

Controlled radical polymerization of vinyl acetate in supercritical CO₂ catalyzed by CuBr/terpyridine

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Abstract—Poly(vinyl acetate) (PVAc) was synthesized by the atom transfer radical polymerization of vinyl acetate (VAc) in supercritical carbon dioxide using CuBr/2,2':6',2''-terpyridine complex as a catalyst and ethyl 2-bromoisobutyrate as an initiator. Polymerization proceeded in a controlled manner, and low to moderate conversion was achieved within a reasonable time. The effects of the monomer amount, temperature, pressure, initiator, and ligand loading on monomer conversion, molecular weight and molecular weight distribution of the polymer were examined. The reaction kinetics was also investigated. The polymerization reaction was found to be first-order with respect to the monomer concentration. The molecular weights of the resulting PVAc increased linearly with increasing VAc conversion.

Keywords: Vinyl Acetate, Living Polymerization, Copper Catalyst, Supercritical CO₂, Atom Transfer Radical Polymerization (ATRP)

INTRODUCTION

Vinyl acetate (VAc) is a representative monomer that can be polymerized only via a free-radical mechanism [1,2]. Control of the radical polymerization of VAc is a challenge because, unlike methacrylates and styrene, VAc lacks a conjugating substituent. Therefore, its propagating radicals are highly reactive, less stable, and tend to undergo chain transfer and termination reactions [3]. Despite the substantial efforts made, control of the polymerization of VAc has been unsuccessful [4-8]. The living radical polymerization of VAc based on degenerative chain transfer promoted by alkyl iodides [4], use of *N,N*-diethyldithiocarbamate in the iniferter technique [5] and reversible addition-fragmentation chain transfer [6-9] have been reported using conventional radical initiators.

Currently, controlled "living" radical polymerization has attracted considerable interest because radical polymerization is generally more tolerant of polar functionalities and impurities than ionic and coordination polymerizations [10]. Among the approaches developed thus far, transition metal-catalyzed atom-transfer radical polymerization (ATRP) has been studied extensively. The ATRP of VAc was first reported by Matyjaszewski et al. using Al(*i*Bu)₃/2,2'-bipyridine/TEMPO (TEMPO=2,2,6,6-tetramethyl-1-piperidinyloxy) as the initiator [11]. On the other hand, polymerization was found to be complicated and difficult to reproduce [12]. The same group reported the polymerization of VAc using CCl₄ as the initiator in the presence of a Fe(OAc)₂/PMDETA (PMDETA=*N,N,N',N'',N'''*-pentamethyldiethylenetriamine) complex [13]. The polymerization process in this case was a redox-initiated telomerization based on the

irreversible activation of a C-Cl bond followed by chain transfer. Furthermore, the polymer molecular weight was independent of the monomer concentration, determined by the [VAc]₀/[CCl₄]₀ mole ratio, which is not a typical characteristic of ATRP. Wakioka et al. [14] reported a promising result of ATRP of VAc using dicarbonylcyclopentadienyl iron dimer, [Fe(Cp)(CO)₂]₂, as the catalyst in the presence of Al(O-*i*-Pr)₃ or Ti(O-*i*-Pr)₄ as additives with an iodide compound as the initiator. The results revealed the reversible activation of a carbon-halogen terminal group, where the molecular weight increased with increasing monomer conversion. Without the additive, as no polymerization occurred or the polymerization rate was very slow. Recently, the ATRP of VAc was performed in the presence of triisobutylaluminum using CuBr/bidentate phosphorus ligand complexes [15]. On the other hand, the molecular weights of the resulting polymers were independent of the monomer conversion, and a broad molecular weight distribution (≤ 2) was obtained. More recently, Tang et al. [16] reported the first copper-based catalyst CuX/2,2':6',2''-terpyridine (CuX/tPy, X=Br or Cl) for the controlled/living polymerization of VAc.

