

# Studies on Novel Surfactant-Free Polystyrene Nanoparticles Formed in Microphase Inversion

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**ABSTRACT:** Randomly carboxylated polystyrene ionomers are insoluble in water. However, we found that when their tetrahydrofuran (THF) solutions are added into an excess of water or vice versa, the ionomer chains can undergo a microphase inversion to form surfactant-free colloidal nanoparticles stable in water. In this study, a combination of static and dynamic laser light scattering (LLS) was used to study the influence of various experiment conditions, such as the initial ionomer concentration in THF, the degree of carboxylation, the type of counterion, the composition of the THF/water mixture, and the order of mixing the ionomer THF solution with water, on the formation and size distribution of the nanoparticles.

## Introduction

Ionomers usually refer to macromolecules containing no more than 10 mol % ionic groups chemically bound to a hydrophobic chain backbone. Ionomers can be homopolymer partially substituted with ionic groups or a random copolymer made of neutral and ionic monomers. Most of the past studies were focused on their bulk properties, including high melting viscosity, toughness, and thermoplasticity.<sup>1,2</sup> Recently, much attention has been paid to their solution behavior. In a nonpolar solvent, ionic groups, existed as solvated ion pairs, can form electric dipoles. The attraction between these electric dipoles can lead to chain aggregation.<sup>3–8</sup> However, in a polar solvent, the ion pairs are dissociated, so that all the phenomena related to the aggregation disappeared.<sup>9–12</sup> Ionomers can also be block copolymers with one nonpolar block and one or two ionic blocks, known as block ionomers. They can display solution behavior as similar to those of homopolymer and copolymer ionomers.<sup>13–15</sup> Block ionomers with a long nonionic block and a short ionized block are polymeric amphiphiles which can form polymeric micelles in aqueous media, resembling small surfactant molecules. They are often used as emulsifiers to stabilize colloidal suspensions.<sup>16–27</sup>

Ionomers are normally insoluble in water. Recently, we found that a slightly carboxylated commercial styrene-(ethylene-*co*-butene)-styrene triblock copolymer (SEBS) can form colloidal particles stable in water.<sup>28</sup> It is worth noting that both of the PS block and EB blocks are insoluble in water, so that the micellization model, i.e., an insoluble hydrophobic core surrounded by a soluble hydrophilic shell, is obviously not applicable to this type of colloidal particles.

In previous studies, we showed that not only could the triblock ionomers form stable colloidal particles but also randomly carboxylated and sulfonated polystyrene ionomers could form stable surfactant-free polystyrene nanoparticles if the ionomer tetrahydrofuran (THF)

solution was added dropwise into an excess amount of water.<sup>29,30</sup> We have already studied how the nanoparticle formation depended on the initial ionomer concentration and on the carboxylation extent when Na<sup>+</sup> was used as a counterion. Very recently, we found (not reported yet) that even the carboxylated polystyrene in its acid form could form polystyrene nanoparticles stable in water, indicating that only a weak stabilization force is required to prevent the aggregation of such formed polymeric nanoparticles. The trick is to slow the inter-chain aggregation process in the microphase inversion so that the polymer chains have enough time to arrange themselves to let all the hydrophobic groups stay on the surface. In this study, we used laser light scattering to study how the formation of these novel nanoparticles takes place under different experimental conditions, such as the initial ionomer concentration in THF, the degree of carboxylation, the type of counterion, the composition of the THF/water mixture, the dilution of the dispersion, and the order of mixing the ionomer THF solution and water.

## Experimental Section

**Materials.** The carboxylation of narrowly distributed polystyrene ( $M_n = 2.36 \times 10^4$  g/mL, polydispersity = 1.45) was described elsewhere.<sup>31,32</sup> The polystyrene ionomers with two different carboxylation contents (4.8 and 6.8 mol %) and two different counterions (Na<sup>+</sup> and Mn<sup>2+</sup>) were used. The counterions were, respectively, introduced by titrating the ionomers with CH<sub>3</sub>ONa and (CH<sub>3</sub>COO)<sub>2</sub>Mn in methanol. According to the extent of carboxylation and the type of counterion, the four ionomer samples used are denoted as 4.8NaCPS, 6.8NaCPS, 4.8MnCPS, and 6.8MnCPS hereafter.

**Sample Preparation.** Each ionomer sample was dissolved in THF under stirring for at least 2 days, wherein a small amount of water (~1 vol %) was added to promote its dissolution. The initial ionomer concentration in THF was  $2 \times 10^{-2}$  g/mL except as stated otherwise. Each ionomer THF solution was divided into two parts. One part was used for the characterization of individual ionomer chains in THF, and the other part was diluted to different concentrations ( $(0.02 - 1) \times 10^{-2}$  g/mL) before it was added dropwise into an excess of water under ultrasonification. The final concentration of

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the dispersion was  $2 \times 10^{-4}$  g/mL or less, depending on the initial ionomer concentration. The volume ratio (v/v) H<sub>2</sub>O:THF in the dispersion was kept at 99:1.

