3492 *Macromolecules* **2000,** *33,* 3492−3494

Light-Scattering Study of a Zwitterionic Polycarboxybetaine in Aqueous Solution

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Received September 24, 1999
Revised Manuscript Received February 9, 2000

Introduction

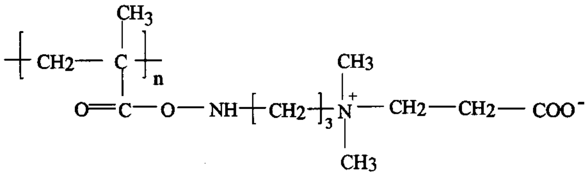
Polyelectrolytes, defined as macromolecules with ∼10 mol % or more ionic groups on their chain backbones, are soluble in highly polar solvents, ubiquitous in biological systems, and useful in environmental friendly polymer processes. The effects of salt on the interaction of polyelectrolytes in aqueous solution have been extensively studied.[1−4] Such a study is difficult because the solution contains at least four components: polyions, 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.[5]

Despite all the difficulties, researchers have recently started to study more complicated stable zwitterionic polymers (also known as betaine) because carboxybetaine and sulfobetaine are widely used in textile, medical, and other industrial branches.[6−8] 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 intercharge length. 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.[9] revealed that the reduced viscosity of polycarboxybetaine was a function of pH. Gnambodoe et al.[10] studied the association behavior of polyisoprenes of carboxylatobetaines with different intercharge lengths and showed that the average aggregation number depended on the molar mass of the aminated precursor polymer as well as the intercharge length. Liaw et al.[11] investigated the properties of an ampholytic poly(3-dimethylacryloxy ammonium propiolactone) 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 propiolactone), in dilute aqueous solution, and the ζ 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 propiolactone)) (poly(DMMPAPL)), with the following chemical structure was prepared by free-radical polymerization:



$$\left[CH_2 - \overset{\overset{CH_3}{|}}{\underset{\underset{O=C-O-NH-(CH_2)_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}}-CH_2-CH_2-COO^-}{|}}{C}} \right]_n$$

The details of synthesis can be found elsewhere.[12] 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 ∼5.2×10^4 g/mol and an average hydrodynamic radius $\langle R_h \rangle$ 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.

ζ Potential. A commercial Brookheaven Zeta Plus analyzer was used to measure the ζ 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 ζ potential study can be found elsewhere.[13,14]

Laser Light Scattering. A modified commercial light scattering spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlator and an ADLAS DPY425II solid-state laser (output power = 400 mW at $\lambda = 532$ nm) was used. The details of the LLS instrumentation and theory can be found elsewhere.[15,16] In static LLS, the angular dependence of the excess absolute time-averaged scattered light intensity, known as the excess Rayleigh ratio $R_{vv}(q)$, of dilute polymer solutions led to the apparent weight-average molar mass $(M_w)_{app}$ and the root-mean square *z*-average radius of gyration $\langle R_g^2 \rangle_z^{1/2}$ (or written as $\langle R_g \rangle$) via a Zimm plot,[15,16] where *q* is the scattering vector. In dynamic LLS, the Laplace inversion of each precisely measured intensity−intensity−time correlation function $G^{(2)}(t,q)$ in the self-beating mode could result in a line width distribution $G(\Gamma)$.[15,16] For a pure diffusive relaxation, $G(\Gamma)$ can be converted to a translational diffusion coefficient distribution $G(D)$ by $\Gamma = Dq^2$ or a hydrodynamic radius weight distribution $w(R_h)$ by the Stoke-Einstein equation. In this study, the CONTIN Laplace inversion algorithm in the correlator was used.[17]

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 ζ 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 carboxylic 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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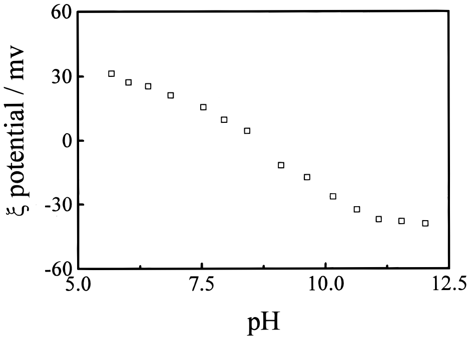

Figure 1. pH dependence of ζ potential of poly(DMMPAPL) in 1 mM potassium nitrate aqueous solution.

