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### Adsorption of Peo-b-Ps Copolymers on Surfaces. Infrared and Surface Force Measurements at XRCC

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ADSORPTION OF PEO-b-PS COPOLYMERS ON  
SURFACES. INFRARED AND SURFACE FORCE  
MEASUREMENTS AT XRCC

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ABSTRACT

Surface force and IR data on polystyrene-b-poly(ethylene oxide) block copolymers adsorbed on mica from toluene will be presented. The copolymers were selected to have a wide range of asymmetry radius ratio ( $\beta = R_{F,PS}/R_{F,PEO}$ )<sup>3/5</sup> as defined by Marques and Joanny. The extended length  $L$  of the block copolymers has been measured with the Surface Force Apparatus and shown to scale as  $L \sim N_{PS} N_{PEO}^{1/3}$  for moderately asymmetric copolymers ( $1 \ll \beta \gg N_{PEO}^{1/2}$ ). Deviations are observed when the nonadsorbing block is either much larger than the anchor block or approximately the same size. A general method using infrared spectroscopy has been developed which can measure the quantity of adsorbed polymers on mica. A FTIR operated in a dual beam mode has been used to increase the sensitivity to a point where it is possible to easily obtain spectra of adsorbed polymers. Thin mica sheets and a transmission-reflectance device are used to suppress optical interference fringes which otherwise dominate the spectrum and mask the infrared bands due to adsorbed polymers. The Alexander-de Gennes scaling law for the surface density,  $LN_B \sigma^{1/3}$ , has been found to be roughly obeyed over a wide range of copolymer molecular weights and radius ratios  $\beta$ . The Marques and Joanny scaling laws for  $\sigma$ ,  $\sigma \sim 1/Na$ , describe well the behaviour of the moderately asymmetric materials. However, their model does not appear to predict the proper surface density for material at the cross over point between the 3D and 2D regimes, near  $\beta \approx N_A^{1/2}$ .

Recently we have extended our infrared studies of PEO-b-PS adsorption to high surface area silica particles. The adsorption of the PEO and PS

units with the surface of the silica can be measured independently by observing the perturbation in the infrared band due to surface hydroxyl groups. Special infrared cells have been designed to allow for thermal pretreatment of the silica and subsequent polymer addition under vacuum conditions. An overview of our initial findings will be discussed.

## INTRODUCTION

The properties of colloidal suspensions depend strongly on the state of aggregation of the particles. Stabilization of colloidal dispersions can be controlled by the adsorption of polymers on the surface of the particle in a process known as steric stabilization. The presence of a polymer anchored to the surface of the particle and extended out into solution provides the necessary stability to prevent the particles from aggregating. In essence, the repulsive forces experienced by the interaction of the extended tails of the polymers overcome the van der Waals attractive forces between the particles. Block copolymers are effective steric stabilizers because the copolymer consists of an anchor block which has a strong affinity for the surface and a nonadsorbing buoy block which is soluble in the solvent and forms a brush layer that can extend into solution up to as much as 10 times its radius of gyration. Adsorption of the copolymer can occur either from a selective solvent or a nonselective solvent. In the first case the buoy block is soluble whereas the anchor block is in a poor solvent and forms a "pancake" layer on the surface. In the second case adsorption can occur from a nonselective solvent (both blocks are soluble) provided there is a specific interaction of the anchor block with the surface. This latter system is experimentally attractive because the polymer is unlikely to form micelles in solution.

