

## Dispersion Polymerization of Vinyl Pivalate in a Green Ionic Liquid

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### Introduction

Due to unique characteristic features of low vapor pressure, high chemical and thermal stability, non-flammability and possible recycling,<sup>1-8</sup> rapidly increasing attention have been paid to ionic liquids (ILs) as environmentally friendly reaction media for chemical processes. It is well known that ILs have been used in the field of free-radical polymerization including traditional free radical polymerization,<sup>2</sup> nitroxide mediated stable free radical polymerization,<sup>4</sup> atom transfer radical polymerization (ATRP),<sup>5</sup> reverse ATRP,<sup>6</sup> and reversible addition fragmentation chain transfer.<sup>7</sup> The green ionic liquid, ([bmim][TFSI]) as the solvent for the free radical polymerization of some monomers,<sup>8</sup> and synthesis of chiral 1-2 diols<sup>9</sup> has been reported. It was demonstrated that radical polymerization in ILs provided higher polymerization rates and higher molecular weights than in the bulk or organic solvents, mainly due to a reduced termination rate not only because of high viscosity of the ionic liquids,<sup>9,10</sup> but also as a result of an increase in the propagation rate coefficients in some case.<sup>10</sup>

Poly(vinyl pivalate) is selectively used as a precursor of poly(vinyl acetate) (PVA) which is widely used as fibers for clothes and industries, binders, films, membranes, and in medicines for drug delivery systems, and cancer cell-killing embolic materials. PVA has good physical properties, such as high tensile and compressive strengths, high tensile modulus, and good abrasion resistance due to its higher crystalline lattice modulus.<sup>11-15</sup> Additionally, PVA obtained from PVPi with the high syndiotacticity and yield via the saponification has been reported.<sup>12,13</sup> In fact, PVPi has been synthesized by bulk, solution, emulsion, and suspension polymerization processes in various organic solvents at room temperature.<sup>11-15</sup> However, to the best of our knowledge, no work has been reported on the synthesis of PVPi by polymerization in ionic liquids.

In this study, we investigated the free radical dispersion polymerization of vinyl pivalate in an ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][TFSI]) using polyvinyl pyrrolidone (PVP) as a stabilizer. The effect of varying the concentrations of monomer, initiator, and stabilizer upon the molecular weight, yield and morphology of the resultant polymer was described.

### Experimental

#### Materials

Vinyl pivalate (99%) from Aldrich was passed through an alumina column to remove inhibitor and then it was dehydrated and degassed by nitrogen. [bmim][TFSI] was kept in vacuum oven at 80°C for 24 h to remove volatile impurities such as water and volatile organic substances remained in ionic liquids before use. The initiator AIBN was recrystallized twice from absolute methanol and dried in vacuum. Poly(vinyl pyrrolidone) (PVP, K-30,  $M_w = 36,000 \text{ g}\cdot\text{mol}^{-1}$ ) and other chemicals were purchased from Sigma-Aldrich and used as received without further purification.

**Dispersion polymerization**

In a typical experiment, the desired amounts of ([bmim][TFSI]), initiator (AIBN) and stabilizer (PVP) were introduced in a round-bottom flask and was agitated with a magnetic stir bar, and the system was purged with nitrogen gas for 30 min to remove any oxygen. Then a predetermined amount of monomer (VPi) was added into the flask. Polymerization was performed into a preheated oil bath under nitrogen atmosphere. After a predetermined time, the flask was cooled by an ice bath to stop the reaction. The resultant polymer was precipitated in methanol and treated with ultrasonic transducer. After centrifugation and washing three times by methanol, the product was dried in vacuum at room temperature for 24 h. The yield was determined gravimetrically. As a comparison, PVPi was prepared in an organic solvent DMSO under precisely the same conditions.

**Polymer characterization**

The number-average molecular weight and polydispersity of the PVPi were measured at 30°C using gel permeation chromatography (GPC), consisted of with a Waters 1515 Pump, Waters 2414 using THF as an eluent (1.0 mLmin<sup>-1</sup>). Calibration was made with a series of standard polystyrenes. Microscopic images of the polymer were obtained by a Hitachi S-4100 field emission scanning electron microscope (FESEM). Thermo gravimetric analysis (TGA) and differential scanning calorimetric (DSC) studies were performed on a TA instruments (SDT Q600 analyzer) from 30 to 800°C at a heating rate of 10°C/min under nitrogen atmosphere. FT-IR characterizations were performed using an Excalibur Series FTS 3000 (Bio-Rad) spectrometer.

