A Biomimetic Modular Polymer with Tough and Adaptive Properties

Aaron M. Kushner, John D. Vossler, Gregory A. Williams, and Zhibin Guan*

Department of Chemistry, University of California, 1102 Natural Sciences 2, Irvine, California 92697-2025
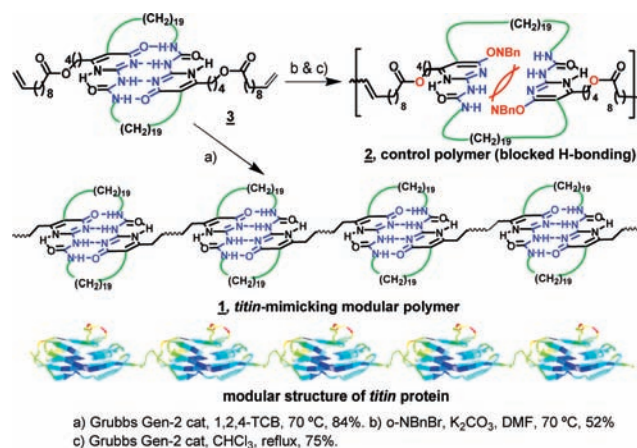
Received February 6, 2009; E-mail: zguan@uci.edu

Whereas man-made polymers can be prepared to meet particular parameters one at a time, it remains a challenge to design synthetic polymers with a combination of mechanical properties such as high modulus, toughness, and resilience. A further challenge is to introduce adaptive properties into polymers. In contrast, many smart strategies have evolved in nature to achieve biopolymers possessing excellent combinations of mechanical properties.[1] To survive in often variable environments, natural materials have also evolved to be adaptive, maintaining functions across a range of stress or strain, or changing properties in response to stimuli such as temperature or moisture level.[2] In recent years, the elucidation of molecular mechanisms for natural materials has prompted many biomimetic materials designs.[3] Herein, we report a biomimetic design of a modular polymer that has a combination of high modulus, toughness, and resilience, while possessing adaptive mechanical properties.

Our biomimetic concept is based on the modular domain design observed in the skeletal muscle protein *titin*, which possesses a remarkable combination of strength, toughness, and elasticity.[4] The ability of *titin* to absorb energy by the reversible rupture of intramolecular secondary interactions, followed by refolding induced recovery, makes it an intriguing model for the design of adaptive materials. Following *titin*'s modular design, our group first synthesized polymers incorporating the quadruple hydrogen bonding 2-ureido-4[1*H*]-pyrimidone (UPy) motif[5] as the modular domain-forming mimic of the Ig domains in *titin*.[6] To overcome issues such as structural heterogeneity and interchain cross-linking, we further developed a cyclic modular polymer using a peptidomimetic β-sheet dimer.[7] Despite the well-defined single molecule unfolding properties, the synthesis of the second generation polymers is tedious, and the rupture forces of the H-bonded modules are much lower than the UPy dimer. To simplify synthesis and improve mechanical strength, the cyclic modular concept was applied to the UPy core. In our previous report, a cyclic UPy dimer was incorporated as a cross-linker into a 3-D network that then showed significant enhancement of mechanical properties,[8] which we attribute to the reversible opening of the closed UPy dimer.

Well-defined hydrogen bonding motifs have been introduced to a number of polymers at chain ends,[5,9,10] in the main chain,[6,11] or at side chains,[12–14] in the pursuit of new material designs. However, most of the studies were focused on the dynamic properties in solution or melt.[9–14] In one study, UPy groups were introduced as thermoreversible interaction sites to a chemically cross-linked polymer network, resulting in shape memory properties.[15] Nevertheless, this thermoset is not processable and its mechanical properties are moderate in terms of strength and extensibility. Here we synthesized a linear polymer composed of a tandem array of biomimetic cyclic UPy modules, closely mimicking the *titin* architecture, yielding a strong, tough, processable, and highly *adaptive* material.