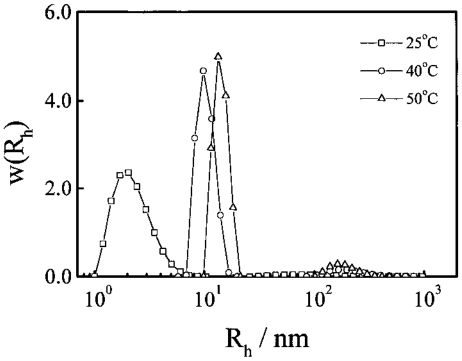

Figure 2. Temperature dependence of weight distribution of hydrodynamic radius $w(R_h)$ of poly(DMMPAPL) in deionized water, where $C = 4.65 \times 10^{-5}$ g/mL.

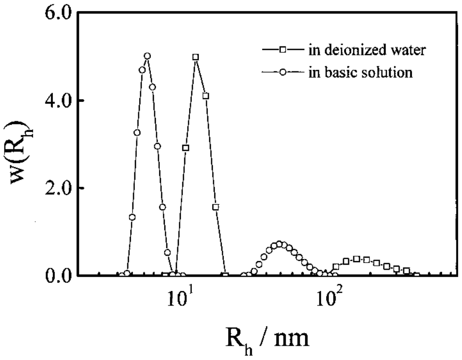

Figure 3. Comparison of weight distribution of hydrodynamic radius $w(R_h)$ of poly(DMMPAPL) in deionized water and in aqueous solution (pH = 12) at 50 °C, where $C_{\text{poly(DMMPAPL)}} = 4.65 \times 10^{-5}$ g/mL.

nm, corresponds to individual chains, while the second broad peak can be related to larger interchain aggregates. The static light-scattering measurements revealed a 10-times higher apparent weight-average molar mass (M_w), clearly indicating the interchain aggregation. Therefore, in deionized water, poly(DMMPAPL) exists as a mixture 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 R_h 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.

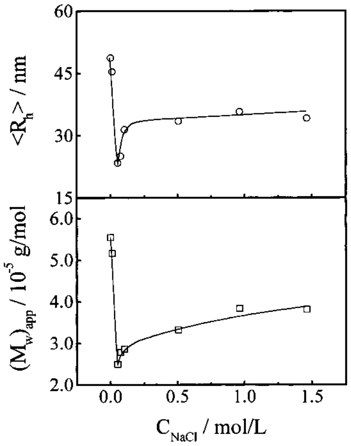

Figure 4. NaCl concentration dependence of average hydrodynamic radius $\langle R_h \rangle$ and apparent weight-average molar mass of poly(DMMPAPL) in aqueous solution (pH = 12) at 50 °C, where $C_{\text{poly(DMMPAPL)}} = 4.65 \times 10^{-5}$ g/mL.

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 $-R_4N^+$ and $-COO^-$ groups. Both $\langle R_h \rangle$ and $(M_w)_{app}$ reach their corresponding minimums at $C_{NaCl} \sim 0.05$ M. Further addition of NaCl results in the increases of both $\langle R_h \rangle$ and $(M_w)_{app}$. A previous study has attributed this increase of $\langle R_h \rangle$ purely to the breaking up of the intrachain association and the chain extension.[18] 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 $\langle R_h \rangle$. Note that in a zwitterionic polymer solution, electrostatic attraction, on the one hand, induces inter- and intrachain 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 $\langle R_g \rangle / \langle R_h \rangle$, which directly reflects the chain conformation.