Controlled radical polymerization is carried out most often in bulk or solution or organic solvents. Supercritical carbon dioxide (scCO₂) has attracted significant attention as an environmentally friendly alternative to volatile organic solvents because of its low cost, abundance, non-toxicity, non-flammability, inert medium, tunable solvent property, and easy recyclability [17,18]. Moreover, the proposed global carbon capture strategies indicated that the scCO₂ will be widely available and inexpensive for widespread future use as a solvent. In the field of synthetic polymers, considerable effort has been devoted to polymerization processes in supercritical fluids. In particular, the conventional free-radical polymerization of vinyl monomers in scCO₂ has received considerable research attention [19-21], whereas only limited research has been carried out on the

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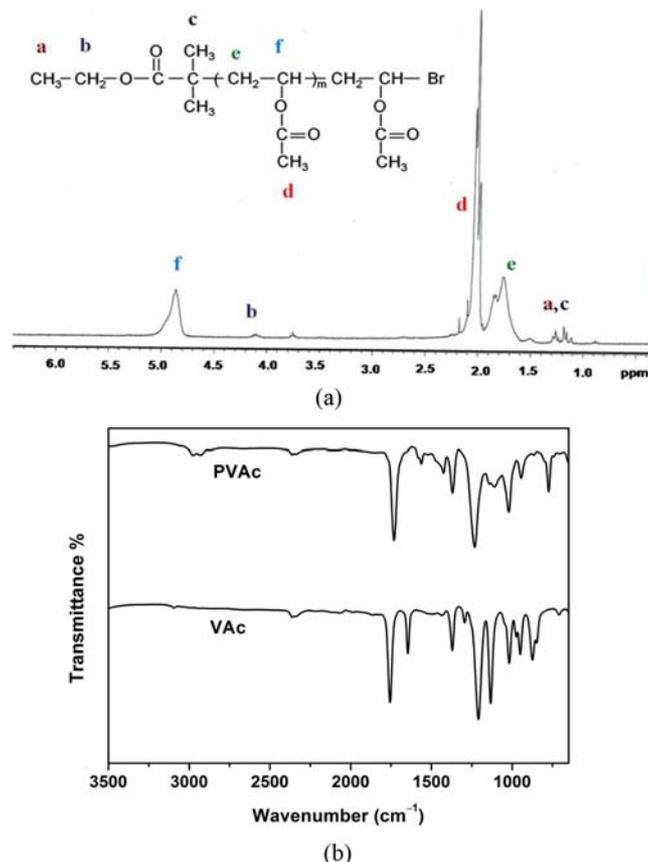


Fig. 2. ¹H-NMR spectrum of PVAc (a) and FT-IR spectra of PVAc and VAc (b).

and catalyst ($[\text{VAc}]_0/[\text{CuBr}]_0=150, 300, 600, \text{ and } 1,200$) at fixed ratio of initiator/catalyst/ligand molar ratio ($[\text{EBiB}]_0 : [\text{CuBr}]_0 : [\text{tPy}]_0=1 : 1 : 1$) in scCO_2 at 65°C and 310 bar for 24 h. In all cases, the ratio of the initiator, catalyst and ligand was constant. Fig. 3(a) shows a plot of the monomer content versus conversion. It is clear from Fig. 3(a) that the conversion was rather insensitive to the monomer content. No significant increases in conversion were observed after reaching approximately 30%. The homogeneous polymerization of vinyl monomers in scCO_2 can be performed provided that the monomer concentration is sufficiently high because the monomer acts as a cosolvent. On the other hand, the propagation rate in scCO_2 was lower due to a decrease in the local monomer concentration in the vicinity of the radical chain end [26,27].

Fig. 3(b) shows the number average molecular weight (M_n) and polydispersity index (PDI), corresponding to the monomer content. The results suggest that both the M_n and PDI increased with increasing monomer content in the feed. The M_n increased from 10 to 46.4 kg/mol (PDI increased from 1.64 to 1.95) nearly linearly when the monomer/catalyst mole ratio changed from 150 to 1200. This is possibly because for a higher amount of monomer, the ratio of initiator to monomer decreases, (i.e., the number of radicals formed decreases) resulting in higher molecular weights. Moreover, when the monomer/catalyst mole ratio was higher, the polymerization was not controlled and a broader MWD (PDI 1.95) was observed. Considering the monomer concentration in the reactor, the molar feed ratio ($[\text{VAc}]_0 : [\text{EBiB}]_0 : [\text{CuBr}]_0 : [\text{tPy}]_0$) of $600 : 1 : 1 : 1$ turned

