Can Fluorescence Anisotropy Probe Conformational Transitions in Polymer Brushes?

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The ability to undergo conformational transitions in response to external stimuli such as pH, ionic strength, or temperature makes polymer brushes promising surface modifications for sensing [1] . The incorporation of fluorescent probes into polymer brushes introduces advanced functionality, enabling non-invasive and highly sensitive real-time spatiotemporal monitoring of structural and dynamic changes. To date, Förster Resonance Energy Transfer (FRET)-based measurements [2,3] or fluorescence lifetime (LT) analysis [4] have been applied to probe conformational transitions in polymer brushes. While fluorescence anisotropy (FA) is conceptually simpler and a self-referencing approach, it remains largely unexplored in this context. Excitation with linearly polarized light leads to depolarization of fluorescence emission due to rotational diffusion of the fluorophore. As a result, fluorescence anisotropy directly reports on molecular rotational mobility and polymer chain dynamics [5] .
Here, we demonstrate the application of fluorescence anisotropy to poly(N-isopropylacrylamide) (pNIPAM) polymer brushes in co-nonsolvency conditions. In response to solvent composition, polymer chains with terminal dye alter their conformations as well as the rotational mobility of chains - changes that are directly reflected in the measured anisotropy. FA increased from 0.10 in the swollen state to 0.26 upon collapsed, revealing conformational transitions under co-nonsolvency conditions. Specifically, enhanced segmental mobility in the swollen brush state allows greater rotational freedom of the incorporated dye, leading to lower anisotropy values. In contrast, the collapsed brush increases steric crowding and restricts rotational motion, resulting in higher anisotropy. These results establish fluorescence anisotropy as a broadly applicable tool for studying stimulus-responsive polymer surfaces. Compared to FRET or fluorescence LT measurements, FA offers a simpler and more direct measure of polymer chain mobility without the need for dual labeling or specialized chromophores.

Keywords:
Polymer brush, fluorescence anisotropy, conformational transitions, stimuli-responsive surface coating

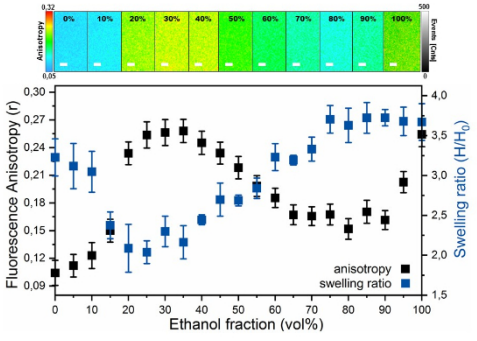

Figure 1. Fluorescence anisotropy images of pNIPAM brushes at varying ethanol fractions; the scale bar represents 10 µm (top). Fluorescence anisotropy and swelling ratio as a function of ethanol fraction (bottom).

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