

Highly Controlled Organotellurium-Mediated Living Radical Polymerization (TERP) in Ionic Liquids (ILs). A New Role of ILs in Radical Reaction

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General. All PDIs were determined by a Waters GPC liquid chromatograph (Waters, USA) equipped with four TSK HxL series polystyrene divinylbenzene gel columns (300 × 7.8 mm; particle size = 5-6 μm). THF was used as eluent with a flow rate of 1.0 mL/min (40 °C). Sample detection and quantification were made with a Waters differential refractometer RI-2414 calibrated with PS narrow standard in THF. The column system was calibrated with standard PSTs. ¹H NMR spectra were recorded by a Varian INOVA-400 (Varian, USA). UV-Vis spectra were obtained by a LabTech's UV Power UV-Vis spectrophotometers (LabTech, USA).

Materials. Methyl methacrylate (MMA), methyl acrylates (MA), styrene (St), 2,2'-azobis(isobutyronitrile) (AIBN) and other solvents were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). MMA, MA and St were distilled under reduced pressure before use. AIBN was recrystallization from ethanol three times. 1-Butyl-3-methylimidazolium hexafluorophosphate (>99%) and 1-butyl-3-methylimidazolium tetrafluoroborate (>99%) which were deoxygenated by bubbling with high purity nitrogen before use were purchased from Lanzhou Greenchem ILS, LICP. CAS. China. Methyl lithium (1.2 M in tetrahydrofuran) was purchased from Boer Chemical Co. Ltd. (Shenzhen, China). Tellurium powder (99.999%) and ethyl 2-bromo-isobutyrate (98%) were purchased from Aladdin Chemical Company (Shanghai, China). Dimethyl ditelluride and ethyl-2-methyltellanyl-isobutyrate (**1**) were synthesized according to the literature.^[1] Those without further descriptions were used as received.

Typical Procedure of TERP of MMA in [Bmim]PF₆. A solution of newly distilled MMA, **1**, AIBN with ILs-deoxygenated by bubbling high purity nitrogen for over 30 min-was charged into a Schlenk tube, and then stirred at 60 °C in an oil bath. After prescribed reaction time, *t*, the reaction was quenched in an ice-water bath. The resulted polymer was precipitated by adding methanol or aqueous ethanol into reaction mixture.

Preparation of Polymer-methyltellurides. The synthesis, distillation, polymerization, purification and storage pertaining to organotelluriums were processed under high purity nitrogen atmosphere in virtue of Schlenk line and glove box. A solution of 3 mL MMA, 1 mmol **1**, and 1 mmol dimethyl ditelluride was heated at 80 °C for 8 h. Methanol which was deoxygenated by bubbling with high purity nitrogen was added, and the macro initiator, PMMA-TeMe, was purified by reprecipitation. A PMMA-TeMe with *M_n* ≈ 3300 and PDI = 1.06 was isolated. The chain extension test^[1] showed that this polymer contained 4% (*f_{dead}* = 0.04) of potentially inactive species without a -TeMe moiety at the chain end, for which the experimental data shown below have been corrected.

PMA-TeMe was prepared analogously by heating a solution of 3 mL MA and 1 mmol **1** at 100 °C for 24 h. After purification, PMA-TeMe with $M_n \approx 2800$, $PDI = 1.11$, $f_{dead} = 0.05$ was obtained. PSt-TeMe was also prepared from a solution of 3 mL St and 1 mmol **1** at 100 °C for 12 h. PSt-TeMe with $M_n \approx 2500$, $PDI = 1.08$, $f_{dead} = 0.03$ was obtained.

Determination of k_{act} for Polymer-methyltellurides. The polymer-methyltellurides were used as probe adducts (P_0 -Xs). A mixture of monomer (5 mL), ILs (20, 2.5, 2.5 mL was added for testing PMMA-TeMe, PMA-TeMe and PSt-TeMe respectively), P_0 -X (5.4 mM), and AIBN (0-5.4 mM or 5-20 mM) in a Schlenk flask was heated at 60 °C. Samples for kinetic studies and polymer analysis were withdrawn at regular time intervals and quenched in cold methanol or aqueous methanol. The resulting precipitate was diluted by tetrahydrofuran (THF) to a known concentration, and analyzed by GPC.

Figure S1 shows the pseudo-first order plot of MMA/IL concentration $[M]$. Each set of results within the examined period was linear, which supports living character of TERP in ILs. A $R_p/[M]$ value of polymerizing MMA, approximately three times higher than that in bulk polymerization, was obtained from the slope of the line Figure S1 for highest [Bmim]PF₆ amount.

