Fluorescence and Light-Scattering Studies on the Formation of Stable Colloidal Nanoparticles Made of Sodium Sulfonated Polystyrene Ionomers

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ABSTRACT: The lightly sulfonated polystyrene ionomer is only soluble in some organic solvents, such as toluene and tetrahydrofuran (THF). The mixture of its organic solution with water normally leads to macroscopic phase separation, namely precipitation. In this study, using the steady-state fluorescence, the nonradiative energy transfer and dynamic laser light scattering, we demonstrate that the sulfonated polystyrene ionomers can form stable colloidal nanoparticles if the THF solution of the ionomers is dropwisely added into an excessive amount of water, or vice verse, water is added in a dropwise fashion into the dilute ionomer THF solution under ultrasonification or fast stirring. The hydrophobic core made of the polystyrene backbone chains is stabilized by the ionic groups on the particle surface. Such formed stable nanoparticles have a relatively narrow size distribution with an average diameter in the range of 5–12 nm, depending on the degree of sulfonation, the initial concentration of the ionomer THF solution, and the mixing order. This study shows another way to prepare surfactant-free polystyrene nanoparticles. © 1997 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 35: 1593–1599, 1997

Keywords: laser light scattering; fluorescence; surfactant-free colloid; nanoparticle; polystyrene ionomer

INTRODUCTION

The association/dissociation of ionomers in nonpolar and polar solvents have been a focused issue for more than 10 years, and the lightly sulfonated polystyrene (SPS) ionomer was usually chosen as a model compound.[1–8] In nonpolar solvents, such as tetrahydrofuran (THF) and xylene, the ionic groups are not completely dissociated, but exist as solvated ion-pairs, which form electric dipoles. The attraction between the electronic dipoles and the repulsion between the dipoles and the hydrocarbon backbone chain lead to the aggregation of the dipoles and the consequent association of the ionomers, which has been experimentally confirmed by rheology, light scattering, small-angle neutron scattering, and fluorescence.[9–16] When dissolving in a polar solvent, such as dimethylformamide (DMF), the ionomer chains in solution behave like polyelectrolytes. All phenomena related to the aggregation in nonpolar solvents disappear because of the dissociation of the ion-pairs.[17–20] On the other hand, the study of the S-PS in aqueous solutions has attracted much less attention because of the poor solubility of its hydrophobic backbone in water. Recently, Jiang et al.[21] reported that the carboxylated poly(styrene-

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block-butadiene-*block*-styrene) triblock copolymer ionomer (SEBS) can form stable colloidal particles in aqueous solution if a dilute THF solution of the ionomer is added in a dropwise fashion into an excessive amount of water. In the present work, fluorescence together with laser light scattering were used to demonstrate that the randomly sulfonated polystyrene ionomers can also form stable colloidal particles in water. The emphasis of this study will be on how the formation of the stable nanoparticles depends on the degree of sulfonation, the method of preparation, and the initial concentration of the ionomer THF solution used in the preparation.

EXPERIMENTAL

Materials

The preparation of sodium sulfonated polystyrene ionomers has been done as described previously.[9] The sulfonation extents were calculated based on sulphur analysis. Three samples were used in this study. Two of them are made by free radical polymerization. The samples are soluble in THF to form a stable solution. The apparent weight-average molar mass of these two ionomers in THF were 2.8×10^5 and 3.1×10^5 g/mol, respectively, which are close to the values before the ionomerization, indicating that the ionomerization did not alter the length of polymer chains. The extents of sulfonation of these two samples are 3.67 and 5.52 mol %, respectively. The third sample was made by anionic polymerization. Its weight-average molar mass and extent of sulfonation are 3.1×10^5 g/mol and 5.23 mol %, respectively. According to the extent of sulfonation, these samples are denoted as 3.67 NaSPS, 5.52 NaSPS, and 5.23 NaSPS hereafter.

