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Characterizations of poly(vinyl pivalate) polymerized in tertiary butyl alcohol and resulting syndiotactic poly(vinyl alcohol) microfibrils saponified

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Abstract

Vinyl pivalate (VPi) was solution-polymerized in tertiary butyl alcohol (TBA) and in dimethyl sulfoxide (DMSO) with low chain transfer constant using a low temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN). TBA was absolutely superior to DMSO in increasing the syndiotacticity and molecular weight of poly(vinyl alcohol) (PVA). Low-temperature solution polymerization of VPi in TBA or DMSO by adopting ADMVN proved to be successful in obtaining PVA of ultrahigh molecular weight (maximum number-average degree of polymerization (P_n): 13,500–17,000) and of high yield (ultimate conversion of VPi into PVPi: 55–80%) to a much higher conversion than that from bulk polymerization. Moreover, PVA from TBA system were fibrous, with a high degree of orientation of the crystallites, indicating the syndiotactic nature of TBA polymerization. © 2001 Published by Elsevier Science Ltd.

Keywords: Vinyl pivalate; Tertiary butyl alcohol; Poly(vinyl alcohol)

1. Introduction

Poly(vinyl alcohol) (PVA) obtained by the saponification of poly(vinyl ester) or poly(vinyl ether) is a linear semicrystalline polymer, which is widely used as fibers for clothes and industries, binders, films, membranes, and in medicines for drug delivery systems, and cancer cell-killing embolic materials [1–13]. PVA fibers have high tensile and compressive strengths, tensile modulus, and abrasion resistance due to its higher crystalline lattice modulus. To maximize these physical properties, molecular weight, degree of saponification and syndiotacticity should be increased [1,2,4–9].

To raise the syndiotacticity as well as molecular weight of PVA, various other vinyl ester monomers like vinyl pivalate (VPi) which reveals strong steric effects of the *t*-butyl group have been used. Lyoo and Ha [14] synthesized ultrahigh molecular weight (UHMW) PVA having a maximum number-average degree of polymerization (P_n) of over 18,000 and syndiotactic diad (S-diad) content of over 63% via UV-initiated low temperature bulk polymerization of VPi [14]. This polymerization method, however, inevitably require very complex and expensive radiation procedures and special polymerization devices. Thus, we utilized a low temperature initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN) in polymerization of vinyl acetate (VAc) and VPi, which can lower the polymerization temperature down to room temperature [15–17].

Recently, Lyoo et al. [17] have found that a PVA fiber of well-oriented microfibrillar structure, similar to a natural cellulose fiber, is formed during saponification of poly(vinyl pivalate) (PVPi) to PVA. This has proved to be the case only for the saponification process of HMW PVPi having a high S-diad content of 57–64% prepared by UV-initiated low-temperature bulk polymerization of VPi [3,6,8,14]. In fact, saponification of poly(vinyl acetate) (PVAc) to PVA with similar molecular weight and an S-diad content of 50–53% did not lead to any fibril formation [8,17]. This fact indicates that tacticity plays an important role in the in situ fibrillation of flexible chain polymers under low shear conditions (shear rates below 100/s). In addition, these microfibrillar PVA fibers are very similar to natural asbestos fibers in structure and physical properties [3].

In this study, a low-temperature initiator, ADMVN [14–16], was selected in solution polymerization of VPi to obtain HMW PVPi with higher conversions, which

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is expected to be a profitable precursor of UHMW syndiotactic PVA with high yield. Tertiary butyl alcohol (TBA) and dimethyl sulfoxide (DMSO) with low chain transfer constants were used as solvents. The effect of polymerization conditions on the molecular parameters of PVPi and PVA such as molecular weight, degree of branching, stereoregularity, morphology and crystal property were investigated.

