

# Preparation of Ultrahigh Molecular Weight Syndiotactic Poly(vinyl alcohol) Microfibrillar Fibers by Low-Temperature Solution Polymerization of Vinyl Pivalate in Tertiary Butyl Alcohol and Saponification

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Received 15 May 2001; accepted 5 December 2001

**ABSTRACT:** Vinyl pivalate (VPi) was solution polymerized in tertiary butyl alcohol (TBA) and in dimethyl sulfoxide (DMSO) with a low chain transfer constant using a low temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN). The effects of polymerization temperature and initiator concentration were investigated in terms of polymerization behavior and molecular structures of poly(vinyl pivalate) (PVPi) and its saponification product poly(vinyl alcohol) (PVA). TBA was absolutely superior to DMSO in increasing the syndiotacticity and molecular weight of PVA. In contrast, TBA was inferior to DMSO in causing conversion to polymer, indicating that the initiation rate of VPi production in TBA was lower than that in DMSO. These effects could be explained by a kinetic order of ADMVN concentration, calculated by the initial rate method. 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: 55–83%). In the case of bulk polymerization of VPi at the same conditions, maximum  $P_n$  and conversion were 14,500–17,500 and 22–36%, respectively. The  $P_n$  and syndiotactic diad content were much higher and the degree of branching was lower with PVA prepared from PVPi polymerized at lower temperatures in TBA. Moreover, PVA from the TBA system was fibrous, with a high degree of orientation of the crystallites, indicating the syndiotactic nature of TBA polymerization. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1992–2003, 2002

**Key words:** vinyl pivalate (VPi); tertiary butyl alcohol (TBA); poly(vinyl alcohol) (PVA); syndiotacticity; ultrahigh molecular weight; high yield; fibrous

## INTRODUCTION

Poly(vinyl alcohol) (PVA), obtained by the saponification of poly(vinyl ester), or poly(vinyl ester) are linear semicrystalline polymers that have

been widely used as fibers for clothes and industries, binders, films, membranes, medicines for drug delivery systems, and cancer cell-killing embolic materials.<sup>1–13</sup> PVA fiber has high tensile and compressive strengths, tensile modulus, and abrasion resistance because of its high crystalline lattice modulus. To maximize these physical properties, molecular weight, degree of saponification, and syndiotacticity should be in-

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*Journal of Applied Polymer Science*, Vol. 85, 1992–2003 (2002)  
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creased.<sup>1,2,4-9</sup> In particular, to increase molecular weight, which is a fundamental factor affecting physical properties, it is necessary to improve polymerization methods of vinyl acetate (VAc)<sup>14-20</sup> or use other vinyl ester monomers, such as vinyl pivalate (VPi).<sup>21-23</sup>

As is well known, it is very difficult to obtain linear high molecular weight (HMW) poly(vinyl acetate) (PVAc), a precursor for HMW PVA, by free radical polymerization because it tends to chain transfer (branching) reactions. Hence, linear HMW PVA has been created only by special polymerization methods, primarily initiation by irradiation.<sup>15</sup> These systems were developed in attempts to produce linear HMW PVAc, which could be used in the production of ultrahigh molecular weight (UHMW) PVA. Wu and West synthesized UHMW PVA with a number-average degree of polymerization ( $P_n$ ) of  $> 15,000$  by low temperature-ultraviolet (UV) radiation polymerization of VAc in a bulk system.<sup>15</sup>

To raise the syndiotacticity as well as molecular weight of PVA, various other vinyl ester monomers have been used, such as VPi, which reveals strong steric effects of the *t*-butyl group. Lyoo and Ha synthesized UHMW PVA with a maximum  $P_n$  of  $> 8000$  and syndiotactic diad (S-diad) content of  $> 63\%$  by UV-initiated low temperature-bulk polymerization of VPi.<sup>22</sup>

These polymerization methods, however, inevitably require very complex and expensive radiation procedures, special polymerization initiator, and lower polymerization temperature. The free radical polymerizations of VAc and VPi are prone to bring about chain transfer (branching) reaction. However, a proper choice of polymerization conditions may suppress the branch formation reaction. As well known, the polymerization temperature has a paramount effect on the conversion and molecular weight of polymer. The type and concentration of initiator have a notable effect on the molecular parameters of polymer as well. We utilized a low temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN), in the polymerization of VAc, which can lower the polymerization temperature to room temperature.<sup>18,20,23</sup>

Recently, Lyoo et al.<sup>3,6,8,22-24</sup> have found that a PVA fiber of well-oriented microfibrillar structure, similar to natural cellulose fiber, is formed during saponification of poly(vinyl pivalate) (PVPi) to PVA. This result has proved to be the case only for the saponification process of HMW PVPi with a high S-diad content of 57–64% pre-

pared by UV-initiated low-temperature bulk polymerization of VPi. In fact, saponification of PVAc to PVA with similar molecular weight and an S-diad content of 50–53% did not lead to any fibril formation.<sup>8,23</sup> This fact indicates that tacticity plays an important role in the *in situ* fibrillation of flexible chain polymer under low shear conditions (shear rates of  $< 100 \text{ s}^{-1}$ ). In addition, these microfibrillar PVA fibers are very similar to natural asbestos fibers in structure and physical properties.<sup>3,24</sup> However, even with omitting spinning, drawing, and heat treatment in PVA fiber preparation in the case of the UV-initiation system of VPi, PVA fiber production is nearly impossible to be commercialized because of the very high cost.

In this study, a low temperature initiator, ADMVN, which can reduce the polymerization temperature to room temperature,<sup>18,20,23</sup> was selected in solution polymerization of VPi to obtain HMW PVPi with higher conversions. The HMW PVPi 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 polymerization behavior of VPi and molecular parameters of PVPi and PVA, such as molecular weight, degree of branching, and stereoregularity, were examined.

## EXPERIMENTAL

### Materials

VPi (Aldrich Company, 99.9%) was washed with an aqueous solution of  $\text{NaHSO}_3$  and water, dried over anhydrous  $\text{CaCl}_2$ , then distilled under reduced pressure of nitrogen. ADMVN (Wako Company, 99%) was recrystallized in methanol. Other extra-pure grade reagents were used without further purification.