Preparation of the NaSPS Nanoparticles

First, each ionomer was dissolved in tetrahydrofuran (THF) to form a solution with a concentration of 2×10^{-2} g/mL or less. Using the THF solution, the stable dispersion of NaSPS in water was made by adding the THF solution in a dropwise fashion into an excessive amount of water under ultrasonification or magnetic stirring. The dispersion contains 1 v % THF and the final ionomer concentration is 2×10^{-4} g/mL or less. Such prepared dispersion is transparent and stable. Further, the dispersion was diluted to a series of desired concentrations with deionized water containing 1 v % THF for fluorescence and light-scattering measurements. The dispersion can also be prepared by very slowly (one drop per minute for the first 10 mL of water) adding 99 mL deionized water into 1 mL ionomer THF solution under fast stirring.

Fluorescence Measurements

The steady-state fluorescence was measured using a Perkin–Elmer Luminescence Spectrometer LS50 with a right-angle geometry (90° collecting optics). The excitation and emission slits were 5 and 3 nm, respectively. Pyrene and naphthalene/anthracene were respectively used here as a fluorescence probe and a pair of donor/acceptors to study the aggregation of the ionomer chains in water. The pyrene concentration was $6 \times 10^{-6} M$. The naphthalene and anthracene concentrations were 2×10^{-5} and $1 \times 10^{-5} M$, respectively. The solutions were ultrasonificated for at least 10 min to ensure a complete dispersion of the fluorescence probe molecules. Then, the solutions were allowed to stand at room temperature for at least 12 h before the fluorescence measurements. The excitation wavelength for the pyrene and the nonradiate energy transfer (NRET) studies are 335 and 275 nm, respectively. The excitation spectra of pyrene were recorded with the emission wavelength of 390 nm.

Laser Light Scattering (LLS)

A commercial LLS spectrometer (ALV/SP-150, Germany) equipped with an ALV-5000 multi-τ digital correlator and a solid-state laser (ADLAS DPY425II, Germany; output power ≈ 400 mw at λ = 532 nm) as the light source was used. The incident light beam was vertically polarized with respect to the scattering plane. The detail of LLS instrumentation and theory can be found elsewhere.[22,23] All LLS measurements were done at 25.0 ± 0.1°C. All samples used in the LLS measurements were clarified by 0.2 μm Anotop filter. The measured time correlation functions were analyzed by both the cumulants and Laplace inversion (CONTIN) programs equipped with the correlator.

RESULTS AND DISCUSSION

Evidence of the Formation of Nanoparticles

Pyrene, as one of the most sensitive probes, has been widely used to study the association and mi-
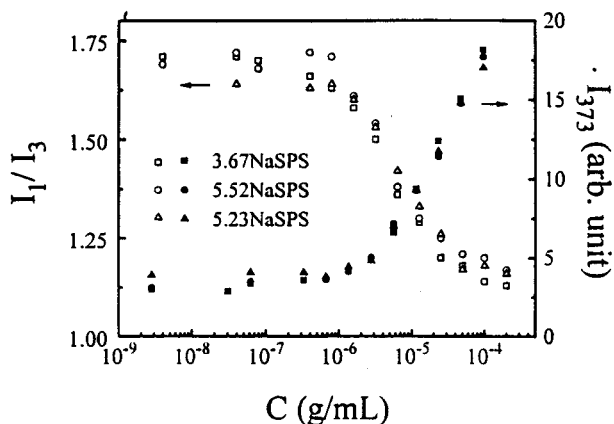
Figure 1. Ionomer concentration dependence of the fluorescence intensity (I_{373}) and the intensity ratio of (I_1/I_3) of pyrene in different NaSPS ionomer dispersions.

cellization of macromolecules in solution because of the remark changes of its photophysical and other properties when it is transferred from a polar environment to a nonpolar one,[24-28] such as an increase in the quantum yield, a change in the fine vibrational structure reflected in the intensity ratio (I_1/I_3) of the first and third bands in its emission spectrum, and a shift of the low energy band of the $L_a(S_2-S_0)$ transition from 333 to 338 nm in its excitation spectrum.

