Supplementary Information

Cu(0)-RDRP of styrene: Balancing initiator

efficiency and dispersity

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General Procedures

Optimised Procedure 1: PS (DP800) Optimised ligand concentration

Styrene (4 mL or 3.64 g, 800 equiv.), pre-activated copper wire (5 cm), methyl- α bromopropionate (6.9 µL or 9.96 mg, 1 equiv.), CuBr₂ via a stock solution (0.49 mg, 0.05 equiv.) and IPA (4 mL) were added to a septum sealed vial. The copper wire was wrapped around the stirrer bar and the mixture was subsequently deoxygenated by bubbling with nitrogen for 20 min. PMDETA (6.4 µL, 0.72 equiv.) was then introduced in the vial via a gastight syringe and the polymerisation was allowed to commence at 60 °C for 36 h. Samples were taken periodically under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ¹H NMR and SEC.

Optimised Procedure 2: PS (DP800) Optimised initiator and solvent

Styrene (4 mL or 3.64 g, 800 equiv.), pre-activated copper wire (5 cm), Ethyl-2bromopropionate (5.6 μ L or 7.8 mg, 1 equiv.) or 2-bromopropionitrile (3.8 μ L or 5.8 mg, 1 equiv.), CuBr₂ via a stock solution (0.49 mg, 0.05 equiv.) and either toluene or dioxane (4 mL) were added to a septum sealed vial. The copper wire was wrapped around the stirrer bar and the mixture was subsequently deoxygenated by bubbling with nitrogen for 20 min. PMDETA (3.2 μ L, 0.36 equiv.) was then introduced in the vial via a gas-tight syringe and the polymerisation was allowed to commence at 60 °C for 36 h. Samples were taken periodically under a nitrogen blanket and passed through a short column of neutral alumina to remove dissolved copper salts prior to analysis by ¹H NMR and SEC.

Supplementary Figures

NMR analysis of Conversion



Figure S1: ¹H NMR of polystyrene synthesised with MBPA as the initiator.

The effect of temperature



Figure S2: SEC analysis of polystyrene (Target DP50) prepared at a) 25 °C, b) 40 °C and c) 50 °C via Cu(0)-RDRP in IPA utilising MBPA at the initiator, under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[50]:[0.05]:[0.36]. Black traces are those samples taken after 18 hours and red traces are samples taken after 36 hours.



Figure S3: SEC analysis of polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP in IPA utilising MBPA at the initiator, under the following reaction conditions $[MBPA]:[S]:[CuBr_2]:[PMDETA]=[1]:[50]:[0.05]:[0.36]$. The black trace is that of a sample taken after 18 hours and the red traces is that of a sample taken after 36 hours.



Figure S4: SEC analysis of polystyrene (Target DP50) prepared at a) 70 °C and b) 80 °C via Cu(0)-RDRP in IPA utilising MBPA at the initiator, under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[50]:[0.05]:[0.36]. Black traces are those samples taken after 18 hours and red traces are samples taken after 36 hours.



Figure S5: SEC analysis of polystyrene (Target DP800) prepared at 60 °C via Cu(0)-RDRP in IPA utilising MBPA at the initiator, under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[800]:[0.05]:[0.36].

The effect of the type and concentration of ligand

Table S1: ¹H NMR and SEC analysis of polystyrene with target DP50 prepared via Cu(0)-RDRPinIPA,underthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[PMDETA]=[1]:[50]:[0.05]:[X], where [PMDETA] was varied between0.18 and 0.72 equivalents with respect to initiator.

Entry	[PMDETA] w.r.t [l]	Conversion (%)	M _{n (Theo.)} (g mol ⁻¹)	M _{n (SEC)}	Ð
1	18%	66	3600	5100	1.13
2	36%	98	5300	8100	1.15
3	54%	94	5100	7000	1.19
4	72%	90	4900	6900	1.23

Table S2: Kinetic analysis of polystyrene with target DP50 prepared via Cu(0)-RDRP in IPA,underthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[PMDETA]=[1]:[50]:[0.05]:[0.72].

