Supporting Information

A healable supramolecular polymer blend based on aromatic π-π stacking and hydrogen bonding interactions

Stefano Burattini,[a] Barnaby W. Greenland,[a] Daniel Hermida Merino,[a] Wengui Weng,[b] Jon Seppala,[b] Howard M. Colquhoun,*[a] Wayne Hayes,*[a] Michael E. Mackay,[b] Ian W. Hamley,[a] Stuart J. Rowan.[c]

Email: h.m.colquhoun@reading.ac.uk; w.c.hayes@reading.ac.uk.

[a] Department of Chemistry, University of Reading, Whiteknights, Reading, RG6 6AD, UK.
[b] Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716, USA.
[c] Department of Macromolecular Science & Engineering, 2100 Adelbert Road, Cleveland, Ohio 44106, USA.

Table of Contents

Experimental Section

General information

All reagents were purchased from Aldrich, except for bis-hydroxy-terminated polybutadiene which was kindly donated by Henkel Ltd., and were used without further purification. Solvents were used as supplied, with the exception of tetrahydrofuran (THF), which was distilled under nitrogen from sodium and benzophenone prior to use. Anhydrous triethylamine was purchased from Aldrich and used as received. Model compound **9** was prepared as previously described.[S1].

Polymer characterization

Polymer molecular weight data were acquired at Smithers-RAPRA Technology Ltd. (Shawbury, Shropshire, UK) using 0.01 M lithium bromide in *N*,*N'*-dimethylformamide as eluent, and PMMA calibration standards. Differential scanning calorimetry (DSC) was carried out under nitrogen using a Mettler-Toledo 823e instrument, at a heating rate of 10 °C min^{-1}.

Spectroscopy

NMR spectra were recorded on Bruker AC250 and Bruker AMX400 instruments, operating at 250 MHz or 400 MHz respectively for ^{1}H nuclei and 62.5 MHz or 100 MHz for ^{13}C nuclei. Infrared (IR) spectroscopic analyses were obtained with a Bruker Equinox 55 infrared microscope, operating in transmission mode and equipped with a variable temperature stage, from polymer films cast onto KBr disks. UV/vis absorption measurements were carried out in 1 cm^2 quartz cuvettes on a double-beam Perkin–Elmer Lambda 25 spectrophotometer, over the wavelength range 400–700 nm, employing a scan speed of 120 nm min^{-1} and slit width of 1 mm. Spectra were recorded using samples dissolved in analytical grade chloroform mixed with hexafluoroisopropanol (6:1 v/v) and were blank-corrected for absorption by the solvent. Fluorescence measurements were carried out in 1 cm^2 quartz cuvettes on a Varian Eclipse spectrometer.

[S1] Greenland, B. W.; Burattini, S.; Hayes, W.; Colquhoun, H. M. *Tetrahedron*, **2008**, *64*, 8346-8354.

Microscopy

Images were recorded using an FEI Quanta FEG 600 environmental scanning electron microscope (ESEM) at ambient temperature, with a magnification of ×500.

Film preparation

Polymer films were cast from 1,1,1–trichloroethanol and dried in a vacuum oven, initially at atmospheric pressure by increasing the temperature from 50 °C to 80 °C over 24 hours, and then at 80 °C under vacuum for further 36 hours.

Rheology

Mechanical testing was carried out on samples ca. 0.10 mm in thickness and 3.50 mm in width, using a TA Instruments RSA III at 30 °C and a constant Hencky strain rate of 0.01 s^{-1}, with a gap of 5 mm. Samples were pre-tensioned, and the Young's Modulus was extracted from the linear region at low strain. Frequency and temperature sweeps were carried out on an ARES-G2 strain controlled rheometer (TA Instruments, New Castle, DE, USA) with 8 mm parallel plates on circular samples with an 8 mm diameter. Frequency sweeps at 10 to 0.1 rad s^{-1} at 0.1% strain were measured from -20 °C to 110 °C in 10 °C increments. Temperature sweeps were run at 10 rad s^{-1} and 0.3–1.0% strain, with the strain automatically increased by the instrument to keep the measured torque at a reasonable value as the sample softened. Contact with the sample was maintained by the autocompression feature set to 0.03+/-0.01 N. Linearity of the viscoelastic region was determined a strain sweep at the lowest temperature and highest frequency. Boltzmann Time-Temperature superposition was used to create a master curve, with a reference temperature of 30 °C from the individual frequency sweeps. Temperature sweep analyses were run at 1 °C min^{-1} between -50 °C and +120 °C.

SAXS and WAXS

SAXS experiments were performed on Beamline A2 of HASYLAB at the Deutsches Elektronen-Synchrotron (DESY) in Hamburg. Samples were encapsulated in aluminium foil and mounted in a heated cell. The temperature profile (5 °C min^{-1} heating and cooling rates) comprised a heating ramp from -20 °C to 80 °C, cooling to -20 °C, and re-heating from -20 °C to 80 °C. The sample was held for two minutes between each temperature reversal. Two linear Gabriel-type detectors were used to acquire SAXS and WAXS data simultaneously. The wavenumber scale $q = 4\pi\sin\theta/\lambda$ (scattering angle 2θ, wavelength $\lambda = 1.5$ Å, 2.2 m) was calibrated for SAXS using mineralized rat tail tendon, and for WAXS using a sample of poly(ethylene terephthalate). Since no orientation was observed in the SAXS patterns, data were reduced to one-dimensional form, with appropriate background subtraction.

Healing studies

The two parts of a ruptured film-sample were positioned with their broken edges in contact (not overlapped) on a preheated (100 °C) PTFE plate, and then annealed in an oven at 100 °C in air for varying periods of time.

