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Redox-Active Cross-Linkable Poly(ionic liquid)s

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Supporting Information

ABSTRACT: The synthesis of a new class of cross-linkable redox-responsive poly(ferrocenylsilane)-based poly(ionic liquid)s (PFS-PILs) is reported. PFS-PILs self-cross-link at low concentrations into nanogels or form macroscopic hydrogel networks at higher concentrations. PFS-PILs proved to be efficient dispersants in the microemulsion polymerization of methyl methacrylate, producing stable PFS−poly(methyl methacrylate) latex suspensions.

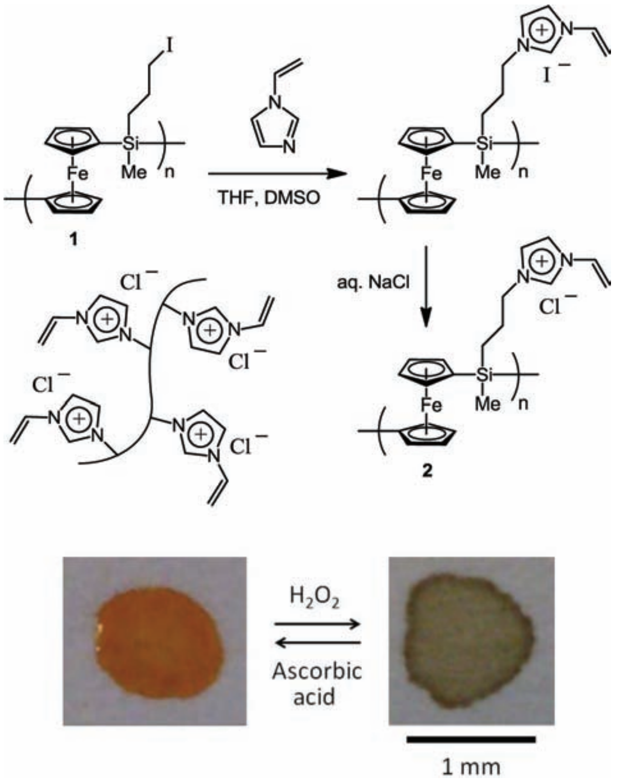
In this work, we describe cross-linkable, redox-active poly(ionic liquid)s (PILs) that were converted into nanogels and macroscopic hydrogels and were demonstrated to be efficient dispersants in microemulsion polymerization. We aimed to use these responsive PILs as encapsulants and redox mediators for enzymes in the development of micro- and nanosphere sensor particles. Over the past decade, ionic liquids (ILs)[1] have evolved from reaction media into highly tailorable polymeric or polymer-supported materials in which the functionality of ILs is combined with the spatial control of IL moieties provided by polymer architectures.[2] Responsive PILs constitute a novel, unexplored class of functional, addressable materials that may serve to create tailored, amendable interfaces between (bio)-active species and their surroundings or act as responsive embedding media for such species.

PILs have attracted much attention in recent years because of their unique properties and broad applicability as dispersants, solid-ion conductors, carbon precursors, etc.[3] In PILs, IL species incorporating cationic groups such as pyridinium, imidazolium, and alkylammonium moieties are part of the repeat units of the polymer chain.[3d] Cross-linked, swellable PILs possess an even wider range of applications, and, although more rarely, some examples of gels and microgels based on PILs have been reported.[4] The area of reactive and responsive PILs and PIL networks is still largely unexplored; however, a first example exhibiting reversible poration of a PIL gel in response to solvent variation[5] underscores the potential of responsive PIL structures as addressable, functional materials. Examples of organic-solvent-swellable, redox-active,[6] cross-linked networks/gels and nanogels from poly(ferrocenylsilane) (PFS)[7] homopolymers and block copolymers have been previously reported.[8]

Here we introduce a novel class of water-soluble PILs composed of PFS chains and polymerizable vinylimidazolium pendant groups. Alkyl-substituted imidazolium cations have attracted much interest, as their delocalized charge and low symmetry lead to ILs with low melting points. Because of the presence of polymerizable IL side groups, these organometallic polymers are easily transformed into redox-responsive PIL networks. A variety of water-swellable redox-responsive structures ranging from intramolecularly cross-linked polymeric nanogels formed from a few polymer chains to intermolecularly cross-linked macroscopic gel structures and tailored hydrogel nano- and microspheres generated by microfluidic methods are therefore within reach.

