

# ATRP of Ionic Liquid Monomers and CO<sub>2</sub> Absorption of the Polymerized Ionic Liquids

*Huadong Tang, Sijie Ding, Jianbin Tang, Maciej Radosz, Youqing Shen\**

*Department of Chemical & Petroleum Engineering, University of Wyoming, Laramie, WY 82071*

Volatile organic compounds (VOCs) have been found to be a major contributor to air pollution in many chemical and industrial processes. Recently, a new class of solvents—ionic liquids, which are chemically stable and non-volatile liquid organic salts at temperatures less than 100 °C, have attracted widespread interest due to its negligible volatility, nonflammability and high ionic conductivity.<sup>1,2</sup> In contrast to volatile organic compounds, ionic liquids have no measurable vapor pressure. Ionic liquids have been explored as green solvents for organic synthesis, liquid-liquid extraction and liquid-gas separation.<sup>3-5</sup>

The polymer forms of ionic liquids may be a new class of polymer materials with exceptional properties such as thermal stability, mechanical properties, electrochemical activity and CO<sub>2</sub> absorption ability, but to date, there is little study on the synthesis of ionic liquid polymers. Ohno and coworkers polymerized imidazolium salt methacrylate derivatives by free radical polymerization and found that the polymer had ionic conductivity.<sup>6,7</sup> Watanabe et al showed the poly(1-butyl-4-vinyl-pyridinium chloride) complexed with butylpyridinium chloride/aluminum trichloride had a ionic conductivity as high as 10<sup>-3</sup> Scm<sup>-1</sup> at room temperature.<sup>8</sup> The synthesis of these polymerized ionic liquids was all by free radical polymerization, and thereby the polymer structures, molecular weight and polydispersity were not controlled.

Another important potential application for polymerized ionic liquids is as sorbents for CO<sub>2</sub> absorption and separation.<sup>9</sup> It has been known that CO<sub>2</sub> is remarkably soluble in imidazolium based ionic liquid in comparison with other gases (e.g. CH<sub>4</sub>, CO, N<sub>2</sub> and O<sub>2</sub>).<sup>10,11</sup> For example, 1-butyl-3-aminopropyl-imidazolium tetrafluoroborate ionic liquid can dissolved 7.4 wt % of CO<sub>2</sub> at room temperature at one atmosphere.<sup>12</sup> Very recently, we found that the solid polymerized ionic liquids had much higher CO<sub>2</sub> absorption capacity and faster absorption kinetics than room-temperature ionic liquids. These polymers can be easily fabricated into sorbents and membranes, and thus may have widespread prospects in industrial applications.<sup>9</sup>

In this work, instead of using free radical polymerization, we use atom transfer radical polymerization (ATRP), a versatile living polymerization process for preparation of (co)polymers with predictable molecular weight, low polydispersity, and well-defined architectures,<sup>13,14</sup> to polymerize two new ionic monomers, 1-(4-vinylbenzyl)-3-butyl imidazolium tetrafluoroborate (VBIT) and 2-(1-butyl imidazolium 3-yl)-ethyl methacrylate tetrafluoroborate (BIMT), and for the first time we report the CO<sub>2</sub> absorption properties of obtained ionic liquid polymers. ATRP of ionic liquids was found very challenging due to its high polarity nature. The effects of varying initiator/catalyst system, monomer concentration, solvent polarity and reaction temperature on the polymerization were examined in detail.

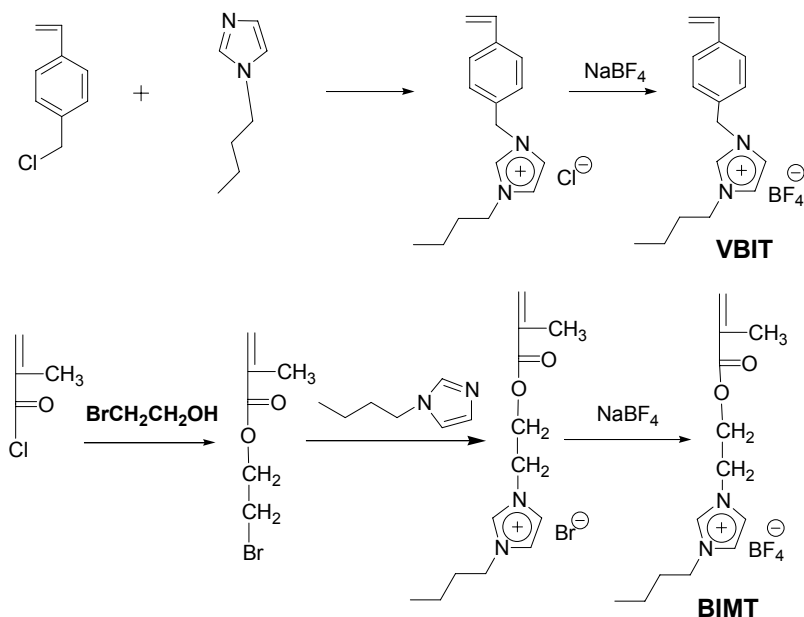
## Experimental

**General.** All chemicals were commercially available and used as received unless otherwise indicated. CuCl and CuBr were purified according to literature.<sup>15</sup> Monomer

conversions were determined by  $^1\text{H}$  NMR which was recorded on a Bruker Advance DRX-400 spectrometer. The X-ray diffraction (XRD) analysis was recorded on a SCINTAG XDS2000 powder diffraction system. DSC experiments were performed on a TA Instruments DSC Q100 differential scanning calorimeter. Gel permeation chromatography (GPC, Waters) was used to determine polymer molecular weights. The eluent was DMF containing 0.05 M lithium bromide at a flow rate of 0.3 mL/min at 50 °C. A series of polyethylene glycol standards were employed to generate the calibration curve.

