

Supporting Information

Visualizing the Efficiency of Rapid Modular Block Copolymer Construction

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Supplementary Experimental Section

¹H-NMR spectroscopy was performed using a Bruker AM 400 spectrometer at 400 MHz for hydrogen nuclei. All samples were dissolved in CDCl₃. The δ -scale is referenced to the internal standard trimethylsilane ($\delta = 0.00$).

GPC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μ m bead-size guard column (50 x 7.5 mm) followed by one PLgel 5 μ m Mixed E column (300 x 7.5 mm), three PLgel 5 μ m Mixed C columns (300 x 7.5 mm) and a differential refractive index detector using THF as the eluent at 35 °C with a flow rate of 1 mL·min⁻¹. The GPC system was calibrated using linear poly(methyl methacrylate) standards ranging from 700 to 2·10⁶ g·mol⁻¹.

Mass spectra were recorded on a LXQ mass spectrometer (ThermoFisher Scientific) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. The instrument was calibrated in the m/z range 195-1822 using a standard comprising caffeine, Met-Arg-Phe-Ala acetate (MRFA), and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage

of 4.5 kV and a dimensionless sweep gas flow rate of 2 and a dimensionless sheath gas flow rate of 12 were applied. The capillary voltage, the tube lens offset voltage and the capillary temperature were set to 60 V, 110 V and 275 °C respectively. The LXQ was coupled to a Series 1200 HPLC system (Agilent) that consisted of a solvent degasser (G1322A), a binary pump (G1312A) and a high-performance autosampler (G1367B), followed by a thermostatted column compartment (G1316A). Separation was performed on two mixed bed GPC columns (Polymer Laboratories, Mesopore 250 x 4.6 mm, particle dia. 3 μ m) with pre-column (Mesopore 50 x 4.6 mm) operating at 30 °C. THF at a flow rate of 0.3 mL·min⁻¹ was used as the eluent. The mass spectrometer was coupled to the column in parallel to an RI detector (G1362A with SS420x A/D). A 0.27 mL·min⁻¹ aliquot of the eluent was directed through the RI detector and 30 μ L·min⁻¹ infused into the electrospray source after post-column addition of a 0.1mM solution of sodium iodide in methanol at 20 μ L·min⁻¹ by a micro flow HPLC syringe pump (Teledyne ISCO, Model 100DM). The polymer solutions (20 μ L) with a concentration of ~ 3 mg·mL⁻¹ were injected into the HPLC system.

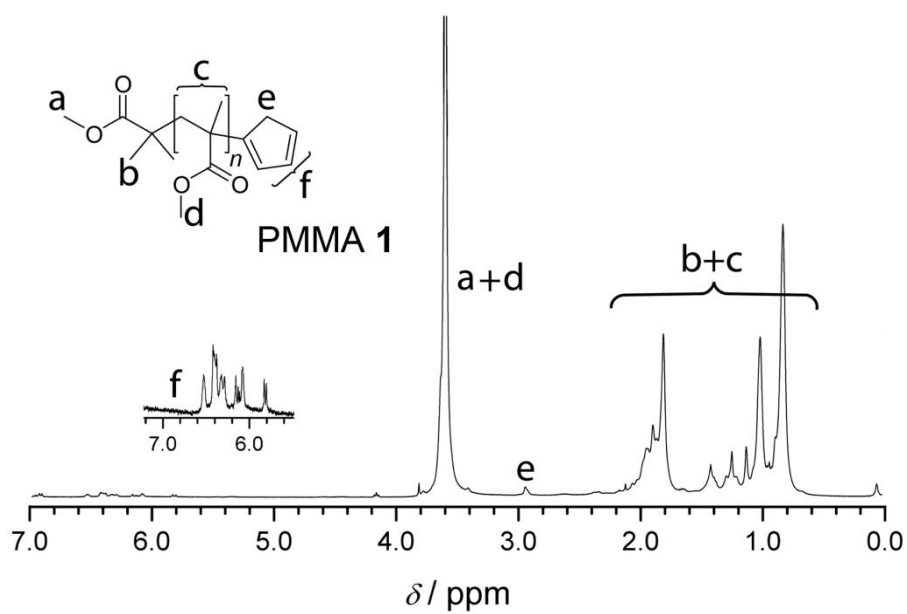


Figure S1. ¹H-NMR spectrum of PMMA 1.