2. Experimental

2.1. Materials

Purified VPi (Aldrich Co., 99.9%) and solvent (TBA or DMSO) were poured into a three-necked round bottom flask and flushed with nitrogen for 3 h to eliminate oxygen. At the polymerization temperatures of 25, 35, and 45°C, recrystallized ADMVN (Wako Co., 99%) was added to the solution. When polymerization was completed for the ADMVN/TBA system (homogeneous solution polymerization), the product polymer was reprecipitated several times from benzene/methanol to eliminate residual monomer and solvent. On the other hand, the product polymerized using the ADMVN/DMSO system (heterogeneous solution polymerization) was filtered and washed several times with methanol and water. Conversion was calculated by measuring the weight of the polymer. Conversions were averages of five determinations. The PVA was prepared by the saponification method of PVPi mentioned in previous papers [3,6,14]. Residual ester groups could not be detected in the ^{1}H-NMR spectra of PVA.

2.2. Characterization

The molecular weight of PVPi was calculated from the intrinsic viscosity of PVPi. On the other hand, the molecular weight of PVA was determined from that of PVAc produced by acetylation of PVA [3,14].

The syndiotactic diad (S-diad) contents of PVAs were determined by 300 MHz ^{1}H-NMR, using 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 100 ×.

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 CuKα radiation and pinhole collimation. The specimens were parallel bundles of (3–5) fibers. The degree of orientation of the crystallite regions was determined using the Hermans equation, based on the azimuthal half width of the meridional reflection on the second layer line measured using an optical densitometer [17].

3. Results and discussion

3.1. Molecular weight and degree of branching

UHMW (PVA)s having various (P_n)s of 13,500–17,000 could be prepared by saponification of UHMW (PVPi)s having (P_n)s of 24,000–39,000. It should be noted that PVA with P_n of up to 17,000 could be prepared from PVPi solution-polymerized in TBA at 25°C at a conversion of ca. 55% using ADMVN concentration of 0.00003 mol/mol of VPi, which is comparable to P_n of PVA (17,500) from PVPi by bulk polymerization using the same polymerization conditions (conversion: ca. 29%) [17]. In the case of the DMSO system, PVA with P_n of up to 15,800 could be prepared from PVPi solution-polymerized in DMSO at 25°C at a conversion of ca. 65% using minimum ADMVN

