Achieving Molecular Weight Distribution Shape Control and Broad Dispersities using RAFT Polymerizations

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Experimental Section

Materials

Unless otherwise noted, all reactions were performed in a Unilab MBraun Glovebox with a nitrogen atmosphere. Methanol (MeOH, 99.8%, Fisher Scientific) was used without further purification. Toluene (>99%, J.T. Baker) and dichloromethane (DCM, >99%, J.T. Baker) were purified by purging with argon for 1 h, followed by passing through two packed columns of neutral alumina under argon pressure. DCM was further purified by distilling over 4Å molecular sieves followed by degassing using 3 freeze pump thaw cycles. DCM was then stored under nitrogen in the glovebox. Azobisisobutyronitrile (AIBN, 98%, Millipore Sigma) was purified by recrystallization from MeOH. 2-Cyano-2-propyl benzodithioate (CTA 1, >97%, Millipore Sigma) and ferrocenium tetrafluoroborate (FcBF4, 97%, Millipore Sigma) were used as received. Methyl methacrylate (MMA, 99%, Millipore Sigma) and benzyl methacrylate (BMA, 96%, Millipore Sigma) were filtered over basic alumina (Oakwood Chemicals) and degassed by three freeze-pump-thaw cycles. Isobutyl vinyl ether (IBVE, 99%, TCI) was dried over calcium hydride (CaH₂, ACROS organics, 93% extra pure, 0-2 mm grain size) for 12 h, distilled under vacuum, and degassed by three freeze-pump-thaw cycles.

Analytical Methods

All polymer samples were analyzed using a Tosoh EcoSec HLC 9320GPC system with two SuperHM-M columns in a series at a flow rate of 0.350 mL/min. Tetrahydrofuran (THF) was used as the eluent and all dispersities (D) and asymmetry factors (A_s) were calculated from refractive index chromatograms against TSKgel polystyrene standards. All homopolymer number-average molecular weights (M_n) were determined by light scattering using a Wyatt miniDawn Treos multi-angle light scattering detector and calculated dn/dc values (0.0812 mL g⁻¹ for PMMA and 0.0381 mL g⁻¹ for PIBVE). Conversions were determined by proton nuclear magnetic resonance (¹H NMR) spectra obtained on a Bruker 500 MHz spectrometer in CDCl₃. The M_n for the PMMA_{broad}-*b*-PBMA diblock copolymer was calculated from ¹H NMR data.

Synthesis

Representative Procedure for Synthesis of Narrow PMMA via Radical RAFT Polymerization.

A 20 mL scintillation vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 1.0 mL of MMA (9.35 mmol), 0.75 mL of a 0.0125 M stock solution of AIBN in toluene (9.35 μ mol), and 0.69 mL of a 0.068 M stock solution of CTA 1 in toluene (0.047 mmol). The reaction was placed in a heating block equipped with a thermocouple. The reaction was heated to 90 °C until ~60% conversion of MMA to PMMA was reached (6.5 h). The reaction vial was removed from the glovebox and the polymerization was terminated by rapidly cooling the reaction vial with an ice bath.

Representative Procedure for Synthesis of Broad PMMA via Radical RAFT Polymerization.

A 20 mL scintillation vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 1.0 mL of MMA (9.35 mmol) and 0.75 mL of a 0.0125 M stock solution of AIBN in toluene (9.35 μ mol). 0.69 mL of a 0.068 M stock solution of CTA 1 in toluene

(0.047 mmol) was drawn into a 1 mL syringe and mounted onto a New Era NE-4000 Double Syringe Pump. The pump was programmed according to the appropriate rate profile (Tables S1-S5). The needle was submerged into the reaction solution, the reaction vial was placed in a heating block equipped with a thermocouple, and the temperature was set to 90 °C. As soon as the vial was warm to touch, the addition program was started. The reaction was stirred at 90 °C until ~60% conversion of MMA to PMMA was reached (~6 h). The reaction vial was removed from the glovebox and the polymerization was terminated by rapidly cooling the reaction vial with an ice bath.

