

ARGET ATRP of Vinyl Acetate: A Green Synthesis in Supercritical CO₂ Catalyzed by Elemental Copper

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ABSTRACT

In this work, poly(vinyl acetate) (PVAc) with narrow molecular weight distribution (MWD) was synthesized implementing Activator Regenerated Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) technique in supercritical carbon dioxide (scCO₂). To synthesize PVAc with better controllability and reaction rate, phenylene bis terpyridine (PBTP) ligand were coordinated with cupric chloride (CuCl₂) at different concentrations. Zerovalent metal was employed as reducing agent in the practice of ARGET ATRP. The concentration of implemented mediator was kept as low as ppm level. Zerovalent metal along with PBTP ligand provided superlative control over MWD (PDI ~ 1.10) without falsifying the reaction rate negatively. Polymers with wide range of molecular weights were also prepared in a controlled fashion by changing the degrees of polymerization.

INTRODUCTION

Recently, supercritical carbon dioxide (scCO₂) has been extensively used for both homogenous and heterogeneous polymerization owing to its unique characteristic features: non-toxicity, non-flammability, low cost, inertness and availability with high purity. Apart from free radical polymerizations (FRP), atom transfer radical polymerization (ATRP) has also been studied in scCO₂ [1]. ATRP is one of the most powerful and versatile methods to synthesize well-defined polymers. It's a radical generation process through a reversible redox reaction, which is catalyzed by a transition metal catalyst and controlled by a dynamic equilibrium between dormant species and growing radicals [2]. However, conventional ATRP has some drawbacks, such as air sensitivity of the lower oxidation state catalyst [3], relatively high concentration of catalyst needed [4] and retention of the transition metal catalyst in the resulting polymers. Considerable numbers of researches have been performed to sort out these shortcomings, and as a result, many new ATRP techniques have been developed, such as activator regenerated by electron transfer (ARGET) ATRP [5], initiators for continuous activator regeneration (ICAR) ATRP [6], single electron transfer (SET) ATRP [7], electrochemically mediated ATRP (eATRP) [8], etc.. ARGET ATRP is a new catalytic activation process that involves the concept of reducing an air stable higher oxidation state catalyst/ligand complex (i.e. Cu^{II}X) to their corresponding lower oxidation state catalyst/ligand complex (i.e. Cu^IX) in situ by the addition of an excess of reducing agents (e.g. ascorbic acid, tin(II) 2-ethylhexanoate, hydrazine, amines, and zerovalent metals etc.) [9].

Poly(vinyl acetate) (PVAc) is an important polymer because of its hydrolyzed product, poly(vinyl alcohol) (PVA). But the synthesis of PVAc with a narrow molecular weight distribution (MWD) is challenging owing to the relatively high reactivity of the propagating radical species [10]. Matyjaszewski et al. [11] first reported the ATRP of VAc using, which resulted in PVAc with poor controllability. Therefore, in this study, a catalyst system was introduced to synthesize PVAc in scCO₂ with controlled MWD by suppressing the probability of chain capping as a chain ending

event and level of bimolecular termination.

EXPERIMENTAL

Materials

Unless stated otherwise, all chemicals were stored in a glovebox. Vinyl acetate (99%, Aldrich) was passed through a neutral alumina column to remove the inhibitor and was dried over calcium hydride (CaH_2) for 24 h. Subsequently, vacuum distillation was performed and the distilled monomer was stored under a nitrogen atmosphere in a refrigerator. Ethyl 2-bromoisobutyrate (EBiB, 98%), CuCl_2 (99.99%), CuCl (99.99%), 4',4''''-(1,4-Phenylene)bis(2,2':6',2''-terpyridine) (PBTP, 96%), 2,2:6';2''-terpyridine (tpy, 98%) and copper wire (Cu^0 , diam. 1.0 mm, $\geq 99.9\%$) were purchased from Aldrich, and used as received. Ultra high purity CO_2 gas (99.999%) was obtained from Deokyang Energy Corp.

