Electronic Supplementary Information (ESI)

Thermo-regulated Phase Separable Catalysis (TPSC)-Based Atom Transfer Radical Polymerization in Thermo-Regulated Ionic Liquid

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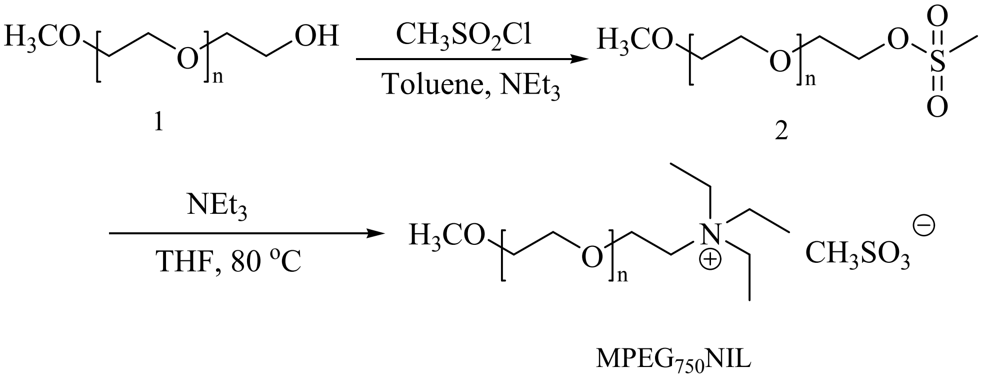
Experimental Section

Materials. Styrene (St, >99%), methyl methacrylate (MMA, >99%), methyl acrylate (MA, >99%) and *n*-Butyl acrylate (*n*-BA, >99%) were purchased from Shanghai Chemical Reagents Co. Ltd. (Shanghai, China). St, MMA, MA and *n*-BA were removed inhibitors by passing through a neutral alumina column. Ethyl 2-bromoisobutyrate (EB*i*B, >98%) was purchased from Acros and used as received. Monomethoxy poly(ethylene glycol)-750 ($MPEG_{750}$), 2,2′-dipyridyl (bpy, >97%), pentamethyldiethylene triamine (PMDETA, >97%) and tris(2-pyridylmethyl)amine (TPMA, 97%) were purchased from Sigma-Aldrich and used as received. Tris(3,6-dioxaheptyl)amine (TDA-1) (97%) was purchased from Linhai Xinghua Chemical Factory (Zhejiang, China) and used as received. Ascorbic acid (AsAc, >98%), sodium ascorbate (AsAc-Na, >98%), tin-2-ethylhexanoate ($Sn(EH)_2$, >98%), glucose (>98%), triethylamine ($N(Et)_3$, analytical reagent), phenol (analytical reagent), toluene (analytical agent), tetrahydrofuran (THF, analytical reagent), *n*-heptane (analytical reagent) and all other chemicals were obtained from Shanghai Chemical Reagents Co. Ltd. (Shanghai, China) and used as received unless mentioned. The ionic liquid, $MPEG_{750}NIL$ was synthesized according to the literature.[S1]

Synthesis of Thermo-Regulated Ionic Liquid, $MPEG_{750}NIL$. All the glass vessels were dried before use. As shown in Scheme S1, poly (ethyl glycol) monomethyl ether **1** (45 g, 0.06 mol) was dissolved in 60 mL toluene for azeotropic removal of water. $MPEG_{750}$ (M_n = 750 g/mol) was converted to the corresponding methanesulfonate by reaction with methanesulfonyl chloride according to the published method.[S1] Then, the methanesulfonate **2** reacted with an excess amount of triethylamine in THF under reflux at 80 °C for two weeks in the atmosphere of Ar. The reaction mixture was evaporated under vacuum to remove the solvent and the excess triethylamine and to give a very viscous product $MPEG_{750}NIL$. The product was characterized by ^1H NMR analysis. ^1H NMR (400MHz, $CDCl_3$): $\delta = 1.39$ (t, 9H, $-CH_2CH_3$), 2.75 (s, 3H, $-SO_3CH_3$), 3.38 (s, 3H, $-OCH_3$), 3.50 (q, 6H,$-CH_2CH_3$), 3.55, 3.64, 3.71, 3.94 [m, 59H, $(OCH_2CH_2)_n$] and its viscosity at different temperature was shown in Figure S1.



