Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Tailoring Polymer Dispersity by Mixing Chain Transfer Agents in PET-RAFT Polymerization

Kostas Parkatzidis,[a‡] Nghia P. Truong,[a‡] Maria Nefeli Antonopoulou,[a] Richard Whitfield,[a] Dominik Konkolewicz[b] and Athina Anastasaki*[a]

a - *Laboratory of Polymeric Materials, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, Zurich, Switzerland.*

b- Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056, United States.

Materials and Methods

Materials

All materials were purchased from Sigma Aldrich or Fischer Scientific and used as received unless otherwise stated. All monomers were filtered through basic alumina, except methyl vinyl ketone which was distilled prior to usage.

NMR

^{1}H NMR spectra were recorded on Bruker DPX-250 or DPX-300 spectrometers in $CDCl_3$. Chemical shifts are given in ppm downfield from tetramethylsilane referenced to residual $CHCl_3$ protons.

SEC

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 bead-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,Ndimethylacetamide (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 1.5×10^6. Samples were passed though basic alumina to remove the eosin y and filtered through 0.45 μm PTFE filters prior to SEC injection.

Procedure for PET-RAFT polymerization of methyl methacrylate (MMA) with CTA 1

Into a 4 mL glass vial, CTA 1 (8.7 mg, 3.1×10^{-2} mmol, 1 equiv.) was dissolved in 1 mL of DMSO. MMA (0.94 g, 9.4 mmol, 300 equiv.), Eosin Y (0.43 mg, 6.3×10^{-4} mmol, 0.02 equiv.) and a stirrer bar were added to the vial and it was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, $\lambda_{max} = 465 \pm 5$ nm) with a 200 rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for PET-RAFT polymerization of MMA with CTA 2

Into a 4 mL glass vial, CTA 2 (13.5 mg, 4.7×10^{-2} mmol, 1 equiv.) was dissolved in 1 mL of DMSO. MMA (0.94 g, 9.4 mmol, 200 equiv.), Eosin Y (0.65 mg, 9.4×10^{-4} mmol, 0.02 equiv.) and a stirrer bar were added to the vial and it was sealed with a

rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for PET-RAFT polymerization of MMA with mixtures of CTAs

The same procedure as for the CTA 2 was repeated with different ratios of CTA 1 and CTA2. In all cases, the molar ratio between total CTA and monomer was kept constant.

Procedure for the *ex-situ* chain extension of poly(methyl methacrylate) (PMMA) macroCTA with MMA

PMMA macroCTA crude mixture was diluted in chloroform and passed through basic alumina to remove Eosin Y. The organic layer was washed with water three times to remove DMSO and dried with $MgSO_4$. The organic layer was concentrated and precipitated into diethyl ether to give PMMA in a solid phase.
Into a 4 mL glass vial, purified macroCTA (CTA 1: CTA 2 0.65: 0.35) with M_n = 10300 and $Đ$ = 1.35 (100 mg, 9.7 × 10^{-3} mmol, 1 equiv.) was dissolved in 1 mL of DMSO. MMA (0.39 g, 3.9 mmol, 400 equiv.), Eosin Y (0.13 mg, 1.9 × 10^{-4} mmol, 0.02 equiv.) and a stirrer bar were added to the vial and it was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. Samples were analysed *via* ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for *in-situ* chain extension of PMMA macroCTA with MMA

Into a 4 mL glass vial, CTA 2 (27.1 mg, 9.4 × 10^{-2} mmol 1 equiv.) was dissolved in 1 mL of DMSO. MMA (0.94 g, 9.4 mmol, 100 equiv.), Eosin Y (1.3 mg, 1.9 × 10^{-3} mmol, 0.02 equiv.) and a stirrer bar were added and the vial was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. After 3h (conversion > 99 %) second aliquot of deoxygenated solution of MMA (0.94 g, 9.4 mmol, equiv. 100) and DMSO (1 ml), was added into the solution under inert atmosphere, and the polymerization was continued in the same manner. Samples were analysed *via* ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for the synthesis of poly(methyl methacrylate-*block*-butyl methacrylate) P(MMA-*b*-BMA) diblock copolymer

