

Synthesis of high molar mass all-(meth)acrylic thermoplastic elastomers by photo-initiated RAFT polymerisation

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Methods

Differential Scanning Calorimetry (DSC). The glass transition temperature (T_g) of triblock copolymer was measured by DSC using Mettler Toledo STARe DSC in nitrogen atmosphere using aluminum crucibles of 40 μL at heating rates of 10 $^\circ\text{C}/\text{min}$. Sample in 15 mg portion was used for analysis. T_g value was obtained from the second ramp to remove the thermal history of the sample.

Light intensity measurement. The light intensity of photoreactors was measured was measured with a GENTEC Maestro power and energy meter equipped with a 12 mm diameter probe. The detector was inserted inside the reactor in 3 different positions, and the light intensity was measured 3 times for 1 minute in each position.

Nuclear Magnetic Resonance (NMR). ^1H NMR spectra of *PnBA*, PMMA, and ABA triblock copolymers were recorded at 25 $^\circ\text{C}$ with a Bruker Avance 300 MHz instrument at an operating frequency of 300.13 MHz. The resonance multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Chemical shifts δ are reported in parts per million (ppm) and are referenced to the residual solvent peak (CDCl_3 : H = 7.26 ppm).

Rheological measurements. Isochronal temperature ramp tests were performed on an Anton Paar MCR 302. The experiments were performed in parallel plate geometry using 8 mm sample disks. A frequency of 1 $\text{rad}\cdot\text{s}^{-1}$, and a strain of 1 % were used to record the evolution of the dynamic moduli as function of the temperature with a heating rate of 2.5 $^\circ\text{C}/\text{min}$.

Size Exclusion Chromatography (SEC). The molecular masses and molecular mass distributions of *PnBA*, PMMA, and ABA triblock copolymers were determined by SEC using THF as an eluent at a flow rate of 1.0 mL min^{-1} at 25 $^\circ\text{C}$. Before the analysis, the polymers were carefully dissolved in the eluent (the final concentration was 5 mg mL^{-1}) and filtered through a 0.45 μm PTFE filter. The samples were analyzed using a two-column set Styragel HR3 and HR4 (Waters) coupled with a three-detector system: refractometer thermostated at 35 $^\circ\text{C}$ (Optilab Rex, Wyatt technology), a UV detector (Prostar, Varian) set at 290 nm, and a multiangle laser light scattering detector (Mini Dawn, 3 angles, Wyatt technology). The dn/dc for PMMA (0.085) and *PnBA* (0.067) were adopted from the literature.^{1,2} The dn/dc of the ABA triblock copolymers were calculated based on the weight fraction of PMMA and *PnBA*.

Thermogravimetric Analysis (TGA). TGA analysis was conducted on a TGA/DSC 3+ Mettler with a temperature ramp of 10 °C/min under N₂ (50 mL/min).

Synthetic protocols

General procedure for the polymerisation of MMA with TTC-bCP. A reaction stock solution of **TTC-bCP** and MMA (70% or 50% w/w) in acetonitrile was prepared. 1 mL of solution was then added to several glass tubes and degassed by three freeze-pump-thaw cycles. The tubes were sealed with an acetylene/oxygen flame and irradiated in a blue or green LED-based photoreactor. Polymerisation was stopped by removing the tube from the light source. The samples were directly analyzed by ¹H NMR. For SEC analysis, the solvent was evaporated, and polymers were dissolved in THF.

General procedure for the polymerisation of *n*BA with TTC-bCP. TTC-bCP was carefully dissolved in *n*-butyl acrylate. 1 mL of solution was then added to several glass tubes and degassed by three freeze-pump-thaw cycles. The tubes were sealed with an acetylene/oxygen flame and irradiated in a blue or green LED-based photoreactor. Polymerisation was stopped by removing the tube from the light source. Samples were directly analyzed by ¹H NMR. For SEC analysis, the residual *n*BA was evaporated, and polymers were dissolved in THF.

