Letter

# Microrheological Approach for Probing the Entanglement Properties of Polyelectrolyte Solutions

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**ABSTRACT:** The entanglement dynamics and viscoelasticity of polyelectrolyte solutions remain active research topics. Previous studies have reported conflicting experimental results when compared to Dobrynin's scaling predictions derived from the Doi–Edwards (DE) tube model for entangled polymers. Herein, by combining classical bulk shear rheometry with diffusing wave spectroscopy (DWS) microrheometry, we investigate how the key viscoelastic parameters (the specific viscosity  $\eta_{sp}$ , the plateau modulus  $G_{e^j}$  and the ratio of the reptation time to the Rouse time of an entanglement strand  $\tau_{rep}/\tau_e$ ) depend on the polymer concentration for semidilute entangled (SE) solutions containing n



concentration for semidilute entangled (SE) solutions containing poly(sodium styrenesulfonate) with high molecular weight. Our experimental measurements yield  $G_e \propto c^{1.51\pm0.04}$ , in good agreement with the scaling of  $G_e \propto c^{1.5}$  predicted by Dobrynin's model for salt-free polyelectrolyte SE solutions, suggesting that the electrostatic interaction influences the viscoelastic properties of polyelectrolyte SE solutions. On the other hand, the deviation in the scaling exponent for  $\eta_{sp} \propto c^{2.56\pm0.04}$  and  $\tau_{rep}/\tau_e \propto c^{1.82\pm0.28}$  is observed between our DWS experiments and Dobrynin's model prediction ( $\propto c^{1.5}$ ), likely due to the fact that Dobrynin's scaling model does not account for mechanisms such as the contour length fluctuation, the constraint release, and the retardation of solvent dynamics, which are known to occur for SE solutions of neutral polymers. Our results demonstrate that DWS serves as a powerful rheological tool to study the entanglement dynamics of polyelectrolyte solutions. The scaling relationships obtained in this study provide new insights to the long-standing debate on the entanglement dynamics of polyelectrolyte solutions.

he conformation of polyelectrolyte chains is known to be strongly influenced by electrostatic interactions acting between the repeating units with dissociated counterions. Accordingly, how the electrostatic interactions modify the dynamics of polyelectrolyte chains is an important question to be answered. Among existing models,<sup>2-7</sup> Dobrynin's scaling model has shown good agreement with many experimental rheology data for polyelectrolyte solutions.<sup>8-16</sup> In their scaling model, the Debye-Hückel theory was first applied to explain the effect of electrostatic interactions on the conformation of polyelectrolyte chains, which was subsequently incorporated into the viscoelastic models to derive the scaling laws of viscoelastic parameters, such as the solution viscosity and relaxation time of the polyelectrolyte solution.<sup>6</sup> However, recent rheological studies on polyelectrolyte solutions in the semidilute entangled (SE) regime have presented conflicting results on the applicability of the tube model for entangled neutral polymers to polyelectrolyte systems.<sup>13-26</sup> For example, Lopez<sup>22</sup> reported that the dependence of the entanglement concentration on the chain length was much weaker than that predicted by Dobrynin's scaling theory for salt-free SE polyelectrolyte solutions. Moreover, Han and Colby<sup>25</sup> showed that the plateau modulus of poly(cesium styrenesulfonate) in glycerol scaled as  $c^{2.3}$  (with c being the molar concentration of the monomers), in agreement with the predicted exponent for

electrically neutral polymers in the SE regime. Hence, independent verification is required to understand the entanglement dynamics of polyelectrolytes given their importance in various biological and industrial processes.<sup>1</sup>

The scaling analysis for polyelectrolyte SE solutions can be challenging because the polyelectrolyte SE regime, where the electrostatic interactions influence the viscoelastic properties of polyelectrolyte solutions, tends to be narrow.<sup>27</sup> Dobrynin et al.<sup>6</sup> defined the polyelectrolyte SE regime in the concentration range of  $c_e \leq c < c_D$  with  $c_e$  being the entanglement concentration at which entanglements start to form and  $c_D$ being a critical polymer concentration at which the electrostatic screening length is equal to the electrostatic blob size. On the basis of Dobrynin's scaling prediction,<sup>6</sup> polyelectrolytes in solutions at  $c \geq c_D$  behave like neutral polymers and their viscoelastic properties follow the scaling laws of neutral polymers in the SE regime. When one considers that the

