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## Supporting Information

# A Self-Repairing Polymer Blend: Healability as a Consequence of Donor-Acceptor π-π-Stacking Interactions

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## General Information

Reagents were purchased from either Aldrich or Acros and were used as received without further purification, except triethylamine which was distilled from $CaH_2$ under nitrogen prior to use. Solvents were used as supplied, with the exception of chloroform ($CHCl_3$), which was distilled under nitrogen from calcium hydride. DMAc (99.8% anhydrous) was purchased from Aldrich and used as received. NMR spectra were recorded on a Bruker AC250 instrument operating at 250 MHz and 62.5 MHz for $^1$H and $^{13}$C nuclei, respectively. Infrared (IR) spectroscopic analyses were performed on a Perkin–Elmer 17 20-X FT-IR spectrometer from thin films cast onto KBr disks. Matrix-assisted laser desorption–ionization time-of-flight mass spectra (MALDI-TOF MS) were obtained using a Scientific Analysis Instruments LT3 LaserTof spectrometer using dithranol as the matrix. A typical sample preparation is described as follows: A solution of the analyte in chloroform 3 μL (1–10 mgmL$^{-1}$) was combined with 10–20 μL of the freshly prepared matrix (40 mg mL$^{-1}$ in $CHCl_3$) in a mini-vial, and an aliquot was transferred onto a sample plate and left to dry in air prior to analysis. UV/vis absorption measurements were carried out in 1 cm$^2$ quartz cuvettes on a double-beam Perkin–Elmer Lambda 25 spectrophotometer, in the wavelength range 400–700 nm, employing a scan speed of 120 nm min$^{-1}$, with a slit width of 1 nm. Spectra were recorded using samples dissolved in analytical grade chloroform mixed 6:1 with hexafluoroisopropanol and blank-corrected for the possible absorption of the solvent. Polymer molecular weight data were acquired at Smithers-RAPRA Technology Ltd using HFIP as eluent and PMMA as standards. Inherent viscosities were measured on a Schott CT52 auto-viscometer and are the average of 5 measurements. ESEM microscopy images were recorded with a FEI Quanta FEG 600 Environmental Scanning Electron Microscope (ESEM) equipped with a hot stage. Mechanical testing was carried out using a TA instruments (New Castle, DE, USA) RSA III at 30 °C and a constant Hencky strain rate of 0.1 $s^{-1}$ using a gap of 5 mm. Samples were approximately 0.10 mm in thickness and 3.50 mm in width. Frequency temperature sweep measurements were acquired on a TA instrument ARES G2 (New Castle, DE, USA). Differential scanning calorimetry (DSC) was carried out under nitrogen using a Mettler-Toledo 823e instrument, at a heating rate of 10 °C $min^{-1}$. Polymer films were cast from solutions in 1,1,1–trichloroethanol and were dried at 80 °C under vacuum for 36 hours.

### Chain folding polyimide 1

A solution of Jeffamine® D-400 (1.20 g, 2.70 mmol) and 2,2'-(ethylenedioxy)bis(ethylamine) (0.48 g, 2.7 mmol) in DMAc (5 mL) 2-ethyl hexylamine (0.07 g, 0.6 mmol) was added to a stirred suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.50 g, 5.6 mmol) in DMAc (10 mL) and toluene (2 mL). The suspension was heated to 135 °C and the reaction became homogeneous. During this time the toluene/water azeotrope was distilled off and additional toluene (2 mL) was added and removed again by distillation. After 18 hours the reaction was cooled to room temperature and the suspension poured into diethyl ether (100 mL). The crude polymer was collected by filtration then subjected to Soxhlet extraction with diethyl ether for 5 hours before being dried in vacuum overnight to give **1** as a tan powder (2.01 g, 74%). $T_g$ = 190 °C; (GPC, HFIP) $M_n$ = 16400, $M_w$ = 27400; $\eta_{inh}$ = 0.127 dL $g^{-1}$; $^1$H NMR ($CDCl_3$/TFA 9:1 v/v, 250 MHz) $\delta$ = 8.80 (s, 8H), 5.51 (m, 1.5H), 3.90 (br, 6H), 4.19-3.50 (br, 26H), 1.90 (m, 0.2H), 1.55 (d, 4H, $J$=6), 1.40-0.80 (m, 14H); $^{13}$C NMR ($CDCl_3$/TFA 9:1 v/v, 62.5 MHz) $\delta$ = 164.1, 164.3, 131.5, 126.7-126.1, 76.0, 74.5, 72.5, 71.8, 69.7, 68.0, 49.6, 39.6, 16.4, 15.9, 14.7, 13.9; IR $\nu_{max}$(KBr)/$cm^{-1}$ 3360, 3083, 2975, 2927, 2872, 1782, 1704, 1666, 1579, 1453, 1373, 1335, 1245, 1098.

