Shear of Telechelic Brushes

Erika Eiser* and Jacob Klein[†]

Department of Materials and Interfaces, Weizmann Institute of Science, Rehovot 76100, Israel

Thomas A. Witten

James Franck Institute, University of Chicago, Chicago, Illinois 60637

Lewis J. Fetters

Exxon Research and Engineering Company, Clinton Township, Annandale, New Jersey 08801

The forces between two surfaces bearing solvated, telechelic polymer chains (terminated at both ends with a dipolar group) exhibit a clear attractive regime. The range and magnitude of this attraction indicate the presence of multimers on each surface, and the formation of entropically favored bridges between them as the telechelic layers overlap. On sliding the surfaces a shear force close to that expected from the stretching of the polymer bridges is observed, suggesting that the frictional forces can be tuned by varying the interaction strength of the telechelic end groups.   [S0031-9007(99)09413-2]

The physics of neutral, flexible polymers attached to surfaces, and their control of long-ranged interactions, has been extensively studied, and is reasonably well understood [1–5]. The next level of understanding involves functionalized polymers with specific interactions, so that both entropic and enthalpic effects may contribute to the surface forces [6]. Here we report the measurements of normal and shear forces between surfaces bearing telechelic chains, where dipolar groups are attached to both ends of an otherwise nonadsorbing polymer. Such a telechelic chain may be tethered to the surface by both ends, in which case it forms a loop, or by one end only, so that its other end—bearing the second functional group—extends tail-like into the solution. Earlier work focused on *ABA* telechelic triblock copolymers. Here the absorbing *A* block is larger and less polar than our end groups, while the *B* block is nonadsorbing. These triblocks appeared to form a predominantly loop layer [7,8] when the *A* moieties were sufficiently strongly adsorbing [8]. Our results reveal a behavior rather different to that of regular brushes [9] or to that of the triblock telechelics [7,8] studies earlier, both in the normal and in the shear interaction modes. Existing theory [6] treats the case where the fraction of tails is small; however, our results suggest that tails predominate and that their free ends associate with those of other chains, either within the layer or—on approach—with those from the opposing layer.

The polymer used, designated *X*-PS-*X*, was polystyrene (PS, molecular weight $M_W = 70\,000$ polydispersity $M_W/M_n = 1.05$) terminated at both ends with the zwitterionic group $-N^+(CH_3)_2(CH_2)_3SO_3^-$ (designated $-X$). Its synthesis was similar to that of singly zwitterion-terminated polystyrene molecules PS-*X* [9,10]. Control experiments confirmed that unfunctionalized polystyrene does not adsorb onto the mica from the toluene solvent (BDH, spectroscopic grade, used as received) in

the conditions of our experiments. A droplet of 10^{-4} ($\pm 10\%$) gm/ml solution of *X*-PS-*X* in toluene was injected between the curved mica surfaces (this concentration is lower than the critical micelle concentration for corresponding PS-*X* chains in toluene [9]), and incubated for 2–3 h, beyond which no further changes in the normal force profiles were observed. Figure 1 shows a series of typical normal force $F_n(D)$ vs surface-separation
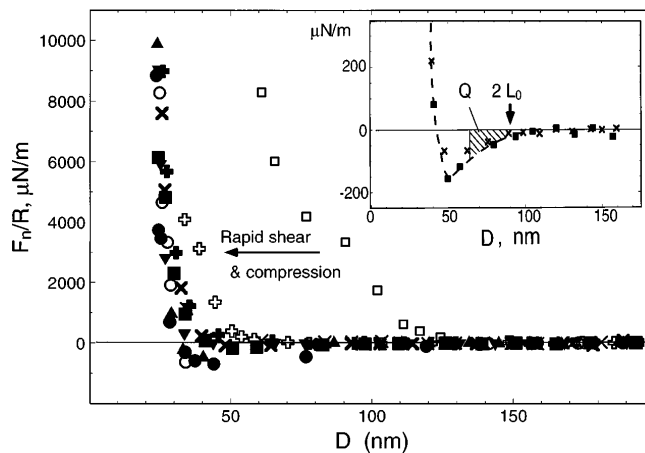

