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## **Supporting Information**

Designing a Robust Recyclable Tricopolymer Poly(Ionic Liquid) Macroligand for Copper-Mediated Atom Transfer Radical Polymerization in Non-Aqueous Biphasic System

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## Materials

Methyl methacrylate (MMA, ≥99%, Shanghai Macklin Biochemical Co. Ltd), was purified by through a column packed with activated neutral alumina, passing while 2.2azobisisobutyronitrile (AIBN, ≥97%, Tianjin Guanfu Fine Chemical Research Institute) was purified from ethanol, dried and then stored in a refrigerator at about -2 °C. Other chemical reagents such as poly(ethylene glycol) methyl ether acrylate-480 (PEG<sub>480</sub>-MA) (Aladdin Industrial Corporation), methyl iodide (99%) (Xiya Reagent Shandong, China), ethyl 2bromoisobutyrate (EBiB, 98%), acrylolyl chloride (96%), 2-[(dimethylamino)ethyl] acrylate (99%), ethanolamine (97%), acetonitrile (+99.9 analytical grade), 1,3,5-trimethylbenzene (97%), dimethyl sulfoxide (DMSO, analytical grade), triethylamine (99%), acetonitrile (99%), 2-(chloromethyl)-4-methoxy-3,5-dimethylpyridine hydrochloride (98%) were all acquired from Shanghai Macklin Biochemical Co. Ltd, while copper(II)bromide (CuBr<sub>2</sub>, 99.95%, Aladdin Chemistry Co. Ltd), anhydrous methanol (+99.5%), tetrahydrofuran (THF, +99.5%), diethyl ether (+99.5%), dichloromethane (+97.5%) from Sinopharm Chemical Reagent Co. Ltd., anhydrous sodium carbonate (+99.8%), anhydrous potassium carbonate (+99%), anhydrous magnesium sulphate (+99%) from Shanghai Lingfeng Chemical reagent Co. Ltd., were all used as received.

## Characterization

The molecular weight distribution  $(M_w/M_n)$  values and number-average molecular weight  $(M_{n,GPC})$  of the polymeric products were analyzed by Angilent Technologies PL-220 gel permeation chromatograph (GPC) equipped with a refractive-index detector (Angilent Technology), using a PLgel 5µL MIXED-C column (300 x 7.5mm) with measurable molecular weights in the range of  $6 \times 10^2$  to  $5 \times 10^5$  g/mol. THF served as the eluent with a flow rate of 1.0

mL/min at a temperature of 40 °C. The GPC samples were injected using Angilent Technologies plus autosampler and calibrated with polystyrene standards purchased from Angilent Technologies. The resultant polymers were analyzed using <sup>1</sup>H NMR spectra recorded on INOVA 600 MHz nuclear magnetic resonance (NMR) instrument where CDCl<sub>3</sub> and DMSO-d<sub>6</sub> served as the solvents and tetramethylsilane (TMS) as the internal standard. The analysis of residual elemental Cu in polymeric solutions was done by inductively coupled plasma mass spectroscopy (ICP-MS).



Fig. S1 <sup>1</sup>H NMR spectrum for the intermediate product 1 using  $CDCl_3$  as a solvent and TMS as the internal standard.



**Fig. S2** <sup>1</sup>H NMR spectrum for the intermediate product **2** using  $CDCl_3$  as a solvent and TMS as the internal standard.



**Fig. S3** <sup>1</sup>H NMR spectrum for intermediate product **3** using DMSO-d<sub>6</sub> as a solvent and TMS as the internal standard.

Solvents (2 mL)	25 °C	70 °C	25 °C
Cyclohexane	Ι	Ι	Ι
Heptane	Ι	Ι	Ι
Anisole	М	М	М
o-Xylene	М	М	М
P-Xylene	М	М	М
m-Xylene	М	М	М
1,3,5-	Ι	S	Ι
Trimethylbenzene			
Benzene	М	М	М
Toluene	М	М	М
n-Hexane	Ι	Ι	Ι

Table S1 Screening of the solvents that successfully coupled with PILLL<sup>a</sup> (200 mg) for the

## TPSC system

I: depicts immiscibility; S: depicts slight miscibility; M: depicts miscibility of PILLL/1,3,5trimethylbenzene solvent pair with MMA under the examined temperatures. <sup>*a*</sup> [MA-sLN]/ [PEG<sub>480</sub>MA]/[TMEAM] = 1/10/10.

Entry	Х	Time.	Conv.	$M_{ m n,th}{}^a$	M <sub>n,GPC</sub>	$M_{\rm w}/M_{\rm n}$
	(mg)	(h)	(%)	(g. mol <sup>-1</sup> )	(g. mol <sup>-1</sup> )	
1	107	12.5	46.7	4900	3000	1.43
2	214	12.5	59.8	6200	3400	1.28
3	321	12.5	61.5	6400	3800	1.27
4	428	12.5	70.2	7200	4200	1.34

**Table S2** Effects of varying the amount of PILLL for TPSC *via* ICAR ATRP system Polymerization conditions:  $[MMA]_o/[EBiB]_o/[CuBr_2]_o/[PILLL]_o/[AIBN]_o = 150/1.5/1/x/1, V_{MMA}$ = 0.75 mL,  $V_{1,3,4-trimethylbenzene} = 2.0$  mL, temperature = 70 °C. <sup>a</sup>  $M_{n,th} = ([M]_o/[initiator]_o) \times M_{w,MMA}$ x Conv.% +  $M_{EBiB}$ .

