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Reversible addition-fragmentation chain transfer polymerization of vinyl acetate and vinyl pivalate in supercritical carbon dioxide

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Abstract−Two highly supercritical CO_2-soluble, poly(vinyl acetate) (PVAc)-based macro-reversible addition-fragmentation chain transfer (RAFT) agents were synthesized. The RAFT agents were used for the first time in RAFT/macromolecular design via the interchange of xanthates (MADIX) and polymerization of vinyl acetate (VAc) and vinyl pivalate (VPi) in supercritical carbon dioxide ($scCO_2$). A homopolymer PVAc and a block copolymer PVAc-*b*-PVPi made by RAFT/MADIX polymerization were characterized, and the effects of time and RAFT agents on polymerization were examined. For the 8.4 wt% RAFT agent in VAc, the molecular mass (M_n) of homopolymer PVAc was 26,000 g mol^{-1} and PDI was 1.35. For the copolymerization of VPi using 9.8 wt% PVAc-RAFT agent in VPi for 24 h, the M_n and PDI of PVAc-*b*-PVPi reached 32,400 g mol^{-1} and 1.42, respectively. These results suggest that the polydispersity can be controlled during the clean production of PVAc and PVPi by RAFT/MADIX polymerization in $scCO_2$.

Keywords: Poly(Vinyl Acetate), Poly(Vinyl Pivalate), Block Copolymer, RAFT Polymerization, Reversible Addition-fragmentation Chain Transfer Polymerization, Supercritical Carbon Dioxide

INTRODUCTION

Poly(vinyl ester), such as poly(vinyl acetate) (PVAc) or poly(vinyl pivalate) (PVPi), is used selectively as a precursor for the preparation of poly(vinyl alcohol) (PVA), which is a colorless, water-soluble synthetic polymer. PVA has been used as an adhesive for paper, wood and textiles, and as a raw material for vinylon, in sizing and finishing textiles and papers, and in the packaging of foods and medicine because of its high tensile strength and flexibility, good oxygen impermeability, and excellent film forming properties. PVA is not obtained by the polymerization of vinyl alcohol, but by the saponification of PVAc or PVPi. PVAc obtained from free-radical polymerization is a structurally heterogeneous material that exhibits a broad molecular weight distribution, variably branched macromolecular architectures, and physical properties that depend sensitively on their precise structures [1]. Therefore, PVAc has also been used widely in water-based paints, adhesives, paper coatings and nonwoven binders. From the early 2000's, PVPi has been an important vinyl ester for the production of PVA with high syndiotacticity because of the pendent tertiary group. On the other hand, a requirement for solvent-free and surfactant-free polymers has arisen in the industry. Therefore, synthesis using supercritical fluids has been studied. In addition, access to the new degradable vinyl ester homopolymers and block copolymers with tunable properties requires the development and optimization of controlled polymerization methods, such as living radical polymerization.

Supercritical carbon dioxide ($scCO_2$) has attracted considerable attention as an environmentally friendly alternative to volatile organic solvents in polymer production processes owing to its low cost, abundance, non-toxicity, non-flammability and tunable solvent properties [2,3]. Polymerization in $scCO_2$ has attracted significant attention as an alternative to the conventional polymerization process [4,5]. Recently, controlled living radical polymerization (CLRP) has allowed access to new classes of well-defined macromolecules with precise architectures, compositions, and chain-end functionalities from a wide range of monomers. Different CLRP techniques have been carried out in $scCO_2$, including nitroxide-mediated polymerization (NMP) [6-9], atom transfer radical polymerization (ATRP) [10-12], and reversible addition-fragmentation chain transfer (RAFT) polymerization [13-16]. Among these techniques, RAFT polymerization has become the most versatile because it is applicable to a wide range of monomers while exhibiting exceptional control over the polymerization kinetics [15,17]. The strong odor and toxicity of common xanthate RAFT agents has prompted increasing interest into more stable and nontoxic macro-RAFT agents.

