Copper(I) mediated living radical polymerization in the presence of oxyethylene groups: Online ^{1}H NMR spectroscopy to investigate solvent effects

*David M. Haddleton**, *Sébastien Perrier and Stefan A. F. Bon*

Supplementary Information

Full Data set for the polymerization of MeO(PEG)MA; $[M]_0/[I]_0/[Cu(I)Br]_0/[n\text{-Pr-L}]_0$ = 10/1/1/2, toluene solution – see Figure 1 of main paper.

T/K	t/min	Conv.[a]	$\langle Mn\rangle_{th}$	$\langle M_n\rangle^a_{exp}$	$\langle M_n\rangle^b_{exp}$	PDI[b]
298	60	13.2	638		1090	1.41
	120	24.9	1204		1800	1.32
	180	34.4	1664		2500	1.16
	240	37.0	1760	2010	2570	1.08
313	20	13.4	648		1240	1.32
	40	22.3	1078		1600	1.32
	60	26.8	1296		1960	1.28
	120	48.3	2336		3700	1.21
	180	56.8	2747		4200	1.16
	240	64.1	3100		5010	1.14
	300	70.4	3405	3700	5820	1.14
333	20	29.3	1417		2110	1.28
	40	42.2	2041		2700	1.15
	60	56.7	2742		3700	1.16
	120	74.6	3608		4480	1.11
	180	78.9	3816		4700	1.10
	240	90.1	4357		5300	1.14
	300	92.8	4488	4620	5390	1.11
363	20	38.7	1872		2710	1.08
	40	56.0	2708		3690	1.13
	60	68.9	3330		4700	1.07
	120	76.8	3716		5020	1.12
	180	81.7	3950		5200	1.13
	240	85.2	4120	5460	5370	1.12

[a] Determined by the ^{1}H NMR peak intensity ratio
[b] Estimated by PMMA-calibrated SEC.

Fitting Results for the Data set for the polymerization of MeO(PEG)MA in d^8 toluene– see Figure 3 of main paper.

$\ln([M]_0/[M]) = a + bt$

T/ °C	*a*	*b*	r^2	Fit st. error
25	0.22445716	0.001255233	0.9736	0.0591
40	0.13511358	0.004311053	0.9989	0.0215
60	0.10216744	0.006543862	0.9978	0.0282
90[a]	-0.28717	0.0456458	0.9898	0.0770

$\ln([M]_0/[M]) = a + bt^{2/3}$

T/ °C	*a*	*b*	r^2	Fit st. error
25	0.019295006	0.013824547	0.9746	0.0580
40	-0.23409561	0.03834569	0.9884	0.0710
60	-0.26047872	0.049957482	0.9944	0.0449
90[a]	-0.8617699	0.20689868	0.9797	0.0770

[a] Data used up to $\ln([M]_0/[M]) = 2.10$.

Fitting Results for the Data set for the polymerization of BzMA in d^8 toluene (I), using MeO(PEG)I (II) and with 1,2-diethoxy ethane as co-solvent (III)– see Figure 4 of main paper.

$\ln([M]_0/[M]) = a + bt$

	a	*b*	r^2	Fit st. error
I	-0.047467	0.001645	0.9983	0.0120
II	-0.053979	0.002420	0.9994	0.0135
III[a]	-0.087659	0.007309	0.9818	0.1024

$\ln([M]_0/[M]) = a + bt^{2/3}$

	a	*b*	r^2	Fit st. error
I	-0.24981268	0.017024731	0.9751	0.0769
II	-0.37013225	0.024740034	0.9793	0.0821
III	-0.4347114	0.054703005	0.9915	0.1233

[a] Data used up to $\ln([M]_0/[M]) = 2.10$.