Entry	Х	Time	Conv.	$M_{ m n, th}$ $^a$	M <sub>n, GPC</sub>	$M_{ m w}/M_{ m n}$
	(mL)	(h)	(%)	(g. mol <sup>-1</sup> )	(g. mol <sup>-1</sup> )	
1	0.75	6.5	6.4	800	1600	1.18
2	1.0	6.5	36.2	7400	3600	1.25
3	1.5	6.5	46.7	9400	4300	1.30
4	2.0	$\mathrm{NA}^b$	NA	NA	NA	NA

Table S3 Effects of varying the amount of monomer for TPSC via ICAR ATRP system

Polymerization conditions:  $[MMA]_o/[EBiB]_o/[CuBr_2]_o/[PILLL]_o/[AIBN]_o = x/1.5/1/3/1$ ; where (x = (100, 200, 300, 400),  $V_{1,3,5\text{-trimethylbenzene}} = 2.0$  mL, temperature = 70 °C. <sup>*a*</sup>  $M_{n,th} = ([M]_o/[initiator]_o) \times M_{w,MMA} \times \text{Conv.} + M_{EBiB}$ . <sup>*b*</sup> No biphasic separation.

Entry	Х	Time	Conv.	$M_{ m n,th}{}^a$	$M_{ m n, GPC}$	$M_{ m w}/M_{ m n}$
	(mL)	(h)	(%)	(g. mol <sup>-1</sup> )	(g. mol <sup>-1</sup> )	
1	2.0	6.5	36.2	7400	3600	1.25
2	2.5	6.5	31.3	4400	3400	1.24
3	3.0	6.5	51.2	6800	5400	1.38
4	3.5	6.5	71.4	9700	6000	1.39

 Table S4 Effects of varying the volume of 1,3,5-trimethylbenzene for TPSC via ICAR ATRP

 system

Polymerization conditions:  $[MMA]_o/[EBiB]_o/[CuBr_2]_o/[PILLL]_o/[AIBN]_o = 200/1.5/1/3/1,$ temperature = 70 °C,  $V_{1,3,5\text{-trimethylbenzene}} = X. \ ^a M_{n,th} = ([M]_o/[initiator]_o) \times M_{w,MMA} \times \text{Conv.} + M_{EBiB}.$ 

Entry	Х	Time	Conv.	$M_{ m n, th}$ $^a$	$M_{ m n, \ GPC}$	$M_{ m w}/M_{ m n}$
	(µL)	(h)	(%)	(g. mol <sup>-1</sup> )	(g. mol <sup>-1</sup> )	
1	3.3	7.5	31.5	12800	8000	1.19
2	5.3	7.5	33.1	8500	7700	1.24
3	6.7	7.5	32.0	6600	7900	1.25
4	10.0	7.5	46.2	6400	7300	1.17

Table S5 Effects of varying the amount of alkyl initiator for TPSC via ICAR ATRP system

Polymerizations conditions:  $[MMA]_o/[EBiB]_o/[CuBr_2]_o/[PILLL]_o/[AIBN]_o = 200/x/1/3/1$ , where (x = (0.5, 0.8, 1, 1.5) temperature = 70 °C,  $V_{1,3,5\text{-trimethylbenzene}} = 2.5 \text{ mL}$ .  ${}^a M_{n,th} = ([M]_o/[initiator]_o) x M_{w,MMA} x \text{ Conv}$ .% +  $M_{EBiB}$ .

Entry			Time	Conv.	$M_{ m n, th}{}^c$	M <sub>n,GPC</sub>	$M_{\rm w}/M_{\rm n}$
	$\mathbf{X}^{a}$	$\mathbf{Y}^b$	(h)	(%)	(g. mol <sup>-1</sup> )	(g. mol <sup>-1</sup> )	
1	0.5	1.0	8.5	51.8	7100	4500	1.27
2	1.0	1.0	8.5	59.4	8100	7900	1.20
3	1.5	1.0	8.5	59.8	8200	8400	1.21
4	2.0	1.0	8.5	$NA^d$	NA	NA	NA
5	1.0	0.5	8.5	$NA^d$	NA	NA	NA
6	1.0	1.5	8.5	57.4	7900	6400	1.36
		5.0	( ) ( ) ( ) ) · · · · ·				

 Table S6 Effects of varying the amount of catalyst and reducing agent for TPSC via ICAR

 ATRP system

Polymerization conditions:  $[MMA]_o/[EBiB]_o/[CuBr_2]_o/[PILLL]_o/[AIBN]_o = 200/1.5/x/3/y,$ temperature = 70 °C,  $V_{1,3,5\text{-trimethylbenzene}} = 2.5 \text{ mL}.^a$  The molar ratio of  $[MMA]_o/[CuBr_2]_o/[AIBN]_o$ = 150/x/1 (x = 0.5, 1, 1.5, 2); <sup>b</sup> the molar ratio of  $[MMA]_o/[CuBr_2]_o/[AIBN]_o = 150/y/1$  (y = 0.8, 1, 1.5); <sup>c</sup>  $M_{n,th} = ([M]_o/[initiator]_o) \times M_{w,MMA} \times \text{Conv.} + M_{EBiB.}^{a}$  No polymers were obtained.