Electronic Supplementary Information (ESI) for Polymer Chemistry

Supporting information

Redox-Induced Temperature Responsive Polymer Solubility

Hui Fu, Danielle Policarpio, James D. Batteas* and David E. Bergbreiter*

Department of Chemistry, Texas A&M University

P.O. Box 30012, College Station, Texas 77842-4719, U.S.A

Table of Contents

Experimental Section

Materials. The chemicals used including 2,2'-azobisisobutyronitrile (AIBN), acryloyl chloride, *N*-hydroxysuccinimide, isopropylamine, 4-amino-2,2,6,6-tetramethylpiperidinoxyl (4-amino-TEMPO), and 4-amino-2,2,6,6-tetramethylpiperidine were obtained from Aldrich and used as received. L-Ascorbic acid (99+ %) and potassium ferricyanide (99+ %) were obtained from Alfa Aesar. The water used in the LCST analyses was obtained from a Milli-Q water purification system.

Synthesis of poly(*N*-acryloxysuccinimide) (PNASI). The *N*-acryloxysuccinimide monomer was prepared from acryloyl chloride and *N*-hydroxysuccinimide following a literature procedure.[1] The PNASI polymer was prepared following a literature procedure.[2] A solution of *N*-acryloxysuccinimide (8.0 g, 47 mmol) and 2,2'-azobisisobutyronitrile (40 mg, 0.24 mmol) in 200 mL of benzene was degassed under positive pressure of N_2 for 1 h. Then the solution was heated to 60° and stirred for 24 h. The resulting mixture was allowed to cool to room temperature. The white precipitate of polymer product which formed was collected by filtration and washed with benzene and THF and dried under vacuum to yield 7.8 g (99 %) of the desired polymer product. ^{1}H NMR (*d*-DMSO) δ 2.05 (bs, 2H), 2.80 (bs, 4H), 3.13 (bs, 1H). ATR-IR (powder) 1813, 1782, 1734, 1204, 1068, 648 cm^{-1}.

Representative synthesis of poly(*N*-isopropylacrylamide)-*c*-poly(*N*-4-amino-2,2,6,6-tetramethyl-piperidineoxylacrylamide) (PNIPAM-*c*-PTEMPOAM) from PNASI. A DMF solution containing the desired molar ratio of isopropylamine and 4-amino-2,2,6,6-tetramethyl-piperidinoxyl (4-amino-TEMPO) was added to a DMF solution of PNASI dropwise. The reaction mixture was allowed to stir under a positive N_2 pressure at ambient temperature overnight. The DMF was then removed from the product under reduced pressure using a rotary evaporator. The polymer isolated after this procedure was redissolved in dichloromethane and the desired polymer was precipitated by addition of anhydrous diethyl ether. After a second dissolution/precipitation using THF as a good solvent and diethyl ether

as the precipitation solvent, the polymer product was isolated by filtration and dried in oven under vacuum overnight.

Synthesis of poly(*N*-isopropylacrylamide)-*c*-poly(*N*-4-amino-2,2,6,6-tetramethylpiperidinylacrylamide) (PNIPAM-*c*-PTEMPAM) Analogue from PNASI. A DMF solution with the molar ratio of isopropylamine and 4-amino-2,2,6,6-tetramethylpiperidine identical to that used for synthesis of the PNIPAM-*c*-PTEMPOAM copolymer above was added dropwise to a DMF solution of the same PNASI used to prepare PNIPAM-*c*-PTEMPOAM. The reaction was allowed to stir under positive N_2 pressure at ambient temperature overnight and then the solvent DMF was removed under reduced pressure. The remaining polymer was redissolved in dichloromethane and the solution was precipitated in ethyl ether anhydrous. The precipitation process was repeated one more time as described for PNIPAM-*c*-PTEMPOAM above and the final polymer product was isolated by filtration and dried in oven under vacuum overnight. The ratio of the piperidinyl/isopropyl groups in this polymer after these two solvent precipitations was analyzed by ^{1}H NMR and was assumed to be the same as that of the PNIPAM-*c*-PTEMPOAM polymer above.

LCST Measurements. An OptiMelt automatic melting point apparatus from Stanford Research Systems was used for all the LCST analyses in this study.[3,4] In a typical experiment, 8 uL of a polymer solution was introduced to a regular capillary melting point tube (Kimble 1.5-1.8 x 90-mm) using a microsyringe and the tube was sealed before placing it into the sample holder. Three sealed sample tubes were placed into the sample holders for simultaneous measurements of their clouding curves using a 0.5 °C/min heating rate. During the heating process, the thermoresponsive polymers underwent a phase transition that changed the optical characteristics of the samples leading to scattering, scattering that in experiments in this paper was found to be enhanced by the addition of 0.1 M Na_2SO_4. This scattering was analyzed using the digital image processing software included with the melting point apparatus to produce a graph of the percent light scattering versus temperature. The resulting usually sigmoidal curve of the extent of clouding and the data for specific scattering percentages (usually at 10%) was then used in our LCST studies.

