Supporting Information

Effect of Radical Copolymerization of the (Oxa)norbornene End-group of RAFT-prepared Macromonomers on Bottlebrush Copolymer Synthesis via ROMP

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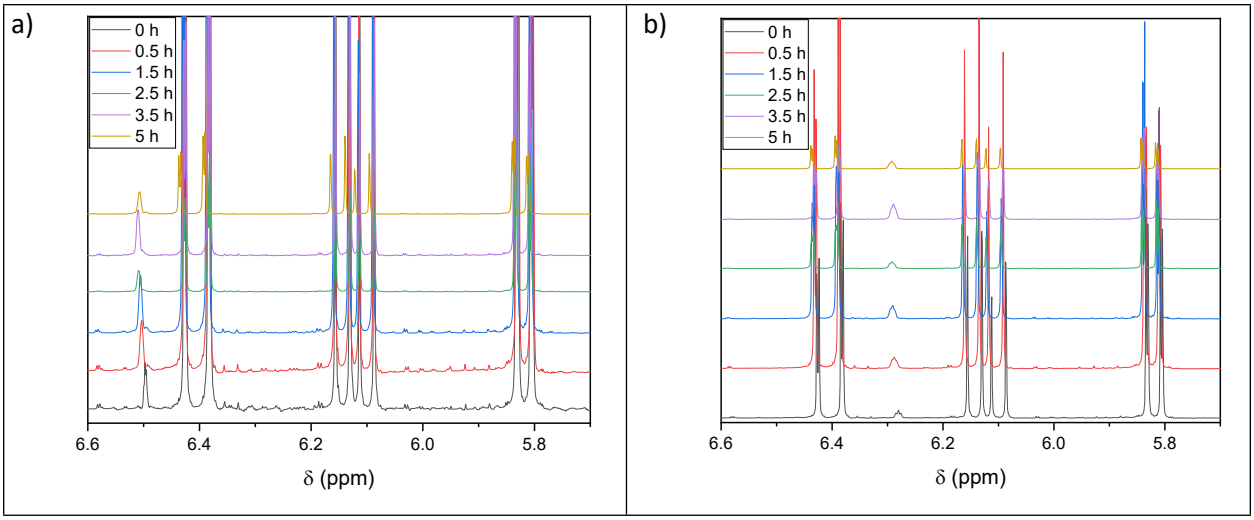


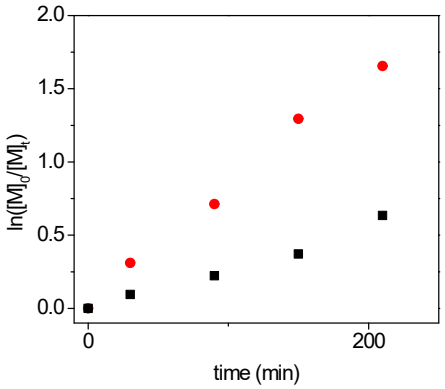
Figure S1: Representative stacked ^{1}H NMR plots for illustrating the resolved vinylic resonances for the methyl acrylate and (a) oxanorbornene (~6.50 ppm) and (b) norbornene (~6.28 ppm) end-groups for experiments reported in Figure 1, and Table1, Entries 1 and 2.

