Role of the Stereosequences of Poly(vinyl alcohol) in the Rheological Properties of Syndiotacticity-Rich Poly(vinyl alcohol)/Water Solutions

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ABSTRACT: Syndiotacticity-rich poly(vinyl alcohols) (s-PVAs) with various syndiotactic dyad (S-dyad) contents were prepared by the copolymerization of vinyl pivalate and vinyl acetate with various monomer feed ratios, which was followed by the saponification of copoly(vinyl pivalate/vinyl acetate) to investigate the effect of the stereosequences of s-PVA on the rheological properties of s-PVA/water solutions. Through a series of experiments, we identified that the syndiotacticity had a profound influence on the rheological properties of s-PVA/water solutions. Over a frequency range of 10^{-1} to 10^2 rad/s, s-PVAs with higher S-dyad contents showed larger values of complex viscosity and storage modulus and more shear thinning at similar molecular weights and degrees of saponification of the polymer, suggesting that poly(vinyl alcohol) molecules were stiffer and more readily oriented as syndiotacticity increased. All the yield stresses of s-PVA represented positive values, and s-PVAs with higher syndiotacticity showed higher yield stresses. This suggests that as syndiotacticity increased, more pseudostructures were present in s-PVA/water solutions. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 1858–1863, 2003

Key words: PVA; stereosequence; rheological properties

INTRODUCTION

Poly(vinyl alcohol) (PVA) has received considerable interest because of its various uses and good properties. PVA is a water-soluble, innocuous, environmentally friendly material that is used for fibers, sizing agents, adhesive, polarizing and packaging films, membranes, drug delivery systems, contact lenses, biomaterials, nanomaterials, and so on.[1–3] However, PVA has poor water resistance and physical properties; therefore, the enhancement of these properties is necessary.

PVA is classified structurally into isotactic PVA, atactic poly(vinyl alcohol) (a-PVA), and syndiotactic PVA with respect to the arrangement of hydroxyl groups attached in main chain. a-PVA, with its irregular arrangement of hydroxyl groups, has a weak structure in water and poor physical properties. Poly(vinyl acetate) (PVAc) is used as a precursor of PVA, for the production of a-PVA. However, because vinyl acetate (VAc), the monomer for PVAc, has a small steric effect during polymerization, a-PVA made from PVAc has a poor stereosequences and is susceptible to water absorption.[4–12] Recently, syndiotacticity-rich poly(vinyl alcohol) (s-PVA) with higher stereosequences was made from poly(vinyl pivalate) (PVPi) having bulky side groups.[13–26] Because s-PVA has a regular structure with hydroxyl groups in the main chains alternately arranged, it packs well with adjacent molecules and can easily form strong intermolecular hydrogen bonds.[14] When PVPi is used as the precursor, s-PVA with a closely packed molecular structure because of higher syndiotacticity does not dissolve in water until it reaches 120°C.[15]

So, to prepare a water-soluble s-PVA, the major molecular parameters of PVA, such as molecular weight, degree of saponification, and stereosequence, need to be controlled with the copolymerization of vinyl pivalate (VPi) and VAc with various monomer feed ratios and the subsequent saponification of copoly(vinyl pivalate/vinyl acetate). Because water-insoluble s-PVA with a strong molecular structure is only soluble in organic solvent, it causes toxicity problems for the organic solvent when used for biomaterial *in vivo*. However, water-soluble s-PVA can be used for innocuous biomaterials. Moreover, because water-sol-

uble s-PVA is superior to a-PVA in many physical properties, water-soluble s-PVAs are able to be prepared as biomaterials with better physical and chemical properties.

To adopt s-PVA/water solutions for industrial applications, it is important to characterize the rheological properties of PVA solution for products such as biofibers, biogels, and bioadhesives with specified biomedical properties.[27] PVA solution shows variable rheological behaviors with regard to temperature, degree of saponification, molecular weight, and so on.[28–30] In this study, the effect of stereosequence on the rheological properties of s-PVA/water solutions was investigated.

EXPERIMENTAL

Materials

VAc and VPi, purchased from Shin-Etsu (Japan), was washed with an aqueous solution of $NaHSO_3$ and water and dried over anhydrous $CaCl_2$, followed by distillation under reduced pressure of nitrogen. The initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (AD-MVN; Wako Co., 99%, Japan), was recrystallized twice from absolute methanol before use. Other extra-pure grade reagents were used without further purification. The water used for all procedures was deionized.

