

Synthesis of Syndiotacticity-Rich High Molecular Weight Poly(vinyl alcohol) by Suspension Polymerization of Vinyl Pivalate and Saponification

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ABSTRACT: Vinyl pivalate (VPi) was suspension-polymerized to synthesize high molecular weight (HMW) poly(vinyl pivalate) (PVPi) with a high conversion above 95% for a precursor of syndiotacticity-rich HMW poly(vinyl alcohol) (PVA). Also, the effects of the polymerization conditions on the conversion, molecular weight, and degree of branching (*DB*) of PVPi and PVA prepared by the saponification of PVPi were investigated. Bulk polymerization was slightly superior to suspension polymerization in increasing the molecular weight of PVA. On the other hand, the latter was absolutely superior to the former in increasing the conversion of the polymer, indicating that the suspension polymerization rate of VPi was faster than that of the bulk one. These effects could be explained by a kinetic order of a 2,2'-azobis(2,4-dimethylvaleronitrile) concentration calculated by

the initial rate method. Suspension polymerization of VPi at 55°C by controlling various polymerization factors proved to be successful in preparing PVA of HMW [number-average degree of polymerization (P_n): 8200–10,500], high syndiotactic diad content (58%), and very high yield (ultimate conversion of VPi into PVPi: 94–98%). In the case of the bulk polymerization of VPi at the same conditions, the maximum P_n and conversion of 10,700–11,800 and 32–43% were obtained, respectively. The *DB* was lower and the P_n was higher with PVA prepared from PVPi polymerized at lower initiator concentrations. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 832–839, 2003

Key words: syndiotactic; branched; suspension polymerization

INTRODUCTION

Poly(vinyl alcohol) (PVA) fibers and films are potentially high-performance materials because they have high tensile and impact strengths, high tensile modulus, high abrasion resistance, excellent alkali resistance, and an oxygen barrier property that is superior to those of any known polymers.^{1–3} To maximize these physical properties, the molecular weight, degree of saponification, and syndiotacticity should be increased.^{4–17} Especially, to increase the molecular weight, which is a fundamental factor affecting the physical properties, improvement of the polymerization methods of vinyl acetate (VAc)^{18–26} is necessary. To enhance the syndiotacticity as well as the molecular weight of PVA, various other vinyl ester monomers such as vinyl pivalate (VPi),^{27–37} which reveals

strong steric effects of the *t*-butyl group, have been used.

In the general bulk polymerization of VPi, high molecular weight (HMW) poly(vinyl pivalate) (PVPi) and PVA can be obtained but it is very difficult to control the viscosity of the reaction mixture. Thus, HMW PVPi with a high conversion is hardly obtained at the same time.^{27,32} Lyoo and Ha synthesized ultra-high molecular weight (UHMW) PVA having a maximum number-average degree of polymerization (P_n) of over 18,000 and a syndiotactic diad (*S*-diad) content of over 63% using ultraviolet ray-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 a high yield is hardly obtained.

To reduce the polymerization heat and the viscosity of the medium, solution polymerization of VPi was tried. Although a relatively higher conversion of VPi into PVPi is attained in the case of solution polymerization than in bulk polymerization, it is nearly impossible to prepare HMW PVPi with a conversion of

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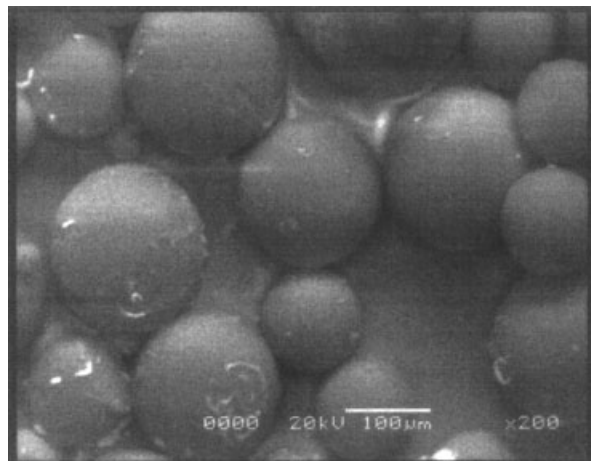


Figure 1 Scanning electron micrograph of PVPi microspheres prepared by suspension polymerization of VPi at 55°C.

