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Reversible Polymer–Metal Mechanical Transitions Enabled by Electrochemical Modulation

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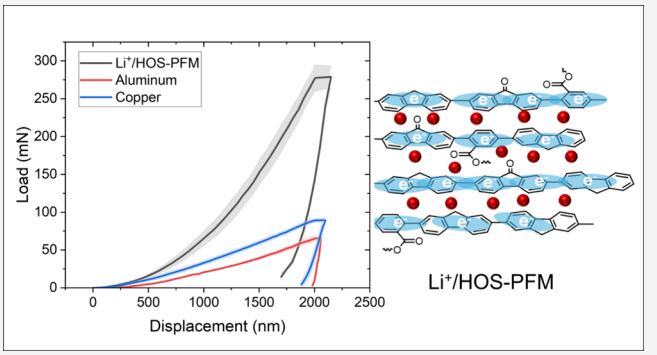
ABSTRACT: The mechanical properties of materials, e.g., elastic modulus and hardness, are important for many engineering applications. Here, we introduce a hierarchically ordered structure (HOS) polymer system that exhibits exceptionally large, reversible changes in mechanical behavior upon electrochemical lithiation and delithiation. Full lithiation of the HOS polymer induces a substantial mechanical transition from polymer-like to metal-like attributes, yielding a 10-fold increase in elastic modulus and a 3-fold increase in hardness, with values comparable to those of aluminum. Upon removal of Li^+ ions, the elastic modulus and hardness return to nearly pristine polymer levels, and this transformation remains highly repeatable over many electrochemical cycles. Reversible transitions between polymer-like and metal-like mechanical behaviors offer a new pathway for engineering materials for applications that require tunable mechanical properties, such as soft robotics and stimuli-responsive systems.



KEYWORDS: *Polymer, Mechanical Property, Energy Storage*

Materials are generally classified into four families: metals, polymers (natural or synthetic), ceramics, and composites. Their physical properties, such as Young's modulus and density, exhibit well-established correlations that can be visualized in Ashby plots on logarithmic scales. Each family occupies a distinct region in this property space, providing a framework for selecting materials for specific applications. Modern engineering materials are typically designed and manufactured with tightly controlled mechanical properties to ensure consistent, reliable, and safe performance.

In contrast, stimuli-responsive materials can alter their properties in response to external stimuli such as mechanical stress, temperature, moisture, pH, light, electric field, or magnetic field.[1−3] Representative examples include shape memory alloys and polymers,[4] piezoelectric materials,[5] photochromic materials,[6] electro responsive polymers,[7] and electrorheological[8] and magnetorheological fluids.[9] These materials have been widely used in sensors, actuators, and biomedical devices.[10,11] In recent years, variable stiffness materials (VSMs) have been actively explored for applications including lightweight morphing aerospace structures, vibration and noise control, soft robotics, and wearable devices, artificial muscles, and neural implants.[12−14] Notable examples include systems based on shape memory alloys and polymers, phase change materials, and multiphase metamaterials that exploit solid–liquid phase transitions to modulate stiffness. Additional approaches for achieving variable stiffness include particle, fiber, and layer jamming, as well as fluidic flexible matrix composites.[15]

In this work, we report a synthetic polymer capable of reversibly transitioning from a polymer-like to a metal-like mechanical state via electrochemical modulation of lithium-ion (Li-ion) content within a hierarchically ordered structure (HOS) polymer. Understanding the mechanism of reversible mechanical transformation in the HOS polymer, which was originally developed as a binder for high-capacity silicon electrodes in solid-state Li-ion batteries, may help create new materials with giant tunable stiffness.

As a binder for silicon electrodes in solid-state Li-ion batteries, the poly(9,9-dioctylfluorene-*co*-fluorenone-comethylbenzoicester) (PFM) polymer was designed to be an electron- and lithium ion-conducting polymer with strong adhesion to silicon. It must also be deformable and flexible as silicon electrodes expand and contract by about 300% during charging and discharging operation. To impart electronic conductivity, the PFM was heat treated from ambient to 500 °C. The results of Fourier transform infrared spectroscopy (FTIR, Figure S1) and