**Laser Light Scattering (LLS).** The detail of LLS instrumentation and theory can be found elsewhere.<sup>33,34</sup> All the LLS measurements were done at  $25.0 \pm 0.1$  °C. The dispersions were clarified by 0.2  $\mu$ m Antop or 0.5  $\mu$ m Millipore filters, depending on the particle size. In static light scattering, the angular and concentration dependence of the time-averaged scattered light intensity were measured, which led to the weight-averaged molar mass  $M_w$ , the second virial coefficient  $A_2$ , and the  $z$ -average square-root-mean radius of gyration  $\langle R_g^2 \rangle_z^{1/2}$  (or written as  $\langle R_g \rangle$ ).

In dynamic LLS, the intensity–intensity time correlation function  $G^{(2)}(\tau, \theta)$  in the self-beating mode was measured, where  $\tau$  is the delay time and  $\theta$  is the scattering angle.  $G^{(2)}(\tau, \theta)$  can be related to the normalized first-order electric field time correlation function  $|g^{(1)}(\tau, \theta)|$  as<sup>33, 34</sup>

$$G^{(2)}(\tau, \theta) = \langle I(0, \theta) I(\tau, \theta) \rangle = A[1 + \beta |g^{(1)}(\tau, \theta)|^2] \quad (1)$$

where  $A$  is the measured baseline;  $\beta$ , a parameter depending on the coherence of the detection; and  $\tau$ , the delay time. For a polydisperse sample,  $|g^{(1)}(\tau, \theta)|$  is related to the line-width distribution  $G(\Gamma)$  as

$$|g^{(1)}(\tau, \theta)| = \langle E(0, \theta) E^*(\tau, \theta) \rangle = \int_0^\infty G(\Gamma) e^{-\Gamma \tau} d\Gamma \quad (2)$$

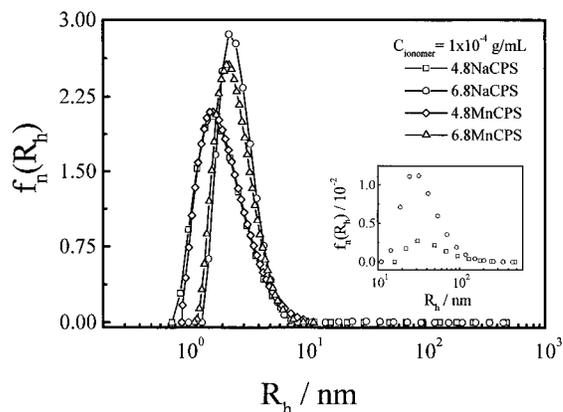
$G(\Gamma)$  can be calculated from the Laplace inversion of the measured  $G^{(2)}(\tau, \theta)$  on the basis of eqs 1 and 2. In this study, the CONTIN program developed by Provencher<sup>35</sup> was used. For a diffusive relaxation, at infinite dilution and  $\theta \rightarrow 0$ ,  $(\Gamma/q^2) \rightarrow D$ , where  $q$  is the scattering vector and  $D$  is the translational diffusion coefficient.  $D$  can be converted to the hydrodynamic radius ( $R_h$ ) by using the Stokes–Einstein equation:  $R_h = k_B T / 6\pi\eta D$ , where  $\eta$ ,  $k_B$ , and  $T$  are the solvent viscosity, the Boltzmann constant, and the absolute temperature, respectively. All the time correlation functions were measured at  $\theta \leq 15^\circ$ .

The specific refractive index increment ( $dn/dC$ ) used in static light scattering was determined by a novel and precise differential refractometer.<sup>37</sup> For the NaCPS and MnCPS ionomers in THF, the values of  $dn/dC$  are 0.183 and 0.156 mL/g, respectively, and for the nanoparticles in water,  $dn/dC$  is 0.250 mL/g, very close to the 0.256 mL/g for conventional polystyrene latex particles in water.