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transition of the polymer concentration regime occurs gradually, the experimental results with narrow SE regimes may over- or underestimate the scaling exponent for the polyelectrolyte SE regime due to different scaling exponents in the surrounding polymer concentration regimes.<sup>22</sup> In addition, probing the entanglement dynamics of polyelectrolyte solutions at high frequencies is difficult. With conventional bulk rheometers, the measurable viscoelastic response of polyelectrolyte SE solutions is limited to that in the terminal regime captured at low frequencies since polyelectrolytes can only dissolve in low-viscosity solvents, such as water.<sup>25</sup> To acquire data at high frequencies, complex modulus  $G^*$ measurements need to be performed at various temperatures to construct the master curve of  $G^*$  by applying the timetemperature superposition (TTS) principle.28 However, the TTS principle often breaks down due to solvent crystallization for polyelectrolyte systems.<sup>25</sup> As a result, only the zero-shear viscosity and the longest relaxation time have been routinely compared with the scaling predictions. To resolve these difficulties, we will use polyelectrolyte solutions possessing a wide SE regime with  $c_{\rm e} \ll c_{\rm D}$  and probe their viscoelastic responses at high frequencies before reaching the terminal regime.

Diffusing wave spectroscopy (DWS) is a dynamic light scattering technique for turbid samples, operating in the multiple light scattering regime. DWS is often employed to perform microrheology with probe particles being embedded within otherwise translucent or transparent materials.<sup>29,30</sup> DWS-based microrheology enables the measurement of the complex modulus  $G^*$  of viscoelastic materials at angular frequencies as large as 10<sup>7</sup> rad s<sup>-1</sup>, depending on the size and concentration of tracer particles. In the past two decades, substantial progress has been made in developing the DWS technique<sup>31-34</sup> to provide reliable linear rheological measurements of polymer solutions,<sup>35-39</sup> wormlike micellar solutions,<sup>40,41</sup> emulsions,<sup>30,42</sup> suspensions,<sup>43</sup> and gels.<sup>44</sup> In particular, the rubber-plateau regime has been successfully observed for aqueous poly(ethylene oxide) solutions,<sup>3</sup> indicating that DWS can provide important information for entangled polyelectrolyte solutions at high frequencies.

Motivated by the encouraging DWS results of aqueous poly(ethylene oxide) solutions, we employ DWS microrheology to study the entanglement dynamics of aqueous solutions of poly(sodium styrenesulfonate) (NaPSS) with a high molecular weight  $(M_{\rm w})$  of 3.16  $\times$  10<sup>6</sup> g mol<sup>-1</sup> and a narrow molecular weight distribution  $(M_w/M_n)$  of <1.35. The NaPSS used in our study has the longest chain length that is commercially available, which yields a smaller entanglement concentration  $c_{e}$ .<sup>6</sup> We choose water as the solvent because it acts as a good solvent and has a small Bjerrum length because of its high dielectric constant,<sup>45</sup> leading to a high  $c_D$  value, and more counterions can dissociate from polyelectrolyte chains (see Section S3.3 for more details).<sup>14,46</sup> Thus, we anticipate that using water as a solvent can maximize the concentration range in the polyelectrolyte SE regime for quantitative scaling analysis of the NaPSS SE solution, while keeping the charge effects on their viscoelastic properties active. Here, we measure and extract four key viscoelastic parameters (the specific viscosity  $\eta_{sp}$ , the plateau modulus  $G_{e}$ , the Rouse time of an entanglement strand  $\tau_{e}$ , and the reptation time  $\tau_{rep}$ ) with respect to the polymer concentration in the SE regime for the NaPSS solutions and compare the experimental data with Dobrynin's scaling model.

