

Supplementary Information

Photoinduced sequence-control via one pot living radical polymerization of acrylates

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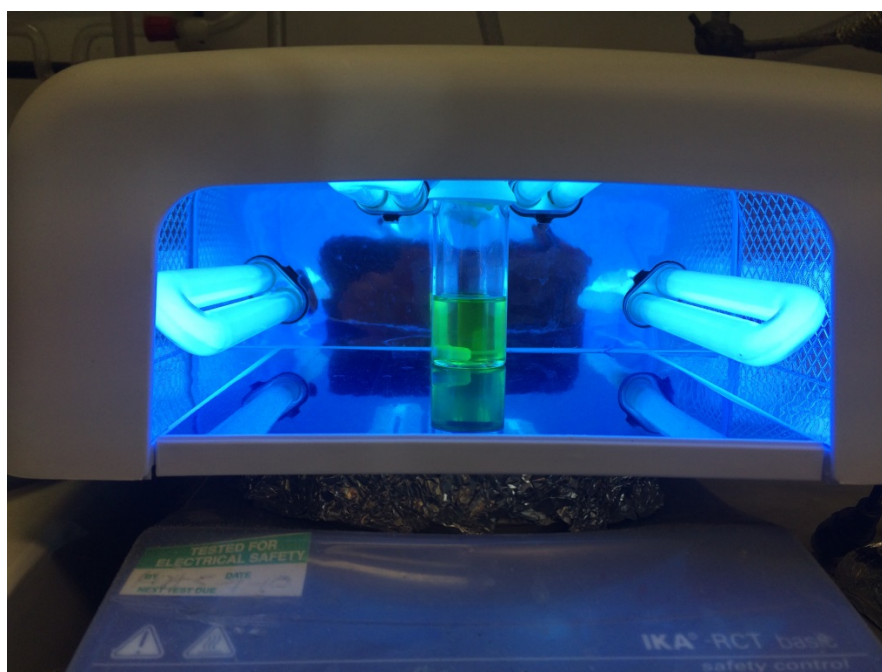


Figure S1: Typical set up for **photoinduced** polymerisation ($\lambda= 360\text{nm}$).

Materials

All materials were purchased from Sigma Aldrich or Fischer Scientific unless otherwise stated. Copper (II) bromide ($\text{Cu}^{\text{II}}\text{Br}_2$) and ethyl 2-bromoisobutyrate (EBiB) were used as received. All monomers were passed through a basic Al_2O_3 chromatographic column prior to use. Tris-(2-(dimethylamino)ethyl)amine (Me_6TREN) was synthesized according to previously reported literature.¹ Solketal acrylate was synthesized according to a reported procedure and distilled under reduced pressure (45°C , 10^{-1} mbar) to yield a colourless liquid.²

Instruments

^1H NMR spectra were recorded on Bruker DPX-250 and DPX-300 spectrometers using deuterated chloroform (CDCl_3) obtained from Aldrich. Chemical shifts are given in ppm downfield from the internal standard tetramethylsilane. Size exclusion chromatography (SEC) measurements were conducted using an Agilent 1260 GPC-MDS fitted with differential refractive index (DRI), light scattering (LS) and viscometry (VS) detectors equipped with $2 \times$ PLgel 5 mm mixed-D columns (300×7.5 mm), $1 \times$ PLgel 5 mm guard column (50×7.5 mm) and autosampler. Narrow linear poly(methyl methacrylate) standards in range of 200 to 1.0×10^6 g·mol⁻¹ were used to calibrate the system. All samples were passed through $0.45 \mu\text{m}$ PTFE filter before analysis. The mobile phase was chloroform with 2% triethylamine eluent at a flow rate of 1.0 mL/min. SEC data was analyzed using Cirrus v3.3 with calibration curves produced using Varian Polymer laboratories Easi-Vials linear poly(methyl methacrylate) standards (200- 4.7×10^5 g/mol). ESI-ToF spectra were recorded on Bruker MicroTOF. Samples were loaded by direct infusion at a flow rate of 240 $\mu\text{L/hr}$ in $\text{MeOH:H}_2\text{O}$. The source of UV light was a UV nail gel curing lamp (available online from a range of suppliers) ($\lambda_{\text{max}} \sim 360$ nm) equipped with four 9W bulbs.

General procedure for the preparation of multiblock (co)polymer by photoinduced living radical polymerization without purification.

Filtered monomer (DP_n eq), EBiB (1 eq), CuBr_2 (0.02 eq), $\text{Me}_6\text{-Tren}$ (0.12 eq) and DMSO (2 mL) were added to a septum sealed vial and degassed by purging with nitrogen for 15 min.

Polymerization commenced upon addition of the degassed reaction mixture to the UV lamp. Samples were taken periodically and conversions were measured using ^1H NMR and SEC analysis.

For the iterative chain extensions, an aliquot of a degassed monomer (DP_n eq), in DMSO (50% *v/v*) was added *via* a nitrogen-purged syringe and again the solution was allowed to polymerize in the lamp. When required (according to the manuscript), a fresh solution of CuBr_2 (0.02 eq), $\text{Me}_6\text{-Tren}$ (0.12 eq) in DMSO was fed together with the monomer *via* a nitrogen-purged syringe. The above polymerization-extension procedure was repeated as required.

DP=3

Scheme S1: Synthesis of **multiblock homopolymers DP=3** by sequential addition of monomers without intermediate purification.

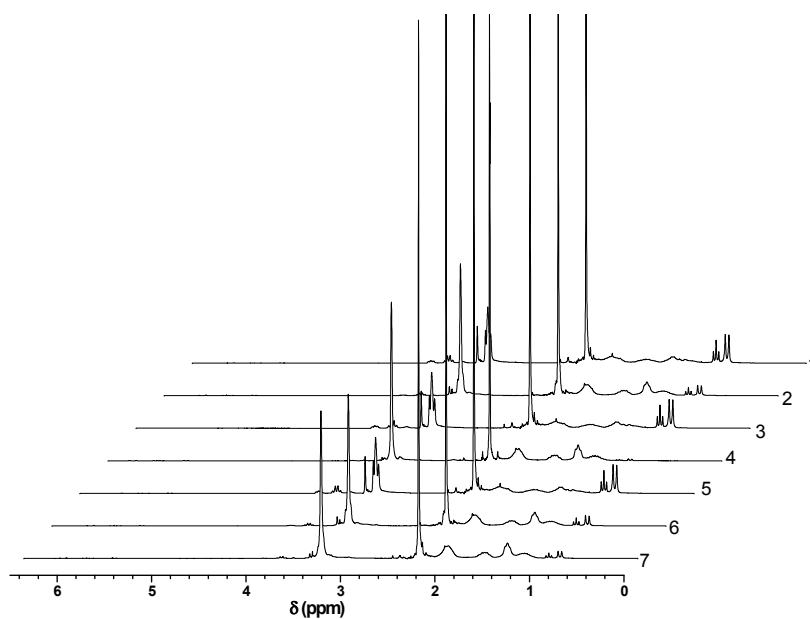
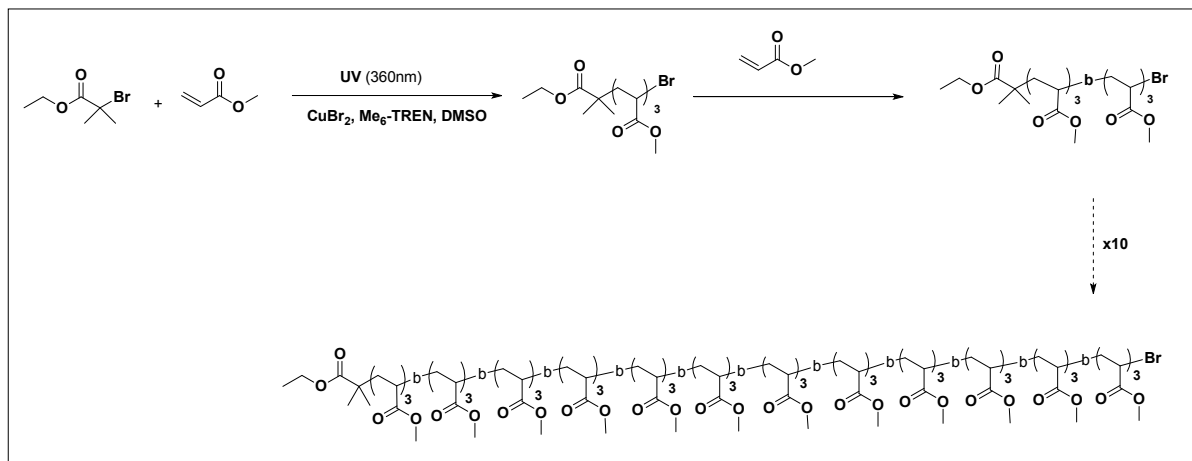


Figure S2: ^1H NMR spectra showing the monomer conversion for each cycle during synthesis of heptablock homopolymer **DP=3** in DMSO at ambient temperature.

Table S1: Characterization data for the synthesis of the pseudo heptablock homopolymer **DP=3** obtained from UV experiment: $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [2]:[1]:[0.02]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock homopolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol ⁻¹]	$M_{n,\text{GPC}}$ ^b [g mol ⁻¹]	\bar{D}
1	Poly(MA ₃)	12	99	450	300	1.39
2	Poly(MA ₃ -MA ₃)	12	100	710	700	1.19
3	Poly(MA ₃ -MA ₃ -MA ₃)	12	100	970	1300	1.17
4	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃)	15	98	1230	2600	1.09
5	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	18	100	1500	3400	1.07
6	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	26	99	1750	4000	1.10
7	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	48	96	2010	4700	1.18

^aDetermined by ¹H NMR. ^bDetermined by CHCl₃ SEC analysis.

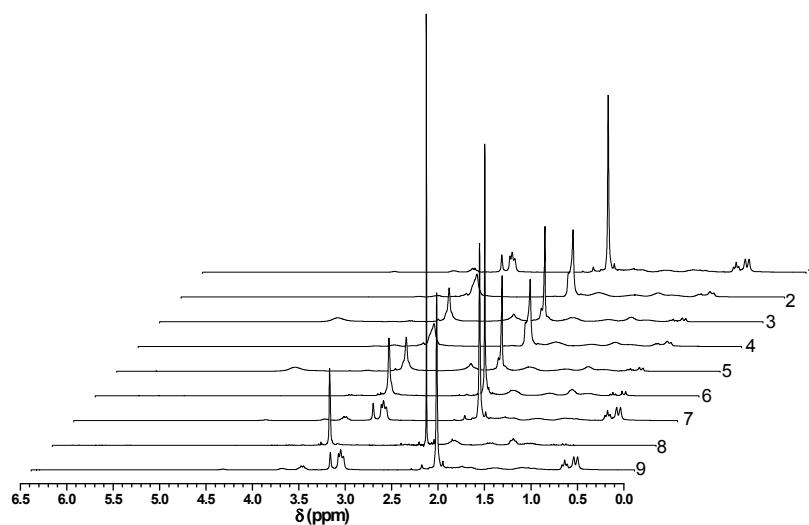


Figure S3: ¹H NMR spectra showing the monomer conversion for each cycle during synthesis of nonablock homopolymer **DP=3** in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [0.02]:[0.12]$, was added together with the monomer upon every 2nd addition. **No additional solvent** was added.

Table S2: Characterization data for the synthesis of the nonablock homopolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [3]:[1]:[0.02]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	M _{n,th} [g mol ⁻¹]	M _{n,GPC} ^b [g mol ⁻¹]	<i>D</i>
1	Poly(MA ₃)	12	100	450	260	1.26
2	Poly(MA ₃ -MA ₃)	12	100	710	650	1.23
3	Poly(MA ₃ -MA ₃ -MA ₃)	12	100	970	1200	1.20
4	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	100	1230	1800	1.18
5	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	100	1500	2400	1.12
6	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	99	1750	3400	1.10
7	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	99	2010	5100	1.15
8	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	99	2270	6100	1.33
9	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	14	95	2530	8000	1.35

^aDetermined by ¹H NMR. ^bDetermined by CHCl₃ SEC analysis.

