A Novel Electrolyte-Responsive Membrane with Tunable Permeation Selectivity for Protein Purification

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Synthesis of Polystyrene Nanoparticles. Polystyrene nanoparticles were synthesized via standard emulsion polymerization procedure. To a jacketed three-neck round bottom flask containing 191.8 gram of DI water, 0.128 gram of cetylpyridinium chloride (CPC) was added and mechanically stirred to ensure complete dissolution. The solution was then bubbled with high-purity nitrogen to remove dissolved oxygen for at least 30 minutes. Predetermined amount of styrene monomer (1 and 3 gram, respectively) was then added with the aid of deoxygenated syringe under nitrogen atmosphere. The temperature was then increased to 70 °C while the mechanical stirring was maintained at 250 rpm. The thermal initiator, 2,2'-Azobis(2-methylpropionamidine) dihydrochloride (V-50) (80mg) was dissolved in 5 gram of pre-deoxygenated DI water and then injected into the flask to commence the polymerization. Within 5 minutes, the solution turned milky. After 4 hours, the polymerization was quenched by decreasing the temperature to 20 °C. The freshly prepared nanoparticle suspension was then cleaned by serum-replacement for at least 1 week, to remove unreacted monomer, emulsifier as well as labile oligomers. The weight concentration of the final product was measured gravimetrically. The morphology of the synthesized styrene nanoparticle was observed using a high-resolution field-emission transmission electron microscope (TEM) (JOEL, JEM-2100P, Japan), operated at accelerating voltage of 200 kV. The effective hydrodynamic diameter of the nanoparticles was measured using dynamic light scattering (DLS) with ZetaPlus-90PLUS (BROOKHAVEN, US).

Morphology and Particle Size of the Polystyrene Nanoparticles.

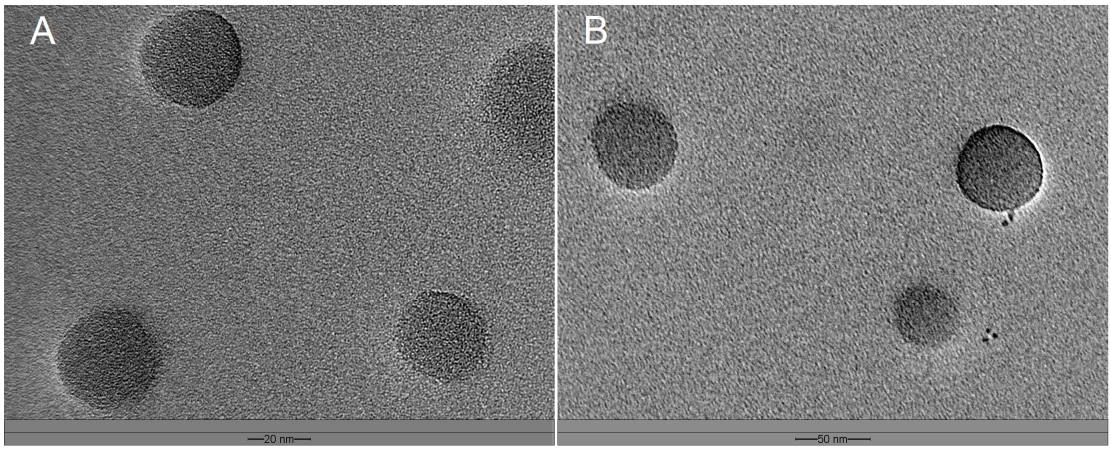

FIGURE S1. TEM images of the polystyrene nanoparticles.

