Supporting Information

Tunable Nanolubrication between Dual-Responsive Polyionic Grafts

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Experimental details

Materials. 2-(dimethylamino)ethyl methacrylate (DMAEMA, Aldrich, 98%) was vacuum distilled before use. 2,2´-azobis(isobutyronitrile) (AIBN, Fluka, 98%) was re-crystallized from ethanol at 40 °C and 1,4-dioxane (Aldrich, 99%) was used as received. The RAFT-agent 2-cyanoprop-2-yl dithiobenzoate (CPDB) had previously been synthesized according to a procedure described elsewhere[1] and was provided by Dr. Nikolas Zwaneveld and Dr. Camilla Nilsson. The water used in all experiments was first pretreated by a Milli-RO Plus unit and then further purified by a Milli-Q Plus185 system and filtered through a 0.2 µm Millipak filter. The resistivity after the treatment was 18.2 MΩ cm, and the total organic carbon content of the water did not exceed 2 ppb.

RAFT polymerization and characterization. The following polymerization procedure is outlined in Figure S1. The chain transfer agent (CPDB, 112 mg, 0.51 mmol) and the initiator (AIBN, 27.8 mg, 0.17 mmol) were dissolved in dioxane (29.4 mL) by stirring for 10 min after which the monomer (DMAEMA, 14.0 g, 15 mL, 89 mmol) was added and the mixture was stirred for another 10 min. The solution was then divided into several smaller vials, sealed off with rubber septa and purged with N_2 for 15 min before being put in an oil-bath at 90 °C. Vials were removed at appropriate times and the polymerization was rapidly quenched in an ice-bath. The conversion was calculated by gravimetric analysis after being dried by evaporation. Molecular weight was determined by size exclusion chromatography (Shimadzu SEC, RI10A refractometer, UV detector) in tetrahydrofuran (THF) at 1 mL/min. The column was calibrated with near mono-disperse poly(methyl methacrylate) standards.

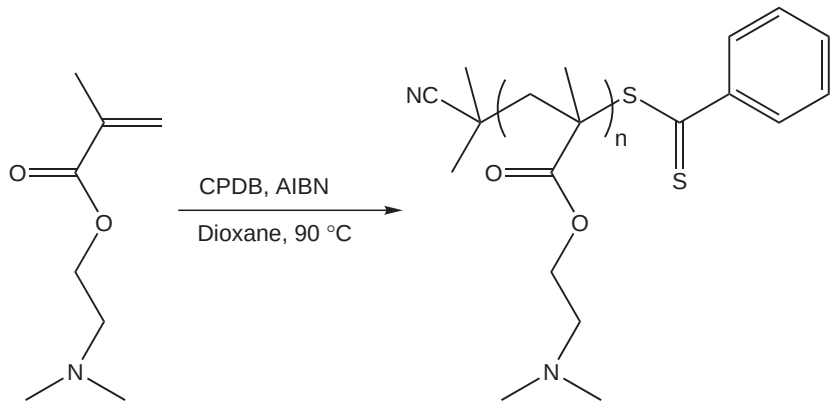

Figure S1: Synthetic pathway for the CPDB mediatied RAFT polymerization of DMAEMA.

The weight-average molecular mass, M_w, for the sample used in the grafting-to procedure was 2.8×10^4 with a polydispersity index (M_w/M_n, where M_n is the number-average molecular mass) of 1.42. Figure S2 summarizes the polymerization and the molecular information. The retention of the dithioester group was confirmed by SEC using UV detection at 310 nm, the wavelength of strong absorption of the dithiobenzoate moiety.

