

Rheological Properties of Water Solutions of Syndiotactic Poly(vinyl alcohol) of Different Molecular Weights

Sam Soo Kim,¹ In Seok Seo,² Jeong Hyun Yeum,² Byung Chul Ji,² Joon Ho Kim,¹ Jin Woo Kwak,¹ Won Sik Yoon,¹ Seok Kyun Noh,³ Won Seok Lyoo¹

¹Advanced PVA Research Center, School of Textiles, Yeungnam University, Kyongsan 712-749, Korea

²Department of Dyeing and Finishing, Kyungpook National University, Daegu 702-701, Korea

³School of Chemical Engineering and Technology, Yeungnam University, Kyongsan 712-749, Korea

Received 11 June 2003; accepted 22 September 2003

ABSTRACT: To precisely identify the effect of the molecular weight of syndiotacticity-rich poly(vinyl alcohol) (s-PVA) on the rheological properties of s-PVA/water solutions, we prepared four s-PVAs with a syndiotactic dyad content of 57%, a degree of saponification (DS) of 99.9%, and number-average degrees of polymerization (P_n 's) of 300, 1300, 2700, and 4000. Through a series of experiments, we found that the molecular weight of poly(vinyl alcohol) had a significant influence on the rheological properties of s-PVA/water solutions. Over a frequency range of 10^{-1} to 10^2 rad/s, the s-PVA/water solution with the highest P_n value showed the largest values of the complex viscosity, storage modulus, and loss modulus at similar syndiotacticity and DS values of

s-PVA, and this suggested that the higher P_n was, the stronger the internal ordered structure was in the molecules. All the s-PVA/water solutions showed shear-thinning behavior, which implied heterogeneity. In a modified Casson plot, Bingham flow behaviors, which gave rise to non-zero yield stress, were evident. This suggested that some pseudostructure existed in the s-PVA/water solutions. The yield stress increased with P_n , and this implied that the pseudostructure was developed as P_n increased. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 1426–1431, 2004

Key words: molecular weight; s-PVA; rheological property

INTRODUCTION

It is well known that the stereoregular configuration of vinyl polymers changes the physical characteristics and enhances the mechanical properties. According to the stereoregularity, vinyl polymers are often classified as isotactic, atactic, and syndiotactic. In the case of poly(vinyl alcohol) (PVA), a polymer with a syndiotactic dyad (S-dyad) content of hydroxyl groups exceeding 54% is conventionally called syndiotacticity-rich poly(vinyl alcohol) (s-PVA). Compared with atactic poly(vinyl alcohol) (a-PVA), s-PVA has been known to have different properties due to the increased intermolecular hydrogen bonding between the adjacent chains.^{1–3}

PVA is commercially produced by the radical polymerization of vinyl acetate (VAc), followed by saponification of the obtained polymer, poly(vinyl acetate). In general, the radical polymerization of VAc produces an atactic polymer. Much attention has been paid to the synthesis of stereoregular PVA because the properties of PVA significantly depend on the stereo-

chemical structure of the main chain. It is known that the solvent and temperature effects on the stereochemistry of the radical polymerization of VAc are generally small.^{4–11} On the contrary, the polymerizations of bulky vinyl ester monomers, such as vinyl pivalate (VPi)^{12–27} and vinyl diphenylacetate,²⁸ produce polymers rich in syndiotacticity.

Water-soluble PVA has been extensively used as a material for drug delivery systems and the immobilization of enzymes.^{29–31} However, in comparison with a-PVA, high-molecular-weight s-PVA has been limited in its biomaterial applications because of its water-insoluble characteristics, which are induced by the high compactness of s-PVA, although s-PVA has superior properties. Therefore, to improve the water solubility of s-PVA while the basic properties of s-PVA are maintained to some extent, fine control of the molecular weight and stereoregularity of PVA is needed. For the preparation of water-soluble s-PVA, the major molecular parameters of PVA, such as the molecular weight, stereoregularity, and degree of saponification (DS), need to be controlled with the copolymerization of VPi and VAc with various monomer feed ratios and the ensuing saponification of the copolymer of VPi and VAc. Because water-insoluble s-PVA with its strong molecular structure can only be dissolved in an organic solvent, the toxicity of organic solvents in biomaterials used *in vivo* is a concern.