Into a 4 mL glass vial, macroCTA with M_n = 10300 and $Đ$ = 1.35 (100 mg, 9.7 × 10^{-3} mmol, 1equiv.) was dissolved in 1 mL of DMSO. Butyl methacrylate (BMA) (0.55 g, 3.9 mmol, 400 equiv.), Eosin Y (0.13 mg, 1.9 × 10^{-4} mmol, 0.02 equiv.) and a stirrer bar were added and the vial was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. Samples were analysed *via* ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for the *in-situ* synthesis of poly(methyl methacrylate-*block*-methyl vinyl ketone) P(MMA-*b*-MVK) block copolymer

Into a 4 mL glass vial, CTA 2 (27.1 mg, 9.4 × 10^{-2} mmol 1 equiv.) was dissolved in 1 mL of DMSO. MMA (0.94 g, 9.4 mmol, 100 equiv.), Eosin Y (1.3 mg, 1.9 × 10^{-3} mmol, 0.02 equiv.) and a stirrer bar were added and the vial was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. After 3h (conversion > 99 %) second aliquot of deoxygenated solution of Methyl vinyl ketone (MVK) (1.32 g, 18.8 mmol, equiv. 200) and DMSO (1.5 ml), was added into the solution under inert atmosphere, and the polymerization was continued in the same manner. Samples were analysed *via* ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for PET-RAFT polymerization of MMA in the presence of oxygen

In the case of oxygen tolerant polymerization, the same amounts of reagents were used as for the deoxygenated polymerization. The polymerization solution was placed into 2 ml glass vial, instead of 4 ml, and the polymerization took place without any deoxygenation procedure.

Procedure for PET-RAFT polymerization of methyl acrylate (MA) with CTA 3

Into a 4 mL glass vial, CTA 3 (12.7 mg, 3.7 × 10^{-2} mmol, 1 equiv.) was dissolved in 1 mL of DMSO. MA (0.95 g, 11 mmol, 300 equiv.), Eosin Y (0.51 mg, 7.4 × 10^{-4} mmol, 0.02 equiv.) and a stirrer bar were added and the vial was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H

NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for PET-RAFT polymerization of MA with CTA 4

Into a 4 mL glass vial, CTA 4 (13.9 mg, 5.5×10^{-2} mmol, 1 equiv.) was dissolved in 1 mL of DMSO. MA (0.95 g, 11 mmol, 200 equiv.), Eosin Y (0.76 mg, 1.1×10^{-3} mmol, 0.02 equiv.) and a stirrer bar were added and the vial was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for PET-RAFT polymerization of MA with a mixture of CTAs

The same procedure as for the CTA4 was repeated with mixtures CTA3 and CTA4 into different rations, keeping the same molar ration between the mixture of CTAs and monomer.

Procedure for PET-RAFT polymerization of dimethyl acrylamide (DMA) with CTA 3

Into a 4 mL glass vial, CTA 3 (11.2 mg, 3.2×10^{-2} mmol, 1 equiv.) was dissolved in 1 mL of DMSO. Dimethyl acrylamide (DMA) (0.96 g, 9.7 mmol, 300 equiv.), Eosin Y (0.45 mg, 6.5×10^{-4} mmol, 0.02 equiv.) and a stirrer bar were added and the vial was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for PET-RAFT polymerization of DMA with CTA 5

Into a 4 mL glass vial, CTA 5 (13.1 mg, 4.8×10^{-2} mmol, 1 equiv.) was dissolved in 1 mL of DMSO. DMA (0.96 g, 9.7 mmol, 200 equiv.), Eosin Y (0.67 mg, 9.7×10^{-3} mmol, 0.02 equiv.) and a stirrer bar were added and the vial was sealed with a rubber septum. The vial was then covered with aluminium foil and the reaction solution was deoxygenated by bubbling with nitrogen for 15 minutes. Polymerization was conducted in a home-made photoreactor using blue LED light (12 W, λ_{max} = 465 ± 5 nm) with a 200 rpm stirring rate. Samples were taken periodically under a nitrogen blanket for ^{1}H NMR analysis and passed through basic alumina and a syringe filter (0.45 μM PTFE membrane) prior to SEC analysis.

