# Novel Surfactant-Free Stable Colloidal Nanoparticles Made of Randomly Carboxylated Polystyrene Ionomers

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Ionomers consist of macromolecules with a few mole percent ionic groups attached to the hydrophobic backbone. The introduction of the ionic groups on a polymer chain can dramatically change the bulk properties, such as the glass transition temperature and miscibility with other materials.[1] Most of the past studies of ionomers were concentrated on their rheological properties. In nonpolar solvents, such as tetrahydrofuran (THF) and xylene, the ionic groups form solvated ion pairs with large electric dipoles. The attraction between the electric dipoles leads to aggregation of the polymer chains. On the other hand, in polar solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), all phenomena related to the aggregation disappear and polyelectrolyte-like behavior appears in dilute solution.[2−12] Up to now, less attention has been paid to ionomers in aqueous solution because they are normally insoluble in water. Recently, Eisenberg *et al.*[13] has found that block copolymers with long nonionic blocks and short ionic blocks can form "crew-cut" micelles in water by (1) dissolving the block copolymer in a nonselective solvent which is not only miscible with water but also a good solvent for the block copolymer, (2) adding a selective solvent and/or water slowly to the polymer solution, and (3) replacing the nonselective solvent with water. Recently, Jiang *et al.*[14] reported that the lightly carboxylated SEBS, a hydrogenated poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer ionomer, can also form stable aggregates in water if a special preparation method is followed.

Our present study shows that not only can block copolymers form stable aggregates in water but randomly carboxylated polystyrene ionomers are also able to form narrowly distributed stable colloidal nanoparticles in water if the carboxylated polystyrene ionomer THF solution is added dropwise to an excess of water, rather than adding water to the polymer solution. Also, by using a combination of static and dynamic laser light scattering (LLS), our present study has revealed that the average surface area occupied by each ionic carboxylate group is nearly constant, governing the final size of the colloidal nanoparticles.

Polystyrene ($M_n = 2.36 \times 10^4$) was made by anionic polymerization and was carboxylated as described elsewhere.[15−17] Two samples with different degrees of carboxylation (4.85 and 6.85 mol %, denoted as 4.85NaCPS and 6.85NaCPS hereafter) were used. First, the ionomer sample was dissolved in THF under continuous stirring for at least 2 days, with a very small amount of water (~1 v/v %) added to the THF solution to promote the dissolution of the ionomers. The initial ionomer concentration was $2 \times 10^{-2}$ g/mL. The ionomer solution was then divided into two parts. One part was further diluted with THF for the characterization of the ionomers in THF. The other part, after dilution to a different initial concentration ($2 \times 10^{-2}$−$6.25 \times 10^{-4}$ g/mL), was added dropwise to an excess of water under ultrasonification or fast stirring, leading to a transparent stable colloidal dispersion of the NaCPS ionomer in water. The final ionomer concentration in the mixture of water and THF was $2 \times 10^{-4}$ g/mL or less, depending on the initial ionomer concentration. The volume ratio (v/v) of $H_2O$:THF in the dispersion was 100:1. The stable colloid dispersion could be further diluted into a series of solutions for laser light scattering experiments, the ionomers THF solutions were clarified using a 0.2-$\mu$m Whatman PTFE filter, and the stable colloidal dispersions were clarified using a 0.5-$\mu$m Millipore filter.

A commercial laser light scattering (LLS) spectrometer (ALV/SP-150) equipped with a solid-state laser (ADLAS DPY425II, output power ≈ 400 mW at $\lambda = 532$ nm) as the light source and an ALV-5000 multi-$\tau$ digital correlator was used. The incident light beam was vertically polarized with respect to the scattering plane. Details of the LLS instrumentation and theory can be found elsewhere.[18,19] All LLS measurements were done at 25.0 ± 0.1 °C. The measured time correlation functions were analyzed by the cumulants and Laplace inversion program (CONTIN) provided with the correlator. The refractive index increment (d$n$/d$c$) was determined by a novel and precise differential refractometer.[20] For the NaCPS ionomers in THF, the value of d$n$/d$c$ is 0.183 mL/g, while for the NaCPS colloid particles in water, the value of d$n$/d$c$ is 0.250 mL/g, which is very close to the value of 0.256 g/mL for normal polystyrene latex particles in water.