The  $\text{CO}_2$  absorption of the polymerized ionic liquids was measured using a CAHN 1000 Electrobalance. The buoyancy effects were corrected according to literature.<sup>16</sup> The fine powder polymer was dried and degassed at 70 °C under vacuum for 12h to remove any water or other volatile contaminants.  $\text{CO}_2$  gas (99.995%) was dried by passing a drying column packed with  $\text{P}_2\text{O}_5$  and then filled into the balance chamber. The absorption was recorded until the weight did not change significantly in 30 min.

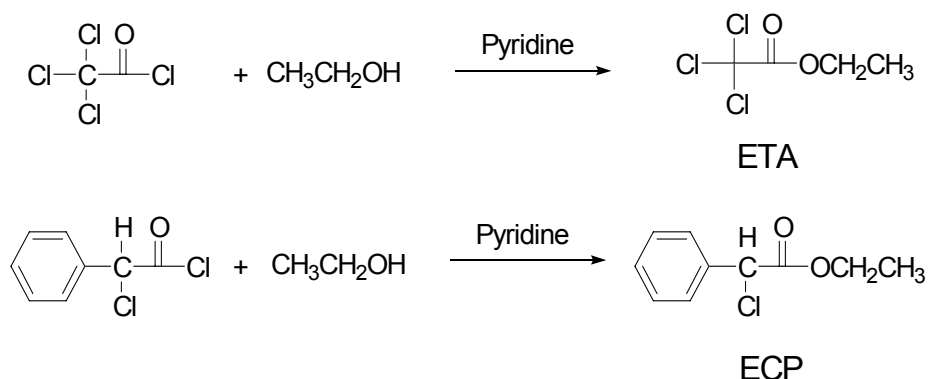
**Synthesis of ionic liquid monomers VBIT and BIMT.** The synthesis of two new monomers was shown in Scheme 1. *N*-butylimidazole and 4-vinylbenzyl chloride were mixed together and stirred at 45 °C for one day. The obtained viscous liquid then reacted with  $\text{NaBF}_4$  in dry acetone at room temperature for three days. The final solution was filtered and the filtrate was evaporated to give VBIT as white powder crystals. M. p. 67 °C.  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta$  9.24 (1H, s), 7.80 (2H, s), 7.51 (2H, d), 7.35 (2H, d), 6.73 (1H, m), 5.89 (1H, d), 5.40 (2H, s), 5.27 (1H, d), 4.14 (2H, t), 1.78 (2H, m), 1.24 (2H, m), 0.88 (3H, t). The liquid BIMT was prepared in similar manner.  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ ):  $\delta$  9.23 (1H, s), 7.80 (2H, s), 6.08 (1H, s), 5.73 (1H, s), 4.51 (2H, t), 4.44 (2H, t), 4.13 (2H, t), 1.83 (3H, s), 1.76 (2H, m), 1.24 (2H, m), 0.88 (3H, t).



**Scheme 1.** Synthesis of ionic liquids VBIT and BIMT

**Synthesis of initiators ethyl trichloroacetate (ETA) and ethyl  $\alpha$ -chlorophenylacetate (ECP).** ETA was synthesized through the reaction of ethyl alcohol with trichloroacetyl

chloride (Scheme 2). The ETA was purified by vacuum distillation (57-58 °C/10 mmHg). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.42 (q, 2H), 1.40 (t, 3H). Similarly, ECP was prepared by the reaction of ethyl alcohol with α-chlorophenylacetic chloride. <sup>1</sup>H NMR (400Hz, CDCl<sub>3</sub>): δ 7.52(m, 2H), 7.41 (m, 3H), 5.36 (s, 1H), 4.27 (q, 2H), 1.28 (t, 3H).



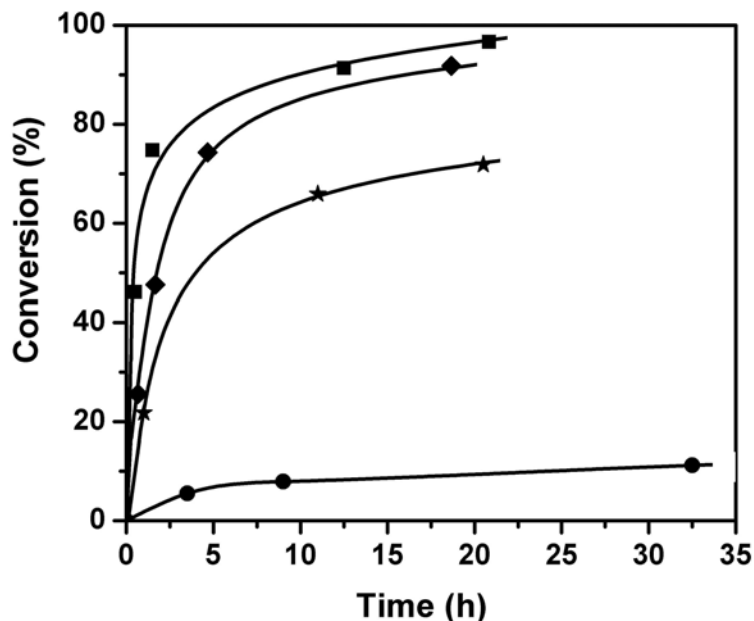
**Scheme 2.** Synthesis of initiators ETA and ECP

