Polymerization of vinyl pivalate in supercritical carbon dioxide and the saponification for the preparation of syndiotacticity-rich poly(vinyl alcohol)

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Abstract–This paper reports a successful free-radical dispersion polymerization of vinyl pivalate in supercritical carbon dioxide using poly(1H,1H-dihydroperfluorooctyl acrylate) and dimethylsiloxane-*g*-pyrrolidone carboxylic acid (Monasil PCA) as stabilizers. In both cases, no spherical polymer particles were obtained, which might be due to the high solubility of poly(vinyl pivalate) (PVPi) in supercritical carbon dioxide. The effects of the reaction time, pressure, temperature, monomer loading, stabilizer concentration and initiator concentration on the polymer yield and molecular weight of PVPi were also investigated. In addition, the formation of poly(vinyl alcohol) via saponification of the resulting PVPi is described.

Key words: Poly(vinyl pivalate), Poly(vinyl alcohol), Supercritical Carbon Dioxide, Dispersion Polymerization

INTRODUCTION

Highly syndioctactic poly(vinyl alcohol) (PVA) has good resistance to weather and alkali, as well as high crystallinity, making it suitable for use as a basic material for high modulus/high strength fibers that can replace carcinogenic asbestos fibers in construction materials, films for food and drug packages, polarization and barrier membranes, and gels for drug delivery systems [1-4]. PVA is synthesized mostly by the saponification of vinyl esters, such as poly(vinyl acetate) (PVAc) [5,6] and poly(vinyl pivalate) (PVPi) [7-23] because vinyl alcohol monomer cannot exist in the free state [4]. PVPi is considered the best precursor for the preparation of highly syndiotactic PVA owing to the strong steric hindrance of the *tert*-butyl group in vinyl pivalate (VPi) [12]. PVA synthesized from PVPi frequently has a syndiotacticdiad (S-diad) content of 58-65%, which is higher than that of commercial PVA products with an atactic body of 53-54% S-diads [7]. Only PVA with a non-descriptive morphology was obtained with a syndiotactic content of less than 55-56%. As the S-diads content was increased to more than 56%, a highly crystalline and well-oriented PVA with a fibrous morphology was observed. The structural changes correlated with the improvements in the tensile properties, melting behavior and solubility [8].

VPi can be polymerized by different methods including bulk, solution, suspension and emulsion. In these methods, the use of 2,2′-azobis(2,4-dimethylvaleronitrile) as a low-temperature activated initiator had a significant effect on the molecular weight of PVPi when an ultrahigh degree of polymerization (P_n) of up to 40,000 was obtained. PVPi synthesized in the bulk [9-12] gave a high molecular weight but very low conversion (36%). Solution polymerization of PVPi [13-17] using DMSO and TBA yielded PVPi with high conversion. Therefore, suspension [18-20] and emulsion [21-23] poly-

merization methods appear to be most successful for the synthesis of PVPi with either high molecular weight of approximately 40,000 or high conversion of up to 98% as well as using water as a medium for the reaction. On the other hand, although the use of water can relieve the environmental problems to some extent, there are still a large amount of hazardous aqueous sewage that requires treatments.

Recently, the use of supercritical carbon dioxide (scCO$_2$) in polymer synthesis has been studied extensively due to the environmental friendliness of this fluid. ScCO$_2$ with an easily accessible critical point (31.1 °C, 73.8 bar) possesses both gas-like diffusivity, which has important implications for the reaction kinetics, and a liquid-like density, which allows the solvation of many compounds [24]. The density of scCO$_2$ correlating with the solvent power can be tuned continuously by simply changing the temperature and/or pressure without altering its composition [25]. This gives rise to the preferential use of CO$_2$ as a solvent for chemical reactions, particularly for polymerization, because scCO$_2$ can dissolve different types of monomers. Moreover, separation of the carbonic solvent from the polymer products by simple depressurization can save a significant amount of energy for the drying process. As an ambient gas, CO$_2$ can be recycled easily after use to negate any contribution to greenhouse gas emissions. In addition, CO$_2$ is inflammable, non-toxic and inexpensive. Moreover, it is naturally abundant and produced readily in high purity. These advantages of CO$_2$ support the growing use of this material in industry as a replacement for current organic solvents.

Since DeSimone [26,27] conducted the first successful free radical dispersion polymerization of methyl methacrylate (MMA) in scCO$_2$ using poly(1H,1H-dihydroperfluorooctyl acrylate) (PFOA) as a stabilizer, many studies have been carried out to synthesize polymers using the same method [28]. The principle of dispersion polymerization, in which the monomer is soluble in the solvent while the polymer product is insoluble, is the formation of polymer particles stabilized with one or more stabilizers. This stabilizer is a macromolecule containing a lipophilic part that can anchor to the growing

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polymer particles and a CO_2-philic part that makes it soluble in a CO_2 continuous phase, thereby imparting a repulsion force between the stabilizer-coated particles and preventing aggregation [24]. The most effective stabilizers used so far are fluorinated and siloxane-based polymers, owing to their high solubility in $scCO_2$. PFOA [27-29] and copolymers with a poly(dimethylsiloxane) (PDMS) part [30-32] are good stabilizers for poly(methyl methacrylate) (PMMA) and polystyrene (PS) as free-flowing polymer powders were obtained in high yield (>90%). Canelas et al. [33] reported the synthesis of PVAc by dispersion polymerization in $scCO_2$ using 2,2′-azobisisobutyronitrile (AIBN) and different stabilizers at 65 °C and approximately 350 bar. Although no particles were formed for all stabilizers, the results suggest that VAc can be polymerized successfully in a $scCO_2$ environment with a high yield of more than 90%. This study has opened the possibility for the synthesis of PVPi in $scCO_2$, which has not been reported.

