polymer communications

Neutron scattering, nuclear magnetic resonance and photon correlation studies of polymers adsorbed at the solid–solution interface

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Introduction

Several experimental techniques now exist for obtaining information on the configuration of polymer molecules absorbed at interfaces. These include infra-red spectroscopy[1] (i.r.), electron spin resonance[2] (e.s.r.), ellipsometry[3], photon correlation spectroscopy[4] (p.c.s.), nuclear magnetic resonance[5] (n.m.r.) and microcalorimetry[6]. Of these methods only i.r., e.s.r. and n.m.r. give direct evidence of two characteristic segment environments, namely: trains which are polymer segments in contact with the surface (2-dimensional), and loops and tails which are segments which protrude into the solution phase. Microcalorimetry gives an indirect measure of the fraction of segments in trains ($\langle p \rangle$) by comparing the enthalpy of polymer adsorption with that for the corresponding adsorbed oligomers. Ellipsometry and p.c.s. experiments both lead to information on the thickness of the adsorbed layer. P.c.s. measures a 'hydrodynamic' thickness (δ) whereas the value obtained from ellipsometry depends on the function chosen to represent the segment density distribution of the adsorbed polymer, $\rho(z)$, normal to the interface.

In this communication, preliminary small-angle neutron scattering SANS, p.c.s. and n.m.r. experiments are described for the system poly(ethylene oxide) adsorbed on polystyrene latex dispersed in water.

Both p.c.s.[4] and n.m.r.[5] experiments on adsorbed polymers have been discussed elsewhere and so only the results of these studies are given. SANS has been used to estimate characteristic correlation functions in polymeric systems[7] as well as the structures of biological units in solution[8,9]. Recently[10] SANS, together with the contrast matching technique, has given information on the density and size of adsorbed laurate ions on polystyrene latex dispersed in H_2O/D_2O mixtures.

For the systems studied here both the finite polydispersity of the latex particles and the finite angular resolution of the detector, at wide angles, mean that a unique Fourier inversion of the particle plus the adsorbed layer is impossible. However, an alternative analysis of the data is possible using the contrast variation technique.

For a layer of thickness t, adsorbed on a particle of radius r_o, ($r_o \gg t$) it can be shown[11] that the scattered intensity $I^o(Q)$ is given by:

$$I^o(Q) = \frac{\text{constant}}{Q^2} \left| \int_0^t \rho(z) e^{iQz} dz \right|^2 \qquad (1)$$

when $Qr_0 \gg 1$ and the particle scattering is contrast-matched with that of the solvent. If it can also be arranged experimentally that $Qt < 1$ then the exponential term in equation (1) can be expanded in a Taylor series. Hence plots of $\ln(Q^2 I^o(Q))$ against Q^2 can be used to obtain σ, the second moment of the distribution $\rho(z)$ about the mean, i.e.:

$$\sigma = (\langle z^2 \rangle - \langle z \rangle^2)^{1/2} \qquad (2)$$

Experimental

The system chosen for these studies was such that comparative studies with SANS, n.m.r. and p.c.s. could be made. The substrate used was polystyrene latex, made with a persulphate initiator, using a surfactant-free method in water. For the neutron scattering, latex deuterated styrene monomer was diluted with 4% protonated monomer in order to achieve a contrast match condition in an H_2O/D_2O dispersion medium ($\sim 1\%$ ^1H). For the n.m.r. experiments, fully deuterated (98%) styrene monomer and D_2O (99.8%) were used. The latices produced were monodisperse and in the range 230–250 nm. The adsorbed polymer used in this initial study was protonated poly(ethylene oxide) of molecular weight 50 000

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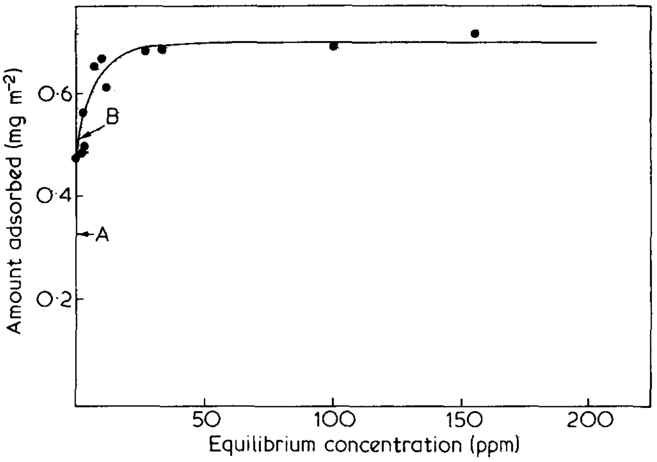

Figure 1 Adsorption isotherms for poly(ethylene oxide) of molecular weight 50 000 adsorbed on polystyrene latex in water

($\bar{M}_w/\bar{M}_n = 1.23$). This sample was prepared by anionic polymerization of ethylene oxide monomer using sodium methoxide initiator in a sealed ampoule. The adsorption isotherm for the polymer on the latex is shown in *Figure 1* and the concentrations of the two samples used in these experiments are indicated.