**ATRP of ionic liquid monomers.** In a typical ATRP procedure, the catalyst copper halides (e.g., CuCl), ligand such as 1,4,7,10,10-Hexamethyltriethylenetetramine (HMTETA) or 2,2'-bipyridine (Bpy) and monomer VBIT or BIMT were charged into a reaction flask. Then the degassed solvents were added. The mixture was stirred and purged with nitrogen for 15 minutes. After the mixture was put in an oil bath and equilibrated to desired temperature, the initiator such as ethyl 2-bromoisobutyrate (EBiB) was introduced via a degassed syringe. Samples were withdrawn at timed intervals using degassed syringes and diluted in DMF containing CuBr<sub>2</sub> for NMR and GPC measurements.

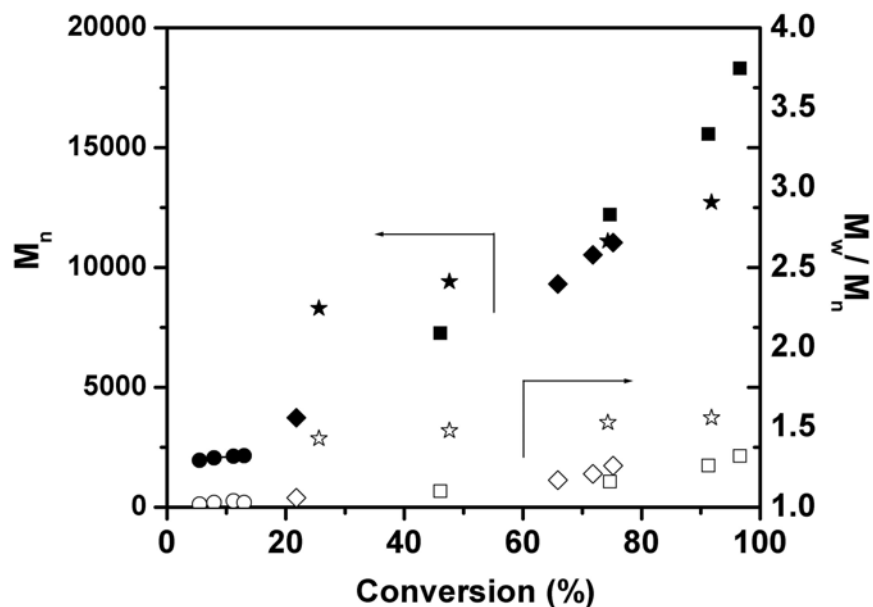
## Results and Discussion

### Determination of catalyst/ligand system for ATRP of VBIT and BIMT.

Copper bromide combined with bromide-based initiator is a highly active for ATRP of styrenic monomers. Several bromide-initiator/catalyst including EBiB/CuBr/HMTETA, EBiB/CuBr/Bpy and EBiB/FeBr<sub>2</sub> without ligand were firstly examined for ATRP of VBIT and the results were shown in Figures 1 and 2. Obviously, FeBr<sub>2</sub> showed very low activity. The polymerization could only reach 10% conversion even after one day, indicating that FeBr<sub>2</sub> could not efficiently catalyze the ATRP of VBIT under experimental conditions. CuBr/HMTETA and CuBr/Bpy polymerized VBIT in a fast polymerization rate (90% conversion in 12 h), producing polymers with low polydispersity (< 1.3). Chloride-initiator/catalyst methyl 2-chloropropionate (MCP)/ CuCl/Bpy was also tried for ATRP of VBIT, but the polymerization could only reach 70% final conversion and produce polymer with a broad molecular weight distribution (PDI ~ 1.6) as shown in Figures 1 and 2.



**Figure 1.** ATRP of VBIT in butyronitrile at 90 °C. [VBIT] = 1.67 M, [EBiB] = [MCP] = 16.7 mM, EBiB/CuBr/HMTETA (1/1/1) (■), EBiB/CuBr/Bpy (1/1/2) (◆), MCP/CuCl/Bpy (1/1/2) (★), EBiB/FeBr<sub>2</sub> (1/1) (●).