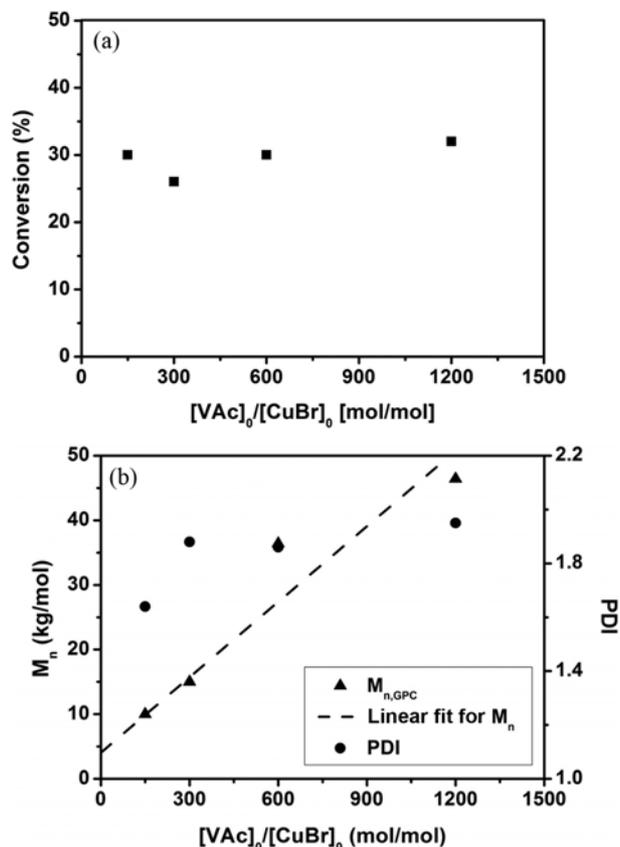


Fig. 3. Conversion (a) and M_n and PDI (b) as a function of monomer content ($[\text{VAc}]_0/[\text{CuBr}]_0$) for the ATRP of VAc in scCO_2 (Reaction conditions: Molar feed ratio of $[\text{EBiB}]_0 : [\text{CuBr}]_0 : [\text{tPy}]_0=1 : 1 : 1$, temperature= 65°C , pressure=310 bar, and time=24 h).

out to be adequate for the ATRP of VAc in scCO_2 .

3. Effect of Reaction Temperature

To examine the effects of temperature, the polymerization reactions were at a molar feed ratio of $[\text{VAc}]_0 : [\text{EBiB}]_0 : [\text{CuBr}]_0 : [\text{tPy}]_0=600 : 1 : 1 : 1$ and at 310 bar for 24 h by varying the temperature from 55 to 70°C . Fig. 4 presents the experimental results. The conversion of PVAc increased slightly with increasing temperature (Fig. 4(a)), whereas the opposite behavior was observed for M_n and PDI (Fig. 4(b)). When the reaction was at 55°C , PVAc with $M_n=38.3$ kg/mol was obtained with a conversion of 26%. When the temperature was increased to 70°C , the polymerization rate was faster and the conversion increased to 32% but M_n decreased significantly to 28.2 kg/mol, as expected. These trends agree well with the theory of radical polymerization that employs thermal dissociation [28]. PDI decreased only 4% for the temperature change from 55 to 65°C but decreased 23% for only 5°C increase from 65 to 70°C (Fig. 4(b)).