The neutron scattering experiments were carried out on the D11 small-angle spectrometer at Grenoble with neutrons of wavelength 7.0 Å and sample detector distances of 2.5 and 5.0 m.

The p.c.s. measurements were carried out at 25°C and results were obtained from the analysis of 45° to 100° angular plots. The experiments used a He–Ne laser at about 25 mW power and homodyne light mixing[4]. The n.m.r. experiments were carried out using a computer controlled pulsed n.m.r. spectrometer operating at 60 MHz. Both solid and liquid spin–echo techniques[5] were used to obtain the experimental data.

Results and discussion

Figure 2 shows the neutron scattering data plotted as $\ln(Q^2 I^\circ(Q))$ vs. Q^2 for sample B (*Figure 1*). As can be seen, a reasonable straight line plot is obtained at small values of Q. Values of σ (Equation 10) have been calculated at the two different coverages and these are given in *Table 1*.

The advantages of using σ instead of δ to describe the adsorbed layer are two-fold. Firstly, and most importantly, σ can be directly related to $\rho(z)$, whereas the meaning of the hydrodynamic radius in terms of $\rho(z)$ is unclear[12]. Secondly, because δ is obtained by subtraction of the radius of the bare particle from the coated particle, it is intrinsically less accurate than the σ value, especially at low coverages, with small molecular weight polymers.

However, it is useful to compare the σ and δ values qualitatively, and from *Table 1* it can be seen that both parameters show the same trend of decreasing thickness with decreasing coverage as would be expected; also δ appears to be larger than σ. Using a rectangular distribution for $\rho(z)$ gives $\delta = \sigma\sqrt{12}$ showing that the absolute values obtained are not unreasonable. At monolayer coverage the δ value is 15.5 ± 2 nm. Comparison of this value with the radius of gyration R_G (*Table 1*), of a free coil in solution[13], shows that at monolayer coverage the adsorbed polymer is not appreciably distorted. At low coverages however, it adopts a flatter configuration.

The $\langle p \rangle$ values (*Table 1*) show that only a few segments of the adsorbed polymer are in static contact with the surface. For sample A ~ 10% of segments are in contact but for sample B the $\langle p \rangle$ value was experimentally indistinguishable from zero, (i.e. less than 5%). However, even this small number of surface contacts can appreciably distort the adsorbed coil configuration. For example, if it were assumed that the adsorbed segments were distributed uniformly along the chain, then this would give a maximum apparent thickness of $\sim 5l$ (where $l = 2.54$ Å) for sample A. This simple calculation shows that small values of $\langle p \rangle$ are not inconsistent with the measured values of σ or δ.

Conclusion

Values of the second moment of the segment density distribution for an adsorbed homopolymer, the hydrodynamic thickness of the adsorbed layer and the fraction of segments in contact with the surface have been measured experimentally. The results are self-consistent and given an overall picture of a weakly adsorbed polymer layer with a few segments actually in physical contact with the surface.

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Table 1 Results for 50 000 molecular weight poly(ethylene oxide) adsorbed on polystyrene latex from water

Sample	Coverage (mg m^{-2})	σ (nm)	δ (nm)	$\langle p \rangle$	R_G ‡ (nm)
A	0.34	0.77 ± 0.05	2.0 ± 1.0*	0.1 ± 0.05	9.5
B	0.51	0.90 ± 0.02	3.0 ± 1.0	†	9.5

* Extrapolated;
† See text;
‡ From ref. 13

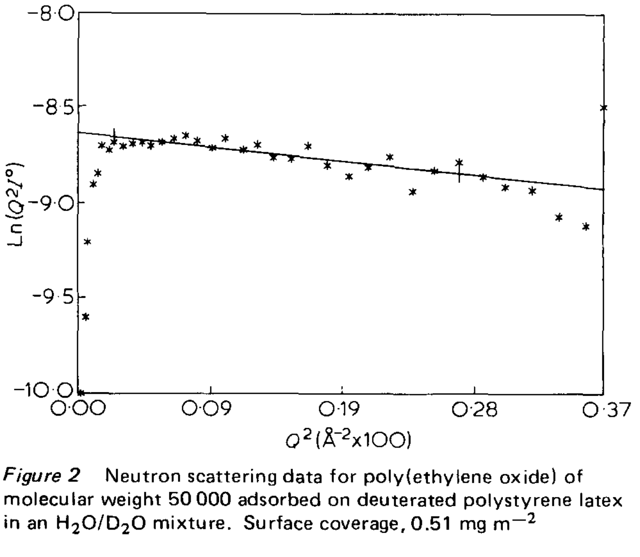

Figure 2 Neutron scattering data for poly(ethylene oxide) of molecular weight 50 000 adsorbed on deuterated polystyrene latex in an H_2O/D_2O mixture. Surface coverage, 0.51 mg m^{-2}