Synthesis

*Pyrenyl end-capped polymer **2**:*

Bis-hydroxy-terminated polybutadiene (2.0 g, 1.0×10^{-3} mol) was dried under vacuum at 100 °C for 1 hour. After cooling to room temperature, a solution of diphenylmethane-4,4'-diisocyanate (MDI) (0.50 g, 2.0×10^{-3} mol) in THF (75 mL) was added under an argon atmosphere, and the stirred solution was heated under reflux. After three hours, a solution of 1-pyrenemethylamine hydrochloride (0.59 g, 2.2×10^{-3} mol) and dry triethylamine (1.1 g, 1.5 mL, 1.1×10^{-2} mol) in THF (20 mL) was added dropwise and heating continued for an additional 3 hours. After cooling to room temperature, the solution was concentrated and the crude product precipitated in water (100 mL), filtered and washed with hot water (3×50 mL) to give a pale yellow gum (83%, 2.5 g). T_g = -30 °C; GPC (DMF/LiBr) M_n = 8,400 g mol^{-1}, PDI = 1.7. ^{1}H NMR (250 MHz, $CDCl_3$), δ 8.14-7.94 (pyrene, br), 7.28-7.20 (m), 7.09-7.00 (m), 6.50 (br), 5.55-5.46 (m), 5.35-5.33 (m), 4.96 (br), 4.13-4.10 (m), 3.87 (br), 3.79 (br), 2.02 (br), 1.40-1.38 (m), 1.25 (br); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 153.7, 144.2-142.4, 136.2-135.9, 131.7-129.4, 128.1-127.2, 125.8, 125.1, 124.6, 122.7, 121.1, 118.9, 115.4-112.8, 64.7, 63.5, 43.6, 41.7-37.4, 35.6, 34.2-33.5, 32.7, 32.6, 32.0, 30.2, 28.8, 27.5, 27.4, 25.0; IR ν_{max}(KBr)/cm^{-1} 3322, 3075, 2974, 2913,2851, 1737, 1717, 1636, 1597, 1524, 1415, 1311, 1222, 911.

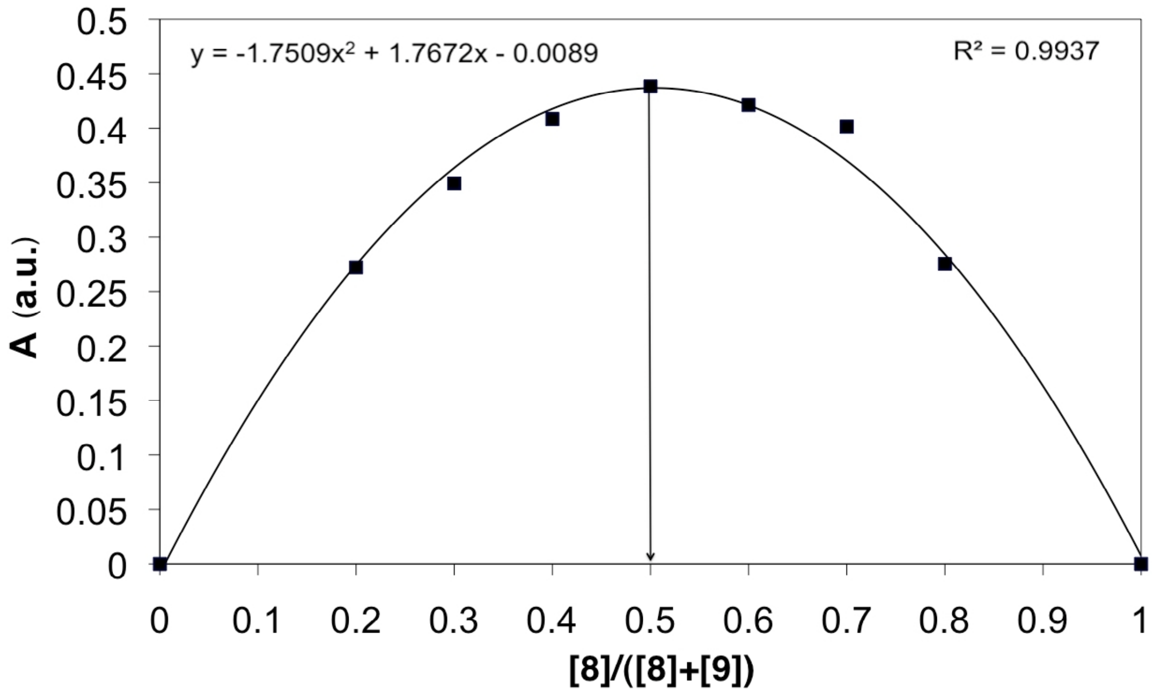
*Benzyl end-capped polymer **6**:*

Bis-hydroxy terminated polybutadiene (4.00 g, 2.0×10^{-3} mol) was dried under vacuum at 100 °C for 1 hour. After cooling to room temperature, a solution of diphenylmethane-4,4'-diisocyanate (MDI) (1.0 g, 4.0×10^{-3} mol) was added under an argon atmosphere and the stirred solution was heated under reflux. After three hours, a solution of benzylamine (0.45 g, 4.0×10^{-3} mol) and triethylamine (1.11g, 1.5mL, 1.1×10^{-2}) in THF (20 mL) was added dropwise and heating continued for an additional 3 hours. After cooling to room temperature, the solution was concentrated and the crude product precipitated from water (100 mL), filtered and washed with hot water (3×50 mL) to give a colourless gum (82%, 4.5 g). T_g = -32 °C; (GPC in DMF/LiBr) M_n = 8,500 g mol^{-1}, PDI = 1.4. ^{1}H NMR (400 MHz, $CDCl_3$), δ 7.34-7.23 (m), 7.17-7.15 (m), 7.10-7.08 (m), 6.52 (br), 6.30 (br), 5.9-5.7 (m) 5.59-5.41 (m), 5.37-5.33 (m), 4.95 (br), 4.43-4.42 (m) 4.15-4.13 (m), 3.87 (br), 3.76 (br), 2.02 (br), 1.40-1.38 (m), 1.25 (br);

