

# Preparation of Poly(Vinyl Acetate) using Supercritical Carbon Dioxide

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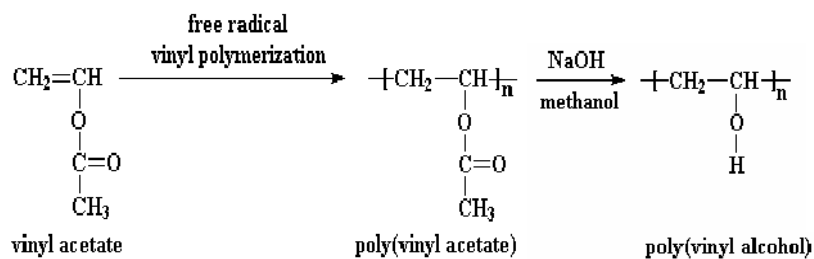
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## ABSTRACT

Since polymers were first synthesized by DeSimone et al. in early 1990s, many kinds of polymers have been prepared using supercritical fluids. Poly(2-ethylhexylacrylate), a rubbery polymer, was synthesized in supercritical carbon dioxide. In this study, another rubbery polymer, poly(vinyl acetate) (PVAc), a precursor of poly(vinyl alcohol) (PVA), was synthesized in supercritical CO<sub>2</sub> at 338.15 K and 345 bar. Molecular weight of PVAc obtained in this study was in the range of 25,000 ~ 190,000, depending on the reaction conditions. As expected, the molecular weight decreased but the yield of PVAc increased with increasing the amount of initiator. A maximum behavior in the molecular weight was observed. The yield of polymer also showed a maximum versus the amount of surfactant. Polymerization with and without surfactant was also investigated.

## INTRODUCTION

PVA is a polymer containing hydroxyl groups, and an extremely hygroscopic organic gel. Due to its high tensile strength and supreme modulus of elasticity of crystal, fibers obtained from this polymer have high tensile strength, high tensile elasticity and high abrasion resistance. Because PVA also has superior properties such as alkali-proof, very low oxygen permeability and good adhesion force, it is used in the industry as an alternative to iron reinforcing rod in concrete, high elastic organic fibers as an alternative to asbestos fibers, and so on [1-3]. PVA is difficult to obtain by directly polymerizing vinyl alcohol. PVA is thus made by saponification of vinyl ester derivative polymers (Figure 1), such as PVAc, polyvinyl pivalate(PVPi), polyvinyl trifluoroacetate(PVTFA), and polyvinyl trichloroacetate (PVTCAc). Although the monomers such as VPi, VTFA and VTCAc are used in the manufacturing excellent syndiotactic PVA, they are expensive and the polymers are hard to be hydrolyzed [4,5]. Thus PVAc is the most popular intermediate as it is inexpensive and easy to be hydrolyzed. However, it has a drawback of branching due to the rapid chain transfer caused by the high heat of reaction. It is difficult to get high molecular weight PVA with good molecular linearity and good spinning property [6,7].



**Figure 1:** The polymerization of vinyl acetate to poly(vinyl acetate), followed by saponification to produce poly(vinyl alcohol).

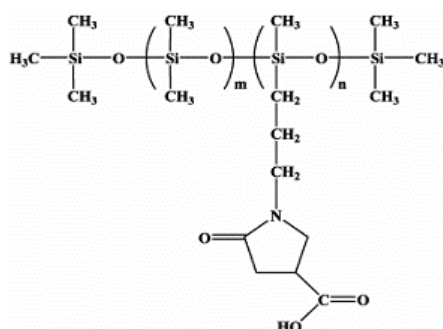
Supercritical fluids have a gas-like diffusivity that promotes the reaction and a liquid-like density that provides a good solubility. It is possible to change the solvent density with a small change in temperature or pressure, without altering the composition of the solvent. The chemical industry has become increasingly aware of environmental concern on using volatile organic solvents in the polymer industry. Therefore, supercritical carbon dioxide has been considered as an environmentally friendly alternative to the organic solvents. Carbon dioxide is not an expensive material as it produced naturally by respiration of plants and animals, or generated artificially as a byproduct from ammonia, hydrogen and ethanol plants and as a combustion product in the thermal power stations. Carbon dioxide has a very mild critical condition ( $T_c = 31.1^\circ\text{C}$ ,  $P_c = 73.8$  bar) and can be recycled easily as it is a gas. Furthermore, as it is inexpensive, nonflammable and nontoxic, carbon dioxide has become an attractive solvent in large scale polymer manufacturing industry.