In the present study, both PFOA and dimethylsiloxane-g-pyrrolidone carboxylic (Monasil PCA) were used as stabilizers for the dispersion polymerization of VPi in $scCO_2$. In both cases, no spherical polymer particles were obtained in the form of free-flowing powder, as observed in the polymerization of MMA. This might result from the high solubility of PVPi in $scCO_2$, which is reminiscent of PVAc reported elsewhere [32] because the structures of these two compounds are similar. The reaction time, pressure, temperature, monomer loading, stabilizer concentration and initiator concentration were examined to determine their influence on the molecular weight and yield of the PVPi product. In addition, the saponification of PVPi was investigated to determine the syndiotacticity, degree of saponification (DS), degree of branching (DB) and thermal behavior of the PVA products.

EXPERIMENTAL SECTION

1. Materials

CO_2 with a purity of 99.999% was purchased from Korea Specialty Gases. VPi (Aldrich) was purified by passage through an alumina column (Aldrich) and flushed with ultrapure nitrogen. AIBN was purified by recrystallization in methanol. Monasil PCA (Uniquema) with a molecular weight of 8.5 kg/mol was used as received. PFOA was prepared by the bulk polymerization of 1H,1H-perfluorooctyl acrylate (FOA) at 65 °C for 24 h using AIBN (1% wt/wt of monomer) as the initiator. Fig. 1 shows the molecular structures of PFOA and Monasil PCA.

2. Dispersion Polymerization of VPi in $scCO_2$

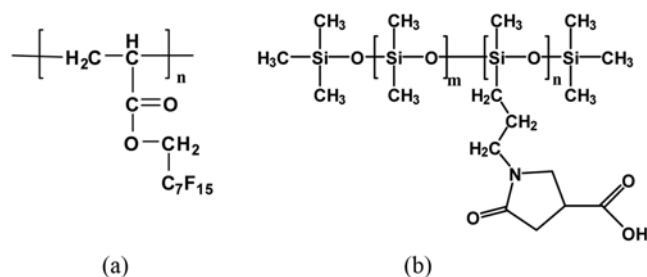Polymerization was conducted in a 20 mL high pressure reactor

equipped with a sapphire window for visual observations of the reaction mixture. The CO_2 pressure and flow rate were controlled with an ISCO pump. AIBN (0.5-3 wt% of monomer) and the desired amount of stabilizer (except for the reaction in which no stabilizer was used) were charged to the front chamber of the reactor and purged with CO_2 for approximately 20 min. Subsequently, 2.0 g of monomer was injected using a degassed syringe. Approximately 10 g of CO_2 was introduced and the entire system was immersed into a water bath equipped with a thermostat. While the system was heated slowly, CO_2 was supplied to the rear chamber to pressurize the system. Once the final condition was reached, the reaction was allowed to proceed with constant stirring by a magnetic stirrer. Once the reaction was complete, the reactor was cooled in an ice bath and the CO_2 was vented slowly from the cell. The polymer was collected and dried overnight under vacuum.

3. Saponification of PVPi

In a typical experiment, approximately 1.2 g of PVPi was dissolved in 120 mL of tetrahydrofuran (THF) in a three-necked round bottom flask equipped with a reflux condenser. Approximately 2.1 g of potassium hydroxide was dissolved in a mixture of MeOH/water (90/10 v/v) to make a 20 wt% alkali solution. The two solutions were deoxygenated by bubbling with nitrogen. The alkali solution was added to the polymer solution with constant stirring by using a magnetic stirrer at 55 °C for 10 min. The reaction was kept for 1-2 h to complete saponification. Subsequently, the reaction was quenched by cooling in water. The precipitated PVA was washed several times with methanol, filtered through a Buchner funnel, and dried under vacuum at 70 °C for 24 h.

4. Characterization

[1]H nuclear magnetic resonance (NMR, Bruker DPX-300 MHz) spectroscopy of PVPi and PVA were obtained by using $CDCl_3$ and DMSO-d_6 as solvents. The morphology of PVPi and PVA was obtained by field emission scanning electron microscopy (FESEM, Hitachi, S-4100). The molecular weight of the PVPi samples was determined by gas permeation chromatography (GPC, Waters 1515 isocratic pump, Waters 717+ Autosampler, and Waters 2414 refractive index detector) equipped with Waters Styragel HR5E column. THF was used as an eluent against narrow standard (Showadenko polystyrene standards M_w=1,310, 3,370, 19,600, 55,100, 275,000, and 815,000). Both calibration and samples analysis were performed at a carrier flow rate of 1 mL/min. The yield was calculated gravimetrically, assuming that the stabilizers were conserved during the venting of CO_2 and drying.

