Electronic Supporting Information

Synthesis of unfunctionalised G1 - Frechét-type CTA

Materials

Acetone (Analytical Grade, Fisher Scientific) was dried over 3 Å molecular sieves under a blanket of dry nitrogen overnight before use. Dichloromethane (Analytical Grade, Fisher Scientific), toluene (HPLC Grade, 99.5%, Fisher Scientific) and hexane (Analytical Grade, Fisher Scientific) were used as received. Benzene (HPLC grade, 99.9+%, Sigma-Aldrich) was freshly distilled over calcium hydride before use. Benzyl bromide (98%, Aldrich) was used as received. 3,5-dihydroxybenzyl alcohol (99%, Aldrich), potassium carbonate (≥98%, Aldrich) and 18-crown-6 ether (≥99.5%, Aldrich) were dried in a vacuum oven and stored in a vacuum desiccator. Anhydrous pyridine (99.8%, Aldrich), thionyl chloride (99+% Aldrich), sodium amide (95%, Aldrich), diphenylamine (99+% A.C.S. Reagent, Aldrich) and carbon disulfide (99.9%, Acros Organics) were used as received.

Synthesis of 3,5-dibenzyloxybenzyl alcohol (G1-OH)

3,5-Dibenzyloxybenzyl alcohol was prepared according to a previously described method. 3,5-Dihydroxybenzyl alcohol (6.15 g, 1.00 equivs, 43.9 mmol), potassium carbonate (15.15 g, 2.50 equivs, 101.0 mmol) and 18-crown-6 ether (4.63 g, 0.20 equivs, 17.5 mmol) were placed in a 2-necked, 500 ml round-bottomed flask equipped with a magnetic stirrer and reflux condenser and the flask flushed with dry nitrogen for 30 minutes. Benzyl bromide (15.00 g, 2.00 equivs, 87.7 mmol) was then injected into the flask, followed by cannulation of 200 ml dry acetone into the flask. The mixture was heated to gentle reflux with efficient stirring under a blanket of dry nitrogen for 48 hours and was then allowed to cool and the solvent was removed by rotary evaporation. The reaction mixture was partitioned between dichloromethane and water, and the aqueous layer extracted a further three times with dichloromethane. The combined organic layers were dried over magnesium sulphate, filtered and evaporated to dryness. The solid residue was recrystallised from 3:1 toluene / hexane and then dried under vacuum to a constant mass to give the final product as a white crystalline powder in 61% yield, MP=79-82°C. 1H NMR (400MHz, CDCl3, δ, ppm) 1.60 (s, 1H, CH2OH), 4.65 (s, 2H, CH2OH), 5.05 (s, 4H, Ar-CH2O-Ar-CH2OH), 6.55 (s, 1H, ArH), 6.65 (s, 2H, ArH), 7.1-7.5 (m, 10H, ArH).

Synthesis of 3,5-dibenzyloxybenzyl chloride (G1-Cl)

3,5-Dibenzyloxybenzyl alcohol (1.00 g, 1.00 equivs, 3.12 mmol) was dissolved in 80 ml dry benzene in a 3-necked, 250 ml round bottomed flask equipped with a magnetic stirrer, dropping funnel and reflux condenser under a blanket of dry nitrogen. To this was added anhydrous pyridine (1.97 g, 8.00 equivs, 24.96 mmol, 2.01 ml) and after 15 minutes the stirring solution was cooled to 0°C. Thionyl chloride (3.71 g, 10.00 equivs, 31.2 mmol, 2.26 ml) was then added dropwise with efficient stirring and after a further 5 minutes the ice bath removed and the reaction mixture allowed to warm to room temperature. It was then heated to gentle reflux for 24 hours. Thionyl chloride, pyridine and solvent were removed by vacuum distillation on a high vacuum line followed by distillation of dry benzene into and
out of the flask twice to azeotropically remove any excess thionyl chloride. The residue was then partitioned between water and dichloromethane and the aqueous layer extracted with dichloromethane a further three times. The combined organic layers were dried over magnesium sulphate, filtered and evaporated to dryness. The product was purification by flash chromatography eluting with dichloromethane followed by recrystallisation from toluene / hexane (1 ml hexane added followed by gentle heating and drop wise addition of toluene until the crude product had completely dissolved). The product was obtained as a light yellow solid in 62% yield.