Table S1: Details of polymers prepared via RAFT Polymerization

Entry	monomer	[M] (mol L^{-1})	RAFT agent	T (°C)	$[M]_0$:$[RAFT]_0$:$[AIBN]_0$	time (h)	M conv. (%)[a]	M_n(calc)[b]	M_n[c]	$Đ$[c]	L% (ω-end)[d]	DB% (NMR)[a,e]	DB % (SEC)[e,f]
1	MA	6.79	**7-ONb**	60	200:1:0.1	0.5	22	3960	5900	1.16	99.9	9	5.2
						1.5	51	9320	12500	1.24	99.6	20	17.6
						2.5	73	13100	18800	1.36	99.4	31	28.8
						3.5	81	14500	22500	1.50	99.2	47	37.8
						5	88	15700	25700	1.68	98.9	62	44.3
2	MA	6.79	**8-Nb**	60	200:1:0.1	0.5	6	1570	1400	1.18	99.9	1	0
						1.5	39	7260	7900	1.12	99.6	10	2.6
						2.5	74	13300	15300	1.20	99.4	17	11.5
						3.5	82	14700	18000	1.23	99.2	23	13.7
						5	88	15700	19400	1.30	98.9	26	19.6
3	BA	4.68	**7-ONb**	60	200:1:0.1	0.5	32	8740	10100	1.24	99.9	13	5.8
						1.5	60	15900	20900	1.41	99.6	27	24.0
						2.5	73	19300	28100	1.46	99.4	39	33.4
						3.5	77	20300	32600	1.56	99.2	42	38.9
						4.5	82	21600	35900	1.67	99.0	46	43.4
						6	88	23100	37300	1.75	98.7	51	47.5
4	BA	4.68	**8-Nb**	60	200:1:0.1	0.5	19	5410	5400	1.19	99.9	6	0
						1.5	55	14600	16400	1.17	99.6	19	6.2
						2.5	72	19000	21400	1.22	99.4	21	10.7
						3.5	79	20800	23700	1.27	99.2	24	14.5
						4.5	84	22100	26200	1.28	99.0	27	17.4
						6	89	23400	28200	1.32	98.7	29	20.6
5	St	8.73	**7-ONb**	65	250:1:0.1	2	3	1300	1900	1.20	99.1	6	0.7
						4	9	2900	3400	1.19	98.3	9	1.9
						7	16	4700	5600	1.22	97.4	12	7.4
						10	23	6500	7400	1.24	96.6	16	12.5
						22.5	39	10700	13800	1.43	94.7	34	31.1
						34	50	13600	18000	1.64	94.0	39	43.6
6	St	8.73	**8-Nb**	65	250:1:0.1	2	4	1580	1900	1.18	99.1	0	1
						4	9	2880	3300	1.16	98.3	0	0
						7	17	4970	5300	1.12	97.4	0	0
						10	23	6530	6800	1.12	96.6	1	0
						22.5	43	11700	10900	1.12	94.7	1	0
						34	51	13800	12900	1.14	94.0	1	1.6

[a]Calculated from ^{1}H NMR; [b]M_n(calc) = $([M]_0 - [M]_t)/([RAFT]_0) \times MW_{monomer} + MW_{RAFT}$; [c]SEC THF eluent, T = 40°C (data reported in polystyrene equivalents); [d]L%= $([CTA]_0/([CTA]_0 + df \times [I]_0 \times 1\text{-}e^{k_d t}) \times 100\%$,[1-2] where f is the initiator efficiency (= 0.7),[3]d is number of chains formed by radical-radical termination (= 1),[4]and k_d = 9.67×10^{-6} s^{-1}at 60°C[5]or k_d = 1.95×10^{-5} s^{-1}at 65°C (calculated from Arrhenius parameters)[5]; [e]DB% = percentage degree of branching; [f]calculated following deconvolution of SEC chromatograms.

a)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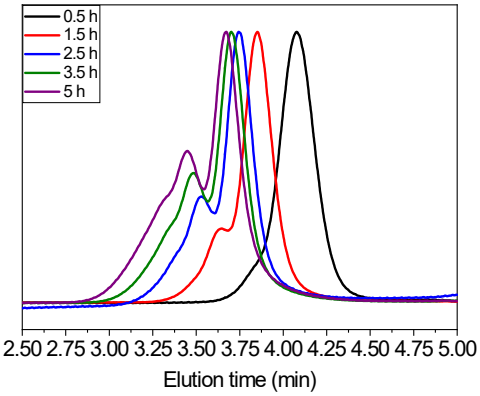
1.5
1.0
0.5
0.0
ln([M]0/[M]t)
0
200
time (min)


