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Structure of Poly(vinyl alcohol) Microfibrils Produced by Saponification of Copoly(vinyl pivalate/vinyl acetate)

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ABSTRACT: High molecular weight specimens of syndiotacticity-rich poly(vinyl alcohol) (PVA) have been prepared by saponification of copolymers of vinyl pivalate (VPi) and vinyl acetate (VAc). VPi and VAc were copolymerized using the low-temperature initiator 2,2′-azobis(2,4-dimethylvaleronitrile) and saponified in KOH/methanol/water with vigorous stirring, i.e., under shear. The PVAs obtained had number-average degrees of polymerization in the range $(5.6-16.5) \times 10^3$ and syndiotactic diad (S-diad) contents of 52.8−61.5%. The highest molecular weight and S-diad content were obtained for specimens derived from homopoly(VPi) prepared at low initiator concentration, and these parameters declined progressively with increasing VAc content in the parent copolymers. The structures of these PVAs show a consistent sharp transition between 55 and 56% S-diad content. Specimens with lower S-diad contents have shapeless morphologies, but at 56% S-diad content the polymers were fibrous, with a higher degree of crystallinity and orientation of the crystallites. The order improves steadily with the S-diad content above the transition and correlates with the observed changes in the thermal and mechanical properties. The results suggest that the small increase in S-diad content from 55 to 56% facilitates a major change in the crystallization process, such that the crystallinity improves, and leads at the same time to the development of a fibrous morphology when the saponification is performed under shear.

Introduction

High molecular weight (HMW), syndiotacticity-rich poly(vinyl alcohol) (PVA) is of considerable interest because of its potential for the preparation of high-strength and high-modulus fibers and for applications as films for food and drug packaging, as barrier membranes, and as gels for drug delivery systems.[1−5] Preparation of PVA is usually via saponification of poly(vinyl acetate) (PVAc) synthesized by free radical polymerization, but the molecular weights are relatively low and the molecules tend to be branched due to chain transfer reactions. Thus there have been many efforts to produce HMW, relatively unbranched PVA using new methods to polymerize VAc[6−11] or using new precursors such as poly(vinyl pivalate) (PVPi).[12−15] Wu and West[9] have prepared ultrahigh molecular weight (UHMW) PVA with a number-average degree of polymerization (P_n) = 15 000 via ultraviolet (UV) initiation polymerization of vinyl acetate (VAc) at −45 °C, and Yamamoto et al.[10] have synthesized UHMW PVA with $P_n = 12\,800$ by UV-initiated emulsion polymerizaion of VAc at 0 °C. In the present paper we describe the synthesis and properties of HMW PVAs produced via saponification of PVPi and copoly(VAc/VPi).

The physical properties of PVA are highly dependent on the degree of syndiotacticity, which is determined primarily by the choice of the vinyl ester monomer precursor. Efforts to produce more syndiotactic PVAs, as well to increase the molecular weight, have centered on the polymerization of vinyl trifluoroacetate,[16] vinyl trichloroacetate,[17] and VPi.[12−15] The best results have been obtained using VPi, due to the strong steric effects of the *tert*-butyl group. Even so, the syndiotactic diad (S-diad) contents do not exceed 50% (i.e., random) by very much: PVAs with S-diad contents exceeding 53−54% (about the maximum value obtained in VAc polymerization) are generally described as "syndiotacticity-rich". (This contrasts with the 95% figure typically used to describe syndiotactic poly(methyl methacrylate)[18] and polystyrene.[19]) Recently, Yamamoto et al.[12,13] have reported the synthesis of UHMW PVA with $P_n > 18\,000$ and an S-diad content of 62.8% via UV-initiated emulsion polymerization of VPi at low temperatures, followed by saponification. Similarly, Lyoo and Ha[15] have synthesized UHMW PVA with a maximum P_n of 18 300 and an S-diad content of 64.1% via UV-initiated bulk polymerization of VPi at low temperature. The above polymerizations are complex and difficult to commercialize. Lyoo and co-workers[11,20,21] found that the use of a low-temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN), in polymerization of VAc, allowed them to lower the polymerization temperature to room temperature, and thereby suppress branching. Polymerization of VPi under the conditions described above (polymerization temperature of −10 to +50 °C) led to HMW PVAs with S-diad contents of 59−65%. Interestingly, saponification under mild shear conditions (shear rates of below 100 s^{-1}) led to PVAs with a well-oriented microfibrillar morphology similar to that seen for cellulose.[22,23] This did not occur for analogous PVA specimens derived from PVAc of similar molecular weight, for which the S-diad content was only 50−53%, and demonstrates the importance of tacticity in the in situ fibrillation. These microfibrillar PVAs are very

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Table 1. Copolymerization Results and Molecular Parameters of PVA

