

# Preparation of High Molecular Weight Poly(vinyl pivalate) with High Yield and High Molecular Weight Poly(vinyl alcohol) by Emulsion Polymerization of Vinyl Pivalate and Saponification

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Received 14 February 2006; accepted 15 May 2006

DOI 10.1002/app.25166

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** To prepare high molecular weight (HMW) poly(vinyl pivalate) (PVPi) with high yield and high linearity which is a promising precursor for syndiotactic poly(vinyl alcohol) (PVA), vinyl pivalate (VPi) was emulsion polymerized, using 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH) as an initiator and sodium dodecyl sulfate (SDS) as an emulsifier. The effect of the polymerization conditions on the conversion, molecular weight, and degree of branching was investigated. PVA with maximum number-average degree of polymerization ( $P_n$ ) of 6200 could be prepared by complete saponification of PVPi, with  $P_n$  of 13,300–16,700 obtained at polymerization tem-

perature of 50°C, using SDS and AAPH concentration of  $2.0 \times 10^{-3}$  mol/L of water and  $1.0 \times 10^{-3}$  mol/L of water, respectively, and the maximum conversion was about 90%. From the emulsion polymerization of VPi, spherical PVPi with high yield was effectively prepared, which might be useful for the precursor of syndiotactic PVA micro- and nano-spheres with various surface properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 410–414, 2007

**Key words:** PVPi; HMW PVA; VPi; 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, which is widely used as fibers for clothes and industries, binders, films, membranes, and in medicines for drug delivery systems, and cancer cell-killing embolic materials 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. To maximize these properties, PVA should retain high molecular weight (HMW), high syndiotacticity, and high degree of saponification.<sup>1–13</sup>

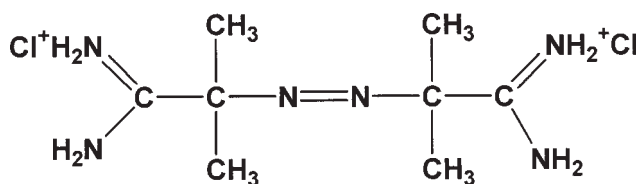
To enhance the syndiotacticity as well as molecular weight of PVA, poly(vinyl pivalate) (PVPi) is selectively used as a precursor of PVA. PVA obtained from PVPi has the highest syndiotacticity among (PVA)s obtained via radical polymerization, and the syndiotactic diad content of PVA prepared by low temperature polymerization of vinyl pivalate

(VPi) comes to over 60%. VPi can be polymerized through bulk, solution, emulsion, and suspension polymerization processes.<sup>14–27</sup> However, in the preparation of PVA from bulk or solution polymerization, there are several technical limitations for obtaining high conversion and HMW simultaneously. The improvement of polymerization method has required to prepare the PVA with high yield and HMW.<sup>19</sup> Emulsion polymerization processes using ultraviolet ray or  $\gamma$ -ray radiation methods<sup>21</sup> and redox initiation methods<sup>22,23</sup> for the preparation the HMW atactic PVA have studied. However, the radiation initiation polymerization processes inevitably require very complicated and expensive polymerization apparatus and special polymerization initiator, preventing commercialization. It has also been known that the redox initiation leads to serious discoloration and low polymerization efficiency.<sup>24</sup>

In this study, we conducted the emulsion polymerization of VPi with azoinitiator, 2,2'-azobis(2-amidinopropane) dihydrochloride (AAPH), and an emulsifier, sodium dodecyl sulfate (SDS) to prepare HMW PVPi with high conversion and resultant HMW syndiotactic PVA by controlling the polymerization factors. The effect of polymerization factors on the conversion, molecular weight, and degree of branching is investigated (Scheme 1).

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Contract grant sponsor: Ministry of Commerce, Industry, and Energy (MOCIE); contract grant number: RTI04-01-04.



Scheme 1 Chemical structure of AAPH.

## EXPERIMENTAL

### Materials

VPI purchased from Shin-Etsu was washed with an aqueous solution of  $\text{NaHSO}_3$  and water and dried over anhydrous  $\text{CaCl}_2$ , followed by distillation under reduced pressure of nitrogen. The initiator, AAPH was recrystallized twice from absolute methanol before use. Other extra-pure grade reagents were used without further purification. Water used for all the procedures was deionized.