One of the most important features of the RAFT process is the ability to reinitiate the polymer chain with a thiocarbonylthio endgroup (a macro-RAFT agent) to continue propagation in the presence of a second monomer [14]. The formation of polymeric macro RAFT agents with thiocarbonylthio end-groups due to homopolymerization in the presence of a xanthate RAFT agent, can be considered the key component in the successful formation of block copolymers [18,19]. Chain extension polymerization including homopolymerization and block copolymerization via a RAFT mechanism has been studied either in organic solvents [18-21] or in the bulk [22]. On the other hand, there are few reports on chain extension

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polymerization in supercritical CO_2. Gregory et al. [14] reported the chain extension homopolymerization of MMA using a PMMA-RAFT agent in $scCO_2$ but a redispersion step with the aid of a stabilizer was needed due to the low solubility of the macro-RAFT agent in $scCO_2$. Without a stabilizer, chain extension could be minimal [14]. Therefore, successful chain extension in $scCO_2$ without a stabilizer requires a macro-RAFT agent with high solubility. Wong et al. [19] reported the chain extension of polystyrene (PS) block copolymers with *N,N*-dimethylacrylamide (DMA) in *N,N*-dimethylacetamide (DMAc) using different PS-RAFT agents. In their study, the experimental number average molecular weights (M_n) deviated significantly from the theoretical number average molecular weights ($M_{n,th}$).

The controlled RAFT polymerization of vinyl acetate (VAc) using xanthates [23,24] and dithiocarbamates [25] was reported to furnish well-defined homopolymers with relatively narrow polydispersity. Lee et al. [26] reported the synthesis of poly(vinyl acetate-*alt*-dibutyl maleate) copolymer using the RAFT technique and checked its phase behavior in CO_2. Girard et al. [27] examined the structural-property relationships between PVAc-based polymers and their solubility in $scCO_2$. They also reported the solubility of fluorinated poly(vinyl ester) in $scCO_2$ [28,29]. Although RAFT polymerization of VAc and its chain extension in normal organic solvents has been studied [22-25], to the best of our knowledge, there are no reports on the polymerization of vinyl esters using highly soluble macro-RAFT agents in $scCO_2$.

Therefore, to develop an environmentally friendly polymerization method for PVAc and PVPi, we examined the RAFT homopolymerization of VAc in $scCO_2$ using highly soluble PVAc macro-RAFT agents (PVAc-X1 and PVAc-X2). Block copolymers of PVAc and PVPi can tune the physical properties of PVA, and have been synthesized by the polymerization of vinyl pivalate (VPi) using a PVAc-X1 macro-RAFT agent. The chain extension study of PVAc in $scCO_2$ offers several benefits, such as a facile process without using an expensive stabilizer, free from stabilizer contaminants in the final products, and the formation of block copolymers with well-defined structures.

EXPERIMENTAL

1. Materials

CO_2 (99.999%) was purchased from Deokyang Energy Corp. Methanol, ethanol, isopropoxyethanol, and carbon disulfide (all ≥99%) were acquired from Aldrich, and methyl bromoacetate (98%) was obtained from Alfa Aesar. These chemicals were used as received. VPi (99%) and VAc (99%) were supplied by Aldrich and purified by passing through an alumina column followed by vacuum distillation over calcium hydride. 2,2′-Azobis(isobutyronitrile) (AIBN, Wako) was recrystallized twice from methanol. Xanthate RAFT agents, such as methyl(ethyloxycarbonothioyl)sulfanyl acetate (X1) and methyl(methyloxycarbonothioyl)-sulfanyl acetate (X2) (Fig. 1), were synthesized using the procedure described elsewhere [22].

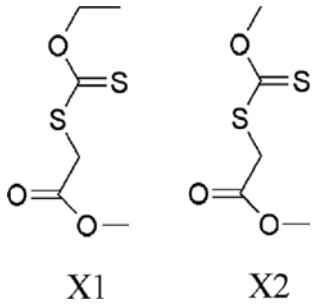

Fig. 1. Structures of the MADIX/RAFT agents methyl(ethoxycarbonothioyl)sulfanyl acetate (X1) and methyl(methoxycarbonothioyl)sulfanyl acetate (X2) used in this study.

2. Synthesis of PVAc Macro-RAFT Agents

Xanthate RAFT agent X1 (0.227 g, 1.17 mmol) and AIBN (0.019 g, 0.116 mmol) were dissolved in freshly distilled VAc (10 ml, 108.5 mmol). The solution was placed in a glass vial, degassed by three freeze-pump-thaw cycles on a vacuum line, and then sealed under argon. Polymerization was carried out at 333.15 K for 2.5 h. The resulting polymer was dissolved in acetone, precipitated in hexane and dried in a vacuum oven. To remove all traces of monomer from the polymer, the solids were freeze-dried in a vacuum at room temperature. A similar protocol was used to synthesize RAFT agent X2. Table 1 lists the experimental conditions.