\(^1\text{H NMR (}400\text{MHz, CDCl}_3, \delta, \text{ppm)} 4.54 (s, 2H, } \text{CH}_2\text{Cl), 5.07 (s, 4H, Ar-CH}_2\text{O-Ar-CH}_2\text{Cl), 6.50 (s, 1H, ArH), 6.68 (s, 2H, ArH), 7.30-7.50 (m, 10H, ArH).}

**Synthesis of G1 Frechét-type dendronised CTA**

95% sodium amide (0.0545 g, 1.00 equivs, 1.33 mmol) was suspended in 2.5 ml benzene in a 3-necked, 100 ml round bottomed flask equipped with magnetic stirrer, dropping funnel and reflux condenser under a blanket of dry nitrogen. To this was added diphenylamine (0.225 g, 1.00 equivs, 1.33 mmol) in 2.5 ml benzene and the mixture stirred overnight at room temperature. Carbon disulphide (0.121 g, 1.20 equivs, 1.59 mmol) in 2.5 ml benzene was added followed by G1-Cl (0.450 g, 1.00 equivs, 1.33 mmol) in 2.5 ml benzene which was slowly added drop wise to the stirring mixture. After 15 minutes the reaction mixture was heated to gentle reflux for 3.5 hours and then allowed to cool. The reaction mixture was washed twice with water and then dried over magnesium sulphate. After filtration the solvent was removed by vacuum distillation on a high vacuum line. The product was obtained as a light yellow solid in 55% yield.

\(^1\text{H NMR (}400\text{MHz, CDCl}_3, \delta, \text{ppm)} 4.44 (s, 2H, } \text{C(=S)SC}_2\text{H}_5\text{), 5.01 (s, 4H, Ar-CH}_2\text{O-Ar-), 6.51 (s, 1H, ArH), 6.61 (s, 2H, ArH), 7.30-7.44 (m, 20H, ArH).}

Elemental analysis calculated for C\(_{34}\)H\(_{29}\)NO\(_2\)S\(_2\): C, 74.56; H, 5.34; N, 2.56; S, 11.71. Found: C, 73.82; H, 5.29; N, 2.51; S, 11.06.

**RAFT polymerisation of N-vinyl pyrrolidone with G1 Frechét-type dendronised CTA (G1-CTA)**

The polymerisation was carried out using N-vinyl pyrrolidone (1.00 ml, 1.045 g, 9.40 mmol), 1ml 1,4-dioxane and the appropriate amount of CTA (0.0484 g, 0.088mmol) aiming for a polymer with \(M_n=10,000\) g mol\(^{-1}\). A 1:8 molar ratio of AIBN:G1-CTA was used, and the G1-CTA and AIBN were placed in a Schlenk tube containing a magnetic stirrer bar. 1.00 ml N-vinyl pyrrolidone was then transferred into the Schlenk tube, along with 1 ml freshly distilled 1,4-dioxane and the tube sealed with a rubber septum. The Schlenk tube was then connected to a vacuum / nitrogen line and its contents subjected to several freeze-pump-thaw cycles until thoroughly degassed. The Schlenk tube was then sealed under vacuum or flooded with nitrogen, and the reaction mixture heated to 80°C in an oil and left for 33 hours with efficient stirring. After this time the polymerisation mixture was cooled, the product dissolved in a few millilitres of dichloromethane and precipitated into diethyl ether (20 × volume excess of diethyl ether over the combined volumes of polymerisation mixture and dichloromethane)
before being recovered by vacuum filtration. The polymer was then dried under vacuum and the final product was a white powder obtained in 42% yield. The polymer was analysed by SEC in order to determine the average molecular weight and its distribution, and $^1$H NMR to verify the presence of the G-1 end group.

Scheme S1. Synthesis of S-3,5-dibenzyloxybenzyl N,N-diphenyldithiocarbamate (G1 CTA).

<table>
<thead>
<tr>
<th>Target $M_n$ / g mol$^{-1}$</th>
<th>$M_n$ (SEC) / g mol$^{-1}$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>10,000</td>
<td>7,900</td>
<td>1.27</td>
</tr>
<tr>
<td>20,000</td>
<td>14,000</td>
<td>1.36</td>
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</tbody>
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Table S1. SEC data for the synthesis of poly(N-vinyl pyrrolidone) by RAFT polymerization using G1-CTA.
Figure S1. Series of NMR spectra (in CDCl₃) showing intermediates and final product of the synthesis of the difunctional fluoroalkyl CTA precursor.
Figure S2. Series of NMR spectra (in CDCl₃) showing intermediates and final product of the synthesis of the trifunctional fluoroalkyl CTA precursor.
Figure S3. NMR spectra (in CDCl₃) of the difunctional and trifunctional fluoroalkyl CTA.

References