Supporting Information

Yb(NTf₂)₃/HFIP Induced High Isotacticity in Atom Transfer Radical Polymerization of Methyl Methacrylate

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1. General information

Unless stated otherwise, all manipulations with air- and moisture-sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold line, or in an inert gas (N₂)-filled glovebox. All solvents and reagents were obtained from commercial sources and were purified according to standard procedures before use. MMA was purchased and dried over activated CaH₂ overnight, followed by vacuum distillation and stored in bottles at -30 °C in a freezer. ¹H NMR spectra were recorded on a Varian Mercury 400 MHz or Agilent Mercury 400 MHz spectrometer in chloroform-d. All signals were reported in ppm with the internal TMS signal at 0.0 ppm or the chloroform signal at 7.26 ppm as a standard. The triad isotacticities (mm) of the polymer samples were measured by ¹H NMR in CDCl₃ at room temperature. They were determined by integrating three resonance peaks for α -CH₃ with different tacticities, which were approximately centered at 0.84 ppm (rr), 1.02 ppm (mr) and 1.21 ppm (mm), respectively, and then calculated according to the formula mm = $I_{1.21 \text{ ppm}}/(I_{1.21})$ $_{\rm ppm} + I_{1.02 \text{ ppm}} + I_{0.84 \text{ ppm}}) \times 100\%$, where $I_{\rm x ppm}$ is the peak integral of proton centered at x ppm. The number-average molecular weight (M_n) and the polydispersity index (D) were measured by gel permeation chromatography (GPC). GPC was performed on a Waters (USA) 1515 gel permeation chromatograph equipped with a Waters 2414 refractive-index detector with three commercial columns (Waters Styragel) connected in series. The analysis was performed at 25 °C with purified high-performance-liquid-chromatography-grade THF as the eluent at a flow rate of 1 mL/min. Calibration was performed with standard PSs. Thermal transition temperatures of polymers were measured by differential scanning calorimetry (DSC) using a TA Instruments Q2000 calorimeter equipped with an automated sampler. Analyses were performed in crimped aluminum pans under nitrogen and data were collected with the heat/cool/heat cycle at a rate of 10 °C/min and processed with TA Q series software.

2. General (SARA) ATRP procedure with Lewis acids

In a Schlenk bomb flask equipped with a magnetic stirrer bar, a mixture of Cu(II) salt, ligand, and Cu(0) powder (fine powder (99.9% metals basis)) in solvent was stirred at room temperature for 3 h under an atmosphere of nitrogen. The monomer was added and stirred for another 1 h. After that, the initiator was added and the Lewis acid was added after an initiation period of 5 min. Then the bomb flask was sealed and placed at specified temperature. After stirred for the allotted time, the reaction mixture was diluted with CH_2Cl_2 and stored for a while waiting for the complete precipitate of excess of the copper. The supernatant was then poured to an approximately 50-fold excess of rapidly stirred methanol. The precipitate was collected by decantation and washed with methanol and pentane, which was dried for 24 h in a vacuum oven at 60 °C. The dried samples were then analyzed by GPC and NMR.

3. General procedures for the synthesis of Lewis acids

3.1 General procedure for the synthesis of M(NTf₂)₃ (M=La, Nd, Gd, Er, Yb, Lu)

The complexes were synthesized according to the literature.¹ A mixture of $HNTf_2$ (12.0 mmol) and M_2O_3 (2.0 mmol) in 20 mL of water was stirred at 90 °C for 2 h. After filtration, the clear solution was completely evaporated at 120 °C for 3 h. The remaining solids were dried at 180 °C for 6 h under high vacuum to give the corresponding $M(NTf_2)_3$ complexes as highly hygroscopic colorless solids. The solids were used and stored in a N_2 filled glovebox.

