Long-ranged surface forces: The structure and dynamics of polymers at interfaces

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Abstract - Polymers that attach at solid-liquid interfaces can considerably modify the long-ranged forces acting between surfaces. Over the past decade or so these forces have been studied directly using a surface-force-balance approach, and the equilibrium force laws between two polymer-bearing surface interacting across a liquid medium are reasonably well understood. Recently we have extended these studies to the case of surfaces with adsorbed and with grafted layers as they *shear* part each other. Our results suggest that the lateral forces depend on the extent of interpenetration of the opposing layers and on their relative shear velocities; they reveal a marked coupling between the normal forces and the shear velocity, beyond a certain critical value of the latter which is probably related to relaxation rates of the end-tethered chains. We find that while non-adsorbing but end-anchored polymer layers are stable with respect to shear and compression, they can be rapidly replaced by addition of *shorter* polymers with the same adhering end-group.

SURFACE-ATTACHED POLYMERS AND EQUILIBRIUM SURFACE INTERACTIONS

Polymers that are adsorbed or grafted at interfaces are frequently used to modify long-ranged surface forces in a variety of applications ranging from colloidal stabilisation toemulsification to lubrication properties (refs. 1-3). The spectrum of spatial scales associated with flexible polymer molecules and their relation to the long-ranged surface forces in the context of this review, is illustrated in Fig. 1. This schematically shows a polymer chain (polystyrene is shown as a typical case) at three different "magnifications", immersed in a monomeric solvent (not shown). Figure 1(a) is on a spatial scale characteristic of the micro-structure and interactions of the individual monomers and the interactions on this scale are determined by the local bond energies and local fields. The structure of the solvent molecules and their distribution is also important on this scale. Fig. 1(b) represents an intermediate length scale; for the case illustrated it is comparable with the 'persistence length' of the polymer (refs.4,5), and bridges the gap between microscopic and global structure of flexible polymers. Fig. 1(c) shows the flexible polymer chain as a whole. Its behaviour on this scale is dominated by internal configurational entropy effects, arising from the vast numbers of possible configurations available to the chain; the interactions between segmentsfrom different chains in this case may be considered in terms of (repulsive) excluded volume interactions on the one hand and the enthalpic interactions between the monomers on the other (refs. 4,5). For the common case of neutral flexible chains these are dispersive in origin, and generally attractive. The nature of the solvent determines the overall segment-segment interactions: in poor solvents the attraction between the segments
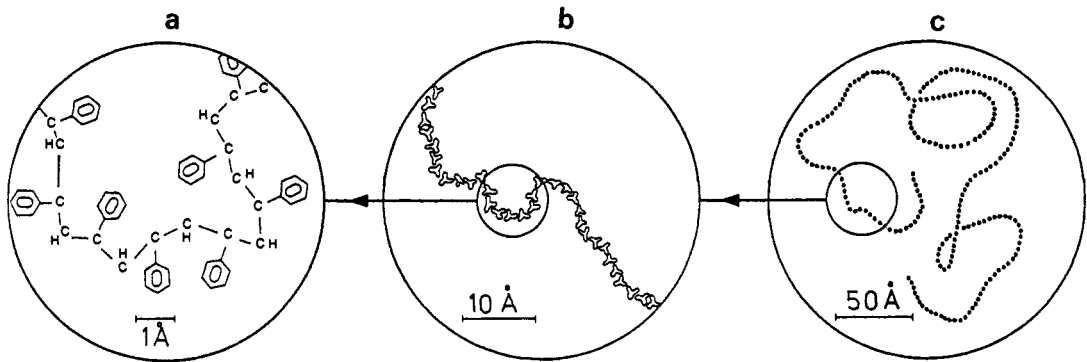
Fig. 1:   Illustrating the length scales on a polymer molecule. It is on the scale of Fig. 1(c) that
long-ranged forces between surfaces are modified by surface-attached chains.

