Supporting Information

An efficient process for the Cu(0)-mediated synthesis and subsequent chain extension of poly(methyl acrylate) macroinitiator

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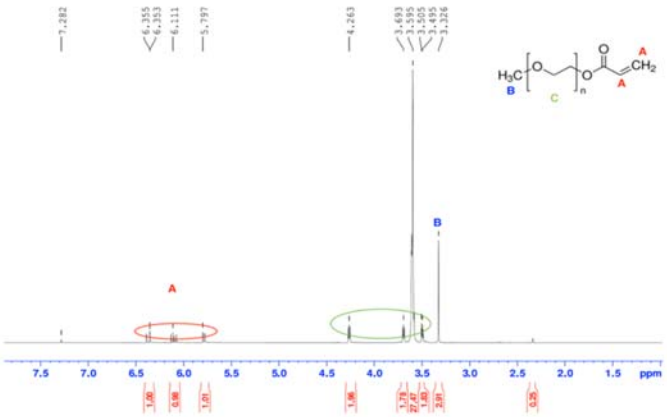
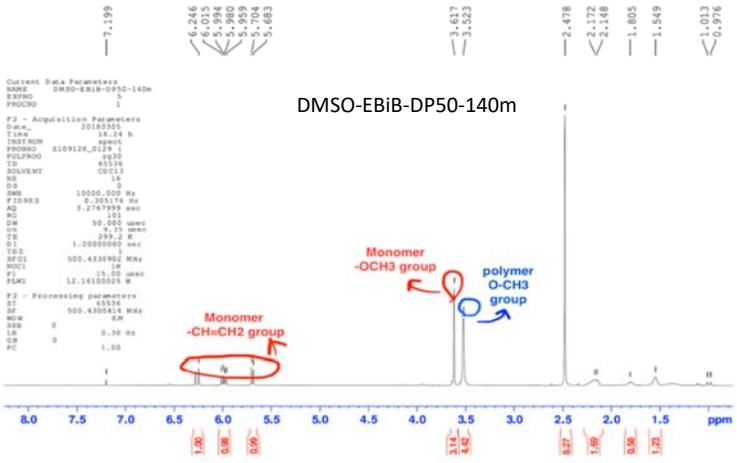
A. Conversion Calculation based on NMR

NMR spectra of poly(ethylene glycol) methyl ether acrylate (M_n=480 g·mol^{-1})



Final conversion of poly(MA)$_{10}$ in DMSO batch system



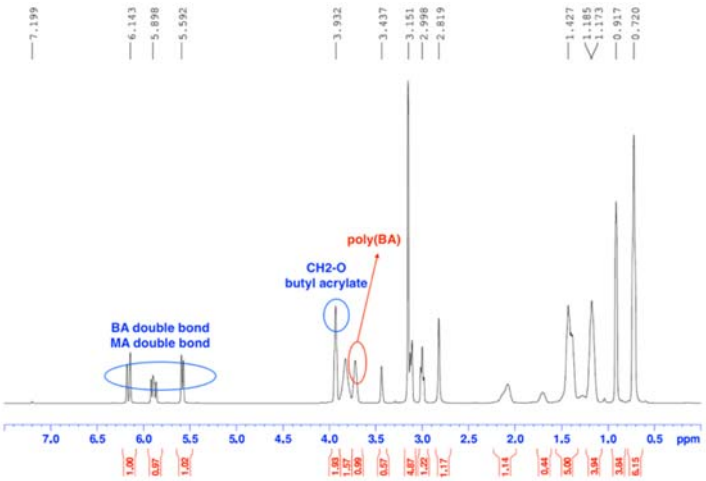
Method #1:

$$conversion = \frac{polymer\ O-CH3\ group\ integral}{polymer\ 0-CH3\ integral + monomer\ O-CH3\ integral} \times 100 = \frac{4.42}{4.42+3.14} \times 100 \approx 58\%$$

Method #2:

$$conversion = \frac{polymer\ O-CH3\ group\ integral}{polymer\ 0-CH3\ integration + sum\ of\ monomer-CH=CH2\ integration} \times 100$$
$$= \frac{4.42}{4.42 + (1 + 0.98 + 0.99)} \times 100 \approx 59\%$$

