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Low-temperature suspension polymerization of vinyl pivalate for the preparation of syndiotacticity-rich ultrahigh molecular weight poly(vinyl alcohol) microfibrils with high yield

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Abstract To prepare ultrahigh molecular weight (UHMW) poly(vinyl pivalate) (PVPi) with high conversion and high linearity for a precursor of syndiotacticity-rich UHMW poly(vinyl alcohol) (PVA), vinyl pivalate (VPi) was suspension polymerized using a low-temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN), and the effects of polymerization conditions on the polymerization behavior and molecular structures of PVPi and PVA prepared by saponifying PVPi were investigated. Suspension polymerization was slightly inferior to bulk polymerization in increasing the molecular weight of PVA. In contrast, the former was superior in increasing the conversion of the polymer. Suspension polymerization of VPi at 25 °C by controlling various polymerization factors proved to be successful in obtaining PVA of UHMW (number-average degree of polymerization (P_n): 14,700–16,700), high syndiotactic diad content (62%), and of high yield (ultimate conversion of VPi into PVPi: 85–90%). In the case of bulk polymerization of VPi under the same conditions, maximum P_n, conversion of 15,800–17,000, and 25–35% were obtained, respectively. The degree of branching was lower and the P_n and syndiotacticity were higher with PVA prepared from PVPi polymerized at lower temperatures. All PVAs from PVPi suspension-polymerized at 25 °C were fibrous, with a high degree of crystallinity and orientation of the crystallites.

Keywords UHMW · PVPi · Syndiotacticity-rich · PVA · VPi · Suspension polymerization · High yield · Fibrous

Introduction

Poly(vinyl alcohol) (PVA) obtained by the saponification of poly(vinyl ester) such as poly(vinyl acetate) (PVAc) or poly(vinyl pivalate) (PVPi) is a linear semicrystalline polymer, which has been widely used as a fiber for clothes and industries, films, membranes, medicines for drug delivery system, and cancer cell-killing embolic materials [1, 2, 3]. PVA fibers and films have high tensile and compressive strengths, high tensile modulus, and good abrasion resistance due to their highest crystalline lattice modulus. To maximize these physical properties, molecular weight, degree of saponification, and syndiotacticity should be increased [4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. To increase molecular weight, which is a fundamental factor affecting physical properties, improvement of polymerization methods of vinyl acetate (VAc) [18, 19, 20, 21, 22, 23, 24, 25, 26] is especially necessary. To raise the syndiotacticity as well as molecular weight of PVA, various other vinyl ester monomers such as vinyl pivalate (VPi) [27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37] which reveals strong steric effects of the *t*-butyl group have been used.

Generally, in the bulk polymerization of VPi, ultra-high molecular weight (UHMW) PVPi and PVA can be obtained, but it is very difficult to control the viscosity of the reaction mixture. Thus, UHMW PVPi with high conversion is hardly obtained at the same time [27, 32]. Lyoo et al. synthesized UHMW PVA with a maximum number-average degree of polymerization (P_n) of over 18,000 and syndiotactic diad (S-diad) content of over 64% through ultraviolet ray (UV)-initiated low-temperature-bulk polymerization of VPi [30]. But, as described above, in the bulk polymerization of VPi, it is so difficult to increase the conversion of the precursor of PVA that the resultant UHMW PVA with high yield is hardly obtained.

To reduce the polymerization heat and the viscosity of the medium, solution polymerization of VPi was tried. Although relatively higher conversion of VPi into PVPi was obtained than in bulk polymerization, it is nearly impossible to obtain UHMW PVPi with conversion of over 80% owing to the high viscosity of reaction solution [33]. It was known that molecular weight and polymerization rate were increased simultaneously by emulsion polymerization of VPi. However, because side chain formation reactions due to a higher propagation rate of VPi in the emulsion system result in branched HMW PVPi, it is nearly impossible to produce syndiotacticity-rich UHMW PVA from PVPi by saponification reaction [31].

The mechanism of suspension polymerization in droplets is basically identical to that of bulk polymerization [38], and water in the polymerization reaction solution diminishes polymerization exothermic heat and prevents viscosity enhancement during polymerization [39]. Owing to these advantages, suspension polymerization of VPi has a possibility of producing UHMW PVPi with the highest conversion, which is a precursor of syndiotacticity-rich UHMW PVA.