### Pyrene-endcapped oligo amide 2

To a stirred solution of Jeffamine® D-400 (4.00 g, 10.0 mmol), 1-pyrenemethylamine hydrochloride (0.53 g, 2.0 mmol) and dry triethylamine (14.04 mL, 10.19 g, 100 mmol) in dry chloroform (100 mL) was added a solution of isophthaloyl dichloride (2.23 g, 11.0 mmol) in dry chloroform (80 mL) over a period of 5 min. The reaction mix was poured into *n*-hexane (200 mL). A white precipitate was formed and filtered off under vacuum. The crude product was washed with hot water (4 × 50 mL), dissolved in chloroform, dried over $MgSO_4$ and the solvent removed under reduced pressure overnight at 50 °C to give pyrene-endcapped oligo-amide **2** as a pale yellow oil in 61% (3.59 g). $T_g$ = -7 °C; (GPC HFIP) $M_n$ = 5900, $M_w$=10400; $\eta_{inh}$ = 0.126 dL $g^{-1}$. $^1$H NMR ($d_6$-DMSO, 250 MHz) $\delta$ = 9.37 (m, 2H), 8.54-7.48 (m, 22H), 5.25 (d, 2H, J = 5.35 Hz), 4.17-4.09 (m, 1H), 3.39 (m, 4H), 1.14 (d, 3H, J = 7.5), 1.02 (m, 3H); $^{13}$C NMR ($d_6$-DMSO, 62.5 MHz) $\delta$ = 165.4, 134.8-120.1, 74.4, 72.3, 72.1, 71.6, 71.3, 45.3, 17.3. IR $\nu_{max}$(KBr)/$cm^{-1}$ 3328, 3061, 2971, 2870, 1723, 1647, 1540, 1455, 1374, 1106. MALDI-ToF MS: m/z for (M) 1027.74, 1085.82, 1143.83, 1201.96, 1638.95, 1687.00, 1754.05, 1814.02, 2307.64, 2365.68, 2424.77, 2481.56. (Calc. for for one repeat unit of oligo-amide **2**, where n = 4 and m = 1: $C_{65}H_{64}N_5O_8$ = 1028.47). NOTE: Jeffamine® D-400, comprises oligomers differing by 58 Da, there are a range of Jeffamine repeat units in the repeat unit of oligo-amide **2**).

## Jeffamine® D-400 polyimide 3

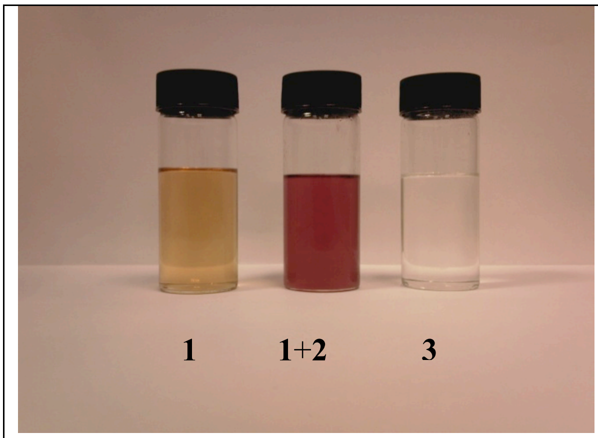
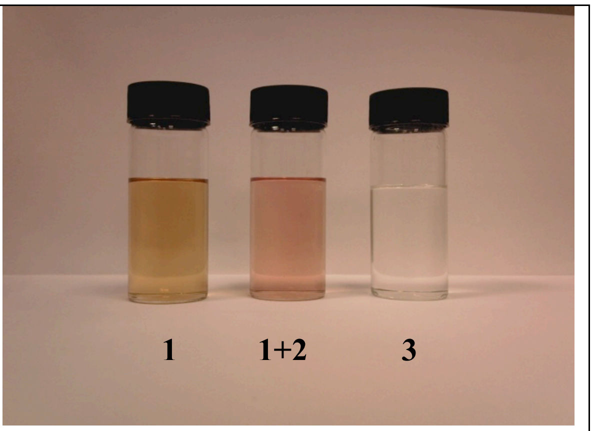
A solution of Jeffamine® D-400 (2.40 g, 5.4 mmol) and 2-ethyl hexylamine (0.07 g, 0.6 mmol) in DMAc (5 mL) was added to a stirred suspension of 1,4,5,8-naphthalenetetracarboxylic dianhydride (1.50 g, 5.6 mmol) in DMAc (10 mL) and toluene (2 mL). The suspension was heated to 135 °C and the reaction became homogeneous. During this time the toluene/water azeotrope was distilled off and additional toluene (2 mL) was added and removed again by distillation. After 18 hours the reaction was cooled to room temperature and the dark solution poured into hexane (100 mL). The light yellow upper layer was decanted to leave a viscous brown oil. The stirring with hexane followed by decanting procedure was repeated an additional 3 times before the brown oil was dried under vacuum at 80 °C overnight to give **3** (1.93 g, 54%). $^1$H NMR ($CDCl_3$/TFA 10:1 v/v, 250 MHz) $\delta$ = 8.80 (m, 4H), 5.51 (m, 2H), 4.4-3.2 (br m, 19H), 1.55 (d, 6H, $J$ = 6 Hz), 1.5-0.8 (m, 20H); $^{13}$C NMR ($CDCl_3$, 62.5 MHz) $\delta$ = 163.2, 133.1, 130.9, 126.7, 75.2, 73.2, 72.8, 69.8, 68.0, 49.6, 49.4, 37.8, 28.6, 23.0, 17.2, 15.1, 14.1, 10.6; IR $\nu_{max}$(KBr)/cm$^{-1}$ 2969,2871, 1705, 1666, 1580, 1453, 1372, 1333, 1246, 1105, 927, 771, 737, 590.