The thermal behavior was tested by thermogravimetric analysis (TGA). The crystalline melting temperature (T_m) was obtained by differential scanning calorimetry (DSC, TA Instrument Q200) at a heating rate of 10 °C min^{-1}. The number average molecular weight M_n of PVPi is related to intrinsic viscosity [η] according to Eq. (1) [34]. P_n of PVA and DB for the pivaloyl group of PVPi were determined by Eq. (2) [35,36] and Eq. (3) [12], respectively.

$$[\eta]=2.88\times10^{-5}[M_n]^{0.77} \text{ (dl g}^{-1} \text{ in Acetone at 25 °C)} \tag{1}$$

$$[\eta]=3.79\times10^{-3}[P_n]^{0.84} \text{ (dl g}^{-1} \text{ in DMSO at 30 °C)} \tag{2}$$

$$DB=(DP_1/DP_2)-1 \tag{3}$$

where DP_1 is P_n of PVPi and DP_2 is P_n of PVA prepared by saponify-

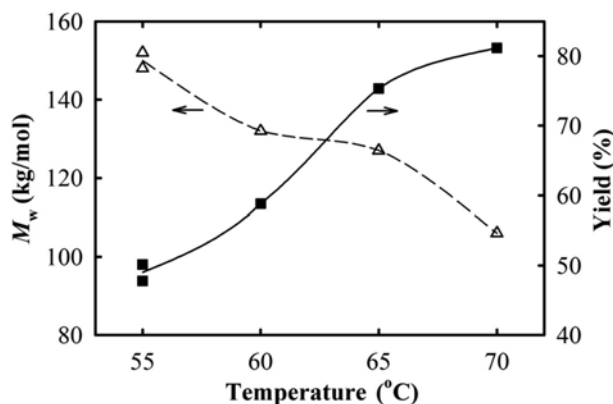**Fig. 1. Chemical structures of (a) PFOA and (b) Monasil PCA.**

Fig. 2. Effect of reaction temperature on the molecular weight and the yield of PVPi. Reaction condition: 2.0 g VPi, 10 g CO_2, 0.02 g AIBN (1%wt/wt monomer), 0.02 g PFOA (1% wt/wt monomer), 34.5 MPa, 10 h. M_w was determined by GPC.

ing PVPi. DS and S-diad content was derived from the ^{1}H NMR spectrum of PVA.

RESULTS AND DISCUSSION

1. Effect of Reaction Temperature

Both the density of the reaction medium and the kinetic behavior of the polymerization system are affected by temperature. Therefore, the molar mass and polymerization yield should change across the range from 55 to 70 °C, as seen from Fig. 2. The yield increased with increasing temperature but the molecular weight decreased. As the reaction was carried out at 55 °C, PVPi product with a high molecular weight of 148 kg/mol was obtained with a yield of 47%. The yield increased significantly to 82% (i.e., enhanced 75%), while the molecular weight decreased to 106 kg/mol (i.e., reduced 28%) when the temperature was increased to 70 °C. The trends were in agreement with the theory [37,38] for radical polymerizations using a thermally dissociating initiator like AIBN. The rate constants for initiation, propagation and termination are dependent on the temperature in a manner that frequently leads to an increase in the polymerization rate or yield and a decrease in the molecular mass of a polymer. At higher temperatures initiators more easily dissociate to radicals than at low temperatures. Therefore, at higher temperatures, a large number of radicals are formed and thus radical chain reactions occur at the same time, depleting the monomers faster, thereby, leading to a higher yield and a lower molecular weight polymer. This is in agreement with the previous study [39].

2. Effect of Initiator Concentration

In general, the yield and the rate of radical polymerization are driven strongly by the initiator concentration. Therefore, we examined the effect of AIBN, a thermally activated initiator, on the polymerization of VPi in an $scCO_2$ environment using different amounts of AIBN, while keeping the same amounts of CO_2, monomer and stabilizer. As shown in Fig. 3, the yield increased with increasing initiator concentration following an exponential rise-to-max function. On the other hand, the molecular weight decreased according to an exponential decay model. Initially, at an initiator concentration of less than 1% (wt/wt monomer), the yield increased rapidly corresponding to a small increase in the initiator content. When the
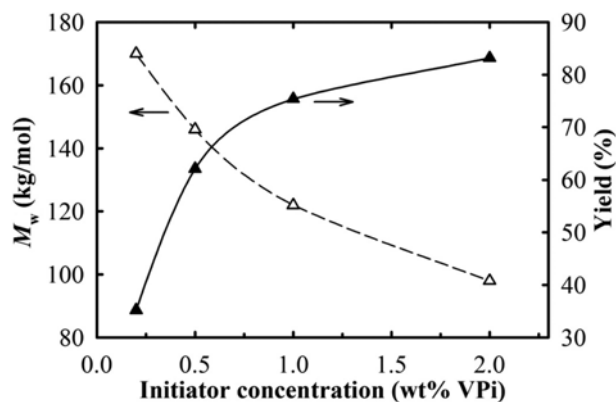

Fig. 3. Effect of initiator concentration on the yield and molecular weight of PVPi. Reaction condition: 2.0 g VPi, 10 g CO_2, 0.02 g PFOA (1%wt/wt monomer), 34.5 MPa, 65 °C, 10 h. M_w was determined by GPC.

concentration was >1%, the yield increased, but its increasing rate decreased with increasing the initiator concentration, reaching a saturated value of 84% with 2% of initiator. In contrast, the weight average molecular weight of PVPi decreased faster from 170 to 98 kg/mol when the initiator concentration was increased from 0.2 to 2.0 wt%. The increase in the yield and decrease in the molecular weight were attributed to the increase in the number of free radicals and thus the increase in the number of polymer chains with increasing initiator concentration [39]. These trends also agree well with Giles et al. [40].