ADMVN concentration, mol/mol of monomer	VPi mol % in feed	conv, %	VPi mol % in copolymer	[η] of copolymer	P_n of PVA	triad tacticity (%)			diad tacticity (%)	
						mm	*mr*	*rr*	*m*	*r*
2.0×10^{-5}	100	18.2	100	3.65	16500	13.2	49.6	37.2	61.5	38.5
1.0×10^{-4}	100	29.5	100	3.81	14300	13.7	49.2	37.1	61.7	38.3
4.3×10^{-4}	100	38.3	100	3.55	8100	13.8	49.4	36.8	61.5	38.5
2.0×10^{-5}	90	16.1	97.5	4.35	15200	13.8	50.5	35.7	60.9	39.1
1.0×10^{-4}	90	30.9	96.6	4.76	12600	14.5	49.9	35.6	60.6	39.4
3.5×10^{-4}	90	35.9	95.1	4.67	7900	14.5	50.2	35.3	60.4	39.6
2.0×10^{-5}	80	16.6	90.8	4.06	13800	14.8	50.8	34.4	59.8	40.2
1.0×10^{-4}	80	32.1	88.8	4.33	10200	15.1	50.8	34.1	59.5	40.5
2.6×10^{-4}	80	36.6	86.4	4.31	8200	14.9	51.0	34.1	59.6	40.4
2.0×10^{-5}	70	17.6	82.5	3.88	10700	15.4	50.9	33.7	59.2	40.8
1.0×10^{-4}	70	33.6	79.7	4.04	8100	15.8	50.6	33.6	58.9	41.1
2.0×10^{-5}	60	19.4	71.6	4.11	10100	15.9	50.6	33.5	58.8	41.2
1.0×10^{-4}	60	25.1	69.5	3.67	8300	15.9	51.0	33.1	58.6	41.8
2.0×10^{-5}	50	12.8	58.5	3.29	8300	16.1	51.1	32.8	58.4	41.6
1.0×10^{-4}	50	23.6	58.6	3.44	6700	16.1	51.1	32.8	58.4	41.6
2.0×10^{-5}	40	15.3	49.7	3.36	8100	16.7	51.4	31.9	57.6	42.4
1.0×10^{-4}	40	26.4	47.4	3.51	6800	16.7	51.2	32.1	57.7	42.3
2.0×10^{-5}	30	16.1	35.2	3.17	7800	18.6	50.4	31.0	56.2	43.8
1.0×10^{-4}	30	28.5	36.4	3.50	7100	18.1	50.8	31.1	56.5	43.5
2.0×10^{-5}	20	13.5	26.3	3.25	7800	19.6	50.2	30.2	55.3	44.7
1.0×10^{-4}	20	22.9	24.8	2.99	6900	20.1	49.6	30.3	55.1	44.9
2.0×10^{-5}	10	13.7	14.7	3.11	7700	20.6	50.3	29.1	54.3	45.7
1.0×10^{-4}	10	25.2	13.5	2.90	6600	20.7	50.8	28.8	54.2	46.1
2.0×10^{-5}	0	10.8	0	2.61	6500	21.4	51.0	27.6	53.1	46.9
1.0×10^{-4}	0	23.5	0	2.59	5600	21.8	50.8	27.4	52.8	47.2

similar to natural asbestos fibers in structure and physical properties.

In the work described below we have compared PVA specimens of different molecular weights and stereoregularities. The specimens were produced by saponification of copoly(VPi/VAc) after bulk copolymerization using ADMVN initiation at low temperatures. The results show that for these specimens there is a critical syndiotacticity for in situ fibrillation, which also correlated with other physical and mechanical properties.

Experimental Section

Bulk Copolymerization. VPi and VAc (Shin-Etsu) were both washed successively with aqueous $NaHSO_3$ and water, dried over anhydrous $CaCl_2$, and redistilled under nitrogen at reduced pressure. ADMVN (Wako) was purified by recrystallization from methanol. Mixtures of VPi and VAc (100 mL) in different mole ratios were flushed with nitrogen at 10 °C for 3 h, after which ADMVN was added, and the mixture was stirred for 10 h at 30 °C. The monomer mole ratios and concentrations of ADMVN are specified in Table 1; the lowest ADMVN concentration used (2.0×10^{-5} mol/mol of monomer) is the minimum practical for this polymerization. Unreacted monomer was removed by distillation under vacuum. The resultant polymers were purified by reprecipitation: PVPi in acetone/water, copoly(VPi/VAc) in methanol/water, and PVAc in acetone/*n*-hexane, respectively. The intrinsic viscosity ([η]) of PVPi was determined in acetone at 25 °C; for P(VPi/VAc) and PVAc, [η] was measured in benzene at 30 °C. The copolymer compositions were determined using a Varian Sun Unity 300 ^{1}H NMR spectrometer, with benzene-d_6 as the solvent, based on the resonance for the *tert*-butyl (pivaloyl) and methyl (acetyl) protons at 1.5 and 2.2 ppm, respectively.