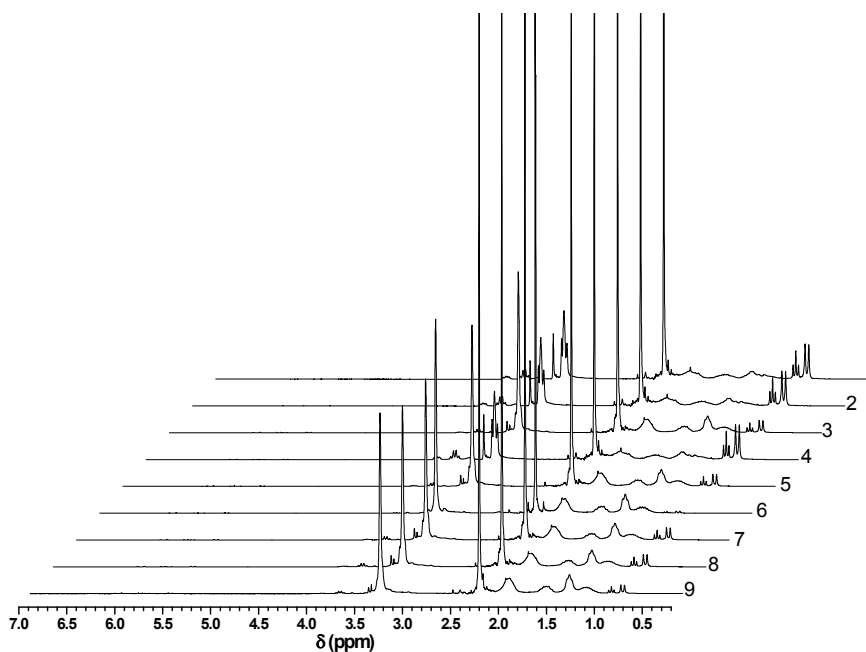


Figure S4: ¹H NMR spectra showing the monomer conversion for each cycle during synthesis of nonablock homopolymer **DP=3** in DMSO at ambient temperature. A fresh solution of [CuBr₂]:[Me₆-Tren] = [0.02]:[0.12], was added together with the monomer upon every 4th addition..

Table S3: Characterization data for the synthesis of the pseudo nonablock copolymer **DP=3** obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [3]:[1]:[0.02]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol ⁻¹]	$M_{n,\text{GPC}}^b$ [g mol ⁻¹]	\bar{D}
1	Poly(MA ₃)	12	>99	450	180	1.30
2	Poly(MA ₃ -MA ₃)	12	>99	710	610	1.23
3	Poly(MA ₃ -MA ₃ -MA ₃)	12	97	970	1200	1.16
4	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃)	15	96	1230	1800	1.16
5	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	95	1500	2800	1.09
6	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	13	99	1750	4000	1.08
7	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	16	97	2010	6900	1.08
8	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	24	96	2270	7900	1.09
9	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	48	50	2530	8400	1.09

^aDetermined by ¹H NMR. ^bDetermined by CHCl₃ SEC analysis.

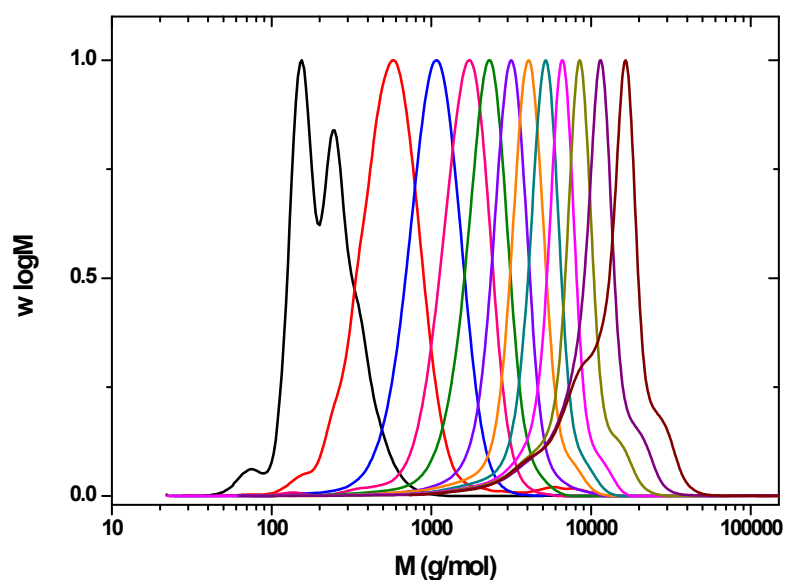


Figure S5a: Molecular weight distributions for successive cycles during synthesis of dodecablock homopolymer **DP=3** in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [0.02]:[0.12]$, was added together with the monomer upon every 3rd addition.

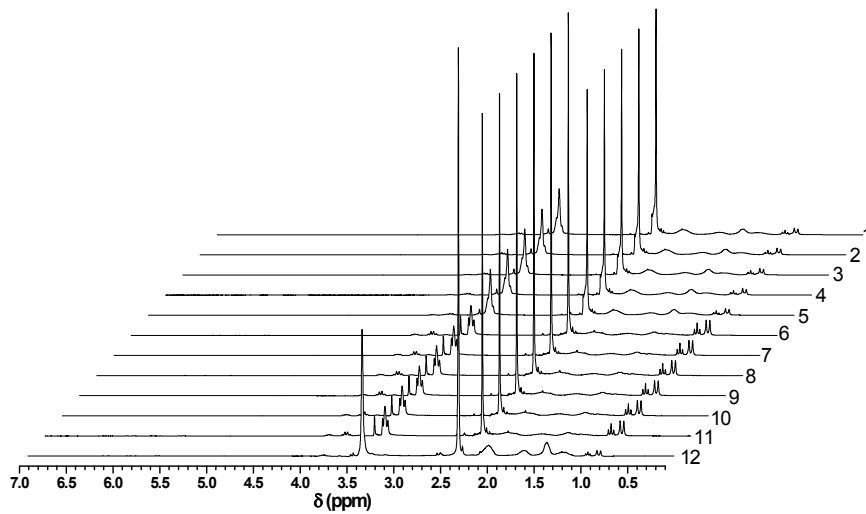
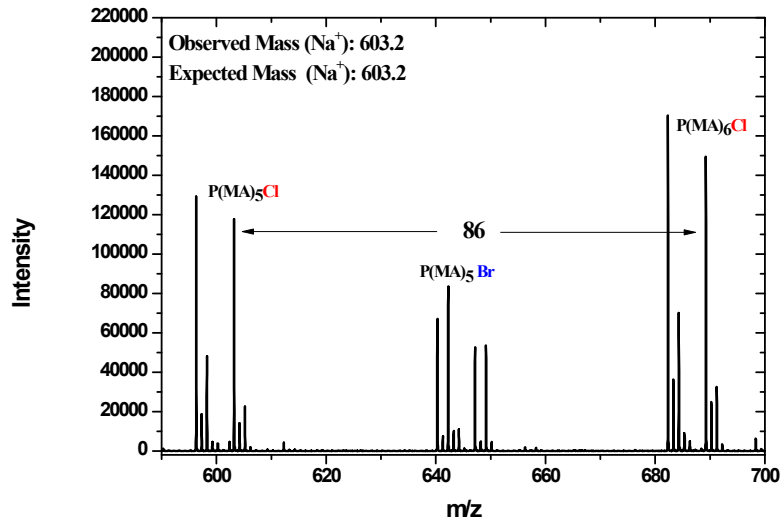
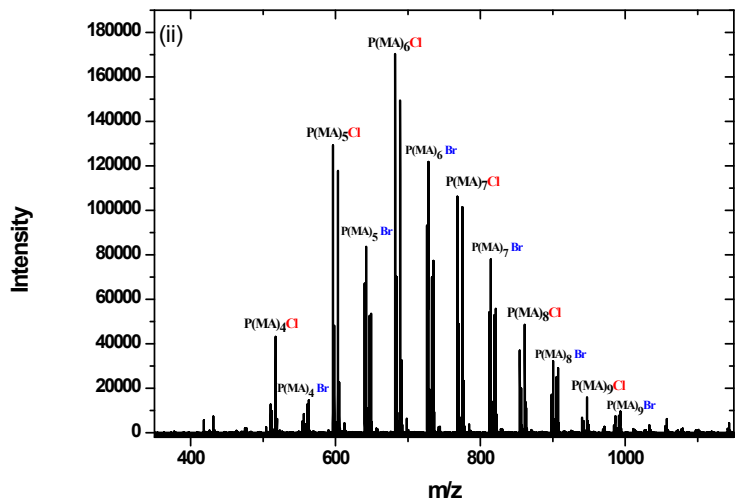
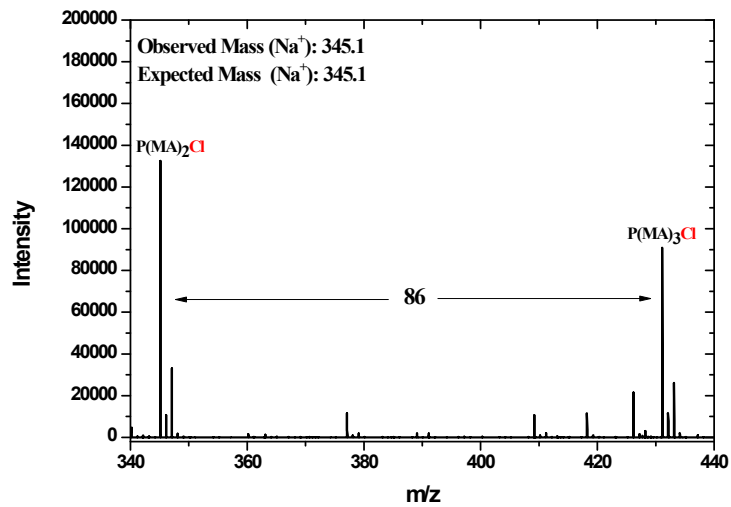
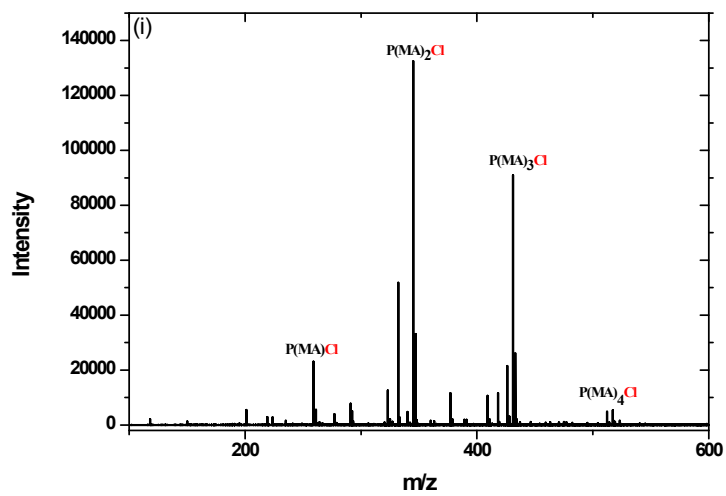


Figure S5b: ^1H NMR spectra showing the monomer conversion for each cycle.