3. Effect of Reaction Pressure

As the density of fluid is the most important property of the fluid phase, polymerization has deep relation with density. The density is directly related to both pressure and temperature of the supercritical fluid medium. In this study, pressure as well as temperature was chosen as an independent variable because it is easily measured. The pressure affects the polymerization in terms of changing the density of a supercritical medium. The change in pressure results in the change in the dielectric constant of the fluid, and thus the solubility of reactants such as monomer, stabilizer, and initiator is deeply attributed to the pressure. Therefore, pressure has a profound effect on the polymerization.
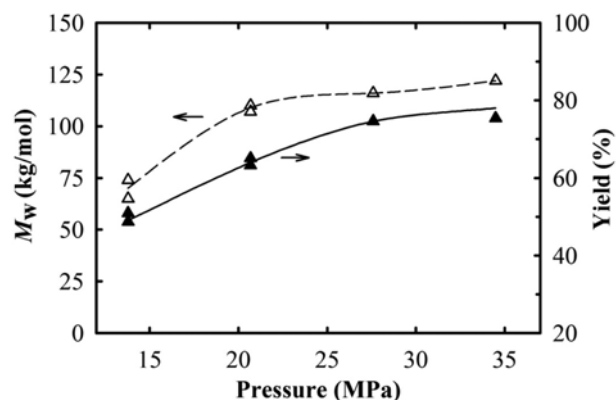

Fig. 4. Effect of pressure on the yield and molecular weight of PVPi. Reaction condition: 2.0 g VPi, 10 g CO_2, 0.02 g AIBN, 0.02 g PFOA, 65 °C, 10 h. M_w was determined by GPC.

The yield and molecular weight of PVPi synthesized with 20 wt% VPi, 2 wt% AIBN, and 2 wt% PFOA at 65 °C and various pressures are shown in Fig. 4. As pressure increased from 13.8 to 34.5 MPa, the yield of PVPi increased from 50 to 75% and the M_w, from 72 to 122 kg/mol. As pressure increases, the density and thus the solubility increase. As solubility is higher at a higher pressure, the stability of polymer particles is better and can stay in the fluid phase longer and can continue polymerization until they are precipitated. Therefore, both yield and molar mass of the polymer increased with increasing pressure.

4. Effect of Monomer Concentration

The effects of the monomer concentration on the yield and molecular weight of PVPi were examined by changing the monomer loading while maintaining the amount of CO_2, initiator, and stabilizer (see Fig. 5). Both yield and molecular weight of the polymer increased with increasing monomer concentration. This might have been resulted from the cosolvent effect that improves the solubility of the initiator and stabilizer because monomer VPi played an important
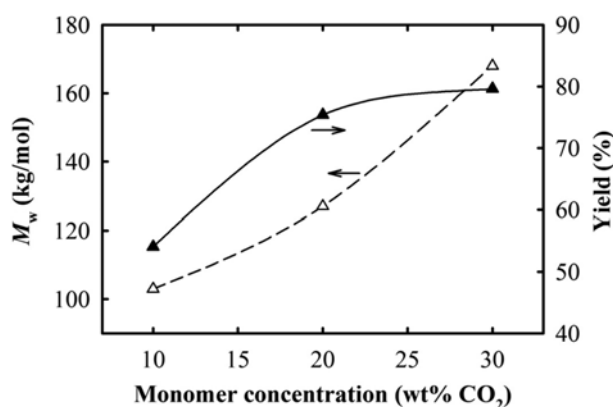

Fig. 5. Effect of monomer concentration on the yield and molecular weight of PVPi. Reaction condition: 10 g CO_2, 0.02 g AIBN, 0.02 g PFOA, 34.5 MPa, 65 °C, 10 h. M_w was determined by GPC.

role as a cosolvent. In particular, a 10% monomer loading resulted in an opaque mixture inside the view cell at the early stages of the reaction, whereas the mixtures appeared transparent at 20 and 30% loadings, showing high solvent power of the fluid incorporated with large amount of monomer. Due to the better solubility of polymer with a larger amount of monomer, polymers stayed longer in the fluid phase, maintaining polymerization longer. When polymer chains grew above a certain length, they must have aggregated to form micro particles that adsorbed the stabilizer, which were stabilized by the fluid mixture of CO_2 and monomer. When the polymer particles grew larger than the size which the fluid mixture can hold, they could have been precipitated and the polymerization could have been stopped. When the monomer loading was increased at a fixed amount of initiator, the relative amount of initiator to the monomer decreased, producing polymers with a larger molecular weight. A molecular weight of 172 kg/mol was obtained in the case of 30% of monomer, which was the highest molecular weight obtained in this research.

5. Effect of Stabilizer Concentration

Table 1 lists the effects of the stabilizer on the molecular weight, yield, and the appearance of the reaction mixture inside the view cell. Without a stabilizer, the color of the mixture was gray and, no matter how high the stirring rate was, the polymer settled at the bottom of the reactor, making two separate phases. When a stabilizer such as PFOA and Monasil PCA was used, the mixture appeared white due to the formation of micron-sized particles.

