UCLA ENGINEERING
Chemical and Biomolecular Engineering

SEMINARS IN CHEMICAL AND BIOMOLECULAR ENGINEERING

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Presented by:

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"Enhancing the Solid-State Properties of Polyethylene by Block Copolymerization"

Polyethylene (PE) is the world's most widely produced synthetic polymer: nearly 100 million tons globally, or about 35% of total thermoplastics production. Yet the mechanical properties of PE (relatively low stiffness and yield strength, poor creep resistance, etc.)—even for the most-crystalline "high density" linear PE—are limiting for many applications. Polymer properties are commonly tuned either through copolymerization, or through blending, but very few polymer species have been identified with sufficiently weak repulsive interactions against PE to yield block copolymers with disordered (homogeneous) melts, or PE-containing miscible blends at high molecular weights. Moreover, most suitably miscible candidates are chemically similar to PE, such as copolymers of ethylene with an α-olefin; these polymers also have low glass transition temperatures (T_g) and thus do not ameliorate the limiting properties outlined above.

We have found that several members of another family of hydrocarbon polymers—hydrogenated substituted polynorbornenes—are substantially miscible with PE in the melt, yielding symmetric block copolymers with homogeneous melts at molecular weights exceeding 100 kg/mol, tunable through the substituent attached to the polynorbornene repeat unit. The polymers are synthesized by "living" ring-opening metathesis polymerization (ROMP) of cyclopentene, as the precursor to perfectly linear PE, and various 5-substituted norbornene monomers (alkyl, cycloalkyl, aryl), yielding narrow-distribution polymers of targeted molecular weight and composition. We characterize the interaction energy density X (proportional to the Flory interaction parameter, ꭓ) by measuring the order-disorder transition temperature of near-symmetric diblocks via small-angle x-ray scattering or dynamic mechanical thermal analysis. These values of X are then compared against various mixing rules proposed to describe the mixing energy in terms of pure-component properties, starting with the classical regular mixing treatment. Attaching relatively short blocks of hydrogenated poly(norbornylnorbornene), with T_g = 115ꭓC, to PE doubles its modulus and yield strength, while retaining an easily-processed single-phase melt.

Richard A. Register is Eugene Higgins Professor in the Department of Chemical and Biological Engineering at Princeton University. His research interests revolve around micro- and nanostructured polymers, such as block copolymers, polymer blends, semicrystalline polymers, and ionomers, ranging across their synthesis, physics, properties, and applications. He served as chair of his department from 2008-2016, and as Director of the Princeton Center for Complex Materials from 2005-2008. He received the Charles M.A. Stine Award from the American Institute of Chemical Engineers in 2002, and was honored with the Distinguished Teacher Award from Princeton's School of Engineering and Applied Science in 2018. He is a Fellow of the American Physical Society, of the American Chemical Society, and of the American Institute of Chemical Engineers.