Supplementary Information

Self Healing Polymers Prepared via Living Radical Polymerisation

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**General Experimental**

All chemicals were purchased from Sigma-Aldrich and used without further purification, unless otherwise stated. Size exclusion chromatography (SEC) was used to determine the molecular weight averages and the PDI with a 390-LC Polymer Laboratories system equipped with a PL-AS RT/MT autosampler, a PL-gel 3 µm (50 × 7.5 mm) guard column, two PL-gel 5 µm (300 × 7.5 mm) mixed-D columns (suitable for separations up to MWt = 2.0 × 10^6 g mol⁻¹) and a differential refractive index and a UV detector, using THF–triethylamine 95 : 5 (v/v) as eluent with a flow rate of 1.0 mL min⁻¹. A high temperature PL 200 GPC also used with a PL-gel 3 µm (50 × 7.5 mm) guard column, three PL-gel 5 µm (300 × 7.5 mm) mixed-D columns using 100 % 1,2,4 trichlorobenzene as the eluent with a flow rate of 0.7 mL min⁻¹. The PL 220 was fitted with a DRI detector, a PL-BV 400 HT viscometer and a dual angle light scattering detector. Narrow molecular weight PMMA standards (1.0 × 10^6–200 g mol⁻¹) were used for calibration. ¹H-NMR spectroscopy was used to determine the monomer conversion. NMR spectra were recorded on Bruker DPX300, Bruker DPX400 and Bruker DRX500 spectrometers as solutions in perdeuterated NMR solvents. FTIR was recorded using a VECTOR-22 Bruker spectrometer using a Golden Gate diamond attenuated total reflection cell to record the infrared absorption.

**Synthesis of 4,10-Dioxatricyclo[5,2,1,0]dec-8-ene-3,5-dione (1)**

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\end{align*}
\]

(1)
Maleic anhydride, toluene and furan were added to a dried round bottom flask, equipped with a magnetic stir bar. The solution was heated under reflux for 24 hours, and then allowed to cool to ambient temperature. The product precipitated out of solution, and was washed with diethyl ether. The resulting white powder was used without further purification. Yield 92%; mpt 114–116 °C; \(^1\)H NMR (CDCl\(_3\)): \(\delta\) (ppm) 6.611 (s, 2H), 5.493 (s, 2H), 3.207 (s, 2H); \(^13\)C NMR (CDCl\(_3\)): \(\delta\) (ppm) 170.6, 136.8, 81.4, 48.8; FT-IR \(\nu = 3087, 3034, 2990, 1785, 1209 \text{ cm}^{-1}\). HRMS-ES Calcd. for C\(_8\)H\(_6\)O\(_4\) (M\(^+\)) = 167.03 Found 167.03.

**Synthesis of 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.0\(_2,6\)]dec-8-ene-3,5-dione (2)**

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\begin{array}{c}
\text{(2)}
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Exact Mass: 209.07

4,10-Dioxatricyclo[5,2,1,0\(_2,6\)]dec-8-ene-3,5-dione (30.0 g, 181.0 mmol) was added to a dried 3 neck round bottom flask, equipped with a magnetic stirred bar, dropping funnel and methanol (750 mL). The solution was purged with nitrogen for 10 minutes on an ice bath, after which ethanolamine (11.9 mL, 181.0 mmol) and triethylamine (25.1 mL, 181.0 mmol) was added. The system was removed from the ice bath, and the temperature steadily increased to 67 °C and left for 12.5 hours, after which a further 10% of ethanolamine (1.2 mL, 1.81 mmol) and reaction left at 70 °C for 2 hours. The flask was cooled to ambient temperature and the product precipitated from solution. The resultant crop of white crystals were washed with IPA and used without further purification. Yield 72%; mpt 134–136 °C; \(^1\)H NMR (CDCl\(_3\)): \(\delta\) (ppm, coupling in Hz) 6.457 (s, 2H), 5.213 (s, 2H), 3.657 (d, 2H, \(J = 5.2\)), 3.687d (2H, \(J = 5.2\)), 2.852 (s, 2H), 2.322 (s, 1H); \(^13\)C
Synthesis of 1-(2-hydroxyethyl)-1H-pyrrole-2,5-dione