General procedure for ABA triblock copolymer synthesis. PMMA-macroCTA was carefully dissolved in *n*-butyl acrylate. 1 mL of solution was then added to several glass tubes and degassed by three freeze-pump-thaw cycles. The tubes were sealed with an acetylene/oxygen flame and irradiated in a blue LED-based photoreactor. Polymerisation was stopped by removing the tube from the light source. Samples were directly analyzed by ¹H NMR. For SEC analysis, the residual *n*BA was evaporated, and polymers were dissolved in THF.

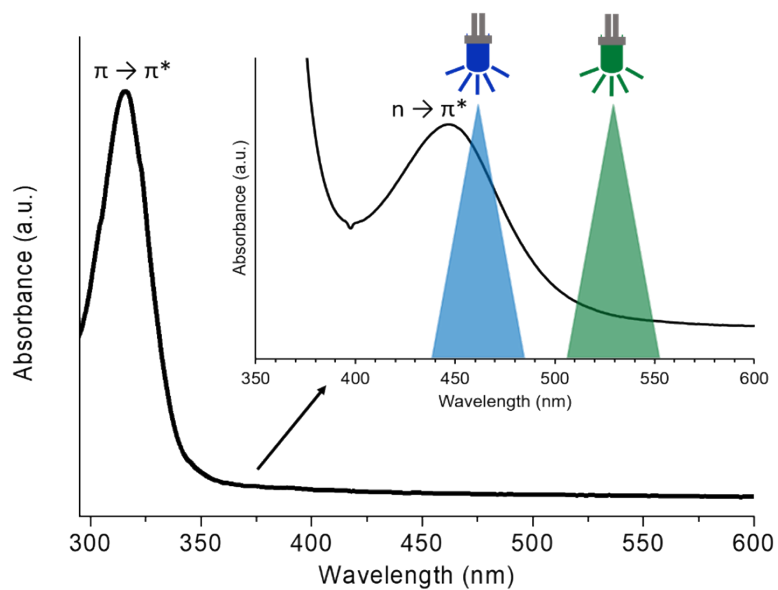


Figure S1. UV-Vis spectrum of bis-(2-methylpropanenitrile)trithiocarbonate (TTC-bCP).

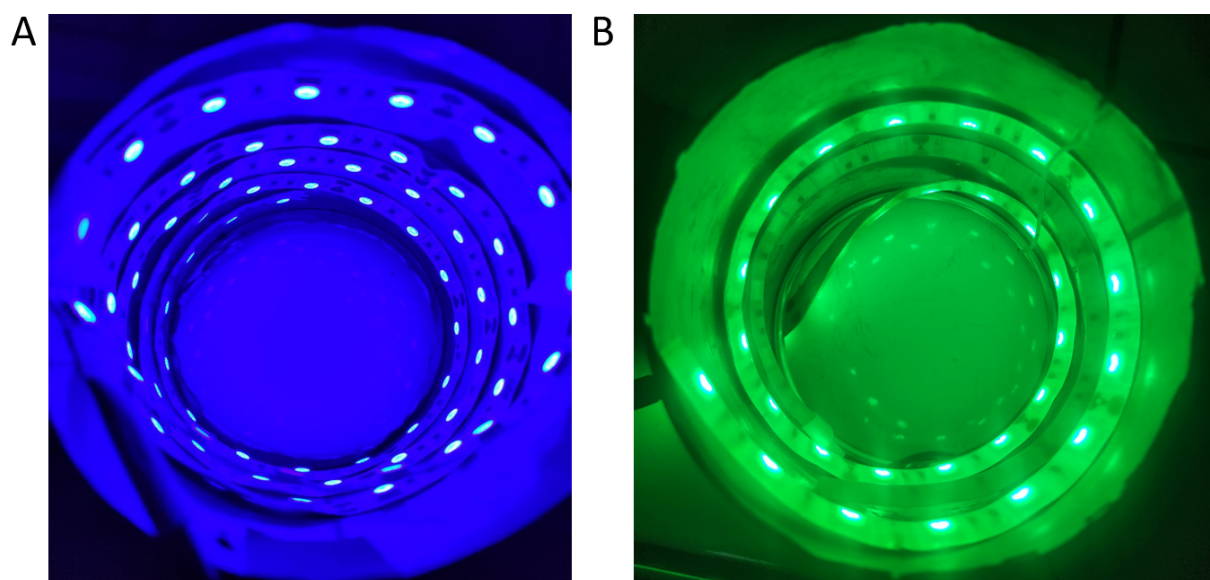


Figure S2. Blue (A) and green (B) LED light photoreactors (view from the top).