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References

1 Fontana, B. and Thomas, J. *J. Phys. Chem.* 1961, **65**, 480
2 Robb, I. D. and Smith, R. *Eur. Polym. J.* 1974, **10**, 1005
3 Grant, W. H., Morrissey, B. W. and Stromberg, R. R. *Polym. Sci. Technol.* (*A*) 1975, **9**, 43
4 van den Boomgaard, Th., King, T. A., Tadros, Th. F., Tang, H. and Vincent, B. *J. Colloid Interface Sci.* 1978, **66**, 68
5 Barnett, K. G. and Cosgrove, T. *J. Mag. Res.* submitted for publication
6 Killmann, E., Eisenlauer, J. and Korn, M. *J. Polym. Sci.* (*C*) 1977, **61**, 413
7 Allen, G. and Maconnachie, A. *Br. Polym. J.* 1977, **9**, 184
8 Stuhrmann, H. B. *J. Appl. Crystallogr.* 1974, **7**, 173
9 Chauvin, C., Pfeiffer, P., Witz, J. and Jacrot, B. *Virology* 1978, **88**, 138
10 Cebula, D., Thomas, R. K., Harris, N. M., Tabony, J. and White, J. W. *Faraday Discuss.* 1978, **65**, 76
11 Crowley, T. *PhD Thesis*, Oxford (1981)
12 Varoqui, R. and Dejardin, P. *J. Chem. Phys.* 1977, **66**, 4395
13 Vincent, B., Luckham, P. F. and Waite, F. A. *J. Colloid Interface Sci.* 1980, **73**, 508

Thermally-induced structural change in polyacrylonitrile

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Introduction

In a recent publication[1] it was pointed out that the dielectric relaxation of polyacrylonitile (PAN) in identical temperature and frequency ranges reported from four different laboratories[1-4], showed some differences, implying differences in the structure of the PAN samples used. Results on the samples used by Hayakawa *et al.*[2] were found to be markedly different from those of the other authors[1,3,4]. Hayakawa *et al.*[2] used a solution-grown PAN film which had undergone heat treatment for 30 h at 130°C, whereas other authors[1,3,4] used powder samples which had not been heat treated. Thus the previous comparative study[1] of the various reports on dielectric relaxation of PAN revealed that the prolonged heat treatment might possibly be responsible for the observed discrepancies in the results. This contention could not be confirmed in the previous investigation[1] because the data on heat treated and untreated PAN were originating from different laboratories and other conditions of sample preparation were not identical.

We have thus attempted a systematic investigation of the effect of heat treatment on the dielectric relaxation of PAN. The heat treated and untreated samples used in this study were identical in all other respects except the heat treatment.

Experimental

PAN used in this work was prepared by free radical polymerization using α,α'-azobisisobutyronitrile as initiator by the method described in detail elsewhere[5].

PAN powder was subjected to heat treatment at 120°C for 24 h under an air atmosphere by keeping the specimen in a closed flask in a constant temperature oven, followed by slow cooling to room temperature. The specimen turned yellow after heat treatment.

For dielectric measurements, discs of about 1 mm thickness and 1 cm diameter were prepared by compressing the pre-dried (vacuum oven at 40°C) PAN powder in a pellet-forming press. The disc surfaces were silver-coated for achieving better electrode contact.

Dielectric measurements at constant frequency (100 Hz) and temperatures varying in the range 30° to 160°C were carried out on a General Radio Bridge (GR 716 CS). Specimens were enclosed in a thermostatically-controlled chamber maintained to within ±0.1°C. A thermocouple placed close to the specimen was used for measurement of specimen temperature.

Results and discussion

Results of dielectric measurements for the untreated PAN and the PAN heat treated at 120°C for 24 h are shown as variations of dielectric constant (ε') *versus* temperature in *Figure 1*, and dissipation factor (tan δ) *versus* temperature in *Figure 2*.

The insignificant rise in dielectric constant with temperature up to about 90°C observed in both these samples (*Figure 1*) may be attributed to the glassy state of the polymer. The glass transition temperature (T_g) of PAN has

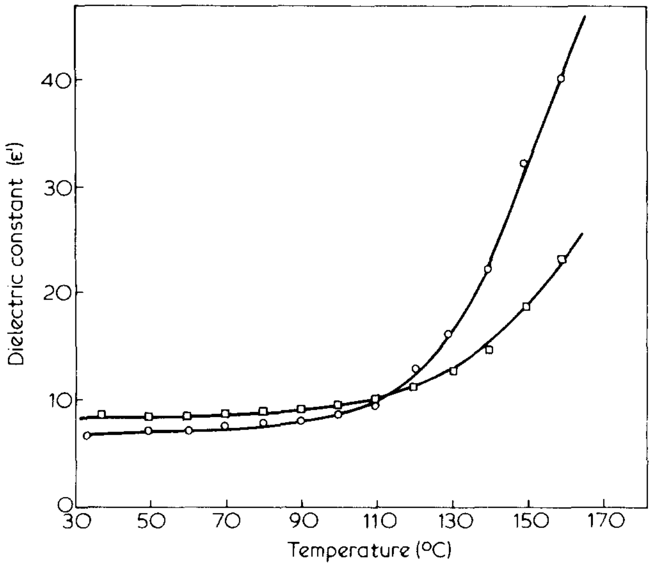

Figure 1 Variation of dielectric constant with temperature for untreated PAN (○) and PAN heat-treated at 120°C for 24 h (□)

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