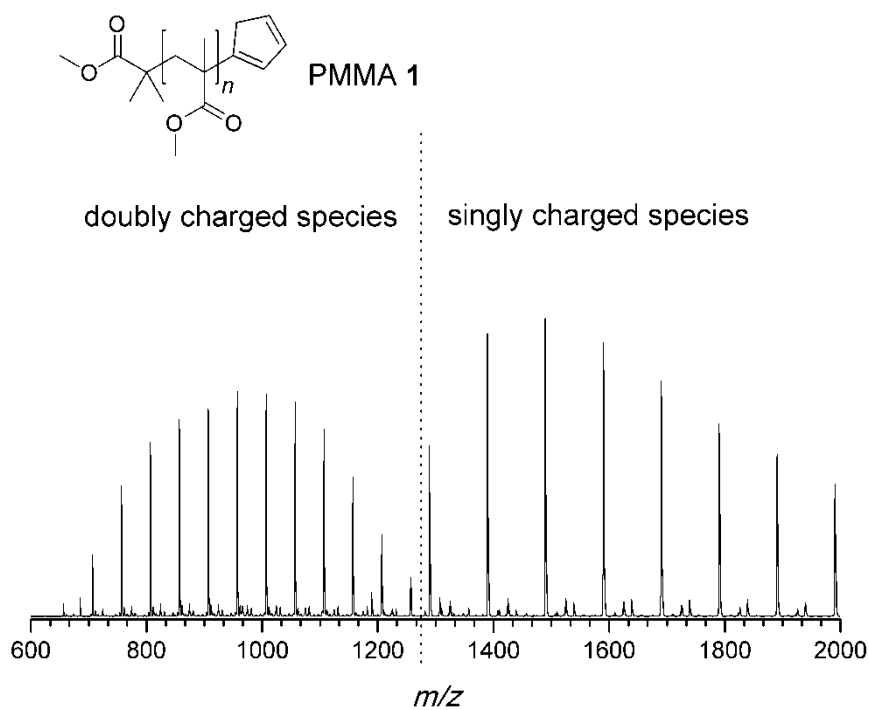


Figure S2. Full ESI-MS Spectrum of PMMA 1.

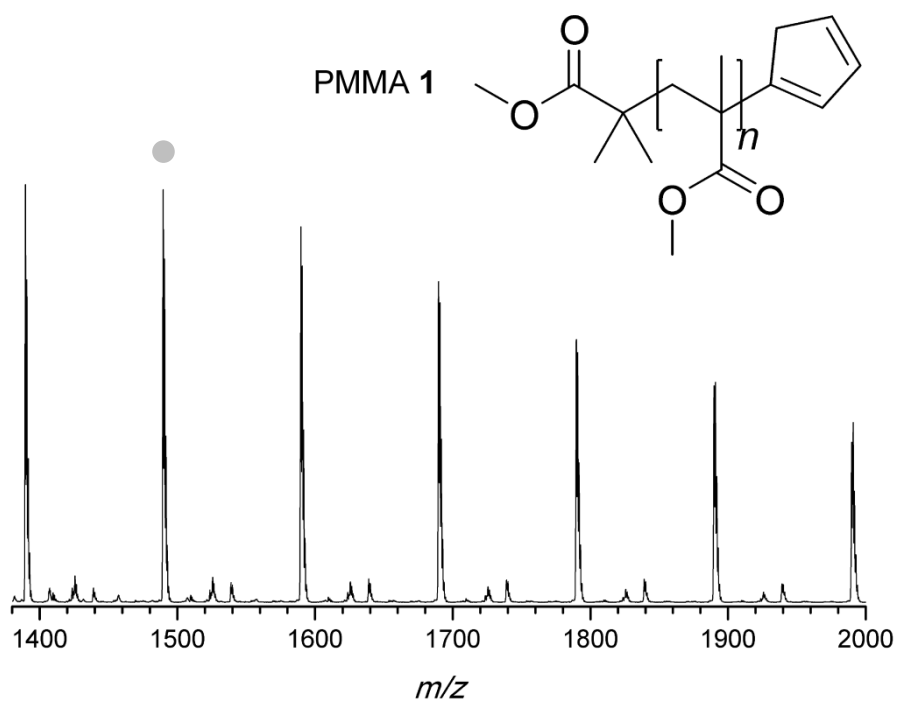


Figure S3. ESI-MS spectrum of PMMA **1** (1400-2000 m/z region). Details of the marked signal are presented in Table S1.

Table S1. Experimental and theoretical m/z values for the first peak in the isotopic distributions for selected signal in Figure S3.

