Role of Degree of Saponification in the Shear-Induced Molecular Orientation of Syndiotacticity-Rich Ultrahigh Molecular Weight Poly(vinyl alcohol)

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ABSTRACT: Rheological and morphological properties as well as crystal characteristics of syndiotacticity-rich ultrahigh molecular weight poly(vinyl alcohol) (PVA) were studied with consideration of degree of saponification (DS). The solutions of syndiotacticity-rich PVA with DS higher than 90% in dimethyl sulfoxide exhibited shear-thinning behavior without lower Newtonian flow region, implying the presence of heterogeneity. From the logarithmic plot of G' vs G'', the modified Casson plot, and the variation of relaxation time with DS, the syndiotacticity-rich PVA chains with high DS were elucidated to have a nature of molecular alignment under shearing deformation through the formation of microgels. These characteristic rheological features have a strong relationship with the development of the microfibrillar structure in the course of saponification of poly(vinyl pivalate). The well-oriented microfibrillar structure was observed in the syndiotacticity-rich PVA with high DS, which resulted from the hydrogen-bonding generation during saponification.

Introduction

Shear-induced alignment of polymer molecules has received considerable interest in recent years. Its importance lies in academic as well as practical aspects. It can offer a clue to assess the colligative behavior of polymer molecules under stress and can suggest a practical method to prepare highly oriented polymeric materials, which is the very essence of obtaining high-performance fibers and films. This phenomenon has been reported for both homogeneous and microheterogeneous systems.[1−12] Examples of the former and the latter include shear-induced molecular orientation of polymer melts and spontaneous fibrillation of the mesophase of liquid crystalline polymers under shear, respectively.

Recently, we found out that the syndiotacticity-rich poly(vinyl alcohol) (PVA) whose syndiotactic diad (*s*-diad) content was higher than 60% formed a microheterogeneous solution system in dimethyl sulfoxide (DMSO).[13] Although the solution system was optically transparent, it gave rise to fibrillation under shear. This has never been reported in the solutions of atactic PVA whose *s*-diad content is lower than 54% in DMSO.

In the case of microheterogeneous polymeric systems the shear-induced alignments of molecules are expected through phase separation. For example, the block copolymers, composed of mutually incompatible block components, generally exhibit a phase transition called the order−disorder transition at certain temperatures. In the ordered state, various periodic morphologies such as lamella are observed. The changes in morphological and rheological properties of block copolymer melts or solutions under shear flow have been extensively studied.[1−12] Assemblies of microdomains are randomly aligned and called isotropic. However, under shear flow, the microdomains give transverse, parallel, and perpendicular alignment along the shear flow, shear gradient, and vorticity (neutral) directions, respectively. In addition, at low shear rates, liquid crystal polymer exhibits a complex supramolecular microstructure that is sensitive to shear deformation. The nematic or smectic mesophases may assume a particular orientation with respect to the principal directions defined by the flow. In both the order−disorder transition of block copolymer system[2,8,11] and the mesophase of liquid crystal polymer system,[12] failure of time−temperature superposition is detected.

Recently, Lyoo et al.[14−18] reported that PVA fiber of well-oriented microfibrillar structure, similar to a natural cellulose fiber, was formed during saponifying poly(vinyl pivalate) (PVPi) to PVA, and syndiotacticity played an important role in the in-situ fibrillation of flexible chain polymer under low shear conditions.[14−17] From the previous investigation of syndiotacticity-rich high molecular weight PVA, it was confirmed that the

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small increase in *s*-diad content from 55 to 56% facilitated a change in crystallization process and led to the development of a fibrous morphology.[14] So, it is quite interesting to investigate the deformation of syndiotacticity-rich PVA chains under shear flow, which may be analogous to the in-situ fibrillation during saponification.

