

Preparation of multi-stimuli-responsive active colloids via polymerization-induced thermal self-assembly

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Collective motions observed in living organism, such as flock of birds, schools of fish, self-organization of bacterial colonies, formation of tissues from cells, *etc.* serve important biological functions. Over the last decades, synthetic materials that mimic those collective motions, so called “active matter”, have attracted increasing attention.¹⁻² When focusing on the molecular scale, self-propelled nano- and micromotors that move in fluids powered by chemical reactions³ have been widely studied since the initial reports in 2004–2005.⁴⁻⁶ Examples of such materials include self-powered filaments of microtubes, spherical Janus particles, and polymer single-crystals. The driving force of the movement is provided by converting the energy of chemical fuels into mechanical motion. For instance, catalytic decomposition of hydrogen peroxide to oxygen and water on one face of Janus particles covered by platinum provides driving force for the collective motion of the particles in fluids. External energy in the form of electric, light, heat, ultrasound, magnetic induction, *etc.* can also induce collective motion of the active matter. Unlike the chemically powered methods, the externally powered approach does not need constant re-fueling of chemical fluids, which is a major advantage for biomedical applications including directed molecular delivery. Therefore, there have been considerable interests in designing active matter consisting of external stimuli-responsive compounds. However, many of those listed active matter consists of hard condensed materials within which guest molecules are hard to be encapsulated. Thus, it is of great importance to prepare externally powered active matter from stimuli-responsive soft materials as potential delivery vehicles.

Self-assembly of block copolymers is a practical strategy to prepare polymer colloids with controlled morphology and desired functionality. Recent advances in polymerization-induced self-assembly (PISA) further facilitate and simplify the preparation of the polymer colloids.^{7,8} This technique enables direct fabrication of polymeric assemblies including spherical micelles, rod-like micelles, vesicles, nanotubes and other aggregates during polymerization. In general, a first polymer block (A) is chain-extended using a second monomer in a solvent which is at once a good solvent for the polymer block A and the second monomer, and a poor solvent for the second polymer block (B). As the polymerization proceeds, the growing polymer block B gradually becomes insoluble, driving *in situ* self-assembly of the A-B diblock copolymer.

Herein, we applied the PISA approach to a reversible addition-fragmentation chain transfer (RAFT) polymerization of *N*-isopropylacrylamide (NIPAM) mediated by poly(methacrylic acid) (PMAA)-macromolecular chain transfer agent (macro-CTA) in the presence of *N,N'*-methylenebis(acrylamide) (MBAM) as a cross-linker in water at 70 °C, a temperature higher than the lower critical solution temperature (LCST) of the PNIPAM to prepare pH- and thermo-responsive nanogels (NGs). The NGs were functionalized with photo-responsive

spiropyran (SP) derivative by post-polymerization functionalization. The hydrodynamic radii (R_h) of the NGs varied with phase transition of the PNIPAM moiety by heating/cooling around their cloud point temperatures (T_{cp}). The T_{cp} and thermo-responsive property of the NGs varied by adjusting pH below/above pK_a of MAA ($pK_{aMAA} = 4.36$) due to protonation/deprotonation of the carboxylic acid groups on the PMAA moiety. Photoisomerization of the SP moiety on the surface of colloidal particles consisting of the NGs from nonionic SP form to highly polarized zwitterionic merocyanine (MC) form induced self-propelled collective motion of the colloids toward UV light source.

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