3.2 General procedure for the synthesis of M(NTf₂)₃ (M=Sc, Y)

The complexes were synthesized according to the literature.² A mixture of $HNTf_2$ (12.0 mmol) and M (4.0 mmol) in 15 mL of water was stirred at 90 °C for 2 h. After filtration, the clear solution was completely evaporated at 120 °C for 3 h. The remaining solids was dried at 180 °C for 6 h under high vacuum to give the corresponding M(NTf₂)₃ complexes as highly hygroscopic colorless solids. The solids were used and stored in a N₂ filled glovebox

3.3. General procedure for the synthesis of Yb(OR)₃ (R=SO₂(CF₂)₃CF₃, COCF₃)

The complexes were synthesized according to the literature.³ A mixture of HOR (16.7 mmol) and Yb_2O_3 (2.78 mmol) in 50 mL of water was stirred at 90 °C for 2 h. After filtration, the clear solution was completely evaporated at 120 °C for 3 h. The remaining solids was dried at 180 °C for 6 h under high vacuum to give the corresponding $Yb(OR)_3$ complexes as highly hygroscopic colorless solids. The solids were used and stored in a N₂ filled glovebox.

4. Reaction optimization

	r		EBPA/CuX ₂ /In-BO 5.0 mol% Yb(C HFIP, RT, 48	X/Cu(0))Tf) ₃ ► h			
		N N In-BOX	ethyl	2-bromo	Br O O phenylacetate (I	EBPA)	
run	CuX ₂	$\operatorname{Yield}^{b}(\%)$	$M_{\rm n}{}^{c}~(imes~10^{3})$	Đc	$\operatorname{mm}^{d}(\%)$	$\operatorname{mr}^{d}(\%)$	rr ^d (%)
1	CuCl ₂	61	36.4	2.07	10.5	40.7	46.8
2	CuBr ₂	50	41.8	2.21	9.2	42.0	44.8
3	$Cu(OAc)_2$	67	44.1	1.84	8.1	34.9	57.0
4	Cu(OTf) ₂	84	42.4	2.01	12.5	40.7	46.8
5	Cu(NTf.).	67	20.4	1.62	14.2	40.9	44 9

Table S1. Screening of CuX₂ in (SARA) ATRP of MMA with Yb(OTf)₃ in HFIP^a

^{*a*}Conditions: 200:2:1:2:4 MMA:EBPA:Cu(X)₂:In-BOX:Cu(0) ratio, 5.0 mol% of Yb(OTf)₃, HFIP/MMA (4/1, v/v), RT. ^{*b*}Isolated yield. ^{*c*}Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards, $D = M_w/M_n$. ^{*d*}Triad tacticity measured by ¹H NMR in CDCl₃.

		EBPA/Cu(NTf ₂) ₂ /In-BOX/Cu(0) 5.0 mol% Yb(NTf ₂) ₃				
		HI	FIP, T °C, 48 h	-		
run	T (°C)	yield	$M_{\rm n}$	$\tilde{\mathbf{D}}^{c}$	mm/mr/rr (%) ^d	
		(%) ^b	(×10 ³) ^c			
1	50	32	12.7	1.42	31.3/32.2/36.5	
2	RT	66	17.3	1.53	38.8/28.3/32.9	
3	10	50	36.4	1.87	46.3/24.5/29.2	
4	5	39	40.1	1.89	41.2/25.5/33.3	

^{*a*}Conditions: 200:2:1:2:4 MMA:EBPA:Cu(NTf₂)₂:In-BOX:Cu(0) ratio, 5.0 mol% of Yb(NTf₂)₃, HFIP/MMA (4/1, v/v), at the specified temperature. ^{*b*}Isolated yields. ^{*c*}Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs narrow PS standards (D = Mw/Mn). ^{*d*}Triad tacticity measured by ¹H NMR in CDCl₃.