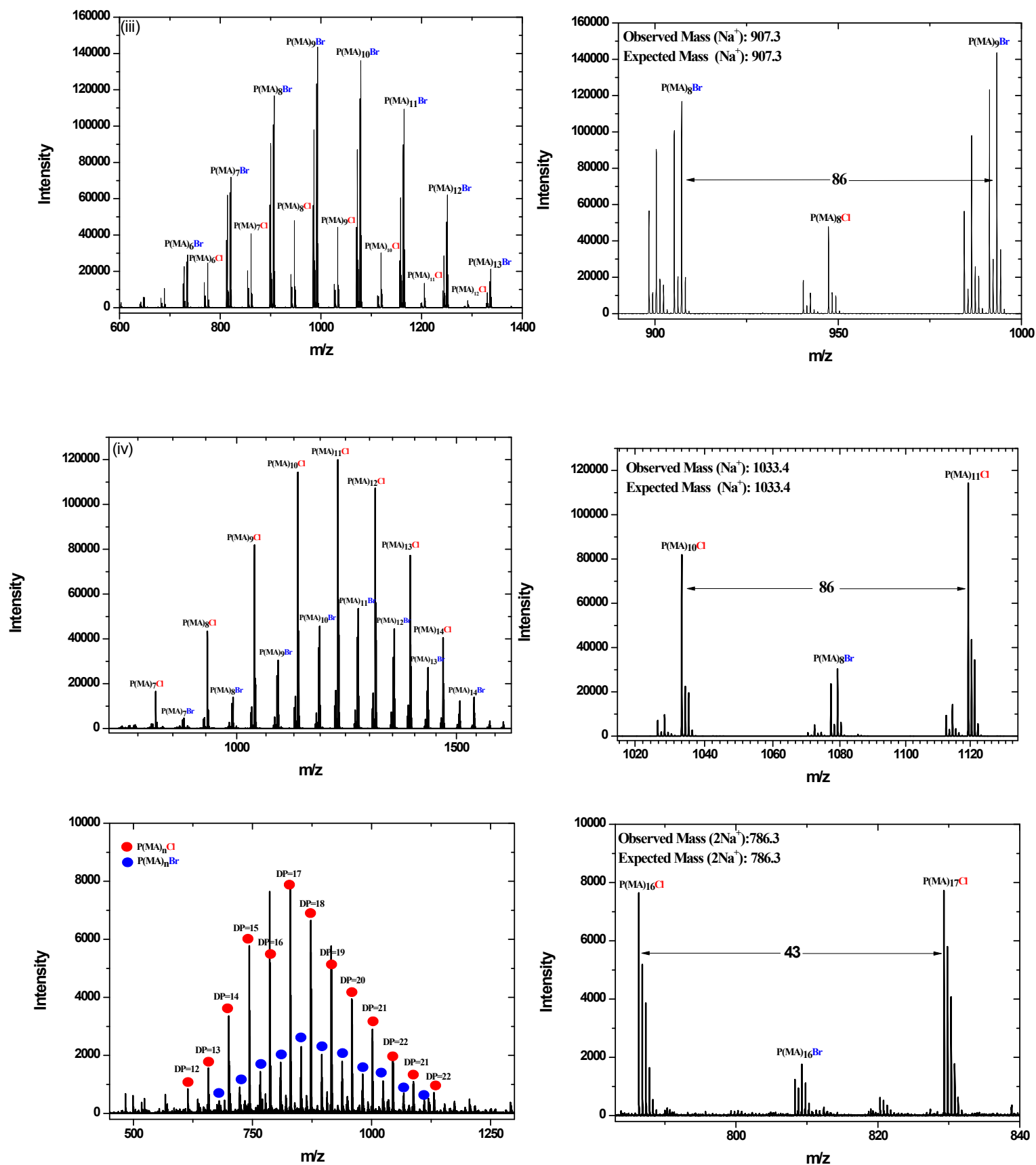


Figure S5c: ESI-MS spectra of the (i) 1st block, (ii) 2nd block, (iii) 3rd block, (iv) 4th block and (v) 5th block (doubly charged) obtained during the synthesis of dodecablock homopolymer DP=3 in DMSO, including the enlargement of the corresponding spectrum.

Table S4: Characterization data for the synthesis of the dodecablock homopolymer obtained from UV experiment. Initial feed ratio = [MA]:[EBiB]:[CuBr₂]:[Me₆-Tren] = [3]:[1]:[0.02]:[0.12] in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	M _{n,th} [g mol ⁻¹]	M _{n,GPC} ^b [g mol ⁻¹]	<i>D</i>
1	Poly(MA ₃)	12	>99	450	190	1.23
2	Poly(MA ₃ -MA ₃)	12	>99	710	480	1.24
3	Poly(MA ₃ -MA ₃ -MA ₃)	12	99	970	920	1.19
4	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	>99	1230	1400	1.16
5	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	98	1500	1900	1.15
6	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	99	1750	2800	1.13
7	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	99	2010	3600	1.13
8	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	14	97	2270	4600	1.12
9	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	16	99	2530	5700	1.10
10	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	17	98	2790	7100	1.19
11	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	24	98	3050	9000	1.20
12	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	30	95	3310	11800	1.30

^aDetermined by ¹H NMR. ^bDetermined by CHCl₃ SEC analysis.

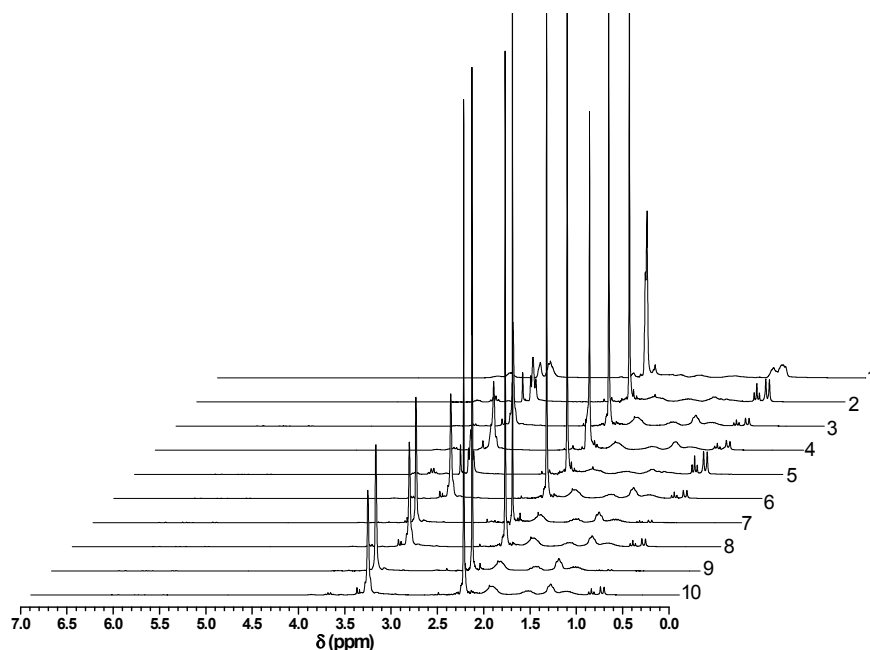


Figure S6: ^1H NMR spectra showing the monomer conversion for each cycle during synthesis of decablock homopolymer $\text{DP}=3$ in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [\mathbf{0.02}]:[\mathbf{0.12}]$, was added together with the monomer upon every 2nd addition.

Table S5: Characterization data for the synthesis of the decablock homopolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [\mathbf{3}]:[\mathbf{1}]:[\mathbf{0.02}]:[\mathbf{0.12}]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol^{-1}]	$M_{n,\text{GPC}}$ ^b [g mol^{-1}]	\bar{D}
1	Poly(MA_3)	12	100	450	180	1.26
2	Poly($\text{MA}_3\text{-MA}_3$)	12	99	710	490	1.23
3	Poly($\text{MA}_3\text{-MA}_3\text{-MA}_3$)	12	100	970	1000	1.18
4	Poly($\text{MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3$)	12	99	1230	1500	1.16
5	Poly($\text{MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3$)	12	99	1500	2000	1.20
6	Poly($\text{MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3$)	12	97	1750	2800	1.22
7	Poly($\text{MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3$)	12	96	2010	4000	1.18
8	Poly($\text{MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3$)	12	96	2270	4900	1.23
9	Poly($\text{MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3$)	14	95	2530	5900	1.32
10	Poly($\text{MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3\text{-MA}_3$)	24	89	2790	6200	1.59

^aDetermined by ^1H NMR. ^bDetermined by CHCl_3 SEC analysis.

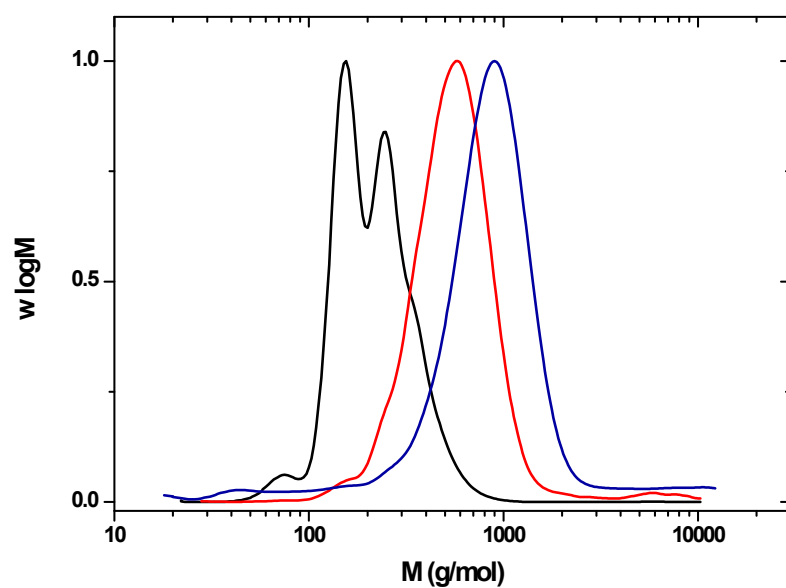


Figure S7a: Molecular weight distributions for successive cycles during synthesis of triblock homopolymer **DP=3** in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2] = [0.02]$ was added together with the monomer upon every 2nd addition.

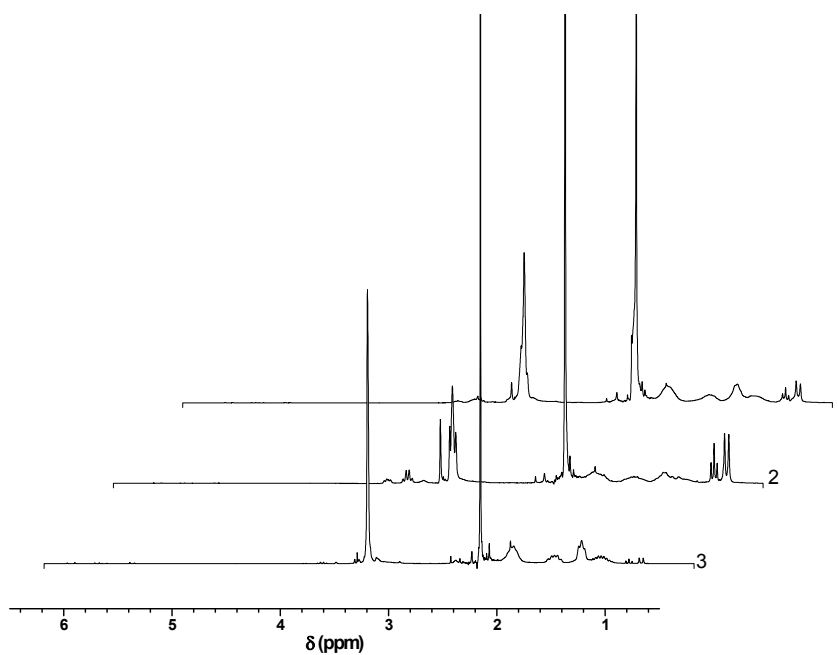


Figure S7b: ^1H NMR spectra showing the monomer conversion for each cycle.

Table S6: Characterization data for the synthesis of the triblock homopolymer obtained from UV experiment. Initial feed ratio = [MA]:[EBiB]:[CuBr₂]:[Me₆-Tren] = [3]:[1]:[0.02]:[0.12] in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	M _{n,th} [g mol ⁻¹]	M _{n,GPC} ^b [g mol ⁻¹]	<i>D</i>
1	Poly(MA ₃)	12	99	450	200	1.23
2	Poly(MA ₃ -MA ₃)	12	99	710	500	1.24
3	Poly(MA ₃ -MA ₃ -MA ₃)	15	97	970	700	1.23

^aDetermined by ¹H NMR. ^bDetermined by CHCl₃ SEC analysis.

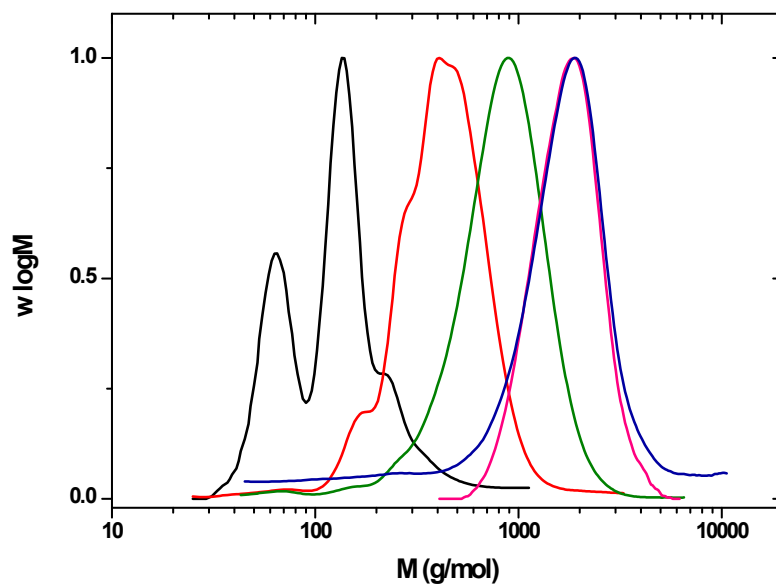


Figure S8a: Molecular weight distributions for successive cycles during synthesis of pentablock homopolymer DP=3 in DMSO at ambient temperature. A fresh solution of [Me₆-Tren] = [0.12], was added together with the monomer upon every 2nd addition.

