*J. Chem. Eng. Data* **2010,** *55,* 3555–3559

# Swelling of Poly(acrylic acid) in Concentrated Sodium Carbonate Solutions

**Xiaohua Fang and Ponisseril Somasundaran***

Columbia University, Langmuir Center of Colloids and Interfaces, New York, New York 10027

Interactions of polymers with salts are of primary importance in industry as well as scientific research. In this paper, we focus on the system of poly(acrylic acid) (PAA) in concentrated sodium carbonate aqueous solutions. From the results obtained by density, static/dynamic light scattering, conductivity, and rheometry, the size/shape of single polymer chains, their effective hydrodynamic region, and the condensation of ionic species were evaluated as a function of salt and PAA concentrations. The formation of special morphological structures of PAA chains in solution and the resultant rheological behavior of the solutions were also examined.

## Introduction

Polyelectrolyte solutions have a wide variety of applications in industries. Charged polymers, for example, poly(acrylic acid) or PAA, are normally used as stabilizers or thickeners to disperse water insoluble components that would otherwise phase segregate or precipitate. The addition of small amounts of appropriate polyanion/polycation chains can achieve this goal and stabilize the formulation. These polymers act as large macroions that can help balance ionic charges in solutions. Their power to stabilize the formula depends considerably on their conformation in the system, which is controlled by the interactions with the solvents and surrounding electrolytes. The addition of any small species of surfactant or salt can provide electrostatic and hydrogen bonding, making the interactions more complex and leading to phase instability as well as poor flow properties.

Previous theoretical and experimental work on the behavior of specific polyelectrolytes in salt solutions has shown charge screening of chain segments by local counterions.[1−3] Under such conditions, the intramolecular interactions would be reduced, while the intermolecular interaction could cause[4] ion condensation on the polymer backbone,[5] inducing collapse-expansion transition on the chains.[3] The above findings, however, are based on the oversimplified cases, for example, PAA in solutions with salt like NaCl. More complex conditions exist when the salt has strong interactions with the solvent and surrounding media components, and there is a lack of systematic experimental studies in this regard. The questions still remain as to how the characteristic concentration (the dilute, semidilute, and the entanglement regions) scales with the ionic strength in different salt−polymer solution systems.[1,6]

This work is based on a model solution system that has a wide variety of applications in the personal care industry, that is, PAA + sodium carbonate + water.[7−9] By measuring the interference of sodium carbonate salt with PAA in aqueous solutions using density, light scattering, and conductivity methods, relevant information on size and shape of the single polymer chains and their effective hydrate region as well as the relative position of the polymer to salt can be evaluated. The information obtained is useful for engineering applications such as the fabrication of nanoscale fibers with a high surface-to-volume ratio, nanoporous structures for biological scaffolds, membranes for wastewater treatment, and the templates for nanostructured assembly materials via micro extrusion/electrospinning.

## Experimental Methods

The sample preparation and characterization techniques are as follows.

***1. Sample Preparation.*** Solutions of PAA were prepared by dissolving different amounts (0.15 mg·cm$^{-3}$, 0.3 mg·cm$^{-3}$, 0.5 mg·cm$^{-3}$, 2 mg·cm$^{-3}$, 10 mg·cm$^{-3}$, 20 mg·cm$^{-3}$) of the polymer in triple-distilled water. The molecular weight $M_w$ of polymers are 2000 (PAA$_{2k}$), 450 000 (PAA$_{450k}$), 1 000 000 (PAA$_{1000k}$), and 4 000 000 (PAA$_{4000k}$) (Sigma-Aldrich). Anhydrous sodium carbonate was then loaded into the above solutions at concentrations of 0 mg·cm$^{-3}$, 50 mg·cm$^{-3}$, 110 mg·cm$^{-3}$, 180 mg·cm$^{-3}$, and 250 mg·cm$^{-3}$. These solutions were equilibrated for 24 h before further characterization.