It is well known that the molecular weight of polymer prepared by the suspension polymerization method is controlled by the type and amount of initiator and suspending agent, the polymerization temperature, the monomer to water ratio, and the agitation speed. It was known that the higher the agitation speed, the higher the molecular weight and the conversion [39, 40, 41]. Compared to the rareness of the study regarding the suspension polymerization of VPi, there has been much research conducted on the suspension polymerization of VAc [42, 43]. Bravar et al. [44] synthesized PVAc with molecular weight of over 1,500,000 by using sodium salt of styrene/maleic acid copolymer as a suspending agent. Gunesch and Schneider [45] reported that the molecular weight of PVAc was increased at lower initiator content and at higher agitation rate, which was concluded by determining polymerization heat and polymerization rate calculated by measuring the heat absorbed in water during suspension polymerization of VAc. Collins [46] prepared PVAc with 50% conversion polymerized at 80 °C by using tragacanth gum and benzoyl peroxide (BPO) as suspending agent and initiator, respectively. Wilson [47] utilized Arabic gum as a suspending agent and $FeCl_3.6\ H_2O$ and hydrogen peroxide as initiators at a polymerization temperature of 85–95 °C to reach conversion of 54–55%. Schouteden and Tristmans [48] polymerized VAc at 50–90 °C by using methyl ether cellulose and BPO as a suspending agent and an initiator, respectively.

These polymerizations, however, were conducted at a polymerization temperature of over 50 °C. In these cases, branch formation in PVAc results in the decrease of molecular weight of the resulting PVA due to a higher polymerization temperature of over 50 °C. Moreover, polymerization at a temperature below 40 °C was only possible by the use of UV or γ-ray radiation methods accompanied by a complicated polymerization apparatus [22, 30]. Redox systems have been explored in the lower temperature polymerization of VAc and VPi to produce HMW PVA [31, 49]. However, discoloration and low polymerization efficiency are two common deficiencies of redox systems. We utilized the low-temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) in the polymerization of VAc and VPi, which can lower the polymerization temperature to room temperature [18, 19, 25, 27, 32, 33].

Recently, Lyoo et al. [16, 27, 29, 30, 37] have found that a PVA fiber of well-oriented microfibrillar structure, similar to a natural cellulose fiber, is formed during saponification of PVPi to PVA. This has proved to be the case only for the saponification process of HMW PVPi with a high S-diad content of 58–65% prepared by low-temperature bulk and solution polymerizations 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 [27, 29, 30, 37]. 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 below 100 s^{-1}). In addition, these microfibrillar PVA fibers are very similar to natural asbestos fibers in structure and physical properties [16, 27, 37]. However, despite omitting spinning, drawing, and heat treatment in the PVA fiber preparation, in the case of UV-initiation system of VPi, it is nearly impossible to be commercialized because of very high cost.

In this study, ADMVN, which can lower the polymerization temperature to room temperature [18, 19, 25, 27, 32, 33] was selected in suspension polymerization of VPi to obtain UHMW PVPi with the highest conversions, which is expected to be a profitable precursor of syndiotacticity-rich UHMW PVA microfibrillar fiber. The effect of suspension polymerization conditions on the polymerization behavior of VPi and molecular parameters of PVPi and PVA such as molecular weight, degree of branching (DB), and stereoregularity were examined.

Experimental

Materials

VPi purchased from Shin-Etsu was washed with an aqueous solution of $NaHSO_3$ and water and dried over anhydrous $CaCl_2$, followed by distillation under a reduced pressure of nitrogen. The initiator ADMVN (Wako Co., 99%) was recrystallized twice from absolute methanol before use. PVA with number-average molecular weight of 127,000 and degree of saponification of 88% (Aldrich Co.) was used as a suspending agent. Other extra-pure grade reagents were used without further purification. Water used for total procedures was deionized.

Suspension polymerization of VPi

In a typical reaction, suspending agent was dissolved in water under a nitrogen atmosphere with constant stirring in a 250 mL reactor fitted with a condenser. After degassing, VPi monomer and the ADMVN were added at once at a fixed polymerization temperature. After predetermined times, the reaction mixture was cooled and kept for one day to separate and to sink spherical PVPi particles (Fig. 1a). To eliminate residual VPi and suspending agent, PVPi polymerized was filtered and washed with warm water and methanol. Conversion was calculated by measuring the weight of the polymer. Conversions were averages of three determinations. The detailed polymerization conditions are listed in Table 1.

Bulk polymerization of VPi [27, 32]

VPi was poured into a 250 mL three-necked round bottom flask and flushed with nitrogen. At the predetermined polymerization temperature, ADMVN was added to the monomer. After predetermined times, the unreacted monomer was distilled out. PVPi was purified by reprecipitation from acetone/*n*-hexane. Conversion was calculated by using the same method adopted in the suspension polymerization.