Scheme S2. The synthetic route of ionic liquid, $MPEG_{750}NIL$.

General Procedure for TPSC-Based AGET ATRP of Styrene. A typical polymerization procedure with the molar ratio of $[St]_0/[EB\textit{i}B]_0/[CuCl_2\cdot 2H_2O]_0/[TPMA]_0/[Glucose]_0 = 400/1/1/1.5/2$ in the presence of a limited amount of air was as follows. Firstly, $CuCl_2\cdot 2H_2O$ (7.67 mg, 0.0436 mmol), TPMA (18.9 mg, 0.0654 mmol) and 0.50 g of $MPEG_{750}NIL$ were added to a dried ampule and stirred with a stir bar for a moment. Secondly, St (2.0 mL, 0.0175 mol), heptane (1.0 mL), toluene (1.0 mL), glucose (15.72 mg, 0.0872 mmol) and EB*i*B (6.33 µL, 0.0436 mmol) were added to the ampule. The ampule was flame-sealed directly without bubbling with the inert gas (argon). At last, the ampule was transferred into a magnetic heated stirrer at the desired temperature (100 °C). The original $[O_2]_0$ = 7.9 × 10^{-3} mol/L (= (3.8 × 0.21/22.4) /4.5) based on the reaction solution (4.5 mL) was calculated from the residual volume (air volume, 3.8 mL) of ampule after adding the reaction mixture and ignoring the amount of oxygen dissolved in the liquids. After the desired time, the polymerization was stopped by immersing the ampule to iced water. Afterward, the ampule was opened. The upper organic phase was drawn out and dissolved in THF (~2 mL), then precipitated into a large amount of methanol (~250 mL) under stirring. The polymers obtained by filtration were dried under vacuum until constant weight at 35 °C. The monomer conversion was determined gravimetrically. The ionic liquid phase containing catalyst complex can be reused in the next polymerization cycle directly.

General Procedure for the Polymerization Based on the Recycled Catalyst. Firstly, a typical polymerization procedure of TPSC-based AGET ATRP with the molar ratio of $[\mathrm{St}]_0/[\mathrm{EB}i\mathrm{B}]_0/[\mathrm{CuCl_2{\cdot}2H_2O}]_0/[\mathrm{TPMA}]_0/[\mathrm{Glucose}]_0$ = 400/1/1/1.5/2 in the presence of a limited amount of air was as mentioned above. After polymerization at 100 °C, the ampule was cooled by immersing into iced water and opened. The upper phase was transferred and dissolved in THF (~2 mL) and precipitated into a large amount of methanol (~200 mL) under stirring. The ionic liquid phase containing Cu catalyst and ligand was collected by a pipettor and then added into a new dried ampule with a stir bar for reuse. A polymerization mixture was obtained by only adding St (2.0 mL, 0.0175 mol), heptane (1.0 mL), toluene (1.0 mL), glucose (15.72 mg, 0.0872 mmol) and EB*i*B (6.33 μL, 0.0436 mmol), TPMA (10.0 mg) when necessary, to the dried ampule with recycled catalyst ionic liquid solution. Similarly, the ionic liquid phase after polymerization was recycled again for the next turn recycling experiments. The rest of the procedure was the same as that described above.