Polymerization of vinyl acetate in scCO_2

A typical polymerization procedure for the ARGET ATRP of VAc using EBiB as an initiator and PBTP/ CuCl_2 / Cu^0 (wire) as the catalyst system with a molar ratio of $[\text{VAc}]_0/[\text{EBiB}]_0/[\text{CuCl}_2]_0/[\text{PBTP}]_0 = 2400:1:1:0.5$, is as follows. A 20 mL deoxygenated stainless steel reactor was equipped with a stir bar. The catalyst consisted of CuCl_2 (3.6×10^{-5} mol, 4.9 mg), Cu^0 wire ($l = 1$ cm, $d = 1$ mm) and PBTP (1.8×10^{-5} mol, 9.8 mg). VAc (0.087 mol, 8 mL) was added to the reactor after purging the nitrogen for approximately 30 min. Subsequently, the reactor was purged with CO_2 at 6.9 MPa at a flow rate of 0.5–0.6 mL/min, and the reaction mixture was stirred for approximately 30 min before adding the initiator to allow proper complex formation to take place. Finally, the initiator (EBiB) (3.6×10^{-5} mol, 5.3 μL) was added to the reactor, which was then heated to 65°C in a water bath. CO_2 was supplied to the reactor until the pressure reached 31 MPa using an ISCO syringe pump. The temperature of the water bath was kept constant within $\pm 0.01^\circ\text{C}$ using a thermostat. The reaction was stopped after 24 h by cooling the reactor in an ice bath, and the CO_2 gas was vented slowly. The polymer was collected by dissolution in THF, followed by precipitation in n-hexane. The polymer product was dried overnight in a vacuum oven to remove the remaining solvents.

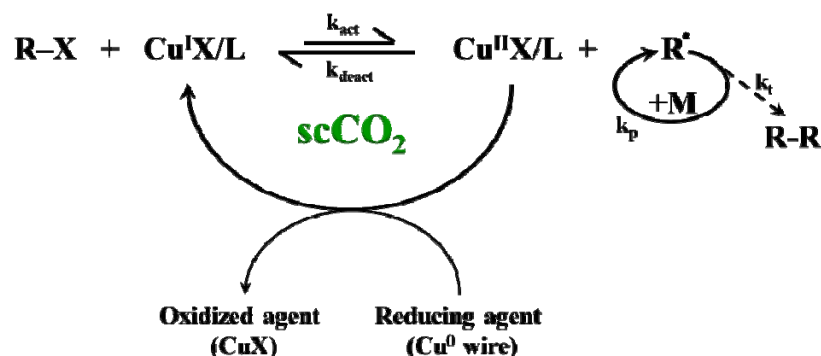
Characterization

Nuclear magnetic resonance (NMR) spectroscopy of PVAc was performed in CDCl_3 using a 300 MHz NMR spectrometer (Bruker, DPX-300). Monomer conversion was determined gravimetrically. The molecular weight (M_n) and polydispersity index (PDI) was obtained by gel permeation chromatography (GPC). GPC was equipped with an isocratic pump (Waters 1515) and a refractive index (RI) detector (Waters 2414). The Waters Styragel columns (HR4E and HR5E) were used in series with THF (HPLC grade) as an eluent and calibrated using polystyrene standards ($M_n = 3.07 \times 10^3 - 2.75 \times 10^5$ and $\text{PDI} = 1.01 - 1.15$). Calibration and analysis were carried out at 35°C and a carrier flow rate of 1 mL/min.

RESULTS AND DISCUSSIONS

ARGET ATRP of VAc

The ARGET ATRP of VAc in scCO_2 was performed using the CuCl_2 /PBTP complex system as a catalyst, Cu^0 wire as the reducing agent and EBiB as the initiator. Scheme 1 shows the proposed mechanism of the ARGET ATRP of VAc in scCO_2 .



Scheme 1: Proposed mechanism for the ARGET ATRP of VAc in scCO₂.

Reaction Kinetics

The reaction kinetics were investigated for the two different catalytic systems (CuCl₂/Cu⁰/tpy and CuCl₂/Cu⁰/PBTP) at 65°C and 34.5 MPa, with a feed ratio of [VAc]:[EBiB]:[Cu(II)X]:[PBTP] = 2400:1:1:0.5 and [VAc]:[EBiB]:[Cu^{II}X]:[tpy] = 2400:1:1:1. To determine the reaction kinetics, a series of experiments were performed for different reaction times (Table 1). First order reaction kinetics plots of the two polymerizations are shown in Fig. 1(a).