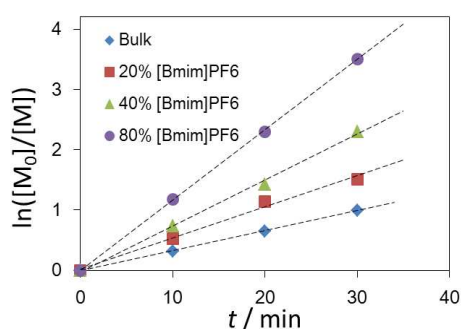


Figure S1. Plot of $\ln([M]_0/[M])$ vs t for the TERP of MMA in bulk and [Bmim]PF₆ at 60 °C. Molar ratio of MMA/ **1**/AIBN fixed at 100/1/1. The $[M]$ is the concentration of monomer.

The pseudo-first order plots in polymerization of MA and styrene in [Bmim]PF₆ are shown in Figures S2 and S3, respectively.

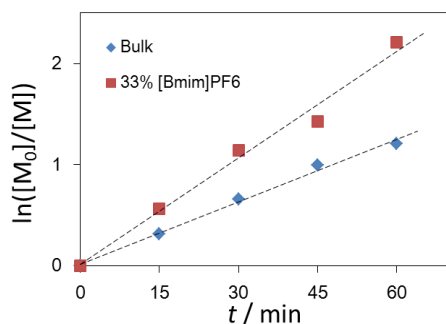


Figure S2. Plot of $\ln([M]_0/[M])$ vs t for the TERP of MA in bulk and [Bmim]PF₆ at 60 °C. Molar ratio of MA/**1**/AIBN fixed at 100/1/1. The $[M]$ is the concentration of monomer.

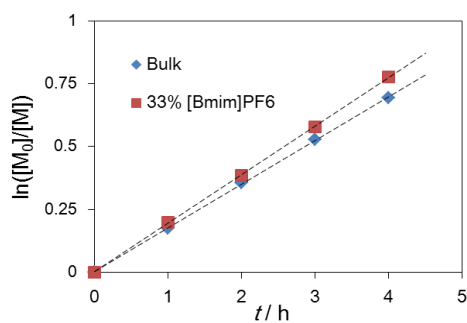


Figure S3. Plot of $\ln([M]_0/[M])$ vs t for the TERP of St in bulk and $[\text{Bmim}]\text{PF}_6$ at 60 °C. Molar ratio of St/1 fixed at 100/1, $[\text{AIBN}] = 100$ mM. The $[M]$ is the concentration of monomer.

The k_{act} was determined by the GPC peak resolution method according to [Eq (S2)].^[1]

$$\ln(I_0 / I) = k_{\text{act}} t \quad (\text{S2})$$

where I_0 and I are the concentrations of $\text{P}_0\text{-X}$ at times 0 and t , respectively. When $\text{P}_0\text{-X}$ is activated, the released $\text{P}_0\cdot$ propagates until it is deactivated to give a chain-elongated dormant species, P-X . Since $\text{P}_0\text{-X}$ and P-X are generally different molecular weights, the amount of them can be determined by GPC (impurities, f_{dead} , was subtracted from both I_0 and I). Figure S4 provides three GPC charts before the chain extension (solid line) and after 120 s in the two experiments carried out without AIBN and in the presence of 1.02 mM of AIBN (dotted lines). Figure S4 exhibits the peak resolution outcome. The slope of each line revealed the value of k_{act} in different amount AIBN. Figure S5 is the plot of k_{act} vs $R_p/[M]$. From Eq. S1 and S2, the exchange constant, C_{ex} , which is 14 in this system was obtained. The k_{act} and C_{ex} of PSt-TeMe and PMA-TeMe were also obtained in 2/1 v/v ratio system similarly, as shown in Figure S7-S9, Figure S10-S12 respectively. The C_{ex} of PSt-TeMe and PMA-TeMe are 25, 22 respectively, higher than each in bulk.

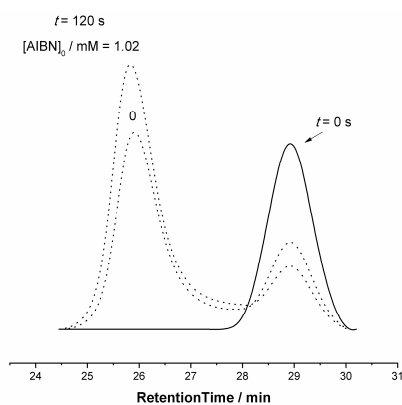


Figure S4. Examples of the GPC charts for the MMA/PMMA-TeMe ($\text{P}_0\text{-X}$)/ $[\text{Bmim}]\text{PF}_6$ /AIBN system at 60 °C after 120 s (feed amount: $[\text{P}_0\text{-X}]_0 = 5.4$ mM; $[\text{AIBN}]_0$ as indicated in the figure).

