Molecular dynamics of poly(ethylene oxide) in concentrated solution

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Incoherent quasi-elastic neutron scattering measurements on aqueous poly(ethylene oxide) solutions show that as the concentration of water is increased to 1:1 mole ratio of water to ethylene oxide monomer units, the polymer chain mobility is not enhanced. Increased mobility is only observed when the water content is increased beyond this ratio. The activation energy for viscous flow shows a similar behaviour, it is unchanged as the system is diluted from the melt to the 1:1 solution and as more water is added it falls sharply. Similar studies on the system poly(ethylene oxide)/toluene show that chain mobility is enhanced and the activation energy for viscous flow falls continuously, at all concentrations. The difference is attributed to the formation of polymer—water hydrogen bonded complexes in aqueous solution. High resolution data for the aqueous systems suggest that the molecular dynamics obey the scattering law predicted for the Zimm model. In the melt the behaviour changes towards the limit given by the Rouse model.

INTRODUCTION

Quasi-elastic neutron scattering has been used to study the dynamics of polymer chains in bulk rubbers[1-4] and in dilute solution[5]. In this paper the technique is extended to study the molecular dynamics of poly(ethylene oxide) (PEO) in concentrated solution in water, where strong specific hydrogen bond interactions exist between polymer and solvent. The molecular behaviour of the poly(ethylene oxide) solutions has been compared with macroscopic behaviour observed by viscometry.

The molecular dynamics are studied by incoherent quasi-elastic neutron scattering (IQNS), the molecular motions causing a Doppler shift of the energy of the scattered neutrons. Because the wavelength of the neutrons is only ~5Å, the technique measures the overall translational diffusive motions of small molecules and diffusive motions of relatively short segments of polymer chains. Measurements on oligomers of poly(dimethyl siloxane) PDMS have shown that the method gives effective diffusion constants which reach a limiting value at chain lengths of about 20 monomer units and thereafter become insensitive to chain length.

Poly(ethylene oxide) is a crystalline polymer melting at 65°C. Various methods have already been used to study poly(ethylene oxide) solutions, including n.m.r.[6-9], infrared and Raman spectroscopy[10], vapour pressure[11] and calorimetric measurements[12]. N.m.r. measurements of the chemical shifts of the CH_2 and OH protons suggest that in aqueous solution a hydrated complex is formed comprising 3 molecules of water per ethylene oxide repeat unit. Raman spectroscopy[10] has given further evidence for this hydrated chain. No such structures can be identified in poly(ethylene oxide) solutions in organic solvents.

Further evidence for the existence of hydrated structures in aqueous solution comes from recent vapour pressure[11]

and calorimetric measurements[12]. In addition to a 3:1 hydrate, there is evidence for hydrates containing 1:1 and 5:1 molecules of water per ethylene oxide repeat unit. Spectroscopic methods have not detected either of these structures.

In this paper we report studies of the dynamics of poly(ethylene oxide) in the melt and in aqueous and toluene solutions. Evidence has been obtained which strongly supports the existence of a 1:1 hydrated complex.

EXPERIMENTAL AND DATA ANALYSIS

Materials

Commercial samples of PEO were used with M_n in the range 200 to 10 000 and $M_w/M_n < 1.1$. Perdeutero-PEO (DPEO) was prepared by anionic polymerization of ethylene oxide-d_4 in a pyrex ampoule at ambient temperature and in a stainless-steel autoclave at elevated temperature. Two samples of DPEO were used having M_n of 3000 and 6000 and $M_w/M_n < 1.1$.

Deuterium oxide (D_2O) was obtained from AERE Harwell, it was untritiated and had a deuterium content >99.8%. Deuterated toluene (C_7D_8) was obtained from Fluorochem and had a deuterium content >98%. The other solvents used were distilled water and Analar grade toluene.

All solutions were made up on a weight to weight basis.

Neutron scattering

Spectrometers. The medium resolution twin-chopper time-of-flight spectrometer 6H[13] at Harwell was used with an incident wavelength of 4.2 Å and resolution ~600 μeV and the data collected at 9 angles of scatter covering the momentum transfer (Q) range 0.46 to 2.1 Å^{-1}.

At higher resolution 2 spectrometers were used. The multi-chopper time-of-flight spectrometer IN5[14] at ILL,

Grenoble had an incident wavelength of 10 Å and resolution ~25 μeV. The data were collected at 16 angles of scatter covering the Q range 0.1 to 1.15 Å^{-1}.