Figure 1 shows typical ionomer concentration dependence of the fluorescence intensity (I_{373}) and the intensity ratio of I_1/I_3 in the pyrene emission spectrum. The enhancement of the fluorescence intensity shows that the quantum yield of pyrene increases as the ionomer concentration increases. For a constant pyrene concentration, the increase in the quantum yield indicates the variation of polarity around pyrene. On the other hand, the increase of I_{373} also reflects a longer life time of the excited state of pyrene, indicating a change in the local environment of pyrene.[25] In the low concentration range, the fluorescence intensity I_{373} of pyrene is nearly a constant, but when the ionomer concentration is higher than 3×10^{-6} g/mL, the intensity rapidly increases as the ionomer concentration increases, indicating the partition of pyrene between water and the hydrophobic microdomain, i.e., between inside and outside of the aggregates of the polystyrene backbone chains.

On the other hand, the intensity ratio I_1/I_3 of pyrene is also sensitive to the polarity of the medium. The ratio can change from a value of $\sim$ 1.8 in water to $\sim$ 1.0 in anionic surfactant micelles or even 0.62 in cyclohexane.[26] Figure 1 shows that the intensity ratio is $\sim$ 1.7 when the ionomer con-

centration is extremely dilute, indicating that most of the pyrene molecules are surrounded by water molecules. When the ionomer concentration is higher than 10^{-6} g/mL, the ratio starts to decrease, very similar to the change of I_{373}. A plateau value of $\sim$ 1.1 at the ionomer concentration higher than 1×10^{-4} g/mL indicates the complete transference of pyrene molecules from water to the hydrophobic environment of the colloidal particles. The plateau value of I_1/I_3 is not as low as 0.95 measured in bulk polystyrene, which is reasonable because the collapsed polymer chain might still containing some water molecules.[29] Figure 1 shows that the type of sample, the polydispersity of molar mass, and the extent of sulfonation have nearly no effect on the aggregation behavior observed in fluorescence.

Moreover, we found that for all of the three NaSPS ionomers in aqueous solution the (0,0) band of the S_2-S_0 absorption of pyrene is shifted $\sim$ 5 nm to red, indicating the aggregation of the ionomer chains because in a micelle system the red shift is 2–3 nm in comparison with that in pure water.[24,26] Wilhelm et al.[26] reported that the intensity ratio I_{338}/I_{333} of the pyrene excitation spectra could give additional information on the onset of block copolymer aggregation because pyrene in water has a maximum absorption at 333 nm, and its absorption at 339 nm is very weak. In contrast, the absorption of pyrene in a less polar solvent at 339 nm increases substantially. Therefore, the shift of the maximum absorption peak and the concentration dependence of the I_{338}/I_{333} ratio are also very sensitive to the formation of a hydrophobic domain.

Figure 2 shows the ionomer concentration dependence of the intensity ratio I_1/I_3 of the emission spectra and the intensity ratio I_{338}/I_{333} of the excitation spectra of pyrene in the 3.67 NaSPS dispersion prepared by different methods: (1) adding the THF solution ($C_{initial} = 2 \times 10^{-2}$ g/mL) into water; (2) diluting the THF solution to $C_{initial} = 2 \times 10^{-3}$ g/mL and then adding it into water; (3) adding water to the THF solution ($C_{initial} = 2 \times 10^{-3}$ g/mL). The decrease of I_1/I_3 and the increase of I_{338}/I_{333} further indicate the formation of colloidal particles. The turning point of the I_{338}/I_{333} curve is close to that of I_{373} and I_1/I_3 shown in Figure 1. At the extremely dilute ionomer concentration, the ratio of I_{338}/I_{333} is only $\sim$ 0.5, characterizing pyrene in pure water. When the ionomer concentration is higher than 3×10^{-6} g/mL, the ratio of I_{338}/I_{333} starts to increase. The plateau value of I_{338}/I_{333} at the high ionomer concentration is typical for pyrene in a hydrophobic environ-
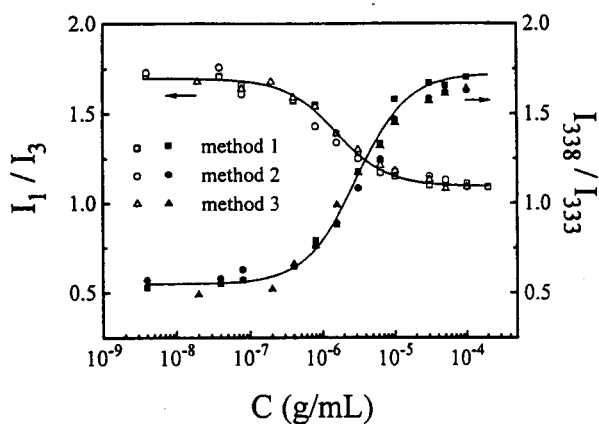
Figure 2. Ionomer concentration dependence of the intensity ratio (I_1/I_3) of the emission spectra and the intensity ratio (I_{338}/I_{333}) of the excitation spectra of pyrene in the 3.67 NaSPS dispersion prepared by different methods.