Typical Procedure of Chain Extension Using the Resultant Polystyrene (PS) as a Macro-initiator. The PS ($M_{\mathrm{n,GPC}}$ = 7000 g/mol, M_w/M_n = 1.12), obtained by TPSC-based AGET ATRP with the molar ratio of $[\mathrm{St}]_0/[\mathrm{EB}i\mathrm{B}]_0/[\mathrm{CuCl_2{\cdot}2H_2O}]_0/[\mathrm{TPMA}]_0/[\mathrm{Glucose}]_0$ = 400/1/1/1.5/2 in the presence of a limited amount of air was used as a macro-initiator for the chain-extension at the molar ratio of $[\mathrm{St}]_0/[\mathrm{PS}]_0/[\mathrm{CuCl_2{\cdot}2H_2O}]_0/[\mathrm{TPMA}]_0/[\mathrm{Glucose}]_0$ = 200/0.5/1/1.5/2. The procedure in detail was as follows: PS (76.40 mg, 7000 g/mol) was dissolved in 1.0 mL (0.909 g, 8.75 mmol) of fresh styrene, $CuCl_2 \cdot 2H_2O$ (7.67 mg, 0.0436 mmol), TPMA (18.9 mg, 0.0654 mmol) and glucose (15.72 mg, 0.0872 mmol) were added to the ampule with a stir bar. Then, the ampule was bubbled with argon for 15 min to eliminate the oxygen. After that, the ampule was flame-sealed. The rest of the procedure was the same as that described above. The monomer conversion was 83.8% in 11.5 h at 110 °C. The M_n and M_w/M_n values were determined by GPC (M_n = 57200 g/mol, M_w/M_n = 1.17).

Characterizations. The number-average molecular weight ($M_{n,GPC}$) and molecular weight distribution (M_w/M_n) results of the resultant polymers were determined using a TOSOH HLC-8320 gel permeation chromatograph (GPC) equipped with a refractive-index detector (TOSOH), using TSKgel guardcolumn SuperMP-N (4.6×20 mm) and two TSKgel SupermultiporeHZ-N (4.6 × 150 mm) with measurable molecular weight ranging from 5×10^2 to 5×10^5 g/mol. THF was used as the eluent at a flow rate of 0.35 mL/min and 40 °C. GPC samples were injected using a TOSOH plus autosampler and calibrated with polystyrene standards purchased from TOSOH. The ^1H NMR spectra were recorded on an Inova 400 MHz nuclear magnetic resonance (NMR) instrument using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard at the ambient temperature. Matrix-assisted laser desorption ionization time-of-flight mass spectra (MALDI-TOF MS) were acquired on a Bruker Ultraflex-III TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a Nd:YAG laser (355 nm). All spectra were measured in positive reflection mode. Cu elemental analysis was made by inductively coupled plasma (ICP) of Vista-MPX. Absorption of the ligand, TPMA was measured by Ultraviolet and visible spectrophotometer (UV-*Vis*) of SHIMADZU UV-2600. Viscosity of the ionic liquid, $MPEG_{750}NIL$, at different temperature was measured by HAAKE RheoStress 6000 rheometer.

Effect of Catalyst, Ligand and Reducing Agent on TPSC-Based AGET ATRP of Styrene. Firstly, the effect of the components of AGET ATRP such as the type of catalysts (e.g., $FeCl_3 \cdot 6H_2O$, $CuBr_2$ and $CuCl_2 \cdot 2H_2O$), ligands (PPh_3, TDA-1, bpy, PMDETA, TPMA) and reducing agents (AsAc, AsAc-Na, glucose, phenol, $Sn(EH)_2$ and triethyl amine) on TPSC ATRP was investigated. The results are shown in Table S1 and Table S2. From Table S1, the polymerization of styrene was out of control when using $FeCl_3 \cdot 6H_2O$ as the catalyst regardless of the type of ligands. While using copper salt as the catalyst, the molecular weight distribution was narrow when using TPMA as the ligand. This is because TPMA is a tetradentate ligand which has better coordination with copper. And polymerization with $CuCl_2 \cdot 2H_2O$ as the catalyst was better controlled than that with $CuBr_2$ as the catalyst, which is in accordance with previous report.[S2] However, the measured molecular weights deviated from the theoretical ones, which indicate low initiator efficiency of the polymerization. It may be caused by the existence of chain transfer reaction to solvent. Comparing Entry 6 and Entry 7, the polymerization rate and the initiator efficiency increased with the concentration of monomer.