## Benzyl end-capped oligoamide 4

To a stirred solution of Jeffamine® D-400 (2.00 g, 5.0 mmol), benzylamine **6** (0.10 g, 0.9 mmol) and dry triethylamine (7.02 mL, 5.09 g, 50 mmol) in dry chloroform (40 mL) was added a solution of isophthaloyl dichloride (1.01 g, 5.0 mmol) in dry chloroform (20 mL) over a period of 5 minutes. The reaction mix was poured into *n*-hexane (200 mL). A white precipitate was formed and filtered off under vacuum. The crude product was washed with hot water (4 × 50 mL), dissolved in chloroform, dried over $MgSO_4$ and the solvent removed under reduced pressure overnight at 50 °C to give **4** as a colourless oil in 73 % (2.01 g) yield. $T_g$ = -1 °C; (GPC HFIP) $M_n$ = 5600, $M_w$ = 10500; $^1$H NMR ($d_6$-DMSO, 250 MHz) $\delta$ = 9.16 (m, 2H), 8.34-8.28 (m, 40H), 8.02-7.93 (m, 14H), 7.58-7.49 (m, 8H), 7.34-7.32 (m, 8H), 4.51-4.48 (d, 4H, J = 5.9 Hz), 4.16-4.09 (m, 12H), 3.50-3.35 (m, 164H), 1.20-1.00 (m, 144H); $^{13}$C NMR ($d_6$-DMSO, 62.5 MHz) $\delta$ = 165.4, 134.8-126.4, 74.6-74.2, 72.3-71.3, 45.3, 17.3. IR $\nu_{max}$(KBr)/cm$^{-1}$ 3478, 3070, 2972, 2929, 2879, 1644, 1540, 1451, 1376, 1103.

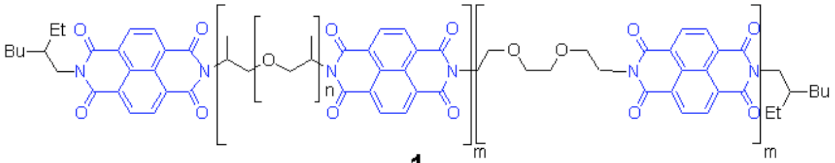
## Film from blend of 1 and 2 (1:3 w/w respectively)

**Solutions at 25 °C of 1 and 2 in isolation and as a blend at 60 °C (right) and at room temperature (left) in hexafluoropropan-2-ol/$CHCl_3$ 1:6 v/v.**