The third spectrometer to be used was the high resolution back scattering spectrometer IN10[15] also at the ILL. This spectrometer had an incident wavelength of 6.28 Å and a resolution of ~1 μeV. Two energy windows, ±6 and ±11 μeV, were used by varying the frequency of the Doppler drive. The data were collected at 5 angles of scatter covering the Q range 0.15 to 1.07 Å^{-1}.

The energy resolution of each spectrometer was obtained by measuring the scattering from a vanadium standard.

The temperature of the samples was controlled electrically to ±1°C.

Data analysis. For each instrument initial data reduction was carried out to take account of background effects, container scattering, detector efficiencies and variations in flight paths and neutron flux[16-18].

The data treated in this way give the scattering function $S(Q, \omega)$ at constant angle. The values of Q given above are the values at zero energy transfer for a particular angle of scatter. Variation of Q across the quasi-elastic peak was taken into account where necessary.

The low resolution data were analysed further using the method described in an earlier paper[1]. Values of the full width at half maximum ($FWHM$), $\Delta\omega_{1/2}$, of the quasi-elastic peak were calculated assuming a Lorentzian form for $S(Q, \omega)$ and a Gaussian resolution function using standard Voigt function tables[19]. The calculated $FWHM$ values were then plotted as a function of Q^2 and D_{eff} calculated from the slope.

After the initial data reduction the high resolution data were analysed using computer fitting techniques. A model function was proposed for $S(Q, \omega)$ convoluted with the resolution function and fitted to the data using iterative computer procedures. The use of these programmes is described in two previous papers on bulk polymers[4] and dilute polymer solutions[5].

All the solutions contained a hydrogenous and a deuterated component and it was assumed, in all cases, that because of the large incoherent hydrogen cross-section the scattering from the hydrogenous component dominated the measured scattering function, therefore no account was taken of the scattering from the deuterated component.

Theoretical models. The scattering law $S(Q, \omega)$ is related to the intermediate scattering function $I(Q, t)$ by the expression:

$$S(Q, \omega) = \frac{1}{2\pi} \int I(Q, t) \exp(i\omega t) dt \qquad (1)$$

For simple diffusion:

$$I(Q, t) = \exp(-DQ^2 t) \qquad (2)$$

where D is the centre of mass diffusion coefficient. Equation (2) gives a Lorentzian scattering law with a $FWHM$ proportional to Q^2. In the case where equation (2) has been applied to the IQNS spectra from polymers the coefficient D is no longer a translation diffusion coefficient since Q is too large and thus is called D_{eff}, the effective diffusion coefficient. D_{eff} characterizes in one simple parameter the IQNS broadening characteristic of a given polymer at a fixed temperature.

For a polymer in solution where there are no hydro-

dynamic interactions[20] (the Rouse model) the expression for the intermediate scattering law is:

$$I(Q, t) = \exp\left[-Q^2 \frac{\sigma^2}{3} \left(\frac{W}{\pi}\right)^{1/2} |t|^{1/2}\right] \qquad (3)$$

where σ is the step length of the polymer and W^{-1} is a correlation time. The $FWHM$ of $S(Q, \omega)$ calculated using equation (3) is proportional to Q^4.

If hydrodynamic interactions are taken into account[21], i.e. using the Zimm model then:

$$I(Q, t) = \exp\left[-Q^2 \frac{\sigma^2}{6\pi} \Gamma\left(\frac{1}{3}\right) |Wt|^{2/3}\right] \qquad (4)$$

and the $FWHM$ of $S(Q, \omega)$ is now proportional to Q^3.

These three models were used to calculate $S(Q, \omega)$ used in the fitting programmes. The shape of the scattering law can be completely characterized by the $FWHM$ and this parameter was extracted from the data and its Q^n-dependence calculated.

Viscometry

From literature data[22-24] and preliminary experiments it was established that the solutions under investigation were Newtonian liquids. The viscosity coefficients could be measured using Ubbelohde and Atlantic capillary viscometers. Each was calibrated according to standard specifications[25]. The viscometric constant K in the equation:

$$\eta = K\rho t$$

where ρ is the density and t the flow time, was determined by using several standard fluids with known viscosity coefficients. The average values of K for the Ubbelohde and the Atlantic viscometer were 4.631 ± 0.005 and 0.985 ± 0.005, respectively. Under the conditions of measurement kinetic energy corrections were found to be negligible.