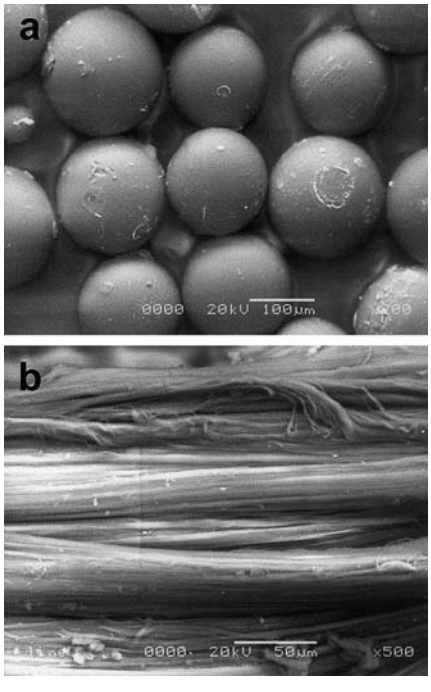

Fig. 1a,b Scanning electron micrographs of PVPi microspheres suspension polymerized at 25 °C (**a**) and PVA microfibrils prepared by the saponification of PVPi (**b**)

Table 1 Molecular parameters of PVA microfibrils from PVPi prepared by suspension polymerization of VPi

Polymerization temperature (°C)	P_n	S-diad content (%)	DS (%)[a]	T_m (°C)[a]
25	16,000	61.4	99.9	243.3
25	15,300	61.7	99.9	243.3
25	14,800	61.2	99.9	244.1
25	12,400	61.7	99.9	244.2
45	12,200	58.2	99.9	240.2
45	11,100	58.9	99.9	240.7
45	10,600	58.8	99.9	240.3
45	9,800	58.3	99.9	239.9

[a]DS and T_m are degree of saponification and crystal melting temperature (2nd heating) of PVA, respectively

Saponification and in situ fibrillation of PVPi

The following is a typical example of PVA fibrillation experiments [16, 29, 37]. 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. 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 of saponification agent/PVPi solution was 0.05–0.25 (*v*/*v*). The alkali solution was added to the PVPi solution while being stirred at 50–60 °C. After the saponification reaction had been completed, the solid saponification product was beaten mechanically, filtered, and washed several times with methanol. A quantitative yield of PVA microfibrils (Fig. 1b) was obtained. Residual ester groups could not be detected in the proton nuclear magnetic resonance (^{1}H NMR) spectra of these specimens.

Acetylation of PVA [50]

A mixture of 1 g of PVA, 2 mL of pyridine, 20 mL of acetic anhydride, and 20 mL of acetic acid was stirred in a three-necked flask at 100 °C for 100 h under an atmosphere of nitrogen. The mixture was then poured into cold water to precipitate PVAc. PVAc thus produced was filtered and purified by repeating the reprecipitation from methanol and water.

Characterizations

The molecular weights of PVPi were calculated using Eq. (1) [51].

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

where $[\eta]$ is the intrinsic viscosity of PVPi and M_n is the number-average molecular weight of PVPi. In contrast, the molecular weight of PVA was determined from that of PVAc produced by acetylating PVA by using Eq. (2) [52].

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

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

The DB for the pivaloyl group of PVPi is calculated by Eq. (3) [3, 30],

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

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

The S-diad contents of the PVAs were determined by 300 MHz ^{1}H NMR spectroscopy in DMSO-d_6, based on the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm. The degree of saponification of PVA was determined by weight loss after saponification and by the ratio of methyl and methylene proton peaks in the ^{1}H NMR spectrum.

The crystal melting temperature (T_m) was 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^{-1}.

The surface morphologies of the PVPi and PVA specimens were investigated using a scanning electron microscope (JSM 5800-LV, JEOL, Japan) with a magnification of 200× and 500×, respectively.

Results and discussion

Suspension polymerization behavior of VPi

Generally, in a free radical polymerization, the rate of conversion is increased with an increase in the initiator concentration as depicted by Eq. (4) [53],

$$P_{eq} = 1 - \exp\left(-2k_p(f[\mathrm{I}]/k_i k_t)^{1/2}\right) \quad (4)$$

where P_{eq}, f, [I], k, k_p, and k_t are conversion at the equilibrium of polymerization, initiator efficiency, concentration of initiator, and reaction rate constants of initiation, propagation, and termination, respectively. Effect of ADMVN concentration on the conversion of VPi into PVPi suspension-polymerized at 25 °C are shown in Fig. 2. It was shown that the greater the initiator concentration, the higher the polymerization rate. That is, the conversion rate was increased as the initiator concentration was increased, which coincided well with the theoretical predictions in Eq. (4). High ultimate conversions (85–90%) were obtained at all ADMVN concentrations. This explains the fact that suspension polymerization at 25 °C by ADMVN is useful for producing PVPi with high yield.