Time (h)	Conversion (%)	-ln([M ₀]/[M _t])	M _{n (SEC)}	Ð
0	0	-	-	-
0.5	0	-	-	-
1	0.5	0.00501	-	-
2	1	0.0101	-	-
4	10	0.104	900	1.15
6	17	0.191	1350	1.19
8	26	0.300	1700	1.17



Figure S6: Kinetic and SEC analysis of polystyrene with target DP50 prepared via Cu(0)-RDRPinIPA,underthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[PMDETA]=[1]:[50]:[0.05]:[0.72].



Figure S7: SEC analysis of polystyrene (Target DP800) prepared at 60 °C via Cu(0)-RDRP inIPAunderthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[PMDETA]=[1]:[800]:[0.05]:[0.72].

Table S3: ¹H NMR and SEC analysis of polystyrene with target DP50 prepared via Cu(0)-RDRPinIPA,underthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[Me_6TREN]=[1]:[50]:[0.05]:[X],where[Me_6TREN]wasvariedbetween 0.18 and 0.54 equivalents with respect to initiator.

Entry	[Me ₆ TREN] w.r.t [l]	Conversion (%)	M _{n (Theo.)} (g mol ⁻¹)	M _{n (SEC)}	Ð
1	18%	31	1800	2100	1.12
2	36%	70	3800	7700	1.35
3	54%	67	3700	10400	3.31

Table S4: ¹H NMR and SEC analysis of polystyrene with target DP50 prepared via Cu(0)-RDRPinIPA,underthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[TREN]=[1]:[50]:[0.05]:[X],where[TREN]was0.18or0.36equivalents with respect to initiator.

Entry	[TREN] w.r.t [l]	Conversion (%)	M _{n (Theo.)} (g mol ⁻¹)	M _{n (SEC)}	Ð	
1	18%	73	3900	6100	1.38	
2	36%	98	5300	13500	1.64	



Figure S8: SEC analysis of polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP in IPA where TREN a) 18% and b) 36% was utilised as the ligand.

Table S5: ¹H NMR and SEC analysis of polystyrene with target DP50 prepared via Cu(0)-RDRPinIPA,underthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[L]=[1]:[50]:[0.05]:[0.36], with BPY, TPMA, cyclam and Me4cyclamrespectively utilised as the ligand.

Entry	Ligand	Conversion (%)	M _{n (Theo.)} (g mol ⁻¹)	M _{n (SEC)}	Ð
1	BPY	0	-	-	-
2	TPMA	63	3500	7100	1.58
3	Cyclam	25	1500	8000	2.38
4	Me ₄ Cyclam	63	3500	11100	2.39



Figure S9: SEC analysis of polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP in IPA with a) TPMA b) Cyclam and c) Me₄Cyclam utilised as the ligand.

Table S6: ¹H NMR and SEC analysis of polystyrene with target DP50 prepared via Cu(0)-RDRPinIPA,underthefollowingreactionconditions[MBPA]:[S]:[CuBr₂]:[HMTETA]=[1]:[50]:[0.05]:[X], where[HMTETA]was0.18or0.36equivalents with respect to initiator.

Entry	[HMTETA] w.r.t [l]	Conversion (%)	M _{n (Theo.)} (g mol ⁻¹)	M _{n (SEC)}	Ð
1	18%	45	2600	3200	1.16
2	36%	92	5000	8000	1.19



Figure S10: SEC analysis of polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP in IPA with HMTETA a) 18% and b) 36% utilised as the ligand.



Figure S11: SEC analysis of polystyrene (Target DP800) prepared at 60 °C via Cu(0)-RDRPinIPAunderthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[HMTETA]=[1]:[800]:[0.05]:[0.36].

The effect of the initiator



Figure S12: SEC analysis of polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP inIPAunderthefollowingreactionconditions[TosylChloride]:[S]:[CuX2]:[PMDETA]=[1]:[50]:[0.05]:[0.36].

Table S7: ¹H NMR and SEC analysis of polystyrene with target DP800 prepared via Cu(0)-RDRPinIPA,underthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[HMTETA]=[1]:[800]:[0.05]:[X], where[HMTETA]was0.18 or0.36equivalents with respect to initiator.

