

Preparation of High Molecular Weight Poly(vinyl alcohol) with High Yield by Emulsion Polymerization of Vinyl Acetate Using 2,2'-Azobis(2-amidinopropane) Dihydrochloride

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ABSTRACT: To prepare high molecular weight (HMW) poly(vinyl acetate) (PVAc) with high yield and high linearity as a precursor of HMW poly(vinyl alcohol) (PVA), vinyl acetate (VAc) was emulsion polymerized using, azo initiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH). This was compared with the polymerization using potassium peroxydisulfate (KPS) as an initiator at various polymerization conditions. PVA, having a maximum number average degree of polymerization (P_n) of 3500 was obtained by the saponification of PVAc with P_n of 13,000–14,000, degree of branching (DB) for the acetyl group of about 3.4–3.5, and a maximum conversion of VAc into PVAc of 95%, which was polymerized by AAPH. These numerical values were superior compared with 14,500–15,000 of P_n of PVAc, obtained by KPS, and 3100 of maximum P_n of resulting PVA, DB of

about 3.7–3.8, and maximum conversion of 90%. From the foregoing experimental results, we found that AAPH was a more efficient initiator than KPS in increasing both conversion of PVAc and molecular weight of PVA. In addition, PVAc microspheres, obtained by these emulsion polymerizations, can be converted to PVA / PVAc shell / core microspheres through a series of surface-saponifications, maintaining their spherical morphology. Various surface morphologies, such as flat or wrinkled and swellable or nonswellable ones formed by the various molecular parameters and saponification conditions, were examined. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2356–2362, 2004

Key words: PVAc; HMW PVA; VAc; emulsion polymerization; AAPH

INTRODUCTION

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

Vinyl acetate (VAc) monomer can be polymerized via bulk, solution, emulsion, and suspension polymerization processes.^{14–27} However, in the preparation of

PVA from bulk or solution polymerization, there are several technical limitations for obtaining high conversion and high molecular weight (HMW) simultaneously. These technical limitations mean difficulties in control of high viscosity and in removal of the heat of the polymerization. Thus, improvement of the polymerization method is necessary to prepare PVA with high yield and with HMW.

In general, it is known that molecular weight and conversion of monomer into polymer can be increased simultaneously by emulsion polymerization. Emulsion polymerization processes using ultraviolet ray or γ -ray radiation methods²¹ and redox initiation methods^{22,23} for the preparation of high molecular weight atactic PVA have been studied. However, the radiation initiation polymerization processes inevitably require very complicated and expensive polymerization apparatus and special polymerization initiators, preventing commercialization. It also has been known that redox initiation leads to serious discoloration and low polymerization efficiency.²⁴

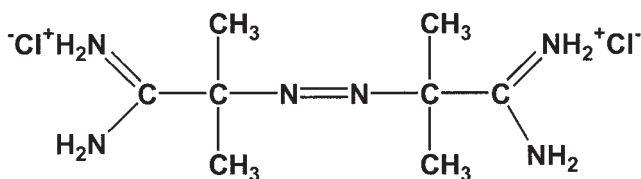
In this study, to prepare poly(vinyl acetate) (PVAc) with high conversion and HMW PVA, VAc was polymerized in emulsion at 50 and 60°C using potassium peroxydisulfate (KPS) and 2,2'-azobis(2-amidinopro-

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pane) dihydrochloride (AAPH) as initiators and sodium dodecyl sulfate (SDS) as an emulsifier, respectively.



Differences between KPS and AAPH on the molecular weight, conversion, and degree of branching (DB) of the resultant polymer were investigated. PVA/PVAc (shell / core) microspheres with various sizes could be prepared through a series of emulsion polymerizations and surface saponification of polymerized PVAc.

EXPERIMENTAL

Materials

VAc (Aldrich Co., Milwaukee, WI) was washed with an aqueous solution of NaHSO_3 and water and dried over anhydrous CaCl_2 , followed by distillation under reduced pressure of nitrogen. Initiator, AAPH (99%; Wako Co., Tokyo, Japan), KPS (99%; Shinyo Pure Chemical Co., Osaka, Japan), the emulsifier, SDS (Daejung Chemical Co., Incheon, Korea), and other reagents were used without further purification. Water used for all of the procedures was deionized.

