

ABSTRACT

One of the contemporary goals of research in polymer chemistry is to achieve control over molecular architectures e.g. block, graft and star polymers, during their synthesis. Controlled radical polymerization (CRP), especially, radical addition fragmentation transfer (RAFT) process has emerged as one of the most promising synthetic routes for this purpose. Here, we have utilized RAFT as a tool to synthesize polymers with precisely controlled chain length, polydispersity and end-functionalities, for different potential applications. In the present dissertation work, we have aimed at establishing a broader approach towards the synthesis and applications of new block copolymers and star polymers. The synthesized polymers were thoroughly characterized using different tools like GPC, NMR and FTIR. The solution properties, especially self-assembling behavior, were studied different physicochemical methods such as DLS, fluorescence, UV-vis spectroscopy, and TEM.

To begin with, we have synthesized different water-soluble and organo-soluble chain transfer agents (CTAs) required for the RAFT polymerizations. PEGylated cationic block copolymers were synthesized and interactions of these cationic polymers with oppositely charged surfactants (SDS and AOT) and a protein (HSA) were investigated. While the polymer-surfactant systems produced various nanostructures, it was concluded that PEG, to some extent, prevented any perturbation caused to the polypeptide chain as a result of interactions with the cationic polymers.

We also synthesized two new block copolymers, poly(ethylene oxide)-*b*-poly(*N*-isopropylacrylamide)-*b*-poly(*t*-butyl acrylate) and poly(ethylene oxide)-*b*-poly(*N*-isopropylacrylamide)-*b*-poly(glycidal methacrylate) and studied their self-assembling behavior in water before and after transformations of the butyl acrylate and epoxy groups present on these copolymers. These copolymers showed thermo-responsive and functional-group dependent formation of various nanostructures. Using these triblock copolymers, we have demonstrated simple synthetic strategies for the preparation of cross-linked stars (CCS) polymers through i) thiol-acrylate Michael addition reaction between acrylate functionalized block copolymers and thiol functionalized two arm cross-linker and ii) diol-aldehyde acetal formation using diol functionalized triblock copolymer and aldehyde functionalized cross-linker. We have further investigated the pH-triggered disassembly of the CCS polymers and demonstrated the capability of these CCS polymers towards pH-dependent controlled release of drug molecules. We have also established a novel and environmentally benign method, whereby 1,3-dipolar cyclo-addition reaction has been applied using non-toxic reagent, iodosobenzenediacetate [PhI(OAc)₂] instead of the conventional copper-based reagents for the synthesis of soluble CCS polymers from polystyrene block copolymers.

Distance and size-dependent nanoparticle SET process was demonstrated by steady-state and timed-resolved fluorescence spectroscopy using gold nanoparticle tagged block copolymers bearing anthracene. We also reported the synthesis of a new block copolymer that was capable of highly selective and sensitive detection of Cu²⁺ and CN⁻ ions in aqueous medium. Cu²⁺ induced opening of the spirolactam ring of the rhodamine units present in the copolymer resulted in rapid and easily noticeable color change that disappeared on interacting with CN⁻, thus enabling a highly selective detection of Cu²⁺ and CN⁻ ions in aqueous medium.

Key words: RAFT polymerization, polyelectrolytes, nanostructures, vesicles, self-assembly, green synthesis, block copolymer, core cross-linked stars, drug delivery vehicles.