Saponification and In Situ Fibrillation. The fibrillation of PVA during saponification of PVPi depends on the molecular weight, the degree of syndiotacticity, the saponification conditions (solvent, concentration, temperature, time, and the presence or absence of oxygen), and the shear speed.[22,23] The conditions used in the present work were those judged to be optimum for saponification of PVPi.[15,22,23]

P(VPi/VAc) copolymer (4 g) was dissolved in tetrahydrofuran (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.) The solid saponification product was tapped mechanically, filtered, and washed several times with methanol. A quantitative yield of bright-yellow PVA (fibrils or precipitates) was obtained. Residual ester groups could not be detected in the ^{1}H NMR spectra of these specimens.

Structure Analysis. P_n's of the PVAs were determined from the viscosities of the benzene solutions of the fully acetylated specimens.[10] The S-diad contents of the PVAs were determined by 300 MHz ^{1}H NMR, using dimethyl sulfoxide-d_6 (DMSO-d_6) as the solvent, based on the ratio of the components of the hydroxyl proton triplet at 4.1−4.7 ppm.

The surface morphology of the PVA specimens was investigated using a Scalar VMS 3000 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. The specimens were parallel bundles of (3−5) fibers. The degree of orientation of the crystallite regions was determined by using the Hermans equation, based on the azimuthal half-width of the meridional reflection on the second layer line measured using an optical densitometer.

PVA densities were determined using a benzene−carbon tetrachloride density gradient at 30 °C. The degree of crystallinity (X_c) was derived from

$$1/d = X_c/1.345 + (1 - X_c)/1.269$$

where *d* is the measured density and 1.345 (g/mL) and 1.269 (g/mL) are the densities of the crystalline[24] and amorphous[25] PVA, respectively. The crystal melting temperatures (T_m) were measured with a Perkin-Elmer DSC 7 differential scanning calorimeter with a sample weight of 10 mg and at a heating rate of 10 °C/min. Stress−strain curves for the fiber specimens were obtained using an Instron model 4201, with a sample length of 3 cm and a 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 30 measurements. The degree of solubility of the

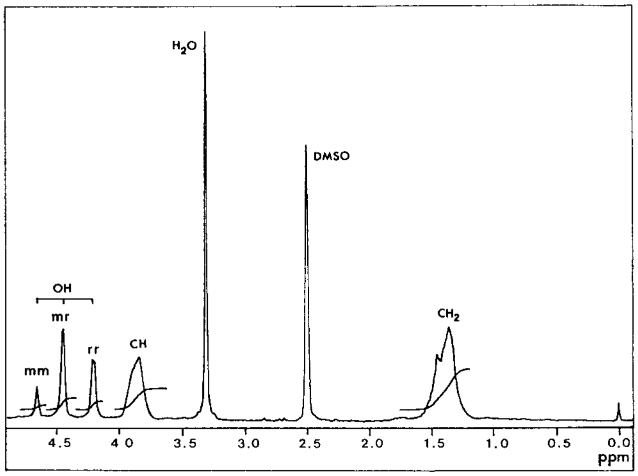

Figure 1. ^{1}H NMR spectrum of PVA with P_n = 8300 and S-diad content = 58.4%.

PVA was determined from the weight of the undissolved residue after 3 h in water at 105 °C.[26]

Results

Copolymerization of VPi and VAc. As expected, the rate of polymerization for pure monomers increased with initiator concentration, and the reaction rate for VPi exceeded that for VAc at the same temperature, by a factor that appeared to be independent of ADMVN concentration. In the radical copolymerization reactions, the monomer reactivity ratios of VPi (r_1) and VAc (r_2) are given by[27]

$$a - (a/b) = (a^2/b)r_1 - r_2$$

where a is the monomer ratio ([VPi]/[VAc]) and b is the ratio of monomer units in the copolymer ([−VPi−]/[−VAc−]) determined by ^{1}H NMR spectroscopy. A plot of $a - (a/b)$ against a^2/b was a straight line, from which r_1 and r_2 were determined to be 3.1 and 1.6, respectively. r_1 is approximately twice r_2, and hence conversion of VPi predominates when VPi and VAc are copolymerized at 30 °C using ADMVN. Both r_1 and r_2 are larger than 1, and thus the VPi/VAc copolymer synthesized should be a block copolymer with relatively short block lengths.

Table 1 shows data for the conversion, monomer composition, and P_n for the copolymers and saponified products. P_n for the latter specimens varied from (5.6−16.5) × 10^3 (number-average molecular weight (M_n) = (2.47−7.26) × 10^4), such that they can be classified as HMW. Progressively higher molecular weights were obtained for higher VPi contents of the copolymer and for lower ADMVN concentrations. In addition, the lower the initiator concentration, the lower the conversion.

