Critical Molecular Weight Required for in Situ Fibrillation of Syndiotactic Poly(vinyl alcohol) during Saponification

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Introduction

This paper describes the effect of molecular weight on fibrillation during synthesis for poly(vinyl alcohol) (PVA) of relatively high syndiotacticity (syndiotactic diad (s-diad) contents of 61−62%). These fibrils may have potential as reinforcing fillers. As an analogy, poly(*p*-phenylene teraphthalamide) forms a fibrillar structure during synthesis as a result of the rigid-rod conformation that leads to a lyotropic liquid crystal in a certain range of concentrations.[1,2] For flexible chain polymers such as PVA, polyethylene, polyacrylonitrile, poly(vinyl chloride), and polystyrene, fibrillar structures have been achieved by extrusion of immiscible polymer blends followed by extraction.[3−8]

Since the first work by Herrmann and Haehnel,[9] high-strength and high-modulus PVA fibers have been achieved by zone drawing,[10,11] cross-linking and wet spinning,[12,13] crystal mat drawing,[14] and gel drawing,[15−17] all of which are relatively complex multistep processes. Recently, Lyoo et al.[18−25] reported that PVAs with well-oriented fibrillar structures are formed by saponification of poly(vinyl pivalate) (PVPi) under low-shear conditions (stirring), provided that the microstructure is significantly syndiotactic. These PVAs had a degree of polymerization $P_n > 4500$ and formed fibrils that were similar in appearance to native cellulose fibers. Lyoo et al.[19] showed that these structures were formed only by PVAs that were significantly syndiotactic. A range of PVAs were produced by saponification of copoly(vinyl acetate/vinyl pivalate) in which the s-diad content ranged from 52 to 63%, and it was found that fibril formation occurred only for s-diad contents greater than ∼57%. At lower s-diad contents (52−55%) only shapeless, globular morphologies were observed.

It is reasonable to expect that in situ fibrillation during stirred saponification will depend on molecular weight, and in the present paper we have extended the above work to consider the effect of lower molecular weight on the fibrillation process. PVAs with P_n in the range 330−820 and s-diad contents 61−63% were prepared by saponification of PVPis that had been synthesized at different temperatures with different amounts of initiator, using tetrahydrofuran (THF) as solvent because of its high chain transfer constant. It will be seen that a fibrous morphology analogous to that for the high molecular weight materials previously studied was obtained only for molecular weights in excess of $P_n \approx 800$. As P_n declines, there is a steady change in morphology to the more globular, shapeless morphology typical of higher molecular weights closer to random microstructure.

Experimental Section

Solution Polymerization of Vinyl Pivalate (VPi). VPi was washed with dilute aqueous $NaHSO_3$ and then with water, dried over anhydrous $CaCl_2$, and redistilled under nitrogen at reduced pressure. Mixtures of VPi and THF were flushed under nitrogen for 3 h, after which specific amounts of the initiator 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN) were added, and the VPi was polymerized at different temperatures with slow stirring. Polymerizations at 25, 35, and 45 °C were conducted using 1/9, 3/7, and 5/5 (v/v) THF/VPi mixtures, with the addition of 1×10^{-4}, 3×10^{-4}, 5×10^{-4}, or 10×10^{-4} mol/mol of VPi (mol/mol$_{VPi}$) of ADMVN initiator. The actual combinations of these parameters used in our preparations are given in Table 1. It was found that polymerization did not occur at initiator and monomer concentrations lower than those listed in the table. In each case, the PVPi product was purified by reprecipitation from a benzene/methanol mixture and dried in a vacuum oven at 60 °C.

Saponification of PVPi. In a 500 mL four-neck round-bottom flask, PVPi (6 g) was dissolved in THF (300 mL), and a solution of potassium hydroxide (7.5 g) in methanol/water (90/10 v/v; 30 mL) was added drop-by-drop with stirring using a H-shaped anchor-type stainless steel stirrer with dimensions in the stirring rod length of 25 cm, in the anchor width of 1.5 cm, and in the anchor length of 2 cm at 15 000 rpm at 55 °C. (No stirring resulted in incomplete saponification, and higher stirring rates (>15 000 rpm) resulted in the breakup of the gel structure that appears to be necessary for fibrillation.) The solid saponification product was broken up mechanically, filtered, and washed several times with methanol. Complete saponification was confirmed by the absence of *tert*-butyl proton peaks in the ^{1}H NMR spectrum,[25] using a Varian Sun Unity 300 spectrometer.