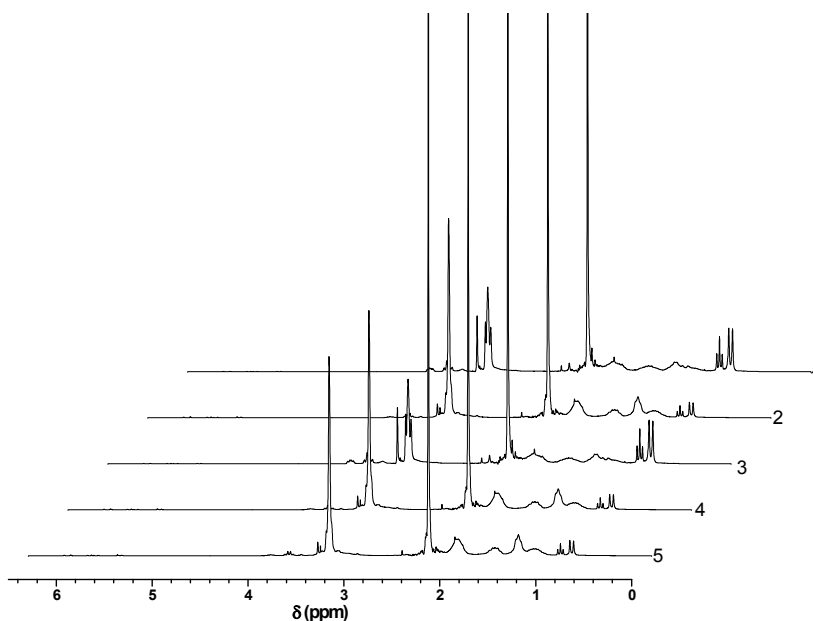


Figure S8b: ^1H NMR spectra showing the monomer conversion for each cycle.

Table S7: Characterization data for the synthesis of the pentablock homopolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [3]:[1]:[0.02]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol ⁻¹]	$M_{n,\text{GPC}}$ ^b [g mol ⁻¹]	\bar{D}
1	Poly(MA ₃)	12	99	450	105	1.45
2	Poly(MA ₃ -MA ₃)	12	99	710	355	1.34
3	Poly(MA ₃ -MA ₃ -MA ₃)	12	99	970	680	1.25
4	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	99	1230	1500	1.15
5	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	100	1500	1560	1.35

^aDetermined by ^1H NMR. ^bDetermined by CHCl_3 SEC analysis.

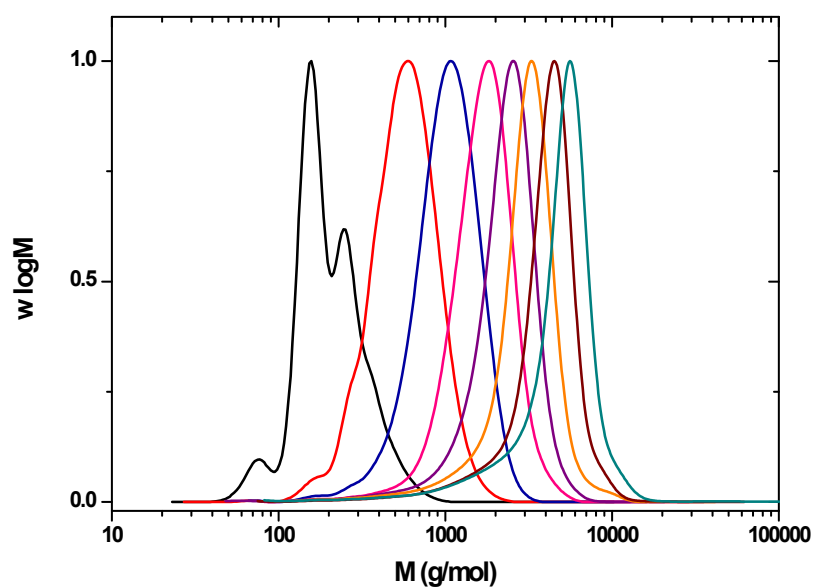


Figure S9a: Molecular weight distributions for successive cycles during synthesis of octablock homopolymer $DP=3$ in DMSO at ambient temperature. A fresh solution of $[CuBr_2]:[Me_6-Tren] = [0.01]:[0.12]$, was added together with the monomer upon every 3rd addition.

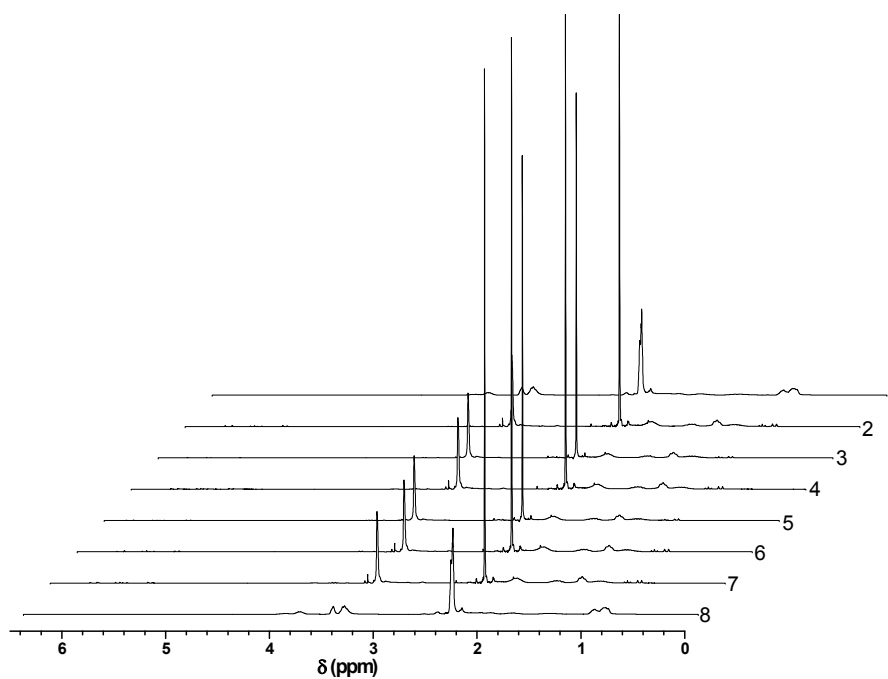


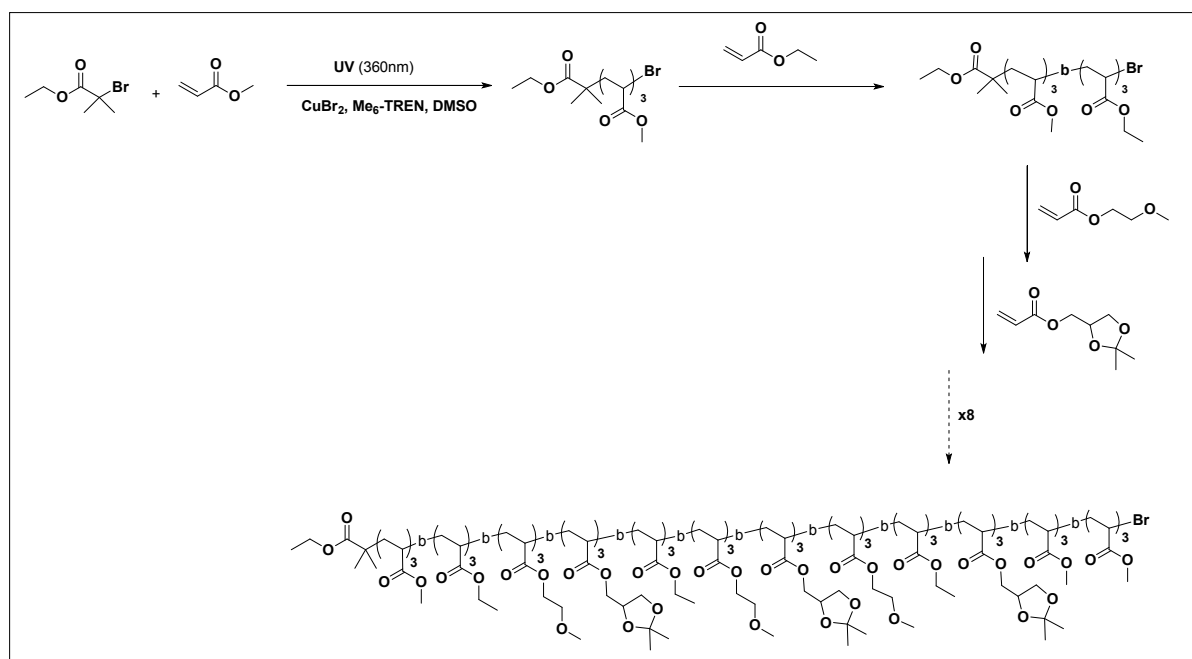
Figure S9b: 1H NMR spectra showing the monomer conversion for each cycle.

Table S8: Characterization data for the synthesis of the octablock homopolymer obtained from UV experiment. Initial feed ratio = [MA]:[EBiB]:[CuBr₂]:[Me₆-Tren] = [3]:[1]:[0.01]:[0.12] in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	M _{n,th} [g mol ⁻¹]	M _{n,GPC} ^b [g mol ⁻¹]	Đ
1	Poly(MA ₃)	12	100	450	200	1.25
2	Poly(MA ₃ -MA ₃)	12	99	710	500	1.24
3	Poly(MA ₃ -MA ₃ -MA ₃)	12	100	970	900	1.23
4	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	99	1230	1500	1.21
5	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	100	1500	2000	1.23
6	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	12	99	1750	2500	1.29
7	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	13	98	2010	3500	1.22
8	Poly(MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃ -MA ₃)	15	95	2270	3800	1.37

^aDetermined by ¹H NMR. ^bDetermined by CHCl₃ SEC analysis.

Scheme S2: Synthesis of multiblock copolymers DP=3 by sequential addition of monomers without intermediate purification.



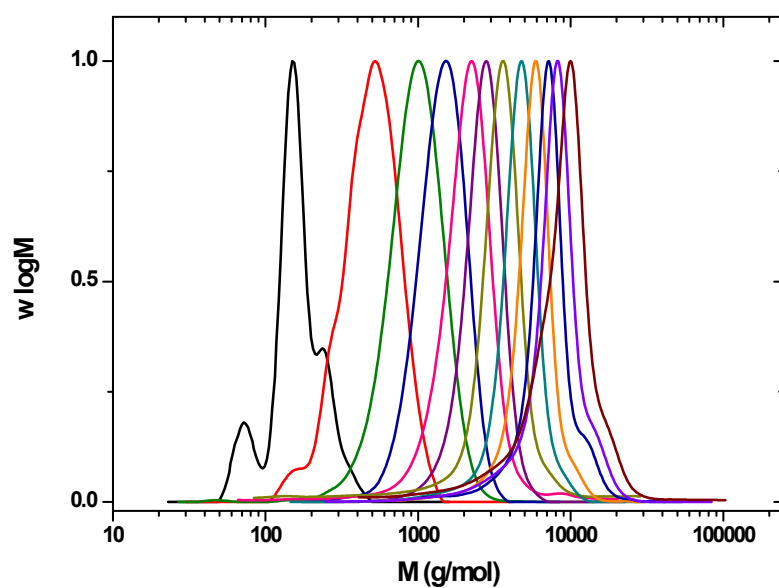


Figure S10a: Molecular weight distributions for successive cycles during synthesis of dodecablock copolymer $DP=3$ in DMSO at ambient temperature. A fresh solution of $[CuBr_2]:[Me_6-Tren] = [0.02]:[0.12]$, was added together with the monomer upon every 3rd addition.