dominates, in good solvents the excluded volume repulsion dominates (leading to swelling of
the chains), while in so-called θ(theta)-solvents the two compensate at low monomer
concentrations - the second virial coefficient of the interaction disappears in these conditions.
Thus by varying solvent conditions it is possible to modify strongly the long-ranged
interactions between polymer-bearing surfaces. Most importantly, the dimensions of the
polymer chains themselves, characterised for a random coil (as in a θ-solvent) by the
unperturbed radius of gyration R_g, can be modified by varying the degree of polymerisation
N:

$$R_g = const. \ N^{1/2}a$$

where a is a monomer dimension and the prefactor is of order unity. In good solvents,
excluded volume effects lead to swollen coil dimensions (refs. 4, 5)

$$R_F \approx N^{3/5} \ a$$

For high polymers N may vary between 10^2-10^5, providing for a large variation in the
spatial scale of figure 1(c), and hence in the range over which forces between polymer-
bearing substrates may be varied.

Polymers frequently adsorb strongly to surfaces, due to their large size and their flexibility,
which enable very many contacts of each adsorbing chain with the surface, and thus overall
sticking energies per chain much larger than their thermal energies of order kT. This fact
has been utilised from antiquity (when the ancient Egyptians stabilised carbon black
dispersions by addition of the naturally occurring polysaccharide gum arabic (ref. 6)), to the
present day, by attaching polymers onto colloidal particles in order to modify the long-
ranged interactions between them. This is because the range over which field-type forces -
such as double-layer electrostatic repulsions or dispersive (van der Waals) attraction -
between *bare* colloidal particles are of order of their thermal energies kT , vary in the range
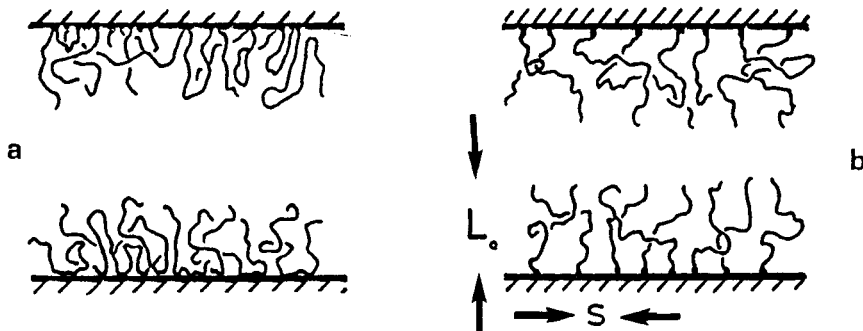

Fig. 2: (a) Adsorbed chains; (b) Grafted chains, forming a 'brush-like layer of
thickness L_o. s is the mean interanchor spacing.

50-5000Å (ref. 9); this is comparable (depending on N and on solvent conditions) with the 'long-ranged' spatial scales indicated in Fig. 1(c). The thickness of a surface layer of adsorbed polymers for a given degree of polymerisation N is proportional to the solution dimensions of the chains, and is clearly larger in good solvents $(R_F > R_g)$; however, for the case of polymers that do not adsorb at all - surface sites being prefentially covered by solvent molecules - but are tethered to a surface by specific adsorbing end-group or end-moiety, extended brush-like layers can arise (as shown in Fig. 2(b)); their thickness L_0 varies *linearly* with N for a given grafting density (ref. 7), as discussed later. Such grafted layers may - for a given N value - form the thickest layers in good solvents (ref. 8).

