Electronic Supplementary Information

Poly(acrylamide) Films at the Solvent-Induced Glass Transition: Adhesion, Tribology, and the Influence of Crosslinking

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Analytical data

^{1}H-NMR spectrum of *iniferter*

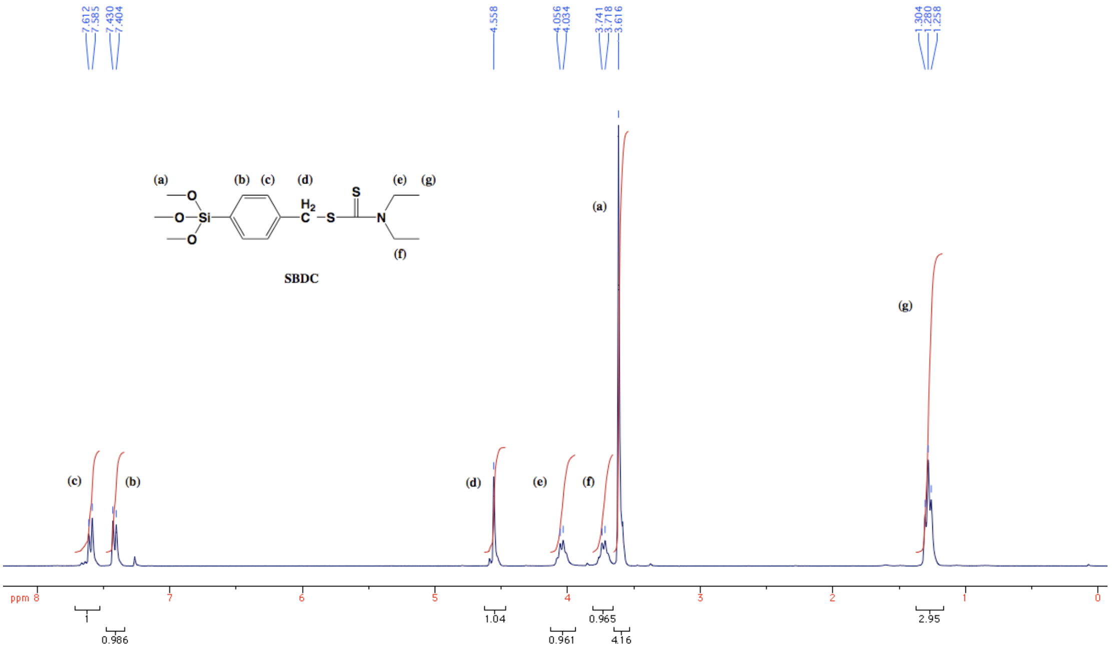


Figure S1: ^{1}H-NMR spectrum of *N*,*N*-(diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane (SBDC) *iniferter*.