4. Effect of Reaction Pressure

The reaction conditions were set to a constant molar feed ratio of $[\text{VAc}]_0 : [\text{EBiB}]_0 : [\text{CuBr}]_0 : [\text{tPy}]_0=600 : 1 : 1 : 1$ at a pressure ranging from 241 to 379 bar. All the experiments were carried out at 65°C for 24 h. Fig. 5 shows that the conversion and M_n increased linearly with pressure, whereas the PDI showed an inconsistent behavior with pressure. At higher pressure (379 bar), the PDI decreased significantly, reaching a comparatively low PDI of 1.69. This is be-

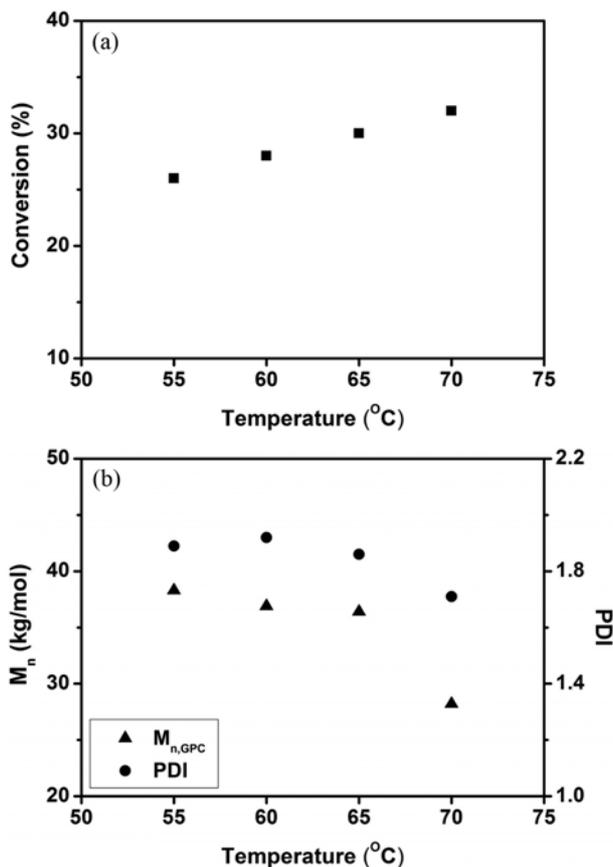


Fig. 4. Conversion (a) and M_n and PDI (b) as a function of temperature for the ATRP of VAc in $scCO_2$ (Reaction conditions: Molar feed ratio of $[VAc]_0 : [EBiB]_0 : [CuBr]_0 : [tPy]_0 = 600 : 1 : 1 : 1$, pressure=310 bar, and time=24 h).

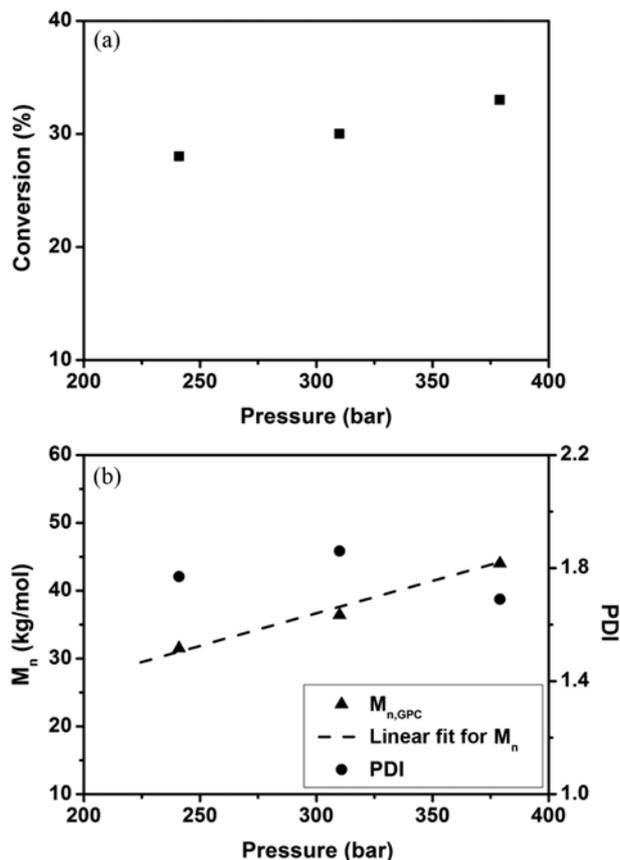


Fig. 5. Conversion (a) and M_n and PDI (b) as a function of pressure for the ATRP of VAc in $scCO_2$ (Reaction conditions: Molar feed ratio of $[VAc]_0 : [EBiB]_0 : [CuBr]_0 : [tPy]_0 = 600 : 1 : 1 : 1$, temperature=65 °C, and time=24 h).

