Supporting Information

Synthesis of Multisegmented Block Copolymer by Friedel-Crafts Hydroxyalkylation

Polymerization

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Materials. Purchased chemicals were used as received, unless otherwise indicated, including dichloromethane (DCM, >99.5%, EMD-Millipore), 4-nitrobenzaldehyde (NBA, 98%, Beantown chemical), 4-tert-butylbenzaldehyde (tBBA, 97%, Sigma-Aldrich), 4-dimethylaminobenzaldehyde (DMABA, TCI, >98%), 4-fluorobenzaldehyde (FBA, 98%, Beantown chemical), methyl 4-formylbenzoate (EBA, 99%, Sigma-Aldrich), 1,4-dimethoxybenzene (DMB, 99%, Sigma-Aldrich), methanesulfonic acid (MSA, >99.0%, TCI), octanol, 4-carboxybenzaldehyde, EDC, and 4-dimethylaminopyridine (DMAP, Matrix Scientific, 98%).

Characterization. A 400 MHz Bruker proton nuclear magnetic resonance (¹H NMR) spectrometer was used to analyze polymer structures and monomer synthesized. Molecular weight and distributions were analyzed by size exclusion chromatography (SEC) with dimethylformamide (DMF) as mobile phase for separation and characterization of oligomer and copolymers. The DMF SEC was equipped with PSS columns (guard, 10⁴, 10³, and 10² Å GRAM columns) at 55 °C with DMF flow rate = 1.00 mL/min and a differential refractive index (RI) detector (Wyatt Technology,
Optilab T-rEX, 658 nm) and contained 0.01M LiBr. All SEC data was analyzed using PSS WinGPC 7.5 software. The apparent number-average molar masses ($M_{n,RI}$) were calculated based on linear poly(methyl methacrylate) (PMMA) calibration standards. The volume-average hydrodynamic sizes of some samples were used to confirm presence of high molar mass polymer in cases where SEC was not possible, which were determined using a dynamic light scattering (DLS) detector (Zetasizer NanoZS, He-Ne laser wavelength at 633 nm, Malvern Instruments, Malvern, UK).

**Thermal Analysis.** Differential scanning calorimetry (DSC) measurements were performed on vacuum dried samples of polymer were analyzed in 40 μL aluminum crucibles with a Mettler Toledo DSC-1 using two heating cycles, first heating from 25 to 250 °C at 20 °C/min before cooling at heating to 250 °C at 10 °C/min. Only the data gathered for the second cycle was used for the analysis. Scanning from -100 to 300 °C was used to identify the typical behavior of the triaryl methane polymers and determined only a glass transition was observed on a second heating cycle. Thermal gravimetric analysis was performed on vacuum dried samples of polymer were analyzed in 40 μL aluminum crucibles with a Mettler Toledo TGA\DSC-1 using single heating cycle was used from 35-500 °C at 10 °C/min to determine the temperature at 90% residual weight.
<table>
<thead>
<tr>
<th>Entry(^a)</th>
<th>DP(_{\text{NMR}})(^b)</th>
<th>(M_{n,\text{RI}})(^c) (g/mol)</th>
<th>(M_{w}/M_{n,\text{RI}})(^c)</th>
</tr>
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<tbody>
<tr>
<td>O-L1</td>
<td>10</td>
<td>3,100</td>
<td>1.35</td>
</tr>
<tr>
<td>O-L2</td>
<td>10</td>
<td>3,800</td>
<td>1.26</td>
</tr>
<tr>
<td>CP @ 0.75 eq MFB</td>
<td>-</td>
<td>12,600</td>
<td>1.51</td>
</tr>
<tr>
<td>CP @ 1.0 eq MFB</td>
<td>-</td>
<td>24,000</td>
<td>1.69</td>
</tr>
<tr>
<td>CP @ 1.2 eq MFB</td>
<td>-</td>
<td>39,000</td>
<td>1.90</td>
</tr>
<tr>
<td>CP @ 1.4 eq MFB</td>
<td>-</td>
<td>111,000</td>
<td>2.45</td>
</tr>
</tbody>
</table>

