Supporting Information

Materials & Methods

PAN was synthesised via slow addition of concentrated nitric acid, HNO_3 (RCI Labscan Ltd., Thailand, 70% w/w), to a chilled solution (< 10 °C) of hydrogenous propylamine (Fluka Analytical, Germany, ≥ 99.0% w/w) and reverse osmosis (RO) water. During the acid addition, the mixture was rapidly stirred to ensure dispersal of any heat generated. The sample was then rotary evaporated for several hours at ~ 50 °C. The resultant solution was heated overnight in an oil bath at ~ 105 °C under a nitrogen atmosphere. The liquid was thoroughly purged with filtered nitrogen gas between rotor evaporation and oil bath steps to prevent the formation of nitrous oxide impurities. The water content of the IL was undetectable by Karl Fischer titration prior to experimentation (< 0.01% w/w). Mica (Pro Sci Tech, Australia) was prepared by using adhesive tape to cleave along the basal plane.

The PAN – mica interface was studied using an Asylum Research Cypher Atomic Force Microscope (Santa Barbara, CA). Data was obtained at a constant temperature of ~ 25 °C. Force curves were recorded in contact mode and AFM images were obtained in soft contact mode to minimise deformation of the surface structure. Silicon nitride tips were used for all experiments (nominal normal spring constant k_z = 0.06 N/m) and were irradiated with UV radiation for 15 minutes prior to experiment. Scan sizes for force curves were between 30 and 50 nm. The environmental cell for the Cypher AFM is still being developed, so experiments were completed in a droplet exposed to the atmosphere within the AFM box (a sealed enclosure). As PAN is hygroscopic, the water content of the liquid will increase over the course of an experiment. The water content of PAN was checked using Karl Fischer titration after each experiment. Even after four hours the water content never exceeded 3% w/w. The images presented in this paper (and the force curve in **Error! Reference source not found.** of the supporting information) were obtained within no more than 30 minutes of the PAN droplet being placed on the mica. Karl Fischer titration of PAN collected from the cell after this time period had a vale of ~ 1% w/w. This value depended slightly on the ambient humidity, so the water concentration in the data presented will be less than this value.

The normal force curve and lateral force measurements presented in Figure 1 of this paper were obtained using a Digital Instruments Nanoscope IV Multimode AFM (Veeco, Santa Barbara, CA) with an EV scanner in contact mode. Colloidal particles were attached to two tipless rectangular cantilevers (model CSC12, Mikromasch, Tallinn, Estonia) using Araldite™ epoxy under an optical microscope. A ~ 5 μm diameter silica particle (Bangs Laboratories, Fishers, IN) was used to obtain the normal force curve, and a ~ 15 μm diameter borosilicate particle (Duke Scientific, Palo Alto, CA) was used to obtain the friction data.

The normal (k_z) and torsional (k_t) spring constants of each cantilever were determined using the Sader method.[1] The spring constants of the cantilever with the 15 μm colloid probe were k_z = 0.329 N/m and $k_t = 2.85\times10^{-9}$ N·m/rad. The spring constants of the cantilever with the 5 μm colloid probe were k_z = 0.580 N/m and $k_t = 4.20\times10^{-9}$ N·m/rad.

Experiments on the Nanoscope AFM were performed in a liquid cell sealed with a silicon rubber O-ring that prevents water ingression. The liquid cell and the O-ring were cleaned by rinsing with distilled ethanol and RO water. Normal force curve measurements and friction force measurements were performed after introducing ~ 1 mL PAN into the cell and equilibrating for at least 30 minutes.

Friction measurements were obtained by performing lateral AFM scans with a scan angle of 90° (with respect to the cantilever long axis) with the slow scan axis disabled. The lateral deflection signal (i.e., cantilever twist) was converted to lateral force using a custom-written function produced in MATLAB 7.11.0 (written by Oliver Werzer) which takes into account the torsional spring constant and the geometrical dimensions of the cantilever. The lateral deflection sensitivity, δ, of the AFM's photodiode was calibrated according to the method of Liu *et al.*[2] and was found to be $\delta = 6.7376\times10^3$ V/radian. Friction force data were obtained for sliding velocities from 5 to 40 μm/s and normal loads from 0 to ~ 34 nN. Each individual lateral force data point is an average of at least sixteen repeat friction loops to produce statistically significant data.