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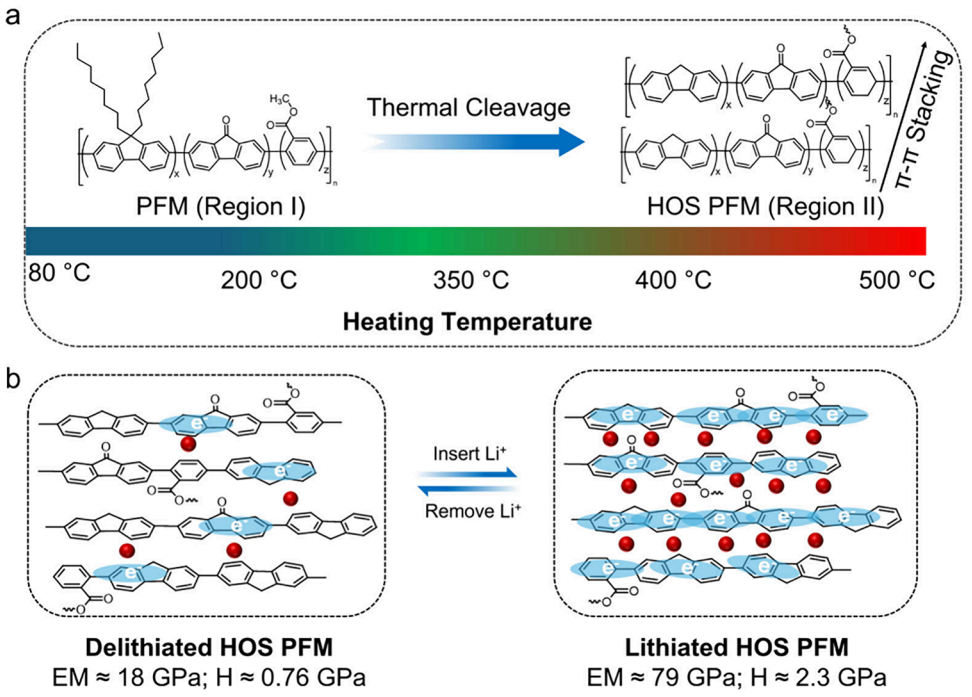

Figure 1. Temperature-dependent structural evolution and mechanical modulation of PFM polymer. (a) Structural evolution of PFM polymer at different temperatures. (b) Schematic illustration of reversible tuning of elastic modulus (EM) and nanoindentation hardness (H) of HOS-PFM polymer via lithiation/delithiation.