Table S1. Detailed information about the photoreactors.

Photoreactor	Light wavelength (nm)	Number of LEDs	Light intensity (mW cm ⁻²)
Blue	460	60	3.33 ± 0.43
		30	2.21 ± 0.16
Green	530	60	2.35 ± 0.17

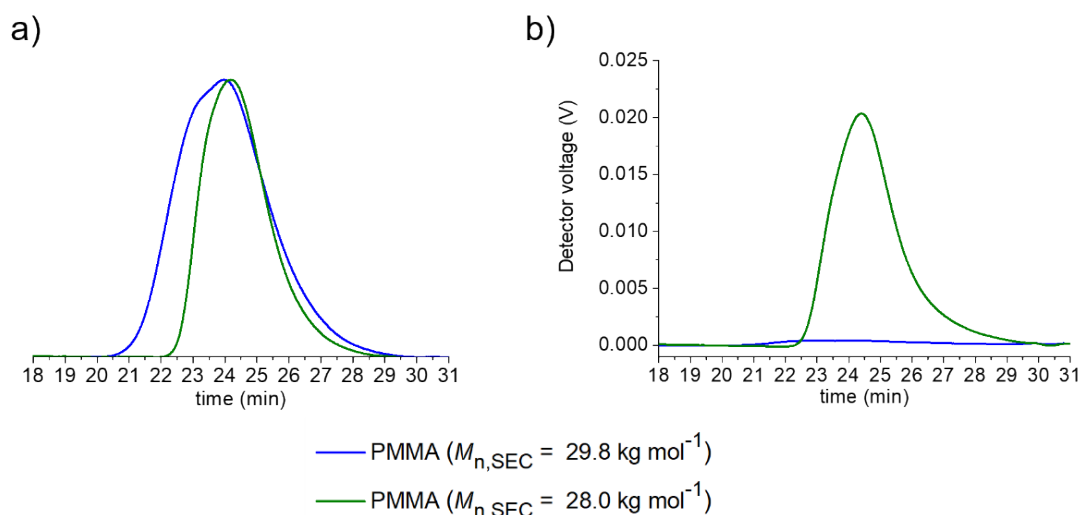


Figure S3. SEC chromatograms of PMMA ($M_{n,th} = 50 \text{ kg mol}^{-1}$) obtained with different sources of visible light: a) normalized RI signal, b) UV detector (290 nm) voltage versus time. Blue SEC traces represent PMMA prepared under blue LED irradiation. Green SEC traces represent PMMA prepared under green LED irradiation.