Procedure for PET-RAFT polymerization of DMA with mixture of CTAs

The same procedure as for the CTA5 was repeated with mixtures CTA3 and CTA5 into different rations, keeping the same molar ration between the mixture of CTAs and monomer.

Figure S1: Experimental setup of PET-RAFT polymerization comprising of blue led strips inside a homemade box with a magnetic stirrer.

Table S1: ^{1}H NMR and SEC analysis of PMMA synthesized with various ratios of CTA 1 and CTA 2 (aligned by M_p value).

Entry	[MMA]:[CTA 1]: [CTA 2]:[Eosin Y]	Time (h)	Conversion (%)*	M_n (Theo.)	M_p (SEC)	M_n (SEC)	M_w (SEC)	$Đ$
1	200:0:1:0.02	1.5	63	12900	**24000**	15500	26600	1.72
2	200:0.1:0.9:0.02	2	68	13900	**24600**	15800	24800	1.57
3	200:0.4:0.6:0.02	8	95	19300	**25100**	20200	27500	1.36

4	200:0.7:0.3:0.02	16	91	18500	**24800**	18600	22800	1.23
5	300:1:0:0.02	28	71	21600	**24600**	22700	24900	1.10

All polymerizations were performed in DMSO under blue light irradiation. The volume ratio of DMSO to monomer was maintained at 1:1. [*] Conversion was calculated by ^{1}H NMR.

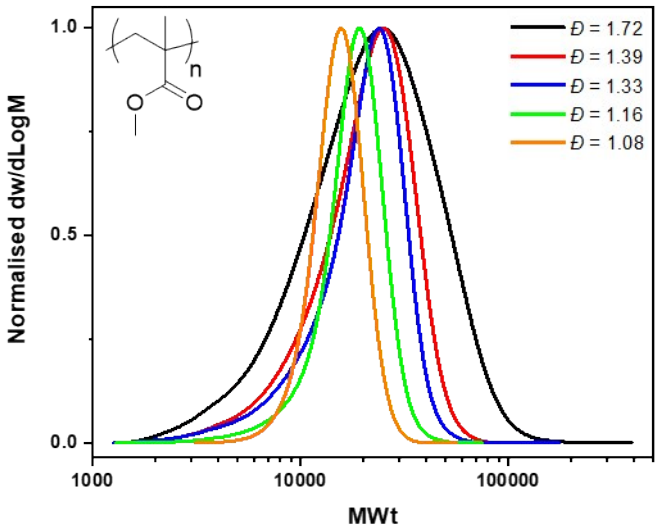

Figure S2: SEC analysis of the polymerization of MMA, illustrating a) the variation in dispersity as CTA 1 and CTA 2 are mixed in different ratios (Aligned by M_n value)

Table S2: ^{1}H NMR and SEC analysis of PMMA synthesized with various ratios of CTA 1 and CTA 2 (Aligned by M_n value).

Entry	[MMA]:[CTA 1]: [CTA 2]:[Eosin Y]	Time (h)	Conversion (%)*	M_n (Theo.)	M_p (SEC)	M_n (SEC)	M_w (SEC)	Đ
1	200:0:1:0.02	1.5	63	12900	24000	**15500**	26600	1.72
2	200:0.5:0.5:0.02	4	81	16500	25100	**16000**	22300	1.39
3	200:0.6:0.4:0.02	4.5	76	15500	23800	**15800**	21000	1.33
4	200:0.8:0.2:0.02	14	73	14900	19200	**15900**	18500	1.16
5	300:1:0:0.02	24	49	15000	15700	**14400**	15600	1.08

All polymerizations were performed in DMSO under blue light irradiation. The volume ratio of DMSO to monomer was maintained at 1:1. [*] Conversion was calculated by ^{1}H NMR.