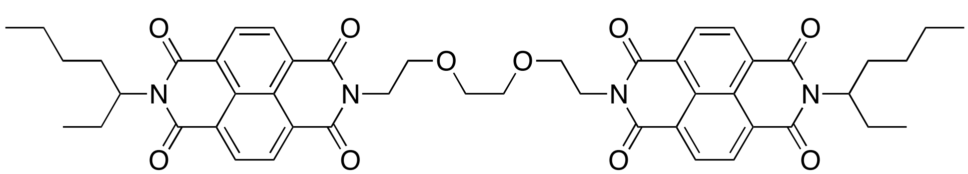
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 153.7, 143.3-143.1, 138.9, 136.0, 131.6, 131.2-127.3, 131.7-129.4, 121.7, 118.9 125.8, 115.1-111.8, 68.0, 64.8, 63.6, 44.2, 43.7, 41.7-38.5, 35.8-35.6, 34.2-33.5, 32.0, 30.2, 28.8, 27.5, 27.4, 25.6; IR ν_{max}(KBr)/cm^{-1} 3316, 3075, 2980, 2924, 2845, 1723, 1630, 1591, 1530, 1412, 1311, 1239, 911.

*End-group model compound **9**:*

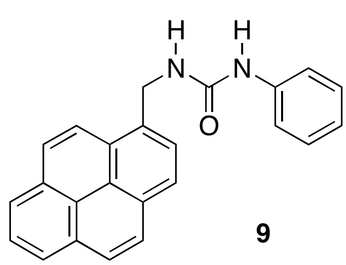
To a stirred solution of phenylisocyanate (0.333 g, 2.8 mmol, 0.304 mL) in dry THF (30 mL) a suspension of 1-pyrenemethylamine hydrochloride (0.670 g, 2.5 mmol) and triethylamine (1 mL) in dry THF (20 mL) was added dropwise. The white suspension was heated to reflux under argon for 18 h. After cooling to room temperature, the solvent was removed under reduced pressure, the crude product stirred in a mixture of chloroform and hexafluoropropan-2-ol (6:1 v/v, 50 mL) and the resulting solution filtered. After removal of the solvents, the resulting pale yellow solid was subjected to column chromatography ($CHCl_3$:MeOH (95:5 v/v) $R_f = 0.6$) to afford the target urea, **9**, as a pale yellow powder (46%, 0.404 g). M.P. 282 °C (dec.); ^1H NMR (400 MHz, d_6-DMSO) δ = 8.61 (s, 1H, Pyr-*H*), 8.50 (d, 1H, Pyr-*H*, *J* = 9.2 Hz), 8.37-8.31 (m, 4H, Pyr-*H* & 1H N-*H*), 8.21 (s, 2H, Pyr-*H*), 8.15-811 (m, 2H, Pyr-*H*), 7.47 (d, 2H, Ar-*H*, *J* = 7.7 Hz), 7.28 (t, 2H, Ar-*H*, *J* = 7.6 Hz), 6.95 (t, 1H, Ar-*H*, *J* = 7.4 Hz), 6.87 (t, CO-N*H*-CH_2, *J* = 5.7 Hz), 5.10 (d, NH-CH_2-Pyr, *J* = 5.7 Hz); ^{13}C NMR (100 MHz, d_6-DMSO) 155.1, 140.4, 133.7, 130.8, 130.3, 130.0, 128.6, 128.0, 127.6, 127.4, 127.0, 126.4, 126.2, 125.2, 125.1, 124.8, 124.0, 123.9, 123.1, 121.1, 117.7, 40.9; IR 3288, 3030, 2879, 2840, 1728, 1627, 1555, 1496, 1233, 1093. HRMS (ESI): found m/z = 351.1499 $[M+H]^+$; calc. for $C_{24}H_{19}N_2O$, 351.1498.