3. Homopolymerization of VAc Using a Macro-RAFT Agent

A 28 ml stainless steel variable-volume view cell equipped with a sapphire window that allows visual observations of the reaction was used. A piston inside the view cell was used to vary the volume of the sample at a constant pressure. Details of the experimental equipment are reported elsewhere [3]. Designated amounts of macro-RAFT agents and 0.0033 g of AIBN were placed in a variable volume view cell, followed by flushing with CO_2 for 20 min to remove all traces of air. 1.1 g of the VAc monomer was injected into the view cell using a degassed syringe under a CO_2 atmosphere and the cell was then filled with approximately 5 g of CO_2. The view cell was placed in a water bath at 338.15 K, whereas CO_2 was supplied by an ISCO pump to increase the pressure to 34.5 MPa. During the reaction, the pressure in the cell was kept constant for 10 h. At the end of the reaction, the reactor was quenched in an ice bath for 20 min.

Table 1. Conditions and results for the synthesis of the PVAc macro-RAFT agents

Macro- RAFT agent	Initial ratio $[M]_0/[X]_0/[I]_0$[a]	Temp. (K)	Time (h)	Conv[b] (%)	M_n[c] (g mol^{-1})	$M_{n,th}$[d] (g mol^{-1})	PDI
PVAc-X1	944/10.1/1	333	2.5	67.5	5,700	5,600	1.16
PVAc-X2	938/10.1/1	335	4	75.2	7,600	6,200	1.12

[a]Initial molar ratio of M: monomer (VAc), X: xanthate (X1 or X2), and I: initiator (AIBN)
[b]Conversion was determined gravimetrically
[c]M_n and PDI were determined by GPC
[d]$M_{n,th}$ was calculated by Eq. (1)

The CO_2 gas was vented until the pressure reached atmospheric pressure. The polymer product was collected carefully from the reactor and dried overnight in a vacuum oven at room temperature to remove the remaining monomer and solvent. The level of monomer conversion was calculated gravimetrically from the amount of polymer, assuming that the entire macro-RAFT agent was collected after the venting and drying processes.

4. Block Copolymerization of VPi with PVAc-X1 Macro-RAFT Agent

The stainless steel high-pressure view cell reactor described above was charged with AIBN (0.006 g, 0.0365 mmol) and PVAc-X1 (0.2 g, 0.035 mmol). The reactor was sealed and purged with CO_2 for 10 min before VPi (2.046 g, 16 mmol) was added under a positive pressure of CO_2. The reactor was pressurized to 4.8 MPa, and heated to 338.15 K. Additional CO_2 was added to reach a final reaction pressure of 34.5 MPa. The reaction was at a constant pressure for different times (5 h and 24 h). After the designated reaction time, the reactor was quenched in an ice bath and depressurized. The product was collected and dried in a vacuum. The conversion of VPi was determined gravimetrically.

5. Determination of Cloud Points

The same stainless steel variable-volume view cell was used to observe the cloud points at a constant weight fraction and pressure. For a typical experiment, 0.11 g of PVAc-X1 and 2 g of VAc were placed in the cell and CO_2 at a particular pressure was introduced using a syringe pump. After a clear homogeneous solution was achieved at approximately 1 MPa over the cloud point pressure, the piston was moved backwards to reduce the pressure inside the cell at a reduction rate of 0.02-0.04 MPa/s and a constant temperature. The cloud point pressure was determined as the pressure at which the stir bar inside the cell could not be seen through the window. Each cloud point was reproduced three times to within approximately ±0.4 MPa. The experiments were repeated using different amounts of the PVAc macro-RAFT agents and VAc at a range of temperatures.

6. Characterization

The ^{1}H nuclear magnetic resonance (NMR) spectrum was recorded in $CDCl_3$ using a 300 MHz NMR spectrometer (Bruker, DPX-300). The molecular weight and molecular weight distribution of the polymers was determined by gel permeation chromatography (GPC) on a Waters System equipped with an isocratic pump (Waters 1515) and a refractive index (RI) detector (Waters 2414). Waters Styragel columns (HR4E and HR5E) were used in series with tetrahydrofuran (Fisher, HPLC grade) as the eluent and calibrated with polystyrene standards (Showa Denko). Calibration and analysis were carried out at 308.15 K and a carrier flow rate of 1 mL min^{-1}.