**RESULTS AND DISCUSSION****Polymer Properties**

PVPi samples were formed in both ionic liquid and DMSO and were analyzed by FT-IR, H<sup>1</sup> NMR, TGA and DSC. It found that PVPi prepared in [bmim][TFSI] is the same as samples obtained in DMSO in FT-IR and H<sup>1</sup> NMR spectrum. The TGA and DSC results indicate that there is no significant difference in the thermal stabilities up to 370°C, although a slight lesser thermal stability was observed in the case of PVPi prepared in DMSO beyond 370°C. The higher thermal stability of the polymers synthesized in ionic liquid might be explained by higher degree of polymerization for these polymers leading to less volatile thermolysis fragments.<sup>23</sup>

**Effect of the stabilizer concentration**

The SEM images for the polymers (Figure 3) shows the discrete particles obtained in the presence of the PVP stabilizer. With 1 and 2 wt% , a relatively large distribution of particle sizes was observed; a selection of large particles (ca. 3.34 μm) surrounded by some smaller ones (ca. 1.03 μm), giving a final yield of 42.25% (Table 1). The yield value for polymers decreases with an increase in the amount of stabilizer present.

**Table 1.** Characterization of PVPi particles prepared at different stabilizer concentrations

Stabilizer concentrations (%w/w to vinyl pivalate)	M <sub>n</sub> (g/mol) <sup>a</sup>	PDI <sup>a</sup>	Yield (%)	D <sub>n</sub> (μm) <sup>b</sup>	Figure
1	298000	2.14	43.25	2.55	1A
2	274000	1.94	46.46	1.77	1B
5	268000	2.23	57.34	1.68	1C
10	253000	1.94	64.23	1.21	1D

Reaction condition: 1% AIBN/VPi (w/w), 65 °C, for 20 h. <sup>a</sup> Obtained by GPC. <sup>b</sup> Mean particle diameter.

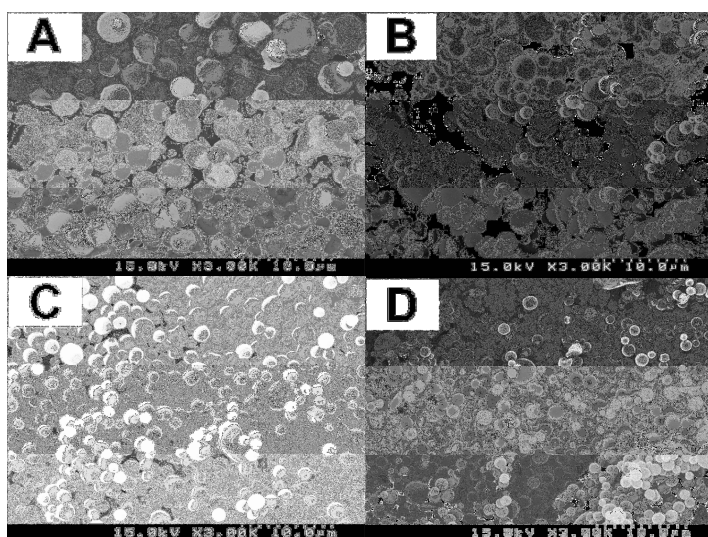
**Effect of the initiator concentration**

The molecular weight of PVPi prepared in [bmim][TFSI] decreased with increasing the amount of initiator (Table 2). When the more initiator is used, the more radicals are formed, shortening the length of each chain and reducing the molecular weight. However, unusual morphologies are also observed at lower initiator concentration (Figure 2).

**Table 2.** Characterization of PVPi particles prepared at different initiator concentrations with 5% (w/w to monomer) of PVP stabilizer

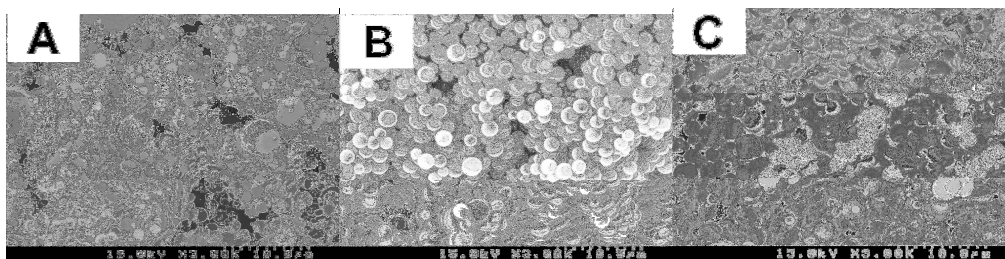
AIBN concentrations (%w/w to VPI)	$M_n$ (kg/mol) <sup>a</sup>	PDI <sup>a</sup>	Yield (%)	$D_n$ ( $\mu\text{m}$ ) <sup>b</sup>	Figure
0.5	274000	1.86	44.21	1.10	2A
1.0	268000	2.23	57.34	1.68	2B
2.0	198000	2.31	59.47	1.91	2C

