SUPLEMENTAL INFORMATION

Diffusion of Labeled Polyelectrolyte Probes in

Unlabeled Polyelectrolyte Matrix Solutions

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Supplemental Information

Experimental

Materials. Fluoresceinamine isomer I was bought from Sigma-Aldrich. Dimethyl sulfoxide (DMSO) and methanol were bought from Fisher Scientific. NaPSS samples were purchased from Polysciences, Inc. or Sp^2, Inc.

Nondialyzed NaPSS is known to contain a certain amount of sodium sulfate.[1] Purification with ionic exchange resin, followed by titration with 1.0 M NaOH, rotary evaporation at 60°C and oven-drying under vacuum were performed on NaPSS-990000. The details were reported in our earlier paper.[2] Unless otherwise indicated, freeze-dried NaPSS powder was used in the preparation of FPR samples.

Labeling. LNaPSS-6500, LNaPSS-70000, LNaPSS-100000, LNaPSS-170000, LNaPSS-350000 and LNaPSS-680000 were obtained through a two-step reaction, chlorination of narrowly distributed NaPSS in POCl$_3$ followed by the attachment of fluoresceinamine isomer 1 (Aldrich). Chlorination can be achieved with a PCl$_3$/POCl$_3$ mixture[3] or pure[4] POCl$_3$. A higher efficiency of chlorination was reported[4] with PCl$_3$/POCl$_3$ mixture than POCl$_3$. Pure POCl$_3$ was chosen because a low efficiency of chlorination will lead to the desired light labeling and minimal disturbances to the NaPSS chain. The detailed procedure was reported earlier.[4] LNaPSS-167000 was obtained from fractionation of LNaPSS-70000. The details of fractionation and characterization were explained earlier.[4] On the basis of a previous investigation using this method of dye attachment, or another using a different approach,[5] it seems unlikely that light labeling ($\cong 0.24\%$ of monomer units) altered the random coil nature of the NaPSS chains, at least in the presence of added salt.

Preparation of FPR samples. Two approaches to sample dissolution were tried, leading to different results. In the first and better of the two (Method 1), LNaPSS-7000, LNaPSS-100000 and LNaPSS-680000 were dissolved in Nanopure[TM] water (Barnstead Int'l.) for at least 48 hours. These solutions were used as pseudosolvents for the NaPSS-990000 matrix. The required amount of NaPSS-990000 was dissolved with pseudosolvent and the samples were slowly rotated with a homemade sample rotor at a speed of 1~2 rpm at room temperature for 48 hours to ensure good mixing.

For one sample at the very high matrix concentration of 167 mg NaPSS/g of water, pseudosolvent (LNaPSS solution) was added to concentrated NaPSS-990000 solution, which was obtained directly from purification with ion exchange and concentration with a rotary evaporator. Drying was avoided to ensure molecular dispersion of NaPSS-990000. The concentration of NaPSS-990000 (174 mg/g) was determined with UV-Vis absorbance as described previously.[2] The solution was mixed with a homemade sample rotor at a speed of 1~2 rpm for 24 hours. All other experimental conditions were the same as above.

Another group of experiments with LNaPSS-70000, LNaPSS-170000 and LNaPSS-350000 was performed using a dissolution method judged to be less effective (Method 2). Instead of using the stock solution of LNaPSS to dissolve the matrix for the entire concentration range as described above, the stock solution of LNaPSS was only used as a pseudosolvent to prepare the first sample. After stirring with a magnetic stirring bar at room temperature for a few hours, a small amount of the sample was taken out for the FPR experiment. The amount of NaPSS-990000 powder required for the next

higher concentration was added directly into the remaining sample. The same procedure

was repeated until a certain concentration of matrix was reached.

As thermal analysis indicates that there are two water molecules bound with each

NaPSS unit,[6] the concentration of LNaPSS or NaPSS-990000 matrix is expressed as the

concentration of NaPSS without the bound water molecules.

Results

Log-log version of Figure 1 of main document.
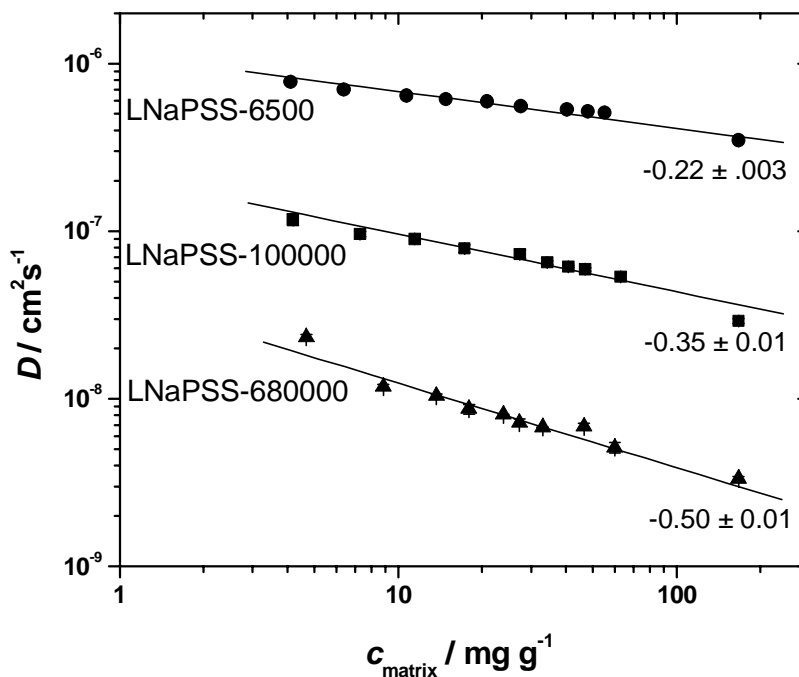
Supplemental Figure 1. Log-log companion to Figure 1 of the main document.
The magnitude of the slope for LNaPSS-100000 slightly exceeds that estimated in
Figure 2 of the main document because an extra data point at higher concentration
appears here.

Effect of Dissolution Procedure. The self-diffusion coefficients of LNaPSS-70000, LNaPSS-170000 and LNaPSS-350000 in NaPSS-990000 at low added salt, when prepared by Method 2, which allowed insufficient time for equilibration, decrease with added matrix concentration but then level out. Although the diffusion values were very different in water, as expected for the molecular weight range, they all converged to about $(3.3 \pm 0.6) \times 10^{-8}$ cm$^2\cdot$s^{-1} when c_{matrix} exceeded about 4 mg$\cdot$mL^{-1}. Thus, the molecular weight dependence of diffusion was severely diminished by the addition of sufficient matrix. This is the result one would expect if many L-NaPSS probes were tied up over long periods of time in aggregates, and the diffusion value is approximately consistent with the temporal aggregates described in the literature. Perhaps this is coincidental; while temporal aggregates do sometimes exhibit interesting time-dependent behavior, they have been monitored for long periods of time in DLS studies.[7]

Reference List

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