RESULTS AND DISCUSSION

1. Preparation of PVAc-X Macro-RAFT Agents and their Solubility in CO_2

Two PVAc macro-RAFT agents, PVAc-X1 and PVAc-X2, containing thiocarbonylthio end groups were synthesized by the bulk polymerization of VAc in the presence of two xanthate RAFT agents, X1 and X2, respectively. The bulk polymerization method was used to prepare the RAFT agents because it is a simple, inexpensive process with a high reaction rate. The chemical structure of PVAc-X1 was verified by ^{1}H NMR spectroscopy (Fig. 2). All the peaks exactly

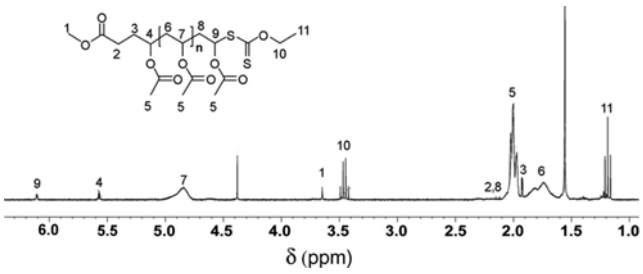

Fig. 2. Chemical structure and NMR spectrum of the PVAc-X1 agent.

matched the hydrogen atoms of the macro-RAFT agent. As shown in Table 1, these macro-RAFT agents had comparable M_n and low polydispersity indices (PDI). $M_{n,th}$ was calculated by using Eq. (1).

$$M_{n,th} = \frac{[M]_0}{[RA]_0} \times m_M \times \rho + m_{RA} \quad (1)$$

where ρ is the monomer conversion, $[M]_0$ is the initial concentration of the monomer, $[RA]_0$ is the initial concentration of xanthate RAFT agent, m_M is the molecular weight of the monomer and m_{RA} is the molecular weight of the xanthate RAFT agent.

M_n of the PVAc macro-RAFT agents synthesized in this study were higher than $M_{n,th}$ (Table 1). On the other hand, the polymerizations were well controlled as the PDIs of the products were close to 1.1. Because positive deviations from the theoretical values indicate the incomplete use of RAFT agents [30], almost all the X1 molecules attached to the polymer chains while a fairly large amount of X2 remained intact during polymerization. The use of an excess of xanthate (10 times that of the initiator) is necessary to ensure a high living content of the PVAc-RAFT agents, which is essential to assist RAFT polymerizations in $scCO_2$.

Owing to the high solubility of PVAc in CO_2 [31-33], PVAc macro-RAFT agents were employed in both homopolymerization with VAc and block copolymerization with VPi. The temperature-dependent cloud-point pressures of the PVAc macro-RAFT agents in CO_2 and in CO_2/VAc mixtures were measured to find the proper pressure

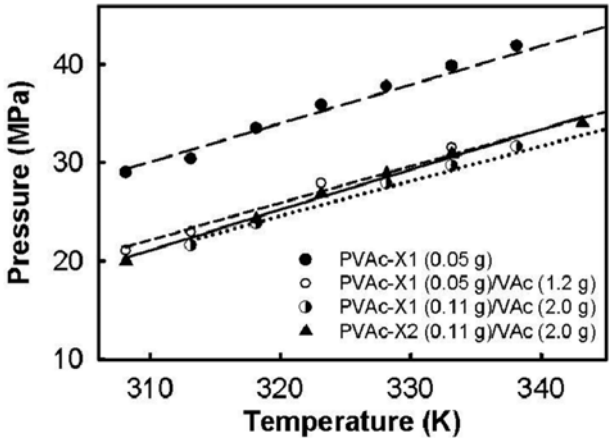

Fig. 3. Temperature dependent cloud point profiles of the PVAc macro-RAFT agents in CO_2 and in CO_2/VAc mixtures. In addition to the PVAc-X agent, 5.0 g of CO_2 was used for all measurements.