Figures

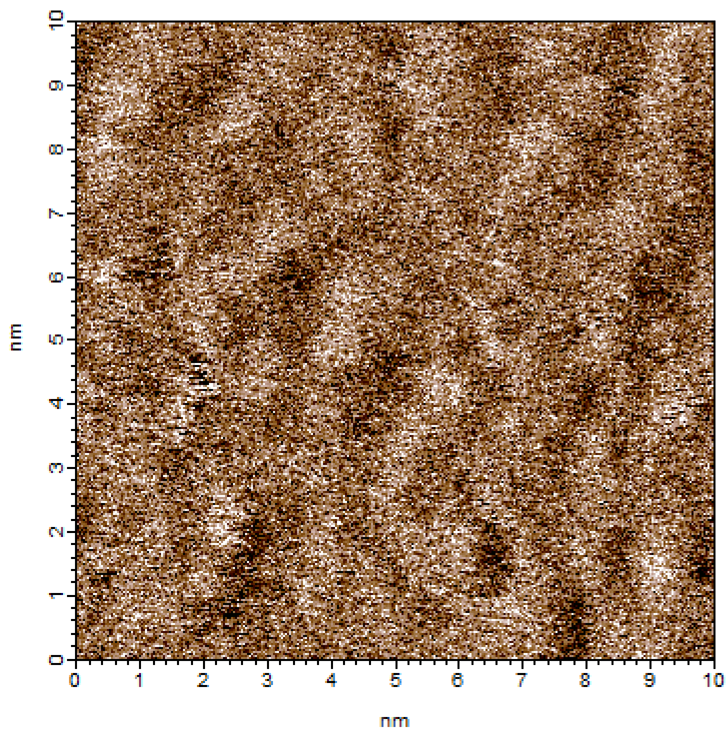

Figure A. A contact mode AFM image of a transition zone layer in the PAN-mica system. The slow scan direction is up the image.

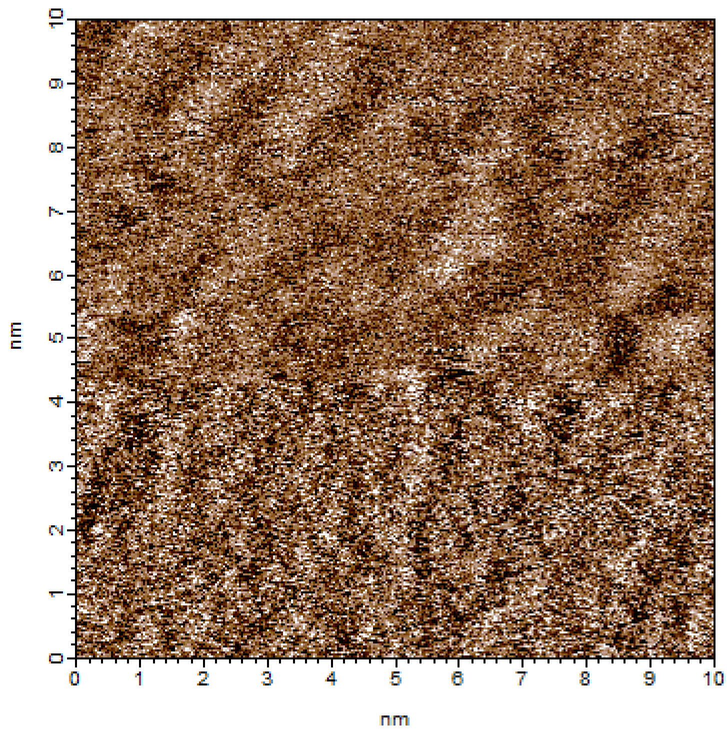

Figure B. A contact mode AFM image of the transition from a near surface layer (top) to the innermost layer (bottom) in the PAN-mica system. The slow scan direction is down the image.