### Polymerization

VPi and solvent (TBA or DMSO) were poured into a three-necked round-bottomed flask and flushed with nitrogen for 3 h to eliminate oxygen. At the predetermined polymerization temperature, ADMVN was added to the solution. When polymerization had been completed for the ADMVN/TBA system (homogeneous solution polymerization), the product polymer was reprecipitated several

**Table I** Parameters for Polymerization of VPi

ADMVN (mol/mol of VPi)	Solvent Type	Solvent Concentration (mol/mol of VPi)	Temp (°C)	Time (h)	Conversion (%)
$3 \times 10^{-5}$	DMSO	0.33	45	14	83.1
$3 \times 10^{-5}$	TBA	0.33	45	20	74.4
$3 \times 10^{-5}$	Bulk	0.00	45	12	36.1
$3 \times 10^{-5}$	DMSO	0.33	35	24	75.6
$3 \times 10^{-5}$	TBA	0.33	35	28	67.1
$3 \times 10^{-5}$	Bulk	0.00	35	16	32.3
$3 \times 10^{-5}$	DMSO	1.00	25	60	78.5
$3 \times 10^{-5}$	TBA	1.00	25	66	66.3
$3 \times 10^{-5}$	DMSO	0.50	25	52	74.4
$3 \times 10^{-5}$	TBA	0.50	25	58	62.8
$3 \times 10^{-5}$	DMSO	0.33	25	32	65.8
$3 \times 10^{-5}$	TBA	0.33	25	40	55.7
$3 \times 10^{-5}$	Bulk	0.00	25	16	22.3

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 detailed polymerization conditions and conversions equilibria are given in Table I.

### Saponification and *In Situ* Fibrillation

The following is a typical example of PVA fibrillation experiments:<sup>3,6</sup> In a flask equipped with a reflux condenser, a thermocouple, a dropping funnel, and a stirring device, 3 g of PVPi was dissolved in 300 mL of tetrahydrofuran (THF). The PVPi solution in the flask and 20% potassium hydroxide/methanol/water (90/10, v/v) solution in the dropping funnel were flushed with nitrogen. The ratio saponification agent/PVPi solution was 0.05/0.25 (v/v). The alkali solution was added to the PVPi solution with stirring at 50–60°C. After the saponification reaction was completed, the solid saponification product was beaten 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 proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra of these specimens.

### Characterizations

The molecular weight of PVPi was calculated with eq. 1:<sup>25</sup>

$$[\eta] = 2.88 \times 10^{-5} [M_n]^{0.77} \quad (\text{in acetone at } 25^\circ\text{C}) \quad (1)$$

where  $[\eta]$  is the intrinsic viscosity of PVPi and  $M_n$  is the number-average molecular weight of PVPi. On the contrary, the molecular weight of PVA was determined from that of PVAc produced by acetylating PVA with eq. 2:<sup>26</sup>

$$[\eta] = 8.91 \times 10^{-3} [P_n]^{0.62} \quad (\text{in benzene at } 30^\circ\text{C}) \quad (2)$$

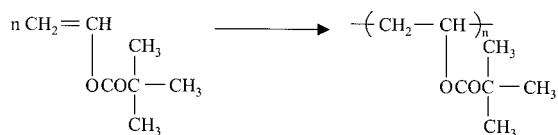
where  $P_n$  is the number-average degree of polymerization of PVAc.

The degree of branching for the pivaloyl group (DB) of PVPi is calculated by eq. 3:<sup>1</sup>

$$\text{DB} = (DP_1/DP_2) - 1 \quad (3)$$

where  $DP_1$  is  $P_n$  of PVPi and  $DP_2$  is  $P_n$  of PVA prepared by saponifying PVPi.

The S-diad contents of the PVA were determined by 300 MHz <sup>1</sup>H NMR, using DMSO-d<sub>6</sub> as



**Scheme 1** Preparation of PVPi by polymerization of VPi.

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 with a Scalar VMS 3000 video microscope with a magnification of  $\times 100$ .

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  $\text{CuK}\alpha$  radiation and pinhole collimation. The specimens were parallel bundles of (3–5) fibers. The degree of orientation of the crystallite regions was determined with the Hermans equation, based on the azimuthal half-width of the meridional reflection on the second layer line, measured with an optical densitometer.<sup>23</sup>

## RESULTS AND DISCUSSION

### Solution Polymerization of VPi

Generally, in a free radical polymerization, the rate of polymerization ( $R_p$ ) increased as the efficiency and concentration of initiator are increased.<sup>27</sup> The initial conversion rates measured within 15% conversion in the solution polymerization of VPi in TBA and DMSO at 25°C using ADMVN are shown in Figures 1a and 1b, respectively. It was shown that the greater the initiator concentration, the higher the polymerization rate. The dependence of polymerization rate on initiator concentration can be determined by the initial rate method.<sup>28</sup> For small changes in initiator concentration, the polymerization rate can be approximated to the corresponding ratio of increments. If a measurement is made at two different initiator concentrations of one component with the other held constant, the order with respect to that component can be simply determined with eqs. 4–10:

$$-(d[M]_1/dt) = (R_p)_1 = k[M]_1^{n_1}[I]_1^{n_2}[S]_1^{n_3} \quad (4)$$

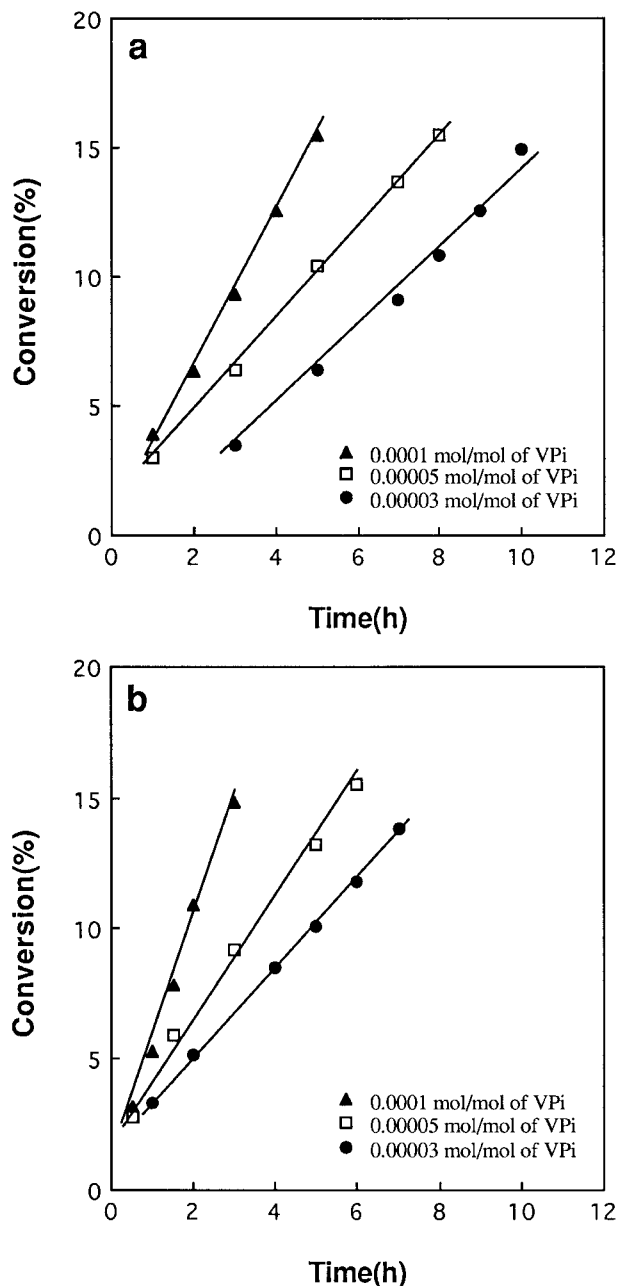
$$-(d[M]_2/dt) = (R_p)_2 = k[M]_2^{n_1}[I]_2^{n_2}[S]_2^{n_3} \quad (5)$$