Entry	Initiator	Conversion (%)	M _{n (Theo.)} (g mol ⁻¹)	M _{n (SEC)}	I _{eff} (%)	Ð
1	MBPA	22	18500	34300	54	1.22
2	EBP	33	27700	38500	72	1.29
3	BPN	27	22700	29600	76	1.32



Figure S13: SEC analysis of polystyrene (Target DP800) prepared at 60 °C via Cu(0)-RDRPinIPAunderthefollowingreactionconditions[I]:[S]:[CuBr2]:[PMDETA]=[1]:[800]:[0.05]:[0.36], with a) MBPA, b) EBP and c) BPN as theinitiator.



Figure S14: SEC analysis of uncontrolled polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP in a) DMSO b) DMF and c) ethanol under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[50]:[0.05]:[0.36].



Figure S15: SEC analysis of polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP in a biphasic system in a) tBuOH b) IPA under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[50]:[0.05]:[0.36].



Figure S16: SEC analysis of well-defined polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP in a) toluene b) acetonitrile c) dioxane under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[50]:[0.05]:[0.36].

Table S8: ¹H NMR and SEC analysis of polystyrene with target DP800 prepared via Cu(0)-RDRP in a) toluene b) acetonitrile and c) dioxane under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[800]:[0.05]:[0.36].

Entry	Solvent	Conversion (%)	M _{n (Theo.)} (g mol ⁻¹)	M _{n (SEC)}	I _{eff} (%)	Ð
1	Toluene	37	31000	45500	68	1.24
2	Acetonitrile	28	23600	64900	36	2.06
3	Dioxane	28	23600	29300	80	1.19



Figure S17: SEC analysis of well-defined polystyrene (Target DP800) prepared at 60 °C via Cu(0)-RDRP in a) toluene b) acetonitrile and c) dioxane under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[50]:[0.05]:[0.36].



Figure S18: SEC analysis of well-defined polystyrene (Target DP50) prepared at 60 °C via Cu(0)-RDRP in toluene: ipa mixtures with a) 1:1 b) 4:1 under the following reaction conditions [MBPA]:[S]:[CuBr₂]:[PMDETA]=[1]:[50]:[0.05]:[0.36].

Combining Optimal Conditions



Figure S19: SEC analysis of polystyrene (Target DP800) prepared at 60 °C via Cu(0)-RDRP in a) dioxane and b) toluene with EBP as the initiator, under the following reaction conditions [EBP]:[S]:[CuBr₂]:[PMDETA]=[1]:[800]:[0.05]:[0.36].



Figure S20: SEC analysis of polystyrene (Target DP800) prepared at 60 °C via Cu(0)-RDRP in a) dioxane and b) toluene with BPN as the initiator, under the following reaction conditions [BPN]:[S]:[CuBr₂]:[PMDETA]=[1]:[800]:[0.05]:[0.36].

Exploring Bulk Conditions



Figure S21: SEC chromatograms of well-defined polystyrene (Target DP800) synthesised in bulk utilising PMDETA (36%) as the ligand and a) MBPA, b) EBP and c) EBiB as the initiator.

It is noted that at lower degrees of polymerization bulk reactions must be stopped at low conversions as control is lost at the threshold in which the polystyrene is no longer soluble in the styrene monomer. Also in a similar manner to the solvated systems, the use of Me_6TREN at 18% or PMDETA at 36% are optimal, with 36% Me_6TREN resulting in a significant loss of control and 18% PMDETA resulting in a slower rate of polymerization and a lower conversion.

Table S9: Kinetic analysis of polystyrene with target DP800 prepared via Cu(0)-RDRP in bulk,underthefollowingreactionconditions[EBiB]:[S]:[CuBr_2]:[Me_6Tren]=[1]:[800]:[0.05]:[0.18].

Time (h)	Conversion (%)	-In([M ₀]/[M ₁])	M _{n (SEC)}	Ð
0	0	-	-	-
0.5	0	-	-	-
1	0	-	-	-
2	0	-	-	-
4	11	0.113	9300	1.09
6	20	0.227	14400	1.07
24	25	0.285	23400	1.10



Figure S22: Kinetic and SEC analysis of polystyrene with target DP800 prepared via Cu(0)-RDRPinbulk,underthefollowingreactionconditions[MBPA]:[S]:[CuBr_2]:[Me_6Tren]=[1]:[800]:[0.05]:[0.18].