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Model Solutions for Studies of Salt-Free Polyelectrolytes

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Introduction. Strong long-range interactions govern the physics of both polymer and electrolyte solutions. Although polyelectrolytes combine features of both, they cannot be understood with a simple combination of the properties of electrolytes and polymers. Because of their significant scientific and technological importance, polyelectrolytes have been the focus of decades of theoretical and experimental efforts, yet we still lack clear molecular interpretations for most of their fundamental properties.

Over the past 20 years there has been continuing interest in the so-called "extraordinary" regime in polyelectrolyte solutions with zero added salt.[1−4] First reported by Lin, Lee and Schurr[5] in 1978, this behavior manifests itself in unusual dynamic light scattering (DLS) correlation functions from low ionic strength polyelectrolyte solutions. Although scattering from high ionic strength solutions shows a diffusive mode of magnitude corresponding to single-chain diffusion, this mode is absent in the low ionic strength extraordinary regime. Lin et al. reported an abrupt order of magnitude decrease in the diffusion coefficient as the concentration of added salt was reduced. Schmitz[6] later demonstrated that in this extraordinary regime, DLS actually measures two modes, bracketing the value expected for single-chain diffusion.

Over the past decade these dilute solution results have been confirmed by numerous investigators and various explanations have been offered.[2,4,6] In general, the unusual scattering is thought to result from strong interactions of unscreened charges along the polymer chain such that the dynamics are dominated by intrachain and interchain electrostatic interactions. However, no theory accounts for all the observed features.

An additional complication for aqueous solutions is the influence of backbone solvation. Generally, experiments have examined polymers with hydrophobic backbones, such as styrene or other vinyl based systems, which are modified with pendant ionic groups to provide water solubility. Nevertheless, the hydrophobic backbone remains poorly solvated and could promote aggregation or microphase separation. The consequences of poor backbone solvation were recently addressed theoretically[7] and experimentally[8] for weakly charged aqueous polyelectrolyte solutions. It was shown that microphase separation can occur as a result of aggregation of hydrophobic regions. However, for strongly charged polyelectrolytes, it is unclear how the hydrophobic character of the chain backbone affects chain interactions.[9] It has again been suggested that the unusual scattering may not be the result of solely electrostatic interactions but that contributions from a phase separation process may be involved.[10,11] To test this hypothesis, it is crucial to develop systems to study the electrostatics of polyelectrolyte solutions independent of any possible hydrophobic interactions.

An additional concern for previous studies in aqueous solutions is that the dielectric constant, ϵ, a variable that should have significant effects on the strength and range of electrostatic interactions, has been constant. A system allowing variation of solvent dielectric constant removes this constraint and by choosing appropriate polymer−solvent pairs we are permitted to vary important experimental parameters such as viscosity, solvent quality, and charge density. In this study, we use dynamic light scattering to investigate the structure and dynamics of poly(*N*-methyl-2-vinylpyridinium chloride) (PMVP) in three nonaqueous solvents. We address some of the problems of previous studies and demonstrate the ability to probe additional experimental parameters.

Experimental Procedures. Many methods to produce high degrees of quaternization of P2VP lead to degradation products, colored samples, or broadening of the molecular weight distribution. Therefore, we have applied the quaternization method recommended by Noda and co-workers in their comprehensive comparison of standard methods.[12] Anionically polymerized P2VP (MW = 281 000) is converted with dimethyl sulfate (DMS) to its methyl-substituted analog in a one-step reaction in dimethylformamide. The resultant PMVP is precipitated into acetone, filtered, and redissolved in aqueous NaCl solution containing at least a 50-fold excess of chloride to pyridinium ion. The solution is then dialyzed against deionized water (18 MΩ) until a permanent low conductivity of the exchange water is achieved. The polyelectrolyte, now at the salt-free limit, is lyophilized and the dry polymer used to prepare light scattering solutions. Prior to measurements, the solutions are filtered through 0.20 or 0.45 μm Millipore membrane filters directly into sealable, dust-free scattering cells. The larger pore size is required for most ethylene glycol solutions due to high solution viscosity. The degree of quaternization (DQ) was determined using standard quantitative analysis of the chloride counterion. All data reported here are for PMVP with a DQ of 30%.

Ethylene glycol (EG, Aldrich, 99.8%, anhydrous: water < 0.005%, $\epsilon = 37.7$, $\eta = 17.3$ cP) was kept in septum-sealed bottles under an inert atmosphere and found to contain very low ionic impurites as measured by conductivity. *N,N*′-Dimethyl formamide (DMF, Aldrich, 99.9+%, HPLC grade, $\epsilon = 36.7$, $\eta = 0.791$ cP), and *N*-methylformamide (NMF, Aldrich, 99%, $\epsilon = 182$, $\eta = 1.65$ cP) were further purified with mixed bed ion exchange resin to remove residual ionic impurities and stored in sealed bottles under an inert atmosphere. All solvent parameters are for 25.0 °C.