Figure 3 illustrates conversion-time histories of suspension and bulk polymerizations for temperature levels of 25, 35, and 45 °C. The rate of conversion was increased with increasing polymerization temperature, and the conversion rates of suspension polymerization were higher than those of bulk polymerization at all polymerization temperatures. In the case of bulk polymerization of VPi, the conversion-time curves had the characteristic sigmoidal shape showing the acceleration in rate of polymerization with conversion at the higher polymerization temperatures of 45 and 35 °C. That is, the rate of conversion was high at the early stage of polymerization at 45 and 35 °C, but the ultimate conversion was lower. These features were clearly observed

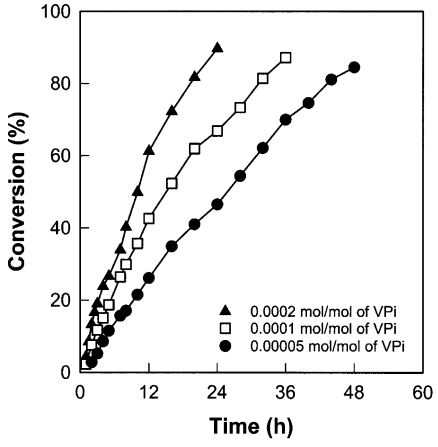

Fig. 2 Conversion of VPi into PVPi suspension polymerized at 25 °C using suspending agent concentration of 1.5 g dL^{-1} water, VPi/water of 0.5 L L^{-1}, and agitation speed of 500 rpm with polymerization times

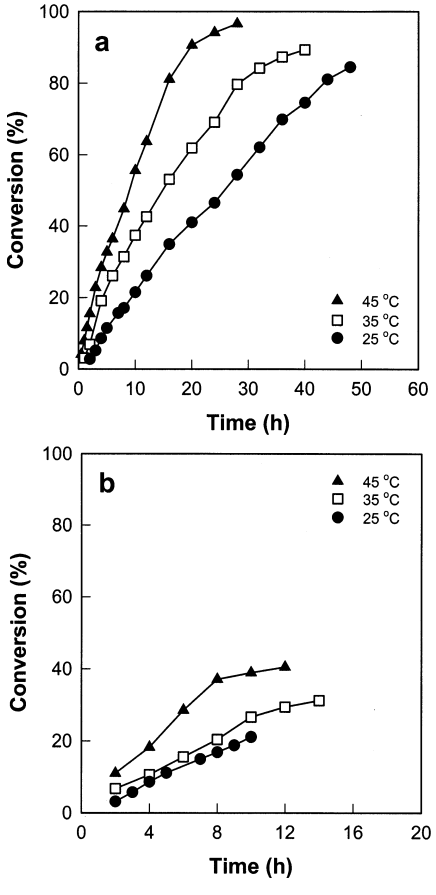

Fig. 3a,b Conversions of VPi into PVPi suspension polymerized using ADMVN concentration of 0.00005 mol mol^{-1} VPi, suspending agent concentration of 1.5 g dL^{-1} water, VPi/water of 0.5 L L^{-1}, and agitation speed of 500 rpm (**a**) and bulk polymerized using ADMVN concentration of 0.00005 mol mol^{-1} VPi (**b**) with polymerization times

in BPO- or azobisisobutyronitrile (AIBN)-initiated free radical polymerization of VPi above 45 °C. In contrast, at 25 °C, the conversion was linearly increased without any abrupt changes in the slope. This might be explained by diminishing heat generated during polymerization at lower polymerization temperature by ADMVN. But the ultimate conversion was low due to a viscosity increase by forming UHMW PVPi molecules. In contrast, in the case of suspension polymerization, the conversions at 25 °C increased linearly up to 85% in spite of a very low ADMVN concentration of 0.00005 mol mol^{-1} VPi, which was absolutely impossible in bulk polymerization. This can be explained by an advantage of heterogeneous (suspension) polymerization of VPi. Furthermore, autoacceleration described above seems not to be so noticeable in the suspension polymerization of VPi at 25 °C using ADMVN, as shown in Fig. 3a. This is indicative of suppression of irregular chain transfer reaction during polymerization. Below an ADMVN concentration of 0.00005 mol mol^{-1} VPi at a polymerization temperature of 25 °C, effective polymerization could not occur.