Among the molecular parameters of PVA, including stereoregularity,[16,19] the degree of saponification (DS) is a quite notable one because residual ester groups on side chains hinder hydrogen-bonding interaction between the chains. As pivaloyl groups change into hydroxyl ones, in other words, as DS increases during saponification, highly crystalline and oriented PVA microfibrillar fibers are produced. Hence, the investigation of syndiotactic PVAs with different DSs is closely analogous to the evolution of microfibrillar structure during saponification. In this study, we traced spontaneous shear-induced alignment of syndiotacticity-rich ultrahigh molecular weight PVA molecules during saponification of PVPi considering DS of the polymer on the basis of rheology, morphology, and crystal structure of PVA.

Experimental Section

Preparation of Polymer. PVPi with high stereoregularity was synthesized by ultraviolet-ray-initiated bulk polymerization of vinyl pivalate at low temperature.[18] The number-average degree of polymerization (P_n) of PVPi prepared is 21 700. The saponification of syndiotacticity-rich PVPi produced ultrahigh molecular weight PVA with *s*-diad content of 64.5% (denoted as syndiotacticity-rich PVA to differentiate it from PVAs prepared from saponification of poly(vinyl acetate) (PVAc), whose *s*-diad content is less than 54%). The saponification conditions of PVPi are as below. PVPi (2 g) was dissolved in tetrahydrofuran (THF) (200 mL), and a solution of potassium hydroxide (5 g) in methanol/water solution (90/10 v/v; 20 mL) was added drop by drop with stirring using an H-shaped anchor-type stainless steel stirrer at 20 000 rpm at 60 °C. (No stirring resulted in incomplete saponification, and the higher stirring rates resulted in the breakup of the gel structure that appears to be necessary for fibrillation.) A solid saponification product was beaten mechanically, filtered, and washed several times with methanol.[16] A quantitative yield of PVA was obtained. PVAs with different DSs were obtained by controlling saponification times. The optimum saponification times for PVAs with DSs of 87.8, 90.3, 95.4, 97.8, and 99.9% were 600, 700, 800, 900, and 1050 s, respectively.

Characterization. The P_n of PVA was determined by measuring viscosity of the fully reacetylated specimen in benzene solution.[18] The *s*-diad content was calculated from the ratio of the components of hydroxyl proton triplet at 4.1−4.7 ppm obtained by 300 MHz ^{1}H NMR scanning using DMSO-d_6 as a solvent. The DS was determined from the peak of residual pivaloyl group in the ^{1}H NMR spectrum. PVA so prepared had a P_n of 14 000 and an *s*-diad content of 64.5%, denoted as syndiotacticity-rich ultrahigh molecular weight PVA.

Changes in the shear viscosity of saponification reaction solution during the saponification of PVPi were observed by using a rheometer (Physica, MC 20) at a constant shear rate of 50 s^{-1}. A Z-1 cell, double-gap coaxial type, was used as a flow cell. A 0.2 g sample of PVPi was dissolved in 20 mL of THF, and 2 mL of solution of potassium hydroxide (0.5 g) in methanol/water solution (90/10 v/v; 2 mL) was used as a saponification agent at 60 °C.

PVA solutions in DMSO were prepared by stirring the polymer/DMSO mixture at 50 °C. For a precise rheological measurement, a Rheometrics fluid spectrometer RFS II was used. Minimum sensitivity and sampling time of RFS II are 2 × 10^{-3} g cm and 5 ms, respectively. In RFS measurement, a cone and plate type flow cell with diameter of 25 mm and deformation degree of 0.02 rad was adopted to effectively accommodate the torque of the solutions. To keep the shear history of the polymer solution minimized, the solution was placed without disturbance between the cone and plate for 90 min before rheological measurement.