As can be seen, there was an increase in the rate of polymerization while CuCl₂/PBTP was used as the catalyst system. However, a nonlinear plot was observed for both catalyst systems, indicating a higher contribution of termination after 24 h of reaction time. The polymerization reactions exhibited first order kinetics in both cases, as shown in Eq. (1).

$$\ln([M]_0/[M]) = k_p^{\text{app}} t \quad (1)$$

where $[M]$ = monomer concentration, k_p^{app} = apparent rate constant and t = reaction time. The apparent rate constant of the polymerization, k_p^{app} , was calculated from the slopes in Fig. 1(a).

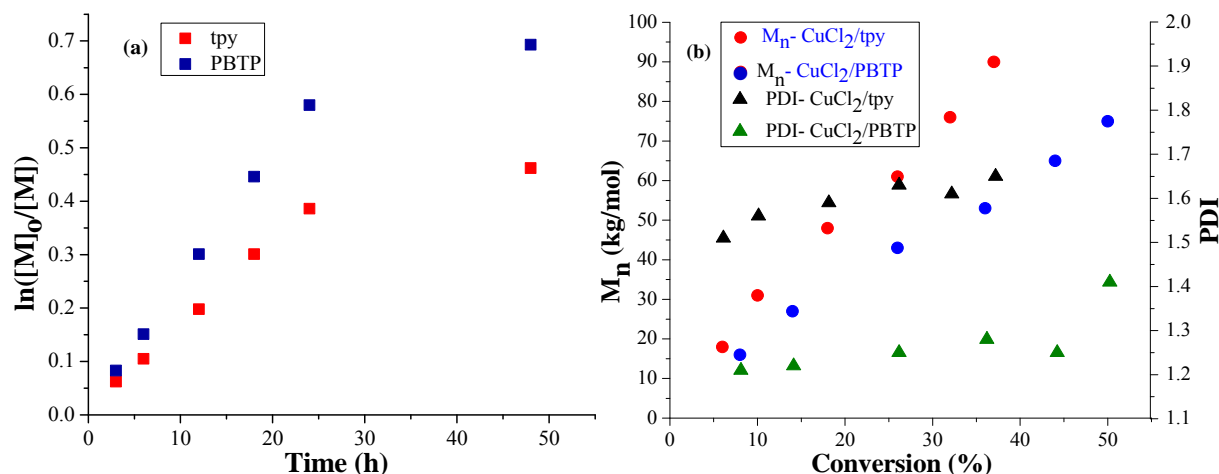


Figure 1: Plot of $\ln([M]_0/[M])$ as a function of time (a) and $M_{n,\text{GPC}}$ and PDI as a function of conversion (b) for the ARGET ATRP of VAc. Feed ratio = [VAc]:[EBiB]:[CuCl₂]:[tpy] = 2400:1:1:1; or [VAc]:[EBiB]:[CuCl₂]:[PBTP] = 2400:1:1:0.5, Cu⁰ wire ($l = 1$ cm, $d = 1$ mm); pressure = 34.5 MPa, temperature = 65°C.

The value of k_p^{app} was $6.5 \times 10^{-6} \text{ s}^{-1}$ and $4.35 \times 10^{-6} \text{ s}^{-1}$ for $\text{CuCl}_2/\text{PBTP}$ and CuCl_2/tpy , respectively. Fig. 1(a) shows that $\text{CuCl}_2/\text{PBTP}$ has a steeper slope than CuCl_2/tpy , indicating an approximately 1.5 times higher polymerization rate. However, for both cases limited monomer conversion was achieved. For both polymerizations with the $\text{CuCl}_2/\text{PBTP}$ and CuCl_2/tpy catalytic systems, linear evolution of molecular weight (M_n) with conversion was observed, which led to an increase in M_n from 18 to 90 and 16 to 75 kg/mol, respectively (Fig. 1b). Polymerization with the $\text{CuCl}_2/\text{PBTP}$ catalyst system showed better control (PDI <1.3), whereas the CuCl_2/tpy catalyst system produced polymers with broader PDIs (PDI <1.5) (Fig. 1b).

CONCLUSIONS

We have successfully prepared narrowly polydispersed PVAc by ARGET ATRP using $\text{CuCl}_2/\text{PBTP}$ and CuCl_2/tpy as a catalyst, EBiB as an initiator and an excess amount of Cu^0 wire as the reducing agent in scCO_2 . PBTP which was used first time as a ligand in ARGET ATRP was found to be an efficient ligand in terms of controllability for preparing PVAc, even with low catalyst concentrations. In this case, PVAc with very narrow MWD ($M_w/M_n \sim 1.20$) was obtained, even though the reaction rate was slightly slower.

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