Table 1 summarizes the scaling laws of the key viscoelastic parameters described above, derived using the Doi-Edwards

Table 1. Comparison of the Scaling Predictions of the Specific Viscosity  $\eta_{sp}$ , the Plateau Modulus  $G_e$ , the Rouse Time of an Entanglement Strand  $\tau_e$ , and the Reptation Time  $\tau_{rep}$  for Salt-Free Polyelectrolytes<sup>6</sup> and Neutral Polymer<sup>47</sup> in Good Solvents and Our Experimental Results for Aqueous NaPSS SE Solutions<sup>*a*</sup>

	semidilute entangled (SE) regime			
	scaling prediction of salt- free polyelectrolytes	scaling prediction of neutral polymers	our experimental measurements	
$\eta_{\rm sp}$	$N^{3}c^{1.5}$	$N^{3}c^{3.9}$	$c^{2.56\pm0.04}$	
G <sub>e</sub>	$N^{0}c^{1.5}$	$N^{0}c^{2.3}$	$c^{1.51\pm0.04}$	
$ au_{e}$	$N^{0}c^{-1.5}$	$N^{0}c^{-2.3}$	$c^{-0.62\pm0.27}$	
$ au_{ m rep}$	$N^3c^0$	$N^{3}c^{1.6}$	$c^{1.19\pm0.08}$	
$ au_{ m rep}/ au_{ m e}$	$N^{3}c^{1.5}$	$N^{3}c^{3.9}$	$c^{1.82\pm0.28}$	

 ${}^a\!\mathrm{More}$  details on the scaling law can be found in the original article by Dobrynin et al.  ${}^6$ 

(DE) tube model for salt-free polyelectrolytes<sup>6</sup> and neutral polymers<sup>47</sup> with a single molecular weight dissolved in good solvents in the SE regime. Here, N and c are the degree of polymerization and the molar concentration of the monomers. The parameters  $G_{\rm e}$ ,  $\tau_{\rm e}$ , and  $\tau_{\rm rep}$  are specific only for SE solutions and can be estimated from the dependence of the complex modulus  $G^*$  on the angular frequency  $\omega$ .<sup>47</sup> It should be noted that the Dobrynin model does not account for polymer relaxation mechanisms, such as the contour length fluctuation (CLF) and the constraint release (CR), which are known to occur for entangled solutions of neutral polymers.<sup>48</sup> In addition, as the polymer concentration increases in the entangled regime, the dynamics of the solvent molecules could be retarded by their cooperative motions with the polymer chains.<sup>49</sup> By measuring glass transition temperatures of polymer solutions, Savin et al.<sup>50</sup> showed that the retardation of solvent dynamics became pronounced at polymer concentrations above 20 wt % and the retardation degree was enhanced with increasing polymer concentrations. Thus, we anticipate that the dependence of  $\tau_{\rm rep}$ ,  $\tau_{\rm e}$ , and  $\eta_{\rm sp}$  on c from our experiments would be different from the scaling laws predicted by the Dobrynin model shown in Table 1.

Among the four parameters listed in Table 1, the specific viscosity, defined as  $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$  with  $\eta_0$  being the zeroshear viscosity of the polymer solutions and  $\eta_s$  being the solvent viscosity, can be easily estimated from the shear viscosity curve measured using a conventional bulk shear rheometer. Therefore, we first investigate how  $\eta_{sp}$  varies against the polymer concentration *c* with a strain-controlled shear rheometer (ARES-G2, TA Instruments).

Figure 1 plots  $\eta_{sp}$  values at 25 °C as a function of *c*. The values of  $\eta_0$  and  $\eta_s$  were estimated by averaging shear viscosities over low shear rates in the Newtonian regime (see Figure S1). The specific viscosity  $\eta_{sp}$  increased monotonically with increasing *c*, consistent with the reported behavior for salt-free polyelectrolyte solutions.<sup>25</sup>

We determined various polymer concentration regimes for our NaPSS solutions by performing power-law fits to the measured  $\eta_{sp}$  in a wide polymer concentration range, as shown in Figure 1. For  $c < 7 \times 10^{-4}$  M, the specific viscosity increased linearly with c ( $\eta_{sp} \propto c^{1.00\pm0.06}$ ). This linear trend is typical for dilute (DL) polymer solutions. At higher *c*, a shift of the



