Adsorption of polymers at the solid-liquid interface: a comparison of the e.p.r. and i.r. techniques

I. D. Robb and R. Smith
Unilever Research Laboratory, Port Sunlight, Wirral, Merseyside L62 4XN, UK
(Received 29 November 1976)

Several experimental techniques are available for studying the adsorption of polymers at the solid–liquid interface, though each is subject to considerable uncertainty, either in measurement or interpretation. We have used electron paramagnetic resonance (e.p.r.) to study the adsorption of PVP and PMMA on carbon and silica, and compared the results with both n.m.r. and i.r. I.r. measures the actual number of segments attached to the surface whereas magnetic resonance measures the number of segments immobilized by close association with the surface. For PMMA adsorbed onto silica from chloroform, e.p.r. indicated a flatter configuration than did i.r., a result consistent with alternative segments being bound to the surface. Differences in flexibility between PVP and PMMA may have given rise to different configurations at the silica–chloroform interface. Conditions under which e.p.r. can be used to study the adsorption of polymers were investigated.

INTRODUCTION

This paper outlines progress in the application of electron paramagnetic resonance (e.p.r.) to the study of the behaviour of polymers adsorbed at the solid–liquid interface. The advantages and disadvantages inherent in the technique are described and comparisons made with the results from other techniques. The method relies on the fact that when a random-coil polymer is adsorbed at a solid–liquid interface, segments in trains (i.e. in close contact with the surface) have a lower mobility than segments in loops or tails (more than 3–4 carbon atoms from the surface). These differences in mobility cause a difference in the magnetic (n.m.r. or e.p.r.) relaxation time of atoms attached to the backbone of the adsorbed polymer. If the signals from the loops and trains can be separated, their relative intensities can be estimated by comparison with standards. This allows an estimate of p, the fraction of segments in trains, to be made. Thus spin labels chemically attached at random to the polymer provide a means of monitoring the behaviour of adsorbed polymers.

The limitations and benefits of the method are as follows. First, introduction of the label causes a perturbation in the adsorption energy per segment, thus changing the behaviour of the segments near the label. Situations where this pertubation is important are discussed below. Secondly, the mobility of the backbone is measured and p estimated from those segments having relatively fast or slow mobilities. Hence for short loops of about 2 or 3 segments, which may occur where the polymer chain lies across some surface defect or pore, the mobility of the loop segments would be largely determined by the adjacent train mobilities, particularly if the trains are long (~10 segments or more). Hence e.p.r. would see the short loops as trains whereas some other techniques, such as infra-red, would not. Thus a comparison of the results from e.p.r. and i.r. could give an indication of the occurrence of short loops. The last major disadvantage is that the method is only useful for random-coil polymers and is not helpful with the adsorption of globular proteins. The advantages of the method are: (1) on colloidal systems with solids of surface area greater than about 1 m^2/g, the behaviour of polymers at low coverage (~10% of plateau adsorption) can be observed; (2) the influence of changes in the solvent, temperature or molecular weight can be investigated; (3) a wide range of high area solids, such as colloidal particles, paper and cotton can be studied; (4) exchange between labelled and unlabelled polymers can be studied, allowing estimates to be made of the time required for equilibrium to be reached. So far, the random-coil polymers that have been spin-labelled include poly(vinyl pyrrolidone)[1], polystyrene[2], poly(methyl methacrylate)[3,4], poly(ethylene imine), gelatin, polysaccharides[5] including heparin, poly(ethylene glycol)[6], polyamides[7] and polyesters[7].

