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A Supramolecular Polymer Based on Tweezer-Type $\pi-\pi$ Stacking Interactions: Molecular Design for Healability and Enhanced Toughness

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Polymeric materials that can recover their mechanical properties after damage are an increasingly active area of research.[1] Such materials can be categorized as undergoing either autonomic healing,[2] where regeneration of the physical properties occurs without external intervention, or induced healing, whereby they regain their original physical properties in response to an external stimulus such as heat,[3] or light.[4] Most healable materials reported to date require the formation of new covalent bonds within the damage zone to achieve healing,[5] although more recent work has demonstrated that certain supramolecular materials can also show healable behavior after fracture, either autonomically[6] or at elevated temperatures,[7] through regeneration of noncovalent bonding interactions.

In supramolecular polymer systems, it is proposed that fractures propagate predominantly by disengagement of the supramolecular interactions between the individual oligomeric components of the material, rather than by scission of covalent bonds.[1a] Only a relatively small input of energy is then needed for molecular motion to allow reassembly of the supramolecular network and enable the mechanical strength of a damaged material to be recovered, ideally at the level of the pristine, undamaged material.

Recent developments in supramolecular polymer chemistry have depended mainly on the exploitation of multiple hydrogen bonded motifs,[8] but complementary aromatic $\pi-\pi$ stacking[9] has also emerged as an important interaction in this field,[7a−c] based largely on polymers containing π-electron deficient aromatic diimide residues in the backbone.[10] Spectroscopic analyses of high molecular weight systems,[11] and crystallographic studies on small molecule analogues of these polymers,[12] have established that addition of π-electron-rich molecules such as pyrene and its derivatives can afford supramolecular complexes that adopt chain-folded secondary structures in order to maximize the number of complementary (donor−acceptor) $\pi-\pi$ stacking interactions.

A readily accessible, chain folding receptor-motif for pyrene derivatives has been described from both computational and experimental standpoints.[7,13] The chain-segment involved comprises two naphthalene-diimide units separated by a simple triethyleneoxy residue (Figure 1A). Binding studies in solution, via UV−visible spectroscopy, revealed an association constant (K_a) of 130 ± 20 M^{-1} for complex **A**.[13] In that work, increasing the number of face-to-face $\pi-\pi$ stacking interactions from two to three to four (Figure 1, complexes **A**−**C**, respectively) resulted in a progressive increase in binding constant of almost 2 orders of magnitude.[13]

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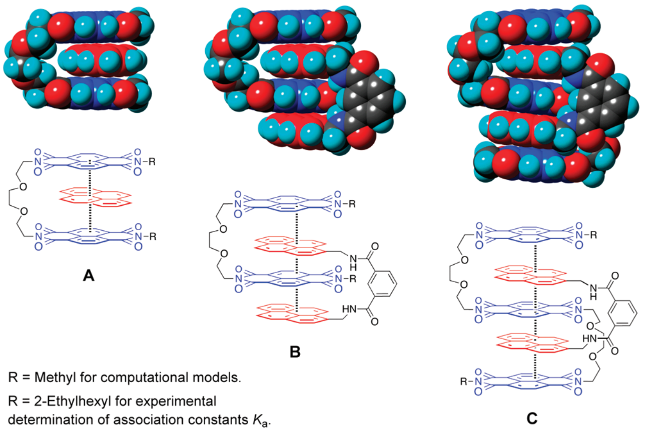


Figure 1. Energy-minimized models (molecular mechanics with charge-equilibration) for complexes formed between pyrene or a tweezer-type derivative (red) and naphthalene diimide oligomers (blue) containing two, three, or four face-to-face $\pi-\pi$ stacking interactions. Experimentally determined association constants, K_a, are 130, 3.50×10^3, and 11.0×10^3 M^{-1} for complexes A, B, and C, respectively.[13]

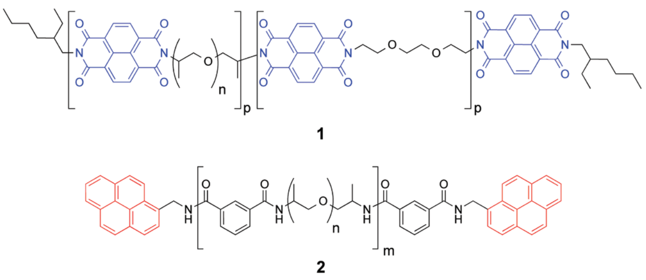


Figure 2. Components of the healable polymer blend [**1**+**2**].

This novel supramolecular motif has been harnessed to produce healable materials from a complementary, two-component polymer blend (see Figure 2).[7a−c] In those studies, $\pi-\pi$ stacking interactions occurred between a low-MW polymer containing a pyrenyl residue at each chain-end (**2**, $M_n \approx 6.0$ kDa) and chain-folded pairs of diimide residues in the mainchain of a second polymer (for example, **1**, $M_n \approx 16.0$ kDa).[7b] The material comprising a 1:3 w/w blend of **1** and **2** (corresponding to a near-equimolar ratio of pyrenyl units and diimide pairs) exhibited a tensile modulus of ca. 1 MPa, and elongation to break of ca. 20%. After breaking this material, the tensile modulus was essentially completely restored after heating for 5 min at 50 °C. This high healing efficiency was retained over multiple break and heal cycles.