$$-(d[M]_3/dt) = (R_p)_3 = k[M]_3^{n_1}[I]_3^{n_2}[S]_3^{n_3} \quad (6)$$

$$(R_p)_1/(R_p)_2 = ([I]_1/[I]_2)^{n_{2a}} \quad (7)$$

$$(R_p)_2/(R_p)_3 = ([I]_2/[I]_3)^{n_{2b}} \quad (8)$$

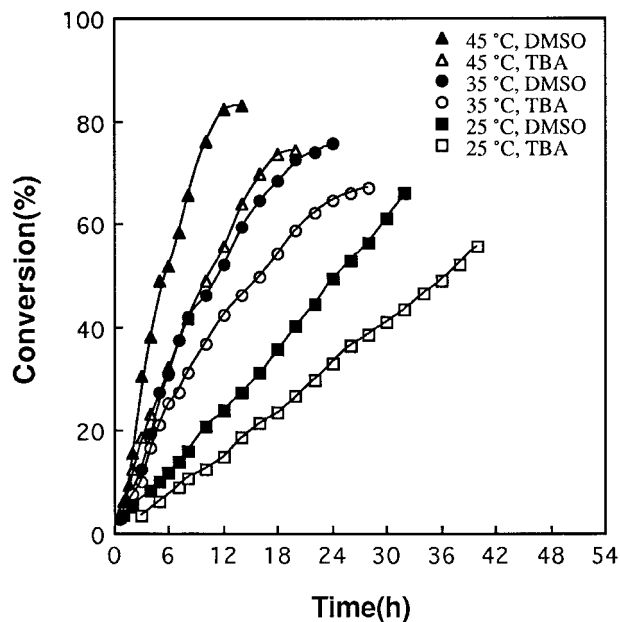
$$(R_p)_3/(R_p)_1 = ([I]_3/[I]_1)^{n_{2c}} \quad (9)$$



**Figure 1** Conversion of VPi into PVPi in early stage of polymerization in (a) TBA and in (b) DMSO at 25°C using VPi concentration of 3 mol/mol of solvent with polymerization time.

$$n_2 = (n_{2a} + n_{2b} + n_{2c})/3 \quad (10)$$

where  $[M]$ ,  $[I]$ , and  $[S]$  are the concentrations of monomer, initiator, and solvent, respectively, and  $k$  is the reaction rate constant. This procedure can be used to determine all exponents like  $n_1$ ,  $n_2$ , and  $n_3$ . From the calculation, it was found that the



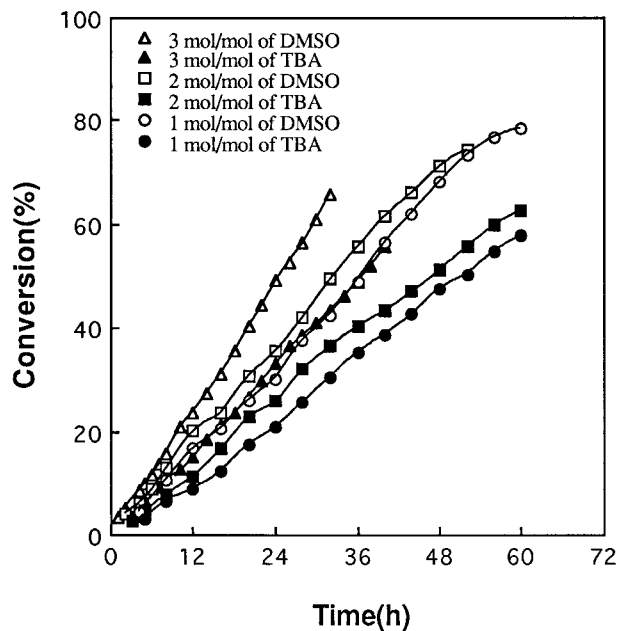
**Figure 2** Conversion of VPI into PVPi using VPI concentration of 3 mol/mol of solvent and ADMVN concentration of 0.00003 mol/mol of VPI with polymerization time.

polymerization rates of VPI in TBA and in DMSO were proportional to the 0.49 and 0.82 powers of ADMVN concentrations, respectively. That is, the polymerization rate of VPI in DMSO was higher than that in TBA. In some accord with general free radical propagation,<sup>27</sup> the polymerization rate in TBA was proportional to  $[\text{ADMVN}]^{0.49}$ . In contrast, in the case of DMSO, there is considerable discrepancy between theoretical (0.5) and experimental (0.82) values. This anomaly with respect to normal kinetic behavior is generally accounted for by assuming that the precipitation of the growing polymers severely restrains bimolecular chain termination and, hence, that the radicals do not reach a stationary concentration. Further, some of the growing chains become buried in the dead polymer, an effect that corresponds kinetically to monomolecular chain termination.<sup>29,30</sup> Therefore, the higher order with respect to ADMVN in the DMSO system (0.82) in this study might be attributed to monomolecular termination involving occlusion of growing chains due to heterogeneous nature of the polymerization of VPI.

The conversion–time plots for temperatures of 25, 35, and 45°C at monomer concentration of 3 mol/mol of solvent and initiator concentration of 0.00003 mol/mol of VPI are illustrated in Figure 2.

The rate of conversion was increased with increasing polymerization temperature, and the rates using TBA were much lower than those using DMSO at all temperatures. At the higher polymerization temperatures of 45 and 35°C, the conversion–time curves had the characteristic sigmoidal shape showing the increase in rate of polymerization with conversion; that is, the rate of conversion was very high in the early stage of polymerization at 45 and 35°C, but the ultimate conversion was lower in both cases. At 25°C, the conversion of TBA system linearly increased without any abrupt changes in the slope. This result might be explained by smaller heating effects during polymerization at lower polymerization temperature using ADMVN. High ultimate conversions (55–83%) were obtained at all ADMVN concentrations, compared with the case of bulk polymerization of VPI using ADMVN at 25°C (22–36%). This result explains the fact that solution polymerization temperature of 25°C by ADMVN is a useful one for producing PVPi with high yield.