EXPERIMENTAL

The experimental methods were basically the same as described in earlier publications[1,8]. The spin-labelled poly (vinyl pyrrolidone) (PVP) had a molecular weight of about 40 000 and the poly(methyl methacrylate) (PMMA) was a sample from BDH, and had a molecular weight of 85 000. determined by viscosity in acetone at 298K. The PMMA was spin-labelled by reacting it with 4-amino-2,2,6,6-tetramethyl piperidinyl-1-oxyl in *p*-xylene. The labelled polymer was collected and purified by several solution and precipitation steps. The carbon black was a sample of Mogul L, of surface area 150 m^2/g, supplied by Cabot Carbon. It was boiled in concentrated nitric acid for 3 h, washed until free of acid, and dried. Adsorption isotherms were determined by adding a known weight of carbon to solutions containing various amounts of polymer, and the mixture ultrasonicated for 15 min. After equilibrating for 24 h, they were centrifuged at 30 000 rev/min, and the concentration of polymer in the supernatant estimated by e.p.r. The adsorption isotherm was calculated from the amount adsorbed. Spectra were recorded on a Varian E-4 spectrometer and subtraction of the spectra was carried out on a Nicolet 1074

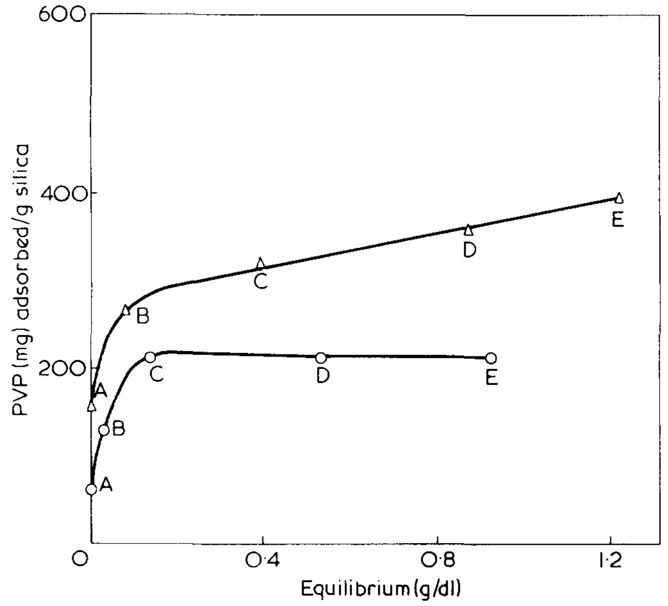

Figure 1 Adsorption isotherm of PVP on carbon from: ○, water; △, 0.5 M Na_2SO_4

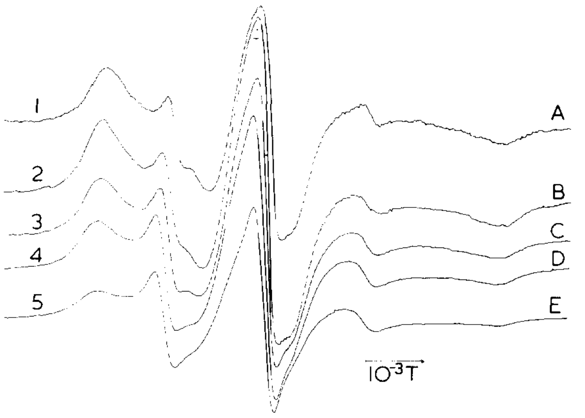

Figure 2 Spectra of PVP adsorbed onto carbon from water. Each spectrum comes from points on the isotherm (*Figure 1*) having a corresponding letter A–E. 1, $p = 0.95$; 2, $p = 0.95$; 3, $p = 0.90$; 4, $p = 0.78$; 5, $p = 0.67$

computer. Values of p were estimated as follows[8]. Spectra from a 2% solution of the spin-labelled polymer in aqueous glycerol (47 %w/w glycerol) were measured at temperatures between 313 and 263K. Spectra taken at lower temperatures (higher viscosities) corresponded to spectra from polymer segments in trains, whereas those taken at higher temperatures corresponded to segments in loops. By adding, on the computer, different proportions of spectra taken in aqueous glycerol at high and low temperatures, the spectra of the adsorbed polymer could be simulated, and from the proportions used the value of p, the fraction of segments in trains, was estimated.