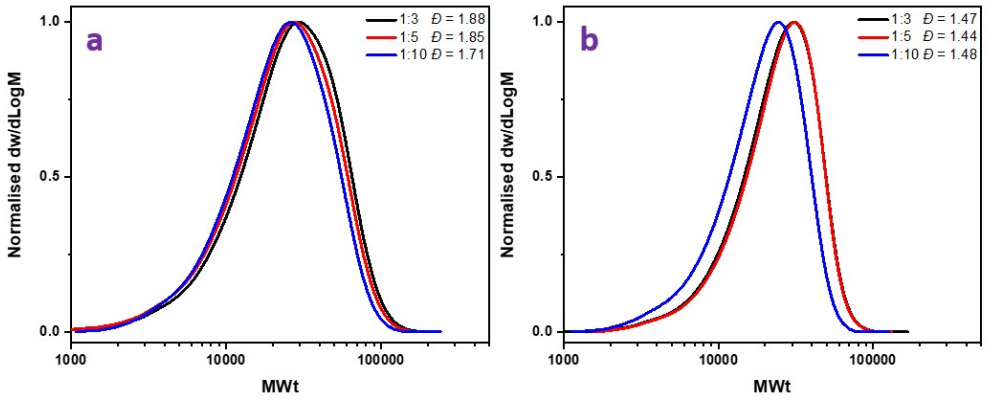

Figure S3: SEC analysis of the polymerization of MMA, illustrating different monomer concentrations (1:3, 1:5 and 1:10 v/v monomer to solvent) a) for low activity CTA2: 1:3 M_n= 16700 C= 80%, 1:5 M_n= 15400 C= 80% and 1:10 M_n= 15800 C= 70% and b) for mixed CTA 1 and CTA 2 in 40:60 ratio: 1:3 M_n= 18400 C= 70%, 1:5 M_n= 18900 C= 70% and 1:10 M_n= 14700 C= 57%.

