

Combining uretdione and disulfide reversibly degradable polyurethanes: route to alternating block copolymers†

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Electronic supplementary information

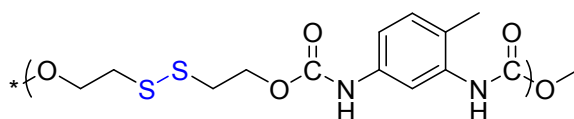
Materials and Analytical Methods

All reagents were purchased from Sigma-Aldrich and used without further purification unless otherwise stated.

Nuclear magnetic resonance (NMR) spectra were recorded on Bruker HD-300 and HD-400 spectrometers with samples prepared in deuterated solvents (Sigma-Aldrich) and chemical shifts were reported in parts per million (ppm) with reference to solvent residual peaks. THF size exclusion chromatography (SEC) was performed on an Agilent 390-LC-MDS system using THF as eluent at 30 °C, 1 ml min⁻¹ flow rate, equipped with refractive index, UV, viscometry and light scattering detectors, 2 x PLgel 5 mm mixed D columns (300 x 7.5 mm), 1 x PLgel 5mm guard column (50 x 7.5 mm) and autosampler. DMF SEC was performed on an Agilent 390-LC-MDS system using DMF (5 mM NH₄BH₄) eluent at 50 °C, 1 ml min⁻¹ flow rate, equipped with refractive index, UV, light scattering and viscometry detectors, 2 x PLgel 5 mm mixed D columns (300 x 7.5 mm), 1 x PLgel 5 mm guard column (50 x 7.5 mm) and autosampler. Agilent Easi-Vials narrow linear poly(styrene) standards in range of 200 to 1 x 10⁶ g mol⁻¹ were used to calibrate the systems. All samples were passed through a 0.22 μm filter prior to analysis. Infrared absorption spectra were recorded on a Bruker VECTOR-22 FTIR spectrometer using a Golden Gate diamond attenuated total reflection cell.

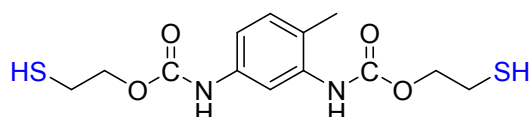
Experimental

(1) Disulfide containing polyurethane synthesis



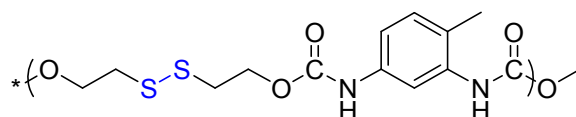
2-Hydroxyethyl disulfide (15 g, 0.0972 mol, 1eq) and toluene diisocyanate (16.936 g, 0.0972 mol, 1eq) were added to a round bottomed flask with a magnetic stirrer. The solids were dissolved in THF (100 ml) and 2 drops of dibutyltin dilaurate added. The solution was heated to 40°C for 2 hours. The polyurethane product precipitated into hexane and vacuum filtered producing a white powder. Yield = 83%.

(2) Reductive degradation of the disulfide containing polyurethanes using tributyl phosphine



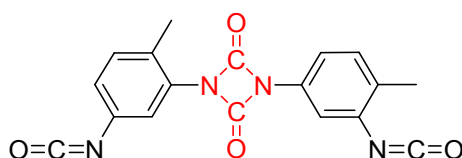
Disulfide containing polyurethane (1) (1 g, 0.00304 mol, 1eq) was dissolved in DMF (ml) in a sealed round bottomed flask equipped with a stirrer bar and bubbled with nitrogen for 20 minutes. Once heated to 40°C tributylphosphine (3 g, 0.0152 mol, 5 eq) was added and samples periodically withdrawn for GPC analysis. Samples taken for GPC analysis were first passed through neutral alumina.

(3) Oxidative reformation of the disulfide containing polyurethanes using iron(III) chloride



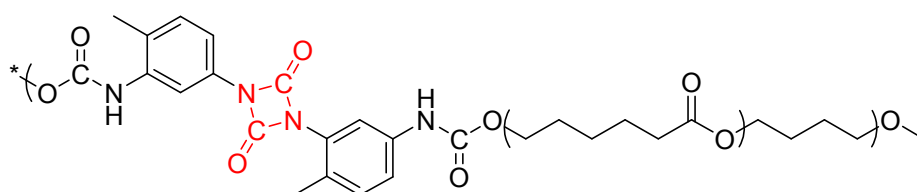
The reduced disulfide polymer (2) (1 g, 0.00304 mol, 1eq) was placed in a round bottomed flask equipped with a stirrer bar and dissolved in DMF (ml). The solution was heated to 40°C and the iron(III) chloride (24.65g, 0.152 mol, 50eq) added. The reaction was heated overnight. Samples taken for GPC analysis were first passed through neutral alumina to remove the iron residue.