Over the past decade the forces as a function of surface separation between substrates bearing both adsorbed and grafted polymers have been directly measured using the mica force-balance method (ref. 9), over a wide spectrum of parameters such as solvent conditions, N values, surface coverage and monomer concentrations both in aqueous and organic liquid media. The results of many studies by several different groups are summarised in Figs. 3 and 4 for high and low coverage of the polymers on the surfaces. At the same time, the question of the structure of surface-attached polymers and the interactions between such surfaces has been treated theoretically by several workers (refs. 7,10,11,14,15), and a reasonable - quantitative - understanding exists today of the equilibrium force laws shown schematically in Figs. 3 and 4. We remark on the characteristic attraction due to bridging in the low surface-coverage case, Fig. 3, for the adsorbed polymers in all solvency conditions: this arises when a given chain spans the inter-surface gap and adheres strongly to both surfaces (ref. 12,13), as sketched. For grafted polymers (where only one end adheres) no such bridging attraction occurs, and the equilibrium surface interactions remain
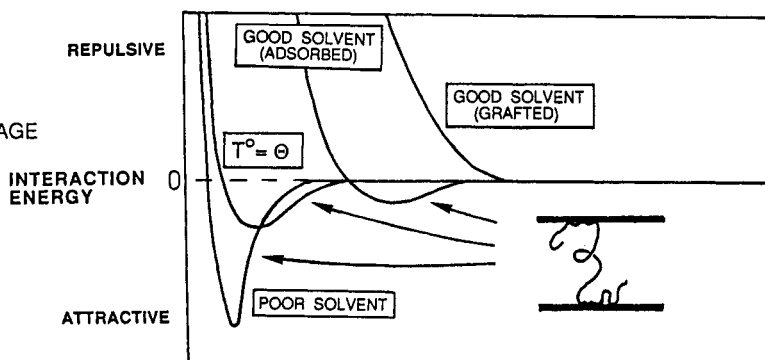

Fig. 3
LOW SURFACE COVERAGE
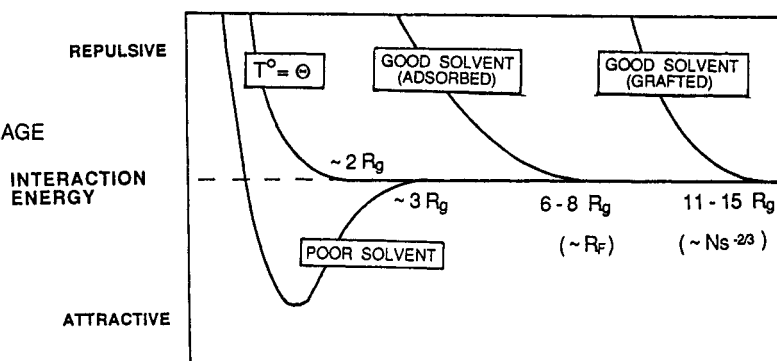

Fig. 4
HIGH SURFACE COVERAGE

Fig. 3 and Fig. 4: The interaction between polymer-bearing surfaces as a function of their separation D, for low and high surface-coverage by the chains, based on experimentally determined force-distance profiles (ref. 9). E(D) is the net interaction energy between unit area of flat parallel plates. In fig. 4 the D-axis is normalised in terms of the unperturbed dimensions R_g of the chains, over the range studied to date in the experiments (ref. 9) and also indicates where appropriate the dependence on swollen coil dimension, R_F, and on 'brush' thickness L_0 ($\sim Ns^{-2/3}$) where s is the interanchor spacing (Fig. 2(b)).

monotonically repulsive at all surface coverages. It is worth remembering that, while the data summarised in Figs. 3 and 4 were obtained for polymers attached to *mica* surfaces, the results are expected to have a much greater generality and to be applicable to other surfaces: this is because for surface-attached flexible polymer chains, all 'memory' of the surface is lost beyond a few statistical step lengths away from the surface (i.e. beyond spatial scales as in Fig. 1(b)). Long-ranged dispersive surface fields are not expected to change significantly the structure of the polymer layers or the form of the interactions (ref. 14), though different surfaces may affect the behaviour through adsorbing different amounts of polymers.

SHEAR FORCES AND DYNAMIC EFFECTS

The previous section considered the equilibrium long-ranged forces between polymer-bearing surfaces. Time dependent effects, on the other hand, are themselves of great importance for polymers at interfaces: they determine the rate at which chains from solution adsorb or graft to form the final surface layers, and their in-plane diffusion. The relaxation of the chains determines also features such as 'breathing modes' and kinetics of interpenetration and bridging (ref. 15) as the polymer-layers on opposing surfaces come into overlap.