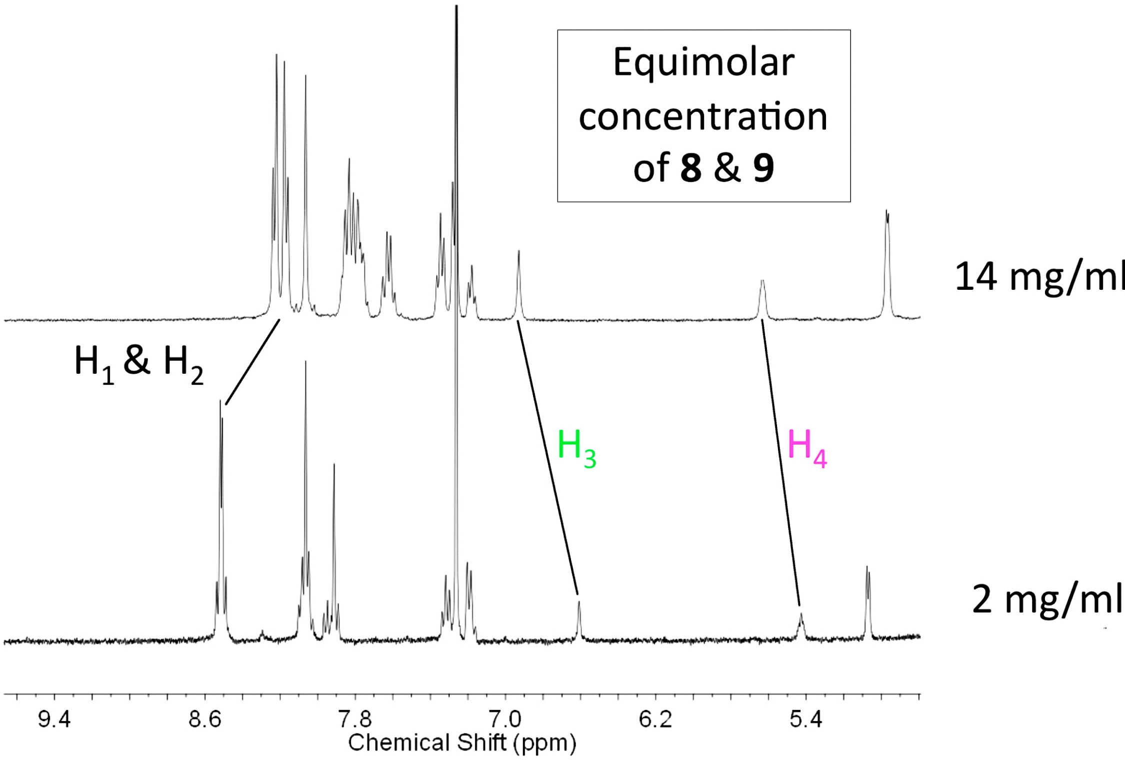
Job plot for complexation of model chain-fold **8** with model end-group **9** (structures shown below), based on absorption by the charge-transfer band at 530 nm in the UV-visible spectrum. Absorbance values for the complex were corrected for absorption by the parent diimide at this wavelength.