RESULTS AND DISCUSSION

The adsorption isotherms for the PVP onto carbon from water and 0.5 M Na_2SO_4 are shown in *Figure 1*. The spectra of the adsorbed polymers are shown in *Figure 2*. The carbon substrate produced a single broad line whose intensity was normally less than 10% of the signal from the adsorbed PVP. The signal from the carbon has been subtracted from the spectra in *Figures 2* and *3*. The spectra from polymers adsorbed from 0.5 M Na_2SO_4 are shown in *Figure 3*. Values of p are shown in all three Figures. The results in *Figure 2* show that the adsorbing molecules tend initially to adsorb in a relatively flat configuration and become more looped (or have longer tails) as saturation polymer coverage is approached. This is essentially the same result as obtained for PVP adsorption onto silica[8].

In order to compare the adsorption behaviour of polymers as studied by i.r. and e.p.r., the adsorption of PMMA on aerosil silica from chloroform was studied. The infra-red data have been reported earlier[10]. The adsorption isotherm for the labelled PMMA is shown in *Figure 4*, and was determined both by direct weighing (of the silica with and without polymer) and from concentrations of unadsorbed polymer measured by e.p.r. intensities. The spectra of the adsorbed polymer taken at the points indicated, are shown in *Figure 5*. In contrast to the PVP adsorption onto silica from chloroform[8], PMMA although initially adsorbing in a flat configuration also had a relatively flat configuration at high coverages, approaching saturation. The observation of a flat configuration at high coverages agrees with the conclusions of Miyamoto and Cantow[9] who could not detect any high resolution n.m.r. spectra of PMMA adsorbed onto

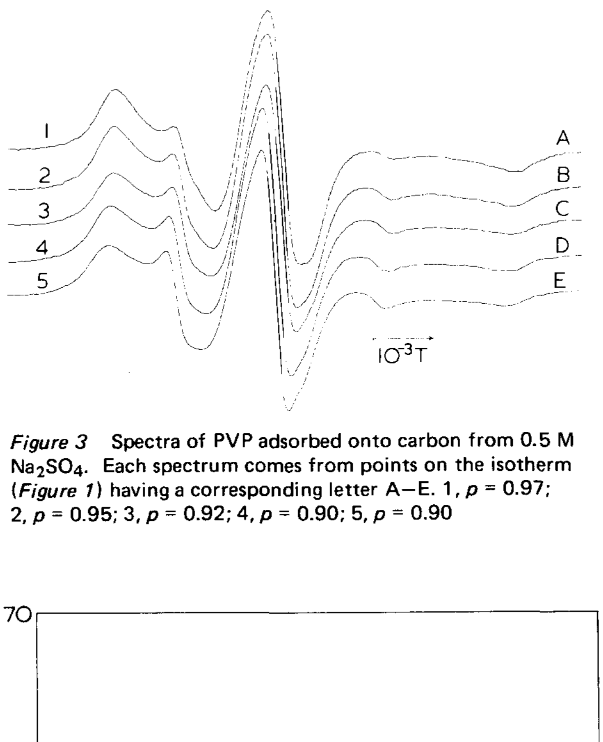

Figure 3 Spectra of PVP adsorbed onto carbon from 0.5 M Na_2SO_4. Each spectrum comes from points on the isotherm (*Figure 1*) having a corresponding letter A–E. 1, $p = 0.97$; 2, $p = 0.95$; 3, $p = 0.92$; 4, $p = 0.90$; 5, $p = 0.90$

