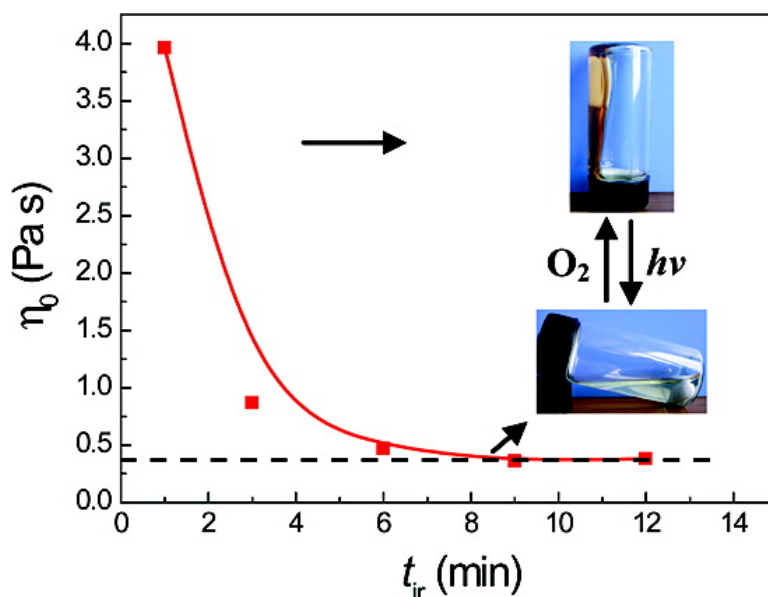


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J. Am. Chem. Soc., **2008**, 130 (48), 16166-16167 • DOI: 10.1021/ja807087z • Publication Date (Web): 11 November 2008

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Redox-Responsive Gel–Sol/Sol–Gel Transition in Poly(acrylic acid) Aqueous Solution Containing Fe(III) Ions Switched by Light

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Polymer gels are considered as a potential “smart” or “intelligent” matter with a specific stimuli-responsive performance. The stimulus includes solvent composition, pH, temperature, addition of salts, electric field, light irradiation, and so on.¹ The three-dimensional network of gels is made of polymer chains cross-linked with chemical junctions and physical interactions.² Up to now, the redox-responsive sol–gel transition in polymer systems has not been reported yet. A few papers concern the sol–gel transition resulting from specific redox reactions of low molecular mass species in organic solvents. Shinkai et al. demonstrated that gelation was induced in some organic solvents by a coordination gelator of a Cu(I)-2,2′-bipyridine derivative complex, in which the gel was turned into sol when the Cu(I) was oxidized to Cu(II).^{3a} Fang et al. showed that some organic solvents were gelled by a low-molecular-mass gelator containing ferrocenyl groups and oxidation of the ferrocenyl group resulted in the gel–sol transition.^{3b} Here, we are reporting a reversible gel–sol/sol–gel transition in poly(acrylic acid) (PAA) aqueous solutions triggered by the redox state of ferric ions conjugated with photoreduction and oxidation. The reversible light-responsive gel–sol/sol–gel transition was observed from some supramolecular organogels containing azobenzene,⁴ stilbene,⁵ or fumaric amide residues.⁶ The cis–trans photoisomerization of the residues connecting to a carbon double bond plays a critical role in this light-switching sol–gel transition.⁷

In the present work, we have developed a redox-responsive gel–sol transition system with an aqueous PAA solution containing an Fe(III)–citrate complex. The gelation of a PAA solution can be induced by trivalent cations, such as Fe(III) and Al(III).⁸ Direct addition of ferric ions into a PAA solution only produces a heterogeneous hydrogel due to the fast binding of Fe(III) to the carboxyl groups. Thus, citric acid was chosen to chelate the ferric ions to slow down the binding rate. The complexation equilibrium constant K_c for Fe(III) and citric acid decreases with decreasing pH.^{9,10} Thus, the ferric ions are gradually released from the complex to form a homogeneous PAA hydrogel at pH 4.0. In this way, a transparent brown PAA hydrogel of Fe/COO (in PAA) = 0.0072 (in mol) was prepared as judged with a tilting tube method. It is interesting that the gel changes to a colorless solution after irradiation with sunlight for several minutes at room temperature. This PAA solution can be recovered to the homogeneous transparent brown gel again after being exposed to oxygen. Figure 1a illustrates the appearance change of the PAA + Fe(III)–citrate system switched by light and oxidation. The hydrogel of the PAA + Fe–citrate system began to flow along the wall of the vial, and the brown color gradually faded after being irradiated for only a few minutes.