Polymerization

Water and emulsifier were poured into a 250-mL three-necked round-bottom flask and flushed with nitrogen through a pyrogallol-alkaline solution trap and a calcium chloride trap and agitated for 30 min, and then monomer VAc was added into the flask with agitation. After 30 min, initiator (AAPH or KPS) was added to the monomer at a predetermined polymerization temperature and polymerization was conducted for a predetermined polymerization time. Sphere-type polymer resin, obtained by coagulation using Na_2SO_4 solution, was washed several times with warm water and dried in a vacuum oven at 60°C for 1 d.

Saponification

General solution saponification was conducted to analyze characteristics of prepared PVAc and PVA. To a solution of 2 g of PVAc in 100 mL of methanol, 2.5 mL of a 40% NaOH aqueous solution was added, and the mixture was stirred for 5 h at room temperature to yield PVA. The PVA produced was filtered and washed well with methanol.

Heterogeneous surface saponification

PVAc microspheres, obtained by emulsion polymerization, were sieved with standardized mesh sieves for heterogeneous surface saponification. Then, 0.5 g of PVAc microspheres was added slowly into a 500-mL flask filled with 200 mL of alkaline solution with agitation at a predetermined temperature. After a predetermined time, reacted microspheres were poured in cool water, filtered with cool water several times, and dried in the vacuum oven at 40°C .

Acetylation of PVA

To estimate the molecular weight of the resulting PVA, acetylation of PVA was conducted. 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 72 h under an atmosphere of nitrogen. Then, the mixture was poured into cold water to precipitate PVAc, which was filtered and purified by repeating the reprecipitation from methanol and water.

Characterizations

The conversion of VAc into PVAc was obtained from the percent ratio of the weight of polymer formed to the weight of monomer used and the molecular weight of PVAc and the DB were calculated by using eqs. (1) and (2), respectively.

$$[\eta] = 8.91 \times 10^{-3} [P_n]^{0.62} \quad (\text{in benzene at } 30^\circ\text{C}) \quad (1)$$

where $[\eta]$ is the intrinsic viscosity and P_n is a number-average degree of polymerization of PVAc. On the other hand, molecular weight of PVAc was determined from that of PVAc produced by acetylation of PVA using eq. (1).²⁸

$$\text{DB} = (\text{DP}_1/\text{DP}_2) - 1 \quad (2)$$

where DP_1 is P_n of PVAc and DP_2 is P_n of PVA prepared by saponifying PVAc in eq. (2). The morphology of microspheres was observed using an optical microscope (BH-2; Olympus Co., Tokyo, Japan) and a scanning electron microscope (SEM; S-360; Cambridge Co., Cambridge, UK).

RESULTS AND DISCUSSION

Emulsion polymerization behavior

It is important to find optimum values among the various emulsion polymerization factors that affect conversion and molecular weight, such as initiation method, volume ratio of monomer to water,²⁹ amount and type of initiator, amount and type of emulsifier,³⁰

agitation method and agitation speed,³¹ polymerization temperature, and polymerization time. In this work, AAPH and KPS were used as initiators in emulsion polymerization of VAc and the effects of initiators on the conversion, and DB of PVAc and the molecular weights of PVAc and PVA.

The function of the initiator is to generate free radicals, thereby initiating the polymerization reaction. Emulsion polymerizations have been restricted almost entirely to catalysis by free-radical initiation. AAPH and KPS, initiators used in these polymerizations, are both water soluble. Azoinitiator AAPH and peroxyinitiator KPS are thermal dissociation-type free-radical initiators. All chemical bonds rupture if sufficient energy of vibration of the atoms is attained. However, only a limited range of bond dissociation values is feasible to allow practical rates of free-radical generation. A very important class of compounds, characterized by O—O and N=N bonds within the molecule, exhibit bond dissociation energies falling within 30–35 kcal / mol. These decompose at very convenient temperatures and at rates commensurate with efficient polymerization times. It is inevitable that emulsion polymerization reactions, using these initiators, require the temperature to be raised above their decomposition temperatures, typically to 50–70°C. Figure 1 illustrates conversion-time plots for temperatures of 60°C for each initiator AAPH and KPS at varying concentrations. The conversion, according to the content of initiator, showed the expected tendency for both initiators: the conversion rate increased as the content of initiator was increased.