$m/z_{\text{expt.}}$	Ion assignment	Formula	$m/z_{\text{theor.}}$	$\Delta m/z$
1489.8	PMMA 1 _(n=13) + Na ⁺	[C ₇₅ H ₁₁₈ O ₂₈ Na] ⁺	1489.8	0.0

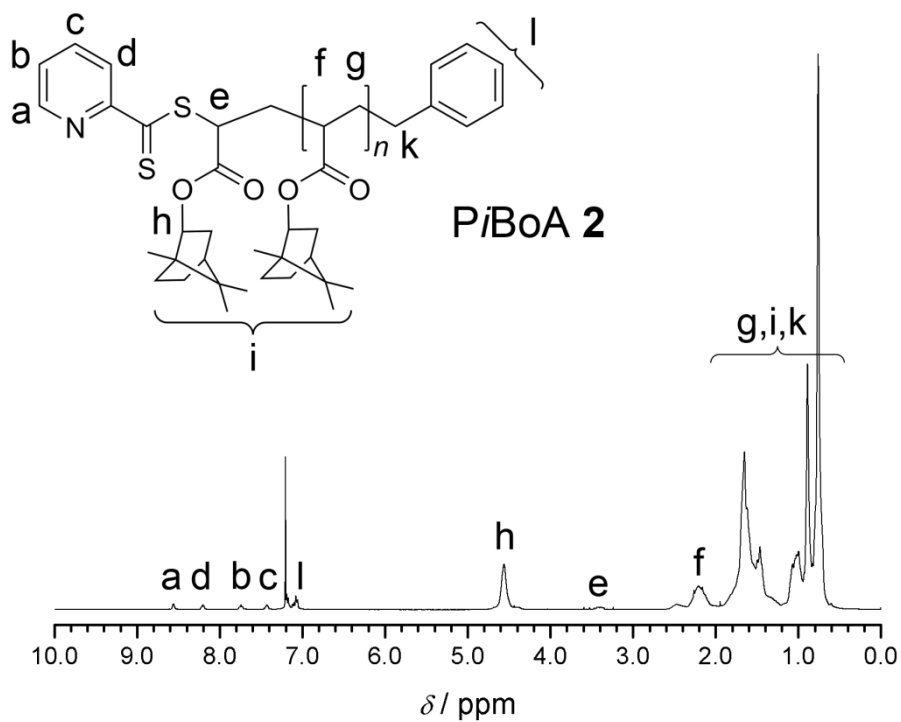


Figure S4. ¹H-NMR spectrum of PiBoA 2.

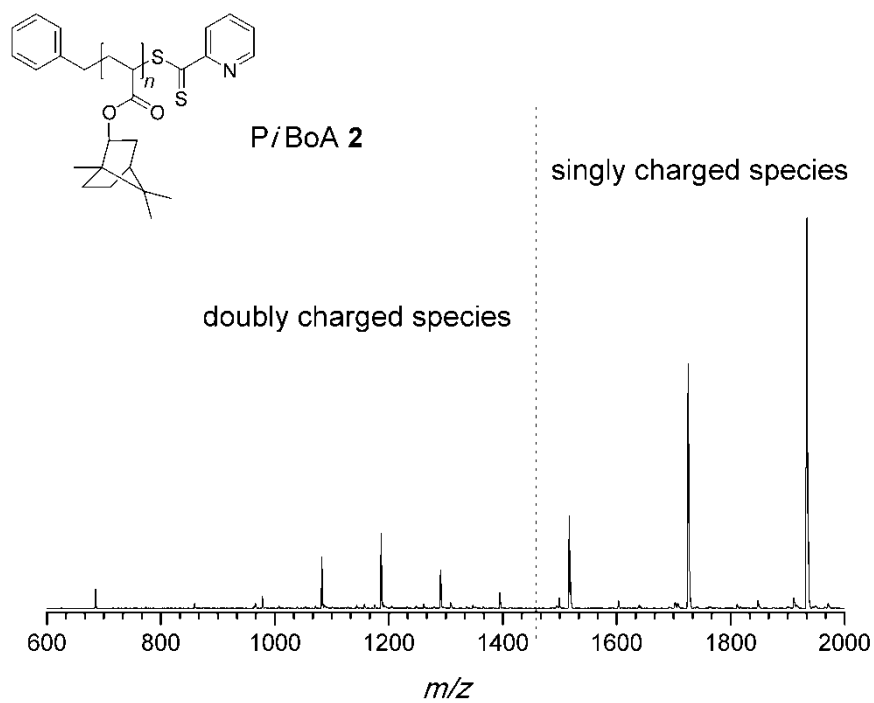


Figure S5. Full ESI-MS spectrum of PiBoA 2.