over 80% owing to the high viscosity of the reaction solution.³³ It is known that the molecular weight and polymerization rate are increased simultaneously by emulsion polymerization of VPi. However, since 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 HMW PVA from PVPi by a saponification reaction.³¹

The mechanism of suspension polymerization in droplets is basically identical to that of bulk polymerization³⁸ and the water used as the reaction medium minimizes exotherm and viscosity enhancement generated during polymerization.³⁹ Owing to these advantages, suspension polymerization of VPi has a possibility of producing HMW PVPi with the highest conversion, which is a precursor of syndiotacticity-rich HMW PVA. As is well known, the molecular weight of a polymer prepared by the suspension polymerization method is controlled by the type and amount of the initiator and the suspending agent, the polymerization temperature, the monomer-to-water ratio, and the agitation speed. It is known that the higher the agitation speed, the higher is the molecular weight and the conversion.^{39–41} Compared with the rare studies regarding suspension polymerization of VPi, there has been much research on the suspension

polymerization of VAc because it is possible to reach higher conversion with it than with other polymerization methods.^{42,43}

To obtain HMW PVPi with the highest conversions, which is expected to be a profitable precursor of syndiotacticity-rich HMW PVA, in this study, suspension polymerization of VPi was conducted at 55°C. The effect of the suspension polymerization conditions on the polymerization behavior of VPi and the molecular parameters of PVPi and PVA such as molecular weight, degree of branching, and stereoregularity were examined.

EXPERIMENTAL

Materials

The VPi purchased from Shin-Etsu was washed with an aqueous solution of NaHSO₃ and water and dried over anhydrous CaCl₂, followed by distillation under a reduced pressure of nitrogen. The initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) (Wako Co., Tokyo, 99%), was recrystallized twice from absolute methanol before use. PVA with a number-average molecular weight of 127,000 and a degree of saponification of 88% (Aldrich Co.) was used as a suspending agent. Other extrapure-grade reagents were used without further purification. The water used for all the procedures was deionized.

Suspension polymerization of VPi

In a typical reaction, the suspending agent was dissolved in water under a nitrogen atmosphere and constant stirring in a 250-mL reactor fitted with a condenser. After degassing, the VPi monomer along with the ADMVN were added all at once at a fixed polymerization temperature. After predetermined times, the reaction mixture was cooled and kept for 1 day to separate and to sink the spherical PVPi particles (Fig. 1). To eliminate residual VPi and the suspending agent, the 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 I.

TABLE I
Suspension Polymerization Conditions of VPi

Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration (mol/mol of VPi)	0.00003, 0.00005, 0.0001
Suspending agent concentration (g/dL of water)	0.5, 1.5, 2.5, 4.5, 9.0
VPi/water (L/L)	0.25, 0.50, 0.75, 1.00
Rpm	100, 300, 500, 1000, 1200
Temperature (°C)	55

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, the initiator 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.

Saponification of PVPi

The following is a typical example of the saponification of PVPi^{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 a 20% potassium hydroxide/methanol/water (methanol/water = 90/10 v/v) solution in the dropping funnel were flushed with nitrogen. The ratio of the 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 filtered and washed several times with methanol. A quantitative yield of PVA was obtained. Residual ester groups could not be detected in the proton nuclear magnetic resonance (¹H-NMR) spectra of these specimens.

Acetylation of PVA⁴⁴

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. Then, the mixture was poured into cold water to precipitate the PVAc. The 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)⁴⁵:

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

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 using eq. (2)⁴⁶:

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

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

The degree of branching for the pivaloyl group (*DB*) of PVPi was calculated by eq. (3)³:

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

where DP_1 is the P_n of PVPi and DP_2 is the P_n of PVA prepared by saponifying PVPi. The *S*-diad contents of the PVAs were determined by 300-MHz ¹H-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 PVPi specimen was investigated using a scanning electron microscope (JSM 5800-LV, JEOL, Japan) with a magnification of 200×.

