Supporting Information

Precision Polyelectrolytes

Sansanee Srichan, Laurence Oswald, Mirela Zamfir and Jean-François Lutz*

Precision Macromolecular Chemistry Group, Institut Charles Sadron, UPR-22 CNRS,
BP 84047, 23 rue du Loess, 67034 Strasbourg Cedex 2, France

E-Mail: jflutz@unistra.fr

Content:

A. Experimental procedures S2

- A.1. Chemicals S2
- A.2. Example of Nitroxide Mediated homopolymerization of **1** S2
- A.3. Example of Nitroxide Mediated copolymerization of **1** and **2** S3
- A.4. Example of NMP of **1** with a kinetically-controlled addition of **2** S3
- A.5. Example of hydrolytic deprotection of a polymer S3

B. Measurements and analysis S4

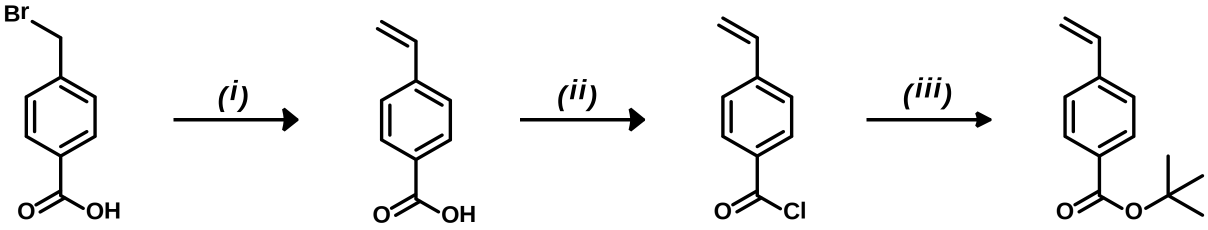
- B.1. Size Exclusion Chromatography (SEC) S4
- B.2. Nuclear Magnetic Resonance (NMR) S4

C. Additional data and Figures S4

- Table S1 S4
- Figure S1 S5
- Figure S2 S5

A. Experimental procedures:

A.1. Chemicals. 4-Bromomethylbenzoic acid (Alfa Aesar, 97%), triphenylphosphine (Alfa Aesar, 99%), acetone (Sigma Aldrich, >99.5%), formaldehyde (Acros Organics, 37% wt. aqueous solution stabilized with 5-15% methanol), NaOH (SDS, 98%), thionyl chloride (Fluka, >99%), 4-*tert*-butylpyrocatechol (Acros Organics, 99%), *tert*-butyl alcohol (Acros Organics, extra pure), potassium *tert*-butoxyde (Acros Organics, 98+%), diethyl ether anhydrous (Sigma Aldrich, 99.7%), BlocBuilder® MA, (Arkema, 97%), *N*-benzylmaleimide (Alfa Aesar, 99%), *N*-(1-pyrenyl)maleimide (Sigma Aldrich), anisole (Sigma Aldrich, 99%), dioxane (Fluka, 99.5%), hydrochloric acid (Sigma Aldrich, 37%), methanol (Carlo Erba, 99.9%), ethanol absolute (Carlo Erba), tetrahydrofuran for SEC (Sigma Aldrich, 99.8% HPLC, stabilizer-free) were used as received. THF (99%, stabilized with BHT) purchased from Aldrich was dried and distilled over sodium-benzophenone. The synthesis of TIPS-protected *N*-propargyl maleimide 1-(3-(triisopropylsilyl)prop-2ynyl)-1H-pyrrole-2,5-dione was described in a previous publication.[1] *Tert*-butyl 4-vinylbenzoate **1** was synthesized in three steps (Scheme S1). Vinyl benzoic acid was first synthesized from 4-bromomethylbenzoic acid.[2] Afterwards, vinyl benzoic acid was transformed in its *tert*-butyl ester in two steps.[3]



Scheme S1. Synthesis of *tert*-butyl 4-vinylbenzoate. Experimental conditions: *(i)* P(Ph)$_3$, acetone, CH$_2$O, NaOH, HCl; *(ii)* SOCl$_2$; *(iii)* *t*-BuO$^-$K$^+$, *t*-BuOH, dry ether.

A.2. Example of nitroxide mediated homopolymerization of 1. Homopolymers of *tert*-butyl 4-vinylbenzoate were synthesized by nitroxide mediated polymerization. A typical procedure is described below. This particular example corresponds to Entry 5 in Table S1. A mixture of **1** (1 g, 20 Eq.), and BlocBuilder MA (0.0962 g, 1 Eq.) were added into a 10 mL Schlenk tube equipped with a magnetic stirring bar and sealed with a rubber septum. After the mixture was degassed, the tube was purged with dry argon for a few minutes and introduced in an oil bath thermostated at 100 °C. Periodically, samples were taken for NMR analysis. After 4 h of reaction, the polymer was precipitated by pouring a concentrated polymer solution in THF into a large volume of methanol while stirring. The precipitate was collected by filtration, washed with methanol and dried in a vacuum oven at room temperature overnight. The purified polymer was characterized by ^{1}H NMR and SEC (M_n = 4400 g·mol^{-1}, M_w/M_n = 1.18).