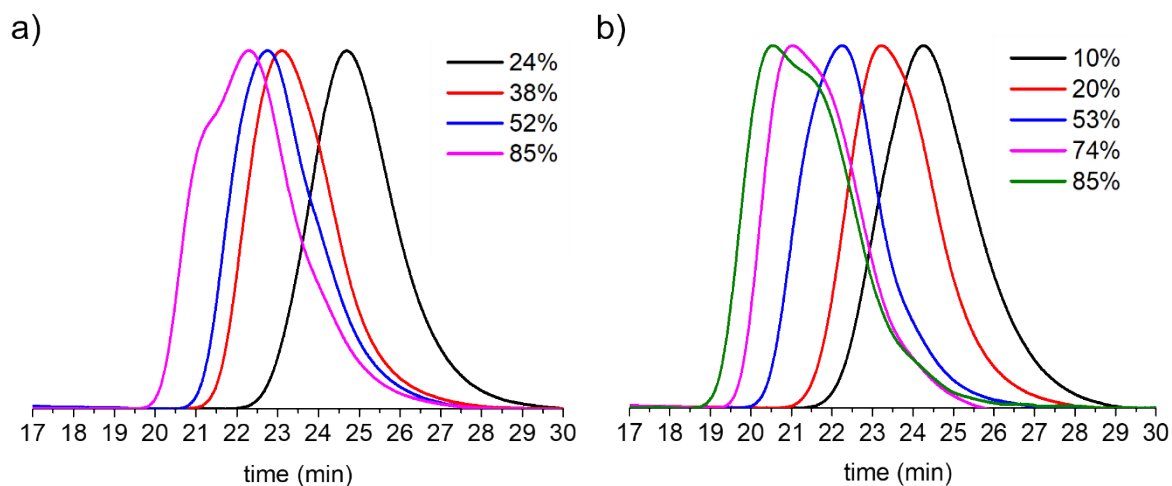


Figure S4. Evolution of PMMA SEC-RI chromatograms with MMA conversion for polymerisations carried out with a) $[MMA]_0 = 4.28 \text{ mol L}^{-1}$ in acetonitrile and b) $[MMA]_0 = 6.21 \text{ mol L}^{-1}$ in acetonitrile. Reaction conditions given in Table S2.