Very recently the forces between polymer bearing surfaces moving *laterally* with respect to each other have been measured (refs.16,17). The geometry is illustrated in Fig. 5.
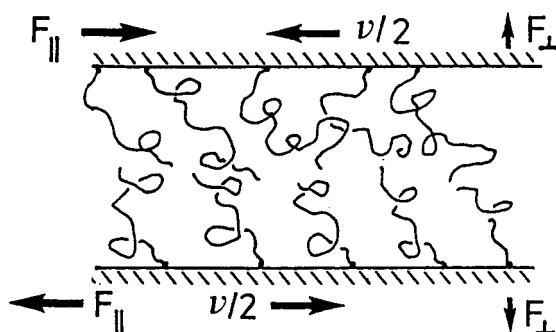

Fig. 5: Illustrating surfaces bearing end-anchored chains shearing past each other at separation D and relative velocity v. $F_\perp$ and $F_\parallel$ are the corresponding normal and shear forces respectively.

Interactions in shear are expected to be relevant in applications such as lubrication, flow of fluids past surfaces, the rheology of stabilised dispersions and of multicomponent polymer blends, and also to the general question of colloidal stability in shear flow, central in many technological contexts (e.g. paper making). Shear interactions between sliding surfaces with confined polymers between them are likely to be dominated not only by the structure and mean segment-segment interactions, but also - to a much greater extent than for normal forces acting between approaching surfaces - by the relaxation behaviour of the surface-attached chains themselves. Shear forces between rubbing *solids* in contact have been studied classically in the investigation of friction (ref. 17), but the shear stress measured in such studies tends to be very much larger than would be expected in a situation such as in Fig. 5. Mica provides an attractive substrate for frictional studies, as the apparent area of contact between atomically smooth mica sheets equals their real contact area , and the mica force apparatus has been extended to study shear forces between sliding mica surfaces that are compressed against each other (refs. 18, 19): for monotonic sliding motion (ref. 19), shear forces as low as 10^{-4} N have been measured in such a geometry. A simple consideration suggests that forces between polymer-bearing layers in the crossed-cylinder configuration of the mica force apparatus may be very much lower: of order 10^{-7} N for a shear stress sufficient to stretch the chain molecules on the surface by their own radius of gyration in the sliding direction. The apparatus we designed to measure such weak forces is schematically shown in Fig. 6. A detailed description is given in ref.16; here we note the main features which enable the necessary sensitivity and resolution in the measurements. A sectored

piezoelectric tube (PZT) holds the upper curved mica surface, as shown in Fig. 6. Such a device can be made to move laterally, as indicated in the inset, when equal and opposite potentials are applied to opposing sectors. By suitable coupling of inner and outer conductors of the PZT, extremely parallel motion is achievable (ref. 16), enabling the simultaneous measurement of both $F_\perp(D)$ and $F_\parallel(D)$, the normal and parallel forces between the curved surfaces when they are a closest distance D apart. This PZT and the upper mica surface which it holds are mounted on a pair of weak, vertical leaf-springs, which bend in response to any shear force $F_\parallel(D)$. This bending is monitored by changes in the capacitance of a parallel air-gap capacitor, as shown in Fig. 6; at the same time the normal force $F_\perp(D)$ is given by the bending of the *horizontal* leaf-spring holding the lower curved mica sheet, and measured by optical interferometry.