Correspondence to: W. S. Lyoo (wslyoo@yu.ac.kr).

Contract grant sponsor: Advanced Research Center in Yeungnam University; contract grant number: 105095.

However, water-soluble s-PVA can be used for biomaterials with no toxicity. In addition, because water-soluble s-PVA is stronger than a-PVA in many physical properties, water-soluble s-PVA can be used to prepare biomaterials with higher physical and chemical properties.

PVA/water solutions show various rheological behaviors with respect to the temperature, DS, molecular weight, stereoregularity, and so on.^{32–35} Therefore, it is important to characterize the rheological properties of PVA solutions to manufacture various products, such as contact lenses, biomaterials, fibers, films, adhesives, and sizing agents, with excellent properties.³⁶ In this study, the effect of the molecular weight of s-PVA on the rheological properties of s-PVA/water solutions was investigated.

EXPERIMENTAL

Materials

VPI and VAc, purchased from Aldrich (St. Louis, MO), were washed with an aqueous solution of NaHSO₃ and water and dried with anhydrous CaCl₂; this was followed by distillation in a nitrogen atmosphere under reduced pressure. The initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN; Wako Co., Osaka, Japan), was recrystallized twice in methanol before being used. Other extrapure-grade reagents were used without further purification. The water used for all the procedures was deionized.

Preparation of s-PVA

To prepare water-soluble s-PVAs with similar stereoregularities, we performed copolymerizations of VPI and VAc in a molar ratio of 3/7 with conversions of 25–35%. For s-PVA with a number-average degree of polymerization (P_n) of 300, VPI and VAc were solution-copolymerized in tetrahydrofuran at 40°C with ADMVN as an initiator and subsequently saponified. To synthesize s-PVA with P_n values of 1300, 2700, and 4000, we bulk-copolymerized VPI and VAc at 40°C with ADMVN concentrations of 0.001, 0.0005, and 0.0001 mol/mol of VPI, respectively, and subsequently saponified them.

Characterization of s-PVA

P_n 's of s-PVAs were determined from the viscosities of benzene solutions of fully acetylated specimens.¹⁴ The S-dyad content of PVA was determined from the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm obtained with ¹H-NMR (Sun Unity 300, Varian, Palo Alto, CA). DS of PVA was determined by the ratio of *tert*-butyl and methylene proton peaks in the ¹H-NMR spectrum.

TABLE I
Molecular Parameters of PVA

P_n	DS (%)	S-dyad content (%)
300	99.9	56.9
1300	99.9	56.8
2700	99.9	57.0
4000	99.9	57.2

Preparation of the s-PVA/water solutions

s-PVA was hard to dissolve in water at room temperature, so it was dissolved in a 5% water solution at 120°C for 1 h and was kept there for 30 min to ensure homogenization.

Measurement of the rheological properties of the s-PVA/water solutions

For more precise rheological measurements, an Advanced Rheometric Expansion System (ARES, Piscataway, NJ), manufactured by Rheometric Scientific, Inc., was used. For the ARES measurements, a cone-and-plate flow cell with a diameter of 25 mm and a degree of 0.04 rad was used to effectively accommodate the torque of the solutions. The test type and measurement type were strain control and dynamic frequency sweep test, respectively, and the measurement was performed at a fixed strain of 5%, at 25°C, and at a low frequency (ω) of 10⁻¹ to 10² rad/s.

RESULTS AND DISCUSSION

Generally, it is known that the rheological behavior of PVA is greatly affected by the molecular parameters of PVA, such as the molecular weight, DS, and stereoregularity. Also, s-PVA with a high stereoregularity and a high molecular weight is a water-insoluble polymer.¹² In this study, to prepare water-soluble s-PVA, we finely controlled the molecular weight, tacticity, and DS of PVA to an appropriate level by solution and bulk copolymerizations of VPI and VAc and subsequent saponification. Table I shows the characteristic features of s-PVA prepared by copolymerization and saponification. All the specimens showed different P_n 's of 300–4000, similar S-dyad contents of 57%, and similar DSs of 99.9%.

