Light-Scattering Study of a Zwitterionic Polycarboxybetaine in Aqueous Solution

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Introduction

Polyelectrolytes, defined as macromolecules with ~10 mol % or more ionic groups on their chain backbones, are soluble in highly polar solvents, ubiquitous in biological systems, and useful in environmental friendly polymer processes. The effects of salt on the interaction of polyelectrolytes in aqueous solution have been extensively studied. Such a study is difficult because the solution contains at least four components: polymers, counterions, co-ions, and solvent and also because different interactions, such as intra- and interchain interactions, long-range electrostatic interaction, hydrophobic interaction, and entropic force, have to be simultaneously considered.

Despite all the difficulties, researchers have recently started to study more complicated stable zwitterionic polymers (also known as betaines) because carboxybetaine and sulfobetaine are widely used in textile, medical, and other industrial branches. These polymers are regarded as a well-identified class of highly dipolar polymeric materials with a wide spectrum of unique and specific properties. In a zwitterionic polymer, each pair of covalently bonded anion and cation leads to a permanent dipole whose value can be varied by the charge. Depending on whether the solution PH is above or below its isoelectric point (IEP), a zwitterionic polymer in solution could be overall anionic or cationic. Asonova et al. revealed that the reduced viscosity of polycarboxybetaine was a function of pH. Gnambodee et al. studied the association behavior of polyisoprenes of carboxylbetaines with different inter-charge lengths and showed that the average aggregation number depended on the molar mass of the amminated precursor polymer as well as the intercharge length. Liaw et al. investigated the properties of an ampholytic poly(3-dimethylacryloxy ammonium propionolactone) in aqueous solution and found that higher ionic strength led to the interchain aggregation.

In this work, a combination of static and dynamic laser light scattering was used to study a polycarboxybetaine, poly(N,N-dimethyl ((methacrylamido) propyl) ammonium propionolactone), in dilute aqueous solution, and the potential was measured to determine the pH dependence of the net charge of poly(DMMPAPL) chains in aqueous solution. We intended to find the effects of pH and ionic strength on inter- and intrachain interactions as well as the chain conformation.

Experimental Section

Sample Preparation. Polycarboxybetaine, poly(N,N-dimethyl ((methacrylamido) propyl) ammonium propionolactone) (poly(DMMPAPL)), with the following chemical structure was prepared by free-radical polymerization:

\[
\begin{align*}
&\text{CH}_2 - \text{CH} - \text{CH}_2 - \text{COO}^+ \\
&\text{CH}_3 \\
&\text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{COO}^- \\
&\text{CH}_3
\end{align*}
\]

The details of synthesis can be found elsewhere. Poly(DMMPAPL) chains are soluble in methanol, and no interchain association in methanol was observed. The light-scattering characterization of poly(DMMPAPL) in methanol showed that poly(DMMPAPL) chains have a weight-average molar mass \(M_w\) of \(~5.2 \times 10^6\) g/mol and an average hydrodynamic radius \(R_h\) of ~11 nm. The resistivity of deionized water used in this study was 18.3 MΩ cm. All the solutions were prepared by dissolving a proper amount of poly(DMMPAPL) directly into the solvent. The solutions were clarified with a 0.5 μm Millipore filter to remove dust.

\[\zeta\text{ Potential.}\] A commercial Brookheaven Zeta Plus analyzer was used to measure the \(\zeta\) potential. The suspension fluid used was 1 mM potassium nitrate aqueous solution. The concentration of poly(DMMPAPL) in this suspension was 1.48 × 10^{-3} g/mL. The pH value was adjusted by 0.1 M potassium hydroxide solution. The details of the \(\zeta\) potential study can be found elsewhere.

Laser Light Scattering. A modified commercial light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-r digital time correlator and an ADLASDPY425I solid-state laser (output power = 400 mW at λ = 532 nm) was used. The details of the LLS instrumentation and theory can be found elsewhere.

In static LLS, the angular dependence of the excess absolute time-averaged scattered light intensity, known as the excess Rayleigh ratio \(R_\alpha(q)\), of dilute polymer solutions led to the apparent weight-average molar mass \(M_w(q)\) and the root-mean square z-average radius of gyration \(R_g(q)\) or written as \(R_g\) via a Zimm plot.

In dynamic LLS, the Laplace inversion of each precisely measured intensity–intensity–time correlation function \(G(t)\) in the self-beating mode could result in a line width distribution \(G(t)\). For a pure diffusive relaxation, \(G(t)\) can be converted to a translational diffusion coefficient distribution \(G(D)\) by \(I = Dq^2\) or a hydrodynamic radius distribution \(w(R_h)\) by the Stoke-Einstein equation. In this study, the CONTIN Laplace inversion algorithm in the correlator was used.

Results and Discussion

Figure 1 shows that poly(DMMPAPL) has an isoelectric point (IEP) of pH 8.6. When pH < 8.6, poly(DMMPAPL) chains are net positively charged. The \(\zeta\) potential decreases as pH increases until pH > 11. The net negative charge of poly(DMMPAPL) chains at high pH values is due to the ionization of the carboxyl groups.

Figure 2 shows the temperature dependence of weight distribution of hydrodynamic radius \(w(R_h)\) of poly(DMMPAPL) in deionized water. The \(w(R_h)\) has two peaks at 25 °C. The first peak, located in the range 1–10

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in 1 mM potassium nitrate aqueous solution.

Figure 1. pH dependence of ζ potential of poly(DMMPAPL) in 1 mM potassium nitrate aqueous solution.

molar mass (Mw) revealed a 10-times higher apparent weight-average molar mass in aqueous solution (pH 4.65) compared to individual chains, while the second peak corresponds to larger interchain aggregates. The static light-scattering measurements of the broad peak can be related to larger interchain aggregates.

