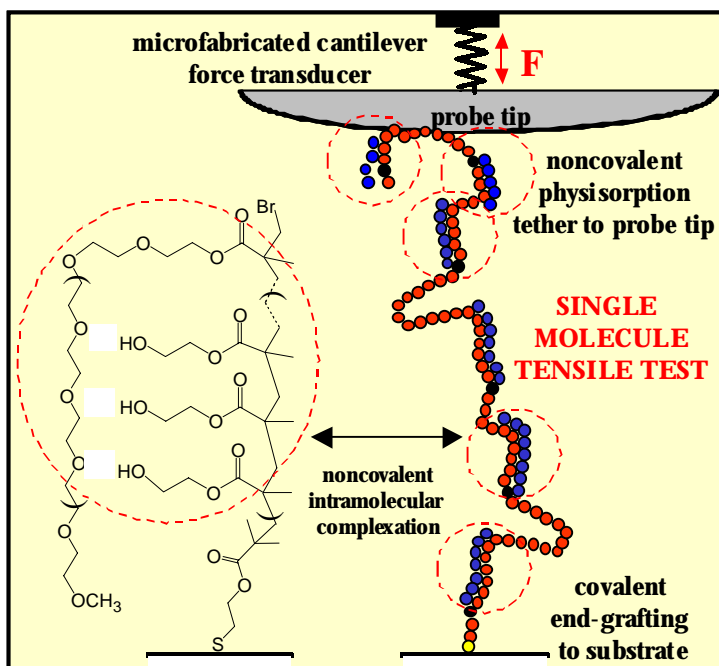


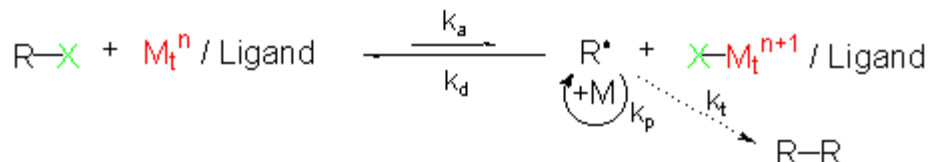
DESIGN AND NANOMECHANICAL TESTING OF SINGLE MACROMOLECULE SPRINGS USING NONCOVALENTLY BONDED BLOCK COPOLYMERS

Springs are fundamental components that form the basis of most macroscopic mechanical systems. With the advent of nanotechnology, it is clear that miniaturized devices will soon need nanoscale springs with well-controlled nanomechanical properties to act as switches, force generators, sensors, motors, shock absorbers, or to control the adhesive interactions between two components. In biological systems, individual polymer chains perform this function and the molecular elastic "spring" properties are controlled through the precise incorporation and organization of multiple, noncovalent intramolecular interactions (e.g.