A.3. Example of nitroxide mediated copolymerization of 1 and 2. Copolymers of **1** with functional *N*-substituted maleimides were synthesized by nitroxide mediated copolymerization in bulk or in anisole solution. Similar procedures were used for comonomers **2**, **3** and **4**. A typical example is shown below and corresponds to Entry 4 in Table 1 (Main document). In a 10 mL Schlenk tube, 1 g of **1** (100 Eq.), 9.25 mg of **2** (1 Eq.), 19.2 mg BlocBuilder MA (1 Eq.) and 1 mL of anisole were added. The tube was capped by a rubber septum, purged with argon for a few minutes and then immersed in an oil bath thermostated at 100 °C for 8 h. Samples were withdrawn at regular intervals for NMR analysis in order to monitor the incorporation of **2** in the growing copolymer chains. The mixture was then diluted in THF which was slowly poured into an excess of methanol under stirring in order to precipitate the polymer. The precipitate was collected by filtration and dried in a vacuum oven at room temperature overnight. The purified polymer was characterized by ^{1}H NMR and SEC (M_n = 11500 g·mol^{-1}, M_w/M_n = 1.21).

A.4. Example of NMP of 1 with a kinetically-controlled addition of 2. The present example corresponds to Entry 6 in Table 1 (Main document). 19.2 mg BlocBuilder MA (1 Eq), 1 g of **1** (100 Eq.) and 0.8 mL anisole, were added in a 10 mL Schlenk tube equipped with a stirring bar. The tube was then sealed with a rubber septum, purged with dry argon and then immersed in an oil bath thermostated at 100 °C. After 2 h of reaction, a degassed solution of **2** (9.25 mg, 1 Eq.) in 0.2 mL of anisole was added with a degassed syringe in the reaction mixture (42 % conversion of **1** at this stage). Samples were withdrawn periodically for NMR analysis in order to monitor the incorporation of **2** in the growing copolymer chains. After 8 h, the reaction mixture was dissolved in THF and the resulting solution was slowly poured into an excess of methanol under stirring in order to precipitate the polymer. The precipitate was collected by filtration, washed with methanol and dried in a vacuum oven at room temperature overnight. The purified polymer was characterized by ^{1}H NMR and SEC (M_n = 15500 g·mol^{-1}, M_w/M_n = 1.13).

A.5. Example of hydrolytic deprotection of a polymer.[4] 0.5 g of a homopolymer of **1** (M_n = 16400 g·mol^{-1}) were dissolved in 4.5 mL of dioxane in a round bottom flask. Then, 0.49 mL of HCl (37%) was added and the flask was capped with a condenser. The mixture was refluxed for approximately 6 h and subsequently cooled at room temperature. The solution was diluted with ethanol and the polymer was precipitated in water. The precipitate was collected by filtration, washed with water and dried in a vacuum oven at room temperature overnight. The purified deprotected polymer was characterized by ^{1}H and ^{13}C NMR.

B. Measurements and analysis:

B.1. Size exclusion chromatography (SEC). Molecular weights and molecular weight distributions were determined using a SEC system equipped with a Shimatzu SPD M20A refractive index detector and five PLgel 10µ Mixed-B columns. The mobile phase was THF with a flow rate of 1 $mL \cdot min^{-1}$ using a Shimadzu LC20AD pump. Toluene was used as internal reference. The molecular weight calibration was based on sixteen narrow molecular weight linear polystyrene standards from Polymer Laboratories.

B.2. Nuclear Magnetic Resonance (NMR). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or in CD_3OD on either a Bruker Avance 400 MHz or on a Bruker Avance 600 MHz spectrometers equipped with Ultrashield magnets. The conversions of monomers **1-4** were calculated from ^{1}H NMR spectra. Different calculation procedures have been used for bulk and anisole solution polymerizations.

C. Additional data and Figures:

Table S1. Properties of homopolymers of **1** prepared by nitroxide mediated polymerization.[a]

	[1]	**[BlocBuilder]**	**T [°C]**	**t_{end}[b]**	**$conv._{1}$[c]**	**M_n[d] [$g \cdot mol^{-1}$]**	**$M_{n\ th}$[e]**	**M_w/M_n[f]**
1	100 Eq.	1 Eq.	120	240	0.89	16400	18600	1.18
2	100 Eq.	1 Eq.	110	240	0.97	17100	20200	1.29
3	100 Eq.	1 Eq.	100	240	0.87	14000	18100	1.35
4	50 Eq.	1 Eq.	100	240	0.92	8300	9800	1.23
5	20 Eq.	1 Eq.	100	240	0.65	4400	3000	1.18

[a] All experiments were performed in bulk. [b] Final polymerization time. [c] Conversion of **1** at the end of the reaction as estimated from ^{1}H NMR spectra in $CDCl_3$. [d] Number average molecular weight measured by SEC in THF. [e] Theoretical number average molecular weight $M_{n\ th} = M_{BlocBuilder} + M_{\mathbf{1}} \cdot conv._{\mathbf{1}} \cdot [\mathbf{1}]/[BlocBuilder]$; where $M_{BlocBuilder}$ and M_1 are the molecular weights of BlocBuilder and **1**, respectively. [f] Molecular weight distribution measured by SEC in THF.

