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論 文 要 旨

THESIS SUMMARY

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要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

Surface coating is a highly effective technique that can be used to modify the surface properties of both inorganic and organic solid materials without changing their inner properties. There are various methods for polymer-based surface modification, including grafting, physical adsorption, layer-by-layer assembly, and plasma-induced polymerization. Within the realm of surface coating approaches, building chemical bonds between polymer and substrate allows the formation of well-defined polymers with precisely controlled surface properties, and the grafting of polymeric brushes stands out as a significant way to modify the surface. By covalently grafting polymer brushes from surfaces using controlled polymerization methods, functionalized surfaces with well-defined polymers can be obtained and precise control of surface properties with low thickness can be achieved.

With the vigorous development of industrial society, some persistent environmental problems have emerged. Issues such as climate change, ocean plastic contamination, and biofouling have led researchers in different fields to find solutions in the emerging field of sustainability. In the field of polymer synthesis, plant-derived bio-based functional polymers have attracted widespread attention due to their eco-friendly properties. Bio-based monomers derived from natural compounds such as agricultural feedstocks, organic wastes, and lignocellulosic biomass have been explored as renewable feedstocks for functional polymeric materials over the past few decades. Among them, vinyl compounds are suitable for producing various bio-based polymers with naturally derived properties, and various polymerization techniques have been developed for vinyl monomers during the past century.

While previous studies have demonstrated that various bio-based monomers can be readily synthesized from abundant bio-based resources such as caffeic acid and glycerol and polymerized to afford well-defined biofunctionalized polymers after concise deprotection, this dissertation focuses on the combination of photoinduced surface-initiated reversible-deactivation radical polymerization (SI-RDRP) with the synthesis of biofunctionalized polymer layers using plant-derived novel bio-based functional monomers. Surface-initiated photoinduced electron transfer-reversible addition-fragmentation chain transfer polymerization (SI-PET-RAFT) was attempted due to its oxygen tolerance and highly versatile monomer choices. Bio-based monomers derived from abundant bio-based resources such as caffeic acid and glycerol are polymerized under a wide wavelength range of visible light to afford well-defined functionalized polymers.

In Chapters 1 and 2, a brief overview of this work as well as a comprehensive academic background of polymer science was provided, detailing various surface-initiated and photoinduced systems based on RDRP that have been extensively investigated.

In Chapter 3, the concept of visible light-mediated PET-RAFT polymerization of caffeic acid-derived *tert*-butoxycarbonyl (Boc)-protected vinyl catechol monomer Boc_2VC was introduced in both solution and surface-initiated controlled radical polymerization systems. The PET-RAFT using exceeded DMSO as solvent provides a high degree of oxygen tolerance in solution systems while allowing polymer brush layers to graft through a surface-initiated mechanism. Functionalized substrates are readily obtained under exposure to visible light with different wavelengths using a 'grafting-from' approach, and well-defined poly(Boc_2VC) brushes were prepared under green light.

Surface properties were discussed and demonstrated by surface water contact angle (WCA) values and ellipsometry measurements. Although the SI-PET-RAFT showed poorer control in an open-to-air system, grafting under a nitrogen atmosphere still provided controlled fabrication of uniform poly(Boc_2VC) layers to yield thick films of $d = 5 \sim 7$ nm. Polymerization in the microliter scale of solution caused by free-RAFT CTA did not show an obvious influence of SI-PET-RAFT. The efficient and quantitative thermal deprotection of poly(Boc_2VC) resulted in the liberation of catechol groups, as evidenced by the significant decrease in WCA.

In Chapter 4, further surface modification via photoinduced RDRP copolymerizations was proposed by introducing a second monomer based on the homopolymerization of Boc_2VC to initiate monolayers. Functionalized substrates were prepared via both SI-PET-RAFT random copolymerization and block copolymerization, showing good control under aerobic environments. The grafting of polymer brushes can be easily observed by examining the WCA changes.

In Chapter 5, photoinduced RDRP of glycerol-derived cyclic vinyl ethers (VEs) was discussed. By applying PET-RAFT copolymerizations with MA, well-defined random copolymers and block copolymers can be readily obtained in solution polymerization systems under visible light irradiation. On glass substrates, the SI-PET-RAFT platform allows the grafting of poly(MA-*co*-DMMDO) copolymer brush layers under green and red light irradiation. Those functionalized substrates can undergo acetal deprotection by acid-washing, with clear decreases in WCA values ($> 10°$) observed across different samples, conforming to the formation of hydrophilic polymeric brushes.

Finally, Chapter 6 concludes the dissertation by summarizing the key findings and emphasizing their significance within the broader context of polymer science. Overall, the author demonstrated that plant-derived monomers including caffeic acid-derived vinyl catechol (VC) and glycerol-derived cyclic vinyl ethers (VEs) can be applied to generate well-defined bio-based polymers as well as functionalized polymeric brushes under various visible light irradiation.