Figure 4. Typical hydrodynamic radius (R_h) distributions of the stable colloidal dispersion made of different NaSPS ionomers. The ionomer concentration in the dispersion was kept at 2×10^{-3} g/mL for all dispersions.

ment, indicating the formation of colloidal particles in aqueous solution. It is clear that the preparation method has little effect on the aggregation of the ionomer chains. Further, the nonradiative energy-transfer (NRET) technique was also used to confirm the formation of stable colloidal particles in aqueous solution.

Figure 3 shows the ionomer concentration dependence of the efficiency of the NRET between naphthalene and anthrance (I_a/I_d). According to the NRET theory, if the emission spectrum of a donor molecule overlaps the absorption spectrum of a acceptor molecule, the NRET will happen due to the dipole–dipole interaction between the donor in its excited state and the acceptor in its ground state leads to the emission spectrum of
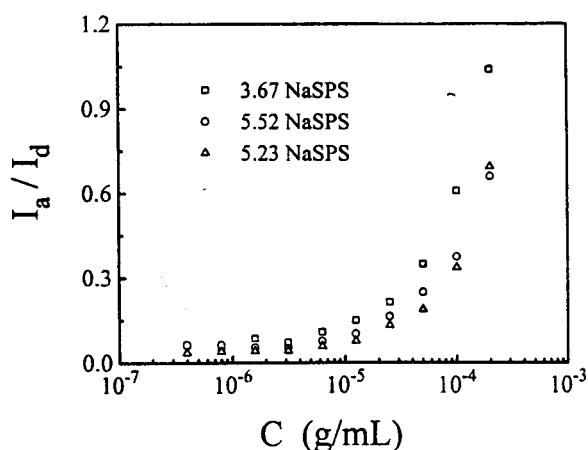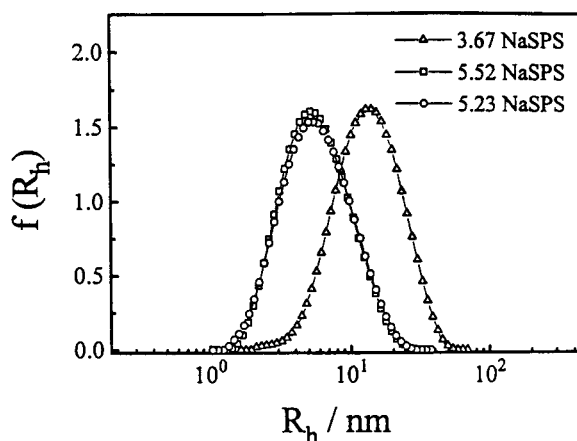
the acceptor. The energy transfer efficiency (E) is directly related to the average distance (R) between donor and acceptor by $E = R_0^6/(R_0^6 + R^6)$, where R_0 is the distance at which 50% of the energy transfer takes place. For a given donor/acceptor pair in a given medium, R_0 is a constant. Experimentally, the efficiency of the NRET is characterized by the intensity ratio of I_a/I_d in the emission spectrum. Figure 3 shows that in the low ionomer concentration range the NRET efficiency between naphthalene and anthrance is very low. When the ionomer concentration is higher than 1 $\times 10^{-5}$ g/mL, I_a/I_d starts to increase, indicating the formation of a hydrophobic microdomains and the partition of naphthalene and anthrance in the hydrophobic microdomains. It has been noted that the concentration at which I_a/I_d starts to increase is $\sim$ 10 time higher than that detected by using pyrene as a probe. This is understandable because the solubility of naphthalene in water is much higher than that of pyrene and only when naphthalene concentration in the hydrophobic microdomain is higher than a certain value can the energy transfer takes place. Figure 3 also shows that the samples with a lower sulfonated degree have a larger NRET efficiency and I_a/I_d starts to increase at a lower concentration, which agrees well with the fact that the polystyrene ionomer with a lower degree of sulfonation is more hydrophobic. Dynamic light scattering as a powerful analytical tool can be used to directly determine the size distribution of the colloidal particles.