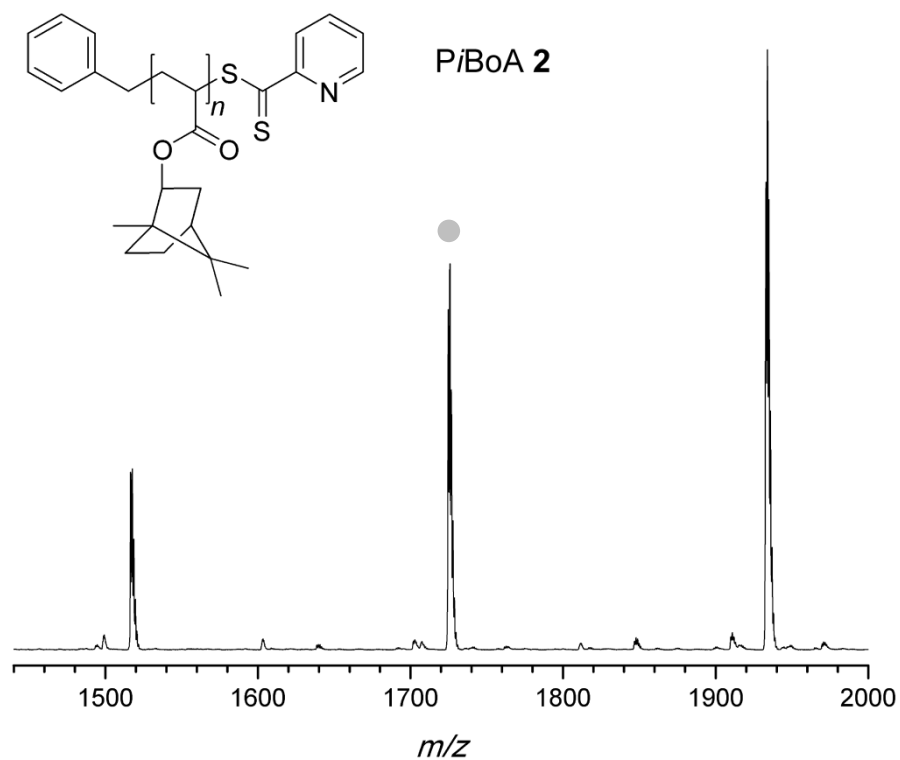


Figure S5. ESI-MS spectrum of PiBoA 2 (1450-2000 m/z region). Details of the marked signal are presented in Table S2.

Table S2. Experimental and theoretical m/z values for the first peak in the isotopic distributions for selected signal in Figure S4.

$m/z_{\text{expt.}}$	Ion assignment	Formula	$m/z_{\text{theor.}}$	$\Delta m/z$
1724.8	PiBoA 2 _(n=6) + Na ⁺	[C ₁₀₄ H ₁₅₁ NO ₁₄ S ₂ Na] ⁺	1725.0	0.2