Recently, a model to describe block copolymer adsorption from a nonselective solvent has been published by Marques and Joanny<sup>1</sup>. They have developed scaling relations describing the surface density and the extended length of the stabilizing block in terms of the number of segments of each block. Their model allows the classification of the adsorbed copolymer into different regimes which are dependent on the relative sizes of the two blocks. These sizes can be defined by an asymmetry radius ratio  $\beta$  which is dependent on the Flory radii of gyration of the individual blocks, ( $\beta = (R_{F,PS}/R_{F,PEO})^{3/5} = (N_{PS}/N_{PEO})^{3/5}$  (where  $R_{F,PS}$  and  $R_{F,PEO}$  are the Flory radii of gyration,  $N_{PS}$  and  $N_{PEO}$  the number of segments of the polystyrene and poly(ethylene oxide) respectively). Depending on the value of  $\beta$ , the anchor block may form a thick, fluffy, continuous adsorbed layer or a thin layer which may be continuous or discontinuous. The scaling laws derived by Marques and Joanny gave rise to the following laws for the surface density  $\sigma$  and extended length  $L$ ;

$$\text{for } 1 \ll \beta \ll N_{PEO}^{1/2}$$

then

$$\sigma \sim 1/N_{\text{PEO}} \quad (1)$$

$$L \sim N_{\text{PS}} N_{\text{PEO}}^{-1/3}. \quad (2)$$

Recently, we have obtained surface force<sup>2</sup> and infrared data<sup>3</sup> on polystyrene-*b*-poly(ethylene oxide) block copolymers adsorbed on mica from toluene and we have interpreted our data using the Marques and Joanny model. A good agreement was found.

Both PS and PEO blocks are soluble in toluene but the PEO block preferentially adsorbs on the mica surface. The copolymers adsorbed on the mica were selected to have a wide range of asymmetry radius ratio  $\beta$ . The extended length  $L$  as well as the adsorbed quantity of the block copolymer were measured with the Surface Force Apparatus and the adsorbed quantity was also measured independently by infrared spectroscopy.

## RESULTS AND DISCUSSION

For a grafted polymer brush the extended length  $L$  is often described by the Alexander-de-Gennes relation<sup>4</sup>

$$L \sim N_B \sigma^{1/3} \quad (3)$$

where  $N_B$  is the number of segments in the brush and  $\sigma$  is the surface density of the adsorbed polymer on the surface. Since the extended length is governed by the surface density it is important to know how this varies as a function of the size of the two blocks. The adsorbed amount of polymer on mica can be calculated from refractive index measurements using the Surface Force Apparatus. However this measurement is nontrivial for PS-*b*-PEO blocks adsorbed from toluene. The small differences in the refractive indices of the copolymer and solvent result in calculated values which are suspect at best. The refractive index problem was overcome by collapsing the polymer layer by the addition of nonsolvent heptane-toluene mixture but this involves the assumption that there is no preferential solvent uptake. Nevertheless the values of the adsorbed amounts obtained in this manner were found to roughly obey the Alexander-de-Gennes scaling law, as reported in Figure 1.

Recently we have developed an independent method based on infrared spectroscopy to determine the amount of adsorbed PS-*b*-PEO on mica<sup>5</sup>. Infrared spectroscopy has been useful in providing information on the interaction of adsorbed polymers and has been used to quantify polymer adsorption on high surface area materials. The main difficulty in extrapolating these measurements to low surface area materials such as mica is that the bands due to adsorbed polymers are weak and difficult to detect. This is compounded further when mica is used as a substrate because although mica is transparent in the infrared region of interest,