Figure 4 shows typical apparent size distributions of the stable colloidal particles made of different sodium sulfonated polystyrene ionomers. It
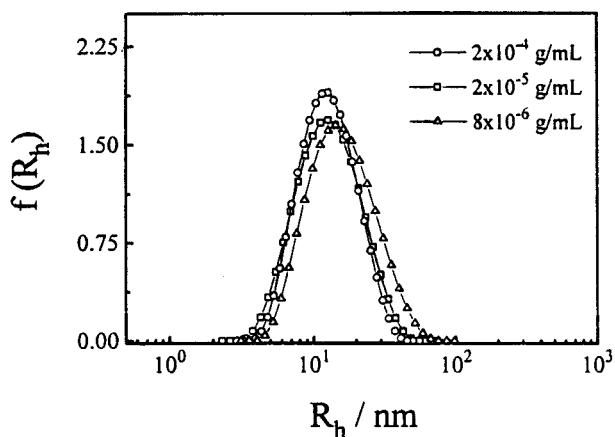

Figure 3. Ionomer concentration dependence of the NRET efficiency between naphthalene and anthrance (I_A/I_d) in different NaSPS dispersions.

Figure 5. Typical hydrodynamic radius (R_h) distributions of the stable colloidal dispersion made of the 3.67 NaSPS ionomer after a successive dilution.

clearly shows that the particles formed through the hydrophobic aggregation of the ionomers in water are very small in the nanometer range and the size distribution is fairly narrow. The more important point is that the average particle size depends on the degree of sulfonation, namely, the higher the degree of sulfonation, the smaller the average particle size, which agrees well with our previous study of the carboxylated ionomers.[30] In static light scattering, we found that the weight-average molar masses of the 3.67 NaSPS, 5.52 NaSPS, and 5.23 NaSPS nanoparticles are 3.9 × 10⁵, 2.9 × 10⁵, and 3.3 × 10⁵ g/mol, respectively, indicating these nanoparticles are nearly made of a single ionomer chain.

Figure 5 shows a successive dilution of the 3.67 NaSPS dispersion in the range of 8 × 10⁻⁶–2 × 10⁻⁴ g/mL has nearly no effect on the particle size distribution. On the one hand, Figure 5 indicates the effect of the ionic interaction on the measured particle size distribution is not significant. Otherwise, the increase of the interparticle distance due to the dilution will decreases the ionic interaction and affect the measured size distribution. On the other hand, Figure 5 shows that the nanoparticles stabilized by the ionic groups on the surface are very stable and they are very different from simple aggregation, namely there is no equilibrium between individual chains and particles. It should be noted that it is difficult to determine the particle size distribution for such small nanoparticles when the concentration is lower than 10⁻⁵ g/mL. In contrast, the intensity ratio of $I_1/$ I_3, I_{338}/I_{333} and I_a/I_d show substantial variations over the same concentration range.

