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Supporting Information

Synthesis of Highly Reactive Polyisobutylene via Cationic Polymerization in a Neutral Ionic Liquid: Characteristics and Mechanism

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Table S1 The screening of ionic liquids for IB polymerization -10 °C

Fig. S1 Microstructures of TiCl$_4$ and anions-TiCl$_4$.

Fig. S2 Typical $^1$H NMR spectrum of PIB obtained in CH$_2$Cl$_2$ in this study. [H$_2$O]=2.5 mmolL$^{-1}$; [TiCl$_4$]= 50 mmolL$^{-1}$. Computation level: GGA/PW91/DNP (3.5).

Fig. S3 GPC curves of PIB obtained in CH$_2$Cl$_2$ and [Bmim][PF$_6$] with different ratios of [H$_2$O]/[TiCl$_4$] at -10 °C. [H$_2$O]=2.5 mmolL$^{-1}$; reaction time= 20 min.

Table S2 Polymerization of IB in [Bmim][PF$_6$] with the addition of pure TiCl$_4$

Fig. S4 Energy change vs. different coinitiator for the effect of solvent polarity, cation and anion in [Bmim][PF$_6$]ionic liquid with H$_2$O as initiator. Computation level: GGA/VWN-BP/DNP (4.4) with COSMO corrected.

Fig. S5 Optimized geometries for isolated IB Trimer (IB$_3$) cation in CH$_2$Cl$_2$ (a), [PF$_6$]$^-$-IB$_3$ cation(b) and [Bmim][PF$_6$]-IB$_3$ Cation (c). Computation level: GGA/VWN-BP/DNP(4.4) level with COSMO corrected energy.

Fig. S6 Optimized geometries for IB Trimer (IB$_3$) (a) and [PF$_6$]$^-$-IB$_3$ (b). Computation level: GGA/VWN-BP/DNP(4.4) level with COSMO corrected energy.
The ionic liquids for IB polymerization were screening at the preliminary experiment. Four ionic liquids ([Bmim][PF₆], [Bmim][BF₄], [Omim][BF₄] and [Bmim][Tf₂N]) were used for IB polymerization as shown in Table S1.

As shown in Table S1, PIB was successfully synthesized for the forming of colloidal precipitation (run 6-7). [Bmim][PF₆] was chosen as solvent in the later polymerization reaction of IB.

Lower molecular weight PIB may be formed in [BF₄]⁻ based ionic liquids (Table S1, 1-2), however, $M_n$ and $M_w/M_n$ were not detected for the very low yield.

The polymerization of IB is failed in [Bmim][Tf₂N]. The reason may be that [Tf₂N]⁻ can coordinate with TiCl₄ and make initiation system poisoning₁.

The interaction between different anions and TiCl₄ was investigated by DFT method with GGA/PW91²⁻³/DNP 3.5. The microstructures of interaction between anions and TiCl₄ are shown in Fig. S1. TiCl₄ can coordinate with [PF₆]⁻, [BF₄]⁻ and [Tf₂N]⁻. Among these ionic liquids, the strongest coordination of [BF₄]⁻ with TiCl₄ is observed. There are multi-sites of coordination in [Tf₂N]⁻. The more coordination sites of leads to better coordination of [Tf₂N]⁻ with TiCl₄ than [PF₆]⁻. Moreover, the coordination ability is also related to the interaction ability between the anions and cations inside the ionic liquid. Strong electrostatic interactions between cations and anions in ionic liquids weaken the coordination of anions with TiCl₄. The better polymerization behavior of IB in [Bmim][PF₆] may result from the strongest electrostatic interactions between [Bmim]⁺ and [PF₆]⁻ which impairs the coordination of [PF₆]⁻ with TiCl₄.
Fig. S1 Microstructures of TiCl$_4$ (a), anions-TiCl$_4$ (b-d) and [Tf$_2$N]-2TiCl$_4$. The anions from (b) to (d) are [PF$_6$]$, [BF$_4$]$^{-}$ and [Tf$_2$N]$^{-}$. Computation level: GGA/PW91/DNP (3.5).
Fig. S2 Typical $^1$H NMR spectrum of PIB obtained in CH$_2$Cl$_2$ in this study. [H$_2$O] = 2.5 mmolL$^{-1}$; [TiCl$_4$] = 50 mmolL$^{-1}$. 
**Fig. S3** GPC curves of PIB obtained in CH$_2$Cl$_2$ and [Bmim][PF$_6$] with different ratios of [H$_2$O]/[TiCl$_4$] at -10 °C. [H$_2$O]=2.5 m mol L$^{-1}$; reaction time= 20 min.

![GPC curves](image)

**Table S2** Polymerization of IB in [Bmim][PF$_6$] with the addition of pure TiCl$_4^a$

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<th>[H$_2$O] mM</th>
<th>[TiCl$_4$] mM</th>
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$^a$ V([Bmim][PF$_6$]): 3 mL; C(IB): 4.7 M; polymerization temperature: -10 °C; time: 30 min; mechanical stirring. H$_2$O was introduced in CH$_2$Cl$_2$ solution.

Because of trace amount of H$_2$O used in our system and the low solubility of H$_2$O in hydrophobic ionic liquids such as [Bmim][PF$_6$], the addition of H$_2$O into the polymerization system was via a saturated amount of water in CH$_2$Cl$_2$.

In order to reduce the impact of CH$_2$Cl$_2$, several polymerization experiments with pure TiCl$_4$ were performed as shown in Table S2. In these systems, about 2.2 or 4.4 vol% CH$_2$Cl$_2$ were introduced for the concentration of 2.5 mM or 5 mM H$_2$O, respectively.

As seen from Table S2, the polymerization of IB with directly introduced pure
TiCl$_4$ need more time to achieve a higher yielding of PIB than that with TiCl$_4$ in CH$_2$Cl$_2$. Meanwhile, the selectivity of exo-olefinic PIB was decreased with pure TiCl$_4$, which indicated that the effect of ionic liquid on the IB polymerization weakened due to the close combination between anions and cations through electrostatic interaction.

Small amount of CH$_2$Cl$_2$ played a role of reducing intermolecular binding capacity of ionic liquid through hydrogen bonding between Cl and H atoms, which weaken the combination of cation-anion and enhance the amount of free ions in ionic liquids. The addition of CH$_2$Cl$_2$ also can enhance the fluidity of ionic liquids especially at low temperature. The increased fluidity of ionic liquids are favorable for the strengthen the effect of [PF$_6$]$^-$ on IB polymerization and then improves the selectivity of exo-olefinic PIB.
**Fig S4** Energy change vs. different cointiator for the effect of solvent polarity, cation and anion in [Bmim][PF$_6$] ionic liquid with H$_2$O as initiator. Computation level: GGA/VWN-BP/DNP (4.4) with COSMO corrected.
Fig. S5 Optimized geometries for isolated IB Trimer (IB₃) cation in CH₂Cl₂ (a), [PF₆]⁻-IB₃ cation (b) and [Bmim][PF₆]-IB₃ Cation (c). Computation level: GGA/VWN-BP/DNP(4.4) level with COSMO corrected energy.
Fig. S6 Optimized geometries for IB Trimer (IB₃) (a) and [PF₆]⁻-IB₃ (b). Computation level: GGA/VWN-BP/DNP(4.4) level with COSMO corrected energy.

References

1 H. Olivier-bourbigou, L. Magna and D Morvan, *Applied Catalysis A: General*, 2010, **373**: 1-56)