FT-IR spectra of PAAm films with different degrees of crosslinking

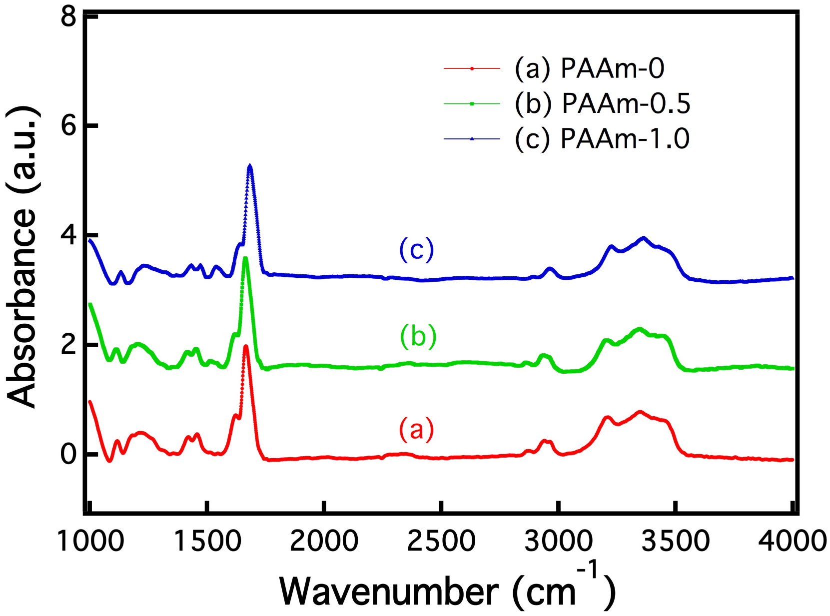
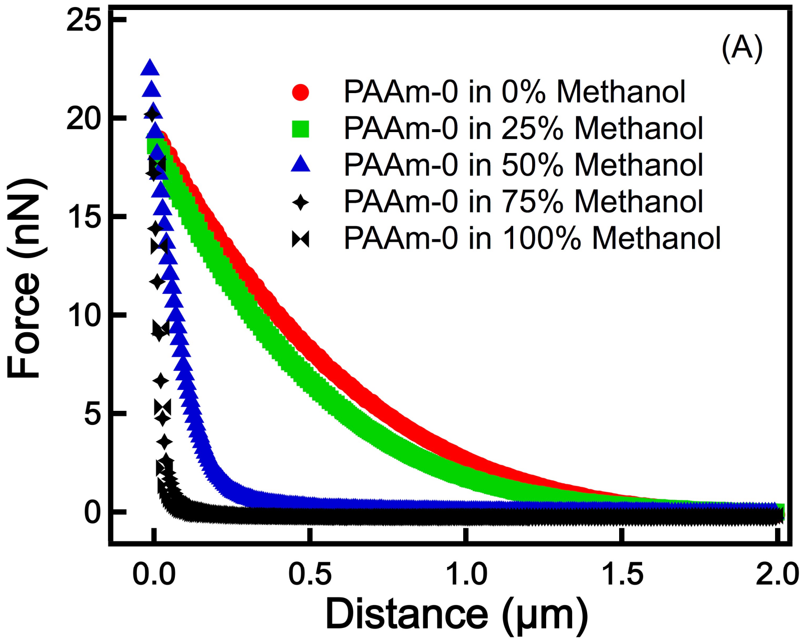
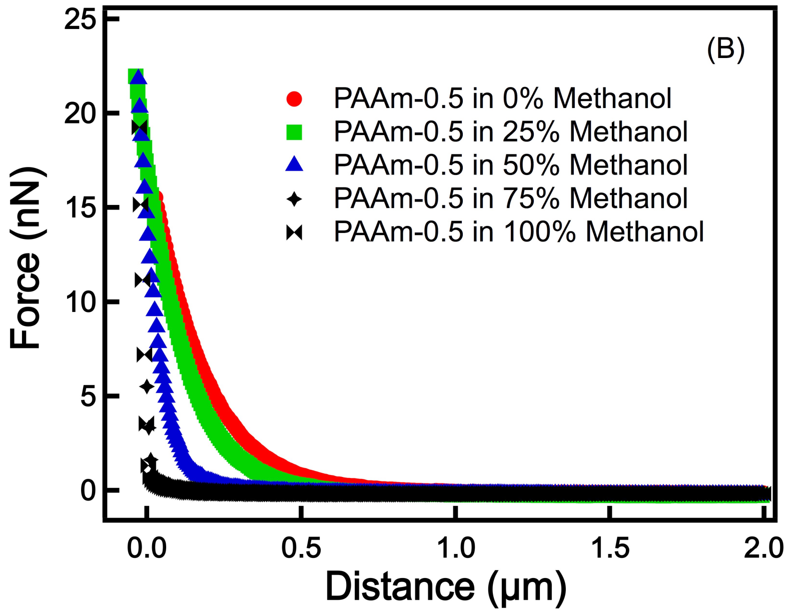


Figure S2: FT-IR spectra of surface-tethered poly(acrylamide) thin films with different crosslinking degrees. Dry thickness of PAAm-0, PAAm-0.5 and PAAm-1.0 are 189 nm, 173 nm and 217 nm, respectively.

Force-distance curves for PAAm films in different solvent mixtures, with different degrees of crosslinking