***2. Characterization Techniques.*** To check whether PAA is swelling in presence of $Na_2CO_3$, the solution density was measured as a function of PAA concentration at each sodium carbonate level using an Anton Paar DMA 5000 density meter. The Zimm plot of the system was acquired by static laser light scattering using a standard Brookhaven BI 200SM goniometer, which yields information on radius of gyration ($R_g$). The laser light was produced from a model 95 ion laser generator (Lexel, 300 mW, 488 nm). The angular dependence of the excess absolute time-averaged scattered intensity, known as the Rayleigh ratio $R_{vv}(\theta)$, was measured from solutions with a series of very dilute PAA concentrations (e.g., 0.04 mg·cm$^{-3}$, 0.09 mg·cm$^{-3}$, 0.25 mg·cm$^{-3}$, 0.48 mg·cm$^{-3}$). Within this range,

$$\frac{HC}{R_{vv}(\theta)} = \frac{1}{M_w}\left(1 + \frac{\langle R_g\rangle^2 q^2}{3}\right) + 2A_2C$$

where $H = 4\pi^2 n_0^2(\mathrm{d}n/\mathrm{d}c)^2/(N_A\lambda^4)$ and $q = (4\pi n_0/\lambda)\sin(\theta/2)$. $N_A$ is the Avogadro constant, $n_0$ is the solvent refractive index, d$n$/d$c$ is the increment in specific refractive index $n$ with respect to the polymer concentration $c$ in a given solvent, and $\lambda$ is the wavelength of laser light in a vacuum.[10,11] The d$n$/d$c$ value was obtained with a BI-DNDC differential refractometer from Brookhaven Instruments Corporation.

The hydrodynamic radius ($R_H$) is the radius of the polymer−solvent−salt sphere that diffuses at the same rate as the PAA molecule. The size of this sphere reflects the ability of a polymer

---

* Corresponding author. E-mail address: ps24@columbia.edu.

10.1021/je100199k

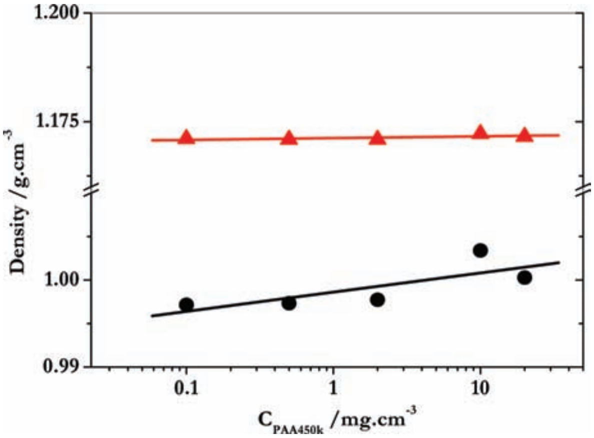

**Figure 1.** Changes in solution density with 450 000 PAA concentration $C_{PAA450k}$ at ●, 0 mg·cm$^{-3}$ and ▲, 250 mg·cm$^{-3}$ salt levels.

coil to affect its surrounding solution. $R_H$ is evaluated by dynamic light scattering (DLS). The diffusion coefficient ($D$) of the hydrated polymer coils is obtained by fitting the intensity correlation curve using the CONTIN model, which further enables the calculation of $R_H$ through the Einstein–Stokes equation $D = (kT)/(6\pi\eta R_H)$,[12] where $k$ is the Boltzmann constant, $T$ is the temperature, $\eta$ is the medium viscosity.

The amount of free ionic species and their mobility in the system was monitored with an Oakton CON 510 benchtop conductivity meter (110/220 VAC, Cole Parmer). Before each measurement, the instrument was calibrated with 5 Oakton conductivity solutions. The rheological behaviors of suspensions are influenced by the size and conformation of the polymer chain, which depends on the relative locations of the salt species. Therefore, the solution viscosity was measured with a Brookfield PVS model rheometer at different temperatures.

## Results and Discussion

The changes in density with PAA ($M_w = 450\,000$) concentration at both 0 mg·cm$^{-3}$ and 250 mg·cm$^{-3}$ $Na_2CO_3$ levels are displayed in Figure 1. Pure polymer solutions show an increase in density. The slope of this density increment was reduced by the presence of 250 mg·cm$^{-3}$ $Na_2CO_3$, indicating the possible swelling of chains and their stronger interaction with surrounding salt−water media. Solutions containing polymers of other molecular weights behave similarly.