The cyclic UPy core was synthesized as described previously[8] and further converted to a terminal diolefin monomer **3**. Catalyzed

Scheme 1. Synthesis of Biomimetic Linear Modular Polymer

a) Grubbs Gen-2 cat, 1,2,4-TCB, 70 °C, 84%. b) o-NBnBr, K₂CO₃, DMF, 70 °C, 52%
c) Grubbs Gen-2 cat, CHCl₃, reflux, 75%.

by the Grubbs Gen-2 catalyst, acyclic diene metathesis (ADMET)[16] polymerization of monomer **3** (Scheme 1) afforded polymer **1** (M_n = 18.0 kDa, PDI = 1.7; see Supporting Information (SI) for experimental details). The polymer is soluble in CHCl₃ or CHCl₃/DMF (9/1 v/v), and homogeneous transparent films are easily prepared from solution casting. Dynamic Light Scattering (DLS) of polymer **1** in solution shows a single peak around 7−8 nm (see Figure S9 in SI), indicating no aggregation present in the polymer solution.

The system was designed so that the polymer backbone has no hydrogen-bonding or other strong interaction sites that may complicate the reversible opening and closing of the UPy modules. ADMET was chosen because it results in a hydrocarbon backbone with minimal secondary interactions, and the hydrocarbon spacer is attached to the UPy module by an ester linkage rather than the H-bonding carbamate linkage of our previous system.[8] We decided to make a homopolymer of **3** by incorporating a UPy module in every repeat unit to minimize the possibility of phase segregation, which would likely prevent the linear tandem UPy modules, trapped in rigid-phase aggregates, from exhibiting *titin*-like sequential unfolding and reversible energy-absorbing behavior. As a control, monomer **3** was protected with the *ortho*-nitrobenzyl (NBn) group to block H-bonding and then polymerized to yield polymer **2**. The control polymer is almost identical to the real sample except that the protected UPy units cannot form dimers. As will be shown later, without reversible hydrogen-bonding capability, the control polymer **2** is drastically different from the real sample (**1**), lacking toughness, extensibility, or any adaptive properties.

Figure 1 compares the stress−strain curves for polymer **1** and the control **2**. While control is brittle and fractures at 7% strain, polymer **1** undergoes large deformation with maximal strain >100%. Polymer **1** is stiff with a relatively high Young's modulus, ∼200 MPa. After yielding at ∼5% strain, it shows a large deformation, with a relatively small increase in stress, resulting in the absorption of a large amount of energy. We postulate that this high toughness
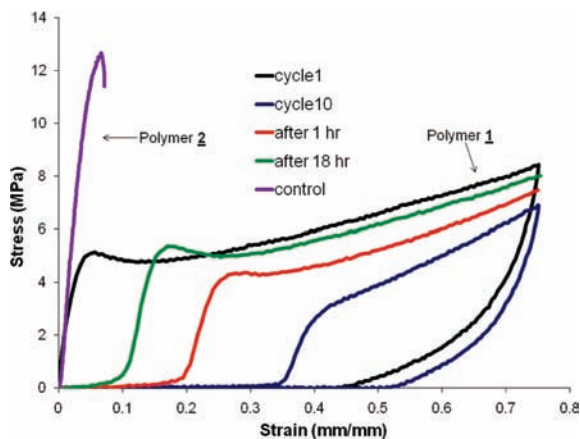
Figure 1. Stress−strain curves for sample **1** and control **2**.

Figure 2. Shape-memory cycle for polymer **1** (color code: red, temperature; blue, stress; and black, strain).

behavior is enabled at the molecular level by the continuous unfolding of UPy dimer modules upon stretching. Whereas traditional thermoplastic polymers can undergo large plastic deformation after yielding, this is usually accomplished through crazing or necking leading to permanent damage.[17] In our case, however, neither necking nor crazing was observed. The specimens remain uniform and transparent throughout the tests.