A dried round bottom flask, fitted with a reflux condenser and magnetic stirrer, was charged with 300 mL of toluene and 4-(2-hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.0²,6]dec-8-ene-3,5-dione (30 g, 142.80 mmol). The reaction was refluxed for 24 hours. The resulting solution was filtered whilst hot, and the product crystallised upon cooling. Yield 92 %. ¹H NMR (CDCl₃): δ (ppm) 6.754 (s, 2H), 3.785 (d, 2H, J = 5), 3.725 (d, 2H, J = 5.2), 2.019 (s, 1H); ¹³C NMR (CDCl₃): δ (ppm) 176.6, 136.3, 80.7, 60.0, 47.3, 41.5; FT-IR v = 3477, 3102, 2971, 2890, 1765, 1681; HRMS-ES Calcd. for C₁₀H₁₁NO₄ (M⁺) = 210.07 Found 210.07

Synthesis of 1-(hydroxymethyl)-10-oxatricyclo[5.2.1.0²,6]dec-8-ene-3,5-dione-2-aminoethanol

Exact Mass: 141.04

HRMS-ES Calcd. for C₁₀H₁₁NO₄ (M⁺) = 141.04 Found 142.04 (+ H⁺)
1-(2-Hydroxyethyl)-1H-pyrrole-2,5-dione (2.94 g, 20.83 mmol), freshly distilled furfuryl alcohol (1.8 mL, 20.83 mmol) and 45 mL of high purity benzene was added to a 150 mL round bottom flask equipped with a condenser and magnetic stirrer. The reaction was refluxed for 24 hours, during which the product precipitated. The reaction was allowed to cool, the product isolated by vacuum filtration, and washed with diethyl ether. Yield 59 %; mpt 112–115; $^1$H NMR (d-DMSO): $\delta$ (ppm) 6.516 (s, 2H), 5.073 (s, 1H), 4.931 (t, $J = 5.7$ Hz, 1H), 4.776 (t, $J = 5.7$ Hz, 1H), 4.022 (dd, $J = 12.6$, 6 Hz, 2H), 3.772 (dd, $J = 12.6$, 5.4 Hz, 1H), 3.395 (br, 4H), 3.060 (d, $J = 6.3$ Hz, 1H), 2.898 (d, $J = 6.3$ Hz, 1H); $^{13}$C NMR (d-DMSO): $\delta$ (ppm) 176.4, 174.9, 138.1, 91.6, 80.2, 58.9, 57.3, 49.9, 47.8, 40.5. IR (solid) $\nu$ = 3423, 3078, 2919, 1692, 1407, 1183, 1029 cm$^{-1}$.

HRMS-ES Calcd. for C$_{17}$H$_{25}$NO$_4$ (M$^+$): 240.0872 Found: 240.0872

Synthesis of 5

1-(2-Hydroxyethyl)-1H-pyrrole-2,5-dione (10.0 g, 0.071 mmol) was placed in a round bottom flask equipped with a magnetic stirrer bar. To it was added 9-anthracenemethanol (14.76 g, 0.071 mmol), and 50 mL toluene. The reaction was heated under reflux for 24 hours, and the product crashed out upon cooling. The crystals were collected by vacuum filtration and used without
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Further purification. A second crop of crystals were obtained after leaving the filtrate in the fridge overnight. Yield 67%; ¹H NMR (d-DMSO): δ (ppm) 7.650 (d, J = 7.2, 1H) 7.413 (d, J = 6.7, 1H), 7.175 – 7.116 (m, 6H), 5.328 (t, J = 4 Hz, 1H), 4.695 (s, 1H) 4.602 (t, J = 4 Hz, 1H), 3.256 (s, 2H) 2.999 (m, 2H), 2.504 (m, 2H); ¹³C NMR : δ (ppm) 176.5, 175.8, 142.5, 139.9, 139.5, 126.3, 126.1, 125.9, 124.7, 124.5, 123.8, 122.5, 58.2, 56.4, 49.2, 47.5; IR (solid) ν = 3565, 3462, 2941, 2879, 1764, 1692, 1422, 1048, 771 cm⁻¹. HRMS-ES Calcd. for C₂₁H₁₉NO₄ (M⁺): 350.1 Found: 350.1

Synthesis of acrylic acid 2-(1-acryloyloxymethyl-3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.0²,6]dec-8-en-4-yl)-ethyl ester (6)