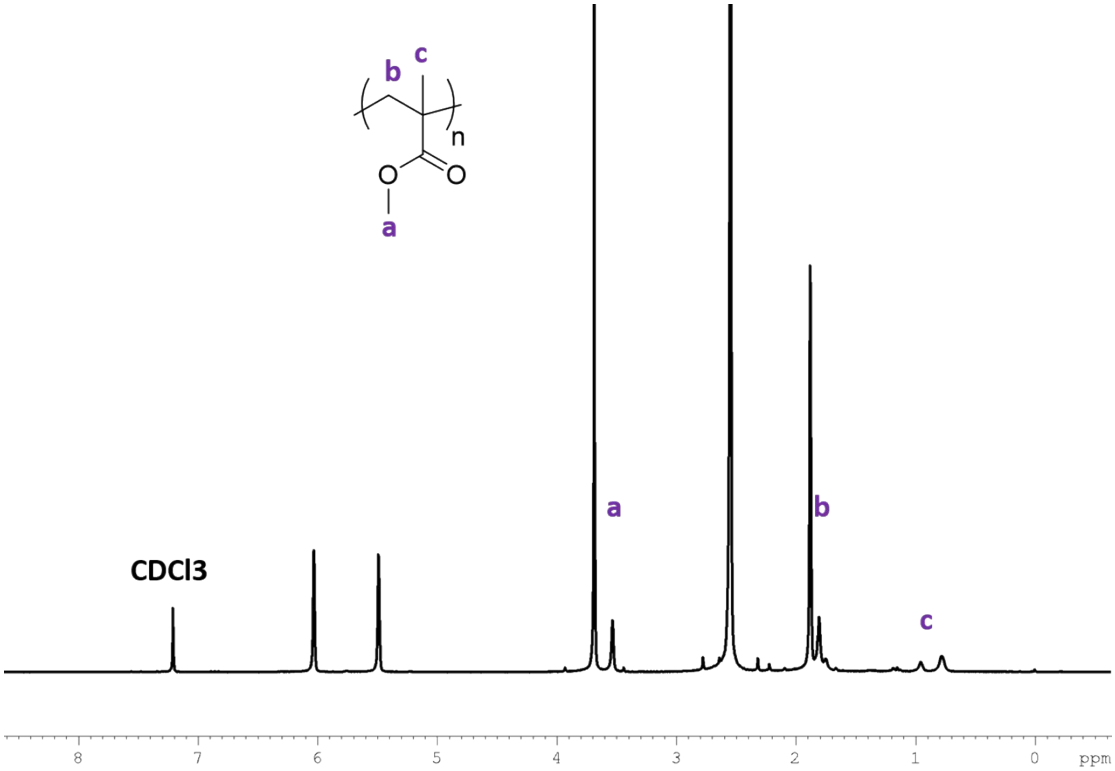

Figure S4: Typical ^{1}H NMR spectrum of crude PMMA in $CDCl_3$ (20% conversion, $M_{n,\,SEC}$ = 10300, $Đ$ = 1.37). Conversion was calculated by integrating the total methoxy (O-CH_3) protons of monomer and polymer (3.5-3.8 ppm) against vinyl protons (5.5-6.5 ppm).

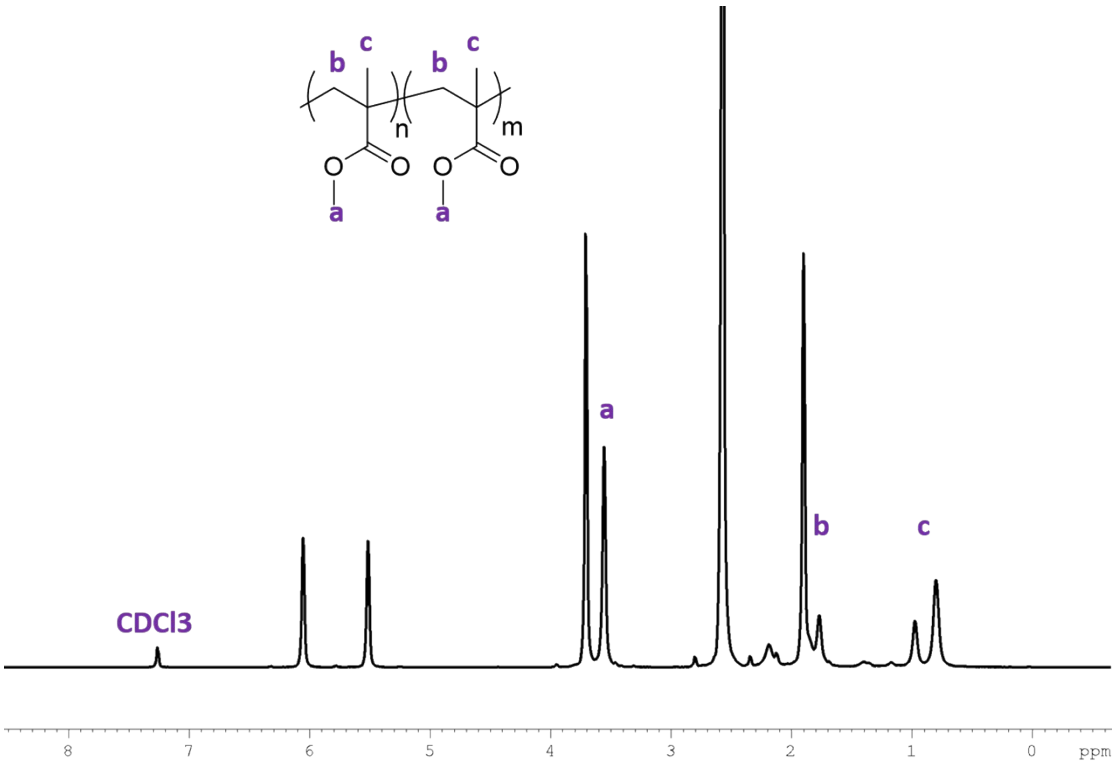

Figure S5: ^{1}H NMR spectrum of crude P(MMA-b-MMA) in CDCl3 (40 % conversion, $M_{n,SEC}$ = 26800, $Đ$ = 1.33). Conversion was calculated by integrating the total methoxy (O-CH3) protons of monomer and polymer (3.5-3.8 ppm) against vinyl protons.