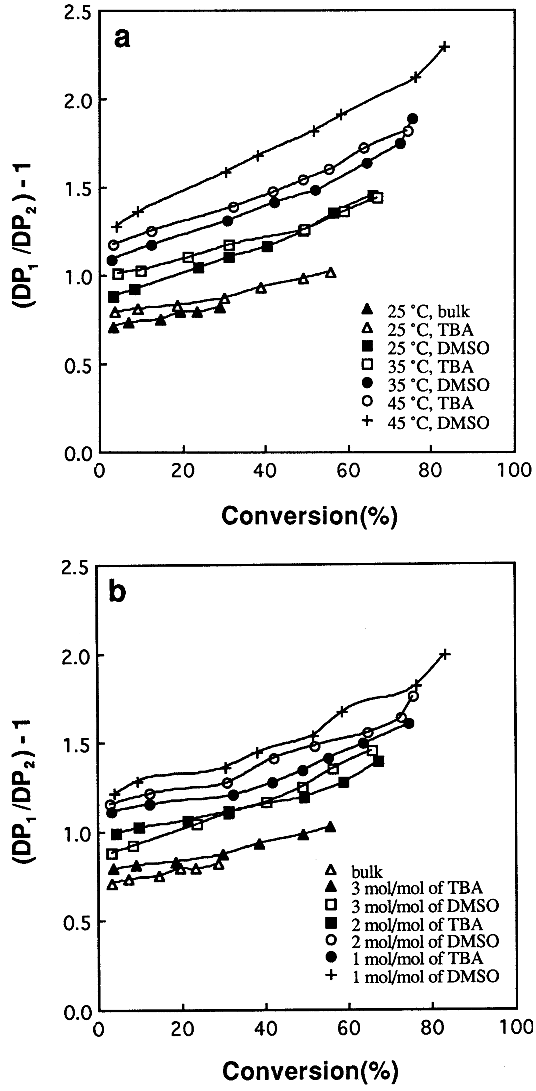


Fig. 1. (a) ((DP_1/DP_2) − 1) in polymerization of VPi using VPi concentration of 3 mol/mol of solvent and ADMVN concentration of 0.00003 mol/mol of VPi and (b) ((DP_1/DP_2) − 1) in polymerization of VPi at 25°C using ADMVN concentration of 0.00003 mol/mol of VPi.

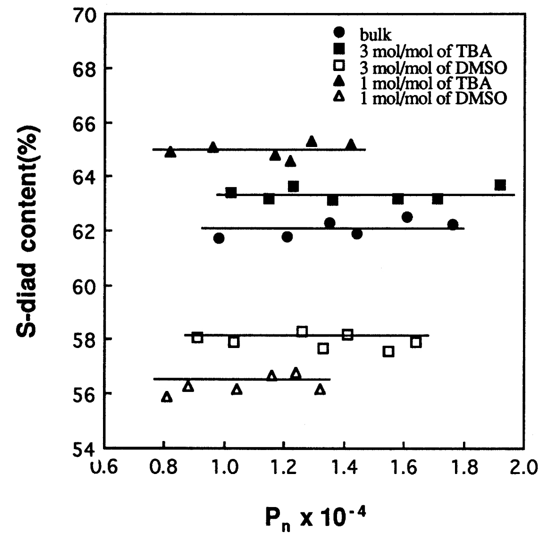
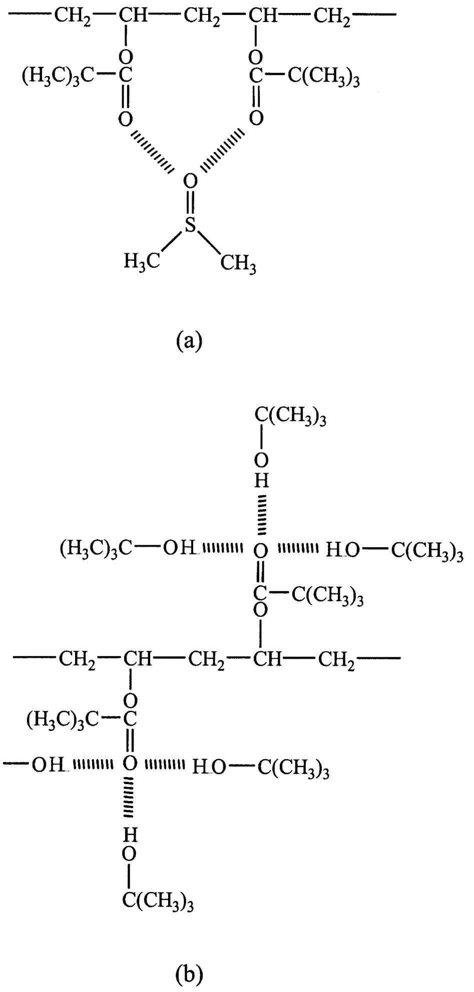


Fig. 2. S-diad content of PVA from PVPi polymerized in bulk, TBA, and DMSO, respectively, with P_n of PVA.