FIG. 1. Normal force $F_n(D)/R$ vs distance D profiles between mica surfaces bearing layers of *X*-PS-*X* telechelic chains. The force axis is normalized as $F_n/R = 2\pi E(D)$ where $E(D)$ is the interaction energy per unit area of flat parallel interacting plates obeying the same force-distance law. The initial long-ranged repulsion on a first approach (□) moves in on rapid shear (frequency ca. 1 kHz, at amplitude ca. 0.5 μm) and compression [11] to progressively shorter ranged profiles, to yield the limiting $F_n(D)$ profiles which have an attractive regime attractive both on approach and on separation of the surfaces. The inset (on a magnified scale) highlights the limiting $F_n(D)/R$ profiles as the surface approach. Symbols: □/○; 1st approach/separation; ✚/●: 2nd approach/separation; ■/▲: 3rd approach/separation; ✕/▼: 4th approach/separation.

D profiles, measured following this incubation. Initial interactions commence at an unexpectedly large distance [11–13], $D \approx 130$ nm, and are repulsive on approach. These long-ranged repulsions may be eliminated by shearing the surfaces rapidly under compression [11] (see Fig. 1), until eventually a limiting profile $F_n(D)$ is observed, this does not change further with time, and shows a marked attractive regime on approach of the surfaces, as highlighted in the inset. The final attractive well is first observed at $D_{\text{onset}} = 85 \pm 10$ nm, and is very different to the monotonic repulsion observed between singly functionalized PS-X brushes [14] or between the telechelic ABA triblock copolymers [7,15]. Insight into the limiting telechelic layer structure, and thus into the origin of the attraction, may be obtained by comparing the measured thickness L_0 and the surface densities of the X-PS-X layers with those of the corresponding PS-X layers. This is shown in Table I.

We see at once that the separations $2L_0$ at onset of interactions (once the limiting profiles are attained) and the mean interanchor spacing s of the X-PS-X layers are very similar to those of PS-X brushes of the same molecular weight $M = 70\,000$ (85 ± 10 nm vs 88 nm and 6.6 ± 0.4 nm vs 6.6 nm, respectively). At the same time, if we evaluate s for the telechelics assuming an all-loop structure, the value of s (4.7 nm) is significantly different from that (5.3 nm) for PS-X brushes of $M = 35\,000$ (equivalent to an X-PS-X of $M = 70\,000$ forming an all-loop structure) to which it should be equal. The onset distance for such PS-X brushes (56 nm) is also appreciably smaller than the observed values (85 nm) for the X-PS-X chains. These comparisons show that the telechelic chain layer on each surface must, at the least, have a substantial fraction of singly end-tethered tails extending away from the surface. This is most likely due to the association of dangling -X groups into dimers

or multimers [16] (see Fig. 4 later). Such association eliminates the energy advantage of forming single-chain loops [17], and has not been previously treated by theories of telechelics [6]. The attractive well (inset to Fig. 1) is then due to the interactions between these multimer entities on the opposing layers, as discussed below. The range of the interaction as the surfaces approach also confirms that single-chain bridging—as would occur via the penetration of a given chain end through the opposing layer, and its attachment to the opposite surface—is negligible [18].

Shear force profiles were measured by moving the top telechelic-bearing surface laterally (by Δx_0) and parallel to the lower telechelic-bearing surface, at a surface separation D. The shear force F_s between the surfaces is measured directly by monitoring the bending (by Δx) of a set of springs, constant k_1 (70 N/m), so that $F_s = k_1 \Delta x$. Figure 2 shows typical traces of a back-and-forth linear motion applied to the top surface (top trace), together with the corresponding shear force F_s between the surfaces (lower traces). The plateau value of $F_s = F_{\text{sp}}$ is indicated, and is the force required to slide the two telechelic-bearing surfaces steadily past each other at the corresponding shear velocity and surface separation.

The variation of F_{sp} with D for a given shear velocity, extracted from traces as in Fig. 2, is shown in Fig. 3, where the normal force profile (taken from Fig. 1) is superposed. We see that the shear forces required to slide the surfaces become significant (i.e., measurable) at about the same separation as the onset of the normal (attractive) forces between them, at $D \cong 80$ nm; the increase of F_{sp} at greater compressions is due in part to the increased overlap area. This is again in marked contrast to the case of interacting surfaces bearing singly end functionalized

TABLE I. Comparison of the measured thickness and inferred surface densities by polymer type.