PMMA_{broad}-b-PBMA via Radical RAFT Polymerization.

This polymerization was performed in a hood using a Schlenk line. The PMMAbroad macro-CTA $(M_n = 12.0 \text{ kg/mol})$ was crashed out of MeOH and dried under vacuum at 40 °C for 12 h. A 0.015 M stock solution of the macro-CTA in toluene was prepared. A 20 mL scintillation vial capped with a screw-cap septa and equipped with a magnetic stir bar was flame dried under vacuum and charged with 0.68 mL of the macro-CTA stock solution (0.01 mmol), 0.16 mL of a 0.0125 M stock solution of AIBN in toluene (0.002 mmol), and 0.54 mL of BMA (3.42 mmol). The reaction mixture was degassed by three freeze-pump-thaw cycles and then placed under nitrogen. The reaction was heated to 90 °C under a nitrogen headspace for 5 h (~43% conversion of BMA to PBMA). The polymerization was terminated by rapidly cooling the reaction vial with an ice bath.

Representative Procedure for Synthesis of Narrow PIBVE via Cationic RAFT Polymerization.

A 3 mL dram vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 0.13 mL of IBVE (1 mmol), 0.1 mL of a 2 mM stock solution of FcBF₄ in DCM (0.02 mol%, 0.2 μ mol), and 0.5 mL of a 0.02 M stock solution of CTA **2** in DCM (0.1 mmol). The reaction was allowed to stir for 5 h (~100% conversion of IBVE to PIBVE) and terminated by opening the reaction vial to air and diluting with DCM outside of the box. Aliquots were taken for GPC and ¹H NMR. The polymer could be isolated by crashing out in cold methanol and drying at 50 °C under vacuum until constant mass is achieved.

Representative Procedure for Synthesis of Broad PIBVE via Cationic RAFT Polymerization.

A 3 mL dram vial equipped with a magnetic stir bar was flame dried, brought into the glovebox, and charged with 0.13 mL of IBVE (1 mmol) and capped with a PTFE septum. 0.5 mL of a 0.01 M stock solution of CTA 2 in DCM (0.1 mmol) was drawn into a 1 mL syringe and mounted onto a New Era NE-4000 Double Syringe Pump. The pump was programmed according to the appropriate rate profile (Tables S6-S8). Upon starting the addition of CTA 2, 0.1 mL of a 2 mM stock solution of FcBF₄ in DCM (0.2 μ mol) was injected through the septa. The reaction was allowed to stir for 5 h (~100% conversion of IBVE to PIBVE) and terminated by opening the reaction vial to air and diluting with DCM outside of the box. Aliquots were taken for GPC and ¹H NMR. The polymer could be isolated by crashing out in cold methanol and drying at 50 °C under vacuum until constant mass is achieved.

Reagent Quantities and Addition Rates of CTA for Skewed Polymers

Radical RAFT Polymerization

Entry	MMA, AIBN Volumes (mL)	Addition Time CTA 1 (h)	Addition Rate CTA 1 (μL/h)	Total Volume CTA 1 (μL)	Molarity CTA 1 Stock Solution (mol/L)
1	1.0, 0.75	0.0		690	0.068
2	1.0, 0.75	0.5	1380	690	0.068
3	1.0, 0.75	1.0	690	690	0.068
4	1.0, 0.75	2.0	345	690	0.068
5	1.0, 0.75	2.5	366	914	0.051

Table S1. Preparation of PMMA Entries 2-5 using Constant Rates of CTA 1 Addition

Reagent	Step #	1	Addition Rate		Volume
Volume			CTA 1		CTA 1
(mL)			(µL/h)		(µL)/Step
MMA = 1.0		Entry 6	Entry 7	Entry 8	[CTA 1] =
AIBN = 0.75		0.25 h	0.5 h	1.0 h	0.068 M
	1	193	97	48	2.4
	2	483	232	116	5.8
	3	733	367	183	9.2
	4	1004	502	251	13
	5	1274	637	318	16
	6	1544	772	385	19
	7	1814	907	453	23
	8	2084	1042	520	26
	9	2355	1177	588	29
	10	2625	1312	655	33
	11	2895	1448	723	36
	12	3165	1583	790	40
	13	3436	1718	858	43
	14	3706	1853	925	46
	15	3976	1988	992	50
	16	4246	2123	1060	53
	17	4516	2258	1127	56
	18	4787	2393	1195	60
	19	5057	2528	1262	63
	20	5327	2663	1330	67