0.5 h
1.5 h
2.5 h
3.5 h
5 h
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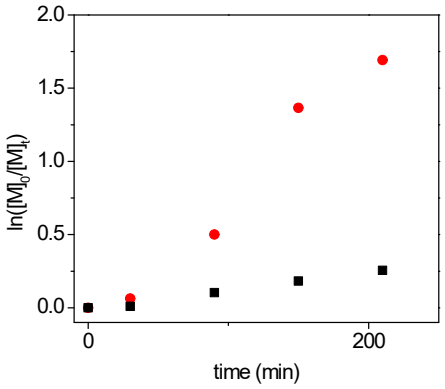
Elution time (min)

b)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1.5
1.0
0.5
0.0
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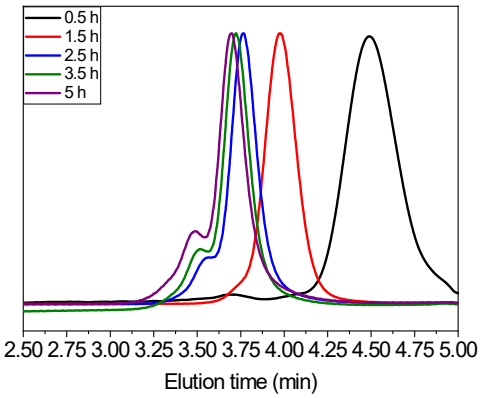
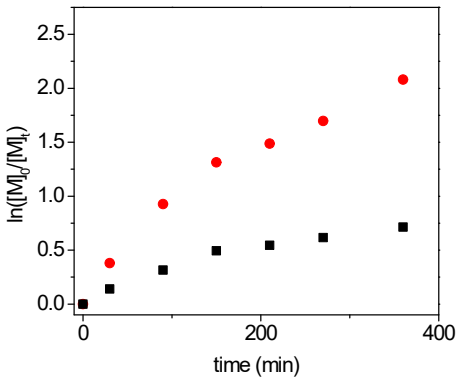
0
200
time (min)


0.5 h
1.5 h
2.5 h
3.5 h
5 h
2.50 2.75 3.00 3.25 3.50 3.75 4.00 4.25 4.50 4.75 5.00
Elution time (min)

c)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1.5
1.0
0.5
0.0
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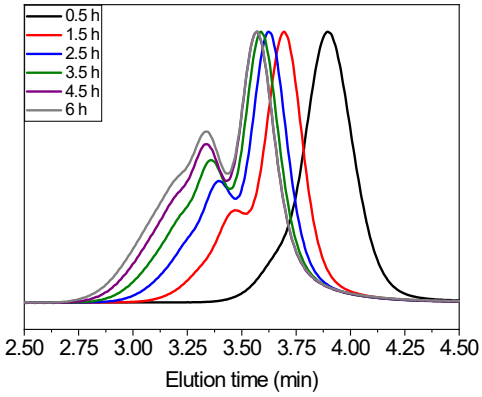
0
200
400
time (min)


0.5 h
1.5 h
2.5 h
3.5 h
4.5 h
6 h
2.50 2.75 3.00 3.25 3.50 3.75 4.00 4.25 4.50
Elution time (min)

