



UNIVERSITY OF DELAWARE

ENGINEERING

DEPARTMENT OF CHEMICAL AND BIOMOLECULAR ENGINEERING



SEMINAR SERIES

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Ph.D., University of Delaware, 2017

Attend virtually: <https://udel.zoom.us/j/99615073260>

BEYOND ALIGNMENT: NEW ROUTES FOR CONTROLLING BLOCK COPOLYMER PHASE BEHAVIOR AND MECHANICAL PROPERTIES VIA MAGNETIC FIELDS

Block copolymers (BCPs) are attractive for developing novel materials due to their tunable properties and self-assembly via block chemistry, composition, and length. However, practical methods for processing BCPs into advanced materials with long-range order remain difficult, where techniques like magnetic field alignment are typically infeasible because of large required field strengths and limited range of responsive chemistries. We recently discovered anomalous magnetic field-induced ordering in weakly diamagnetic, aqueous block polymers (BCPs) exposed to low intensity magnetic fields ($B \leq 0.5$ T). Prior work on magnetic field-directed assembly in BCPs has focused on alignment of a structure or phase with inherent anisotropy which leads to anisotropy in the magnetic susceptibility, $\Delta\chi$. However here, ordered phases are created by temporarily applying magnetic fields to low viscosity solutions of spherical BCP micelles with no inherent anisotropy, causing up to a six order of magnitude increase in the dynamic moduli. Using a combination of magnetorheology (MR), small angle neutron and x-ray scattering (SANS/SAXS), and vibrational spectroscopy, we demonstrate that low intensity magnetic fields likely facilitate these phase transitions by altering polymer-solvent interactions and hydrogen bonding, which in turn modify amphiphile packing. We then show that this assembly strategy can be used to produce two types of ordered materials: those that remain composed of isotropic micelles (i.e. cubic phases), and those that transform into aligned phases like cylinders or lamellae. Here, the induced elastic modulus, $G'B$, is up to three orders of magnitude larger than the maximum modulus that results from an analogous thermal ordering transition at 0 T. Additionally, this anomalous assembly behavior is time-dependent, where the critical induction time t_c and resulting phase can be controlled by altering amphiphile molecular weight and processing conditions like field strength, magnetization time, and temperature. Finally, in a promising sign for practical applications, this transition is robust to shear processing and cycling, where t_c is largely independent of strain amplitude $\gamma\theta$ up to 100%. While applying large $\gamma\theta$ during magnetization reduces G' and G'' , the moduli rapidly recover upon cycling, when $\gamma\theta$ is repeatedly reduced to 0.01% following high shear. This new assembly strategy enables the discovery of structures and d-spacings inaccessible via traditional self-assembly, thus providing a platform for developing materials with long-range order using mild conditions and little energy input from external fields.

ABOUT THE SPEAKER

Michelle A Calabrese is an assistant professor in the Department of Chemical Engineering and Materials Science at the University of Minnesota. She received her BS in Chemical Engineering from the University of Pennsylvania in 2012. She completed her PhD in Chemical Engineering at the University of Delaware in 2017, where she focused on developing new techniques in rheology and neutron scattering to understand the flow properties of complex fluids. Following her postdoc in chemical engineering at MIT, she joined the faculty at UMN in mid-2019. Her research group employs rheology, soft matter physics, and polymer and nanoparticle synthesis to address a range of fundamental and applied problems in polymer and soft materials engineering. Her recent recognitions include the 3M Non-tenured Faculty Award, NSF CAREER Award, and NIH NIDCD Early Career Research Award (R21).