

Dispersion Polymerization of Vinyl Pivalate in Supercritical Carbon Dioxide: An Environmentally Benign Synthesis

Long Quang Pham, Nguyen Van Hoa, Yuvaraj Haldorai, Jae-Jin Shim*
(jjshim@yu.ac.kr*)

1. Introduction

Poly (vinyl alcohol) (PVA) has attracted much attention as basic material for high modulus/high strength fibers which can replace the carcinogenic asbestos fiber in construction materials, films for food and drug packages, polarization, and barrier membranes, and gel for drug delivery systems¹. It is impossible to synthesize PVA by polymerization of Vinyl Alcohol because this is unstable at normal condition. Therefore, many works have taken advantages of the precursor polymers most of which were vinyl ester compounds including poly (vinyl acetate)^{7,8} and poly (vinyl pivalate) (PVPi)¹⁻⁶. PVPi has been demonstrated a good precursor for preparing PVA with high syndiotacticity¹⁻⁶. Different polymerization methods have been used to polymerize vinyl pivalate (VPi) such as bulk¹, suspension^{4,6}, solution^{2,3} and emulsion⁵. However, most of these methods dealt with the use of volatile organic compounds which have prompted considerable worldwide environmental concern.

Recently, the use of supercritical carbon dioxide (scCO₂) in polymer synthesis has been extensively studied. This is due to the environmental benefits of scCO₂ when it is used as a medium for polymerization reactions⁹. ScCO₂ also has gaslike diffusivities while possessing liquidlike densities that allow for solvation of many compounds¹⁰. Moreover, CO₂ is inexpensive, nonflammable and nontoxic and it has an easily accessible critical point (T_c=31.1⁰C; P_c=73.8 bar). Since Desimone successfully studied the free radical dispersion polymerization of methyl methacrylate (MMA) in scCO₂ employing poly(1,1-dihydroperfluorooctyl acrylate) (PFOA) as a stabilizer¹¹, many works has been carried out to synthesize polymers using the same method¹³⁻¹⁶. It is well known that the principle of the dispersion polymerization method in which monomer is soluble in the solvent while polymer product is insoluble is the formation of polymer particles stabilized with one or more stabilizers. This stabilizer contained a lipophilic part that can anchor onto the growing polymer particles and a CO₂-philic part that makes it soluble in the CO₂ continuous phase, thus giving rise to the steric stabilization and preventing particle flocculation⁹. The most effective stabilizers have been used so far were fluorinated and siloxane-based polymers due to their high solubility in scCO₂. PFOA¹¹ and poly (dimethylsiloxane-g-pyrrolidone carboxylic acid) (Monasil PCA)¹⁵ have been proved to be good stabilizers for PMMA as free-flowing polymer powder was obtained with high yield (>90%) and high molecular weight (>2.10⁵ g/mol). In the present study, we employ both PFOA and Monasil PCA as the stabilizers for the dispersion polymerization VPi in scCO₂. In both the cases, no spherical polymer particles could be obtained in the form of free-flowing powder as could be seen from MMA. Reaction time, pressure, temperature, stabilizer concentration and initiator concentration were investigated to evaluate their influence to the molecular weight and yield of PVPi product.

2. Experimental

Materials

CO₂ with purity of 99.999% was purchased from Korea Specialty Gases. Vinyl Pivalate (Aldrich) was purified by passage through an alumina column (Aldrich) and flushed with nitrogen. 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol. Monasil PCA (Uniquema) having molecular weight of 8500g/mol was used without further purification¹⁴. PFOA having molecular weight of 58kg/mol was prepared by bulk polymerization of 1H,1H-perfluorooctyl acrylate (FOA) at 65⁰C, 24h using AIBN as initiator.

Dispersion polymerization of VPi in scCO₂

Polymerization was conducted in a high pressure reactor equipped with a sapphire window for visual observation of the reaction mixture. CO₂ pressure and flow rate were controlled using an ISCO pump. The equipment set-up was similar to what given by Park¹⁴. AIBN (0.5–3 wt% of monomer) and a desired amount of stabilizer (2–15 wt% of monomer) were charged into the reactor and then purged with CO₂ in about 20 min. Then 2g monomer was injected using a syringe. About 10g of CO₂ was introduced and the whole system was immersed into a water bath equipped with a thermostat. While the system was slowly heating, CO₂ was applied to the back chamber to pressurize the system. Once reaching the final condition, the reaction was allowed to proceed with stirring by a magnetic stirrer. Once the reaction finished, the reactor was cooled in an ice bath and CO₂ was slowly vented from the cell. Polymer was collected and dried. The yield was measured gravimetrically. Molecular weight of PVPi samples was determined by Gel Permeation Chromatograph (GPC) (Waters 515) using tetrahydrofuran (THF) as eluent and polystyrene as standards.