The effect of monomer concentration on the conversion of VPI into PVPi polymerized in TBA and in DMSO at 25°C using ADMVN at 0.00003 mol/mol of VPI is shown in Figure 3. In all conditions, the conversion of the DMSO system was higher than that of the TBA system. At higher

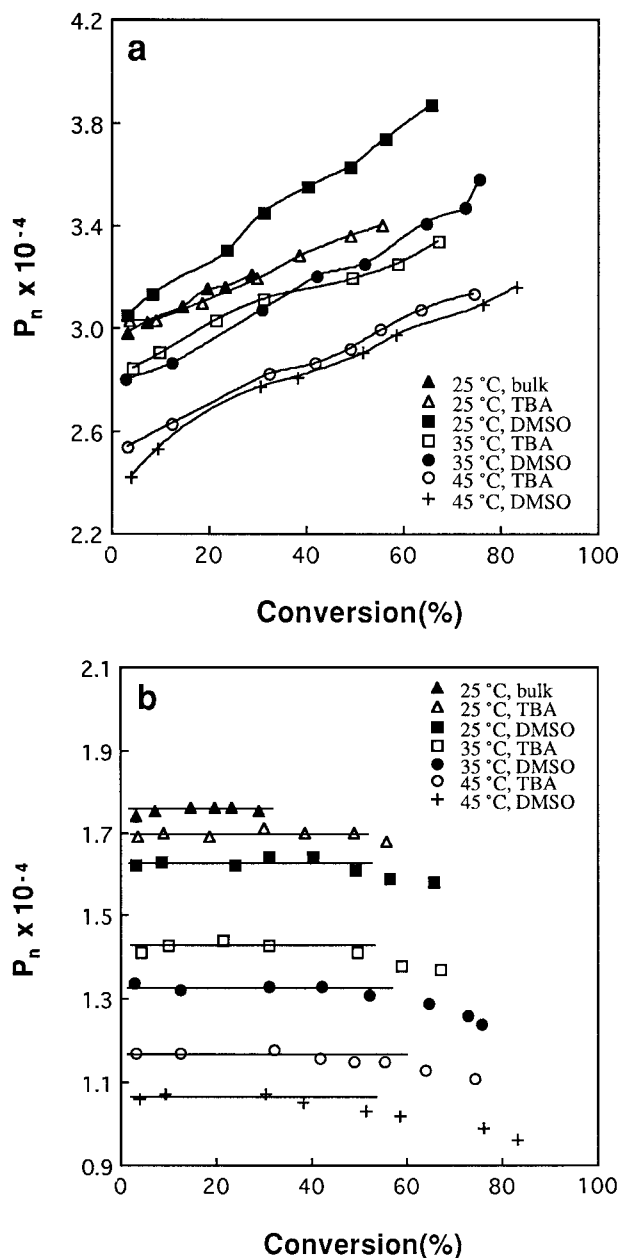


**Figure 3** Conversion of VPI into PVPi polymerized at 25°C using ADMVN concentration of 0.00003 mol/mol of VPI with polymerization time.

monomer concentration, the radicals generated from the initiator largely attack the double bonds of monomer molecules that possess high electron density. Conclusively, a higher rate of polymerization results. It has been known that, in the case of solution polymerization of VPi, it is very difficult to control the process if the monomer concentration is high because the excessive polymerization exotherm accelerates the polymerization. This fact indicates that autoacceleration may lead to excessive chain transfer during polymerization if the monomer concentration is high. However, the results in Figure 3 show that such autoacceleration seems not to be so noticeable during the low-temperature polymerization of VPi in TBA and DMSO using ADMVN. This result is indicative of suppression of irregular chain transfer reaction during polymerization. In contrast, the rate of polymerization may be decreased at lower monomer concentrations.

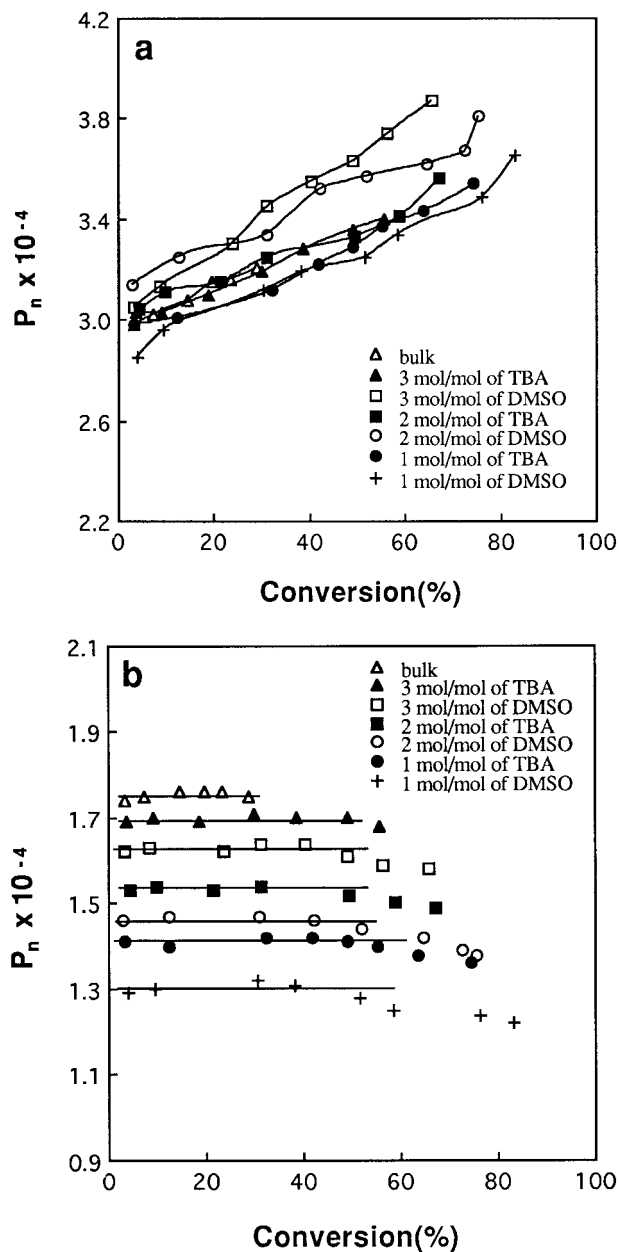
#### Molecular Weight and Degree of Branching

