A self-repairing, supramolecular polymer system: healability as a consequence of donor–acceptor π–π stacking interactions†

Stefano Burattini,[a] Howard M. Colquhoun,*[a] Justin D. Fox,[b] Donia Friedmann,[c] Barnaby W. Greenland,[a] Peter J. F. Harris,[a] Wayne Hayes,[a] Michael E. Mackay[c] and Stuart J. Rowan[b]

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A novel supramolecular polymer system, in which the terminal pyrenyl groups of a polyamide intercalate into the chain-folds of a polyimide *via* electronically-complementary π–π stacking, shows both enhanced mechanical properties relative to those of its individual components and facile healing characteristics as a result of the thermoreversibility of non-covalent interactions.

The development of new materials with stimuli-responsive physical properties is a rapidly expanding area of research.[1] Notable recent developments in this field include self-healing polymers[2] which, when fractured, can regain the physical properties of the original polymer either autonomically,[3] or in response to an external stimulus such as heat[4] or pressure.[5] Healable polymeric systems may for example contain encapsulated monomers and polymerisation catalysts,[3,6] or latent functionalities which are able to participate in thermally-reversible, covalent bond-forming reactions.[4,7] It has also been shown that non-covalent interactions, specifically hydrogen bonds,[8] may be used to effect healing within a supramolecular polymer blend (albeit in the presence of a plasticising solvent).[5] In the latter system, it is proposed that fracture propagates *via* dissociation of the weak supramolecular interactions rather than by scission of covalent bonds, so that re-assembly of the supramolecular network restores the original physical properties of the material.

A number of recent reports describe chain-folding copolymers containing π-electron-deficient diimide units in the backbone.[9] Spectroscopic and crystallographic analyses of these polyimides and related model-compounds have shown that they can adopt chain-folded conformations on interacting with π-electron-rich aromatic molecules, the folded conformations maximising the number of complementary π–π stacking interactions.[10] We have also designed a novel receptor motif comprising two naphthalene-diimide units linked by a triethylenedioxy residue:[11] a model compound containing this motif was found to complex to a pyrene derivative in a 1 : 1 molar ratio, with a binding constant of 130 M^{-1}. Blending a polyimide based on this motif with a pyrene end-capped polysiloxane afforded a visually-healable though extremely fragile material.[12]

Here we report the realisation of a new, mechanically robust, re-healable polymer system, based on complexation of a chain-folding copolyimide **1** (tan powder, M_n = 16 000, M_w = 27 000; T_g = 190 °C) with the pyrenyl end-capped polyamide **2** (pale yellow oil, M_n = 6000, M_w = 10 000, T_g = −7 °C). Both components (Fig. 1) were synthesised in one-pot procedures from commercially available starting materials (see ESI†). Polymers **3** and **4** were also synthesised as control materials, each lacking just one of the key design-elements needed to form a supramolecular network based on the intercalation of the pyrenyl end-groups of polyamide **2** into the chain-folds of polyimide **1** (Fig. 2).

Initial evidence for polyimide–pyrene complexation came from ^{1}H NMR spectra (in $CDCl_3$–trifluoroacetic acid; 9 : 1 v/v) of solutions containing **1** and end-group model compound **5**,[11] which showed substantial upfield shifts of the diimide resonances ($\Delta\delta$ up to 0.6 ppm) as a result of magnetic ring-current shielding by the intercalating pyrenyl residues.† More graphically, mixing a pale yellow solution of polyimide **1** with a colourless solution of polyamide **2** produced an immediate deep red colour arising from a new absorption band at 521 nm, indicative of complementary π–π stacking and charge-transfer between the pyrenyl end-groups of one component and the diimide residues of the other. Heating the solution to *ca.* 60 °C resulted in a very obvious fading of the deep red colour, but the intensity of colour was restored on cooling to room temperature,† clearly demonstrating the thermal reversibility of inter-polymer π–π stacking in this system.

