

Mechanical Denaturation of High Polymers in Solutions. XXXIX. Flow-Induced Crystallization of High Molecular Weight Syndiotactic-Rich Poly(vinyl Alcohol)

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Synopsis

The crystallization of syndiotactic-rich poly(vinyl alcohol) (*s*-PVA) with a molecular weight of 6.73×10^5 from aqueous solutions was carried out under Couette flow with or without seed crystals. The crystallization of *s*-PVA from aqueous solutions occurred below the surface of the solutions even in the presence of seed placed in the solution; whereas, in the case of aqueous *s*-PVA solutions containing 0.02% octyl alcohol (antifoaming reagent) only the longitudinal growth of seed occurred. The lengths of the fibers obtained were 2.5 to 3.0 cm.

INTRODUCTION

Flow-induced crystallization of polymers from solution depends on the molecular weight¹⁻⁸ and the stereoregularity^{5-7,9,10} of polymer. Flow-induced crystallization of polyethylene (PE) from solutions was first carried out under the combination of shearing and elongation flows¹¹ and then in the presence of seed crystals.^{12,13} Ultrahigh-molecular-weight (UHMW) PE was used in the presence of seed crystals. These studies contributed much to the recent development for production of gel-drawn PE fibers or films with high modulus.¹⁴⁻¹⁷

In this article, the flow-induced crystallization of syndiotactic-rich poly(vinyl alcohol) (*s*-PVA) with high-molecular-weight (HMW) from solutions and the preparation of *s*-PVA filaments using seed crystals are presented.

EXPERIMENTAL

Sample

An unfractionated *s*-PVA sample was used, which was prepared from polymers obtained from a two-month bulk polymerization of vinyl trifluoroacetate (VTFA) at room temperature without an initiator. The degree of polymerization (DP) was 15300 and the syndiotactic diad content [*s*-(diad) %] was 57.4. The DP and the *s*-(diad) % were determined by the methods described previously.⁷

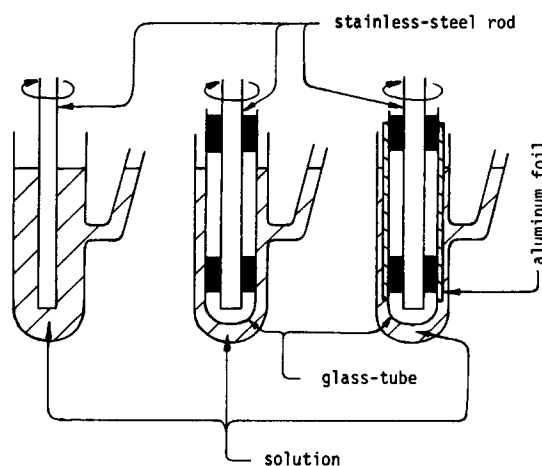


Fig. 1. Apparatus used for crystallization.

Flow-Induced Crystallization Under Couette Flow

Aqueous solutions of *s*-PVA were prepared at about 130°C in sealed glass tubes. The flow-induced crystallization was carried out at 30°C under Couette flow. The solution in a test tube (22 mm i.d.) was stirred by a stainless steel rod (15 mm diam). The volume of solution was 15 mL. The grown crystallites were separated and dried.

Crystallization with Seed Crystals

Figure 1 is a schematic representation of the apparatus used for the crystallization. The aqueous *s*-PVA solutions or those containing octyl alcohol were poured in a glass tube (inner diameter: 30 mm) with a side tube. Three kinds of stirrers of different diameters were used to flow the solutions under various shear rates. Namely, the solutions were allowed to flow by rotating a stainless-steel rod (diameter: 15 mm), a test tube (diameter: 25 mm) fixed coaxially on the stainless-steel rod, and the test tube (diameter: 28 mm) covered with aluminum foil (to reduce the distance between a stirrer and a container) at rates of 810, 410, and 70 rpm in the presence of a fibrous seed crystal inserted through the side tube.

Tensile Test

Tensile tests were performed using a Shinko Model TOM/5 tensile tester at a cross-head speed of 10 cm/min and an original sample length of 20 mm.

