

Electronic Supplementary Information
for
Scalable Syntheses of Well-defined
Pentadecablock Bipolymer and Quintopolymer

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1.1 Materials

Tetrahydrofurfuryl methacrylate (THFMA, 97%), 2-(diethylamino)ethyl methacrylate (DEAEMA, 99%), ethyl methacrylate (EtMA, 99%), ethylene glycol methyl ether methacrylate (MEGMA, 99%), 2-(dimethylamino)ethyl methacrylate (DMAEMA, 98%), 1-methoxy-1-trimethylsiloxy-2-methyl propene (MTS, initiator, 95%), deuterated chloroform (CDCl_3), triethylamine (Et_3N), HPLC grade tetrahydrofuran (THF, $\geq 99.9\%$), n-hexane, methanol, calcium hydride (CaH_2 , $\geq 90\%$), basic aluminum oxide (Al_2O_3), 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH, free radical inhibitor), sodium metal and potassium metal were purchased from Aldrich, United Kingdom.

2.1 GPC analysis

The final copolymers and precursory blocks were analysed by GPC to obtain their number average molar masses (M_n) and dispersity indices (\mathcal{D}). The GPC system used is an Agilent SECurity GPC system with a Polymer Standard Service (PSS) SDV analytical linear M column (Agilent technologies UK Ltd., Shropshire, UK). This system is equipped with a "1260 Iso" isocratic pump and an Agilent 1260 refractive index (RI) detector. THF with 5% vol triethylamine was used as the mobile phase at a flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$. The column is calibrated with six different linear poly(methyl methacrylate) (PMMA) standard samples of MM 2000, 4000, 8000, 20,000, 50,000, and $100,000 \text{ g}\cdot\text{mol}^{-1}$, purchased from Fluka, Sigma Aldrich Co Ltd.

2.2 NMR analysis

The final copolymers and their precursory blocks were analysed by NMR using a 400 MHz Avance Bruker NMR spectrometer (Bruker UK Ltd., Coventry, UK). Samples were partially dried in a vacuum oven at room temperature on the day of polymerization and diluted with CDCl_3 (the samples for the quintopolymer were dried more extensively to remove THF traces which would have otherwise affected the compositional analysis). Fig. S1 and S3 show the spectra for the final pentadecablock copolymers.

3.1 Purification of materials

All methacrylate monomers were passed twice through basic Al_2O_3 columns, stirred over CaH_2 for several hours. Subsequently DPPH was added and the flask was purged with argon before storing in the fridge for several days. Monomers are distilled prior to polymerisation. THF was dried over sodium/potassium amalgam in an inert atmosphere. The catalyst, tetrabutylammonium bibenzoate (TBABB), was previously synthesized by tetrabutylammonium hydroxide and benzoic acid, as reported by Dicker et al.¹ TBABB was dried and kept under vacuum until use.

3.2 Method

The multiblock copolymers were synthesized using group transfer polymerization (GTP) by sequential addition of monomers. For example $(\text{EtMA}_5\text{-}b\text{-DMAEMA}_5)_7\text{-}b\text{-EtMA}_5$ was synthesized as follows: TBABB (10 mg) was added into an oven-dried 250 mL flask containing a stirrer bar. The flask was sealed and purged with argon, followed by the addition of dry THF (90 mL). A thermostat is affixed to the flask to monitor the exotherm and MTS (0.46 mL, 0.39g, 2.3 mmol) is added. EtMA (1.41 mL, 1.29g, 11.3 mmol) is added and the exotherm is observed ($24.1 \text{ }^\circ\text{C}$ to $26.1 \text{ }^\circ\text{C}$) over the subsequent 4 minutes. After 10 minutes from the first addition, two samples of 0.1 mL were obtained for GPC and NMR analysis. DMAEMA (1.91 mL, 1.78g, 11.3 mmol) is added, the exotherm monitored and samples taken after 10 minutes. The samples were partially dried in a vacuum oven at room temperature before analysis. Alternating additions of EtMA and DMAEMA are polymerized in the same manner until 15 blocks are achieved. The polymerization is terminated by the addition of methanol (0.1 mL) and the polymer is precipitated in methanol. The polymer is dried in a vacuum oven at room temperature for several days.