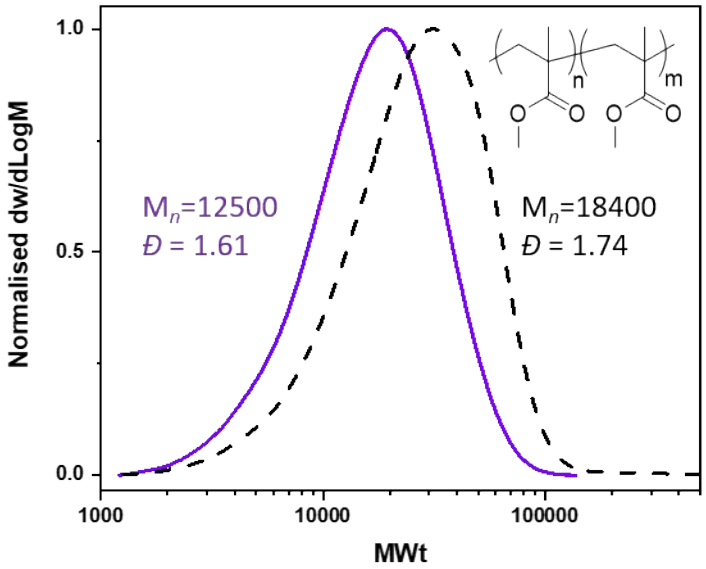

Figure S6: *In-situ* chain extension of a PMMA macroCTA prepared with only CTA 2 with MMA.

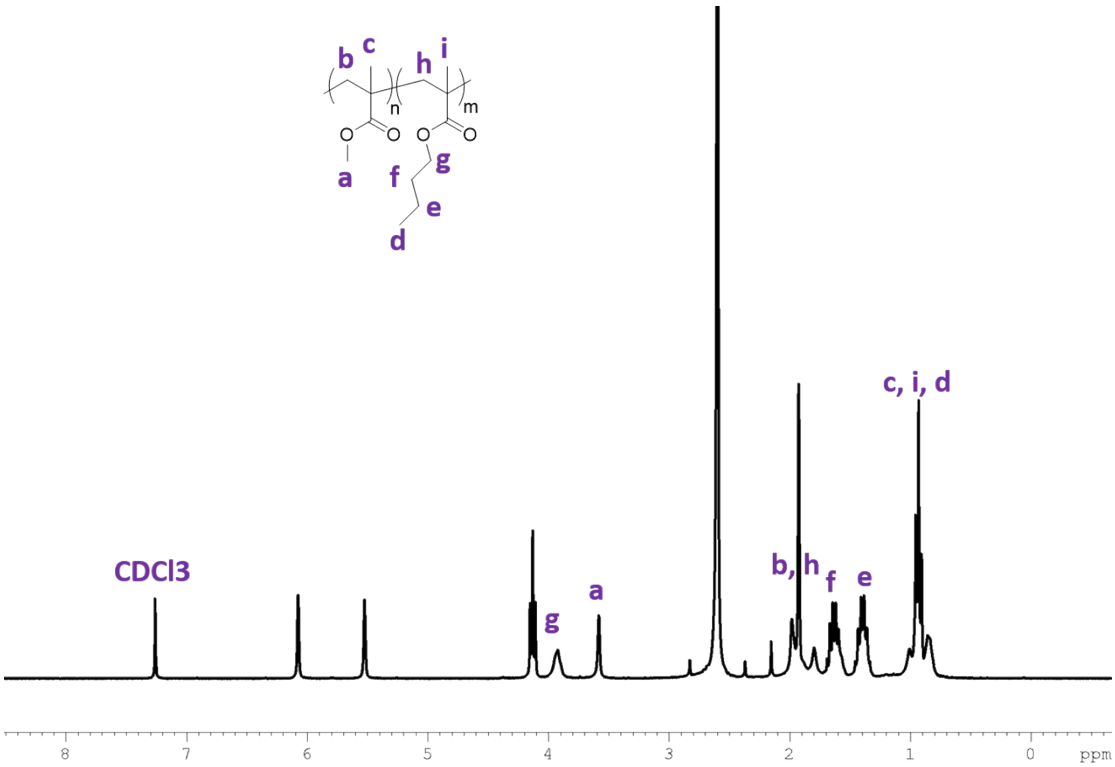

Figure S7: Typical ^{1}H NMR spectrum of crude P(MMA-b-BMA) in CDCl3 (10 % conversion, $M_{n,\,SEC}$ = 21400, $Đ$ = 1.35). Conversion was calculated by integrating the total ester (O-CH2) protons of monomer and polymer (3.8-4.2 ppm) against vinyl protons.