Stereoregularity and Blockiness. The diad and triad tacticities for all the PVA specimens studied are listed in Table 1, as determined from the ^{1}H NMR spectra. Figure 1 shows the ^{1}H NMR spectrum for a typical PVA prepared from P(VPi/VAc) copolymerized using an equimolar ratio of VPi and VAc. The tacticities estimated from the three OH peaks at 4.1−4.7 ppm are 16.1, 51.1, and 32.8% for isotactic, heterotactic, and syndiotactic triads, respectively. The absence of the pivaloyl proton peak at 1.1 ppm indicates that PVPi had been completely saponified. As can be seen Table 1, all the PVA specimens had heterotactic triad contents of approximately 50%. However, the syndiotacitic triad contents increased from 27.4% to 37.1% with increasing VPi content of the parent copolymer, while the isotactic triad content decreased from 21.8% to 13.5%. This trend appeared to be independent of molecular weight, in that the tacticities were nearly same for copolymers prepared at different ADMVN concentrations. Figure 2 shows the S-diad contents of PVAs prepared from copolymers polymerized at ADMVN concentration of 2.0 × 10^{-5} mol/mol of monomer, which increased from 53.1% to 61.5% as the VPi content increased from 0 to 100%. The difference in syndiotacticity across all the PVA specimens was only about 8−9%, but it will be seen that these specimens show remarkably different morphologies.

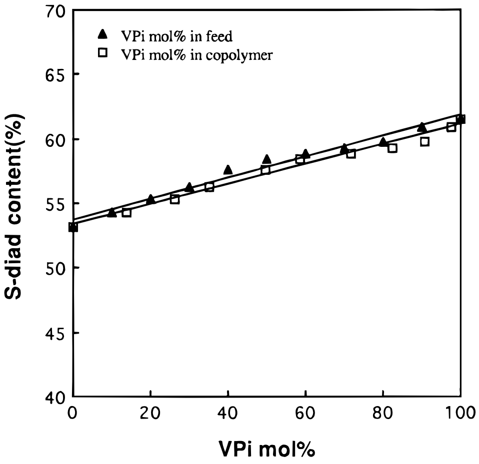

Figure 2. Plot of S-diad content against VPi mol % in the feed and in the intermediate copolymer prepared at an ADMVN concentration of 2 × 10^{-5} mol/mol of monomer.

The number-average lengths of isotactic, syndiotactic, and all blocks, n_m, n_r, n, respectively, were calculated from[28]

$$n_m = 1 + 2(mm)/(mr)$$

$$n_r = 1 + 2(rr)/(mr)$$

$$n = 0.5(n_m + n_r)$$

where mm, mr, and rr are the fractions of isotactic, heterotactic, and syndiotactic triads of PVA, respectively. These data for the PVA specimens derived from VPi/VAc copolymers prepared at an ADMVN concentration of 2.0 × 10^{-5} mol/mol of monomer are shown in Figure 3. All specimens had similar values for n of 1.95−2.00, indicating the presence of short blocks. In addition, n_r increased from 2.1 to 2.5 while n_m decreased from 1.8 to 1.5 in PVAs derived from intermediates with increasing VPi contents; i.e., higher VPi contents in both feed and copolymer led to longer syndiotactic blocks.

Structure and Morphology of In Situ Fibrillated PVAs. Figure 4 compares the morphologies of PVA specimens with different syndiotacticities. The PVA produced by saponification of PVPi homopolymer with an S-diad content of 61.5% (Figure 4J) consists of very fine microfibrillar fibers. The specimens prepared from PVAc having an S-diad content of 52.8% and 53.1% (Figure 4A,B) initially formed a gel and gave rise to irregularly shaped precipitates. We also see a shapeless gross morphology for the specimens in which the initial VPi contents were 13.5 and 14.7% (Figure 4C,D), but

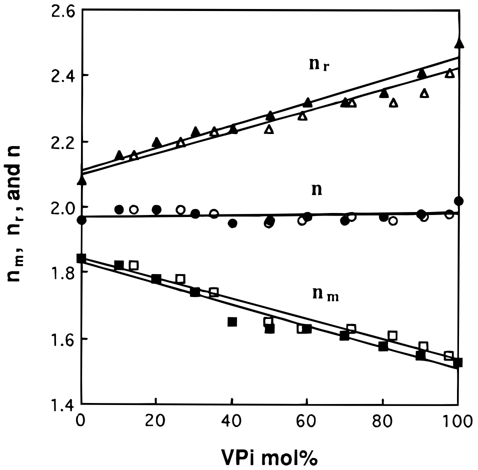

Figure 3. Plots of n_m, n_r, and n against VPi mol % in the feed (filled symbols) and in the intermediate copolymer (open symbols) for PVAs prepared from copolymers polymerized at an ADMVN concentration of 2×10^{-5} mol/mol of monomer.