### Emulsion polymerization of VPI

Water and emulsifier were poured into a 250 mL three-necked round bottom flask and flushed with nitrogen through the pyrogallol-alkaline solution trap and calcium chloride trap, and agitated for 30 min and then emulsifier, SDS and VPI were added into the flask with agitating. After 30 min, initiator AAPH was added to the monomer at predetermined polymerization temperature. And then, the polymerization was conducted for predetermined polymerization time. Sphere-type polymer particle obtained by the de-emulsification using  $\text{Na}_2\text{SO}_4$  solution was washed several times with warm water and dried in vacuum oven at  $40^\circ\text{C}$  for a day. The detailed polymerization conditions are listed in Table I.

### Saponification of PVPi

In a flask equipped with a reflux condenser, a thermocouple, a dropping funnel, and a stirring device, 2 g of PVPi was dissolved in 200 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 was 0.05–0.25 (v/v). The alkali solution was added to the PVPi solution while being stirred at  $55^\circ\text{C}$  after the saponification reaction had been completed, the solid saponification product was filtered and washed several times with methanol and dried in vacuum oven at  $40^\circ\text{C}$ . A quantitative yield of PVA was obtained. Residual ester groups could not be detected in the proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra of these specimens.

### Acetylation of PVA

To estimate the molecular weight of 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  $100^\circ\text{C}$  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 molecular weights of PVPi was calculated using eq. (1).

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

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).

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

where  $P_n$  is the number-average degree of polymerization of PVAc. The conversion and the degree of branching (D.B.) were calculated by using eqs. (3) and (4), respectively.

$$\text{Conversion (\%)} = \left( \frac{\text{the weight of polymer formed}}{\text{the weight of monomer used}} \right) \times 100 \quad (3)$$

$$\text{DB} = (\text{DP}_1 / \text{DP}_2) - 1 \quad (4)$$

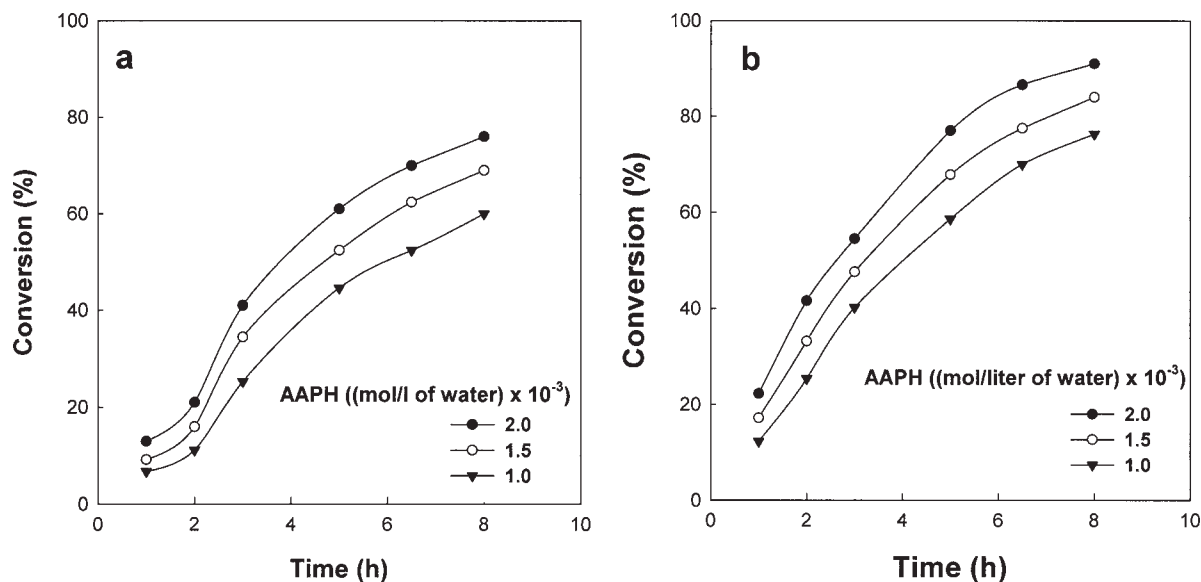
where  $\text{DP}_1$  is the  $P_n$  of PVPi and  $\text{DP}_2$  is the  $P_n$  of PVA prepared by saponifying PVAc. The s-diad contents of the PVAs were determined by 300 MHz  $^1\text{H}$  NMR, using  $\text{DMSO-d}_6$  as the solvent, based on the ratio of the components of the hydroxyl proton triplet at 4.1–4.7 ppm. The surface morphologies of the PVPi and PVA specimens and particles were investigated, using a scanning electron microscope (JSM 5800-LV, JEOL, JAPNA) with a magnification of  $200\times$  and  $500\times$ , respectively, and optical microscope.

