Supporting Information

Cationic Polymerization of *p*-Methylstyrene in Selected Ionic Liquids and Polymerization Mechanism

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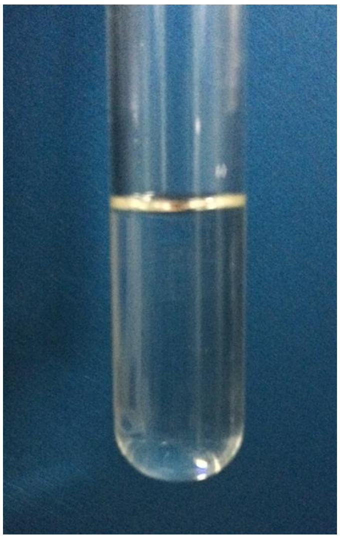


Fig. S1. Photograph of the homogeneous mixture of *p*-MeSt and IL.

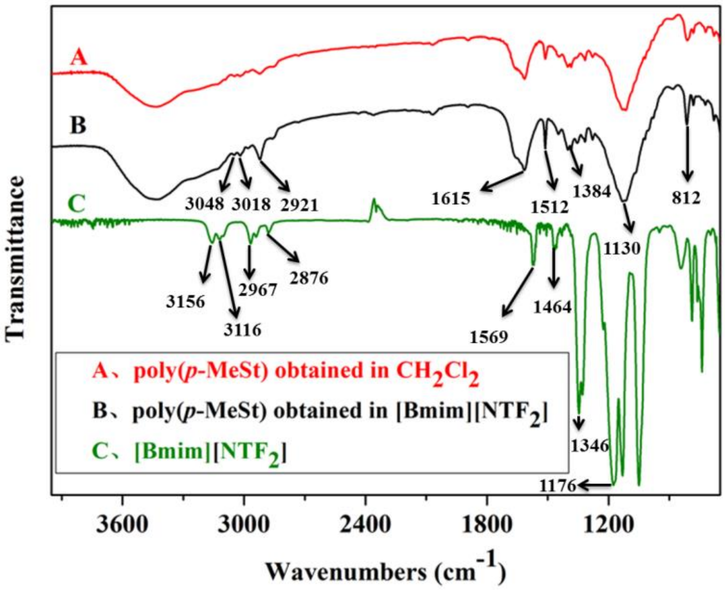


Fig. S2. FT-IR spectra of poly(*p*-MeSt) obtained in CH_2Cl_2 (A) and in [Bmim][NTF_2] (B) and FT-IR spectra of [Bmim][NTF_2] (C).

The FT-IR spectra of products (polymerized in [Bmim][NTF_2] and CH_2Cl_2) and the FT-IR spectra of pure [Bmim][NTF_2] are illustrated in Fig. S2. In Fig. S2 A and S2 B, the bands at 3,018 and 3,048 cm^{-1} were attributed to the C-H in phenyl ring, and that at 2,921

cm^{-1} was assigned to the CH_2 stretching band. The bands at 1,615 and 1,652 cm^{-1} were believed to be related to the C=C in phenyl ring, and that at 1,384 cm^{-1} was caused by the stretch of $-CH_3$. Out-of-plane CH bending of two adjacent aromatic hydrogen was represented by peak at 812 cm^{-1}.[1, 2]

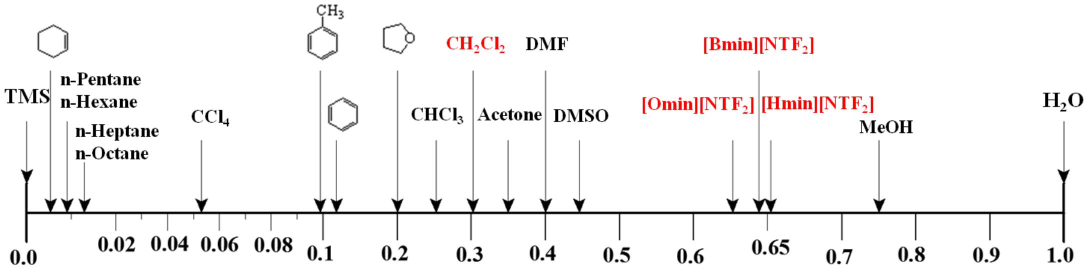
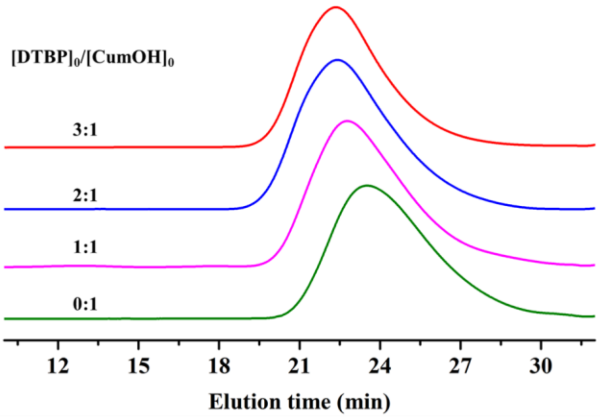
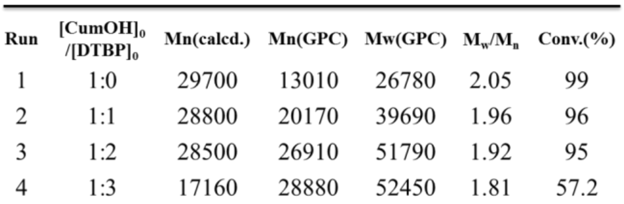


Fig. S3. Normalized solvent polarity scale E_T^N with $E_T^N = 0.00$ for tetramethylsilane (TMS) and $E_T^N = 1.00$ for water as arbitrarily fixed points, with ordering of eighteen selected molecular solvents and the inclusion of the ionic liquids used in our polymerization on this scale.