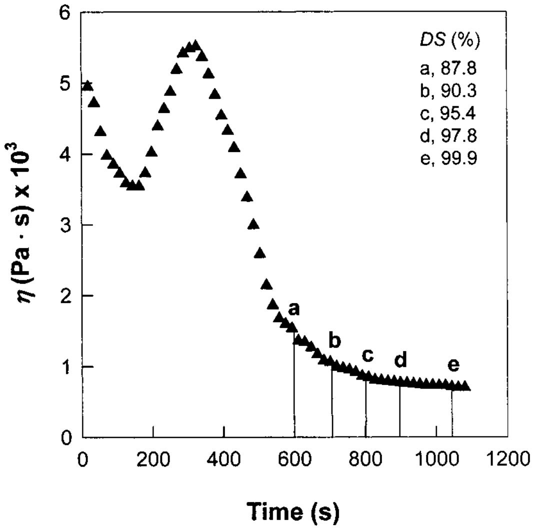

Figure 1. Changes in shear viscosity and DS during the saponification of PVPi having P_n of 21 700 at 60 °C.

The surface morphology of the PVA specimen was investigated using a Scalar VMS 300 video microscope with a magnification of ×200.

Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) data were recorded on Kodak direct exposure X-ray film using Ni-filtered Cu Kα radiation and pinhole collimation under vacuum.

Stress−strain curves for the PVA microfibrillar fibers were obtained using an Instron model 4201, with a sample length of 3 cm and cross head speed of 10 mm/min. The specimens appeared very similar to those of native cellulose, notably ramie, jute, and linen, so, in calculating tensile strength of the PVA specimens, we used a similar method adopted in the calculation of the tensile properties of these cellulose fibers. The tensile strength was taken as the average of 20 measurements.

Results

Rheological Characterization. The changes in shear viscosity (η) and DS during the saponification of PVPi with P_n of 21 700 were checked by using a rheometer (Figure 1). During the initial reaction stage, the η decreased due to the mixing of PVPi/THF and alkali solutions. As the saponification proceeded, the pivaloyl groups of PVPi were converted into hydroxyl groups, and the η increased, exhibiting a maximum η, at which the Weissenberg effect was observed. While the saponification proceeded to the points a (87.8%), b (90.3%), and c (95.4%), the gel was converted into fibril. The η decreased as the gel was phase-separated and fibrillated. From the fact that the η in this system changed little near point d (97.8%), it was apparent that the fibrillation was almost finished. In this study, we identified five syndiotacticity-rich PVA solutions having different DSs of a (87.8%), b (90.3%), c (95.4%), d (97.8%), and e (99.9%), presented in Figure 1, on the basis of rheology. In the case of PVA with DS of below 85%, it was impossible to dissolve it in DMSO.

Figure 2 compares behavior of the complex viscosities (η*) of 2% (g/dL) solutions of PVAs with different DSs at 30 °C. As expected, DS had a profound influence on the viscoelastic properties of PVA solution. Over the

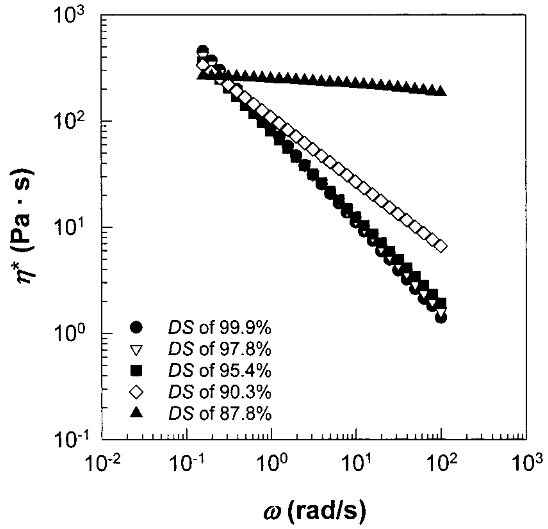

Figure 2. Complex viscosity curve of 2% (g/dL) PVA solutions in DMSO at 30 °C.