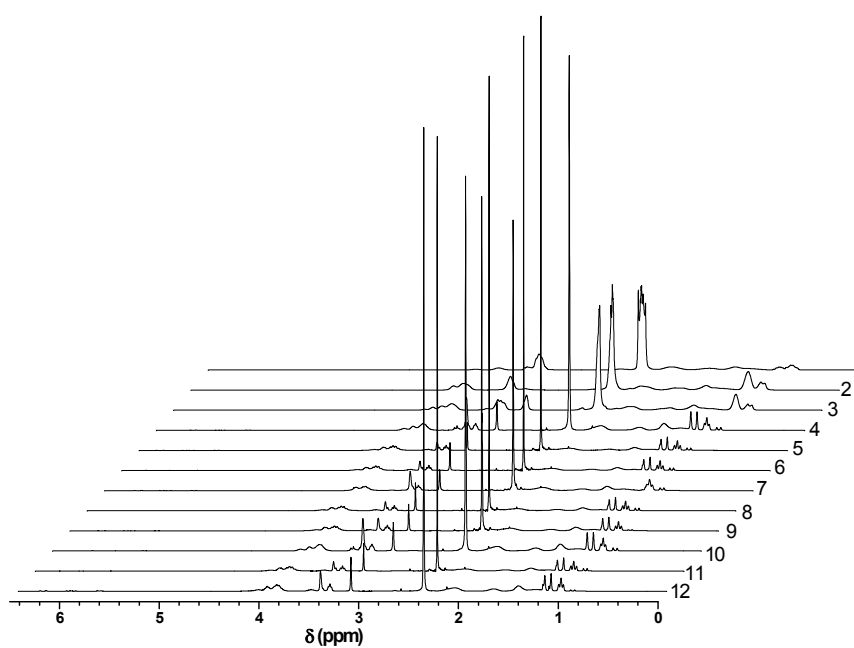


Figure S10b: 1H NMR spectra showing the monomer conversion for each cycle.

Table S9: Characterization data for the synthesis of the dodecablock copolymer obtained from UV experiment. Initial feed ratio = [MA]:[EBiB]:[CuBr₂]:[Me₆-Tren] = [3]:[1]:[0.02]:[0.12] in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	M _{n,th} [g mol ⁻¹]	M _{n,GPC} ^b [g mol ⁻¹]	<i>D</i>
1	Poly(MA ₃)	12	99	450	144	1.17
2	Poly(MA ₃ -EA ₃)	12	99	760	430	1.21
3	Poly(MA ₃ -EA ₃ -EGA ₃)	12	98	1150	800	1.20
4	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃)	12	99	1700	1300	1.14
5	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃ -EA ₃)	12	98	2000	1800	1.15
6	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃ -EA ₃ -EGA ₃)	12	96	2400	2480	1.11
7	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃ -EA ₃ -EGA ₃ -SA ₃)	12	96	3000	3200	1.13
8	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃ -EA ₃ -EGA ₃ -SA ₃ -EGA ₃)	12	96	3400	4200	1.12
9	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃ -EA ₃ -EGA ₃ -SA ₃ -EGA ₃ -EA ₃)	15	97	3600	5400	1.11
10	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃ -EA ₃ -EGA ₃ -SA ₃ -EGA ₃ -EA ₃ -SA ₃)	19	99	4200	6600	1.12
11	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃ -EA ₃ -EGA ₃ -SA ₃ -EGA ₃ -EA ₃ -SA ₃ -MA ₃)	24	99	4500	7000	1.19
12	Poly(MA ₃ -EA ₃ -EGA ₃ -SA ₃ -EA ₃ -EGA ₃ -SA ₃ -EGA ₃ -EA ₃ -SA ₃ -MA ₃ -EGA ₃)	48	92	4900	10000	1.39

^aDetermined by ¹H NMR. ^bDetermined by CHCl₃ SEC analysis.

DP=10

Scheme S3: Synthesis of **multiblock copolymers DP=10** by sequential addition of monomers without intermediate purification.

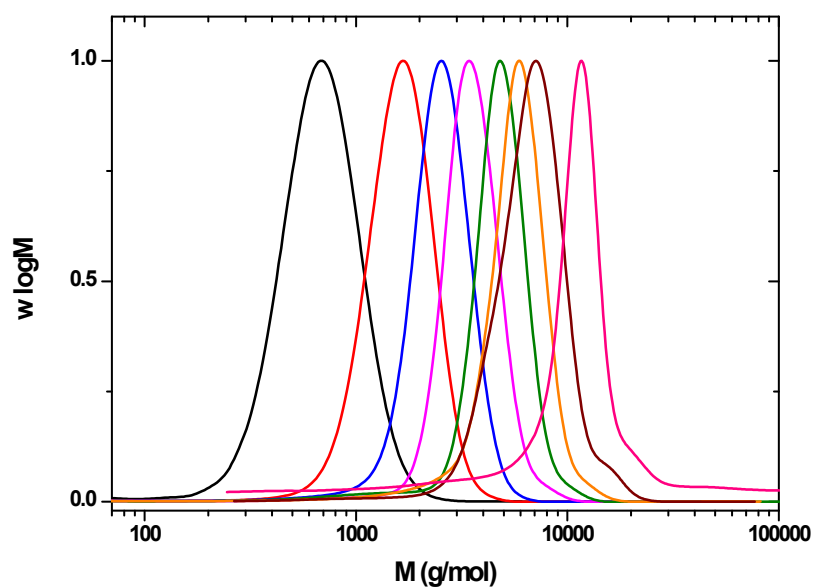
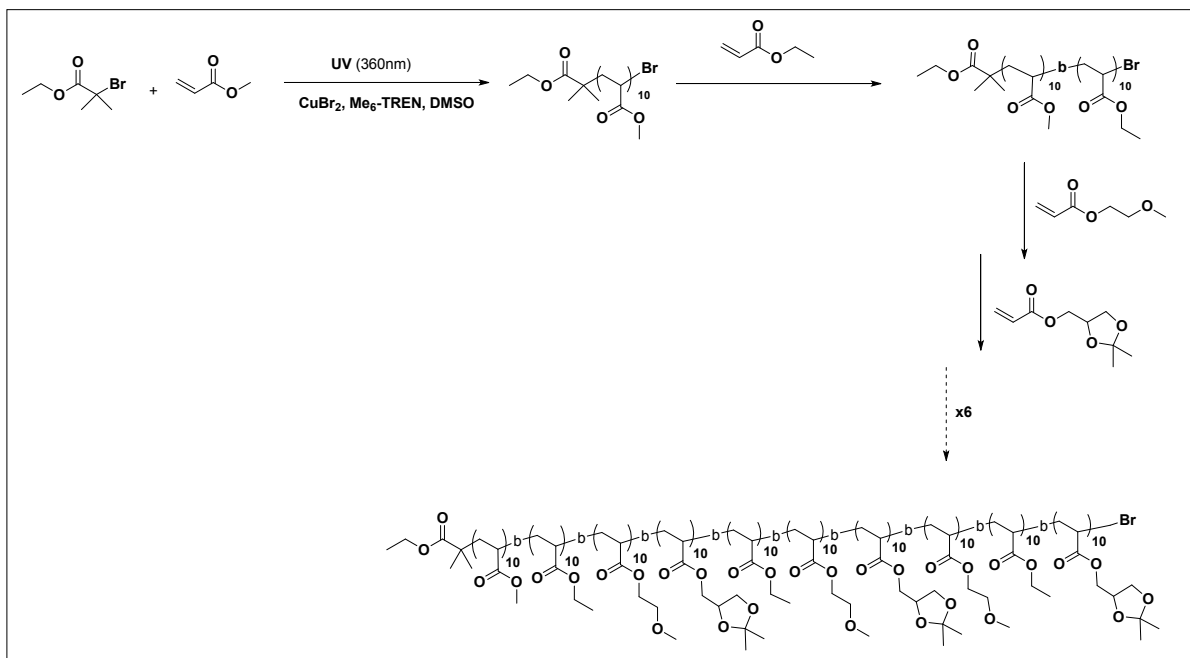


Figure S11a: Molecular weight distributions for successive cycles during synthesis of octablock copolymer **DP=10** in DMSO at ambient temperature. A fresh solution of [CuBr₂]:[Me₆-Tren] = [0.02]:[0.12], was added together with the monomer upon every 3rd addition.

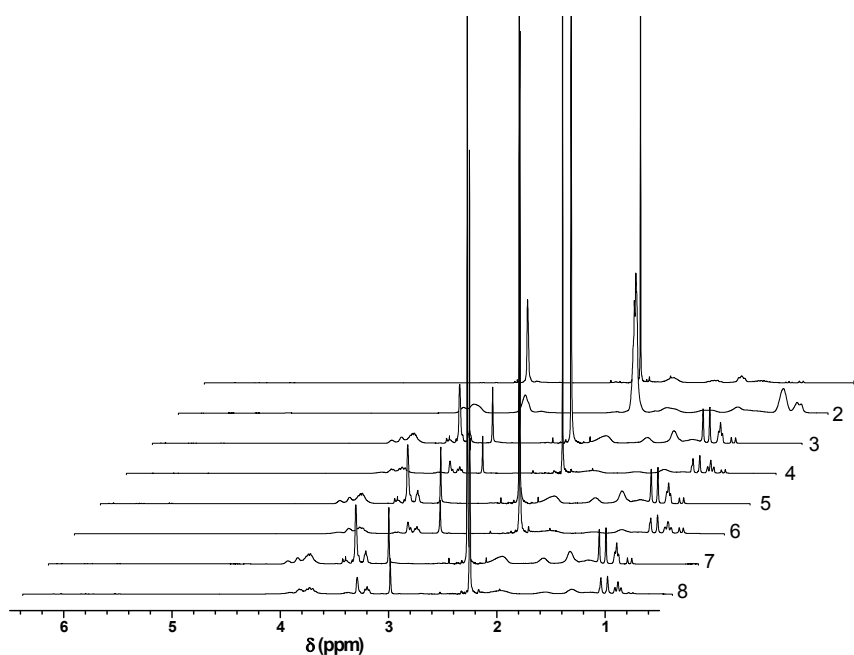


Figure S11b: ^1H NMR spectra showing the monomer conversion for each cycle.

Table S10: Characterization data for the synthesis of the octablock copolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [10]:[1]:[0.02]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol^{-1}]	$M_{n,\text{GPC}}$ ^b [g mol^{-1}]	\bar{D}
1	Poly(MA_{10})	2	99	1060	600	1.24
2	Poly($\text{MA}_{10}\text{-EA}_{10}$)	6	99	2100	1500	1.15
3	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}$)	12	100	3400	2300	1.15
4	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}$)	12	97	5200	3300	1.12
5	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}$)	12	99	6200	4000	1.19
6	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}$)	14	99	7600	5000	1.17
7	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}$)	16	98	9400	6000	1.15
8	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EGA}_{10}$)	24	97	11200	8000	1.35

^aDetermined by ^1H NMR. ^bDetermined by CHCl_3 SEC analysis.

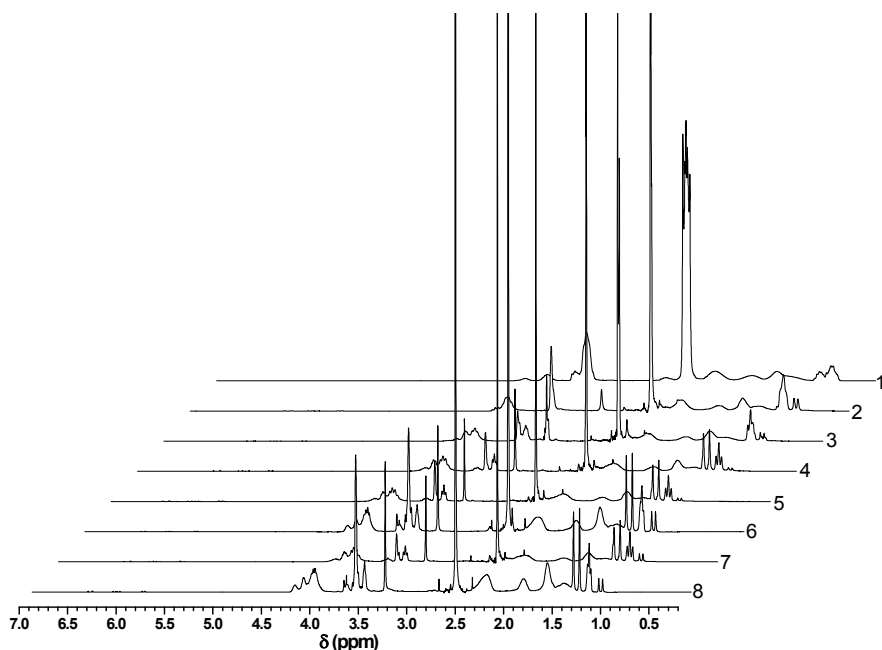


Figure S12: ^1H NMR spectra showing the monomer conversion for each cycle during synthesis of octablock copolymer $\text{DP}=10$ in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [\mathbf{0.02}]:[\mathbf{0.12}]$, was added together with the monomer upon every 2nd addition.