A combination of the LLS and fluorescence re-

sults leads us to the following picture: it is not difficult to realize that when the ionomer THF solution was added into water in a dropwise fashion the hydrophobic polystyrene backbone chains start to collapse, in which the ionic groups will have a tendency to stay at the surface of the interchain aggregates. Assuming these aggregates are spherical with an average radius of R, we have that the particle surface area (S) is proportional to R^2. On the other hand, the number (N_{ionic}) of the ionic groups should be proportional to the number of the ionomer chains incorporated inside the particle, or equivalent, to the particle mass (M). Therefore, assuming all the ionic groups are on the particle surface, $S/N_{ionic} \propto R^2/M \propto R^{-1}$ because $M \propto R^3$, where S/N_{ionic} represents the average surface area occupied by each ionic group. During the aggregation, the size of the particles increases, so that S/N_{ionic} decreases. Eventually, the particles will be stabilized by the ionic groups on the surface because for a given polymer/solvent system S/N_{ionic} should has a minimum value that corresponds to a fully covered surface by the ionic groups. Therefore, diluting the dispersion has no effect on the particle size, but the relative amount of the particles. When the concentration is lower than 10^{-7} g/mL, the value of I_1/I_3 remains ~ 1.7, which is typical for pyrene in aqueous media. However, we still cannot exclude the possibility of the existence of the hydrophobic microdomains because the ionomer concentration is extremely low, even if the ionomer chains could form the hydrophobic microdomains rather than existing as individual chains. The relative amount of pyrene in the microdomains might not be high enough to make a detectable change in I_1/I_3. The LLS study in this extremely dilute range is also very difficult, but still undergoing, which might be able to provide evidence to answer this question.

Effect of Dialysis on the NaSPS Nanoparticles

In order to remove the 1 v % THF introduced in the preparation, the dispersion was dialyzed for 1 week. Figures 6 and 7 indicate that the dialysis has nearly no effect on the stability of the colloidal particles in water; namely, there is no change in the minimum value of I_1/I_3, the concentration at which the ratio of I_1/I_3 starts to drop, and the particle size distribution. These results in Figures 6 and 7 imply that there is no strong preferential adsorption of THF inside the colloidal particles. Otherwise, the removal of THF would change the hydrophobility inside the particle and alter the
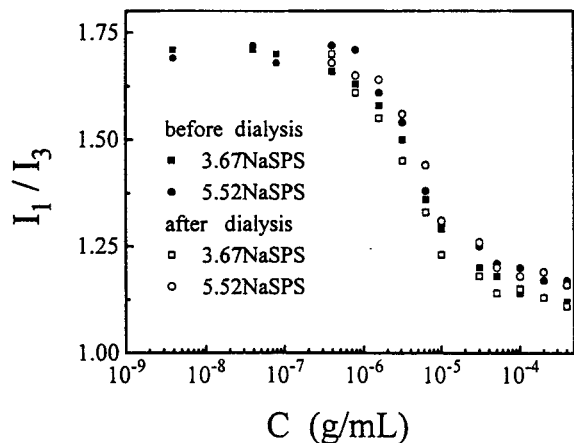
Figure 6. Concentration dependence of the intensity ratio I_1/I_3 of pyrene in the 3.67 NaSPS ionomer dispersion before and after 1-week dialysis of the dispersion.

particle size distribution. Therefore, we can assume that when the ionomer THF solution is dropwisely added into a large amount of water the THF molecules immediately diffuse into water resulting in the collapse and aggregation of the hydrophobic polystyrene backbone chains because THF is infinitely soluble in water.

Influence of the Sample Preparation Methods

Figure 8 shows the initial ionomer concentration dependence and the influence of the preparation method on the particle size distribution. It clearly shows that ultrasonification and stirring essentially lead to the same particle size distribution when the 3.67 NaSPS THF solution with an initial concentration of 2×10^{-2} g/mL was added in a dropwise fashion into water. It also shows that
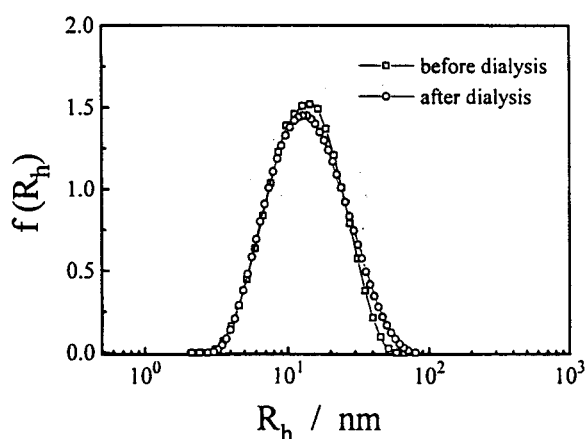