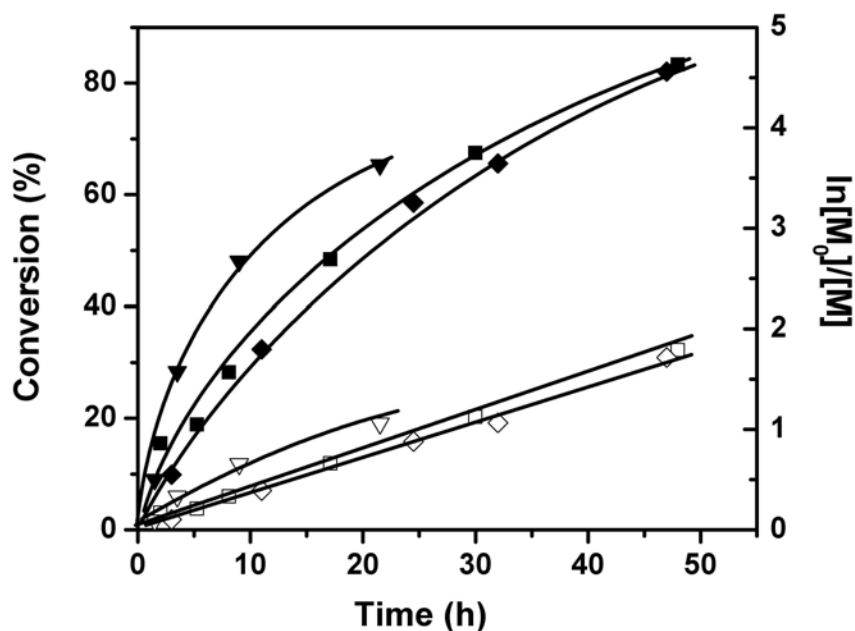


**Figure 2.** Molecular weight and polydispersity versus conversion plots of the ATRP of VBIT in butyronitrile at 90 °C. See Figure 1 for experimental conditions. EBiB/CuBr/HMTETA (■, □), EBiB/CuBr/Bpy (◆, ◇), MCP/CuCl/Bpy (★, ☆), EBiB/FeBr<sub>2</sub> (●, □).

The GPC traces of PVBIT showed a unimodal molecular weight distribution. The measured  $M_n$  of PVBIT by CuBr/HMTETA and CuBr/Bpy increased linearly with monomer conversion (Figure 2), indicating living features of the polymerization of VBIT. However, the measured molecular weights were much lower than the theoretical values. This is

understandable because the  $M_n$  of PVBIT were measured by GPC using polyethylene glycol (PEG) standards. PEG is a neutral polymer and its hydrodynamic volume is significantly different from that of positive-charged PVBIT even with same molecular weight.<sup>17</sup>

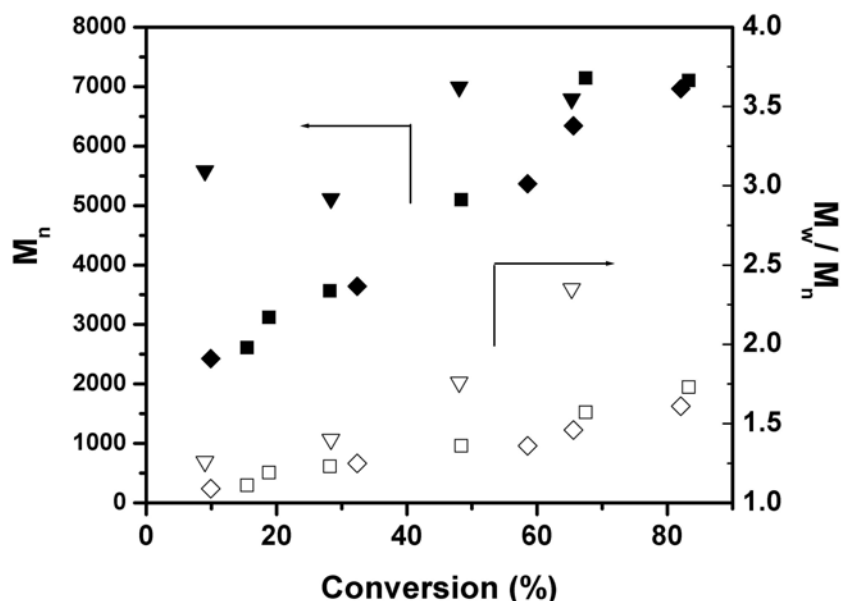
Though EBiB/CuBr/HMTETA and EBiB/CuBr/Bpy are suitable for ATRP of VBIT, they are not good initiator/catalyst systems for polymerization of BIMT. The ATRP of BIMT by EBiB/CuBr/Bpy or EBiB/CuBr/HMTETA was out of control. For example, the polymerization of BIMT in acetonitrile at 60 °C with BIMT/EBiB/CuBr/ Bpy = 100:1:1:2 and [BIMT] = 2.56 mol/L was very fast. The conversion could reach 72% in five minutes, but the prepared polymer had a polydispersity as high as 1.93. On the other hand, chloride-based initiator/catalyst system was found to be very effective for ATRP of BIMT. Figures 3 and 4 showed the results of ATRP of BIMT using CuCl/Bpy or CuCl/HMTETA as catalyst and ETA, ECP or CCl<sub>4</sub> as initiators.



**Figure 3.** ATRP of BIMT in acetonitrile at 60 °C using CuCl/Bpy or CuCl/HMTETA as catalysts and ETA, ECP or CCl<sub>4</sub> as initiators. [BIMT] = 2.3 mol/L, [CuCl] = 0.023 mol/L; CCl<sub>4</sub> /CuCl/Bpy = 1:1:2 (■), ETA/CuCl/Bpy] =1:1:2 (◆), ECP/CuCl/HMTETA = 1:1:1 (▼)