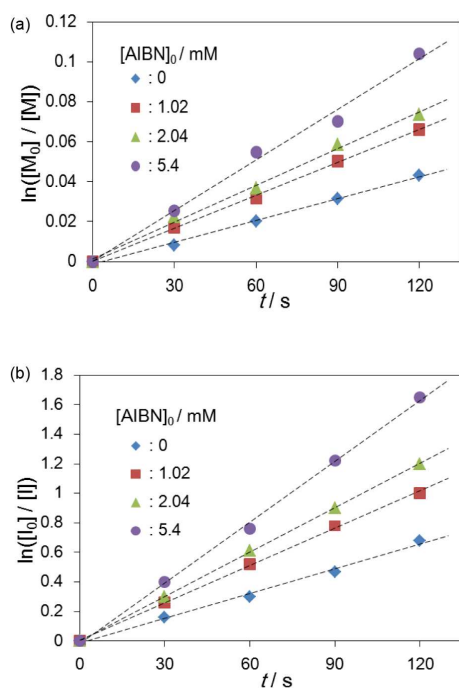


Figure S5. Kinetic plot of $\ln([I]_0/[I])$ vs t of (a) MMA and (b) P₀-X for MMA/PMMA-TeMe (P₀-X)/ [Bmim]PF₆ system at 60 °C (feed amount: [Bmim]PF₆ 20 mL, MMA 5 mL, P₀-X fixed to 5.4 mM, AIBN varied from 0-5.4 mM). The [M] and [I] is the concentration of MMA and P₀-X respectively.

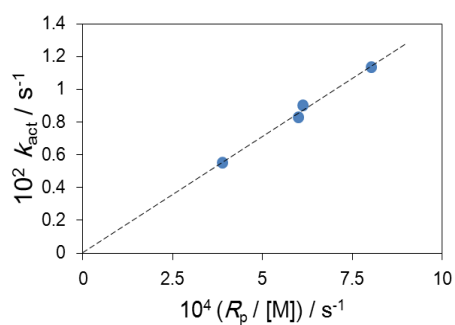


Figure S6. Plot of k_{act} vs $R_p/[M]$ for MMA/PMMA-TeMe (P₀-X)/[Bmim]PF₆ system at 60 °C. The pseudo first order activation of constant k_{act} , defined in [Eq. (S2)], was determined by peak resolution method. R_p and [M] is the polymerization rate and the concentration of MMA respectively.

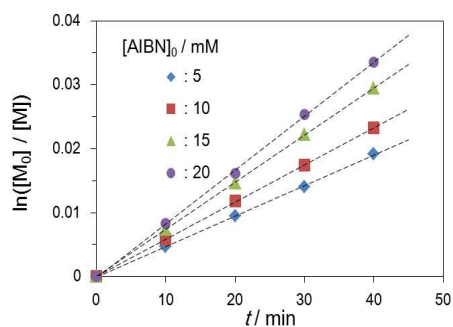


Figure S7. Kinetic plot of $\ln([M]_0/[M])$ vs t of St for St/StPSt-TeMe (P₀-X)/[Bmim]PF₆ system at 60 °C (feed amount: [Bmim]PF₆ 2.5 mL, St 5 mL, P₀-X fixed to 5.4 mM, AIBN varied from 5-20 mM). The [M] is the concentration of St.

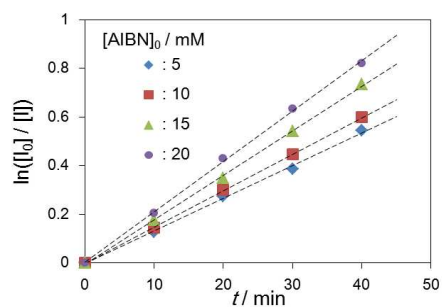


Figure S8. Kinetic plot of $\ln([I]_0/[I])$ vs t of P_0 -X for St/PSt-TeMe (P_0 -X)/[Bmim]PF₆ system at 60 °C (feed amount: [Bmim]PF₆ 2.5 mL, St 5 mL, P_0 -X fixed to 5.4 mM, AIBN varied from 5-20 mM). The $[I]$ is the concentration of P_0 -X.