Figure 2 illustrates conversion-time plots of emulsion polymerizations by the two initiators for temperatures of 50 and 60°C using emulsifier SDS. The initial conversion of VAc into PVAc was 75–80% for KPS in 2 h at 60°C and was higher than that of the 60–70% for AAPH. The rate of conversion was increased with increasing polymerization temperature for both initiators. For the case of ultimate conversion, PVAc using AAPH was higher than that for PVAc using KPS. The rate of conversion using KPS was faster at the early stage of polymerizations at both temperatures but the ultimate conversion was lower. This result might be because of the faster initiation rate for KPS at the early stage of polymerization.

Molecular weight and DB

The effect of emulsion polymerization temperature on the conversion of VAc into PVAc and the P_n of PVAc and resulting PVA is shown in Figure 3 a and b. The P_n of PVAc using KPS (Figure 3 b) was higher than that using AAPH (Figure 3 a). However, this tendency was not evident with the case of PVA. At all conversions of VAc into PVAc polymerized at 50°C, as expected, we obtained larger P_n than at 60°C as shown in

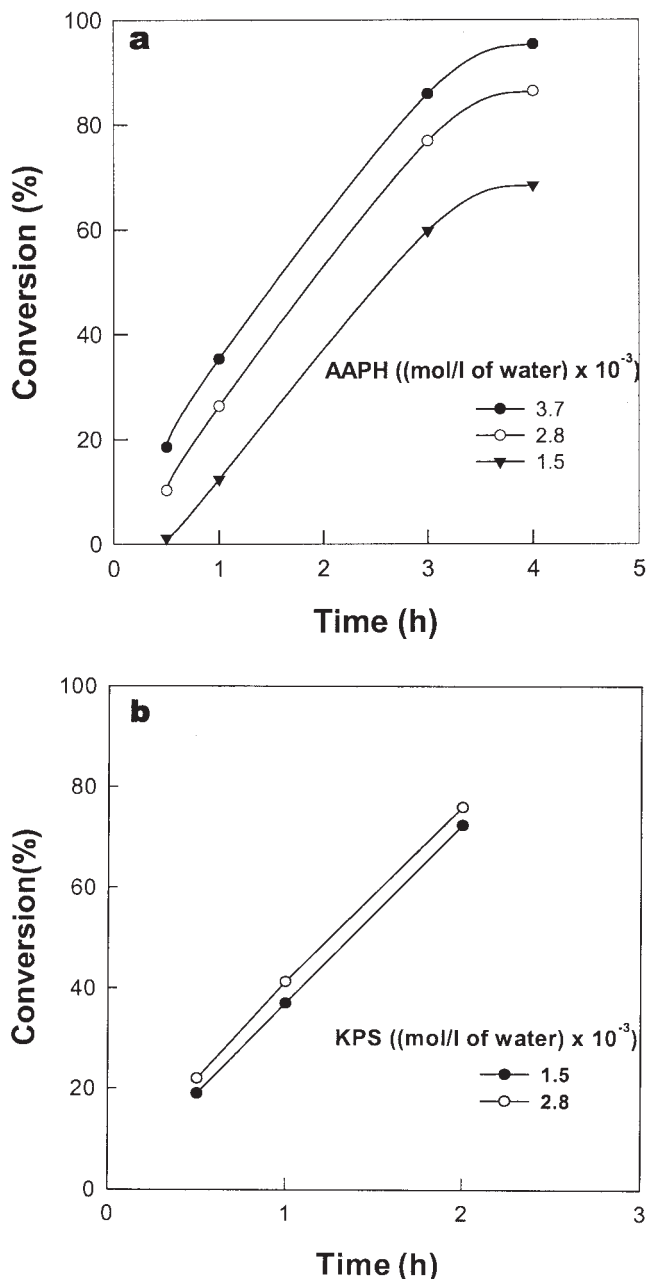


Figure 1 Conversions of VAc into PVAc obtained by emulsion polymerization of VAc at 60°C using an initiator concentration of 3.7×10^{-3} mol / L of water and SDS concentration of 1.7×10^{-2} mol / L of water with polymerization times (a) AAPH and (b) KPS.

