Multi-valent interactions in systems of polyelectrolytes can exhibit dramatic, non-monotonic effects, for example, switching forces from repulsive to attractive, and back to repulsive again, in some cases. We have been studying these patterns of behavior with the surface forces apparatus (SFA) and with electrochemical methods, such as cyclic voltammetry, which enables the quantitative determination of the number of multi-valent ions residing in thin layers of charged polymers. At fixed ionic strength, all cause strong shrinkage and condensation of poly(styrene sulfonate) brushes over a narrow range of ratio multi-valent to mono-valent ions. When the multi-valent ion is an oppositely charged polymer, new fluid phases can form. We have clarified the quantitative aspects of the phase diagram for a simplified polyelectrolyte complex system. See Figure 1. Charged blocks in copolymers leads to materials with new types of ordered phases. Effects of these multi-valent interactions on supermolecular and biomolecular assembly will be discussed. There are many possibilities for the creation of new materials based on electrostatic assembly involving multi-valent interactions.

Figure 1. Complete polyelectrolyte complexation phase diagrams. (a) Phase diagram for solutions comprising PLK100 and PRE100. Two experimental approaches were employed to map the phase boundaries (blue symbols) and were in excellent agreement with the simulation results (red + symbols). The filled circles (complex phase) and open circles (supernatant phase) are the results from TGA; × are the results from salt resistance methods. Representative tie-lines are shown as dotted lines to demonstrate their negative slope, which are contrary to the predictions from the Voorn-Overbeek theory. (b) Phase diagram for PLK20+PRE20 (red), PLK50+PRE50 (yellow), and PLK400+PRE400 (green). The solid (complex phase) and open (supernatant phase) squares, diamonds and triangles are the results from TGA on the three respective systems; × are the results from salt resistance methods. The overall shape of the binodal phase boundary was preserved, while the two-phase region became larger with increasing polymer chain lengths.

Biography:
Matthew Tirrell’s research has been in the fields of polymer interfaces, dynamics, fluid phase behavior and nanomedicine. He is particularly known for his work on polymer brushes, surface force measurement, peptide amphiphiles and polyelectrolyte complex phase behavior. In 2011, Matthew Tirrell was appointed as the founding Pritzker Director and Dean of the Faculty of the Institute for Molecular Engineering and established the first University of Chicago engineering program, which he continues to oversee (now the Pritzker School of Molecular Engineering). Professor Tirrell simultaneously served as Deputy Laboratory Director for Science (September 2015 - April 2018) and Chief Research Officer (January 2017 - March 2018) at Argonne National Laboratory. Immediately prior to joining the University of Chicago, he was the Arnold and Barbara Silverman Professor and Chair of Bioengineering at the University of California, Berkeley, with
additional appointments in chemical engineering and materials science & engineering, as well as a Faculty Scientist appointment at the Lawrence Berkeley National Laboratory. Dr. Tirrell completed ten years as Dean of Engineering at the University of California, Santa Barbara on June 30, 2009. From 1977 to 1999, he was on the faculty of Chemical Engineering and Materials Science at the University of Minnesota, where he served as department head from 1994 to 1999. Tirrell received a B.S. in Chemical Engineering at Northwestern University in 1973 and a Ph.D. in 1977 in Polymer Science from the University of Massachusetts. He has co-authored about 400 papers and one book, has supervised about 100 Ph.D. students and 50 postdoctoral researchers. Professor Tirrell is a member of the National Academy of Engineering, the National Academy of Sciences, the American Academy of Arts & Sciences and the Indian National Academy of Engineering, and is a Fellow of the American Institute of Medical and Biological Engineers, the AAAS, and the American Physical Society.