

Supporting information for

**Improved Photo-Induced Cobalt-Mediated Radical Polymerization in Continuous Flow
Photoreactors**

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Table S1. CMRP of VAc conducted in a 2 mL continuous flow-reactor.

Entry	Conditions ^a	Time (h)	Conv (%) ^b	M_{nSEC}^c (g/mol)	M_w/M_n^c
1	40 °C	1	4	2500	1.06
		2	7	3900	1.12
		4	15	9200	1.09
		8	25	16200	1.21
2	40 °C + UV	0.33	10	5.700	1.09
		0.66	23	9.800	1.24
		1	30	14200	1.28
		2	53	17500	1.50

^aConditions: VAc/Co-R molar ratio of 529/1 using a 2 mL reactor in 20% VAc solution in EtOAc, UV irradiation using 200 W lamp; ^b VAc conversion determined by ¹H NMR; ^c M_n and M_w/M_n determined by SEC-THF using PS cal.

Table S2. CMRP of VAc performed at 40 °C in bulk or in solution in EtOAc (20%)

Entry	Conditions ^a	Time (h)	Conv (%) ^b	M_{nSEC}^c (g/mol)	M_w/M_n^c
1	bulk	1	3	2200	1.09
		2	7	4100	1.05
		4	15	7000	1.07
		6	22	10200	1.09
		8	28	13600	1.10
		10	33	16300	1.13
2	EtOAc solution	1.5	1	2250	1.05
		4.5	4	4700	1.05
		8	8	6400	1.04
		10	10	7800	1.06
		24	20	14400	1.19
		30	26	18500	1.33

^a Conditions: VAc/Co-R molar ratio of 529/1, in bulk using 5 mL of VAc (54.2 mmol) and 2.4 mL of R-Co(acac)₂ solution in CH₂Cl₂ (0.10 mmol) under argon, in 20% VAc solution in EtOAc using 1 mL of VAc (10.8 mmol), 4 mL of EtOAc and 0.5 mL of R-Co(acac)₂ solution in CH₂Cl₂ (0.02 mmol) under argon; ^b VAc conversion determined by ¹H NMR; ^c M_n and M_w/M_n determined by SEC-THF using PS cal.

Table S3. CMRP of VAc conducted in a 19.5 μ L flow microreactor.

Entry	Conditions ^a	Time (min)	Conv (%) ^b	M_{nSEC}^c (g/mol)	M_w/M_n^c
1	60 °C	1	1	1300	1.09
		2.5	3	2300	1.05
		5	9	3800	1.04
		10	14	6100	1.10
		20	23	8900	1.11
2	80 °C	1	5	3700	1.04
		2.5	13	5800	1.06
		5	20	8800	1.10
		10	36	13000	1.29
		20	68	17500	1.64
3	100 °C	0.25	5	4600	1.07
		0.5	9	6000	1.12
		1	16	7900	1.22
		2.5	29	10900	1.59
		5	47	13700	1.70
		10	53	14000	1.68

^a Conditions: VAc/Co-R molar ratio of 529/1 in a 20% VAc solution in EtOAc; ^b VAc conversion determined by ¹H NMR; ^c M_n and M_w/M_n determined by SEC-THF using PS cal.

Table S4. CMRP of VAc conducted in a 19.5 μ L flow microreactor under UV irradiation.