Table S11: Characterization data for the synthesis of the octablock copolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [\mathbf{10}]:[\mathbf{1}]:[\mathbf{0.02}]:[\mathbf{0.12}]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol^{-1}]	$M_{n,\text{GPC}}^{\text{b}}$ [g mol^{-1}]	\bar{D}
1	Poly(MA_{10})	2	99	1060	880	1.17
2	Poly($\text{MA}_{10}\text{-EA}_{10}$)	6	99	2100	2000	1.12
3	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}$)	12	100	3400	3400	1.09
4	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}$)	12	97	5200	4800	1.07
5	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}$)	12	95	6200	6500	1.08
6	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}$)	14	99	7600	8400	1.07
7	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}$)	16	98	9400	10200	1.11
8	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EGA}_{10}$)	24	99	11200	12400	1.10

^aDetermined by ^1H NMR. ^bDetermined by CHCl_3 SEC analysis.

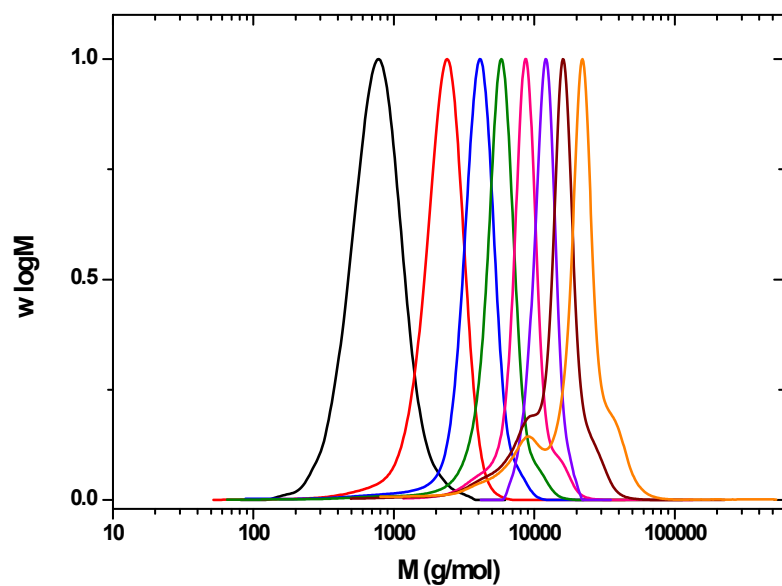


Figure S13a: Molecular weight distributions for successive cycles during synthesis of octablock copolymer DP=10 in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [0.02]:[0.12]$, was added together with the monomer upon every addition.

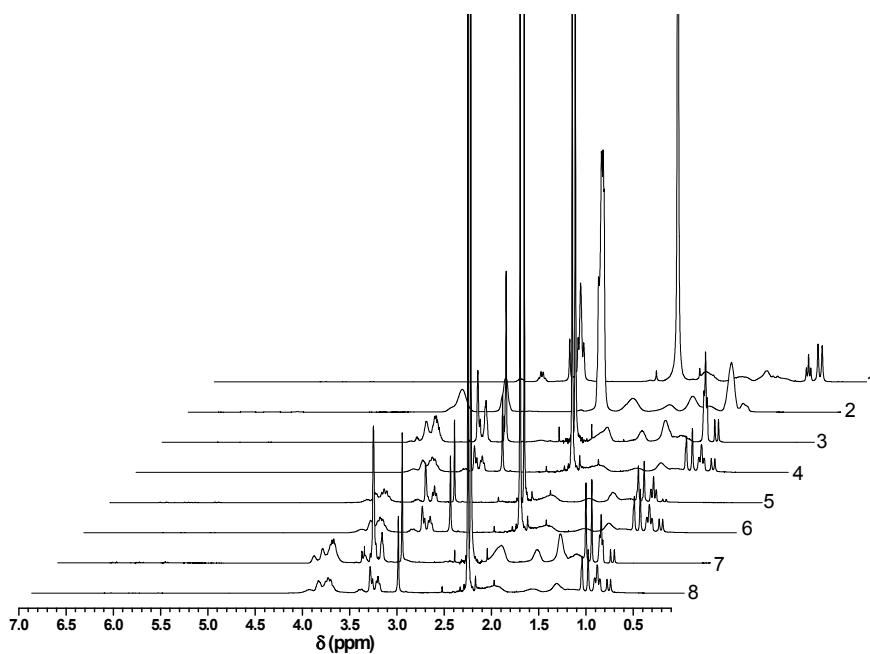


Figure S13b: ^1H NMR spectra showing the monomer conversion for each cycle.

Table S12: Characterization data for the synthesis of the octablock copolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [10]:[1]:[0.02]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol ⁻¹]	$M_{n,\text{GPC}}$ ^b [g mol ⁻¹]	\mathcal{D}
1	Poly(MA ₁₀)	2	100	1060	700	1.22
2	Poly(MA ₁₀ -EA ₁₀)	6	100	2100	2000	1.17
3	Poly(MA ₁₀ -EA ₁₀ -EGA ₁₀)	12	100	3400	3800	1.10
4	Poly(MA ₁₀ -EA ₁₀ -EGA ₁₀ -SA ₁₀)	12	99	5200	5200	1.13
5	Poly(MA ₁₀ -EA ₁₀ -EGA ₁₀ -SA ₁₀ -EA ₁₀)	12	97	6200	8000	1.11
6	Poly(MA ₁₀ -EA ₁₀ -EGA ₁₀ -SA ₁₀ -EA ₁₀ -EGA ₁₀)	14	99	7600	11500	1.05
7	Poly(MA ₁₀ -EA ₁₀ -EGA ₁₀ -SA ₁₀ -EA ₁₀ -EGA ₁₀ -SA ₁₀)	16	97	9400	10800	1.29
8	Poly(MA ₁₀ -EA ₁₀ -EGA ₁₀ -SA ₁₀ -EA ₁₀ -EGA ₁₀ -SA ₁₀ -EGA ₁₀)	24	99	11200	15900	1.36

^aDetermined by ¹H NMR. ^bDetermined by CHCl₃ SEC analysis.

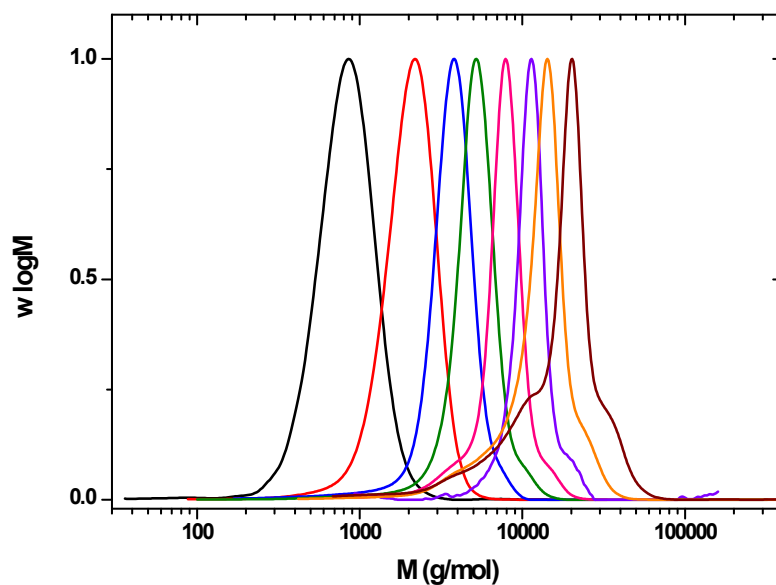


Figure S14a: Molecular weight distributions for successive cycles during synthesis of octablock copolymer DP=10 in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [0.01]:[0.12]$, was added together with the monomer upon every addition.

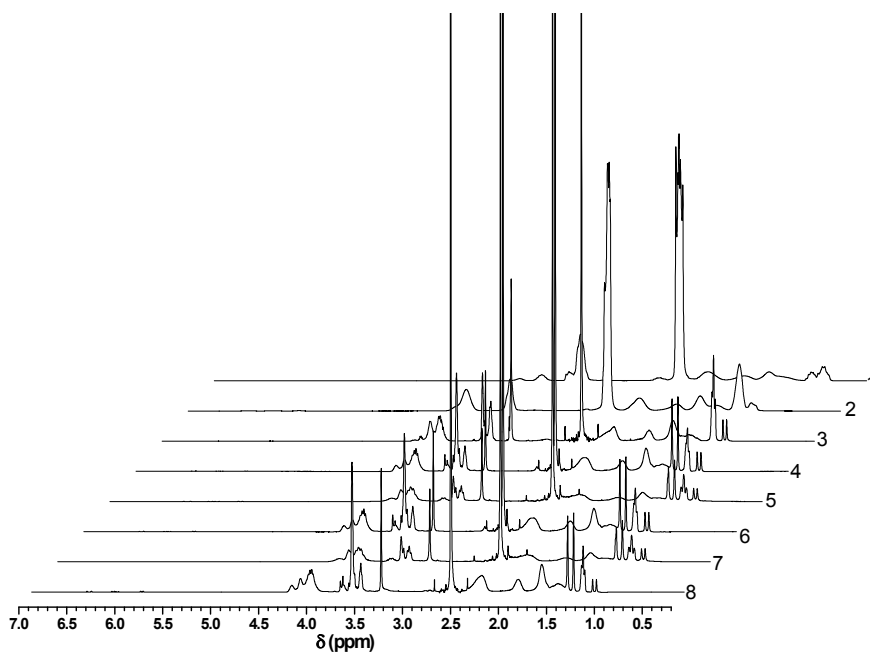


Figure S14b: ^1H NMR spectra showing the monomer conversion for each cycle.

Table S13: Characterization data for the synthesis of the octablock copolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [10]:[1]:[0.01]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol^{-1}]	$M_{n,\text{GPC}}$ ^b [g mol^{-1}]	\bar{D}
1	Poly(MA_{10})	2	100	1060	800	1.19
2	Poly($\text{MA}_{10}\text{-EA}_{10}$)	6	99	2100	1800	1.19
3	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}$)	12	100	3400	3500	1.11
4	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}$)	12	99	5200	4600	1.15
5	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}$)	12	97	6200	7100	1.12
6	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}$)	14	99	7600	10000	1.10
7	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}$)	16	99	9400	10500	1.32
8	Poly($\text{MA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EA}_{10}\text{-EGA}_{10}\text{-SA}_{10}\text{-EGA}_{10}$)	24	99	11200	14000	1.36

^aDetermined by ^1H NMR. ^bDetermined by CHCl_3 SEC analysis.

DP=25

Scheme S4: Synthesis of **multiblock copolymers DP=25** by sequential addition of monomers without intermediate purification.