Table S2. Preparation of PMMA Entries 6-8 using Linearly Increasing Rates of CTA 1 Addition

Reagent	Step #	Addition Rate	Volume		
Volumes		CTA 1	CTA 1		
(mL)		(μL/h)	(µL)/Step		
MMA = 0.7			[CTA 1] =		
AIBN = 0.53		1.1 h	0.054 M		
	1	40	2.2		
	2	95	5.2		
	3	151	8.2		
	4	207	11		
	5	262	14		
	6	318	17		
	7	374	20		
	8	429	23		
	9	484	26		
	10	541	29		
	11	596	32		
	12	652	35		
	13	707	38		
	14	763	41		
	15	819	44		
	16	874	47		
	17	930	50		
	18	986	53		
	19	1041	56		
	20	1097	59		

Table S3. Preparation of PMMA Entry 9 using a Linearly Increasing Rate of CTA 1 Addition

Reagent	Step #	Addition Rate	Volume		
Volumes		CTA 1	CTA 1		
(mL)		(μL/h)	(µL)/Step		
MMA = 0.7			[CTA 1] =		
AIBN = 0.53		1.25 h	0.037 M		
	1	49	3.1		
	2	118	7.4		
	3	188	12		
	4	257	16		
	5	326	20		
	6	395	25		
	7	464	29		
	8	533	33		
	9	602	38		
	10	671	42		
	11	740	46		
	12	809	51		
	13	878	55		
	14	947	59		
	15	1016	64		
	16	1086	68		
	17	1155	72		
	18	1224	76		
	19	1293	81		
	20	1362	85		

Table S4. Preparation of PMMA Entry 10 using a Linearly Increasing Rate of CTA 1 Addition

Reagent	Step #	Addition Rate	Volume
Volumes		CTA 1	CTA 1
(mL)		(μL/h)	(µL)/Step
MMA = 1.0			[CTA 1] =
AIBN = 0.75		2.0 h	0.068 M
	1	3.3	0.3
	2	4.6	0.5
	3	6.5	0.6
	4	9.0	0.9
	5	13	1.3
	6	18	1.8
	7	25	2.5
	8	35	3.5
	9	49	4.9
	10	68	6.8
	11	95	9.5
	12	134	13
	13	187	19
	14	262	26
	15	366	37
	16	513	51
	17	718	72
	18	1005	101
	19	1408	141
	20	1971	197

Table S5. Preparation of PMMA using an Exponentially Increasing Rate of CTA 1 Addition

Cationic RAFT Polymerization

Entry	IBVE (mL), FcBF4 (mol %)	Addition Time	Addition Rate	Total Volume
		CTA 2 (h)	CTA 2 (μL/h)	CTA 2 (μL)
11	0.13, 0.02	0.0	-	500
12	0.13, 0.02	1.0	500	500
13	0.13, 0.02	1.5	333	500
14	0.13, 0.02	2.0	250	500

Table S6. Preparation of PIBVE Entries 11-14 using Constant Rates of CTA 2 Addition

Reagent	Step #	Addition Rate	Volume
Volumes		CTA 2	CTA 2
(mL)		(μL/h)	(µL)/Step
IBVE = 0.13			[CTA 2] =
$FcBF_4 = 0.1$		2.0 h	0.02 M
	1	17	2
	2	42	4
	3	66	7
	4	91	9
	5	115	12
	6	140	14
	7	164	16
	8	189	19
	9	213	21
	10	238	24
	11	262	26
	12	287	29
	13	311	31
	14	336	34
	15	360	36
	16	385	38
	17	409	41
	18	434	43
	19	458	46
	20	483	48