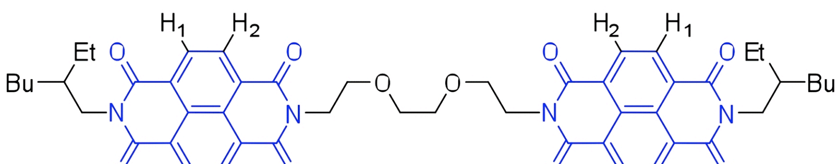


8

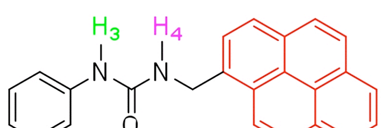


9



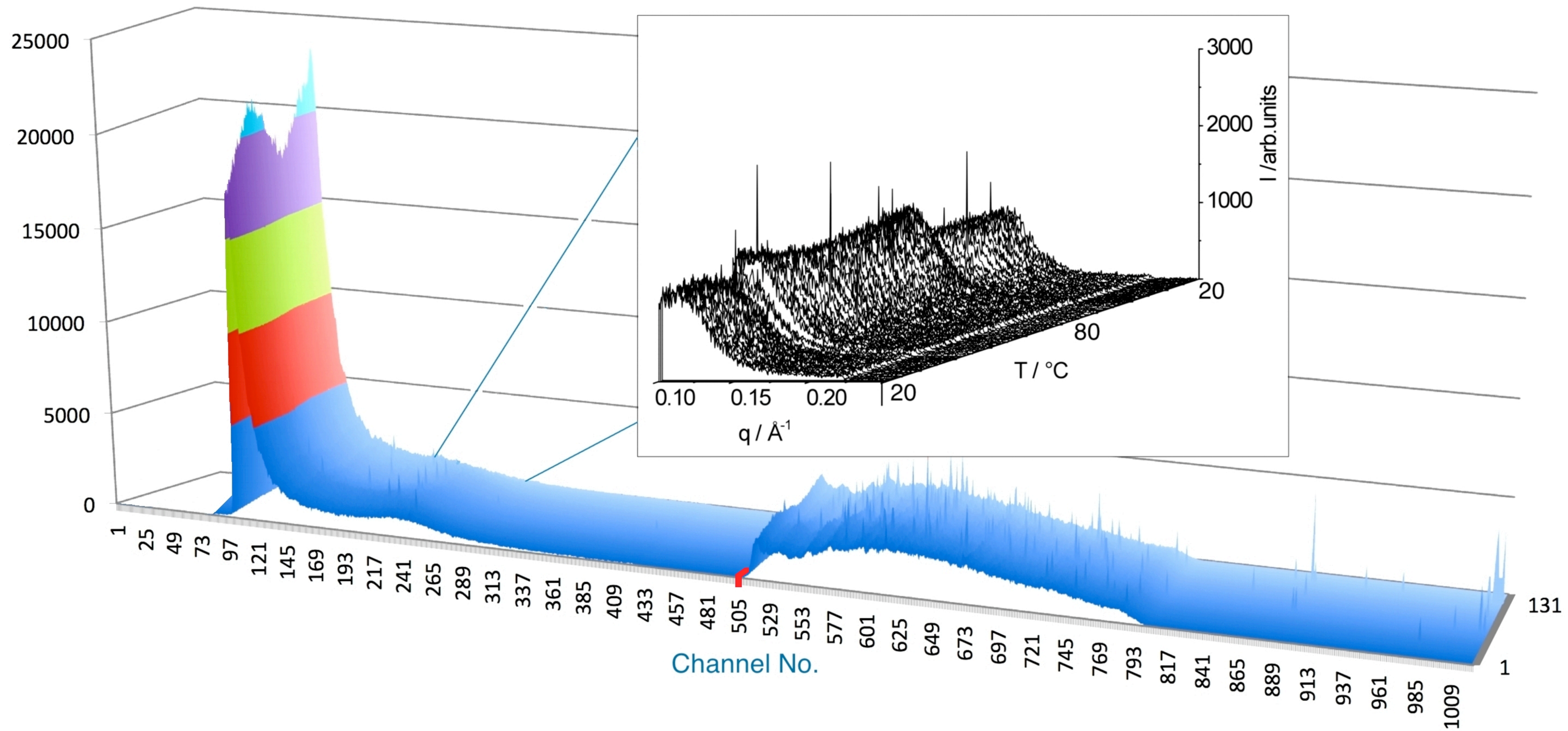


8

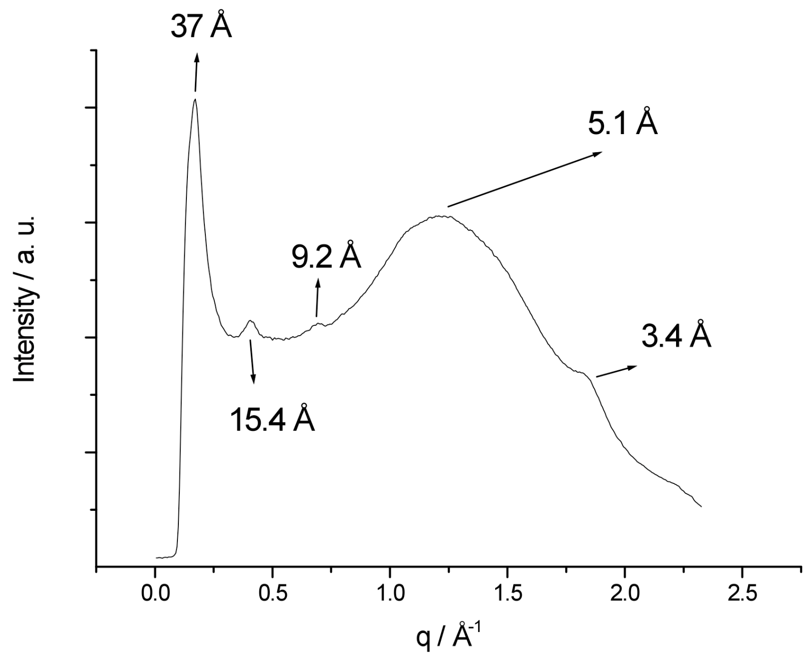


9

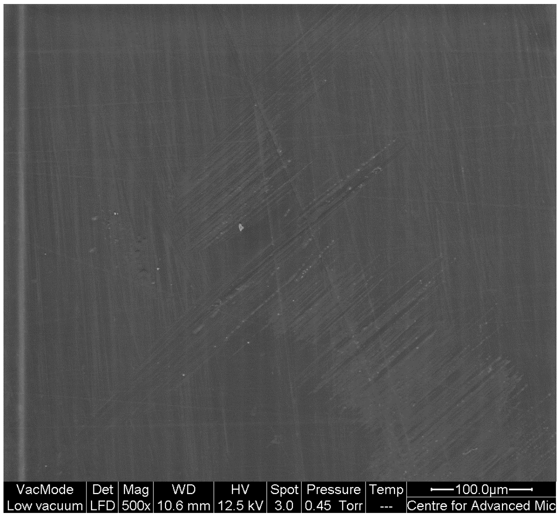
[1]H NMR spectra (400 MHz, $CDCl_3$/hexafluoropropan-2-ol) of equimolar mixtures of the model chain-fold **8** and model end-group **9**. The downfield shift of both NH protons in compound **9** as concentration increases confirms the presence of hydrogen bonding between these groups and compound **8**. Similarly, the upfield shift of the diimide proton resonances is consistent with the proposed complementary π-π stacking between **8** and **9**.



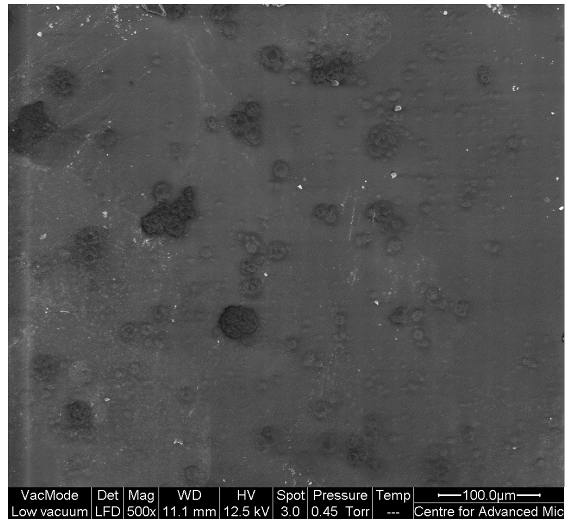
Variable temperature X-ray scattering (SAXS/WAXS) profile (raw data) of the supramolecular network [**1**+**2**] over the range -20 to +80 °C (two cycles). The mark at channel 505 indicates a break between SAXS and WAXS data. Inset shows an expansion of data in the SAXS range.



WAXS profile of the supramolecular network [**1**+**2**].