The complex viscosities (η^*) of 5% (g/dL) s-PVA/water solutions of different P_n 's with ω is shown in Figure 1. Specimens of higher P_n 's had higher η^* values at given values of ω , and all the specimens showed shear thinning behavior, η^* decreasing with ω . An increase in P_n led to greater intermolecular hydrogen bonding of hydroxyl groups, and the molecular structures were more rigid; this led to higher η^* values. Because s-PVA of a higher P_n value forms greater

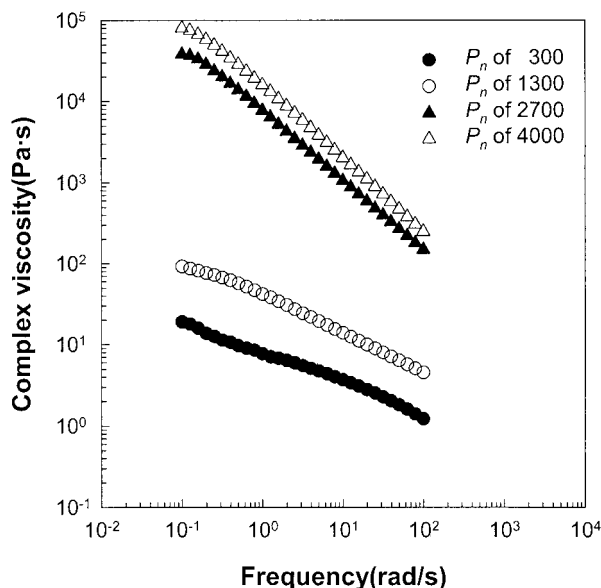


Figure 1 η^* of a 5% (g/dL) s-PVA/water solution versus ω at 30°C.

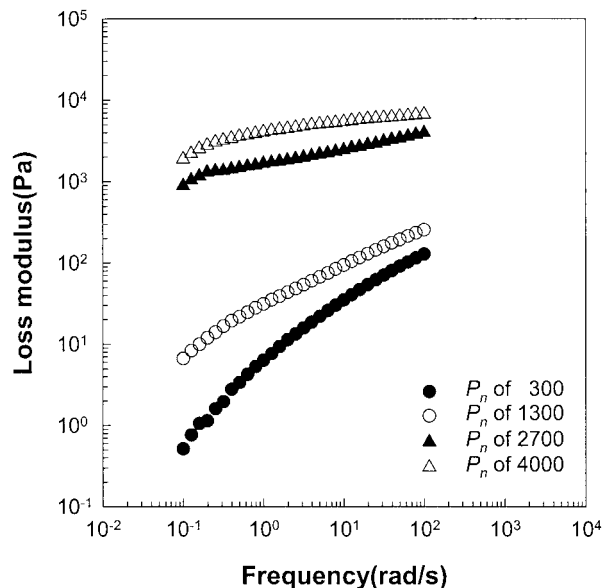


Figure 3 G'' of a 5% (g/dL) s-PVA/water solution versus ω at 30°C.

molecular orientation and a heterogeneous system like a liquid crystal, the molecules are arranged along the shear force direction, and η^* decreases with shear. Specimens with P_n 's of 300 and 1300 showed poorer shear thinning than those with P_n values greater than 2700. This suggests the presence of a critical point, at which a change in the internal structure of the molecules occurs, between 1300 and 2700. From this viscosity behavior, we found that the molecular weight has a significant influence on the viscoelastic properties of s-PVA/water solutions.

