

SUPPLEMENTARY MATERIAL

α -Amido Trifluoromethyl Xanthates: a New Class of RAFT/MADIX Agents

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Table S1. Data used to determine transfer constants to xanthates C_{tr} (X) in RAFT/MADIX polymerization of styrene in bulk at 110°C (self-initiation).

Entry	Xanthate	[St] ₀ /[X] ₀	t (min)	Conv (%)	M_n (g/mol)	\bar{D}
1	9	41	90	11.9	2060	2.10
2		80	90	10.1	3550	2.17
3		120	90	13.0	4680	2.26
4		197	90	12.1	6960	2.35
5	10	39	45	12.8	1700	1.85
6		76	60	8.4	2680	2.08
7		96	45	4.3	3560	2.24
8		151	45	7.9	4610	2.29
9	11	38	45	9.7	1980	1.85
10		74	60	11.1	3420	2.11
11		131	45	4.8	5420	2.21
12		160	45	8.1	6360	2.17
13	13	38	30	1.0	980	1.43
14		82	30	1.2	1730	1.68
15		120	30	1.3	2440	1.88
16		178	30	0.9	3800	2.10

Figure S1. Mayo plot for the determination of chain transfer constant to xanthate **9** in styrene polymerization. Conditions of Table S1 (entries 1-4).

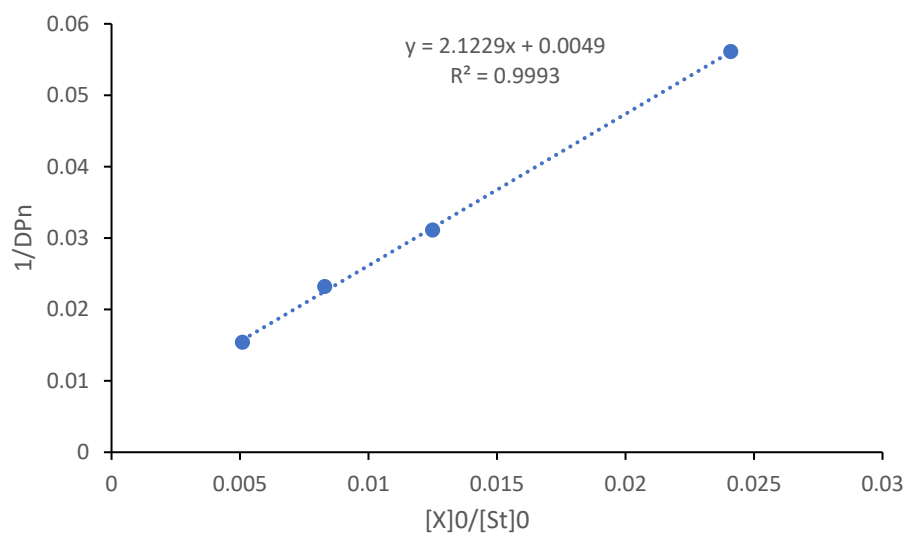


Figure S2. Mayo plot for the determination of chain transfer constant to xanthate **10** in styrene polymerization. Conditions of Table S1 (entries 5-8).

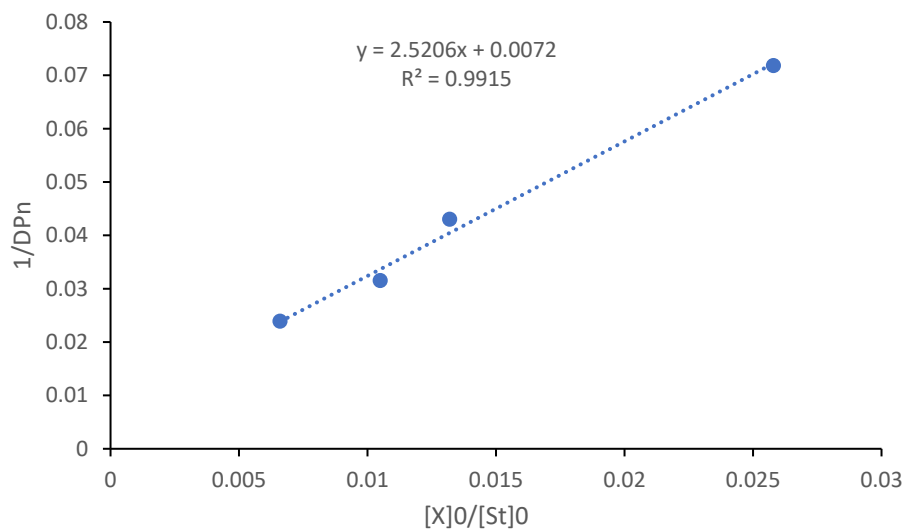


Figure S3. Mayo plot for the determination of chain transfer constant to xanthate **11** in styrene polymerization. Conditions of Table S1 (entries 9-12).