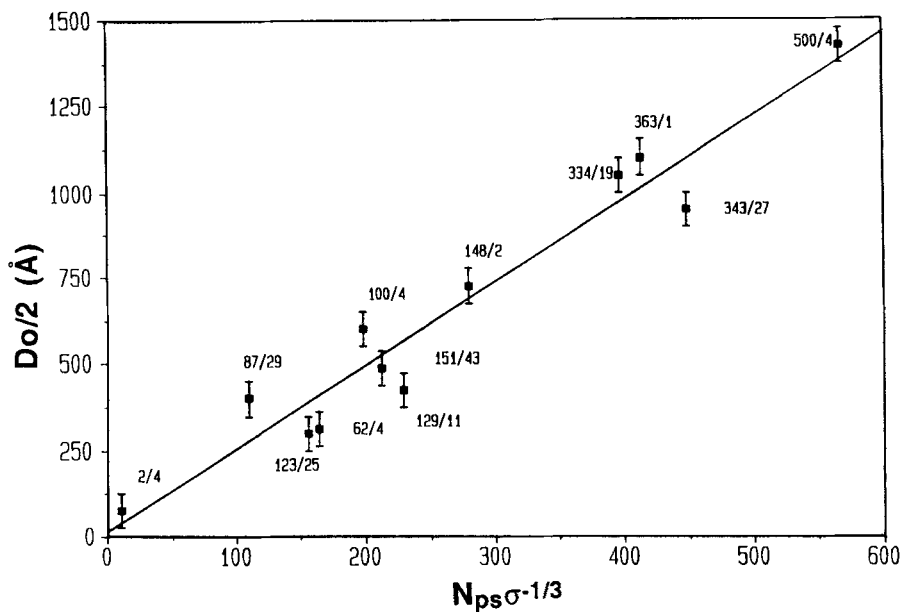


Fig. 1.  $Do/2$  as a function of surface coverage and segment density of polystyrene.

Table I: Adsorbed Amounts Measured by Infrared and Surface Forces Experiments

POLYMER	DATA FROM FTIR			DATA FROM SURFACE FORCES		
	$s$ (mg/m <sup>2</sup> )	$\sigma$ (nm <sup>-2</sup> )	$a$ (nm <sup>2</sup> )	$s$ (mg/m <sup>2</sup> )	$\sigma$ (nm <sup>-2</sup> )	$a$ (nm <sup>2</sup> )
100/4	1.5	0.0087	115	2.8	0.01667	60
87/29	0.43	0.00223	448	2.1	0.0109	92
148/2	1.9	0.0076	131	---	---	---
151/43	1.0	0.0031	323	2.5	0.0077	130
2/4	1.2	0.121	8	2.7	0.25	4
334/19	1.4	0.0025	400	2.6	0.0047	213
62/4	2.3	0.021	48	4.0	0.0385	26
500/4	1.3	0.0016	625			
363/1	1.0	0.0028	356	---	---	---
65/0.7	0.0			---	---	---
700/1	0.3	0.0258	39	---	---	---

when recorded in transmission large interference fringes result from multiple reflections from the back and front surface of the mica. These dominate the spectrum and mask the bands due to adsorbed polymers. The problem associated with the interference fringes was sufficiently reduced by using a combination of thin mica sheets and a transmission reflectance device. The transmission reflectance device suppressed the intensity of the interference fringe and the use of thin mica sheets increased the period of the oscillation to a level at which it appeared as a gentle sloping background in the spectrum.

In infrared spectroscopy, the light not adsorbed by the sample is measured and therefore the attenuation of the signal by a monolayer of polymer is small and under these circumstances the upper limit in sensitivity is usually determined by the dynamic range of the analog-to-digital converters (ADC). Attempts to increase the sensitivity by increasing the amount of sample analyzed by using multiple pass geometries or multiple sheets of mica stacked in series proved impractical. The second possibility for increased sensitivity is to reduce the noise level of the spectrometer (i.e., the ADC noise limitation). We have accomplished this by using a dual beam FTIR in combination with optical filters. By operation in a dual beam mode the signal measured is due to the light adsorbed by the sample. For weakly adsorbing samples such as polymers on mica this signal is small and can be amplified until detector noise is detected. The improvement in the detection limit is equal to the amount of amplification.

The adsorbed amount, surface density and area per molecule obtained using both the infrared spectroscopy and the refractive index data from a polymer layer collapsed in heptane/toluene solvent mixture are shown in Table 1.

For almost all polymers measured the infrared values are approximately 50% of those obtained using the surface force apparatus. The discrepancy between these two values can be accounted for by preferential solvent uptake. If one assumes that upon addition of the toluene/heptane mixture that the polymer surrounds itself with only the good solvent molecules then the calculated values from the refractive index measurements agree with those measured by infrared spectroscopy. Confirmation was obtained when, after collapsing the polymer, the solvent was drained out of the apparatus and the surfaces allowed to dry under a gentle flow of dry nitrogen. Then the adsorbed amounts obtained by the refractive indices measurements agreed with the values obtained by infrared.