RESULTS AND DISCUSSION

Flow-Induced Crystallization Under Couette Flow

The authors and their co-workers have reported that the crystallization of *s*-PVA under Couette flow from aqueous solution occurred below the surface of the solution and was significantly influenced by generation of foam.¹⁸⁻²¹ In

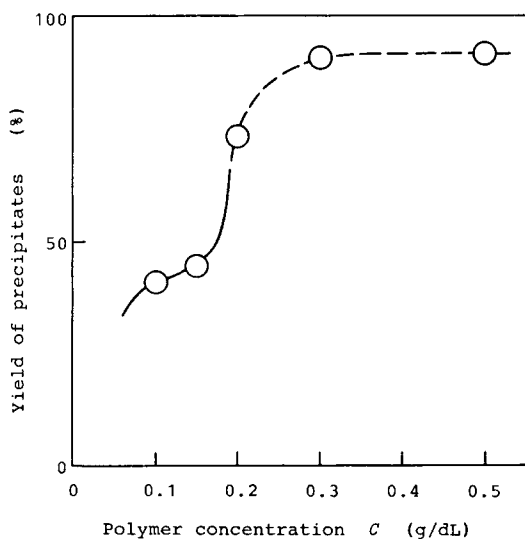


Fig. 2. Relation between the yield of precipitates and the polymer concentration for an aqueous *s*-PVA solution stirred at a rate of 810 rpm for 4 h at 30°C. Solid line indicates the region where no air bubbles were formed. Broken line indicates the region where air bubbles were formed.

this experiment, the process of crystallization under Couette flow of *s*-PVA with high-molecular-weight (HMW) were the same as reported previously.¹⁸⁻²¹

Figure 2 shows the relation between the yield of precipitates and the polymer concentration obtained by stirring for 4 h at a rate of 810 rpm and 30°C. After a few seconds of stirring, fibrillar crystals were produced just under the surface of solution. Even in the case of 0.1 g/dL, a considerable amount of precipitate was obtained. This was due to enhanced nucleation at the solution surface owing to the higher molecular weight of PVA used. In the case of aqueous solutions of 0.1 and 0.15 g/dL *s*-PVA, almost no air bubbles appeared during stirring for 4 h and the fibrillar crystals wound themselves around the stirrer. In the case of aqueous solutions of 0.2, 0.3, and 0.5 g/dL *s*-PVA, air bubbles were produced after 3 h, 40 min, and 30 min, respectively. The yield of precipitates increased rapidly after air bubbles were produced, since air bubbles induced turbulent flow and promoted precipitation. The curve in Figure 2 is caused by both the contact between polymer chains and the production of air bubbles with increasing polymer concentration. Figure 3 shows the relation between the yield of precipitate and the rate of stirring obtained by stirring for 4 h at various rates for an aqueous solution of 0.2 g/dL *s*-PVA. At a rate of 420 rpm, though the yield of precipitates was about 60%, very few air bubbles were produced. The steep increase in precipitates in the range between 300 and 400 rpm is considered to be related to the enhanced extensibility of this sample at this rpm range.

Figure 4 shows the relation between precipitate yield and stirring time obtained by stirring at a rate of 810 rpm for aqueous solution of 0.1 g/dL *s*-PVA. Although the yield of precipitates was about 50% after stirring for 7 h, air bubbles were not produced in significant amounts. The curve was sigmoidal, that is, the yield of precipitates increased rapidly after 2 h and slowly after

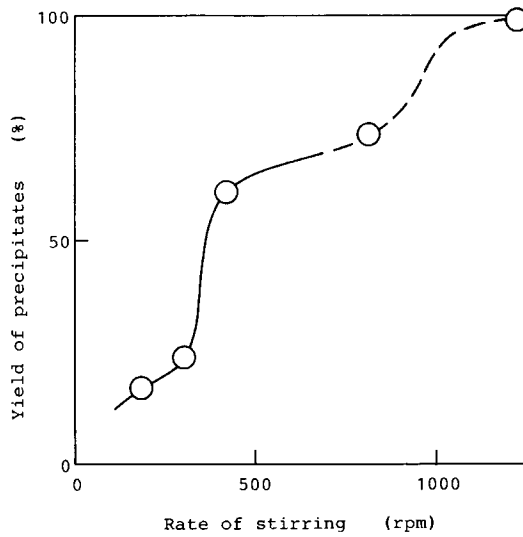


Fig. 3. Relation between the yield of precipitates and the rate of stirring for an aqueous solutions of 0.2 g/dL *s*-PVA stirred for 4 h at 30°C. Solid line indicates the region where air bubbles were formed. Broken line indicates the region where air bubbles were not formed.