during each reaction (Fig. 3). The solubility was attributed to a two-point interaction between the pendant groups on the PVAc backbone and CO_2, including a Lewis acid-Lewis base interaction between the carbonyl group and CO_2, and a weak interaction between the hydrogen atom of the methyl group and the oxygen atom of CO_2 [32,33]. Generally, higher pressures were required for the complete dissolution of PVAc at higher temperatures. When the temperature was increased from 310 to 340 K, the cloud-point pressure of PVAc-X1 was increased linearly from 30 to 41 MPa in the presence of $scCO_2$ and from 21 to 32 MPa in the presence of VAc-laden $scCO_2$. The cloud-point pressure in the CO_2/VAc mixtures was approximately 9 MPa lower than that of PVAc-X1 in CO_2 because the monomer acted as a cosolvent [34]. Higher VAc content in the mixtures resulted in lower cloud-point pressures. On the other hand, the cloud point pressure of PVAc-X2 was approximately 0.5 MPa higher than that of PVAc-X1 because higher pressures are needed to dissolve the higher molecular weight PVAc [32]. Note that the M_n of PVAc-X1 and PVAc-X2 are 5,700 and 7,600 g mol^{-1}, respectively (Table 1). Another interesting behavior of the cloud-points is that the cloud-point pressure lines for mixtures of different amounts of VAc in supercritical solvents were parallel to each other. Together with the linearity of the cloud point pressure with temperature, this behavior appeared because the density of the fluid varies almost linearly with temperature for small change in temperature, but the pressure effect on the density between 20 and 40 MPa was relatively small.

2. Homopolymerization of VAc with PVAc-X Macro-RAFT Agent

The cloud points for PVAc-X1/CO_2 were not measured, as shown in Fig. 3, but a similar cloud point for PVAc-X2/CO_2 was expected. The addition of PVAc macro-RAFT agents had profound effects on the homopolymerization of VAc in $scCO_2$. Fig. 4 shows a plot of the concentration of macro-RAFT agents versus M_n and PDI. Table 2 lists the results of polymerization. When the concentrations of RAFT agents (for both X1 and X2) were increased, the probability of transferring the growing polymeric radicals to the RAFT agent increased (from 0 to 10 wt%), reducing the molecular weight of the polymers but allowing better control over polymerization. In the absence of RAFT agents, a radical polymerization reaction of VAc at 34.5 MPa for 10 h produced PVAc with a M_n of 60,900 g mol^{-1} and a PDI of 2.05 (Table 2), showing no control over polymerization. On the other hand, the presence of PVAc-X1 or PVAc-X2 in the polymerization reaction produced polymers with lower molecular weights and lower PDIs: 25,900 g mol^{-1} and 1.35 in the case of PVAc-X1, and 26,700 g mol^{-1} and 1.56 in the case of PVAc-X2 (Fig. 4). This suggests that the addition of these macro-RAFT agents improves the living nature of the system by reducing the molecular weight distribution compared to the reaction using the initiator only. PVAc-X1 exhibited much better controllability than PVAc-X2, showing considerably lower PDI values for the same amount of the RAFT agent. The lowest PDI of 1.35 was obtained when 8.4 wt% PVAc-X1 (based on the amount of monomer) was used. In addition, the variation in PDI was very small when the amount of RAFT agent was more than 5 wt%.

Table 2. Homopolymerization of VAc at 338.15 K and 34.5 MPa for 10 h using PVAc-X macro RAFT agents in $scCO_2$

Entry	RAFT agent	Initial amount of RAFT agent (wt% of VAc)[a]	Conv[b] (%)	M_n[c] (g mol^{-1})	PDI
1	PVAc-X1	0	33	60,900	2.05
2	PVAc-X1	2.6	37	48,800	1.58
3	PVAc-X1	5.2	25	28,500	1.39
4	PVAc-X1	8.4	31	25,900	1.35
5	PVAc-X2	0	33	60,900	2.05
6	PVAc-X2	3	29	45,400	1.76
7	PVAc-X2	5	37	42,500	1.62
8	PVAc-X2	10	34	26,700	1.56

[a]Amount of reactants: 1.1 g of VAc, 0.0033 g of AIBN, and 5.0 g of CO_2

[b]Conversion was determined gravimetrically

[c]M_n and PDI were determined by GPC

Fig. 5 shows a plot of M_n versus the conversion of VAc when PVAc-X1 was used as a RAFT agent. M_n increased almost linearly with conversion due to the livingness of polymerization. The dashed and solid lines represent the $M_{n,th}$ calculated using Eqs. (1) and (2),

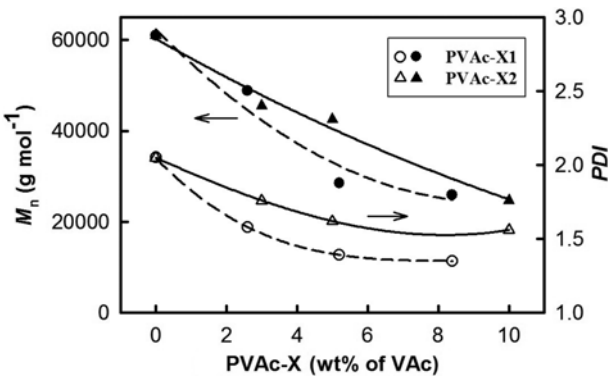

Fig. 4. Effect of the PVAc macro-RAFT agent concentration on the homopolymerization of VAc in $scCO_2$ (Reactions conditions: VAc 22 wt% of CO_2, initiator 0.3 wt% of VAc and various concentration of RAFT agents at 338.15 K and 34.5 MPa for 10 h).