1-(Hydroxymethyl)-10-oxatricyclo[5.2.1.0²,6]dec-8-ene-3,5-dione-2-aminoethanol and triethylamine was added to a round bottom flask, equipped with a magnetic stirrer and placed on an ice bath. Anhydrous DCM was canulated into the flask. To this solution, acryloyl chloride was added drop wise via a dropping funnel and the reaction was left to stir for 24 hours. The extraction process involved washing with NH₄Cl, H₂O and brine, with the organic layer dried with MgSO₄. The product was recovered as a colorless oil after the volatiles were removed under vacuum. Yield 75%; ¹H NMR (d-CDCl₃): δ (ppm) 6.631 (s, br, 2H), 6.375 – 5.776 (m, 6H), 5.226 (s, 1H), 4.990 (d, J = 5.8 Hz, 1H), 4.466 (d, J = 12.8 Hz, 1H), 4.259 (m, 2H), 3.765 (m, 2H), 2.990 (dd J = 6.5 Hz + 6.3 Hz, 2H); ¹³C NMR (d-CDCl₃): δ (ppm) 175.2, 174.2, 165.7, 165.5, 139.2, 136.8, 132.8,
Synthesis of 2-bromo-2-methyl-propionic acid 2-[1-(2-bromo-2-methyl-propionyloxymethyl)-3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-en-4-yl]-ethyl ester (7)

1-(Hydroxymethyl)-10-oxatricyclo[5.2.1.02,6]dec-8-ene-3,5-dione-2-aminoethanol (3 g, 12.54 mmol) and triethylamine (6.0 ml, 26.33 mmol) was added to 3 neck round bottom flask equipped with a magnetic stirrer. 200 mL of anyhydrous THF was canulated into the flask placed in an ice bath and purged with nitrogen for 15 minutes. 2-Isobutyrylbromide (6.0 mL, 26.33 mmol) was added dropwise over a period of 15 minutes. The reaction was left to stir for a period of 6 hours. The solution was filtered to remove the salt, and the volatiles removed under reduced pressure. White powder. Yield 78%; $^1$H NMR (CDCl$_3$): $\delta$ ppm 6.490 (br, 1H), 6.412 (br, 1H), 5.191 (s, 1H), 4.903 (d, $J = 4.1$, 1H), 4.512 (d, $J = 4.1$, 1H), 4.156 (m, 2H), 3.663 (m, 2H), 2.92.0 (dd, $J = 4.9$ Hz, 2H), 1.811 (br s, 12H); $^{13}$C NMR (CDCl$_3$): $\delta$ ppm 175.2, 173.8, 171.3, 170.9, 137.3,
Synthesis of 8

(5) (10 g, 27.5 mmol) and triethylamine (8.4 mL, 57.7 mmol) was added to 3 neck round bottom flask equipped with a magnetic stirrer. 300 mL of anyhydrous THF was canulated into the flask, put on an ice bath and purged with nitrogen for 15 minutes. 2-Isobutyrylbromide (7.1 mL, 60.0 mmol) was added dropwise over a period of 15 minutes. The reaction was left to stir for a period of 6 hours. The solution was filtered to remove the salt, and the volatiles removed by vacuum. The oil was passed down a silica column using 1:1 Pet Ether:Et2O. The volatiles were removed under vacuum, to yield a white powder. Yield 81 %; \(^1H\) NMR (DMSO): \(\delta\) (ppm) 7.338 – 7.092 (m, 8H), 5.546 (d, \(J = 11.1, 1\)H), 5.390 (d, \(J = 10.8, 1\)H), 4.717 (s, 1H), 3.579 (s, 2H), 3.29 – 3.24 (m, 4H), 1.783 (br s, 12H); \(^13\)CNMR (DMSO): \(\delta\) (ppm) 175.9, 175.2, 170.5, 141.9, 140.8, 138.9, 138.0, 126.6, 126.1, 125.0, 124.2, 123.2 122.3, 62.9, 61.9, 57.1, 56.9, 47.3, 44.6, 36.0, 30.1; IR (solid) \(\nu\) 3653, 1774, 1735, 1695, 1461, 1417, 1312, 1291, 1275, 1161, 1103, 984 (cm\(^{-1}\)); HRMS-ES Calcd. for C\(_{29}\)H\(_{29}\)Br\(_2\)NO\(_6\) (M\(^+\)): 648.3 Found: 648.3
Polymerisation

General polymerisation procedure.

Cu(I)Br/DA1 catalysed polymerisation of MMA in toluene – Target 5 000 Da (9)

Cu(I)Br (0.1 g, 0.74 mmol) and DA1 (0.2 g, 0.37 mmol) was added to a clean, oven dried Schlenk tube, along with a magnetic follower. The Schlenk tube was sealed with a suba-seal, and purged with nitrogen several times. This was carried out by deoxygenating the tube via a high vacuum followed by flushing with nitrogen. Toluene (4 mL, 50% solids), MMA (3.9 mL, 37 mmol) and propyl-pyridin-2-ylmethylen-amine (0.27 mL, 1.48 mmol) were all added to the tube via a degassed syringe. Three freeze pump thaw cycles were then carried out using liquid nitrogen. The tube was placed in an oil bath at 50 °C (t = 0), and samples were taken every 45 minutes via a degassed syringe for conversion and molecular weight analysis. The reaction mixture was washed with toluene and passed through a neutral alumina column in order to remove copper salts. The solvent was removed on a rotary evaporator and the resulting polymer dissolved in a minimum THF. A total of 200 mL of methanol and 20 mL of water was measured into to a beaker and was left stirring in a dry ice/acetone bath. The polymer was then slowly dropped into the beaker with a pipette, and once completely added, was filtered out with a Buchner flask and funnel under high vacuum. The polymer was then dried in a vacuum oven at 45 °C.
Cu(I)Br/DA1 catalysed polymerisation of MMA in toluene – Target 5 000 Da (10)