4 h. The steep increase in precipitate with time near 0.3 g/dL is caused by the enhanced growth of crystals due to increasing concentration. As the solution is dilute, the rate of precipitation decreased after 4 h. After a gel-like film formed on the stirrer had dried, the solid film was drawn 1.7 times its original length in water at 80°C. The drawn film was annealed at 200°C for 10 min and the stress-strain curve was obtained. The Young's modulus and the

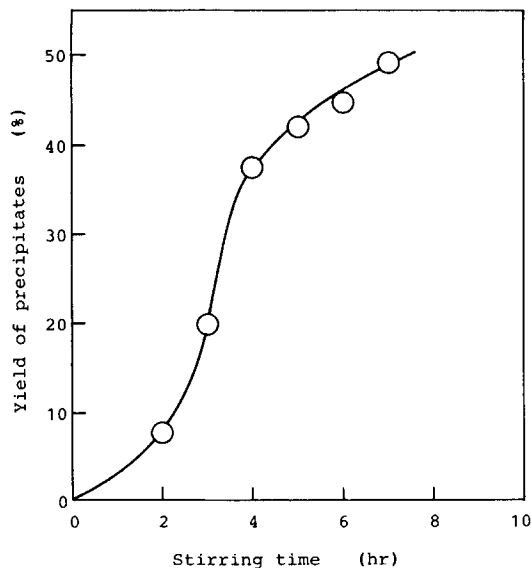


Fig. 4. Relation between the yield of precipitates and the stirring time for an aqueous solutions of 0.1 g/dL *s*-PVA stirred at a rate of 810 rpm at 30°C.

strength at break for the drawn annealed film were 7.05 GPa and 0.15 GPa, respectively. Those values were lower than that of the drawn annealed casting films or the drawn annealed fibers of *s*-PVA.^{22,23} That is, the molecular orientation in the crystals of *s*-PVA obtained under Couette flow is considered to be low.

Crystallization with Seed Crystals

The crystallization with seed crystals was tried by stirring an aqueous solution of 0.15 g/dL *s*-PVA at rates of 70, 420, and 810 rpm using a rod stirrer with a diameter of 15 mm, that is, at shear rates of 19.5, 117, and 226 s⁻¹, respectively. Although no air bubbles were produced, the fibrous crystals were formed just under the solution surface and the seed crystal did not grow. The authors have reported that the flow-induced crystallization under Couette flow just below the surface was prevented by addition of small amounts of octyl alcohol (OA), an antifoaming reagent.²¹ Therefore, the crystallization with seed crystals was carried out by the addition of 0.02% OA to the aqueous solution. The longitudinal growth of fibrillar crystals on seeds was not observed at a rate of 70 rpm, although at rates of 420 and 810 rpm it was