So far, only a few studies have been reported for the polymerization of vinyl acetate in supercritical  $\text{CO}_2$ . In this study, we have performed the polymerization of vinyl acetate in supercritical carbon dioxide to obtain PVAc - a precursor of PVA - using a surfactant (stabilizer) that adsorb physically or chemically on the surface of polymer particles and prevent them from coalescing each other by electrostatic force or steric stabilization. A silicone-derivative polymer was adopted as the stabilizer. The effect of the type and amounts of initiator and surfactant as well as the reaction time on the yield and molecular weight of PVAc has also been investigated.

## MATERIALS AND METHODS

### Materials

Vinyl acetate (99%) is a monomer that was purchased from Aldrich. 20 ml of vinyl acetate was treated with 1.5 g of  $\text{K}_2\text{CO}_3$  to remove the moisture and passed through a small alumina column to remove the inhibitor. It was then purged with nitrogen for 30 minutes and was put into a vial to keep cold in a freezer at 253.15 K. 2,2-Azobisisobutyronitrile (AIBN) and potassium persulfate (KPS) from Aldrich were used as the initiator. Monasil PCA (poly(dimethylsiloxane)-*g*-pyrrolidonecarboxylic acid) (Figure 2) from Uniquima and sodium dodecyl sulfate (SDS) from Aldrich were used as stabilizers. AIBN was recrystallized with methanol to remove impurities before putting into polymerization vessel. KPS, SDS, and Monasil PCA were used without further purification. Ultrahigh purity carbon dioxide (99.995%) was purchased from Korea Industrial Gas Co.

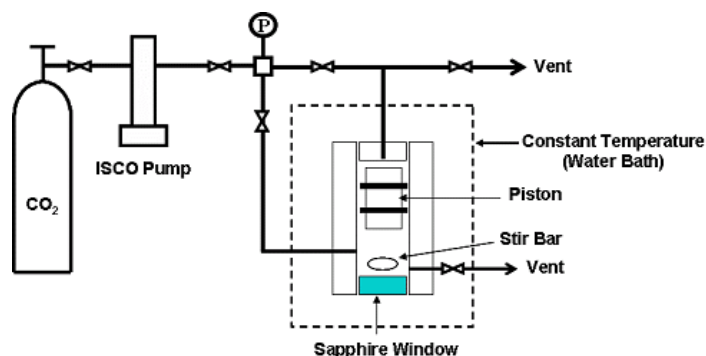


**Figure 2:** The molecular structure of Monasil PCA.

### Experimental Equipment and Procedures

An apparatus was set up as shown in Figure 3. The reactor was a variable-volume view cell with a piston to keep the pressure constant using an automatic syringe pump (ISCO Model 260D) throughout the reaction. After putting a known amount of initiator and surfactant into the cell, it was capped and purged with carbon dioxide for 10 minutes. A small amount of monomer was then injected into the cell by a graduated syringe. All the surfactant, initiator and monomer samples were accurately measured the weights (to  $\pm 0.0001$  g) by a balance (Mettler Model AG204) before putting into the cell.

A known amount of carbon dioxide was supplied to the cell and was agitated with a magnetic bar. The cell was then placed in the constant temperature water bath kept to a reaction temperature. The reactor was heated to the bath temperature while agitated. It was then kept at the temperature to incur the polymerization reaction. After a certain reaction time, the cell was quenched by placing in an ice bath to stop the polymerization. When the temperature was fully lowered, the pressure in the cell was reduced as much as possible by venting the rear chamber of the cell. The front chamber was vented to remove monomer and CO<sub>2</sub>. The polymer and surfactant that were deposited at the bottom of the chamber were collected using a spatula. The remaining polymer attached to the wall was also collected by dissolving it with acetone. These polymer samples were dried at room temperature for 24 hours to remove the remaining monomer.