The  $P_n$ s of PVPi polymerized in bulk, in TBA, and in DMSO and corresponding PVA obtained by saponifying PVPi with conversions are shown in Figures 4 and 5. The temperature effect is shown in Figure 4 and the monomer concentration effect is shown in Figure 5. The difference between the  $P_n$ s of PVPi and PVA is mostly obliged to branched structures, which may be broken down when saponified. It is interesting to see that the  $P_n$  of PVA remained almost constant up to  $\sim 45$ – $55\%$  conversions and nearly independent of the  $P_n$  of PVPi, and then the  $P_n$  of PVA decreased slightly at higher conversion of  $> 44$ – $55\%$ . This result was attributed to the frequent chain transfer reactions between polymers, resulting in termination and branch formation reactions at higher conversions, whereas chain transfer reactions between monomers prevail at lower conversions. The  $P_n$  of PVA was increased with a decrease in the polymerization temperature or the solvent concentration. In addition, the  $P_n$  of PVA by the TBA system was much higher than that by the DMSO system at all polymerization conditions (see Figures 4 and 5). This result was due to a lower polymerization rate of TBA system. UHMW (PVA)s with various  $P_n$ s of 13,500–17,000 could be prepared by saponifying UHMW PVPi polymers with  $P_n$ 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  $25^\circ\text{C}$  at conversion of  $\sim 55\%$  using



**Figure 4**  $P_n$  values of PVPi polymerized using VPi concentration of 3 mol/mol of solvent and ADMVN concentration of 0.00003 mol/mol of VPi (a) and resulting PVA with conversion (b).

an ADMVN concentration of 0.00003 mol/mol of VPi, which is comparable to a  $P_n$  of PVA (17,500) from PVPi by bulk polymerization using the same polymerization conditions (conversion:  $\sim 29\%$ ). 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  $25^\circ\text{C}$  at conversion of  $\sim 65\%$  using minimum ADMVN concentration of

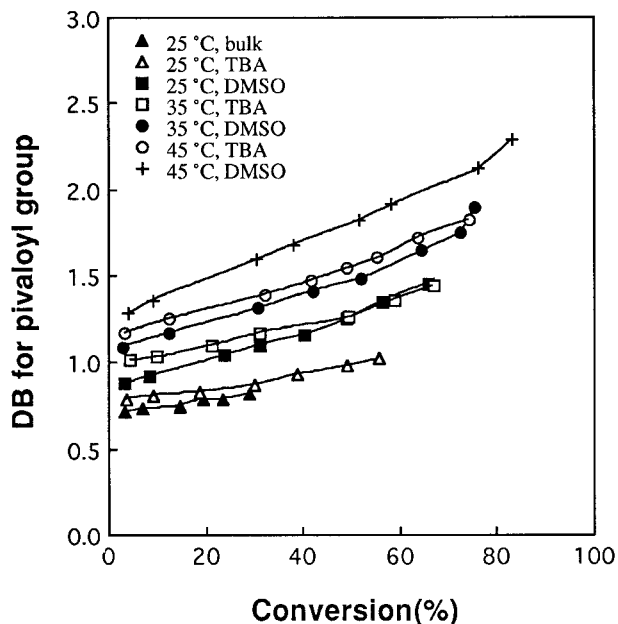


**Figure 5**  $P_n$  values of PVA polymerized at 25°C using ADMVN concentration of 0.0003 mol/mol of VPi (a) and resulting PVA with conversion (b).

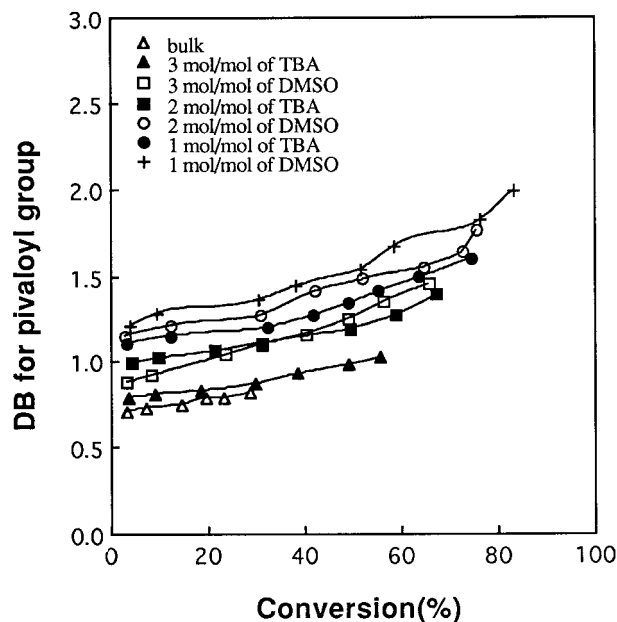
0.00003 mol/mol of VPi. Therefore, it can be concluded that the solution polymerization of VPi at 25°C using low temperature initiator ADMVN and TBA and DMSO with low chain transfer constants is an effective method to increase both yield and molecular weight at the same time.

As a rule, the difference between the  $P_n$ s of PVPi and PVA is due to a branched structure. In this study, the effect of conversion, polymeriza-

tion temperature, and type and amount of solvent on the DB pivaloyl group of PVPi was investigated. The variation of DB for the pivaloyl group of PVPi polymerized at three different temperatures with conversion is shown in Figure 6. DB increased with an increase in the conversion for all the cases. In addition, the rate of increasing DB with conversion was decreased as the polymerization temperature was lowered. At the high polymerization temperatures, the accelerated polymerization reaction may bring about a chain transfer (branching) reaction more easily. Also, the rate of increasing DB with conversion of TBA system was much lower than that of DMSO system. This result might be ascribed to a polymerization rate difference between the two solvents. From the fact that the DB of PVPi polymerized at 25°C in TBA was a very low value of  $< 1$ , it was identified that the low temperature solution polymerization of VPi using ADMVN and TBA produced PVPi with high linearity. The monomer concentration effect is presented in Figure 7. As VPi concentration was increased, the DB was decreased in all cases. This result is explained by increasing chain transfer reaction with an increase in the solvent concentration.



**Figure 6** DB for the pivaloyl group of PVPi polymerized using VPi concentration of 3 mol/mol of solvent and ADMVN concentration of 0.00003 mol/mol of VPi (a) and resulting PVA with conversion (b).



**Figure 7** DB for the pivaloyl group of PVPi polymerized at 25°C using ADMVN concentration of 0.00003 mol/mol of VPi (a) and resulting PVA with conversion (b).

