Single-Molecule Manipulation Experiments Reveal the Onset of Excluded Volume in Poly(Ethylene Glycol)

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Summary: Single-molecule data on the structural features of poly(ethylene glycol) are presented and compared to biomolecules such as DNA, RNA, proteins, and bottle-brush polymers. Our quantitative measurements provide the microscopic parameters needed to predict real-polymer structure. This information may be used in the rational design of future biomaterials.

Poly(ethylene glycol) (PEG) is an important polymer in many biotechnological applications due to its exceptional inertness and large excluded volume in water. However, the microscopic parameters describing the real-polymer structure of PEG have never before been measured, due to a lack of sensitivity in existing bulk characterization techniques. Moreover, these microscopic parameters should depend on PEG’s complex interactions with water. Here, we present single-molecule elasticity measurements on PEG and show that as the chain length increases, it transitions from a rod-like polymer to a Gaussian coil, and only becomes swollen by excluded volume past a critical molecular weight (Fig. 1). We then vary the solvent quality using chaotropic salts and observe that the microscopic parameters change in the expected manner. We identify a room-temperature theta point at which PEG behaves as an ideal polymer for any length of chain, and see poor-solvent collapse at higher salt.

Fig. 1. a) Our method of measuring the microstructural parameters of a polymer from single-molecule elasticity data at low force. The effective size of polymer being measured is inversely related to the applied tension. Data are shown for PEG in water with the expected behavior indicated by grey lines. b) Schematic phase diagram in force-solvent space. The vertical grey line corresponds to the data in (a). The shaded region indicates the loss of equilibrium during poor-solvent collapse. Data in good, theta, and poor solvent can be found in our paper [1].