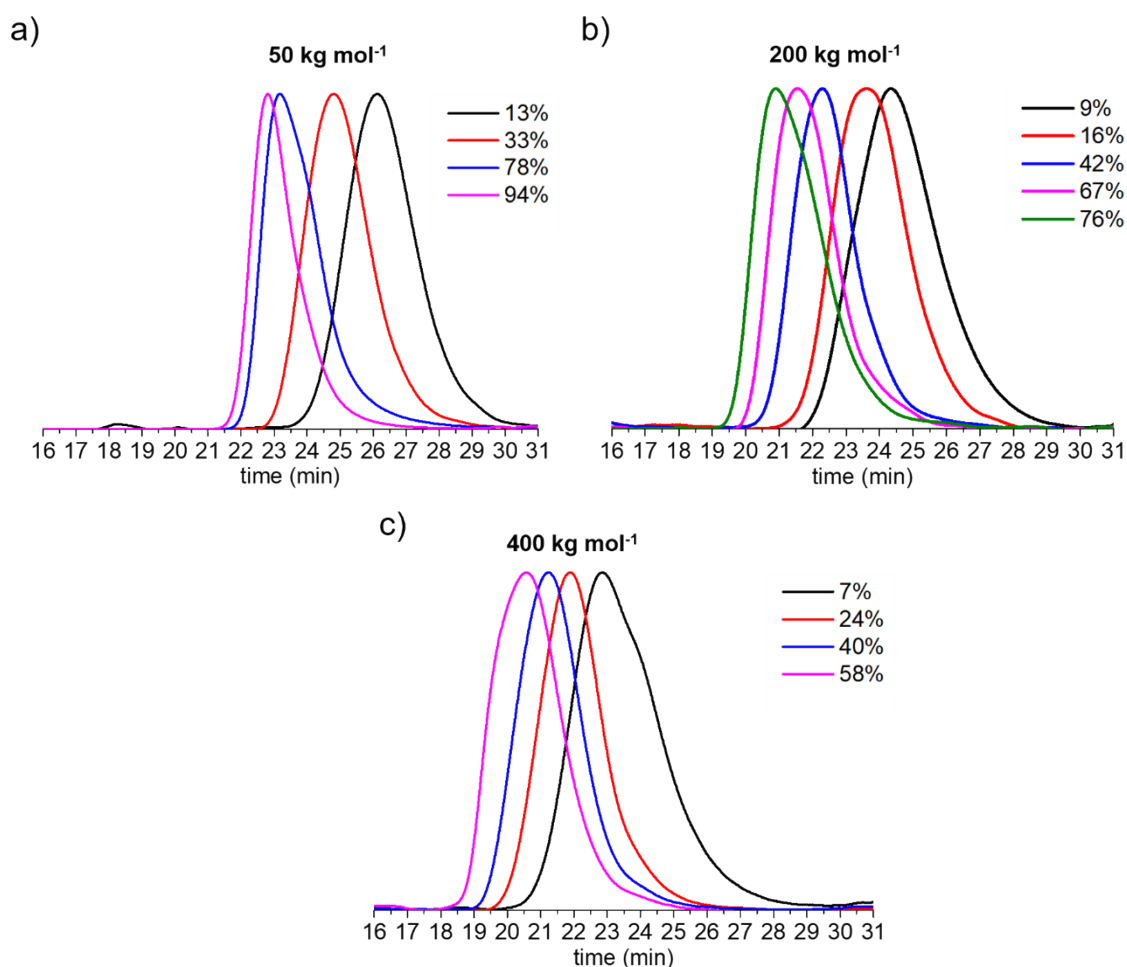


Figure S5. Evolution of SEC-RI chromatograms of PMMA prepared with TTC-bCP with MMA conversion for different targeted molar masses corresponding to $[\text{TTC-bCP}]_0 = 12.49, 3.11, 1.55 \text{ mmol L}^{-1}$ respectively. Reaction conditions given in Table S3.

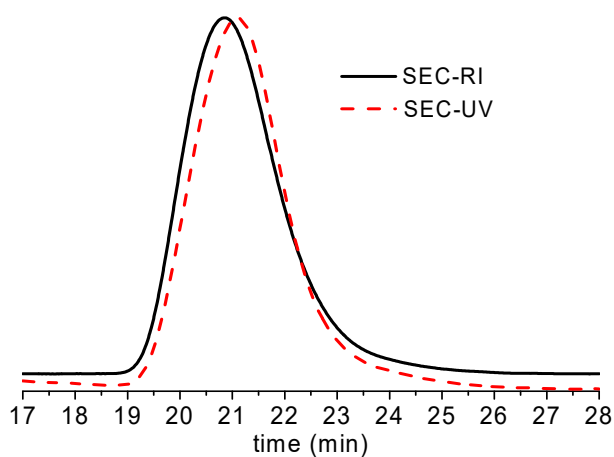


Figure S6. SEC chromatograms of PMMA ($M_{n, \text{SEC}} = 192 \text{ kg mol}^{-1}$, $\text{Đ} = 1.24$) prepared by bulk polymerisation.