The synthesis of a PFS-PIL is depicted schematically in Scheme 1. PFS-PIL chains bearing vinyl side groups were obtained by allowing poly(ferrocenyl(3-iodopropyl)-methylsilane)[9] (**1**) to react with 1-vinylimidazole at 60 °C for 24 h. To increase the water solubility of the formed polycation, its iodide counterions were exchanged with chloride

Scheme 1. Synthesis of Cross-Linkable PFS-PIL 2 and the Color Change of PFS-PIL Associated with Its Reversible Oxidation and Reduction on a Paper Substrate



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counterions by dialysis in 0.1 M aqueous sodium chloride. The counterion identity strongly influences the PFS polyelectrolyte solubility and swellability.[9,10] The resulting PFS-PIL (**2**) was characterized by means of ^{1}H and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), FTIR spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and X-ray photoelectron spectroscopy (XPS) [see the Supporting Information (SI)]. NMR spectroscopy indicated a quantitative conversion of **1** into **2** and showed that polymerization of the vinyl groups did not occur in this step. GPC showed **2** to be a high-molar-mass material with the same polydispersity as **1**, indicating that the molar mass did not decline during the interconversion. The XPS results showed almost complete counterion exchange from I^- to Cl^-. Importantly, a relatively low glass transition temperature of 48 °C was found for **2** by DSC. The presence of nonvolatile elements in **2** was confirmed by TGA. PFS-PIL **2** underwent thermal decomposition beyond 350 °C and left a high residual mass (40%).

The electrochemical properties of PFS-PIL were studied using cyclic voltammetry (CV). We noticed that in aqueous PFS-PIL, the CV peak currents displayed a "break-in" behavior,[11] increasing gradually with each successive sweep and then reaching a steady state at which stable and reproducible current–potential curves were obtained (see the SI). This behavior is typical of redox-active films into which the diffusion of solvent molecules and supporting electrolyte ions is slow, as observed for thick redox-active films or films that do not swell readily in the employed CV solvent. Chemical oxidation of the ferrocene units in PFS is accompanied by a very distinct color change from amber to blue/green.[12] To illustrate this, spots of PFS-PIL deposited on a paper support were observed to undergo a clear color change upon oxidation by, for example, H_2O_2 (Scheme 1).

Irradiation[13] of a dilute solution of PFS-PIL in water (0.5 mg/mL) with 365 nm UV light in the presence of a photoinitiator (Irgacure 2959) yielded a stable, translucent dispersion (Figure 1A).

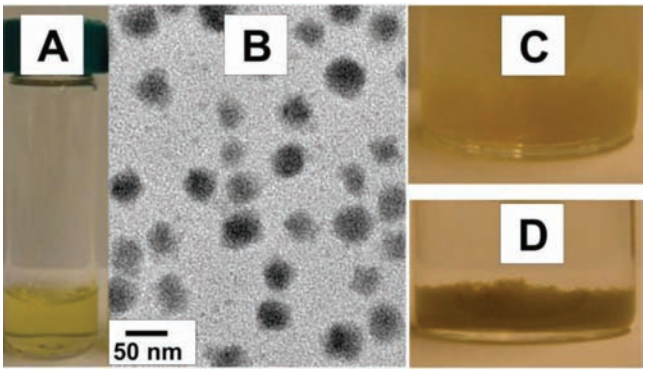

Figure 1. (A) PFS nanogels dispersed in water. (B) TEM image of PFS nanogels. (C) PFS nanogels dispersed in 0.1 M KPF_6 solution. (D) PFS nanogels dispersed in 0.1 M aqueous KPF_6 after 12 h.

Transmission electron microscopy (TEM) analysis (Figure 1B) showed the formation of cross-linked PFS-PIL nanogels[14] with diameters of 20–50 nm. Energy dispersive X-ray (EDX) measurements obtained from these PFS-PIL nanogels demonstrated the presence of Fe (see the SI). The excellent dispersibility of the formed nanoparticles in water is due to their small size and the electrostatic repulsion of the imidazolium moieties.[4a] The nature of the counterion significantly influenced the stability of the PFS-PIL nanogel dispersions. In solutions containing relatively hydrophobic PF_6^- anions,[15] the gel particles aggregated dramatically (Figure 1C). In addition, PFS-PIL dispersions aggregated in the presence of KPF_6 underwent oxidation simply upon exposure to air (Figure 1D), indicating that the PFS oxidation potential was significantly reduced by the PF_6^- counterions, likely as a result of ion-pairing effects.[16] A cyclic voltammogram of the nanogel particles recorded in aqueous $NaNO_3$ (Figure 2) showed the two oxidation and reduction waves typical of PFSs.[17]