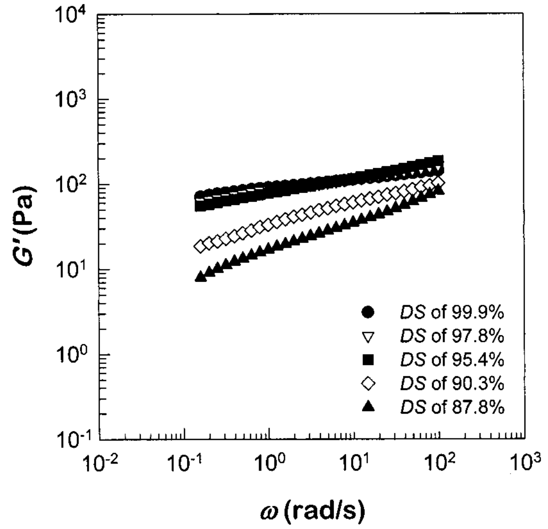

Figure 3. Storage moduli of 2% (g/dL) PVA solutions in DMSO at 30 °C with frequencies.

frequency ranges examined, the solution of PVA with DS of 87.8% exhibited almost Newtonian flow behavior whereas the solution of PVA with DS over 90% was shear thinning at the identical polymer concentration. The disappearance of a lower Newtonian flow region in the case of the PVA solution with DS over 90% is indicative of the presence of heterogeneity in the system. This kind of viscosity behavior is reported to be frequently encountered in inhomogeneous systems such as polymer gels, block copolymers, and liquid-crystalline polymers. It is worth mentioning that the magnitude of viscosity is smaller when DS is higher.

Change of storage modulus (G') of the PVA solutions with frequency is presented in Figure 3. The slopes of PVA solutions are in the range 0.1−0.4. It should be noticed that the slope is decreased with increasing DS, but the magitude of G'' is increased. In this case one can see the rheological responses more clearly by replacing frequency, a processing parameter, with loss modulus (G''). The so-called Cole−Cole plot was empirically found out that the logarithmic plot of G' against G'' gives slope of 2 for most homogeneous and isotropic polymer melts and solutions and eliminates temperature effects on G'. Han and John[20] theoretically related

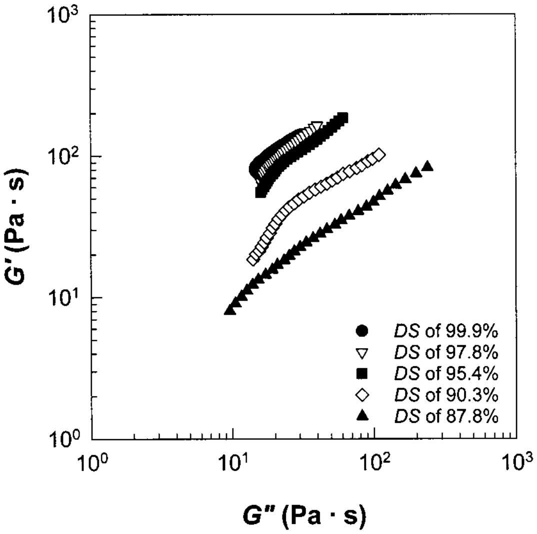

Figure 4. Storage moduli of 2% (g/dL) PVA solutions in DMSO at 30 °C with loss moduli.

G' to loss modulus (G'') by the following equation:

$$\log G' = 2 \log G'' + \log(6/5G_0{}^n) \qquad (1)$$

in which $5G_0{}^n = \rho RT/M_e$, ρ is density, R is the gas constant, T is temperature, and M_e is the entanglement molecular weight. This equation has been derived from molecular viscoelasticity theory for entangled flexible homopolymers. According to this equation, the slope of homogeneous isotropic polymer solutions should be 2. As one may imagine, however, the slope would be reduced in the case of the heterogeneous phases because it contains pseudostructures of microdomains through physical aggregations, which may be easily oriented even by low shear. This was successfully adapted to characterize phase transition of block copolymers. Further, the orientation relaxation would be much slower than in homogeneous isotropic solutions. Thus, the degree of increasing energy dissipation will be increased with increasing frequency by increased breakdown and orientation of the microdomains.