Conversion of poly(MA_{10}-*block*-BA)$_{90}$ in PGME solvent

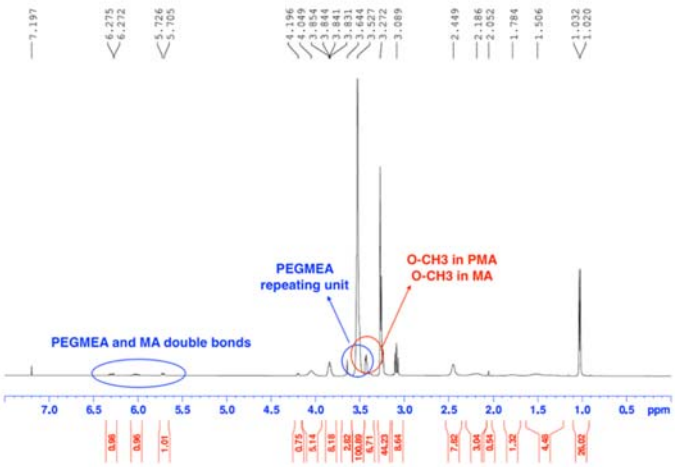


$$conversion = \frac{polymer\ integral}{polymer\ integral + monomer\ O-CH2\ integral} \times 100 = \frac{0.99}{0.99 + 1.93} \times 100 \approx 34\%$$

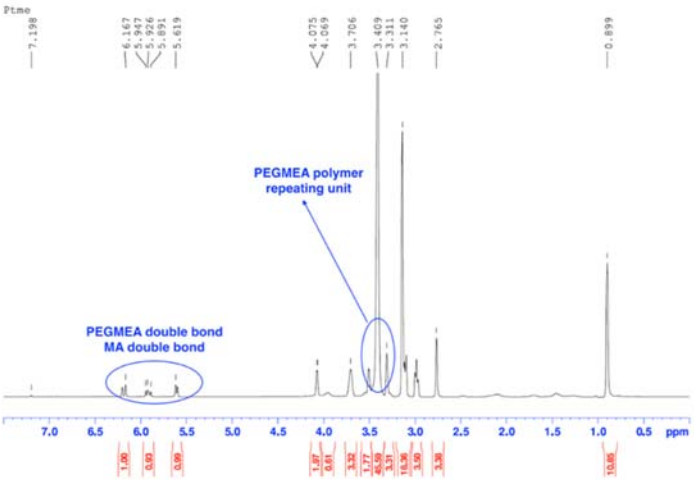
Because BA and MA double bonds peaks are overlapping, second method of conversion calculation cannot be used.

Conversion of poly(MA_{10}-*block*-PEGMEA$_{50}$-*block*-MA_{50}) in PGME semi-batch system

Because the O-CH_3 groups in MA monomer and poly(MA) are overlapping with PEGMEA repeating unit the conversion cannot be calculated by NMR spectra.



Conversion of poly(MA_{10}-block-$PEGMEA_{100}$) in PGME

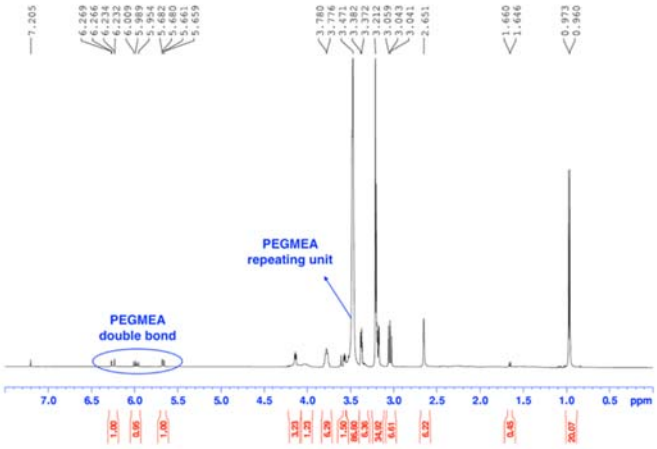


$$\frac{1}{CA} = \frac{1}{CA_0}(1 - Conv.) \quad \rightarrow \quad \frac{1}{chain\ extended\ Polymer\ integral} = \frac{1}{macroinitiator\ \ integral\ (Section\ A\ appendix)}(1 - conv.)$$

$$conv. = (1 - \frac{27.47}{45.59}) \times 100 \approx 39\%$$

Although PEGMEA repeating unit and O-CH_3 group in P(MA) and MA monomer are overlapping, the conversion was calculated by assuming MA monomer and polymer integration (DP10) negligible compared to PEGMEA groups (DP100) at 3.3-3.6 ppm. Thus, the peak in 3.4 ppm was considered as the PEGMEA repeat unit.