The radius of gyration ($R_g$), being the average radius of the polymer coil cross-section from the center of the gravity,[13] describes the conformation of the polymers and their interactions with the solvent. $R_g$ varies with salt concentration if the solvency near the polymer chain is influenced by the ionic species of salt. Figure 2a displays the salt effect on the polymer chain size ($R_g$). For $PAA_{450k}$, the coils remain roughly constant upon the addition of sodium carbonate. When the salt concentration reaches 180 mg·cm$^{-3}$, $R_g$ becomes larger, indicating the stronger interactions between the chain segments and the surrounding solvent or ionic molecules. This obeys the general polyelectrolyte chain behaviors in previous studies, which show that polymer chains undergo chain collapse and re-expansion process when the ionic strength of the media was elevated.[3] Therefore, 180 mg·cm$^{-3}$ is considered the collapse salt concentration $C_z$, at which $PAA_{450k}$ chains pack themselves most efficiently. When the salt level exceeds $C_z$, the polymer coils re-expand themselves, showing a higher affinity to the surrounding media. This phenomenon is also observed for polymers with larger molecular weights of 1 million and 4 million, with $C_z$ being shifted to less than 50 mg·cm$^{-3}$ salt concentration range. Moreover, it is also seen that larger molecules have larger $R_g$ as compared with smaller molecules at similar salt levels. A swell of the polymer chain makes it easier for the chains to contact each other due to the space limit in solution. Therefore, any contributing factors that swell the polymer chains (i.e., an increment in salt levels or polymer chains size) would make the system more crowded with interpenetrated or entangled polymers. This can be tested by measuring the hydrodynamic radius of the polymer chains.

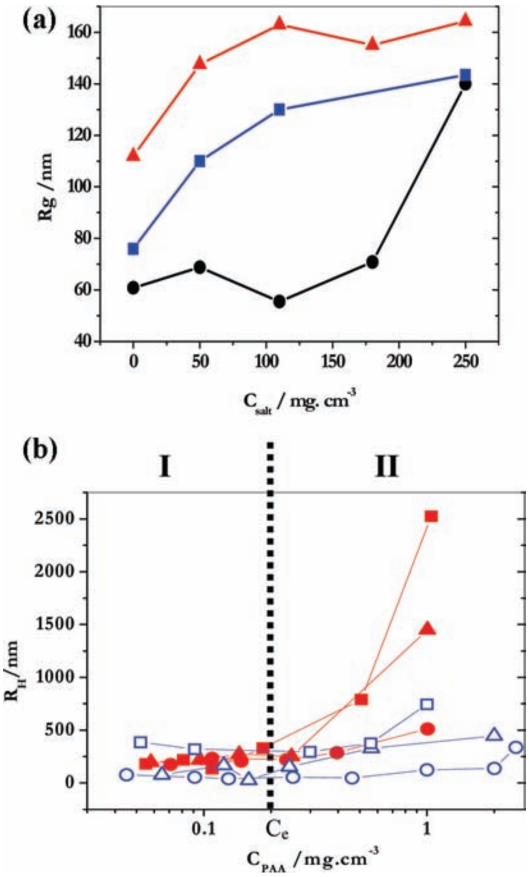

**Figure 2.** Results from the static light scattering technique. (a) The radius of gyration $R_g$ of ●, $PAA_{450k}$; ■, $PAA_{1M}$; and ▲, $PAA_{4M}$ at different $Na_2CO_3$ levels ($C_{salt}$). (b) The hydrodynamic radius $R_H$ as a function of PAA concentration $C_{PAA}$ for $PAA_{1M}$ and $PAA_{4M}$. The dotted line indicates the entanglement concentration $C_e$ between regime I and regime II for $PAA_{4M}$ at the 250 mg·cm$^{-3}$ salt level. $PAA_{4M}$: ●, 0 mg·cm$^{-3}$ salt; ▲, 50 mg·cm$^{-3}$ salt; ■, 250 mg·cm$^{-3}$ salt. $PAA_{1M}$: ○, 0 mg·cm$^{-3}$ salt; △, 50 mg·cm$^{-3}$ salt; □, 250 mg·cm$^{-3}$ salt.

The hydrodynamic radius, $R_H$, is the size of the light scattering center in solution. In pure polymer solutions, it is expected that, with more polymer chains in the system, each chain's effective region shrinks a little with lower $R_H$. The PAA-sodium system, on the other hand, shows (Figure 2b) two distinct regimes on the $R_H$-PAA concentration curve. In the dilute solution regime, $R_H$ remains roughly constant with polymer concentration. In the more concentrated PAA regime, $R_H$ increases sharply with PAA concentration $C_{PAA}$. The slope of regime II depends on the sodium carbonate loading, with an increase in salt level showing steeper slopes. In general, larger PAA chains show higher $R_H$ than smaller chains at the same salt level.