\(^a\)Copolymerization conditions for a series of CP-L1-L2 MSBCPs: \([\text{O-L1}]_0:[\text{O-L2}]_0:[\text{MFB}]_0:[\text{MSA}]_0=0.5:0.5:X:40\), where X = 0.75, 1.0, 1.2, 1.4 equivalents. \(^b\)Number-average degree of polymerization (DP\(_{\text{NMR}}\)) calculated from integration of peaks of chain-end protons and methine proton in triarylmethane backbone units. \(^c\)Apparent \(M_{n,\text{RI}}\) and polydispersity (\(M_{w}/M_{n,\text{RI}}\)) measured by DMF SEC with RI detector, based on linear PMMA standard calibration.
**Synthesis of octyl 4-formyl benzoate (OFB).** To a 250 mL round bottom flask was added 1.2 g (9.2 mmol) octanol, 1.94 g (7.7 mmol) 4-carboxybenzaldehyde, 0.28 g (2.3 mmol) 4-dimethylaminopyridine, 100 mL of DCM and a magnetic stir bar. The solution was stirred, cooled to 0 °C in an ice bath and 1.79 g (11.5 mmol) 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide was added slowly. The solution was allowed to warm to room temperature and stirred overnight. The organic phase was filtered and washed with 1M HCl, 1M NaOH, DI water and brine. The solvent was removed under reduced pressure and the product was purified by silica column chromatography with 5:1 hexanes to ethyl acetate, yielding 1.95 g (97% yield) of a clear oil. $^1$H NMR spectrum of the purified product in CDCl$_3$ is shown in Figure S1.

**A typical procedure for synthesis of MSBCP.** To a 1.8 mL vial was added 0.025 mmol of O-H1, 0.025 mmol O-H2, 0.150 mmol DMABA, 0.750 mL DCM and a magnetic stir bar. The contents of
the vial were mixed until homogenous before 2 mmol MSA was added to initiate the reaction. The reaction was monitored by taking samples at timed intervals for precipitation in MeOH and analysis in SEC until the \( M_n \) ceased to increase, typically 24-72 hours. In cases where solubility in DMF became too poor to analyze by SEC, samples were monitored by \(^1\)H NMR spectroscopy for disappearance of chain-end signals and by DLS to confirm particle size when reaching > 10 nm.

