The Effect of Counterion Size and Valency on the Increase in Viscosity in Polyelectrolyte Solutions

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Abstract

Entangled polymer solutions play an important role in many industries, however the dynamics of these solutions are poorly understood. Here, the addition of salt to entangled polylectrolyte solution results in an increase in viscosity. The rheological properties of Sodium Alginate solutions above the critical concentration cD are examined in a number of inorganic salt solutions. The effect of salt counterion size and valency on the magnitude of the viscosity increase is elucidated. Lastly, an alternative hypothesis incorporating ion bridging between polymer chains is proposed to explain the effect of counterion valency in the observed viscosity differences.

Keywords

Polyelectrolytes; rheology; viscosity.

1. Introduction

Charged polymer systems are encountered daily in nature as many biological polymers,are polyelectrolytes. Polyelectrolytes are used extensively in many industrial applications such as food additives, drilling fluids, and drag reducers.[1-7] Because polyelectrolytes are such an important part of so many different systems and industries, a fundamental understanding of the rheology of polyelectrolyte solutions is critical. SA solution properties have been studied extensively over the past 20 years. The main topics of interest have included solution viscosity, polymer conformation, temperature effects on polymer conformation, and the effects of salt on both solution properties and chain conformation. SA exhibits both anisotropic and isotropic phases in solution. The relative amount of each phase present in solution depends on polymer molecular weight, polymer concentration and solution ionic strength. The highest SA concentration used in the current study remains well below the biphasic regime.[8-11] Further, SA has been shown to exhibit two different conformational states: an ordered, helical conformation and a disordered conformation that can be described as a broken or imperfect helix.[12-14]

2. Methods

2.1 Materials

GO and SA (molecular weight of 380000 g·mol-1. Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ultrapure water (18.2 MΩ·cm) was used to prepare all solutions. Rotational rheometer. (MCR301, Anton Paar Instrument) The salts used in this study are all reagent grade salts obtained from Aldrich, Mallinckrodt Chemicals (NaCl, KCl, LiCl, NaBr, NaI). For reference, a table of the effective ionic radius and hydrolyzed radius for each of the ions used here is included (Table 1). The glass ware used for mixing and storage of SA solutions was carefully cleaned with either ethanol or acetone, then rinsed with purified deionized water to remove all traces of salt finally used for rheological testing.

2.2 Sample Preparation

SA solutions were prepared by dissolving the polymer powder in deionized water to obtain the desired polymer concentration. The solutions were stirred using a magnetic stir bar for approximately one hour then allowed to rest for approximately 24 h at room temperature. Following the period of rest, enough salt in powder form was added to the SA solutions to obtain the desired salt concentration in solution. The salt solutions were shaken vigorously to homogeneously distribute the salt then allowed to rest for at least one hour before rheological testing. In all cases, measurements were made one to four days following solution preparation. In the period of one to four days following sample preparation, no measurable change in the rheological properties of the solutions was observed. The solutions were discarded six days following preparation, as polymer degradation became evident (e.g., significant decrease in viscosity and loss of optical clarity).were conducted using either a stainless steel cone (50 mm diameter, 2 degree) and plate or a concentric cylinder geometry (of outer diameter 30.0 mm and inner diameter 25.0 mm) in steady or oscillatory shear. Sample evaporation was minimized by using a solvent trap in conjunction with the appropriate geometry. The temperature was controlled using a Peltier plateor a Peltier jacket. Calibration with viscosity standard oils showed agreement with an error of less than 2%. The rheometer has a torque range of 0.01–100 mN, which is sufficiently sensitive to measure zero shear rate viscosities at very low shear rates for the polymer solutions used here. For each polyelectrolyte solution tested here, a zero shear rate plateau was observed. The data reported here are the averages of at least three replicate data sets and the associated error bars represent one standard deviation unless otherwise noted