Figure 3. The (P_n)'s of PVA obtained using AAPH were very slightly larger than those by KPS, but the difference was small. The P_n of PVA remained almost constant and nearly independent of initiator.^{10,11,14,16,20,25}

The general role of emulsifier in emulsion polymerization is to reduce the interfacial tension between the monomer phase and the water phase so that, with agitation, the monomer is dispersed in the water phase. Emulsifiers act to stabilize the monomer drop-

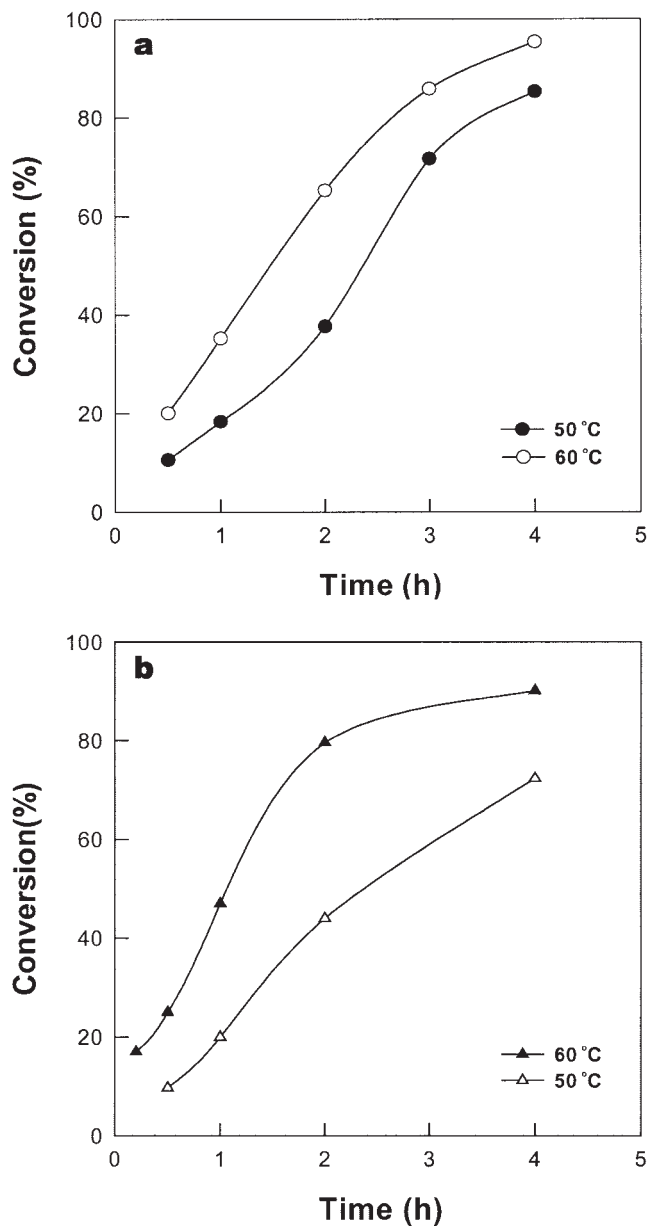


Figure 2 Conversions of VAc into PVAc obtained by emulsion polymerization of VAc at 50 and 60°C using an initiator concentration of 3.7×10^{-3} mol / of water and an SDS concentration of 1.7×10^{-2} mol / L of water with polymerization times (a) AAPH and (b) KPS.

lets in an emulsion form, serve to solubilize monomer within micelles, stabilize the formed monomer-swollen polymer particle during propagation and, after the polymerization process, act to solubilize the polymer in the aqueous phase to a lesser extent, and sometimes serve as the site for the nucleation of particles, and sometimes act as chain transfer agents and retarders.³² Therefore, it is important to find optimum emulsifier concentration for obtaining HMW PVAc and PVA. The emulsifier SDS, used in this study, is one of the most commonly used anionic surfactants having a sulfate ionic group.