**Figure 3:** Schematic diagram of the supercritical fluid polymerization equipment.

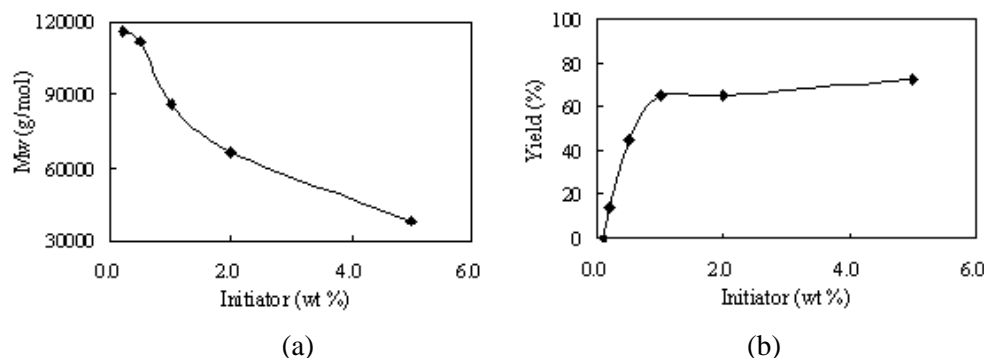
The molecular weight of the polymer prepared from the experiment was measured by gas permeation chromatography (GPC), consisted of Waters 515 Pump, Waters 2410 Differential Refractometer, and Rheodyne 7725I Injector and equipped with a column (Waters Stryagel HR5E). As a reference material for measuring the molecular weight of polymer, the Showadenko's polystyrene standards ( $M_w = 1310, 3370, 13900, 303000, 52400, 205000, 736000, 1190000, 2060000, 3850000$ ) were employed in the analysis. The polymer solutions for GPC analysis was prepared by dissolving the polymer in tetrahydrofuran. The column temperature was room temperature and the flow ratio of carrier is 1 ml/min.

## RESULTS

### Effect of Initiator

The molecular weight of PVAc prepared in the presence of supercritical carbon dioxide decreased with increasing the amount of initiator (Figure 4). When the more initiator is used, the more radicals are formed, shortening the length of each chain and reducing the molecular weight. At the initiator concentrations lower than 1 wt%, the molecular weight decreased sharply, but after 1 wt% the decreasing rate got much smaller. When the amount of initiator increases, the number of radicals that are involved in the reaction increases. Therefore, the molecular weight decreases but the yield increases. As the amount of initiator increases over 1 wt%, the number of radicals are so large that the radical forming rate might have been diminished. On the other hand, the yield of PVAc was increased sharply with increasing the amount of initiator up to 1 wt%. Between 1 and 5 wt%, the increasing rate of the yield was almost stopped. After 5%, the yield was increasing again but very slowly. We can see that the polymerization continued for 1 wt% or more initiator but was started from new radicals, making the yield almost the same. Thus, the amount of initiator necessary in the polymerization of vinyl acetate is 1.0 wt%. There are some research that used KPS and V-50 (2,2'-azobis(2-amidinopropane) dihydrochloride) as initiator [9-13] in the polymerization of vinyl acetate at atmospheric pressure. When KPS or V-50 was used, no polymer was formed. It was not even dissolved

well in CO<sub>2</sub>.



**Figure 4:** Variation of molecular weight (a) and yield (b) of PVAc upon the amount of initiator in the polymerization of vinyl acetate at 345 bar and 338.15 K for 10 hours.