a

b

Fig. 7: Schematic illustration of (a) compressed grafted chains in a good solvent , and (b) compressed adsorbed chains in a θ-solvent .
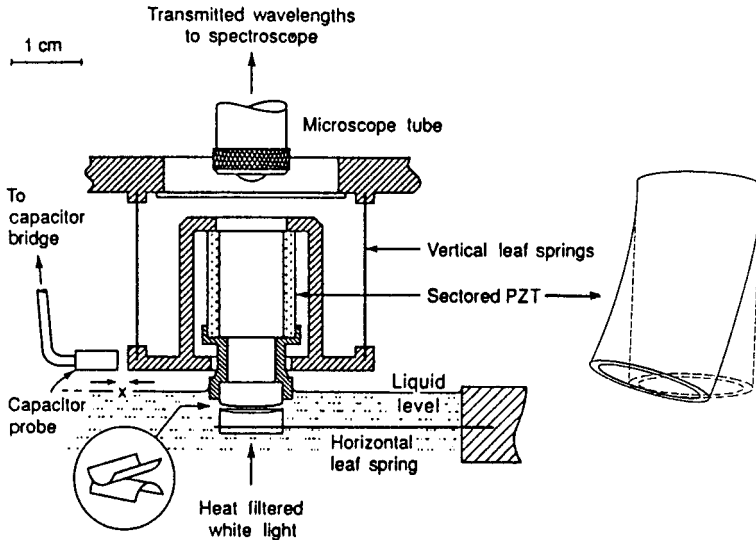
Fig. 6: The main elements of the apparatus used to measure shear and normal forces between mica surfaces in a crossed-cylinder configuration. Shear forces $F_\parallel$ (D) are measured by the bending of vertical leaf-springs, monitored via an air-gap capacitor, while normal forces $F_\perp(D)$ are measured via bending of the horizontal leaf-spring, monitored via optical interferometry. Lateral motion of the upper mica surface is provided by the sectored PZT. (taken from ref. 16).
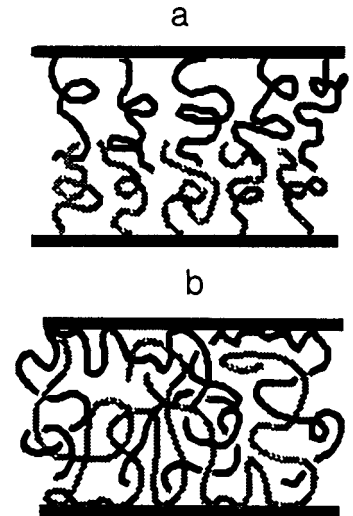
Measurements have been made of the shear and normal forces between mica sheets bearing adsorbed polystyrene across a close-to-θ-solvent (cyclopentane), and bearing end-anchored but non-adsorbing polystyrene in a good solvent (toluene). Both these systems have been investigated earlier extensively in the context of studying the normal force profiles $F_\perp(D)$ (refs. 8,12). Our preliminary results (ref. 16) with sheared layers reveal several new features:

a) At low sliding velocities, the shear forces $F_\parallel(D)$ (Fig. 5) for the case of grafted chains in a good solvent remain extremely low even at high compressions $F_\perp(D)$. This contrasts with the behaviour of adsorbed chains in a θ-solvent, where lateral forces are marked at much lower relative compressions. This difference is probably because little interpenetration occurs between the polymer brushes in the good solvent, compression leading rather to a distortion of each brush layer, as indicated in Fig. 7(a). The sliding between the layers is then mediated by a lubricating layer at the interface between the brushes: it is rather fluid (i.e., presents little viscous dissipation) because the chain lengths needing to slide through each other are short and have low relaxation times (comparable with the relaxation time of a correlation length ξ of the polymer at the relevant local concentration at the interface (ref.5)).

For the case of the adsorbed chains near θ-conditions, considerably more interpenetration occurs as indicated in Fig. 7(b), because the segmental interactions are very weak and the layers telescope easily into each other (ref. 12); as the surfaces slide past each other, the interpenetrated chains need to disentangle, a process involving much longer portions of each chain and considerably longer relaxation times . Indeed, for the case of the adsorbed layers sliding past each other in the θ-solvent, the shear force $F_{\parallel}$ is an increasing function of the shear velocity, indicating a dissipative process as the chains disentangle .

