Measurement of the interaction force profiles between block copolymers of poly(2-vinylpyridine)/poly(t-butylstyrene) in a good solvent

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Direct measurements of the interaction forces $F(D)$ between two atomically smooth solid (mica) surfaces immersed in toluene have been performed as a function of surface separation. Interaction profiles were also measured following adsorption of the AB block copolymer poly(2-vinylpyridine)/poly(t-butylstyrene) and incubating the surfaces overnight in these solutions. Toluene is a poor solvent for poly(2-vinylpyridine) and a good solvent for poly(t-butylstyrene) implying that on adsorption the poly(t-butylstyrene) chain will extend away from the mica surface, i.e. act as a stabilizing chain. Three molecular weight poly(t-butylstyrene) chains ($M_w = 4700$, 15 100, 30 700) anchored by poly(2-vinylpyridine) have been studied. The pure toluene results showed an attraction between the surfaces at distances $\leqslant 10$ nm in agreement with our earlier findings[13]. Following overnight incubation of the surfaces in the copolymer solutions long range repulsive interactions were observed which increased approximately exponentially with decreasing surface separation. The form of the force profile and the dependence of the distance of onset of interaction with the molecular weight of the stabilizing chain are compared with theoretical predictions from scaling theory. Good agreement is found for the dependence of the adsorbed layer thickness with molecular weight, however scaling ideas do not describe the form of the force profile.

(Keywords: interaction forces; poly(2-vinylpyridine); poly(t-butylstyrene); block copolymers; adsorption; mica)

INTRODUCTION

For many years macromolecules have been used by man to stabilize colloidal dispersions[1,2], but it is only recently that interactions between polymer bearing surfaces, which are responsible for steric stabilization, have been measured directly. Early studies involved surface balance[3,4] and compression cell techniques[5,6], however, recently the 'mica technique' developed by Tabor and coworkers to study Van der Waals forces[7,8], has been extended to the case where the interactions between mica sheets bearing adsorbed polymer layers have been measured. The majority of these studies have involved measuring the interactions between high molecular weight homopolymers. Interactions between polymers in poor solvents[9,10] (polystyrene in cyclohexane at 23°C), theta solvents[10,11] (polystyrene in cyclohexane at 37°C), and good solvents[12–14], (poly(ethylene oxide) in aqueous 0.1 M potassium nitrate solution[12] and toluene[13], and polystyrene in cyclopentane[14]), have been studied. The results have shown that at full surface coverages of polymer, repulsion between the polymer layers is observed in a good solvent, whilst in both poor and theta solvents attractions are noted. These results agree qualitatively with the observation that colloidal particles bearing adsorbed polymer layers flocculate near the theta point for the polymer in solution[1,2].

From a practical viewpoint, it is found that homopolymers are not, in general, good stabilizers of colloidal dispersions. This is a consequence of the requirements for steric stabilization. These are first that the polymers adsorb strongly to the surface and second that the polymer extends sufficiently far from the particle surface to prevent the Van der Waals forces between the surfaces becoming predominant[1]. These criteria are mutually exclusive for homopolymers. If the polymer adsorbs too strongly to the particle surface, then the polymer will lie in a flat configuration on the surface and not impart stability, on the other hand, if the polymer extends too far from the particle surface, adsorption will be weak and in some cases no adsorption occurs. The two criteria may be met using a specifically designed block or graft copolymer, where one chain adsorbs strongly to the surface and the second one extends into solution. Such polymers are widely used as stabilizers of particles. In the current experiments we have studied the interactions between adsorbed layers of poly(2-vinylpyridine)/poly(t-butylstyrene) (P2VP/PBS) AB block copolymers. The solvent chosen was toluene, which is a good solvent for poly(t-butylstyrene) (PBS), and a poor one for poly(2-vinylpyridine) (P2VP). Therefore, the P2VP block will anchor the PBS to the mica surface. Preliminary experiments have shown that PBS does not adsorb to mica, therefore the polymer will be adsorbed with the PBS tail extending away from the mica surface as shown in *Figure 1*. This is a similar system to that studied by Hadziiannou *et al.* who have measured the interaction between high molecular weight block copolymers of polystyrene and P2VP[15].

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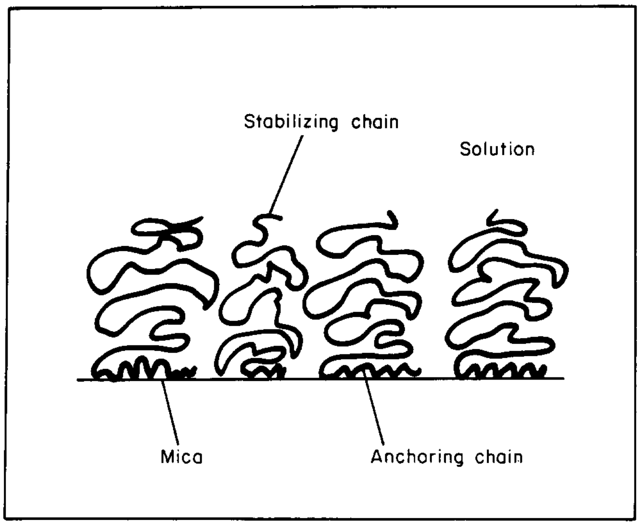

Figure 1 Schematic representation of the configuration of the block copolymers adsorbed onto mica

EXPERIMENTAL

Materials

The polymers used in these experiments were P2VP/PBS block copolymers. They were prepared by sequential anionic polymerization of t-butylstyrene and 2-vinyl pyridine, and terminated with methanol. The molecular weights of the block copolymers are given in *Table 1*. Further details of the polymerization procedure and characterization of these polymers will be given elsewhere.