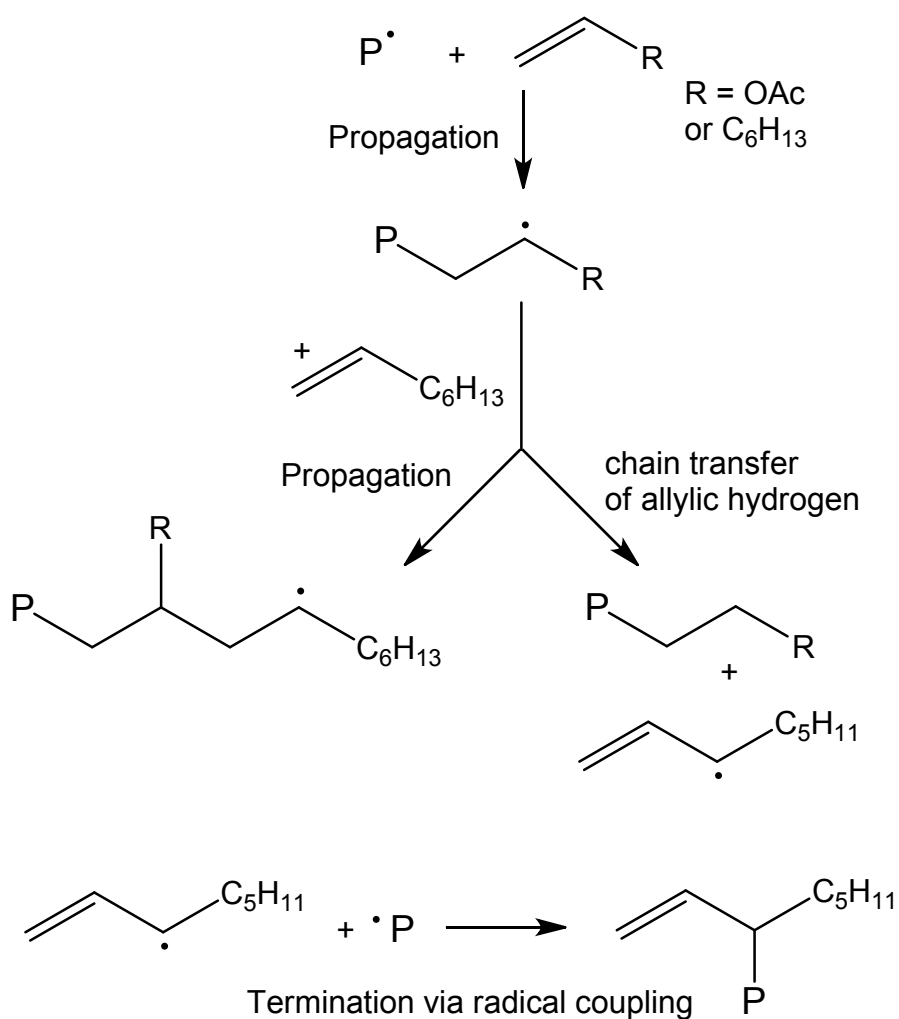
Entry	Conditions ^a	Time (min)	Conv (%) ^b	M_{nSEC}^c (g/mol)	M_w/M_n^c
1	40 °C + UV	1	<1	900	1.15
		2.5	2	1200	1.07
		5	5	1900	1.14
		10	9	4300	1.11
		20	12	6100	1.19
2	60 °C + UV	1	1	2100	1.08
		2.5	4	3300	1.10
		5	9	5500	1.06
		10	18	8300	1.09
		20	31	12600	1.15

^a Conditions: VAc/Co-R molar ratio of 529/1 in a 20% VAc solution in EtOAc using a 100 W UV lamp; ^b VAc conversion determined by ¹H NMR; ^c M_n and M_w/M_n determined by SEC-THF using PS cal.

Table S5. Copolymerization of VAc and 1-Oct in bulk and initiated by R-Co(acac)₂ at 40 °C.^a

Time (h)	VAc Conv (%) ^b	1-Oct Conv (%) ^b	M_{nSEC}^c (g/mol)	M_w/M_n^c	F_{1-Oct}^d
1	6	1	2400	1.09	0.11
3	10	1	3600	1.07	0.10
4.5	11	1	4100	1.08	0.10
6	14	6	4700	1.10	0.10
7.5	15	2	5300	1.12	0.10
10	17	4	6000	1.14	0.10
12	18	3	6700	1.20	0.10
29	28	6	9700	1.43	0.10
36	32	5	9600	1.53	0.11
50	35	7	10100	1.69	0.10
72	38	7	11900	1.83	0.11

^a Conditions: VAc/1-Oct/Co-R molar ratio of 383/127/1 using 5 mL of VAc (54.2 mmol), 2.8 mL of 1-Oct (17.8 mmol) and 0.14 mmol of R-Co(acac)₂ (from a CH₂Cl₂ solution) under argon; ^b monomer conversion determined by ¹H NMR; ^c M_n and M_w/M_n determined by SEC-THF using PS cal.; ^d 1-Oct fraction in copolymer determined by ¹H NMR after elimination of volatiles.



Scheme S1. Competition between propagation, degradative chain transfer of allylic hydrogens and termination via radical coupling reactions occurring during VAc/1-Oct radical copolymerization