N.M.R. Relaxation Studies on Poly(ethylene oxide) Terminally Attached at the Polystyrene/Water Interface

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N.m.r. spin relaxation studies have been used to investigate the concentration histogram of poly(ethylene oxide) terminally attached to polystyrene latex in water.

The structure of polymers at interfaces has been the subject of considerable experimental and theoretical study.[1,2] In this communication we report results obtained using the n.m.r. Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence,[3,4] which has been used previously to study small molecules, adsorbed at an interface. Here it is used to determine the magnetisation decay curve of adsorbed polymer molecules. The result is compared with data derived from small-angle neutron scattering (SANS) measurements on the same sample.

The proton spin–spin relaxation time, T_2, of a polymer segment, depends on the segment's local magnetic environment and its characteristic correlation times. For a homogeneous system, the component of magnetisation in the y-direction, $M_y(t)$, as a function of time, t, is given by equation (1), where $M_y(0)$ is the value of $M_y(t)$ at $t = 0$ and is proportional to the number of protons in the sample. In the case of an adsorbed polymer layer, the concentration of segments varies across the interface. Each concentration corresponds to a different magnetic and dynamic environment and consequently has a different relaxation time. In the case of segments which are one or two bonds away from the interface, there will also be an anisotropic effect on their mobility, above that due solely to concentration effects. However, such segments, which are subject to large magnetic dipole–dipole interactions are not seen in the CPMG experiment. When the exchange of segment environments in the adsorbed layer is slow compared to the lifetime of the magnetisation, each relaxation function will have the same form as equation (1). The total magnetisation is then given by equation (2).

$$M_y(t) = M_y(0)\exp(-t/T_2) \qquad (1)$$

$$M_y(t) = \sum_{i=1}^{n} M_y(0)_i \exp(-t/T_{2_i}) \qquad (2)$$

In the concentration regimes typical of adsorbed polymer layers (up to ~50%) it has been found, experimentally, that the T_2 of a proton in a polymer segment varies inversely with concentration.[5] Given that T_2 is concentration dependent, the magnetisation decay can, in principle, be used to obtain information on the concentration of segments at an interface by an inverse Laplace transform of equation (2). However, no distinction can be made between segments at the same concentration (or mobility) but at different distances from the interface. The resulting concentration histogram does not, therefore, contain any spatial information about the segments with respect to the interface. Hence, whilst the shape of a volume fraction profile, $\phi(z)$, normal to the interface, will directly determine the magnetisation decay, the resulting curve may not be unique to that profile. However, it is possible to calculate the expected magnetisation, from either an experimentally determined or theoretically predicted volume fraction profile, and compare this to the observed decay.

The chosen experimental system was poly(ethylene oxide) (PEO), terminally attached at the [$^2H_8$]polystyrene latex (dPS)/D_2O interface. This system has many useful characteristics with regard to the n.m.r. experiments. The protons in the adsorbed PEO are magnetically identical and this should lead to a single exponential decay for the calibration solutions. The mobility of any residual protons in the deuteriated latex particles would be considerably less than that of the protons in the adsorbed polymer layer and, consequently, they would have very short T_2 values (~1 ms). The effect of these protons could be eliminated from the experimental data by deleting the first 100 of the 5000 points of the magnetisation decay. Any protons present as H_2O in the D_2O are magnetically dilute and would have very long spin–lattice relaxation times (~10 s). By having a pulse repeat time of ~1 s these protons could be saturated and their effect on the magnetisation decay also eliminated. The observed decay would then contain information concerning only the adsorbed layer. One further advantage of this system is that it is suitable not only for the n.m.r. studies but also for the SANS experiments: D_2O and dPS have similar neutron scattering densities.

The latex sample was prepared by the copolymerisation of [$^2H_8$]styrene and methacrylate-terminated PEO ($\bar{M}_n = 5000$, $R_g = 3$ nm) in water, using potassium persulphate as the initiator.[6] The latex was then centrifuged and redispersed four times in H_2O/D_2O mixtures before finally being redispersed in pure D_2O. The latex particle diameter was 180 nm, with a polymer coverage of 4 mg m^{-2}.

The polymer solutions were prepared in D_2O at volume fractions covering the range from 0.01 to 0.40. The polymer (PEO 5000) was the same as that used in the latex preparation.

The volume fraction profile was obtained by using SANS on the D17 camera at the ILL, Grenoble. The sample–detector distance was 2.8 m and the neutron wavelength was 0.9 nm. The data were analysed by using the procedure described by Crowley.[7] A similar volume fraction profile, calculated from data obtained at 1.45 nm, has been published previously.[8]

The n.m.r. experiments were performed on a 100 MHz pulsed n.m.r. spectrometer which was constructed in this laboratory. The 90° pulse length was 3 μs and the probe recovery time ~2 μs. The data were collected on a PDP 11/23 computer.