b) Polystyrene chains attached by one end only (via a zwitterionic group at that end) to the mica surface, which form extended brush-like layers , are very robust with respect to strong shear. i.e. even when strongly stretched by the sliding motion between the mica sheets the chains do not come off the surface. This is shown in Fig. 8 where the force profile $F_{\perp}(D)$ is shown both prior to and following strong shear of the grafted layers. The similarity of the profiles indicates the integrity of the layers. This behaviour of the zwitterion-anchored but otherwise non-adsorbing polystyrene contrasts with that of the adsorbed polystyrene in the θ-solvent (cyclopentane), which is clearly observed to detach from the surface under similar shear conditions (to be published). The reasons for this are as follows: stretching of the chains (whether grafted or adsorbed) induces a tension along each polymer. In the case of the end-tethered polystyrenes this tension is insufficient to detach the polymer from the surface , even when the overall stretching *energy* in the chain is very much higher than the zwitterion-mica adhesion energy of ca. 8kT (ref. 8) . If the range of this adhesive (dipole-dipole-like) interaction is of order 10Å then a tension around 1kT/Å is needed to pull off the zwitterion from the mica ; the total stretching energy in the highly elongated chain may be of order 100kT or more, but this is distributed over some 2000Å for the chains shown in fig. 8 (ref. 20), so that the mean tension in each chain - ca. .05kT/Å - is insufficient to remove it from the mica. For the adsorbed chains, however, such a tension *does* suffice to 'unzip' the 'trains' of each adsorbed chain on the surface, since the polystyrene monomer-mica adhesion is typically very weak, ca. 0.01-0.1 kT acting over a monomer size of 5Å; i.e. chain tensions
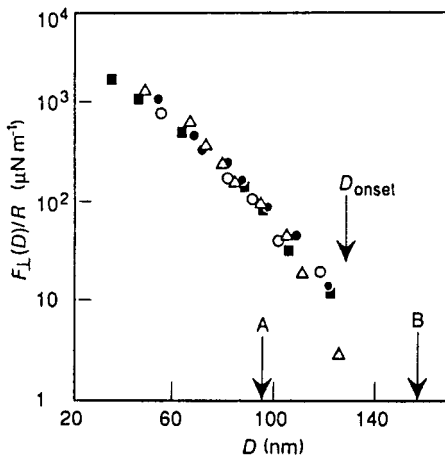

Fig. 8: Force-distance profiles (normalised by the mica curvature R) between mica sheets bearing polystyrene terminated by the zwitterionic group $-N^{+}(CH_3)_2(CH_2)_3SO_3^{-}$ and tethered by this group to the surfaces . The molecular weight is M=141,000. Profiles both prior to shear (■) and after strong shear (● O △) are shown (taken from ref. 16).
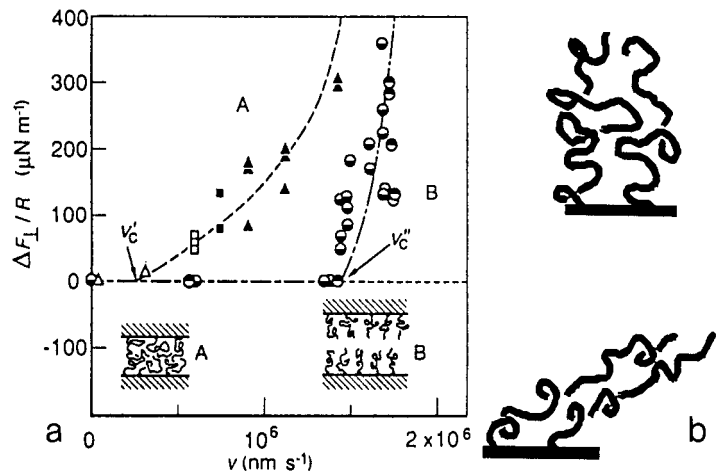D_{onset} is the separation at onset of repulsion.

Fig. 9:

a) The increase $\Delta F_{\perp}(D)$ in the normal repulsion between mica surfaces bearing end-tethered polystyrene as in fig. 8, at two values of D as indicated in fig.8 by positions A and B. v_c' and v_c'' are the critical velocities above which increased repulsion is observed (from ref. 16).
b) Illustrating the origin of the increased repulsion: in the unstretched brushes most monomers from different chains are screened from mutual interaction (top), but stretching (bottom) reduces this screening (ref. 20).

greater than 0.002 - 0.02 kT/Å will detach the polymers, as indeed observed. This distinction between chain tension and stored energy is important in the context of stability of surface-attached chains to shear, and may be of considerable practical relevance.

c) There is a strong coupling between the normal force $F_\perp(D)$ and the shear motion whenever the shear velocity v_s exceeds some critical value v_c. In this case ($v_s > v_c$) we find a marked increase $\Delta F_\perp(D)$ in the repulsion between the surface, as shown in Fig. 9(a). This is probably due to the stretching of the chains for $v_s > v_c$. The effective shear rates at which $v_s = v_c$ are probably related to some local relaxation rate of the end-anchored chains, and at higher shear rates they undergo what resembles a 'coil-to-stretch' transition on the surface. (it is important to recall that - as a result of their being anchored at one end on the surface - the shear field between the mica surface is effectively an elongational field as far as the polymer chains are concerned). Once the chains have stretched the screening between monomers in considerably reduced, resulting in increased local osmotic pressure and hence an increase in $F_\perp(D)$, as illustrated schematically in Fig. 9(b). (Ref. 20).