cause the density of the continuous phase increases at higher pressures. At higher pressures, the monomer, catalyst and ligand dissolved comparatively better in the initial polymerization mixture, resulting in a higher reaction rate and higher M_n [28]. The increasing polymerization rate might be caused by an increase in the equilibrium constant and propagation rate coefficient, and a decrease in the termination rate [29,30]. Moreover, the denser CO_2 at higher pressures will have greater solvating power on the growing PVAc chains. Therefore, the chains will grow to a longer length prior to precipitation. In this way, the molecular weight of the polymer can be tailored simply by tuning the pressure. In addition, higher pressures induce greater plasticization of the polymer phase, which in turn leads to enhanced monomer diffusion within the polymer phase [29]. Furthermore, under higher pressures, the total living chains became notably higher compared to the dead chains, which is also a reason for the low PDI [32].

5. Reaction Kinetics

To examine the kinetics of VAc polymerization in $scCO_2$, a series of experiments were performed with a molar feed ratio of $[VAc]_0 : [EBiB]_0 : [CuBr]_0 : [tPy]_0 = 600 : 1 : 1 : 1$ at 65 °C and 310 bar for various reaction times (3, 6, 12, 24, 48 and 72 h). Fig. 6(a) shows a semi-logarithmic kinetic plot of the polymerization of VAc promoted by the CuBr/tPy catalyst complex in $scCO_2$. Polymerization was faster in the initial period but slower in the latter periods. The

concentration of the propagating radicals must have been nearly constant showing a linear increase of $\ln[M]_0/[M]$ vs. time (a characteristic of the first-order reaction), where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration at time t , until the conversion reached approximately 30%. The polymerization rate decreased abruptly after 24 h, suggesting that a significant degree of termination had occurred (Fig. 6(a)). The conversion was approximately 22% at 6 h, whereas it was 34% at 72 h, showing that the rate of polymerization was slower than the typical ATRP. This might be due to the poor solubility of the polymer in $scCO_2$ [29]. Although the monomer VAc is soluble in $scCO_2$, precipitation of the polymer occurred during the reaction. Lyoo et al. [15] reported a similar polymerization rate, where the ATRP of VAc was performed in the presence of triisobutylaluminum using CuBr/bidentate phosphorus ligand complexes.

The linear relationship between M_n and conversion (Fig. 6(b)) suggested that polymerization proceeded in a controlled manner. The experimental M_n determined by GPC is in agreement with the theoretical M_n . On the other hand, the PDIs obtained were fairly high for a controlled system and certainly higher than those obtained for the ATRP of VAc in the bulk [16]. After 6 h, the control of polymerization appeared to be lost, as indicated by the dramatic increase in PDI from 1.68 to 1.94. This might be due to the low deactivation rate constant (k_{deact}) of CuBr/tPy as a result of frequent chain

