

Critical Syndiotacticity Required for In-Situ Fibrillation of Poly(vinyl Alcohol) during Saponification of Poly(vinyl Ester)

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1. Introduction

The physical properties of poly(vinyl alcohol) (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,¹ vinyl trichloroacetate,² and vinyl pivalate (VPi).^{3, 4} 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 exceed 53-54% (about the maximum value obtained in vinyl acetate (VAc) polymerization) are generally described as "syndiotacticity-rich". (This contrasts with the 95% figure typically used to describe syndiotactic poly(methyl methacrylate)⁵ and polystyrene.⁶) Recently, Yamamoto et al.³ have reported synthesis of ultrahigh molecular weight (UHMW) PVA with number-average degree of polymerization (P_n) > 18,000 and S-diad content of 62.8% *via* UV-initiated emulsion polymerization of VPi at low temperature, followed by saponification. Similarly, Lyoo and Ha⁴ have synthesized UHMW PVA with maximum P_n of 18,300 and 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 coworkers,⁷⁻⁹ 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 - 50 °C) led to high molecular weight (HMW) PVAs with S-diad contents of 59-65%.⁴ 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.^{10, 11} This did not occur for analogous PVA specimens derived from poly(vinyl acetate) (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.^{12, 13}

In this work we have compared PVA specimens of different stereoregularities, which 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 properties.

2. Experimental

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 polymerized for 10 h at 30 °C.

The fibrillation of PVA during saponification of poly(vinyl ester) depends on the molecular weight, the degree of syndiotacticity, the saponification condition (solvent, concentration, temperature, time, and the presence or absence of oxygen), and the shear speed.^{10, 11} The saponification conditions (fibrillation conditions of PVA) used were those judged to be optimum for saponification of PVPi.^{4, 10, 11, 14}

P_n of the PVAs were determined from the viscosities of the benzene solutions of the fully acetylated specimens. The S-diad contents of the PVAs were determined by 300 MHz ¹H-NMR, using dimethylsulfoxide-*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 x 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 CuK α radiation and pinhole collimation. The degree of orientation of the crystallite regions was determined using the Hermans equation, based on the azimuthal halfwidth 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 crystal melting temperature (T_m) were measured using 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.

3. Result and Discussion

The monomer reactivity ratios of VPi (r_1) and VAc (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. P_n for the latter specimens varied from (5.6 - 16.5) x 10³ (number-average molecular weight = (2.47 - 7.26) x 10⁴), such that they can be classified as HMW. All the PVA specimens had heterotactic triad contents of approximately 50%. However, the syndiotactic 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%. The difference in S-diad content across all the PVA specimens was only about 8-9%, but it will be seen that these specimens show remarkably different morphologies.

The PVA produced by saponification of PVPi homopolymer with S-diad content of 61.5% (Figure 1J) consists of very fine microfibrillar fibers. The specimens prepared from PVAc having S-diad content of 52.8% and 53.1% (Figures 1A and 1B) 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 1C and 1D), but there is a distinct difference in that the particles can be seen to be composed of short fiber-like 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 1E and 1F) the fully saponified products had a fiber-like appearance. Fibrous morphology is also obtained for higher S-diad contents (Figure 1G-1J) with the general trend that the fibrils become longer and narrower as the degree of syndiotacticity increases.

SAXS analysis for four PVA specimens with S-diad contents of 55.3, 56.2, 58.4, and 61.5% were conducted. 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 S-diad content of 56.2%. At 58.4% S-diad content, we observed strong elliptical micro-void scattering, with the long axis of the ellipse parallel to the equator, and this was converted to a strong diamond-shaped micro-void scattering for the specimen with S-diad content of 61.5%. The PVAs with S-diad contents exceeding 56% all have orientation parameters in the range 82-89%, increasing steadily with syndiotacticity. The specimens with S-diad content of 55.3% has a much lower degree of orientation (62%) even though it had a distinct fibrous morphology. The specimens with S-diad contents less than 55% were unoriented and could not be prepared as fibers.

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 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. 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 describes above, and suggest that the increased tacticity facilitates a more ordered crystal structure.

