Electrochemical Control of Coil-Globule Transition of Ureido Polymer with Iron Hexacyanide Redox Couple

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Stimuli-responsive polymers, which undergo coil-globule transitions between dissolved and aggregated states in response to external stimuli, are expected to find applications in sensors, actuators, and shape-memory materials. Most stimuli-responsive polymers are responsive to temperature, humidity, pH, and chemicals, however limited numbers of polymers are known to undergo coil-globule transitions by electrochemical stimuli.[1] Here we report that the coil-globule transition of poly(allylamine-*co*-allylurea) can be controlled by the electrochemical redox reaction of hexacyanoferrate/ferrite ($[Fe(CN)_6]^{3-/4-}$) anions (**Figure 1**).

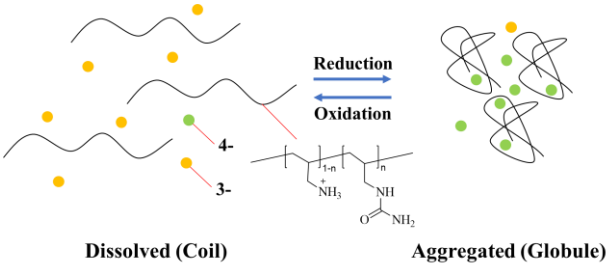

Figure. 1 Coil-globule transition of PAU triggered by electrochemical redox reaction of $[Fe(CN)_6]^{3-/4-}$ anions

Poly(allylamine-*co*-allylurea) (PAU) is known to undergo coil-globule transition at upper critical solution temperature (UCST).[2] We discovered that the strong coulombic interaction between the protonated amine group ($-NH_3^+$) and $[Fe(CN)_6]^{4-}$ anion induces the aggregation of PAU chains (globule state). When $[Fe(CN)_6]^{4-}$ is oxidized to $[Fe(CN)_6]^{3-}$, the coulombic interaction is weakened, and the PAU chains redissolve in the solution (coil state).

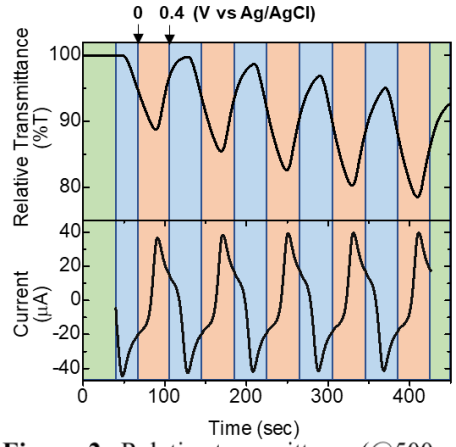

Figure. 2 Relative transmittance (@500 nm) of PAU solution containing $[Fe(CN)_6]^{3-}$ during CV mesurment (scan rate : 10 mV/sec)
: OCV : negative scan : positive scan

An aqueous solution of $[Fe(CN)_6]^{3-}$ containing PAU was cycled between 0 and 0.4 V with cyclic voltammetry (CV) technique, and the transmittance of the solution was monitored *in situ*. (**Figure 2**). The transmittance decreases (transition to globule state) at the negative scan and increases (transition to coil state) at the positive scan. This result indicates that the reversible coil-globule transition of PAU can be realized by the electrochemical method.

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