This change was followed by the zero shear viscosity η_0 as a function of the irradiation time^{4,11} shown in Figure 2. η_0 sharply decreases with increasing irradiation time at the beginning, which suggests dissolution of the three-dimensional network of PAA due to light irradiation. The final value of η_0 after 12 min of irradiation

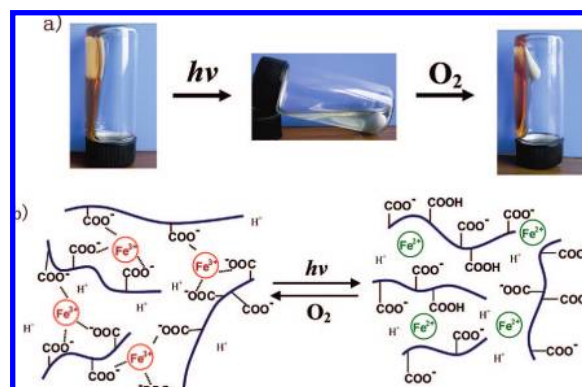


Figure 1. (a) Switching gel–sol–gel transition in PAA (20 wt%) + Fe(III) (0.02 mol/L)–citrate (0.04 mol/L) aqueous system at pH 4.0 and room temperature. A homogeneous hydrogel of PAA + Fe(III) was dissolved into solution after irradiation by simulated sunlight of 80 mW/cm² for 12 min, and then the solution was recovered to a homogeneous hydrogel again after exposure to oxygen in dark for 5 days. (b) Schematic illustration of the gel–sol transition in the PAA + Fe(III)–citrate aqueous system switched by photoreduction and oxidation.

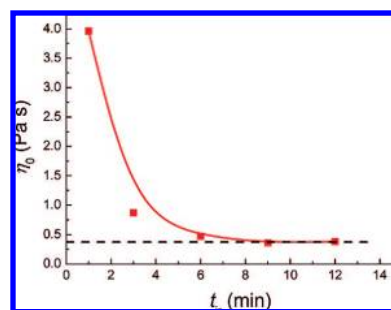


Figure 2. Zero shear viscosity η_0 at 25 °C of the PAA + Fe(III)–citrate system as a function of irradiation time t_{ir} when irradiated by simulated sunlight of 80 mW/cm². The dashed line indicates the η_0 value for the original PAA aqueous solution at the same concentration of 20 wt% without iron ions.

is ~ 0.38 Pa s, which agrees well with that for the original PAA aqueous solution of 20 wt% without iron ions. This confirms that the PAA chains are neither degraded nor connected during irradiation.

The dynamic moduli were monitored within the linear viscoelastic region over this gel–sol–gel transition process.¹² The storage modulus is somewhat higher than the loss modulus with a small slope for the as-prepared PAA + Fe(III) gel, indicating the formation of a weak network due to cross-linking PAA chains with Fe(III) cations. In contrast, for the PAA + Fe(III) gel after irradiation for 12 min, the dynamic moduli show obvious characters of a viscoelastic solution and completely overlap the corresponding data for the original PAA solution, implying the complete dissolu-

tion of the PAA + Fe(III) gel by irradiation. We found from the frequency sweep that this gel dissolution gradually progressed to the solution with increasing irradiation time. For the PAA + Fe(III) gel after irradiation for 12 min and oxidation for 5 days, however, the dynamic moduli recover the same level of the as-prepared PAA + Fe(III) gel, suggesting the PAA chains are cross-linked to a network again after oxidation. The reversible photoswitch of association has been reported for the hydrophobically modified PAA in aqueous systems only involving the photoisomerization of azobenzene residues and irrelevant to the redox activity.^{7,13}

If the Fe(III)–citrate complex was added into the PAA solution at pH < 4.0, more Fe(III) ions were released due to the decrease in the complexation equilibrium constant K_c . This resulted in stronger PAA + Fe(III) gels as known from the storage modulus.