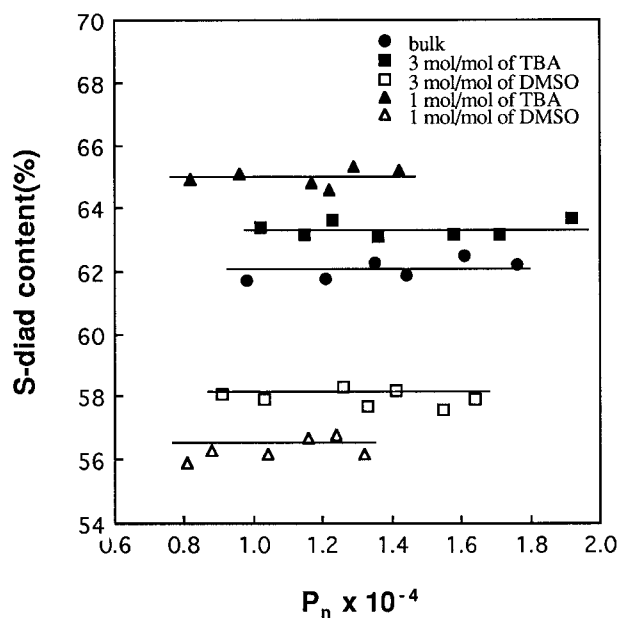
### Characteristics of PVA Saponified

The saponification of PVPi<sup>3,6,22-24</sup> or PVPi/PVAc<sup>23</sup> 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.<sup>23</sup> 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.<sup>31,32</sup> investigated the effect of 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, syn-

diotactic configuration is favored when alcohol is used as a solvent.<sup>31,32</sup> The effect of solvent on the syndiotacticity of PVA is depicted in Figure 8. PVPi and resulting PVA were sampled at similar conversions of ~ 30% to clarify the solvent effects only. As expected, TBA, 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. S-diad content seems not to have a close relationship with molecular weight of PVA.

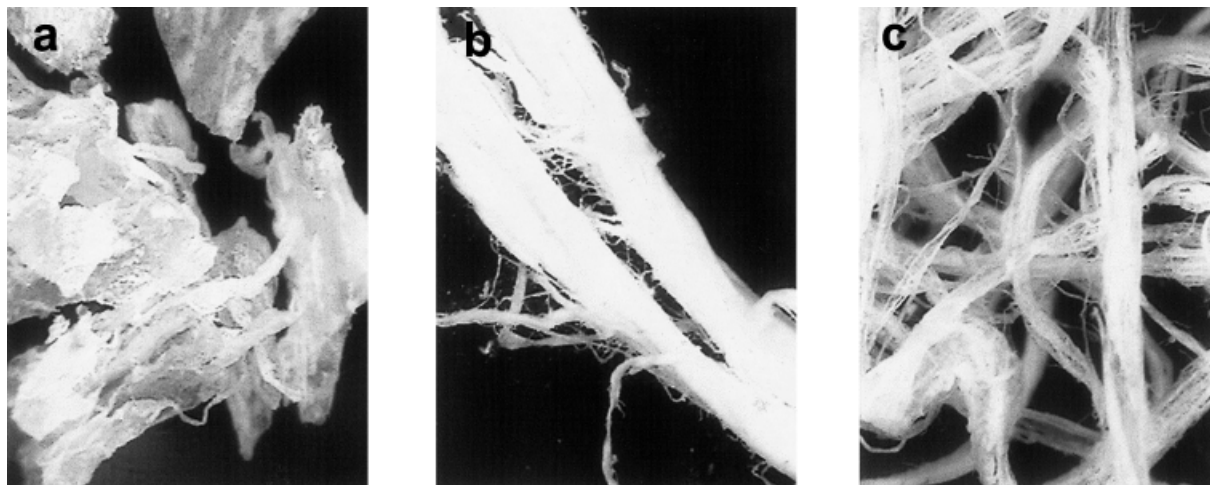
From the morphological point of view, the role of solvent is obvious. The optical micrographs of PVA obtained by the saponification of PVPi polymerized in DMSO, bulk, and TBA are illustrated in Figure 9. Three specimens had similar  $P_n$  of ~ 12,000 and different syndiotacticities. In the case of DMSO, 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.

The SAXS patterns of those PVAs are shown in Figure 10. No scattering in small angle region



**Figure 8** S-diad content of PVA from PVPi polymerized in bulk, TBA, and DMSO, respectively, with  $P_n$  of PVA.





**Figure 9** Optical micrographs ( $\times 100$ ) of PVA from PVPi polymers polymerized in (a) DMSO, (b) bulk, and (c) TBA. S-diad content and  $P_n$  are, respectively, (a) 56.8% and 12,400; (b) 61.8% and 12,100; and (c) 65.1% and 11,700.

was found for the PVA obtained by 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 result is related to 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, the diamond-shaped scattering and the strong line scattering are observed in SAXS patterns of ramie and bamboo fibers, respectively.<sup>33,34</sup> As seen in Figure 11, a WAXD pattern representing a high degree of crystal orientation of 0.9 was found when TBA was used, whereas 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.

