Polymer Brush Mobility Revealed by Integrated Viscosity-sensitive Fluorescent Molecular Rotors

László Mérai [a], Holger Merlitz [a], Quinn Alexander Besford [a,b]

[a] Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, Dresden 01069, Germany, [b] Faculty of Chemistry and Food Chemistry, Technische Universität Dresden, Dresden 01069, Germany

merai@ipfdd.de

As polymer brushes are gaining increasing relevance in numerous fields, including separation, coating and sensing technologies, or as model systems to biological barriers, there is an emerging need for a better comprehension over the material transport within. In the context of material transport, viscosity is a crucial parameter, but the conventional, shear-based and tracer-involving microviscosity measurement approaches are non-applicable for its experimental determination inside the surface-tethered, nanoscopic polymer brushes. To address this issue, brush-bound viscosity-sensitive fluorescent molecular rotors (FMRs) offer a viable route, as their fluorescence lifetime and intensity are indicative of the viscosity of their microenvironment, which - applying fluorescence lifetime-imaging microscopy (FLIM) – allows for visualizing local variations in brush viscosity with diffraction-limited resolution. In this work, we achieved this through the coupling of a rhodamine-derivative molecular probe (RV-1 [1]) to N-isopropyl acrylamide-co-2-hydroxyethyl acrylate (NIPAM-co-HEA) polymer brushes. According to FLIM and in-situ ellipsometry measurements under different water-ethanol mixtures and solvency conditions, the apparent viscosity within the brush increased with decreasing solubility (Fig. 1.), leading to maximum observed fluorescence lifetime and viscosity under cononsolvency conditions (20 V/V% EtOH). As the fluorescence lifetime was proven to be not entirely proportional to the brush expansion, we also ran molecular dynamics simulations to uncover the underlying mechanisms.

Keywords:
polymer brush, microviscosity, fluorescence, cononsolvency, FLIM

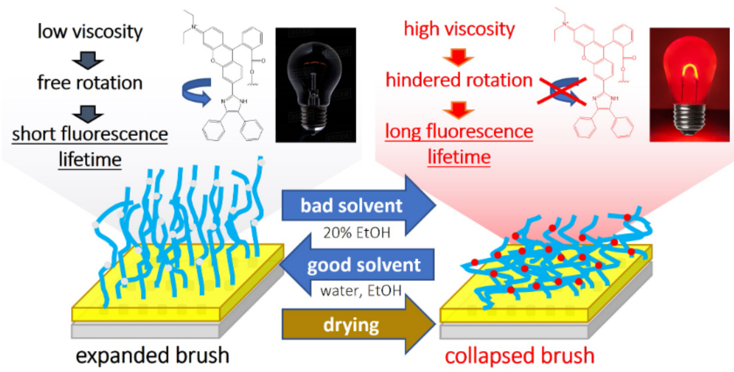

Figure 1. Mechanism of action of polymer brush-integrated fluorescent molecular rotors

References:

[1] Rui Guo. Jungling Yin. Yanyan Ma. Qiuan Wang. Weiying Lin. Journal of Materials Chemistry B 6, 2894-2900. 2018

Acknowledgements:

The authors acknowledge the Deutsche Forschungsgemeinschaft (DFG, Project Nr. 496201730) (L.M., Q.A.B.) and the DFG Walter Benjamin Programme (L.M.) for funding.