The toluene used was Analar grade material, which was dried over calcium hydride and doubly distilled prior to use.

The mica used was best quality FS/GS, Grade 2, Muscovite ruby mica and was obtained from Mica and Micanite Ltd, London. The cleaving of mica and assembly of the surface forces apparatus were carried out in a class 1000 clean room.

Methods

The surface forces apparatus and the experimental procedure have been extensively documented[7-17] and only a summary will be presented here. Two mutually perpendicular cylindrical glass formers, each having a $\simeq 2$–$4\,\mu$m thick mica sheet attached with molten glucose, were brought together in a controlled manner (to an accuracy of ± 1.0 nm), using a piezoelectric crystal and a combination of stepper and synchronous motors. The upper cylinder was rigidly fixed whilst the lower cylinder was attached to a moveable spring of known spring constant, k ($\simeq 100\,\mathrm{N\,m^{-1}}$). The back surfaces of the mica were previously silvered to a thickness of $\simeq 46$ nm. This arrangement formed an interferometer when collimated white light was passed up through the apparatus. The resulting fringes of equal chromatic order (FECO)[17], were visualized using a spectrometer (0.5 m spectrometer with a 32 Å mm^{-1} diffraction grating), and the wavelengths of the FECO were measured by a micrometer eyepiece. By measuring both the applied motion (ΔD_0) and the actual motion (ΔD) of the mica surfaces, the force $F(D)$ between the two surfaces is simply given by the difference in the motions multiplied by the spring constant (k) i.e.

$$F(D) = k(\Delta D_0 - \Delta D) \tag{1}$$

The experiments were carried out by bringing the mica surfaces together in air and measuring the wavelengths of the FECO when the surfaces were in contact. Toluene was then introduced into the apparatus and the surfaces were left to thermally equilibrate in the liquid for 1–24 h. (The length of time was to ensure that no long-term changes occurred in the force profile, typically the surfaces were left to equilibrate for 1 h.) The force profile in toluene was then measured. This was achieved by bringing the surfaces together from a distance of approximately 200 nm, and measuring the wavelengths of the FECO until the surfaces were in contact. This procedure enabled the force–distance profile and contact position for the mica surfaces in toluene to be measured. The toluene was drained from the apparatus, and a solution of the block copolymer in toluene was introduced. Measurement was normally started 16 h after the introduction of the polymer solution. Longer time periods did not alter the form of the force profile. The force profile was redetermined and the change in the force profile due to the adsorption of the polymer was measured. The force profile was redetermined several times under varying rates of compression and decompression of the surfaces. The block copolymer solution was then drained from the apparatus and replaced by pure toluene, this had the effect of reducing the polymer concentration in the toluene by a factor of $\simeq 100$. The force profile was then redetermined following incubation in the fresh toluene for 1–24 h. The temperatures of all the experiments were 22 ± 2°C.

RESULTS

Before the addition of polymer in any experiment the $F(D)$ profile between the bare mica surfaces immersed in toluene was determined. *Figure 2* shows a typical force profile. The force axis is normalized as F/R, where R is the mean radius of curvature of the mica surfaces in their mutual cross cylinder configuration. According to the Derjaguin approximation, which is nearly exact for $R \gg D$, as in the current experiments, this gives the interaction profile per unit area $E(D)$ of flat parallel surfaces a distance D apart, obeying the same force law, i.e.

$$F/R = 2\pi E(D) \tag{2}$$

This normalization is used in all subsequent force distance profiles. No forces were detected as the surfaces approached from large D ($\simeq 300$ nm) down to $D \leqslant 10$ nm, when an attraction was observed; on further compression

Table 1 Characteristics of polymers

Molecular weight (M_w) total	Molecular weight (M_w) PBS	Molecular weight (M_w) P2VP	M_w/M_n (total)	$\langle r_a^2 \rangle^{1/2}$ PBS (nm)
33 000	30 700	2 300	1.5	9.4
21 400	15 100	6 300	2.2	6.6
6 200	4 700	1 500	2.3	4.3