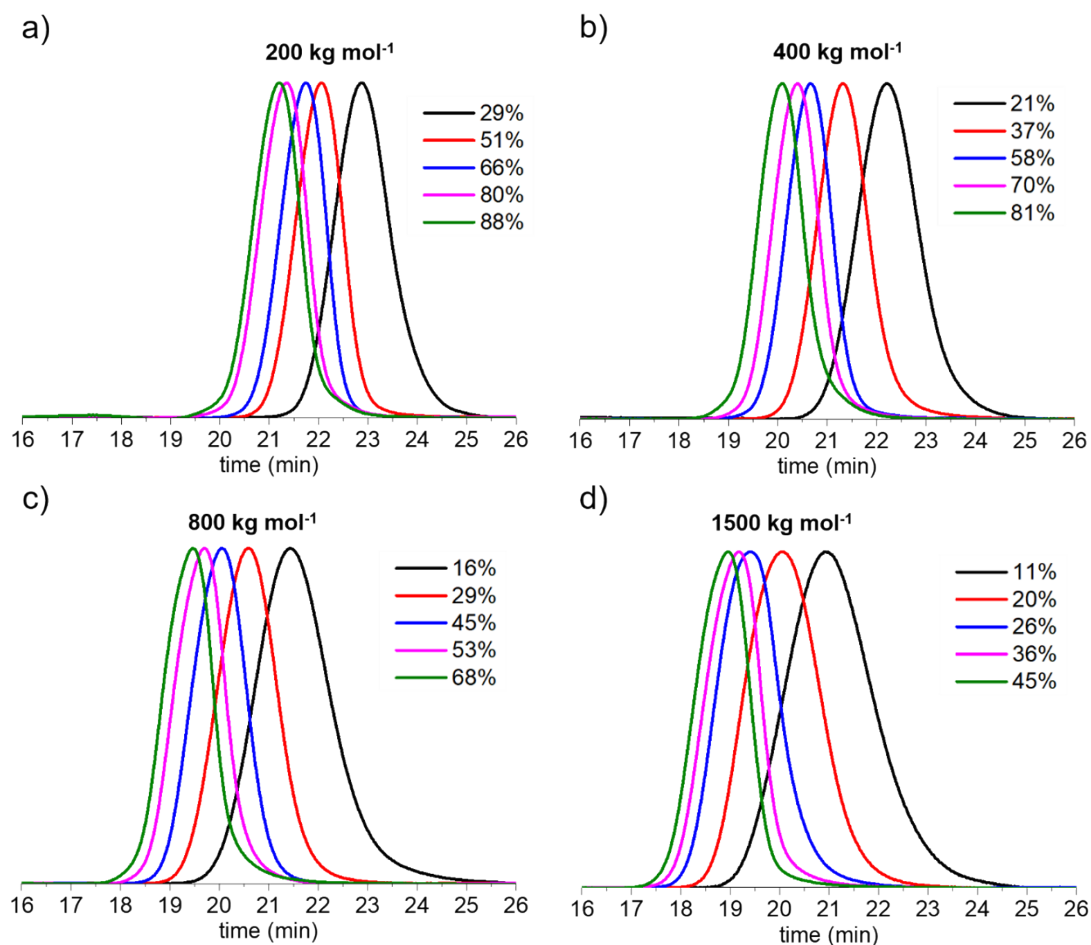


Figure S7. Evolution of SEC-RI chromatograms of PnBA with nBA conversion for different molar masses. Reaction conditions given in Table S4.

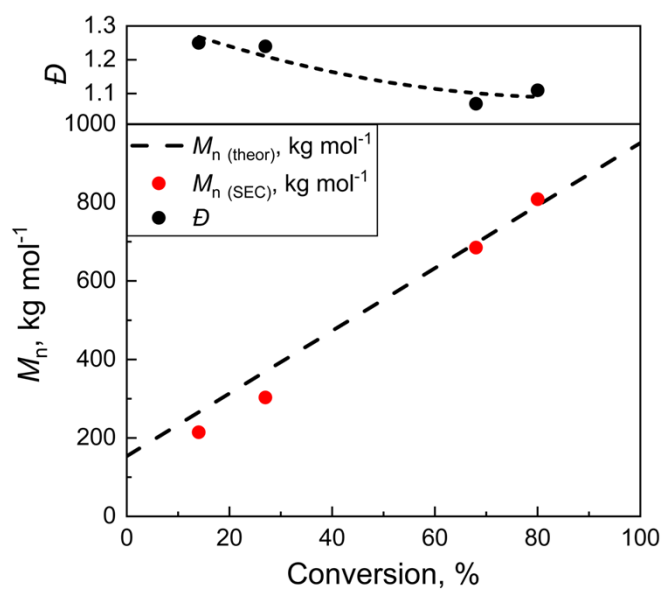


Figure S8. Evolution of M_n and \bar{D} during PI-RAFT polymerisation of PMMA-*b*-PnBA-*b*-PMMA from PMMA_{154k}. Reaction conditions given in Table S5.

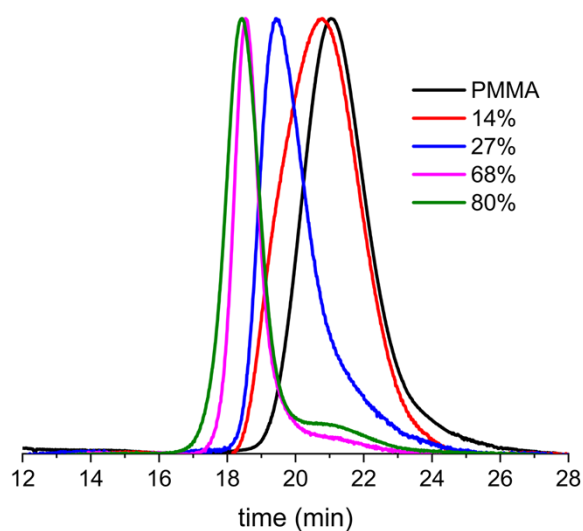


Figure S9. Evolution of SEC-RI chromatograms of PMMA-*b*-PnBA-*b*-PMMA synthesis from PMMA macro-CTA with *n*BA conversion for different molar masses. Reaction conditions given in Table S5.