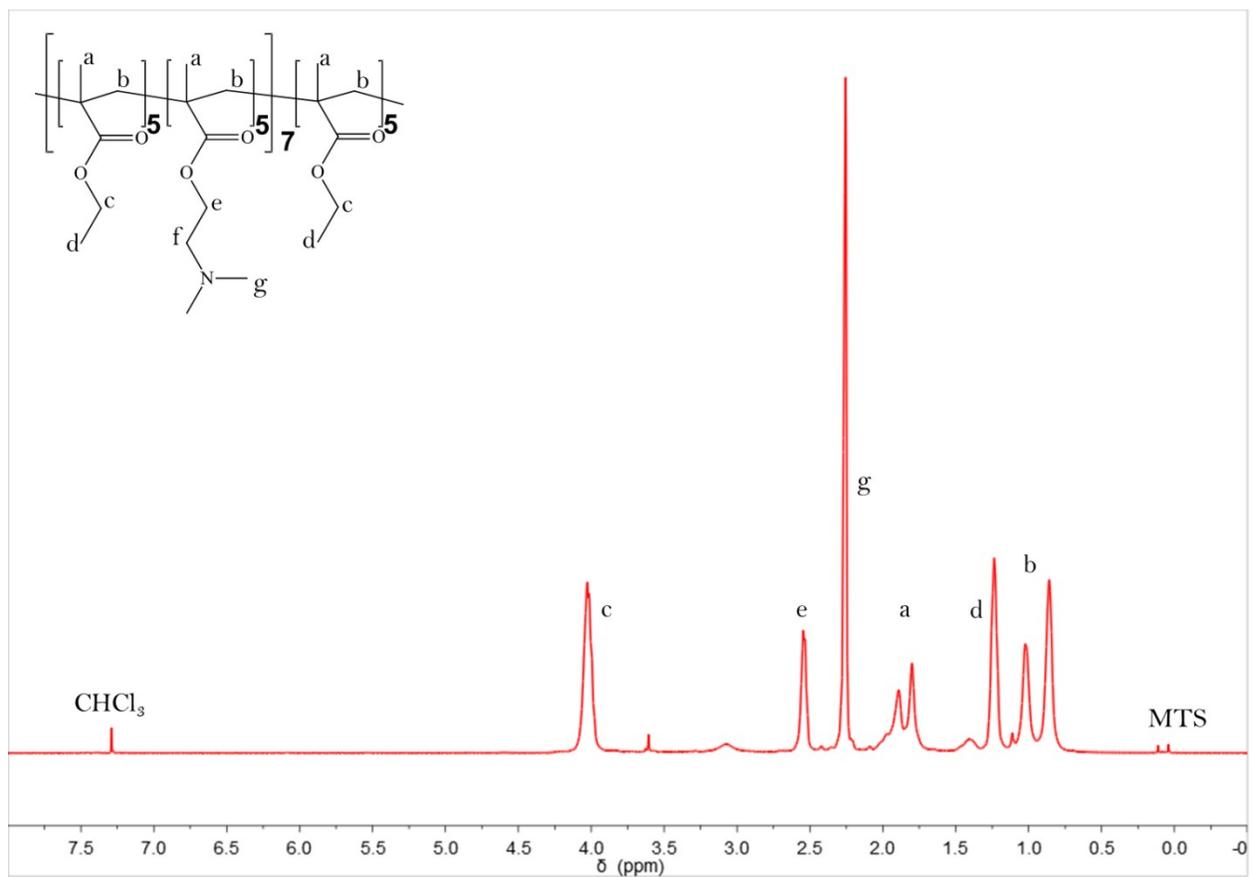


Fig. S1. Assigned proton NMR spectrum of the final sample taken during the synthesis of the copolymer $(\text{EtMA}_5\text{-}b\text{-DMAEMA}_5)_7\text{-}b\text{-EtMA}_5$.