**Spin-coating of homopolymers and MSBCPs.** Solutions of 2 wt% polymer in DCM (except CP-H2-H3) were deposited on square borosilicate slides at 750 RPMs followed by a speed ramp up to 2000 RPMs for 30 seconds. The coated slides were placed in a desiccator for 48 hours before a 5 \( \mu \)L drop of water was applied on the top of polymer coating using an auto-pipet. The droplet was photographed, and the image was analyzed using Image-J with the Contact Angle analysis plugin by Marco Brugnara. For copolymer CP-H2-H3 with pH-switchable contact angles, solution of 2 wt% CP-H2-H3 in acidic N-methyl pyrrolidone were deposited on square borosilicate slides at 750 RPMs followed by a speed ramp up to 2000 RPMs for 30 seconds. The coated slide was placed in a desiccator for 48 hours before being immersed for 10 minutes in 1M HCl solution. Then a 5 \( \mu \)L drop of water was applied using an auto-pipet. The droplet was photographed, and the image was analyzed using Image-J with the Contact Angle analysis plugin by Marco Brugnara. The coated slide was then immersed in 0.25 M NaOH and DI water sequentially for 10 minutes each before being dried. The contact angle was then re-measured and the procedure was repeated for 3 total cycles of HCl and NaOH treatments as described.
**Figure S2.** Size elution chromatograms for O-L1, O-L2, O-L3, O-L4, O-L6 measured by SEC in DMF. Oligomer O-L5 was insoluble in DMF for SEC characterization.
Figure S3. Size elution chromatograms for O-H1, O-H2, O-H3, O-H4 and O-H6 measured by SEC in DMF. Oligomer O-H5 was insoluble in DMF for SEC characterization.
Figure S4. Stacked $^1$H NMR spectra of oligomers O-L1 through O-L6 comparing the integration of the 4 terminal proton signals with the integrations of the triarylmethane proton signal, the pendent aryl and backbone aryl proton signals, demonstrating the linear structure of these oligomers with well-defined structural regularity.
Figure S5. Stacked $^1$H NMR spectra of oligomers O-H1 through O-H6 comparing the integration of the 4 terminal proton signals with the integrations of the triarylmethane proton signal, the pendent aryl and backbone aryl proton signals, demonstrating the linear structure of these oligomers with well-defined structural regularity.
Figure S6. $^1$H NMR spectra of oligomers O-H1, O-H3, O-H4, and O-H5 displaying the shifts of the triarylmethane proton signals where electronic de-shielding shows a proportional response to electron withdrawing group (EWG) and an inverse response to electron donating group (EDG).
Figure S7. Stacked $^1$H NMR spectra of CP-L1-L2, the constituent oligomers O-L1 and O-L2, and O-L4 that corresponds to the linking monomer.
Figure S8. Region of $^1$H NMR spectra showing methoxy proton signal of two MSBCPs, CP-L1-L2 & CP-H1-H2, where oligomer block lengths are varied from O-L1 & O-L2 to O-H1 & O-H2.
Figure S9. Stacked $^1$H NMR spectra for CP-H1-H4, the constituent oligomers O-H1 and O-H4, and O-H3 which corresponds to the linking monomer, synthesized using conditions $[O-H1]_0:[O-H4]_0:[DMABA]_0:[MSA]_0 = 0.5:0.5:1.5:40$, $[DMABA]_0 = 0.2\text{M}$. 
Figure S10. Stacked $^1$H NMR spectra for CP-H2-H5, the constituent oligomers O-H2 and O-H5, and O-H4 which corresponds to the linking monomer, synthesized using conditions $[O-H2]_0:[O-H5]_0:[MFB]_0:[MSA]_0 = 0.5:0.5:1.5:40$, $[MFB]_0 = 0.2M$. 
Figure S11. Stacked $^1$H NMR spectra for CP-H2-H3, the constituent oligomers O-H2 and O-H3, and O-H4 which corresponds to the linking monomer, synthesized using conditions [O-H2]₀:[O-H3]₀:[MFB]₀:[MSA]₀ = 0.5:0.5:1.5:40, [MFB]₀ = 0.2M.
Figure S12. Stacked $^1$H NMR spectra for CP-H2-H6, the constituent oligomers O-H2 and O-H6, and O-H3 which corresponds to the linking monomer, synthesized using conditions $[O-H2]_0:[O-H6]_0:[DMABA]_0:[MSA]_0 = 0.5:0.5:1.5:40$, $[DMABA]_0 = 0.2\,\text{M}$. 
Figure S13. Size elution chromatograms measured by SEC in DMF for MSBCPs synthesized using conditions \([\text{Oligomer A}]_0:[\text{Oligomer B}]_0:[\text{BA}]_0:[\text{MSA}]_0 = 0.5:0.5:1.5:40\), \([\text{BA}]_0 = 0.2\text{M}\), where the oligomers and coupling monomer were a) \(\text{O-H1, O-H2 and MFB}\), b) \(\text{O-H1, O-H4, and DMABA}\), and c) \(\text{O-H2, O-H3 and MFB}\).
Figure S14. $^1$H NMR spectrum for CP-L1b-H4 synthesized using conditions [O-L1b]₀:[O-H4]₀:[DMABA]₀:[MSA]₀ = 0.5:0.5:1.5:40.
Figure S15. a) Oligomer DSC measurements showing $T_g$ for O-H1 to O-H6 where DP > 10. b) First and second scans by DSC of O-H4 at 10 °C/min.

Figure S16. a) Residual mass and heat flow from thermal gravimetric scan of CP-H1-H4, and b) comparison of thermal mass loss profile of CP-H1-H4 with constituent oligomers and additive curve of O-H1 and O-H4.
Figure S17. Thermal gravimetric mass loss profiles for oligomers O-H1 to O-H6.
Figure S18. $^1$H NMR spectra for CP-H2-H3 synthesized using conditions $[O-H2]_0:[O-H3]_0:[MFB]_0:[MSA]_0 = 0.5:0.5:1.5:40$ in a) neutral state in CDCl$_3$ and b) protonated state in DMSO-d$_6$ with HCl.