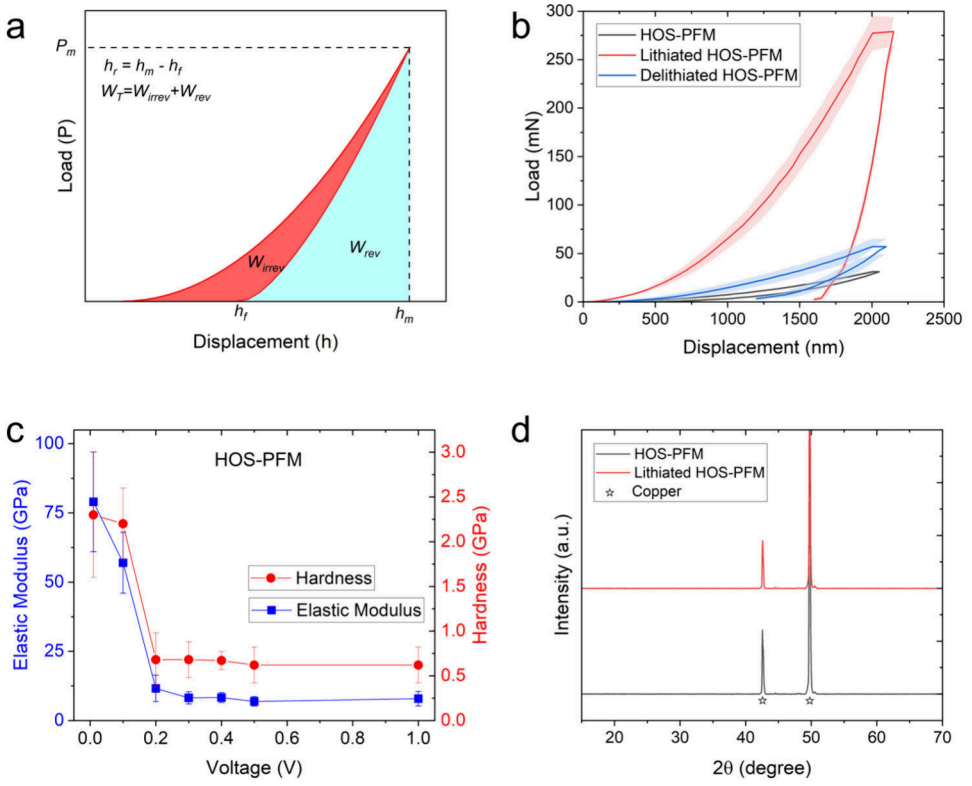

Figure 2. Mechanical property evolution of HOS-PFM polymers under varied Li^+ doping conditions. (a) Schematic illustration of a typical load−displacement curve obtained from indentation, highlighting the shaded regions for irreversible (W_{irrev}) and reversible (W_{rev}) indentation work; h_r denotes the elastic recovery distance. (b) Load−displacement curves for pristine, lithiated, and delithiated HOS-PFM. (c) Elastic modulus and hardness of HOS-PFM at varying lithiation voltages. (d) XRD patterns of pristine and fully lithiated HOS-PFM.

Thermogravimetric Analysis (TGA, Figure S2) elucidate the molecular structural evolution of PFM under thermal treatment, along with complementary insights from previous solid-state nuclear magnetic resonance (ssNMR) studies.[16]

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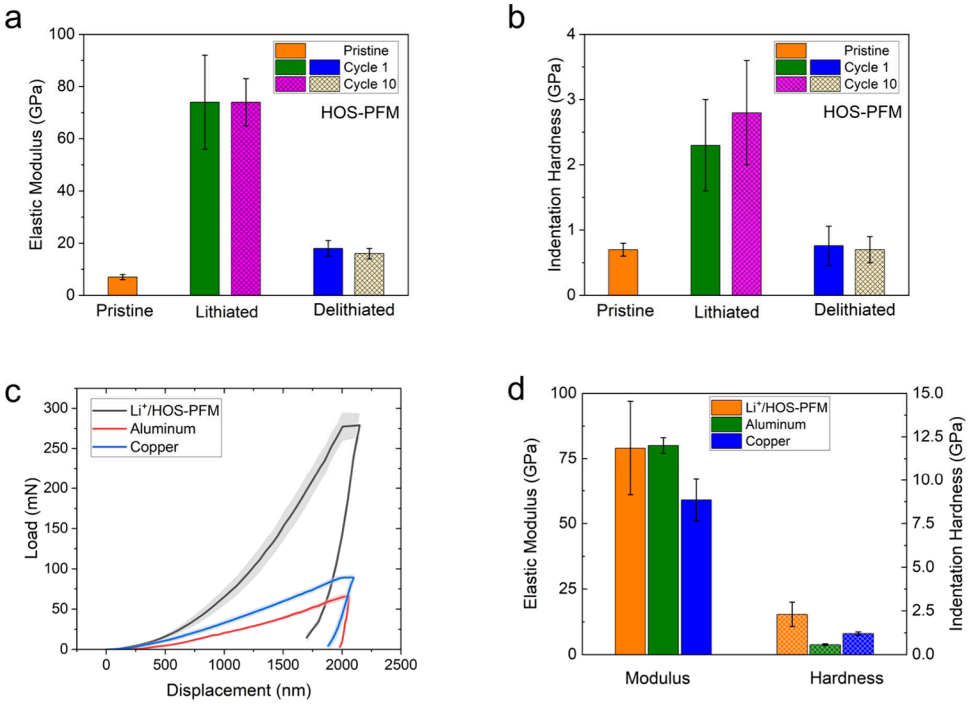

Figure 3. Reversible and superior mechanical properties of HOS-PFM polymers. (a) Elastic modulus and (b) indentation hardness of HOS-PFM after the first and 10th cycles in both lithiated and delithiated states. (c) Load−displacement curves and (d) elastic modulus and indentation hardness of lithiated HOS-PFM, aluminum, and copper.

In the pristine state, PFM comprises three monomeric repeating units: 9,9-dioctylfluorene, fluorenone, and methyl-benzoic ester (Figure 1a). The long, flexible alkyl side chains impart high solubility in organic solvents and enable solution processability; however, their steric bulk disrupts backbone packing and chain alignment, leading to an amorphous polymer morphology. At approximately 400 °C, the alkyl side chains and methyl groups on the ester moieties underwent thermal cleavage, yielding HOS-PFM (Figure 1a). Removal of these bulky side chains exposed the conjugated backbone,[16] enabling dense nanoscale packing with increased structural order and alignment, thereby strengthening $\pi-\pi$ interactions and enhancing electronic conductivity by 3 orders of magnitude.[17] Benefiting from enhanced $\pi-\pi$ stacking and improved electronic conductivity, HOS-PFM exhibits a lithium-ion capacity of approximately 400 to 1000 mAh g^{-1}, depending on polymer thickness and cycling rate.[16] During lithiation, Li^+ ions intercalate into the interspaces between conjugated backbones of HOS-PFM, while electrons migrate along the conjugated backbones (Figure 1b). Upon delithiation, most intercalated Li^+ ions are extracted from the polymer; however, a small fraction of Li^+ ions remains trapped within the polymer. The large capacity of HOS-PFM, combined with its reversible lithiation/delithiation behavior, enables tunable control over its mechanical properties.