Prepared as (9) with the following changes in quantities:

Cu(I)Br (0.05 g, 0.37 mmol), DA 1 (0.1 g, 0.185 mmol), MMA (1.0 mL, 9.25 mmol) and propylpyridin-2-ylmethylene-amine (0.13 mL, 0.74 mmol) and toluene 3 mL.

Cu(I)Br/DA1 catalysed polymerisation of MMA in toluene – Target 50 000 Da (11)

Prepared as (9) with the following changes in quantities:

Cu(I)Br (0.05 g, 0.37 mmol), DA 1 (0.1 g, 0.185 mmol), MMA (10.0 mL, 92.5 mmol) and propylpyridin-2-ylmethylene-amine (0.13 mL, 0.74 mmol) and toluene 10 mL.

Cu(I)Br/DA2 catalysed polymerisation of MMA in toluene – Target 10 000 Da (12)

Prepared as (9) with the following changes in quantities:

Cu(I)Br (0.22 g, 1.517 mmol), DA 2 (0.5 g, 0.75 mmol), MMA (8.0 mL, 75.8 mmol) and propylpyridin-2-ylmethylene-amine (0.45 mL, 3.03 mmol) and toluene 8 mL. The reaction was carried out at 70 °C.

Cu(I)Br/Ethyl-2-bromoisobutyrate catalysed polymerisation of MMA arm first star in toluene (13)

Cu(I)Br (0.2 g, 1.4 mmol) and was added to a clean, oven dried Schlenk tube, along with a magnetic follower. The Schlenk tube was sealed with a suba-seal, and purged with nitrogen several times. This was carried out by deoxygenating the tube via a high vacuum followed by flushing with nitrogen. Toluene (3 mL), MMA (1.9 mL, 47.2 mmol) and propyl-pyridin-2-ylmethylene-amine (0.45 mL, 2.8 mmol) were all added to the tube via a degassed syringe, and the flask was freeze pump thawed as described above. The flask was placed in an oil bath at 50 °C, and monitored every 30 minutes. At 90 % conversion, DA-XL (6) (1.0 g, 2.8 mmol) was added and left for a further 45 minutes. The polymer
Cleavage of polymers 9 – 11, 13

The respective polymer (0.5 g) was placed into a round bottom flask equipped with a magnetic stirrer. The flask was charged with 6 ml of toluene, and fitted with a reflux condenser. The solutions were refluxed for 24 hours, and precipitated as in the method described in (9) for NMR and GPC analysis.

Reformation of polymers 9 – 11

0.1 g of each polymer was placed in a sample vial and placed in an oil bath at 60 °C. This was left for 24 hours. The polymer was analysed by NMR and GPC, used without further purification.

Cleavage of polymer 12

Polymer 12 (0.5 g) was placed into a round bottom flask equipped with a magnetic stirrer. The flask was charged with 6 ml of DMSO, and fitted with a reflux condenser. The solutions were refluxed for 24 hours at 160 °C, and precipitated as described for (9) for NMR and GPC analysis.