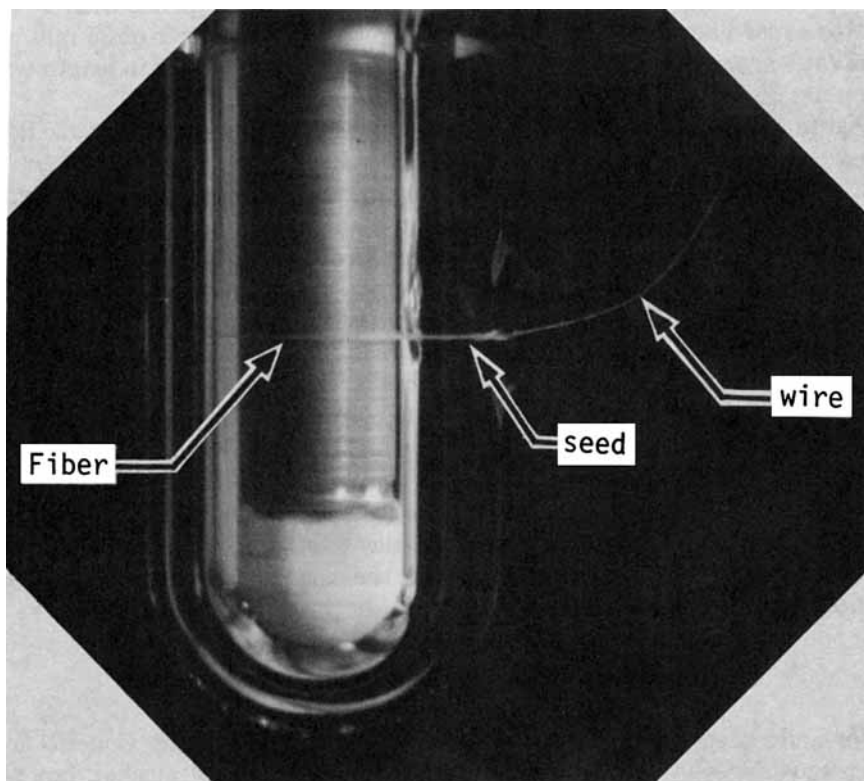


Fig. 5. Photograph of the appearance of the crystallization induced by seed crystals under Couette flow for HMW *s*-PVA from an aqueous solution with 0.02% octyl alcohol. The diameter of stirrer is 25 mm.

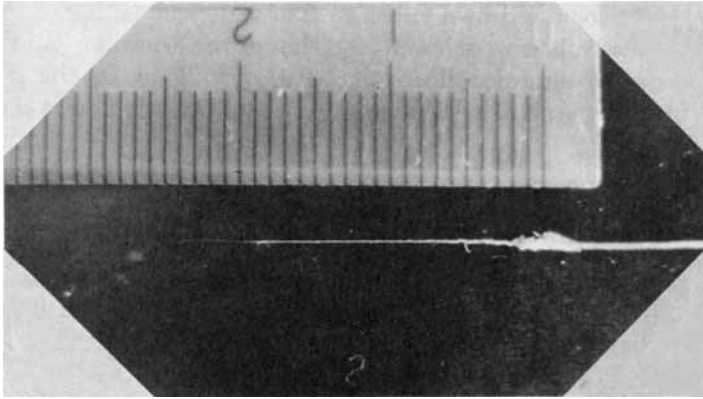


Fig. 6. Photograph of a fiber obtained in Fig. 5.

observed. This means that the shear rate of 19.5 s^{-1} is not sufficient to cause impingement and extension of PVA molecules to crystallize on the seed.

After the fibrillar crystals on seeds grew 5 to 10 mm, the propagated fibers on seed crystals were broken by high-speed stirring. The flow-induced crystallization using stirrers with diameters of 25 and 28 mm was performed at low-speed stirring of 70 rpm in order to give shear rates higher than 20 s^{-1} and to avoid fiber breakage. When the stirrer with a diameter of 25 mm was used (at a shear rate of 48 s^{-1}), fibrillar crystals of 25 to 30 mm in length were often obtained, but not always.

Figure 5 shows crystallization induced by seed crystals under Couette flow, using the 25-mm-diameter stirrer, for HMW *s*-PVA from the aqueous solution with 0.02% octyl alcohol. Figure 6 is a photograph of a fiber obtained in Figure 5. When the 28-mm stirrer was used (at a shear rate of 113 s^{-1}), fibrillar crystals of 25 to 30 mm in length were always obtained. The fibrillar crystals obtained were always present in trace amounts. The longer continuous fiber as shown in UHMW PE^{12,13} was not produced. This is considered to be due to the lower molecular weight ($\text{MW} = 6.7 \times 10^5$) of *s*-PVA as compared to $1\text{--}5 \times 10^6$ for the UHMW PE. The PVA sample used in our study was unfractionated and is considered to contain some UHMW PVA. Therefore, propagated fibers on seed crystals was present in trace amounts. We cannot obtain UHMW *s*-PVA (above $\text{MW} = 10^6$) at this time. Moreover, the propagated fiber on seed crystals could not be wound off continuously through a guide pipe of the fiber because of its tendency to stick to the fiber to the pipe wall. This may be another reason that the continuous filament was not produced.

CONCLUSIONS

We could prepare *s*-PVA fibers grown on seed crystals under Couette flow from aqueous solution containing a small amount of octyl alcohol, but the fibers obtained were short. In order to prepare continuous filaments, it is necessary to prepare UHMW *s*-PVA of molecular weight above 10^6 . Moreover, solvents other than pure water such as water/dimethyl sulfoxide mixture, for

example, might be useful. With such a solvent system, breakage of fibers caused by sticking to the wall of the guide pipe might be avoided.

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