Polymer type	M	$2L_0$ (nm)[a]	Mean interanchor spacing s (nm)[b]
X-PS-X	70 000	85 ± 10	6.6 ± 0.4 [tethered at one end (tails)]
			4.7 ± 0.3 [tethered at both ends (loops)]
PS-X	70 000[c]	88	6.6
PS-X	30 000[c]	56	5.3

[a]Taken as distance for onset of interactions (attractive for the X-PS-X, repulsive for the PS-X layers).
[b]Inferred from the $F(D)$ profiles at high compressions, as described in Ref. [9]. For polystyrene in toluene at room temperature, for $F(D')/R = 10^4 \; \mu$N/m, $s = s_1 \cong 0.98 M^{1/2}/(D')^{1/4}$ if attachment is at one end only (tails), and $s_2 = s_1/\sqrt{2}$ if both ends are attached (loops), where both s and D' are in Å.
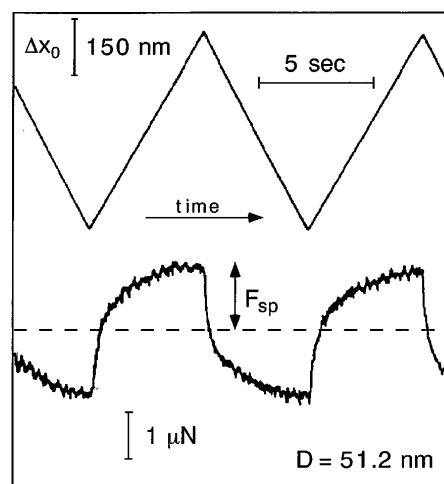[c]By interpolation of measurements in Ref. [9].

FIG. 2. Directly measured traces of the applied back-and-forth lateral motion (top trace) and the corresponding shear force across the interacting telechelic layers (lower trace), at a surface separation $D = 51.2 \pm 0.5$ nm. The shear velocity in each direction is 130 nm/sec.
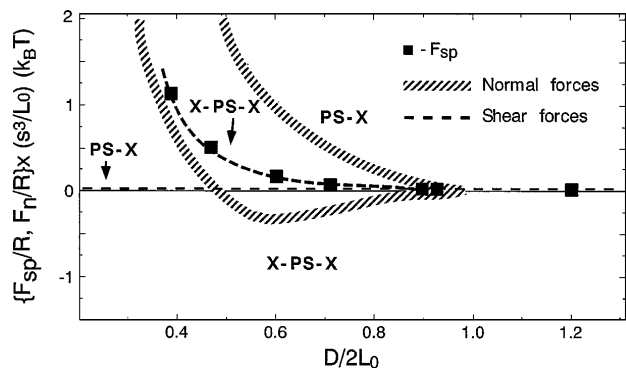
5077

FIG. 3. Variation of the limiting (plateau) value F_{sp} (Fig. 2) for different D values, all at shear velocity 130 nm/sec (broken line is a guide to the eye). Also shown as a shaded band is the normal force profile $F_n(D)$, taken from the inset to Fig. 1. For comparison, the force profiles for normal and shear interaction between PS-X brushes are also shown (shaded and broken curves indicated), taken from Ref. [19]. The surface separation axis is normalized as $D/2L_0$ with respect to the unperturbed thickness of the brushes (taken as $2L_0 = 850$ Å for the telechelic chains, Table I), while the force axis is normalized with respect to the chain length and interanchor spacing (see Ref. [19]).

(PS-X) brushes at comparable compression ratios and shear velocities, also shown in Fig. 3.

Further insight is obtained by analyzing the nature and magnitude of the interactions in both the normal and the shear modes. As noted, each zwitterionic -X group may adhere not only to the mica substrate (with interaction energy ε_{zm} [10]) but also—with comparable energy—to another zwitterion. This may occur between two or more dangling -X groups within a layer, forming multimer structures, or it may occur between -X groups on opposing layers, forming bridges as illustrated in Fig. 4. The former case is associated with greater constraint on the translational freedom of the interacting end moieties. Thus we expect an effective net energy gain of entropic origin, of order $k_B T$, for each dipolar end that is free to associate with ends on the other layer as well as within the same layer. We also expect the entropic attraction
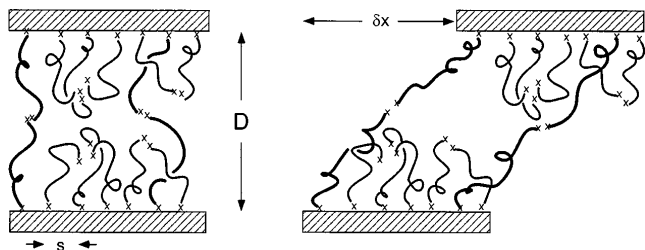