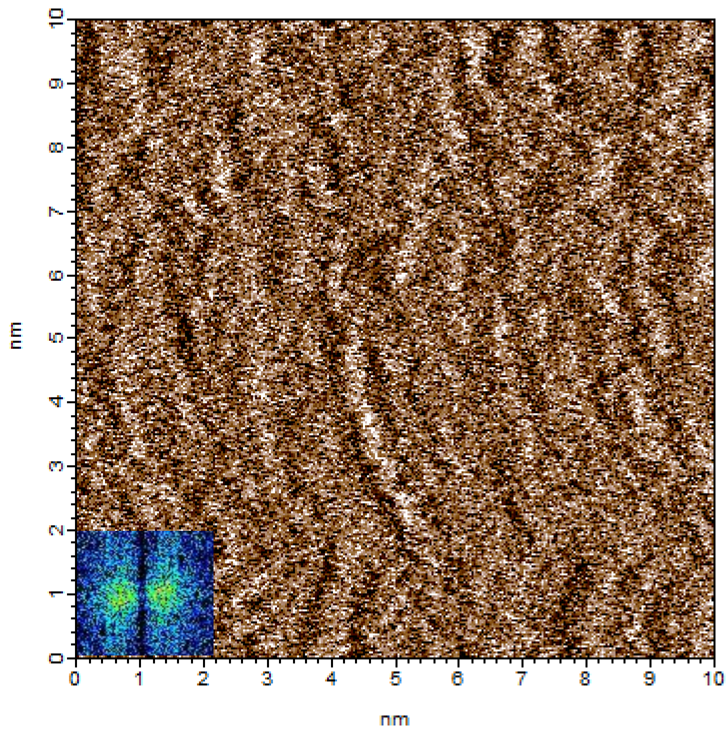

Figure C. A contact mode AFM image of the innermost layer of the PAN-mica system. The slow scan direction is up the image. The inset gives the 2D Fourier transform, indicating that the interaggregate periodicity repeat length is 5 ± 0.3 Å.

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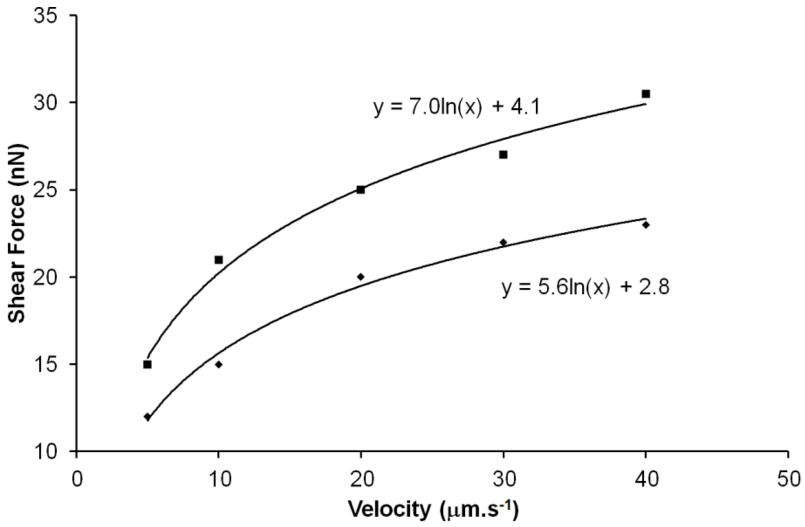

Figure D. Representative plots of shear force versus colloid probe sliding velocity at 20 nN (diamonds) and 32 nN (squares) that demonstrate the logarithmic dependency of shear force with sliding velocity.

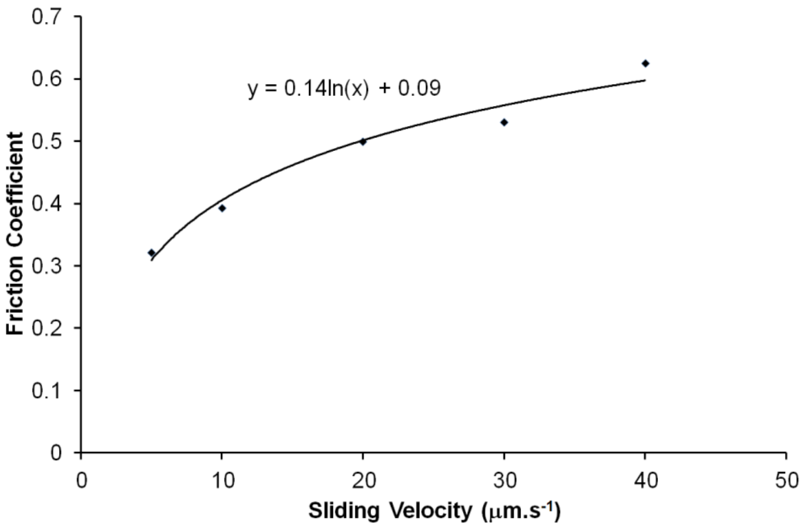

Figure E. Colloid probe speed dependant friction coefficient for Region II.

References

(1) Green, C. P.; Lioe, H.; Cleveland, J. P.; Proksch, R.; Mulvaney, P.; Sader, J. E. *Rev. Sci. Instrum.* **2004**, *75*, 1988.

(2) Liu, E.; Blanpain, B.; Celis, J. P. *Wear* **1996**, *192*, 141.