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Adsorption of Polystyrene-*b*-Poly(ethylene oxide) on Mica: Scaling Concepts

In the past decade there has been tremendous interest in the structure of polymers adsorbed on surfaces. Much of the early work concentrated on homopolymers, but the past few years have seen an increasing use of block copolymers. This is mostly mediated by the fact that one block of the copolymer will preferentially adsorb on the surface (the "anchor" block, usually called the A block), with the other blocks dangling freely into solution (the "buoy" or B blocks). In many cases the chains are sufficiently close together that the buoy blocks overlap and the polymer becomes well extended beyond its normal radius of gyration (i.e., forms the so-called "brush"). The elongated length, L, thus becomes a measurable parameter of importance, and the surface force apparatus as developed by Israelachvili[1] has proved useful in demonstrating and measuring this elongation.[2]

Many of the early studies of adsorption using block copolymers in the surface force apparatus utilized copolymers of poly(vinylpyridine) (PVP) and polystyrene (PS). In this case the organic solvents generally used (i.e., toluene) are selective solvents in that the B block (in this case polystyrene) is preferentially soluble while the A block [in this case poly(vinylpyridine)] is insoluble. The insoluble block adsorbs onto the mica surface in the form of a pancake. This type of adsorption has been discussed theoretically by Marques et al.,[3] investigated by Hadziioannou et al.,[4] and reviewed by Patel and Tirrell.[5]

A second type of block copolymer is that in which both blocks are soluble in the (nonselective) solvent. Adsorption is then completely from solution, and any problems associated with insolubility, precipitation, or micelle formation are avoided. A block copolymer of poly(ethylene oxide) (PEO; A block) and polystyrene (PS; B block) in toluene provides an example. In this case, the poly(ethylene oxide) adsorbs preferentially to the mica surface (presumably via an ion–dipole interaction), and the polystyrene brush is extended in the usual manner. Theoretically, it is known that, provided the area of surface occupied by the polymer molecule can be determined, the length of the brush and its dependence on molecular weight can be calculated by using either scaling or mean-field theory.[6,7] Determining this area, however, is not trivial, and we have found that values of the adsorbed amount of PEO-*b*-PS measured by using the surface force apparatus are larger by at least 50% than values obtained by an infrared spectroscopic technique.[8]

Experimental results relating length measurements for adsorbed PEO-*b*-PS polymers adsorbed from toluene on mica were first published by Marra and Hair[9] (MH). Interpretation was based on both determination of area/molecule and a suggested scaling with PEO molecular weight. Subsequent to this, an accurate scaling theory was proposed by Marques and Joanny[10] (MJ) that predicted the dependence of the length on the molecular weight of both PS and PEO blocks. More recently, Taunton et al.[11] (TTFK) (as part of a work that dealt primarily with investigation of end-functionalized polystyrene) have reported length measurements for two samples of PEO-*b*-PS.

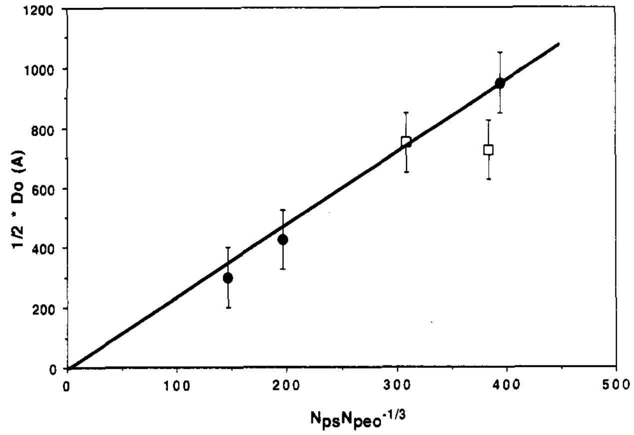

Figure 1. Scaling plot for PEO/PS polymers. The extended polymer length is taken to be half the distance at which the repulsive force is first measurable; i.e., $^1/_2\ D_0$. Circles refer to Marra/Hair data and squares to Taunton et al. The straight line is arbitrarily drawn between the origin and the highest M_w polymer. Error bars are those quoted by the above authors.

Table I
Properties of Polymers and Experimental Length As Determined in the Surface Force Apparatus

source	PS/PEO[a]	$D_0/2$	β
MH[9]	123/25[b]	300	1.56
MH[9]	129/11[b]	425	2.58
MH[9]	343/27[b]	950	2.72
TTFK[11]	184/7	750	4.04
TTFK[11]	150/2	725	7.40

[a] The nomenclature refers to the M_W of each block in units of thousands; i.e., the sample 123/25 had a measured M_W of 123 000 for the PS block and 25 000 for the PEO block. [b] These polymers were originally labeled in ref 5 on the basis of M_N rather than M_W as 90/18, 90/8, and 250/20, respectively.