The effect of the amount of SDS on P_n of PVAc at each polymerization temperature is presented in Figure 4. The emulsion system with AAPH was unstable below an SDS concentration of 1.15×10^{-2} mol / L of water because this amount of SDS was not enough to emulsify VAc effectively so that effective polymerization could not occur. Likewise, there existed an optimum concentration of SDS for effective emulsion polymerization with KPS as for the emulsion system with AAPH. From the foregoing results, it is found

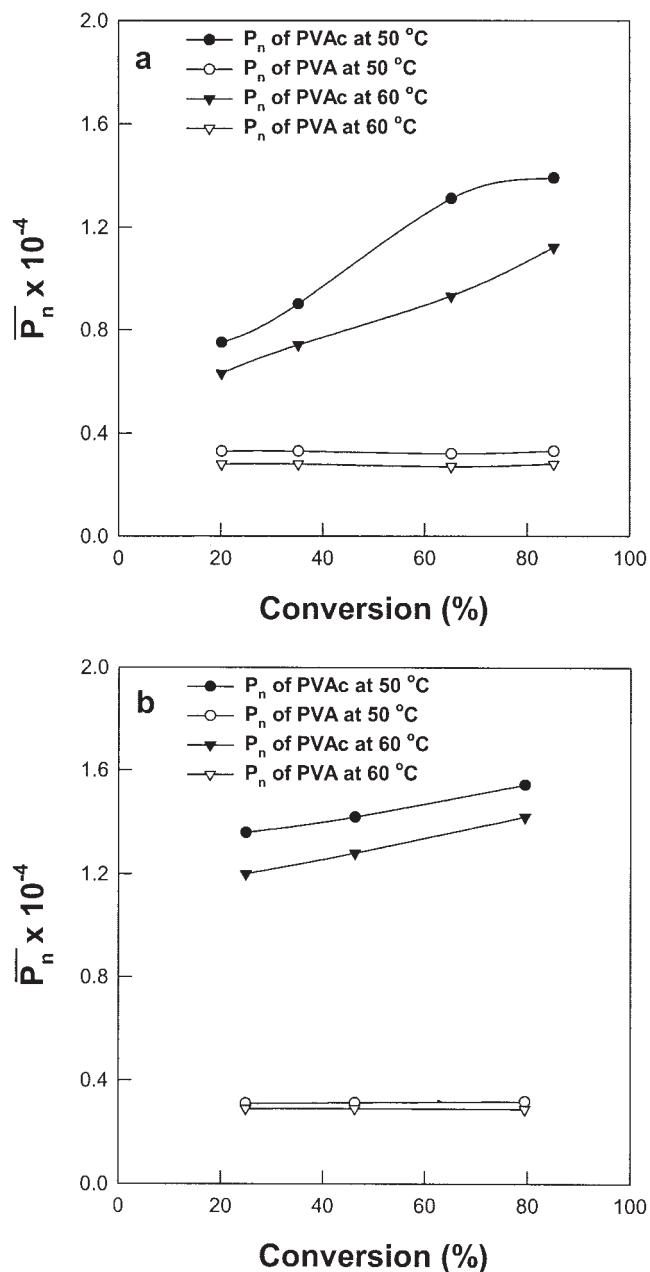


Figure 3 (P_n)'s of PVAc obtained by the emulsion polymerization of VAc at 50 and 60°C using an initiator concentration of 3.7×10^{-3} mol / L of water and an SDS concentration of 1.7×10^{-2} mol / L of water and resulting PVA with conversions (a) AAPH and (b) KPS.