Table 1 summarizes all static and dynamic LLS results. It is known that the carboxylation has little effect on the molar mass distribution of initial polystyrene chains.[17] In comparison with the weight-average molar mass of initial polystyrene chains ($M_w = 3.42 \times 10^5$ g/mol), Table 1 clearly shows an ionic association of the ionomer chains in THF even with ~1 v/v % of added water. In the measured concentration range of $1 \times 10^{-4}$−$5 \times 10^{-4}$ g/mL, the average association numbers of 4.85NaCPS and 6.85NaCPS in THF are ~9 and ~10, respectively. It should be noted that both of the ionomer samples are difficult to dissolve completely in THF without adding a small amount of water (~1 v/v %). Therefore, the association of the ionomer chains in THF is expected. It should also be noted that the driving force for the association of the carboxylated polystyrene in THF is *the ionic pair interaction* because THF is a good solvent for the polystyrene backbone.

Table 1 also shows that after the dropwise addition of the ionomer THF solution into water, much larger particles are formed and the weight-average molar masses ($M_w$) of the particles are much higher than those in THF, indicating two simultaneous processes: the collapse of the hydrophobic polystyrene backbone chains in water accompanied by the transfer of the ionic groups toward the surface of the collapsed particles, and the interchain aggregation of the carboxylated polystyrene chains.

Figure 1 shows two typical particle size distributions of the stable colloidal particles respectively prepared from 4.85NaCPS and 6.85NaCPS. The dispersion is very stable and the particle size distributions are fairly narrow, which is reflected in the smaller values of the relative distribution width ($\mu_2/\langle\Gamma\rangle^2$). There is no detectable change in the particle size distribution for more

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**Table 1. Summary of the Light Scattering Results of the Stable Nanoparticles Made of Randomly Carboxylated Polystyrene Ionomers**[a]

| sample | ionomer concn in THF (g/mL) | solvent | $M_w$ (g/mol) | $\langle R_g \rangle$ (nm) | $\langle R_h \rangle$ (nm) | $\mu_2/\langle \Gamma \rangle^2$ | $N_{agg}$ | $\langle R_g \rangle/\langle R_h \rangle$ | $s_{ionic}$ (nm$^2$/ionic group) | $\rho$ (g/cm$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|
| 4.85NaCPS | $(1.0-5.0) \times 10^{-4}$ | THF | $3.2 \times 10^5$ | ~21 | 18 | ~0.2 | ~9 | | | |
| 6.85NaCPS | $(1.0-5.0) \times 10^{-4}$ | THF | $3.6 \times 10^5$ | ~29 | 22 | ~0.2 | ~10 | | | |
| 4.85NaCPS | $2.0 \times 10^{-2}$ | $H_2O$ | $5.5 \times 10^6$ | ~21 | 20 | ~0.1 | ~160 | ~1.0 | 2.8 | 0.27 |
| 6.85NaCPS | $2.0 \times 10^{-2}$ | $H_2O$ | $3.4 \times 10^6$ | ~13 | 18 | ~0.1 | ~100 | ~0.7 | 2.6 | 0.23 |
| 6.85NaCPS | $5.0 \times 10^{-3}$ | $H_2O$ | $2.9 \times 10^6$ | ~15 | 17 | ~0.1 | ~84 | ~0.9 | 2.8 | 0.23 |
| 6.85NaCPS | $1.2 \times 10^{-3}$ | $H_2O$ | $9.5 \times 10^5$ | | 10 | ~0.2 | ~28 | | 3.1 | 0.33 |
| 6.85NaCPS | $6.2 \times 10^{-4}$ | $H_2O$ | $6.1 \times 10^5$ | | 8 | ~0.2 | ~18 | | 3.1 | 0.42 |

[a] Relative errors of $M_w$, $R_g$, $R_h$, $\mu_2/\langle \Gamma \rangle^2$, $N_{agg}$, $s_{ionic}$, and $\rho$ are ±5%, ±20%, ±1%, ±20%, ±5%, ±10%, and ±10%, respectively.

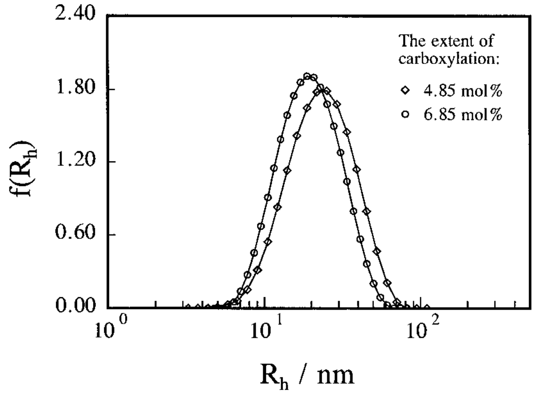

**Figure 1.** Typical hydrodynamic radius distributions of the stable nanoparticles made of randomly carboxylated polystyrene ionomers with different extents of carboxylation. The initial ionomer concentration in THF is $2 \times 10^{-2}$ g/mL.