there is a distinct difference in that the particles can be seen to be composed of short fiberlike structures. This is a remarkable change considering that the S-diad contents have increased by less than 1% to 54.2 and 54.3%, respectively. At S-diad contents of 55.1 and 55.3% (Figure 4E,F) the fully saponified products had a fiberlike appearance. Fibrous morphology is also obtained for higher S-diad contents (Figure 4G−J) with the general trend that the fibrils become longer and narrower as the degree of syndiotacticity increases. The fibrils had irregular cross-sections and needlepoint-like ends and resembled the ultrafine microfibril structure observed in native cellulose fibers.[29−33]

SAXS data for four PVA specimens with S-diad contents of 55.3, 56.2, 58.4, and 61.5% are shown in Figure 5. For the 55.3% specimen there was essentially no scattering in the small angle region, even after long exposure times. In contrast, weak scattering due to voids was observed on the equator at an S-diad content of 56.2% (Figure 4B). At 58.4% S-diad content, we observed strong elliptical microvoid scattering, with the long axis of the ellipse parallel to the equator, and this was converted to a strong diamond-shaped microvoid scattering for the specimen with an S-diad content of 61.5%. The difference between the scattering patterns for 58.4 and 61.5% S-diad content are reminiscent of those between the SAXS data for cellulose acetate fibers and ramie fibers[34] and point to the development of more regular and more elongated microvoids.[34−36]

Figure 6 shows WAXD data for fibers of four saponified PVAs with different syndiotacticities. The degrees of crystal orientation determined for these and other PVA specimens are given in Table 2. The PVAs with S-diad contents exceeding 56% all have orientation parameters in the range 82−89%, increasing steadily with syndiotacticity. The specimen with an S-diad content of 55.3% has a much lower degree of orientation (62%) even though it had a distinct fibrous morphology (Figure 4F). The specimens with S-diad contents less than 55% were unoriented and could not be prepared as fibers.

The degree of crystallinity of the PVA specimens derived from their measured densities are shown in Figure 7. The crystallinity increases with increasing syndiotacticity, and the data fall approximately on two straight lines that intersect at an S-diad content of 56.2%. The main changes occur at lower syndiotacticities. The crystallinities rise only slightly after the transition, when they are in the 45−47% range. Note that such high crystallinities in conventional PVA fibers are only achieved by heat treatment or hot drawing. The transition at 56.2% S-diad content occurs in the vicinity of those seen in the morphology and orientation, and thus there appears to be a critical syndiotacticity for PVA crystallization and in situ fibrillation, for which a crystallinity exceeding 45% may be required. The above results are consistent with those of Nakamae et al.,[37] who reported differences in the temperature dependence of the elastic moduli of PVA fibers with S-diad contents of 55.4% and 63.0%, respectively. These workers suggested that this could be due to the presence of kink