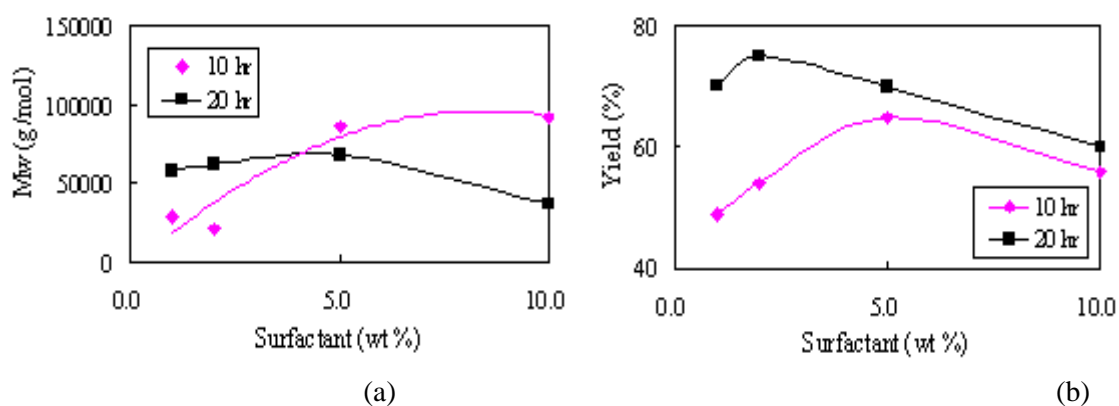
### Effect of Surfactant

When a reaction occurs in the supercritical fluid, a dispersion polymerization or a suspension polymerization takes place. Surfactants added to the reactor must have the bifunctional structure that has a part with affinity with carbon dioxide and the other part with affinity with polymer. We tested two surfactants: Monasil PCA and SDS (Table 1). Monasil PCA has CO<sub>2</sub>-philic groups and lipophilic groups. SDS has lipophilic groups and hydrophilic groups. Therefore, we can expect that these two surfactants should have different properties. When Monasil PCA (5 wt% of the monomer) was used in the reaction (the amount of initiator: 1 wt% of the monomer, reaction time: 5 hrs), the molecular weight of the resulting polymer was twice as large as that obtained without surfactant. The yield was also larger for the polymer obtained with Monasil PCA than that without the surfactant. When SDS was used in the same reaction, there have been essentially no changes in the molecular weight and the yield between the polymers prepared with the surfactant and without surfactant. We can see that SDS did not function at all as a surfactant. The following experiments are all done with Monasil PCA.

**Table 1:** Effect of surfactant on the polymerization

Monomer (g)	wt % of Initiator	wt % of Surfactant	Mw (g/mol)	Mn (g/mol)	Yield (%)	Time (hr)	Rxn	Surfactant Type
2.0516	1.0	0	61,000	46,000	16.72	5	O	-
2.0173	1.0	5.0	140,000	82,000	36.36	5	O	Monasil PCA
2.1677	1.0	5.0	62,000	45,000	32.57	5	O	SDS

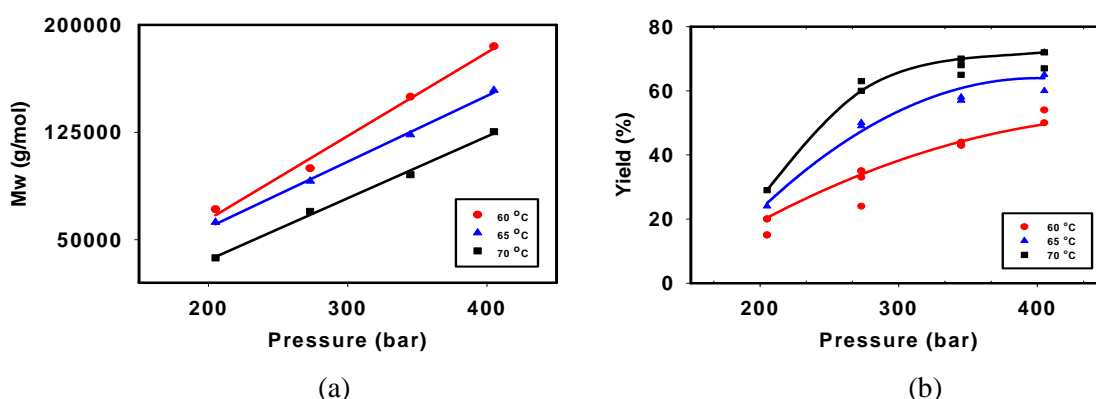
Figure 5 shows that, for the reaction time of 20 hours, the molecular weight increased slightly with increasing the amount of surfactant up to 5.0 wt%, but decreased thereafter. But, for the reaction time of 10 hours, the molecular weight was smaller than that for 20 hours but increased monotonically with the amount of surfactant and became higher than that for 20 hours. There was almost no change in the molecular weight for surfactant larger than 5 wt% at a fixed reaction time of 10 hours. The yield of PVAc showed a maximum at 2 wt% surfactant for the 20 hour reaction but for the 10 hour reaction, it was at 5wt% surfactant. We observed the effect of surfactant in the reaction mixture: (1) when was no surfactant, the reaction mixture was only a little opaque but (2) when Monasil PCA was used in the reaction, the reaction mixture became white milky state.