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 zig-zag backbone can be

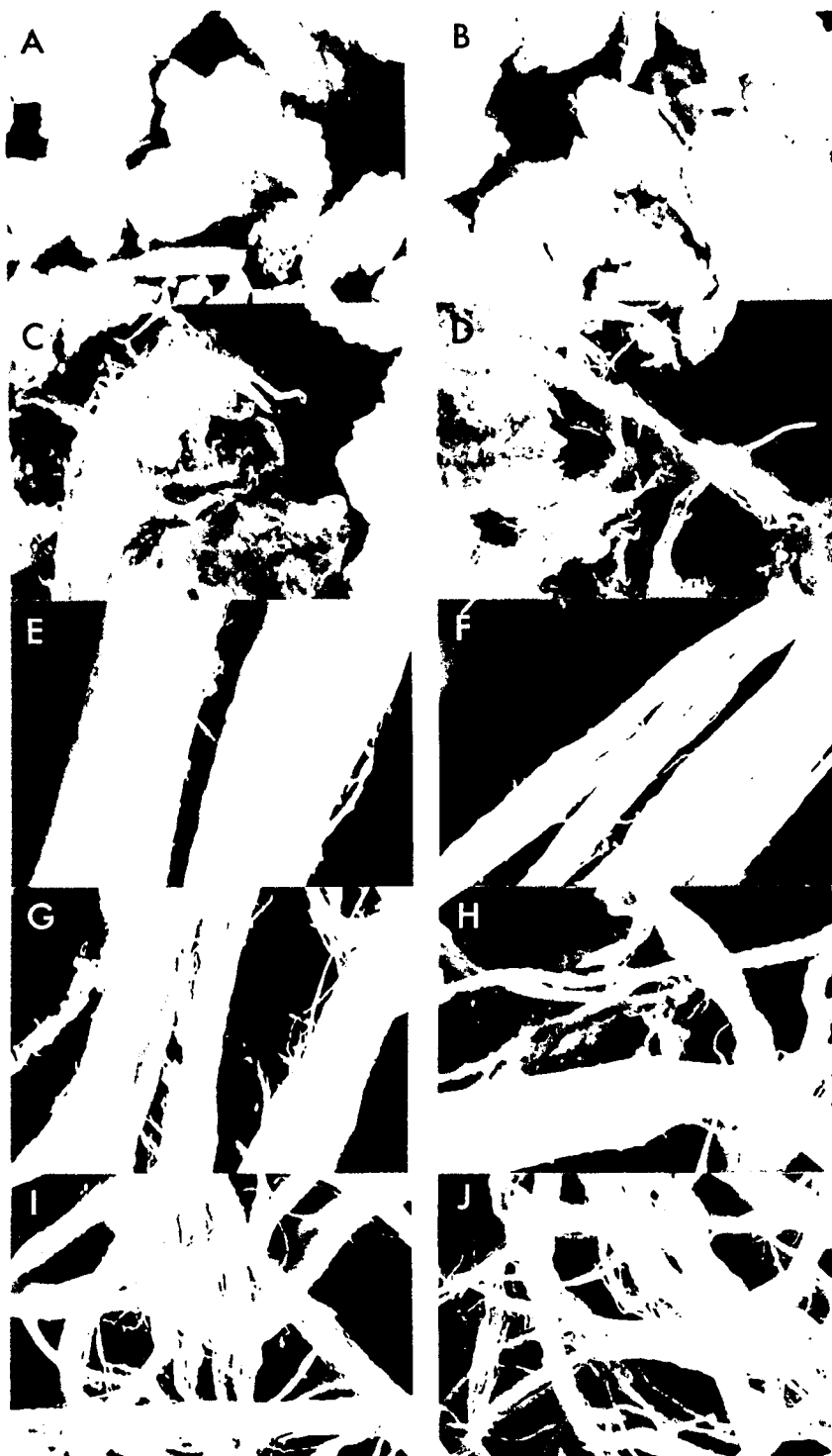


Figure 1. Effect of syndiotacticity on the fibrillation of PVA during saponification of copoly(VPi/VAc): S-diad content: A, 52.8%; B, 53.1%; C, 54.2%; D, 54.3%; E, 55.1%; F, 55.3%; G, 56.2%; H, 58.4%; I, 59.6%; J, 61.5%.

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.

Finally we note that the fibers produced by “self assembly” under shear for the specimens with highest 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.

4. Conclusion

HMW specimens of syndiotacticity-rich PVA have been prepared by saponification of copolymers of VPi and VAc. 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 structure of these PVAs show a consistent sharp transition in 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 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.

5. References

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