Dynamic light scattering measurements were performed with a Brookhaven (BI-200SM) light scattering goniometer over an angular range 30−145°, using an Ar ion laser (Spectra Physics 2020-3) operating at 514.5 nm as the light source. The measurement temperature was controlled at 25.00 ± 0.05 °C using a circulating bath. Photon autocorrelation functions were acquired with a log τ digital correlator (ALV-5000). The correlation curves were analyzed using the CONTIN program. Diffusion coefficients were determined from the slope of τ^{-1} vs q^2 plots, where τ is the characteristic decay time and q is the scattering vector defined as $q = (4\pi n/\lambda_0)\sin(\theta/2)$, with n the solution refractive index, λ_0 the laser wavelength, and θ the scattering angle.

Results. Ethylene glycol is a good solvent for neutral and protonated P2VP in either low- or high-salt condi-

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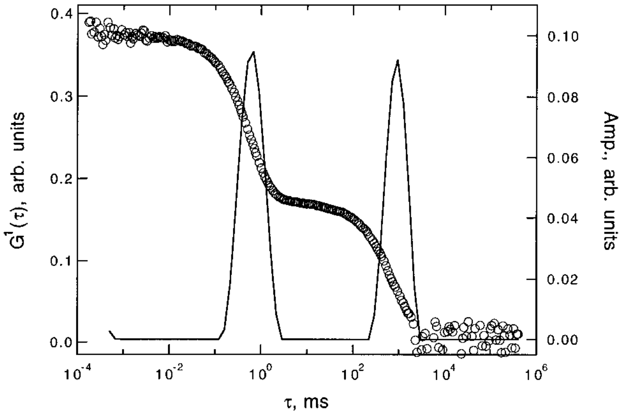

Figure 1. Representative dynamic light scattering correlation function for PMVP in ethylene glycol showing two widely separated relaxations. The solid line is the spectrum of relaxation times obtained by CONTIN analysis.

tions[13] with Mark–Houwink exponents for intrinsic viscosity of 0.715–0.840. It was therefore a logical first choice for studying solutions independent from possible hydrophobic interactions. Over a broad concentration range, the DLS correlation functions show double exponentials yielding two diffusive relaxations. At lower concentrations, the two diffusion coefficients seem to approach a single value.

Figure 1 shows a typical correlation function covering over 8 decades of time together with the spectrum of characteristic relaxation times obtained by CONTIN. The slow and fast relaxations, τ_f and τ_s, respectively, are separated by over 3 decades and are easily resolved by the CONTIN program. Both modes are q^2 dependent and show no evidence of nondiffusive behavior. This clear observation of two diffusive modes, in a solvent for which the chain backbone is well solvated, demonstrates that the slow-mode scattering in salt-free solutions cannot be attributed to hydrophobic interactions or phase separation.

Using ethylene glycol as the solvent also means that we have changed the dielectric constant, an important, yet neglected variable affecting the strength and range of electrostatic interactions. In the absence of a theoretical model for the multimodal DLS, it is difficult to predict how varying solvent dielectric constant should affect the scattering. Polyelectrolyte theories[6,14] predict that the dynamics of such systems will be governed by strong electrostatic interactions over length scales on the order of the inverse Debye screening length, κ^{-1}, which is defined as

$$\kappa^{-1} = \left(\frac{2q^2\mu}{\epsilon_0\epsilon k_b T}\right)^{-1/2} \tag{1}$$

where μ is the ionic strength of the solution, q is the elementary charge, ϵ is the solvent dielectric constant, and ϵ_0 is the dielectric constant in vacuum. The length scales for which electrostatic interactions are important are thus proportional to $\epsilon^{1/2}$. Therefore, the choice of solvent affects the distance over which the electrostatic effects are important. To investigate these effects, the polyelectrolyte system must be chosen to permit variation of solvent. PMVP is suited for such a study because it is soluble in most polar solvents, such as dimethylformamide, dimethyl sulfoxide, ethanol, and water.

Three solvents were chosen for this initial study, ethylene glycol, *N*,*N*′-dimethylformamide, and *N*-methylformamide. These solvents have dielectric constants from 36.7 to 182. Figure 2 shows representative correlation functions for the PMVP in DMF, NMF, and EG, where all three correlation functions display the two relaxations. Although in aqueous solutions similar behavior has been referred to as extraordinary,[1–4,8] it now appears to be quite universal.