3. Results and Discussion

3.1 Monovalent Salts

To test the effect of monovalent salt ion size on the degree of viscosity increase for SA concentrations above cD, chloride salts of several of the alkali metals (LiCl, NaCl, KCl) were tested (Fig. 1a). Qualitatively, the shear viscosity of SA in the presence of each of the monovalent salts is similar to that of the salt free case. A Newtonian plateau is observed at low shear rates followed by a region of shear thinning at higher shear rates (Fig 1a). The magnitude of the zero shear rate viscosity (as well as the shear viscosity) increases with the size of the added salt ion. The effect of salt ion size on viscosity is readily seen when the normalized zero shear rate viscosity is compared for each of the monovalent salts (Fig 1b). In every case, the addition of salt results in a dramatic increase in viscosity over the salt free solution, however the magnitude of the increase is markedly different, which represents the smallest of the alkali metal salts, produced the smallest viscosity increase while KCl, the largest of the metal salts, produced the largest viscosity increase .
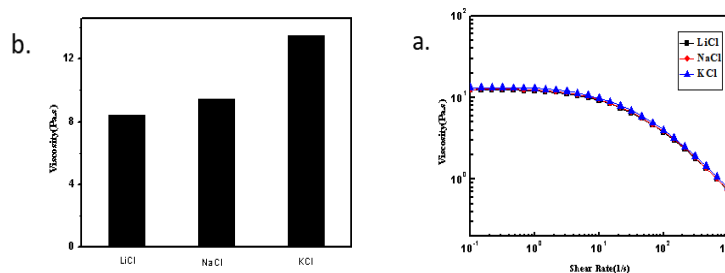

Figure 1a. Viscosity versus shear rate for 2000 ppm SA in 0.2 M solutions of various monovalent salts.b. Normalized zero shear rate viscosity for 2000 ppm SA in several monovalent salts
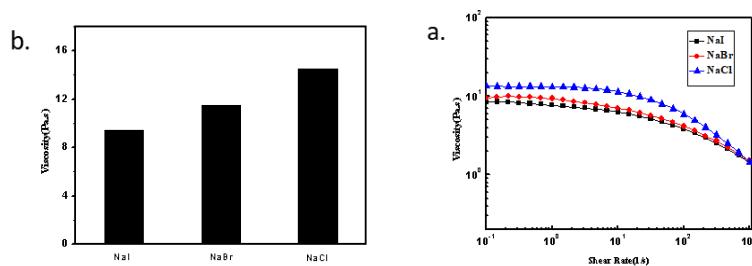
Figure 2a. Viscosity versus shear rate for 2000 ppm SA in 0.2 M solutions of various monovalent salts.b. Normalized zero shear rate viscosity for 2000 ppm SA in several monovalent salts

Next, the effect of the salt anion size on the viscosity was tested using the sodium salts of several halides (NaCl, NaBr, NaI) (Fig 2a). Again, the shear viscosity is qualitatively similar to the salt free solution (i.e., a Newtonian plateau and shear thinning). However, significant differences are observed in the normalized viscosity for each salt (Fig 2b). For the sodium salts of the halides tested, the smallest salt anion (Cl-) produces the largest viscosity increase while the largest salt anion (I- produces the smallest viscosity increase. The diminishing effect on the viscosity with increasing salt anion size may be due to the effectiveness of the salt anions in screening the salt cations from one another which, in turn, results in less Coulombic repulsion between the salt cations. The reduced Coulombic repulsion between salt cations results,.[15-16] in turn, in a lesser degree of expansion of the polymer chain between entanglements. Since the polymer chains are not highly expanded between entanglements, the magnitude of the viscosity increase is diminished.

4. Conclusion

Previous work has shown that polyelectrolytes in excess of the critical concentration cD exhibit an increase in viscosity upon addition of salt.[17-19] It was hypothesized that the increase in viscosity could be attributed to a local charge inversion and subsequent chain expansion between entanglements. It was further hypothesized that the effect would be strongly dependent on the size and valency of the salt counterions added with the bigger or more heavily charged ions inducing the largest effects.[20-26] The latter part of this hypothesis was confirmed with rheological measurements on SA solutions above CD. The viscosity increases observed with addition of different salts are dependent on the size of the salt counterions used, with lithium (the smallest monovalent ion tested) producing the smallest gain in viscosity and caesium (the largest monovalent ion tested) producing the largest increase in viscosity. Further, the viscosity increases are also dependent on the size of the salt anion used with fluorine (the smallest anion) giving the highest viscosity and iodine (the largest anion) giving the smallest viscosity.

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