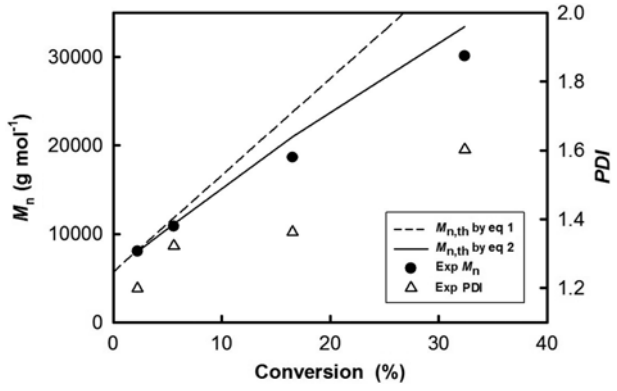

Fig. 5. M_n and PDI versus conversion of PVAc obtained by the homopolymerization of VAc using a macro-RAFT agent PVAc-X1 (Reactions conditions: VAc 22 wt% of CO_2, $[VAc]_0$: $[AIBN]_0$: $[PVAc\text{-}X1]_0$=1267 : 1.16 : 1 at 338.15 K and 34.5 MPa).

respectively. When the initiator concentration is negligible, Eq. (1) can be used, where $[RA]_0$ is the initial concentration of the macro-RAFT agent. Otherwise, Eq. (2) should be used [24].

$$M_{n,th}=\frac{[M]_0}{[RA]_0+df([I]_0-[I]_t)}\times m_M\times\rho+m_{RA} \quad (2)$$

where $[M]_0$ is the initial concentration of monomer, $[RA]_0$ is the initial concentration of macro-RAFT agent, $[I]_0$ is the initial concentration of the initiator, $[I]_t$ is the initiator concentration at reaction time t, d is the mode of termination, and f is the initiator efficiency (approximately 0.83); d is normally set to 1 for termination by coupling and 2 for termination by disproportionation. According to Bamford et al. [35], in which the extent of disproportionation in the polymerization of VAc was less than 10%, it was assumed that termination by coupling is predominant up to 90%. Therefore, d was set to 1.1 for the polymerization of VAc. The amount of initiator consumed during the reaction ($[I]_0-[I]_t$) was calculated using Eq. (3).

$$[I]_0-[I]_t=[I]_0(1-e^{-k_d t}) \quad (3)$$

where k_d is the decomposition rate constant of AIBN ($=3.5\times10^{-6}$ s^{-1}) [36].

Fig. 5 shows that $M_{n,th}$ calculated using Eq. (1) (dashed line) has larger deviations from the experimental values (M_n) than that calculated using Eq. (2) (solid line). Because Eq. (2) produces approximately 20% smaller Mn values than Eq. (1) due to the term, $df([I]_0-[I]_t)$, in the denominator, the initiator concentration and its change with time should not be neglected. The negative deviations from M_n (Eq. (1)) might be due to the significant formation of the polymer chains via the side reactions, including the initiator-derived chains [28]. This means that $M_{n,th}$ (Eq. (2)) is affected by both the initiator and RAFT agent concentration. Guan et al. [36] reported that the decomposition rate of AIBN in $scCO_2$ at 27.6 MPa was only 73% that of benzene at 332.5 K. In contrast, the initiation efficiency in $scCO_2$ of 27.6 MPa was 56% higher than that in benzene. This was attributed to the good transportation properties of $scCO_2$, such as the gas-like diffusivity and gas-like viscosity. In particular, the viscosity in CO_2 under this condition was much smaller and the diffusivity in CO_2 was much larger than that in benzene, allowing the significantly faster movement of radicals in $scCO_2$. The greater diffusivity in $scCO_2$ might also increase the termination by the coupling of radicals, resulting in a smaller number of polymer chains.