The Marques and Joanny model predicts that the surface density scales as the inverse of the number of segments of the anchor block for the continuous regime ( $1 \ll \beta \ll N_{\text{PEO}}^{1/2}$ ) and as a function of both block size ( $\sigma \sim \beta^{-2}$ ) for the discontinuous regime. A plot of the surface density ( $\sigma$ ) as a function of  $1/N_{\text{PEO}}$  is shown in Figure 2.

The data for which  $1 \ll \beta \ll N_{\text{PEO}}^{1/2}$  is depicted as filled circles. A linear least square fits all data points except the 100/4 (filled triangle).

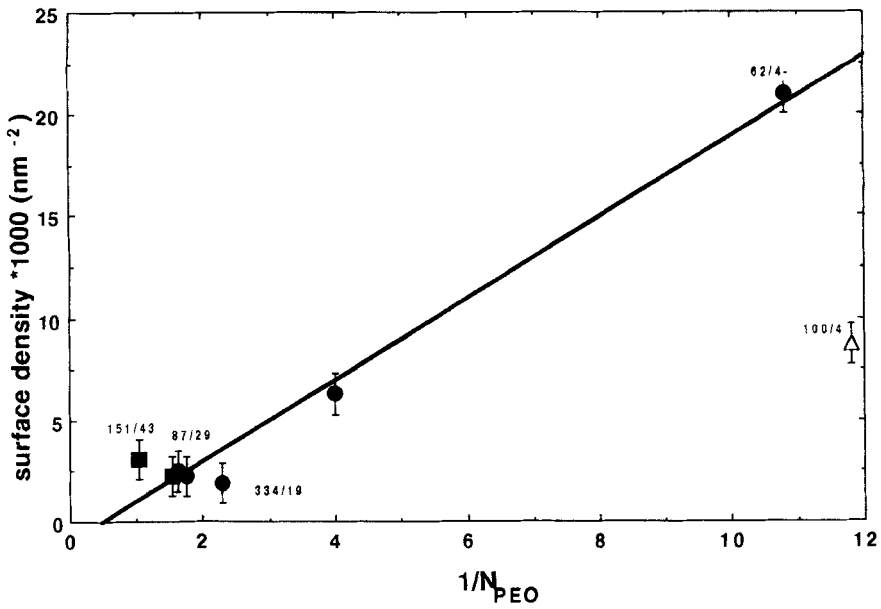


Fig. 2 Surface density ( $\sigma$ ) plotted versus  $1/N_{PEO}$  ( $\bullet$ :  $1 \ll \beta \ll N_{PEO}^2$ ;  $\blacksquare$ :  $\beta \sim 1$ ;  $\Delta$ : 100/4.)

