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Surface Diffusion of Single Molecules on Poly(N-isopropylacrylamide) Brush Surfaces SHENGQIN WANG, University of Notre Dame, Y. ELAINE ZHU, Univeristy of Notre Dame — How molecules and macromolecules diffuse at polymer surface remain inadequately understood. In this talk, we present a recent single-molecule spectroscopy study of fluorescent probes molecules at surface-tethered polymer brush surfaces. We focus on the dynamics of fluorescent molecules, Rhodamine110 (RG110) on thermo-responsive poly(N-isopropylacrylamide) (PNIPAM) brush thin films as a model system of tunable molecule-polymer surface interactions by varying temperature (T) across the LCST of PNIPAM brushes. The diffusion coefficient, D of RG110, measured by fluorescence correlation spectroscopy (FCS) at a single molecule resolution, decreases as increasing the solution T across the LCST of PNIPAM brush thin films, due to the enhanced hydrophobic interaction at the molecule-polymer interfaces. However, it is surprising to observe the faster diffusion of RG110 on the self-assembled monolayer of octadecyltriethoxylsilane (OTE) than that on the PNIPAM brush surface, despite the stronger RG110 interaction with OTE than PNIPAM. Additionally, we observe that reduced PNIPAM brush thickness lead to further slowing down the diffusion dynamics of RG110 on PNIPAM brush surfaces at constant T. We thus speculate that the retarded diffusion process of small molecules on soft polymer brush surfaces, in comparison to the faster diffusion on hard surfaces, is a result of the coupling between molecule surface diffusion and the relaxation of wiggling polymer brush chains at the interface.

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