**Figure 1.** Specific viscosity  $\eta_{\rm sp}$  at 25 °C plotted against the monomer molar concentration *c* for salt-free aqueous NaPSS solutions. Dashed lines represent the power-law fits to the  $\eta_{\rm sp}$  data for dilute ( $\eta_{\rm sp} \propto c^{0.51\pm0.04}$ ), semidilute unentangled ( $\eta_{\rm sp} \propto c^{0.51\pm0.04}$ ), and semidilute entangled ( $\eta_{\rm sp} \propto c^{2.56\pm0.04}$ ) solutions. Arrows indicate the monomer concentrations at the overlap *c*<sup>\*</sup> and entanglement *c*<sub>e</sub> concentrations.

power-law regime occurred at  $\eta_{\rm sp} \sim 1$  with  $\eta_{\rm sp} \propto c^{0.51 \pm 0.04}$  up to  $c = 6 \times 10^{-3}$  M. This highlights the transition from the DL to semidilute unentangled (SU) regimes.47 Indeed, the observed scaling exponent agreed well with the predicted scaling exponent  $(\eta_{sp} \propto c^{0.5})$  for polyelectrolyte SU solutions. We determined the overlap concentration  $c^* \sim 7 \times 10^{-4}$  M as the crossover concentration of the two power-law fits for DL and SU regimes. This estimated  $c^*$  was much larger than the value predicted by Dobrynin's scaling model ( $c^* = 3 \times 10^{-6}$  M), probably due to the salt residues (on the order of  $10^{-5}$  M) in our system; see Section S3.1 for more details. As the polymer concentration is further increased, another power-law relationship  $(\eta_{sp} \propto c^{2.56\pm0.04})$  emerged in the concentration range of 0.09 M < c < 1.12 M. We denote this power-law regime as the polyelectrolyte SE regime because the entanglement concentration  $c_{\rm e} \sim 7 \times 10^{-2}$  M, estimated as the crossover concentration of the two power-law fits for SU and SE regimes, agrees well with the predicted value of  $c_e = 7.2 \times 10^{-2}$ M from Dobrynin's scaling model for salt-free polyelectrolyte SE solutions. This  $c_{\rm e}$  value is further validated using the terminal modulus and complex modulus data (see details and comprehensive scaling analysis in Section S3.2).

Next, we evaluate  $\tau_{rep}$ ,  $\tau_{e}$ , and  $G_{e}$  from the measurement of  $G^*$  using a DWS microrheometer (DWS RheoLab, LS Instruments) for NaPSS solutions at 25  $^{\circ}$ C and 0.0941 M  $\leq$  $c \leq 1.12$  M, spanning the SE regime (the detailed rational for the concentration range can be found in Section S4.1). Polystyrene particles of 211 nm in diameter at 0.3 wt % were suspended in NaPSS solutions for DWS microrheology. More details about the DWS experiments including a discussion of the effects of the embedded tracer particles on the  $G^*$  data (Section S4) and data processing (Section S5) are provided in the Supporting Information. Using the DWS technique, the complex modulus was successfully measured over a wide frequency range at  $10^1-10^7$  rad s<sup>-1</sup>. The representative G\* spectra at 25 °C for a NaPSS solution at c = 0.297 M were shown in Figure 2. We observed a full width of the rubberyplateau regime, evidenced by the two crossovers of G' and G''at  $1.0 \times 10^2$  and  $3.5 \times 10^4$  rad s<sup>-1</sup>. With the full rubbery-



**Figure 2.** Frequency dependence of the complex modulus  $G^*$  and the loss tangent at 25 °C for a semidilute entangled NaPSS solution at c = 0.297 M. The values of  $G^*$  were measured by DWS microrheology (DWS RheoLab). The black and red curves represent the storage G' and loss G'' modulus, while the blue curve represents loss tangent estimated as tan  $\delta = G''/G'$ . Green dashed arrows guide the determination of  $G_e$ ,  $\tau_{rep}$ , and  $\tau_e$ .

plateau regime of  $G^*$  spectra, we estimated  $\tau_{\rm rep}$   $(1.0 \times 10^{-2} \text{ s})$ and  $\tau_{\rm e}$   $(2.9 \times 10^{-5} \text{ s})$  as the inverse of the crossover frequency of G' and G'' at low and high frequencies, respectively. The plateau modulus  $G_{\rm e} = 1.4 \times 10^2$  Pa was estimated as the storage modulus at a frequency where the loss tangent  $\tan \delta = \frac{G''}{G'}$  displays a minimum (i.e., the so-called MIN method)<sup>51</sup> ( $\tan \delta = \frac{G''}{G'}$ . See the schematics shown in Figure 2.