Fig. 6 shows the morphology of PVPi samples synthesized by using two different amounts of PFOA. The polymer obtained from the reaction with 1% PFOA for 10 h (with the yield of approximately 75%) appeared shapeless, whereas the polymer obtained with 3% PFOA for 18 h (with the yield of approximately 90%) showed aggregated and coagulated polymer particles. In the former case with a lower yield, the unreacted monomer acted as an effective solvent for the polymer particles, which deformed the morphology of the final product. In the latter case the stabilizer PFOA concentration was higher and the stabilization of particles was better than the former,

Table 1. Effect of the stabilizer concentration on the polymerization of VPi[a]

Entry	Stabilizer (% wt/wt monomer)	Time (h)	Yield (%)[b]	M_w (kg/mol)[c]	Appearance[d]
PFOA					
1	0	10	63.33	113	Gray, oily, settle
2	0.5	10	74.23	117	White, partially settle
3	1	10	75.38	121	White stable latex
4	2	10	76.62	119	White stable latex
5	3	10	76.47	117	White stable latex
6	3	18	88.66	130	White stable latex
Monasil PCA					
7	2	5	40.76	127	White, settle
8	5	5	39.06	132	White, settle
9	5	12	70.85	139	White, settle
10	5	15	77.31	146	White, settle

[a]Reaction conditions: 2.0 g VPi, 0.02 g AIBN, 10 g CO_2, 34.5 MPa, 65 °C

[b]As determined gravimetrically

[c]As determined by GPC

[d]According to the observation from the view cell during the reaction time
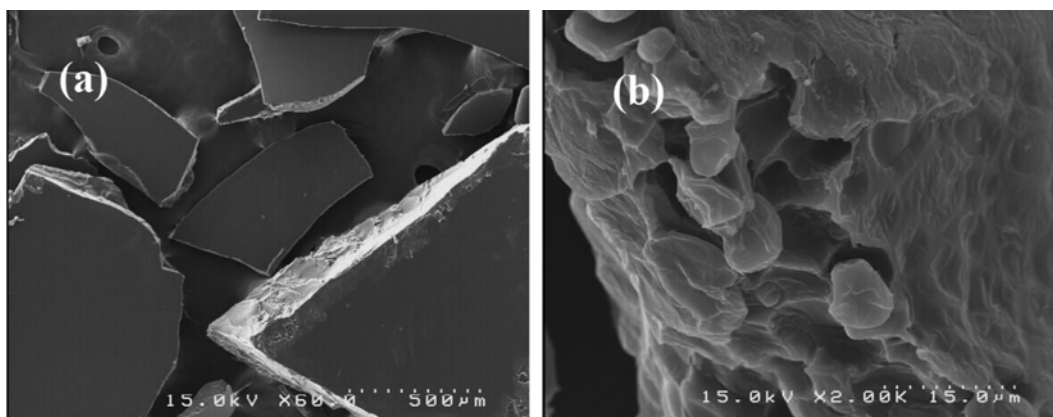
Fig. 6. FESEM images of PVP that were synthesized with (a) 1 wt% PFOA in 10 h and (b) 3 wt% PFOA in 18 h.

producing PVPi at a higher yield and therefore leaving a smaller amount of monomer after the reaction. The latter case had a smaller plasticization effect and provided a better morphology.

Different from the PMMA, PS, and polyacrylonitrile, all attempts to obtain free-flowing PVPi powder failed because of the bulky pivaloyl side chains and the high solubility of PVPi in CO_2. PVPi dissolves well in CO_2 because of the many ester groups connecting tertiary butanes to polyvinyl backbone that have very high compatibility with CO_2. During the depressurization after quenching, some of the low molecular weight polymer was collected in the cold trap while most of the polymer precipitated at the bottom of the reactor. All the polymer particles and droplets seen in the fluid phase during the polymerization were not seen anymore. When the polymer particles precipitated at the bottom, they aggregated and coagulated easily, as shown in Fig. 6, because the particles are very soft and flexible.

Canelas et al. [33] showed that PVAc is soluble in $ScCO_2$ because of Lewis acid-base interaction with the carbonyl group of PVAc. This interaction results in the solvation of CO_2 in the polymer and a high degree of swelling, resulting in the high plasticizing effect of PVAc in $scCO_2$. PVPi must have a similar effect to PVAc. Increase in the mobility of polymer chains enhances the diffusion of the chain ends and prevents the gel effect. Therefore, PVPi cannot get a high molecular weight as was seen for PMMA. The highest molecular weight of PVPi that we have obtained is 172 kg/mol.

In the reaction that contained a siloxane-based stabilizer, Monasil PCA, the latexes were stable only at low conversion but were unstable at high conversion, as proven by the settlement of polymer particles. At low conversion, the VPi monomer served as a cosolvent for the PDMS chains and allowed them to extend into the continuous phase as shown by Yates et al. [41]. On the other hand, as the VPi concentration decreased during polymerization, the dielectric constant of the solution became lower and the PDMS chains began to collapse. At this point, the flocculation and coagulation of the particles was imminent.

Increasing the concentration of PFOA from 0.5 to 3% improved the yield slightly but did not affect the molecular weight much, as shown in Table 1. Compared with the polymerization without stabilizer, a polymer with a considerably higher yield and a higher molecular weight was obtained from the polymerization using only 0.5% PFOA. In this case, the reaction system was stabilized with an excellent stabilizer, PFOA, and formed smaller size polymer particles, thereby imparting a larger surface area to the polymer so that it could contact easily with the continuous fluid phase. As a result, the efficiency of capturing the oligomeric radicals generated in the continuous phase increased, giving rise to a higher yield of polymer. As many small polymer particles were formed, polymerization must have been predominant inside the particles [32]. As polymer chains grew, the chain transfer reaction was reduced due to the gel effect, and therefore a higher molecular weight polymer could be obtained.