RESULTS AND DISCUSSION

Suspension polymerization behavior of VPi

The dependence of the polymerization rate on the initiator concentration can be determined from the initial-rate method.^{47,48} For small changes in the 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 by using eqs. (4)–(10):

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

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

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

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

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

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

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

where $[M]$ and $[I]$ are the concentrations of the monomer and initiator, 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 . Thus, in this study, from the calculation using the kinetic parameters obtained from the plots of conversion of up to 15% with the polymerization time in Table II, it was found that the suspension and bulk polymerization rates of VPi were proportional to the exponents 0.88 and 0.56 of the initiator ADMVN concentrations, respectively, that is, the suspension polymerization rate of VPi was higher than that by bulk polymerization. In accor-

TABLE II
Kinetic Parameters Used for the Calculation of the Initiator Exponent at a Polymerization Temperature of 55°C

Parameter	Suspension	Bulk
$(R_p)_1$ (% h ⁻¹)	13.93	9.73
$(R_p)_2$ (% h ⁻¹)	9.01	6.65
$(R_p)_3$ (% h ⁻¹)	4.97	4.94
$[I]_1$ (mol/mol of VPi)	0.0001	0.0001
$[I]_2$ (mol/mol of VPi)	0.00005	0.00005
$[I]_3$ (mol/mol of VPi)	0.00003	0.00003
$(R_p)_1/(R_p)_2$	1.55	1.46
$(R_p)_2/(R_p)_3$	1.81	1.35
$(R_p)_3/(R_p)_1$	0.36	0.51
$[I]_1/[I]_2$	2.00	2.00
$[I]_2/[I]_3$	1.67	1.67
$[I]_3/[I]_1$	0.30	0.30
n_{2a}	0.63	0.55
n_{2b}	1.16	0.58
n_{2c}	0.86	0.56
n_2	0.88	0.56

dance with the theoretical predictions of general radical polymerization,⁴⁹ the bulk polymerization rate was proportional to $[\text{ADMVN}]^{0.56}$. In contrast, in the case of suspension polymerization, some discrepancy appeared between the theoretical (0.5) and the experimental (0.88) values. The higher order of the initiator concentration of the suspension polymerization (0.88) in this study might be supposed to occur according to monomolecular termination by occlusion of growing chains due to the heterogeneous polymerization of VPi.

The conversion rate is increased with an increase in the initiator concentration as depicted by eq. (11)⁴⁹:

$$P_{\text{eq}} = 1 - \exp(-2k_p(f[I]/k_t k_i)^{1/2}) \quad (11)$$

where P_{eq} , f , $[I]$, k_i , k_p , and k_t are the conversion at the equilibrium of polymerization, the efficiency of the concentration of initiator, and the reaction rate constants of initiation, propagation, and termination, respectively. Figure 2 presents conversion–time plots of the (a) suspension and (b) bulk polymerizations for initiator concentrations of 0.00003, 0.00005, and 0.0001 mol/mol of VPi. The conversion rate increased as the initiator concentration was increased, which was well coincident with the theoretical predictions in eq. (11) and the conversion rates of the suspension polymerization were higher than those of the bulk polymerization at all initiator concentrations. The ultimate conversion in the bulk system was low due to a viscosity increase by forming HMW PVPi molecules. In contrast, in the case of suspension polymerization, the conversions increased linearly up to 94% in spite of a very low initiator ADMVN concentration of 0.00003 mol/mol of VPi, which was absolutely impossible in bulk polymerization. This can be explained by an

advantage of the heterogeneous (suspension) polymerization of VPi. Below an ADMVN concentration of 0.00003 mol/mol of VPi at a polymerization temperature of 55°C, effective polymerization could not occur. Very high ultimate conversions (94–98%) were obtained at all ADMVN concentrations. This explains the fact that suspension polymerization at 55°C by ADMVN is a useful one for producing HMW PVPi with a high yield.

