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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 (*t*BMA/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 *t*BMA/EGDMA to higher values (Figure SI 1).

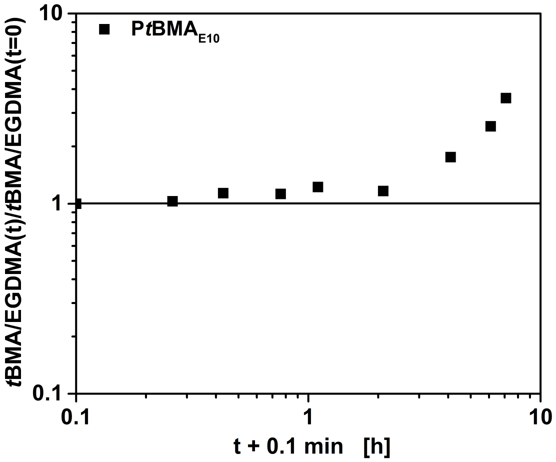

Figure SI 1. NMR study to monitor the changes of the ratio monomer/crosslinker remaining in solution during the polymerization (*t*BMA/EGDMA = 10; time shifted by 0.1 min to allow represenation on a logarithmic plot).

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 P*t*BMA$_{E/Dx}$ 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 P*t*BMA$_{E500}$ latex particles into hydrophobilic 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 diapperaence of the *tert.*-butyl group after the hydrolysis of

P*t*BMA$_{Ex}$ (Figure SI 2b). The spectra are normalized to the –CH$_2$ deformation peak at ca. 1477 cm^{-1}, which remains roughly constant before and after hydrolysis. The two peaks associated with the *tert.*-butyl part at 1350 to 1390 cm^{-1} disappear after hydrolysis and a shift of the carbonyl band from 1730 cm^{-1} towards lower wavenumber of 1709 cm^{-1} is observed.[1] The carbonyl band of PMAA$_{E10}$ stays at slightly higher wavenumber in comparison to PMAA$_{E500,}$ 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.

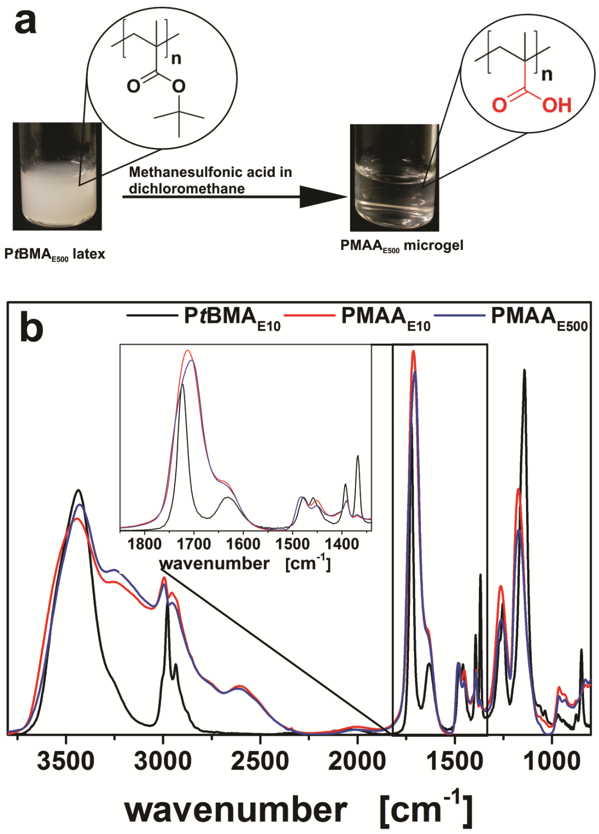

Figure SI 2. Hydrolysis of P*t*BMA/EGDMA latex particles into PMAA microgels. (a) Changes in the chemical structure and photographs of P*t*BMA$_{E500}$ latex in water (c = 0.1 wt%) and PMAA$_{E500}$ microgels (c = 0.1 wt%) in water after acid hydrolysis of crosslinked P*t*BMA/EGDMA after freeze drying at room temperature. (b) FTIR of P*t*BMA$_{E10}$, PMAA$_{E10}$ and PMAA$_{E500}$.

Incremental conversion of monomer/comonomer during the reaction

The changes of the monomer/comonomer ratio during the reaction for starting ratios of *t*BMA/MMA and *t*BMA/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).