Scheme 1. Effect of solvent on the stereoregularity of PVPi during polymerization of VPi.

concentration of 0.00003 mol/mol of VPi. As a rule, the difference between (P_n)s of PVPi and PVA is due to branched structures. In this study, the effect of conversion, polymerization temperature, and type and amount of solvent on the degree of branching of PVPi was investigated (Fig. 1). Fig. 1a shows the variation of $((DP_1/DP_2) - 1)$ at three different polymerization temperatures with conversion. DP_1 is P_n of PVPi and DP_2 is P_n of PVA prepared by saponification of PVPi. $((DP_1/DP_2)-1)$ increased with an increase in the conversion for all the cases. In addition, the rate of increase of $((DP_1/DP_2) - 1)$ with conversion was decreased as the polymerization temperature was lowered. At higher polymerization temperatures, the accelerated polymerization reaction may bring about a chain transfer (branching) reaction more easily. Also, the rate of increase of $((DP_1/DP_2) - 1)$ with conversion of TBA system was much lower than that of the DMSO system. This might be ascribed by a polymerization rate difference between two solvents. From the fact that $((DP_1/DP_2) - 1)$ of PVPi polymerized at 25°C in TBA was a very low value (below 1), it was identified that the low-temperature solution polymerization of VPi using ADMVN and TBA produced PVPi with high linearity. Fig. 1b shows the monomer concentration effect. As VPi concentration was increased, $((DP_1/DP_2) - 1)$ was decreased in all cases. This is explained by increasing chain transfer reactions with an increase in the solvent concentration.

3.2. Characteristics of PVA saponified

The saponification of PVPi [3,6,14,17] or PVPi/PVAc [17] copolymer with high syndiotacticity gives rise to the in situ formation of microfibrillar PVA fibers. The governing factor of the in situ fibrillation of PVA is syndiotacticity. In the vicinity of critical syndiotacticity of PVA, morphological and crystal characteristics were changed [17]. The syndiotacticity of PVA depends on polymerization conditions as well as side group bulkiness of the monomer. In general, a slight increase of syndiotacticity has been observed with decreasing polymerization temperature. Meanwhile, in this study, we considered the solvent effect on the stereoregularity of PVA. Imai et al. [18,19] investigated the effect of polymerization solvents such as DMSO, methanol, and phenol in solution polymerization of VAc, vinyl butyrate, and vinyl propionate on the stereoregularity of PVA. Polar aprotic solvents like DMSO promote isotactic configuration, resulting from electrostatic interaction between the solvent molecules and acetyl groups. On the contrary, in the course of the solution polymerization of VAc in alcohols including methanol and phenol, hydrogen-bonding interaction between the solvent molecules and acetyl groups increases the steric hindrance between the monomers. So, syndiotactic configuration is favored when it is used as a solvent [18,19]. In Fig. 2, the effect of solvent on the syndiotacticity of PVA is depicted. PVPi and resulting PVA was sampled at similar conversions of about 30% to clarify the solvent effects only. As expected, TBA,

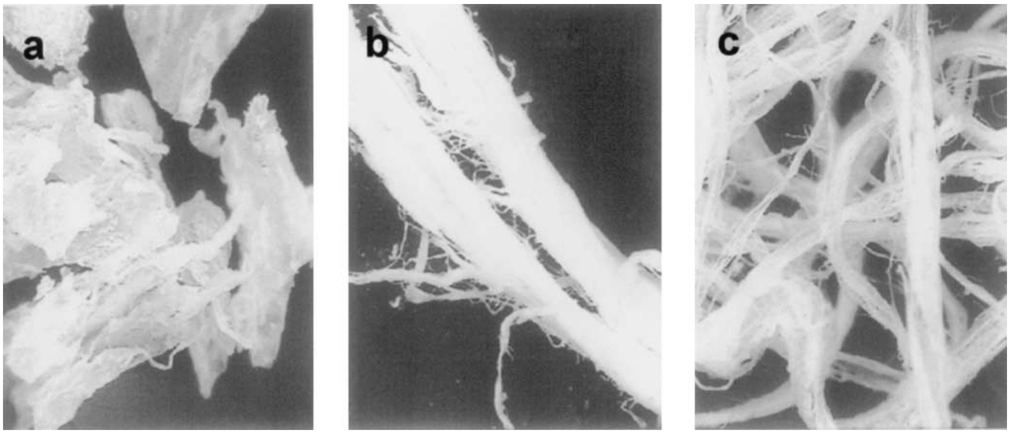


Fig. 3. Optical micrographs (× 100) of (PVA)s from (PVPi)s polymerized in (a) DMSO, (b) bulk, and (c) TBA, respectively. S-diad content and P_n: (a) 56.8%, 12,400; (b) 61.8%, 12,100; (c) 65.1%, 11,700.