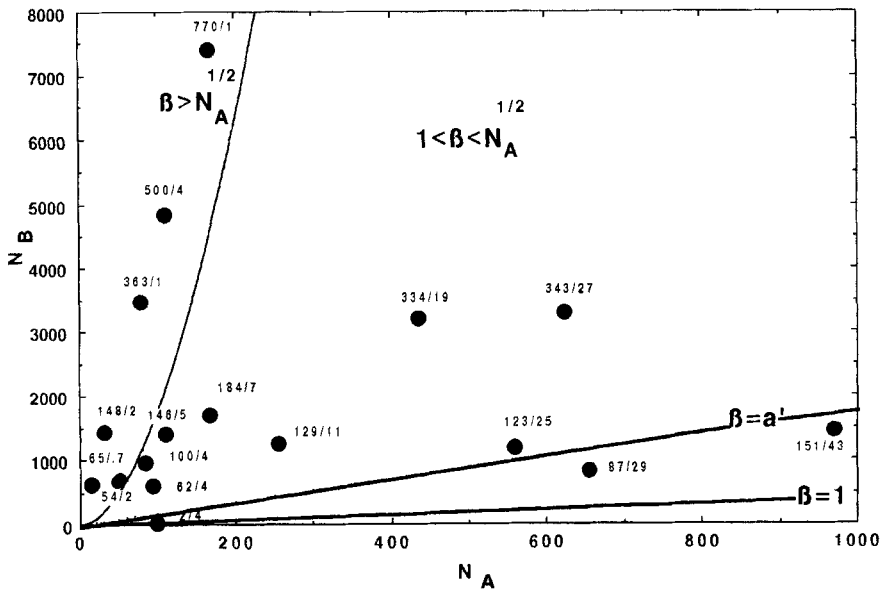


Fig. 3 Space diagram defining the limits of Marques and Joanny model. ( $N_B$  and  $N_A$ : number of segments of polystyrene and poly(ethylene oxide) respectively).

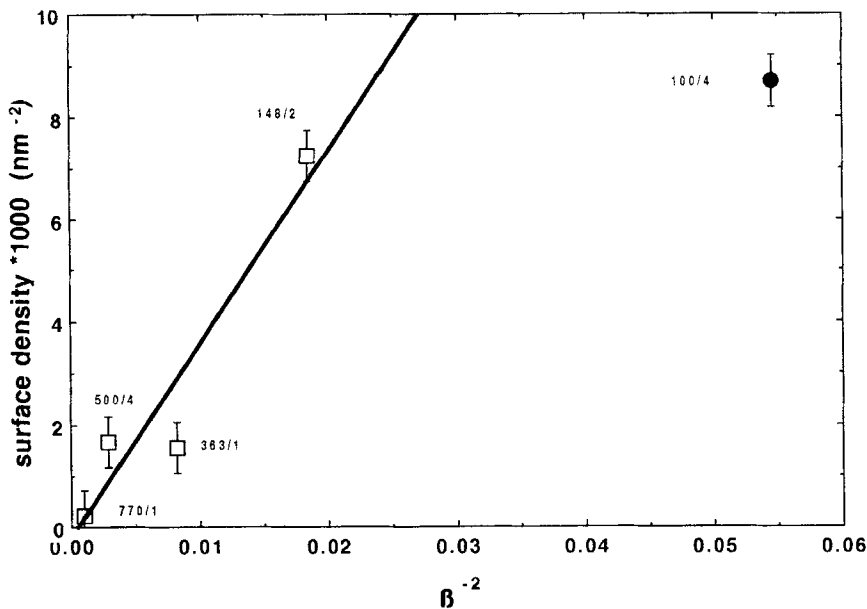


Fig. 4 Surface density ( $\sigma$ ) plotted  $\beta^{-2}$  ( $\square$ :  $\beta > N_{PEO}^{1/2}$ ;  $\bullet$ : 100/4).

Although this point falls inside the Marques and Joanny criteria for moderately asymmetric materials, its  $\beta$  value (7.6) is close to  $N_{PEO}^{1/2}$  (9.2) and it seems to adsorb with a lower surface density than predicted by Marques and Joanny model. As we have shown in a previous paper<sup>2</sup> this polymer lies very close to the cross over between the 3D and 2D semidilute regimes. This can be seen from Figure 3 where a so-called space diagram of all the polymer studied is represented.

The polymers for which  $\beta$  is close to 1 (filled rectangles) also scale reasonably well with  $1/N_{PEO}$ , except for the 2/4 material which would lie far off the top of the figure and is not shown.

The surface density for the polymers belonging to the discontinuous regime ( $\beta > N_{PEO}^{1/2}$ ) should scale as  $\beta^{-2}$ . Our data are plotted as filled circles in Figure 4.

The best fit straight line is shown but the results are less convincing as we have less data. As we suggested that the 100/4 material is too asymmetric to lie into regime II, we have included it in Figure 4 (filled triangle). It is apparent that it does not fit there either.



These results show that our data can be fairly well accommodated within the Marques and Joanny model. However, this model does not seem to predict the proper surface density for materials at the cross over between the continuous and discontinuous regimes, near  $\beta = N_{PEO}^{1/2}$ .

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