Conversion of poly$(PEGMEA)_{10}$ in PGME

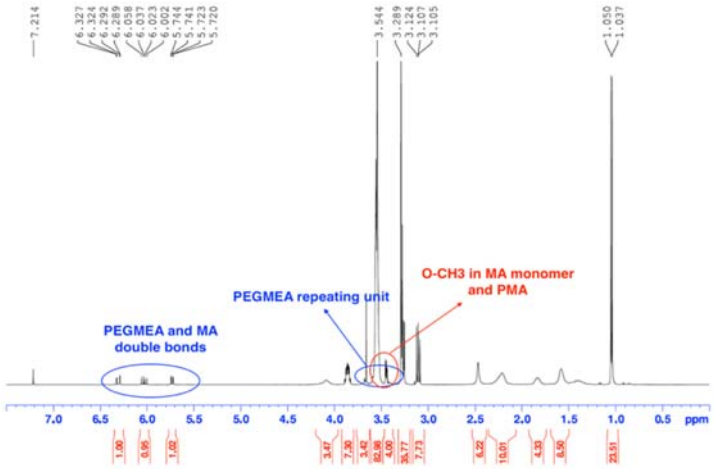


$$\frac{1}{CA} = \frac{1}{CA_0}(1 - Conv.) \quad \rightarrow \quad \frac{1}{chain\ extended\ Polymer\ integral} = \frac{1}{macroinitiator\ \ integral\ (Spectra\ on\ page\ 84)}(1 - conv.)$$

$$conv. = (1 - \frac{27.47}{86.80}) \times 100 \approx 68\%$$

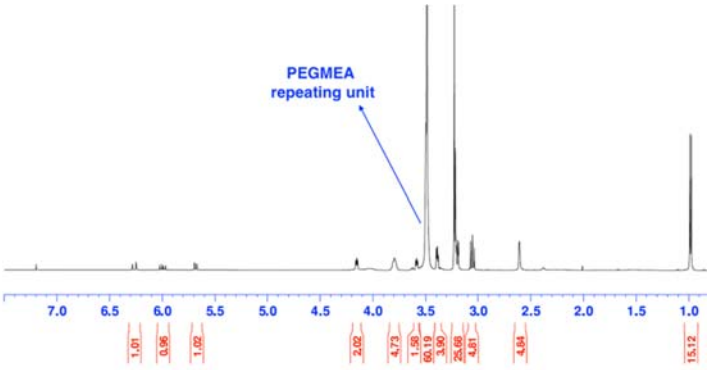
Conversion of poly(PEGMEA$_{10}$-*block*-MA)$_{50}$ in PGME solvent

Because the O-CH_3 groups in MA monomer and poly(MA) overlap with PEGMEA repeat units the conversion cannot be calculated by using just the final NMR spectra. Assuming that in chain extension reaction MA was the only polymer that grow, the conversion can be calculated by subtracting the integral of PEGMEA repeating group in macroinitiator spectra from integral of overlapped area in chain extended spectra:



$$conv. = \frac{82.98 - 60.19}{(82.98 - 60.19) + 3(O - CH3\ in\ MA\ monomer\ )} \approx 88$$

NMR spectra of poly(PEGMEA)$_{10}$ macroinitiator produced in the copper tube



B. Polymerizations and Chain Extensions in Batch Mode.

Experimental : Experiments were done in batch mode to explore the influence of solvent and initiator choice as well as reagent ratios on methyl acrylate polymerization rate and control; in all cases, reactions were conducted at ambient temperature, solvent level was 30 wt%, and 2 g of copper wire wrapped around the stirrer bar was used as the catalyst. EBiB and MBP were used as initiators, DMSO, methanol, PGME and isopropanol were explored as solvents, and target chain length was varied from 10 to 100 by controlling the amount of alkyl halide initiator added, with the amount of Me_6TREN ligand used adjusted to keep the level at 1 mol% relative to initiator. As an example with $[MA]_0$:$[initiator]_0$:$[Me_6TREN]_0$ = 10:1:0.01 (target DP=10), MA (35.0 g, 0.407 mol), Me_6TREN (0.096 g, 0.407 mmol) and solvent (18.8 g) were added to a 100 mL round-bottomed flask containing a stirrer bar wrapped with Cu wire. The system (generally at room temperature in an oil bath, with a few experiments conducted at 50 °C) was purged with N_2 for 30 min, at which point MBP (6.79 g, 40.7 mmol) or EBiB (8.09 g, 40.7 mmol) initiator was injected to the system with a syringe. This action was considered as the start of reaction. Samples (0.1 mL) were withdrawn via syringe at 20 min intervals and added to deuterated chloroform for determination of MA conversion by NMR, shaking well to stop the reaction by exposure to air. The reaction was stopped after 2 h, also by exposure to air. The stirrer bar/Cu wire was removed, with the solution saved without purification for chain extension studies. Samples were analyzed by NMR and, in some cases, by size exclusion

chromatography (SEC), using procedures described in the paper. Results obtained are summarized in Table S1, with discussion presented in the manuscript. Good control (Đ<1.15) was maintained as target chain length was reduced from 100 to 10, with the resulting MMDs shown as Fig. S1(a), and selected conversion profiles shown as Fig. S1(b).