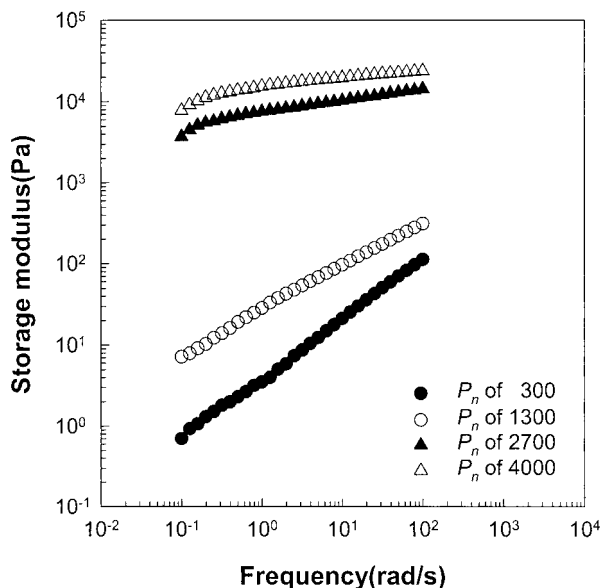


Figure 2 G' of a 5% (g/dL) s-PVA/water solution versus ω at 30°C.

Figures 2 and 3 show the changes in the storage modulus (G') and loss modulus (G'') of 5% (g/dL) s-PVA/water solutions with ω . s-PVAs with higher P_n 's had greater G' and G'' values. Because s-PVA has stronger intermolecular hydrogen bonding with respect to P_n , much higher values of G' and G'' with increasing P_n are evident in Figures 2 and 3.³⁷ This may be due to the fact that the internal structure in an s-PVA/water solution with a higher P_n value is much tighter. That is, the rigidity of PVA chains generated from the intermolecular hydrogen bonds is greater in s-PVA/water solutions with higher P_n values. s-PVA solutions with P_n 's of 300 and 1300 showed increasing values of G' and G'' with ω , whereas specimens with P_n 's over 2700 had nearly similar values of G' and G'' with ω . This implies that s-PVA solutions with P_n 's below 1300 are different from s-PVA solutions with P_n 's over 2700 in their molecular structure. Because s-PVA with P_n 's over 2700 has superior intermolecular bonding with its regular arrangement of hydroxyl groups, it shows nearly constant G'' values against deformation because of the presence of strong interactions in the molecules.

Figure 4 shows the behavior of η^* of 5% (g/dL) s-PVA/water solutions with G'' . The slopes of the viscosity curves indicate the effect of P_n on the shear dependence of viscosity. PVAs of higher P_n values produce viscosity curves with greater slopes. Lyoo et al.³⁷ reported that a-PVA had a constant value of η^* with G'' ; that is, it showed the behavior of Newtonian flow. In Figure 4, all the specimens show reductions in η^* with G'' , that is, non-Newtonian flow. The disappearance of the lower Newtonian flow region indi-

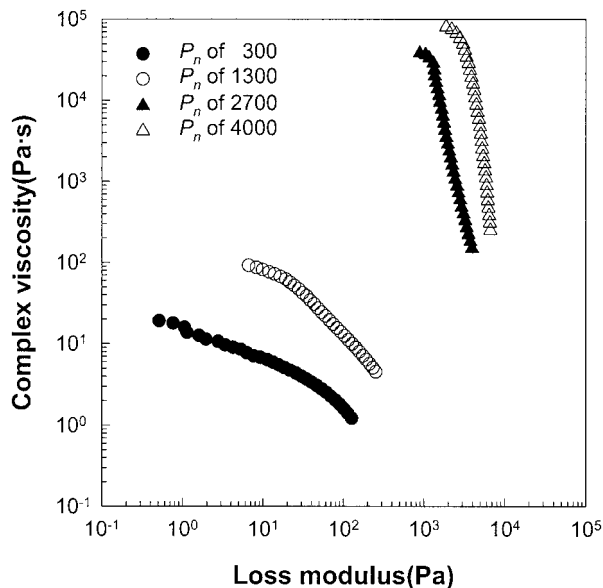


Figure 4 η^* of a 5% (g/dL) s-PVA/water solution versus G'' at 30°C.