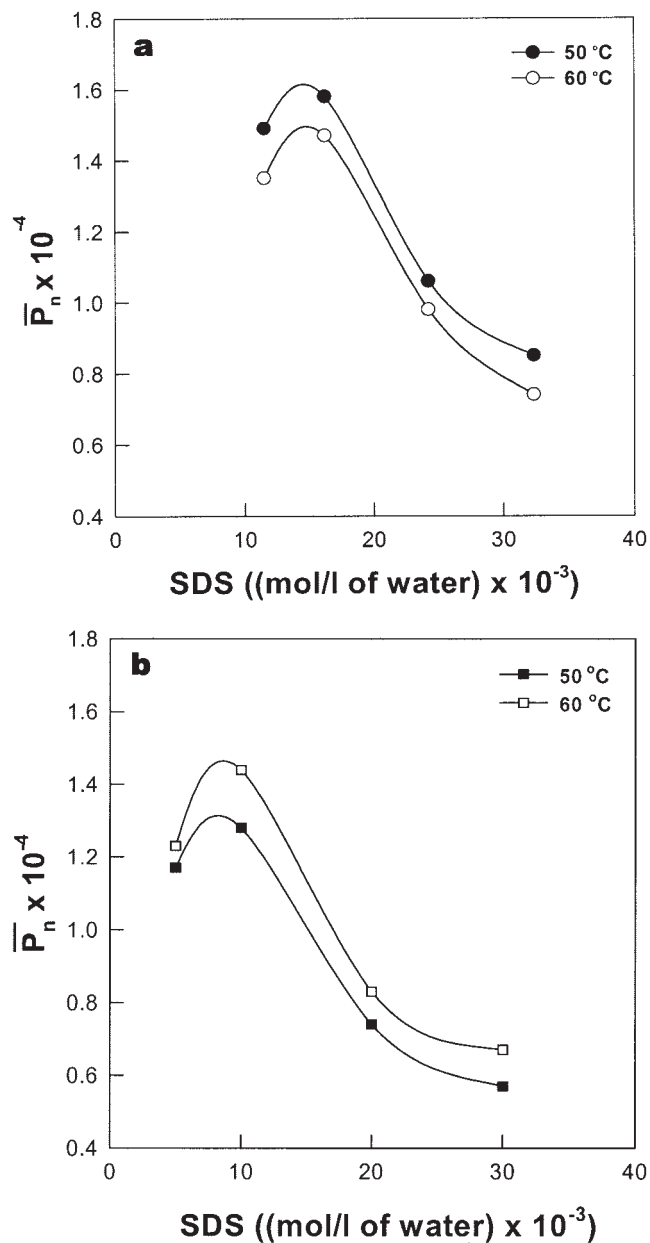


Figure 4 Effect of the amount of SDS on the P_n of PVAc: (a) AAPH, 3.7×10^{-3} mol / L of water, at 50 and 60°C for 4 h; (b) KPS, 1.02×10^{-3} mol / L of water, at 50 and 60°C for 4 h.

that there exists an optimum emulsifier concentration, for higher PVAc molecular weight, than with other emulsifier concentrations at the same polymerization condition. The conversion and P_n of PVAc have the same relationship with polymerization temperatures regardless of emulsifier concentration. Initiators AAPH with a concentration of 3.7×10^{-3} mol / L of water and KPS with a concentration of 1.02×10^{-3} mol / L of water were used in these polymerizations because high conversion polymerization occurred at these concentrations.

Branching reactions during polymerization generally lead to broadening of the molecular weight dis-

tribution, and it is often difficult to distinguish between the effects of branching and polydispersity. The extent of branching is great for PVAc, which has a very reactive propagation radical. PVAc has a transfer to polymer value C_P , which is probably in the range of $(1-5) \times 10^{-4}$. In addition, VAc monomer has a high transfer to monomer value C_M of about $(1.75-2.8) \times 10^{-4}$. Transfer to monomer yields radicals having the acetoxy methyl group, which can initiate polymerization at its radical end and can enter into the propagation reaction of some other propagating radical. The result of this behavior is the formation of a branched polymer. Thus, extensive branching occurs in PVAc because a branch is formed for each act of