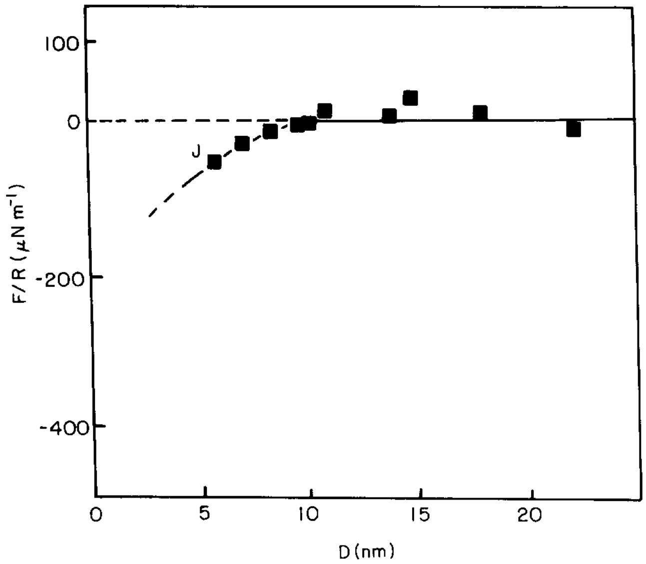

Figure 2 Force–distance profile between mica surfaces immersed in pure toluene, where the force axis is normalized as F/R. J represents the position of an inward jump due to the mechanical instability of the force measuring spring

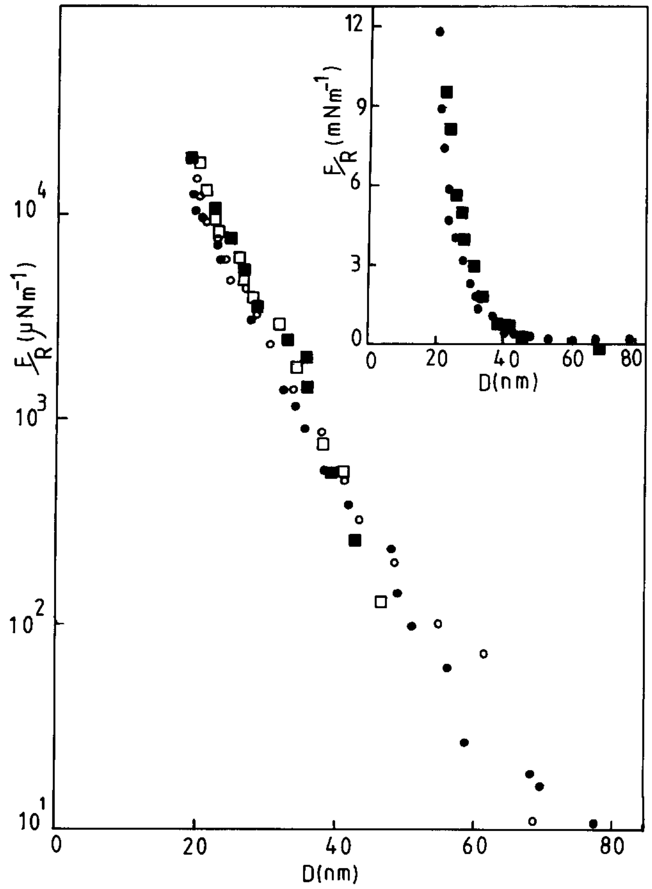

Figure 3 Force–distance profile (with log force scale) following 16 ± 4 h incubation of the mica surfaces in a $100\,\text{mg dm}^{-3}$ solution of P2VP/PBS of $M_w = 33\,000$: ● = first compression; ■ = first decompression; ○ = second compression; □ = second decompression. The inset is an expansion of the force profile showing the initial stages of interaction

the surfaces jumped spontaneously from $D \simeq 5 \pm 1$ nm to a new position very close to the 'contact' position of the mica surfaces in air. Such jumps are due to the mechanical instability of the spring on which one of the mica surfaces is attached, and are expected whenever $\mathrm{d}F(D)/\mathrm{d}D \geqslant k$.

Figure 3 shows the force profiles determined after introducing the $M_w = 33\,000$ P2VP–PBS block copolymer into the apparatus (at a concentration of $10\,\text{mg dm}^{-1}$) and allowing the mica surfaces to incubate in the solution at a separation of 2 mm for 16 h. The results are presented on a semilogarithmic scale to enable the display of several orders of magnitude in $F(D)$. The salient features of these profiles are characteristic of other molecular weight block copolymers studied.

On approach of the surfaces, following incubation in the polymer solution, no interaction was measurable from large surface separations down to $D = 75$ nm, when a monotonically increasing repulsion was observed. The surfaces could be compressed to separations of 20 nm whereupon a steep repulsion was observed, and, using the present apparatus, it was not possible to compress the surfaces any further together. On separation of the surfaces the same (within error) force profile was observed. *Figure 4* shows the data corresponding to *Figure 3* plotted on a linear scale, the inset shows the initial stages of interaction on an expanded linear scale. The main feature to note here is the absence, within error, of any attractive or adhesive component in the interaction. *Figure 5* shows the results following replacement of the block copolymer solution by fresh toluene for varying time intervals.