Both ETA and CCl<sub>4</sub> initiated BIMT with an appropriate polymerization rate and the final conversions were higher than 80%. Just like PVBIT, the measured molecular weights of PBIMT were much low than theoretical values because of the large difference in structure between the positive-charged PBIMT and neutral PEG standard, but they did increased linearly with the monomer conversion, demonstrating that the polymerization is a living process. The polydispersity of PBIMT was 1.1-1.2 at low conversion but gradually increased to 1.5-1.6 at high conversions (>70%). This broadening in molecular weight distribution could be probably attributed to the fact that at the later stage of polymerization, the reaction medium became very viscous, resulting in poor transportation of the activator and deactivator, and thus more pronounced irreversible radical termination.<sup>18</sup> In comparison with ETA or CCl<sub>4</sub>, ECP polymerized BIMT with faster reaction rate because the phenyl group of ECP could provide strong conjugative and inductive effects and thus stabilize radical intermediates, resulting in

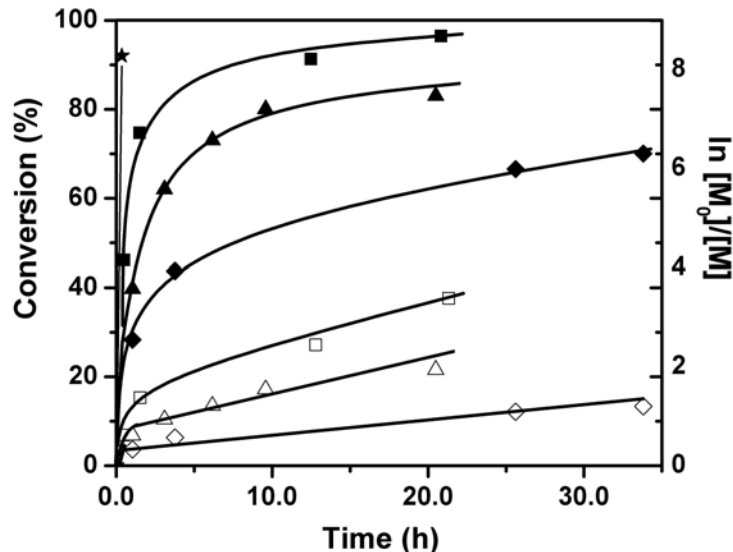
higher radical concentration and faster activation rate, and inevitably leading to more irreversible radical termination and broader molecular weight distribution ( PDI ~ 2.3).



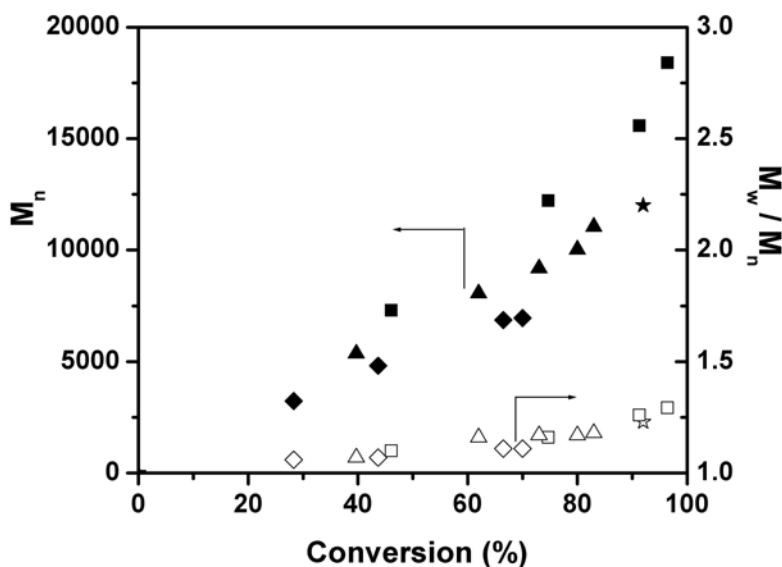
**Figure 4.** Molecular weight and polydispersity versus conversion plots of the ATRP of BIMT in acetonitrile at 60 °C. See Fig. 3 for experimental conditions.  $\text{CCl}_4/\text{CuCl}/\text{Bpy} = 1:1:2$  (■),  $\text{ETA}/\text{CuCl}/\text{Bpy} = 1:1:2$  (◆),  $\text{ECP}/\text{CuCl}/\text{HMTETA} = 1:1:1$  (▼)

#### Effect ion of monomer concentration on ATRP of VBIT and BIMT.

The polymerization rate of ATRP of VBIT and BIMT had a strong dependence on the monomer concentration. Figures 5 and 6 showed the result of ATRP of VBIT in bulk and in butyronitrile with different monomer concentrations using  $\text{CuBr}/\text{HMTETA}$  as catalyst and  $\text{EBiB}$  as initiator. The bulk polymerization at 90 °C was so fast that the liquid monomer turned into solid in less than 10 minutes with a conversion of 92%. The resulting polymer had a  $M_n$  of 12400 with polydispersity of 1.24, indicative of a good control in spite of fast reaction rate. The solution polymerization at VBIT concentration of 1.67 mol/L could reach 90% conversion in 10 h with a final conversion higher than 95%, 80% in 20 h with final a conversion of 83% at VBIT concentration of 1.11 mol/L, and 65% in 25 h at VBIT concentration of 0.83 mol/L with a final conversion of 68%.