Preparation of s-PVAs

To prepare water-soluble s-PVA, the copolymerization of VPi and VAc with various feed ratios of mol_{VPi}/mol_{VAc} (mol of VPi/mol of VAc) (1/9, 2/8, 3/7, and 4/6) with ADMVN as an initiator, with conversions of 25–35%, was performed, followed by the saponification of the copoly(vinyl pivalate/vinyl acetate) with NaOH aqueous solution at 30°C for determined time intervals. Water-soluble (s-PVAs) with various syndiotactic dyad (S-dyad) contents ranging from 55.3 to 58.6% were prepared.

Characterization of s-PVAs

The number-average degree of polymerization (P_n) of s-PVA was determined by the measurement of the viscosity of the fully reacetylated specimen in benzene solution with an Ubbelohde viscometer.[10] The syndiotactic triad and S-dyad content of PVA were determined by a Varian Sun Unity 300-MHz ^{1}H-NMR spectrometer, with dimethylsulfoxide-d_6 as the solvent, on the basis of the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm. The degree of saponification was determined by the ratio of tert-butyl and acetyl and methylene proton peaks in the ^{1}H-NMR spectrum.

TABLE I
Molecular Parameters of the Prepared PVA

S-dyad content (%)	Degree of saponification (%)	P_n
55.3	93.7	3900
56.8	93.5	3900
57.7	93.8	3900
58.6	93.7	3900

Preparation of the s-PVA/water solutions

s-PVA was hard to dissolve in water at room temperature, so it was dissolved to a 10% water solution at 120°C for 1 h and was kept for 30 min to ensure homogenization.

Measurement of the rheological properties of the s-PVA/water solutions[31]

For more precise rheological measurement, an advanced rheometric expansion system (ARES), manufactured by Rheometric Scientific, Inc., was used. In ARES measurement, a cone-and-plate-type 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. 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%, 25°C, and low frequency (ω) with range of 10^{-1} to 10^2 rad/s.

RESULTS AND DISCUSSION

It is known that s-PVA with high tacticity and high molecular weight is a water-insoluble polymer. In this study, to prepare a water-soluble s-PVA and to precisely identify tacticity effect only, we finely controlled molecular weight, tacticity, and degree of saponification to an appropriate level by the copolymerization of VPi and VAc and the resultant saponification. Specimens were prepared by copolymerization with an appropriate control of feed ratio of mol_{VPi}/mol_{VAc}, and as feed quantities of VPi increased, S-dyad contents increased from 55.3 to 58.6%. Table I shows characteristic features of s-PVAs prepared by saponification. All specimens showed different S-dyad contents of 55.3–58.6%, similar P_n's of 3,900, and a similar degree of saponification of 94%, respectively.