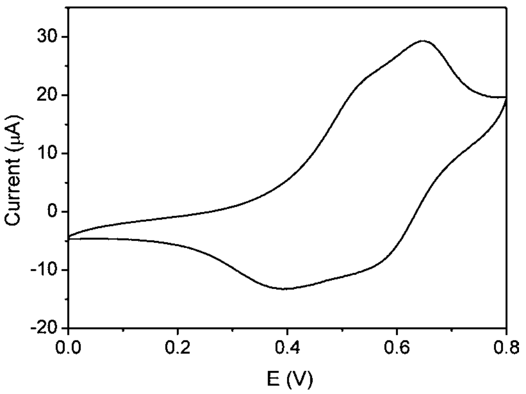

Figure 2. Cyclic voltammogram of PFS nanogel particles. Working electrode, Au; reference electrode, Ag/AgCl; counter electrode, Pt disk; scan rate, 50 mV/s in 0.1 M $NaNO_3$.

Cross-linking of PFS-PIL **2** in water at higher concentrations (60 mg/mL) led to the formation of transparent amber-colored PFS hydrogels (Figure 3A).[7d,18] Porous structures with pore diameters of 15–20 μm were observed by scanning electron microscopy (SEM) imaging (Figure 3B).

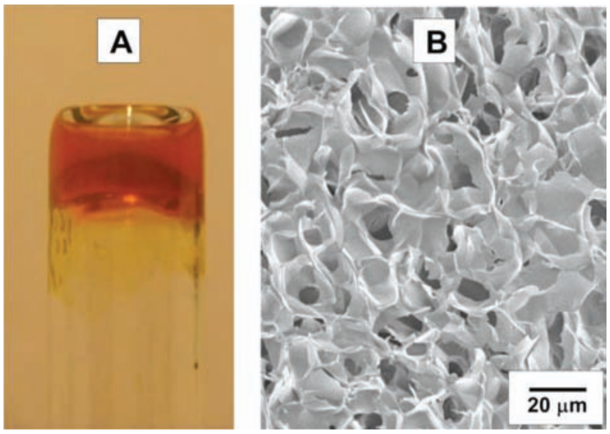

Figure 3. (A) Photograph of a PFS-PIL macroscopic hydrogel. (B) SEM image of a PFS-PIL hydrogel after freeze-drying.

Because PFS-PIL **2** possesses charged, hydrophilic imidazolium chloride units and a hydrophobic main chain, it may potentially be useful as a stabilizer in microemulsion polymerizations in aqueous media.[19] To demonstrate this, PFS-PIL was added to stabilize methyl methacrylate (MMA) polymerization in water. At a PFS-PIL/MMA/H_2O ratio of 1/100/1000, bulk photopolymerization resulted in stable polymer latex suspensions. The small particle size obtained (45 ± 5 nm) is evidence of the powerful stabilizing capability of the imidazolium-based PILs[5,15,19] (Figure 4). Copolymerization of MMA and PFS-PIL

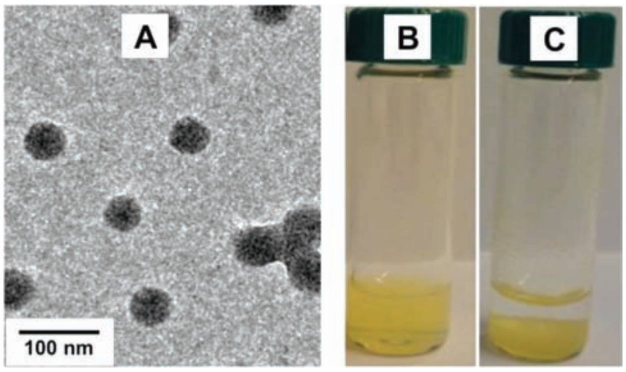

Figure 4. (A) TEM image of PFS−PMMA hybrid latexes from microemulsion polymerization. (B, C) Photographs of hybrid latexes dispersed in (B) water and (C) 0.1 M KPF_6 solution.

was proved by recording FTIR and XPS spectra of the formed particles (see the SI). The nanoparticles also aggregated strongly in KPF_6 solution as the surface of the PFS−PMMA latexes became more hydrophobic because of the anion exchange.[20]

In conclusion, a new class of redox-responsive organometallic polymers composed of a redox-active PFS main chain and cross-linkable IL side groups was synthesized. By tuning of the concentration of the cross-linkable PFS-PIL in water, nanogel and macroscopic hydrogel structures were successfully prepared. Microemulsion polymerization with PFS-PIL as a surfactant produced stable polymer latex suspensions. Moreover, the redox-responsive behavior of the generated structures was demonstrated.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and additional characterization data (CV, FTIR, TGA, and DSC of **2**; EDX of PFS nanogels; photographs of PFS nanogels dispersed in water after addition of H_2O_2; and FTIR and XPS spectra of PFS−PMMA latexes). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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