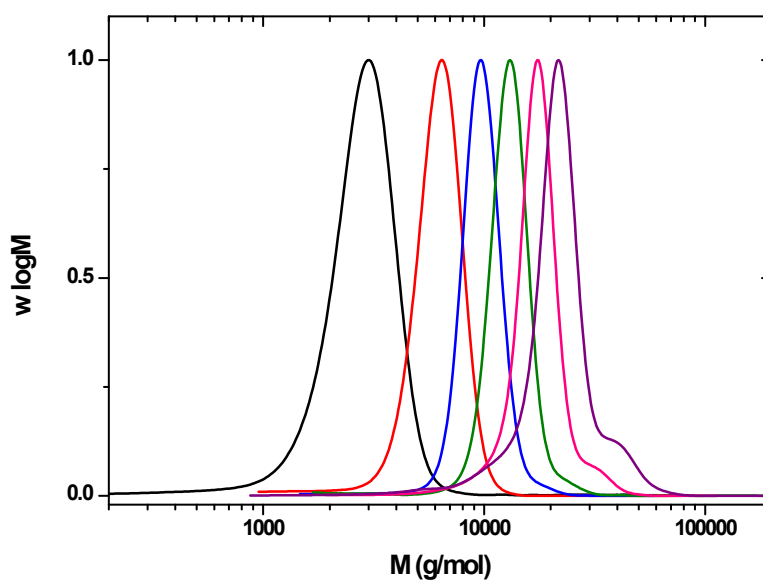
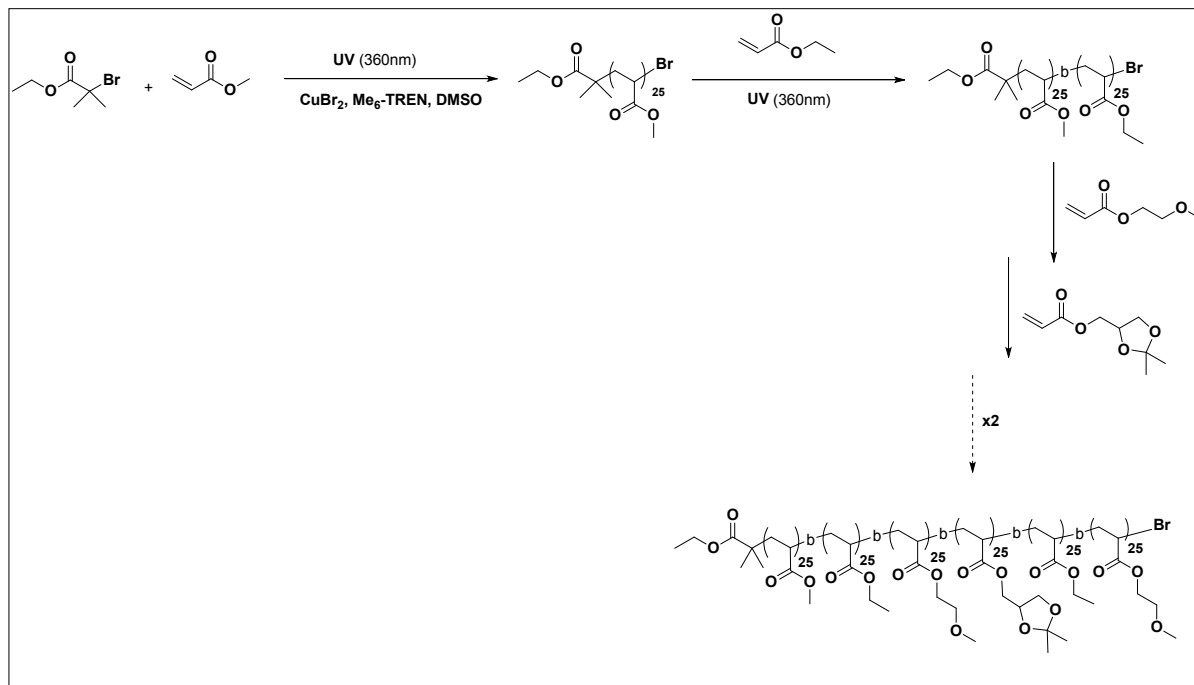


Figure S15a: Molecular weight distributions for successive cycles during synthesis of hexablock copolymer **DP=25** in DMSO at ambient temperature. A fresh solution of [CuBr₂]:[Me₆-Tren] = [0.02]:[0.12], was added together with the monomer upon every 2nd addition.

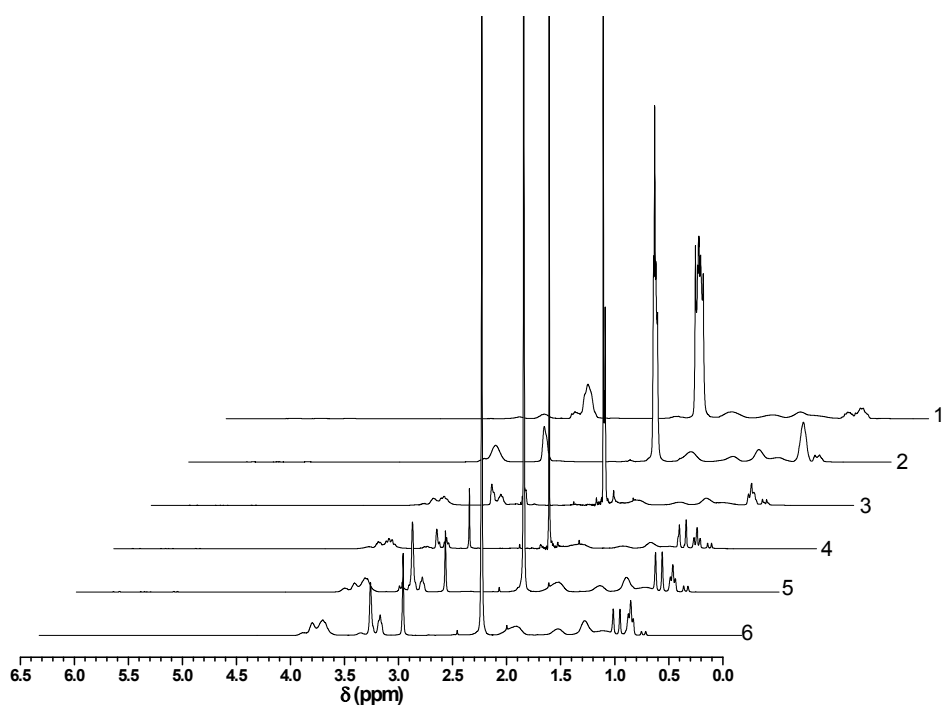


Figure S15b: ^1H NMR spectra showing the monomer conversion for each cycle.

Table S14: Characterization data for the synthesis of the hexablock copolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [25]:[1]:[0.02]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol^{-1}]	$M_{n,\text{GPC}}$ ^b [g mol^{-1}]	\bar{D}
1	Poly(MA_{25})	2	99	2400	2600	1.14
2	Poly($\text{MA}_{25}\text{-EA}_{25}$)	4	99	4900	6000	1.06
3	Poly($\text{MA}_{25}\text{-EA}_{25}\text{-EGA}_{25}$)	7	98	8200	9500	1.05
4	Poly($\text{MA}_{25}\text{-EA}_{25}\text{-EGA}_{25}\text{-SA}_{25}$)	8	99	12700	13000	1.05
5	Poly($\text{MA}_{25}\text{-EA}_{25}\text{-EGA}_{25}\text{-SA}_{25}\text{-EA}_{25}$)	12	97	15200	16600	1.08
6	Poly($\text{MA}_{25}\text{-EA}_{25}\text{-EGA}_{25}\text{-SA}_{25}\text{-EA}_{25}\text{-EGA}_{25}$)	20	99	18200	19900	1.15

^aDetermined by ^1H NMR. ^bDetermined by CHCl_3 SEC analysis.

DP=100

Scheme S5: Synthesis of **multiblock copolymers DP=100** by sequential addition of monomers without intermediate purification.

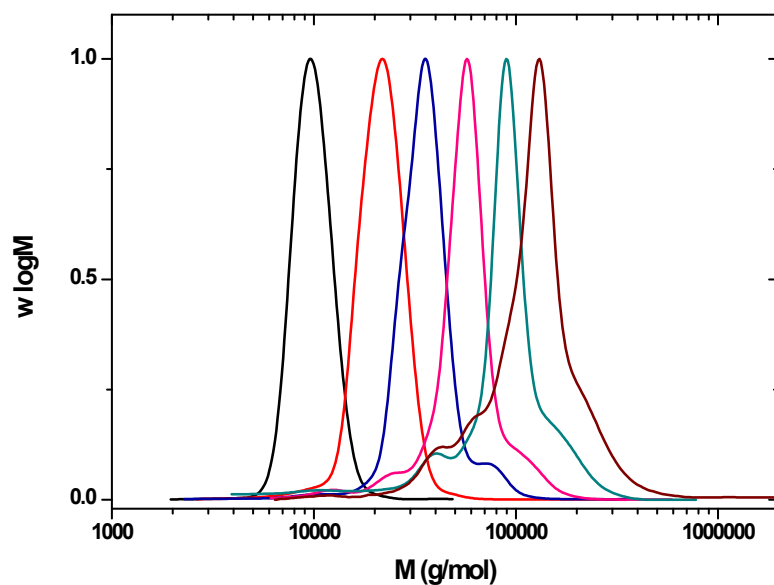
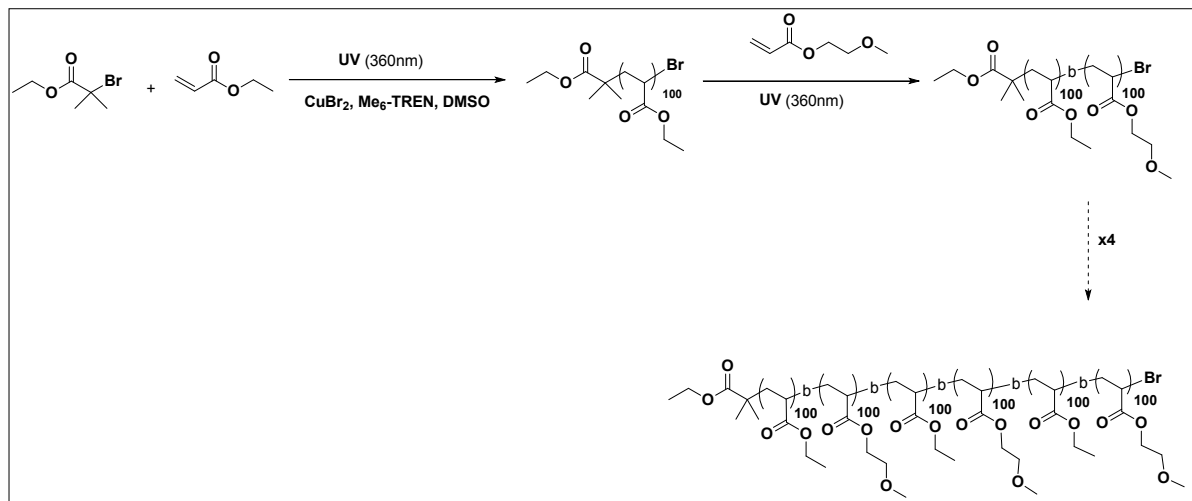


Figure S16a: Molecular weight distributions for successive cycles during synthesis of hexablock copolymer **DP=100** in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [0.02]:[0.12]$, was added together with the monomer upon every 2nd addition.

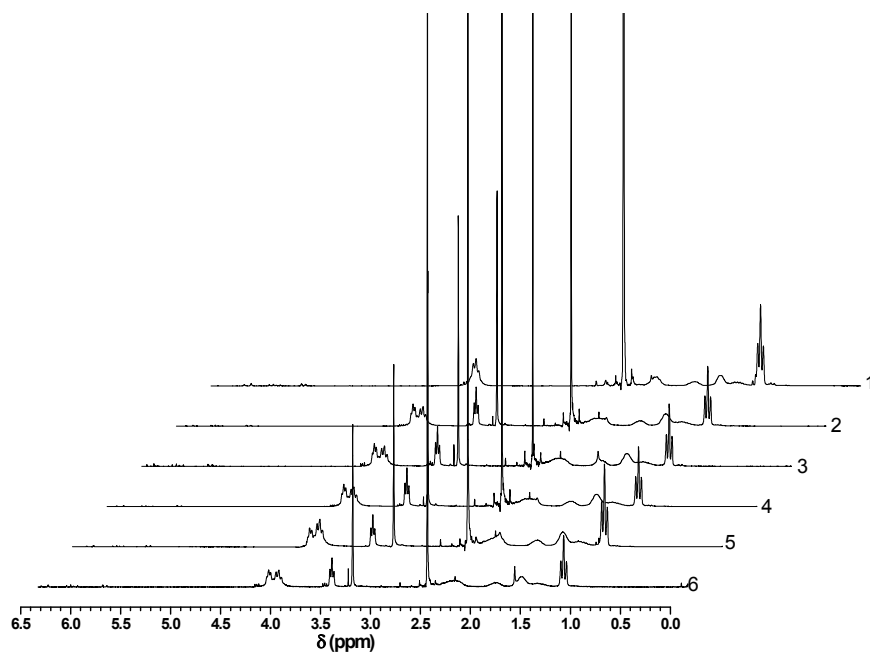


Figure S16b: ^1H NMR spectra showing the monomer conversion for each cycle.

Table S15: Characterization data for the synthesis of the hexablock copolymer obtained from UV experiment. Initial feed ratio = $[\text{MA}]:[\text{EBiB}]:[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [100]:[1]:[0.02]:[0.12]$ in DMSO at ambient temperature.