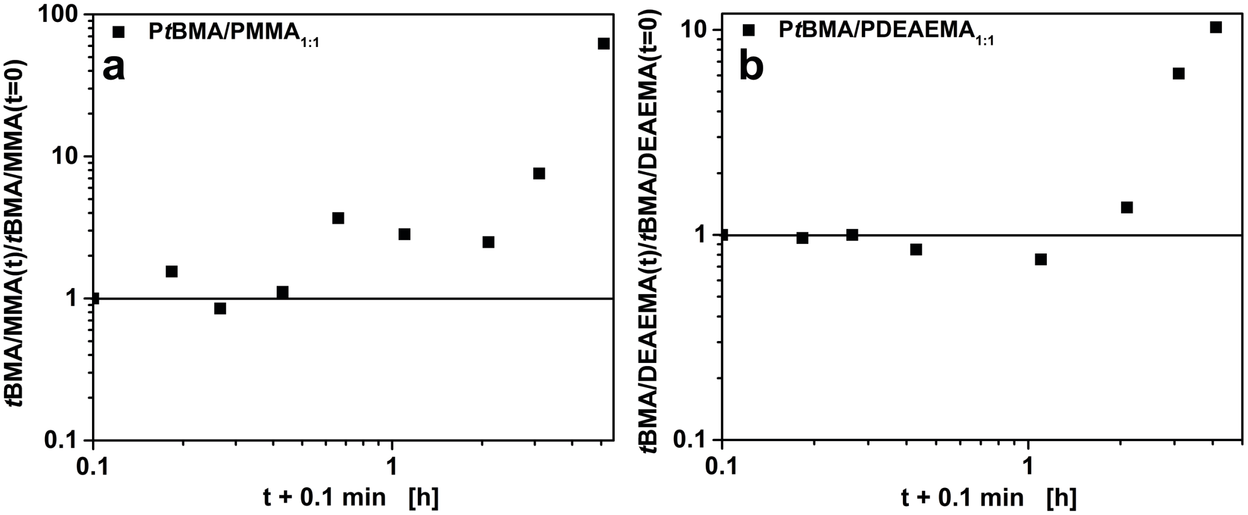

Figure SI 3a and b. NMR study to monitor the changes of monomer/comonomer ratio remaining in solution during the polymerization ((a) P*t*BMA/PMMA$_{1:1}$ and (b)P*t*BMA/PDEAEMA$_{1:1}$; time shifted by 0.1 min to allow represenation on a logarithmic plot).

Potentiometric and Conductivity titration of PMAA/PDEAEMA$_{1:1}$

The potentiometric and conductivity titration of PMAA/PDEAEMA$_{1:1}$ 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_2H_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.

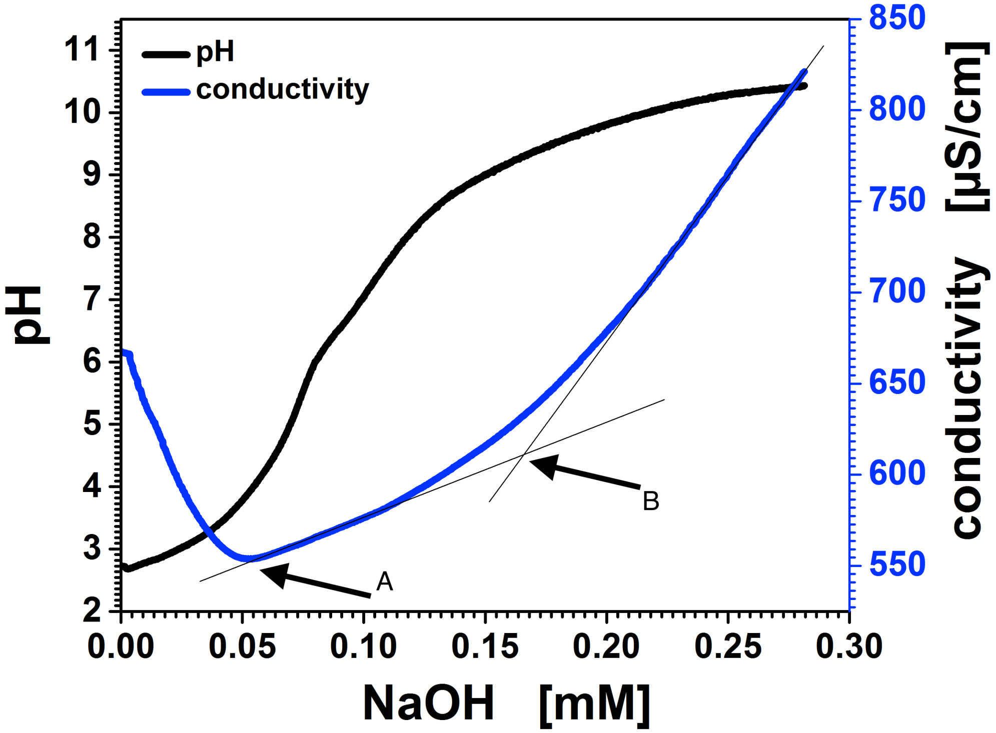

Figure SI 4. Potentiometric and conductvity titration of 0.05 wt% PMAA/PDEAEMA$_{1:1}$ with 0.1 N NaOH.

1. M. Retsch, A. Walther, K. Loos and A. H. E. Müller, *Langmuir*, 2008, 24, 9421-9429.
2. J. Dai, Z. Bao, L. Sun, S. U. Hong, G. L. Baker and M. L. Bruening, *Langmuir*, 2006, 22, 4274-4281.