FIG. 4. Schematic illustration of the structure of interacting telechelic layers suggested by the results of this study. The zwitterionic head groups interact either within a layer to form multimers, or across a layer to bridge the gap, shown in bold lines. On sliding, the bridges initially stretch to provide the shear forces shown in Fig. 2.

per chain to be reduced due to compression of each chain within the overlapped telechelic layers, to some effective value ε_{eff}, say. This mechanism accounts well for the observed attraction between the surfaces as they approach (inset to Fig. 1). The net attractive interaction energy $Q(D)$ of the two curved surfaces at separation D is given by $Q(D) = \int_{2L_0}^{D} F(D') \, dD'$ (corresponding to the shaded region in the inset to Fig. 1). At surface separation D the overlap area between the curved telechelic layers is $A(D) = 2\pi R(2L_0 - D)$, and the total number of chains per surface in this overlap region is $n(D) = A(D)/s^2$. If we assume that a substantial fraction of these have tails that can associate either between or within the grafted layers, then we expect the attraction due to the mechanism described to be roughly $n(D)\varepsilon_{eff}$. Setting $Q(D) \approx n(D)\varepsilon_{eff}$, we find from Fig. 1 (inset) that at $D = 60$ nm, say, $Q(D) = (2.0 \pm 0.4) \times 10^{-14}$ J, so that [setting $R = 1$ cm, $2L_0 = 85$ nm, $s = 6.6$ nm (Table I)], $\varepsilon_{eff} \approx 0.13 \, k_B T$. This value, comparable with though smaller than $k_B T$, is fully consistent with our expectations from the mechanism above of an entropic attraction reduced by steric repulsion [20].

We attribute the shear forces encountered as the telechelic layers slide past each other at surface separation $D < 2L_0$ to stretching of the telechelic chains bridging the gap (Fig. 4). The elastic tension $f(d)$ in a chain when it is initially stretched by an extent d is given by $f(d) = Kd$, where $K \cong [k_B T/(R_F)^2]$ is the spring constant of a chain in a good solvent [21] (R_F being the unperturbed end-to-end dimension of the bridging telechelics). When two flat parallel telechelic-bearing surfaces slide past each other by an amount $\delta x = (\Delta x_0 - \Delta x)$ from an unsheared configuration ($F_s = 0$), the total shear force F_s between them may be evaluated [22] as

$$F_s \cong n_b(D)(k_B T/DR_F)\delta x, \tag{1}$$

where $n_b(D)$ is the total number of bridges between the unsheared surfaces at this separation. This relation applies best at small values of δx since at larger extensions the excess elastic energy will lead to significant breaking of the bridges and a reduction in n_b (we attribute the observed reduction in $\partial F_s/\partial(\delta x)$ at increasing δx, Fig. 2, to the breaking of these bridges). The initial variation of the shear force in the elastic (entropic) regime of the bridges is clearly seen in the traces in Fig. 2. From Eq. (1) the initial slope is $\partial F_s/\partial(\delta x)|_{(F_s=0)} \cong n_b(D)(k_B T/DR_F)$; here $n_b(D)$ is taken as the number of bridges in the overlap area $A(D)$ [$= 2\pi R(2L_0 - D)$] of the two telechelic layers. We initially expect roughly equal partitioning of the total number of chains $n(D) = [A(D)/s^2]$ between bridging and nonbridging chains [22], so that $n_b(D) \cong n(D)/2$. From the shear force traces we may now compare directly the predicted and experimental values. Putting $R_F = 32$ nm [23], $2L_0 = 85$ nm, and $s = 6.6$ nm (Table I), we obtain $n_b(D)(k_B T/DR_F) = 61$ N/m. From the trace in Fig. 2

($D = 51.3$ nm), the experimental value of the slope is $\partial F_s / \partial(\delta x)|_{(F_s=0)} \cong 35 \pm 10$ N/m. The predicted value is thus closely comparable (within a factor 2 or so) with the measured slope at $F_s = 0$; comparisons at other surface separations D give similar agreement. This supports our picture for the origin of the shear forces, and is fully consistent also with the magnitude of the normal surface attraction measured. We note the measurement of tension in the stretched polymer chains in the entropic regime, which (in Fig. 2, for example) is of the order of $F_s/n_b = 2 \times 10^{-14}$ N per bridge.