The densities of the PEO/water solutions were obtained from data available in the manufacturers specifications. Since similar data were not available for PEO/toluene these were determined by pycnometry. The error in the density values was ±0.2%. To minimize errors caused by dilution each concentration was prepared separately by wt. Measurements were made at temperatures controlled to ±0.05°C. The viscosity coefficients at a given composition could be reproduced to within ±2%.

RESULTS

Neutron scattering

Low resolution. From the low resolution data the parameter D_{eff} was calculated from the slope of the plot of $FWHM$ against Q^2. As in previous work[1,2] it was found that the variation of $FWHM$ with Q^2 was linear in this Q-range. It is very difficult because of the poor resolution to determine the correct shape of the scattering function. Although the values of D_{eff} might not have any absolute meaning it is possible to compare the relative values.

In *Figure 1*, D_{eff} for PEO is plotted as a function of chain length at two temperatures. At 65°C, just above the melting point, D_{eff} is essentially constant over the whole range but at 120°C a decrease takes place before the curve flattens off. For chain lengths greater than about 70 monomers
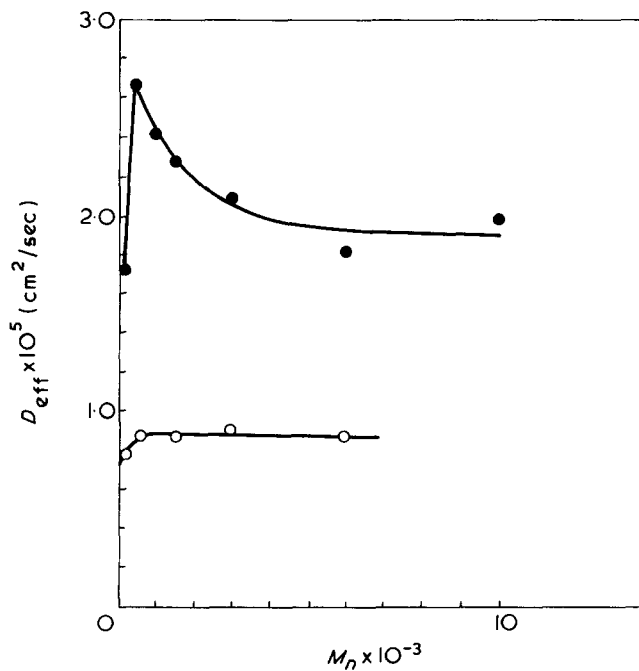
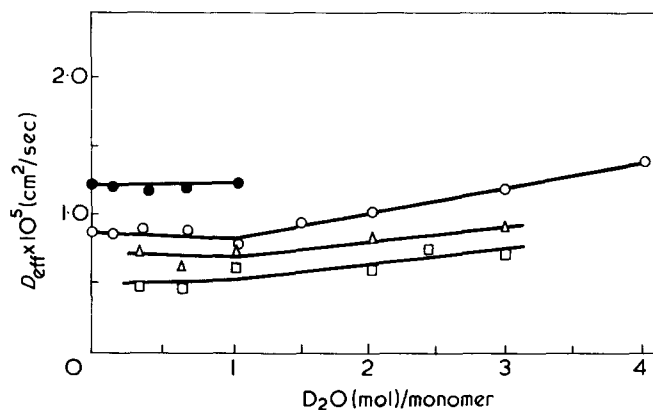**Figure 1** Variation of D_{eff} of PEO with molecular weight at 65°C (O) and 120°C (●)

Figure 2 Variation of D_{eff} of PEO 6000 as a function of D_2O concentrations at 4 temperatures: 45°C (□), 55°C (△), 65°C (O) and 85°C (●)

D_{eff} tends to a limiting value. Previous measurements on PDMS as a function of chain length exhibited similar behaviour but the limiting value of D_{eff} was reached at much shorter chain lengths, i.e. approximately 20 monomer units. This difference in the chain length at which limiting behaviour is observed reflects the relative flexibility of PDMS and PEO chains. PDMS has the lower glass transition temperature and is considered to be a very flexible polymer whereas PEO, having a glass temperature some 50K higher, is considered to be stiffer which will result in a larger statistical segment involved in chain motion.

