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# Coil-Globule Transition: Self-Assembly of a Single Polymer Chain

by

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## ABSTRACT

The coil collapse problem is of interest not only because it represents the simplest model of protein folding, but also because of its fundamental importance as related to polymer nanostructures and fractionation. It is extremely difficult to observe the coil-to-globule transition experimentally because at finite concentrations in a poor solvent, the macromolecules tend to aggregate due to phase separation when the collapsed state is being achieved. In the mid-1980s, two-stage kinetics of a single-chain collapse was proposed theoretically.[1,2] The first successful experimental observation of a two-stage coil-to-globule transition was achieved by quenching a dilute solution of polystyrene (PS) in cyclohexane.[3]

By using a thinnest capillary tube cell with a wall thickness of 0.01 mm and a diameter of 5 mm for dynamic light scattering, two relaxation times, $\tau_{crum}$ for the crumpled globule state and $\tau_{eq}$ for the compact globule state, were determined[4] for the first time. The relaxation times were much slower than expected. From the size of the crumpled globule

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and that of the compact globule and by *assuming* the intraglobular density to be uniform, the volume fraction of the PS chain in the crumpled globule state, $\phi_{crum}$, and that in the compact globule state, $\phi_{comp}$, can be estimated, with $\phi_{crum} \approx 0.02$ and $\phi_{comp} \sim 0.24$-$0.4$ at 28°C for polystyrene in cyclohexane. The results imply that a single-chain globule contains a large amount of solvent. It should also be noted that $\phi_{comp}$ is temperature dependent, i.e., one would have to go to hypothetically low temperatures in order to squeeze out all the solvent (cyclohexane) in the compact PS globule.

The single-chain coil collapse state could be achieved under *equilibrium* conditions by using a high molecular weight, $M_w \sim 1.08 \times 10^7$ g/mol; $M_w/M_n < 1.06$) poly(N-isopropylacrylamide) (PNIPAM) in water,[5] even though the ten million molecular weight for PNIPAM was substantially lower than that for polystyrene ($M_w \sim 50 \times 10^6$ g/mole).[6] Under equilibrium conditions, it was feasible to determine both the hydrodynamic radius $R_h$ and the radius of gyration $R_g$. The ratio of $R_g/R_h$ changed from 1.45 to 0.77, clearly demonstrating the transition from the theta coil state to the compact globule state. At the maximum value of the scaled expansion factor $\alpha_s^3|\tau|M_w^{1/2}$, $R_g/R_h \approx 1.33$ where $\alpha_s = R_g/R_g(\Theta)$ and $\tau = |T-\Theta|/\Theta$ with $\Theta$ being the theta temperature. In the compact globule, $R_g/R_h$ was of the order of 0.7, implying that the PNIPAM compact globule in water still contained ~80% water, of the same order of magnitude as the PS compact globule in cyclohexane at 7° below its theta temperature (35°C).

## References

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