Cycle	Multiblock copolymer composition	Time (h)	Monomer conversion ^a (%)	$M_{n,\text{th}}$ [g mol^{-1}]	$M_{n,\text{GPC}}$ ^b [g mol^{-1}]	\bar{D}
1	Poly(EA ₁₀₀)	3	98	10200	9600	1.05
2	Poly(EA ₁₀₀ -OEGMA ₁₀₀)	8	99	23200	21000	1.08
3	Poly(EA ₁₀₀ -OEGMA ₁₀₀ -EA ₁₀₀)	12	98	33200	37000	1.17
4	Poly(EA ₁₀₀ -OEGMA ₁₀₀ -EA ₁₀₀ -OEGMA ₁₀₀)	15	99	46200	52000	1.18
5	Poly(EA ₁₀₀ -OEGMA ₁₀₀ -EA ₁₀₀ -OEGMA ₁₀₀ -EA ₁₀₀)	24	97	56200	80000	1.21
6	Poly(EA ₁₀₀ -OEGMA ₁₀₀ -EA ₁₀₀ -OEGMA ₁₀₀ -EA ₁₀₀)	48	85	59200	102000	1.33

^aDetermined by ^1H NMR. ^bDetermined by CHCl_3 SEC analysis.

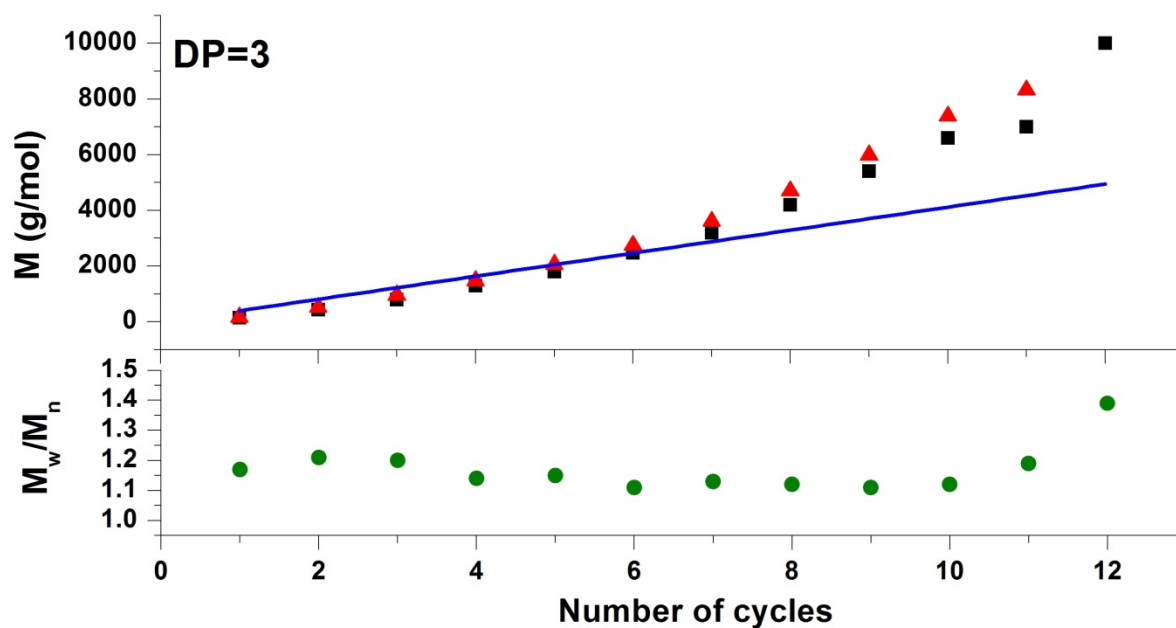


Figure S17: Evolution of theoretical (blue straight line) and experimental molecular weight (M_n (■) and M_w (▲) determined by SEC and M_w/M_n (●) versus the number of cycles during synthesis of dodecablock homopolymer **DP=3** in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [0.02]:[0.12]$, was added together with the monomer upon every 3rd addition.

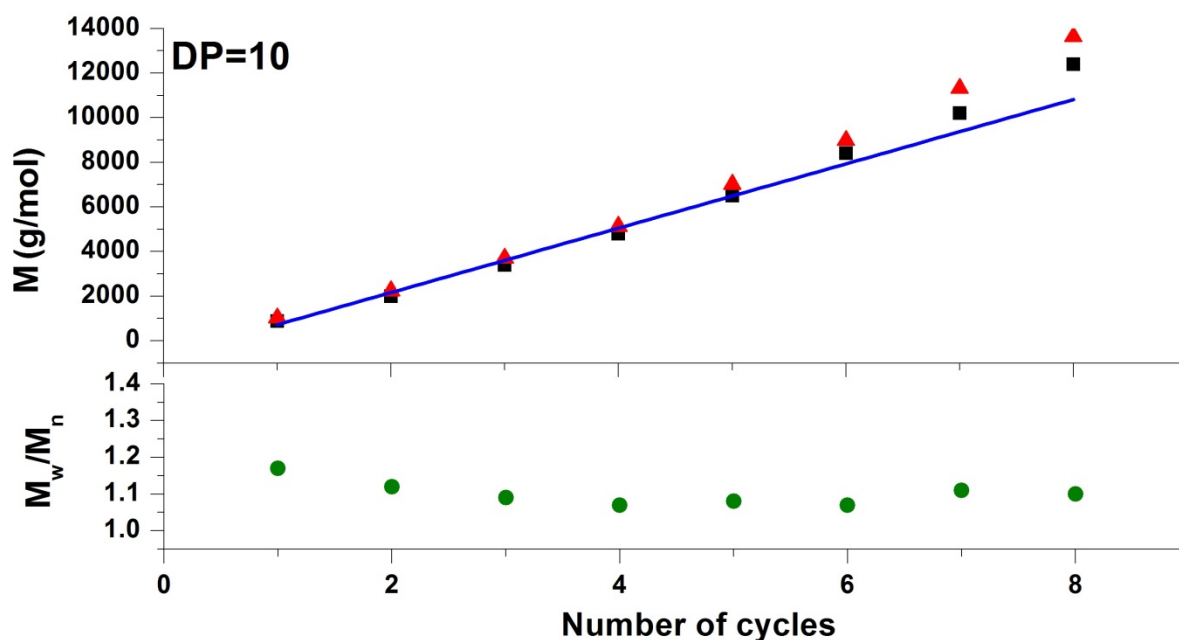


Figure S18: Evolution of theoretical (blue straight line) and experimental molecular weight (M_n (■) and M_w (▲) determined by SEC and M_w/M_n (●) versus the number of cycles during synthesis of octablock copolymer **DP=10** in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [0.02]:[0.12]$, was added together with the monomer upon every 2nd addition.

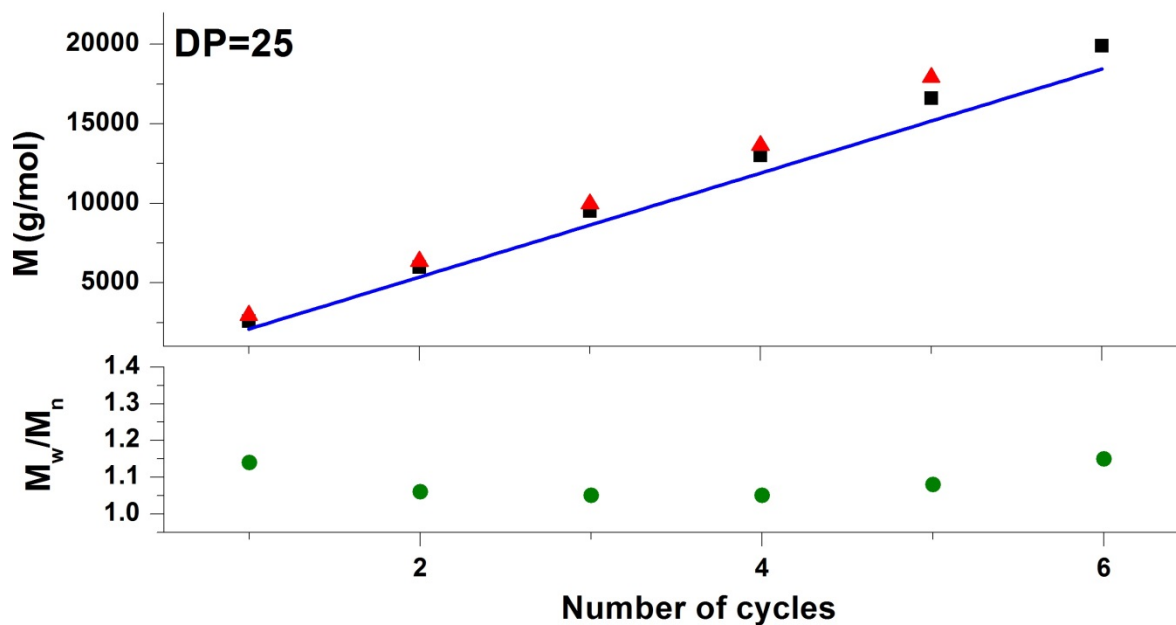


Figure S19: Evolution of theoretical (blue straight line) and experimental molecular weight (M_n (■) and M_w (▲) determined by SEC and M_w/M_n (●) versus the number of cycles during synthesis of hexablock copolymer **DP=25** in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{-Tren}] = [0.02]:[0.12]$, was added together with the monomer upon every 2nd addition.

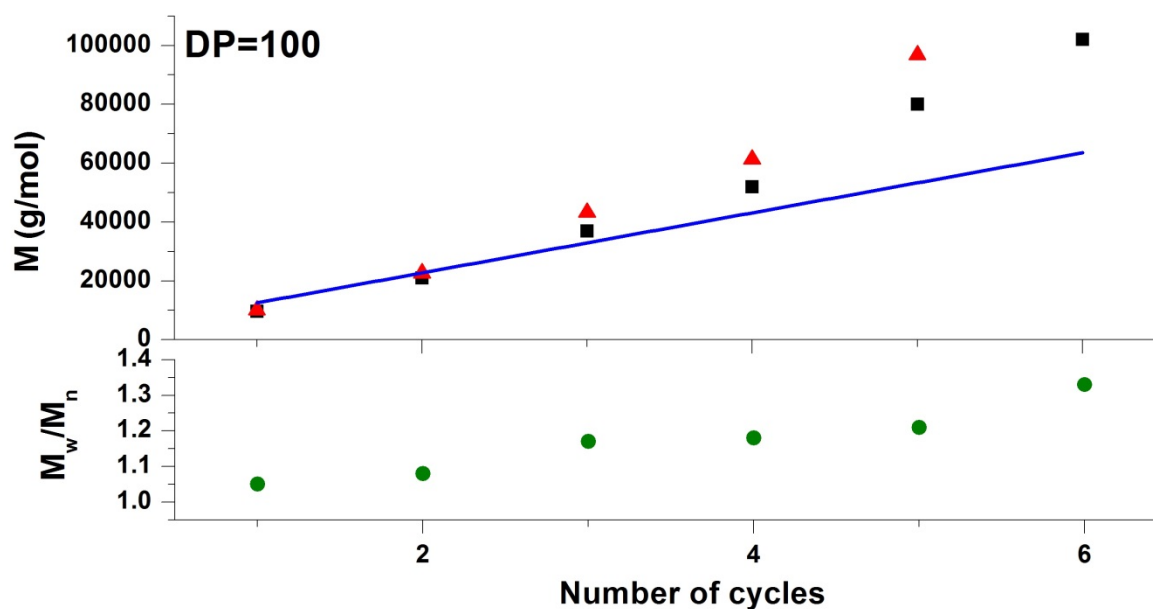


Figure S20: Evolution of theoretical (blue straight line) and experimental molecular weight (M_n (■) and M_w (▲) determined by SEC and M_w/M_n (●) versus the number of cycles during synthesis of

hexablock copolymer **DP=100** in DMSO at ambient temperature. A fresh solution of $[\text{CuBr}_2]:[\text{Me}_6\text{Tren}] = [0.02]:[0.12]$, was added together with the monomer upon **every 2nd** addition.

References

1. M. Ciampolini and N. Nardi, *Inorg. Chem.*, 1966, 5, 41-44.
2. K. Oguchi, K. Sanui, N. Ogata, Y. Takahashi and T. Nakada, *Polym. Eng. Sci.*, 1990, 30, 449-452.