3. Result and Discussion

Temperature effect

The effect of temperature on the yield and molecular weight of PVPi is shown in Figure 1. Yield and molecular weight followed different trends when temperature was increased. While the yield went up at elevated temperature, the molecular weight decreased significantly. These trends naturally take place in the polymerization initiated by the thermal dissociating of an initiator¹⁸. Therefore, increasing temperature results in higher polymerization rate and reducing molecular weight of the polymer.

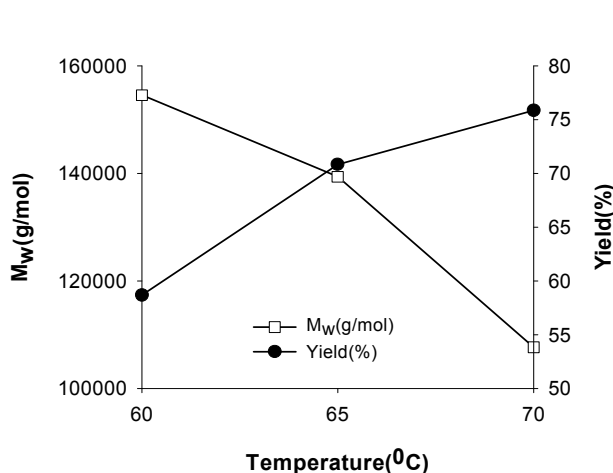


Figure 1. The effect of reaction temperature on the yield and molecular weight of PVPi. Reaction condition: 2g monomer, 10g CO₂, 1% wt/wt monomer AIBN, 5% wt/wt monomer Monasil PCA, 345 ± 1 bar, 12h.

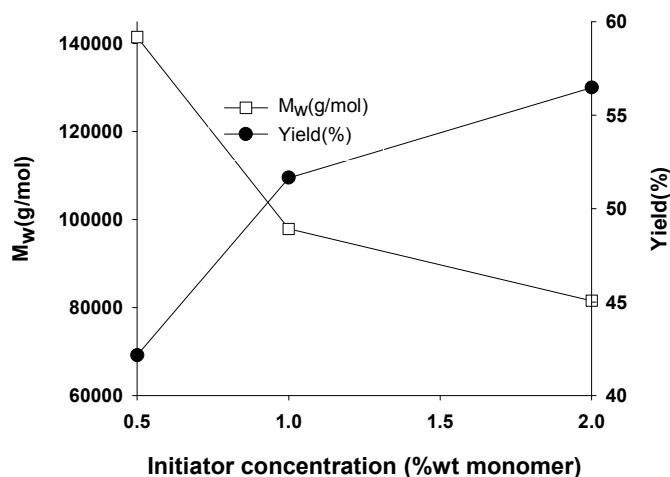


Figure 2. The effect of initiator concentration on the yield and molecular weight of PVPi. Reaction condition: 2g monomer, 10g CO₂, 5% wt/wt monomer Monasil PCA, 65°C, 345 ± 1 bar, 10h.

Initiator concentration

The effect of initiator concentration is illustrated in figure 2. Increasing the concentration of AIBN led to the increase in the yield of PVPi but decreased the molecular weight. These trends properly follow

the kinetic theory in which the kinetic chain length is reciprocal to the initiator concentration while the conversion increases as the initiator concentration increases¹⁸.

Pressure effect

An advantage of employing scCO₂ lies in the ability to tune the solvent density and dielectric constant by simply changing either temperature or pressure. Since these changes can alter the solubility of stabilizer in scCO₂, the polymerization was influenced by changing pressure as can be seen from the Table 1.

In general, the molecular weight increases as the pressure increases and the molecular weight distributions at low pressure were narrower than those at high pressure due to lower density solvent that made a more even distribution of monomer molecules.

Table 1. Effect of pressure on the yield and molecular weight of PVPi. Reaction condition: 2g monomer, 10g CO₂, 1%wt /wt monomer AIBN, 5%wt/wt monomer Monasil PCA., 65°C, 12h.

Entry	Pressure (bar)	Yield (%) ^a	M _w (kg/mol) ^b	PDI
1	206	40.4	69	1.7
2	275	44.5	86	1.8
3	310	73.6	127	2.2
4	345	70.8	139	1.9
5	379	71.7	144	1.9

Reaction time

Polymerization of VPi was done in different reaction time employing Monasil and PFOA as stabilizers. In both the cases, either the yield or molecular weight of PVPi increased as the reaction time increased as can be seen from the Table 2. This trend naturally occurs in conventional radical polymerization and can be obtained in different system like styrene^{14,17}, VPi¹⁻⁷, and MMA¹⁶.

Stabilizer concentration

Different Monasil PCA concentration was used to investigate the effect of the stabilizer on the yield and the molecular weight of PVPi. It can be seen from the Table 3 that when the Monasil PCA content increases the yield slightly increases but the molecular weight decreases. By observation during the

Table 2. The effect of reaction time on the polymerization of VPi. Reaction condition: 2g monomer, 10g CO₂, 1%wt/wt monomer AIBN, 65°C, 345 ± 1 bar.