As shown in Figure 4, PVA solutions give rise to slopes much smaller than 2, which is further decreased as DS increased. Hence, it is suggested that the phase of PVA solutions in DMSO is heterogeneous rather than homogeneous, which is preferred as DS increases. A similar phenomenon, decrease of the slope to below 2 on the logarithmic plot of G' against G'', has been reported for thermotropic liquid-crystalline polymers and block copolymers over a range of temperatures in which nematic phase and heterogeneous phase are formed, respectively. In addition, the PVA solutions give rise to an inflection point on the logarithmic plot of G' against G'' particularly for PVAs with DS over 90%. The inflection point at a certain G'' means that the ratio of viscous dissipation to elastic storage is abruptly increased above G''. This may be attributable to the fact that some heterogeneous domains with internal order are oriented to a great extent at this frequency range. This inflection temperature is indicative of a transition of anisotropic to isotropic phase for thermotropic liquid crystalline polymers and a transition from heterogeneous to homogeneous phase for block copolymers. It should be noted that solutions of PVAs with *s*-diad content of below 54% in DMSO gave the slope of 2

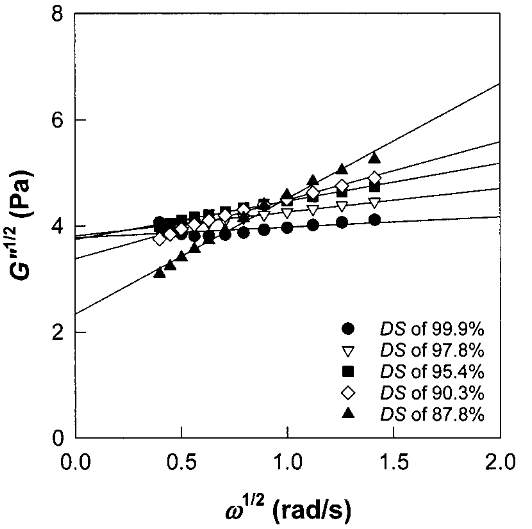

Figure 5. Plots of square root of loss modulus vs square root of frequency for 2% (g/dL) PVA solutions in DMSO at 30 °C.

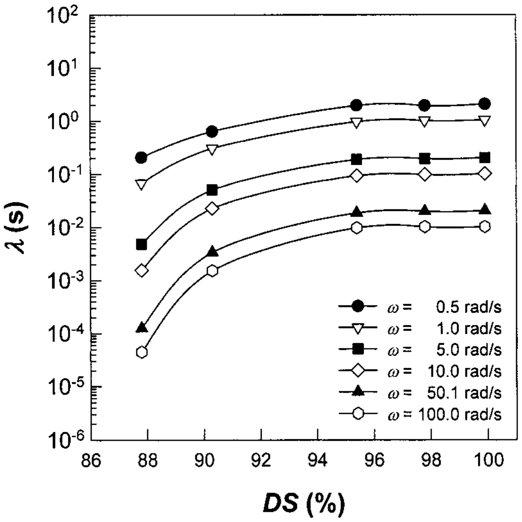

Figure 6. Change in relaxation time of 2% (g/dL) solutions in DMSO at 30 °C with DS.