The reason for the difference in behaviour of D_{eff} at 65° and 120°C is not certain. One explanation could be that there is still some residual hydrogen bonding at 65°C between the —OH groups which would give rise to a high apparent molecular weight which would result in anomalously low D_{eff} values. As the limiting behaviour of D_{eff} with respect to chain length at both temperatures is attained at a molecular weight of 6000, this molecular weight fraction was used in all the solution experiments.

Figure 2 shows D_{eff} for PEO 6000 solutions as a function of D_2O concentration at 4 temperatures. Measurements were made in the concentration range 6.8% to 71% D_2O by wt (0.16 to 5.38 molecules of D_2O per monomer unit) At temperatures below the melting point of bulk PEO it was impossible to measure any broadening of the elastic peak until approximately 13% of D_2O had been added. Below this concentration the resolution is not good enough to be able to measure any quasi-elastic broadening.

At 65°C, as D_2O is added the values of D_{eff} remain essentially constant until approximately 1 mole of D_2O per monomer, 1:1, has been added after which point there is a sharp increase in D_{eff}. These results supercede preliminary results reported elsewhere[26] which indicated a decrease in D_{eff} as water was added. The behaviour of PEO in water seems to be essentially similar at temperatures above and below the melting point which is at variance with Raman measurements[10] made on solutions containing 70% water.

In order to examine the diffusive motion of the water, measurements were made of the translational diffusion constant, D, for H_2O in the system $DPEO/H_2O$. In *Figure 3*, D is plotted as a function of H_2O concentration. The value of D below the concentration ratio 1:1 is slightly lower than the corresponding value of D_{eff} for PEO but above 1:1, D increases much more rapidly than D_{eff}. The value of D for pure water at 65°C is 5×10^{-5} cm²/sec a factor of 2 greater than the values shown in *Figure 3* for H_2O in solution.

Measurements have also been made of the quasi-elastic broadening generated by PEO 6000 in an organic solvent, deuterated toluene, which does not hydrogen bond and these results are shown in *Figure 3*. Note the difference in behaviour of PEO and D_2O and C_7D_8, D_{eff} increases rapidly as soon as C_7D_8 is added to the polymer.

High resolution. To obtain accurate information about the shape of $S(Q, \omega)$ and thus the type of behaviour shown by PEO and PEO in water, measurements were made at high resolution over a wide Q-range.

IQNS measurements were made on PEO and PEO/D_2O solutions at 3 concentrations at 67°C. The IN5 data covered the same Q-range for each measurement although indi-
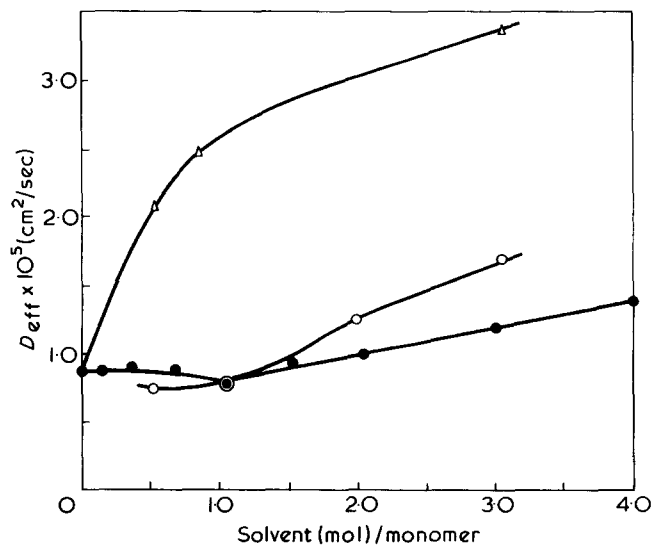