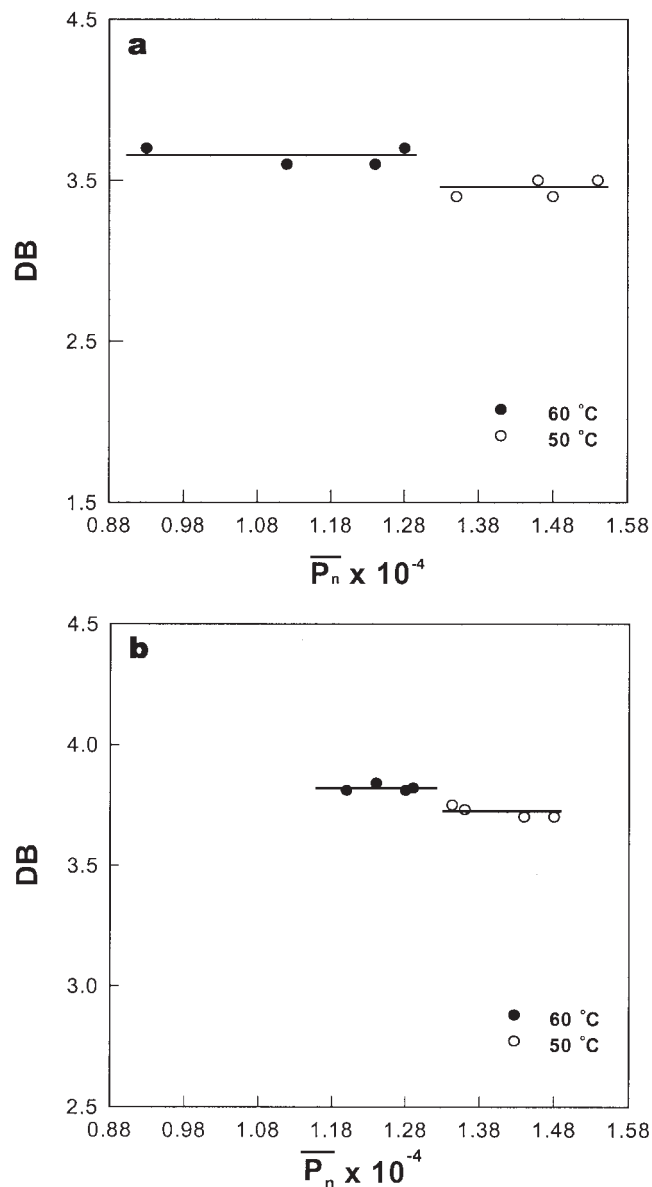


Figure 5 DB for the acetyl group of PVAc obtained by emulsion polymerization of VAc with P_n of PVAc: (a) AAPH and (b) KPS.

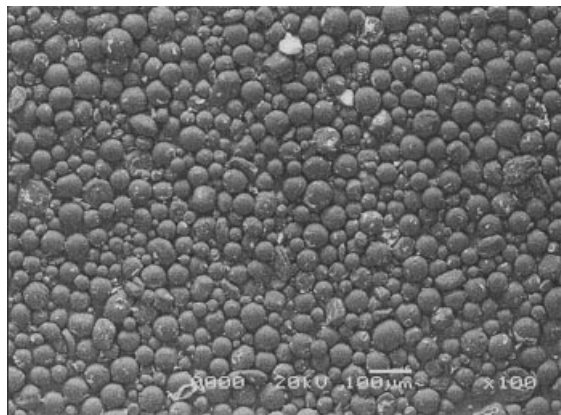


Figure 6 SEM photograph of PVAc microspheres obtained by the emulsion polymerization of VAc at 60°C using an AAPH concentration of 3.7×10^{-3} mol / L of water and an SDS concentration of 1.7×10^{-2} mol / L of water.

transfer to either monomer or polymer. In this study, the effect of polymerization temperature on the DB for the acetyl group of PVAc at a similar conversion was investigated. DB can be a useful index that estimates linearity of the polymer chain indirectly; thus, DB is proportional to polymerization temperature and conversion and also is related to the initiation method. General DB of PVAc is 3–5 and, DB, in the case of high molecular weight PVA obtained by saponification of HMW PVAc, is below 1.

Figure 5 shows DB for acetyl groups of PVAc, obtained by emulsion polymerization of VAc at the same conditions and similar conversions (20–40%), with P_n at two different temperatures of each initiator. Overall, DB was increased with increasing AAPH and KPS contents at polymerization temperature of 50 and 60°C. DB of AAPH and KPS at 60°C were 3.6–3.7 and 3.8–3.9 and were 3.4–3.6 and 3.7–3.8 at 50°C, respectively. Like this, the extent of increasing DB was more prominent at a higher polymerization temperature and emulsion polymerization of VAc by AAPH and saponification produced higher molecular weight PVA with lower DB than those by KPS. In conclusion, AAPH is more efficient than KPS for obtaining HMW PVA and high-conversion PVAc.

PVA/PVAc (shell / core) microspheres

PVAc microspheres obtained by emulsion polymerization of VAc using AAPH were saponified, at predetermined alkaline concentration and time, and then PVAc / PVA core / shell microspheres, revealing about 16% of the degree of saponification, were prepared. Figure 6 is the SEM photograph of PVAc microspheres and Figure 7 shows particle size distribution of PVAc. The average diameters were in the range of 125–150 μm, and polydispersity index was 1.03.

