Polymeric Micellar Nanoreactors for Chemical Reactions in Water

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Several chemical reactions are performed in organic solvents which are mostly toxic and eventually become problematic from both economical and environmental perspectives. To make chemical process "greener", this research aims to develop micellar nanoreactors that can accommodate chemical reactions in water, the most well-known and environmentally friendly media. Sequential post-polymerization modification of poly(pentafluorophenyl acrylate) (PPFPA), a hydrophobic and functionalizable polymer precursor with benzylamine and 1-amino-2-propanol yielded poly(benzylacrylamide)-*ran*-poly(*N*-(2-hydroxypropyl)acrylamide), PBzA-*ran*-PHPA. The random copolymers of controlled composition can self-assemble into well-dispersed nanoparticles in water having size in a range of 150-200 nm. These polymeric micellar nanoassemblies were used as nanoreactors for the Thia-Michael addition between various thiols and nitrostyrene derivatives. The nanoreactors of 0.5 wt% was found to increase the conversion up to 100% for all thiols at room temperature within 24 h in the absence of catalyst. Without the nanoreactors, the reaction conversion decreased with increasing alkyl chain length of thiol due to the solubility limitation in aqueous media. The micellar nanoreactors can be re-used for up to ten times while reasonably high reaction conversion was still maintained. On the other hand, post-polymerization modification of PPFPA with 1-amino-2-propanol and 1-(3-amipropyl)imidazole gave imidazolium-conjugated random copolymers that can self-assemble into water-dispersible micelles upon Cu coordination. Preliminary investigation suggested that the developed imidazolium-Cu micelles can serve as effective nanocatalysts for azide-alkyne click reactions. Since a wide range of chemical functionalities can be proportionally incorporated and varied as a function of selected nucleophilic modifiers, it is strongly believed that post-functionalization of polymer precursor to generate functional random copolymer followed by self-assembly would be a versatile route to customized nanoreactors/nanocatalysts for a variety of chemical and biochemical processes in aqueous media. This would not only comply well with "the 12 Principles of Green Chemistry" but also satisfy "the BCG economic model".