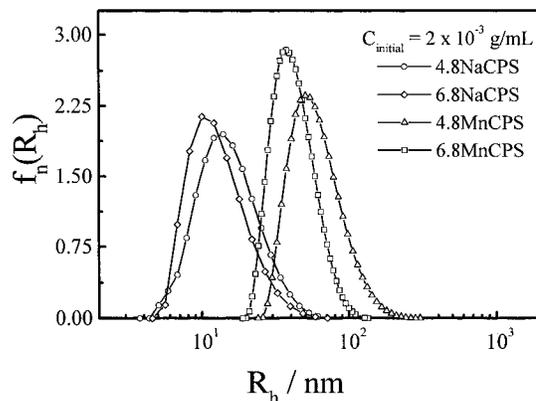
## Results and Discussion

First, we characterized the initial state of the ionomer chains in THF before adding the THF solution dropwise into water to form the nanoparticles. Figure 1 shows that most of the ionomer chains existed as individual CPS ionomer chains in THF with a hydrodynamic radius in the range  $\sim 1$ –10 nm. The second peak (enlarged 100 times) located at  $\sim 70$  nm indicates a very small number of interchain aggregates due to the ionic association. Figure 1 also shows that the higher carboxylation extent leads to more extended chains, reflecting the fact that the nature of the interchain interaction in THF is *ionic*.

Figure 2 shows that the size of the nanoparticles formed by adding the NaCPS and MnCPS THF solution dropwise in an excess of water is in the range  $\sim 10$ –100 nm, depending on the extent of the carboxylation and the kind of metal ion used. It is worth noting that such formed nanoparticles were so stable that there were no change in particle size distribution even after 4 months at room temperature. We also found that the NaCPS ionomer chains could form nanoparticles ( $\sim 20$  nm) that were stable in water even if the initial ionomer concentration was as high as  $2 \times 10^{-2}$  g/mL, but in the

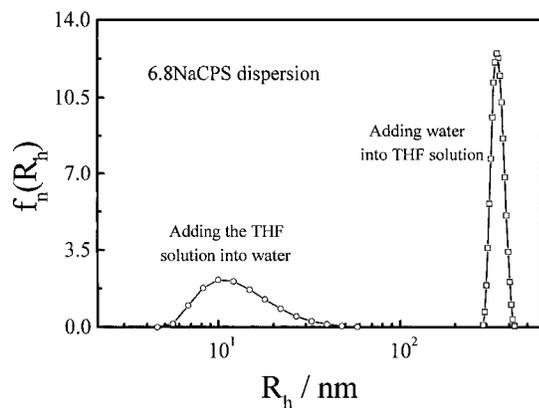


**Figure 1.** Typical number distributions  $f_n(R_h)$  of the hydrodynamic radius of the NaCPS and MnCPS chains in THF, where the ionomer concentration is  $1 \times 10^{-4}$  g/mL. The insert shows a 100-time enlargement of the second peak in  $f_n(R_h)$ , indicating that there exists a very small number of large interchain aggregates.



**Figure 2.** Typical number distributions  $f_n(R_h)$  of the hydrodynamic radius of the CPS nanoparticles stable in water, where the CPS nanoparticles were formed by adding the CPS ionomer THF solution dropwise in an excess of water.

case of MnCPS, the high initial ionomer concentration resulted in precipitation. The stable MnCPS nanoparticles could be obtained only if the initial MnCSP concentration is lower than  $2 \times 10^{-3}$  g/mL. Figure 2 clearly shows that using Mn<sup>2+</sup> instead of Na<sup>+</sup> as a counterion leads to much larger particles. The weight-average molar masses ( $M_w$ ) and hydrodynamic radii ( $\langle R_h \rangle$ ) of the 4.8MnCPS and 6.8MnCPS nanoparticles are  $1.2 \times 10^8$  g/mol and 54 nm and  $5.5 \times 10^7$  g/mol and 48 nm, respectively. In comparison with the initial molar mass ( $M_w = 3.4 \times 10^4$  g/mol) of individual MnCPS ionomer chains, we know that the 4.8MnCPS and 6.8MnCPS nanoparticles, respectively, consist of  $\sim 3500$  and  $\sim 1600$  chains. The ratio of  $\langle R_g \rangle / \langle R_h \rangle \sim 0.8$  indicates that the nanoparticles were uniform spheres. Assuming that all the ionic group were on surface, we estimated that the average surface area ( $s_{\text{ionic}}$ ) per ionic group on the particle surface are  $\sim 0.9$ – $1.0$  nm<sup>2</sup> from  $\langle R_h \rangle$  and  $M_w$ , which is lower than  $\sim 3$  nm<sup>2</sup> found for the NaCPS nanoparticles,<sup>29</sup> and the density of the particles is  $\sim 0.2$ – $0.3$  g/cm<sup>3</sup>, which is much lower than the density ( $\sim 1.0$  g/cm<sup>3</sup>) of the bulk polymer. The lower chain density indicates that the MnCPS nanoparticles have a loose structure, which is also reflected from the ratio of  $\langle R_g \rangle / \langle R_h \rangle$ ,  $\sim 1.0$  instead of  $\sim 0.774$  predicted for a uniform compact sphere, where  $\langle R_g \rangle$  is the radius of gyration. The loose structure also explains why the MnCPS particles are much larger and why the estimated  $s_{\text{ionic}}$



**Figure 3.** Comparison of the number distributions  $f_n(R_h)$  of the hydrodynamic radius of the CPS nanoparticles formed by the two different ways of mixing the CPS ionomer THF solution and water.