Complex viscosities (η^*'s) of s-PVA/water solutions of different S-dyad contents with ω are shown in Figure 1. Specimens of higher S-dyad contents had higher η^*'s at given ωs, and all specimens showed shear thinning behavior, a decrease in η^* with ω. An increase in S-dyad content led to greater intermolecular hydrogen bonding of hydroxyl groups and more rigid molecular structures with the higher η^*. Because s-
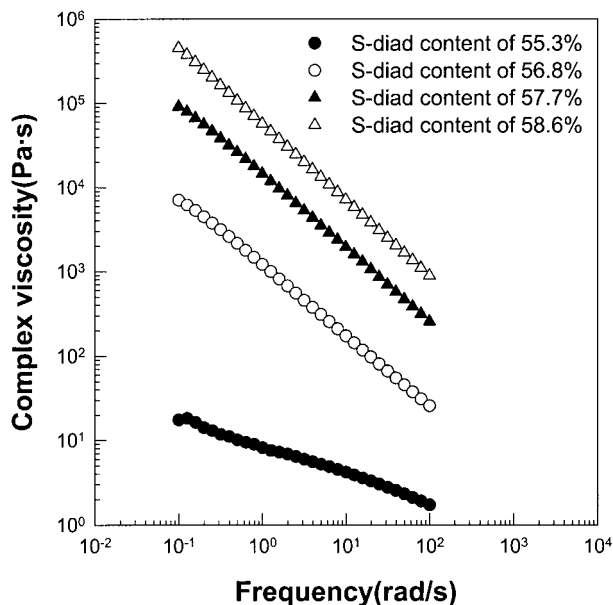
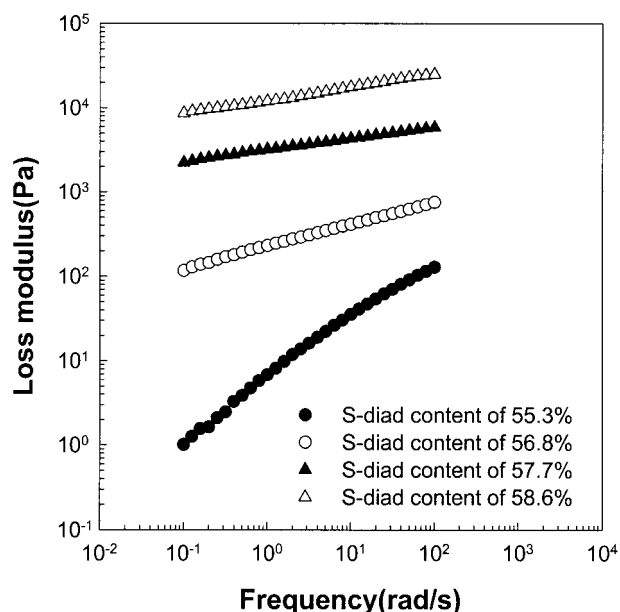**Figure 1** η^* of 10% (g/dL) s-PVA/water solution with ω at 30°C.
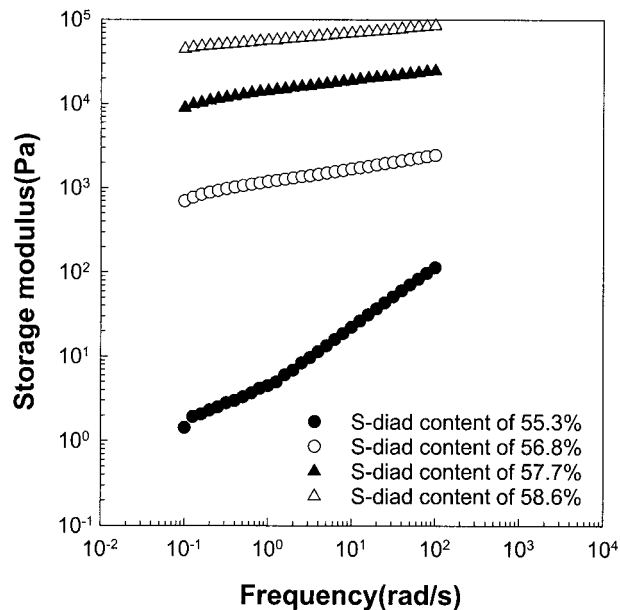
Figure 2 G' of 10% (g/dL) s-PVA/water solution with ω at 30°C.

PVAs with higher S-dyad content formed greater molecular orientation and a heterogeneous system like a liquid crystal, molecules were arranged along the shear force direction, and η^* decreased with shear. The specimen with an S-dyad content of 55.3% had a poorer shear thinning effect than did those with S-dyad contents over 56.8%. This suggests the presence of a critical point at which a change of internal structure in molecules occurred between 55.3 and 56.8%. From this viscosity behavior, we could conclude that stereosequence had a profound influence on the viscoelastic properties of the s-PVA/water solutions.

The change in storage modulus (G') and loss modulus (G'') of s-PVA/water solutions with ω is presented in Figures 2 and 3, respectively. s-PVAs with higher S-dyad contents had greater G'''s and G''''s. Because s-PVA had strong intermolecular bonding related to tacticity, much higher values of G' and G'' with S-dyad content are easily observed in Figures 2 and 3.[32] The s-PVA solution with an S-dyad content of 55.3% had increased G' and G'' with ω, whereas specimens with S-dyad contents over 56.8% had nearly similar values of G' and G'' with ω. This implies that s-PVA with an S-dyad content of 55.3% was different from s-PVAs with S-dyad contents over 56.8% in molecular structure. Because s-PVAs with S-dyad contents over 56.8% had superior intermolecular bonding, due to their regular arrangement of hydroxyl groups, it showed nearly constant G'' against deformation.

Figure 4 shows the η^* behavior of s-PVA/water solutions with G''. The slopes of the viscosity curves indicate the effect of S-dyad content on the shear dependence of viscosity: PVAs of higher S-dyad content had progressively steeper slopes in their viscosity

curves. Lyoo et al.[32] reported that a-PVA had a constant value of η^* to G'', indicating Newtonian flow behavior. As shown in Figure 4, all specimens showed decreases of η^* with G'', which is non-Newtonian flow. Disappearance of the lower Newtonian flow region indicates a heterogeneity of a system frequently observed in liquid crystalline polymers and block copolymers. The specimen with an S-dyad content of 55.3% showed lower slope behavior than the other three specimens, and specimens with S-dyad contents over 56.8% showed nearly unchanged G'' with changes in

