Star-like Molecular Brushes with Poly(2-oxazoline)-based Amphiphilic Diblock Copolymer Side Arms

W. Xu^{1*}, L. Fietzke², R. Gumerov³, P. Zhang¹, F. Zheng¹, C. Jeffreis⁴, I. Potemkin³, R. Jordan², C. Papadakis¹

Soft Matter Physics Group, Technical University of Munich, Garching, Germany
Faculty of Chemistry and Food Chemistry, Technical University of Dresden, Dresden, Germany
DWI Leibniz-Institute for Interactive Materials, RWTH Aachen University, Aachen, Germany
European Molecular Biology Laboratory (EMBL), Hamburg, German
*wengi.xu@tum.de

Poly(2-oxazoline)s (POx) are a class of biocompatible polymers which have attracted great interest in biomedicine [1]. In this study, we focus on the structure of several star-like molecular brushes, which feature stars of poly(methyl methacrylate) having different functionalities as the backbones. They are grafted by amphiphilic diblock copolymers of poly(2-methyl-2-oxazoline) (PMeOx) and poly(n-butyl-2-oxazoline) (PBuOx). A molecular brush having fully hydrophilic side arms is studied as well. The sizes and inner structures of the star-like molecular brushes are investigated in dilute aqueous solution using dynamic light scattering, synchrotron small-angle X-ray scattering and computer simulations. Our results show that, at room temperature, the molecular brushes with amphiphilic side arms form small ellipsoidal clusters, while the fully hydrophilic brushes remain molecularly dissolved. Upon heating, an unexpected size growth is observed for the clusters. This is tentatively attributed to a change in the compatibility between the PMeOx and the PBuOx blocks [2], which is reflected by structural rearrangements of the individual brushes inside the cluster. The findings may offer a new approach to the development of stimuli-responsive polymers.

Keywords: Poly(2-oxazoline)s, polymer brush, polymer solution, light scattering

References

[1] Glassner M.; Vergaelen, M.; Hoogenboom, R.; Poly(2-oxazoline)s: A comprehensive overview of polymer structures and their physical properties. *Polymer International* **2017**, *67*, 32-45.

[2] Daoud L.; Arsenie, L. V.; Benkhaled, B. T.; Caillaud, K.; Semsarilar, M.; Picton, L.; Le Cerf, D.; Lapinte, V.; Shorter might be better: oligo(oxazoline)s for thermoresponsive polymersomes. *Polymer Chemistry* **2024**, *36*, 3641-3656.