Table S7. Preparation of PIBVE using a Linearly Increasing Rate of CTA 2 Addition

Reagent	Step #	Addition Rate	Volume
Volumes		CTA 2	CTA 2
(mL)		(μL/h)	(µL)/Step
IBVE = 0.13			[CTA 2] =
$FcBF_4 = 0.1$		2.0 h	0.02 M
	1	2.4	0.24
	2	3.6	0.35
	3	4.7	0.47
	4	6.6	0.66
	5	9.2	0.92
	6	12.9	1.3
	7	18	1.8
	8	25	2.5
	9	35	3.5
	10	49	4.9
	11	69	6.9
	12	97	9.7
	13	136	14
	14	190	19
	15	266	27
	16	372	37
	17	521	52
	18	730	73
	19	1022	102
	20	1430	143

Table S8. Preparation of PIBVE using an Exponentially Increasing Rate of CTA 2 Addition

Entry ^a	Addition Type, Time (h) ^b	Reaction Time (h)	Conversion (%) ^c	M ^{ntheo} (kg/mol) ^c	M ^{exp} (kg/mol) ^d	${oldsymbol{ar{D}}}^{ m d}$	A_{s}^{d}	α ₃ ^e
1	I, 0	6.5	59.7	11.9	10.3	1.17	1.53	-0.24
2	C, 0.5	5.0	62.5	12.5	10.4	2.04	0.55	7.83
3	C, 1.0	5.5	60.6	12.1	9.8	2.03	1.28	2.81
4	C, 2.0	6.3	51.6	10.3	13.0	2.87	1.46	3.19
5	C, 2.5	5.0	61.7	12.3	12.0	1.47	3.51	3.26
6	LI, 0.25	6.0	59.3	11.8	10.3	2.07	0.68	6.72
7	LI, 0.50	6.3	59.0	11.8	10.1	2.61	0.37	8.30
8	LI, 1.0	5.3	56.7	11.3	11.1	3.52	0.35	8.25
9	LI, 1.1	6.3	54.8	10.9	7.3	5.51	0.43	11.18
10	LI, 1.25	5.0	55.9	11.1	7.7	6.23	0.69	9.66
11	I, 0	5.0	100	10.0	12.7	1.22	1.35	1.70
12	I, 1.0	5.0	90	9.0	11.1	1.29	1.32	1.45
13	I, 1.5	5.0	100	10.0	12.9	1.78	1.70	2.85
14	I. 2.0	5.0	100	10.0	11.3	1.98	2.20	1.85

Table S9. Summary of Polymerization Results

^aRed cells indicate radical RAFT and blue cells indicate cationic RAFT. ^bI = instantaneous, C = constant, LI = linearly increasing. ^cDetermined from ¹H NMR spectra. ^dDetermined from RI GPC relative to PS standards. ^cCalculated from LS values of M_n , M_w , and M_z using equation 1, according to the method described by Rudin.¹

Supplemental Figures and Equations



Figure S1. Comparison of GPC traces for PMMA produced using a (a) 2.5 h or (b) 3 h constant rate of CTA 1 addition.



Figure S2. Exponentially increasing rate of CTA 1 addition produces PMMA having a bimodal MWD.



Figure S3. 500 MHz ¹H NMR spectrum of PMMA_{broad}-*b*-PBMA displaying relevant equations for calculating conversion, M_n^{theo} , and M_n^{exp} .



b.

Figure S4. Bimodal MWDs produced from (a) a linearly increasing rate and (b) an exponentially increasing rate of CTA **2** addition in the redox-initiated cationic polymerization of IBVE.



Figure S5. Depiction of Asymmetry Factor Calculation

Equation 1. Calculation of Skewness (α_3):

a.

$$\alpha_3 = \frac{M_Z M_w M_n - 3M_n^2 M_w + 2M_n^3}{(M_w M_n - M_n^2)^{3/2}}$$

References

1. Rudin, A. Molecular Weight Distributions of Polymers. J. Chem. Educ. 1969, 46, 595-600.