The MIN method has been frequently used to estimate the plateau modulus of viscoelastic fluids.<sup>51</sup> However, the estimated  $G_e$  is not always equivalent to the real plateau modulus because the magnitude of the measured storage modulus in the rubbery-plateau regime decreases as the CLF and CR modes progress, i.e., with decreasing frequencies.<sup>52</sup> As a result, a clear plateau regime, where the storage modulus is independent of frequency, eventually disappears from the observed complex modulus spectra.<sup>51,52</sup> This leads to uncertainties in the magnitude between the estimated and the real  $G_{e}$ , in particular for entangled polymer systems with poor entanglement degrees in semidilute solutions.<sup>51,52</sup> In theory, the plateau modulus should not be affected by the CLF and CR modes.<sup>48,52</sup> In order to confirm that the uncertainties originated from the MIN method do not influence the resulting scaling exponent, we also evaluated the value of  $G_{\rm e}^{\rm cross}$ as the storage modulus at the high frequency crossing of G'and G'' (i.e., the inverse of  $\tau_e$ ). We obtained  $G_e^{cross} \propto c^{1.48\pm0.06}$ confirming that the MIN method did not affect our scaling analysis for the plateau modulus (see Figure S15).

Figure 3 shows various  $G^*$  spectra with different polymer concentrations in the SE regime (0.0941 M  $\leq c \leq 1.12$  M) measured by DWS at 25 °C. The absolute values of the storage G' (solid curves) and loss G'' (dashed curves) moduli increased with increasing polymer concentrations, since the number of polymer chains increases with increasing *c*. Our DWS experiments also captured the expected increase in the width of the rubbery-plateau regime with increasing *c* without applying the TTS method required when using conventional bulk rheometers.<sup>25</sup> We observed that the Rouse time of an entanglement strand  $\tau_e$  decreased with increasing *c*, while the reptation time  $\tau_{rep}$  increased with increasing *c*.

To visualize the behavior of the key viscoelastic parameters described earlier, Figure 4 shows the values of  $G_e$ ,  $\tau_{e}$  and  $\tau_{rep}$  as



**Figure 3.** Frequency dependence of the complex modulus  $G^*$  at 25 °C for NaPSS solutions at various monomer concentrations in the SE regime.

a function of *c* in the range of 0.0941 M  $\leq c \leq$  1.12 M. Here, the magnitude of experimental errors was estimated from three individual DWS experiments under the same experimental condition with larger errors in lower and higher monomer concentrations (see more details in Section S6). Both  $G_{e}$  and  $au_{
m rep}$  increased with increasing *c*, while  $au_{
m e}$  decreased with increasing *c*. In addition, the observed  $G_{e}$ ,  $\tau_{e}$ , and  $\tau_{rep}$  showed a power-law dependence on *c* over the measured polymer concentration range with  $G_{\rm e} \propto c^{1.51\pm0.04}$ ,  $\tau_{\rm e} \propto c^{-0.62\pm0.27}$ , and  $\tau_{\rm rep}$  $\propto c^{1.19\pm0.08}$ . Note that the obtained scaling exponent for  $G_{\rm e}$ showed good agreement with the predicted value for polyelectrolyte SE solutions, indicating that the conformation and the resulting viscoelastic properties of polyelectrolytes in the SE regime are influenced by the electrostatic interaction as predicted by the Dobrynin model. On the other hand, the scaling exponents for  $au_{\rm e}$  and  $au_{\rm rep}$  are different from those predicted by Dobrynin's scaling predictions, probably due to the combined effects from the CLF/CR modes and the retardation of solvent dynamics.