Figure 3 Comparison of the behaviour of D_{eff} of PEO 6000 in D_2O (●) and in C_7D_8 (△) and D of H_2O in DPEO (O) as a function of solvent concentration at 65°C
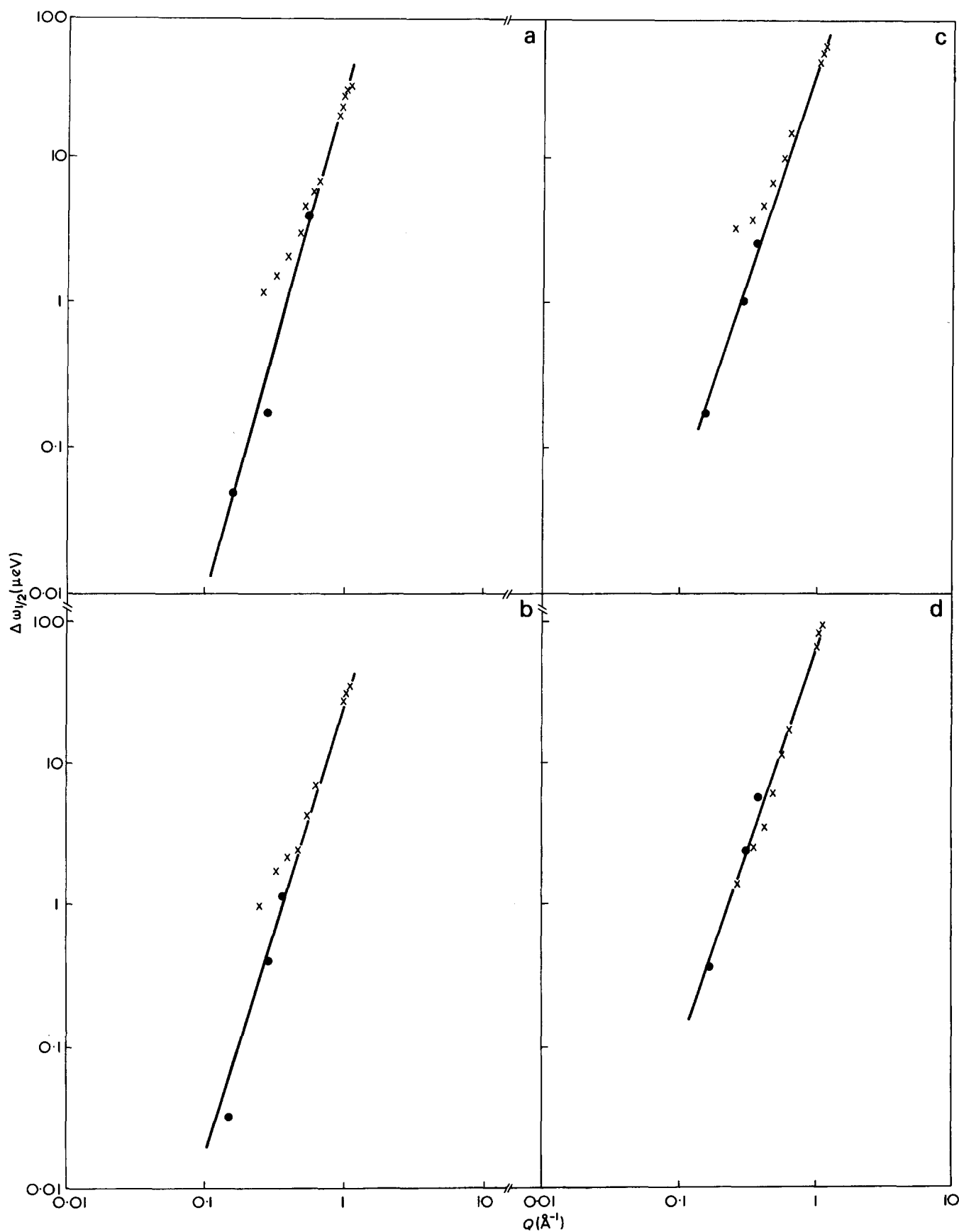
Figure 4   Double logarithmic plots of $\Delta\omega_{1/2}$ against Q where $\Delta\omega_{1/2}$ is the FWHM of the model which gives the best fit. Data are plotted from IN5 (X) and IN10 (●). (a) PEO best fit model Q^4, slope = 3.3, 67°C. (b) PEO/D_2O concentration 0.5 mol D_2O/monomer, best fit model Q^4, slope = 3.2, 65°C. (c) PEO/D_2O concentration 1 mol D_2O/monomer, best fit model Q^3, slope = 2.9, 65°C. (d) PEO/D_2O concentration 3 mol D_2O/monomer best fit model Q^3, slope = 2.9, 65°C
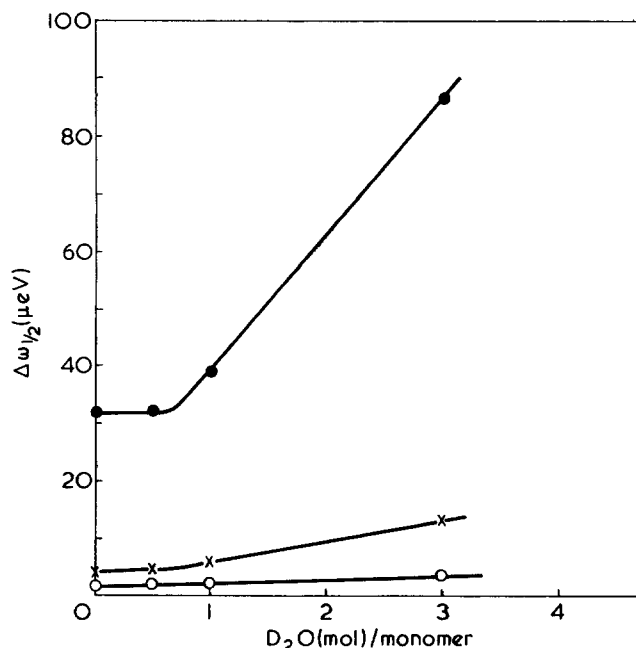
Figure 5 Variation of $\Delta\omega_{1/2}$, calculated using the Q^4-model, as a function of D_2O concentration at different values of Q. Q = 1.1 A^{-1} (●), Q = 0.56 A^{-1} (X) and Q = 0.33 A^{-1} (O)