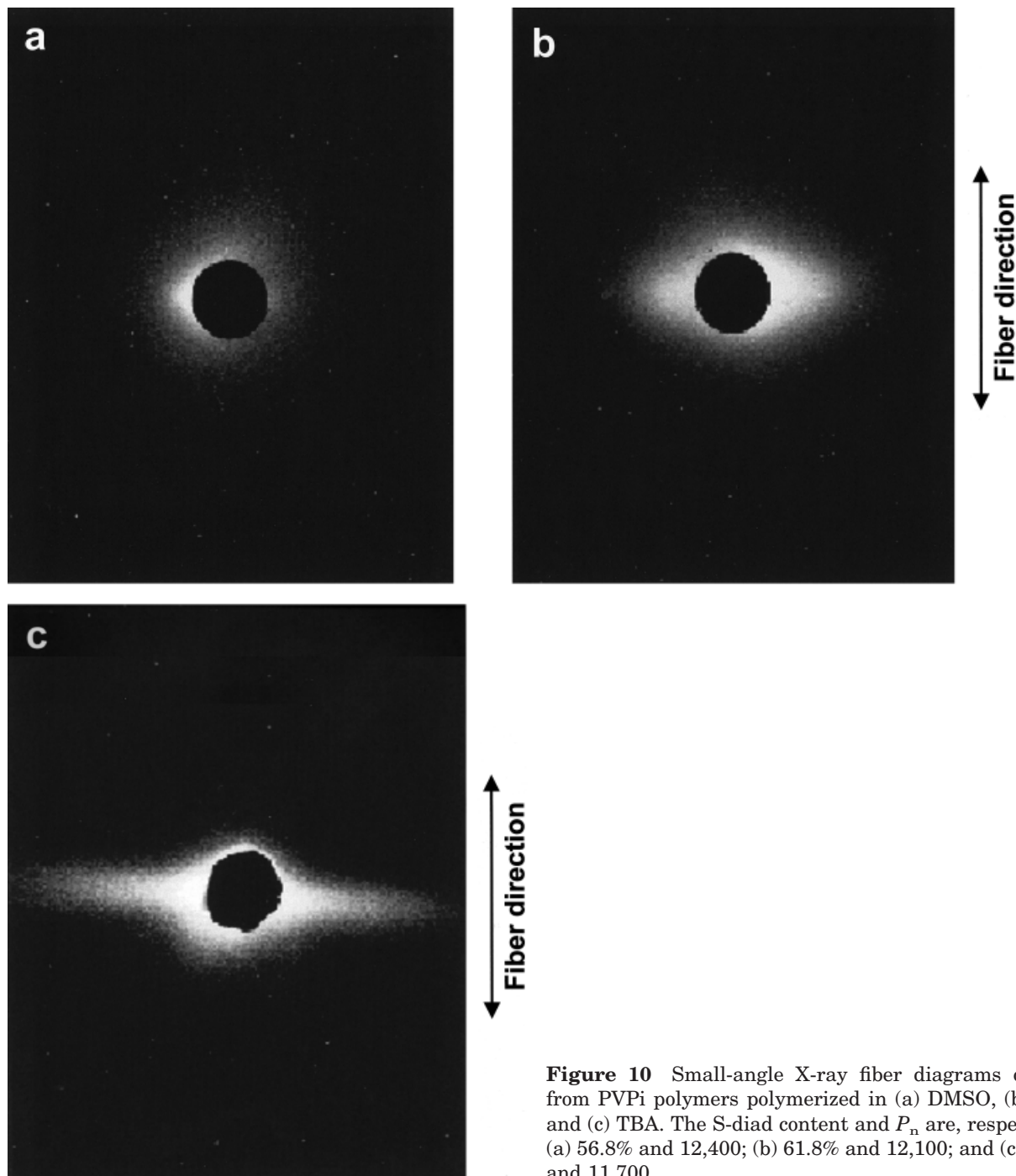
## CONCLUSIONS

To obtain UHMW PVPi with high syndiotacticity and high conversion for a precursor of UHMW syndiotactic PVA, VPi was solution polymerized using a low temperature initiator, ADMVN, and low chain transfer constants, TBA and DMSO, at 25, 35, and 45°C. It is very difficult task to obtain

UHMW PVPi with high conversion, a precursor of UHMW syndiotactic PVA, by free radical polymerization initiated with azobisisobutyronitrile or benzoyl peroxide in bulk because of polymerization exotherm, high viscosity, and chain branching during polymerization of VPi. However, ADMVN and TBA seem to be advantageous in lowering polymerization temperature to  $\sim 25^\circ\text{C}$  and in suppressing chain transfer reaction, respectively. In summary, ADMVN is more effective in preparing UHMW PVA with high syndiotacticity. Furthermore, solution polymerization is a powerful method for enhancing conversion.

Through a series of calculation using initial rate method, it was found that the solution polymerization rates of VPi at  $25^\circ\text{C}$  in TBA and in DMSO were proportional to the exponent 0.49 and 0.82 of ADMVN concentrations, respectively. At the same polymerization conditions, TBA was clearly superior to DMSO in increasing molecular weight of PVA. On the other hand, TBA was inferior to DMSO in causing conversion to polymer, indicating that the initiation rate of VPi in TBA was lower than that in DMSO. These effects could be explained by a kinetic order of ADMVN concentration calculated by initial rate method and by an activation energy difference of polymerization from the Arrhenius plot.

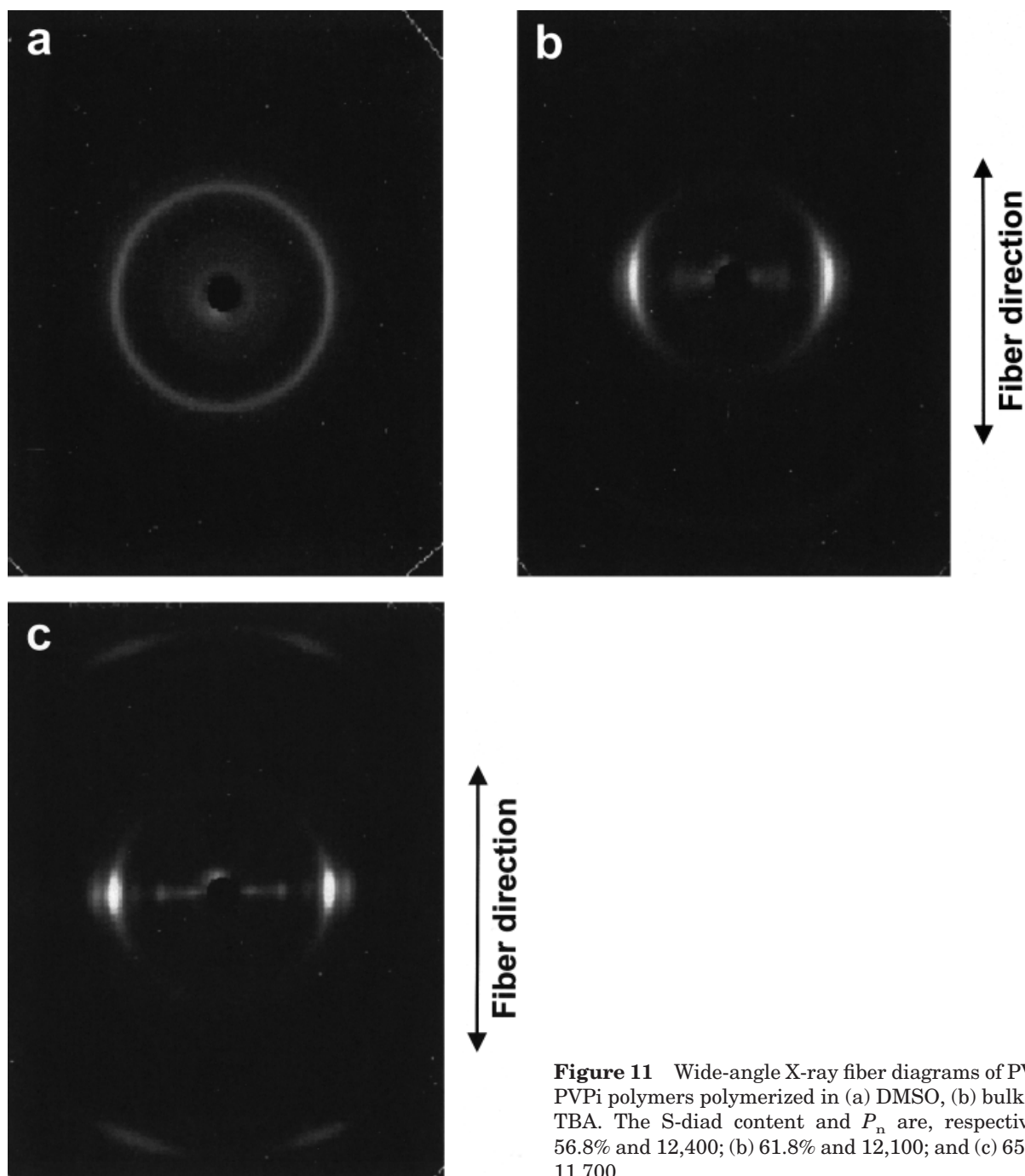
Solution polymerization of VPi at  $25^\circ\text{C}$  by ADMVN and saponification produced UHMW syndiotactic PVA with  $P_n$  of 13,000–17,000 and with maximum conversion of VPi into PVPi of 55–83% with diminishing heat generated during polymer-