Effect of polymerization conditions on molecular weight

In a free radical polymerization process, the kinetic chain length (v) is expressed by Eq. (5) [53].

$$v = k_p[M] \Big/ 2\left(fk_dk_t[\mathrm{I}]^{1/2}\right) \tag{5}$$

Referring to Eq. (5), the degree of polymerization may be decreased as the efficiency and concentration of initiator are increased. P_ns of PVPi prepared by suspension and bulk polymerizations at 25 °C and corresponding PVA obtained by saponifying PVPi with conversions are shown in Fig. 4. Difference between P_ns of PVPi and PVA is mostly due to branched structures, which may be broken down when saponified. It is interesting to see that P_n of PVA remained almost constant up to approximately 40% conversion and nearly independent of P_n of PVPi, and then slightly decreased at higher conversions of over 40–50%. This was attributed to frequent chain transfer reactions between polymers resulting in termination and branch formation reactions at higher conversions, whereas chain transfer reactions between monomers were prevailing at lower ones. In accordance with the theoretical prediction, P_ns of PVPi and PVA were increased with a decrease in the ADMVN concentration in Fig. 4. UHMW PVAs with various P_ns of 14,700–16,700 could be prepared by saponification of UHMW PVPis with P_ns of 27,100–32,300 polymerized in suspension. It should be noted that PVA with P_n of up to 15,900 could be prepared from PVPi suspension-polymerized at a conversion of around 85% by using

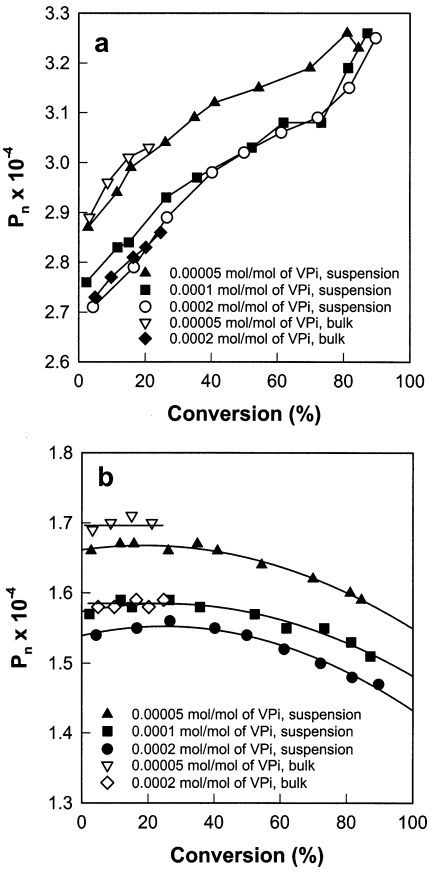

Fig. 4a,b P_ns of PVPi obtained by the suspension polymerization at 25 °C by using suspending agent concentration of 1.5 g dL^{-1} water, VPi/water of 0.5 L L^{-1}, and agitation speed of 500 rpm and by the bulk polymerization at 25 °C (**a**) and resulting PVA (**b**) with conversions

minimum ADMVN concentration of 0.00005 mol mol^{-1} VPi, which is comparable to P_n of PVA (17,000) from PVPi by bulk polymerization using the same polymerization conditions (conversion: ca. 20%). Therefore, it can be concluded that the suspension polymerization of VPi using the low-temperature initiator ADMVN is an effective method to increase both yield and molecular weight at the same time. Figure 5 shows the effect of polymerization temperature on the P_ns of PVPi prepared by suspension and bulk polymerizations and the corresponding PVA obtained by saponification of PVPi. P_n of PVA was increased with a decrease in the polymerization temperature as shown in Fig. 5b. UHMW PVAs with various P_ns of 11,900–16,700 could be prepared by saponification of UHMW PVPis with P_ns of 27,600–43,000 suspension-polymerized at three different temperatures.