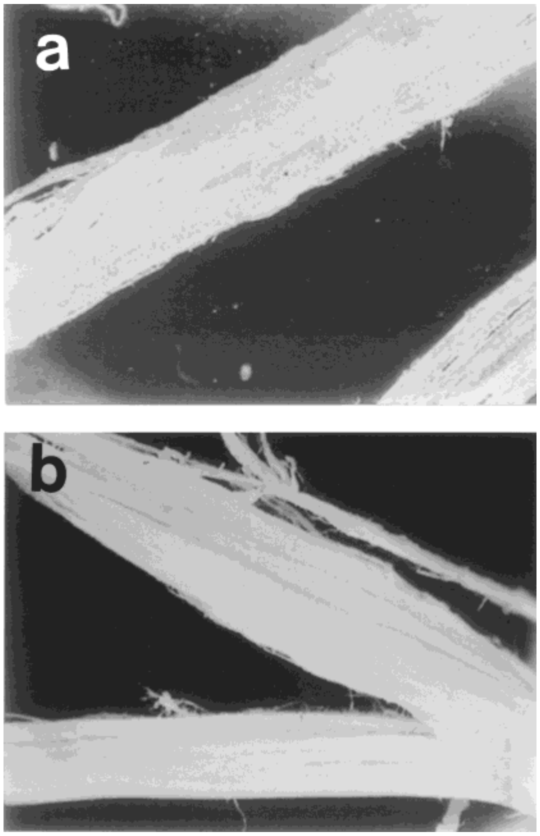

Figure 7. Optical micrographs (×200) of PVAs with different DSs: (a) 87.8%; (b) 90.3%.

irrespective of DS, which were obtained by saponification of PVAc.[13]

Bingham flow behavior gives rise to a nonzero yield stress, which represents minimum energy required to break pseudostructures such as gels and microdomains. The yield stress of heterogeneous systems can be determined from the Casson plot, a plot of the square root of shear stress (τ) against square root of shear rate (γ) in steady shear flow. The yield stress (τ_0) is obtained from eq 2.[21]

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

Similarly, the intercept of G'' axis (G_0'') on the plot of the square root of G'' against square root of frequency (ω) may be regarded as a measure of yield stress in oscillatory shear experiment as eq 3.[22]

$$G''^{1/2} = G_0''^{1/2} + K'\omega^{1/2} \qquad (3)$$

The square roots of G'' of the PVA solutions with different DSs are plotted against the square root of ω in Figure 5. In the case of atactic PVA, all the intercepts reduce to zero in the so-called Casson-type plots whatever the molecular weight of polymer. Syndiotacticity-rich PVA produced nonzero intercepts on the plot, pointing out the existence of yield stress of positive values. This suggests that some pseudostructure was present in solutions of syndiotacticity-rich PVA in DMSO. The yield stress (the intercept) notably increased with DS, implying that the pseustructure was developed significantly as DS increased.

The relaxation time (λ) under dynamic shear is calculated as eq 4.[23]

$$J' = G'/([\eta^*]\omega)^2 = \lambda/[\eta^*] \qquad (4)$$

where J' is compliance. As shown in Figure 6, the PVA with DS lower than 90% exhibited relaxation times typical of flexible chain polymers. However, relaxation time increased with an increase of DS. The fully saponified PVA solution has a long relaxation time particularly at low frequencies. Relaxation time may be much longer if some molecular order exists. For instance, a rigid-rod polymer such as thermotropic liquid-crystal polyester exhibits a very long relaxation time when it forms an anisotropic phase.[23] Accordingly, the molecular orientation in syndiotacticity-rich PVA solution evolves as hydroxyl groups generate, resulting in a long relaxation time comparable with anisotropic mesophase in the liquid-crystal system.

Morphology and Crystal Structure. The hydrogen-bonding generation during saponification is expected to cause the change of morphology and crystal. In Figure 7, the morphologies of PVA specimens with different DSs are illustrated. The microfibrillar structure of the PVA with DS of 90.3% is more developed than that of the PVA with DS of 87.8%. The fibrous morphology developed as DS increased with trends that the fibrils