vidual scattering angles varied slightly. The energy window for IN10 was ±11 μeV for the PEO bulk measurement and ±6 μeV for the PEO solutions.

After the initial reduction the data were fitted to the three laws described earlier. In order to establish the Q^n-dependence the FWHM calculated from the fitting program were plotted against Q. In *Figure 4* best fit data for both machines are plotted as a function of Q. For PEO the best fit was obtained using the Q^4 law and as the amount of D_2O increased the dependence on Q changed to Q^3. In all cases the Lorentzian Q^2-dependent law considerably underestimated the intensity in the wings of the quasi-elastic peak.

At high resolution the variation of FWHM for a particular Q value follows the same general trend shown by D_{eff} values calculated from the low resolution data as shown in *Figure 5* where $\Delta\omega_{1/2}$ is plotted as a function of composition.

Viscosity coefficients

Earlier workers[23] had found that at low temperatures plots of log η versus $1/T$ for PEO solutions tended to curve upwards, this has been verified. However, we are only interested in small ranges of temperature, 45° to 65°C and 65° to 85°C and in these intervals η is an essentially linear function of T.

In *Figure 6* the apparent activation energies for viscous flow, E_{vis}, are plotted against composition for the two systems in the two temperature intervals. Our value for E_{vis} for PEO is in good agreement with the value quoted by Teramoto *et al.*[23], ~6 kcal/mol. The variation of E_{vis} with composition is similar for both temperature intervals and is complementary to the behaviour found for D_{eff}. E_{vis} for the PEO/water system shows little or no variation until the ratio 1:1 is reached where a sharp decrease occurs. The trend when toluene is present is quite different, E_{vis} decreases smoothly and continuously as toluene is added to the polymer as might be expected intuitively for a normal polymer/solvent system.

DISCUSSION

Effect of water on chain mobility

One can divide the behaviour of PEO in water into two distinct regimes, (a) concentrations representing up to approximately 1 mole of water per monomer unit and (b) concentrations above this value.

In regime (a) the mobility of the PEO chains is restricted by the presence of water. This is shown by the negligible variation in D_{eff} as water is added to PEO. The restriction in mobility must be caused by specific polymer/solvent interactions which cause both water and PEO to have approximately the same value of the diffusion coefficient in this region. This type of behaviour is most likely to be due to the hydrogen bonding of the water molecules onto the polymer chain and this is supported by earlier vapour pressure measurements[11]. In a system where no specific interaction between polymer and solvent occurs, i.e., PEO/toluene, the mobility of the PEO/toluene, the mobility of the PEO chains increases as soon as solvent is added to the melt.

In regime (b) D_{eff} increases, and so does the diffusion coefficient of the water molecules. The diffusion coefficient of the water is now much larger than the value of D_{eff} for the polymer indicating that free water is now present. No change in behaviour of either the polymer or solvent was observed when the ratio of solvent to monomer reached 3:1, at which concentration other techniques indicate the formation of another hydrate. The reason why IQNS does not measure any change in the dynamics of the polymer is not clear. It may be that in this region the amount of scattering from the D_2O itself is becoming more important and it is possible that the assumption that the scattering from the deuterated component can be ignored breaks down. However, in the system H_2O/DPEO the scattering from the water relative to the polymer is increasing so this should be more sensitive. But even so, no change in the behaviour of the water was observed at low resolutions, corresponding to the effects found in n.m.r., infra-red and Raman spectra.