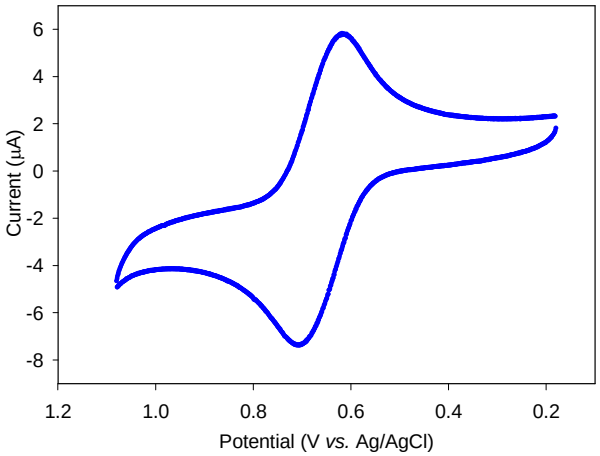

Figure SI-1. Cyclic voltammogram of **2** in aqueous solution measured with a glassy carbon electrode and a Pt wire electrode at 0 °C. The sweep rate is 10 mV/s and the supporting electrolyte was 0.1 M KCl.

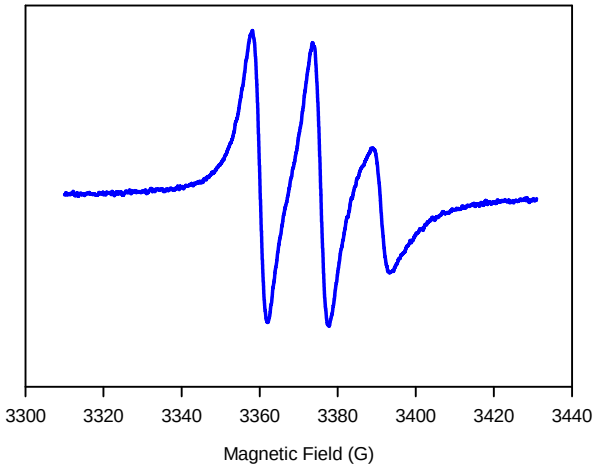

Figure SI-2. Electron spin resonance spectrum of polymer **2** in THF at room temperature.