Table S1. Effect of catalysts and ligands on the polymerization of styrene at 100 °C

Entry	$[Cat]_0/[Ligand]_0$	R	Time (h)	Conv (%)	$M_{n,th}$ [a] (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n
1	$[Cat\text{-}1]_0/[PPh_3]_0$	200/1/1/3/1	20	47.2	9800	26200	3.29
2	$[Cat\text{-}1]_0/[TDA\text{-}1]_0$	200/1/1/3/1	20	47.2	9800	26200	3.29
3	$[Cat\text{-}2]_0/[PMDETA]_0$	200/1/0.5/1/0.5	7.5	61.3	12800	32600	2.34
4	$[Cat\text{-}2]_0/[bpy]_0$	200/1/0.5/1/0.5	24	25.9	5400	19400	2.20
5	$[Cat\text{-}3]_0/[TPMA]_0$		19	22.0	4600	34500	1.32
6	$[Cat\text{-}2]_0/[TPMA]_0$	200/1/1/1/1	21	20.4	4200	9700	1.10
7[b]	$[Cat\text{-}2]_0/[TPMA]_0$	200/1/1/1/1 400/1/1/1/1	21	36.8	15400	23100	1.17

Polymerization conditions: Cat-1 = $FeCl_3 \cdot 6H_2O$, Cat-2 = $CuCl_2 \cdot 2H_2O$, Cat-3 = $CuBr_2$; R = $[St]_0/[EBiB]_0/[Cat]_0/[Ligand]_0/[AsAc]_0$; $V_{St} = 1.0$ mL, $V_{heptane} = 0.7$ mL, $V_{toluene} = 1.2$ mL, $MPEG_{750}NIL = 0.5$ g. [a] $M_{n,th} = [M]_0/[I]_0 \times M_{monomer} \times$ Conversion%, [b] $V_{St} = 2.0$ mL, $[O_2]_0 = 7.9 \times 10^{-3}$ mol/L.

Table S2. Effect of reducing agents on the polymerization of styrene at 100 °C

Entry	RA	Time (h)	Conv. (%)	$M_{\mathrm{n,th}}$ (g/mol)	$M_{\mathrm{n,GPC}}$ (g/mol)	M_w/M_n	$I_{\mathrm{eff.}}$ (%)
1	AsAc	26	50.4	21000	34300	1.24	61.2
2	AsAc-Na	21	59.0	24600	42700	1.35	57.5
3	Glucose	26	51.7	21600	22200	1.30	97.1
4	Phenol	26	44.9	18700	21000	1.25	88.9
5	$Sn(OH)_2$	26	60.2	25100	31700	1.26	79.0
6	NEt_3	26	62.2	25900	31000	1.29	83.4

Polymerization conditions: $[St]_0/[EB\textit{i}B]_0/[CuCl_2 \cdot 2H_2O]_0/[TPMA]_0/[RA]_0 = 400/1/1/1/1$; $MPEG_{750}NIL = 0.5$ g, $V_{\mathrm{heptane}} = 1.0$ mL, $V_{\mathrm{toluene}} = 1.0$ mL, $V_{\mathrm{St}} = 2.0$ mL. $I_{\mathrm{eff.}} = M_{\mathrm{n,th}}/M_{\mathrm{n,GPC}} \times 100\%$, $[O_2]_0 = 7.9 \times 10^{-3}$ mol/L.

The results in Table S2 indicate that the type of reducing agent has significant effect on the polymerization. With different reducing agents, the polymerization rates are decreasing with the sequence AsAc-Na > NEt_3 > $Sn(OH)_2$ >Glucose > AsAc > PhOH. All the polymerizations were under control; however, the initiator efficiency was not high except the case with glucose as the reducing agent (97.1%). This was probably ascribed to better solubility of glucose in ionic liquid than other reducing agents. Therefore, the glucose can reduce Cu (II) species into Cu (I) species rapidly and the polymerization can be conducted more efficiently.