SURFACE EXCHANGE OF POLYMERIC AMPHIPHILES

End-anchored but otherwise non-adsorbing polymers, as in Fig. 2(b), form extended brush-like structures in a good solvent, whose thickness L_0 varies with N and mean interanchor distance s as $L_0 = \text{const.} N s^{-2/3} a^{5/3}$, where a is a monomer size. Such layers are stable with respect to strong compression and to dilution of the surrounding solution (ref. 8), and, as noted above, also to strong shear. It is, however, readily possible to replace a polymer brush, where each N-mer chain is anchored to the surface by an end group with adhesive energy γkT, by adding to the surrounding fluid medium identical but shorter polymeric amphiphiles with the same end-group. This is because for an N-mer end-adsorbed to equilibrium onto a
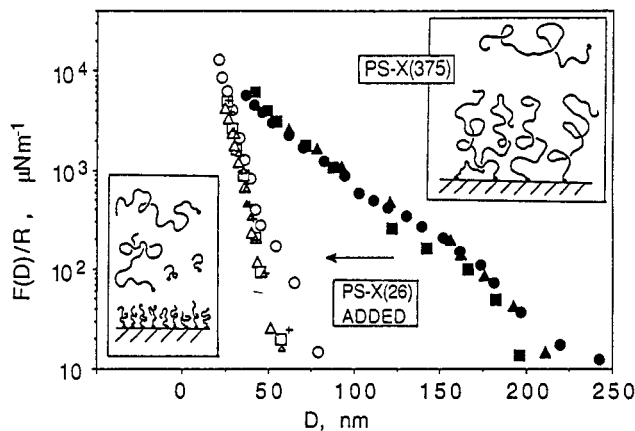

Fig. 10: Zwitterion-terminated polystyrene chains with M = 375×10^3 end-adsorb from toluene onto mica to yield the force profiles shown on the right. Within two hours following addition of identically terminated polystyrene chains of M = 26.5×10^3 the force profiles shift sharply to shorter separations, on the left, indicating essentially complete replacement - as schematically illustrated - of the longer by the shorter amphiphiles (from ref. 21).

surface from a surrounding solution, the free energy per unit area of surface, ΔG, is approximately given by (ref. 21)

$$\Delta G = - \text{const.} (\gamma^{11/5} kT)/(N^{6/5} a^2)$$

Thus brushes consisting of shorter chains (smaller N) would have much lower surface free energies, for a given anchoring end-group (given γ), and in equilibrium would be expected to replace brushes consisting of longer chains. We have very recently demonstrated this directly via surface-force measurements, by first creating a polymer brush consisting of end-tethered zwitterion-terminated polystyrene chains of molecular weight M = 375×10^3, then adding identical but shorter polymeric amphiphiles (M = 26.5×10^3), and observing that the longer amphiphiles are rapidly replaced by the shorter ones on the surface. The corresponding force profiles and the schematic representation of the exchange are shown in Fig. 10. This replacement of long by shorter polymeric amphiphiles runs counter to the conventional behaviour of adsorbing chains (where each monomer has a propensity to adhere to the surface), where it is long chains that replace shorter ones on the adsorbing substrate at

equilibrium (ref. 22). This suggests not only a means for tailoring surface layers in a controlled fashion by varying N and the value of the end-group adhesion energy γkT (or, in the case of amphiphilic diblock copolymers, the length of the adsorbing moiety), but also an interesting strategy for separating polymeric amphiphiles from a mixture of different lengths.

ACKNOWLEDGEMENTS

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