Figure 2. Temperature dependence of weight distribution of hydrodynamic radius (Rg) of poly(DMMPAPL) in deionized water, where C = 4.65 × 10^{-3} g/mL.

Figure 3. Comparison of weight distribution of hydrodynamic radius (Rg) of poly(DMMPAPL) in deionized water and in aqueous solution (pH = 12) at 50 °C, where C_poly(DMMPAPL) = 4.65 × 10^{-3} g/mL.

nm, corresponds to individual chains, while the second broad peak can be related to larger interchain aggregates. The static light-scattering measurements revealed 10-times higher apparent weight-average molar mass (Mw), clearly indicating the interchain aggregation. Therefore, in deionized water, poly(DMMPAPL) exists as a mixture of individual chains and interchain association due to its zwitterionic nature. As the temperature increases, the first peak shifts into the range 7–20 nm, while the second peak becomes narrower. The shifting of the first peak can be attributed to the breaking up of the intrachain association and the extension of individual chains.

Figure 3 shows that adjusting pH to 12 shifts the two peaks toward the left (small Rg direction) because, on one hand, the addition of NaOH completely ionized the carboxylic groups and reduced the hydrogen bonding so that the interassociation was suppressed, leading to the shift of the second peak and, on the other hand, the presence of NaOH increased the ionic strength and decreased electrostatic repulsion so that individual chains contracted, resulting in the shift of the first peak.

Figure 4 reveals that the addition of a very small amount of NaCl into the solution at pH 12 leads to the decrease of the hydrodynamic radius and molar mass, indicating a further dissociation of the interchain association, because of higher ionic strength and weaker electrostatic attraction between −RgN+ and −COO− groups. Both (Rg) and (Mw) reach their corresponding minimums at C_NaCl = 0.05 M. Further addition of NaCl results in the increases of both (Rg) and (Mw). A previous study has attributed this increase of (Rg) purely to the breaking up of the intrachain association and the chain extension. However, the increase of molar mass in Figure 4 reveals that there exists an interchain aggregation, which is at least partially attributed to the increase of (Rg). Note that in a zwitterionic polymer solution, electrostatic attraction, on the one hand, induces inter- and intra-chains associations, but on the other hand, electrostatic repulsion leads to the solvation of the polymer chains. Therefore, suppressing electrostatic interactions by the addition of NaCl has a double effect. This is why there is a change from dissociation-and-extension to aggregation-and-contraction accompanying the increase of the NaCl concentration. This change can be better viewed from the ratio of (Rg)/(Rg)h, which directly reflects the chain conformation.

Figure 5 shows that (Rg)/(Rg)h first increases and then decreases as the NaCl concentration increases. It is known that, for a uniform and nondraining sphere, (Rg)/(Rg)h ≈ 0.8; for a loosely connected hyperbranched chain or aggregate, (Rg)/(Rg)h ≈ 1.0; for a linear flexible random coil chain, (Rg)/(Rg)h ≈ 1.5; and for an extended rigid chain, (Rg)/(Rg)h ≥ 2.0. A combination of Figures 4 and 5 shows that the initial increase of (Rg)/(Rg)h reflects the dissociation of intra- and interchain associations and chain extension because NaCl weakens electrostatic attraction, while the decrease of (Rg)/(Rg)h at higher salt concentrations indicates interchain aggregation and intra-chain contraction. If the increase of (Rg)h in Figure 4 is only attributed to the chain extension, we would observe an increase of (Rg)/(Rg)h.

Figure 6a shows that the addition of a small amount of NaCl further broke up inter- and intra-associations...
because of the increase of ionic strength and electrostatic repulsion, leading to the shifting of the aggregation peak toward the small $R_h$ direction. The peaks of the interchain aggregates and individual chains overlapped when $C_{NaCl} = 0.05$ M. Figure 6b shows that further addition of NaCl leads to the shifting of the aggregation peak toward the higher $R_h$ direction, reflecting the decrease of electrostatic repulsion. The further increase of ionic strength results in the hydrophobic aggregation of the contracted chains.

Figure 7 shows a schematic of the effects of adding NaOH and NaCl into a poly(DMMPAPL) aqueous solution.

leads to a higher ionic strength, a weaker electrostatic attraction, and the breakup of the inter- and intrachain associations, resulting in smaller interchain aggregates. On the other hand, it decreases both electrostatic repulsion and solvation and makes the polymer chains more hydrophobic. The hydrophobic attraction results in intrachain contraction and interchain aggregation.


References and Notes

(7) Schulz, D. N.; Peffer, D. G.; Agarwal, P. K. Polymer 1986, 27, 1734.

Figure 5. NaCl concentration dependence of ratio of average radius of gyration ($R_g^{\prime}$) to average hydrodynamic radius ($R_h^{\prime}$) of poly(DMMPAPL) in aqueous solution (pH = 12) at 50 °C, where $C_{poly(DMMPAPL)} = 4.65 \times 10^{-5}$ g/mL.

Figure 6. NaCl concentration dependence of weight distribution of hydrodynamic radius $w(R_h)$ of poly(DMMPAPL) in aqueous solution ($C_{poly(DMMPAPL)} = 4.65 \times 10^{-5}$ g/mL, pH = 12) at 50 °C: (a) $C_{NaCl} \leq 0.05$ M and (b) $C_{NaCl} > 0.05$ M.

Figure 7. Schematic of effects of adding NaOH and NaCl into a poly(DMMPAPL) aqueous solution.

Notes

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