Characterization of PVPi and PVA. The molecular weight of PVPi was determined from viscosity measurements on solutions in acetone at 25 °C using using[25]

$$[\eta] = 2.88 \times 10^{-5}[\mathrm{M}]^{0.77}$$

where $[\eta]$ is the intrinsic viscosity and M is the average molecular weight. The molecular weight of PVA was determined from viscosity data for fully acetylated specimens (PVAc) dissolved in benzene at 30 °C using[25]

$$[\eta] = 5.63 \times 10^{-4}[\mathrm{M}]^{0.62}$$

The s-diad content of the PVA was determined by ^{1}H NMR using dimethyl-d_6 sulfoxide as the solvent, based on the ratio of the components of hydroxyl proton triplet at 4.1−4.7 ppm.[25]

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Table 1. P_n and s-Diad Content for the Specimens of PVPi and PVA Prepared under Various Conditions

sample number	polymerization temperature (°C)	THF/VPi (v/v)	ADMVN concentration ($mol/mol_{VPi} \times 10^4$)	P_n of PVPi	P_n of PVA	S-diad content (%)
1	25	1/9	10	1140 (±1%)	800 (±1%)	62.5 (±0.2)
2			5	1150	820	62.7
3		3/7	10	1090	720	62.2
4			5	1080	740	62.3
5	35	1/9	10	1140	660	62.4
6			5	1110	690	62.3
7			3	1110	700	62.4
8		3/7	10	1130	580	61.3
9			5	1150	600	61.5
10			3	1190	640	61.6
11	45	1/9	10	1340	600	61.5
12			5	1380	620	61.7
13			3	1460	680	61.7
14			1	1610	780	61.9
15		3/7	10	1300	530	61.2
16			5	1300	550	61.2
17			3	1280	560	61.3
18			1	1310	580	61.3
19		5/5	5	830	330	61.1

The surface morphology of PVA was examined by Olympus BH-2 optical microscope at magnification ×200. Specimens of the PVAs with fibrous morphology were prepared as aligned bundles; for the shapeless, globular morphologies the data were recorded for the as-prepared powders.

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

The internal morphology of the specimens was examined at 120 kV using a PHILIPS CM-20 TEM. Bright field phase contrast TEM micrographs were obtained by low-dose procedures.[26,27] Thin films suitable for transmission electron microscopy (TEM) were prepared by (i) ultra-microtome of fibers and (ii) collecting small dispersed particles. The fiber sample was embedded with epoxy resin at ~60 °C, 15 h, and ultrathin sections (~50 nm) were microtomed parallel to fiber axis at room temperature and collected on carbon-supported copper mesh grids. For the particle specimens, TEM samples were prepared by sonicating the particles for ~10 min in water and drop-drying them onto carbon-supported TEM grids.

Results and Discussion

Table 1 lists P_n for 19 PVPis produced under different preparation conditions and for the PVAs derived therefrom by saponification. The specimens are numbered for reference in the text. Saponification leads to a lower molecular weight for the PVAs, consistent with removal of branching units: the data are consistent with 0.4−1.5 branching units per backbone pivalate. The table also includes the s-diad contents determined by NMR for the PVAs.

As is to be expected, P_n for the PVAs increased as the initiator concentration decreased; P_n fell as the THF content increased, when the chain transfer reaction is favored, as confirmed by the increased degree of branching for the parent PVPi. In addition, synthesis of PVPi at higher temperatures also favored chain transfer and branching, such that increasing the temperature lowers P_n for the resultant PVA. Variation of the three synthesis parameters has generated a range of molecular weights (for PVA) from 14 500 to 36 100, P_n = 330−820.

