Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

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

Xiaoning Li,[a,b,c] Yibo Wu,*[b,c] Jinghan Zhang,[a,b,c] Shuxin Li,[b,c] Min Zhang,[b,c] Dan Yang,[b,c] Hao Wang,[b,c]
Yuwei Shang,[b,c] Wenli Guo,*[a,c] and Penghua Yan[d]

a. College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing, 100029, China.

b. Department of Materials Science and Engineering, Beijing Institute of Petrochemical Technology, Beijing, 102617, China.

c. Beijing Key Lab of Special Elastomeric Composite Materials, Beijing, 102617, China.

d. Lanzhou Petrochemical Research Center, Petrochina, Lanzhou, 730060, China.

* Corresponding author: wuyibo@bipt.edu.cn; guowenli@bjzx.gov.cn

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Table S2 Polymerization of IB in [Bmim][PF_6] with the addition of pure $TiCl_4$

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Fig. S5 Optimized geometries for isolated IB Trimer (IB_3) cation in CH_2Cl_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.

Table S1 The screening of ionic liquids for IB polymerization -10 ^{o}C ^{a}

Run	Solvent	$[H_2O]$(mM)	$[TiCl_4]$(mM)	Experimental phenomena
1	$[Bmim][BF_4]$	5	50	A little of oil-like products formed.
2	$[Omim][BF_4]$	7	70	A little of oil-like products formed.
3	$[Bmim][Tf_2N]$	13	33	No product formed.
4	$[Bmim][Tf_2N]$	5	35	No product formed.
5	$[Bmim][Tf_2N]$	5	50	No product formed.
6	$[Bmim][PF_6]$	13	33	Colloidal precipitation formed.
7	$[Bmim][PF_6]$	5	50	Colloidal precipitation formed.

[a] V(IL): 3 ml; C(IB): 4.7 mol L^{-1}; temperature: -10 °C; time: 30 min.

The ionic liquids for IB polymerization were screening at the preliminary experiment. Four ionic liquids ($[Bmim][PF_6]$, $[Bmim][BF_4]$, $[Omim][BF_4]$ and $[Bmim][Tf_2N]$) 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). $[Bmim][PF_6]$ was chosen as solvent in the later polymerization reaction of IB.

Lower molecular weight PIB may be formed in $[BF_4]^-$ 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 $[Bmim][Tf_2N]$. The reason may be that $[Tf_2N]^-$ can coordinate with $TiCl_4$ and make initiation system poisoning[1].

The interaction between different anions and $TiCl_4$ was investigated by DFT method with GGA/PW91[2-3]/DNP 3.5. The microstructures of interaction between anions and $TiCl_4$ are shown in Fig. S1. $TiCl_4$ can coordinate with $[PF_6]^-$, $[BF_4]^-$ and $[Tf_2N]^-$. Among these ionic liquids, the strongest coordination of $[BF_4]^-$ with $TiCl_4$ is observed. There are multi-sites of coordination in $[Tf_2N]^-$. The more coordination sites of leads to better coordination of $[Tf_2N]^-$ with $TiCl_4$ than $[PF_6]^-$. 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 $TiCl_4$. The better polymerization behavior of IB in $[Bmim][PF_6]$ may result from the strongest electrostatic interactions between $[Bmim]^+$ and $[PF_6]^-$ which impairs the coordination of $[PF_6]^-$ with $TiCl_4$.

Fig. S1 Microstructures of $TiCl_4$ (a), anions-$TiCl_4$ (b-d) and $[Tf_2N]^-$-$2TiCl_4$. The anions from (b) to (d) are $[PF_6]^-$, $[BF_4]^-$ and $[Tf_2N]^-$. Computation level: GGA/PW91/DNP (3.5).