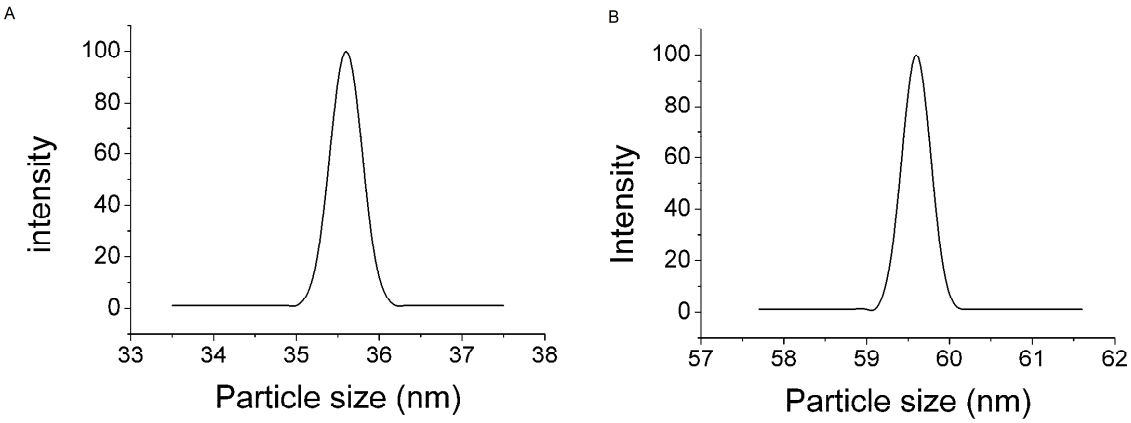

FIGURE S2. Size distribution of the nanoparticles. A: 35.6 nm; B: 59.8 nm.

Estimation of Membrane Pore Size.

The proximate pore size of a porous membrane may be estimated using the classical Hagen-Poiseuille equation:

$$J=\frac{V}{\Delta t}=\frac{\pi \Delta P r^4}{8\eta L} \qquad (1)$$

where V is the volume of the permeate relating to a single membrane pore, Δt is the time interval, ΔP is the trans-membrane pressure, r is the pore radius, η is the viscosity of liquid, and L is the capillary length (representing the membrane thickness). Therefore, based on the DI water fluxes of the RC and RC-*g*-PSBMA membranes, the approximate relative pore size change due to the variation of grafting conditions may be estimated using the following relationship:

$$\frac{r}{r_0}=\sqrt[4]{\frac{V}{V_0}} \qquad (2)$$

Where r_0 is the pore radius and V_0 the DI water flux of the unmodified RC membrane. Here, it is assumed that the pore density of the membrane surface did not change after the grafting polymerization and all pores had equal pore size. The calculated results are given in Figure S3. It can be seen that the value of r/r_0 deceased when the ATRP reaction time increased, suggesting the decrease in the effective pore sizes of the membranes.

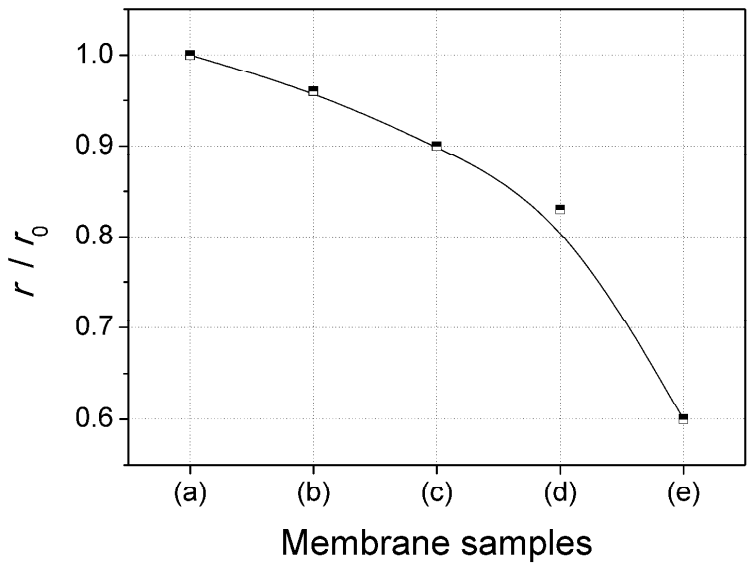

FIGURE S3. Relative pore size change due to the variation of ATRP grafting conditions. (a) RC, (b)-(e) RC-*g*-PSBMA (ATRP conditions: [CuBr]/[$CuBr_2$]/[Bpy]/[SBMA]=1/0.25/2/7.5; solvent, water/methanol=1/1; ATRP reaction time, b: 6 h, c: 12 h, d: 18 h and e: 24 h).