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Self-diffusion of short-chain polystyrenes in deuterochloroform solution

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(*Received* 14 *June* 1980)

This report details investigations concerning determination of the translational self-diffusion coefficients for monodisperse short-chain polystyrenes ($M = 510$, 1010, and 3300, $\bar{M}_w/\bar{M}_n \leqslant 1.11$) in deuterochloroform (99.8%) at 25°C within the polymer weight fraction interval $\omega_{PS} = 0.13$–0.61, through proton (99.6 MHz) pulsed magnetic field gradient spin–echo nuclear magnetic resonance measurements. The technique employed has been described elsewhere[1,2] and uses a pulsed field gradient, generated through the software-controlled spectrometer (JEOL FX-100) homogeneity-spoiling (homospoil) coils. Fourier transformation of the spin–echoes allows determination of the D and T_2 values from the signal attenuation with increasing gradient duration, for an observed individual proton spin group in the molecule.

The polystyrene samples, obtained from Polymer Laboratories Ltd, and used as received, were chain-terminated with an n-butyl group. This terminal methylene chain group provided an ideal proton signal with relatively long values of T_2 and, unlike the aromatic protons, did not display disturbing J modulation effects upon Fourier transformation of the accumulated spin–echoes. The T_2 values, measured in the same manner as in the diffusion experiment albeit with the gradient switched-off, were of the order of 120–160 ms and decreased with molecular weight. No drastic changes in T_2 could be observed around the critical concentration, c^*, for coil overlap (evaluated earlier[3] to be approximately $\omega_{PS} = 0.43$, 0.33 and 0.19 for molecular weights 510, 1010, and 3300, respectively).

As the diffusion experiment measures spatial proton displacements during a time duration of roughly 0.1 s, which corresponds to a traversed distance of approximately 5×10^4 Å (assuming $D \sim 10^{-10}\ \mathrm{m^2\ s^{-1}}$) or about 100–500 times the chain diameters, chain segment reorientational displacements and overall chain rotation should not contribute and the measured quantity should indeed by the self-diffusion coefficient, similar to earlier arguments presented elsewhere[4].

For these short-chain polystyrenes, well below the critical molecular weight for the occurrence of intramolecular entanglements in solution[5], the self-diffusion coefficients were found to decrease rapidly with increasing concentration and molecular weight (*Figure* 1), such that log D decreased linearly with increasing concentration, the slopes increasing with molecular weight (*Figure* 2). These results are in qualitative agreement with earlier n.m.r. pulsed-gradient spin–echo studies[4] on short-chain ($\bar{M}_n = 590$) poly(ethylene oxide) and poly(dimethyl siloxanes) in dilute to concentrated solutions and on concentrated polystyrene solutions in toluene-d_8 [6] and with Rayleigh light-scattered linewidth measurements on low molecular weight polystyrenes in dilute solutions[7].

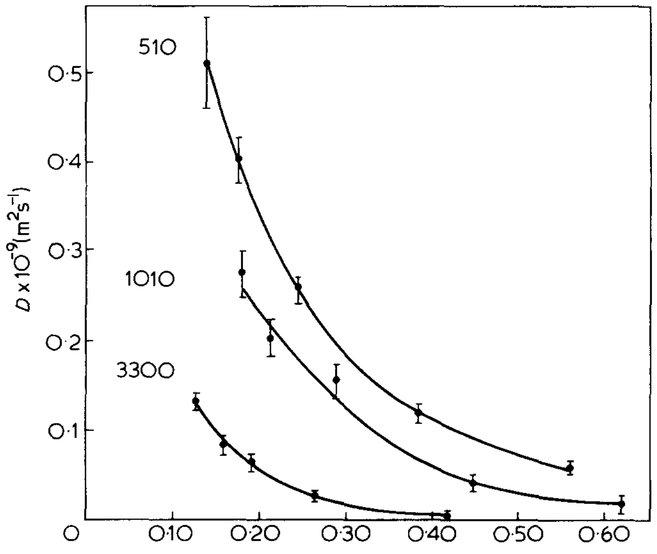

Figure 1 Self-diffusion coefficients for short-chain polystyrenes (molecular weights 510, 1010 and 3300) in deuterochloroform at 25°C as a function of polymer weight fraction

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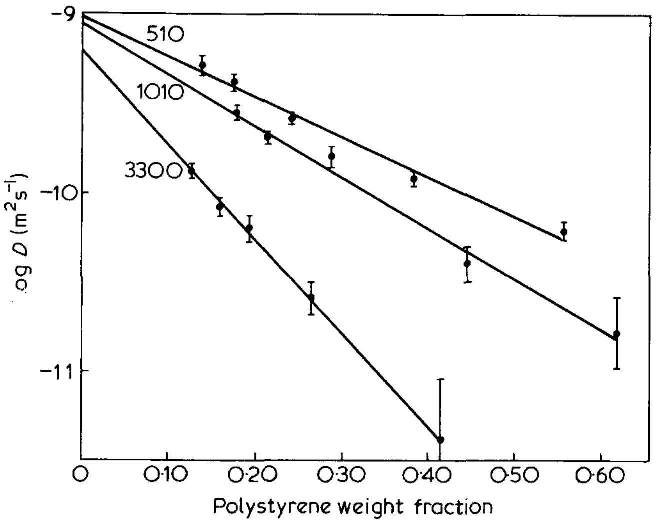

Figure 2 Concentration and molecular weight dependence of log*D* for short-chain polystyrenes in deuterochloroform

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

$$\tau_r = 0.22R^2/D_t \tag{1}$$

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, $\tau_r = 3 \times 10^{-10}$ s, $9 \pm 1 \times 10^{-10}$ s, and $117 \pm 23 \times 10^{-10}$ s for molecular weights 510, 1010 and 3300, respectively. Lauprêtre *et al.*[10], through $^1HT_1$ 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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(*Received* 27 *May* 1980)

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

0032-3861/80/1480–02$02.00