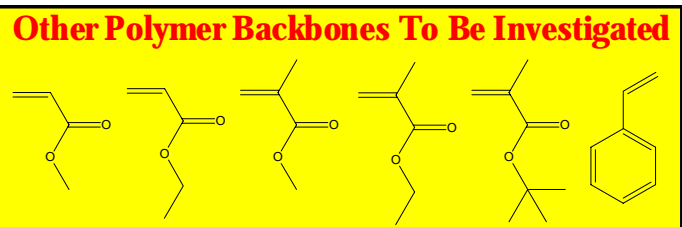
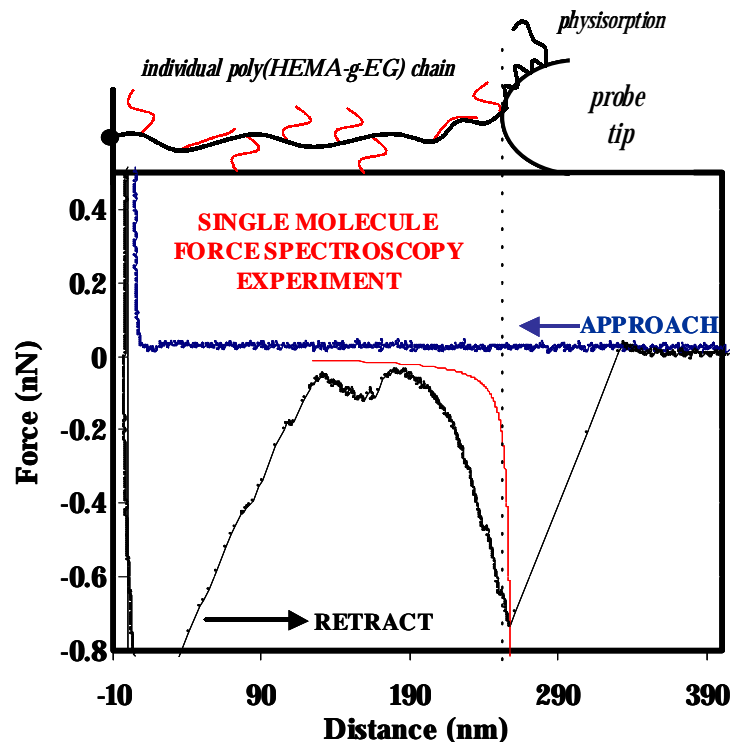
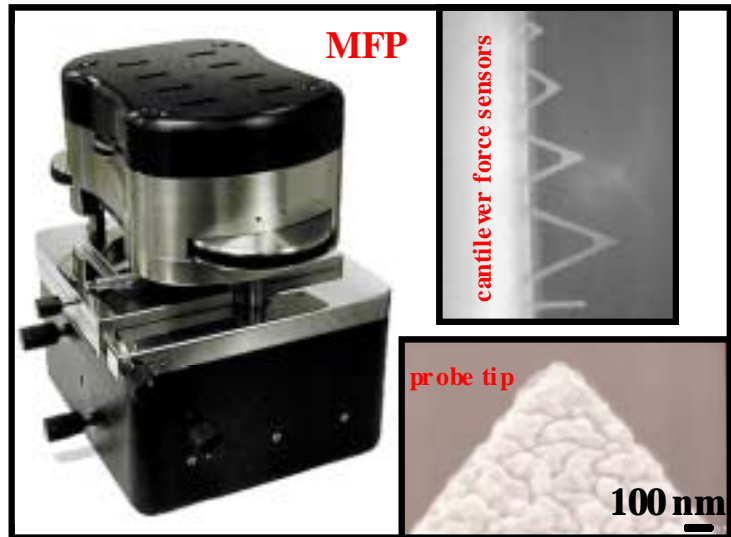
electrostatic, hydrophobic, H-bonds, van der Waals forces, etc.). The goal of this research is to design and synthesize comb-type graft copolymers where specific types of noncovalent intramolecular interactions are incorporated between the side chains and main chain backbone in order to understand and control the single macromolecule elastic properties, i.e. force vs separation distance profile, spring constant, extensibility, heterogeneity, nonlinearity, etc. Variation in the nanomechanical properties can be achieved through the length of side chain, the side chain grafting density,

the type of side chain-main chain interactions. One may think of this as the nanotechnological analogue of understanding structure-property relationships and controlling the stress versus strain curve of a macroscopic material. In order to facilitate the ease of single macromolecule "tensile testing," a number of other properties were designed in including water solubility, end-functionalization, and appropriate molecular weight (~50K). *Atom transfer radical polymerization*¹⁻⁵ in solution using a thiol-protected alkyl halide initiator enabled the synthesis of the first prototype system at a variety of molecular weights and side chain graft densities, poly(hydroxyethyl methacrylate-g-ethylene glycol) or



(* <http://polymer.chem.cmu.edu/Center/ATRP.html>) poly(HEMA-g-EG) where the side EG side chains have the capability to undergo both hydrogen bonding and hydrophobic interactions with the HEMA main chain (shown above). The polymers were characterized by NMR,

GPC, and light scattering, chemically end-grafted to gold surfaces, and tested with a new nanomechanical instrument, called the *Molecular Force Probe* (MFP) (Asylum Research, Inc <http://www.asylumresearch.com/>) which employs a soft microfabricated cantilever with fine probe tip at the end as a force transducer (limit of force detection ~ 5 pN, limit of displacement detection ~ 0.3 Å). The figure to the right displays a typical result of the first series of single molecule force spectroscopy experiments conducted on a single end-grafted chain of Poly(HEMA-g-EG) (MW=50K, in phosphate buffered saline solution (PBS, pH=7.4, 130 mM NaCl). Here we can see a dramatic departure of the experimental data to higher forces compared to the standard model of polymer entropic elasticity, the freely jointed chain model (red line), indicating the presence of additional forces contributing to the uncoiling process. Currently, control experiments on linear poly(HEMA) and PEG are being conducted and a series of other types of side chains are being synthesized (see lower figure to the right) including poly(MMA-g-EG) whose nanomechanical properties will be environmental sensitive, e.g. at high pH, the carboxylic acid groups of the MAA are deprotonated and negatively charged forming carboxylate anions which then loses its capability to form hydrogen bonds with the side chains.



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