

Supporting information

For

Cu(0)-RDRP of acrylates using an alkyl iodide initiator

Cu(0)-RDRP of acrylates using an alkyl iodide initiator

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Materials

All monomers and solvents (except tetraethylene glycol dimethyl ether) were obtained from Sigma Aldrich. Tetraethylene glycol dimethyl ether was obtained from Tokyo Chemical Industry (TCI). The alkyl iodide initiator, Ethyl 2-Iodo-2-methylpropionate (EIP), was obtained from Tokyo Chemical Industry. Tris-(2-(dimethylamino)ethyl)amine (Me₆Tren) was prepared following literature procedures and vacuum distilled before use.¹ Cu(0) wire with diameter of 0.025 mm, were obtained from Thermo Scientific - Alfa Aesar (ALF). The monomers were purified by passing through a column of basic alumina before being used. Other chemicals were used as received.

¹H NMR spectra were recorded on a Bruker DPX-300 spectrometer in deuterated chloroform (CDCl₃). Chemical shifts are given in ppm downfield from tetramethylsilane referenced to residual CHCl₃ protons. Monomer conversions were determined via proton ¹H-NMR spectroscopy by comparing the integrals of monomeric vinyl protons to monomer and polymer signals.

Size exclusion chromatography (SEC) analysis of polymer samples was performed using a Shimadzu modular system comprising of a CBM-20A system controller, an SIL-20A automatic injector, a 10.0 μm beads size guard column (50 × 7.5 mm) followed by three KF-805L columns (300 × 8 mm, bead size: 10 μm, pore size maximum: 5000 Å), an SPD-20A ultraviolet detector, and an RID-20A differential refractive-index detector. The temperature of the columns was maintained at 40 °C using a CTO-20A oven. The eluent was N,N-dimethylacetamide (HPLC grade, with 0.03% w/v LiBr) and the flow rate was kept at 1 mL min⁻¹ using an LC-20AD pump. A molecular weight calibration curve was produced using commercial narrow molecular weight distribution poly(methyl methacrylate) standards with molecular weights ranging from 5000 to 1.5 × 10⁶. Samples were filtered through 0.45 μm filters prior to injection.

MALDI-ToF-MS was conducted using a Bruker Daltonics Ultraflex II MALDI-ToF mass spectrometer, equipped with a nitrogen laser delivering 10 ns laser pulses at 337 nm with positive ion ToF detection performed using an acceleration voltage of 25 kV. Solutions in acetonitrile of dithranol as the matrix (40 mg mL⁻¹), sodium trifluoroacetate as the cationisation agent (1.0 mg mL⁻¹) and sample (1 mg mL⁻¹) were prepared. 10 μL of matrix solution was mixed with 2 μL of cationisation agent solution and 10 μL of sample solution, and 0.7 μL of the mixture was applied to the target plate. Spectra were obtained in reflectron mode calibrated with PEG 1900.

General procedure for polymer synthesis

In a 15 ml glass vial 4 ml of DMSO was added followed by addition of 4 ml methyl acrylate (MA, 4 mL, 200 equiv.), Me₆Tren (10.68 μL, 0.18 equiv.) and (EIP, 53.8 mg, 1 equiv.). A stirring bar wrapped around with 5 cm of copper wire was subsequently added to the vial. The vial was then sealed with a septum, followed by deoxygenation by bubbling with nitrogen for 10 minutes. The polymerization was allowed to take place at ambient conditions and stirred at 200 rpm. Samples were taken periodically under a nitrogen blanket for ¹H NMR analysis and passed through a short column of basic alumina to remove dissolved copper salts prior to SEC analysis.

General procedure for *in-situ* chain extension

For the first block PMA₅₀ was synthesized according to the aforementioned procedure. After the monomer conversion of the first block has reached almost quantitative conversion (>95%), a degassed solution of methyl acrylate (4 mL, 200 equiv.) and DMSO (4 mL), was injected into the polymerization mixture. After 2 hours, the polymerization was stopped by exposing to air. Samples were taken for ¹H NMR analysis and passed through a short column of basic alumina to remove dissolved copper salts prior to SEC analysis.