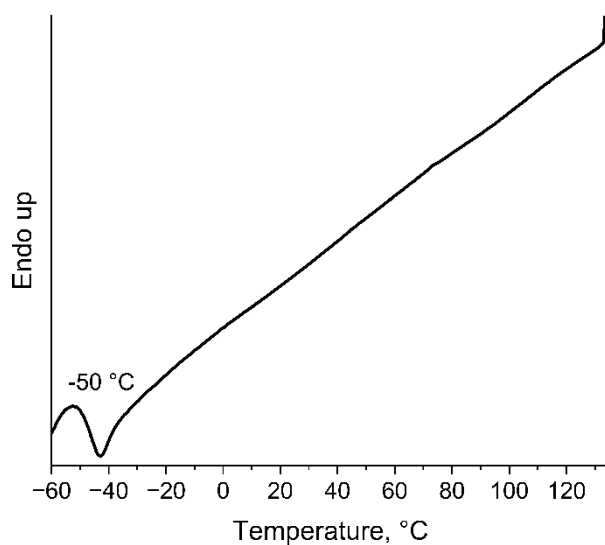


Figure S10. DSC thermogram of PMMA_{77k}-*b*-PnBA_{531k}-*b*-PMMA_{77k}.

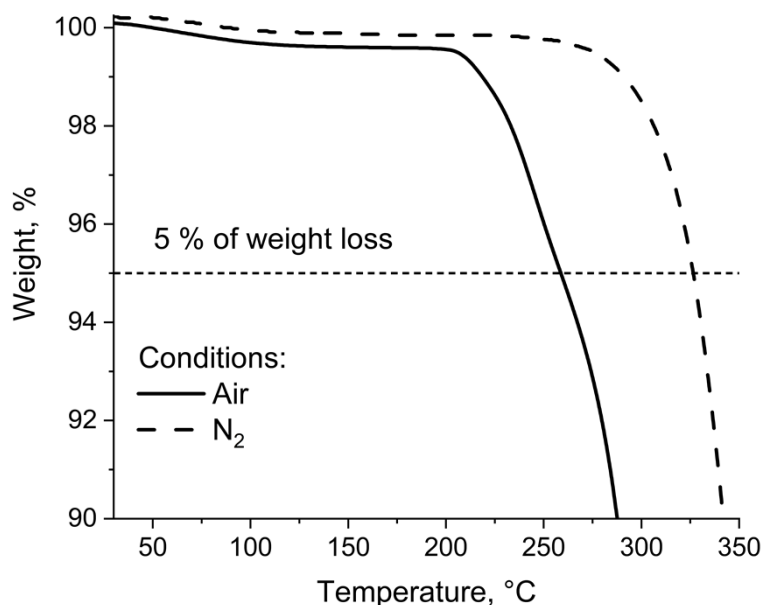


Figure S11. TGA of PMMA_{77k}-*b*-PnBA_{531k}-*b*-PMMA_{77k} in air and N₂ atmosphere.

Table S2. PI-RAFT polymerisation of MMA with **TTC-bCP** at ambient temperature with different MMA concentrations.

Entry	Concentration of MMA in acetonitrile	Time (h)	Conversion ^a (%)	$M_{n,th}^b$ (kg mol ⁻¹)	$M_{n,SEC}^c$ (kg mol ⁻¹)	\bar{D}
1	50% w/w	8	24	49	22	1.25
2		16	38	76	45	1.29
3		24	52	104	567	1.28
4		32	85	170	80	1.46
5	70% w/w	4	10	20	25	1.38
6		8	20	40	42	1.31
8		16	53	106	86	1.29
8		24	74	148	131	1.32
9		32	85	170	145	1.48

Notes: ^acalculated by ¹H NMR in CDCl₃, ^b $M_{n,th} = [MMA]_0/[TTC-bCP]_0 \cdot M_{MMA} \cdot Conv. + M_{TTC-bCP}$, ^c $M_{n,SEC}$ measured by SEC in THF with a RI-MALS detection.