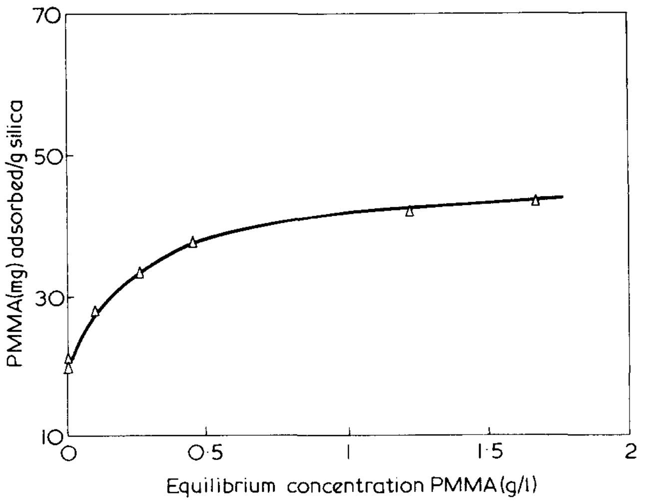

Figure 4 Adsorption isotherm for PMMA on silica from $CHCl_3$

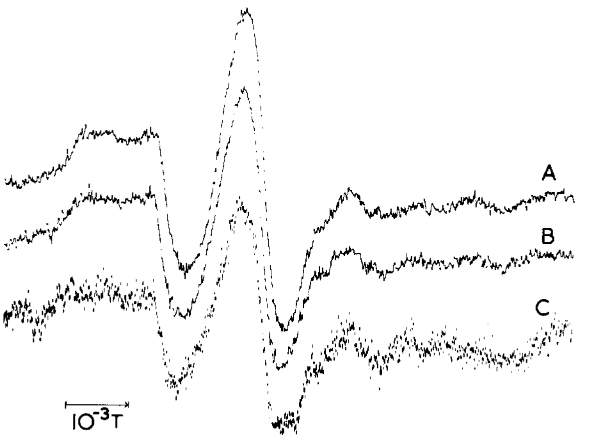

Figure 5 Spectra taken from labelled PMMA on silica at equilibrium concentrations: A, 1.25 g/l; B, 0.1 g/l; C, 0 g/l

silica from chloroform. As for e.s.r., n.m.r. relies on mobility to determine whether segments of polymer are in trains or loops. The i.r. data on PMMA adsorbed onto silica from $CHCl_3$ or similar solvents[10,11] suggest that about 40% of the segments form bonds through the carbonyl group onto the silica surface and that this fraction of segments is almost independent of surface coverage. This is also the case for other poly(acrylate esters)[12,13].

The different results from e.s.r. and i.r. might be understood as follows. Infra-red measures the actual number of bonds formed between the surface and polymer (if inherent assumptions about extinction coefficients are justified), whereas with e.s.r. the mobility of one segment is influenced by whether the neighbouring segments are in loops or trains. Thus if a polymer had each alternate segment in contact with the surface, e.s.r. would indicate a flat configuration with all segments in trains whereas i.r. would see a value of p of 0.5. Such a model, although not proven, would explain the differences observed by e.s.r. and i.r. for PMMA adsorbed onto silica from chloroform. Both techniques show little or no change in the value of p with surface coverage as would be expected if PMMA were flat at all coverages. For PVP there does not appear to be any comparable i.r. data to check the changing value of p with surface coverage.

The cause of the different behaviour of PVP and PMMA adsorbed onto silica is not clear. Both are adsorbed from chloroform via a carbonyl group onto silica so that the difference in the energy of adsorption per segment is probably small. Since chloroform is a good solvent for both PVP and PMMA, a more sensitive indication of the relative adsorbing affinities of the two polymers might be obtained from a study of their competitive adsorption/desorption behaviour. This was carried out in the following way. Spin-labelled PVP was adsorbed onto silica from chloroform at saturation coverage and unadsorbed PVP removed by washing. The silica was divided into three equal fractions. To the first was added unlabelled PVP (similar molecular weight) at the same concentration in $CHCl_3$ as the removed labelled PVP (i.e. 0.45 g/dl); to the second, unlabelled PMMA at a concentration corresponding to that at which saturation coverage was just reached (i.e. 0.18 g/dl); the third fraction was left in contact with pure solvent. The rate of desorption of the adsorbed spin-labelled PVP in contact separately with PVP, PMMA and pure solvent was monitored over a period of several days by simply measuring the amount of labelled PVP in solution.

The results are shown in *Figure 6*. A similar set of experiments was performed but having spin-labelled PMMA adsorbed on the silica instead of PVP. Rates of desorption of PMMA into solutions of PVP, PMMA and solvent were measured as for PVP and the results are shown in *Figure 6*. If one of the polymers were adsorbed with greater binding energy per segment than the other, it would be expected that the stronger binding polymer would displace the weaker. The results show that adsorbed PVP is desorbed more rapidly in the presence of PVP than PMMA; PMMA is also desorbed more rapidly by PVP than PMMA. Both these show that PVP is adsorbed more strongly than PMMA though, compared to the differences between polystyrene and PMMA[11], the differences in energies of adsorption per segment for PVP and PMMA are small. The molecular weight of the PMMA is larger than that of PVP and thus this is not the cause of the greater adsorption affinity of the PVP.