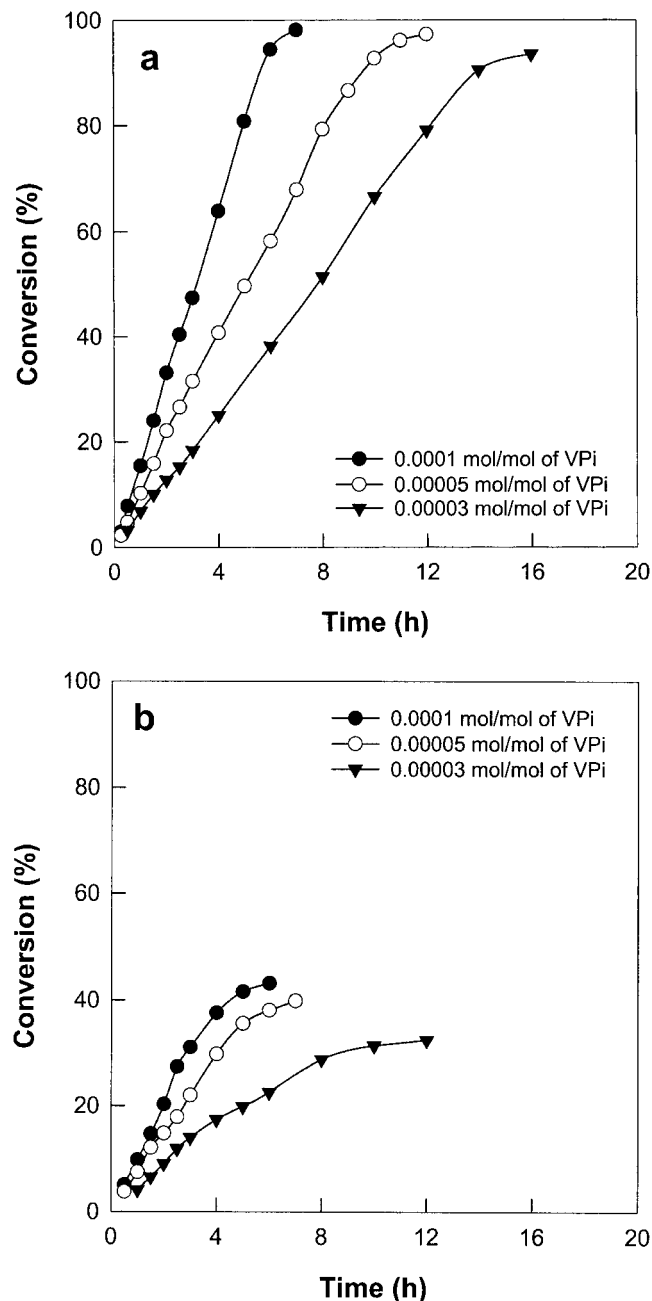


Figure 2 Conversions of VPi into PVPi (a) suspension polymerized at 55°C using suspending agent concentration of 1.5 g/dL of water, VPi/water of 0.5 L/L, and agitation speed of 500 rpm and (b) bulk polymerized at 55°C with polymerization times.

Molecular characteristics of PVPi and PVA

In a free-radical polymerization process, the kinetic chain length, ν , is expressed by eq. (12)⁴⁹:

$$\nu = k_p[M]/2(fk_dk_t[I])^{1/2} \quad (12)$$

Referring to eq. (12), the degree of polymerization may be decreased as the efficiency and concentration of the initiator are increased. The P_n 's of PVPi prepared by suspension and bulk polymerizations at 55°C and the corresponding PVA obtained by the saponification of PVPi with conversions are shown in Figure 3. The difference between the P_n 's of PVPi and PVA is mostly due to the branched structures, which may be broken down when saponified.^{3,30} It is interesting to observe that the P_n of PVA remained almost constant up to about 35% conversion and nearly independent of the P_n of PVPi, and then the P_n of PVA slightly decreased at higher conversions of over 35–45%. This was attributed to frequent chain-transfer reactions between the polymers, resulting in termination and branch formation reactions at higher conversions, whereas chain-transfer reactions between the monomers prevailed at lower ones. In accordance with the theoretical prediction in eq. (12), the P_n 's of PVPi and PVA increased with a decrease in the ADMVN concentration, as shown in Figure 3. HMW PVAs having various P_n 's of 8200–10,500 could be prepared by saponifying UHMW PVPi's having P_n 's of 28,200–43,200 polymerized in suspension. It should be noted that PVA with a P_n of up to 9700 could be prepared from PVPi suspension-polymerized at a conversion of about 94% using a minimum ADMVN concentration of 0.00003 mol/mol of VPi, which is comparable to the P_n of PVA (11,800) from PVPi by bulk polymerization using the same polymerization conditions (conversion: ca. 32%). Therefore, it can be concluded that the suspension polymerization of VPi is an effective method to increase both the yield and molecular weight at the same time.