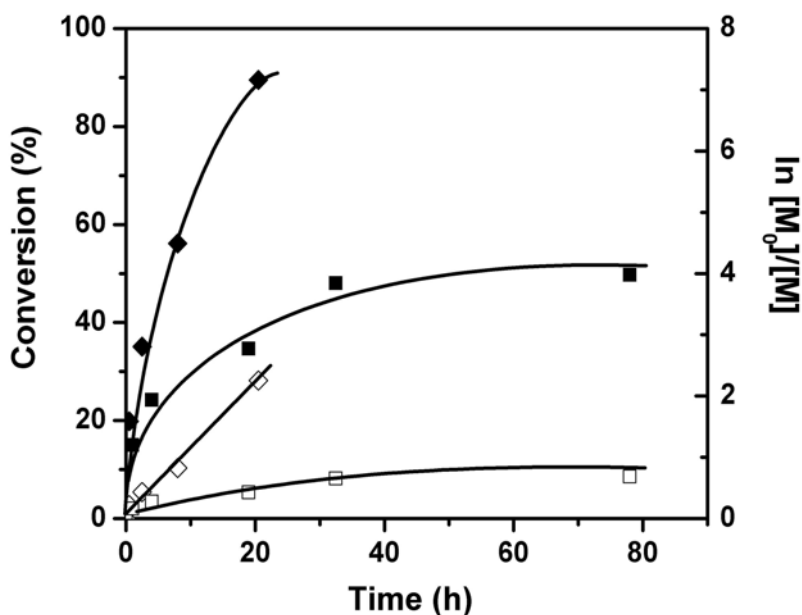
**Figure 5.** ATRP of VBIT by EBiB/Cu/Br in butyronitrile at 90 °C with different monomer concentrations. [EBiB] = [CuBr] = [HMTETA] = 16.7 mM; bulk polymerization ( $\star, \star$ ), [VBIT] = 1.67 M ( $\blacksquare, \square$ ), 1.11 M ( $\blacktriangle, \triangle$ ), 0.83 M ( $\blacklozenge, \lozenge$ ).



**Figure 6.** Molecular weight and polydispersity versus conversion plots of the ATRP of VBIT in butyronitrile at different monomer concentration. See Fig. 5 for experimental conditions; bulk polymerization ( $\star, \star$ ), [VBIT] = 1.67 M ( $\blacksquare, \square$ ), 1.11 M ( $\blacktriangle, \triangle$ ), 0.83 M ( $\blacklozenge, \lozenge$ ).

Similar results were found in the ATRP of BIMT in acetonitrile (Figures 7). At the BIMT concentration of 2.3 mol/L, ECP/CuCl/Bpy initiated polymerization could reach 70% conversion in 10 hours with a final conversion near to 90%. However, when the BIMT concentration decreased to 1.54 mol/L while other components kept unchanged, the polymerization became quite slow, 45% in 40 hours with a final conversion less than 50%.

The so strong effects of monomer concentration on the ATRP polymerization rate may be contributed to the high polarity of the ionic liquid monomer. Ionic liquids are highly polar compounds (similar to *N*-methylformamide).<sup>19</sup> Several groups have reported that polar solvents such as ethylene carbonate or additives such as phenol could accelerate ATRP polymerization rate because these polar compounds molecules can affect the structures of the Cu(I)/ligand and form more active Cu(I) catalyst.<sup>13,20-22</sup> Polar compounds can form the complex with copper-based catalyst or displace halide ligands from the catalyst.<sup>23,24</sup> Such complexation or halogen-displacement may destroy deactivating Cu(II)/ligand species and thus accelerate the activation reaction but slow the deactivation reaction in the ATRP equilibrium,<sup>13</sup> resulting in a high radical concentration and thereby fast polymerization rate. At higher monomer concentration, due to the exceptionally high polarity of VBIT or BIMT, the reaction medium is more polar, leading to much faster activation reaction than in less polar medium at low monomer concentration, and consequently the polymerization rate increased dramatically with the increase of monomer concentration but also decrease significantly with the decrease of concentration.

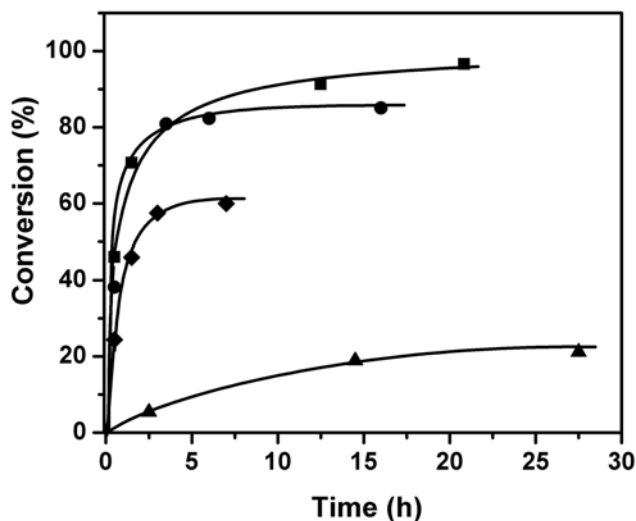


**Figure 7.** ATRP of BIMT in acetonitrile by CuCl/Bpy/ECP at 60 °C with different monomer concentration. [ECP] = [CuCl] = [Bpy] = 23.1 mM, [CuCl<sub>2</sub>] = 3.5 mM, [BIMT] = 2.31 mol/L (◆, ◇), [BIMT] = 1.54 mol/L (■, □).