Table S1 Conversions and molar masses (number average and dispersity) of poly(methyl acrylate) formed by Cu(0)-catalyzed batch polymerization after 140 min. Experiments conducted in 30 wt% solvent using EBIB or MBP as initiator and Me_6TREN as ligand for different target chain lengths with initial reactant molar ratios $[MA]_0$:$[Initiator]_0$:$[lig]_0$ set to Target DP:1:0.01, unless otherwise noted.

EXP.	Solvent	Initiator	Target DP	Temp (°C)	Conversion	M_n (g·mol^{-1})	Đ
D1	DMSO	MBP	100	25	82%	8075	1.17
D2	DMSO	EBiB	100	25	81%	7263	1.13
D3	DMSO	EBiB	50	25	72%	3504	1.11
D4	DMSO	EBiB	20	25	76%	1705	1.12
D5	DMSO	EBiB	10	25	81%	873	1.12
M1	Methanol	MBP	100	25	69%	6207	1.10
M2	Methanol	EBiB	100	25	36%	3076	1.12
M3	Methanol	EBiB	50	25	31%	1736	1.09
M4	Methanol	EBiB	20	25	22%	-	-
M5	Methanol	EBiB	10	25	29%	-	-
M6	Methanol [a]	EBiB	10	25	75%	892	1.09
M7	Methanol	EBiB	10	40	20%	-	-
I1	Isopropanol	EBiB	10	25	80%	877	1.14
I2	Isopropanol [a]	EBiB	10	25	96%	1128	1.09
P1	PGME	EBiB	100	25	81%	5909	1.40
P2	PGME [a]	EBiB	100	25	97%	1066	1.11
P3	PGME	EBiB	10	25	91%	976	1.10
P4	PGME	EBiB	10	60	71%	757	1.12

[a] $[MA]_0$:$[EBiB]_0$:$[Me_6TREN]_0$ set to Target DP:1:0.05

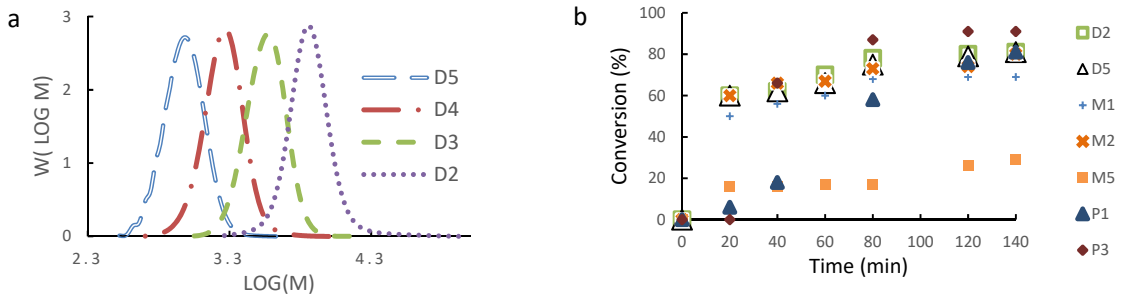


Fig. S1 (a) MMDs of poly(MA) produced in DMSO by batch polymerization over Cu wire at room temperature. (b) Evolution of monomer conversion vs. time for batch methyl acrylate polymerizations in different solvents with various target chains. Experimental details are summarized in Table S1.