Figures 4–6 show the effects of various suspension polymerization conditions of VPi on the molecular weights of both PVPi and PVA. PVPi was sampled at a similar conversion of about 80% to precisely clarify the effect of the polymerization conditions. Figure 4(a,b) shows the effect of the concentration of the suspending agent. At a concentration of 1.5 g/dL of water, maximum P_n 's of PVPi (42,400) and PVA (10,100) were obtained and this tendency was nearly the same irrespective of the ADMVN concentration. Below this concentration, the suspending agent could not produce the stable dispersion required for effective suspension polymerization owing to an insufficient concentration. In contrast, at a higher concentration of 9.0 g/dL of water, a significant increase of the viscosity of the polymerization medium made it diffi-

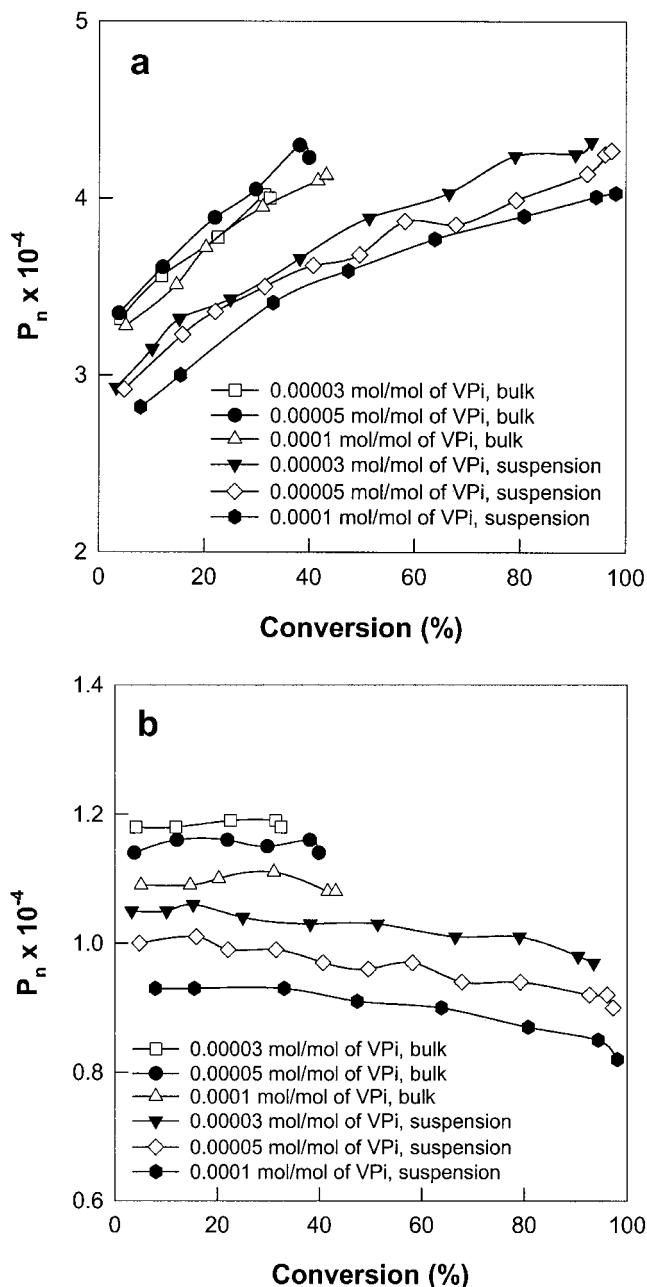


Figure 3 P_n 's of (a) PVPi obtained by suspension polymerization at 55°C using suspending agent concentration of 1.5 g/dL of water, VPi/water of 0.5 L/L, and agitation speed of 500 rpm and by bulk polymerization at 55°C and (b) the resulting PVA with conversions.

cult to agitate the system. From these results, it was found that the optimum concentration of the suspending agent is about 1.5 g/dL of water in this polymerization of VPi at 55°C. Figure 5(a,b) shows the P_n 's of PVPi and PVA with the VPi/water ratio, which indicates that the lower the value, the higher the molecular weight (maximum P_n of PVA:10,300). The effect of the agitation speed is shown in Figure 6(a,b). The molecular weight of both PVPi and PVA increased with an increase in the agitation speed, which well coincided

