Abstract

Biomedical applications often rely on surface adherent architectures such as polymer brushes to prevent adverse nonspecific interactions between materials used in biomedicine and contacting biological fluids. Commonly, “grafting-to” (GT) and “grafting-from” (GF) methods are used to attain the polymer brush architecture on various surfaces. This study investigates the grafting density and antifouling effectiveness of poly[*N*-(2-hydroxypropyl) methacrylamide] (poly(HPMA)) brushes synthesized via reversible addition-fragmentation chain-transfer (RAFT) polymerization, employing both GT and GF techniques.

To determine the molar masses of solution-born and GF poly(HPMA), size exclusion chromatography (SEC) equipped with multiple angle laser light scattering (MALS) and atomic force microscopy (AFM)-based single-molecule force spectroscopy (SMFS) were combined and thoroughly used. Furthermore, the impact of solvent effects on polymer brush propagation kinetics during the concomitant surface-initiated- (SI-) RAFT process between surface and solution was investigated. Experimental findings revealed discrepancies between GF and solution-born poly(HPMA) chains. Notably, solvent composition influenced both the propagation rate and the inferred grafting density of surface-grafted poly(HPMA) due to variations in polymer swelling states attributed to hydrogen bonding.

Building upon established methodologies involving SEC-MALS and AFM-SMFS, along with investigations into the effects of solvent properties on SI-RAFT polymerization, this thesis expands further. Notable additions include: (1) probing the density profile distribution of polymer brushes utilizing neutron reflectometry and electrokinetic methods; (2) exploring the effects of various physical parameters of polymer brushes on hemocompatibility, such as controlling the degree of polymerization and initial grafting density, alongside developing hierarchical structures and biomarker conjugation; (3) advancing biomaterial development through the fabrication of hybrid materials containing antifouling polymer segments via digital light processing to synthesize MRI traceable hydrogel materials of high biocompatibility, thus broadening avenues in biomaterials research.