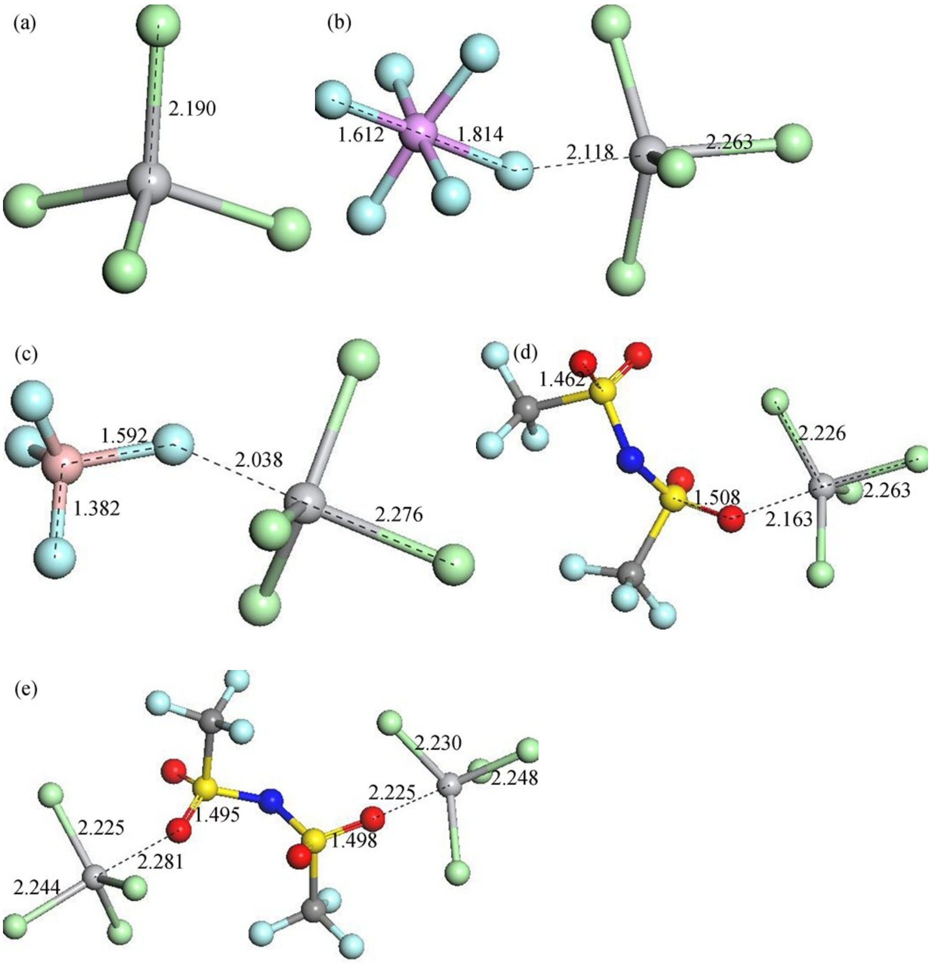
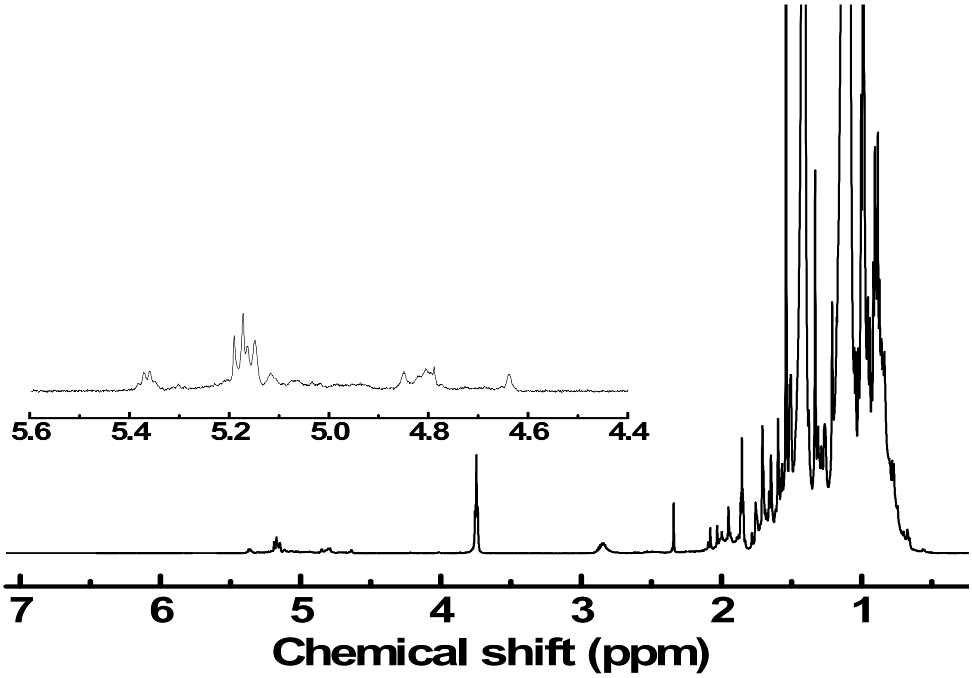


Fig. S2 Typical ^{1}H NMR spectrum of PIB obtained in CH_2Cl_2 in this study. [H_2O]= 2.5 mmolL^{-1}; [$TiCl_4$]= 50 mmolL^{-1}.