6. Thermal Analysis

Fig. 7 shows the thermal behavior of PVPi. The dramatic weight loss observed at approximately 300 $^{\circ}$C was due to the decomposition of the polymer, while the slow decrease above 400 $^{\circ}$C was due to the pyrolysis. At 500 $^{\circ}$C the pyrolysis was completed. The DSC curve shows that the glass transition T_g of the polymer is approximately 70 $^{\circ}$C, as evidenced by the small peak in the DSC curve.

7. Effect of the Reaction Time

The reactions were quenched at various reaction times to examine polymerization as a function of time. Figs. 8 shows the yields and molecular weights of PVPi with respect to the reaction time. An increasing trend was observed for both the yield and molecular weight. The yield increased rapidly for the first 10 h, then continued to increase at a slower rate and finally reached 93% at 20 h. The molecular weight increased rapidly for the first 5 h and then increased at a decreasing rate thereafter. Eventually, a molecular weight of
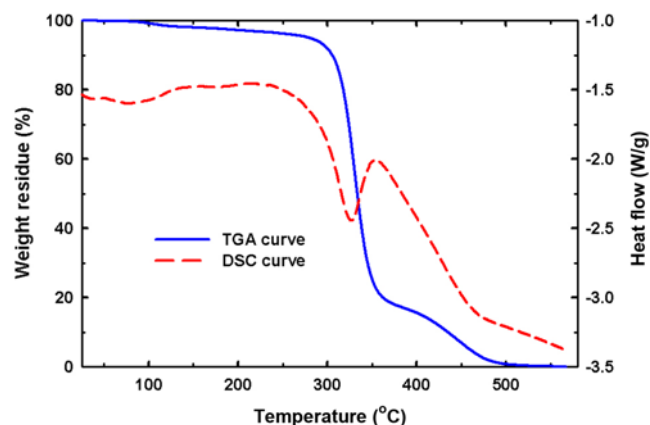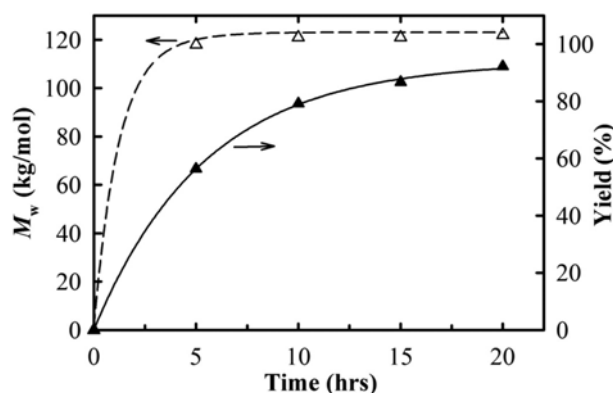

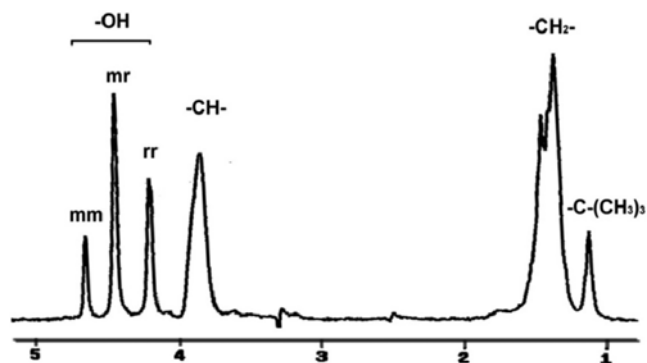**Fig. 7. Results of thermal analysis of PVPi.**

Fig. 8. Effect of reaction time on the yield and the molecular weight of PVPi. Reaction condition: 2 g VPi, 10 g CO₂, 0.02 g AIBN (1%wt/wt monomer), 0.02 g PFOA (1%wt/wt monomer), 65 °C, 34.5 MPa. M_w was determined by GPC.

127 kg/mol was obtained after a 20 h reaction. The slower increase in the yield and M_w with time after 5 h of polymerization was due to the mass transfer limitation of the monomer molecules to the chain reaction sites.

8. Saponification of PVPi

Table 2 lists the properties of PVPi samples synthesized at different conditions and PVAs obtained by saponification of these PVPi samples. The saponification of PVPi with M_n of 113 kg/mol resulted in PVA with P_n of 654. These values are much lower than the ultrahigh molecular weight PVPi synthesized by using the methods reported in the literature [6-20]. Because AIBN was used as an initiator at high concentrations (approximately 8×10^{-3} mol/mol VPi) and was activated at elevated temperatures (over 55 °C), it was difficult to obtain a PVPi product with an ultrahigh molecular weight. The reason was the same as reported elsewhere [40]. Another reason with respect to the solvent effect should be considered. Because PVPi is soluble in CO₂, the critical chain length for precipitation, J_{crit}, of the polymer is high, thus encouraging polymerization in the continuous phase. This often leads to a higher chain transfer reaction rate compared to the polymerization inside the polymer particles owing to the gel effect [42]. Consequently, a lower molecular

weight PVPi was produced.

