

Redox-active Poly(ferrocenylsilane)s as Responsive Materials

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Stimuli-responsive polymers have proved their versatility in a variety of application areas as these materials often display dramatic changes in properties in response to minute stimuli, enabling their use in sensing and actuation. Poly(ionic liquids), a subclass of polyelectrolytes featuring an ionic liquid species in each monomer repeat unit have emerged as promising materials. By employing a redox responsive organometallic polymers: poly(ferrocenylsilane), we have demonstrated a broad range of applications in hydrogel actuators, smart windows, nanoparticle pre-paration, electrochemical sensors, breathing porous membranes.

Interfacial polycondensation

PFS-based thin films and hollow capsules fabricated from interfacial Nylon reaction.

- Oil: Sebacyl chloride in trichloroethane (t150)
- Water: PFS-amine 30 mg/ml with 12 mg/ml NaOH
- Crosslinked PFS-Nylon film was quenched by hexylamine and EtOH

Sebacoyl chloride

Dry film and capsules showing interference color under microscope

Redox responsive hydrogel

was immediately formed via one-step thiol-Michael addition reaction from cross-linkable PFS-based cationic polyelectrolyte and PEG.

Neutral (reduced) hydrogel Oxidized hydrogel

Hydrogel actuator

displays a reversible change in color and size in physiological salt condition (0.1 M Tris/HCl), even under high stress.

- Load: up to 4.5 g
- Work: up to 45 μJ
- G: ~10 kPa
- G': 40 Pa

Porous membrane

can be readily formed from PFS-based poly(ionic liquids) and organic acids: PAA.

Ammonia solution

initiates pore formation by deprotonating COOH to COO⁻, activating electrostatic complexation.

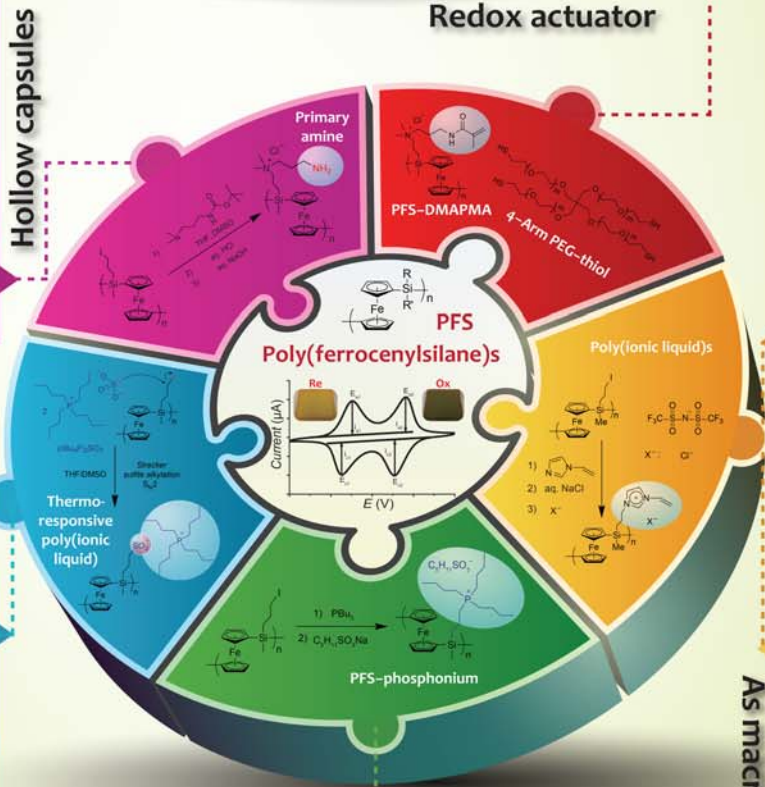
Redox induced changes

were demonstrated: reversible switching between more open and more closed porous structures.

In-situ small-angle x-ray scattering (SAXS)

Reversible permeability control over the porous membrane

Macromolecules, 2017, 50, 296-303
Angew. Chem. Int. Ed., 2014, 53, 13789-13793



Smart window

Coil-globule transitions from a classical LCST-type phase transition and an "isothermal" phase transition, respectively, forming the basis for an electrically switched smart window.

Controllable LCST-type transition temperature in terms of concentration as well as additional salts and redox states.

Adv. Funct. Mater., 2017, 27, 1702784

Bi-stable conductive hydrogel

The PFS-PEG hydrogel exhibits strong hysteric volume phase transition and shows bistable states at room temperature by choosing specific phosphonium/acrylamide repeat unit ratios and counter ion (C₅⁺ or C₆⁺). This PFS-based poly(ionic liquid) can also be used as a dispersant for MWCNT.

The as-formed conductive PFS-CNT hybrid hydrogel shows bistable states and tunable resistance upon heating and cooling.

Relative size (%) vs Temperature (°C)

Free energy vs Volume

J. Am. Chem. Soc., 2017, 139, 10029-10033

Breathing pores

Highly swellable, dual-responsive poly(N-isopropylacrylamide)/poly(ferrocenylsilane) vinylimidazolium hydrogels are fabricated and used as the reducing environment to produce gold nanoparticles inside the hydrogel in situ.

Localized surface plasmon resonance (LSPR) peak of the hybrid system could be tuned reversibly by the volume-phase transition of the stimuli-responsive hydrogel.

Macromol. Rapid Commun., 2016, 37, 1939-1944