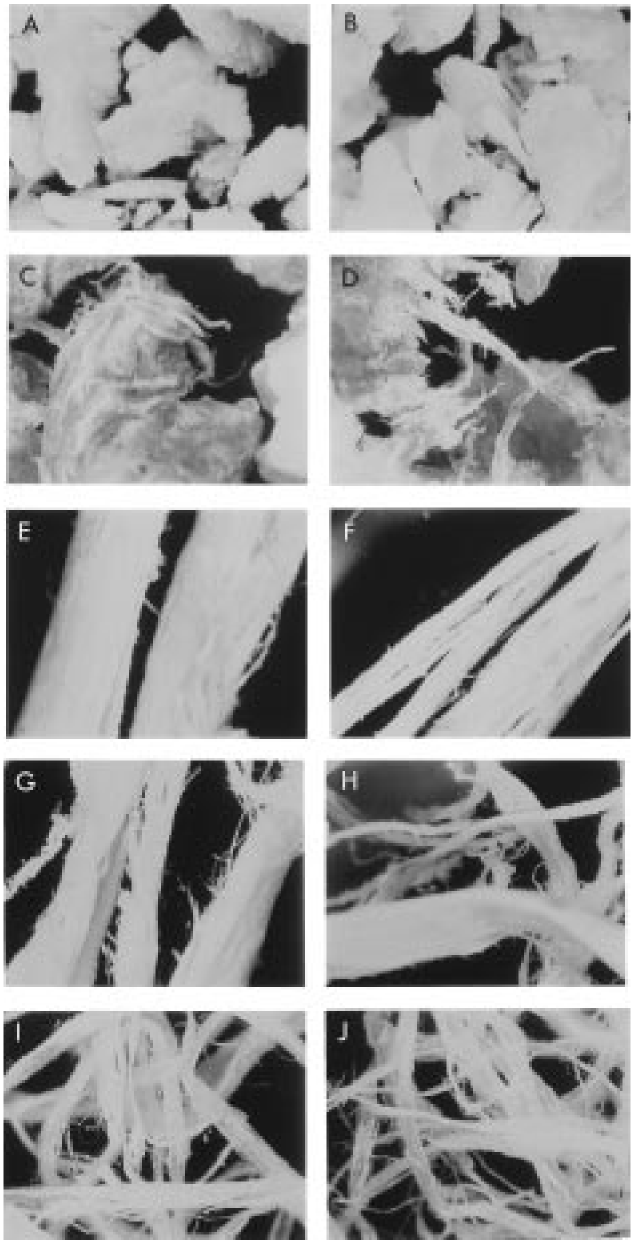

Figure 4. Optical micrographs (×200) of PVAs with different S-diad contents: (A) 52.8% ($P_n = 5600$); (B) 53.1% ($P_n = 6500$); (C) 54.2% ($P_n = 6600$); (D) 54.3% ($P_n = 7700$); (E) 55.1% ($P_n = 6900$); (F) 55.3% ($P_n = 7800$); (G) 56.2% ($P_n = 7800$); (H) 58.4% ($P_n = 8300$); (I) 59.6% ($P_n = 8200$); (J) 61.5% ($P_n = 8100$). Figure reduced to 52% for publication.

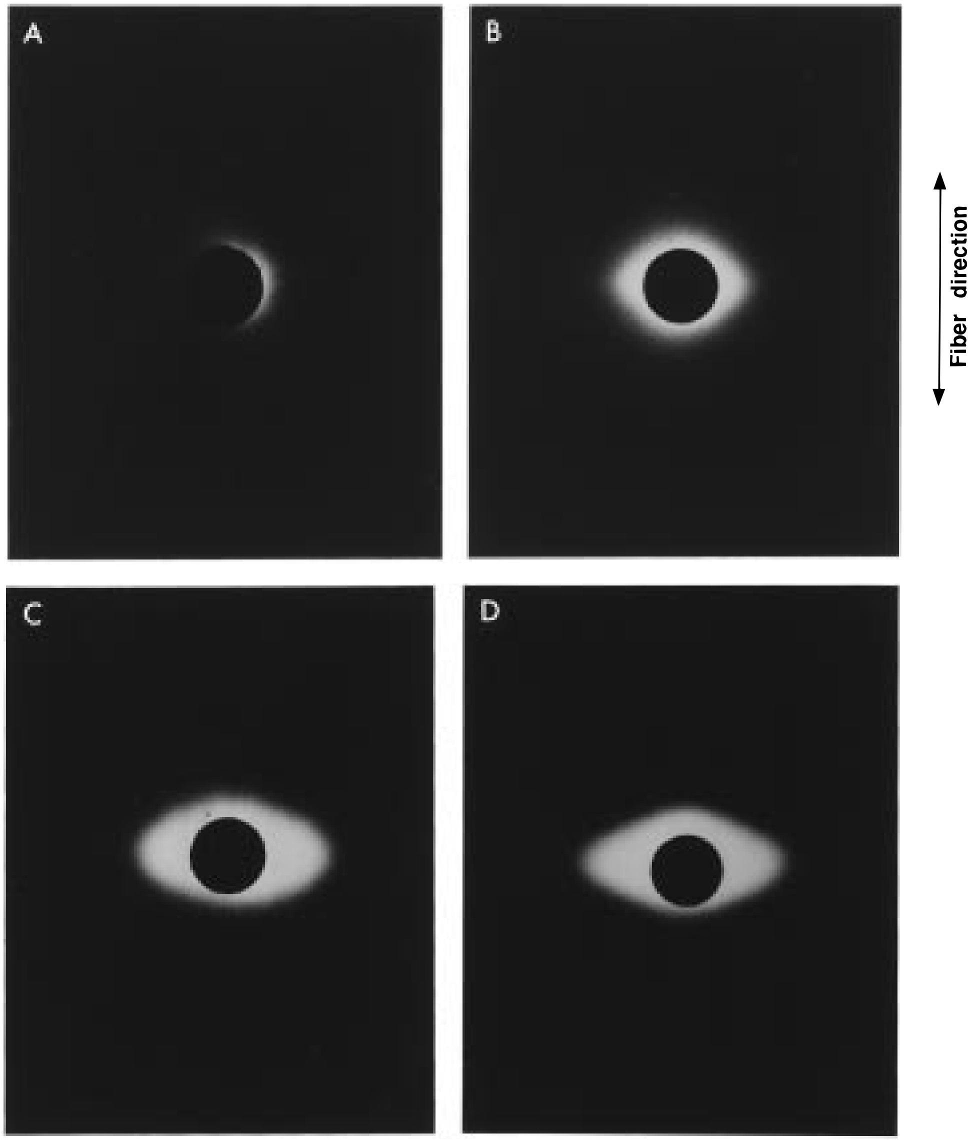

Figure 5. Small-angle X-ray fiber diagrams of PVAs with different S-diad contents: (A) 55.3% ($P_n = 7900$); (B) 56.2% ($P_n = 7800$); (C) 58.4% ($P_n = 8300$); (D) 61.5% ($P_n = 8100$).

defects or other conformational differences in the chains with a lower S-diad content.