Figure 6 and *7* summarize the $F(D)$ profiles following incubation of the mica surfaces in $10\,\text{mg dm}^{-3}$ P2VP–PBS block copolymers of $M_w = 21\,400$ and 6200, respectively. The basic features of the profiles are similar

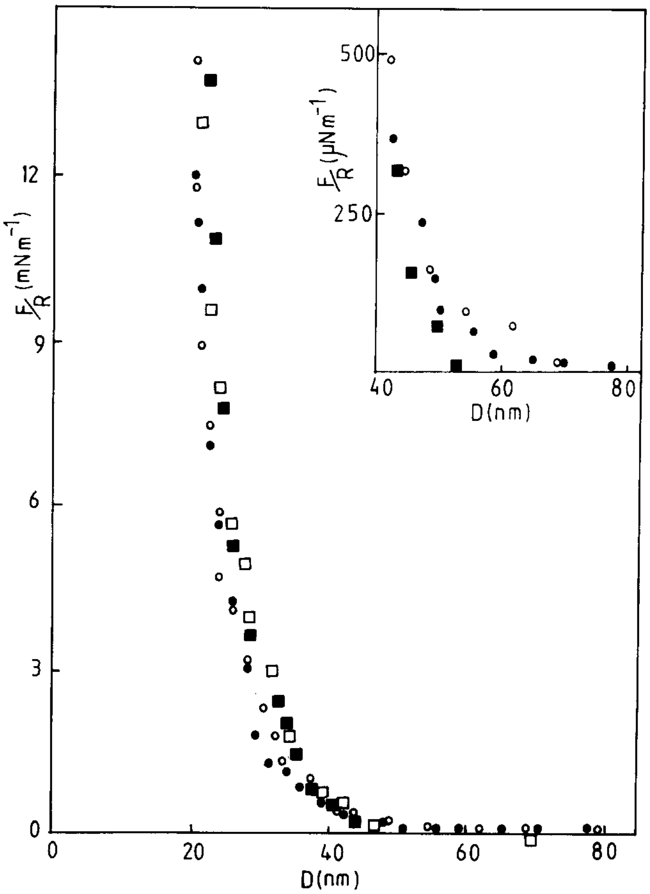

Figure 4 Force–distance profile (plotted with a linear force axis) of the data presented in *Figure 3*. The inset is an expansion of the force profile showing the initial stages of interaction. Symbols as in *Figure 3*

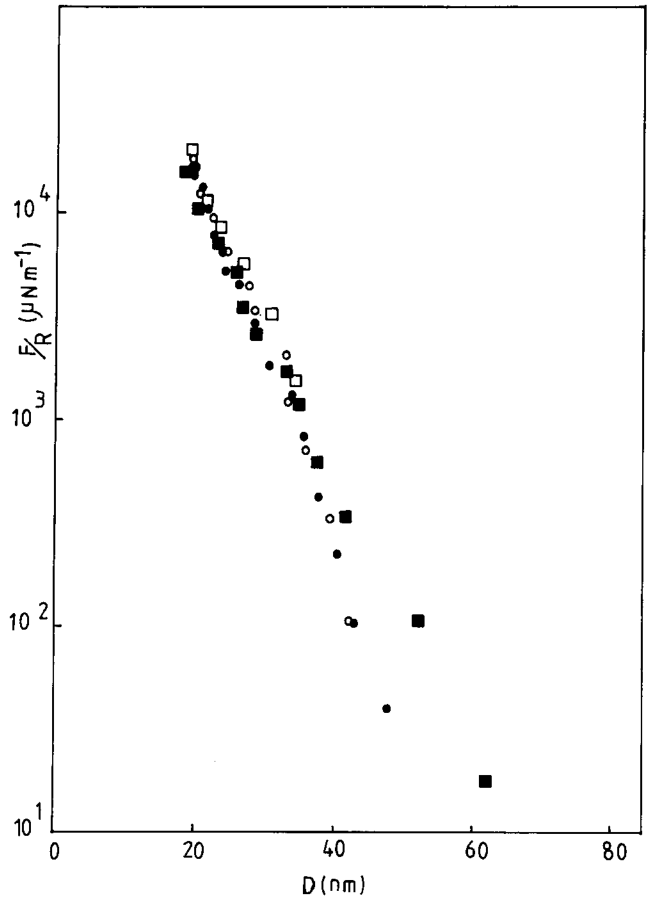

Figure 5 Force–distance profile of a semi-logarithmic scale, following replacement of the copolymer solution with toluene. Symbols as in *Figure 3*

to those obtained for the higher molecular weight block copolymers. The main difference in the results concerns the range of interaction over which the forces apply. The initial stages of interaction are reduced to 50 and 20 nm, respectively, and the surfaces may be compressed to surface separations of 12 and 3 nm, indicating a lower extension from the surface of the adsorbed layer, for the smaller block copolymers.

DISCUSSION

The short range attraction between the bare mica surfaces in pure toluene resembles a Van der Waals type interaction with a suitable Hamaker constant, and is similar to that obtained previously[13], with the exception that in the current studies the mica surfaces came into a flat molecular contact, whilst in our earlier studies the surfaces approached to within 1 nm of the mica contact. Despite the extensive drying of the solvent no molecular structuring of toluene close to the mica was noted, as has been observed previously for organic solvents (not toluene). This may be due to the disruption of the packing of the planar phenyl ring of toluene by the methyl group. The absence of any repulsive force between the mica surfaces greatly simplifies the results obtained in the presence of adsorbed polymer.

Before commencing the discussion of the results for the adsorbed copolymers it is necessary to comment on the results obtained for the two homopolymers, P2VP and PBS. Toluene is a non-solvent for P2VP, and P2VP of $M_w = 5000$ proved to be insoluble in toluene. Therefore, no force measuring experiments were conducted with this polymer. The results for the second homopolymer indicate that there was no adsorption of PBS onto mica from toluene. (The force profile was essentially identical to that obtained in pure toluene.) This may, perhaps, be expected since polystyrene does not adsorb onto mica from toluene, although it does from cyclohexane[9,10].

