Supporting Information

Tunable and switchable nanoparticle separation with thermo-responsive track-etched membranes prepared by controlled surface-initiated polymerization of poly(N-isopropylacrylamide)

Kevin Daumann, Sven Frost, Mathias Ulbricht*

Lehrstuhl für Technische Chemie II, Universität Duisburg-Essen, Universitätsstr. 7, 45141 Essen, and Center for Nanointegration Duisburg-Essen (CENIDE), 47057 Duisburg, Germany.

Detailed synthesis procedure

All the ATRP reactions were performed in a house made setup containing a series of 100 mL 3-neck flasks with septum and gastight screw caps under argon atmosphere. The ATRP reaction solution was prepared in a 4-neck flask with septum. For a typical experiment with a series of membrane samples, 11.3 g of NIPAAm, 11 mg of CuCl₂ and 344 μ L of Me₆TREN were dissolved in DMF to yield 100 mL solution, i.e., the NIPAAm concentration was 1 mol/L. This solution was used for the PET80 membranes, while a NIPAAm concentration of only 0.5 mol/L was used for PET30 membranes, with the respective analogous dilution of all other components. After 30 min of degassing this solution with argon, 83 mg of CuCl was added under a continuous argon stream. The molar ratio for all experiments was [NIPAAm]: $[Me_6TREN]$: $[CuCl_2] = [120]$: [1.5]: [1]: [0.1]. When a light green-brown solution had been formed, 10 mL of the solution was injected with a gastight syringe with silicon plunger (B. Braun Melsungen AG, Melsungen, Germany) through the septum into the 3-neck flask which contained one membrane example. Reaction for the individual membrane sample proceeded for a predetermined reaction time between 1 and 3 h. To stop the polymerization 10 mL of a solution of 500 mg CuBr₂ and 1.25 mL PMDETA in DMF to yield 100 mL solution was added to the in ATRP solution immersed membrane sample. After that the screw caps were removed and the samples were washed as follows: To remove copper traces they were first immersed in a solution of PMDETA in DMF, and then washed one time in DMF and twice in methanol. Each washing step took 30 min and the membranes were moved inside the washing solutions by a horizontal shaker. After drying at 55°C for 1 h the samples were weighed to determine the degree of graft functionalization (DG) which was calculated according to:

$$DG = (m_{gr} - m_0) / A \tag{1}$$

where m_0 is the membrane weight after initiator immobilization, m_{gr} is the membrane weight after grafting and A is the surface area of the used 44 mm diameter membrane sample which is 903 cm² (65 cm²/cm² specific surface area). The surface area of the membranes had been determined by nitrogen adsorption isotherm measurement and BET analysis.



Figure S1: Size distribution from dynamic light scattering (DLS) of lysozyme (blue curve) and BSA (black curve) in aqueous phosphate buffer (pH 8).



Figure S2: Temperature stability of BSA in aqueous phosphate buffer (pH 8) at 40°C demonstrated by DLS data.