Other Properties. The values of T_m recorded during the first and second heating DSC scans for the PVA specimens are plotted against S-diad content in Figure 8. T_m for the first heating increases with S-diad content, but the rate of increase is slowed when the S-diad content exceeds 56%. The data are approximated to two different straight lines, strongly suggesting different crystal structures and/or morphologies above and below this tacticity level. These observations correlate well with the fibrillation at higher S-diad content described above and suggest that the increased tacticity facilitates a more ordered crystal structure. In contrast, T_m for the second heating exhibits a single linear relationship to the S-diad content, and the actual melting temperatures are lower than those for the first heating scans. This is probably explained by the fact that the premelted PVA has lost the structural history induced by fibrillation under shear.

Figure 9 shows the tensile strength of the PVA fibers plotted against S-diad content. The tensile strength increased steadily with increasing S-diad content and exceeded 20 g/denier when the S-diad content were 61.5%. This compares well with the tensile strength of 25 g/denier reported for conventionally spun fibers of atactic UHMW PVA[38] and is impressive considering the simplicity of the processing method. The solubility in hot water decreased with increasing S-diad content and was essentially zero for S-diad contents over 56%.

Discussion

We have demonstrated that HMW PVAs with different stereoregularities can be prepared by saponification of copoly(VPi/VAc) under shear conditions. S-diad contents varying continuously from 52.8 to 61.5% were obtained by variation of the monomer feeds and initiator concentrations. Sequence analysis pointed to a microstructure containing relatively short blocks (average length ~2 monomers): heterotactic triads made up ~50% of the total for all specimens, but the proportions of syndiotactic triads exceeded those of the isotactic triads. Analysis of the structure and properties of these specimens showed a consistent transition at an S-diad content of 55−56%. The specimens with S-diad contents below this region had shapeless morphologies and relatively low crystallinities. For specimens with higher syndiotacticities, the shear conditions result in a fibrous

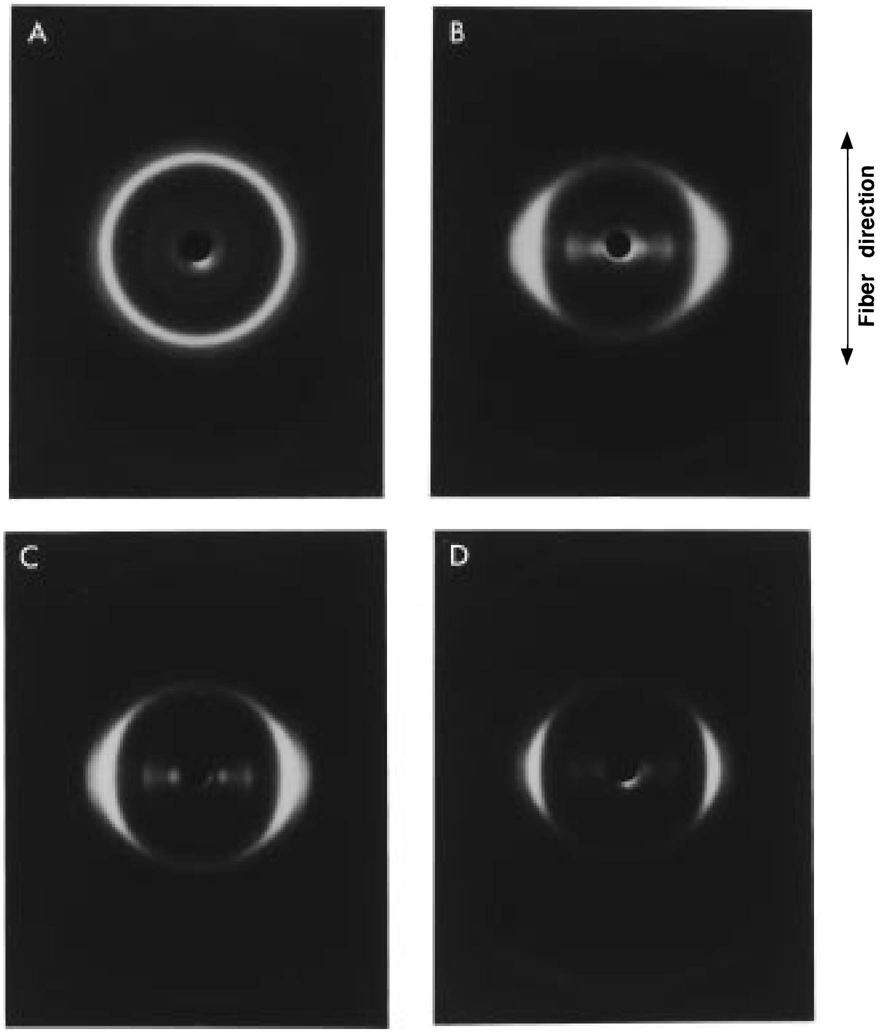

Figure 6. Wide-angle X-ray fiber diagrams of PVAs with different S-diad contents: (A) 55.3% (P_n = 7900); (B) 56.2% (P_n = 7800); (C) 58.4% (P_n = 8300); (D) 61.5% (P_n = 8100).