Effect of Molar Ratio of the Reagent on TPSC-Based AGET ATRP of Styrene. To further obtain the optimal polymerization condition, different molar ratios of the reagent were investigated. Entries 1-4 in Table S3 show the results of the polymerizations with different amount of ligands. The results showed that the polymerization rates increased obviously with the amount of ligands. However, higher polymerization rate resulted in broader molecular weight distribution and lower initiator efficiency. Entries 5-9 in Table S3 list the results of the polymerizations with different amount of reducing agents. The results showed that the polymerization rates increased slightly with the amount of reducing agent and the molecular weight distributions kept almost the same. Entries 10-14 present the results of the polymerizations with different amount of catalysts. The results indicated that the polymerization rates increased with the amount of catalysts and the polymerizations were all under good control. The results in Table S4 were the investigation of the range of the designed molecular weight, which indicated that the polymerization of styrene was well controlled at 100 °C with targeted degrees of 200 to 1000. All the results generally indicated that the polymerization mainly affected by the ligand and affected slightly by the amount of the reducing agent and the catalyst. The more the amount of the ligand used, the faster of the polymerization rate and the broader of the molecular weight distribution were. And with the amount of the reducing agent and the catalyst increasing, the polymerization rate increased slightly and the molecular weight distribution became negligible broader. Besides, a wide range of the molecular weight of the polymer could be designed under good control.

Table S3. Effect of molar ratio on the polymerization of styrene at 100 °C

Entry	R	Time (h)	Conv. (%)	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	M_w/M_n	$I_{eff.}$ (%)
1	400/1/1/1/1	16	14.9	6200	7300	1.11	85.6
2	400/1/1/1.5/1	14	46.3	19300	20900	1.18	92.2
3	400/1/1/2/1	12	50.3	21000	24300	1.28	86.3
4	400/1/1/2.5/1	12	53.9	22500	29800	1.32	75.5
5	400/1/1/1.5/0.5	15	41.8	17400	21200	1.14	81.9
6	400/1/1/1.5/1	13	40.5	16900	18700	1.16	90.0
7	400/1/1/1.5/2	13	43.7	18200	20200	1.18	90.2
8	400/1/1/1.5/2.5	12	43.1	18000	20400	1.19	88.1
9	400/1/1/1.5/3	12	47.0	19600	23600	1.20	83.1
10	400/1/0.5/0.75/1	13	39.1	16300	19600	1.19	83.0
11	400/1/1/1.5/2	7	15.3	6400	7000	1.12	91.4
12	400/1/1.5/2.25/3	8	21.8	9100	9900	1.12	91.3
13	400/1/2/3/4	8	22.8	9500	11300	1.13	84.5
14	400/1/2.5/3.75/5	8	25.5	10600	12500	1.15	85.1

Polymerization conditions: R = $[St]_0/[EB\textit{i}B]_0/[CuCl_2{\cdot}2H_2O]_0/[TPMA]_0/[Glucose]_0$, V_{St} = 2.0 mL, $V_{heptane}$ = 1.0 mL, $V_{toluene}$ = 1.0 mL, $MPEG_{750}NIL$ = 0.5 g, $[O_2]_0 = 7.9 \times 10^{-3}$ mol/L.

Table S4. Effect of the amount of initiator on the polymerization of styrene at 100 °C

Entry	R	Time (h)	Conv. (%)	$M_{\text{n,th}}$ (g/mol)	$M_{\text{n,GPC}}$ (g/mol)	M_w/M_n	$I_{\text{eff.}}$ (%)
1	200/1/1/1.5/2	8	33.8	7000	9400	1.16	74.6
2	300/1/1/1.5/2	11	41.5	13000	16700	1.18	77.5
3	400/1/1/1.5/2	11	35.5	14800	16300	1.20	90.7
4	500/1/1/1.5/2	11	34	17700	20700	1.18	85.6
5	600/1/1/1.5/2	15	40.6	25300	28700	1.22	88.3
6	800/1/1/1.5/2	15	37.1	30900	33700	1.23	91.7
7	1000/1/1/1.5/2	15	39.0	40600	41700	1.28	97.2