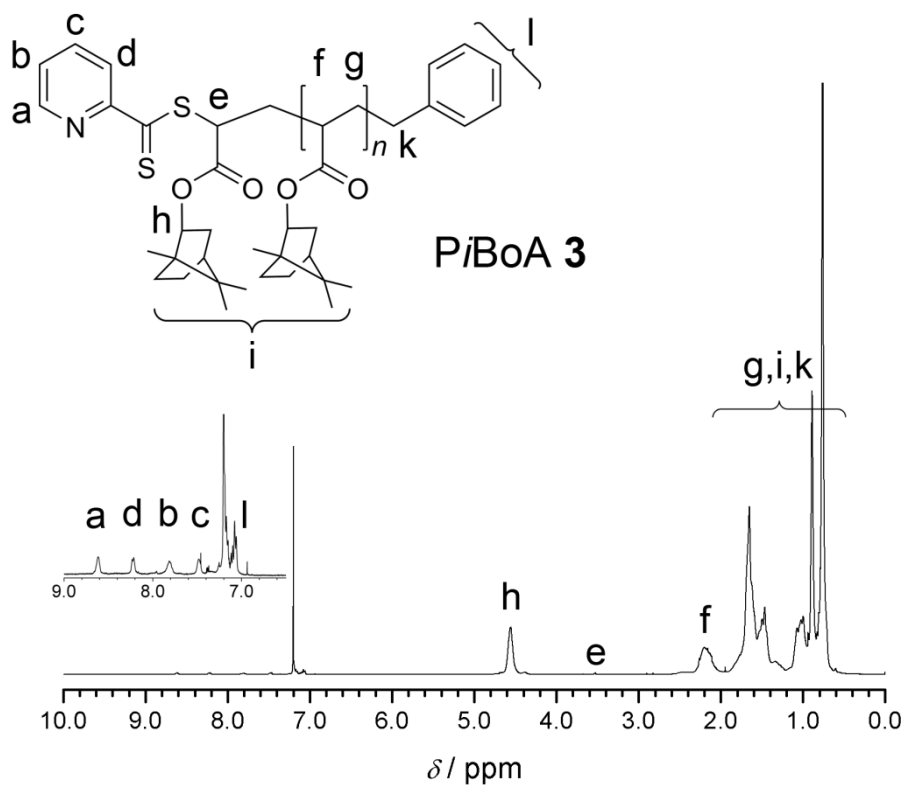


Figure S6. ¹H-NMR spectrum of PiBoA 3.

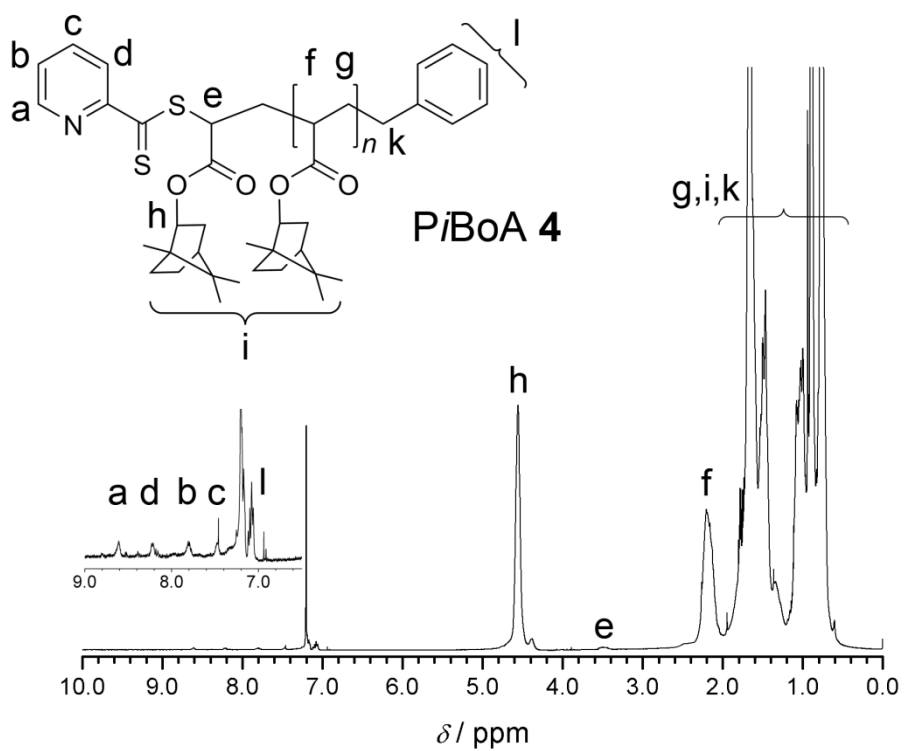


Figure S7. ¹H-NMR spectrum of PiBoA 4.

Theoretical Block Copolymer Composition- Example Calculation

Taking a basis of 1 mol of PMMA **1** ($M_n = 3200 \text{ g}\cdot\text{mol}^{-1}$), there will be:

0.97 mol (3104 g) of functional polymer, and

0.03 mol (96 g) of dead polymer

To achieve equimolar stoichiometry 1.02 mol of PiBoA **2** ($4600 \text{ g}\cdot\text{mol}^{-1}$) is required as it contains:

0.97 mol (4462 g) of functional polymer, and

0.05 mol (236 g) of dead polymer

Therefore, under the assumption of 100 % conjugation efficiency, one can expect:

$3104 + 4462 = 7566 \text{ g}$ of block copolymer

96 g of remaining dead PMMA **1**, and

236 g of remaining dead PiBoA **2**

Thus, the corresponding mass fractions of these components will be:

$$7566/7898 = 0.958 \rightarrow 95.8 \text{ wt\% block copolymer}$$

$$96/7898 = 0.012 \rightarrow 1.2 \text{ wt\% dead PMMA } \mathbf{1}$$

$$236/7898 = 0.03 \rightarrow 3 \text{ wt\% dead PiBoA } \mathbf{2}$$