an alcoholic solvent, caused a definite increase in the S-diad content of PVA up to 65%. In contrast, S-diad content of PVA obtained by the solution polymerization in DMSO fell off to much lower levels (56%) than that of PVA obtained by the bulk polymerization. This behavior is described well in Scheme 1. S-diad content does not seem to have a close relationship with molecular weight of PVA.

From the morphological point of view, the role of solvent is obvious. In Fig. 3, the optical micrographs of PVA obtained by the saponification of PVPi polymerized in DMSO, bulk, and TBA are illustrated. Three specimens had similar P_n of about 12,000 and different syndiotacticities. In the case of DMSO, the particles composed of short fiber-like structures were observed. Fibrous morphology was obtained for specimens from bulk polymerization. Finely developed microfibrils were found when using TBA, arising from the fact that the fibrous morphology develops as syndiotacticity increases with trends that the fibrils become longer and narrower.

Fig. 4 shows the SAXS patterns of the PVAs. No scattering in small angle region was found for the PVA obtained by

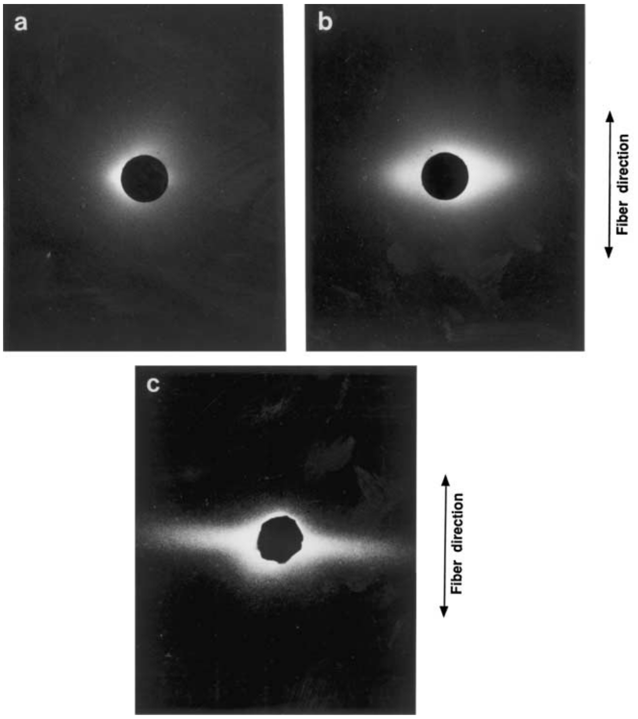


Fig. 4. Small-angle X-ray fiber diagrams of (PVA)s from (PVPi)s polymerized in (a) DMSO, (b) bulk, and (c) TBA, respectively. S-diad content and P_n: (a) 56.8%, 12,400; (b) 61.8%, 12,100; (c) 65.1%, 11,700.