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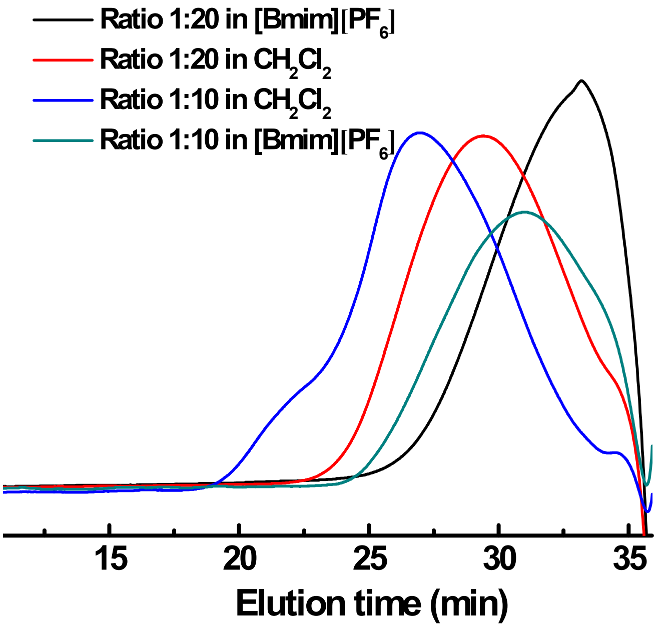


Table S2 Polymerization of IB in [Bmim][PF_6] with the addition of pure $TiCl_4$[a]

run	[H_2O] mM	[$TiCl_4$] mM	Conv %	$M_{n,GPC}$ $gmol^{-1}$	M_w/M_n	$M_{n,NMR}$ $gmol^{-1}$	End group structure contents (%) exo	endo+tri	tetra	coup	PIBCl
1	2.5	50	12.1	3118	2.3	3078	52.7	23.4	15.1	4.7	4.1
2	2.5	50	11.7	3746	2.2	3675	61.8	13.8	16.5	5.6	2.2
3	5	50	13.3	2285	2.3	2446	78.0	9.9	5.0	4.6	2.5
4	5	50	10.4	2177	2.2	2764	75.7	15.9	3.1	2.8	2.5

[a] V([Bmim][PF_6]):3mL; C(IB): 4.7 M; polymerization temperature: -10 °C; time: 30 min; mechanical stirring. H_2O was introduced in CH_2Cl_2 solution.

Because of trace amount of H_2O used in our system and the low solubility of H_2O in hydrophobic ionic liquids such as [Bmim][PF_6], the addition of H_2O into the polymerization system was via a saturated amount of water in CH_2Cl_2.

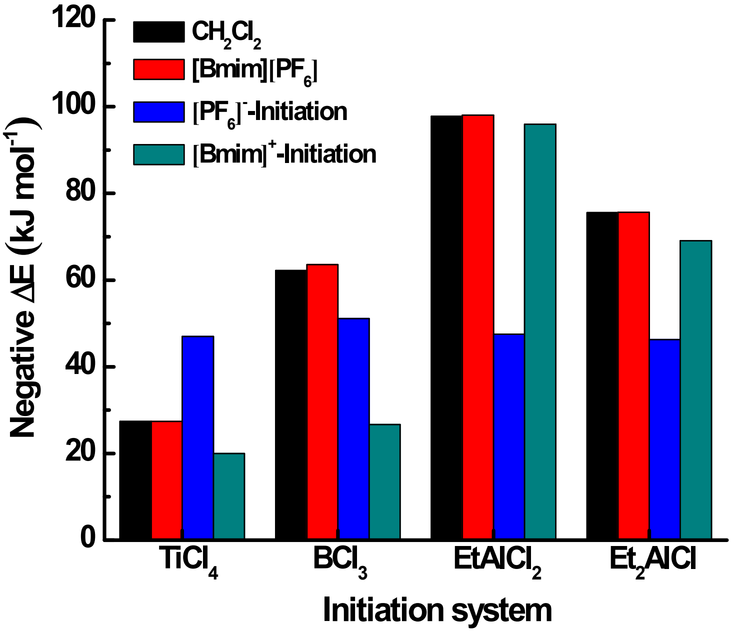
In order to reduce the impact of CH_2Cl_2, several polymerization experiments with pure $TiCl_4$ were performed as shown in Table S2. In these systems, about 2.2 or 4.4 vol% CH_2Cl_2 were introduced for the concentration of 2.5 mM or 5 mM H_2O, respectively.

