Abstract

This thesis reports the synthesis of a specialty functional hydrogel system consisting of derivatives of ionic polymer moieties via conventional Free Radical Polymerization (FRP) and Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization and their utilizations in the biomedical applications. To impart dual responsive self-healablity induced by heat as well as water in the hydrogel sytem, a core-crosslinked (CCL) cationic poly(furfuryl methacrylate)-*b*-poly(2-(methacryloyloxy)ethyltrimethyl ammonium chloride) (PFMA-*b*-PMTAC) and anionic poly(furfuryl methacrylate)-*b*-poly(sodium 4-vinylbenzenesulfonate) (PFMA-*b*-PSS) amphiphilic block copolymers (Am-BCPs) were prepared via RAFT polymerization. The self-assembly of the polyelectrolyte CCL BCP micelle was able to show dual responsive self-healing characteristics. A fluorescence active self-healable ionic hydrogel was also prepared via combination of ring opening polymerization (ROP) of ε-caprolactone and xanthate mediated RAFT polymerization. In this case, a polycaprolactone (PCL) based macro-RAFT reagent was utilized to prepare fluorescence active cationic PMTAC (PCL-*b*-PMTAC) and anionic PSS (PCL-*b*-PSS) BCPs in the presence of fluorescent precursors. This fluorescence active BCPs were incorporated into a poly(acrylamide) based hydrogel to prepare a self-healable hydrogel that can be utilized in sensing and fluorescence guided operations. To introduce an antifouling activity along with the self-healability in a hydrogel system, a zwitterionic BCP of PFMA and poly(sulfobetaine) was prepared and subsequently core-crosslinked with disulphide based crosslinker. It was observed that presence of the zwitterionic moiety imparts the anti-protein adhesive surface to the hydrogel and it also induces the self-healing activity by participating in a synergistic action with the disulphide metathesis reaction under UV irradiation. In another work, an antifouling and self-healable poly(dimethyl siloxane) (PDMS) hydrogel consisting of curcumin loaded BCP polymersome was prepared via RAFT polymerization and Schiff base reaction. This hydrogel can be used as a potential material for soft contact lens. In this regard, an amine modified and zwitterionic modified ABA tri-block copolymers of PDMS was prepared. Due to the presence of zwitterionic polymersomes, the soft contact lens showed self-healing behaviour as well as antifouling activity. Presence of the curcumin in the zwitterionic polymersome system imparts a detrimental effect towards both Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Escherichia coli*) bacteria. In another attempt, an inter-polyelectrolyte system (IPEC) was prepared via a self-assembly of silver nanoparticles (Ag NPs) entrapped cationic thiolated poly(2-hydroxyethyl methacrylate-*b*-(2-(methacryloyloxy)ethyltrimethyl ammonium chloride) (SH-PHEMA-*b*-PMTAC) BCP and anionic poly(N-isopropylacrylamide-b-sodium 4-vinylbenzenesulfonate) (PNIPAAm-*b*-PSS) BCP. This IPEC material showed thermoresponsive gelation behaviour at body temperature (37°C). Because of the presence of the Ag NPs, it could heal the artificial wound created over the NIH 3T3 fibroblast cell line (*in-vitro* study). Finally, a nanocomposite hydrogel was also prepared via an *in-situ* free radical polymerization of sodium acrylate (SA) and successive crosslinking in the presence of starch grafted with PMTAC and cetyl ammonium bromide modified montmorillonite (OMMT). Here, a non-covalent (ionic interlocking and hydrogen bonding) strategy of self-healing was adopted in a covalently crosslinked organic-inorganic hybrid nanocomposite hydrogel, with specific emphasis on tuning its properties to a muscle mimetic material.

Key words: Functional hydrogel, ionic polymer, zwitterionic BCP, FRP, RAFT, biomedical applications.