Our results suggest that telechelic chains with interacting end groups may form predominantly multimerlike aggregates on a surface, rather than loops. When two such surfaces approach, the formation of entropically favored bridges between the opposing layers results in a net attraction, while a shear force due to the stretching of the bridges arises on sliding the surfaces. During steady sliding, bridges appear to break and reform to maintain a constant shear force resisting the motion. These observations imply strategies for controlling surface and tribological interactions, using telechelics, that go beyond the classic modifications achievable by unfunctionalized adsorbed or grafted chains.

———————

*Present address: GDPC case 026, University of Montpellier, 34095 Montpellier Cedex 5, France.
†Corresponding author.
Email: bpklein@weizmann.weizmann.ac.il

[1] D. H. Napper, *Steric Stabilisation of Colloidal Dispersions* (Academic, London, 1983).

[2] A. K. Dolan and S. F. Edwards, Proc. R. Soc. London A **343**, 427 (1975).

[3] P. G. deGennes, Adv. Colloid Interface Sci. **27**, 189 (1987).

[4] G. J. Fleer, M. A. Cohen-Stuart, J. M. H. M. Scheutjens, T. Cosgrove, and B. Vincent, *Polymers at Interfaces* (Chapman and Hall, London, 1993).

[5] J. Klein, Annu. Rev. Mater. Sci. **26**, 581 (1996).

[6] S. M. Milner and T. A. Witten, Macromolecules **25**, 5495 (1992).

[7] M. Tirrell, S. Patel, and G. Hadziiaonnou, Proc. Natl. Acad. Sci. U.S.A. **84**, 4725 (1987).

[8] L. Dai and C. Toprakcioglu, Europhys. Lett. **16**, 331 (1991).

[9] H. J. Taunton, C. Toprakcioglu, L. J. Fetters, and J. Klein, Macromolecules **23**, 571 (1990).

[10] Solvated PS-X brushes in toluene have been extensively characterized [9], and the net zwitterion-mica sticking energy evaluated as $\varepsilon_{zm} = \sim(6-8)k_B T$.

[11] The initial long-ranged repulsion is believed to be due to the presence of free X-PS-X molecules from solution loosely associated with the adsorbed layers [12,13]. Compression under rapid shear appears to break up and squeeze out these associated structures.

[12] T. A. Witten, J. Phys. (Paris) **49**, 1055 (1988).

[13] A. N. Semenov, J.-F. Joanny, and A. R. Khoklov, Macromolecules **28**, 1066 (1995).

[14] H. J. Taunton, C. Toprakcioglu, and J. Klein, Macromolecules **21**, 3333 (1988).

[15] L. Dai, C. Toprakcioglu, and G. Hadziioannou, Macromolecules **28**, 5512 (1995).

[16] See, for example, W. Li and A. C. Balazs, Mol. Simul. **13**, 257 (1994).

[17] E. Kumacheva, J. Klein, P. Pincus, and L. J. Fetters, Macromolecules **26**, 6477 (1993).

[18] We note, however, that following strong compression, the attraction observed on separating the surfaces was markedly larger—by a factor of 4 or so relative to the values on approach shown in the inset to Fig. 1— and at somewhat lower D values, suggesting that single-chain bridging may have occurred during the compression [E. Eiser *et al.* (to be published)].

[19] J. Klein, E. Kumacheva, D. Mahalu, D. Perahia, and S. Warburg, Faraday Discuss. Chem. Soc. **98**, 173 (1994).

[20] We note that at separations $D \lesssim 2L$ near the onset of interactions we expect the steric repulsion component in ε_{eff} to be small (see Fig. 3).

[21] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, New York, 1979).

[22] E. Eiser, J. Klein, T. A. Witten, and L. J. Fetters (to be published).

[23] For a PS chain in toluene [9] of $M = 140\,000$, corresponding to a telechelic bridge consisting of two X-PS-X chains.