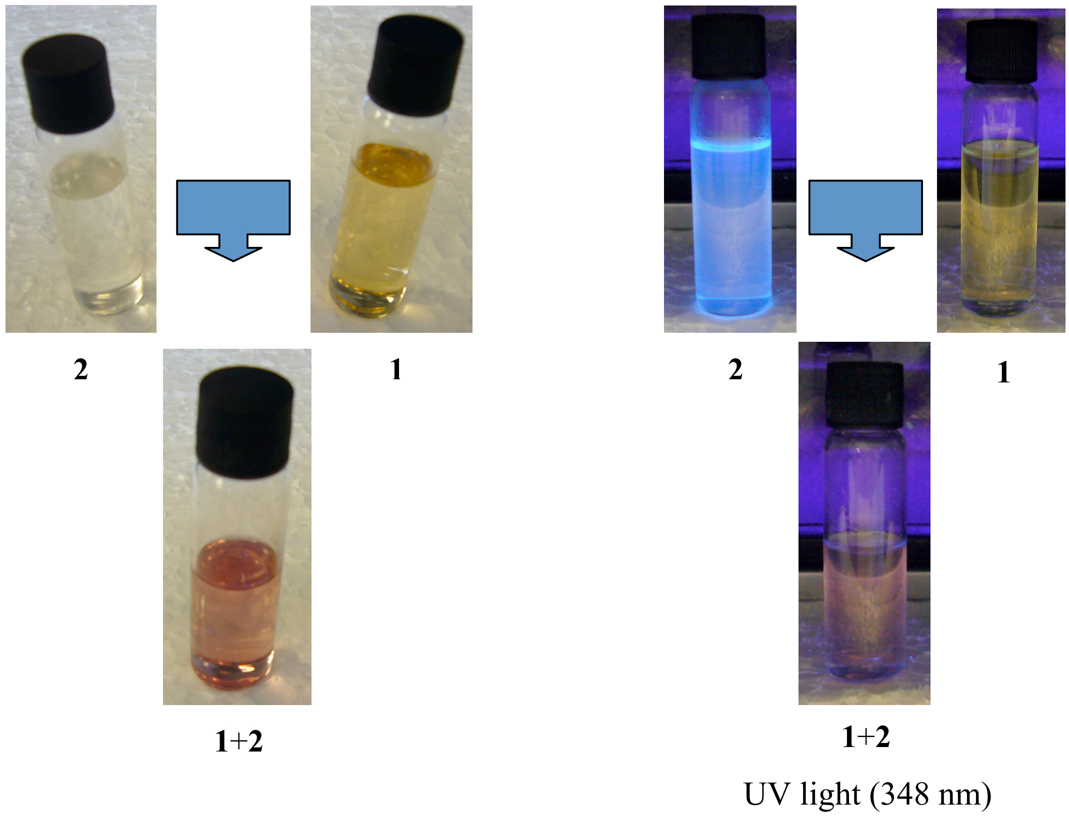


a



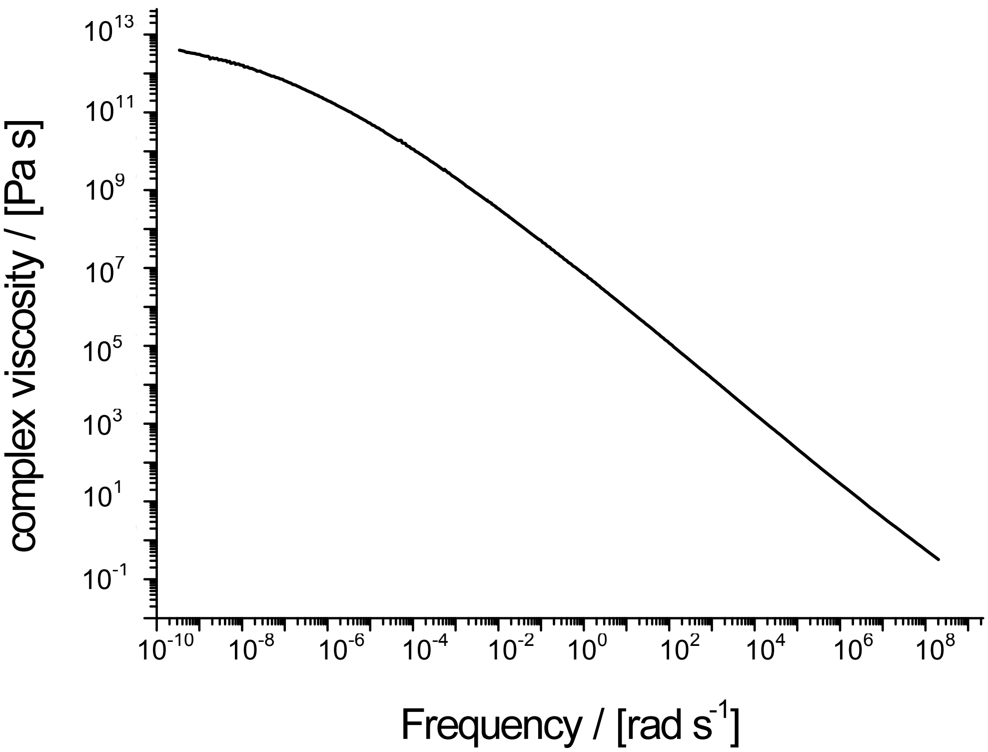
b

a) ESEM image of the network **[1+2]**; b) ESEM image of the blend **[1+6]**.
(Unprocessed micrographs)