### Solvent effects on ATRP of VBIT and BIMT.

Solvent played an important role in ATRP of ionic liquids. Monomer VBIT and BIMT are not soluble in low polar solvents (e.g., toluene, CH<sub>2</sub>Cl<sub>2</sub> and THF). Figure 8 showed the results of ATRP of VBIT in highly polar solvents such as *N,N*-dimethylformamide (DMF), *N*-methylpyrrolidone (NMP) and butyronitrile.





**Figure 8.** ATRP polymerization of VBIT in different solvents at 90 °C (except methanol at 50 °C). Conditions: [VBIT] = 1.67 M, [EBiB] = [CuBr] = [HMTETA] = 16.7 mM; butyronitrile (■, □), NMP (●, ○), DMF (◆, ◇), methanol (▲, △).

The polymerizations of VBIT in NMP, DMF and butyronitrile were all very fast at the early stage of the polymerization, but slowed down significantly afterward. The polymerization actually leveled off at 60% conversion in DMF and 80% in NMP, but polymerization in butyronitrile could reach about 95% conversion. Similar results were found in ATRP of BIMT in acetonitrile (final conversion ~ 90%, Figure 7). This phenomena is typical for ATRP in polar solvents.<sup>25,26</sup> As discussed above, polar solvents can affect the structures of the copper-based catalysts, especially for solvents capable of coordination with Cu(II) such as DMF and water,<sup>23</sup> they may destroy the deactivating Cu(II)/ligand species. In addition, CuCl<sub>2</sub> or CuBr<sub>2</sub> may also disassociate into free Cu<sup>2+</sup> cation and Cl<sup>-</sup> or Br<sup>-</sup> anions in polar solvents, and thus lose the deactivation ability of Cu(II)/ligand, which led to slow deactivation reaction and high radical concentration,<sup>24</sup> and thereby very fast polymerization rate during the initial period of polymerization. However, irreversible radical termination occurs at high radical concentration and thus produces an excess of Cu(II) (persistent radical effect), causing a decrease in polymerization rate afterward.

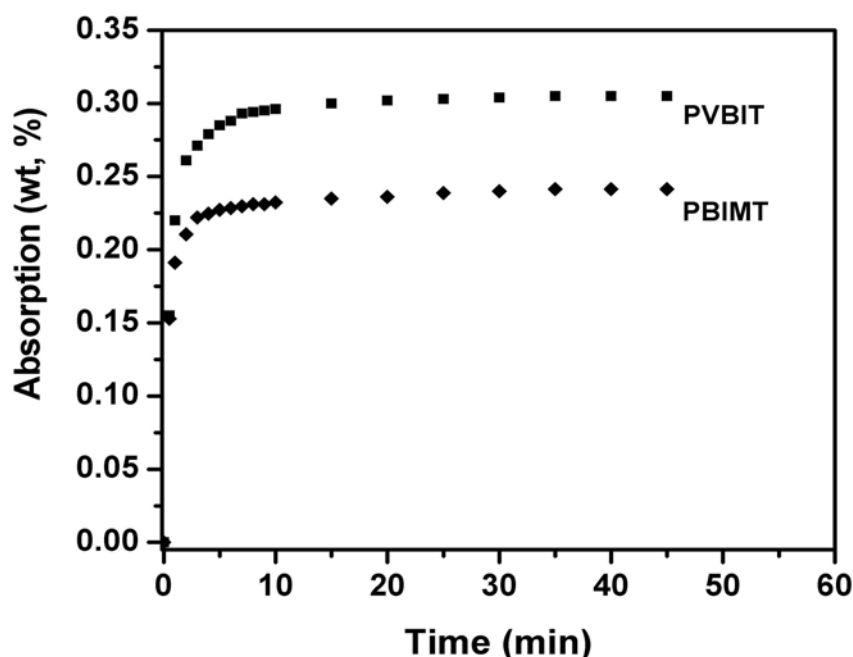
### Characterization of polymerized ionic liquids PVBIT and PBIMT.

PVBIT and PBIMT are not soluble in low polar solvents because of their high polarities. They can only dissolve in high polar solvents such as DMF, NMP and acetonitrile. Scanning calorimetric analysis of PVBIT and PBIMT showed clear glass transitions at 84 °C for PVBIT and 69 °C for PBIMT. It's very interesting that even though PVBIT or PBIMT has very strong inter-chain charge interaction, their *T<sub>g</sub>*'s are lower than those of PS (*T<sub>g</sub>* ~ 100 °C) and PMMA (*T<sub>g</sub>* ~ 114 °C) respectively.<sup>27</sup> It may be because that the anions of ionic liquid such as bis(trifluoromethane-sulfonyl)imide and tetrafluoroborate anion have very strong plasticizing effect.<sup>28</sup> These anions can improve the flexibility of polymer chains and facilitate the segment motion, and consequently decrease the glass transition temperature of the polymers. There was no melting peak observed, indicative of that PVBIT and PBIMT have no crystal structures.

Wide-angle X-ray scattering studies further confirmed that PVBIT and PBIMT are amorphous polymers. The XRD patterns of both PVBIT and PBIMT showed no diffraction peak.