Polymerization conditions: R = $[\text{St}]_0/[\text{EB}i\text{B}]_0/[\text{CuCl}_2\cdot 2\text{H}_2\text{O}]_0/[\text{TPMA}]_0/[\text{Glucose}]_0$, $V_{\text{St}} = 2.0$ mL, $V_{\text{heptane}} = 1.0$ mL, $V_{\text{toluene}} = 1.0$ mL, $\text{MPEG}_{750}\text{NIL} = 0.5$ g, $[O_2]_0 = 7.9 \times 10^{-3}$ mol/L.

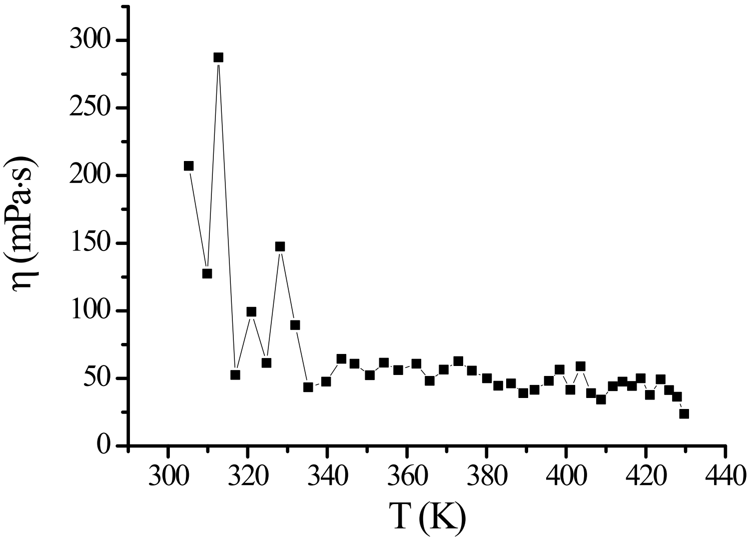


Figure S1. The viscosity of the ionic liquid, $\text{MPEG}_{750}\text{NIL}$, at different temperatures (from 303K to 433K)

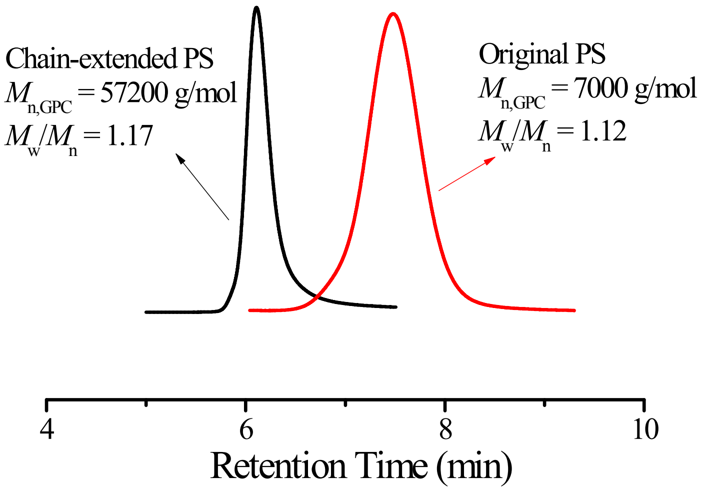


Figure S2. GPC traces of PS macroinitiator before and after chain extension with St. Polymerization conditions for chain-extension with St: $[St]_0/[PS]_0/[CuCl_2 \cdot 2H_2O]_0/[TPMA]_0/[Glucose]_0$ = 400/0.5/1/1.5/2, V_{St} = 1.0 mL, t = 11.5 h, in bulk, conversion = 83.8 %, temperature = 110 °C.