This gel dissolution is due to the photoreduction of ferric ions in the presence of reductive citric acid under sunlight.¹⁴ As schematically illustrated in Figure 1b, the PAA chains in aqueous solution are joined together to form a hydrogel through binding with trivalent ferric ions. When irradiated under sunlight, the Fe(III) ion is reduced to the Fe(II) ion in the presence of citric acid; the latter cannot cross-link PAA chains. The binding affinity of Fe(III) to a carboxyl group is stronger due to the stronger electrostatic attraction of trivalent cations and much lower solubility of Fe(III) carboxylate in water. Therefore, we have observed the dissolution of the PAA hydrogel after irradiation due to the photoreduction of Fe(III) ions. This gel–sol/sol–gel transition switched by light irradiation and oxygen exposure can be repeated if we repeat the photoreduction and oxidation as long as citric acid remains.

Furthermore, variation of the concentration of Fe(II) and Fe(III) ions in the aqueous solution containing citric acid with irradiation time was determined and shown in Figure 3. The Fe(III) concentration sharply decreases and Fe(II) concentration increases within the first 4 min. After 6 min of irradiation, ~90% of Fe(III) ions are reduced to Fe(II) ions and the brown color of the gel turns to light yellow, accompanying dissolution of the PAA gel. Finally after irradiation of the PAA + Fe(III) gel for 12 min, there remains only 0.0010 mol/L of Fe(III) ions and the other 0.019 mol/L of Fe(II) ions are transformed to Fe(II) ions.

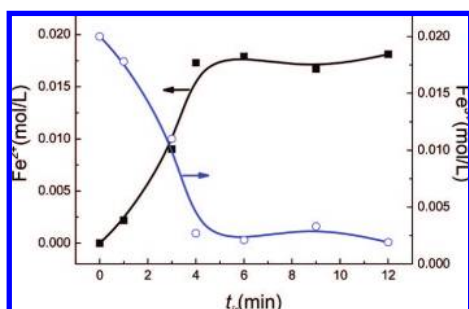


Figure 3. Irradiation time t_{ir} dependence of Fe(II) and Fe(III) concentrations in the Fe(III)-citrate solution of 0.02 mol/L at pH = 4 under simulated sunlight of 80 mW/cm².

Normally, Fe(II) will be oxidized to Fe(III) by air in pH = 4 aqueous solution.¹⁵ When PAA or other chelates are present in the solution, the Fe(II) ion may be bound to form Fe(II)–PAA or other complexes, which will reduce the Fe(II) oxidation rate.¹⁶ Therefore, it took ~5 days to gelate again by exposing to oxygen the dissolved PAA + Fe–citrate aqueous system after irradiation.

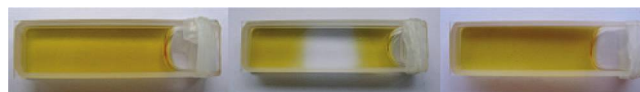


Figure 4. Left: PAA + Fe(III) gel 3 days after preparation. Center: the gel irradiated for 12 min at the center part. Right: the same gel after exposure to oxygen for 5 days.

The phototriggered gel–sol transition makes it possible to photopattern the PAA + Fe(III) hydrogel with the photolithographic technique. Figure 4 depicts an example of the selected gel–sol–gel transition. Only the center part of the gel was irradiated by sunlight and dissolved with color change, which produced a fluid sol phase within the gel matrix. After exposure to oxygen, the solution was transformed to gel again.

In conclusion, we have demonstrated an interesting gel–sol/sol–gel transition in a homogeneous aqueous PAA system containing an Fe(III)–citrate complex by switching the redox states of Fe(III)/Fe(II) ions. When Fe(III) ions in the PAA hydrogel containing citric acid are reduced to Fe(II) by light irradiation, the PAA hydrogel dissolves to solution. The PAA solution can be recovered to the homogeneous hydrogel again by oxidating Fe(II) to Fe(III). This reversible transition is indicated chromatically by the Fe(III) ions and can be repeated many times provided there is enough citric acid. The photochemical or electrochemical control to this transition will be a convenient method. The redox-responsive hydrogel is also promising as a unique material that can encapsulate and localize bioactive molecules and cells within the gel matrix.

Acknowledgment. This work was supported by the NSF of China (20534020 and 50773024).

Supporting Information Available: Experimental details, photoreduction reaction, dynamic moduli, calibration curves for determining the concentration of Fe(III) and Fe(II). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA807087Z