The mechanical behavior of the PFM and HOS-PFM was investigated via nanoindentation using a diamond Berkovich indenter. From a representative load−displacement curve illustrated in Figure 2a, the elastic modulus, hardness, work of indentation (area under the loading curve, W_T), recoverable work (area under the unloading curve, W_{rev}), and depth recovery ratio $\left(\frac{h_r}{h_m}\right)$ can be calculated and measured. These mechanical properties provide valuable insights into PFM and HOS-PFM polymers under various thermal treatment histories and Li^+ doping states, while offering a comparison with existing polymers and metals.

The structural evolution of PFM polymers under varying thermal processing temperatures dictates their nanoindentation-derived mechanical properties. As shown in Figures S3(a, b) and S4, PFM at 80 and 200 °C exhibits similar load−displacement responses, elastic moduli, and hardness values, as thermal treatment below 200 °C does not change their molecular structure. In these polymers, the long, flexible aliphatic side chains occupy the space and act as intrinsic plasticizers to attenuate the van der Waals force and $\pi-\pi$ stacking interactions between conjugated backbones, thereby softening the polymer matrix. Consequently, the PFM polymers in Region I (Figure 1a) display relatively low elastic modulus and hardness. Upon heating to 350 °C, partial thermal decomposition of these side chains occurs, leading to increases in elastic modulus and hardness by 142% and 187% (Figures S3, S4), respectively, compared with the pristine PFM. At elevated processing temperatures of 400 and 550 °C (Region II), the mechanical properties reach a plateau, with both elastic modulus and hardness exhibiting comparable values (Figures S3, S4). In Region II, the long side chains undergo complete thermal cleavage, resulting in more rigid, densely packed, and highly ordered conjugated backbone chains. When the heating temperature increases from 80−200 °C (Region I) to 400−550 °C (Region II), the PFM polymer experiences a plastic-elastic transition. In Region I, the polymer features poor displacement recovery. In comparison, in Region II, the reversible-to-total work ratio and displacement recovery, $\frac{W_{rev}}{W_T}$ and $\frac{h_r}{h_m}$ have significantly increased due to stronger $\pi-\pi$ interactions as shown in Table S1.

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PFM and HOS-PFM are two representative polymers in Region I and Region II, respectively. The PFM exhibits almost negligible lithium-ion doping (~0 mAh g^{-1}), leading to nearly unchanged load−displacement profiles across pristine, lithiated, and delithiated states (Figures S5, S6). In Li||PFM half-cells, the voltage was set to a target voltage (e.g., 0.01 V) under potentiostatic control but immediately returned to the original open-circuit voltage (OCV) upon removal of the applied potential. In contrast, HOS-PFM-based cells sustained the set potential after lithiation, due to their significant Li^+ storage capacity (≈300 to 1000 mAh g^{-1}),[16] which varies with polymer thickness, lithiation rate, and duration of the potential hold. Evidently, fully lithiated HOS-PFM can sustain a substantially higher load than the pristine HOS-PFM at the same displacement (Figure 2b). Upon lithiation, the elastic modulus and hardness increased by factors of approximately 10 and 3 respectively, relative to the original condition (Figure S6). Following delithiation, these values largely recovered, approaching-but remaining slightly above-those of pristine HOS-PFM (Figure S6). This phenomenon is attributed to the partial retention of lithium ions within the polymer matrix, which cannot be completely removed during delithiation. In addition, lithiation decreased the displacement recovery of HOS-PFM from 78% to in the pristine state to 26% in the lithiated state (Figure 2b). This reduction arises because inserted Li^+ ions occupy the interstitial regions between polymer chains, thereby disrupting $\pi-\pi$ interactions between the conjugated backbones. After delithiation, the displacement recovery returned to 43%, indicating partial restoration of elasticity. Figure 2c shows that discharging the Li||HOS-PFM cell from OCV (~2.0 to 2.5 V) to 0.2 V resulted in negligible changes in the mechanical properties of HOS-PFM. In contrast, further reducing the potential to 0.1 or 0.01 V leads to a pronounced increase in both elastic and hardness, indicating that HOS-PFM possesses a low lithiation potential (<0.2 V).