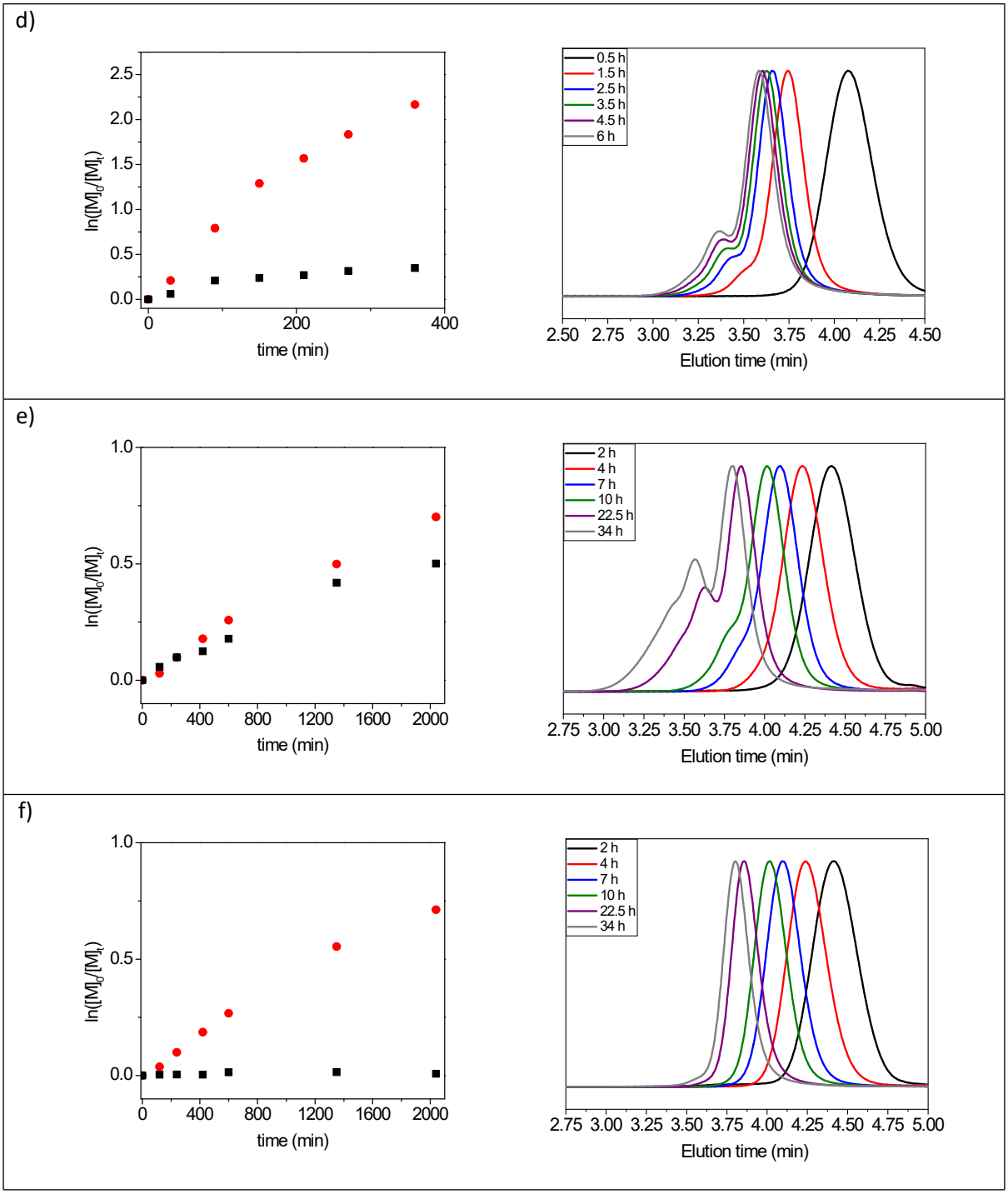


Figure S2: Pseudo-first order kinetics plots (left) for conversion of monomer (red circles) and (oxa)norbornene end-group (black squares), and SEC chromatograms illustrating the evolution of the molar mass distribution with reaction time (right) for polymerizations of MA (a, b), BA (c,d) and St (e,f) with the RAFT agents **7**-**ONb** (a,c,e) or **8-Nb** (b,d,f). Polymerizations of MA and BA performed with [M]:[RAFT] = 200:1; polymerizations of St performed with [M]:[RAFT] = 250:1.

Table S2: Details of DP 50 targeted bottlebrush polymers prepared via ROMP

Entry[a]	Macromonomer (MM)	MMM_n (g mol^{-1})[b]	Residual MM %	M_n(GPC) (g mol^{-1})[c]	$Đ$[c]
1	**PMA-7-ONb**	2700	15	>197000[d]	>1.49[d]
2	**PMA-8-Nb**	3100	5	187000	1.45
3	**PBA-7-ONb**	4300	54	>219000[d]	>1.36[d]
4	**PBA-8-Nb**	3200	4	198000	1.36
5	**PSt-7-ONb**	2900	15	66000	1.54
6	**PSt-8-Nb**	2800	5	>114000[d]	>1.77[d]

