Supporting information

Micellization Coupled with Facilitation of J-Aggregation for Poly(1,3-Cyclohexadiene)-Based Amphiphilic Block Copolymers

Jiaping Lin,*[a] Weiwei Ding, [a] Kunlun Hong,*[b] Jimmy W. Mays,[b,c] Zhongde Xu,[a] and

Yizhong Yuan[a]

[a]Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China

[b]Center for Nanophase Materials Sciences and Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

[c]Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA.

Supplementary information 1

Experimental Procedures

1. Synthesis of PS-*b*-PCHD block copolymers.

All polymerizations were carried out under high vacuum, in *n*-Butyllithium (*n*-BuLi) washed and benzene rinsed all-glass reactors, using breakseal and constriction techniques. *sec*-BuLi was the initiator, benzene was the solvent, and 1,4-Diazabicyclo[2.2.2]octane (DABCO) was used as polar modifier in appropriate ratios ([*sec*-BuLi]/[DABCO] = 1/1.5). All polymers were made by sequential addition of monomers, where 1,3-CHD was always added last.

In a typical polymerization procedure, PS⁻Li⁺ with targeted M_n = 7600 was synthesized by reacting 18.0 mL of styrene (16.4 g, 157.7 mmol) with 3.1 mL *sec*-BuLi (0.69 M, 2.14 mmol) in 175 mL of C_6H_6 for overnight. About 2 mL of the living polymer solution was sampled for characterization. After adding 9.8 mL DABCO solution in benzene (0.33 M, 3.23 mmol), the PS⁻Li⁺/DABCO solution was reacted with 7.3 mL 1,3-cyclohexadiene(6.1 g, 76.3 mmol). The polymerization continued for ~8 hrs and was terminated with about 1 mL methanol. The polymer solution was precipitated in ~ 7-fold excess of methanol. The polymer was collected and dried under high vacuum. The yield was quantitative.

2. Sulfonation of PS-*b*-PCHD block copolymers.

A typical sulfonation procedure is as follows. In a 500 mL two-neck flask, 5.5 mL melted SO_3 in 20 mL dry CH_2Cl_2 was added dropwise to a solution of 17.3 mL dry 1,4-dioxane in 100 mL CH_2Cl_2 and the solution was stirred for 30 min at 0 °C (ice bath). Still at ice bath temperature, 6.2 g of PS-*b*-PCHD with PCHD content of 28.7 wt% (dissolved in $CHCl_3$) was added slowly. The solution was stirred for 4 h. $NaHCO_3$ was added slowly to quench the reaction and then all solvents were removed by evaporating under reduced pressure. The residue was dialyzed against deionized water for 7 days using Spectrum cellulose ester dialysis membrane tube (1000 molecular weight cut-off). Dry samples of the polymers were obtained by freeze-drying.

3. Characterization of PS-*b*-sPCHD block copolymers.

The PS-*b*-PCHD block copolymers were characterized via size exclusion chromatography (SEC) equipped with refractive index and light scattering detectors (Polymer Laboratories PL-120 size exclusion chromatography system equipped with two PL-gel 10 mm MIXED-B columns, chloroform as the eluent at a flow rate of 1 mL min^{-1}, and a Precision Detectors PD-2040 Two-Angler Laser Light Scatter Detector) and ^{1}H-NMR spectra (Bruker Advance 400) in CDCl$_3$. The specific refractive index increments (dn/dc) of the copolymers were measured in CHCl$_3$ at 25 °C using an OPTILAB DSP refractometer (Wyatt Technology, 690 nm).

The degree of sulfonation was calculated from elemental analysis results (performed at Galbraith Laboratories, Inc. Knoxville, TN) by taking into account the relative masses of atoms in a monomer unit: sulfonation % = (72/32) × (%S/%C) × 100%. As schematically represented in Scheme 1, the sulfonation of PCHD blocks yielded two products: one in which the C=C bonds were regenerated and the other one contains saturated C-C bonds. The molecular structure of the sulfonated products was estimated from solid state ^{1}H-NMR (substituted alkene product (80 mol %), and addition product (20 mol %)), since ^{1}H or ^{13}C NMR spectra in solution only yielded very broad peaks due to strong aggregations.

4. Preparation of micelle solutions.

Micelle solutions were prepared by first dissolving PS-*b*-sPCHD in dimethyl sulfoxide (DMSO) to give a stock solution of 8 g/L, and then adding 5 wt% deionized water to the copolymer solution at a rate of 1 drop every 8-10 s with vigorous stirring. The obtained micelle solution was kept at 35 °C for 24 h to reach equilibrium, then dialyzed against deionized water using dialysis tubing (3500 molecular weight cut-off) to remove the organic solvent for one week at room temperature.

5. Measurements.

The morphologies of the micelles were observed by TEM (JEM-1200-EX11). Drops of micelle solution were place on a carbon film coated copper grid, and then were dried at

room temperature. The TEM bright field imaging was performed with 120 KV accelerating voltage.

For laser light scattering, a commercial LLS spectrometer (ALV/SP-125) equipped with a multi-tau digital time correlator (ALV-5000) and a solid state laser (ADLAS DPY425, output power $\approx$ 400 mV at λ = 632.8 nm) was used. All the measurements were carried out at 25 °C. In static LLS, the angular dependence of the excess absolute time-average scattered intensity, i.e., Rayleigh ratio $R_{vv}(q)$ of a dilute dispersion leads to the root-mean square z-average radius of gyration $\langle R_g^2 \rangle^{1/2}$ (or simply $\langle R_g \rangle$), where $q = 4\pi n \sin(\theta/2)/\lambda$ is the scattering vector as a function of scattering angle θ, n is the refractive index of the solution, and λ is the wavelength of the incident beam. In dynamic LLS, the Laplace inversion of a measured intensity-intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode could result in a line-width distribution $G(\Gamma)$. For a pure diffusive relaxation, $(\Gamma/q^2)_{q\to 0,\ c\to 0}$ can lead to hydrodynamic radius R_h by the Stokes-Einstein equation $R_h = k_B T/(6\pi\eta D)$, where k_B is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent, and D is the translational diffusion coefficient (given by the slope of the Γ vs q^2 plot).

The fluorescence spectra of PS-b-sPCHD in aqueous solutions with various copolymer concentrations were recorded at 25 °C on a Fluorolog-3-P fluorescence spectrophotometer (Jobin Yvon Inc., France). The excitation and emission wavelengths were 377 nm and 412 nm for the emission and excitation measurements, respectively. The slit widths for both excitation and emission were 1 nm.