



# Synthesis of poly(vinyl pivalate) by atom transfer radical polymerization in supercritical carbon dioxide



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## ABSTRACT

Atom transfer radical polymerization of vinyl pivalate was carried out in supercritical carbon dioxide using CuBr or CuCl/terpyridine (tpy) complex system and ethyl 2-bromoisobutyrate as an initiator. The reaction kinetics of the two different catalytic systems (CuBr/tpy and CuCl/tpy) was investigated. In addition, the effects of temperature, pressure, and catalyst/ligand concentration were examined systematically to obtain an acceptable rate of polymerization and control over the number-average molecular weight ( $M_n$ ) and polydispersity index (PDI). The result showed that relatively low PDIs were obtained and polymerization rates were enhanced at higher pressures. The CuCl/tpy complex exhibited the maximum conversion of 90% with a  $M_n$  and PDI of 60.2 kg/mol and 1.29, respectively. The CuCl/tpy catalyst system showed better agreement between theoretical and experimental  $M_n$  compared to the CuBr/tpy. The living character of poly(vinyl pivalate) (PVPi) was proven by <sup>1</sup>H NMR spectrum and chain extension reaction. The formation of poly(vinyl alcohol) via saponification of the resulting PVPi was also carried out. The structures of both PVPi and PVA were examined by <sup>1</sup>H NMR and FTIR spectra.

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## 1. Introduction

The rapid technological revolution over the past few decades has provoked several complex ecological issues. The polymer industries consume huge amounts of volatile organic solvents (VOC) as media or solvents, which are environmentally unfavorable. To deal with these environmental concerns, a number of studies have been performed on polymerization in supercritical fluids [1–3], ionic liquids [4–6], and aqueous media [7–9]. Among them, supercritical carbon dioxide (scCO<sub>2</sub>) has many commercial and industrial applications because it is non-toxic, non-flammable, inexpensive, environmentally benign, and inert [10]. The excellent transport properties of scCO<sub>2</sub>, such as gas-like diffusivity and liquid-like density, are the most

promising features, making scCO<sub>2</sub> more suitable for many more reactions than environmentally hazardous VOCs. The properties of scCO<sub>2</sub> can be tuned to a significant extent above the critical conditions by changing the temperature and pressure [11]. Additionally, the critical condition (31.1 °C and 7.39 MPa) of CO<sub>2</sub> is reached readily, and CO<sub>2</sub> can be separated easily from the product by depressurizing it to a lower pressure [12]. Consequently, scCO<sub>2</sub> has drawn considerable interests to be used as a medium for polymerization. In recent years, dispersion, solution, emulsion, and precipitation radical polymerizations have been successfully performed in scCO<sub>2</sub> [2]. Owing to the growing demand for polymers with controlled molecular weight distribution (MWD) or functional end groups, the use of controlled radical polymerization (CRP) in scCO<sub>2</sub> has started to attract attention. The term ‘CRP’ was used to describe polymerization techniques that enable the formation of polymers with predetermined molecular weights

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and controlled MWD. Recently, several methods of CRP such as nitroxide-mediated polymerization (NMP) [13], atom transfer radical polymerization (ATRP) [14], and reversible addition-fragmentation chain transfer (RAFT) polymerization [15] have been performed in  $scCO_2$  that offer much better control over polymer microstructure. Among the three methods, ATRP has been extremely successful in synthesizing well-defined polymers with a controlled polydispersity index (PDI) and novel polymer architecture [16,17]. It can also produce polymers with high chain end-functionality that may serve as macroinitiators in the synthesis of block copolymers and participate in various post-polymerization modifications [18,19]. Therefore, ATRP is considered the most promising among all of the CRP methods.