Since $R_H$ denotes the interaction volume of the polymer chains in media, the above observations of the two regions indicate a possible transition of the solvency conditions when solution gets crowded with polymer chains. Below the transition point $C_e$ shown in Figure 2b, the insensitivity of $R_H$ to $C_{PAA}$ indicates

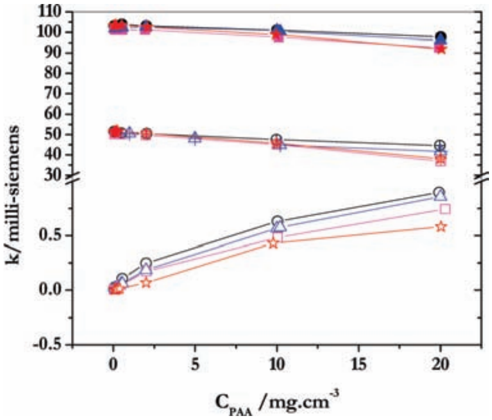

**Figure 3.** Conductivity $k$ of PAA solutions at different $Na_2CO_3$ levels. 250 mg·cm$^{-3}$ salt: ●, 2000; ▲, 450 000; ■, 1 000 000; ★, 4 000 000. 50 mg·cm$^{-3}$ salt: ⊕, 2000; △ with cross, 450 000; ⊞, 1 000 000; ☆ with cross, 4 000 000. 0 mg·cm$^{-3}$ salt: ○, 2000; △, 450 000; □, 1 000 000; ☆, 4 000 000.

the isolated state of chains. Above the transition point (in regime II), the fast $R_H$ progression denotes a larger area of influence by the single polymer chain on its surroundings. Since this change is due to the addition of more chains, it is reasonable to consider $C_e$ to be the critical polymer concentration at which chain entanglement begins to play an important role. $C_e$ gets smaller with an increase in the salt level and molecular weight. According to previous discussion, at $C_z$, the collapse salt concentration, the PAA chains would pack themselves efficiently. This collapse does not cause any observable hydrodynamic radius change below the entanglement PAA concentration $C_e$, where the $R_H$ curves at different salt levels almost overlap each other (Figure 2b). When PAA composition gets higher than $C_e$, divergence in $R_H$ would be observable regardless of chain collapse.

The conductivity of the polymer solutions at different sodium carbonate levels is shown in Figure 3. Pure PAA solutions display a microsiemenz level increase in conductivity with respect to $C_{PAA}$ in regime I, which is much less than the millisiemenz level shown by the salt/PAA/water mixtures. In the entangled range (regime II), the increment with respect to $C_{PAA}$ was lowered. This suggests a more confined situation when more chains exist in the system, although the charged chain/segments are still capable of moving freely under the electrical field of the conductivity meter. In the presence of sodium carbonate, the overall solution conductivity is seen to decrease with polymer concentration, indicating a reduction in the number of free moving ionic species or a decrease in their mobility. Thus, polymers confine some ionic species locally in the solution. The drop in conductivity is proportional to the polymer amount in solution. It is also apparent that, although $PAA_{2k}$ has the same number of monomers in the system as the larger molecules ($PAA_{450k}$, $PAA_{1M}$, $PAA_{4M}$), long chains are more efficient in holding ions locally. This is in support for the necklace-like chain model,[14,15] which describes a polyelectrolyte as a chain consisting of globules of densely packed thermal blobs of size $\xi_T$.[16] Larger chains form more globules that can hold the ions from solution. High salt concentration, for example, 250 mg·cm$^{-3}$, leads to the saturation of the polymer globules, and therefore, the slopes of the conductivity versus $C_{PAA}$ curves will be relatively independent of the polymer concentration.