n $HFIP, 10 °C, 48 h$ O EBPA/Cu(NTf ₂) ₂ /In-BOX/Cu(0) $n = \frac{5.0 \text{ mol}\% \text{ M}(\text{NTf}_2)_3}{\text{HFIP}, 10 °C, 48 h}$							
run	M(NTf ₂) ₃	Yield ^b (%)	$M_{\rm n}{}^{c}$ (× 10 ³)	Đc	mm ^d (%)	mr ^d (%)	rr ^d (%)
1	Sc	36	23.2	1.61	54.3	23.4	22.3
2	Y	48	28.1	1.75	54.9	24.7	20.4
3	La	53	24.9	1.76	55.6	28.9	15.5
4	Gd	64	30.4	1.81	47.2	27.8	25.0
5	Er	28	20.7	1.52	60.2	21.7	18.1
6	Yb	37	36.7	1.88	68.5	18.5	13.0
7	Lu	34	23.0	1.62	50.3	26.6	23.1

Table S3. Screening of M(NTf₂)₃ in (SARA) ATRP of MMA with Cu(NTf₂)₂ in HFIP^a

^{*a*}Conditions: 200:2:1:2:4 MMA:EBPA:Cu(NTf₂)₂:In-BOX:Cu(0) ratio, 5.0 mol% of M(NTf₂)₃, HFIP/MMA (12/1, v/v), 10 °C. ^{*b*}Isolated yield. ^{*c*}Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards, $D = M_w/M_n$. ^{*d*}Triad tacticity measured by ¹H NMR in CDCl₃.

Table S4. Concentration Effects of Yb(NTf₂)₃ in (SARA) ATRP of MMA in HFIP^a

	n 🔌		/Cu(NTf ₂) ₂ /In-B X mol% Yb(NTf HFIP, 10 °C, 48	OX/Cu(0 ^F 2) ₃ 3 h			
run	Yb(NTf ₂) ₃ (X%)	$\operatorname{Yield}^{b}(\%)$	$M_{\rm n}^{\ c} (\times 10^3)$	\mathbf{D}^{c}	$\operatorname{mm}^{d}(\%)$	$\operatorname{mr}^{d}(\%)$	$\operatorname{rr}^{d}(\%)$
1	0	30	20.3	1.51	2.2	25.8	72.0
2	1	29	31.5	1.77	28.9	24.6	46.5
3	2	31	35.3	1.88	46.3	22.7	31.0
4	5	37	36.7	1.88	68.5	18.5	13.0
5	8	47	46.5	2.03	69.0	18.6	12.4

^{*a*}Conditions: 200:2:1:2:4 MMA:EBPA:Cu(NTf₂)₂:In-BOX:Cu(0) ratio, X mol% of Yb(NTf₂)₃, HFIP/MMA (12/1, v/v), 10 °C. ^{*b*}Isolated yield. ^{*c*}Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards, $D = M_w/M_n$. ^{*d*}Triad tacticity measured by ¹H NMR in CDCl₃.



Table S5. Comparison of Ligands in (SARA) ATRP of MMA in HFIP^a

^{*a*}Conditions: 200:2:1:2:4 MMA:EBPA:Cu(NTf₂)₂:L:Cu(0) ratio, 5.0 mol% of Yb(NTf₂)₃, HFIP/MMA (12/1, v/v), 10 °C. ^{*b*}Isolated yield. ^{*c*}Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PMMA standards, $D = M_w/M_n$. ^{*d*}Triad tacticity measured by ¹H NMR in CDCl₃.



Table S6. The (SARA)ATRP of different monomers in HFIP with or without the addition of Yb(NTf₂)_{3^a}

^{*a*}Conditions: 200:2:1:2:4 monomer:EBPA:Cu(NTf₂)₂:In-BOX:Cu(0) ratio, HFIP/MMA (4/1, v/v), 10 °C for runs 1-2 and 4-5, 50 °C for run 3. ^{*b*}Isolated yield. ^{*c*}Number-average molecular weights and polydispersity indices determined by GPC at 25 °C in THF vs. narrow PS standards, $D = M_w/M_n$. ^{*d*}Triad tacticity measured by ¹H NMR or ¹³C NMR.

