Supporting Information for

Polyacid Microgels with Adaptive Hydrophobic Pockets and Ampholytic Character: Synthesis, Solution Properties and Insights into Internal Nanostructure by cryogenic-TEM

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Incremental monomer consumption during copolymerization

The incremental consumption of monomer/crosslinker (tBMA/EGDMA = 10) during the reaction was monitored by tracking the remaining monomers during the polymerization using $^1$H-NMR. The data indicate that the crosslinker is consumed slightly faster in the reaction mixture as we find depletion and a shift of the ratio of tBMA/EGDMA to higher values (Figure SI 1).

**Figure SI 1.** NMR study to monitor the changes of the ratio monomer/crosslinker remaining in solution during the polymerization (tBMA/EGDMA = 10; time shifted by 0.1 min to allow representation on a logarithmic plot).

Acidic hydrolysis of PtBMA latex particles into PMAA microgels

PMAA microgels can be easily obtained by mild and selective acidic deprotection of the tert.-butyl side group of the crosslinked PtBMA$_e$/D$_x$ latex particles using 0.01 v/v methane sulfonic acid in dichloromethane, which runs to completion within one minute reaction time.$^{1, 2}$ The aqueous dispersion turn near transparent when converting the milky dispersions of hydrophobic PtBMA$_{E500}$ latex particles into hydrophoblic PMAA$_{E500}$ microgels (Figure SI 2a). This already allows to macroscopically conclude a successful hydrolysis and a swollen gel character with a drastically reduced refractive index contrast. Further Fourier Transform Infrared Spectroscopy (FTIR) confirms the disappaerance of the tert.-butyl group after the hydrolysis of
PtBMA<sub>ex</sub> (Figure SI 2b). The spectra are normalized to the –CH<sub>2</sub> deformation peak at ca. 1477 cm<sup>-1</sup>, which remains roughly constant before and after hydrolysis. The two peaks associated with the tert.-butyl part at 1350 to 1390 cm<sup>-1</sup> disappear after hydrolysis and a shift of the carbonyl band from 1730 cm<sup>-1</sup> towards lower wavenumber of 1709 cm<sup>-1</sup> is observed. The carbonyl band of PMAA<sub>E10</sub> stays at slightly higher wavenumber in comparison to PMAA<sub>E500</sub>, which is due to more carbonyl groups from EGDMA crosslinker. This confirms a successful and quantitative hydrolysis of the ester to the acid, and a remaining integrity of the ester functionality of the EGDMA crosslinker.

**Figure SI 2. Hydrolysis of PtBMA/EGDMA latex particles into PMAA microgels.** (a) Changes in the chemical structure and photographs of PtBMA<sub>E500</sub> latex in water (c = 0.1 wt%) and PMAA<sub>E500</sub> microgels (c = 0.1 wt%) in water after acid hydrolysis of crosslinked PtBMA/EGDMA after freeze drying at room temperature. (b) FTIR of PtBMA<sub>E10</sub>, PMAA<sub>E10</sub> and PMAA<sub>E500</sub>.
Incremental conversion of monomer/comonomer during the reaction

The changes of the monomer/comonomer ratio during the reaction for starting ratios of tBMA/MMA and tBMA/DEAEMA = 1:1 were monitored by $^1$H-NMR, indicating that the comonomer (MMA and DEAEMA) in both reactions polymerizes faster. This points to a slight enrichment of the comonomers (MMA and DEAEMA) in the core of the microgels (Figure SI. 3a and b).

**Figure SI 3a and b.** NMR study to monitor the changes of monomer/comonomer ratio remaining in solution during the polymerization ((a) PtBMA/PMMA$_{1:1}$ and (b)PtBMA/PDEAEMA$_{1:1}$; time shifted by 0.1 min to allow representation on a logarithmic plot).
Potentiometric and Conductivity titration of PMAA/PDEAEMA\textsubscript{1:1}

The potentiometric and conductivity titration of PMAA/PDEAEMA\textsubscript{1:1} was conducted by titration of an acidified microgel dispersion (HCl) using 0.1 N NaOH solution at 25 °C. Two transition points (pH ~ 4 and 9.5) are observed from the conductivity curve as A and B (Figure SI 4). The first point A corresponds to the onset of neutralization of the –COOH groups, while the second point B is related to the end of deprotonation of the –N(C\textsubscript{2}H\textsubscript{5}) groups. Below pH = 4 and above pH = 9.5, the steep increase in the conductivity is due to the excess of HCl and NaOH respectively.

![Figure SI 4](image-url)

**Figure SI 4.** Potentiometric and conductivity titration of 0.05 wt% PMAA/PDEAEMA\textsubscript{1:1} with 0.1 N NaOH.