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_2Cl_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_2Cl_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_2Cl_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 coinitiator for the effect of solvent polarity, cation and anion in [Bmim][PF_6]ionic liquid with H_2O as initiator. Computation level: GGA/VWN-BP/DNP (4.4) with COSMO corrected.



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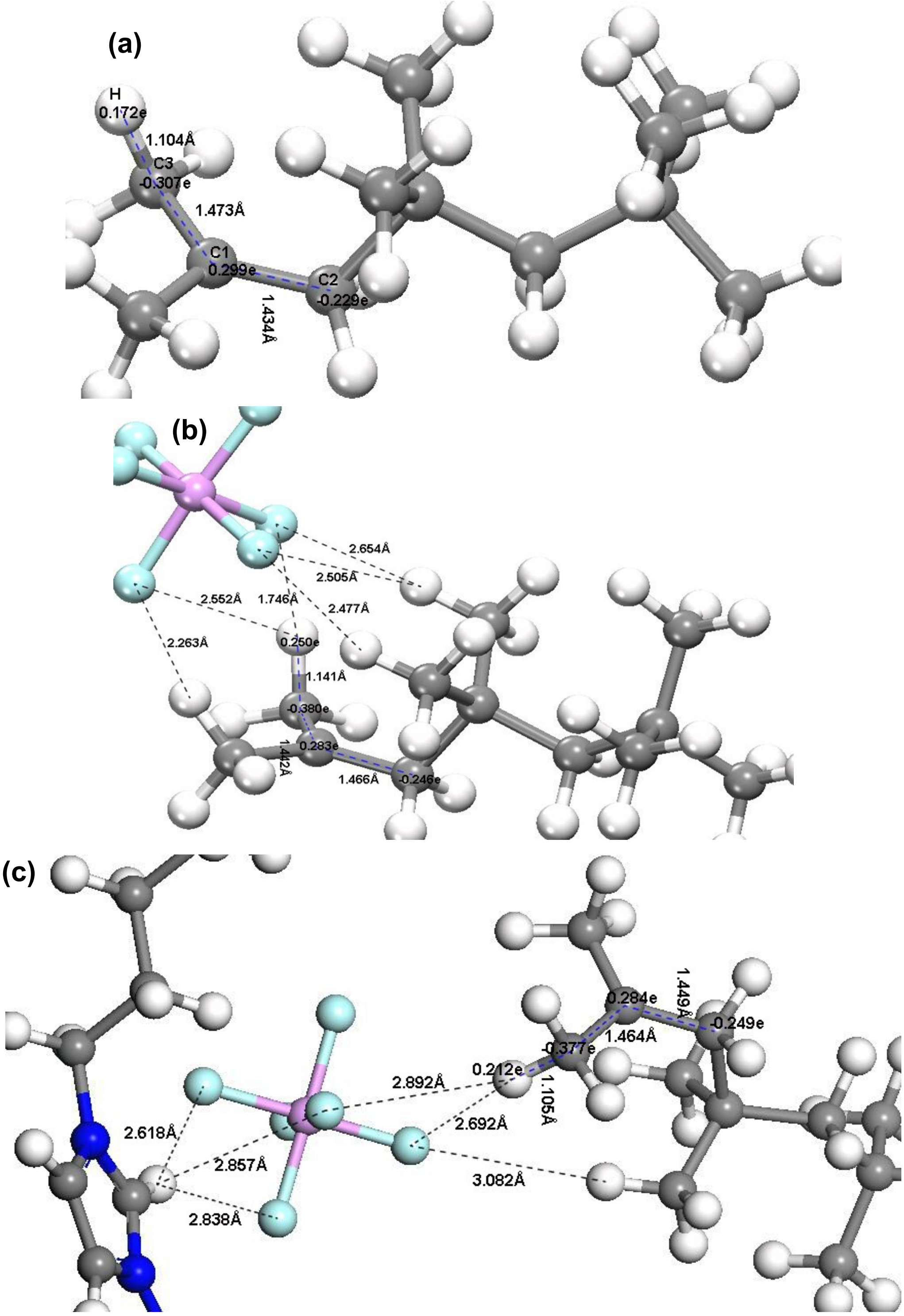