The synthesis conditions also have a small effect on the microstructure of PVA, in that there were small decreases in the s-diad content with the synthesis temperature and THF content. The changes with initiator content appear to be negligible. But for the 19 samples the s-diad contents were in a relatively narrow range: 61.1−62.7%. The data for the triads (not shown here) were also very similar across the range of specimens; i.e., there is no evidence of differences in the microstructure that are not revealed by the s-diad contents**.** Such small changes like in s-diad content are consistent with the fact that all these PVAs were derived from PVPis. To obtain wider ranges in s-diad content (with the same synthesis route), it was necessary to first prepare copolymers of VPi and vinyl acetate.

Figure 1 presents optical micrographs of as-prepared specimens 1, 5, 15, and 19. Specimen 1 (P_n = 800) consists of well-defined fibrils (Figure 1a) that are striated, suggesting that each fibril is composed of microfibrils. This morphology is very similar to that seen for a much higher molecular weight PVA with the same s-diad content. Specimen 5 (P_n = 660) has a longitudinally developed morphology (Figure 1b) and appears to consist of microfibrils, especially on the exterior, that surround and interweave with shapeless, more globular structures. For specimen 15 (P_n = 530) we also see a fibrous morphology in which the individual fibrils appears to consist of microfibrils and shapeless globular regions (Figure 1c), but overall there is a lower proportion of microfibrils, and the gross fibrils are shorter than those in specimen 5 (Figure 1b). Finally, for specimen 19 (P_n = 330) we see irregular-shaped particles, i.e., a powder morphology (Figure 1d); there is no trace of a microfibrillar component.

The data for specimens 1, 5, 15, and 19 are representative sampling of the entire series of PVAs produced here. We see a steady transition in morphology from the extremes in Figure 1a,d: from striated fibrils, through a mixture of microfibrils and shapeless units, to a sample that contains only the shapeless units. This change in morphology parallels the approximately 3-fold decrease in molecular weight, which seems to be its most likely cause. We note that there has also been a small change in the microstructure across the series, from s-diad content of 62.7−61.1%. Although this is small, we cannot rule out some effect on the morphology given the changes seen for higher molecular weight PVAs with s-diad contents of 52−63%. But it would seem likely that molecular weight is a more important parameter determining the morphology.

The fibrous morphology probably is at least partly due to the effects of shear when the saponification mixture is stirred, so it is possible that P_n for the transition from

