Supporting Information

Thin Polymer Film Force Spectroscopy: Single Chain Pull-out and Desorption

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1) Optimizing the Experimental Procedure

Prior to the main experiments in the manuscript, thorough investigations were carried out to optimize the experimental system. Initially, AFM tips were dip-coated in SBR solutions and then used to interact with blank substrates. However, the results showed increased adhesion due to capillary forces on the more hydrophilic substrates.[1] Furthermore, as the overall adhesion in the system was large, it significantly reduced the probability of observing individual desorption events. To overcome these issues, the experimental system was altered so that the AFM tips were left blank and the substrates were dip-coated to physically adsorb the polymers to their surface. This eliminated any influence from capillary forces as each substrate was coated in hydrophobic SBR.[2] Additionally, the overall adhesion in the experiments was lower which significantly increased the probability of observing desorption events (98%, 94%, and 99% probability for the mica, silicon, and graphite substrates, respectively).

2) AFM Images of SBR Thin Films

AFM imaging demonstrated that the SBR formed mostly continuous thin films on each substrate. A small amount of dewetting occurred in the films leading to surface coverages of 99%, 95%, and 99% for the mica, silicon, and graphite substrates, respectively. Figure S1 shows typical AFM images of the SBR films on each substrate.
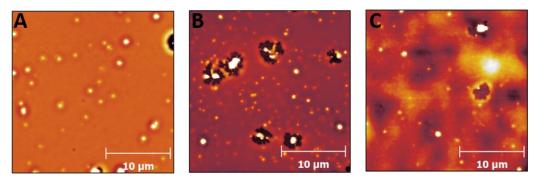

Figure S1. Typical AFM images of the SBR thin films on each substrate. (A) Mica, (B) silicon, (C) graphite.

3) Molecular, Chain Pull-out and Friction Equations and Calculations

GPC performed by Michelin demonstrated that the chains had a molar mass (M_n) of 355 kg/mol and were monodisperse with a Đ of 1.02. The number of Kuhn monomers (N) in the SBR chains could be calculated using:[3]

$$N = \frac{M_n}{M_o} = 1365, \tag{1}$$

where M_0 is the molar mass of the Kuhn monomers (0.26 kg/mol). Values of M_0 for butadiene and styrene were taken from the literature, and the value for SBR was calculated using the styrene-butadiene ratio of 25.9:74.1.[3] The length of the SBR chains (L) could then be calculated using:[3]

$$L = Nb, \tag{2}$$

where b is the polymer Kuhn length (1.19 nm), which was also calculated using values from the literature and the styrene-butadiene ratio of 25.9:74.1.[3] Consequently, the length of the SBR chains was calculated as 1.62 μm.

When chains are pulled-out from their own melt quasi-statically, i.e. close to thermodynamic equilibrium, the associated adhesive energy is related to the change of the intermolecular interactions as they are taken out of their own melt to air, and therefore is related to the polymer surface energy.[4] An elegant estimation of the related force at the single chain level has been given by Raphael and de Gennes,[5] and its connection to adhesion is further explained by Brochard-Wyart et al.[6] This force is essentially the same as the force during the "extraction" of a chain from its own collapsed coil (globule) derived by Halperin et al.[7] which was later used and measured experimentally by Haupt et al.:[8]

$$F = 2\pi r \gamma, \tag{3}$$

where r is a distance of the order of the monomer radius (seen as a cylinder) and γ is the polymer surface energy. It is independent of the chain length and it is a plateau force.

In addition to this "surface energy" force, frictional forces of viscous origin at the monomer scale could develop at finite speeds.[4] For a single chain with N number of monomers embedded in the thin film and pulled-out at velocity, v, the frictional force (F_{fr}), can be estimated by the following equation:[9]

$$F_{fr} = N\zeta v, \tag{4}$$

where ζ is the monomeric friction coefficient, for a styrene-butadiene copolymer a reasonable value is $\zeta = 2.5 \times 10^{-9}$ Ns/m. [10,11] For our experiments, $v = 1.5 \times 10^{-6}$ m/s and the maximum number of monomers is 1365. For these values, the maximum frictional force on a single chain is of the order of 5 pN, which is at the limit of our experimental resolution. Furthermore, it has to be stressed that the frictional force is not a plateau force (in our experiments force plateaus are observed which are consistent with a surface-energy origin); the frictional force drops as the chain is extracted and thus there are fewer monomers of this chain embedded in the thin film. At our detection point during the force-distance curve, most of the chain is already extracted and the friction force contribution is expected to be much lower than 5 pN. For these reasons, its contribution is negligible to our observations.

4) Components of Surface Energy

Table S1. The components of surface energy for each material.[2,12-14]

Surface Energy (mJ/m^2)	Mica	Silicon	Graphite	SBR
Dispersive Component	30.0	35.0	41.9	27.3
Polar Component	90.0	0.5	8.0	0.004
Total	120.0	35.5	49.9	27.304

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