## RESULTS AND DISCUSSION

It is important to find out the optimum values among the various emulsion polymerization factors that affect

TABLE I  
Emulsion Polymerization Condition of VPI

Monomer/ water (volume ratio)	1/2
Emulsifier concentration (mol/L of water)	$1.5 \times 10^{-3}$ , $2.0 \times 10^{-3}$ , $3.0 \times 10^{-3}$ , $4.0 \times 10^{-3}$
Initiator concentration (mol/L of water)	$1.0 \times 10^{-3}$ , $1.5 \times 10^{-3}$ , $2.0 \times 10^{-3}$
Temperature ( $^\circ\text{C}$ )	50, 55
rpm	170, 300



**Figure 1** Conversions of VPi into PVPi obtained by emulsion polymerization of VPi, using AAPH content of  $2.0 \times 10^{-3}$  mol/L of water and SDS content of  $2.0 \times 10^{-3}$  mol/L of water with polymerization times: (a) 50°C and (b) 55°C.

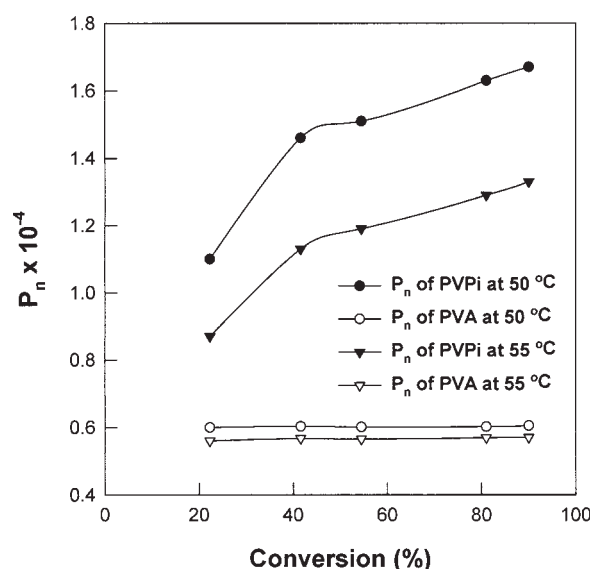
the conversion and molecular weight such as initiation method, volume ratio of monomer to water,<sup>28</sup> amount and type of initiator, amount and type of emulsifier,<sup>29</sup> agitation method and agitation speed,<sup>30</sup> polymerization temperature, and polymerization time. Generally, in a free radical polymerization process, the rate of polymerization is increased as the efficiency of initiator is enhanced. Thus, the rate of conversion is increased by raising the temperature or increasing initiator content. In this work, AAPH were used as initiators in emulsion polymerization of VPi, and the effects of initiators on the conversion, and DB of PVPi and the molecular weights of PVPi and PVA were investigated. AAPH initiators used in these polymerizations are water soluble initiators. AAPH 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 N=N bonds within the molecule, exhibit bond dissociation energies falling with 30–35 kcal/mol. These decompose at very convenient temperature 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 of emulsion polymerization of VPi for temperature 50 and 55°C. The rate of conversion was increased at higher polymerization temperature and higher AAPH concentration. Especially maximum conversion of over 90% was obtained at 55°C (Table II).

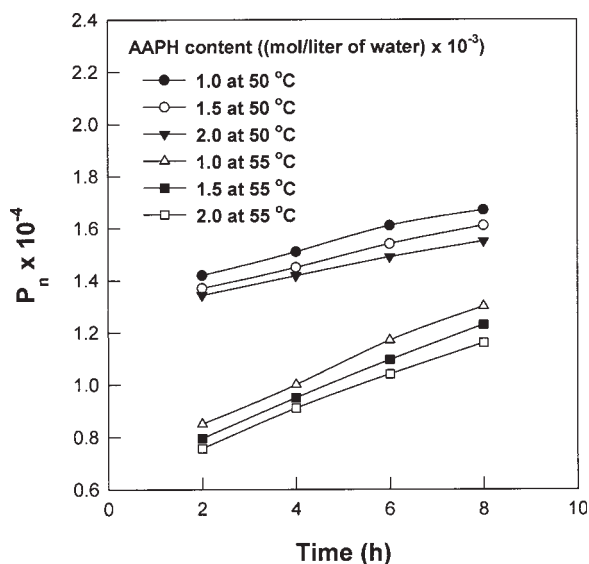
Figures 2 and 3 show the effects of various emulsion polymerization conditions of VPi on the molecular weights of both PVPi and PVA. The  $P_n$  may be decreased as the efficiency and concentration of initiator are increased. ( $P_n$ )s of PVPi prepared by emulsion