To remove the effect of the retarded solvent dynamics on the polymer relaxation times, we adopt the approach proposed by Han and Colby<sup>25</sup> to analyze the ratio of  $\tau_{rep}/\tau_{e'}$  assuming that both  $\tau_e$  and  $\tau_{rep}$  can be retarded similarly with respect to the polymer concentration. Figure 5a shows the monomer concentration dependence of the measured  $\tau_{rep}/\tau_e$  for our NaPSS solutions at 25 °C. This relaxation time ratio also characterizes the width of the rubbery plateau regime. The value of  $\tau_{rep}/\tau_e$  increased with increasing *c* with a power-law dependence  $\tau_{\rm rep}/\tau_{\rm e} \propto c^{1.82\pm0.28}$ . The estimated scaling exponent was slightly larger than that predicted by the Dobrynin model  $(\tau_{\rm rep}/\tau_{\rm e} \propto c^{1.5})$ . We attribute this deviation to the CLF and CR relaxation processes, which are not considered in the Dobrynin model.

In order to confirm our hypothesis, we applied the method proposed by Shahid et al.<sup>52</sup> on the basis of a modified tube model accounting for the CLF and CR modes. They showed that if the CLF and CR modes did influence the reptation dynamics for a given entangled polymeric system, the measured reptation time  $( au_{
m rep})$ , normalized by the ideal reptation time  $(\tau_e Z_{2,0}^3 c)$  in the absence of the CLF and CR modes, would be proportional to the number of entanglement strands  $Z_2 = Z_{2,0}c$  in the solutions. Namely, their modified tube model accounting for the CLF and CR processes predicts the scaling of  $\tau_{\rm rep}/(\tau_{\rm e}Z_{2,0}^3c) \propto Z_2$ . Here,  $Z_{2,0} = M_{\rm w}/(N_{\rm e}M_0)$ represents the number of entanglement strands of the polymer in the melt state, where  $N_{\rm e}$  and  $M_0$  are the number of monomers in an entanglement strand and the molar mass of polymer repeating units. Figure 5b plots the estimated  $\tau_{\rm rep}$  $(\tau_e Z_{2,0}^3 c)$  on  $Z_2$  for our NaPSS solutions. Since the literature data of  $N_{\rm e}$  for NaPSS is not available, we assume  $N_{\rm e}$  = 144 on the basis of the value for polystyrene melts, which yields  $Z_{2,0}$  = 106 with  $M_0 = 206.19$  g mol<sup>-1</sup> for NaPSS. We chose polystyrene because its chemical structure is similar to that for NaPSS. Figure 5b shows  $\tau_{\rm rep}/(\tau_{\rm e}Z_{2,0}^{3}c) \propto c^{1.03\pm0.16}$ , supporting our hypothesis that the CLF and CR modes likely influence the reptation dynamics of our NaPSS solutions in the SE regime.

On the basis of various scaling analyses performed above, we demonstrate that the original Dobrynin model needs to be modified to account for both the CLF/CR modes and the retardation of solvent dynamics to capture the viscoelastic properties of polyelectrolyte SE solutions. We also point out that our observed dependences of  $G_e$  and  $\tau_{rep}/\tau_e$  on *c* is different from those reported by Han and Colby.<sup>25</sup> They used glycerol solutions with a high molecular weight cesium polystyrenesulfonate (similar repeating unit chemical structure to that of NaPSS) and showed that  $G_e \propto c^{2.3}$  and  $\tau_{rep}/\tau_e \propto c^{4.0}$ , which followed the scaling laws of neutral polymers. Although we do not have conclusive evidence to prove our hypothesis, we suspect that the use of glycerol as a solvent may reduce the value of  $c_D$ , so entanglements might be formed after the charge effects are screened; i.e., the entanglement concentration might



Figure 4. Dependence of (a) the plateau modulus  $G_{e}$  (b) the Rouse time of an entanglement strand  $\tau_{e^{\prime}}$  and (c) the reptation time  $\tau_{rep}$  at 25 °C on the monomer concentration *c* of aqueous NaPSS solutions in the semidilute entangled (SE) regime. Dashed lines represent the best fit curves to the measured  $G_{e}$  ( $\propto c^{1.48\pm0.06}$ ),  $\tau_{e}$  ( $\propto c^{-0.62\pm0.27}$ ), and  $\tau_{rep}$  ( $\propto c^{1.19\pm0.08}$ ) data.