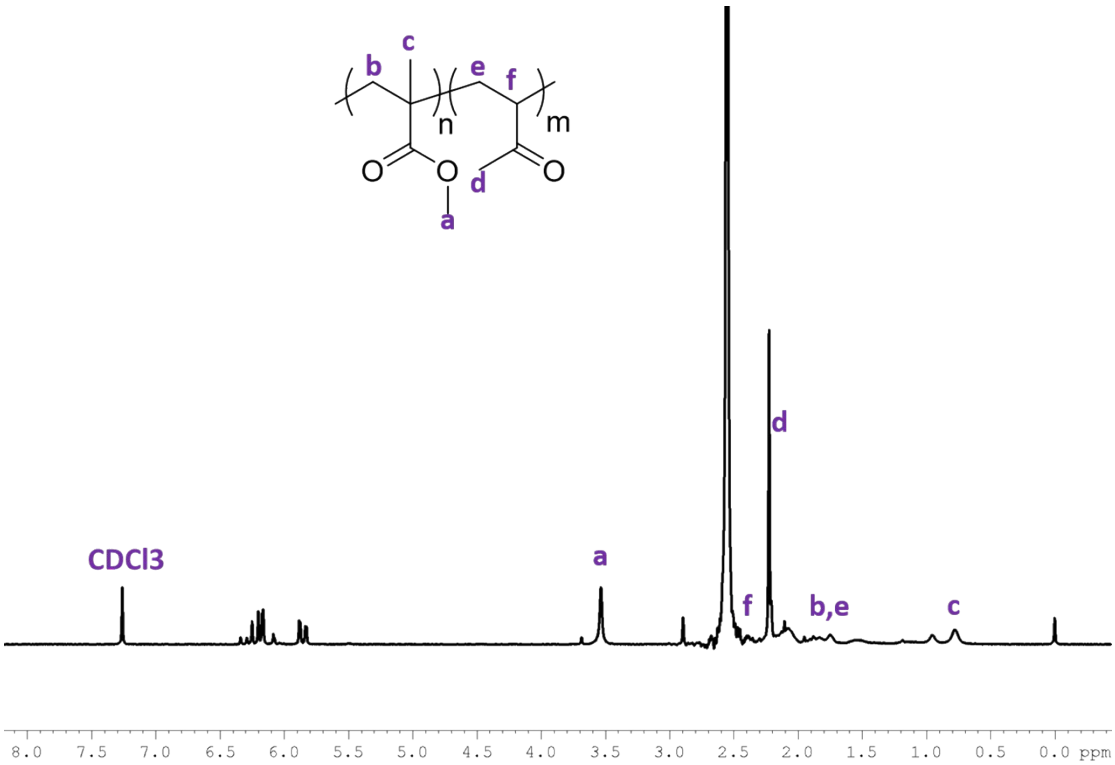

Figure S8: Typical ^{1}H NMR spectrum of crude P(MMA-b-MVK) in CDCl3 (16 % conversion, $M_{n,\,SEC}$ = 18400, $Đ$ = 1.50). Conversion was calculated by integrating the combined monomer and polymer protons 1.1-2.3 ppm, minus the backbone protons (b) of the PMMA block against remaining vinyl protons.