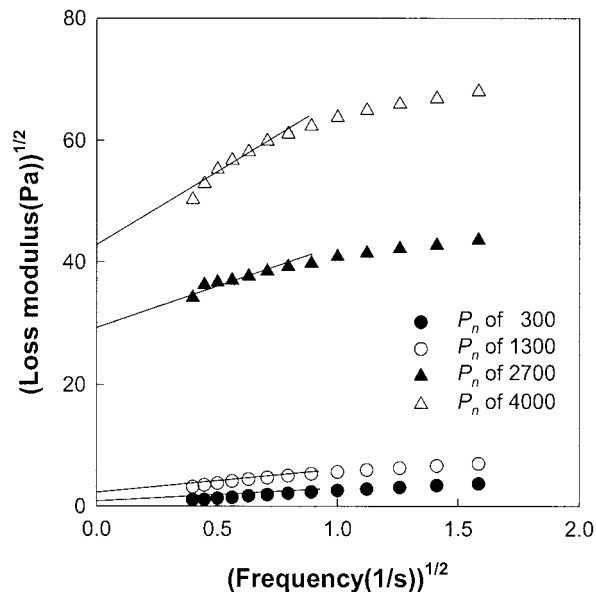


Figure 6 Square root of G'' of a 5% (g/dL) s-PVA/water solution versus the square root of ω at 30°C.

icates the heterogeneity of a system, which is frequently observed in liquid-crystalline polymers and block copolymers. Specimens with P_n 's of 300 and 1300 showed lower slope behavior than the other two specimens, and specimens with P_n 's over 2700 showed the behavior of nearly unchanged G'' values as the viscosity changed. It is thought that s-PVA with a higher P_n value has greater interactions in its molecules and that a critical point of deformation of the system is present.

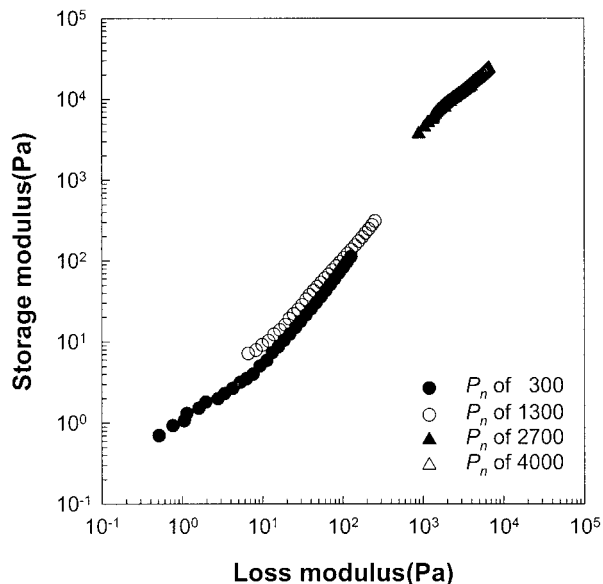


Figure 5 G' of a 5% (g/dL) s-PVA/water solution versus G'' at 30°C.

The behavior of G' of 5% (g/dL) s-PVA/water solutions with G'' is shown in Figure 5. We can see the rheological responses more clearly by replacing ω with G'' in Figure 2. This plot, which is called a Cole-Cole plot, shows that a logarithmic plot of G' versus G'' gives a slope of 2 for most homogeneous and isotropic polymer melts and solutions. The slope of a homogeneous isotropic solution such as a-PVA is nearly 2, but the slope of a heterogeneous solution such as s-PVA is lower than 2.³⁸ In this plot, all the specimens had slope values lower than 2, which represent heterogeneous forms. Specimens with P_n 's over 2700 had slopes remarkably lower than those with P_n 's of 300 and 1300. This indicates that s-PVA solutions with P_n 's over 2700 have systems similar to a mesophase. The difference in the molecular weights is confirmed to influence the appearance of the heterogeneous structure.