5. Control experiments

A control experiment was set up using Et_3B (1 M in Hexane)/O₂ as the radical initiator system for the conventional radical polymerization of MMA in the presence of 5% Yb(NTf₂)₃ in HFIP at 10 °C. The reaction proceeded with a yield of 29%. The mm value was 49% and thus comparable with that (46%) achieved in the (SARA) ATRP of MMA under the similar conditions. The results are as follows:



Scheme S1 Free radical polymerization of MMA in presence of Yb(NTf₂)₃.

The detailed reaction procedure was as follows:

To a Schlenk bomb flask equipped with a magnetic stirrer bar were subsequently added MMA, HFIP, and Yb(NTf₂)₃. The reaction mixture was cooled to 10 °C before Et₃B (1 M in hexane) was added followed by the addition of O_2 . The mixture was stirred at 10 °C for 48 h. The reaction mixture was diluted with CH₂Cl₂ and poured to an approximately 50-fold excess of rapidly stirred methanol. The precipitate was collected by decantation and washed with methanol and pentane, which was dried for 24 h in a vacuum oven at 60 °C. The dried samples were then analyzed by GPC and NMR.

The radical character of the polymerizations was also underlined by a control experiment in which the reaction was efficiently suppressed in the presence of 10 mol% TEMPO. Furthermore, control experiments were run in absence of the initiator as well as in absence of the copper catalyst system which both led to a complete suppression of the reaction. The results are as follows:

MMA _	In-BOX/Cu(0)/Cu(NTf ₂) ₂				
	EBPA, HFIP RT, 48 h				
	5 mol% Yb(NTf ₂) ₃				
Yield=0%	in presence of 10 mol%TEMPO				
Yield=0%	in absence of EBPA				
Yield=0%	in absence of Cu(NTf ₂) ₂				

Conditions: $n(M):n(EBPA):n(CuBr_2):n(Ligand):n(Cu(0)) = 200:$ 2:1:2:4, HFIP was used as the solvent (HFIP/MMA = 4/1 (v/v))

Scheme S2 Further control experiments underlining the radical polymerization process.

Finally we set up the control experiment without Cu(0) where no conversion was detected, underlining the SARA process. The results are as follows:



Scheme S3 Control experiment to underline the (SARA) ATRP mechanism

Additional experiment with a HFIP/MMA ratio of 1/1 was set up to see if this improves the D. Unfortunately, the D for HFIP/MMA=1/1 was broad since the reaction system is a very sticky mixture that could not be stirred when the conversion reached a certain level. The results are as follows:



Scheme S4 Control experiment at high MMA concentrations (MMA/HFIP=1/1)

To underline the activity of the In-BOX ligand under our reaction conditions, we conducted a control experiment furnishing 61% yield compared to 35% yield using Me₆TREN as ligand after 12 h reaction time. Furthermore, the reaction control under these conditions was much better when In-BOX was used as the ligand compared to Me₆TREN, as shown in the following scheme:



Conditions: $n(M):n(EBPA):n(Cu(NTf_2)_2):n(Ligand):n(Cu(0)) = 200:2:1:2:4, HFIP was used as the solvent (HFIP/MMA = 1/1 (v/v)), 25 °C, 12 h$

Scheme S5 Control experiments to illustrate the activity

6. Cyclic voltammetry for CuBr₂/L

The cyclic voltammetry measurements were done in accordance to the literature⁴ and recorded at 25 °C with a CHI660E potentiostat. Solutions of CuBr₂/L (1.0 mM) were prepared in dry CH₃CN containing 0.1 M Bu₄NPF₆ as the supporting electrolyte. Measurements were carried out under nitrogen at a scan rate of 0.1 V·s⁻¹ using a glassy carbon disk as the working electrode and a platinum wire as the counter electrode. Potentials were recorded versus SCE using a 0.1 M Bu₄NPF₆ salt bridge. K_{ATRP} value was estimated through correlation to Figure 2 in the literature.⁴