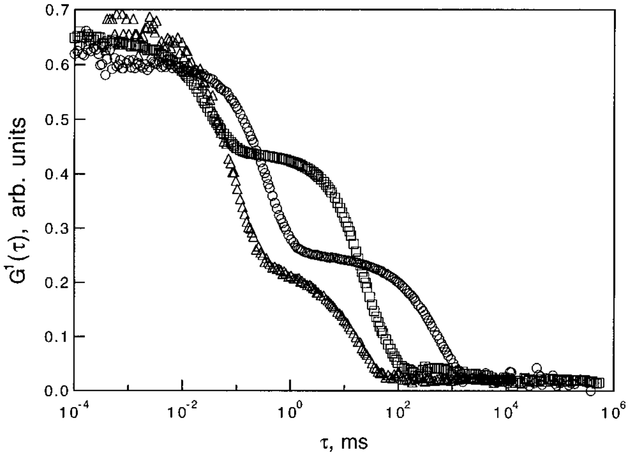

Figure 2. Sample DLS correlation functions for PMVP in (○) ethylene glycol, (□) *N*,*N*-dimethylformamide, and (△) *N*-methylformamide.

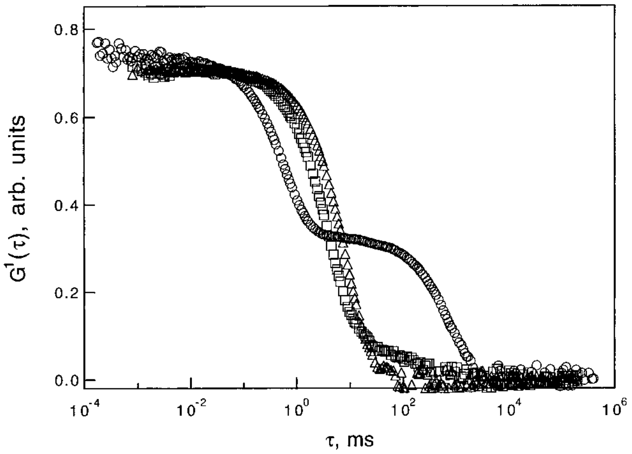

Figure 3. DLS correlation functions for (○) PMVP in salt-free EG, (□) PMVP in EG with excess NaCl, and (△) PVP in EG.

Table 1. Calculated Diffusion Coefficients, Scaled by Solvent Viscosity for PMVP in Three Solvents as Shown in Figure 2

solvent	$D_{\mathrm{fast}}(\eta_{\mathrm{solvent}}/\eta_{\mathrm{water}})$, cm^2 s^{-1}	$D_{\mathrm{slow}}(\eta_{\mathrm{solvent}}/\eta_{\mathrm{water}})$, cm^2 s^{-1}
DMF	2.5×10^{-6}	6.6×10^{-9}
NMF	2.0×10^{-6}	6.8×10^{-9}
EG	3.2×10^{-6}	4.2×10^{-9}

Table 1 displays the values of the calculated diffusion coefficient, scaled by the ratio the solvent viscosity to the viscosity of water at 25 °C. Qualitatively, the diffusion coefficients in DMF and NMF are nearly identical, with the values in EG slightly out of agreement. Contrary to our expectations, a fivefold increase in solvent dielectric constant had little effect on the values of the apparent diffusion coefficients.

As noted earlier, EG is a good solvent for neutral P2VP as well as the quaternized polyelectrolyte in salt-free or added-salt conditions.[13] Figure 3 displays correlation functions for these three conditions. Scattering from the polyelectrolyte, screened by the addition of excess salt, is nearly identical to the equivalent neutral polymer and is in sharp contrast to that from the salt-free solutions. Clearly, addition of excess salt to the zero-salt polyelectrolyte solution causes the two modes to merge to a single relaxation that is approximately equal to the value obtained for the neutral chain. To our knowledge, this is the first unambiguous demonstration of the dynamics of a neutral polymer compared in a common solvent to its polyelectrolyte analogue, in salt-free and high-salt solutions.

Conclusion. From this study we see that if the influences of poor backbone solvation are eliminated, multiple relaxation modes persist in the dynamic light scattering of salt-free polyelectrolyte solutions. Using multiple solvents to vary the dielectric constant by a factor of 5, we see no qualitative effect and little quantitative effect on the extraordinary regime scattering. DLS from solutions of the neutral chain and salt-free solutions of the polyelectrolyte displays dramatic differences whereas the scattering from a high-salt solution of the polyelectrolyte parallels the scattering from the neutral chain. These results demonstrate the flexibility and merits of this system, which we expect to exploit in more detailed investigations of polyelectrolytes and ion-containing polymers.

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