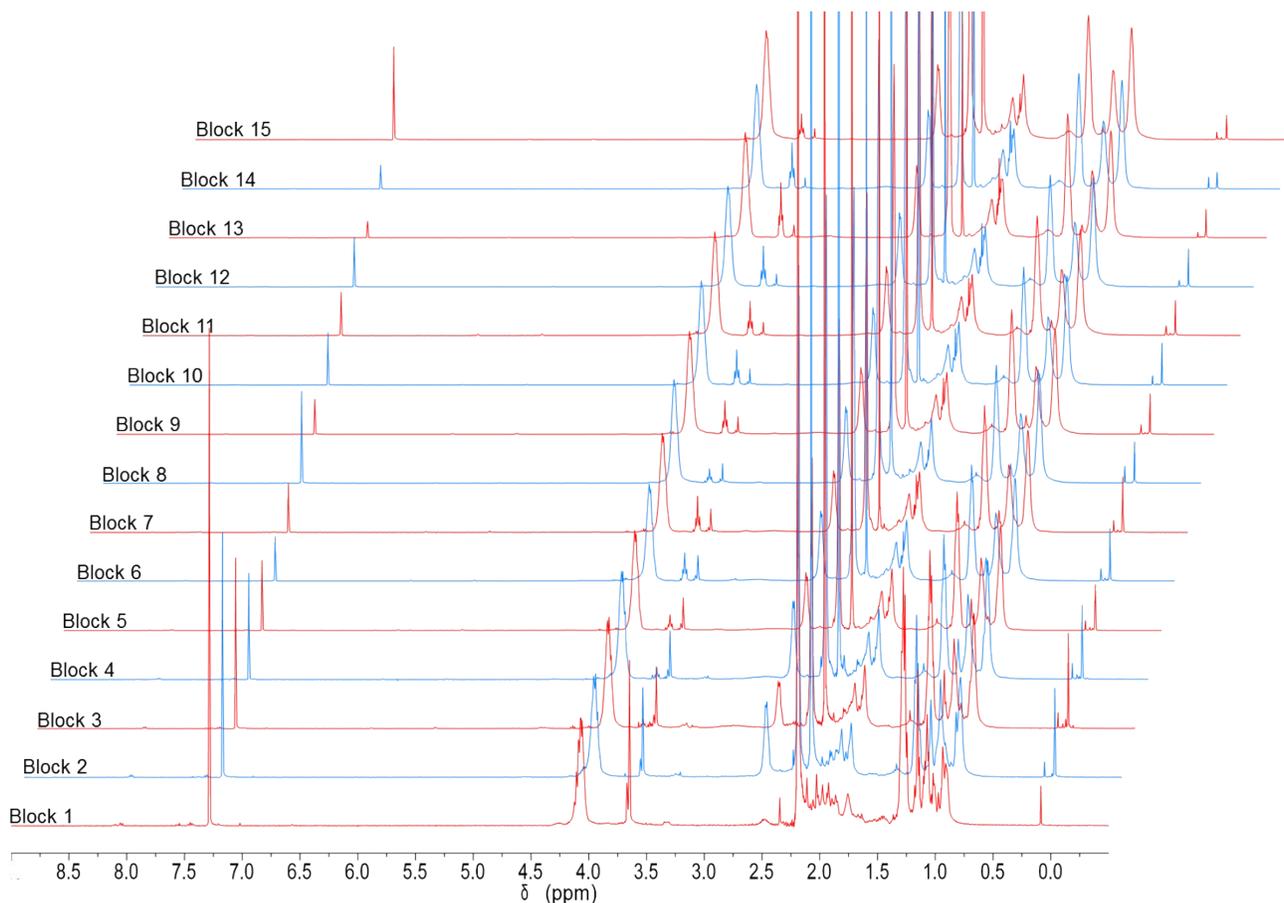


Fig. S2. ¹H-NMR spectra for all samples from the synthesis of (EtMA₅-*b*-DMAEMA₅)₇-*b*-EtMA₅. Spectra are normalized to the peak at 4.1 ppm.

The CHCl₃ peak decreases with block number because the concentration of polymer in the polymerization flask increases. The amount of sample removed was approximately 1 ml. THF is still detectable in the samples (peak at 2.2 ppm). Variation in the amount of polymer collected and the volume of THF removed during drying contribute to differences in the CHCl₃ peak intensity. The alkenyl protons in methacrylate monomers have peaks at 5.5 and 6.1 ppm. Monomer is not present in most cases or at less than 1 mol% in all samples.