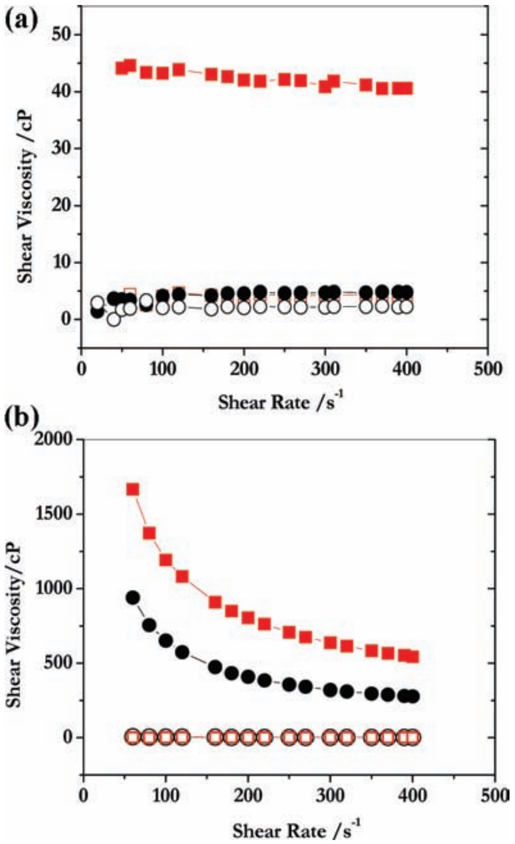

**Figure 4.** Rheological behavior of solutions containing 0 mg·cm$^{-3}$ and 250 mg·cm$^{-3}$ $Na_2CO_3$ in the PAA concentration regimes of I and II as shown in Figure 2b. 0 mg·cm$^{-3}$ salt: ○, 0.2 mg·cm$^{-3}$ (a) $PAA_{450k}$, (b) $PAA_{4M}$; ●, 20 mg·cm$^{-3}$ (a) $PAA_{450k}$, (b) $PAA_{4M}$. 250 mg·cm$^{-3}$ salt: □, 0.2 mg·cm$^{-3}$ (a) $PAA_{450k}$, (b) $PAA_{4M}$; ■, 20 mg·cm$^{-3}$ (a) $PAA_{450k}$, (b) $PAA_{4M}$.

As stated previously, the ionic species collapse into the globules and swell the polymer, which further lower the critical entanglement concentration. In this case, the rheological behavior of the polymer solutions would be affected considerably by salt. In Figure 4 we show the rheological behavior for solutions containing 0 mg·cm$^{-3}$ and 250 mg·cm$^{-3}$ salt in the polymer concentration regimes of I and II, along with the molecular weight effects (Figure 4b). The overall shear viscosity for $PAA_{450k}$ remains constant with respect to shear rates at both salt levels. Larger chains ($PAA_{1M}$ and $PAA_{4M}$), however, showed a shear thinning behavior at high shear rates in regime II. This is reasonable, since according to the conductivity results obtained, larger molecules have a greater chance to form globules, which would unfold during shear. Solutions in regime I show little salt concentration dependence, as compared with the solutions in regime II, which display a significant improvement in shear viscosity at the 250 mg·cm$^{-3}$ salt level. In other words, the polymer shows a higher rheological sensitivity to salt when they entangle. This actually suggests that the globular structure does not actually exist at low PAA concentrations.

In Figure 5 we show the schematic representation of the PAA/sodium carbonate/water system. Without salt, the PAA chains behave like random coils consisting of only thermal blobs. The addition of salt causes the expansion of the chain as well as the formation of globular structures on the chain backbone, which contains localized salt species. The swelling of polymers makes it favorable for the chains to reach the entangled state. Larger molecules (Figure 5b), with a similar amount of monomers but a smaller number of chains, show lower critical polymer concentrations of globule formation as well as chain intertwining. At a high enough temperature to break the globular structures, more significant rheological performance changes

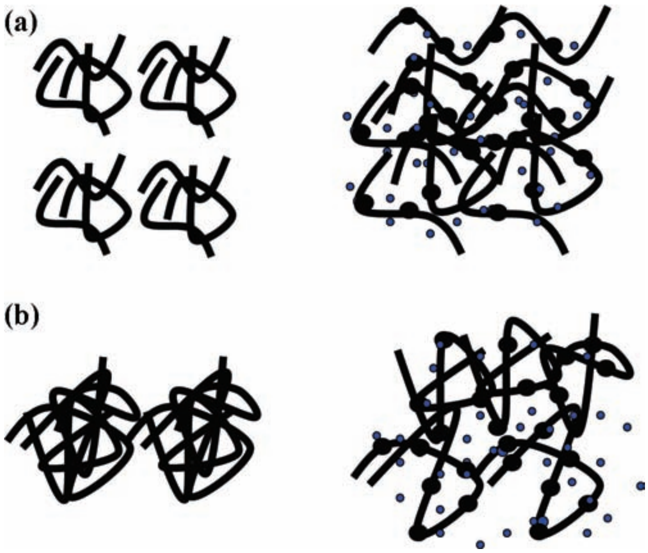

**Figure 5.** Schematic drawing of the interactions in the PAA/$Na_2CO_3$/water system: (a) small chains and (b) large chains. The black disks on the chain backbone represent the globular structure, while the blue disks surrounding the backbone represent the ionic species of salt.