The main features of the force profile for all the block copolymers studied are very similar. A long range repulsive force, which increases approximately exponentially with decreasing distance was observed, following overnight equilibration of the mica surfaces in the copolymer solution. Within the error of the experiment the same force profile was observed on decompression of the surfaces as in compression. Since PBS itself does not adsorb onto mica and P2VP is insoluble in toluene, the conformation of the adsorbed polymer must have the P2VP part of the block adsorbed directly on the mica and have the PBS extended away from the mica (as shown in *Figure 1*). Recently, Fetters *et al.*[18] have shown that the characteristic ratio of poly(t-butylstyrene) to be 13.2 enabling an estimation of the unperturbed radius of gyration to be made (*Table 1*). The distances for the onset of interaction, namely 75, 50 and 20 nm, (*Figure 8*) for the three molecular weight polymers studied, correspond to several (9–12) unperturbed radii of gyration of the PBS. A significant feature is that the extension is considerably greater than the adsorbed layer thickness of

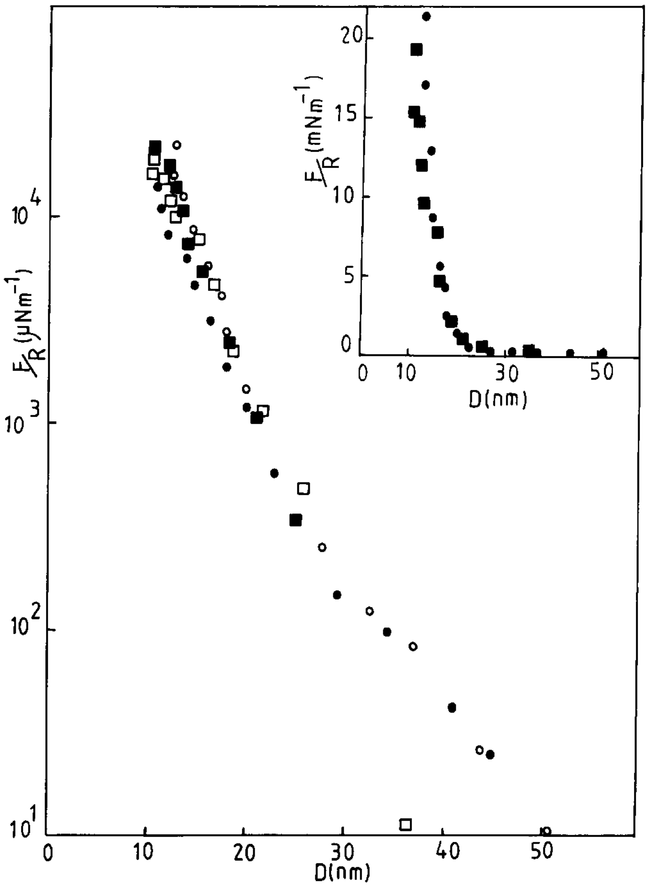

Figure 6 Force–distance profile (on a log force linear distance scale) following 16±4 h incubation of a 100 mg dm^{-3} solution of P2VP/PBS copolymer of $M_w = 21\,400$. Symbols as in *Figure 3*. The inset is a linear force plot of the same data

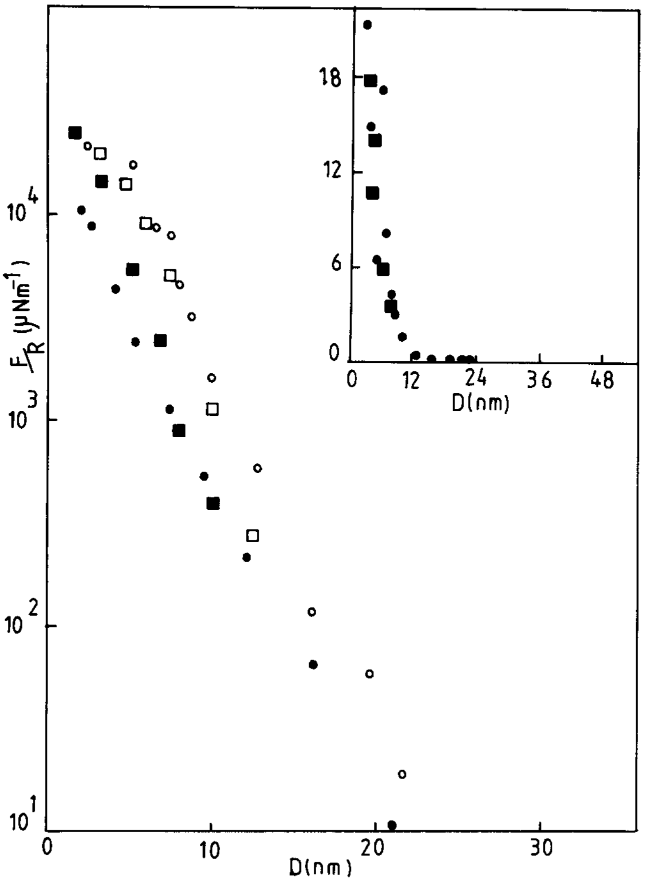

Figure 7 Force–distance profile (on a log force linear distance scale) following 16±4 h incubation of the mica surfaces in a 100 mg dm^{-3} solution of P2VP/PBS copolymer of $M_w = 6200$. Symbols as in *Figure 3*. The inset is a linear force plot of the same data