The PDI of PVAc increased from 1.2 to 1.6 with increasing conversion from 2 to 33% (Fig. 5). The increasing trend of PDI was attributed to chain transfer to the monomer and polymer during polymerization. Similar results were reported for the RAFT mini-emulsion polymerization of VAc [37,38]. The PDI will approach 1 if chain transfer is minimized.

3. Synthesis of PVAc-*b*-PVPi in $scCO_2$

A macro-RAFT agent, PVAc-X1, was used to produce a block copolymer from the VPi monomer in the presence of $scCO_2$. The cloud point of PVAc in the VPi/CO_2 mixture was not examined because VAc and VPi are similarly structured vinyl esters, and have similar properties. The reaction was also performed after observing the homogeneity of the mixtures inside the reactor at the beginning of the reaction. The initial molar ratio of the reactants was $[VPi]_0$: $[PVAc\text{-}X1]_0$: $[AIBN]_0$=457 : 1 : 1.04. The resulting polymer was confirmed by ^1H NMR to be a PVAc-*b*-PVPi block copolymer (Fig. 6). Table 3 lists the conversions and properties of the resulting polymers. As expected, the reaction for 24 h yielded higher conversion, molecular weight, and PDI than that for 5 h. The number average molecular weight of the polymer obtained from a 5 h reaction was 11,000 g mol^{-1} and the conversion of VPi was 12.7%. The mass ratio of the PVAc and PVPi blocks was 51 : 49. Note that the M_n of the polymers was measured by GPC and the PVAc block originated from the PVAc-X macro RAFT agent. On the other hand, for the 24 h reaction, M_n was 32,400 g mol^{-1} and the conversion was 41.5%, whereas the mass ratio of PVAc and PVPi was 17 : 83. The M_n of the block copolymer obtained from a 5 h reaction was approximately 15% lower than the $M_{n,th}$ (calculated by Eq. (1)) and 13% lower than the $M_{n,th}$ (calculated by Eq. (2)). On the other hand, that obtained from the 24 h reaction was 8% higher than $M_{n,th}$ (calculated by Eq. (1)) and 36% higher than $M_{n,th}$ (calculated by Eq. (2)). The current results cannot explain this behavior, highlighting the necessity for further study.

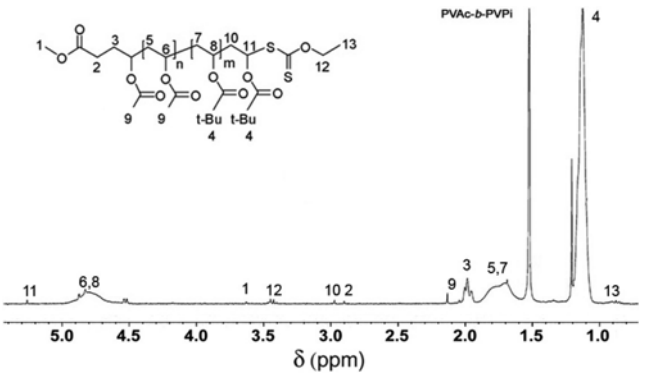

Fig. 6. ^1H-NMR spectrum of PVAc-*b*-PVPi. Chemical shift (ppm): d=0.89 (13), 1.12 (4), 1.19 (initiator-derived chains), 1.53 (AIBN), 1.74 (5,7), 2.00 (9), 2.89 and 2.99 (2 and10), 3.44 (12), 3.61 (1), 4.8 (6,8), 5.26 (11).

Table 3. PVAc-*b*-PVPi block copolymers synthesized by RAFT polymerization[a] and PVPi synthesized by dispersion polymerization, both at 338.15 K and 34.5 MPa in $scCO_2$

Time (h)	Conv[b] (%)	M_n[c] (g mol^{-1})	$M_{n,th}$[d] (g mol^{-1})	$M_{n,th}$[e] (g mol^{-1})	PDI
5	12.7	11,000	13,000	12,600	1.31
24	41.5	32,400	30,000	23,900	1.42
20	48.0	88,000[f]	-	-	1.82