The observed magnetisation decays of the PEO solutions could each be fitted to a single exponential function, of time constant, T_2. Figure 1 shows the resulting calibration curve of T_2 as a function of concentration. Figure 2 shows the volume fraction profile for the terminally attached PEO sample, obtained by using SANS. Using the data shown in Figures 1 and 2 and equation (2), it is possible to construct the T_2 relaxation function for this system. The result is shown in Figure 3, along with the decay determined experimentally by using n.m.r. The comparison is very favourable. Neither data

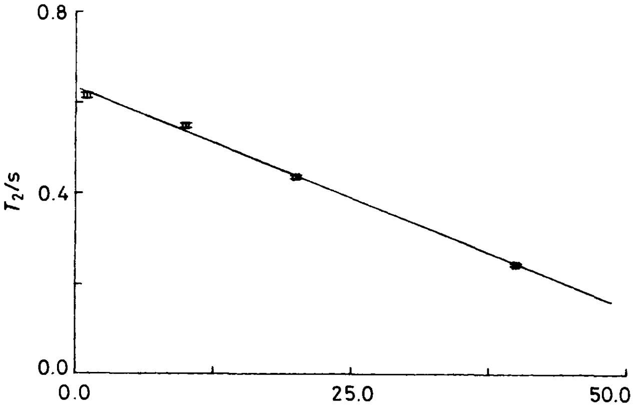

Figure 1. Variation of relaxation time, T_2, with polymer concentration, for PEO 5000 in solution in D_2O.

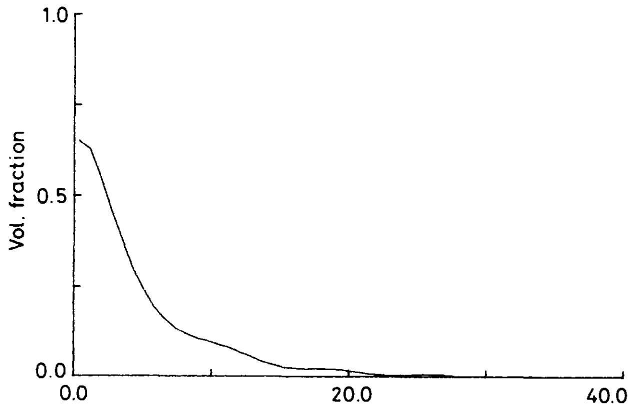

Figure 2. Volume fraction profile of PEO 5000 adsorbed at the polystyrene/D_2O interface.

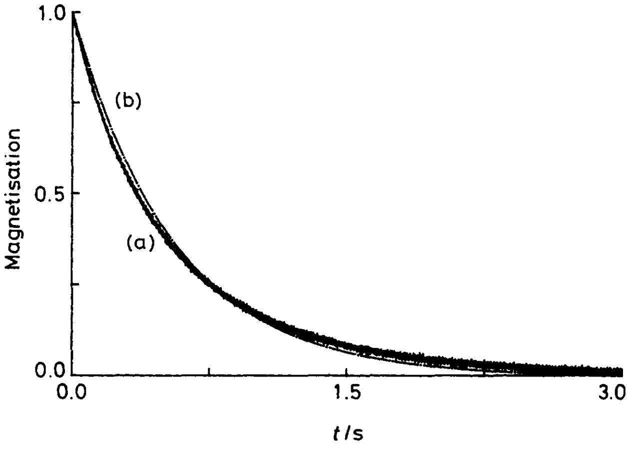

Figure 3. Magnetisation decay for PEO 5000 adsorbed at the polystyrene/D_2O interface; (a) determined using n.m.r.; (b) calculated from the volume fraction profile.

set can be fitted to a single exponential function, suggesting that the method *is* sensitive enough to distinguish between segments of different mobility. The data can be approximated by a double exponential function, with time constants of 0.28 ± 0.03 s (corresponding to a volume fraction of ~35%) and 0.72 ± 0.01 s (corresponding to a volume fraction of ~0.5%). Taking into account the relative initial heights, these figures correspond to an average volume fraction of 10 ± 1%. For comparison, the average volume fraction of the SANS profile is 13%. This difference reflects the insensitivity of the SANS experiment to low polymer volume fractions ($< \sim 1\%$).[9] Furthermore, the greater mobility of segments in tails leads to an average relaxation function for segments near the periphery of the adsorbed layer. This will tend to over-emphasize the importance of segments in tails, leading to an underestimate of the average volume fraction.

Ideally, one would like to take the inverse Laplace transform of the n.m.r. data to obtain the concentration histogram and this is being actively pursued in this laboratory, using a maximum entropy formalism.[10]

In conclusion, we find that the n.m.r. relaxation function, T_2, can be used to probe the structure of an interfacial region. The results compare favourably with those simulated using experimental data obtained by SANS.

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