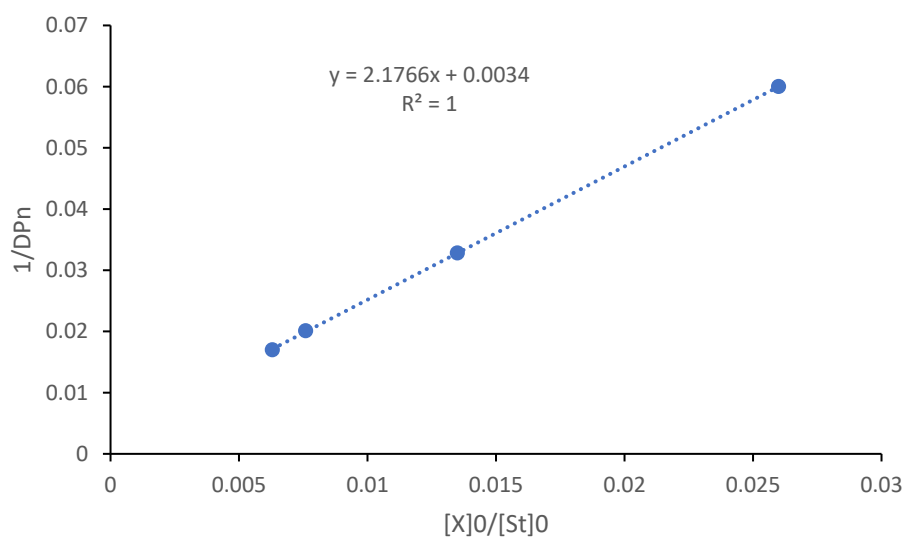


Figure S4. Mayo plot for the determination of chain transfer constant to xanthate **13** in styrene polymerization. Conditions of Table S1 (entries 13-16).

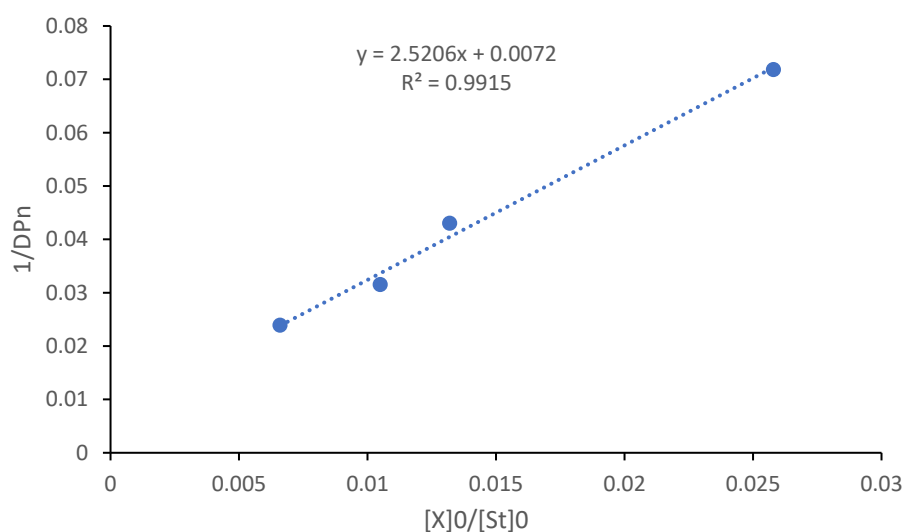


Table S2. **13**- and **14**-mediated RAFT/MADIX polymerization of styrene at 110°C (self-initiation). $[St]_0/[X]_0=80$.

Entry	Xanthate	t (h)	Conv (%)	M_n (g/mol)	$M_{n\ th}$ (g/mol)	\bar{D}
1	13	0.5	0.8	2060	387	1.69
2		1	3.4	3550	601	1.75
3		2	9.6	4680	1119	1.87
4		5	28.3	6960	2690	2.29
5		24	96.0	8220	8361	2.39
6	14	1	4.12	1190	658	1.69
7		2	12.1	1470	1323	1.80
8		5	25.8	2570	2461	1.92
9		24	85.0	6700	7393	1.49

Figure S5. An example of SEC chromatograms during St polymerization in the presence of PSt-14, for a given $[BPO]_0$ at 80°C. Plotting $\ln(S/S_0)$ as a function of time gives access to k_{act} .

