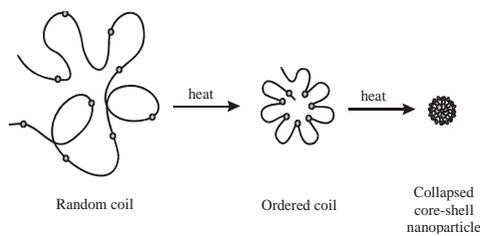
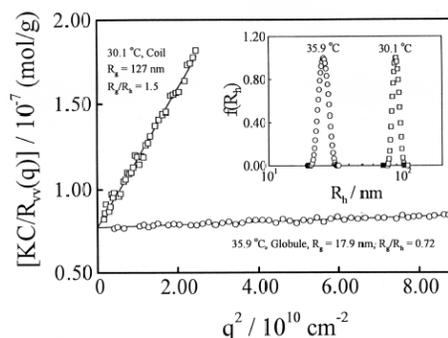


Poly(*N*-isopropylacrylamide) - from single-chain dynamics in polymer physics to intelligent gels in biomedical applications

Zhuojun Dai and Chi Wu

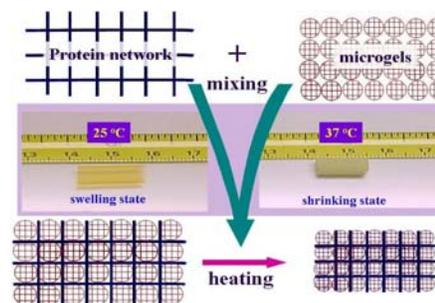
Department of Chemistry, The Chinese University of Hong Kong, Sha Tin, N.T. Hong Kong, China

As a thermally sensitive polymer, poly(*N*-isopropyl acrylamide) (PNIPAM), especially its so-called volume phase transition, has been extensively studied because of its convenient and adjustable (by copolymerization) lower critical solution temperature (LCST ~ 32 °C). Among these studies, our bottom-up approach is rather different and unique. Namely, we started from the coil-to-globule transition of individual chains, which had been predicted in theory, but not been observed, for a long time because interchain aggregation always spoils intrachain contraction. After a lengthly preparation of narrowly distributed linear PNIPAM chains, we have finally shown that individual coiled chains can form single-chain globules by passing a newly discovered molten globular state when solvent is switched from good to poor [1-4]. The right figure shows static and dynamic laser light-scattering results; namely, the solution temperature dependence of “the Rayleigh ratio ($R_v(q)$) vs the scattering vector (q)” and the hydrodynamic radius distribution ($f(R_h)$). We found that even at the collapsing limit, each globule still contains $\sim 70\%$ of water in their hydrodynamic volume, not as “dry” as we thought. The time of transition, involving an initial nucleation followed by a coarsening process, is in the order of ms, too short to support a previously suggested highly chain-knotting inside each globule. Our study



has been extended to some PNIPAM copolymers. We have revealed that after the introduction of second hydrophilic or hydrophobic monomer into the PNIPAM chain backbone [5,6], the chain folding could lead to some unique nanostructures, such as a single-chain micelle and an ordered coil state, as shown in the right figure. We have successfully explained the formation of stable mesoglobules made of a limited number of collapsed chains on the basis of the viscoelasticity in dilute

copolymer solutions. Further, by cross-linking linear chains into a microgel with a size comparable to a long chain, we have demonstrated that the previously observed sharp shrinking of PNIPAM gels is not a volume phase transition, but due to a sudden breakdown of the balance between the bulk shear module and the inhomogeneous shrinking-induced internal stress built up during the coil-to-globule transition of sub-chains between two neighboring cross-linking points. Armed with a fundamental understanding of such a wonderful system, we have developed and patented some fast-shrinking, biocompatible and biodegradable thermally sensitive hydrogels with potential biomedical applications, as shown in the right figure [7]. In this lecture, we would like to illustrate and emphasize how important to combine synthetic chemistry, polymer physics and biology together because our future in education and research must be multi-disciplinary.



[1] C. Wu, S.Q. Zhou, *Macromolecules*, **28**, 5388; and 8381 (1995); **29**, 1574; and 4998 (1996)
 [2] C. Wu, S.Q. Zhou, *Physics Review Letters*, **77**(14), 3053 (1996)
 [3] X.H. Wang, X.P. Qiu, C. Wu, *Macromolecules*, **31**, 2972 (1998)
 [4] C. Wu, X.H. Wang, *Physical Review Letters*, **80**(18), 4092 (1998); and **83**, 4105 (1999)
 [5] C. Wu, X.P. Qiu, *Physical Review Letters*, **80**(3), 620 (1998)
 [6] G.Z. Zhang, C. Wu, *Physical Review Letters*, **86**(5) 822 (2001).
 [7] C. Wu, J. Hong,, U.S. Patent 6,030,634 (2000); & 6,238,688 (2001); Chinese Patent 971 80823.6 (2003)