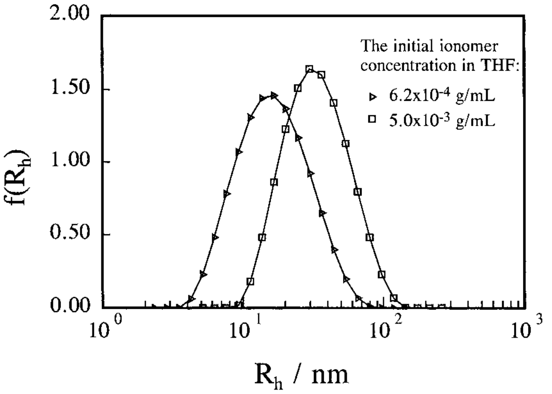

**Figure 2.** Typical hydrodynamic radius distributions of the stable nanoparticles made of the 6.85NaCPS THF solution with different initial ionomer concentrations.

than 2 months. The lower values of $\langle R_g \rangle/\langle R_h \rangle$ listed in Table 1 also indicate that these colloidal nanoparticles are sphere-like, more compact, and less draining. Table 1 shows that for the same initial concentration the average size of the particles made of the ionomer chains with a lower degree of carboxylation is larger. Now the question is what is the exact correlation between the particle size and the degree of carboxylation.

Let us reexamine the particle formation process. During the aggregation, the surface area of the particle ($S$) is proportional to the square of its radius ($R$), i.e., $S \propto R^2$, and the number ($N_{ionic}$) of the ionic groups on the surface is proportional to the number of the ionomer chains in the particle, i.e., $N_{ionic} \propto M_{particle}$, where $M_{particle}$ is the mass of the particle. Since $M \propto R^3$, the average surface area occupied by each ionic group ($s_{ionic} = S/N_{ionic}$) is proportional to $R^{-1}$. In the aggregation process, the particle size increases so that $s_{ionic}$ decreases. For a given ionomer in water, there should exist a minimum value of $s_{ionic}$ at which the particle surface is fully covered by the ionic groups and further coagulation becomes impossible because of the electrostatic repulsion between the ionic groups between two particles. A combination of the static and dynamic LLS results in Table 1 leads to $s_{ionic} = 2.8$ and 2.6 nm$^2$, respectively, for the 4.85NaCPS and 6.85NaCPS nanoparticles in water. Note that the values of $s_{ionic}$ for different degrees of carboxylation are very close because for a given polymer/solvent system the minimum surface area occupied by each ionic group should be a constant. Therefore, a higher degree of carboxylation leads to smaller particles. It should be stated that a full coverage of the particle surface might not be absolutely necessary to prevent coagulation and all the carboxylate groups might not be necessarily on the surface. However, the essence of the simplified picture still remains. For example, we can introduce an effective $N_{ionic}$ as $\beta N_{ionic}$, with $\beta$ being the fraction of the ionic groups on the surface.

Further, we studied the influence of the initial ionomer concentration in THF, i.e., before its addition to water, on the final particle size distribution. Figure 2 shows the initial concentration dependence of the particle size distribution. It clearly shows that the average particle size decreases as the initial polymer concentration decreases, which is understandable because at a lower initial ionomer concentration the ionomer chains have more time to collapse before they have a chance to combine with each other to form larger aggregates. The microscopic parameters of these stable colloidal particles such as the average particle density ($\rho$) and aggregation number ($N_{agg}$) are also summarized in Table 1. The values of $s_{ionic}$ are close to each other, i.e., $s_{ionic} \sim 3$ nm$^2$, even though their average particle sizes are quite different, which supports our above argument that for a given polymer/solvent system $s_{ionic}$ is a fundamental parameter governing the particle size. The nanoparticles prepared with a lower initial ionomer concentration have a higher apparent density ($\rho$), where $\rho = (M_w/N_A)/[(4/3)\pi R_h{}^3]$.

In conclusion, we found that randomly carboxylated polystyrene ionomer chains are also able to form stable colloidal nanoparticles in water if a special preparation method is followed. The formation of these colloidal particles involves the collapse of the hydrophobic backbone chains, the transfer of the ionic groups toward the particle surface, and the interchain aggregation. The fundamental parameter controlling the final particle size of the dispersion is the surface area occupied per ionic group on the particle surface. The size and density of these stable nanoparticles can be varied by the initial ionomer concentration in THF and by the extent of carboxylation. Our finding provides a novel way to prepare surfactant-free polymer nanoparticles in aqueous solution for various potential applications.

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