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.† 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 poly electrolyte-like behavior appears in dilute solution.‡–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, Jang et al.14 reported that the lightly carboxylated SEBS, a hydrogenated polystyrene-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 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 (Mn = 2.36 × 104) 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 × 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 × 10–2–6.25 × 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 × 10–4 g/mL or less, depending on the initial ionomer concentration. The volume ratio (v/v) of H2O:THF in the dispersion was 100:1. The stable colloidal 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-μm Whatman PTFE filter, and the stable colloidal dispersions were clarified using a 0.5-μm 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 λ = 532 nm) as the light source and an ALV-5000 multi-r 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 (dn/dc) was determined by a novel and precise differential refractometer.20 For the NaCPS ionomers in THF, the value of dn/dc is 0.183 mL/g, while for the NaCPS colloid particles in water, the value of dn/dc is 0.250 mL/g, which is very close to the value of 0.256 mL/g 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 (Mw = 3.42 × 106 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 × 10–4–5 × 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 ion 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 (Mw) 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 (ω2/Γ2). 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

<table>
<thead>
<tr>
<th>sample</th>
<th>ionomer concn in THF (g/mL)</th>
<th>solvent</th>
<th>(M_w) (g/mol)</th>
<th>(R_\text{f}^{(1/2)}) (nm)</th>
<th>(\mu_s\Gamma^2)</th>
<th>(N_{\text{agg}})</th>
<th>(S_{\text{ionic}}) (nm²/ionic group)</th>
<th>(\rho) (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.85NaCPS</td>
<td>(1.0–5.0) × 10⁻⁴</td>
<td>THF</td>
<td>3.2 × 10⁵</td>
<td>21</td>
<td>18</td>
<td>~0.2</td>
<td>~9</td>
<td></td>
</tr>
<tr>
<td>6.85NaCPS</td>
<td>(1.0–5.0) × 10⁻⁴</td>
<td>THF</td>
<td>3.6 × 10⁵</td>
<td>29</td>
<td>22</td>
<td>~0.2</td>
<td>~10</td>
<td></td>
</tr>
<tr>
<td>4.85NaCPS</td>
<td>2.0 × 10⁻²</td>
<td>H₂O</td>
<td>5.5 × 10⁴</td>
<td>21</td>
<td>20</td>
<td>~0.1</td>
<td>~160</td>
<td>2.8</td>
</tr>
<tr>
<td>6.85NaCPS</td>
<td>2.0 × 10⁻²</td>
<td>H₂O</td>
<td>3.4 × 10⁴</td>
<td>13</td>
<td>18</td>
<td>~0.1</td>
<td>~100</td>
<td>0.23</td>
</tr>
<tr>
<td>4.85NaCPS</td>
<td>2.0 × 10⁻²</td>
<td>H₂O</td>
<td>2.9 × 10⁴</td>
<td>15</td>
<td>15</td>
<td>~0.1</td>
<td>~95</td>
<td>2.8</td>
</tr>
<tr>
<td>6.85NaCPS</td>
<td>2.0 × 10⁻²</td>
<td>H₂O</td>
<td>9.5 × 10⁴</td>
<td>10</td>
<td>10</td>
<td>~0.2</td>
<td>~28</td>
<td>0.33</td>
</tr>
<tr>
<td>4.85NaCPS</td>
<td>1.2 × 10⁻²</td>
<td>H₂O</td>
<td>6.1 × 10⁴</td>
<td>8</td>
<td>~0.2</td>
<td>~18</td>
<td>3.1</td>
<td>0.42</td>
</tr>
<tr>
<td>6.85NaCPS</td>
<td>6.2 × 10⁻⁴</td>
<td>H₂O</td>
<td>6.1 × 10⁴</td>
<td>8</td>
<td>~0.2</td>
<td>~18</td>
<td>3.1</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*Relative errors of \(M_w\), \(R_\text{f}\), \(\mu_s\Gamma^2\), \(N_{\text{agg}}\), \(S_{\text{ionic}}\), and \(\rho\) are ±5%, ±20%, ±1%, ±20%, ±5%, ±10%, and ±10%, respectively.

![Figure 1](image1.png)  
**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 × 10⁻² g/mL.

![Figure 2](image2.png)  
**Figure 2.** Typical hydrodynamic radius distributions of the stable nanoparticles made of the 6.85NaCPS THF solution with different initial ionomer concentrations.

The extent of carboxylation:  
- 4.85 mol%  
- 6.85 mol%  

The initial ionomer concentration in THF:  
- 6.2×10⁻⁴ g/mL  
- 5.0×10⁻³ g/mL  

The value of \(S_{\text{ionic}}\) is the agglomeration density of the particle, which is the number of the surface area occupied by each ionic group. It is proportional to \(R^{-1}\). The values of \(S_{\text{ionic}}\) are close to each other, i.e., \(S_{\text{ionic}} \sim 3\) nm², even though their average particle sizes are quite different, which supports our argument that for a given polymer/solvent system \(S_{\text{ionic}}\) is a fundamental parameter governing the particle size.

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 backbones, 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 ionomer 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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References and Notes