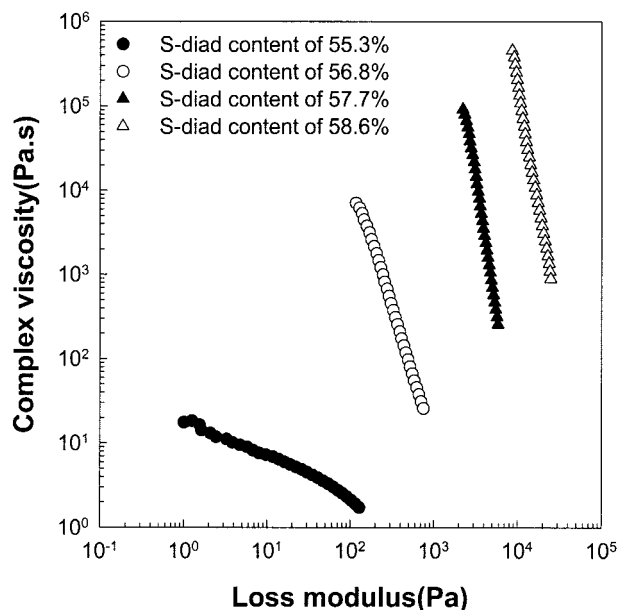**Figure 3** G'' of 10% (g/dL) s-PVA/water solution with ω at 30°C.

Figure 4 η^* of 10% (g/dL) s-PVA/water solution with G'' at 30°C.

viscosity. We believe that s-PVAs with higher S-dyad contents had greater molecular interactions and that a critical point of deformation of the system was present.

The behavior of G' of s-PVA/water solutions with G'' is shown in Figure 5. In this plot, one sees the rheological responses more clearly by the replacement of ω with G'' in Figure 2. This logarithmic plot of G' against G'', a Cole–Cole plot, gives a slope of 2 for most homogeneous and isotropic polymer melts and solutions. The slope of an homogeneous isotropic solution
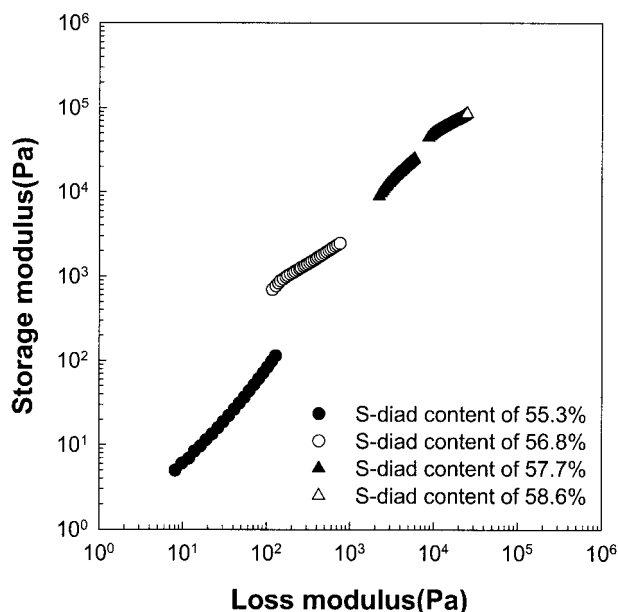

Figure 5 G' of 10% (g/dL) s-PVA/water solution with G'' at 30°C.
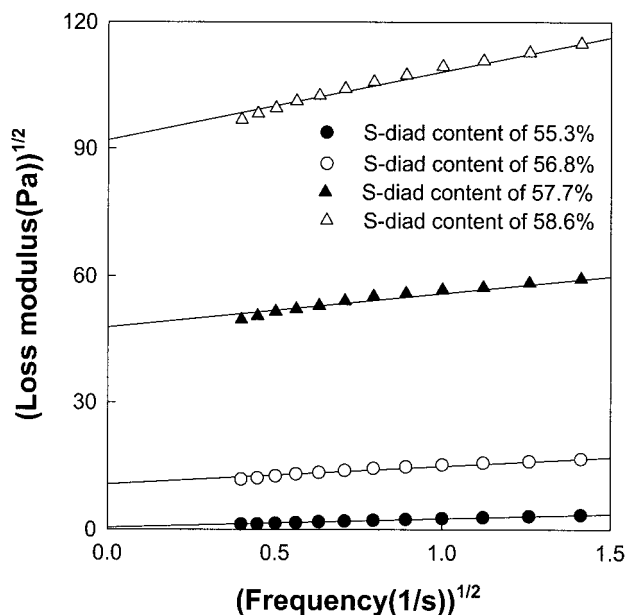

Figure 6 Square root of G'' of 10% (g/dL) s-PVA/water solution with the square root of ω at 30°C.

such as a-PVA is nearly 2, but the slope of a heterogeneous solution such as s-PVA is a lower value than 2.[33] In our plots, all specimens had slope values lower than 2, which represented heterogeneous forms. Specimens with S-dyad contents over 56.8% had significantly lower slopes than that with a content of 55.3%. This indicates that s-PVA solutions with S-dyad contents over 56.8% had structures akin to mesophase. This confirms that the difference in stereoregularities influenced the appearance of the heterogeneous structure.