Table 2. Crystallite Orientation for PVAs with Different S-Diad Contents

P_n	S-diad content (%)	orientation	P_n	S-diad content (%)	orientation
7800	55.3	0.615	8100	58.9	0.867
7800	56.2	0.822	8200	59.6	0.872
8100	57.6	0.831	7900	60.4	0.883
8300	58.4	0.858	8100	61.5	0.887
8300	58.6	0.869			

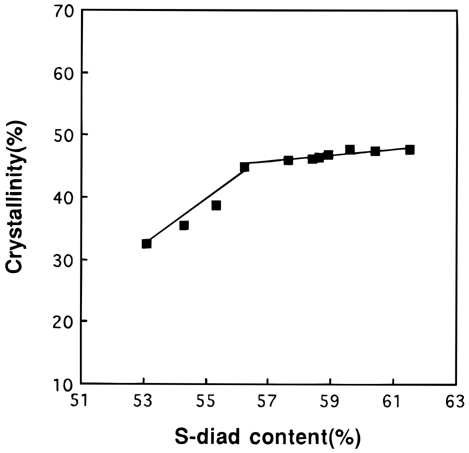

Figure 7. Plot of degree of crystallinity (based on density) against S-diad content for PVA with P_n = 8000.

morphology containing oriented PVA crystallites. As the S-diad content increases from 56 to 61.5%, we see a progressive increase in the degrees of crystallinity and orientation, in the regularity and elongation of the voids between the fibrils, and in the overall gross aspect ratio of the fibers. These structural changes correlate fully with improvements in the tensile properties and changes in the melting behavior and solubility.

In the above results one is struck by the sharpness of the transition at 55−56% S-diad content. The data are for 25 specimens in which the triad contents vary continuously, with relatively small changes from one to the next, and thus there are no major differences in blockiness between the PVAs close to the transition. Atactic PVA is crystalline, meaning that two alternative positions for the hydroxyl group on the planar zigzag backbone can be accommodated such that the structure can be described by an "average" unit cell. It appears that this small increase in S-diad content facilitates a major change in the crystallization process, such that the crystallinity improves and leads at the same time to the development of a fibrous morphology when the saponification is performed under shear. We are currently investigating the improvement in the chain packing by wide-angle X-ray methods, which will be the subject of a future paper.

Finally, we note that the fibers produced by "self-assembly" under shear for the specimens with highest

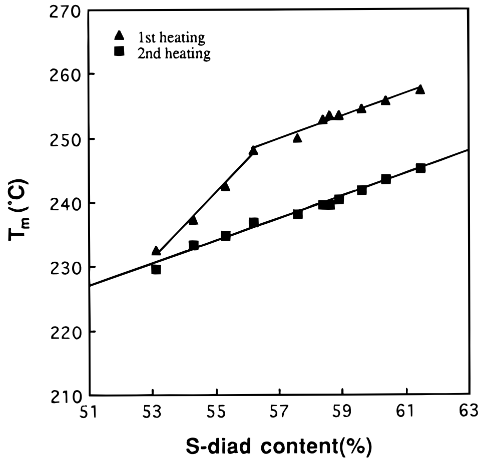

Figure 8. T_m for the first and second heatings plotted against S-diad content for PVAs with $P_n = 8000$.

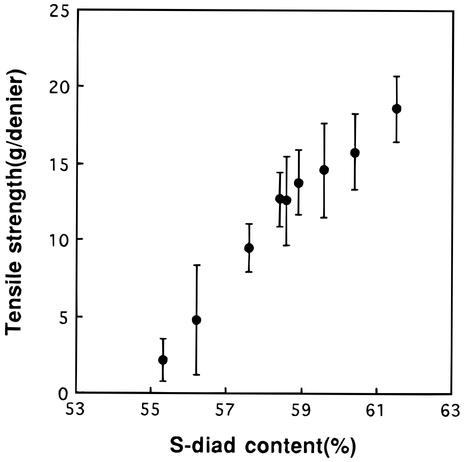

Figure 9. Plot of tensile strength against S-diad content for PVAs with $P_n = 8000$.

tacticity (S-diad content 61.5%) had mechanical properties comparable to those for high-strength spun PVA fibers. Although relatively imperfect, these highly syndiotactic fibers may have considerable commercial potential given the ease of synthesis by saponification of copoly(VPi/VAc) under shear.

References and Notes

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