**TABLE II**  
Maximum Conversion and ( $P_n$ )s of PVAc and PVA in this Study

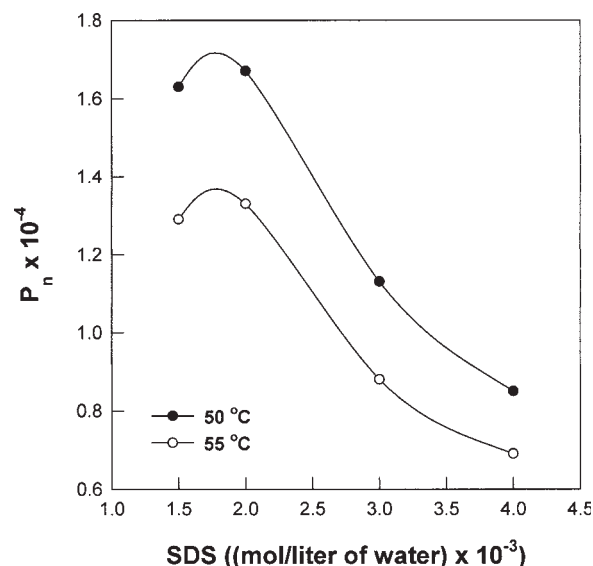
Initiator type	Conversion (%)	$P_n \times 10^{-4}$	
		PVPi	PVA
AAPH	91	1.67	0.62



**Figure 2** ( $P_n$ )s of PVPi obtained by the emulsion polymerization of VPi at 50 and 55°C, using AAPH content of  $1.0 \times 10^{-3}$  mol/L of water and SDS content of  $2.0 \times 10^{-3}$  mol/L of water and resulting PVA with conversions.



**Figure 3** Effect of the AAPH content on the  $P_n$  of PVPi obtained by the emulsion polymerization of VPi at 50 and 55°C, using SDS content of  $2.0 \times 10^{-3}$  mol/L of water.

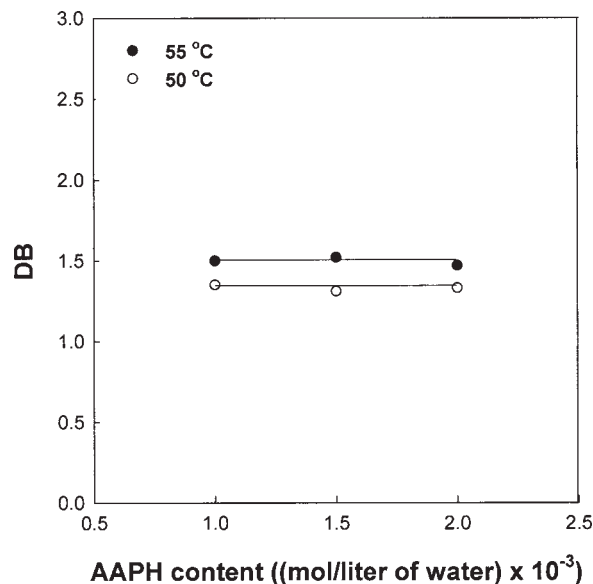


**Figure 4** Effect of the amount of SDS on the  $P_n$  of PVPi obtained by the emulsion polymerization of VPi at 50 and 55°C, using AAPH content of  $1.0 \times 10^{-3}$  mol/L of water.