[a]Initial molar ratio of reactants: $[VPi]_0$: $[PVAc\text{-}X1]_0$: $[AIBN]_0$=457 : 1 : 1.04. The amount of PVAc-X1 equals 9.8 wt% of VPi
[b]Conversion was determined gravimetrically
[c]M_n and PDI were determined by GPC
[d]$M_{n,th}$ was calculated by Eq. (1)
[e]$M_{n,th}$ was calculated by Eq. (2)
[f]Dispersion polymerization of VPi in $scCO_2$ using PFOA (1 wt% of VPi) as stabilizer at 338.15 K and 34.5 MPa. Initial molar ratio $[VPi]_0$: $[AIBN]_0$=457 : 1.04. Detailed procedure is given in the ref. [39]

Fig. 7 shows the molecular weight distributions of the block copolymers synthesized using PVAc-X1 in $scCO_2$ for 5 and 24 h together with that of the PVAc-X1 macro-RAFT agent. PVAc-*b*-PVPi

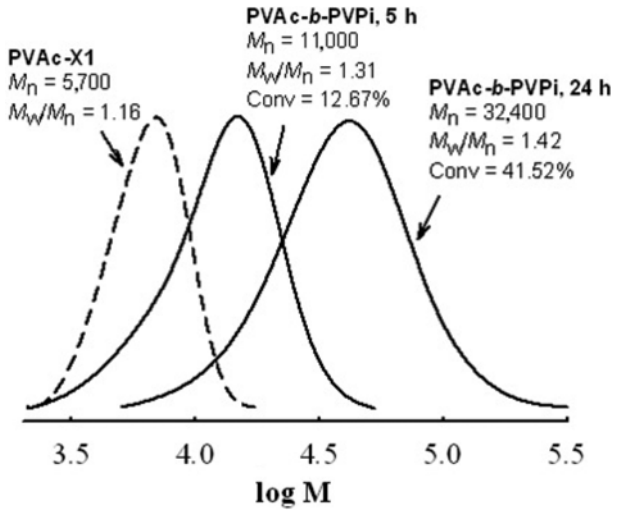

Fig. 7. Evolution of the molecular weight distributions of block copolymers synthesized using the macro RAFT agent PVAc-X1 at 338.15 K and 34.5 MPa in $scCO_2$.

diblock copolymers with a slightly broader polydispersity than the PVAc homopolymer shown above were obtained from this block copolymerization. The GPC curves of the diblock copolymers showed that these highly efficient chain extension reactions produce unimodal peaks of polymers with relatively narrow molecular weight distributions. The unimodal distribution showed that RAFT polymerization increased the M_n from 5,700 to 32,400 g mol^{-1} and the PDI from 1.16 to 1.42 after a 24 h reaction. Therefore, the block copolymerization is controlled under a PDI of 1.5. Block copolymerization using the PVAc-X2 macro RAFT agent will be performed in a future study.

Lipscomb et al. [22] also synthesized diblock copolymers of VAc and VPi but by bulk sequential RAFT polymerization with a PVAc-X2 macro-RAFT agent with a small amount of AIBN (10% of RAFT agent). Zong et al. [15] reported a relatively low conversion for highly efficient PMMA synthesis in $scCO_2$ using a larger amount of AIBN (50% of the RAFT agent). Our reaction was first conducted with a small amount of AIBN (20% of macro-RAFT agent), but the conversion was negligible. When the same amount of AIBN as reported by Zong et al. [15] was used (50% of macro-RAFT agent), only a low conversion of 6.5% was obtained after 5 h. Therefore, to obtain a high conversion, an AIBN to PVAc-X1 molar ratio of 1 : 1 was chosen in the block copolymerization.

CONCLUSIONS

PVAc-b-PVPi block polymer was synthesized in $scCO_2$ by RAFT/MADIX polymerization using a PVAc-xanthate macro-RAFT agent at 9.8 wt% in VPi. After a 24 h reaction, the conversion of VPi and the M_n of the block copolymer reached 41.5% and 32,400 g mol^{-1}, respectively. On the other hand, the PDI was 1.42, which was higher than expected. PVAc homopolymers with a controlled molecular weight distribution were also synthesized in $scCO_2$ by RAFT/MADIX polymerization. An increase in the initial loading of RAFT agent resulted in a decrease in both M_n and PDI, whereas the conversion was not affected. The PVAc macro-RAFT agent with an ethoxy group showed better controllability (with lower PDI value) than that with a methoxy group. The former RAFT agent of 8.4 wt% in VAc showed the best PDI of 1.35. Both M_n and PDI increased with increasing conversion, confirming the presence of living (RAFT) polymerization. Further research into this subject would be beneficial in developing an environmentally friendly RAFT/MADIX-controlled polymerization process using $scCO_2$.

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