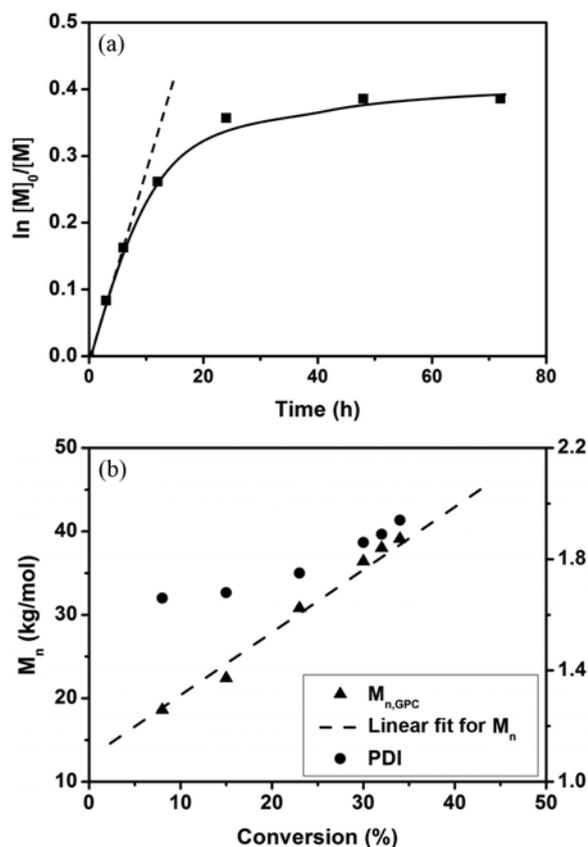


Fig. 6. Kinetic plot (a) and conversion versus M_n and PDI (b) for the ATRP of VAc in $scCO_2$ (Reaction conditions: Molar feed ratio of $[VAc]_0 : [EBiB]_0 : [CuBr]_0 : [tPy]_0 = 600 : 1 : 1 : 1$, temperature = $65^\circ C$, and pressure = 310 bar).

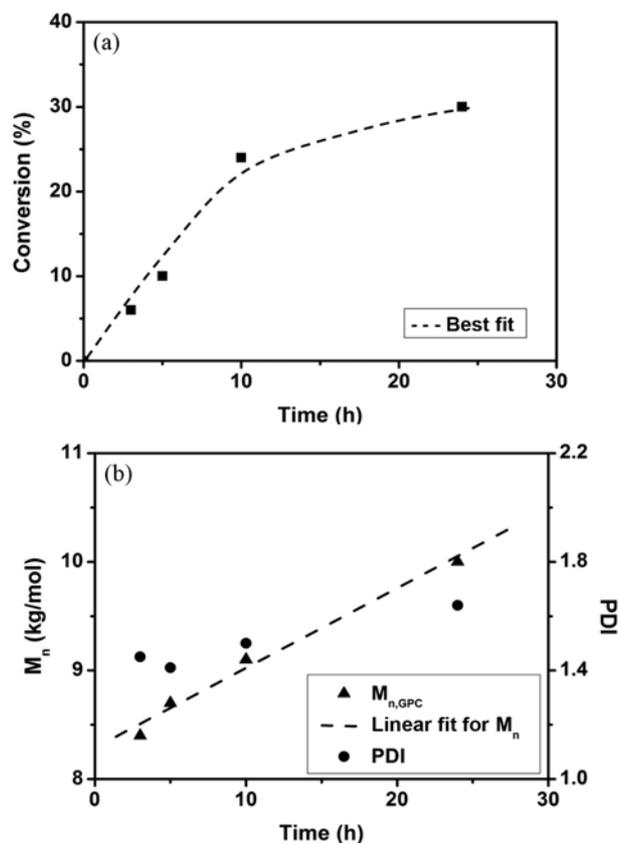


Fig. 7. Conversion (a) and M_n and PDI (b) as a function of time for the ATRP of VAc in $scCO_2$ (Reaction conditions: Molar feed ratio of $[VAc]_0 : [EBiB]_0 : [CuBr]_0 : [tPy]_0 = 150 : 1 : 1 : 1$, temperature = $65^\circ C$, and pressure = 310 bar).

transfer reactions. To obtain a successful catalyst system for living radical polymerization, the catalyst system should provide a high equilibrium constant (K_{eq}) and high deactivation rate constant (k_{deact}) to return the propagating radical to a dormant species before any transfer or termination reaction [33].

A molar feed ratio of $[VAc]_0 : [EBiB]_0 : [CuBr]_0 : [tPy]_0 = 150 : 1 : 1 : 1$ was chosen for further study to allow a comparison with the corresponding ATRP system in bulk, where they used the same monomer content [16]. The reactions were carried out at $65^\circ C$ and 310 bar for different reaction times (3, 5, 10 and 24 h). A linear increase in conversion and M_n with time was observed (Fig. 7). Overall, the experimental results (M_n and PDI) were within the expected range, except for the conversion. In addition, the experimental results observed for 10 h polymerization were comparable to the ATRP of VAc in the bulk [16]. The ATRP of VAc in the bulk showed $M_n = 11.6\text{ kg/mol}$ and $PDI = 1.74$, whereas this system exhibited a M_n and PDI of 9.1 kg/mol and 1.50 , respectively. These results are in good agreement with the ATRP of VAc in the bulk in terms of controllability.