Figure 6 presents the effects of various suspension polymerization conditions of VPi on the molecular weights of PVPi and PVA, respectively. PVPi was

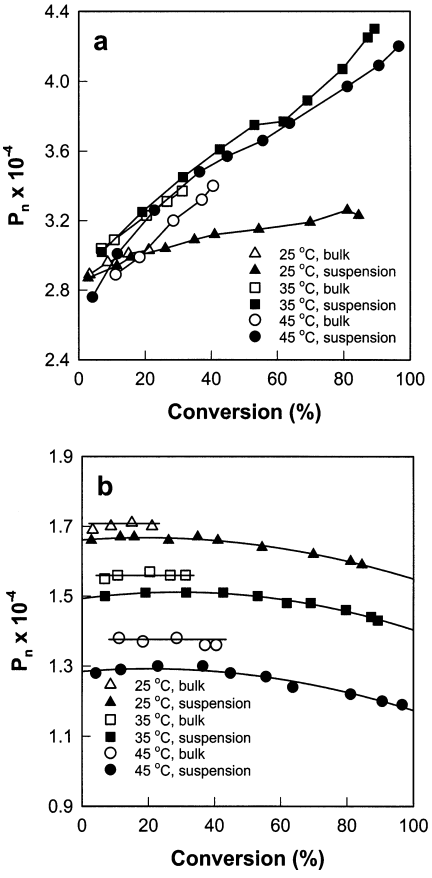

Fig. 5a,b P_ns of PVPi obtained by the suspension polymerization using ADMVN concentration of 0.00005 mol mol^{-1} VPi, suspending agent concentration of 1.5 g dL^{-1} water, VPi/water of 0.5 L L^{-1}, and agitation speed of 500 rpm and by the bulk polymerization using ADMVN concentration of 0.00005 mol mol^{-1} VPi (**a**) and resulting PVA (**b**) with conversion

sampled at a similar conversion of about 80% to precisely clarify the effect of polymerization conditions. Figures 6a and 6b show the effect of concentration of suspending agent. At concentration of 1.5 g dL^{-1} of water, maximum P_ns of PVPi (32,600) and PVA (16,000) were obtained and this tendency was nearly the same irrespective of the ADMVN concentration. Below this concentration, the suspending agent could not make stable dispersions required for the effective suspension polymerization owing to an insufficient concentration. In contrast, at the higher water concentration of 9.0 g dL^{-1}, significant increase of viscosity of the polymerization medium made it difficult to agitate the system. From these results, it was found that the optimum concentration of suspending agent is about 1.5 g dL^{-1} of water in this polymerization of VPi at 25 °C. Figures 6c and 6d are plots of P_ns of PVPi and PVA with VPi/water ratio, which show that the lower the value, the higher the molecular weight (maximum P_n of PVA: 16,100). This might be explained by the fact that the lowered polymerization, termination, and chain transfer rates by an increase ability of water to effectively spread the high exotherm of VPi generated during polymerization and to cool the medium, increased the linearity of PVPi and the molecular weight of PVA. The effect of agitation speed is shown in Figs. 6e and 6f. Molecular weight of both PVPi and PVA increased with an increase in the agitation speed, which coincided well with the results of Gunesch and Schneider [45]. But, above 1200 rpm there was no difference in molecular weight and the highest P_n of PVA was 12,300 at this rpm.

Molecular structure of PVPi and PVA

As a rule, the difference between P_ns of PVPi and PVA is due to a branched structure. In this study, the effect of conversion, polymerization temparature, and ADMVN concentration on the degree of branching of PVPi was investigated. Figure 7 shows variation of DB for the pivaloyl group of PVPi at a suspension polymerization temperature of 25 °C and at three different ADMVN concentrations with conversion. As might be imagined, DB was increased with increasing conversion for all the cases. Furthermore, the rate of increasing DB with conversion was decreased as ADMVN concentration was lowered. Figure 8 presents the suspension polymerization temperature effect on the DB. It was shown that DB value was increased with an increase in the polymerization temperature. This may be ascribed to the fact that at higher polymerization temperatures, the accelerated polymerization reaction may bring about a chain transfer (branching) reaction more easily.

As described above, Lyoo et al. could directly prepare well-oriented-high strength PVA microfibril through the saponification reaction of HMW PVPi synthesized by the low-temperature bulk and solution polymerizations of VPi. This microfibrils had P_n of 4,500-20,000, degree of saponification of 85.0–99.9%, S-diad content of 58–65%, crystal orientation index of over 0.88, crystallinity of over 48%, and crystal melting temperature (1st heating) higher than 260 °C [16, 27, 29, 30, 37]. Figure 1b is a scanning electron micrograph of PVA with a P_n of 10,600 and S-diad content of 58.8% prepared by the saponification of PVPi polymerized at 45 °C using an ADMVN concentration of 0.0002 mol mol^{-1} VPi. From Fig. 1b, it was identified that PVA microfibrils with an S-diad content of 58–62% could be prepared by saponification of PVPi suspension-polymerized by simple chemical initiation at polymerization temperature of 25–45 °C into a very high conversion as well as PVPi prepared by photo polymerization at 0–10 °C (S-diad content of 63–65%) [16, 30].