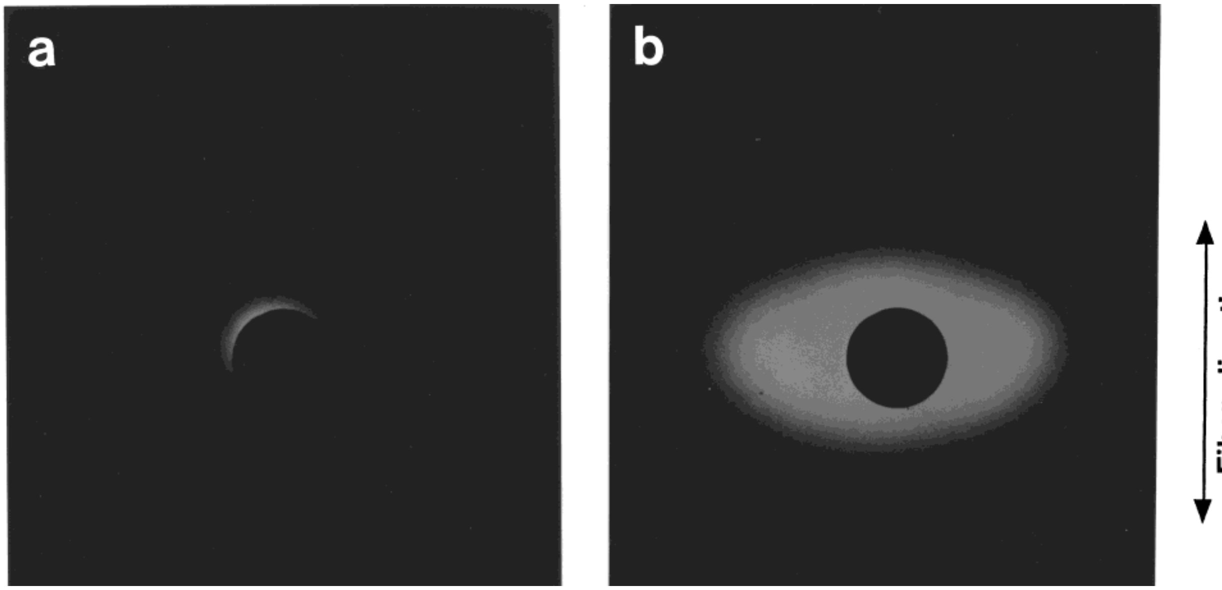

Figure 8. SAXS patterns of PVAs with different DSs: (a) 87.8%; (b) 90.3%.

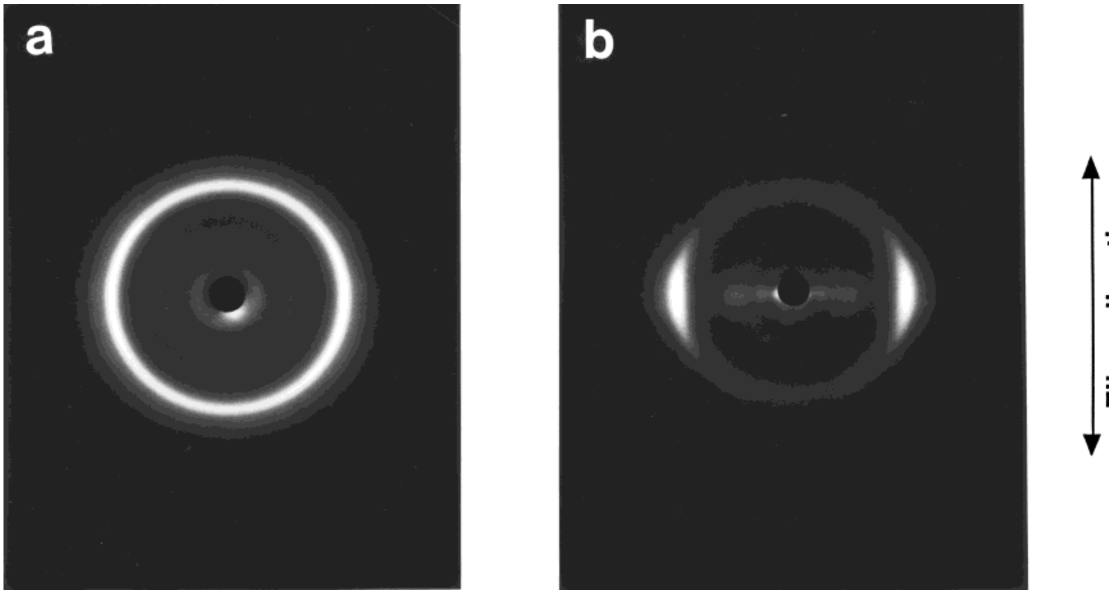

Figure 9. WAXD patterns of PVAs with different DSs: (a) 87.8%; (b) 90.3%.

become longer and narrower. It is interesting that although two PVA specimens in Figure 7 had similar fibrillar morphologies, the tensile strength of the PVA with DS of 90.3% (over 12 g/d) was much higher than that of 87.8% (easily breaking into pieces and nearly no tensile strength). Thus, to identify an obvious tensile strength difference between two specimens, we characterized microstructure and crystal orientation of the two PVAs using X-ray analysis.