6. Effect of Initiator Content

To determine the effects of initiator content on the polymerization, a series of experiments with four different initiator content per catalyst ($[EBiB]_0/[CuBr]_0 = 0.5, 1, 2, \text{ and } 4$) were performed at a molar feed ratio of $[VAc]_0 : [CuBr]_0 : [tPy]_0 = 600 : 1 : 1$ and $65^\circ C$ and 310 bar for 24 h. Fig. 8 presents plots of the initiator content against con-

version, M_n , and PDI. The results show that the conversion increased rapidly with initiator content from 0.5 to 1.0 and slowly, thereafter (Fig. 8(a)), showing that the initiator with the content up to 1.0% can be used completely in the polymerization. M_n decreased nearly linearly (Fig. 8(b)), which results from the increase in the number of radicals with increase in the initiator content for a smaller monomer content. Increasing the initiator content has only a small effect on the PDI. On the other hand, the M_n 's were significantly higher than the ATRP of VAc in the bulk [16], suggesting that the initiation efficiency was lower in $scCO_2$. All the polymers showed broad MWDs, irrespective of the conversion and M_n . The slow initiation rate might be one of the reasons for the broad MWD. In general, the initiation rate should be sufficiently high compared to the propagation rate to obtain a polymer with a narrow MWD through ATRP.

7. Effect of Ligand Content

To examine the effect of ligand content on the polymerization, a series of experiments were performed with three different ligand contents per catalyst ($[tPy]_0/[CuBr]_0 = 0.5, 1, \text{ and } 2$) at a fixed molar feed ratio of $[VAc]_0 : [EBiB]_0 : [CuBr]_0 = 600 : 1 : 1$, $65^\circ C$ and 310 bar for 24 h. Fig. 9 shows that both the conversion and M_n of PVAc decreased with increasing the ligand content per catalyst. This might have two explanations. First, the ligand tPy and its complex with CuBr decreased the solubility of the ligand in $scCO_2$. Moreover, the monomer acted as a cosolvent so that the solubility of the ligated catalyst decreased as the monomer was consumed. A second expla-