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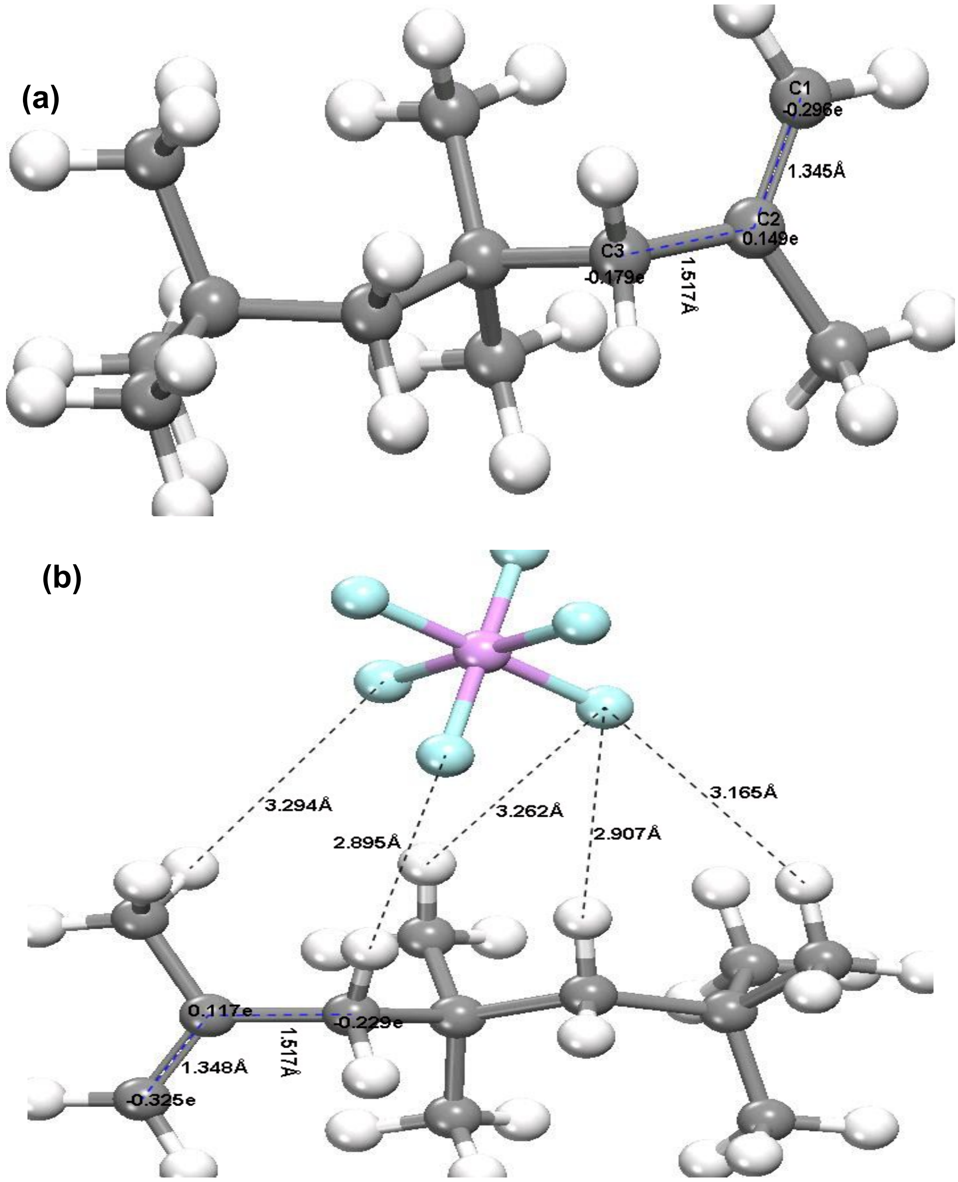

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