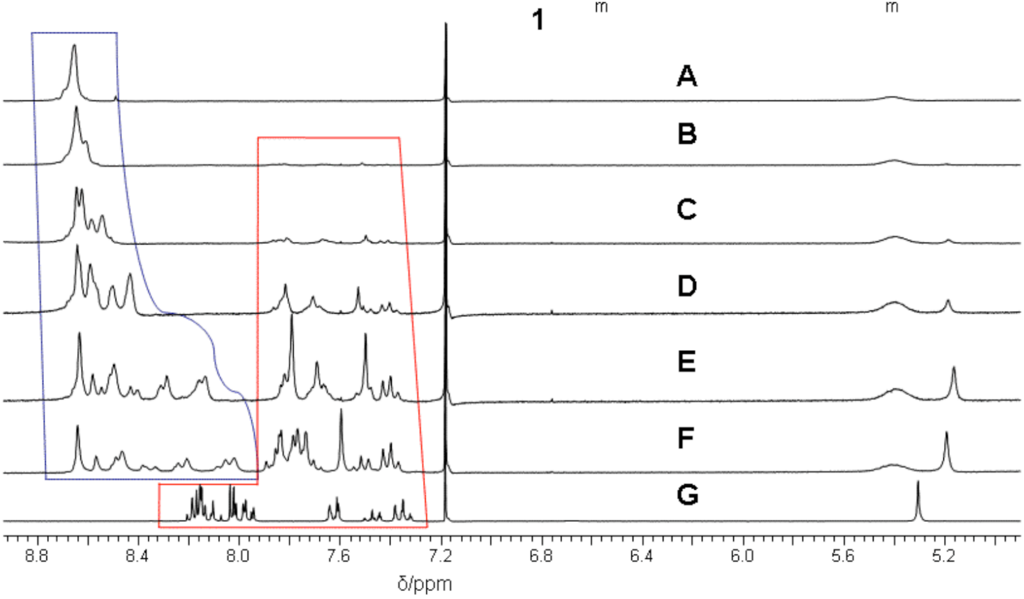
| | |
|---|---|
|  |  |
| Room temperature | ≈ 60 °C |

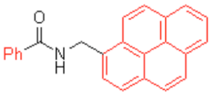
**$^1H$ NMR spectra (250 MHz, $CF_3CO_2H/CDCl_3$ 1:9) of polyimide 1 (10 mg/mL) with increasing concentration of model pyrenyl derivative 5 (spectra B to F)**

Spectra A and G are of polydiimide **1** and pyrenyl derivative **5** respectively. Signals relating to the aromatic protons of the polyimide and pyrene derivative are enclosed within the blue and red boxes respectively. Final concentration (Spectrum F) of **5** was 0.5 mole equivalents of the diimide units in the chain-folding motif ("m" at right in the formula of **1** below).