SAXS patterns of the PVAs with DSs of 87.8% and 90.3% are displayed in Figure 8. No scattering in small angle region was found for the PVA with DS of 87.8% as shown in Figure 8a, indicating there is no microstructure. This pattern is similar to that of atactic PVA.[14] However, in the case of the PVA with DS of 90.3%, a strong elliptical scattering was observed (Figure 8b) due to the presence of regular and elongated microvoids. This is strongly related with the development of well-oriented microfibrillar structure because there should be a lot of microvoids in PVA fiber which is a bundle of microfibrils. From WAXD patterns in Figure 9a, the specimens with DS of 87.8% was unoriented. In contrast, it is ascertained that the crystal orientation of the PVA with DS of 90.3% was favored as shown in Figure 9b. It is postulated that the high tensile strength of the PVA with DS of 90.3% described above was caused by the orientation of the crystal in microfibrils.

Discussion

In this study, the chain deformation of syndiotactic PVA molecule during saponification was simulated by rheological investigation of syndiotacticity-rich ultrahigh molecular weight PVA solutions with different DSs. Considering the molecular structure of polymer, it is assumed that syndiotacticity-rich PVA possesses a much stereoregular sequences, so the polymer chains may be readily stiffened by effective intermolecular interactions between hydroxyl groups. Thus, PVA may form microgels, which includes internal orders or internal structures at high DS. However, in the case of the PVA with lower DS than 90%, the hydrogen bonding between the hydroxyl groups was reduced by the residual pivaloyl groups to reveal a rheological response close to typical Newtonian flow.[13] The smaller absolute value of viscosity when DS is higher at a given frequency supports this phenomenon. That is, the microgels with internal molecular order would be readily oriented by shearing, resulting in Bingham flow behavior, that is, pseudoplasticity from very low frequency. However, it should be noted that atactic PVAs with *s*-diad content of less than 54%, prepared from PVAc, does not exhibit Bingham flow behavior but Newtonian flow behavior even at the DS higher than 99% at similar molecular weight. The intermolecular interactions through polar hydroxyl groups may be less effective with atactic PVA since hydroxyl groups are poorly arranged along the molecule axis. Hence, atactic PVA molecules may acquire smaller chain stiffness in solution than syndiotacticity-rich PVA molecules because the irregularly distributed hydroxyl groups make packing of the polymer chains less compact and dense. On the other hand, the molecules may be greatly stiffened and densely packed to produce microgels in the case of syndiotacticity-rich PVA, particularly at high DS by virtue of more effective hydrogen bonding. Thus, it stands to reason that the shear-induced molecular orientation results from increased stiffness of the polymer molecules. Higher melting temperature of syndiotacticity-rich PVA than that of atactic PVA with the same molecular weight reflects that syndiotacticity-rich PVA possesses higher chain stiffness than atactic PVA. These characteristic features may arise from the generation of strong intermolecular hydrogen bondings during saponification, which promotes the ordering of self-assembled macromolecular domains of PVA molecules.

The development of microfibrillar structure is achieved by orientation of PVA molecules along with crystal formation in the course of saponification, in other words, hydrogen-bonding generation. This result supports evidently that higher DS gives rise to the molecular orientation of syndiotacticity-rich PVA under shear. From a series of rheological and morphological investigations of syndiotacticity-rich PVA with different DSs, it is postulated that the strong nature of molecular alignment along the shear direction progresses as DS increases, and this is definitely related with the microfibrillar formation during saponification.

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