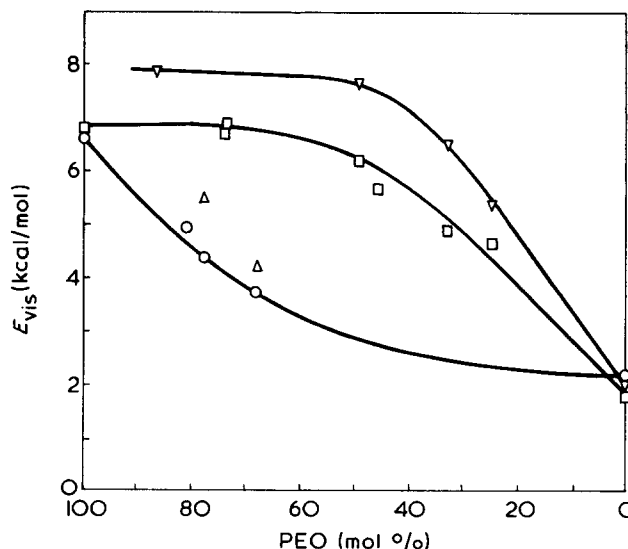The viscosity measurements in this work and those of Teramoto *et al.*[23] also indicate a change in the viscosity

Figure 6 Variation of E_{vis} with the concentration of PEO in water and in toluene for 2 temperature ranges: (a) 45° to 65°C (▽) water and (△) toluene; (b) 65° to 85°C (□) water and (O) toluene

coefficient and particularly in the activation energy for viscous flow composition. Here too, the reduction in E_{vis} is consistent with the transition from a tightly bound PEO–water complex to a more flexible system of the water/PEO system at 1:1 and again no change in E_{vis} is detected at the composition 3 moles of H_2O to 1 ethylene oxide unit. In toluene the variation of E_{vis} is consistent with a smooth increase in the mobility as the system becomes more dilute in polymer. In this respect the microscopic segmental diffusion measured by IQNS is mirrored by the macroscopic viscosity behaviour of PEO in both water and toluene.

Scattering law

The high resolution data give more information about the effect of the presence of water on the PEO chains in terms of the form of the scattering law. As in earlier work on PDMS[4] it was found that the Q^4-law was the best fit to the quasi-elastic scattering envelope but unlike PDMS, as can be seen in *Figure 4a*, the slope of the plot of *FWHM* against Q is less than 4 and has a value of 3.3. As for the PDMS data the low-Q values measured on IN5 do not fall on the same line as the IN10 data. As the amount of water increases the data from IN5 fall nearer the line. This is not a consequence of the resolution of IN5 since the half-widths measured in each case do not vary by very much. However, if the model for the scattering law used in the fitting procedure is not correct then the data will not fall on the line[4].

It is apparent that although the Q^3 law seems to fit the data very well for the most dilute solution the Q^4 law is not quite adequate to explain the behaviour of PEO alone—a point which was also noticed for PDMS[4]. Even at the lowest concentration of water added to PEO there is evidence that the scattering law is changing. The slope of the plot of *FWHM* against Q shown in *Figure 4b* has dropped to 3.2 and this is true of all three solutions.

We conclude that in dilute aqueous solutions the chain dynamics are closely represented by the Zimm model, i.e. by a Q^3 scattering law. The results in the melt are intermediate between the Zimm and Rouse model, in that the overall IQNS curves are best fitted by a Q^4 law, but the slope of log $\Delta\omega_{1/2}$ vs. log Q is only 3.2. This feature has been noted for other rubbers in bulk, it may be the effect of chain stiffness (or the relatively large values of Q studied) which does not allow the Q^4 dependence of the Rouse model to develop in full.

Finally, it is worth noting that the ratios of $\Delta\omega_{1/2}$ (solution)/$\Delta\omega_{1/2}$ (PEO) for the concentrations 0.5:1 and 1:1 calculated from the high resolution data were effectively constant over the entire range of Q. This is not so for the 3:1 concentration, for this solution the ratio varies, increasing as Q increases, indicating a different Q-dependence for the *FWHM* of the most dilute solution compared to that of bulk PEO. This is entirely consistent with the idea that when this concentration is reached the scattering law has changed from the Rouse to the Zimm limit.

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