The existence of strong inter-chain interactions between these polymers in solution was also demonstrated by viscometric studies. Independently, **1** and **2** showed identical inherent viscosities in 1,1,1-trichloroethanol (η_{inh} = 0.13 dL g^{-1}), but a 1 : 3 w/w blend of the two components (equimolar in chain-folding diimide units and pyrenyl end-groups) at the same overall concentration displayed a threefold enhancement of inherent viscosity (η_{inh} = 0.40 dL g^{-1}). Conversely, a control experiment using polyimide **1** and the *benzyl* end-capped polyamide **4** showed no increase in solution viscosity relative to the individual components. Proof that polyimide chain-folding is essential to achieving strong inter-polymer interactions came from the ^{1}H NMR spectrum

[a] *Department of Chemistry, University of Reading, Whiteknights, Reading, UK RG6 6AD. E-mail: h.m.colquhoun@rdg.ac.uk; Fax: +44 (0)118 378 6717; Tel: +44 (0)118 378 6717*
[b] *Department of Macromolecular Science and Engineering, 2100 Adelbert Road, Kent Hale Smith Building, Cleveland, OH 44106, USA*
[c] *Department of Materials Science and Engineering, University of Delaware, Newark, DE 19716, USA*

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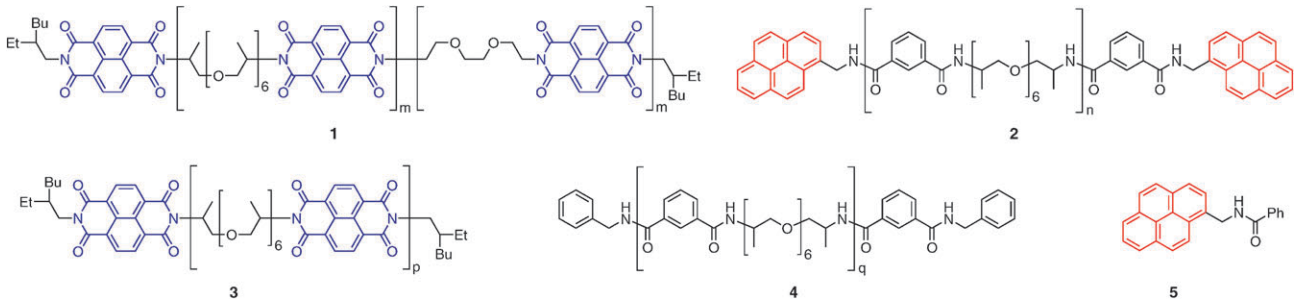

Fig. 1 Polyimides and polyamides developed in this work.† Components **1** and **2** afford a π−π-stacked supramolecular polymer, while **3** and **4** are "control" materials lacking either, in **3**, the chain-folding triethylenedioxy–diimide motif or, in **4**, the terminal pyrenyl residues.

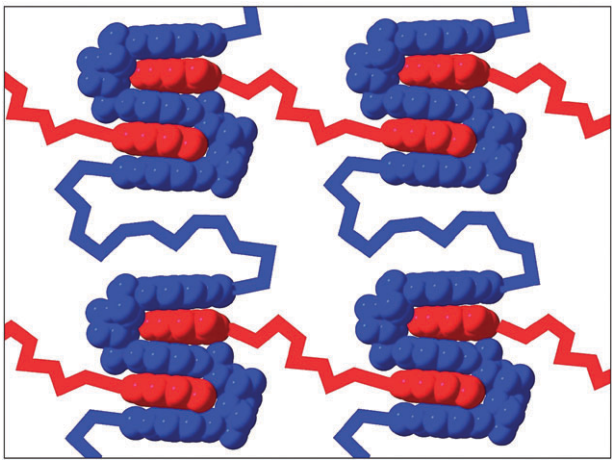

Fig. 2 Schematic showing the potential for non-covalent cross-linking of polyimide chains by multiple intercalation of π-electron-rich pyrenyl end-groups (red) into designed polyimide chain-folds (blue).