In addition, the solvent polarity turned out to be an important factor that affected the rate and the living nature of the monomers polymerization in cationic polymerization. Due to their ionic nature, the ionic liquids have been seen as highly polar yet noncoordinating solvents. A graphical representation of the E_T^N solvent polarity scale is given in Fig. S3. There is a selection of eighteen molecular solvents, including about ten molecular solvents often used in cationic polymerization, like CH_2Cl_2, $CHCl_3$, toluene, CCl_4, *n*-hexane, cyclohexane, and so on, and the three ionic liquids, [Bmim][NTF$_2$], [Hmim][NTF$_2$] and [Omim][NTF$_2$] used in our polymerization above the line. In going from left to right above the line, with increasing solvent polarity, the range of E_T^N values were determined by many research groups. [3-6] From Fig. S3, it is visual that those three ILs were all more polar than the molecular solvents used in cationic polymerization. In our research, the most commonly used and relatively high polar CH_2Cl_2 was selected as the traditional molecular solvent to compare with the selected ILs for researching the *p*-MeSt cationic polymerization.





Run	$[CumOH]_0$ /$[DTBP]_0$	Mn(calcd.)	Mn(GPC)	Mw(GPC)	M_w/M_n	Conv.(%)
1	1:0	29700	13010	26780	2.05	99
2	1:1	28800	20170	39690	1.96	96
3	1:2	28500	26910	51790	1.92	95
4	1:3	17160	28880	52450	1.81	57.2

Fig. S4. GPC curves of polymers at different concentration of DTBP with $CumOH/BF_3OEt_2$ at −25 ℃ in $[Bmim][NTf_2]$. $[p\text{-MeSt}]_o = 1.880\ mol\cdot L^{-1}$, $[CumOH]_o = 7.427\ mmol\cdot L^{-1}$, $[BF_3OEt_2]_o = 133.686\ mmol\cdot L^{-1}$, T = −25 ℃, and t= 120 min.

The results for effects of DTBP concentration on the polymerization of *p*-MeSt with $CumOH/BF_3OEt_2$ are shown in Fig. S4. In absence of DTBP, 100% conversion was reached in about 120 min. The molecular weight was lower than the expected theoretical molecular weight (M_n = 13013, MWDs = 2.05 vs. theoretical M_n, $M_{n,thero}$=29700). When the polymerization was carried out in the presence of DTBP, the molecular weight increased and the molecular weight distribution narrowed. At $[DTBP]_0/[CumOH]_0$ = 2:1, the molecular weight was close to theoretical M_n and relatively narrow molecular weight distribution were observed. As [DTBP] was higher than 2:1, the percent conversion decreased and the M_n was larger than the theoretical value. This is probably because DTBP operate in a similar fashion with n-Bu_4NCl through the formation in situ a salt ($DTBP$-H^+ BF_3OH^-) after DTBP trapping the proton[7,8]. In other words, DTBP confer “livingness” through the formation of common anions that suppress propagation via free ions. So in the following controlled polymerization in $[Bmim][NTF_2]$, $[DTBP]_0/[CumOH]_0$ = 2:1 was used in the polymerization.

Table S1 Cationic polymerization of *p*-MeSt initiated by *p*-MeSt-HCl/$SnCl_4$/DTBP initiating system in $[Bmim][NTf_2]$

Run	Solvent	M_n(theor)	M_n(GPC)	M_w(GPC)	M_w/M_n	Yield (%)
1	CH_2Cl_2	15000	14350	17370	1.21	99.0
2	CH_2Cl_2	7000	6860	8510	1.24	98.4
3	$[Bmim][NTf_2]$	20000	20230	28330	1.40	98.6
4	$[Bmim][NTf_2]$	10000	9640	14840	1.54	96.3
5	$[Bmim][NTf_2]$	7000	6560	10430	1.59	95.8

$[p\text{-MeSt}]_o$ = 1.880 mol·L^{-1}, $[SnCl_4]_o$ = 133.686 mmol·L^{-1}, $[DTBP]_o$ = 14.854 mmol·L^{-1}, Run 1: $[p\text{-MeStCl}]_o$ = 14.850 mmol·L^{-1}; Run 2 and Run 5: $[p\text{-MeStCl}]_o$ = 31.830 mmol·L^{-1}; Run 3: $[p\text{-MeStCl}]_o$ = 11.140 mmol·L^{-1}; Run 4: $[p\text{-MeStCl}]_o$ = 22.280 mmol·L^{-1}. $T = -25$ ℃. The reaction time was 2.5 h.

The cationic polymerization of *p*-MeSt initiated by *p*-MeStCl/$SnCl_4$/DTBP initiating system in [Bmim][NTF_2] is also estimated, as shown in Table S1. The influence of initiator concentration on the polymerization process was studied. In [Bmim][NTF_2] and CH_2Cl_2 M_ns were inversely proportional to initiator concentration and approached the calculated values. In addition, in IL the M_w/M_n leveled of in the range of 1.4-1.6. Here, the effect of DTBP for *p*-MeStCl/$SnCl_4$/DTBP initiating system in the IL is the same as that for CumOH/BF_3OEt_2/DTBP initiating system. These results confirmed that the cationic polymerization of *p*-MeSt in [Bmim][NTF_2] with *p*-MeStCl/$SnCl_4$/DTBP initiating system proceeded also in a controlled fashion.

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