### CO<sub>2</sub> absorption of PVBIT and PBIMT.

The absorptions of CO<sub>2</sub> into PVBIT and PBIMT were measured at room temperature using CAHN 1000 microbalance under local atmosphere pressure (Laramie, 0.78 standard atmosphere pressure). The CO<sub>2</sub> absorption capacity of a room temperature ionic liquid [bmim][BF<sub>4</sub>] was 0.256 wt% (1.30 mol%) at 592.3 mmHg CO<sub>2</sub> and 22 °C, consistent with the value reported. When 1.0 g of the polymer was exposed to dry CO<sub>2</sub> for 1.5 h under the same conditions, a mass gain was 3.05 mg (0.305 wt%, 2.22 mol% of VBIT units) for PVBIT, and 2.41 mg (0.241 wt%, 1.77 mol% of BIMT units) for PBIMT. This is about 71 mol% (PVBIT) and 36.2 mol% (PBIMT) higher than the capacity of [bmim][BF<sub>4</sub>]. Most significantly, the absorption of the poly(ionic liquid)s is extremely fast: in less than 15 min they could reach their full absorption capacity. In contrast, the absorption of room temperature ionic liquids, such as [bmim][BF<sub>4</sub>], needed more than 300 min to reach their full capacity.



**Figure 9.** CO<sub>2</sub> absorption curve of PVBIT and PBIMT at room temperature at 0.77 atm

### Conclusions

New ionic liquid monomers, 1-(4-vinylbenzyl)-3-butyl imidazolium tetrafluoroborate (VBIT) and 2-(1-butyl imidazolium 3-yl)-ethyl methacrylate tetrafluoroborate (BIMT), were prepared and polymerized by ATRP to synthesize ionic liquid polymers. The catalyst, initiator and solvent had strong effects on the ATRP of VBIT and BIMT. The polymerizations were well controlled and exhibited living characteristics when using bromide-based initiator/catalysts (e.g. EBiB/CuBr/HMTETA) for ATRP of VBIT and chloride-based initiator/catalysts (e. g., CCl<sub>4</sub>/CuCl/Bpy) for BIMT. The polymerized ionic liquids PVBIT and PBIMT showed CO<sub>2</sub> absorption ability: PVBIT absorbed 0.30 wt% CO<sub>2</sub> and PBIMT absorbed 0.24 wt% CO<sub>2</sub> at

room temperature at 0.77 atmosphere with very fast absorption rate.

### Acknowledgement:

We thank the State of Wyoming (EORI project) and the University of Wyoming for financial support.

### References

- (1) Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed.* **2000**, *39*, 3772.
- (2) Welton, T. *Chem. Rev.* **1999**, *99*, 2071.
- (3) Sun, D.; Houghbanks, T. *Inorg. Chem.* **2000**, *39*, 1964.
- (4) Armstrong, J. G.; He, L.; Liu, Y. S. *Anal. Chem.* **1999**, *71*, 3873.
- (5) Seddon, K. R. *Kinet. Catal.* **1996**, *37*, 693.
- (6) Masahiro, Y.; Ohno, H. *Chem. Let.* **1999**, *9*, 889.
- (7) Masahiro, Y.; Ogihara, W.; Ohno, H. *Polym. Adv. Technol.* **2002**, *13*, 589.
- (8) Watanabe, M.; Yamada, S. I.; Ogata, N. *Electrochim. Acta* **1995**, *40*, 2285.
- (9) Shen, Y.; Radosz, M. Pending Patent Application, 2004.
- (10) Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B* **2002**, *106*, 7315.
- (11) Cadena C.; Anthony J. L.; Shah J. K.; Morrow T. I.; Brennecke J. F.; Maginn E. J. *J. Am. Chem. Soc.* **2004**, *126(16)*, 5300.
- (12) Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis, J. H. Jr. *J. Am. Chem. Soc.* **2002**, *124(6)*, 926.
- (13) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
- (14) Patten, T. E.; Matyjaszewski, K. *Chem. Res.* **1999**, *32*, 895.
- (15) Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* **2000**, *33*, 8629.
- (16) Macedonia, M. D.; Moore, D. D.; Maginn, E. J.; Olken, M. M. *Langmuir* **2000**, *16*, 3823.
- (17) Tang, H.; Ding, S.; Shen, Y.; Radosz, M. submitted to *Macromolecules*.
- (18) Sarbu, Traian; Matyjaszewski, K. *Macromol. Chem. Phys.* **2001**, *202*, 3379.
- (19) Park, S.; Kazlauskas, R. J. *J. Org. Chem.* **2001**, *66*, 8395.
- (20) Matyjaszewski, K.; Nakagawa, Y.; Jasieczek, C. B. *Macromolecules* **1998**, *31*, 1535.
- (21) Wang, X. S.; Armes, S. P. *Macromolecules* **2000**, *33*, 6640.
- (22) Wang, X.; Luo, N. Ying, S. *Polymer* **1999**, *40*, 4175.
- (23) Goodwin, H. A.; Lions, F. *J. Am. Chem. Soc.* **1960**, *82*, 5013.
- (24) Tsarevsky, N. V.; Pintauer, T.; Matyjaszewski, K. *ACS Polym. Prepr.* **2002**, *43*, 203.
- (25) Li, Y.; Armes, S. P.; Jin, X.; Zhu, S. *Macromolecules* **2003**, *36*, 8268.
- (26) Zeng, F.; Shen, Y.; Zhu, S.; Pelton, R. J. *Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 3821.
- (27) Brandrup, J.; Immergut, E. H. *Polymer Handbook*; John Wiley & Sons: New York, 1989.
- (28) Ohno, H. *Electrochim. Acta* **2001**, *46*, 1407.