Fig. 9 provides the tacticity information from the three separate peaks between 4 and 5 ppm in the ^{1}H NMR spectrum of PVA. These peaks were assigned to the difference in configuration of the polymer chain. Syndiotacticity (S-diad content) represented by the ratio of racemic diad (r) content to the total *racemic* and *meso* (m) content was calculated by using Eq. (4):

$$r(\%) = \frac{rr + (mr/2)}{rr + mr + mm} \times 100\% \qquad (4)$$

where rr, mr and mm are the integration values of the peak areas corresponding to syndiotactic, atactic, and isotactic triads shown in Fig. 9.

According to the s-diad values in Table 2, these PVA samples were syndiotacticity-rich with relatively high racemic-diad contents (>57%), and the highest syndiotacticity of 59.4% was attributed to the PVPi synthesized at 55 °C for 22 h. From the data obtained by thermal analysis, the PVA samples were found to have a high crystallinity with a melting temperature ranging from 220 to 234 °C.

9. Degree of Branching

DB is important because it is the main reason for the inferior P_n of PVA to its precursor PVPi due to the cleavage of pivaloyl groups on the polymer backbone during the hydrolysis of PVPi. In an ideal

Fig. 9. ^{1}H NMR spectrum of PVA (H₂O and solvent peaks were suppressed using WET solvent suppression technique). rr: syndiotactic triad, mr: atactic triad, and mm: isotactic triad).

Table 2. Effect of different factors on PVPi and its hydrolysis product PVA

Entry	VPi conc. (%wt CO₂)	Initiator conc. (%wtVPi)	Temp. (°C)	PVPi[a]				PVA			
				Time (h)	$[\eta]^b$ (dl g⁻¹)	M_n^c (kg/mol)	Yield[d] (%)	P_n	S-diad[e] (%)	DS[f] (%)	T_m^g (°C)
1	20	2	65	10	0.14	62	83.2	388	57.14	92	219.6
2	20	0.5	65	19	0.20	96	76.2	403	58.31	98	-
3	20	1	55	22	0.21	102	76.3	571	59.41	97	234.1
4	20	1	70	10	0.14	58	81.2	374	58.13	96	230.7
5	30	1	65	10	0.22	113	79.6	654	59.02	94	230.5

[a]Reaction condition: 0.02 g PFOA (1%wt/wt monomer), 10 g CO₂, 34.5 MPa
[b]Intrinsic viscosity measured in acetone at 25 °C
[c]Number average molecular weight calculated from intrinsic viscosity
[d]Calculated gravimetrically
[e]Syndiotactic content calculated from ^{1}H NMR spectra
[f]Degree of saponification calculated from ^{1}H NMR spectra
[g]Melting point (2nd heating) obtained from DSC

case, where the ester polymer is linear and converted completely to PVA, the P_n of PVA must be equal to that of its precursor, leaving zero for DB. On the other hand, during the polymerization of VPi, radical sites are generated not only at the alpha and beta carbon positions but also at the methyl groups [5], giving rise to the formation of branches by the inter-combination of those radicals. Branching becomes more significant at high conversions and varies with varying polymerization conditions, shifting the DB to the values greater than zero. Because the synthesis of a linear polymer requires a very low temperature from −40 to −15 °C, this system using elevated temperatures must carry a certain DB value. The DB values were <1 under the conditions investigated, as listed in Table 3. The highest DB of 0.86 was attributed to polymerization using an initia-

Table 3. Degree of branching of PVPi samples under different polymerization conditions

Entry	Monomer (%wt/wt CO_2)	Time (h)	Initiator (%wt/wt monomer)	T (°C)	DB
1	20	10	2	65	0.25
2	20	19	0.5	65	0.86
3	20	22	1	55	0.40
4	20	10	1	70	0.21
5	30	10	1	65	0.35

