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**Understanding Unimer Exchange Processes in Block Copolymer Micelles using NMR Diffusometry, Time-Resolved NMR, and SANS** LOUIS MADSEN, BRYCE KIDD, XIULI LI, KATHERINE MILLER, Virginia Tech, TYLER COOKSEY, MEGAN ROBERTSON, University of Houston — Our team seeks to understand dynamic behaviors of block copolymer micelles and their interplay with encapsulated cargo molecules. Quantifying unimer and cargo exchange rates micelles can provide critical information for determining mechanisms of unimer exchange as well as designing systems for specific cargo release dynamics. We are exploring the utility of NMR spectroscopy and diffusometry techniques as complements to existing SANS and fluorescence methods. One promising new method involves time-resolved NMR spin relaxation measurements, wherein mixing of fully protonated and 2H-labeled PEO-b-PCL micelles solutions shows an increase in spin-lattice relaxation time (T1) with time after mixing. This is due to a weakening in magnetic environment surrounding 1H spins as 2H-bearing unimers join fully protonated micelles. We are measuring time constants for unimer exchange of minutes to hours, and we expect to resolve times of <1 min. This method can work on any solution NMR spectrometer and with minimal perturbation to chemical structure (as in dye-labelled fluorescence methods). Multimodal NMR can complement existing characterization tools, expanding and accelerating dynamics measurements for polymer micelle, nanogel, and nanoparticle developers.

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