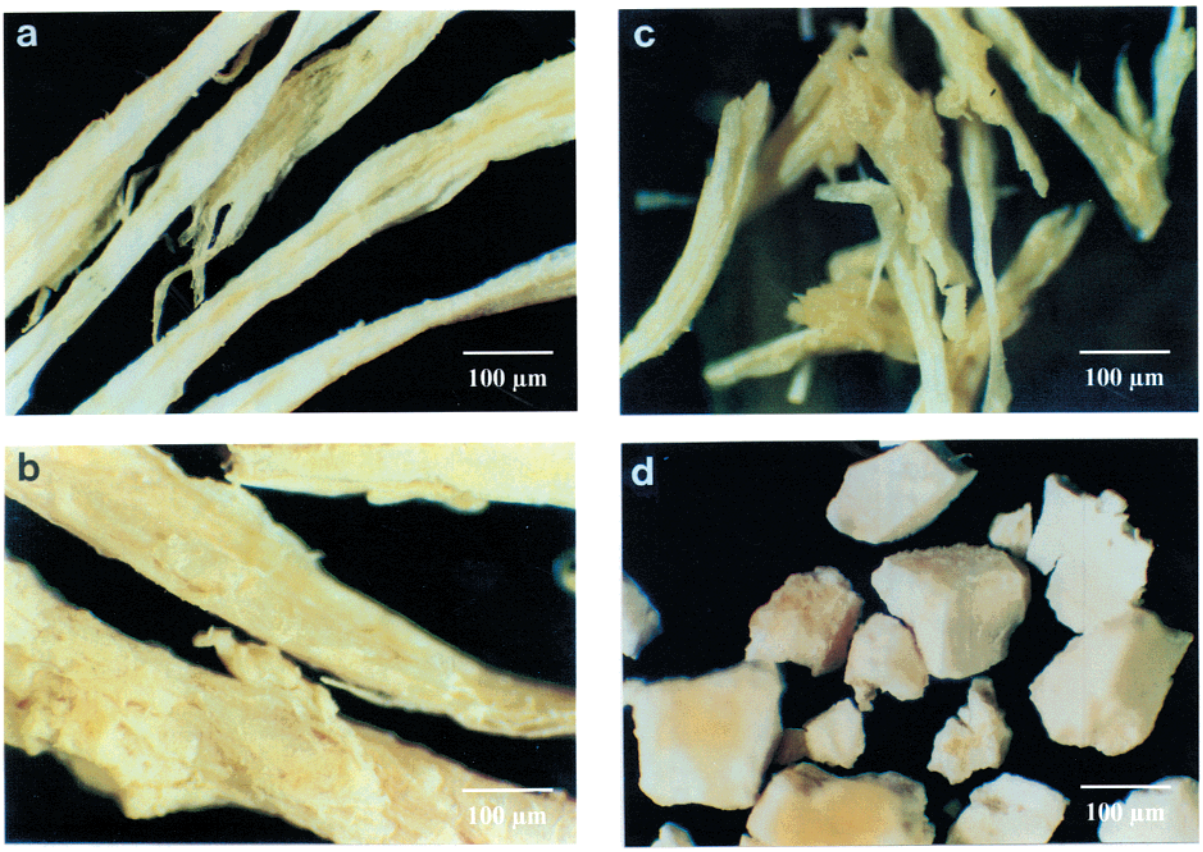

Figure 1. Optical micrographs of PVAs with different molecular weights: (a) specimen 1, $P_n = 800$; (b) specimen 5, $P_n = 660$; (c) specimen 15, $P_n = 530$; (d) specimen 19, $P_n = 330$.

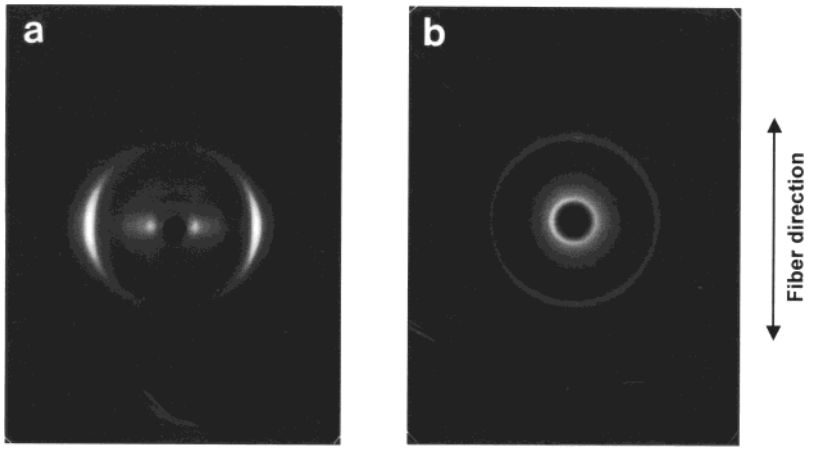

Figure 2. WAXD patterns of PVAs with different molecular weights: (a) specimen 1, $P_n = 800$; (b) specimen 19, $P_n = 330$.

fibrous to globular structure may depend on shear rate. However, when we performed syntheses with different stirring speeds from 200 to 15 000 rpm, we did not see any changes in specimens produced. For the higher molecular weight samples, fibrillation did not occur above 15 000 rpm, probably breakup of the gel structure. Further work is in progress on the effect of shear rate in this process.

The PVAs gave rise to small-angle X-ray scattering that correlated exactly with those reported previously for the high molecular weight specimens with fibrous and shapeless morphologies.[19] The oriented fibrous bundle prepared for specimen 1 ($P_n = 800$) gave an elliptical SAXS pattern typical of fibers containing microvoids, which are suggested by the striations seen in the optical micrographs (Figure 1a). In contrast, no SAXS pattern is detected for specimen 19 ($P_n = 330$), just as was the case for the high molecular weight samples with shapeless, particulate morphology. Indeed, we did not detect SAXS scattering for any specimen with $P_n < 660$, suggesting that any voids in the fibrous fraction are too few in number to be detected or that the nonfibrous material serves as a filler.