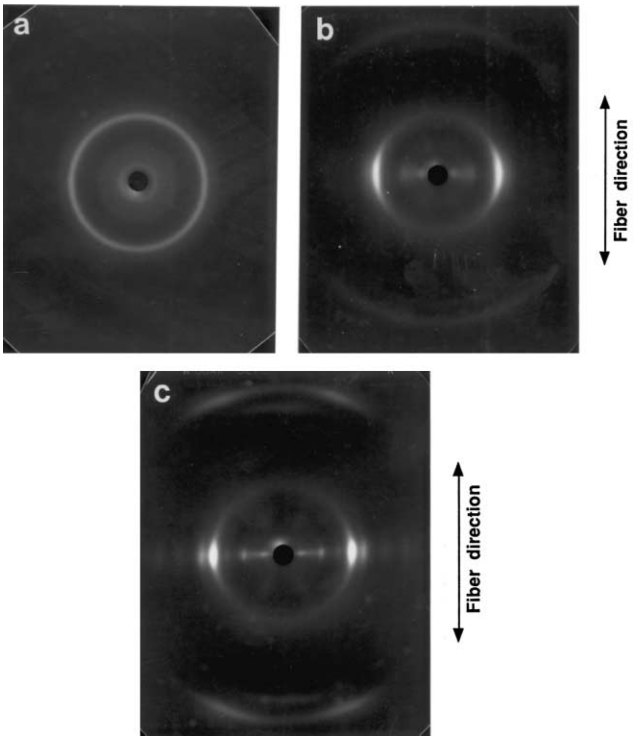


Fig. 5. Wide-angle X-ray fiber diagrams of (PVA)s from (PVPi)s polymerized in (a) DMSO, (b) bulk, and (c) TBA, respectively. S-diad content and P_n: (a) 56.8%, 12,400; (b) 61.8%, 12,100; (c) 65.1%, 11,700.

the saponification of PVPi polymerized in DMSO. However, in the case of PVA from bulk-polymerized PVPi, diamond-shaped scattering was observed. The SAXS pattern was converted to a strong line scattering parallel to the equator when TBA was used, resulting from the presence of more regular and more elongated microvoids. This is related with the development of well-oriented microfibrillar structure because there should be a lot of microvoids in the PVA microfibril bundles. These SAXS patterns are similar to those of native cellulose fibers. That is, diamond-shaped scattering and strong-line scattering are observed in SAXS patterns of ramie and bamboo fibers, respectively [20,21]. In Fig. 5, the WAXD pattern representing a high degree of crystal orientation of 0.9 was found when TBA was used, while the PVA was almost unoriented when DMSO was used. Hence, the in situ formation of PVA microfibrils with high degree of orientation is achieved by TBA, which promotes the syndiotacticity of PVA.

4. Conclusions

Solution polymerization of VPi at 25°C by ADMVN and saponification produced UHMW syndiotactic PVA with P_{n} of 13,500–17,000 and with maximum conversion of VPi into PVPi of 55–80% with diminishing heat generation during polymerization. This compares well with the bulk polymerization of VPi at 25°C using ADMVN with P_{n} of 14,500–17,500 and with the maximum conversion of about 20–35%. The P_{n} and syndiotacticity were higher and $((DP_1/DP_2) - 1)$ was lower with PVA from PVPi polymerized at lower temperatures in TBA ($((DP_1/DP_2) - 1)$ below 1 at 25°C). Syndiotactic configuration was favored when TBA was used due to hydrogen-bonding interaction between the solvent molecules and pivaloyl groups. In contrast, in the case of DMSO, lowest S-diad content was obtained. The in situ formation of PVA microfibrils with high degree of orientation was achieved when TBA was used as a polymerization solvent, which promotes the syndiotacticity of PVA.

Conclusively, this solution polymerization is expected to be an easy way of producing UHMW syndiotactic PVA microfibrils with high yield by simple chemical initiation without using special devices such as irradiation. It is expected that these PVA microfibrils can be used as a high performance replacement material for natural carcinogenic asbestos fiber, reinforcing fiber, water-soluble fiber for non-woven fabric, ultra-low denier fiber, embolic fiber for cancer-cell killing, and pulp for paper-based product owing to its high tensile strength, high modulus, high fineness, excellent alkali and chemical resistance, good biocompatibility, and good binding property [1–3,7]. In the near future, we will report on the low-temperature solution polymerizations of VPi using other solvent systems for producing stereoregular PVA microfibrils to maximize syndiotacticity, molecular weight, and yield.

Acknowledgements

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