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b. Project Title: **Mapping Mechanically Activated Pathways of Metal Coordination Complexes**

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Objective

The objective of the proposal remains unchanged and focuses on the question: What forces are necessary to mechanochemically distort coordination environment and release stored length of transition metal complexes embedded along overstressed polymer chain? This question probes the hypothesis that mechanical force provides an opportunity to develop new chemistry of coordination compounds that is inaccessible by other means. We proposed two Specific Aims: 1) design and synthesize novel metallomechanophore constructs containing polydentate ligands intimately connected within polymer chains, and 2) use single molecule force spectroscopy to measure force-extension curves for these new metallopolymers as a method to quantitate the forces necessary to release length stored in polydentate metal-ligand coordination complexes. Over two years of funding of the project, we have made significant progress on Aim 1 and faced some obstacles to accomplish Aim 2.

Progress of research

In order to quantify force-coupled reactivity of metallomechanophores via single molecule force-spectroscopy (SMFS), it is crucial to ensure that dissociation of metal-ligand bonds does not inherently dismantle the integrity of the polymer's primary structure, a polymer system contains multiple coordination complexes susceptible for mechanochemical activation and has strong adhesion to a cantilever of the SMFS setup. With these requirements in mind, we have previously successfully synthesized and characterized polymeric systems containing dipirydylamine (dpa) as the metal-binding motif utilizing both RCM/ROMP (ring closing metathesis/ring-opening metathesis polymerization) and polycondensation containing different adhesive units embedded within polymer backbone (Figure 1). The epoxy-containing polymer provides good adhesion to non-coated silicon tips that have high spring constant around 20 pN/nm, while thioether-based polymer has greater affinity to the gold-coated cantilever with a smaller spring constant (~6 pN/nm) that provides better resolution of small force regimes (<200 pN).

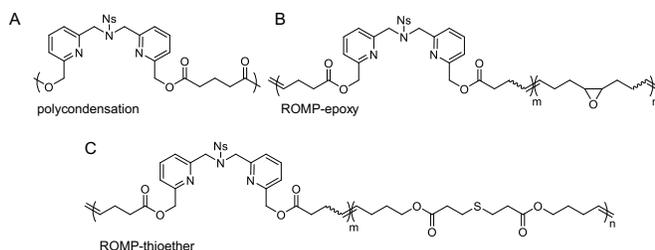


Figure 1. Structures of a) polycondensation, b) epoxy- and c) thioether-containing ROMP polymers suitable for SMFS studies. The dpa to epoxy/thioether ratio in the resulting ROMP polymers is controlled by feed ratio of the corresponding monomers in the reaction mixture.

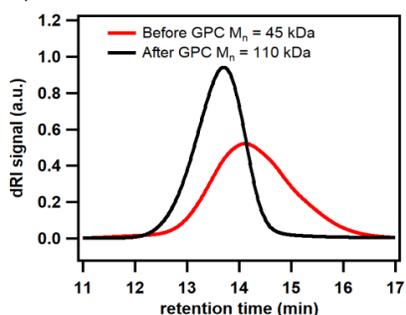


Figure 2. Differential refractive index (dRI) trace before (red) and after (black) preparative GPC. ROMP polymer had 10% of ligand incorporation and $M_n = 45$ kDa. Higher MW fraction of $M_n = 110$ kDa was isolated on about 2 mg scale.

Since high molecular weight polymers (>100 kDa) are desired for SMFS experiments, we have optimized synthetic and postsynthetic polymer modification protocols towards obtaining high degree of polymerization polymers. The MW is controlled by variety of additives, solvents, temperatures, ratios of the monomers, reaction times, chain extension reaction, as well as selective precipitation and preparative gel permeation chromatograph techniques (Figure 2). We now have reliable methods that enable synthesis of both ROMP and polycondensation polymers with molecular weights up to 110 kDa, suitable for SMFS.

Successfully synthesized polymers with high MW were metallated using $Zn(NTf_2)_2$ as the Zn(II) source to form a 1:1 ligand to Zn complex confirmed by UV-visible spectroscopy, 1H NMR, mass-spectrometry (data not shown, see previous progress report for more information), and single crystal structure of the model complex (Figure 3). Equimolar complexation of Zn(II) with the ligand ensures absence of cross-linking between two or more polymer chains that significantly simplifies interpretation of force extension curves.