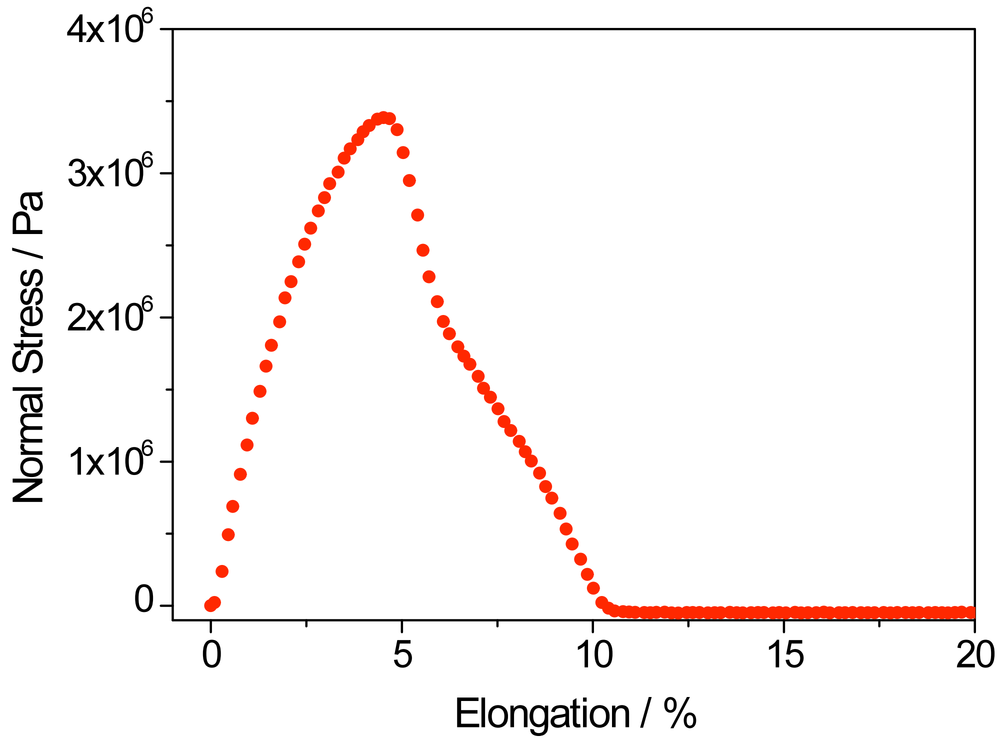


Photographs of the polyimide **1**, pyrenyl endcapped polyurethane **2**, and healing polymer blend [**1**+**2**] in solution in $CHCl_3$/hexafluoro-propan-2-ol (6:1, v/v) under visible light (at left) and under UV irradiation (at right).

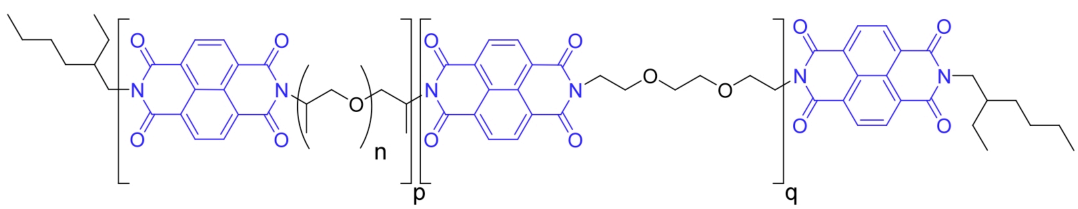
The polyimide/polyurethane blend [**1**+**2**]

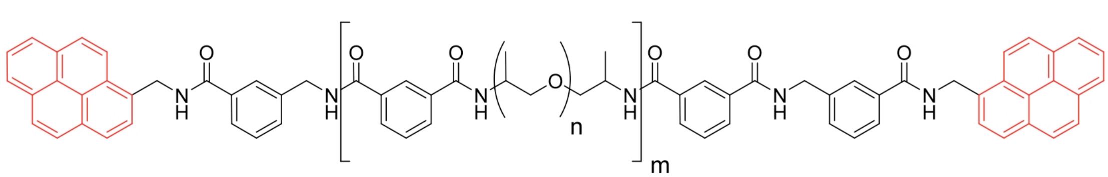


Plot of complex viscosity η* of the polyimide/polyurethane blend [**1**+**2**] vs frequency



Stress/strain plot for the supramolecular, π-stacking polymer blend reported in ref. 5a of the present paper (components shown below).





Atomic Cordinates for the model shown in Figure 7.

This file generated by CrystalMaker 8.0.3, (c) 1994-2008 CrystalMaker Software Limited

Total of 134 atoms in range

		Orthogonal Coordinates [A]		
Elmt	Label	xor	yor	zor
C	C2	-1.37720	-5.24864	-6.13931
C	C3	-3.35156	1.66653	-7.04475
C	C4	-3.35607	-2.26329	-4.99501
C	C5	-3.46582	0.86116	-5.72200
C	C6	-3.84143	-1.50495	-6.25317
C	C8	-1.66759	-3.75201	-5.92570
C	C10	0.14167	1.26754	-8.46487
C	C11	0.65765	0.01957	-11.98634
C	C12	1.48898	1.52171	-8.10881
C	C13	2.54028	1.26027	-9.00903
C	C14	-0.13254	0.76557	-9.76437
C	C15	2.28245	0.75362	-10.30443
C	C16	0.93467	0.51172	-10.68342
C	C17	-1.48043	0.52538	-10.14363
C	C18	-1.74063	0.04950	-11.45108
C	C19	-0.69160	-0.20242	-12.35309
C	C20	-0.94696	1.50481	-7.57939
C	C22	-2.51616	0.78720	-9.20591
C	C23	3.31691	0.49088	-11.24374
C	C25	1.74088	-0.21295	-12.87653
C	C30	5.33258	-6.34194	-10.28192
C	C31	3.77486	-7.01023	-11.94713
C	C32	-0.52783	-5.94566	-8.35120
C	C33	1.33604	-7.03731	-11.44461
C	C34	1.03283	-5.26523	-6.69217
C	C35	0.27551	-6.75754	-10.56201
C	C37	2.12776	-5.52892	-7.55807
C	C38	2.67989	-6.78902	-11.06805
C	C39	2.94234	-6.29562	-9.76182
C	C40	0.51918	-6.24008	-9.26599
C	C42	4.53236	-5.60704	-8.04376
C	C43	4.28655	-6.07752	-9.35695
C	C44	1.86418	-6.02165	-8.86318
C	C45	3.47188	-5.33551	-7.16147
C	C49	6.15932	-7.08234	-12.49915
C	C50	4.14115	-0.11029	-13.47202
C	C77	2.34893	-1.92088	-7.77761
C	C78	1.44033	-2.91776	-10.26245