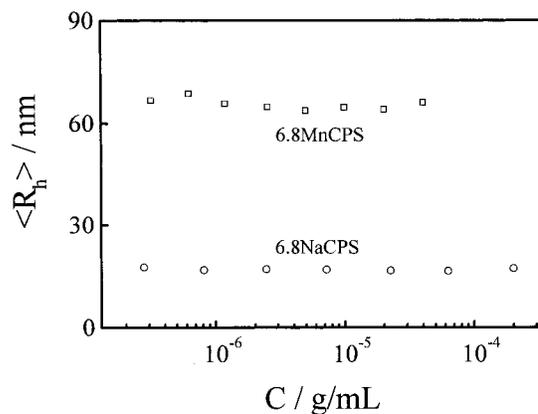
is small, because for a given  $\langle R_h \rangle$ , the loose structure should have a much larger surface area than that estimated from  $\langle R_h \rangle$  on a uniform compact sphere.

Furthermore, our results showed that removing the 1% THF from the dispersion leads to smaller particles, i.e., the contraction of the particles, supporting the point that the MnCPS nanoparticles have a loose structure. On the other hand, the addition of THF into the dispersion leading to the swelling of the 4.8MnCPS nanoparticles, indicating that there is a preferential adsorption of THF onto the nanoparticles to which the loose structures can be attributed. Our results also showed that higher initial ionomer concentrations resulted in larger particles with a broader size distribution. On the other hand, for a given initial ionomer concentration, higher carboxylation extents led to smaller particles. This can be attributed to the fact that each ionic group can only cover a certain area of the particle surface. When the carboxylation extent is higher, each particle requires less ionomer chains to reach the same charge density on the particle surface, so that the particle size is smaller. The same argument can also be used to explain why using  $Mn^{2+}$  instead of  $Na^+$  as counterions led to larger particles because  $Na^+$  can induce a stronger ionic repulsion so that each  $Na^+$  stabilizes a more surface area.

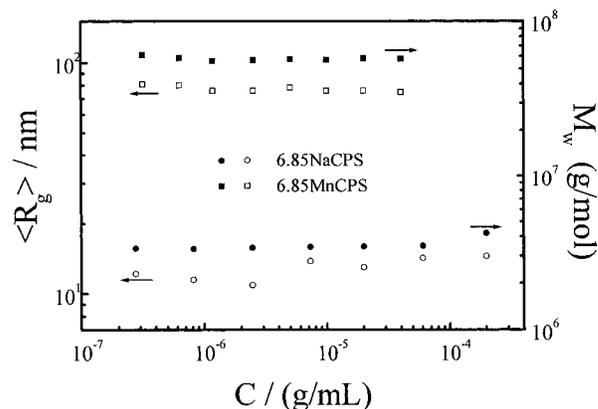
Figure 3 shows that the addition of water into the ionomer solution resulted in larger nanoparticles with a narrower distribution than the reversed process. It can be imagined that in the case of adding the ionomer THF solution dropwise into water, the local environment of the ionomer chains changes rapidly from THF to almost pure water, so that individual ionomer chains quickly collapse and disperse in water under ultrasonication and the ionomer chains have less chance to form large particles through the interchain aggregation. In process of adding water dropwise into the ionomer THF solution, the polystyrene chains around the water droplet collapse into the water droplet and then aggregate with each other to form large particles because the local ionomer concentration is relatively higher.

Figures 4 and 5 clearly reveal that the dilution has no effect on the hydrodynamic radius, the radius of gyration and the apparent weight average molar mass of the CPS nanoparticles, indicating such formed CPS nanoparticles are very stable even in an extremely dilute solution.

In summary, randomly carboxylated polystyrene ionomer chains can form stable surfactant-free colloidal



**Figure 4.** Concentration dependence of the average hydrodynamic radius  $\langle R_h \rangle$  of the CPS nanoparticles.



**Figure 5.** Concentration dependence of the average radius of gyration  $\langle R_g \rangle$  and the apparent weight averaged molar mass  $M_w$  of the CPS nanoparticles.

nanoparticles if the ionomer THF solution is added dropwise into an excess of water or vice versa via a microphase inversion. The trick is to slow the inter-chain aggregation so that the ionomer chains are able to arrange themselves to let as many as ionic groups on the surface of the aggregates. The particle size distribution can be well controlled by varying various experimental conditions. The method and principle presented in this study can be used to prepare other types of surfactant-free polymeric nanoparticles for various potential applications.

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