Figure S1. Cyclic voltammetry measurements of CuBr₂/L, Conditions: 0.1 M NBu₄PF₆, 1.0 mM CuBr₂/L complex, scan rate 0.10 V·s⁻¹ at 25 °C. Potentials are reported vs SCE. $E_{1/2} = (E_{p,a} + E_{p,c})/2$

a: CuBr₂/In-BOX: $E_{1/2} = 0.276$ V; b: CuBr₂/PMEDTA: $E_{1/2} = -0.092$ V



7. DSC determination of $T_{\rm g}$ for PMMAs



Figure S2. T_g values for PMMA with regularly increasing triad isotacticity (mm): (a) $T_g = 128$ °C, mm = 2.6% (Table 1, run 13). (b) $T_g = 111$ °C, mm = 14.2% (Table 2, run 1). (c) $T_g = 96$ °C, mm = 28.9% (Table S3, run 2); d) $T_g = 84$ °C, mm = 46.3% (Table 4, run 1); e) $T_g = 67$ °C, mm = 69.0% (Table 4, run 6)



Figure S3. Plot of T_g over triad isotacticity (mm) for PMMAs with increasing mm: (a) $T_g = 128$ °C, mm = 2.6% (Table 1, run 13). (b) $T_g = 111$ °C, mm = 14.2% (Table 2, run 1). (c) $T_g = 96$ °C, mm = 28.9% (Table S3, run 2). (d) $T_g = 84$ °C, mm = 46.3% (Table 4, run 1). (e) $T_g = 67$ °C, mm = 69.0% (Table 4, run 6).

8. Typical ¹H NMR spectra of PMMAs and other polymers



Figure S4. ¹H NMR spectrum (CDCl₃, 25 °C) of PMMA with mm = 3.2% (Table 1, run 1).



Figure S5. ¹H NMR spectrum (CDCl₃, 25 °C) of PMMA with mm = 5.5% (Table 1, run 11).



Figure S6. ¹H NMR spectrum (CDCl₃, 25 °C) of PMMA with mm = 9.2% (Table 1, run 12).



Figure S7. ¹H NMR spectrum (CDCl₃, 25 °C) for PMMA with mm = 2.6% (Table 1, run 13).



Figure S8. ¹H NMR spectrum (CDCl₃, 25 °C) of PMMA with mm = 14.2% (Table 2, run 1).



Figure S9. ¹H NMR spectrum (CDCl₃, 25 °C) of PMMA with mm = 38.8% (Table 2, run 4).



Figure S10. ¹H NMR spectrum (CDCl₃, 25 °C) for PMMA with mm = 46.3% (Table 3, run 3).



Figure S11. ¹H NMR spectrum (CDCl₃, 25 °C) for PMMA with mm = 68.5% (Table 4, run 4).



Figure S12. ¹³C NMR spectrum (1,2,4-trichlorobenzne+ C_6H_6 , 100 °C) for P^{*n*}BuMA with mm = 14.5% (Table S6, run 1).



Figure S13. ¹³C NMR spectrum (1,2,4-trichlorobenzne+ C_6H_6 , 100 °C) for P^{*n*}BuMA with mm = 58.9% (Table S6, run 2).



Figure S14. ¹³C NMR spectrum (1,2,4-trichlorobenzne+ C_6H_6 , 25 °C) for P^{*n*}PrMA with mm = 50.8% (Table S6, run 3).



Figure S15. ¹H NMR spectrum (D₂O, 25 °C) for PAM with mm = 19.7% (Table S6, run 4).



Figure S16. ¹H NMR spectrum (D₂O, 25 °C) for PAM with mm = 40.5% (Table S6, run 5).

9. References

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