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

Figure 6a shows that the addition of a small amount of NaCl further broke up inter- and intra-associations

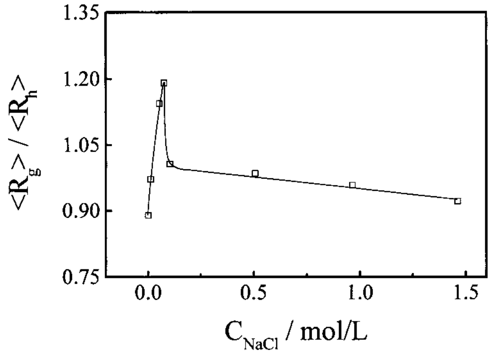

Figure 5. NaCl concentration dependence of ratio of average radius of gyration $\langle R_g \rangle$ to average hydrodynamic radius $\langle R_h \rangle$ of poly(DMMPAPL) in aqueous solution (pH = 12) at 50 °C, where $C_{poly(DMMPAPL)} = 4.65 \times 10^{-5}$ g/mL.

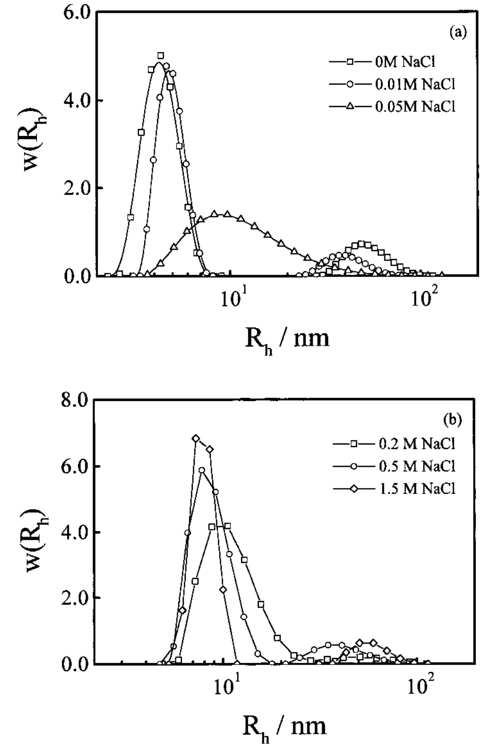

Figure 6. NaCl concentration dependence of weight distribution of hydrodynamic radius $w(R_h)$ of poly(DMMPAPL) in aqueous solution ($C_{poly(DMMPAPL)} = 4.65 \times 10^{-5}$ g/mL, pH = 12) at 50 °C: (a) $C_{NaCl} \leq 0.05$ M and (b) $C_{NaCl} > 0.05$ M.

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 $C_{NaCl} \sim 0.05$ 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 zwitterionic poly(DMMPAPL) aqueous solution. The hydrophilic–hydrophobic balance inside a polymer chain is a primarily important factor to determine its association behavior in aqueous solution. In deionized water, the zwitterionic polymer chains exist as a mixture of interchain aggregates and individual chains due to the zwitterionic interaction. On one hand, the addition of NaOH and small amount of NaCl 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.

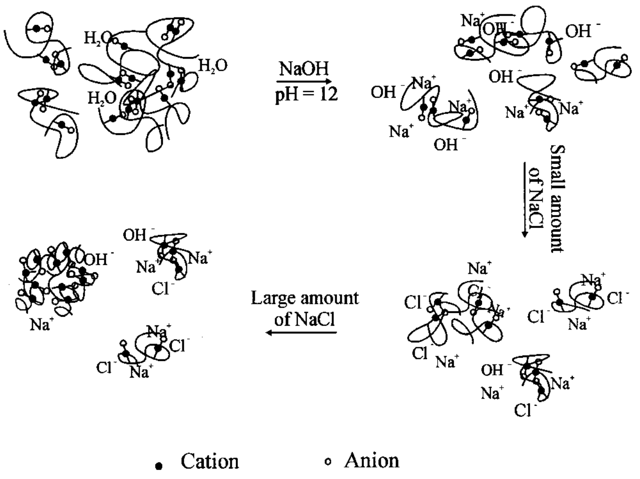

Figure 7. Schematic of effects of adding NaOH and NaCl into a poly(DMMPAPL) aqueous solution.

Acknowledgment. Financial supports of this work by The Research Grants Council of The Hong Kong Special Administration Region Earmarked Grants (1998/99 CUHK4123/98P, 2160111) and The China National Distinguished Young Investigator Fund (1996, A/C No. 29625410) are gratefully acknowledged.

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