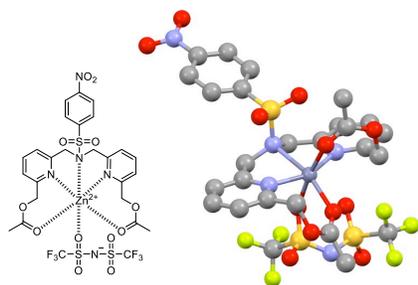


Figure 3. (left) ChemDraw and (right) solid state structure of the Zn-dpa model complex bearing methyl ester groups. Hydrogen atoms and second NTf_2^- anion are omitted for clarity.

SMFS experiments were conducted on a ROMP Zn metallopolymer utilizing both silicon tip with a high spring constant that allow to probe high force regime (>200 pN) and gold-coated cantilevers that have smaller spring constant for better resolution of small forces (<200 pN). In a typical experiment, the metallopolymer was deposited onto the stage by evaporation of a dilute polymer solution in THF. As the polymer-bound microscope tip was retracted, the measured force as a function of tip-surface separation distance were generated. We then analyzed generated curves to select those with separation distance high enough (>200 nm) for detection of plateau putatively assigned to the release of stored length from metal-ligand bond dissociation. The apo-polymers bearing free ligand were subjected to the similar treatment, and the separation distances of the generated force extension curves were normalized to 1 at 60 pN of force. Both Zn- and apo-polymer curves were overlaid on a single graph for direct comparison (Figure 4 top). Analysis of multiple overlays did not reveal apparent plateau regardless of the type of the polymer and tip used. Fitting the polymer extension curve to the worm-like chain (WLC) model of polymer elasticity before expected plateau (>50 pN) and extrapolating these curves onto lower forces regime using obtained fitting parameters also did not help to unambiguous determine presence of transformations at the metal center that are occurring in response to force (Figure 4 bottom).

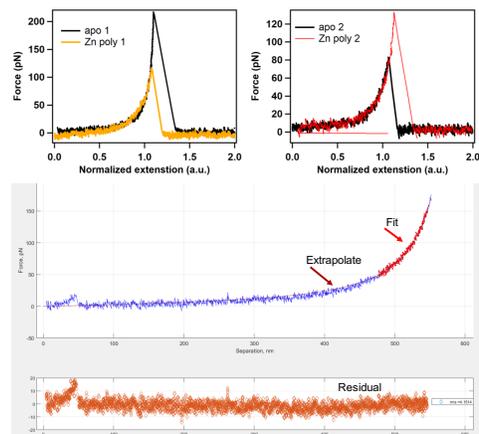


Figure 4. (top) 2. Representative SMFS curves of Zn and apo-polymers. (bottom) Force extension curve of Zn-polymer fit to the WLC model at force > 50 pN. Residual fit does not reveal significant deviation from the experimentally obtained and extrapolated curves in low forces regime.

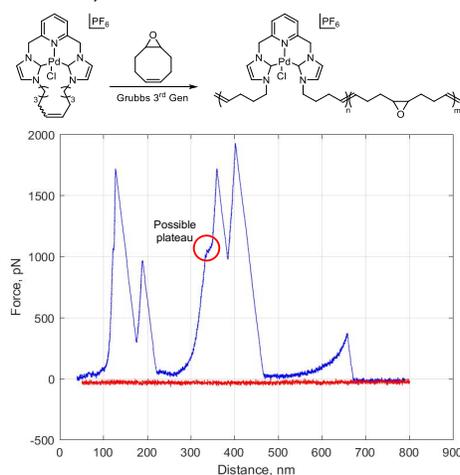


Figure 5. (top) ROMP polymers with 10% Pd-NHC units and MWs up to 80 kDa have been prepared. (bottom) SMFS curve shows multiple polymer strands being pulled simultaneously. Highlighted in the red circles is expected plateau for the Pd-carbene bond dissociation.

While we were able to synthesize polymers with high MW (>100 kDa) and overcome poor adhesion of the metallopolymer to the AFM tip to obtain longer force-extension curves (>250 nm), no obvious plateau is apparent. We hypothesize then the force at which this potential plateau occurs is very low and is at the limit of detection of the instrument. Utilizing metallomechanophore that forms thermodynamically strong and kinetically inert coordination bonds may increase force required for mechanochemical activation of the metal-ligand bond. Pd-NHC complexes bearing strong carbene-Pd bond are suitable candidates to address this challenge. We have already synthesized ED-ROMP Pd-NHC containing polymer and subjected it to preliminary SMFS experiments that appeared to have a plateau around 1 nN (Figure 5). Further experiments, however, required for optimization of force extension curves to obtain a pull on a single isolated polymer chain.

In summary, we have made several key accomplishments in the preparation and characterization of novel metallopolymers. Our next steps are focused on optimizing these systems for single molecule force measurements.