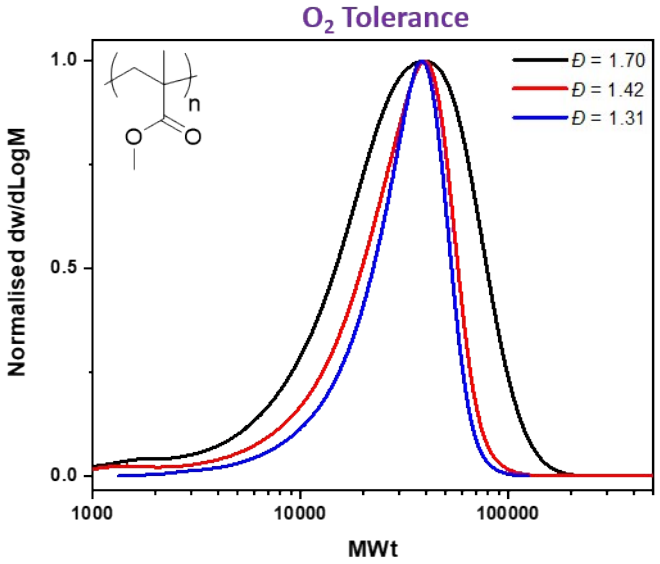

Figure S9: SEC analysis of the polymerization of MMA, illustrating the variation in dispersity as CTA 1 and CTA 2 are mixed in different ratios, in the absence of external deoxygenation (Aligned by M_p value).

Table S3: ^{1}H NMR and SEC analysis of PMMA synthesized with various ratios of CTA 1 and CTA 2 in the absence of external deoxygenation (Aligned by M_p value).

Entry	[MMA]:[CTA 1]:[CTA 2]:[Eosin Y]	Time (h)	Conversion (%)*	M_n (Theo.)	M_p (SEC)	M_n (SEC)	M_w (SEC)	$Đ$
1	200:0:1:0.02	4	99+	2300	**39900**	23800	40200	1.70
2	200:0.5:0.5:0.02	8	99+	20300	**39900**	24700	35200	1.42
3	200:0.6:0.4:0.02	12	99+	20300	**38500**	26400	34700	1.31

All polymerizations were performed in DMSO under blue light irradiation. The volume ratio of DMSO to monomer was maintained at 1:1. [*] Conversion was calculated by ^{1}H NMR.

Table S4: ^{1}H NMR and SEC analysis of PMA synthesized with various ratios of CTA 3 and CTA 4 (Aligned by M_p value)

Entry	[MA]:[CTA 3]:[CTA 4]:[Eosin Y]	Time (h)	Conversion (%)*	M_n (Theo.)	M_p (SEC)	M_n (SEC)	M_w (SEC)	$Đ$
1	200:0:1:0.02	14.5	92	16100	**26100**	18100	27500	1.52
2	200:0.35:0.65:0.02	14.5	89	15600	**26100**	18200	24100	1.32
3	200:0.6:0.4:0.02	14.5	82	14400	**25900**	18600	23500	1.26
4	200:0.8:0.2:0.02	14.5	99	17300	**25900**	21000	24400	1.16
5	300:1:0:0.02	14	88	23000	**26100**	23400	26100	1.11

All polymerizations were performed in DMSO under blue light irradiation. The volume ratio of DMSO to monomer was maintained at 1:1. [*] Conversion was calculated by ^{1}H NMR.

Table S5: ^{1}H NMR and SEC analysis of PDMA synthesized with various ratios of CTA 3 and CTA 5, at high conversions (Aligned by M_p value).

Entry	[DMA]:[CTA 3]:[CTA 5]:[Eosin Y]	Time (h)	Conversion (%)*	M_n (Theo.)	M_p (SEC)	M_n (SEC)	M_w (SEC)	$Đ$
1	200:0:1:0.02	1.5	91	18300	**28400**	17000	30900	1.82
2	200:0.35:0.65:0.02	2.5	87	17500	**29000**	18500	27700	1.50
3	200:0.6:0.4:0.02	6	80	16100	**28600**	17800	24200	1.34
4	300:1:0:0.02	10	94	28200	**28600**	27400	29900	1.10

All polymerizations were performed in DMSO under blue light irradiation. The volume ratio of DMSO to monomer was maintained at 1:1. [*] Conversion was calculated by ^{1}H NMR.