tor concentration of 0.5% wt/wt monomer at 65 °C for 19 h, whereas the lowest DB of 0.21 was attributed to the synthesis of PVPi at
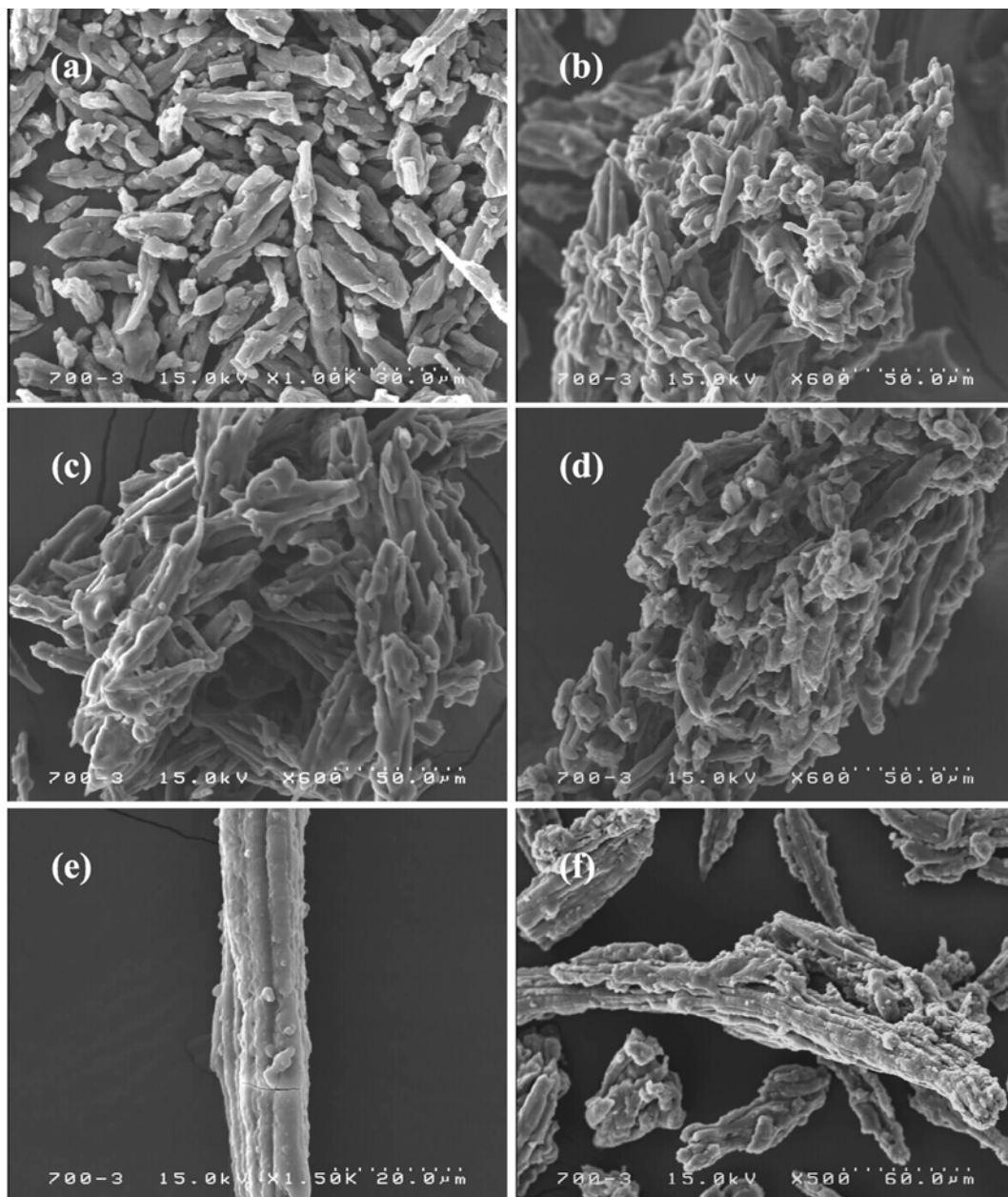
Fig. 10. Morphology of the PVA samples after the saponification of PVPi polymerized under different conditions listed in Table 2. (a) P_n=403, S-diads=58.31%, DS=98%;(b) P_n=388, S-diads=57.14%, DS=92%; (c) P_n=374, S-diads=58.13%, DS=96%; (d) P_n=571, S-diads=59.41%, DS=97%; (e) and (f) P_n=654, S-diads=59.02%, DS=94%.

70 °C for 10 h.

10. Morphology of *In Situ* Fibrillated PVAs

The PVAs that were formed during saponification reactions precipitated from the continuous phase due to their low solubility in THF (medium for saponification). The shear force caused by stirring contributed to the resulting morphology of the PVA product, in which fibers are often acquired, particularly with a high syndiotacticity and a high molecular weight [8]. Fig. 10 shows the morphology of different PVA specimens obtained from the saponification of different PVPi samples. In most cases, the PVA had fairly undefined morphologies, which could be either the sets of isolated short segments with irregular cross sections or the clumps of these due to the agglomeration. A well-defined morphology was only observed in the case of the PVA sample, whose mother PVPi was synthesized using a 30% monomer concentration (Table 2, entry 5, Figs. 10(e) and 10(f)). Fig. 10 shows that both tacticity and M_w (or P_n) are important to get the fibrillated morphology. Though P_n leads to its distinctive morphology of PVA, P_n value of 654 was not high enough to form the fine microfibrillar fibers that Lyoo et al. [16] obtained in their research. According to their investigation, P_n of PVA should be >800 to obtain a fibrous morphology via *in situ* fibrillation. Polymers with globular and shapeless morphologies are normally acquired if P_n is lower than this value. All the samples shown in Fig. 10 have smaller P_n values than the critical number. Fig. 10(e) shows a nearest fiber morphology as it has a high syndiotacticity of 59 as well as the highest P_n value of 654.

CONCLUSIONS

PVPi was synthesized in scCO$_2$ by using a dispersion polymerization with either stabilizer PFOA or Monasil PCA. The polymer product had a range of average molecular weights of up to 172 kg/mol with respect to a 30% monomer loading. A yield of 93% could be obtained after a 20 h reaction. In all cases, the PVPi particles were either coagulated and collapsed due to the high solubility of PVPi in CO$_2$ or shapeless due to the dissolution of the polymer particles in the unreacted monomer and smaller molecular weight oligomers. Saponification of the PVPi samples yielded PVA of fairly rich syndiotacticity (59.4%) with a degree of saponification of up to 654 and a degree of branching between 0.21 and 0.86. Thermal analysis suggested that the PVPi samples had a T_g of 70 °C and the melting temperature of high crystalline PVA samples was in the range from 219 to 234 °C.

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