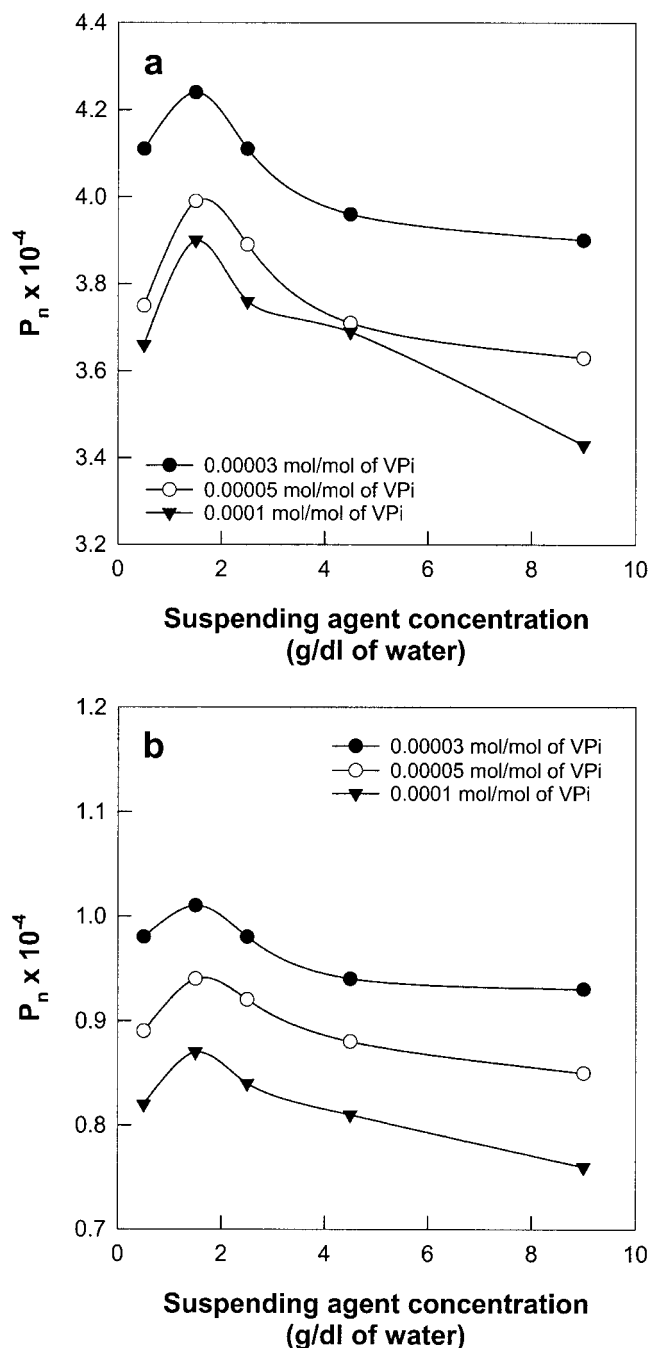


Figure 4 Dependence of suspending agent concentration on the P_n 's of (a) PVPi polymerized at 55°C using VPI/water of 0.5 L/L and agitation speed of 500 rpm and (b) the resulting PVA.

with the results of Gunesch and Schneider.⁵⁰ But over 1200 rpm, there was no difference in the molecular weight, and the highest P_n of PVA was 10,400 at this rpm.

It is known that the difference between the P_n 's of PVPi and PVA is due to a branched structure.^{3,30} In this study, the effect of the ADMVN concentration and conversion on the DB of PVPi was investigated. Figure 7 shows the variation of the DB for the pivaloyl group

of PVPi polymerized at 55°C in suspension and in bulk using three different ADMVN concentrations with the conversion. DB increased with an increasing conversion for all the cases. Further, the rate of the increasing DB with the conversion was decreased as the ADMVN concentration was lowered.