of a second control material,† comprising a blend of model-amide **5** and polyimide **3**. The latter lacks the chain-folding triethylenedioxy–diimide motif present in **1**, but retains the diimide units in the chain. This polymer system showed only minimal complexation shifts ($\Delta\delta_{obs} \leq 0.1$ ppm).†

Solution-cast films of the 1 : 3 w/w blend of **1** and **2** retained the deep red colour observed in solution and, most importantly, the films were flexible and self-supporting.† In contrast, control films cast from either of the two components separately, or from a mixture of benzyl end-capped polyamide **4** and chain-folding polyimide **1**, showed no mechanical strength whatsoever. Similarly, films of the blend [**1** + **2**] appeared homogeneous by both transmission light microscopy and environmental scanning electron microscopy (ESEM),† whereas a control film containing polyimide **1** and the benzyl-terminated polyamide **4** was heterogeneous by ESEM,† with large-scale phase separation of the two components. It seems clear that complexation between the pyrenyl end-groups of **2** and the chain-folded binding segments of polyimide **1** is essential to drive compatibilisation of these materials.

Rheometric analysis of the 1 : 3 w/w blend of **1** and **2** revealed a tensile modulus of *ca.* 1 MPa at 30 °C. A very sharp drop-off in modulus and melt-viscosity above *ca.* 40 °C was indicated by the change in rheometric shift factor, a_T, which falls by five orders of magnitude between 35 and 60 °C (Fig. 3).

In contrast, polystyrene shows a fall-off of only one order of magnitude in a_T, over the corresponding temperature range relative to T_g.[13] This result strongly suggested that the new material should show a markedly enhanced ability to flow and re-heal when compared to conventional thermoplastics. Indeed, it was found that a broken film of [**1** + **2**] could be re-healed by simply pressing the broken ends gently together (*cf.* ref. 5) and heating briefly at 80 °C. The recovered tensile modulus was identical to the original value, and this cycle of test–break–heal–test was repeated three times on a single film, each time with complete recovery of the original modulus.† At 80 °C the healing process was too rapid (a few seconds) to follow as a function of time. At 50 °C however, the rate of repair was slow enough to be monitored. Here, 100% recovery of tensile modulus was achieved after *ca.* 5 minutes (Fig. 4), even though the material retained significant mechanical strength (tensile modulus $> 10^4$ Pa) at this temperature.

A visual demonstration of the healing characteristics of [**1** + **2**] is given in Fig. 5. A damaged film-sample (with a 75 μm wide cut) was heated at 5 °C min^{-1} in an environmental scanning electron microscope (ESEM). As the temperature reached *ca.* 80 °C the material surrounding the cut was clearly seen to flow into the void and, at 90 °C, the film became essentially homogenous, with the position of the cut being

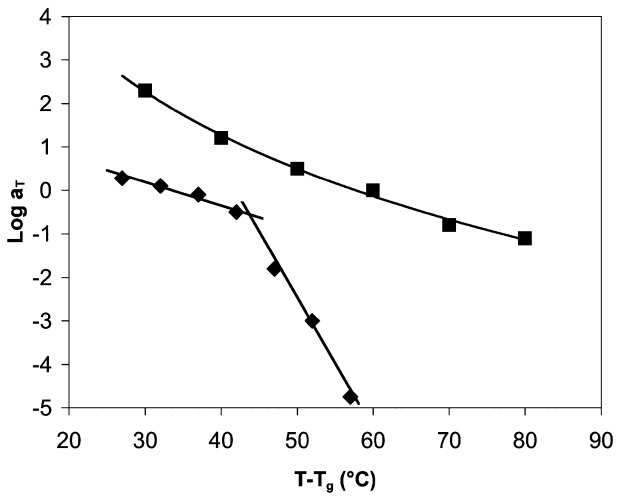

Fig. 3 Variation of rheometric shift factor, a_T (a function of melt-viscosity), with temperature, relative to T_g, for the supramolecular polymer system [**1** + **2**] (◆) and for polystyrene (■).