Moreover, after 10 cycles, the elastic modulus and hardness of HOS-PFM in both lithiated and delithiated states remained comparable to those measured in the first cycle (Figure 3a, 3b, Figure S7), underscoring its excellent reversibility in mechanical behavior under repeated lithiation-delithiation cycling. This mechanical reversibility is consistent with the good electrochemical cycling stability of HOS-PFM films. As long as Li^+ ions can be reversibility inserted into and extracted from the HOS-PFM polymer matrix (Figure S7), the material can maintain reversible mechanical properties through successive lithiation-delithiation processes.

Although the detailed mechanisms underlying the significant enhancement of elastic modulus and hardness in Li^+/HOS-PFM remain unclear, certain observations permit the exclusion of several specific hypotheses. For instance, the measured values far exceed the average of those for Li metal and HOS-PFM polymer, thereby ruling out a simple physical mixture of the two components as the origin of the mechanical reinforcement. In addition, the air-free XRD results (Figure 2d) showed no detectable crystalline inorganic phases, and the observed tuning of mechanical property from polymer-like to metal-like behavior during lithiation-delithiation further supports the process reversibility. Consequently, the contribution of inorganic compound formation, e.g., LiF, to the change in mechanical properties can be excluded, as such processes are typically irreversible. These findings strongly suggest that ionic interactions between Li^+ and the HOS-PFM polymer matrix are the most probable origin of the observed changes in elastic modulus and hardness.

The indentation energy, quantified as the area under the load−displacement curve, encompasses contributions from both recoverable elastic deformation and irreversible plastic deformation. Brittle materials typically have a small plastic deformation zone and can be easily fractured with low energy absorption. However, the tougher materials have larger plastic zone and absorb large energy before failure. As shown in Figure 3c, d and Figure S8, the load−displacement curves show the nanoindentation energy of fully lithiated HOS-PFM (Li^+/HOS-PFM) exceeds that of Al and Cu by 282% and 143%, respectively, which are commonly used as current collectors for positive and negative electrodes. This finding highlights the superior capacity of Li^+/HOS-PFM to absorb mechanical energy at an equivalent displacement as well as its improved ability to withstand impact, shocks, and vibrations compared to metals. Interestingly, Li^+/HOS-PFM exhibits an elastic modulus compared to that of Al and Cu, with a hardness value greater than both metals (Figure 3d). This suggests that full lithiation of HOS-PFM imparts metal-like characteristics and produces synergistic enhancements in its mechanical performance, whereby the elastic modulus and hardness values far exceed that of either the Li metal or pristine HOS-PFM polymer. Owing to its unique mechanical attributes and the inherently low density of polymers, the Li^+/HOS-PFM type of polymers shows strong potential for applications that demand both lightweight design and high energy absorption, such as protective components in aerospace structures, soft robotics, and stimuli-responsive systems.

In conclusion, we demonstrate a PFM-based polymer capable of a reversible transition from polymer-like to metal-like mechanical behavior via electrochemical lithiation and delithiation. Prior to thermal treatment, PFM exhibited negligible changes in mechanical properties upon lithiation or delithiation. In contrast, lithiation of thermally treated HOS-PFM resulted in a pronounced increase in both elastic modulus and hardness, reaching values comparable to metals such as copper and aluminum. Upon Li^+ extraction, delithiated HOS-PFM recovered most of its pristine mechanical properties, while retaining a slight increase due to residual Li^+ trapped within the polymer matrix. Notably, this mechanically adaptive behavior was fully reversible over at least ten lithiation/delithiation cycles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.5c05837.

Experimental details, additional characterizations (FT-IR and TGA), nanoindentation figures and analysis, and a supplementary table (PDF)

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Author Contributions

‖S.T. and D.L. contributed equally to this work. Y.-T.C. and G.L. conceptualized and supervised the study. S.T. and D.L. designed the experiments. D.L. carried out polymer characterization, sample preparation, and the lithiation/delithiation procedures. S.T. performed mechanical property measurements of the polymers. Y.-T.C. and S.T. analyzed and interpreted the changes in mechanical properties. G.L. and D.L. proposed the mechanisms underlying these changes in mechanical properties. D.L. and S.T. completed the initial draft of this manuscript. All authors provided comments and revisions on this manuscript.

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Notes

The authors declare no competing financial interest.

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