**1**

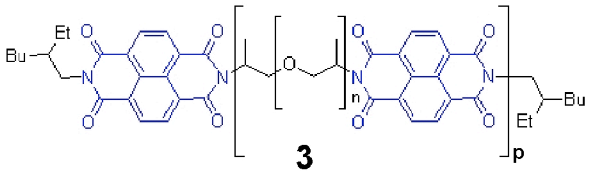




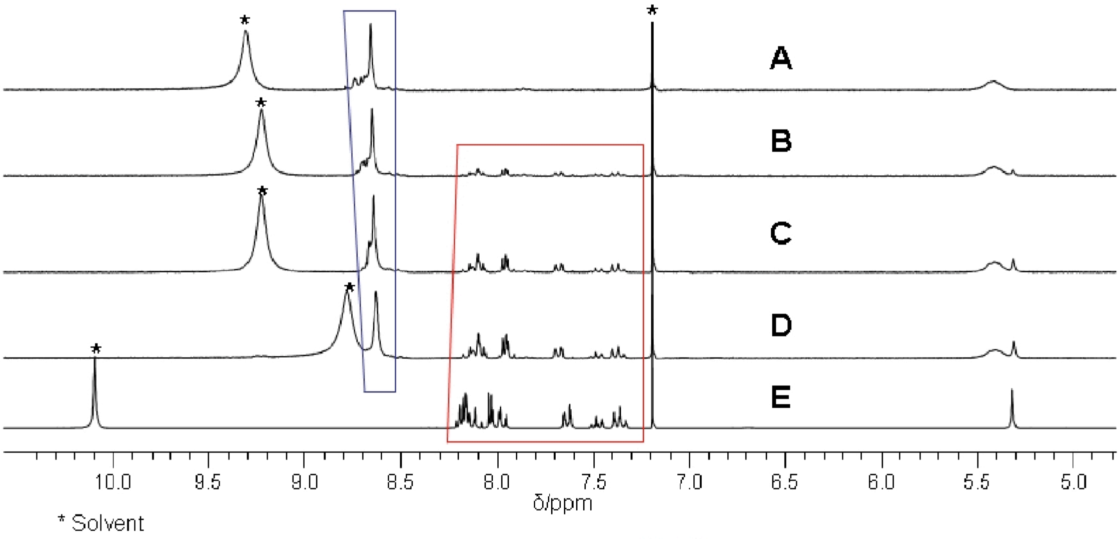
**5**

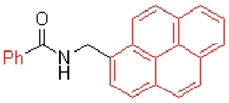
### ${}^1$H NMR spectra (250 MHz, $CF_3CO_2H/CDCl_3$ 1:9) of polydiimide 3 (10 mg/mL) with increasing concentration of and model pyrenyl derivative 5 (spectra B to D)

Spectra A and E are of pure samples of polydiimide **3** and pyrenyl derivative **5** for comparison. Signals relating to the aromatic protons of the polyimide and pyrene derivative are enclosed within the blue and red boxes respectively. Final concentration (Spectrum D) of **5** was 0.5 mole equivalents of the diimide units of **3**, below.



**3**



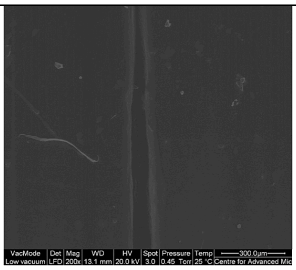


**5**

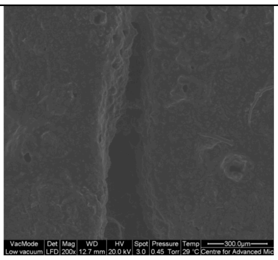
### ESEM experimental details and unprocessed images

ESEM images were recorded using an FEI Quanta FEG 600 Environmental Scanning Electron Microscope equipped with a hot stage. A cut was made in a 0.5 x 0.5 cm square of film with a scalpel, and the sample placed in the ESEM. The temperature was increased at a rate of 5 °C $min^{-1}$ with images acquired periodically throughout the temperature ramp.

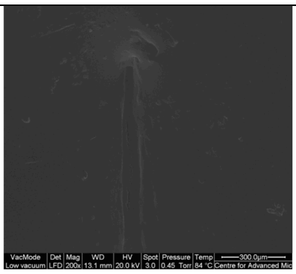
**Unprocessed variable temperature ESEM data for the healable blend of 1 and 2 (A, B and C) and the non-healing blend between 1 and 4 (A’, B’ and C’).**



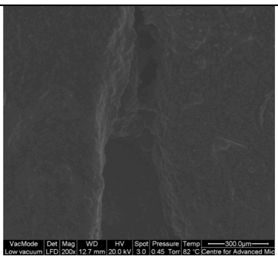
A



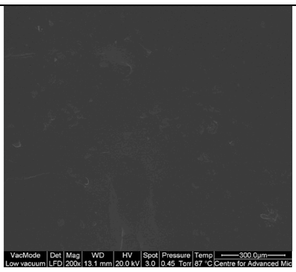
A’



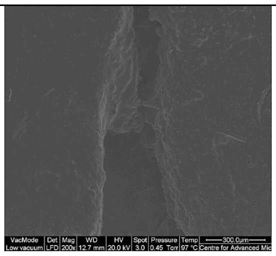
B



B’



C



C’

**Rheometric experimental details and analysis**

Rheometry was carried out using a TA instruments (New Castle, DE, USA) RSA III at 30 °C and a constant Hencky strain rate of 0.1 $s^{-1}$ using a gap of 5 mm and samples of approximately 0.10 mm in thickness and 3.50 mm in width. The tensile modulus was computed from the slope of the low strain linear region of the stress-strain curve.

A smooth, dark red, self-supporting film of [**1**+**2**] (1:3 w/w, 0.10 mm in thickness) was cut into strips 3.5 mm in width and 4 cm in length for testing. Tensile experiments were conducted at 30 °C on the pristine strips, and on the re-healed samples. Healing was achieved by overlapping the broken edges, pressing gently on a pre-heated Teflon plate, and finally heated in an oven at 50 °C for increasing time-periods. (Extremely rapid recovery of mechanical properties was achieved using healing temperatures significantly above 60 °C).

The Figure below shows recovery of tensile modulus for [**1**+**2**] after repeated cycles of breaking and re-healing. The time between breaking and healing had no significant effect on the recovered tensile modulus, even up to 24 hours (column in black).