[a][MM] = 0.33M in THF, [MM]/[G3]=50, t = 3 h, [b]Calculated from ^{1}H NMR; [c]From SEC THF eluent, T = 40°C (data reported in polystyrene equivalents);[d]peak truncated due to the sample reaching the exclusion limit of the SEC column

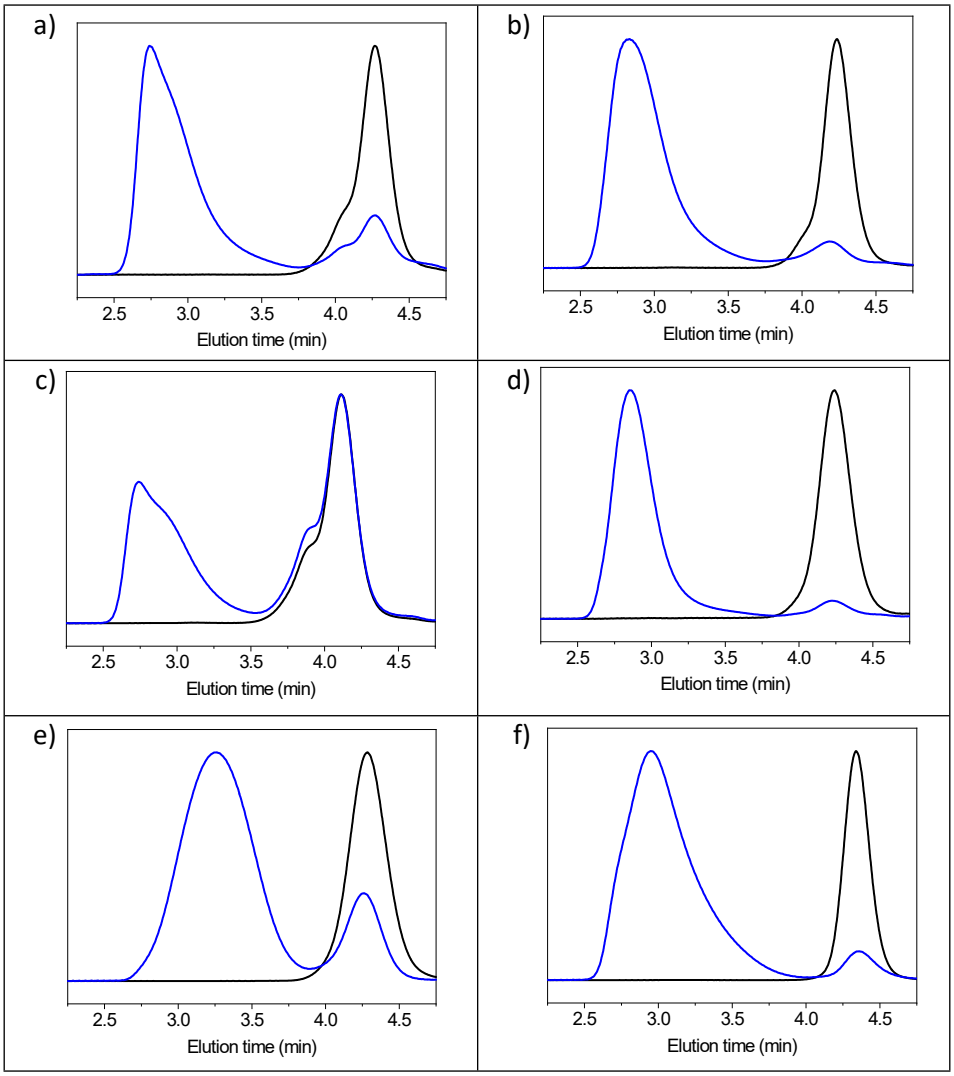


Figure S3: SEC chromatograms of macromonomers (black) and bottlebrush copolymers (blue) for polymerizations of (a) **PMA-7-ONb**, (b) **PMA-8-Nb**, (c) **PBA-7-ONb**, (d) **PBA-8-Nb**, (e) **PSt-7-ONb** and (f) **PBA-8-Nb**. Polymerization were performed at: [Macromonomer]:[G3] = 50:1.

References

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