Thermoresponsive self-assembled NiPAm-zwitterion copolymers

Ya Zhao,[a] Tao Bai,[b] Qing Shao,[b] Shaoyi Jiang,[b] and Amy Q. Shen[a,c*]

Zwitterionic polymers are well known for their non-fouling properties due to their unique pendant side chain structures. In this work, we incorporated temperature-responsive *N*-isopropylacrylamide (NiPAm) with zwitterionic monomers (Carboxybetaine methacrylate (CBMA) and Sulfobetaine methacrylate (SBMA)), and synthesized statistical copolymers poly(NiPAm-*co*-CBMA) and poly(NiPAm-*co*-SBMA). Above the low critical solution temperature (LCST), a clear sol-gel transition was observed, accompanied by an increase in turbidity and elastic modulus in the copolymer solution. The self assembly and thermoresponsive properties of these statistical copolymers under large strains and different temperatures were characterized by UV-visible spectroscopy, dynamic light scattering, and rheological characterizations. We showed that poly(NiPAm-*co*-CBMA) copolymers consisted both mechanically and thermally reversible networks, favoring them as reusable and biocompatible elastic materials. As a comparison, incorporating SBMA with NiPAm inhibited the thermo-sensitive and viscoelastic features from the pure NiPAm based polymer, causing a delayed LCST and weakened viscoelastic response in poly(NiPAm-*co*-SBMA) copolymers at both room and body temperatures. Our work demonstrates that CBMA monomers in poly(NiPAm-*co*-CBMA) copolymer act as stronger ionic bridges to form elastic networks when compared with poly(NiPAm-*co*-SBMA) copolymer. As a result, poly(NiPAm-*co*-CBMA) possess both non-fouling and thermo-sensitive features, without compromising its mechanical properties.

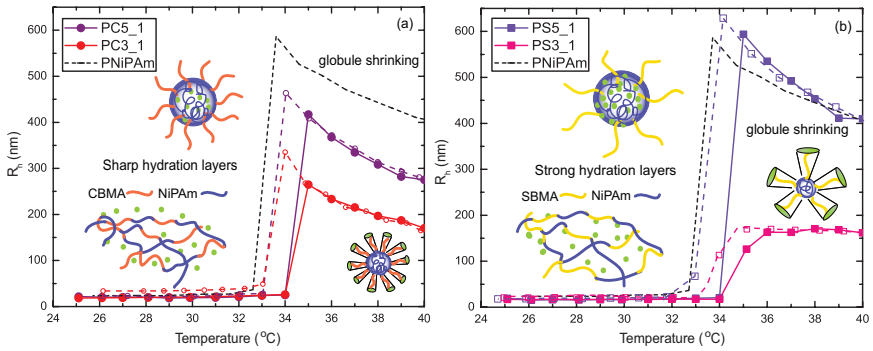

Fig. 1 Hydration radius R_h plotted against temperature from dynamic light scattering measurements for (a) 0.8 wt% PC copolymer solutions; (b) 0.8 wt% PS copolymer solutions. The dashed line corresponds to the hydration radius R_h of PNiPAm as a function of temperature. Single coil-blobs structure was shown to simplify the illustration.The green dots represent water molecules. The cones around C(S)BMA chains represent hydration layers. Solid curves with filled symbols represent heating processes, while dashed lines with hollow symbols correspond to cooling processes.