The cause of the different configurational behaviour (i.e. value of p) of PVP and PMMA on silica with changing surface coverage is difficult to explain. The competitive desorption experiments indicate that PVP has a stronger adsorption affinity than PMMA, although at high coverage it is more 'loopy' than PMMA. Factors such as the thermodynamic quality of the solvent, adsorption energy/segment and solvent/surface interactions should be reflected in the competitive desorption. One factor that may cause the PVP to be more loopy is the difference in flexibility of PVP and PMMA. A more rigid polymer, when adsorbed onto an irregular surface, is likely to have fewer segments in contact that could follow the contours of the surface, compared with a flexible polymer.

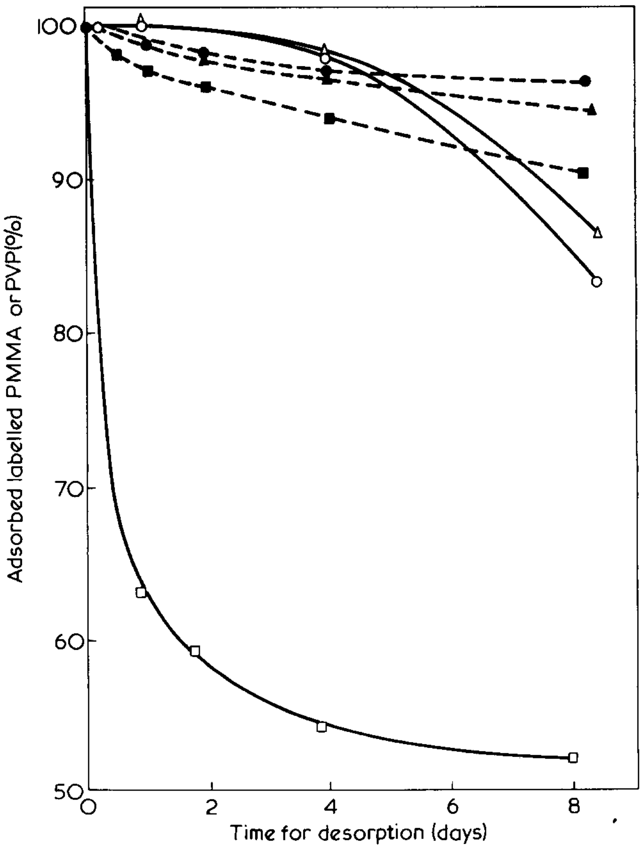

Figure 6 Competitive desorption experiments. Desorption of labelled PMMA in the presence of: △, unlabelled PMMA; ○, $CHCl_3$; □, unlabelled PVP. Desorption of labelled PVP in the presence of: ●, $CHCl_3$; ▲, unlabelled PMMA; ■, unlabelled PVP

The flexibility of a polymer (related here to the *trans–gauche* energy difference rather than the energy maximum of the intermediate configurations, sensed by n.m.r.) may be estimated from viscosity data. Under theta conditions the mean square radius of gyration can be calculated from K, where K is defined in the well-known Mark–Houwink–Sakurada equation, $[\eta]_\theta = KM^{0.5}$. Thus K reflects the backbone rigidity of the polymer as well as its chemical nature. The values of K reported in the literature are about $55 \pm 10 \times 10^{-5}$ dl/g for PMMA[14,15], and 74×10^{-5} dl/g for PVP[16], indicating that PVP is more rigid than PMMA. As the difference in their flexibilities is not large, the explanation for the different behaviours of adsorbed PVP and PMMA, based on flexibilities, must be regarded as tentative.