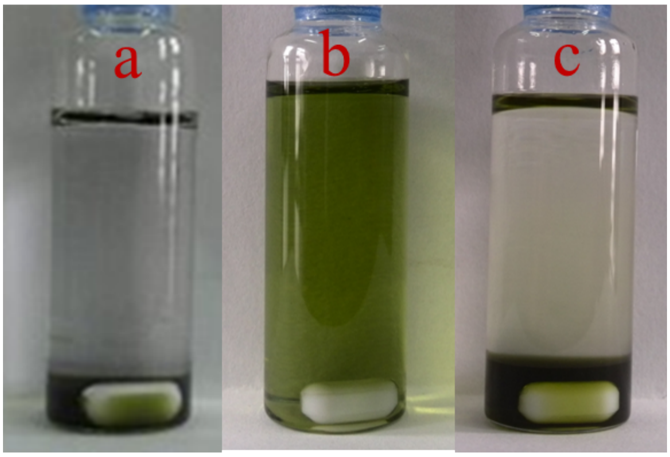


Figure S3. Photographs of TPSC–based AGET ATRP of n-butyl acrylate in ionic liquid: (a) before polymerization at room temperature; (b) during polymerization at 90 °C; and (c) after polymerization and cooled down to room temperature. The copper content in $MPEG_{750}NIL$ was 99.5% after the first cycle based on the original amount of copper.

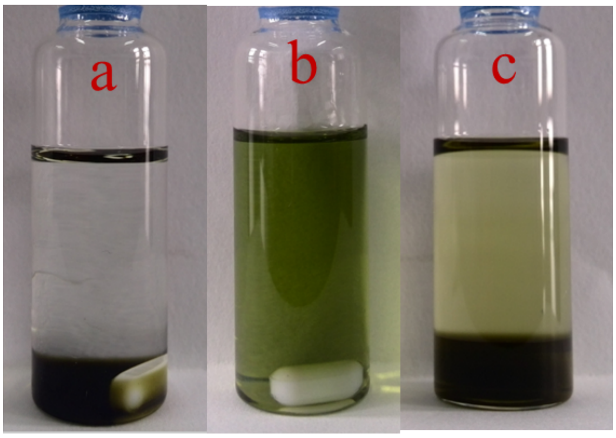


Figure S4. Photographs of TPSC–based AGET ATRP of methyl acrylate ionic liquid: (a) before polymerization at room temperature; (b) during polymerization at 90 ^{o}C; and (c) after polymerization and cooled down to room temperature. The copper content in MPEG$_{750}$NIL was 97.5% after the first cycle based on the original amount of copper.

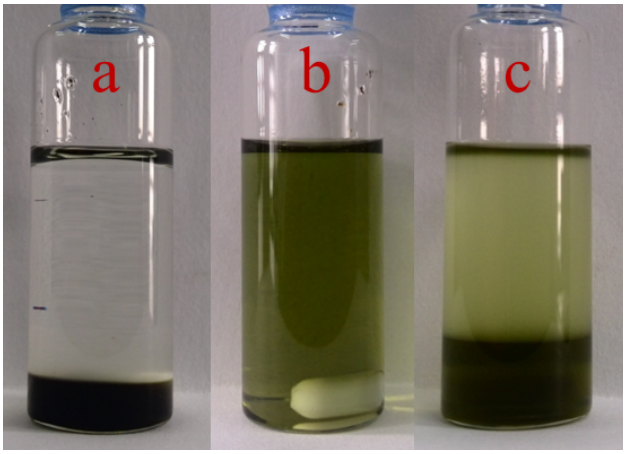


Figure S5. Photographs of TPSC–based AGET ATRP of methyl methacrylate in ionic liquid: (a) before polymerization at room temperature; (b) during polymerization at 90 ^{o}C; and (c) after polymerization and cooled down to room temperature. The copper content in MPEG$_{750}$NIL was 99.6% after the first cycle based on the original amount of copper.

[S1] B. Tan, J. Jiang, Y. Wang, L. Wei, D. Chen and Z. Jin, *Appl. Organomet. Chem.*, 2008, **22**, 620.

[S2] K. Matyjaszewski, D. A. Shipp, J. L. Wang, T. Grimaud and T. E. Patten, *Macromolecules,* 1998, **31***,* 6836.