homopolymers adsorbed onto mica of a similar chain length. For example PEO of M_w 40000 which has $\simeq 2700$ bonds in the polymer backbone adsorbed onto mica from toluene has an adsorbed layer thickness of $\simeq 50.0$ nm, whilst the P2VP–PBS block copolymer with a PBS block $M_w = 30700$ and $\simeq 400$ bonds in the polymer backbone has an adsorbed layer thickness of $\simeq 38.0$ nm. This is of significance in the stabilization of colloidal dispersions by adsorbed polymers. In order to stabilize particles the adsorbed polymer must extend away from the particle surfaces over a distance sufficiently great in order to prevent a strong attraction between the particles due to Van der Waals forces. From these results it is clear that block copolymers of a much lower molecular weight than homopolymers are capable of stabilizing particles. The reason for this is that block copolymers are adsorbed to the surface at only one point (*Figure 1*), whereas homopolymers adsorb as a series of loops, trains and tails, resulting in block copolymers extending further from the surface than homopolymers of a similar chain length.

Alexander[19] and de Gennes[20] have recently considered the conformation of polymers grafted to an interface and, using scaling ideas, related the adsorbed layer thickness to the length of the polymer chain. Their analyses assumed the polymer was terminally attached to the surface and no other segments were attached to the surface; as discussed above, this is the situation in the present case. Two limiting cases were distinguished, for low and high surface coverages.

The low surface coverage case is a particularly simple one. Each chain occupies roughly half a sphere with a radius comparable to the radius of gyration in a good solvent R_g,

$$R_g = N^{3/5}a \tag{3}$$

where a is the monomer size and N the number of units in the polymer chain. Thus the thickness of the polymer layer, δ, will scale directly with R_g and with $N^{3/5}$.

The high surface coverage case is a more complex regime. Alexander has shown that the fundamental distance of the model, L, is the average distance between the grafting sites on the surface. In terms of the fraction of the surface covered by grafted polymer, σ, L is defined as:

$$L = a\sigma^{1/2} \tag{4}$$

The grafted chain was subdivided into 'blobs' of radius L each containing g monomers. Each 'blob' essentially acts as a random coil, thus the relation between g and L is similar to that between N and R_g, i.e.

$$L = ag^{3/5} \tag{5}$$

Thus when $L < R_g$ (in the overlap regime), $g < N$, thus the polymer concentration, $\phi = \sigma^{2/3}$, is

$$\phi a^{-3} = g/L^3 \tag{6}$$

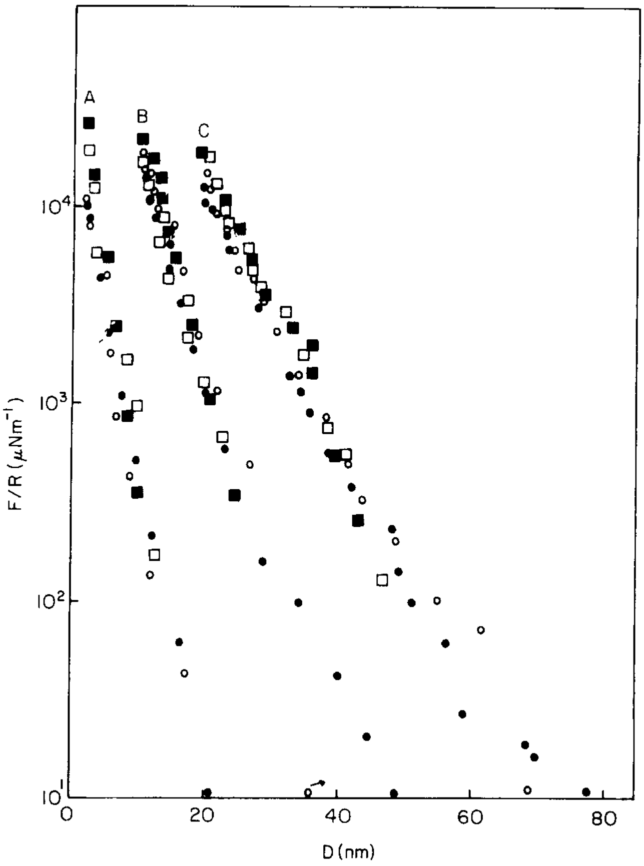

Figure 8 Force–distance profiles (on a log force linear distance scale) following 16±4 h incubation of the mica surfaces in a 100 mg dm^{-3} solution of P2VP/PBS copolymer of M_w = A, 6200; B, 21400; C, 33000, showing the molecular weight dependence of the force profile. Symbols as in *Figure 3*

