

MICRORHEOLOGY OF POLYELECTROLYTE SOLUTIONS IN THE SEMIDILUTE ENTANGLED REGIME

Atsushi Matsumoto¹, Chi Zhang², Frank Scheffold², and Amy Q. Shen³

¹Graduate School of Engineering, University of Fukui, 3-9-1 Bunkyo, Fukui-shi, Fukui 910-8507, Japan

²Department of Physics, University of Fribourg, Chemin du Musée 3, 1700, Fribourg, Switzerland

³Micro/Bio/Nanofluidics Unit, Okinawa Institute of Science and Technology Graduate University, 1919-1 Tancha, Onna-son, Kunigami-gun, Okinawa 904-0495, Japan

ABSTRACT

Entanglements and their effects on the polymer dynamics for polyelectrolyte solutions have been a long-standing debate over the past 30 years since many experimental studies reported conflicting information on their viscoelastic properties when compared with those predicted based on the tube model developed for electrically neutral polymers. These existing rheological studies of polyelectrolyte systems with low-viscosity solvents are limited by the accessible frequency range ($\leq 100 \text{ rad s}^{-1}$) provided by conventional shear rheometers. To overcome this issue, we employed diffusing wave spectroscopy (DWS) based microrheological technique to investigate the linear viscoelastic response of aqueous polyelectrolyte solutions containing poly(sodium styrene sulfonate) (NaPSS) at different degrees of polymerization N . We found that the entanglement monomer concentration c_e , determined by the presence of the plateau regime in the complex modulus spectra, followed the scaling of $c_e \propto N^{-0.77}$ for $N < 7000$, in good agreement with the predicted scaling law of c_e for electrically neutral polymers. However, the estimated scaling exponent changed to -2 when $N > 7000$, the value agreeing well with the predicted value for salt-free polyelectrolyte solutions. We also found the critical monomer concentration at which the charge effects are fully screened by polyelectrolyte itself to be 0.03 M for NaPSS in water. These results indicate that NaPSS can behave as both neutral polymer and polyelectrolyte chains in the entangled regime, depending on the degree of polymerization. We confirmed the observed transition of the NaPSS chain behavior through the scaling analysis of the reptation time τ_{rep} and the Rouse time of an entanglement strand τ_e with respect to the molar concentration of NaPSS monomers c_p , showing $\tau_{\text{rep}}/\tau_e \propto c_p^{1.2}$ for $N > 7000$ and $\tau_{\text{rep}}/\tau_e \propto c_p^{3.3}$ for $N < 7000$, both of which agree well with the predicted scaling law of τ_{rep}/τ_e for salt-free polyelectrolyte and neutral polymer solutions in the semidilute entangled regime, respectively. Our results demonstrate that the observation of the charge effects on the entanglement properties of polyelectrolytes requires the use of high molecular weight polyelectrolytes having c_e much smaller than the polymer concentration where the self-screening of charge effects occurs. Moreover, we show that the scaling theory proposed by Dobrynin et al. [1] can capture the entanglement dynamics of polyelectrolytes.

[1] Dobrynin et al., *Macromolecules*, 1995, 28, 1859-1871