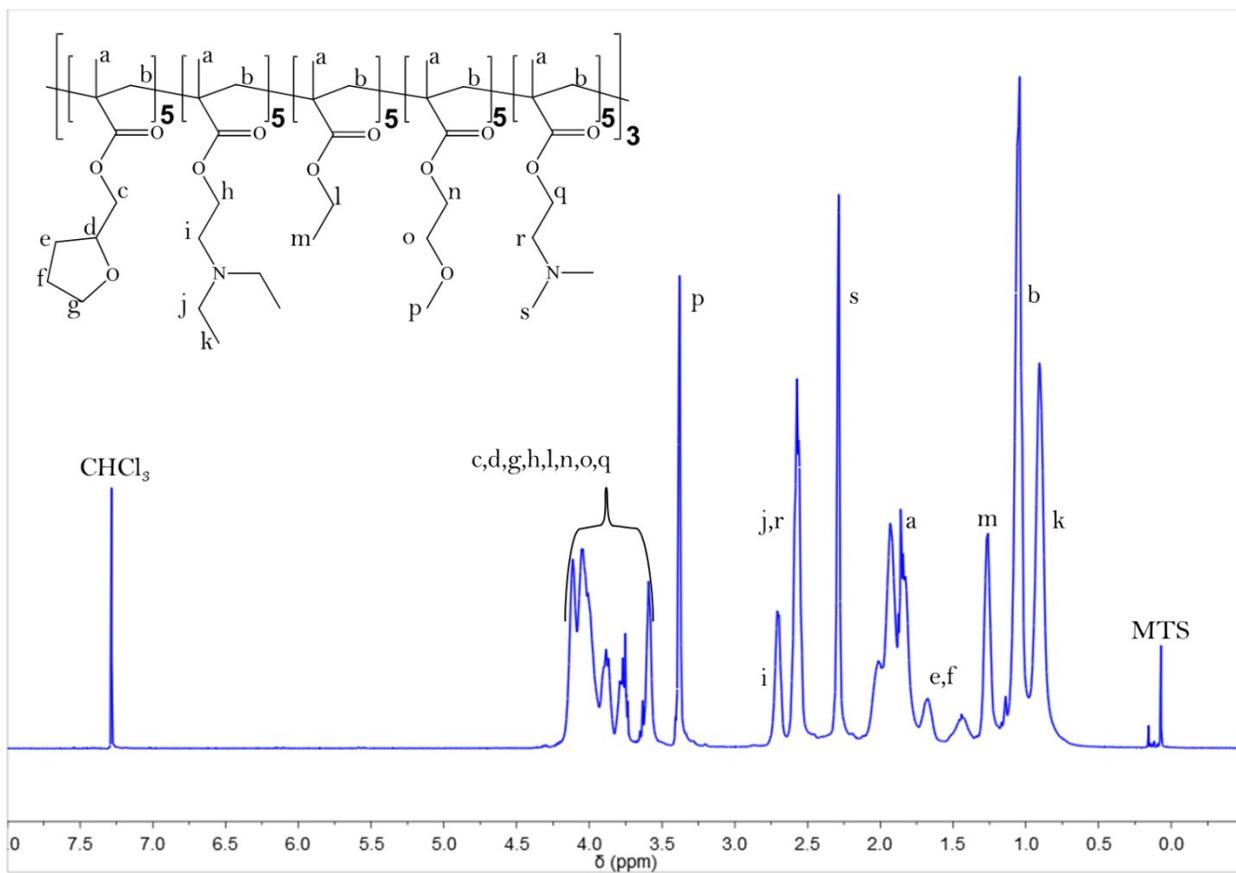


Fig. S3. Assigned proton NMR spectrum of the final sample taken during the synthesis of the copolymer $(\text{THFMA}_5\text{-}b\text{-DEAEMA}_5\text{-}b\text{-EtMA}_5\text{-}b\text{-MEGMA}_5\text{-}b\text{-DMAEMA}_5)_3$.