Synthesis of rhodamine tag and subsequent cleavage with polymers 12 + 13

Synthesis of (6-diethylamino-9-{2-[2-(3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-en-4-yl)-ethoxycarbonyl]-phenyl}-xanthen-3-ylidene)-diethyl-ammonium (14)
[9-(2-Carboxy-phenyl)-6-diethylamino-xanthen-3-ylidene]-diethyl-ammonium, rhodamine B, (9.5 g, 19.9 mmol), 4-(2-hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-ene-3,5-dione (5 g, 23.9 mmol), dicyclohexylcarbodiimide (4.9 g, 23.9 mmol) and 4-dimethylaminopyridine (0.58 g, 4.7 mmol) were all added to a round bottom flask equipped with a magnetic stirrer, and the flask sealed with a suba-seal. The flask was purged with nitrogen for 15 minutes, after which dry DCM (300 Ml) was added via a cannula prior to cooling in an ice bath for 2 hours. The reaction was left at ambient temperature for 72 hours. The volatiles were removed under vacuum, to yield a purple solid. This was purified by flash chromatography with 100 % DCM as eluent, with the product being the second fraction. Yield 79 %; \(^1\)H NMR (CDCl\(_3\)): \(\delta\) (ppm) 8.328 (d, \(J = 8\) Hz, 1H), 7.828 (t, \(J = 6.3\) Hz, 1H), 7.726 (t, \(J = 6.2\) Hz, 1H), 7.339 (d, \(J = 7.5\) Hz, 1H), 7.31 (s 2H), 6.961 (dd, \(J = 2.5\) Hz, 2H), 6.828 (d, \(J = 2.2\) Hz, 2H), 6.566 (s, 2H), 5.220 (s, 2H), 4.2428 (t, \(J = 5.3\) Hz, 2H), 3.853 (t, \(J = 5.2\) Hz, 2H), 3.517 (br s, 8H), 2.946 (s, 2H), 1.361 (t, \(J = 7.3\) Hz, 12H); \(^{13}\)CNMR (CDCl\(_3\)): \(\delta\) (ppm) 157.8, 155.7, 131.6, 130.3, 114.3, 96.4, 81.1, 65.9, 61.8, 47.6, 46.2, 15.4, 12.8 ; IR (solid) \(\nu\) 3321, 2979, 1769, 1719, 1695, 1471, 1414, 1336, 1181, 1073, 1010, 975, 851 (cm\(^{-1}\)); HRMS-ES Calcd. for C\(_{38}\)H\(_{40}\)N\(_3\)O\(_6\) (M\(^+\)): 635.2 Found: 635.2

### Cleavage of 12 in presence of rhodamine tag (14)

0.2 g of polymer 12 and (6-diethylamino-9-{2-[2-(3,5-dioxo-10-oxa-4-aza-tricyclo[5.2.1.02,6]dec-8-en-4-yl)-ethoxycarbonyl]-phenyl}-xanthen-3-ylidene)-diethyl-ammonium (0.63 g, 1 mmol) was placed into a round bottom flask equipped with a magnetic stirrer. The flask was charged with 6 ml of DMSO and fitted with a reflux condenser. The reaction mixture was left refluxing for 24 hours at 160 °C. The reaction was allowed to slowly cool to ambient temperature over a period of 6 hours, and the DMSO was removed under vacuum, and the resulting polymer was dissolved in 10 mL of THF. The resulting
solution was centrifuged for 15 minutes at 5000 rpm, after which the excess rhodamine tag precipitated out in solution. The solution was then isolated for GPC analysis with a UV/Vis detector.

Cleavage of 13 in presence of rhodamine tag (14)

The cleavage of the DA star was carried out in the same way as above except 0.1 g of 13 and 0.79 g of 14 were used.

S.I Fig. 1 - DSC data for polymer 10 run on a Mettler Toledo DSC/TGA 1 from 40 to 400 °C at a heating rate of 5 °C per minute.

The DSC data gave us an indication as to the temperature the Retro Diels reaction proceeded at. (i) The run was taken up to 400 °C. After 200 °C, the polymer back started to degrade. Despite the high sensitivity of the DSC instrument used, it was difficult to see the retro Diels Alder reaction as it was just one bonding breaking in a polymer of Mₙ 12 000 g mol⁻¹, with no phase change.

(ii) Expansion shows the r-DA at 126 °C.
SI Fig. 2 - (i) First order kinetic plot for polymer (9) (50 °C). (ii) $M_n$ vs. conversion for the polymer (9). 

\[ [\text{Cu(I)Br}]/[\text{ligand}]/[\text{initiator}]_0/[\text{MMA}]_0 \ 2:4:1:50 \]

SI Fig. 3 - (i) First order kinetic plot for polymer (11) (ii) $M_n$ vs. conversion for the polymer (11). 

\[ [\text{Cu(I)Br}]/[\text{ligand}]/[\text{initiator}]_0/[\text{MMA}]_0 \ 2:4:1:500 \]
S.I Figure 4 - $^{13}$C-NMR showing (i) the original polymer (ii) cleaved polymer and (iii) the reformed polymer, under the conditions described in scheme 2.

S.I. Figure 5 - High temperature GPC. Run at 140 °C on a PL 200 using 100 % 1,2,4 Trichlorobenzene as the eluent with a flow rate of 0.7 mL min$^{-1}$
The data at 140 °C shows little change to the original polymer, with very small changes in Mn, Mw and Mw / Mn. This indicates that the polymer is constantly cleaving and reforming throughout the heating process in the absence of a trapping agent.