CONCLUSIONS

Through a series of calculations using the initial-rate method, it was found that the suspension and bulk

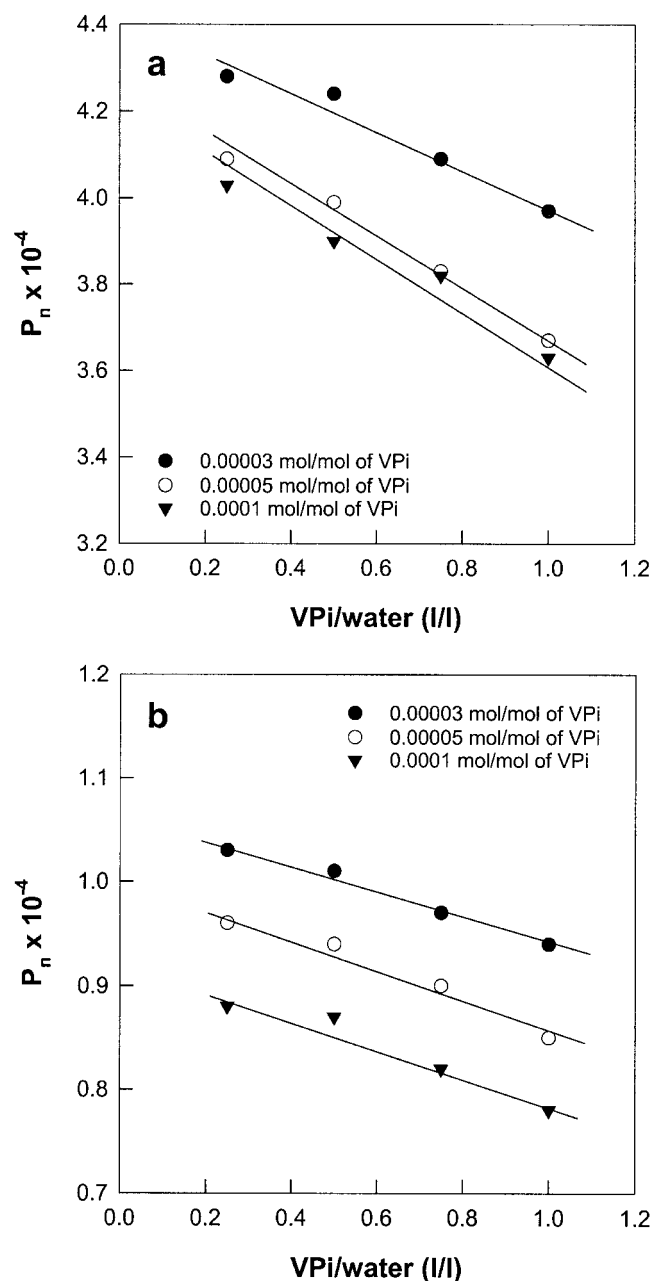


Figure 5 Dependence of VPI/water ratio on the P_n 's of (a) PVPi polymerized at 55°C using suspending agent concentration of 1.5 g/dL of water and agitation speed of 500 rpm and (b) the resulting PVA.

polymerization rates of VPi at 55°C were proportional to the exponents 0.88 and 0.56 of the initiator ADMVN concentrations, respectively. At the same polymerization conditions, the suspension method was absolutely superior to the bulk method in increasing the conversion of PVPi. In contrast, the suspension method was slightly inferior to the bulk method in increasing the molecular weight of the polymer, which indicated that the bulk polymerization rate of VPi by ADMVN was lower than that in suspension. But the molecular weight difference between the two methods was very small.

