Supplementary Material (ESI) for Chemical Communications

A thermoreversible ion gel by self-assembly of a triblock copolymer in an ionic liquid

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Experiments

Triblock Copolymer Synthesis. All reagents were used as received unless otherwise noted. 2,2′-Azobis-isobutyronitrile (AIBN) and *N*-isopropylacrylamide (NIPAm) were purchased from Aldrich and purified by recrystallization from methanol and benzene/*n*-hexane (65/35 v/v), respectively. Poly(ethylene glycol) (PEG) was purchased from Polymer Source, Inc. and purified by reprecipitation in *n*-hexane. It has a molecular weight of M_n = 25 kg/mol and a polydispersity of M_w/M_n = 1.10, as characterized by gel permeation chromatography based on PEO standards. *S*-1-Dodecyl-*S′*-(α,α'-dimethyl-α''-acetic acid)trithiocarbonate (CTA) was generously provided by Prof. Marc Hillmyer.[1, 2]

The first step is to prepare the CTA-PEO-CTA macroinitiator. Oxalyl chloride (0.11 ml, 1.3 mmol) and CTA (0.095 g, 0.26 mmol) were mixed in dry CH_2Cl_2 (5 ml) under nitrogen atmosphere and stirred at room temperature until gas evolution stopped (~ 2 h). Excess reagents were then removed under vacuum, and the residue was redissolved in dry CH_2Cl_2 (15 ml), followed by the addition of PEG (1.25 g, 0.05 mmol). The reaction was allowed to proceed for 24 hours at room temperature, after which the contents were precipitated in *n*-hexane and dried in a vacuum oven. Yied = 1.07 g (86%). ^{1}H NMR: conversion > 90%.

Then CTA-PEO-CTA macroinitiator (1.0 g), NIPAm (1.0 g), AIBN (2.7 mg), and DMF (15 ml) were placed in a high-pressure glass reactor, bubbled with argon for 20 min, sealed, and placed in an oil bath at 60 °C. After 2 h, the reaction was stopped by quenching to 0 °C. Most of the DMF were removed under vacuum. The residual mixture were diluted with CH_2Cl_2 and precipitated in *n*-hexane. ^{1}H NMR: NIPAm conversion ≈ 12%

Ion Gel Preparation. The ion gel were made by mixing weighed amounts of PNIPAm-PEO-PNIPAm triblock copolymer and [EMIM][TFSI] ionic liquid, and adding CH_2Cl_2 as a cosolvent.

After stirring the mixture for 2 h, the cosolvent was removed by evaporation at ambient temperature for 24 h, followed by placing in a vacuum oven at 70 °C until constant weight was achieved. To avoid effect from moisture, in the following experiments, all ion gel samples were subjected to vacuum pumping before measurements until no further weight loss was detected.

Ionic Conductivity Measurements. The ionic conductivity was determined in a home-made cell by means of impedance measurements using a Solartron 1255B Frequency Response Analyzer at an AC amplitude of 10 mV. The frequency range employed for the measurements was typically 1 MHz to 1 Hz. The cell was made of two stainless steel discs (electrodes) separated by a Teflon spacer. It has a defined volume with 7 mm inner diameter and 2 mm inner depth. The measured samples were filled in the cell, which was then enclosed in a sealed Teflon bag and immersed in a thermostatted water bath. The temperature was controlled to within ± 0.5 °C of the set point. All samples were thermally equilibrated at each temperature for 20 minutes prior to the measurements. The cell constant was calibrated before and after each experiment using a KCl conductivity standard solution purchased from Sigma-Aldrich.

Rheology. Oscillatory shear measurements were performed on a RFS II (Rheometric Fluids Spectrometer) and ARES (Rheometric Scientific) rheometers using the parallel plate geometry. Both 50 and 25 mm diameter plates were employed, depending on the amplitude of modulus. A gap spacing of approximately 1 mm was used for all measurements. The gap was adjusted at each temperature to compensate for the thermal expansion of the tool set. The frequency dependences of dynamic storage (G') and loss (G'') moduli were examined in the linear viscoelastic regime (pre-determined at each temperature). The temperature dependences of G' and G'' were measured with a strain amplitude of 5%, a frequency of 0.1 rad/s, and a heating rate of 0.5 °C/min. Temperature were controlled to within ± 0.2 °C of the set points.

References and Notes

1. J. Rzayev and M. A. Hillmyer, *J. Am. Chem. Soc.*, 2005, **127**, 13373-13379.

2. J. T. Lai, D. Filla and R. Shea, *Macromolecules*, 2002, **35**, 6754-6756.