

피발산비닐과 아세트산비닐의 현탁공중합을 이용한 폴리(피발산비닐/아세트산비닐) 입자의 제조 및 특성

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Preparation of Poly(vinyl pivalate/vinyl acetate) Microspheres Using Suspension Copolymerization of Vinyl Pivalate and Vinyl Acetate and its characterization

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1. Introduction

Poly(vinyl alcohol) (PVA) obtained from VPi has the highest syndiotacticity among (PVA)s obtained via radical polymerization, and the s-diad content of PVA prepared by low temperature polymerization of vinyl pivalate (VPi)[1-5] comes to over 60%. Therefore, we can obtain (PVA)s with various tacticities through the copolymerization of vinyl acetate (VAc) and VPi and can examine the relation between physical properties of (PVA)s and their tacticities.

Suspension polymerization is a powerful process for many reasons, including the ease with which the heat produced by the strongly exothermic reaction can be removed and the possibility of producing polymer particles with diameters in the range 50-1000 μm which can be appropriate for many industrial applications.[6-7]

In this study, a room-temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN), was selected in suspension copolymerization of VPi and VAc to obtain ultrahigh molecular weight (UHMW) syndiotactic poly(vinyl pivalate/vinyl acetate) P(VPi/VAc) microspheres with higher conversions, various particle size and uniform size distribution, which is expected to be a profitable precursor of UHMW syndiotactic PVA microspheres with high yield.

2. Experimental

2.1. Materials

VPi and VAc 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 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.

2.2. Suspension Copolymerization of VPi and VAc

In a typical reaction, suspending agent was dissolved in water under nitrogen atmosphere and constant stirring in a 250 ml reactor fitted with a condenser. After degassing, VPi and VAc 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 spherical P(VPi/VAc) particles. To eliminate residual VPi and VAc and suspending agent, P(VPi/VAc) polymerized was filtered and washed with warm water. 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. The suspension copolymerization conditions of VPi and VAc

Type of initiator	ADMVN
Type of suspending agent	PVA
Initiator concentration	0.0001 mol/mol of monomers
Suspending agent concentration	1.5 g/dl of water
VPi/VAc	1/9, 2/8, 3/7, 4/6, and 5/5 mol/mol
Monomers/water	0.50 l/l
Rpm	300 and 500
Temperature	30 °C

2.3. Characterizations

Viscosities of P(VPi/VAc) microspheres were measured. Relative and specific viscosities were calculated according to

$$\eta_{rel} = t/t_0, \eta_{sp} = \eta_{rel} - 1, \eta = \eta_{sp}/c$$

where t , t_0 , and c are the flow time for the given polymer solution, the solvent, and the given polymer solution concentration, respectively.

The surface morphology of particle was investigated using a scanning electron microscope (SEM) (JSM 5800-LV, Jeol, Japan) with a magnification of 200 and optical microscope. The particle diameters of some samples were also measured directly from SEM.

3. Results and discussion

Effects of polymerization conditions were examined to find the optimum conditions for the production of P(VPi/VAc) particles. The microspheres of P(VPi/VAc) having various diameters from 75 μm to 600 μm and higher conversion were obtained at polymerization temperature of 30 °C by controlling the stirring rate at the fixed conditions of the other factors (Figure 1). And microspheres of P(VPi/VAc) having various s-diad contents of 56.2%-58.5% were obtained by varying VAc/VPi feed ratio (Figure 2).

Table II shows data for the monomer composition for the intrinsic viscosity of the copolymers. Higher intrinsic viscosities were obtained for higher VPi contents of the copolymer. So, P(VPi/VAc) microspheres with various s-diad contents and intrinsic viscosities were produced by controlling VPi content.

4. References

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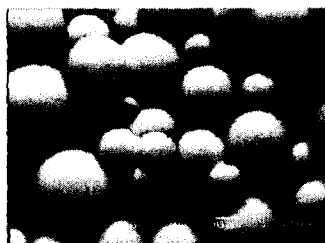


Figure 1. Scanning electron micrograph of non-sieved P(VPi/VAc) microspheres prepared by suspension copolymerization of VPi and VAc at 30 °C using suspending agent concentration of 1.5 g/dl of water, monomer/water of 0.5 l/l, VPi/VAc feed mole ratio of 4/6, and agitation speed of 300 rpm using ADMVN concentration of 0.0001 mol/mol of monomers with polymerization times.

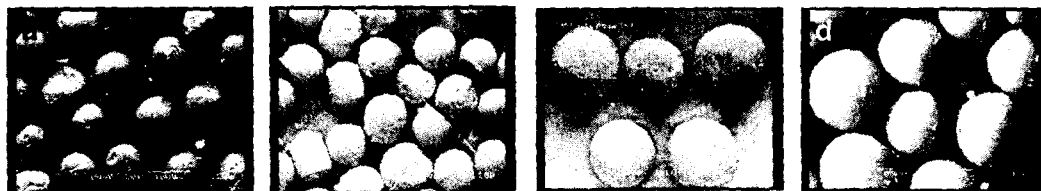


Figure 2. Scanning electron micrograph of sieved monodisperse P(VPi/VAc) microspheres prepared by suspension copolymerization of VPi and VAc at 30 °C using suspending agent concentration of 1.5 g/dl of water, monomers/water of 0.5 l/l, agitation speed of 300 rpm, and the various VPi/VAc feed mole ratio, D_{voadr} , PI: a, 2/8, 107 μm , 1.01; b, 3/7, 154 μm , 1.04; c, 4/6, 208 μm , 1.07; d, 5/5, 352 μm , 1.14 using ADMVN concentration of 0.0001 mol/mol of monomers with polymerization times.

Table II. The intrinsic viscosity of P(VPi/VAc) microspheres with an increase of VPi content

VPi/VAc	Intrinsic viscosity (η)
2/8	2.65
3/7	2.68
4/6	2.92
5/5	3.28
6/4	3.36