

Supporting Information

Bisphosphine Monoxide-Ligated Ruthenium Catalysts: Active, Versatile, Removable, and Cocatalyst-Free in Living Radical Polymerization

Yusuke Fukuzaki, Yusuke Tomita, Takaya Terashima, Makoto Ouchi, and Mitsuo Sawamoto**

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku,

Kyoto 615-8510, Japan

Corresponding Authors:

Makoto Ouchi (ouchi@living.polym.kyoto-u.ac.jp)

Mitsuo Sawamoto (sawamoto@star.polym.kyoto-u.ac.jp)

Table S1. Cp*Ru-Catalyzed Living Radical Polymerizations of MMA, MA, and St with BPMO Ligands in Toluene.^a

Entry	Monomer	Initiator ^b	Ligand	[Ru] ₀ /[Ligand] ₀	Cocatalyst	Temp. °C	Time h	Conv	M _n	M _w /M _n
1	MMA	Cl	PO-2	1/1	None	80	48	86%	10 900	1.04
2		Cl	PO-1	1/2	None	80	48	88%	9 300	1.08
3		Cl	PO-2	1/2	None	80	34	92%	9 800	1.05
4		Cl	PO-1	1/1	<i>n</i> -Bu ₂ NH ^c	80	24	91%	11 800	1.09
5		Cl	PO-2	1/1	<i>n</i> -Bu ₂ NH ^c	80	24	93%	10 600	1.07
6		Br	PO-2	1/2	None	80	70	87%	10 400	1.36
7	MA	Cl	PO-2	1/2	None	80	85	91%	7 400	1.26
8		Br	PO-1	1/1	None	80	14	86%	8 600	1.23
9		Br	PO-1	1/2	None	80	24	95%	8 600	1.37
10		Br	PO-2	1/2	None	80	24	86%	8 100	1.22
11		Br	PO-1	1/1	<i>n</i> -Bu ₂ NH ^c	80	48	90%	8 300	1.29
12		Br	PO-2	1/1	<i>n</i> -Bu ₂ NH ^c	80	24	94%	8 700	1.19
13	St	Cl	PO-1	1/2	None	80	420	86%	9 100	1.03
14		Cl	PO-2	1/2	None	80	280	85%	8 200	1.03
15		Br	PO-1	1/1	<i>n</i> -Bu ₂ NH ^c	100	72	88%	10 400	1.33
16		Br	PO-2	1/1	<i>n</i> -Bu ₂ NH ^c	100	72	93%	12 300	1.09

^a [Monomer]₀/[Initiator]₀/[[RuCp*(μ₃-Cl)]₄]₀/[Ligand]₀ = 4000/4.0/1.0/4.0 or 8.0 mM.

^b Cl: H-(MMA)₂-Cl, Br: H-EMA-Br.

^c [*n*-Bu₂NH]₀ = 40 mM.

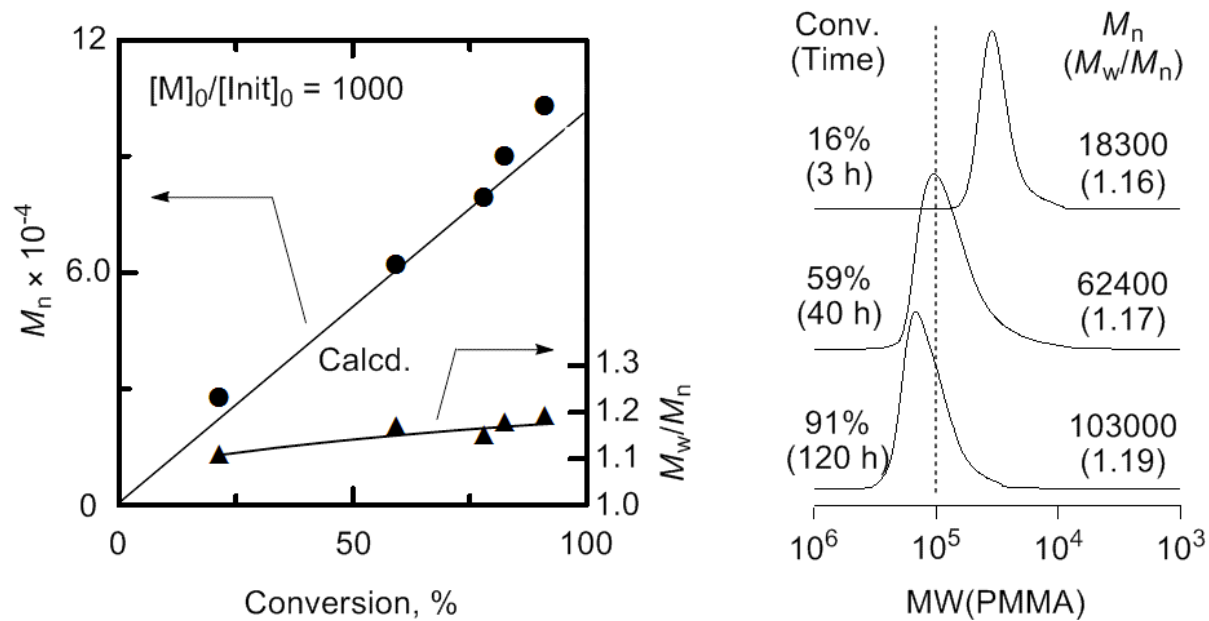


Figure S1. Living radical polymerization of MMA with H-(MMA)₂-Cl/[Cp*Ru(μ_3 -Cl)]₄/PO-2 in toluene at 80°C: [MMA]₀ = 5.0 M, [H-(MMA)₂-Cl]₀ = 50 mM, [[Cp*Ru(μ_3 -Cl)]₄]₀ = 0.25 mM, [PO-2]₀ = 2.0 mM