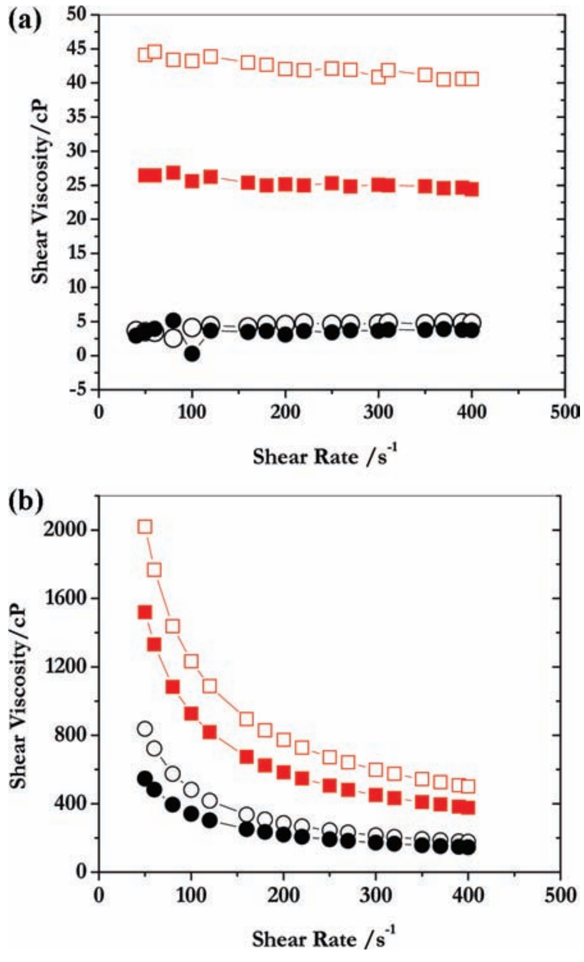

**Figure 6.** Rheological responses of the 20 mg·cm$^{-3}$ (a) $PAA_{450k}$ and (b) $PAA_{4M}$ solutions to temperature. 0 mg·cm$^{-3}$ salt: ○, 25 °C; ●, 45 °C. 250 mg·cm$^{-3}$ salt: □, 25 °C; ■, 45 °C.

might be expected in the high salt samples. This hypothesis was tested, and the results from rheology measurement are shown in Figure 6, which displays the shear viscosity versus shear rate graphs for 20 mg·cm$^{-3}$ $PAA_{450k}$. Solutions of larger chains ($PAA_{1M}$ and $PAA_{4M}$) show similar rheological behavior (Figure 6b). When there is no sodium carbonate in solution, the globules do not form. Therefore, the viscosity response of the pure polymer solutions to temperature is less significant as compared with the solutions at high salt levels. On the other hand, although it is easier to form the globules on larger molecules, the severe entanglement and interpenetration of the chains compromise the influence of the disassembly of the globules under thermal input and shear conditions. As a result, the percentage drop in shear viscosity with temperature is less significant for larger molecules than smaller chains.

Theoretical predictions indicate a re-expansion only in the case when the counterion is multivalent. This is based on the oversimplified salt model, for example, $CaCl_2$, in which the anions do not interfere significantly with the solution compositions.[1−3] The PAA re-expansion detected in this study with the monovalent sodium cation indicates that complex anions like $CO_3^{2-}$ can also influence the morphology of polymer chains, which could be attributed to their strong interaction with the polymer and the solvent.

## Conclusions

The sodium carbonate/PAA interaction in aqueous solutions was studied using density, static/DLS, conductivity, and rheological techniques. It was found that high salt levels swell the polymer more by causing the formation of globular structures, which holds ions and increases the possibility of entanglement. The entanglement of PAA depends on their molecular weight. The morphological variation in turn influences the rheological properties of the solution significantly.