Bingham flow behavior gives rise to a nonzero yield stress (τ_0), which represents the minimum energy required to break pseudostructures such as gels and microdomains.[34] τ_0 of heterogeneous systems can be determined from the Casson plot, the plot of the square root of shear stress (τ) against square root of shear rate (γ) in steady shear flow. K is constant. τ_0 is obtained from[35]

$$\tau^{1/2} = \tau_0^{1/2} + K\gamma^{1/2} \qquad (1)$$

Similarly, the intercept of G'' axis (G_0'') on the plot of the square root G'' against the square root of ω may be regarded as a measure of τ_0 in dynamic shear measurement as.[36] K' is constant.

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

Figure 6 shows plots of the square root of G'' of s-PVA/water solutions with the square root of ω. All specimens with S-dyad contents over 56.8% represented the nonzero intercepts on the Casson-type plot, implying that pseudostructure existed in the systems.
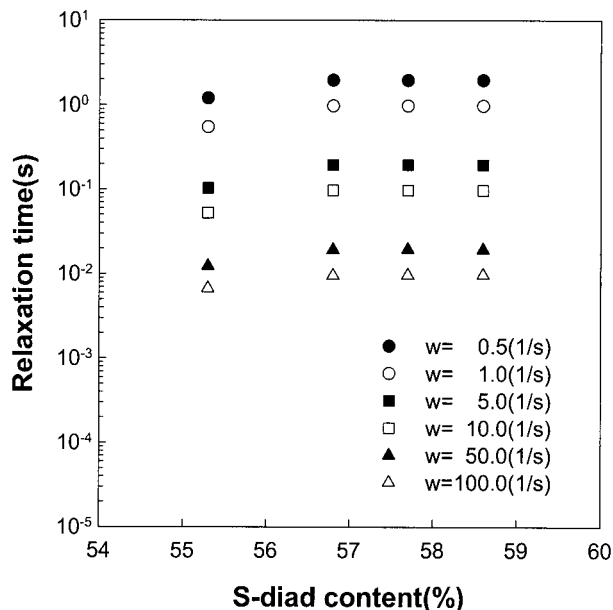
Figure 7 λ of 10% (g/dL) s-PVA/water solution at various S-dyad contents at 30°C.

The intercept values increased with S-dyad contents, indicating that s-PVAs of higher S-dyad contents had greater pseudostructure development. The higher stereoregularity led to a stronger molecular structure, and s-PVAs with higher stereoregularity needed greater energy to break the pseudostructure.

The relaxation time (λ) under dynamic shear may be calculated as[37]

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

where J' and G' are the compliance and storage moduli, respectively, and η^* and η' are the complex and dynamic viscosities, respectively. As shown in Figure 7, λ increased with S-dyad content and decreased with ω. In the plot, it was confirmed that the specimen with high tacticity had a more ordered structure. The difference between λs of 55.3 and 56.8% syndiotacticity were very large, indicating a critical point, which showed that a long λ, due to the internally strong structure in the system, existed between 55.3 and 56.8%.

CONCLUSIONS

After characterizing the rheological properties of s-PVA/water solutions with stereosequences, we conclude the following. As S-dyad content increases, s-PVA solutions had higher η^* values and higher values G' and G''. This might be explained by the fact that the higher the S-dyad content was, the greater the intermolecular hydrogen bonding in PVA was. Above an S-dyad content of 55.3%, a higher shear thinning effect occurred, and nearly constant values of G' and G'' were obtained over a ω range of 10^{-1} to 10^2 rad/s. At the S-dyad content of 55.3%, the plot showed lower τ_0 with poor internal order, whereas above 55.3%, the solution system had a higher degree of internally ordered structure like mesophase, arising from a higher τ_0 and a longer λ. At the critical point, a change from homogeneous properties to heterogeneous properties existed between S-dyad contents of 55.3 and 56.8%, and increased pseudostructure was evident at higher S-dyad contents beyond the critical point.

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