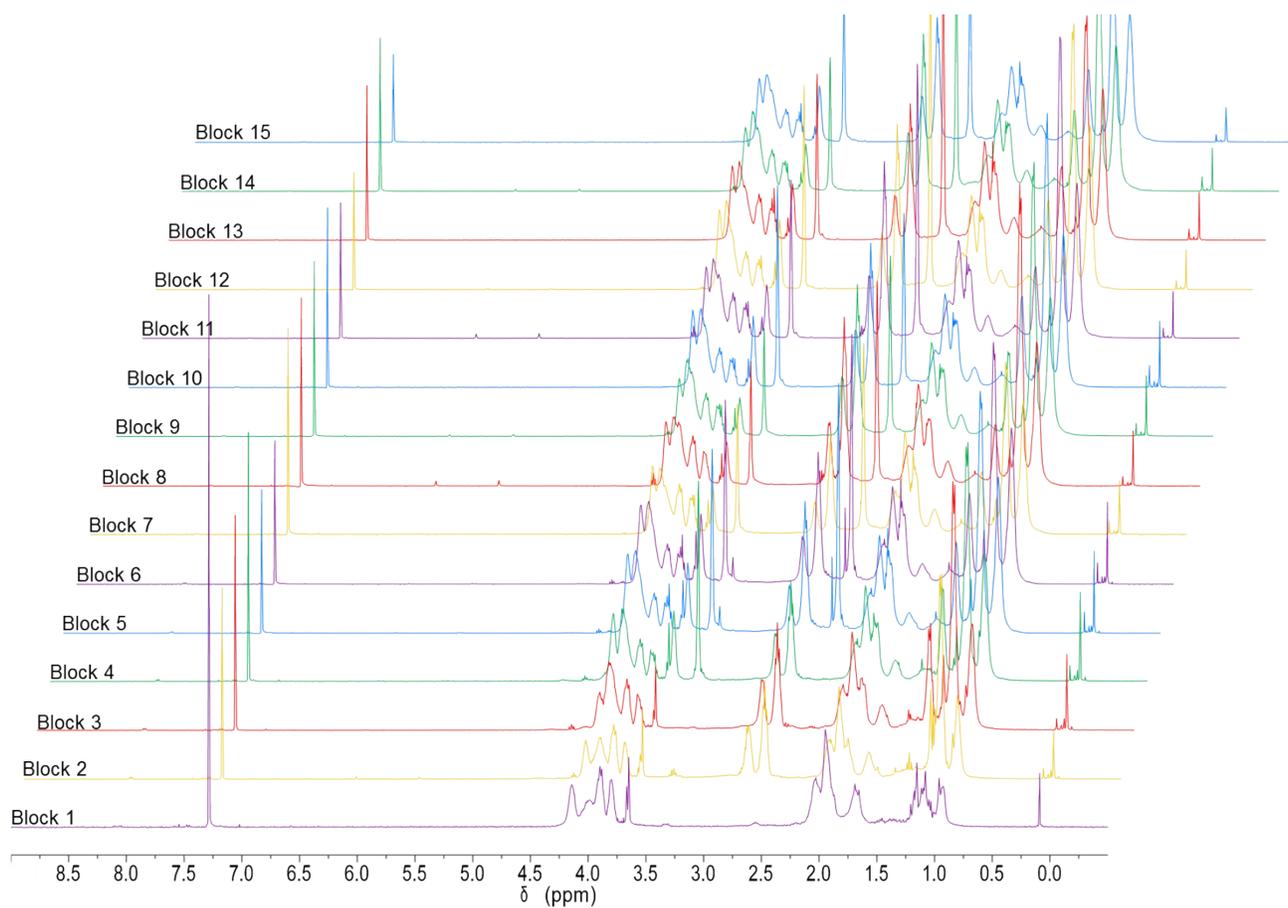


Fig. S4. Stacked NMR spectra for all samples taken during the synthesis of $(\text{THFMA}_5\text{-}b\text{-DEAEMA}_5\text{-}b\text{-EtMA}_5\text{-}b\text{-MEGMA}_5\text{-}b\text{-DMAEMA}_5)_3$.

Table S1

Theoretical and experimental molar masses (M_{th} and M_n , respectively), dispersity (\mathcal{D}) and composition of the $(EtMA_5-b-DMAEMA_5)_7-b-EtMA_5$ and precursory blocks.