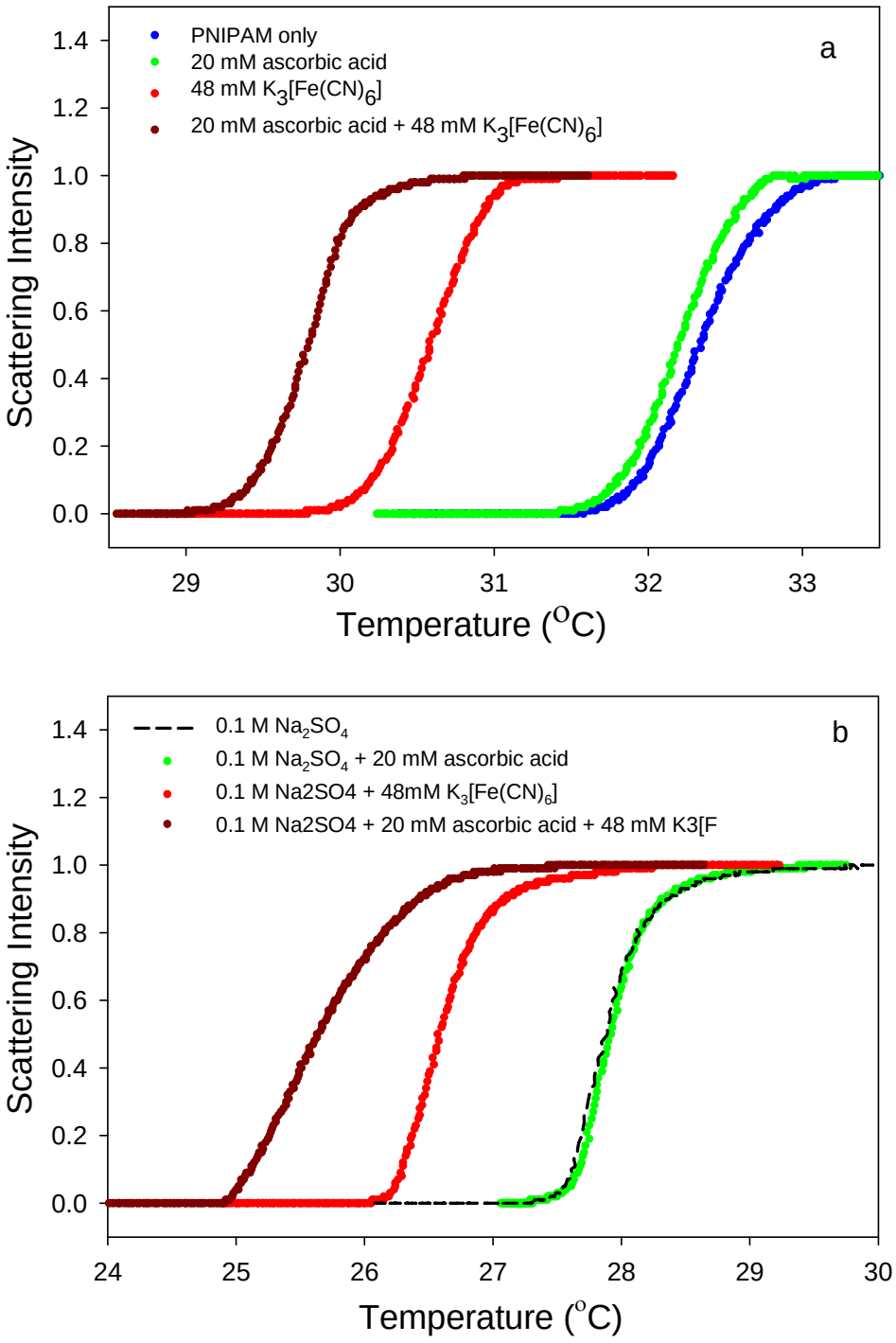

Figure SI-3. Clouding curves of 10 mg/mL PNIPAM sample in the control experiments with ascorbic acid and $K_3[Fe(CN)_6]$: (a) control experiments without addition of 0.1 M Na_2SO_4, (b)control experiments with addition of 0.1 M Na_2SO_4.

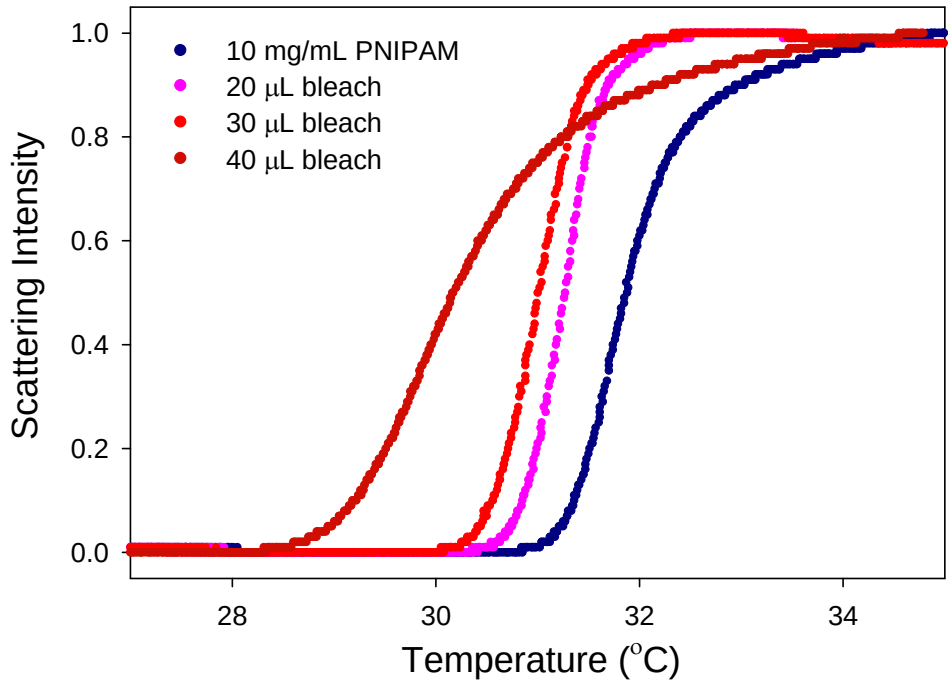

Figure SI-4. Clouding curves of 10 mg/mL PNIPAM sample in the control experiments with varied amounts of bleach.

References:

(1) H.-G. Batz, G. Franzmann, H. Ringsdorf, *Angew. Chem. Int. Ed. Engl.* 1972, **11**, 1103-1104.

(2) S. Furyk, Y. Zhang, D. Ortiz-Acosta, P. S. Cremer, D. E. Bergbreiter, *J. Polym. Sci., Part A: Polym. Chem.* 2006, **44**, 1492-1501.