Figure 5. (a) Dependence of the relaxation time ratio  $\tau_{rep}/\tau_e$  at 25 °C on the monomer concentration c for aqueous NaPSS solutions. (b) The normalized relaxation time ratio  $\tau_{rep}/(\tau_e Z_{2,0}^3 c)$  is plotted as a function of the number of entanglement strands  $Z_2$  in NaPSS solutions. The red dashed lines represent the best fit curves to the measured  $\tau_{rep}/\tau_e$  ( $\propto c^{1.82\pm0.28}$ ) and  $\tau_{rep}/(\tau_e Z_{2,0}^3 c)$  ( $\propto c^{1.03\pm0.16}$ ) data.

be greater than the critical polymer concentration  $(c_e > c_D)$  in their system.

In conclusion, we investigated the entanglement dynamics in the semidilute entangled regime for a model polyelectrolyte NaPSS system by using both the classical bulk shear rheology and the diffusing wave spectroscopy microrheology (DWS) methods. By measuring the shear viscosity at various monomer concentrations, we determined the dilute (DL) regime (c < 7 $\times$  10<sup>-4</sup> M) and semidilute unentangled (SU) regime (7  $\times$  10<sup>-4</sup>  $M \le c < 7 \times 10^{-2} M$ ) of aqueous NaPSS solutions. We probed viscoelastic properties of the aqueous NaPSS solutions in the semidilute entangled (SE) regime (focusing on  $7 \times 10^{-2}$  M < c  $\leq$  1.12 M) and found that the specific viscosity scaled as  $\eta_{sp} \propto c^{(2.56\pm0.04)}$  with an exponent much larger than the Dobrynin's scaling prediction for salt-free SE polyelectrolyte solutions. The complex modulus  $G_e \propto c^{(1.51\pm0.04)}$  displayed good agreement with the scaling law of  $G_e \propto c^{1.5}$ , suggesting that the viscoelastic properties of polyelectrolyte SE solutions are influenced by the electrostatic interaction. On the other hand, we observed a slightly larger scaling exponent for the measured  $\tau_{\rm rep}/\tau_{\rm e} \propto c^{(1.82\pm0.28)}$  than the predicted value  $(\tau_{\rm rep}/\tau_{\rm e} \propto c^{1.5})$ . By scrutinizing the assumptions made in Dobrynin's model, we hypothesized that the observed deviation in the  $\eta_{sp}$  and  $\tau_{rep}/\tau_{e}$ data were likely caused by the contour length fluctuation and the constraint release relaxation processes as well as the retardation of solvent dynamics. Our work lays foundations for more in-depth studies of the entanglement dynamics of polyelectrolytes with different types of polyelectrolyte systems, such as those with varying degrees of polymerization and salt concentrations. We also demonstrate that DWS can be used as a powerful rheological tool to study the entanglement dynamics of polyelectrolyte solutions at room temperature.

# ASSOCIATED CONTENT

## Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.1c00563.

Section S1: Materials; Section S2: Bulk shear rheometry (Section S2.1: Shear viscosity; Section S2.2: Complex modulus); Section S3: The overlap, entanglement, and critical polymer concentrations (Section S3.1: Overlap concentration  $c^*$ ; Section S3.2: Entanglement concentration  $c_{ei}$ ; Section S3.2.1: Dobrynin's scaling prediction; Section S3.2.2: Estimation from the specific viscosity  $\eta_{sp}$ 

data; Section S3.2.3: Estimation from the measured terminal modulus  $G_{tj}$  Section S3.2.4: Further validation using the complex modulus  $G_{DWS}^*$ ; Section S3.2.5: Dependence of  $c_e$  on the polymer concentration; Section S3.3: Critical polymer concentration  $c_D$ ); Section S4: Complex modulus measurements using DWS (Section S4.1: Effects of bead and medium inertia; Section S4.2: Effect of tracer particles; Section S4.3: Effect of the tracer particle size); Section S5: DWS data processing; Section S6: The magnitude of experimental errors; Section S7: Plateau modulus  $G_e^{cross}$  plotted against the monomer concentration c for NaPSS solutions at 25 °C (PDF)

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## Notes

The authors declare no competing financial interest.

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