Supplementary Information

Extremely Rapid and Versatile Synthesis of High Molecular Weight Step Growth

Polymers via Oxime Click Chemistry

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Materials and Instrumentation

Chemicals were purchased from Sigma Aldrich or Alfa Aesar and used without further purification. ¹H-NMR spectra were recorded using a Varian 400 MHz spectrometer. Differential Scanning calorimetry (DSC) was recorded on a Perkin Elmer DSC8500. For differential refractive index (DRI) traces, DMF was used as an eluent and the size exclusion chromatography (SEC) analysis was conducted on a Shimadzu liquid chromatography system equipped with a Shimadzu RID-10 refractometer (λ = 633 nm) and Shimadzu SPD-20A UV-vis detector using two Phenomenex Phenogel columns (5 µm bead size, 10⁴ and 10⁶ Å porosity) in series operating at 70°C. DMF with 0.05 mol·L⁻ ¹ LiBr (>99%, Aldrich) was employed as the mobile phase at a flow rate of 1 mL·min⁻¹. The system was calibrated using polystyrene standards. All samples were filtered through 0.45 µm nylon filters prior to injection. Molecular weight distributions (PDIs) were calculated relative to linear polystyrene standards.

Synthesis

Propane-1,3-Bishydroxylamine (**M1**): Synthesis of propane-1,3-bishydroxylamine (**M1**) was carried out according to a reported literature procedure.¹ ¹H-NMR (400 MHz, CDCl₃): δ 3.97 (t, 4H, *J* = 8 Hz, - CH₂), 1.89 (m, 2H, *J* = 8 Hz, -CH₂).



Dibenzaldehyde Tetraethylene Glycol (M2): Tetraethylene glycol (TEG) (5.00 g, 25.7 mmol), 4formyl benzoic acid (7.92 g, 52.8 mmol) and dimethylaminopyridine (DMAP) (0.47g, 3.85 mmol) were dissolved in DCM (100 mL). N,N'-Dicyclohexylcarbodiimide (DCC) (10.88g, 52.7 mmol) in DCM (20 mL) was added to the solution dropwise. The reaction was left to stir for 24hours at room temperature. The crude reaction mixture was concentrated under reduced pressure then filtered. The filtrate was purified by column chromatography using hexane/ethyl acetate (80/20). The product was collected as a white solid (10.47g, 89%). ¹H-NMR (400 MHz, CDCl₃): δ 10.07 (s, 2H, -COOH), 8.18 (d, 4H, *J* = 8 Hz, Ar), 7.91 (d, 4H, *J* = 8 Hz, Ar), 4.47 (4H, t, *J* = 4 Hz, -CH₂), 3.82 (t, 4H, *J* = 4 Hz, -CH₂), 3.66 (m, 8H, *J* = 4 Hz -CH₂).



Oxime-Linked Polymers (Pa-c, P1-8): Polymerizations were undertaken in DMF using a range of monomer and aniline concentrations (Scheme 1, Table 1). Typically, **M2** was dissolved in DMF to make a final concentration of 150mmolL⁻¹. To this was added **M1** in equimolar amounts and a desired volume of aniline (between 2 – 40%). Polymerization occurred either at room temperature or at 60° C for between 5 minutes – 6 hours. Following polymerization, the product was repeatedly precipitated in water and filtered to afford a white solid. ¹H NMR (400 MHz, CDCl₃): δ 8.1 (s, 2H, - O=NCH), 8.03 (d, 4H, *J* = 8 Hz, Ar), 7.63 (d, 4H, *J* = 8 Hz, Ar), 4.46 (t, 4H, *J* = 4 Hz, -CH₂), 4.32 (t, 4H, *J* = 4 Hz -CH₂), 3.81 (t, 4H, *J* = 4 Hz -CH₂), 3.67 (s, 8H, -CH₂), 2.15 (quin, 2H, *J* = 4Hz. -CH₂).



Figure S1. SEC trace of polymer product formed after 4 hrs at room temperature according to reaction conditions outlined in Scheme 1, Condition A.



Figure S2. ^{14 of SI}H-NMR spectra of polymers formed over time according to reaction conditions outlined in Scheme 1, Condition A.



Figure S4. SEC trace of polymers formed with varying reactant concentrations. All reactions were undertaken at 60° C for 6 hrs with 20% aniline.