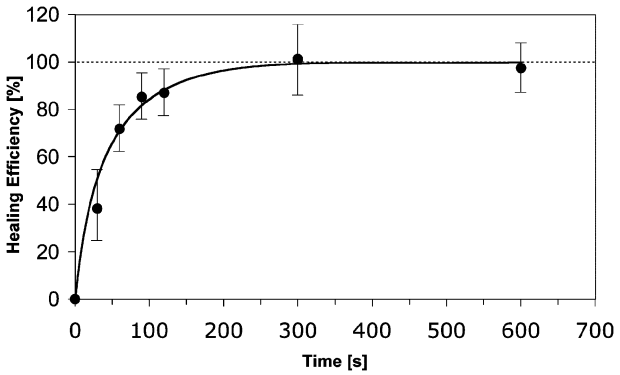

Fig. 4 Recovery of tensile modulus as a function of healing time for samples of [**1** + **2**]. Error bars represent the standard deviation from the mean of multiple measurements.

scarcely visible. In contrast, ESEM analysis of a damaged film of the phase-separated material cast from a solution of **1** and **4** showed that the sample remained inhomogeneous up to 100 °C. Spontaneous healing did not occur; indeed, the width of the break increased as the experiment progressed (Fig. 5).

In conclusion, we have shown unambiguously that self-repairing materials which exploit non-covalent cross-linking of polymer chains can be generated through π–π stacking interactions involving the intercalation of pyrenyl end-groups into polyimide chain-folds. At ambient temperatures such interactions generate a *pseudo*-high-molecular-weight network which transforms the two components from a viscous oil and non-coherent powder into a dimensionally stable, flexible and self-supporting material. As the temperature is increased, reversible dissociation of the supramolecular cross-links occurs, drastically lowering the melt-viscosity and allowing the polymer system to heal the damaged areas. Control experiments indicate that the mechanical strength, homogeneity and healability of the system are driven almost entirely by π–π stacking interactions between the two electronically-complementary components of the blend.

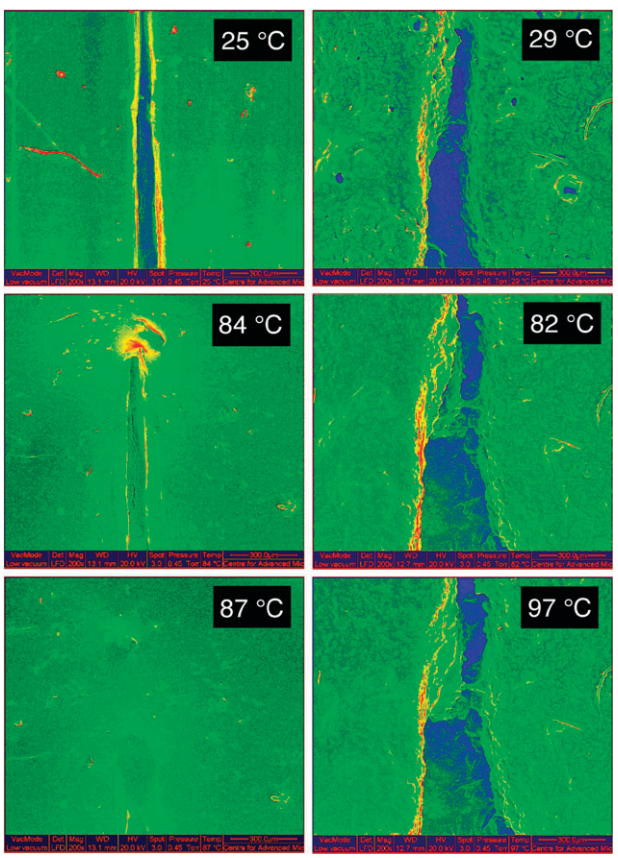

Fig. 5 False-colour ESEM images (×200) demonstrating the homogeneity and healing characteristics of the supramolecular polymer system [**1** + **2**] (left hand column), and the absence of such characteristics for the phase-separated control material [**1** + **4**] (right hand column). The heating rate was 5 °C min^{-1}.

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