Bingham flow behavior gives rise to a non-zero yield stress, which represents the minimum energy required to break pseudostructures such as gels and microdomains.³⁹ The yield stress of heterogeneous systems can be determined from a Casson plot, a plot of the square root of the shear stress (τ) versus the square root of the shear rate ($\dot{\gamma}$) in steady shear flow. The yield stress (τ_0) is obtained from eq. (1).⁴⁰

$$\tau^{1/2} = \tau_0^{1/2} + K\dot{\gamma}^{1/2} \tag{1}$$

Similarly, the intercept of the G'' axis (G_0'') on the plot of the square root of G'' against the square root of ω may be regarded as a measure of the yield stress in dynamic shear measurements:⁴¹

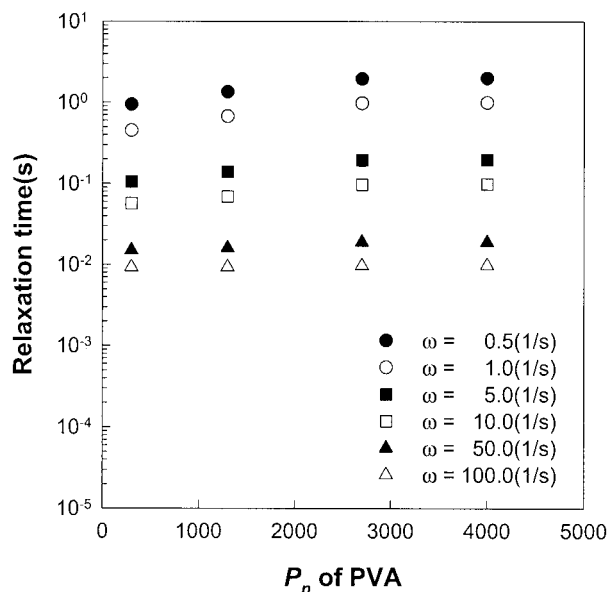


Figure 7 λ of a 5% (g/dL) s-PVA/water solution at various S-dyad contents at 30°C.

$$G''^{1/2} = G_0''^{1/2} + K' \omega^{1/2} \quad (2)$$

Figure 6 shows plots of the square root of G'' of 5% (g/dL) s-PVA/water solutions versus the square root of ω . Two specimens with P_n 's over 2700 represent the non-zero intercepts on the Casson-type plot, and this implies that a pseudostructure exists in the system. The values of the intercepts increase with P_n , and this indicates that s-PVAs of higher P_n 's have a greater development of the pseudostructure. The higher molecular weight leads to a stronger molecular structure, and s-PVAs with higher molecular weights need more energy to break the pseudostructure.

The relaxation time (λ) under dynamic shear may be calculated as follows:⁴²

$$J' = G' / ([\eta^*] \omega)^2 = \lambda / [\eta'] \quad (3)$$

where J' is the compliance, ω is the frequency, and η' is the dynamic viscosity. As shown in Figure 7, λ increased with P_n and decreased with ω . It is confirmed that a specimen with a high P_n value has a rich ordered structure. λ values of 1300 and 2700 are somewhat different. This indicates that the critical point, which shows a large λ value because of a strong internal structure in the system, exists between 1300 and 2700.

CONCLUSIONS

Having investigated the relationship between the molecular weight and rheological properties of four solutions of s-PVAs with different P_n 's of 300, 1300, 2700,

and 4000, we can make the following conclusions. s-PVA with a higher P_n value has a higher η^* value and a greater shear thinning effect. Because s-PVA with a high P_n value has a regularly arranged structure and the large number of hydrogen bonds and s-PVA molecules are stiff and well oriented, it has higher values of G' and G'' . Above a P_n value of 2700, higher shear thinning occurs, and nearly constant values of G' and G'' are obtained over an ω range of 10^{-1} to 10^2 rad/s. This suggests that s-PVA molecules are more oriented as P_n increases. At P_n 's of 300 and 1300, there is lower yield stress with a poor internal ordered structure. However, s-PVAs with P_n 's of 2700 and 4000 have greater pseudostructures, like a mesophase, with higher non-zero yield stress and larger λ values. In the near future, we will report on the effect of the microstructure of PVA on the rheological properties of s-PVA solutions.

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