Entry	Time(h)	Yield(%)	M _w (kg/mol)	PDI
PFOA (1%wt/wt monomer)				
1	10	54.04	100	1.6
2	20	82.15	123	1.8
3	30	86.25	170	2.1
Monasil PCA (5%wt/wt monomer)				
4	5	46.85	92	1.7
5	10	59.43	113	2.1
6	15	76.91	117	1.7

reaction, we could see the stabilization happened inside the reactor through the sapphire window. Initially, the mixture appeared opaque as monasil PCA was dispersed in to the continuous phase. For the time being, the mixture became cloudier as more polymer particles were formed. Finally, only quite homogeneous white mixture could be seen. Generally, a good stabilization system should form stable homogeneous latex in scCO₂ even when stirring is stopped, however, monasil PCA could only

form a weak dispersion system with PVPi evidenced by the quick settlement of polymer particles. This is derived from the ineffective anchoring of the pyrrolidone carboxylic acid group onto the growing PVPi particles and hence, the particles easily collapse at the depressurization stage, one of the reasons why we could not get the polymer as free – flowing powder.

Table 3. The effect of stabilizer concentration on the polymerization of VPI. Reaction condition: 2g monomer, 10g CO₂, 1%wt AIBN, 65°C, 345 ± 1bar, 10h.

Entry	Monasil PCA(%wt)	Yield (%) ^a	M _w (kg/mol) ^b	PDI
1	5	43.7	82	2.1
2	10	43.8	74	2.0
3	15	45.8	71	1.7
4	20	49.2	60	2.1

4. Conclusion

We have successfully synthesized PVPi in supercritical carbon dioxide by dispersion polymerization method using PFOA and Monasil PCA. Different experimental parameters were also investigated to get the optimum reaction conditions. From the results, it can be realized that PVPi can be polymerized in a benign solvent like scCO₂ with relative high yield and high molecular weight.

Acknowledgements

This research is supported by grant number RT104-01-04 from the Regional Technology Innovation Program of the Ministry of Knowledge and Economy (MOKE).

Reference

- (1) Lyoo, W. S.; Han, S.S; Kim, J.H and Yoon, W.H. *D.A Makro Chemie*, **271**, 46 – 52 (1996)
- (2) Lyoo, W. S.; Kim, S.S; Ghim, H.D and Kim, J. P. *J.Appl Polym Sci*, **85**, 1992 – 2003 (2002)
- (3) Lyoo, W. S.; Ghim, H.D and Kim, J.H. *Macromolecules*, **36**, 5428 – 5431 (2003)
- (4) Lyoo, W. S.; Park, C.S; Yeum, B.C and Ji, C.J Lee. *Colloid Polym Sci*, **280**, 1075 – 1083 (2002)
- (5) Song D. H and Lyoo, W.S. *J.Appl Polym Sci*, **104**, 410 – 414 (2007)
- (6) Lyoo, W. S.; Park, C.S; Kim, J.H and Ghim, H.D. *J.Appl Polym Sci*, **88**, 832 – 839 (2003)
- (7) Lyoo, W. S.; Lee, Sung Min; Koo, Kang; Lee. *J.Appl Polym Sci*, **82**, 1897-1902 (2001)
- (8) Lyoo, W. S.; Song, Du H.; Lee, Won C. *J.Appl Polym Sci*, **102**, 4831-4834 (2006)
- (9) Cooper, Andrew I. *J. Mat Chem*, **10**, 207-234 (2000)
- (10) J.L Kendall, D.A Canelas, J.L Young, J.M Desimone. *Chem. Rev*, **99**, 543 – 563 (1999)
- (11) DeSimone, J. M.; Maury, E. E. *Science*, **265**, 356-9 (1994)
- (12) DeSimone, J. M.; Guan, Zihubin; Elsbernd, C. S. *Science*, **257**, 945-947 (1992)
- (13) Canelas, D. A.; Betts, D. E.; DeSimone, J. M. *Macromolecules*, **29**, 2818-2821 (1996)
- (14) Canelas, Dorian A.; DeSimone, Joseph M. *Macromolecules*, **30**, 5673-5682 (1997)
- (15) Hsiao, Y.L, Mauri, E.E. *Macromolecules*, **28**, 8159 – 8166 (1995)
- (16) Park, Jin-Yeol; Shim, Jae-Jin. *J. Supercrit Fluids*, **27**, 297-307 (2003)
- (17) Wang, Ruolei; Cheung, H. Michael. *J. Appl Polym Sci*, **93**, 545-549 (2004)
- (18) G. Odian, Principles of polymerization, Wiley, New York, ed 3, 1981
- (19) A. Kumar, R.K Gupta. Fundamentals of polymer engineering, ed 2, CRC, 2003