### Supporting Information Available:

Conductivity and rheological data, in tables. This material is available free of charge via the Internet at http://pubs.acs.org.

## Literature Cited

(1) Ashok, B.; Muthukumar, M. Crossover Behavior of the Viscosity of Dilute and Semidilute Polyelectrolyte Solutions. *J. Phys. Chem. B* **2009**, *113* (17), 5736–5745.
(2) Kanemaru, E.; Terao, K.; Nakamura, Y.; Norisuye, T. Dimensions and viscosity behavior of polyelectrolyte brushes in aqueous sodium chloride. A polymacromonomer consisting of sodium poly(styrene sulfonate). *Polymer* **2008**, *49* (19), 4174–4179.
(3) Hsiao, P. Y.; Luijten, E. Salt-induced collapse and reexpansion of highly charged flexible polyelectrolytes. *Phys. Rev. Lett.* **2006**, *97*, 148301.
(4) Yethiraj, A. Liquid State Theory of Polyelectrolyte Solutions. *J. Phys. Chem. B* **2009**, *113* (6), 1539–1551.
(5) Chang, R. W.; Yethiraj, A. Dilute solutions of strongly charged flexible polyelectrolytes in poor solvents: Molecular dynamics simulations with explicit solvent. *Macromolecules* **2006**, *39* (2), 821–828.
(6) Litmanovich, E. A.; Zakharchenko, S. O.; Stoichev, G. V. Influence of chain charge and complexation on the overlap and entanglements formation in poly(acrylic acid) salt-containing aqueous solutions. *J. Phys. Chem. B* **2007**, *111* (29), 8567–8571.
(7) Huan, Z. G.; Chang, J. Effect of Sodium Carbonate Solution on Self-setting Properties of Tricalcium Silicate Bone Cement. *J. Biomater. Appl.* **2008**, *23* (3), 247–262.
(8) El Kazzouli, S.; Koubachi, J.; Berteina-Raboin, S.; Mouaddib, A.; Guillaumet, G. A mild and selective method for the N-Boc deprotection by sodium carbonate. *Tetrahedron Lett.* **2006**, *47* (48), 8575–8577.
(9) Zhang, Z.; Dong, Y. W.; Wang, G. W. Efficient and clean aldol condensation catalyzed by sodium carbonate in water. *Chem. Lett.* **2003**, *32* (10), 966–967.
(10) Chu, B.; Wu, C.; Buck, W. Light-Scattering Characterization of an Alternating Copolymer of Ethylene and Tetrafluoroethylene 0.3. Temperature Behavior of Polymer Size. *Macromolecules* **1989**, *22* (1), 371–374.
(11) Lin, W. R.; Zhang, J.; Wan, X. H.; Liang, D. H.; Zhou, Q. F. Solvent-Induced Association and Micellization of Rod-Coil Diblock Copolymer. *Macromolecules* **2009**, *42* (12), 4090–4098.
(12) Chen, X. M.; Burger, C.; Wan, F.; Zhang, J.; Rong, L. X.; Hsiao, B. S.; Chu, B.; Cai, J.; Zhang, L. Structure study of cellulose fibers

wet-spun from environmentally friendly NaOH/urea aqueous solutions. *Biomacromolecules* **2007**, *8* (6), 1918–1926.

(13) Doi, M.; Edwards, S. *The Theory of Polymer Dynamics, International Series of Monographs on Physics 73*; Oxford Science Publications: Oxford, U.K., 1986.

(14) Dobrynin, A. V.; Rubinstein, M.; Obukhov, S. P. Cascade of transitions of polyelectrolytes in poor solvents. *Macromolecules* **1996**, *29* (8), 2974–2979.

(15) Chepelianskii, A.; Mohammad-Rafiee, F.; Trizac, E.; Raphael, E. On the Effective Charge of Hydrophobic Polyelectrolytes. *J. Phys. Chem. B* **2009**, *113* (12), 3743–3749.

(16) Dobrynin, A. V.; Rubinstein, M. Theory of polyelectrolytes in solutions and at surfaces. *Prog. Polym. Sci.* **2005**, *30* (11), 1049–1118.

Received for review March 3, 2010. Accepted May 25, 2010. The authors acknowledge the support from the National Science Foundation (Grant No. 0328614) and industry sponsors of the Industry/University.

JE100199K