Reaction condition: 10% VPI/[bmim][TFSI] (w/w), 65 °C, for 20 h. <sup>a</sup> Obtained by GPC. <sup>b</sup> Mean particle diameter.

**Figure 1:** SEM images of PVPi with (A) 1%, (B) 2 %, (C) 5%, (D) 10% wt PVP (w/w to VPI); reaction conditions: 1.5g Vpi, 1 %wt AIBN, T = 65°C, t = 20 h.

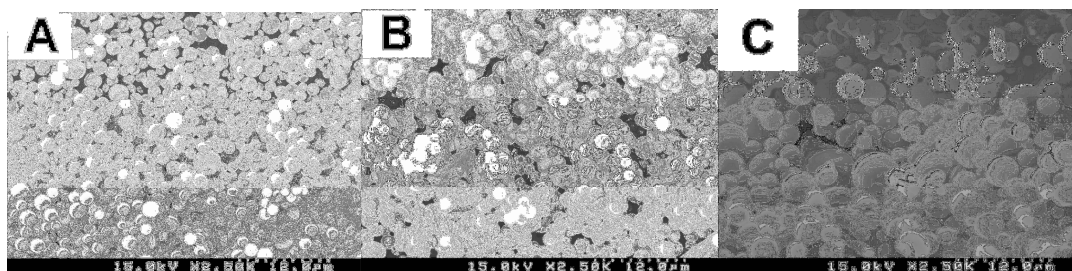
### Effect of the monomer concentration

Figure 3 and Table 3 show the results of the PVPi obtained at different monomer concentrations. When the monomer concentration increased, the dispersion formed was initially stable, but flocculation during polymerization occurred and the morphology of the resulting polymer was found by SEM to be large distribution of some particle sizes. As the monomer concentration increased, the solvency of the medium for growing polymer chain also increased, and this resulted in an increase of critical molecular weight for precipitation or surface activity of the growing oligomeric radicals.

**Figure 2:** SEM images of PVPi with (A) 0.5%, (B) 1%, (C) 2% wt AIBN (w/w to VPI); reaction conditions: 1.5g Vpi, 5 %wt PVP, T = 65°C, t = 20 h.**Table 3.** Characterization of PVPi particles prepared at different monomer concentrations with 5% (w/w to monomer) of PVP stabilizer

Vinyl pivalate concentrations (%w/w to [bmim][TFSI])	$M_n$ (kg/mol) <sup>a</sup>	PDI <sup>a</sup>	Yield (%)	$D_n$ ( $\mu\text{m}$ ) <sup>b</sup>	Figure
10	268000	2.23	57.34	1.68	3A
15	221000	2.01	50.12	1.93	3B
20	193000	1.85	44.52	2.19	3C

Reaction condition: 1% AIBN/VPI (w/w), 65 °C, for 20 h. <sup>a</sup> Obtained by GPC. <sup>b</sup> Mean particle diameter.



**Figure 3:** SEM images of PVPi with (A) 10%, (B) 15%, (C) 20% wt VPI in bmim[TFSI]; reaction conditions: 1.5g Vpi, 1 %wt AIBN, T = 65°C, t = 20 h.

### Conclusion

We have succeeded in preparing PVPi with high molecular weight by dispersion polymerization in [bmim][TFSI] for the first time. The effects of reaction parameters on molecular weight and molecular weight distributions of the polymer formed in ionic liquids are the same as previous reports in organic solvents. Ionic liquids offer new possibilities as green media for producing polymer by dispersion polymerization. The obtained polymers were measured by GPC, NMR, FT-IR, SEM and TGA. We expect that the novel polymer can be prepared by application of ionic liquids as green media. Further work to investigate the effects of the nature of the various ionic liquid on dispersion polymerizations of vinyl pivalate are in progress and will be reported in future publications.

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