An important question regarding the application of e.p.r. to the study of polymers adsorbed at the solid–liquid interface is to what extent does the presence of the spin–label alter the adsorption of the polymer, thus giving false or misleading results? Considering the results from several systems, it appears that there are situations where the label does not seriously interfere with the adsorption, and also where it interferes to such an extent as to invalidate the method. These different results are governed largely by the adsorption energy of the label on the substrate. The spin-labels 4-amino-2,2,6,6-tetramethyl piperidinyl-l-oxyl-(I) and 2,2,6,6-tetramethyl piperidinyl-l-oxyl-(II), when dissolved in the solvents H_2O or $CHCl_3$, showed no detectable change in their molecular motion in pure solution and when 10% phase volume of silica was present, indicating weak adsorption of the label onto the silica from these solvents. Polymers adsorbed from these solvents (e.g. PVP from H_2O or $CHCl_3$) have shown[8] values of p as high as 0.90, particularly at low coverages, where the label would tend to lower p. Thus in these systems the weak adsorption of the label does not prevent the polymer adopting a relatively flat configuration, or the label's reflecting this. The isotherms for the labelled and unlabelled polymers were the same, although the isotherm is not likely to be sensitive to small amounts of impurities.

In another system, spin-labelled polystyrene was adsorbed onto silica from cyclohexane, at 313K. The spectrum from the spin-labels was a typical powder spectrum at all points on the adsorption isotherm, indicating a flat configuration with all segments in trains at both high and low coverages. However, the isotherm of the labelled polymer showed almost double the plateau adsorption level of that of the unlabelled polymer. As this may have been due to the strong adsorption of the label itself, the adsorption isotherm of the labels I and II onto silica from cyclohexane, chloroform and mixtures of the two were studied. The spin-labels (4×10^{-4}g) were dissolved in 5 ml of various chloroform–cyclohexane mixtures, silica (50 mg) added and the suspension shaken gently for 3 h. The suspension was centrifuged and the concentration of the unadsorbed label estimated from the intensity of its signal in the supernatant. The results are plotted in *Figure 7* as percentage of label adsorbed onto the silica against composition of the solution. Clearly, as the chloroform content is increased, the adsorption affinity of the label for the silica decreases until, at about 40–50% $CHCl_3$, no adsorption can be detected. Assuming a thickness of the absorbed layer of 0.6 nm for the label on silica, free energies of adsorption for the label in kJ/mol were calculated and are shown in *Figure 7*. The strong adsorption of both labels from pure cyclohexane is likely to be a consequence of the interaction between the surface hydroxyl group of the silica and the polar groups of the labels. Added chloroform would not only tend to compete with the label for the silanol groups but also provide a more favourable solvent for the label. Thus for adsorption of labelled polymers, the e.p.r. method is invalid if the label itself is strongly adsorbed onto the solid–liquid interface. An example of such a system occurs when polymers containing nitroxide spin labels are adsorbed onto a polar surface from a non-polar solvent. Preliminary results with the adsorption of labelled polymers onto non-polar surfaces (graphitized carbons) from a non-polar solvent indicate that the perturbation caused by the label is small.