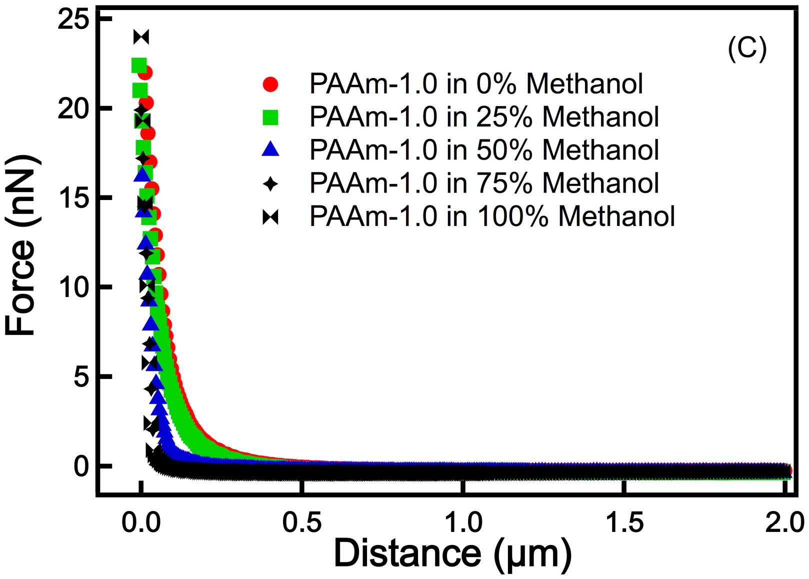


Figure S3: Force-distance curves of PAAm films with different crosslinking degrees measured by colloidal-probe atomic force microscopy (CPM) (spring constant: 0.511 N/m, radius of silica probe: 14 μm, applied load: 21.4 nN, testing speed: 3.97 μm/s) in aqueous methanol mixtures with various solvent qualities (only approach curves are shown). (A) PAAm-0 films (dry thickness: 189 nm). (B) PAAm-0.5 films (dry thickness: 173 nm). (C) PAAm-1.0 films (dry thickness: 217 nm).

Variation of T_g of PAAm-0 brushes with solvent-mixture composition

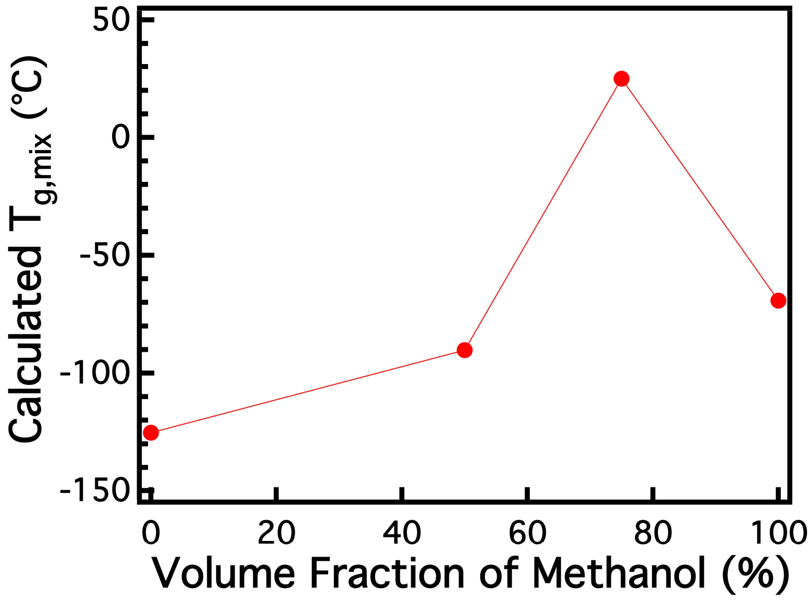


Figure S4: Glass-transition temperatures of PAAm-0 brushes in aqueous methanol solutions with different qualities, calculated using swelling-ratio data from ellipsometry, according to the Gordon-Taylor equation (Lines are shown as a guide to the eye).

Pull-off force between gold-coated silica probe and PAAm films in water-methanol mixtures

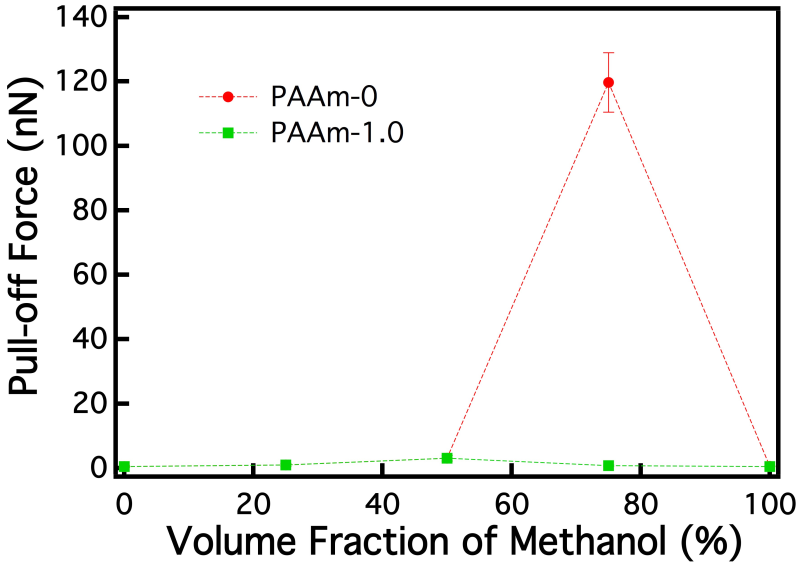


Figure S5: Pull-off force of PAAm films (dry thickness of PAAm-0: 189 nm, dry thickness of PAAm-1.0: 217 nm) measured by CPM (spring constant: 0.508 N/m, radius of gold-coated silica probe: 8.66 μm, applied load: 35.2 nN, testing speed: 3.97 μm/s) in aqueous methanol mixtures of varying composition (Lines are shown as a guide to the eye).