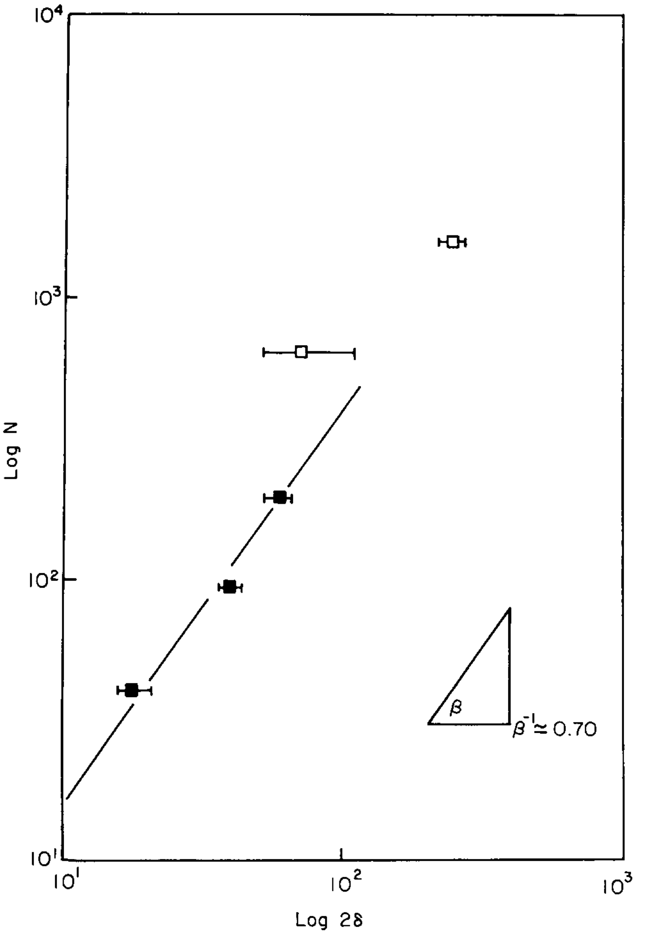

Figure 9 Plot of the distance of onset of interaction (taken to be $F/R = 50\,\mu\mathrm{N\,m^{-1}}$), against degree of polymerization of the stabilizing chain, N. |-■-| = data taken from *Figures 3*, *6* and *7*; |-□-| = data taken from ref. 15

The thickness of the adsorbed polymer layer, δ, which should determine the range of the forces in our experiment, is readily estimated. The polymer segment density, $a^{-3}\phi$, must be equal to the total number of monomers (N) per unit volume of grafted chain, (δL^{-2}), i.e.

$$a^{-3}\phi = N/(\delta L^{-2}) \tag{7}$$

and from equation (4) we find

$$a^{-3}\phi = N/(\delta a^{-2}\sigma^{-1}) \tag{8}$$

thus

$$\delta = Na\sigma^{1/3} \tag{9}$$

i.e. δ scales directly with N.

Thus we find that the molecular weight dependence of the adsorbed layer thickness will depend upon the degree of surface coverage of the grafted polymer. At low surface coverages δ scales with $N^{3/5}$, whilst at high surface coverages δ will scale linearly with N. It is of interest therefore to examine our results in this respect.

The results are shown on a log 2δ vs. log (number of monomers) plot in *Figure 9*, where 2δ is the surface separation where the interaction is first measured. The main feature is that the distance of the onset of interaction varies as

$$2\delta \propto N^{\beta} \tag{10}$$

where $\beta = 0.70$. Also included in *Figure 9* are the results obtained by Hadziioannou *et al.*[15], who have measured the interaction between adsorbed layers of a very similar copolymer (polystyrene/poly(2-vinylpyridine)). The molecular weights of their polymers were considerably higher enabling two orders of magnitude variation in degree of polymerization to be compared. It may be seen that both sets of data may be described by the same exponent despite the slight difference in molecular structure. We have used a power law representation of the data to highlight the difference between the variation of δ with N and the power laws predicted in the preceding discussion. Thus it appears in the current experiments as though the degree of surface coverage is at an intermediate level. However, it should be noted that in the case of adsorbed homopolymers on mica, the molecular weight dependence of the adsorbed layer thickness β, was 0.43 (ref. 21), where scaling theory predicts a hydrodynamic dependence of 0.60 (ref. 22). It has been shown that the reason for such a dependence was due to the surface forces technique being unable to detect the very distal segments of the adsorbed polymer. If in the current experiments the polymer segments furthest from the mica surface are not detected then again the actual molecular weight dependence of the adsorbed layer will be less than the predicted value. (Indeed it is tempting to speculate that β would be lowered by a similar proportion to that of the homopolymer case in which case $\beta = 1.0 \times 0.43/0.60 = 0.72$, a similar value to that measured.) Thus in conclusion, the block copolymers are adsorbed on the mica surface in a reasonably compact configuration, although it is not possible to say how compact.

The repulsive forces between the mica plates as they approach are due to osmotic interactions between the segments from opposing adsorbed layers as they come into overlap. We note that the forces measured on separation of the surfaces are, within error, identical to the forces measured on approach, irrespective of the rate of decompression. This is in contrast to the results observed for the interactions between adsorbed homopolymers[10,12,13], where the forces measured on separation of the surfaces were the same only when the rate of separation was slow ($\simeq 60$ min).