(4) Dimerisation of toluene diisocyanate



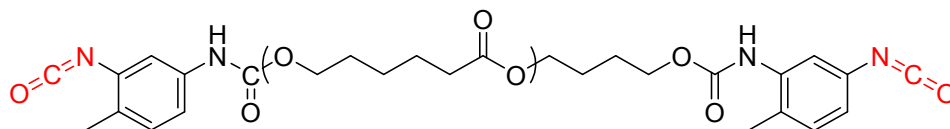
Toluene diisocyanate (4 g, 0.0229mol, 1eq) was placed in a round bottomed flask with a magnetic stirrer. Toluene diisocyanate was dissolved in toluene (30 ml) and cooled under ice while stirring. Tributylphosphine (0.14 g, 0.0007 mol, 0.03 eq) was added and the solution left to stir under ice for 2 hours. The white precipitate isolated by filtration, washed with toluene and hexane and volatiles removed under vacuum resulting in a white crystalline powder. Yield 2.44 g, 41%.

(5) Uretdione containing polyurethane synthesis



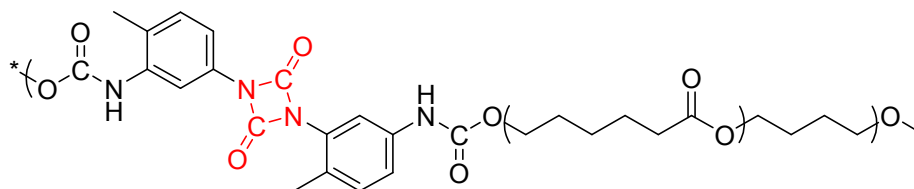
Toluene diisocyanate dimer (4) (0.436 g, 0.0025 mol, 1 eq) and 2,000 M_n polycaprolactone polyol (5 g, 0.0025 mol, 1 eq) were added to a round bottomed flask with a magnetic stirrer. The solids were dissolved in THF (15 ml) and 1 drop of dibutyltin dilaurate added. The solution was heated to 40°C for 2 hours. The polyurethane product was precipitated into hexane and vacuum filtered producing a white powder. Yield 5 g, 92%.

(6) Degradation of the uretdione containing polyurethanes using tributyl phosphine



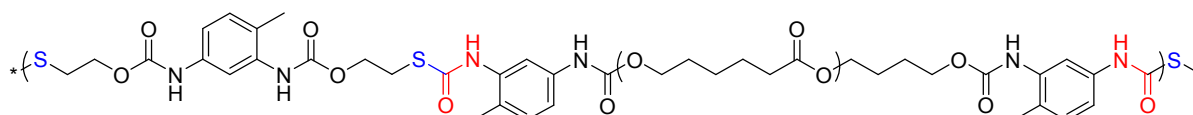
Uretidone containing polyurethane (5) (2 g, 8.52×10^{-4} mol, 1eq) was dissolved in THF (10 ml) in a round bottomed flask equipped with a stirrer bar. Once heated to 60°C tributylphosphine (0.005 g, 2.555×10^{-5} mol, 0.03 eq) was added and samples periodically withdrawn for GPC analysis.

(7) Reformation of the uretdione containing polyurethanes using tributyl phosphine



The reduced uretdione polymer (6) (1 g, 0.00181 mol, 1 eq) was placed in a round bottomed flask equipped with a stirrer bar and dissolved in THF (ml). The solution was cooled while stirring in ice for 30min. Tributylphosphine (0.005 g, 2.555×10^{-5} mol, 0.03 eq) was added and the solution left to stir under ice for 2 hours. Samples were periodically withdrawn for GPC analysis.

(8) Polythiourethane synthesis from disulfide and uretdione containing polyurethanes



Disulfide containing polyurethane (1) (0.14 g, 0.00181 mol, 1 eq) and uretdione containing polyurethane (5) (1 g, 0.00181 mol, 1 eq) were placed in a round bottomed flask and DMF (1 ml) added. The mixture was heated to 60°C and tributyl phosphine (g, mol, 0.03 eq) was added and left to stir for 15 minutes. THF (9ml) was added along with 2 drops of dibutyltin dilaurate and the solution left to stir overnight. Samples were periodically withdrawn for GPC analysis.