In our further studies, we observed that this plastic deformation is not permanent and could gradually recover with time or upon heat treatment, suggesting an interesting "self-healing" property for polymer **1**. After each loading−unloading cycle, the sample did not return to its original length, resulting in a temporary set. After 10 strain cycles, the material was set at ∼135% of its original length (blue curve, Figure 1). With time this sample gradually regained its shape and properties, recovering to 110% of its original length overnight at rt (green curve, Figure 1). In addition to slow spontaneous recovery, heating the material to ∼80 °C induced full recovery of dimension, stiffness, strength, and toughness in ∼30 s, returning these properties to a level comparable to that achieved by slow healing at rt. It should be noted that the unusual stress−strain behavior reflects the inherent mechanical properties of the polymer and is highly reproducible.[18] Because the sample did not recover to its original length following the loading−unloading cycle, the initial region of subsequent stretching showed zero-stress until the sample reached the new set length. During unloading, the sample tension reaches zero-stress before the strain reaches the new temporary set point and then recovers fully over ∼60 s, so that stress again increases when the new set strain is reached on the next loading cycle. Similar stress−strain behavior has been observed in biological materials such as silks,[19] though, in that case, the postloading strain at zero-stress represents a *permanent* set. Finally, to test the sensitivity of the polymer to water, we performed static tensile tests on a polymer **1** sample after incubating it in water for 18 h. Excitingly, very little change was observed in its tensile mechanical properties after this treatment (see SI, Figure S17). Presumably, due to the hydrophobic nature of the polymer, water was not able to effectively permeate the material and, thus, had no detrimental effect on the mechanical properties.

To further explore the adaptive properties of this material, we investigated the temperature dependence of the self-healing process and observed an interesting shape-memory behavior (Figure 2). After heating to 80 °C, the sample was extended to 250% strain and then cooled to 5 °C to freeze the shape. The stress was then released, and then the temperature was ramped up gradually. After reaching ∼27 °C, the sample specimen began to retract and then
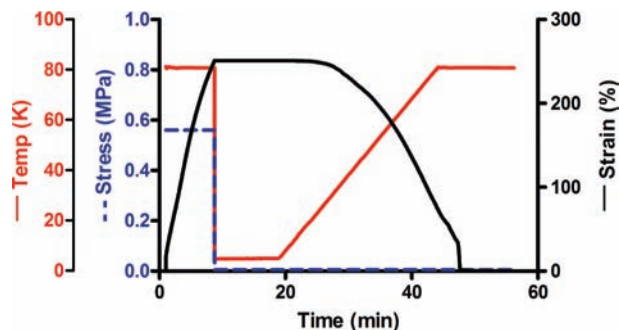
quickly recovered to its original dimension upon further heating, with both shape fixity and recovery approaching 100% (Figure 2).

The unusual stress−strain behavior (Figure 1) and the unique shape-memory properties (Figure 2) indicate that the modular polymer **1** exhibits a *combination* of mechanical properties found in *titin*, including high modulus, toughness, large extensibility, and intriguing *adaptive* behavior. In contrast, the H-bonding blocked control polymer **2** is a simple brittle material, suggesting that the reversible rupture of UPy dimer modules contributes to the macroscopic properties. Our proposed mechanism for these observed properties is illustrated in Figure 3. Upon stretching, the modules gradually unfold, resulting in a large extension and absorption of energy. When the polymer is cooled and stress is removed, many of the unfolded UPy units are in close proximity to other opened units on neighboring chains, with which they can dimerize to form a temporary network, freezing the new polymer shape. When temperature/time is applied to the system, the newly formed interchain UPy dimers become dynamic, and the modules can return to their original more stable cyclic self-dimerized state, regaining their original dimensions and properties.
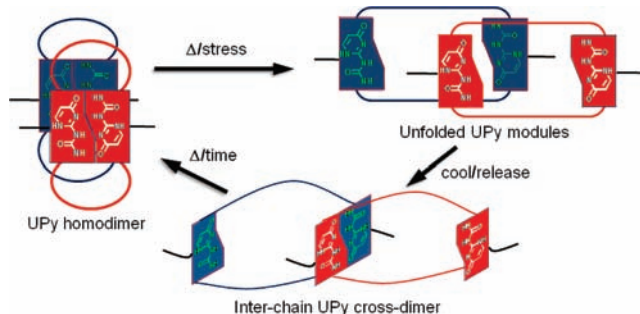

Figure 3. Proposed molecular mechanism.