The present study is sufficiently direct to permit comparison of the results with predictions of various theoretical models of interactions between polymer-bearing plates. The results obtained with the homopolymers suggest that the copolymer is adsorbed with the P2VP portion flat on the mica surface and the PBS being extended away from the surface. Thus, as was the case for the adsorbed layer thickness measurements, the best model for our system is one of the polymer chains grafted at one end onto a surface.

We have previously noted a strong correlation between the polymer adsorbed layer thickness and predictions from scaling theory, it is therefore instructive to compare our experimental force profiles with predictions from scaling arguments. De Gennes[23] has analysed the two limiting cases for terminally attached chains, namely at low and high surface coverages, the two cases treated earlier for adsorbed layer thickness measurements.

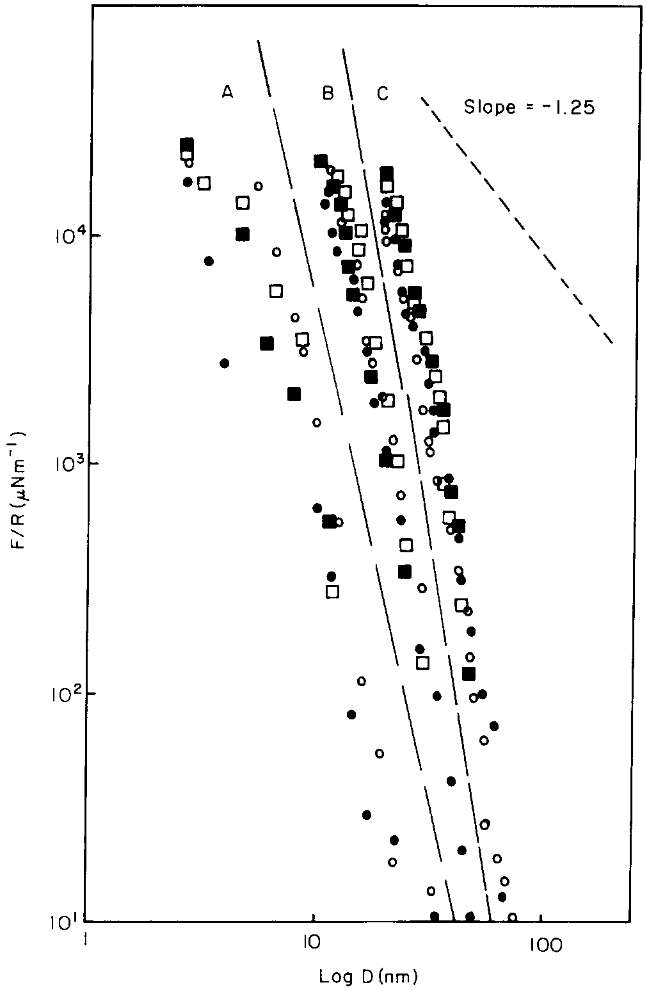

Figure 10 Force–distance profiles plotted on a logarithmic scale following 16±4 h incubation of the mica surfaces in a 100 mg dm^{-3} of P2VP/PBS copolymers of M_w=A, 6200; B, 21 400; C, 33 000. Also shown is the theoretical force law dependence predicted by De Gennes of −1.25 for high surface coverages (broken line)

The interaction between the adsorbed layers commences at a surface separation of 2δ. At separations less than 2δ the chain is squeezed in a thin gap and scaling arguments predict a force F:

$$F \simeq \frac{kT}{L^2 2\delta}\left(\frac{2\delta}{D}\right)^{8/3} \tag{11}$$

i.e. F scales as the surface separation $D^{-8/3}$, or the energy E scales as $D^{-5/3}$.

For the high surface coverage case the force is given by

$$F \simeq \frac{kT}{L^3}\left(\frac{2\delta}{D}\right)^{9/4} - \left(\frac{D}{2\delta}\right)^{3/4} \tag{12}$$

which for $D \ll \delta$ is given by

$$F \simeq \frac{kT}{L^3}\left(\frac{2\delta}{D}\right)^{9/4} \tag{13}$$

or the force scales as $D^{-9/4}$ and the energy scales as $D^{-5/4}$.

Thus the dependence of the force with distance predicted by the two models is rather similar. It is nonetheless instructive to compare our results with these simple scaling predictions. As mentioned previously, the force between the two cylindrical surfaces is in the Derjaguin approximation (which is nearly exact for $D \ll R$, the radius of curvature of the cylinders) equivalent to $2\pi RE$ where E is the energy of interaction between two flat plates. Thus F/R is directly proportional to the energy of interaction between two flat plates. Probably the most striking feature of the results is the linearity of the log (F/R) *versus* D plots, indicating that experimentally $E \propto \exp(-D)$. Scaling ideas do not predict such a dependence, however. A plot of log (F/R) against log (D) (*Figure 10*) will give the exponent. The exponent calculated for all molecular weight polymers is approximately −4, which is a considerably stronger dependence on force with distance than is estimated theoretically from scaling principles. It is not clear why there is little correlation between theory and experiment, particularly since scaling arguments predict the adsorbed layer thickness dependence. De Gennes' theory is based on the model of polymers terminally grafted onto a surface whilst in our experiments a block copolymer is adsorbed onto mica, thus comparison may be invalid.

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