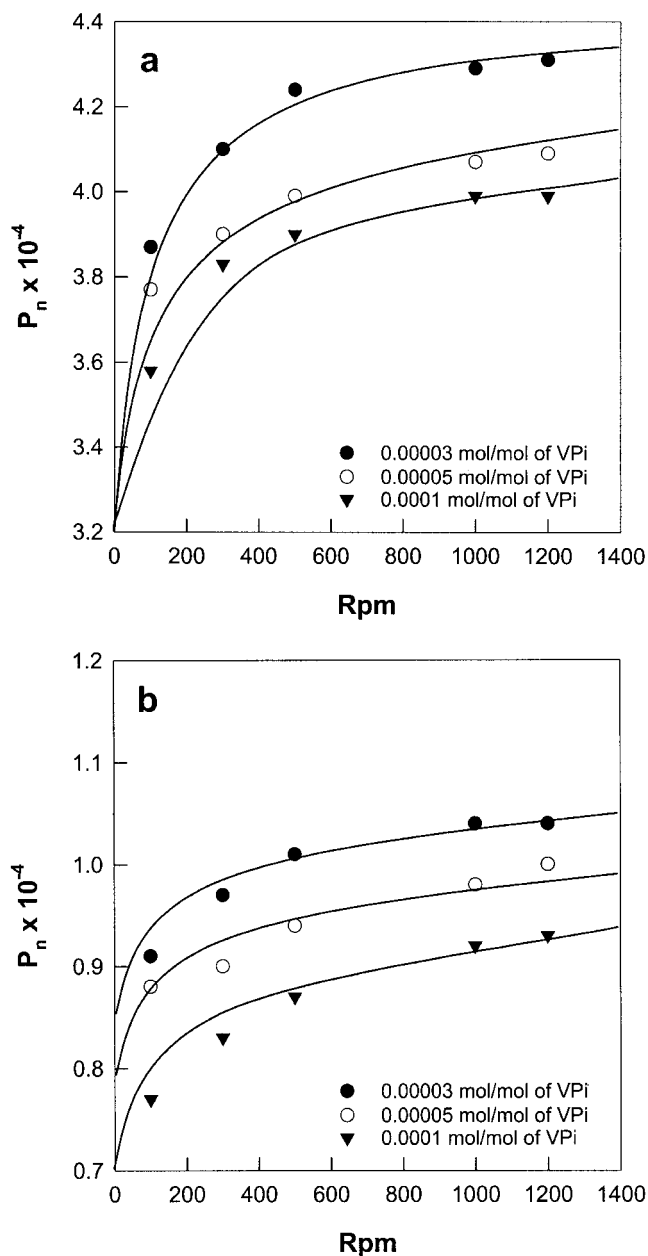


Figure 6 (a) Dependence of agitation speed on the P_n 's of PVPi polymerized at 55°C using suspending agent concentration of 1.5 g/dL of water and VPi/water of 0.5 L/L and (b) the resulting PVA.

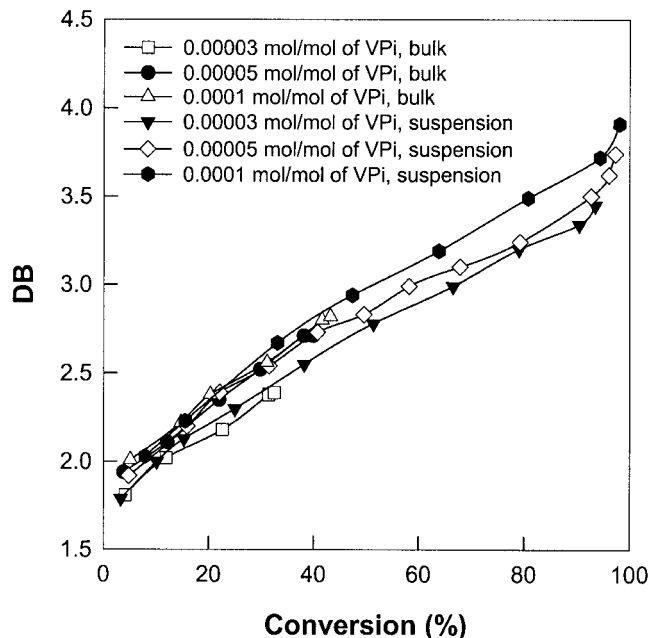


Figure 7 DB for the pivaloyl group of PVPi obtained by the suspension polymerization at 5°C using suspending agent concentration of 1.5 g/dL of water, VPi/water of 0.5 L/L, and agitation speed of 500 rpm.

The suspension polymerization of VPi at 55°C by ADMVN and the saponification-produced HMW PVA with a P_n of 8200–10,500 and an *S*-diad content of 58% and with the maximum conversion of VPi into PVPi of 94–98%. This compares well with the bulk polymerization of VPi at 55°C using ADMVN with a P_n of 10,700–11,800 and with the maximum conversion of about 32–43%.

Conclusively, this suspension polymerization is expected to be an easy way of producing HMW PVA with a high yield by simple chemical initiation without using special devices such as irradiation. Moreover, it has the advantage that the separated spherical PVPi microspheres having various particle sizes and size distributions can be saponified directly as a heterogeneous state for preparing stable syndiotactic PVA microspheres for drug-delivery systems and for cancer cell-killing embolic treatments according to the increased requirement for biomedical materials.^{3,12} 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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