Block #	Theoretical Structure ^a	M_{th}^b (g mol ⁻¹)	M_n^c (g mol ⁻¹)	\mathcal{D}^d	% w/w Composition EtMA-DMAEMA	
					Theoretical	¹ H NMR
1	A	671	820	1.16	100-0	100-0
2	AB	1457	1680	1.13	50-50	50-50
3	ABA	2027	2260	1.11	67-33	68-32
4	(AB) ₂	2814	3120	1.11	50-50	50-50
5	(AB) ₂ A	3384	3790	1.10	60-40	60-40
6	(AB) ₃	4170	4710	1.11	50-50	50-50
7	(AB) ₃ A	4741	5290	1.11	57-43	57-43
8	(AB) ₄	5527	6340	1.10	50-50	50-50
9	(AB) ₄ A	6098	6930	1.11	56-44	55-45
10	(AB) ₅	6884	8050	1.10	50-50	50-50
11	(AB) ₅ A	7454	8780	1.12	55-45	54-46
12	(AB) ₆	8241	9630	1.12	50-50	50-50
13	(AB) ₆ A	8811	10300	1.11	54-46	54-46
14	(AB) ₇	9597	11100	1.13	50-50	50-50
15	(AB) ₇ A	10168	12200	1.15	53-47	53-47

^a A and B are EtMA₅ and DMAEMA₅, respectively. ^b The M_{th} of the polymer was calculated as the sum of the monomer masses plus an additional 100 g mol⁻¹ (part of the MTS initiator which remains on the polymer chain); ^c The M_n was determined by GPC; ^d The \mathcal{D} was determined by GPC.

Table S2

Theoretical and experimental molar masses (MM), dispersity (\mathcal{D}) and composition of the (EtMA₅-*b*-DMAEMA₅)₇-*b*-EtMA₅ and the precursory blocks.

Block #	Theoretical Structure ^a	M _{th} ^b (g mol ⁻¹)	M _n ^c (g mol ⁻¹)	\mathcal{D} ^d	% w/w THFMA-DEAEMA-EtMA-MEGMA-DMAEMA	
					Theoretical	¹ H NMR
1	A	951	1150	1.25	100-00-00-00-00	100-00-00-00-00
2	AB	1877	2050	1.17	50-50-00-00-00	48-52-00-00-00
3	ABC	2448	2810	1.12	33-33-33-00-00	34-33-33-00-00
4	ABCD	3169	3830	1.11	25-25-25-25-00	24-23-26-27-00
5	ABCDE	3955	4400	1.12	20-20-20-20-20	21-20-20-19-20
6	ABCDEA	4806	5840	1.08	33-17-17-17-17	26-15-23-16-22
7	ABCDEAB	5732	6940	1.10	29-29-14-14-14	24-22-22-15-19
8	ABCDEABC	6303	7690	1.09	25-25-25-13-13	22-22-24-13-18
9	ABCDEABCD	7024	8220	1.12	22-22-22-22-11	21-17-22-24-17
10	(ABCDE) ₂	7810	9290	1.13	20-20-20-20-20	18-20-24-22-16
11	(ABCDE) ₂ A	8661	10500	1.12	27-18-18-18-18	19-21-19-20-21
12	(ABCDE) ₂ AB	9587	11100	1.17	25-25-17-17-17	19-20-22-19-20
13	(ABCDE) ₂ ABC	10158	12600	1.15	23-23-23-15-15	19-17-23-17-24
14	(ABCDE) ₂ ABCD	10879	12300	1.20	21-21-21-21-14	19-22-22-16-21
15	(ABCDE) ₃	11665	13000	1.28	20-20-20-20-20	18-20-22-20-20

^a A, B, C, D and E are THFMA₅, DEAEMA₅, EtMA₅, MEGMA₅ and DMAEMA₅, respectively. ^b The M_{th} of the polymer was calculated as the sum of the monomer masses plus an additional 100 g mol⁻¹ (part of the MTS initiator which remains on the polymer chain); ^c The M_n was determined by GPC; ^d \mathcal{D} was determined by GPC.

1. W. J. Brittain and I. B. Dicker, *Macromolecules*, 1989, **1057**, 1054–1057.