Determination of maximum pull-off force measured between a silica probe and PAAm-0 brushes as a function of methanol volume fraction in water-methanol mixtures

Prior to the study of the pull-off force of PAAm-0 brushes conducted by means of CPM in an open fluid cell, the variation of the methanol volume fraction in water-methanol mixtures upon continuous evaporation of the mixture was examined.

Aqueous methanol solutions are known to be non-azeotropic mixtures,[1] the evaporation rate of methanol being faster than that of water due to their different vapor pressures (vapor pressure of water and methanol at 20 °C are 2.30 kPa and 13.02 kPa, respectively). Constant evaporation rates (0 – 100 min) of pure water (0.7 mg/min), pure methanol (8.0 mg/min) and 75% (volume fraction) aqueous methanol solutions (7.0 mg/min) were measured by using an analytical balance (METTLER TOLEDO® XS105) in accompanying experiments under the same conditions as later used for pull-off force measurements (sample volume: 3.0 ml). According to the vapor-liquid coexistence line for the water-methanol system at standard atmospheric pressure,[2] the molar fractions of methanol (y_1) and water (y_2) in the vapor phase during the evaporation process can be estimated making the assumption that the evaporation rate of the two components results from the individual evaporation rate of each component. Thus, for the 75 vol.% mixture:

$$8.0 \cdot y_1 + 0.7 \cdot y_2 = 7.0$$

$$y_1 + y_2 = 1$$

It follows that $y_1 = 0.863$, and $y_2 = 0.137$.

Furthermore, the evaporation rates of methanol (k_1) and water (k_2) in aqueous methanol mixtures with an initial methanol volume fraction of 75% within the experimental time scale can be calculated from:

$k_1 = 8.0 \cdot y_1 = 6.904$ mg/min

$k_2 = 0.7 \cdot y_2 = 0.096$ mg/min

The time-dependent volume of methanol ($V_{methanol}$) and water (V_{water}) can be determined accordingly:

$V_{methanol}\ (t) = 3.0 \cdot 0.75 - k_1 \cdot t\ /\ \rho_{methanol} = 2.25 - 0.00863 \cdot t$

$V_{water}\ (t) = 3.0 \cdot 0.25 - k_2 \cdot t\ /\ \rho_{water} = 0.75 - 0.000096 \cdot t$

since $\rho_{methanol}$ and ρ_{water} are 0.8 g/ml and 1.0 g/ml, respectively.

Finally, the methanol volume fraction during evaporation in mixed solutions with an initial methanol volume fraction of 75% within the experimental time scale (0 – 100 min) results from:

$V_{methanol}\ (\%) = 100 * V_{methanol}\ /\ (V_{methanol} + V_{water}) = 100 * (2.25 - 0.00863 \cdot t)\ /\ (3 - 0.008726 \cdot t)$

The methanol volume percentage in the binary solution decreases with respect to time, as shown in Figure S6.

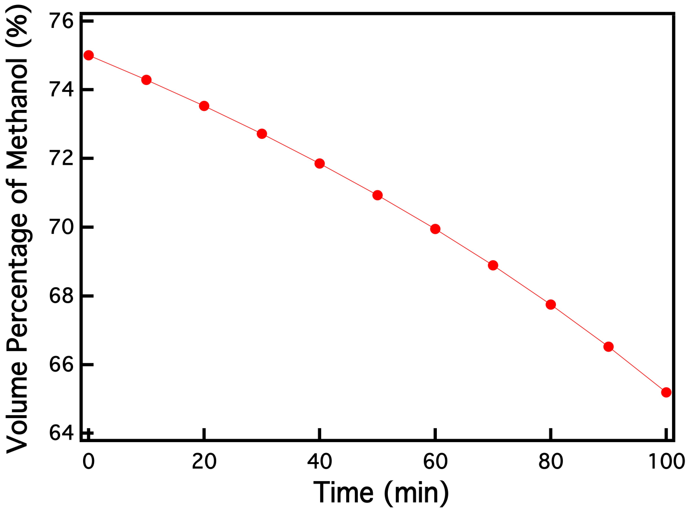


Figure S6: Methanol volume percentage in mixed water-methanol solutions, changing upon evaporation with respect to time.