Figure 7. Typical hydrodynamic radius (R_h) distribution of the 3.67 NaSPS ionomer dispersion before and after 1-week dialysis of the dispersion.
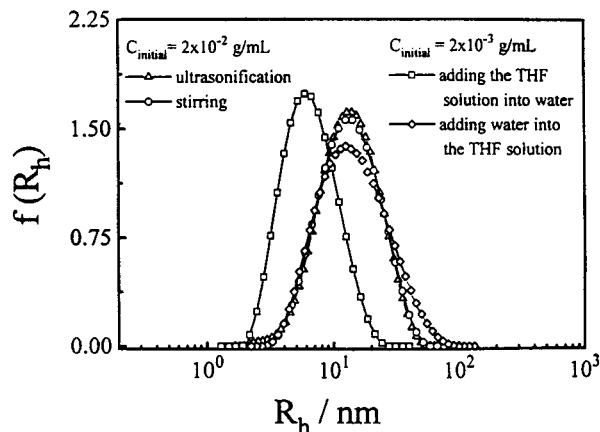

Figure 8. Initial ionomer concentration dependence and the preparation method influence on the hydrodynamic radius (R_h) distributions of the stable polystyrene nanoparticles made of the 3.67 NaSPS chains.

the initial ionomer concentration can greatly affect the final particle size distribution, namely a 10-time dilution of the 3.67 NaSPS THF solution from 2×10^{-2} g/mL to 2×10^{-3} g/mL leads to much smaller particles. This is understandable because when the ionomer THF solution is diluted the number of the ionomer chains in each drop, i.e., the local ionomer concentration decreases, so that the collapsed ionomer chains have less chance to form larger particles before they are stabilized by the ionic groups. On the other hand, Figure 8 shows that adding water in a dropwise fashion into the ionomer THF solution can also form stable colloidal particles as long as the initial ionomer concentration is lower than 2×10^{-3} g/ mL. It should be stated that at a higher initial ionomer concentration, such as 2×10^{-2} g/mL, adding water into the ionomer THF solution resulted in a milky dispersion. The particles formed by adding water in the ionomer THF solution is twice as large as those obtained by adding the same ionomer THF solution into water. This can also be explained in terms of the local ionomer concentration. When the ionomer THF solution is added into water in a dropwise fashion, the number of the polystyrene chains in each drop is limited. In this case, the local environment of the ionomer molecules changes rapidly from THF to almost pure water, the collapsed and aggregated polystyrene chains are rapidly dispersed into the surrounding water by ultrasonification or stirring, and the particles are relatively small. In contrast, when water is added in a dropwise fashion into the ionomer THF solution, the polystyrene chains around the water droplet are collapsed and the local ionomer concentration is much higher,

so that larger particles are formed. In contrast, Figure 2 shows no difference in the excitation and emission spectra of pyrene in the solutions prepared by different methods, indicating that fluorescence is insensitive to the particle size distribution, but only to the amount of the hydrophobic microdomains (nanoparticles) formed in the dispersion because the change of fluorescence signals is related to the change of the hydrophility around the probe molecules.

CONCLUSIONS

By adding a THF solution of the sodium sulfonated polystyrene ionomers into water in a dropwise fashion under ultrasonification (or stirring) or vice verse, the ionomer chains can form surfactant-free polystyrene nanoparticles stabilized by the electrostatic repulsion between the ionic groups on different particles. The particle size distribution is strongly dependent on the extent of sulfonation, the initial concentration of the ionomer THF solution, and the order of mixing the ionomer THF solution with water. However, the dilution of the dispersion, the type of the sample, and the polydispersity of the ionomer chains have much less effect on the nanoparticle formation. This study demonstrates another way to prepare surfactant-free polystyrene nanoparticles that could be used to encapsulate or carry hydrophobic drugs or other hydrophobic molecules for different applications.

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