Poly(vinyl esters) are used selectively as precursors to prepare poly(vinyl alcohol) (PVA). PVA is a hydrophilic and water soluble polymer, and is used widely in a range of applications, such as membranes, clothes, binders, films, and medicines for drug delivery system. These esters also have very good physical properties, such as high tensile and compressive strengths, high tensile modulus, and good abrasion resistance, owing to its high crystalline lattice modulus. The physical properties of PVA are controlled by the molecular weight and stereoregularity. PVA can be obtained easily from poly(vinyl pivalate) (PVPI) via a saponification reaction [20]. PVA synthesized from PVPI has the highest syndiotacticity among the (PVA)s obtained by radical polymerization [21]. Vinyl pivalate (VPi), which has a similar structure to that of vinyl acetate, is one of the most representative monomers that can be polymerized only by a free-radical polymerization [20,22–24]. On the other hand, controlling the radical polymerization of VPi is a challenge because unlike methacrylates and styrene, VPi lacks a conjugating substituent and its propagating radicals are quite reactive, less stable, and tend to undergo chain transfer and termination reactions. Living radical polymerization methods have been investigated to control the polymerization of VPi, such as the reversible addition-fragmentation chain-transfer (RAFT) polymerization [15] and telomerization of VPi followed by block co-polymerization with styrene [25]. Recently our group reported the dispersion polymerization of VPi and CRP of vinyl acetate

in  $scCO_2$  [26,27]. Controlled synthesis of PVPI homopolymer [15], PVAc-s-PVPI [15,28] random copolymer, PVPI-*b*-PVAc and PVAc-*b*-PVPI block copolymer [28] by RAFT polymerization in  $scCO_2$  were reported elsewhere. However, to the best of the authors' knowledge, this is the first effort of synthesizing PVPI by ATRP in  $scCO_2$ .

In this study, we examined the optimal reaction conditions to synthesize PVPI in  $scCO_2$  with a controlled number-average molecular weight ( $M_n$ ) and PDI. The aims of this study were to (i) determine the optimal reaction conditions to obtain polymers with a controlled  $M_n$  and MWD, (ii) extend the chain length of the PVPI macroinitiator and (iii) saponification of PVPI.

## 2. Experimental

### 2.1. Materials

Vinyl pivalate (99%, Aldrich) was passed through an alumina column to remove the inhibitor and dried over calcium hydride ( $CaH_2$ ). Subsequently, a vacuum distillation was performed and the purified monomer was stored under nitrogen atmosphere in a freezer before using in the polymerization. Ethyl 2-bromoisobutyrate (EBiB, 98%), CuBr (99.99%), CuCl (99.99%) and 2,2':6';2''-terpyridine (tpy, 98%) were purchased from Aldrich and used as received. Ultra-high purity  $CO_2$  gas (99.999%) was purchased from Deokyang Energy Corp.

### 2.2. Polymerization of vinyl pivalate in $scCO_2$

The schematic diagram of the experimental setup for the ATRP of VPi in  $scCO_2$  is shown in Fig. 1. The polymerization reaction was carried out in a 20 mL stainless steel reactor, which was deoxygenated inside a glove box before starting the experiment. The reactor was then charged with a stirring bar, a catalyst, either CuBr (0.105 mmol or 0.015 g) or CuCl (0.105 mmol or 0.0105 g), and tpy (0.105 mmol or 0.0245 g). The monomer, VPi (52.3 mmol or 7.7 ml), was bubbled with nitrogen for approximately 30 min to remove the dissolved oxygen and added to the reactor. Subsequently, the reactor was purged with 6.9 MPa  $CO_2$  and the reaction mixture was stirred for

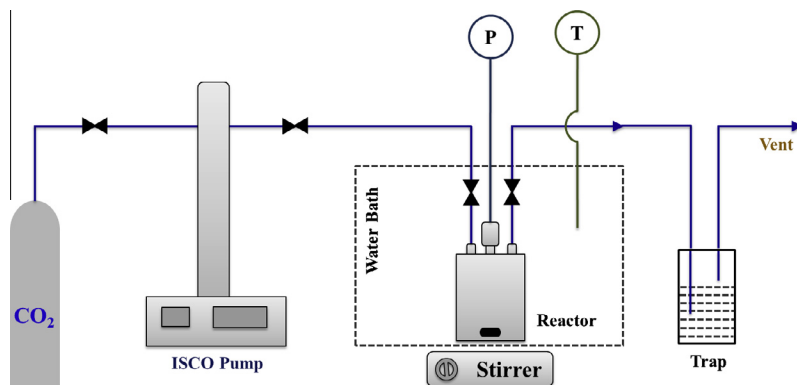


Fig. 1. Schematic diagram of the experimental setup for the ATRP of VPi in  $scCO_2$ .

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