Figure S5. Scatter Plot showing the change in molecular weight of polymer **Pc** (blue diamonds), PCL (red squares) and PBA (green triangles) over seven days when exposed to acidic conditions (0.1M acetic acid, 50° C). No change in mass is observed for any of the polymers studied indicating their stability under acidic conditions.



Figure S6. Scatter plot showing the change in molecular weight of polymer **Pc** (blue diamonds), PCL (red squares) and PBA (green triangles) over seven days when exposed to basic conditions (0.1M NaOH, $50^{\circ}C$). No change in mass is observed for **Pc**, indicating its stability under basic conditions.



Figure S7. Differential Scanning Calorimeter (DSC) trace for **Pc.** Glass transition point (Tg) can be seen at 20° C.



Figure S8. SEC trace of polymers formed over time according to reaction conditions outlined in Scheme 1, Condition C.



Figure S9. SEC trace of polymers formed after 10 minutes at 60° C.

Figure S10. SEC trace of polymers formed over time according to reaction conditions outlined in Scheme 1, Condition B.

Figure S11. ¹H-NMR spectra of polymers formed over time according to reaction conditions outlined in Scheme 1, Condition B. (a) Spectrum taken at time zero, before the addition of the catalyst, (b) spectrum taken 3 min after the addition of 40% aniline, (c) spectrum taken 8 min after the addition of 40% aniline, (d) spectrum taken 13 min after the addition of 40% aniline.

Figure S12. SEC trace of aldehyde terminated polymer before precipitation (dotted line), Mn = 28 kDa, and after precipitation (solid line), Mn = 35 kDa.

Figure S13. SEC trace of hydroxylamine terminated polymer before precipitation (dotted line), Mn = 17 kDa, and after precipitation (solid line), Mn = 30 kDa.

Figure S14. ¹H-NMR spectra of hydroxylamine terminated polymer. Peaks corresponding to the terminal hydroxylamine monomer can be identified and their integration gives a polymer molecular weight of between 35 - 40 kDa.

Figure S15. ¹H-NMR spectra of P_{Bipy10} (red), P_{Bipy20} (green) and P_{Bipy30} (blue). Characteristic bipyridine peaks can be identified: a, b, c, and d which confirms the successful incorporation of 2,2-bipyridine-4,4-dicarboxaldehyde.

Figure S16. ¹³C-NMR spectra of P_{Bipy30} . Identification of characteristic bipyridine peaks l, m, n, o, p and q indicate successful incorporation of the monomer into the polymer.

Figure S17. UV-Vis spectra of P_{Bipy10} (purple), P_{Bipy20} (green) and P_{Bipy30} (orange). A new absorbance band at approximately 330nm appears which is attributed to the bipyridine group. The increase in intensity of the band at 330nm can be seen with increasing bipyridine incorporation.

Figure S18. SEC trace of P_{Bipy10} (blue solid line) P_{Bipy20} (red dashed line) and P_{Bipy30} (green dotted line). Mn of P_{Bipy10} , P_{Bipy20} and P_{Bipy30} calculated to be 34 kDa, 55 kDa and 106 kDa respectively.

Figure S19. ¹H-NMR spectra of $P_{Boron10}$ (red), $P_{Boron20}$ (green) and $P_{Boron30}$ (blue). A change in the shape of the aromatic peaks (h and g) as well as the oxime peak (f) indicates the incorporation of the 3,5-diformylphenyl boronic acid whose peaks (a, b and c) overlap in this region.

Figure S20. ¹³C-NMR spectra of $P_{Boron30}$. The appearance of peaks I, m, n and o indicate the successful incorporation of the monomer.

Figure S21. SEC trace of $P_{Boron10}$ (blue solid line) $P_{Boron20}$ (red dashed line) and $P_{Boron30}$ (green dotted line). Mn of $P_{Boron10}$, $P_{Boron20}$ and $P_{Boron30}$ calculated to be 26 kDa, 20 kDa and 18 kDa respectively.

Figure S22. ¹H-NMR spectra of $P_{10/10}$ Characteristic bipyridine peaks can be identified: I, m, n and o as well as the overlap of the phenyl boronic acid peaks with the aromatic peaks f, g and h.

Figure S23. SEC trace of $\mathsf{P}_{10/10}$ (blue solid line). Mn calculated to be 28 kDa.

References

(1) Taraballi, F.; Russo, L.; Battocchio, C.; Polzonetti, G.; Nicotra, F.; Cipolla, L. *Org. Biomol. Chem.* **2014**, *12*, 4089.