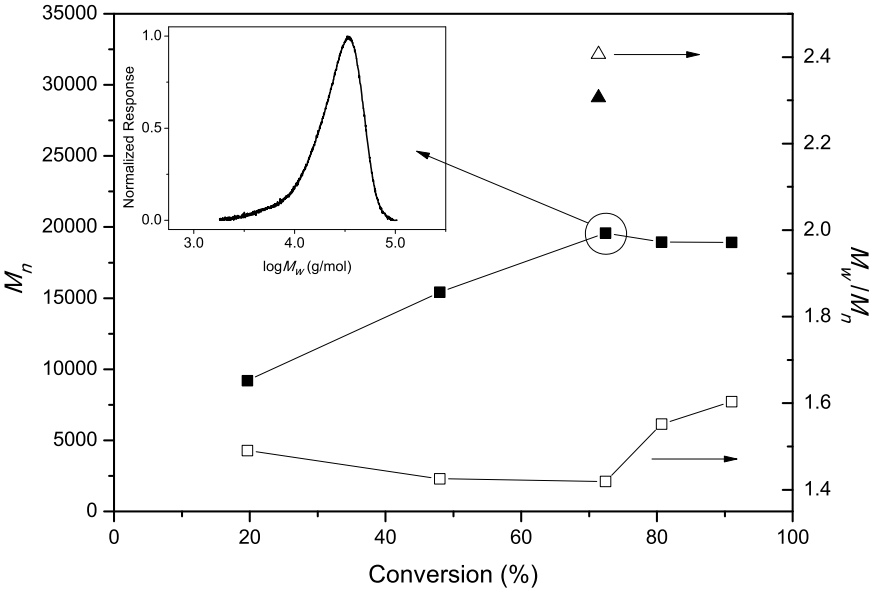

Figure S2: M_n (filled squares) and M_w/M_n (open squares) evolution versus monomer conversion for CPDB mediated RAFT polymerization of DMAEMA. The M_n (filled triangle) and M_w/M_n (open triangle) for the control experiment without the chain-transfer agent (CPDB) is displayed in the upper right corner. The inset shows the size exclusion chromatogram for the sample used in the grafting-to procedure (as indicated by the circled data point).

QCM-D. The quartz crystal microbalance with dissipation (QCM-D) consisted of 4 flow modules that were configured to run in parallel (Q-Sense E4 system). All throughout, standard QSX 301 crystals (Q-Sense) made of quartz with a thin evaporated gold electrode attached via a chromium adhesive layer were used. In order to remove any organic residues from the gold surface, the crystals were first cleaned with bichromatic sulphuric acid for 15 min, flushed with copious amounts of water, rinsed with ethanol and dried under N_2 flow prior to being mounted in the measuring chamber. During adsorption measurements the initial flow rate was set to 150 µL/min and the pump turned off once the appropriate time for filling the measuring chamber was reached. The experiments performed at elevated temperature vary in terms of absolute frequency compared to the ambient temperature conditions. However the mass changes are entirely comparable, via Sauerbrey[2] (Equation 1), because the prefactor varies on the ppm scale over the temperature range used.

AFM. Friction and force measurements were carried out on a MultiMode Picoforce with Nanoscope III (AFM) controller (Veeco, USA). The microscope was further equipped with a thermal application controller attached to a Bio-Heater element mounted on top of the PF-scanner. The cantilevers used were rectangular uncoated tipless silica cantilevers (CSC12/NoAl with approximate dimensions: length 250 µm, breadth 35 µm; MikroMasch, Esonia). In order to obtain accurate normal and torsional spring constants the cantilevers were calibrated using the AFM Tune IT v2.5 software (ForceIT, Sweden), based on thermal noise with hydrodynamic damping.[3, 4] Force measurements were performed with ramp size 1 µm at a rate of 2 µm/s. The lateral photodetector sensitivity was calibrated using the procedure of tilting the photodetector.[5] The gold spheres (approximate diameters of 10 µm) were produced under a gentle nitrogen flow by bringing together two gold wires and applying a current (approximately 10 A) inducing an electrical discharge. The particles were then attached to the end of the cantilever using a tiny amount (~1 fL) of epoxy resin (Araldite Rapid, Casco).

References

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