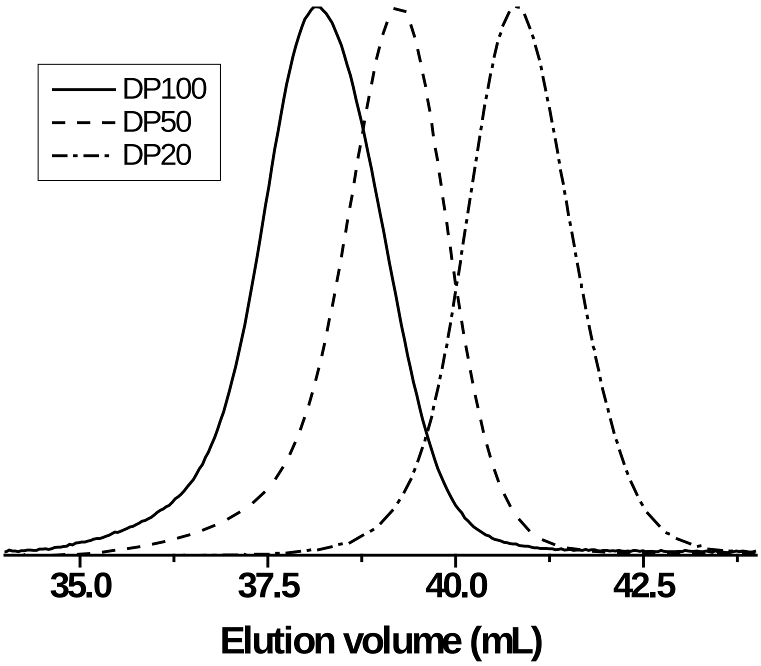


Figure S1. Chromatograms recorded in THF for homopolymers of **1** synthesized by nitroxide mediated polymerization in bulk (Table S1, Entries 3-5).

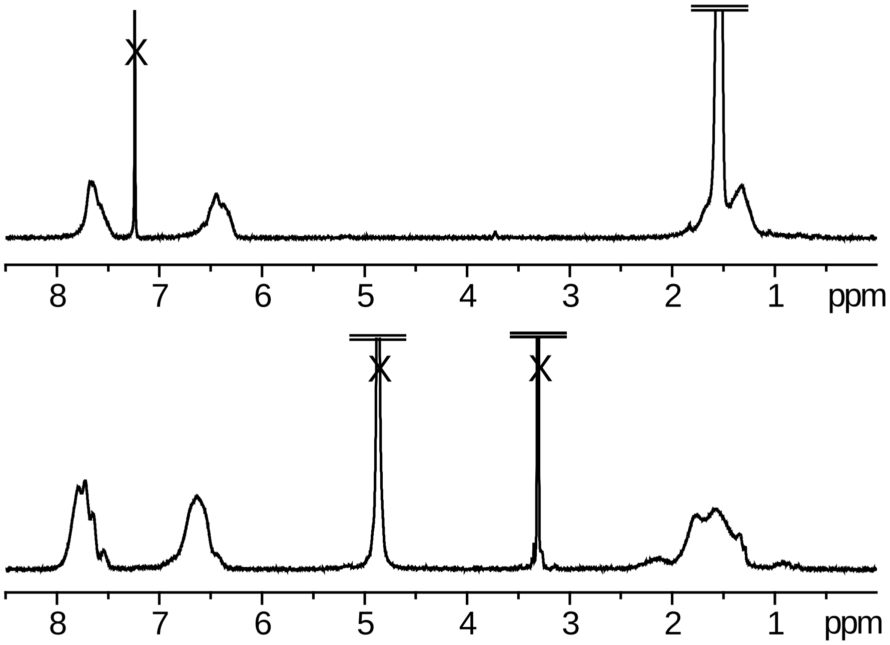


Figure S2. ^{1}H NMR spectrum measured for a well-defined homopolymer of **1** (Table S1, Entry 4) before (top) and after (bottom) deprotection in acidic conditions. The top and bottom spectra were recorded in $CDCl_3$ and CD_3OD, respectively.

References and notes.

1. Schmidt, B. V. K. J.; Fechler, N.; Falkenhagen J.; Lutz, J.-F., *Nature Chem.* 2011, **3**, 234.
2. Wang, R.; Lowe, A. B., *J. Polym. Sci. Part A Polym. Chem.* 2007, **45**, 2468.
3. Ishizone, T.; Hirao, A.; Nakahama, S., *Macromolecules* 1989, **22**, 2895.
4. Davis, K.A., Matyjaszewski, K., *Macromolecules* 2000, **33**, 4039.