**Figure 10** Small-angle X-ray fiber diagrams of PVA from PVPi polymers polymerized in (a) DMSO, (b) bulk, and (c) TBA. The S-diad content and  $P_n$  are, respectively: (a) 56.8% and 12,400; (b) 61.8% and 12,100; and (c) 65.1% and 11,700.

ization. This result compares well with the bulk polymerization of VPi at 25°C using ADMVN which has a  $P_n$  of 14,000–17,500 and a maximum conversion of ~22–36%. The  $P_n$  and syndiotacticity were higher and DB was lower with PVA from PVPi at polymerized at lower temperatures in TBA (DB of < 1 at 25°C). Syndiotactic configuration was favored when TBA was used because of

the hydrogen-bonding interaction between the solvent molecules and pivaloyl groups. In contrast, in the case of DMSO, the 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.



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

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 used as a high-performance replacement material for natural carcinogenic asbestos fiber, reinforcing fiber,

water-soluble fiber for nonwoven fabric, ultra-low denier fiber, embolic fiber for cancer-cell killing, and pulp for paper-based product because of its high tensile strength, high tensile modulus, high fineness, excellent alkali and chemical resistance, good biocompatibility, and good binding property.<sup>1-3,7</sup> In the near future, we will report on the low-temperatures solution polymerization of VPi

using other solvent systems for producing stereoregular PVA microfibrils to maximize syndiotacticity, molecular weight, and yield.

This work was supported by Korea Research Foundation Grant (KRF-2000-041-E00417).

## REFERENCES

- Masuda, M. In *Polyvinyl Alcohol—Developments*; Finch, C. A., Ed.; John Wiley and Sons: New York, 1991; pp. 403–422, 711.
- Sakurada, I. In *Polyvinyl Alcohol Fibers*; Lewin, M., Ed.; Marcel Dekker: New York, 1985; pp. 3–9, 361–386.
- Lyoo, W. S.; Ha, W. S. *Polymer* 1996, 37, 3121.
- Cho, J. D.; Lyoo, W. S. Chvalun, S. N.; Blackwell, J. *Macromolecules* 1999, 32, 6236.
- Choi, J. H.; Lyoo, W. S.; Ko, S. W. *Macromol Chem Phys* 1999, 200, 1421.
- Lyoo, W. S.; Ha, W. S. *Polymer* 1999, 40, 497.
- Lyoo, W. S.; Kim, B. C.; Ha, W. S. *Polym J* 1997, 30, 424.
- Lyoo, W. S.; Yeum, J. H.; Chim, H. D.; Ji, B. C.; Yoon, W. S.; Kim, J. P. Ha, J. *Korean Fiber Soc* 2000, 37, 487.
- Lyoo, W. S.; Kim, B. C.; Ha, W. S. *Polym Eng Sci* 1997, 37, 1259.
- Choi, J. H.; Cho, Y. W.; Ha, W. S.; Lyoo, W. S.; Lee, C. J.; Ji, B. C.; Han, S. S.; Yoon, W. S. *Polym Int* 1998, 47, 237.
- Lyoo, W. S.; Han, S. S.; Choi, J. H.; Cho, W. W.; Ha, W. S. *J Korean Fiber Soc* 1995, 32, 1023.
- Lyoo, W. S.; Han, S. S.; Yoon, W. S.; Ji, B. C.; Lee, J.; Cho, W. W.; Choi, J. H.; Ha, W. S. *J Appl Polym Sci* 2000, 77, 123.
- Kinoshita, A.; Yamada, K.; Ito, M.; Yamasaki, M.; Taneda, M.; Hayakawa, T. *Neuroradiology* 1994, 36, 65.
- Rozenberg, M. E.; Nikitina, S. G.; Khvatova, G. I. U.U.S.R. Pat. 594124, 1978.
- Wu, T. C.; West, J. C. U.S. Pat. 4463138, 1982.
- Kamiake, K.; Ueda, F. Japan Pat. 62-064807, 1987.
- Lyoo, W. S.; Ha, W. S. *J Korean Fiber Soc* 1996, 33, 156.
- Lyoo, W. S.; Kim, B. C.; Lee, C. J.; Ha, W. S. *Eur Polym J* 1997, 33, 785.
- Kim, S. G.; Lee, W. S.; Jo, S. M.; Kim, B. C.; Lyoo, W. S.; Han, J. R. *J Korean Fiber Soc* 1999, 36, 354.
- Lyoo, W. S.; Kwark, Y. J.; Ha, W. S. *J Korean Fiber Soc* 1996, 33, 321.
- Lyoo, W. S.; Kim, B. J.; Ha, W. S. *J Korean Fiber Soc* 1996, 33, 231.
- Lyoo, W. S.; Ha, W. S. *J Polym Sci, Polym Chem Ed* 1997, 35, 55.
- Lyoo, W. S.; Blackwell, J.; Chim, H. D. *Macromolecules* 1998, 31, 4253–4259.
- Ha, W. S.; Lyoo, W. S.; Choi, Y. G. US Patent 2000, 6124033.
- Kurata, M.; Tsunashima, Y. In *Polymer Handbook*; Brandrup, J.; Immergut, E.H., Eds.; John Wiley and Sons: New York, 1989; 3rd ed., p. VII/13.
- Nakajima, I. *Kobunshi Kagaku* 1954, 11, 142.
- Odian, G. In *Principles of Polymerization*; John Wiley and Sons: New York, 1981, pp. 179–318.
- Cox, B.G. In *Modern Liquid Phase Kinetics*; Oxford University Press: Oxford, 1994.
- Bamford, C. H.; Jenkins, A. D. *J Polym Sci* 1956, 20, 405.
- Bern's, A.; Board, M. *J Polym Sci* 1960, 48, 167.
- Imai, K.; Shimmy, T.; Ode, N.; Stoke, H. *J Polym Sci, Polym Chem Ed* 1986, 24, 3225.
- Imai, K.; Shimmy, T.; Tesuque, Y.; Kiwanis, T.; Jin, T. *J Polym Sci, Polym Chem Ed* 1988, 26, 1962.
- Kissing, H. *Colloid-ZZ* 1957, 152, 62.
- Stratton, W.O. *J Polym Sci* 1962, 58, 205.