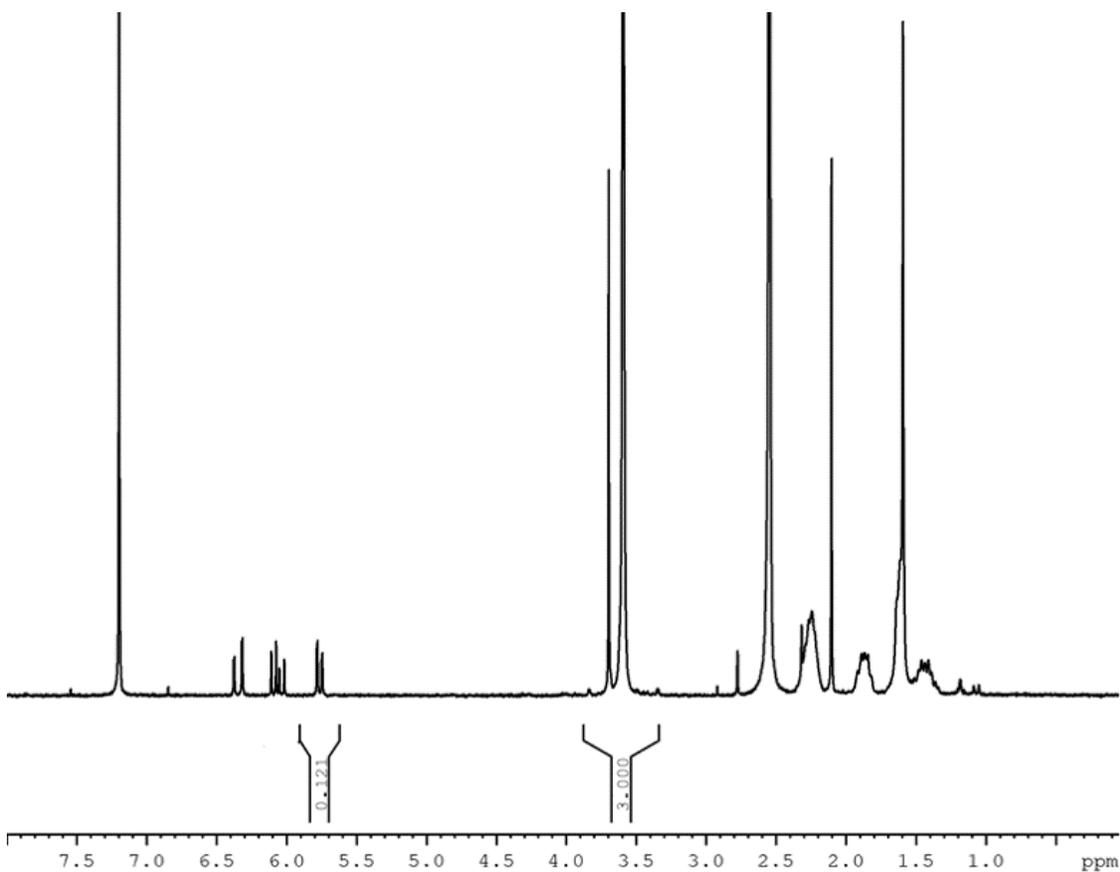


Figure S1: ¹H NMR spectra of polymerization kinetic of methyl acrylate obtained via Cu(0)-RDRP utilizing alkyl iodide initiator. The spectrum corresponds to the last time point of the kinetic reaction (100 min, 88%).

Table S1: ¹H NMR and SEC analysis of polymerization kinetic of methyl acrylate obtained via Cu(0)-RDRP utilizing alkyl iodide initiator.

[MA]:[EIP]:[Cu(0)]:[Me ₆ Tren]	Time (min)	Conversion (%)	<i>M_n</i> (Theo.) (Da)	<i>M_n</i> (SEC) (Da)	<i>D</i>
200:1:5cm:0.18	20	20	3700	4700	1.15
	30	41	7300	10300	1.07
	40	57	10000	14200	1.05
	50	67	11800	17100	1.05
	60	74	13000	18400	1.05
	70	79	13800	19800	1.05
	80	83	14500	20600	1.05
	110	88	15400	22100	1.05

Table S2: ¹H NMR and SEC analysis for PMA synthesized *via* different approaches.

Entry	[MA]:[EIP]:[Cu(0)]:[Me ₆ Tren]:[AIBN]	Temperature (°C)	Time	Conversion (%)	<i>M_n</i> (SEC) (Da)	<i>D</i>
1	100:1:5cm:0.18:0	110	5min	64	8200	1.09
2	100:1:5cm:0.18:0	80	10min	80	10200	1.06
3	100:1:5cm:0.18:0	60	20min	66	8200	1.06
4	100:1:-:-:0.1	80	1h	69	8900	1.69
5	100:1:-:-:0.2	80	1h	82	9700	1.66
6	100:1:-:-:0.3	80	1h	86	8300	1.74
7	100:1:-:-:0.18:0.2	80	1.5h	98	10800	1.75

Table S3: ¹H NMR and SEC analysis for PMA with different targeted DPs obtained via Cu(0)-RDRP utilizing alkyl iodide initiator.

Entry	[MA]:[EIP]:[Cu(0)]:[Me ₆ Tren]	Time (h)	Conversion (%)	<i>M_n</i> (Theo.) (Da)	<i>M_n</i> (SEC) (Da)	<i>D</i>
1	25 : 1:5cm:0.18	2.5	96	2200	3200	1.06
2	50 :1:5cm:0.18	2.5	88	4300	5400	1.07
3	100:1:5cm:0.18	2.5	96	8200	10300	1.10
4	200:1:5cm:0.18	2.5	88	15400	19700	1.05
5	400:1:5cm:0.18	2.5	99	33800	40300	1.13
6	800:1:5cm:0.18	20	95	59700	76400	1.15
7	1600:1:5cm:0.18	20	92	127000	157600	1.11
8	2400:1:5cm:0.18	20	87	180000	200000	1.13

Table S4: ¹H NMR and SEC analysis for different polyacrylates obtained via Cu(0)-RDRP utilizing alkyl iodide initiator.

Monomer	[MA]:[EIP]:[Cu(0)]:[Me ₆ Tren]	Time (min)	Conversion (%)	<i>M_n</i> (<i>Theo.</i>) (Da)	<i>M_n</i> (<i>SEC</i>) (Da)	<i>D</i>
tBA	200:1:5cm:0.18	75	94	24300	26600	1.11
TFEA	200:1:5cm:0.18	300	85	26400	23300	1.08
EGA	200:1:5cm:0.18	75	98	25700	23800	1.08
PEGA	50:1:5cm:0.18	300	99	24000	20500	1.09

References:

1. Ciampolini, M.; Nardi, N., *Inorg. Chem.*, **1966**, 5 (1), 41-44.