**Figure 5:** Variation of molecular weight (a) and yield (b) of PVAc upon the amount of surfactant for 2 different reaction time at 345 bar and 338.15 K.

### Effect of Pressure

Figure 6 shows the effect of pressure and temperature on the yield and molecular weight of PVAc. When the pressure was raised from 205 bar to 405 bar, the molecular weight continuously increased from 37,000 to 185,000 g/mol for all temperatures. The yield was increased at the lower pressure from 205 bar to 345 bar, whereas at the higher pressure from 345 bar to 405 bar, the increasing rate of the yield very small, approximately 2% at 343.15 K. The higher the temperature is, the more yield can be obtained from the reaction.



**Figure 6:** Variation of molecular weight (a) and yield (b) of PVAc with pressure and temperature for the reaction at 10hr.

### CONCLUSION

AIBN and Monasil PCA were functioning well as initiator and stabilizer, respectively, in the polymerization of vinyl acetate. Other initiators such as KPS and V-50 did not work at all in this reaction. As the amount of initiator increased, the molecular weight decreased monotonically, while the yield increased sharply up to 1 wt% of initiator. However, the yield did not increase much thereafter. For the reaction time of 10 hours, the molecular weight increased up to 10 wt% of surfactant but the yield increased at first but decreased. The maximum in yield occurred at the 5 wt% surfactant. Also, both the molecular weight and the yield increased with increasing reaction time. The yield and the molecular weight increased with the increasing of pressure at all temperatures. However, the increasing rate of the yield became smaller at the higher pressure.

## ACKNOWLEDGMENT

This work was supported by grant No. RTI04-01-04 from the Regional Technology Innovation Program of the Ministry of Commerce, Industry, and Energy (MOCIE). We thank Uniquima for providing us the surfactant.

## REFERENCES

- [1] MAQRTEEN, F., L., in Encyclopedia of Polymer Science and Technology, MARK, H., F., BIKALES, N., M., OVERBERGER, C., G., MENGES, G., KROCHWITZ, J., I., Ed., John Wiley and Sons, N. Y., **1985**, p.167
- [2] TOYOSHIMA, K., in Polyvinyl Alcohol, FINCH, C., A., Ed., John Wiley and Sons, N. Y., **1973**, p.339
- [3] SAKURADA, I., in Polyvinyl Alcohol Fibers, LEWIN, M., Ed., DEKKER, M., N. Y., **1985**, p.3 and p.361
- [4] MASUDA, M., in Polyvinyl Alcohol-Development, FINCH, C., A., Ed., John Wiley and Sons, N. Y., **1991**, p.403
- [5] COOPER, W., JOHNSON, F., R., VAUCHAN, G., J. Polym. Sci., Part A, Vol. 1, **1963**, p. 1509
- [6] IMAI, K., SHIOMI, T., ODA, N., OTASUKA, H., J. Polym. Sci., Part A, Polym. Chem., Vol. 24, **1986**, p. 3225
- [7] KENDALL, J., L., CANELAS, D., A., YOUNG, J., L., DESIMONE, J., M., Chem. Rev., Vol. 99, **1999**, p. 543
- [8] RUSSUM, J., P., BARBRE, N., D., JONES, C., W., SCHORK, F. J., J. Polym. SCI. Part A: Polym. Chem., Vol. 43, **2005**, p. 2188
- [9] WU, X., Q., SCHORK, F., J., J. App. Polym. Sci. Vol. 81, **2001**, p. 1691
- [10] LYOO, W., S., KWAK, J., W., CHOI, K., H., NOH, S., K., J. App. Polym. Sci. Vol. 94, **2004**, p. 2356
- [11] CISNEROS, M., G., TREVINO, M., E., PERALTA, R., D., RABELERO, M., MENDIZABAL, E., PUIG, J., E., CESTEROS, C., LOPEZ, R., G., Polymer, Vol. 46, **2005**, p. 2900
- [12] OKAYA, T., KIKUCHI, K., SUZUKI, A., IKEDA, N., Polym. Int., Vol. 54, **2005**, p. 143
- [13] BEUERMANN, S., BUBACK, M., NELKE, D., Macromolecules, Vol. 34, No.19, **2001**, p. 6637