Batch chain extensions were conducted at room temperature using poly(MA) macroinitiator solution produced in batch without purification, with additional MA added to increase final target chain length to 100, assuming full conversion. Additional solvent was also added to keep the level at 30 wt%. A series of experiments were performed to determine the amount of reducing agent (Asc) and additional Me_6TREN ligand required for effective chain extension. As an example, 5 g of macroinitiator solution made in batch was added with MA (31.0 g, 0.36 mol) and solvent (10.0 g) to a 100 mL flask and purged with N_2 for 1h; no additional Cu was added to the system. After purging, Me_6TREN (0.011 g, 0.04 mmol) and ascorbic acid (7.0 mg, 0.04 mmol) dissolved in 3 g of solvent were injected with separate syringes to the flask to

start the reaction. The reaction proceeded for 2 h, with samples collected every 20 min. Dispersities remained low as the poly(MA) chains grew from length 10 to 100, and there is no evidence of tailing in the resulting MMDs (Fig. S2). It should be noted that, while the initial macroinitiator (with DP10) solution had a greenish hue, the solution was colorless after chain extension in the presence of Asc. It is also noted that excellent chain extension was achieved using a macroinitiator batch (B0-3) that SEC analysis indicated had a high-MW tail. This last set of batch chain extensions demonstrates the feasibility of storing the macroinitiator solution for an extended period before its use.

Table S2 Batch chain extension of poly(MA) macroinitiator solutions to a target DP of 100 in 30 wt% solvent at room temperature by addition of Me_6TREN ligand and/or ascorbic acid (Asc). CE indicates the chain extended polymers synthesized using the macroinitiator solution B_0 made by batch polymerization using EBiB initiator, with CE molar ratios of components specified relative to macroinitiator chains added.

EXP.	Solvent	Storage Time	$[MA]_0$:$[EBiB]_0$:$[lig]_0$:$[Asc]_0$	Time (min)	Conversion	M_n ($g \cdot mol^{-1}$)	Đ
$B_{0\text{-}1}$	DMSO	-	10:1:0.01:0	140	91%	980	1.11
CE1	DMSO	-	90:0:0.01:0	120	69%	6945	1.05
CE2	DMSO	-	90:0:0:0.01	120	78%	7243	1.09
CE3	DMSO	-	90:0:0.01:0.01	120	84%	7245	1.10
CE4	DMSO	1 day	90:0:0:0.01	120	83%	7979	1.09
CE5	DMSO	1 day	90:0:0.01:0	120	72%	6616	1.05
CE6	DMSO	1 day	90:0:0.01:0.01	120	91%	9041	1.07
$B_{0\text{-}2}$	PGME	-	10:1:0.01:0	140	91%	907	1.11
CE7	PGME	1 day	90:0:0:0.01	120	15%	-	-
CE8	PGME	1 day	90:0:0:0.02	120	15%	-	-
CE9	PGME	1 day	90:0:0.01:0	120	22%	-	-
CE10	PGME	1 day	90:0:0.01:0.01	120	38%	3655	1.12
CE11	PGME	-	90:0:0.02:0.01	120	37%	-	-
CE12	PGME	-	90:0:0.01:0.02	120	51%	5310	1.09
CE13	PGME	1 day	90:0:0.01:0.04	120	72%	7592	1.09
CE14	PGME	2 days	90:0:0.01:0.06	120	84%	8129	1.29
CE 15	PGME	2 days	90:0:0.01:0.07	120	78%	6072	1.16
$B_{0\text{-}3}$	PGME	-	10:1:0.01:0	140	75%	741	1.87
CE 16	PGME	7 days	90:0:0.01:0.06	120	91%	9348	1.15
CE 17	PGME	10 days	90:0:0.01:0.06	120	53%	4049	1.14

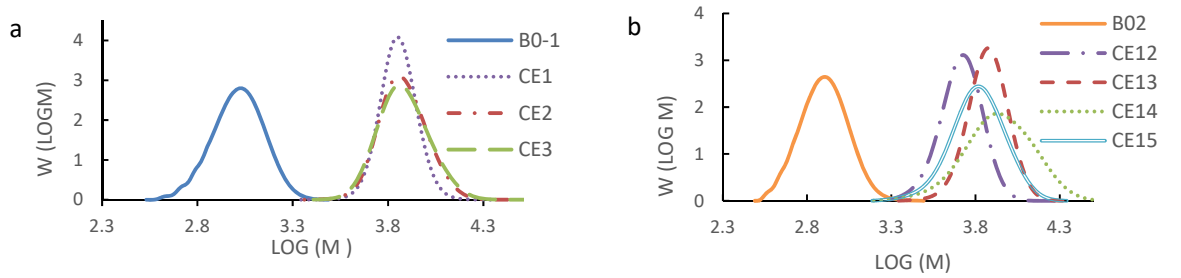


Fig. S2 MMDS of poly(MA) macroinitiator (B0-1; B0-2) after batch chain extension to target DP of 100 in DMSO (CE1-3) and PGME (CE12-CE15); experimental details are summarized in Table S2.