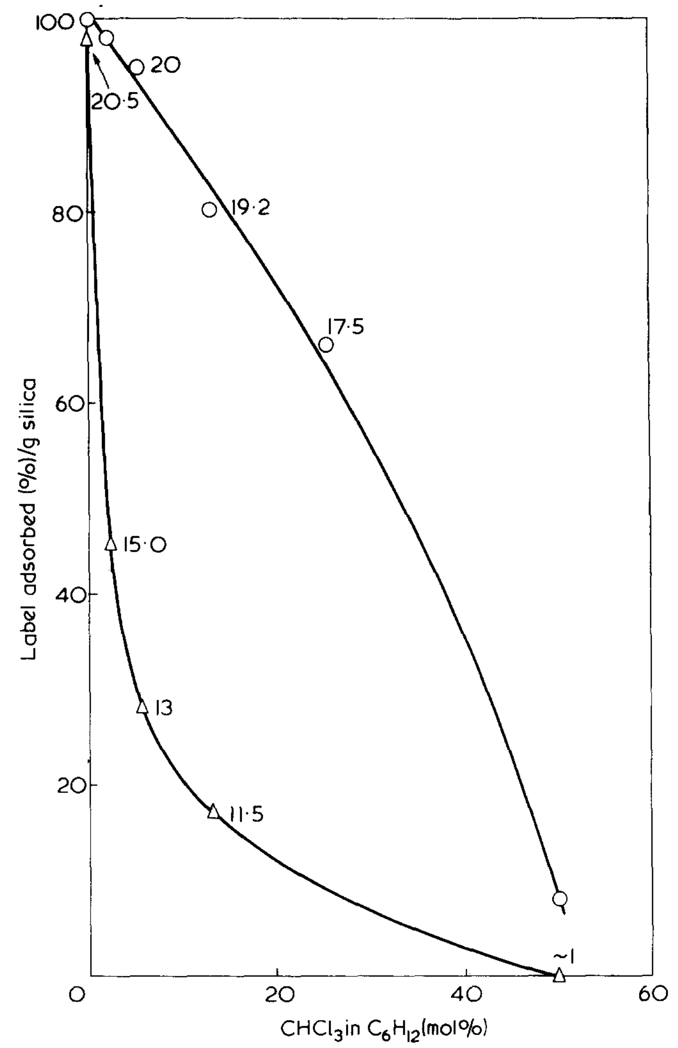

Figure 7 Adsorption of nitroxide labels onto silica from mixtures of chloroform and cyclohexane. Adsorption energies, expressed in kJ/mol are shown on the curves. ○, label (I); △, label (II)

CONCLUSION

For the adsorption of PVP onto a polar carbon surface from chloroform, the fraction of segments in trains decreases with increasing surface coverage (as observed previously for adsorption of PVP onto silica). In contrast, PMMA adsorbed onto silica remains in a flat configuration over the whole of its adsorption isotherm. Competitive desorption experiments using PVP and PMMA indicate that the PVP is slightly more strongly adsorbed than PMMA. The different configurations of PVP and PMMA on silica may be the result of PVP's being a more rigid molecule than PMMA. It is shown that spin-labelled polymers should not be used in systems where the label itself is strongly adsorbed at the solid–liquid interface, but when the adsorption of the label is weak, meaningful results on the behaviour of adsorbed polymers can be obtained.

REFERENCES

1 Fox, K. K., Robb, I. D. and Smith, R. *JCS Faraday Trans. 1.* 1974, **70**, 1186

2 Bullock, A. T., Cameron, G. G., and Smith, P. *Polymer* 1972, **13**, 89

3 Bullock, A. T., Cameron, G. G. and Elsom, J. M. *Polymer* 1974, **15**, 74

4 Shiotani, M. and Sohma, J. *Rep. Prog. Polym. Phys. Japan* 1974, **17**, 505

5 Cafe, M. C., Pryce, N. G. and Robb, I. D. *Polymer* 1976, **17**, 91

6 Törmälä, P., Martinmaa, J., Silvennoinen, K. and Vaahtera, K. *Acta. Chem. Scand.* 1970, **24**, 3066

7 Törmälä, P., Silvennoinen, K. and Lindberg, J. J. *Acta. Chem. Scand.* 1971, **25**, 2659

8 Robb, I. D. and Smith, R. *Eur. Polym. J.* 1974, **10**, 1005

9 Miyamoto, T. and Cantow, H. -J. *Makromol. Chem.* 1972, **162**, 43

10 Thies, C., Peyser, P. and Ullman, R. *Proc. Int. Congr. Surf. Activity 4th, Brussels, September 1964* p 1041

11 Thies, C. *J. Phys. Chem.* 1966, **70**, 3783

12 Botham, R. and Thies, C. *J. Colloid Inter. Sci.* 1969, **31**, 1

13 Fontana, B. J. and Thomas, J. R. *J. Phys. Chem.* 1961, **65**, 480

14 Sakurada, I., Nakajima, A., Yoshizaki, O. and Nakamae, K. *Kolloid Z. -Z. Polym.* 1962, **186**, **41**

15 Inagaki, H., and Kawai, S. *Makromol. Chem.* 1964, **79**, 42

16 Elias, H. -G. *Makromol. Chem.* 1961, **50**, 1