Table S3. PI-RAFT polymerisation of MMA with **TTC-bCP** at ambient temperature with 30 LEDs.

Entry	Targeted M_n (kg mol ⁻¹)	Time (h)	Conversion ^a (%)	$M_{n,th}^b$ (kg mol ⁻¹)	$M_{n,SEC}^c$ (kg mol ⁻¹)	\bar{D}
1	50	4	13	7	9	1.33
2		8	33	17	20	1.22
3		16	78	39	40	1.24
4		24	94	47	46	1.27
6	200	4	9	18	23	1.44
7		8	16	32	38	1.28
8		16	42	84	80	1.23
9		24	67	134	109	1.28
10		32	76	152	153	1.25

11		4	-	-	-	-
12		8	7	28	43	1.40
13	400	16	24	97	103	1.29
14		24	40	160	145	1.33
15		32	58	232	219	1.35

Notes: ^acalculated by ¹H NMR in CDCl₃, ^b $M_{n,th} = [MMA]_0/[TTC-bCP]_0 \cdot M_{MMA} \cdot Conv. + M_{TTC-bCP}$, ^c $M_{n,SEC}$ measured by SEC in THF with a RI-MALS detection, $[MMA]_0 = 6.21 \text{ mol L}^{-1}$.

Table S4. PI-RAFT polymerisation of *n*BA with **TTC-bCP** at ambient temperature.

Entry	Targeted M_n (kg mol ⁻¹)	Time (h)	Conversion ^a (%)	$M_{n,th}$ ^b (kg mol ⁻¹)	$M_{n,SEC}$ ^c (kg mol ⁻¹)	\bar{D}
1		2	29	58	53	1.05
2		4	51	102	92	1.01
3	200	8	66	132	116	1.02
4		16	80	160	144	1.02
5		24	88	176	155	1.02
6		2	21	84	74	1.01
7		4	37	148	134	1.03
8	400	8	58	232	207	1.01
9		16	70	280	247	1.02
10		24	81	324	287	1.03
11		2	16	128	110	1.12
12		4	29	232	203	1.05
13	800	8	45	360	310	1.02
14		16	53	424	413	1.01
15		24	68	544	471	1.02
16		2	11	165	159	1.22
17		4	20	300	287	1.01
18	1 500	8	26	390	417	1.07
19		16	36	540	588	1.03
20		24	45	675	718	1.02

Notes: ^acalculated by ¹H NMR in CDCl₃, ^b $M_{n,th} = [nBA]_0/[TTC-bCP]_0 \cdot M_{nBA} \cdot Conv. + M_{TTC-bCP}$, ^c $M_{n,SEC}$ measured by SEC in THF with a RI-MALS detection, $[nBA]_0 = 6.92 \text{ mol L}^{-1}$.

Table S5. PI-RAFT polymerisation of *n*BA with PMMA_{154k}-**TTC-bCP** at ambient temperature.

Entry	Targeted M_n (kg mol ⁻¹)	Time (h)	Conversion ^a (%)	$M_{n,th}$ ^b (kg mol ⁻¹)	$M_{n,SEC}$ ^c (kg mol ⁻¹)	\bar{D}
1		0	-	163	154	1.25
2		2	14	265	214	1.25
3	800	5	27	369	303	1.24
4		16	68	696	685	1.07
5		24	80	792	808	1.11

Notes: ^acalculated by ¹H NMR in CDCl₃, ^b $M_{n,th} = [nBA]_0/[PMMA_{154k}]_0 \cdot M_{nBA} \cdot Conv. + M_{PMMA}$, ^c $M_{n,SEC}$ measured by SEC in THF with a RI-MALS detection.

1. Z. Huo, S. Arora, V. A. Kong, B. J. Myrka, A. Statt and J. E. Laaser, *Macromolecules*, 2023, **56**, 1845–1854.
2. W. Lu, A. Goodwin, Y. Wang, P. Yin, W. Wang, J. Zhu, T. Wu, X. Lu, B. Hu, K. Hong, N.-G. Kang and J. Mays, *Polym. Chem.* 2017, **9**, 160–168.