The proposed molecular mechanism accounting for the rare combination of mechanical properties of polymer **1** is supported by the following factors. *First*, our single molecule force spectroscopy (SMFS) for previous and current modular polymers shows sawtooth force−extension curves corresponding to tandem unfolding of biomimetic modules,[6,7,20] indicating that, at molecular scale, UPy modules can unfold sequentially under stress. *Second*, computer modeling demonstrates that cross-dimerization of unfolded UPy units from adjacent chains is totally feasible (see SI, Figure S18−20). *Third*, the transition temperature of the shape-memory cycle (T_{trans}) of polymer **1** matches the UPy dimer unfolding temperature, suggesting a direct connection between the UPy module unfolding event and the observed macroscopic properties. The T_{trans} of the shape-memory cycle for polymer **1** centers at ∼50 °C (Figure 2), agreeing with a T_α transition (∼52 °C) observed in

the tan δ peak of its DMA temperature scan (see SI, Figure S10), which, most importantly, matches the UPy unfolding temperature.[15] *Fourthly*, our negative control polymer **2** has shown that blocking the hydrogen bonds of the UPy unit completely destroys the high toughness and adaptive properties, confirming the importance of reversible hydrogen bonding for the macroscopic properties. *Lastly*, our X-ray, DSC, and AFM data have ruled out the possibility that microphase separation or crystallinity is responsible for the observed properties. SAXS data reveal a complete lack of phase separation on the scale of 2−45 nm for both untreated and prestretched samples (see SI, Figure S11−12). AFM imaging further confirms no microphase separation in polymer **1** (see SI, Figure S15). The WAXS (see SI, Figure S14) pattern reveals a broad peak at ∼4.6 Å, which molecular modeling indicates is a reasonable match with the spacing between two adjacent UPy dimers. An additional peak is observed in the WAXS spectrum at ∼2.2 nm, corresponding to the approximate molecular size of the UPy dimer macrocycle.[21] The DSC trace shows no crystallinity for polymer **1** (see SI, Figure S16), confirming its amorphous nature in bulk.

For shape-memory polymers, the molecular mechanism for "memorizing" the initial permanent shape is usually one of the following: (1) permanent covalent cross-links; (2) physical cross-links such as crystalline domains or segregated microphases; or (3) chain entanglement for polymers with very high molecular weight.[22] For polymer **1**, the first two possibilities are ruled out because there are no covalent cross-links and the system is totally amorphous. This leaves the third one, chain entanglement, as the most probable mechanism for holding the permanent shape and preventing permanent flowing at elevated temperature. Although our polymer **1** molecular weight is not particularly high, the unusual molecular topology should contribute to the formation of stable entanglements. With bulky and rigid UPy modules dispersed between flexible alkene spacers, the chains can easily be trapped in entangled states, as was shown with the iptycene polymers by Swager and co-workers.[23] Though interchain UPy cross-dimerization is feasible and, as discussed above, plays a key role in the temporary fixation of polymer shape, it should be noted that this temporary cross-linking cannot be responsible for holding the permanent initial shape, as deformation at elevated temperature would lead to a whole new H-bond network, replacing the initial one, and the original shape would be completely erased.

Finally, the nature of the T_α/T_g transition (∼52 °C) deserves further discussion. The consistency of this T_α/T_g transition with the UPy unfolding temperature reported in another system[15] strongly suggests that this transition is due to UPy dynamic dissociation. In polymer **1**, the relaxation temperature for the flexible hydrocarbon segments (classically defined T_g) should be very low (e.g., T_g for polyethylene is < −60 °C) and, thus, is irrelevant to the temperature window for this study. For the rigid UPy-dimer components, hydrogen bonding between UPy units is the weakest linkage, which will be disrupted by heat, contributing to the T_α/T_g transition. Based on all these considerations, we propose that the observed T_α/T_g relaxation is due to the dissociation of temporary UPy networks and that the thermodynamic reversibility of the cyclic UPy dimer yields an entropic driving force for macroscopic shape and property recovery. At relatively low temperature, the UPy exchange rate is slow, so that it takes a long time to observe the "self-healing" process. As the temperature reaches T_α, the UPy exchange rate increases exponentially, resulting in fast recovery to the original shape.

In summary, we have demonstrated the first biomimetic modular polymer that exhibits a rare *combination* of high modulus, high toughness, and *adaptive* properties, including self-healing and shape memory. Notably, this new polymer combines high toughness and self-healing properties in one material, something that has proven extremely difficult to achieve.[24] Our ongoing research seeks to elucidate the structure property relationships of various aspects of the modular polymer architecture, such as the loop size and intermodule chain length, as well as new UPy module macrocycle morphology. These studies are expected to yield further novel biomimetic polymeric materials with advanced properties.

Supporting Information Available: Synthesis and characterization of monomers and polymers, stress−strain, DMA, X-ray, AFM, and molecular modeling experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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