Wide-angle X-ray patterns of specimens 1 and 19 are shown in Figure 2; for specimens 1 (Figure 2a) the fiber axis is vertical. The data for specimen 1 are the fiber diagram of crystalline PVA, with the polymer chains parallel to the fiber axis. Much of the arcing of the reflections correlates with relatively poor orientation of the (nonlinear) fibrils in the bundle, and the molecular orientation in the individual fibrils is probably much higher than suggested by the data. For specimen 19,

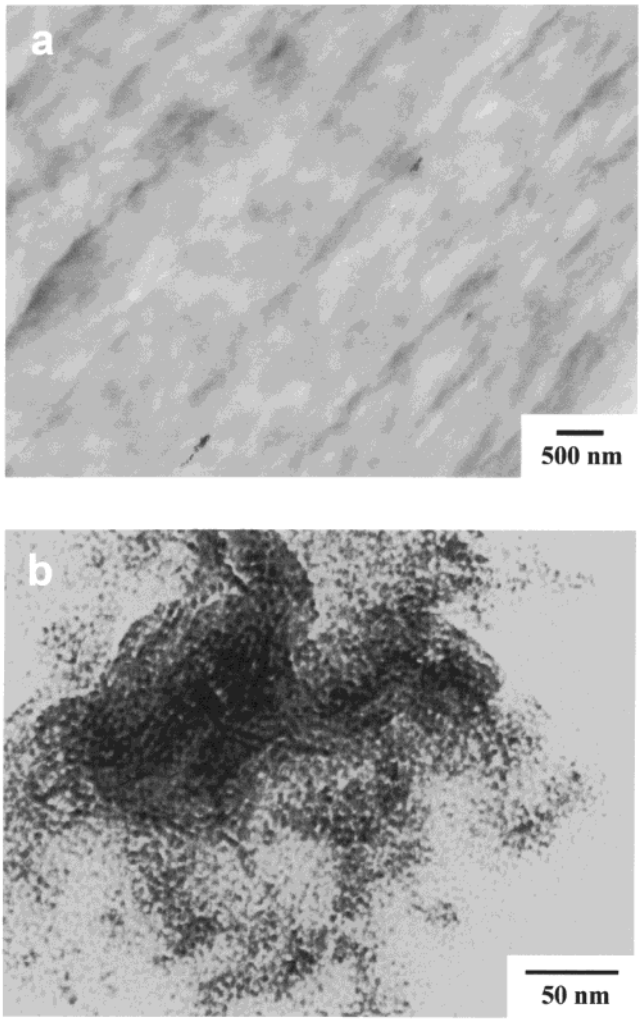

Figure 3. TEM micrographs of PVAs with different molecular weights: (a) specimen 1, $P_n = 800$; (b) specimen 19, $P_n = 330$.

the data are simply those for an unoriented powder pattern, but it is clear that there is substantial crystallinity and crystallite size despite the shapeless morphology.

The TEM image of longitudinal sections of specimen 1 ($P_n = 800$) consisting of well-defined fibrils is shown in Figure 3a. As is to be expected, the image exhibits the presence of uniform individual fibrils with diameter of a few hundred nanometers. The microfibrils with similarity in lateral size appear to proceed in a parallel manner although each fibril has some distorted junctions along their length. Figure 3b depicts the TEM image of specimen 19 ($P_n = 330$). It is obvious that there is no trace of a microfibrillar component.

Conclusions

The results presented here show a fibrous morphology for PVAs with $P_n \approx 800$ and s-diad content of ~62%, which were prepared by from the stirred saponification of PVPi. The fibrils are crystalline and well-oriented, with the polymer chains parallel to the fiber axis. Striations seen in the optical micrographs, and also the SAXS data, suggest a microfibrillar substructure with the presence of microvoids. This morphology is very similar to that reported previously for much higher molecular weight PVAs ($P_n > 4500$) with similar s-diad contents. As the molecular weight is progressively decreased (at approximately the same s-diad content), we obtain samples of mixtures of microfibrils and shapeless globular regions, and there is a steady transition to a shapeless particulate morphology that is complete at $P_n = 330$, the lowest molecular weight examined here. These structures are similar to those seen for high molecular weight PVAs with lower s-diad content (52−55%), and the X-ray data point to significant crystallinity. At the higher end of the range of P_n the fibrils appear to be at the edges of the agglomerates, leading to significant anisotropy.

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