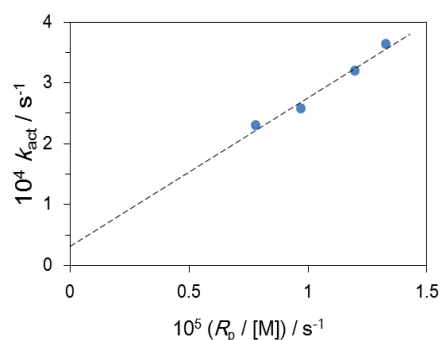


Figure S9. Plot of k_{act} vs $R_p/[M]$ for St/PSt-TeMe (P_0 -X)/[Bmim]PF₆ system at 60 °C. The pseudo first order activation of constant k_{act} , defined in [Eq. (S2)], was determined by peak resolution method. R_p and $[M]$ is the polymerization rate and the concentration of St respectively.

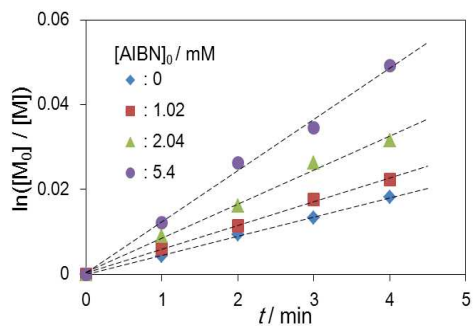


Figure S10. Kinetic plot of $\ln([M]_0/[M])$ vs t of MA for MA/PMA-TeMe (P_0 -X)/[Bmim]PF₆ system at 60 °C (feed amount: [Bmim]PF₆ 2.5 mL, MA 5 mL, P_0 -X fixed to 5.4 mM, AIBN varied from 0-5.4 mM). The $[M]$ is the concentration of MA.

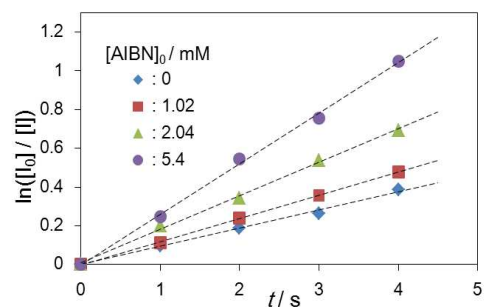


Figure S11. Kinetic plot of $\ln([I_0]/[I])$ vs t of P_0 -X for MA/PMA-TeMe (P_0 -X)/[Bmim]PF₆ system at 60 °C (feed amount: [Bmim]PF₆ 2.5 mL, MA 5 mL, P_0 -X fixed to 5.4 mM, AIBN varied from 0-5.4 mM). The $[I]$ is the concentration of P_0 -X.

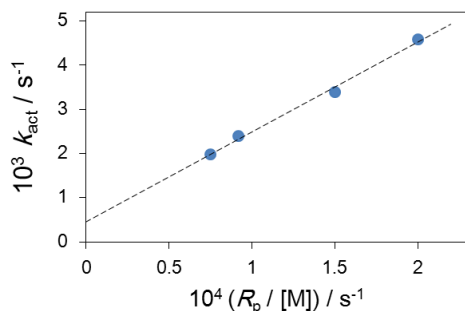


Figure S12. Plot of k_{act} vs $R_p/[M]$ for MA/PMA-TeMe (P_0 -X)/[Bmim]PF₆ system at 60 °C. The pseudo first order activation of constant k_{act} , defined in [Eq. (S2)], was determined by peak resolution method. R_p and $[M]$ is the polymerization rate and the concentration of MA respectively.

Measurements of ¹²⁵Te NMR. ¹²⁵Te NMR (400 MHz) spectra were measured for a CD₂Cl₂ solution of a sample containing MMA (0.1 ml), organotellurium initiator **1** (1.67 μL) and [Bmim]PF₆ (0, 1.08, 1.62, 2.7, 5.4, 13.5, 27.0 mg) in CD₂Cl₂ at 25 °C.

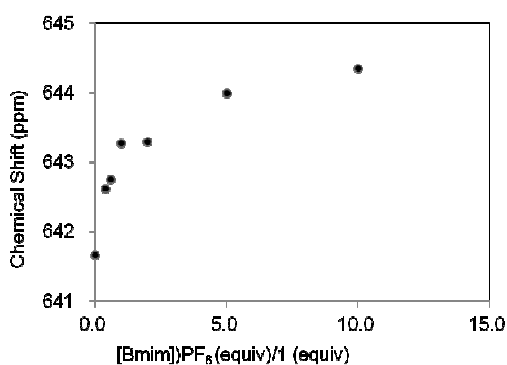


Figure S13. Effect of the ¹²⁵Te NMR chemical shift of **1** on [Bmim]PF₆ in CD₂Cl₂ at 25 °C.

Reference

- (1) Yamago, S.; Iida, K.; Yoshida, J.-i. *J. Am. Chem. Soc.* **2002**, 124, 13666-13667.