The molecular characteristics of PVA prepared in this study are listed in Table 1. The S-diad content appeared to be independent of P_n of PVA, and

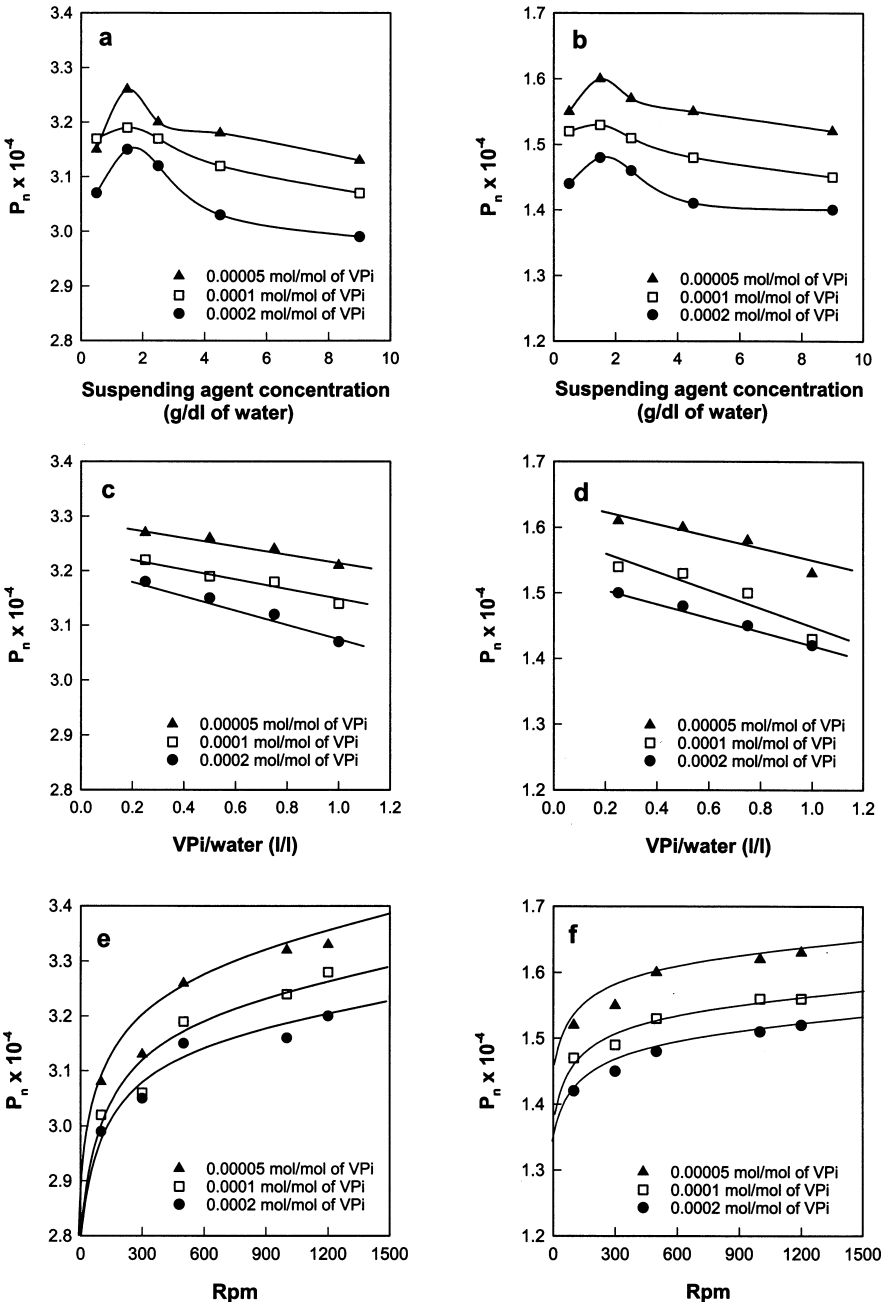

Fig. 6a–f Dependences of suspending agent concentration on the P_ns of PVPi polymerized at 25 °C using VPi/water of 0.5 L L^{-1} and agitation speed of 500 rpm (**a**) and resulting PVA (**b**), of VPi/water ratio on the P_ns of PVPi polymerized at 25 °C using a suspending agent concentration of 1.5 g dL^{-1} water and agitation speed of 500 rpm (**c**) and resulting PVA (**d**), and of agitation speed on the P_ns of PVPi polymerized at 25 °C using suspending agent concentration of 1.5 g dL^{-1} water and VPi/water of 0.5 L L^{-1} (**e**) and resulting PVA (**f**)

obviously increase with lowering polymerization temperature. Generally, PVA with S-diad contents exceeding 53–54%, which is the maximum value obtained in VAc polymerization, are described as syndiotacticity-rich. Thus, it was found that PVA prepared in this study was fairly syndiotactic. T_m values of PVAs from PVPis polymerized at 25 and 45 °C were constant, being about 244 and 240 °C, respectively, and independent of P_n of the PVA, which agrees well with tacticity data illustrated in Table 1. A negligible effect of molecular weight on T_m of PVA suggests that the shape and size of the crystal are almost the same over the molecular weight range observed.