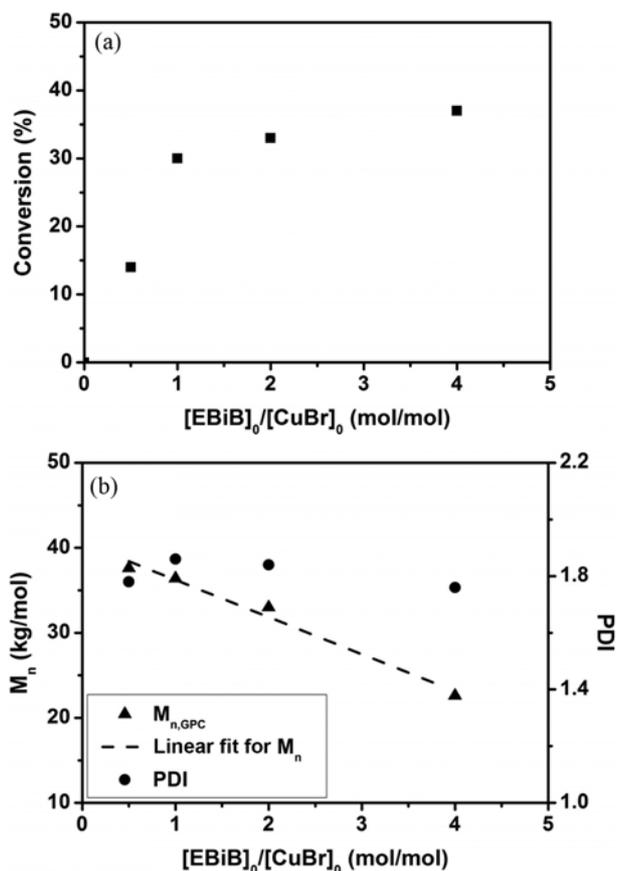


Fig. 8. Conversion (a) and M_n and PDI (b) as a function of initiator content ($[EBiB]_0/[CuBr]_0$) for the ATRP of VAc in $scCO_2$ (Reaction conditions: Molar feed ratio of $[VAc]_0 : [CuBr]_0 : [tPy]_0 = 600 : 1 : 1$, temperature = 65 °C, pressure = 310 bar, and time = 24 h).

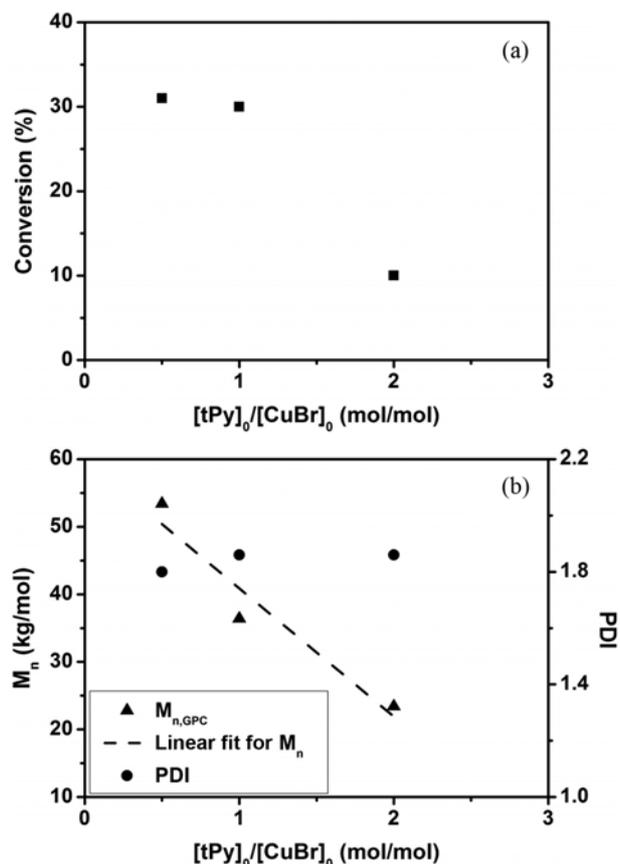


Fig. 9. Conversion (a) and M_n and PDI (b) as a function of ligand content ($[tPy]_0/[CuBr]_0$) for the ATRP of VAc in $scCO_2$ (Reaction conditions: Molar feed ratio of $[VAc]_0 : [EBiB]_0 : [CuBr]_0 = 600 : 1 : 1$, temperature = 65 °C, pressure = 310 bar, and for 24 h).

nation could be the structural effect. Earlier studies with flexible linear aliphatic triamine systems suggested that one equivalent of ligand per Cu(I) atom was sufficient to form a coordination sphere, which provided well-controlled ATRP and assured sufficient solubility of the catalytic system [33]. Apparently, two equivalents of triamines could saturate the coordination sphere around copper, preventing atom transfer, whereas an excess of ligand leads to some additional termination reactions. Fig. 9 shows that PDI was insensitive to the ligand content per catalyst.

CONCLUSIONS

PVAc was synthesized by ATRP using CuBr/(tPy) as the catalyst and EBiB as an initiator in $scCO_2$. The effects of the monomer, initiator, ligand, pressure, and temperature on the conversion, M_n and PDI were investigated. The most significant features of these results is that the M_n of PVAc was independent of the conversion, only low to moderate conversions were achieved, and the PDI values were high. The polymerization reaction was first-order with respect to the monomer in the early stage of reaction. A linear increase in conversion and M_n with time was observed. As reported in the literature, the controlled polymerization of VAc was limited by the ATRP, even in $scCO_2$. Further research will be needed to expand the range

of catalyst/ligand complexes, initiators and the operational conditions for the controlled ATRP of VAc in $scCO_2$.

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