-acids[4], and the general phenomenon has been treated theoretically by a number of authors[5].

One of the results which emerges from such treatments is that under certain limiting conditions the transition may be regarded as a co-operative first order change, analogous in some ways to melting. Experimentally it is found, however, that the transition is 'smeared' over a number of degrees and that an observable helix–random coil equilibrium exists in the vicinity of the transition temperature, T_c. By the application of the van't Hoff equation to this equilibrium an apparent heat of transition, ΔH, may be calculated. In the formulation of Zimm and Bragg[3] and of Applequist[6] ΔH is related to the true heat of transition ΔH_0 by the equation:

$$\Delta H = \frac{\Delta H_0}{\sigma^{1/2}} \qquad (1)$$

where ΔH_0 is the heat associated with the transfer of one amide residue from a random coil configuration to the end of an existing helical section, and σ is a parameter related to the average length of the helical sections at T_c. Zimm, Doty and Iso[3] have provided an estimate of 2×10^{-4} for σ in the PBG–dichloroacetic acid (DCA)–dichloroethane (DCE) system from an examination of the effect of chain-length on the shape of the transition curve, and thus, using equation 1, ΔH_0 may be derived.
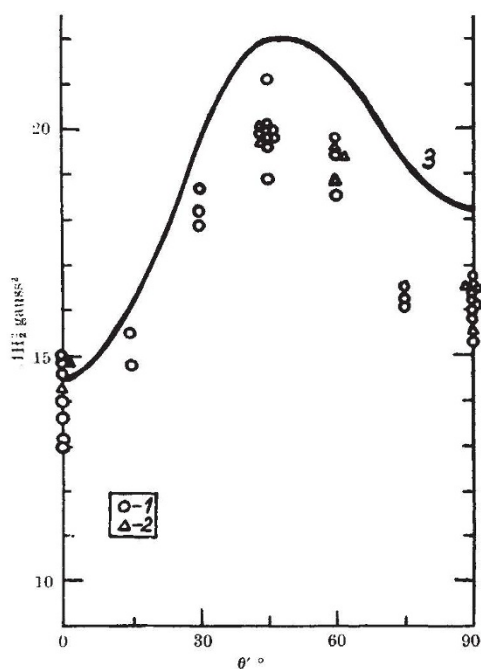

Fig. 1. Second moment of the nuclear magnetic resonance line (ΔH_2^2) as a function of the angle θ' between the 'monocrystal' axis and the magnetic field. 1 and 2, Experimental values for two samples; 3, theoretical function (full line)