It is well-accepted that, if the area occupied by a polymer molecule on a surface is known, and that, provided these molecules are in the semidilute regime, then the length of that polymer molecule will scale as

$$L \sim Na\sigma^{1/3} \tag{1}$$

where N is the chain length, a is the size of a polymer segment, and σ is the surface density.[6,7,12] In the case of the PEO-*b*-PS copolymers it was not until the recent work of MJ that sound theoretical interpretation was given showing how the molecular weight of the PEO block affected σ and hence the total extended length of the polystyrene on the surface. In their original work MH suggested that the polymer packing density on the surface was solely the result of the size of the PEO chain in solution. Thus taking

$$\sigma = 1/R_{\mathrm{g,peo}}^{\;2} \tag{2}$$

(i.e., good solvent conditions), it was derived that

$$L \sim N_{\mathrm{ps}}N_{\mathrm{peo}}^{-0.4} \tag{3}$$

Experimental results obtained on three polymers (i.e., two polymer pairs) were in very reasonable agreement with these scaling arguments.

MJ argue that the soluble A block (i.e., PEO) will adsorb on the mica surface to form a "fluffy" layer, and, using the fact that the area per molecule of A will be the same as the area per molecule of B, they minimized the total free energy of the block polymer chains. Using this approach, they have shown that the length of extended B (i.e., in our case PS) should be given by the relation

$$L \sim N_{\mathrm{B}}N_{\mathrm{A}}^{-1/3} \tag{4}$$

The slight change in the scaling power of the N_{A} block

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(from −0.4 to −0.33) is not sufficiently sensitive to be easily demonstrated by length measurements in the surface force apparatus. Results obtained by using the original MH data are shown in Figure 1: An excellent correlation is observed between L and $N_{ps}N_{peo}^{-1/3}$.

Also shown in Figure 1 are the data by TTFK on the two PEO-*b*-PS block copolymers that they report. It is interesting to note that one of these polymers lies superimposed on the straight line relationship suggested by the MH data whereas the other copolymer shows significant deviation. An interesting explanation for this is found in the theory of MJ. Those authors pointed out the actual form of scaling is dependent upon the asymmetry ratio, β, which they define as

$$\beta = R_{FB}/R_{FA} = (N_B/N_A)^{3/5} \tag{5}$$

where R_F is the Flory radius of gyration. (The model assumes that the solvent is truly nonselective and that the monomer size, a, is equal for both blocks. N is the degree of polymerization.) The scaling relationship shown in eq 4 is only applicable when the block copolymers are moderately asymmetric ($1 < \beta < N_A^{1/2}$). Values for the asymmetry of five published PEO-*b*-PS polymers are given in Table I. It is noted that only four of these polymers have an asymmetry value for which $1 < \beta < N_A^{1/2}$, and these four polymers all fit the scaling relationship of Figure 1. In the case of the fifth polymer, $\beta > N_A^{1/2}$ and the adsorbed copolymer layer thus breaks into a patchwork of individual chains. Under these circumstances, Marques and Joanny determine a scaling relationship

$$L \sim N_B^{3/5}N_A^{2/5}a \tag{6}$$

It is noted that the main thrust of the TTFK work was the use of end-terminated polystyrene chains and the use of such materials to form a well-defined brush. The small zwitterionic end group adsorbs on the mica surface to give an extreme case of a discontinuous pancake in contact with the wall. It is noted that, even given the difficulties of obtaining accurate data using refractive index measurements in the surface force apparatus, those workers determined that the extended length of the adsorbed polymer molecules did indeed scale with $N_B^{3/5}$.

New data have now been obtained in this laboratory for several PEO-*b*-PS polymers. These confirm the generality of the scaling equations and the limits of their applicability.

References and Notes

(1) Israelachvili, J. N.; Adams, G. *J. Chem. Soc., Faraday Trans. 1* **1978**, *79*, 975.
(2) Klein, J. *Nature* **1988**, *288*, 248.
(3) Marques, C. M.; Joanny, J. F.; Leibler, L. *Macromolecules* **1988**, *21*, 1051.
(4) Hadziioannou, G.; Patel, S.; Granick, S.; Tirrell, M. *J. Am. Chem. Soc.* **1986**, *108*, 2869.
(5) Patel, S.; Tirrell, M. *Annu. Rev. Phys. Chem.* **1989**, 40.
(6) Alexander, S. *J. Phys. (Les Ulis, Fr.)* **1977**, *38*, 983.
(7) de Gennes, P.-G. *Macromolecules* **1981**, *14*, 1637.
(8) Tripp, C. P.; Guzonas, D. A.; Boils, D.; Hair, M. L., to be published.
(9) Marra, J.; Hair, M. L. *Colloids Surf.* **1988**, *34*, 215.
(10) Marques, C. M.; Joanny, J. F. *Macromolecules* **1989**, *22*, 1454.
(11) Taunton, H. J.; Toprakcioglu, C.; Fetters, L. J.; Klein, J. *Macromolecules* **1990**, *23*, 571.
(12) Milner, S.; Witten, T.; Cates, M. *Europhys. Lett.* **1988**, *5*, 413.

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