Well-defined poly(HPMAm) brushes via surface-initiated RAFT polymerization; a mixed-chain transfer agent approach

Manisha Singh*, Zdeňka Sedláková, Jan Svoboda, Eliezer Jäger* and Rafal Poreba*

Institute of Macromolecular Chemistry, Czech Academy of Sciences, Heyrovsky sq. 2, Prague, 162 00, Czech Republic

Developing well-defined antifouling coatings remains a challenge in biomaterials research. This study presents an optimized protocol for the surface-initiated reversible addition-fragmentation chain transfer (SI-RAFT) polymerization of poly(N-(2-hydroxypropyl) methacrylamide) (poly(HPMAm)) brushes, employing a mixed-chain transfer agent (CTA) approach, Figure 1. By systematically evaluating different combinations of surface-tethered and free CTAs, we demonstrate that utilizing structurally distinct CTA classes simultaneously; dithiobenzoate (DTB) and trithiocarbonate (TTC), enhances polymerization control and brush growth rates. Our optimized conditions enable the fabrication of poly(HPMAm) brushes exceeding 70 nm in thickness within only 4 hours at 50 °C, and in aqueous media. Spectroscopic ellipsometry confirmed that the mixed-CTA approach significantly outperforms single-CTA systems, yielding higher polymerization efficiency and greater brush thickness. X-ray photoelectron spectroscopy (XPS) analysis revealed that the enhanced surface coverage achieved with DTB-based CTAs plays a crucial role in facilitating rapid brush growth. Additionally, size exclusion chromatography (SEC) confirmed that the solution-born polymers exhibited narrow dispersity (Đ = 1.05–1.15), ensuring well-defined polymer structures. Our findings highlight the advantages of combining different CTAs in a single polymerization system, leading to a more efficient and scalable method for fabricating antifouling poly(HPMAm) coatings. This approach offers a significant potential for biomedical applications, including biosensors, blood-contacting devices, and implantable materials.

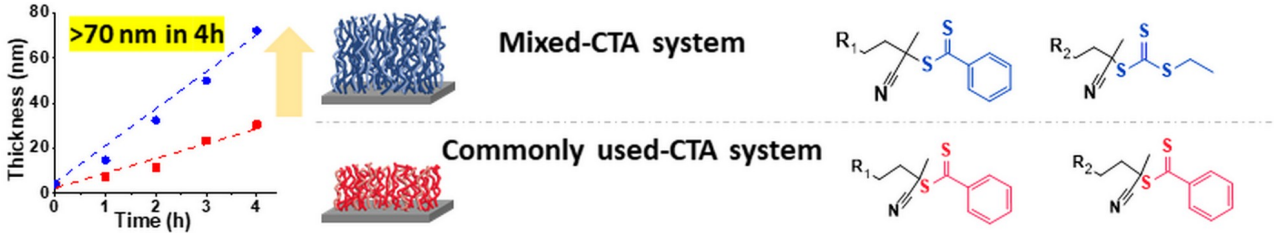

Figure 1. surface-initiated RAFT polymerization using a mixed chain transfer agent (mixed-CTA) approach to grow well-defined poly(HPMAm) brushes with precise control, achieving >70 nm thickness in 4 hours at moderate temperature, 50 °C.

Keywords: surface-Initiated RAFT, poly(HPMAm) brushes, poly(HPMA) brushes

Acknowledgments

The authors thank to the project New Technologies for Translational Research in Pharmaceutical Sciences/NETPHARM, project ID CZ.02.01.01/00/22_008/0004607, co-funded by the European Union, and to the Ministry of Education, Youth and Sports of the Czech Republic (grant # LUAUS24137).