Conclusions

It is notoriously a very difficult job to obtain UHMW PVPi with ultimately high conversion, a precursor of UHMW PVA, by free radical polymerization initiated with AIBN or BPO in bulk because of polymerization exotherm and chain branching during polymerization

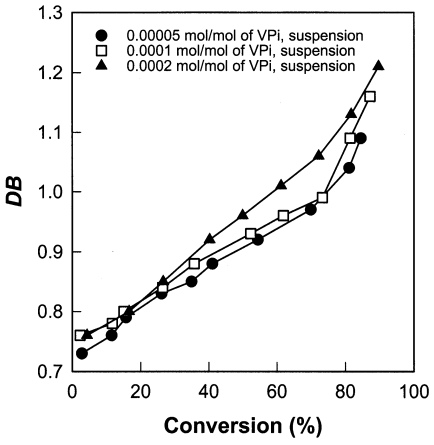

Fig. 7 DB for the pivaloyl group of PVPi in suspension polymerization of VPi at 25 °C using a suspending agent concentration of 1.5 g dL^{-1} of water, VPi/water of 0.5 L L^{-1}, and agitation speed of 500 rpm

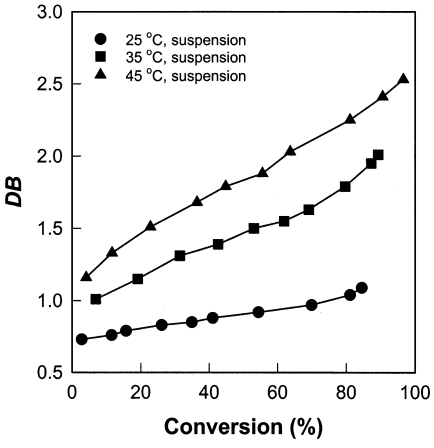

Fig. 8 DB for the pivaloyl group of PVPi in suspension polymerization of VPi using an ADMVN concentration of 0.00005 mol - mol^{-1} VPi, suspending agent concentration of 1.5 g dL^{-1} water, VPi/water of 0.5 L L^{-1}, and agitation speed of 500 rpm

of VPi. However, a low-temperature initiator, ADMVN seems to be advantageous in suppressing the chain transfer reactions because it can lower the polymerization temperature to approximately 25 °C. Hence, ADMVN is more effective in preparing UHMW PVPi with less branches. Furthermore, suspension polymerization is a powerful method for enhancing conversion. Under the same polymerization conditions, the suspension method was superior to the bulk method in increasing conversion of PVPi. On the other hand, the suspension method was slightly inferior to the bulk method in increasing molecular weight of the polymer. But the molecular weight difference between the two methods was very small.

Suspension polymerization of VPi at 25 °C by ADMVN and saponification produced UHMW PVA with a P_n of 14,700–16,700, an S-diad content of 62%, and a maximum conversion of VPi into PVPi of 85–90%. This compares well with the bulk polymerization of VPi at 25 °C using ADMVN with a P_n of 15,800–17,000 and with the maximum conversion of about 25–35%. The P_n and syndiotactic diad content were higher with PVA prepared from PVPi polymerized at lower temperatures. It was found that all PVAs from PVPi suspension-polymerized at 25 °C were fibrous, with a high degree of crystallinity, and orientation of the crystallites.

Conclusively, this suspension polymerization is expected to be an easy way of producing syndiotacticity-rich UHMW PVA microfibrils (Fig. 1b) with high yield by simple chemical initiation without using special devices such as irradiation. Moreover, it has an added advantage in that the separated spherical PVPi microspheres (Fig. 1a) with various particle sizes and size distributions can be saponified directly as a heterogeneous state for preparing stable syndiotactic PVA particles for drug delivery system and for cancer cell-killing embolic treatments according to the increased requirement for biomedical materials [3, 4]. In the near future, we will report on the preparation of monodisperse syndiotactic PVA microspheres by controlling various factors of low-temperature suspension polymerization and saponification.

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