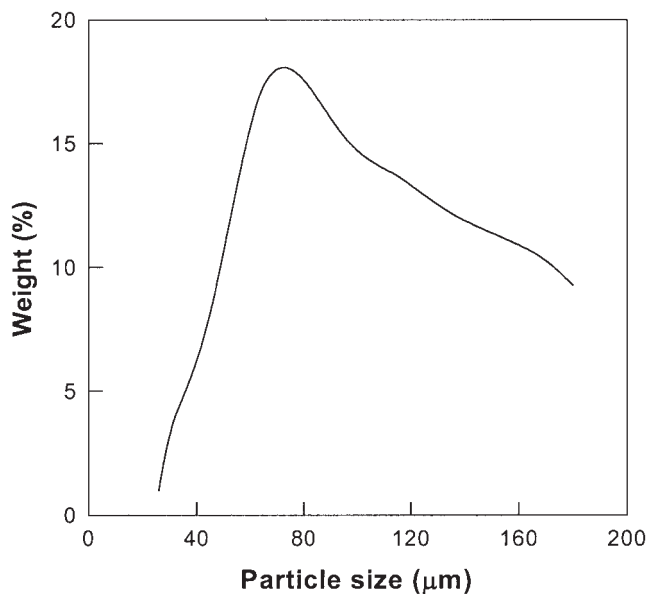


Figure 7 Particle size distribution of PVAc microspheres prepared by emulsion polymerization of VAc at 60°C using an AAPH concentration of 3.7×10^{-3} mol / L of water and an SDS concentration of 1.7×10^{-2} mol / L of water.

Figure 8 is the optical micrograph of PVA / PVAc microspheres with core / shell structure obtained by surface saponification in alkaline solution at 40°C for 10 h.

CONCLUSION

To prepare high-yield PVAc and HMW PVA, VAc was polymerized in emulsion at 50 and 60°C using KPS and AAPH as initiators, respectively, by controlling various polymerization factors. A difference between KPS and AAPH in the molecular weight, conversion, and DB of the resultant polymer was investi-

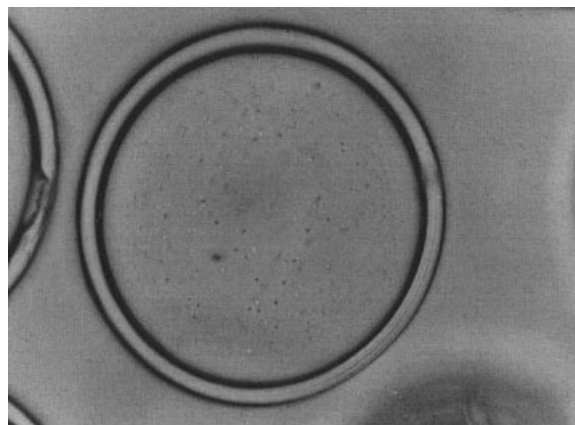


Figure 8 Optical micrograph of PVA / PVAc microspheres of skin / core structure obtained by the surface saponification of PVAc in alkali solution at 40°C for 10 h.

TABLE I
**Maximum Conversion and (P_n 's) of PVAc
 and PVA in This Study**

Initiator type	Conversion (%)	$P_n \times 10^{-4}$	
		PVAc	PVA
AAPH	95.3	1.40	0.35
KPS	90.1	1.55	0.31

gated: the initial rate of conversion by KPS was faster, compared with that by AAPH; however, in the case of ultimate conversion, PVAc by AAPH was higher than PVAc by KPS. Emulsion polymerization of VAc by AAPH and saponification produced HMW PVA with lower DB than those by KPS. This might be caused by the fact that the initially accelerated polymerization reaction may bring about a chain transfer reaction like branching when KPS was used. As a result, as described previously, AAPH might be more efficient in the production of PVAc with high conversion and HMW PVA, as presented in Table I. Emulsion polymerization of VAc by AAPH is a useful method for the preparation of PVAc microspheres with high yield. The PVA / PVAc microspheres with perfect shell / core structure could be prepared successfully through a series of heterogeneous saponification experiments. Separated PVA / PVAc microspheres are expected to be a promising material for biomaterials such as embolic materials and electronic applications such as toner particles. In the near future, we will report on the emulsion polymerization of vinyl pivalate for the production of stereoregular PVA.

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