C	C79	3.29703	-3.49233	-12.32707
C	C80	0.97726	-2.11365	-8.00072
C	C81	0.52290	-2.61601	-9.23240
C	C82	5.16387	-2.75981	-10.87978
C	C83	0.99521	-3.41339	-11.50406
C	C84	1.91441	-3.69885	-12.52798
C	C85	4.65530	-1.97704	-8.59916
C	C86	4.22008	-3.77925	-13.35070
C	C87	5.57466	-2.23394	-9.62772
C	C88	2.83093	-2.70755	-10.04871
C	C89	5.59259	-3.56595	-13.15067
C	C90	3.28198	-2.20543	-8.79800
C	C91	6.09051	-3.06556	-11.92484
C	C92	3.76807	-2.98814	-11.08337
C	C104	8.89180	-3.67363	-9.78868
N	C106	8.89184	-4.69232	-8.91693
C	C111	9.65524	-4.92652	-7.82221
C	C112	10.64527	-4.05965	-7.30179
C	C114	11.37180	-4.40672	-6.14745
C	C116	11.13232	-5.62945	-5.48245
C	C118	10.14586	-6.49757	-6.00121
C	C120	9.41914	-6.14790	-7.15377
C	C122	13.35530	-6.12458	-4.48728
C	C123	13.84018	-7.13841	-5.34877
C	C125	15.22167	-7.30481	-5.56027
C	C127	16.13999	-6.45711	-4.91449
C	C129	15.67409	-5.44223	-4.05862
C	C131	14.29117	-5.27826	-3.84708
H	H51	1.71162	1.90758	-7.18478
H	H52	3.50658	1.44347	-8.71399
H	H53	-2.70665	-0.11022	-11.75732
H	H54	-0.92305	-0.54554	-13.29219
H	H55	-3.23372	2.72767	-6.79417
H	H56	-4.33620	1.59091	-7.51971
H	H57	-2.48669	0.55859	-5.34388
H	H58	-3.89553	1.51028	-4.95808
H	H59	-4.63526	-2.09593	-6.71645
H	H60	-3.04806	-1.39214	-6.99704
H	H61	-2.56413	-1.70591	-4.49028
H	H62	-4.19795	-2.31125	-4.29878
H	H63	-1.68181	-3.26911	-6.90638
H	H64	-0.86764	-3.31691	-5.31703
H	H65	-1.16343	-5.70729	-5.16732
H	H66	-2.32135	-5.70223	-6.46298
H	H67	1.11912	-7.42820	-12.36966
H	H68	-0.68637	-6.93779	-10.87037
H	H69	5.49488	-5.45981	-7.72194
H	H70	3.68402	-4.99243	-6.21768

H	H71	6.03162	-6.49629	-13.41229
H	H72	7.15762	-6.86254	-12.11346
H	H73	6.14832	-8.14038	-12.77795
H	H74	4.62574	0.85257	-13.64755
H	H75	4.90043	-0.78466	-13.08221
H	H76	3.83770	-0.50097	-14.44815
H	H93	4.99993	-1.61263	-7.70624
H	H94	6.23238	-3.78899	-13.91907
H	H95	6.55596	-2.01923	-9.43963
C	H96	7.56874	-2.91596	-11.76444
H	H97	1.56324	-4.05371	-13.42433
H	H98	-0.00264	-3.56965	-11.67384
H	H99	-0.48266	-2.75253	-9.37299
H	H100	0.31086	-1.87945	-7.26208
H	H101	2.65702	-1.56016	-6.86927
H	H102	3.89934	-4.15127	-14.25066
H	H107	7.46505	-4.65591	-10.66959
H	H108	7.81379	-1.87651	-11.51832
H	H109	8.12039	-3.16542	-12.67685
H	H110	8.20422	-5.34386	-9.12045
H	H113	10.84784	-3.16754	-7.75013
H	H115	12.07833	-3.75839	-5.78999
C	H117	11.89310	-5.97429	-4.25264
H	H119	9.94834	-7.39006	-5.54227
H	H121	8.71002	-6.79791	-7.50570
H	H124	13.18489	-7.76281	-5.82563
H	H126	15.56066	-8.04293	-6.18368
H	H128	17.14470	-6.57786	-5.06589
H	H130	16.34095	-4.82555	-3.58774
H	H132	13.97636	-4.53787	-3.21597
H	H133	11.68581	-5.19401	-3.51688
H	H134	11.53121	-6.90890	-3.81450
N	N21	-2.25598	1.29025	-7.95036
N	N24	3.04296	0.04004	-12.51526
N	N36	-0.27312	-5.47613	-7.08268
N	N41	5.07846	-6.80039	-11.55477
N	N103	7.95928	-3.83101	-10.73721
O	O1	6.52100	-6.13769	-9.91964
O	O7	-2.94769	-3.61937	-5.26956
O	O9	-4.39474	-0.23422	-5.86609
O	O26	1.48646	-0.62286	-14.03875
O	O27	4.51325	0.69912	-10.90878
O	O28	-0.70202	1.93581	-6.42427
O	O29	-3.70515	0.55892	-9.54894
O	O46	1.24909	-4.86224	-5.51953
O	O47	-1.71850	-6.14114	-8.70861
O	O48	3.53764	-7.38944	-13.12310
O	O105	9.63492	-2.67123	-9.74307