

# Mixed Micelles of Oppositely Charged PNIPAAm Diblock Copolymers

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Mixed micelle formation between two oppositely charged diblock copolymers that have a common thermosensitive neutral block of poly(*N*-isopropylacrylamide), PNIPAAm, has been investigated. The charged block of the first copolymer was poly((3-acrylamidopropyl)trimethylammonium chloride) (PAMPTMA(+)) and in the second copolymer it was poly(sodium 2-acrylamido-2-methyl-1-propanesulfonate) (PAMPS(-)). The block copolymers are symmetrical in terms of blocks lengths and denoted: PNIPAAm<sub>26</sub>-*b*-PAMPTMA(+)<sub>15</sub> and PNIPAAm<sub>27</sub>-*b*-PAMPS(-)<sub>15</sub>. The block copolymer solutions mixed under equimolar charge conditions were investigated as a function of both temperature and total polymer concentrations by turbidimetry, differential scanning calorimetry, two-dimensional proton nuclear magnetic resonance Overhauser effect spectroscopy (2D <sup>1</sup>H NMR NOESY), dynamic and static light scattering (DLS and SLS), small angle X-ray scattering (SAXS) and electrophoretic mobility measurements. Well-defined and electroneutral micelles were formed at all concentrations studied up to (0.5 wt %), except for at 0.1 wt %, where the solution instead contained single copolymer chains and a small amount of clusters of undefined structure. The 2D <sup>1</sup>H NMR NOESY experiments showed that the charged blocks are in close proximity to each other but a minor block mixing occurs. Upon increasing temperature the solutions underwent clouding at a temperature, which is close to the lower critical solution temperature of PNIPAAm. The charged blocks built up a core, which was surrounded by a corona of PNIPAAm chains. By approaching the cloud point the PNIPAAm chains collapsed, which induced aggregation of the micelles. The structure of the micelles was cylindrical with a radius of about 3 nm and a rod length of 300 nm. The diffusion coefficient of the micelles from DLS agreed well with the theoretical value estimated for a rod.