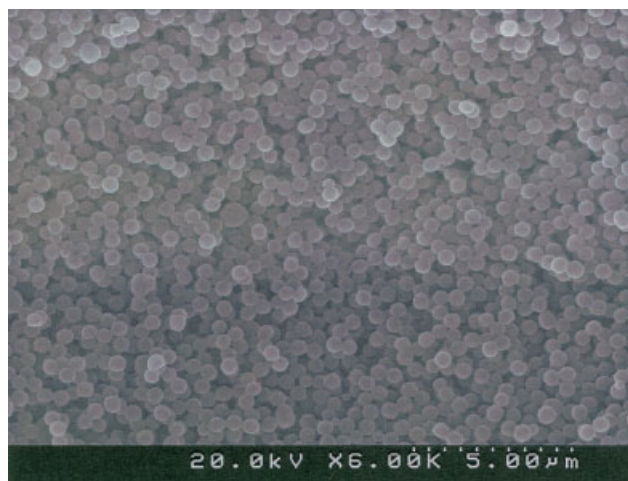
polymerization at 50 and 55°C and corresponding PVA obtained by saponifying PVPi with conversions are shown in Figure 2. Difference between ( $P_n$ )s of PVPi and PVA is mostly obliged to branched structures, which may be broken down when saponified.  $P_n$  of PVA remained almost constant and nearly independent of  $P_n$  of PVPi, and then  $P_n$  of PVA slightly decreased at higher conversions. It might be caused by frequent chain transfer reactions between polymers resulting in termination and branch formation reactions at higher conversions, whereas chain transfer reactions between monomers were prevail at lower ones.<sup>31</sup> The ( $P_n$ )s of PVPi and PVA were increased with a decrease in the AAPH concentration. HMW (PVA)s having various ( $P_n$ )s of 6200 could be prepared by saponifying HMW (PVPi)s having ( $P_n$ )s of 13,300–16,700 polymerized in emulsion.

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 water phase. Emulsifier act to stabilize the monomer droplets 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 aqueous phase to a lesser extent, sometimes serves as the site for the nucleation of particles, and sometimes act as chain transfer agents and retarders.<sup>32</sup> Therefore, to find out optimum emulsifier concentration is important for obtaining HMW PVPi and HMW PVA. The emulsifier, SDS, used in this study, is one of the most commonly used anionic surfactants having a sulfate ionic group. Effect of the amount of SDS on  $P_n$  of PVPi at each polymerization

temperature is presented in Figure 4. The emulsion system by AAPH was unstable below an SDS concentration of  $1.5 \times 10^{-3}$  mol/L of water because this amount of SDS was not enough to emulsify VPi effectively so that, the effective polymerization could not occur. Likewise, there existed the optimum concentration of SDS for effective polymerization in the emulsion polymerization by AAPH. From the above results, it was found that there existed the optimum emulsifier concentration, revealing higher molecular weight of PVPi, than other emulsifier concentrations at same polymerization condition.



**Figure 5** DB for pivaloyl group of PVPi obtained by emulsion polymerization of VPi with AAPH content.



**Figure 6** SEM photograph of PVPi microspheres obtained by the emulsion polymerization of VPi at 55°C, using an AAPH concentration of  $2.0 \times 10^{-3}$  mol/L of water and an SDS concentration of  $2.0 \times 10^{-3}$  mol/L of water. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

Figure 5 shows DB for pivaroyl group of PVPi obtained by emulsion polymerization of VPi at same conditions and similar conversions of about 30% with  $P_n$  at two different polymerization temperatures. On the whole, DB was increased with increasing AAPH contents at polymerization temperature of 50 and 55°C. DB of AAPH at 55°C were 1.4–1.5 and were 1.3–1.4 at 50°C, respectively. Like this, the extent of increasing DB was more prominent at higher polymerization temperature.

In this study, PVPi micro- and nano-spheres was obtained by emulsion polymerization of VPi using AAPH. Figure 6 shows the SEM photograph of PVPi microspheres. Despite of original PVPi specimen directly prepared from emulsion polymerization of VPi without separation procedures like sieving. It is shown that uniform PVPi spheres with diameter of 400–500 nm could be obtained.

## CONCLUSIONS

To prepare high yield PVPi and HMW PVA, VPi was polymerized in emulsion at 50 and 55°C using AAPH as initiators, respectively, by controlling various polymerization factors. Conversion of VPi into PVPi obtained by the emulsion polymerization of VPi according to the polymerization time at lower temperature is lower than that of emulsion polymerization at higher one. Molecular weight of PVPi at lower temperature is higher than that of PVPi at higher one. PVA having maximum  $P_n$  of 6200 could be prepared by complete saponification of PVPi having maximum  $P_n$  of 16,700 obtained with  $2.0 \times 10^{-3}$  mol/L of water of SDS and  $1.0 \times 10^{-3}$  mol/L of

water of AAPH at 50°C. Emulsion polymerization of VPi is a good method for producing HMW PVPi, with high yield (maximum conversion of over 90%). In the near future, we will report on the preparation and characterization of PVPi and syndiotactic PVA micro- and nano-spheres obtained by this emulsion polymerization technique.

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