After establishing the variation of methanol volume fraction in solution with respect to time, we further investigated the variation of pull-off force of PAAm-0 brushes in mixed solutions by means of monitoring pull-off force upon continuous evaporation of methanol. Figure S7 (A) shows the time-dependent pull-off force (obtained at intervals of five minutes) of PAAm-0 brushes in an open liquid cell containing an aqueous methanol solution with an initial methanol volume fraction of 75%. The pull-off force decreased moderately at the beginning of the evaporation process (0 – 20 min); a sharp decrease of pull-off force being observed upon further evaporation of water and methanol (20 min – 80 min); finally, pull-off force reached a steady value. Three representative retraction force curves are taken from the data shown in Figure S7 (A), shown in Figure S7 (B), corresponding to initial (a), intermediate (b) and final (c) states of PAAm-0 brushes during the evaporation process. As described above, the methanol volume fraction in the solution varied roughly from 75% to 65% (mole fraction: 57.5% – 45.5%) over the experimental time scale (Figure S6).

In the initial phase (a), the volume fraction of methanol in solution decreased gradually from 75% to 73% over 20 min, which did not lead to a significant decrease in pull-off force, indicating that PAAm-0 brushes were still at the (solvent-induced) glass transition. Upon further evaporation, the decreasing methanol volume fraction in solution (73% – 67%) led to a shift of the glass transition to values below room temperature and a consequent decrease in pull-off force, as the brushes began to become more mobile (and to swell). In the final stage of the experiment (below 67% methanol vol.%), the residual methanol volume fraction was too low to influence the pull-off force significantly; therefore, a plateau in pull-off force was obtained for the swollen PAAm-0 brushes.

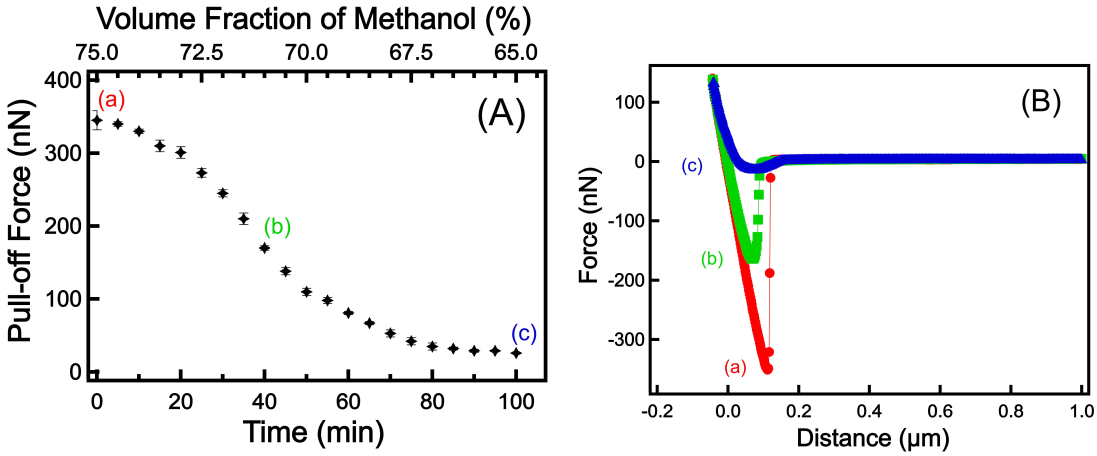


Figure S7: Variation of pull-off force of PAAm-0 Brushes (dry thickness: 133 nm) measured by CPM (spring constant: 3.02 N/m, radius of silica probe: 12.5 μm, applied load: 123.9 nN, testing speed: 3.97 μm/s): (A) Variation of pull-off force of PAAm-0 brushes exposed to ambient environment in aqueous methanol mixtures with an initial methanol volume fraction of 75%. (B) Exemplary retraction force curves of polymer brushes at different time indicated by (a), (b) and (c).

Notes and references

1 *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide, CRC Press, Boca Raton, FL, 75th edn., 1913 – 1995; Chapter 6, pp. 206.

2 K. Kojima, H. M. Moon and K. Ochi, *Fluid Phase Equilib*. 1990, **56**, 269.