Here we report the synthesis of a new type of polymer (**3**, Scheme 1) that has a polyamide backbone identical to that of **2**, but differs in that it possesses tweezer-type[11,14] bis-pyrenyl end groups. Earlier investigations of complementary, chain-folding small molecules (Figure 1) suggested that end groups of this type would interact much more strongly than simple pyrenyl units with the chain-folding polyimide **1**.[13] Direct comparison of the properties of the new blend, [**1** + **3**], to those of the previously studied system [**1**+**2**][7b] enables the effects of supramolecular interactions involving chain-ends to be evaluated in terms of the mechanical properties and healing efficiency of the system.

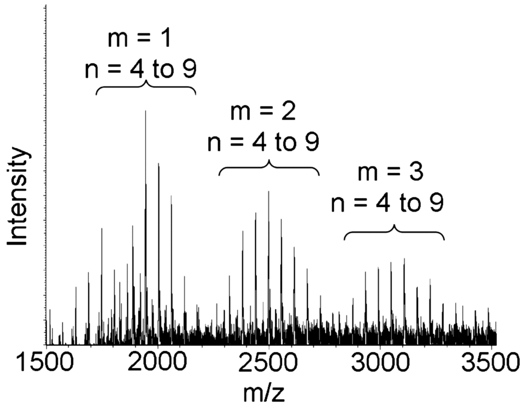
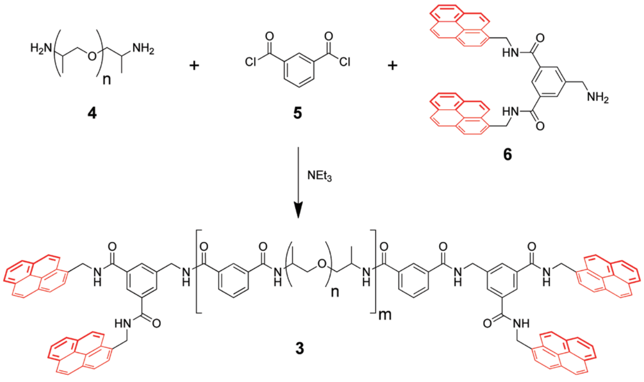


Figure 3. MALDI-ToF mass spectrum of tweezer-end-capped polymer **3**. The increasing dispersity of peaks for each value of “m” (Scheme 1) reflects the number of (polydisperse) Jeffamine 400 units per chain.

Scheme 1. Synthesis of Bis-tweezer-end-capped Polyamide 3



As shown in Scheme 1, the synthesis of polyamine **3** involved reaction of Jeffamine 400 (**4**) with isophthaloyl dichloride in the presence of ca. 20 mol % (relative to **4**) of the aminomethyl-substituted tweezer-molecue **6**,[15] to end-cap the chains and control the degree of polymerization. The resulting polymer had an M_n of 4.9 kDa and a PDI of 2.7, as measured by GPC using PMMA standards.

The MALDI-ToF mass spectrum of **3** exhibited well-resolved signals consistent with the production of bis-end-capped chains (rather than the monoend-capped material) containing up to three Jeffamine 400 segments (≈ 3000 g mol^{-1}: see Figure 3). The discrepancy between molecular weight data from GPC and MS results from the established mass-sensitivity of the MALDI-ToF technique, where relative intensities fall off rapidly with increasing molecular weight.

Polymers **1** and **3** were fully soluble in 1,1,1-trichloroethanol, each producing yellow solutions. However, a blend of the two solutions (one to three weight ratio of the two polymers respectively) produced an immediate color change to yield a deep red solution (see the Supporting

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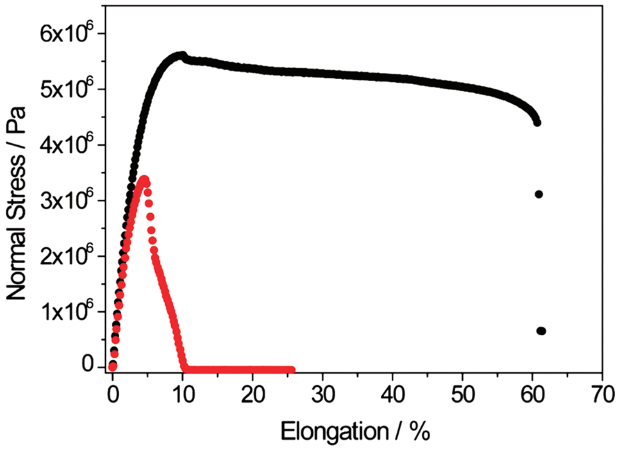

Figure 4. Stress−strain curves for the novel supramolecular material [**1**+**3**] (black) and for blend [**1** + **2**] (red). Initial slope gives the tensile modulus and the area under the curve gives the modulus of toughness.

Table 1. Tensile Measurements for Blends [1+**3] and [1**+**2]**[a]

blend	tensile modulus (MPa)	ultimate tensile strength (MPa)	modulus of toughness (MPa)	elongation to break (%)
[**1**+**3**]	1.8 (0.4)	6.7 (1.2)	299 (28)	53 (7)
[**1**+**2**]	1.2 (0.2)	2.7 (0.7)	14.1 (4.7)	9.3 (1.5)

[a] Values are the average of 3 repeats, with standard deviations shown in parentheses.

Information). This color is the result of a charge-transfer band centered on 526 nm, which is indicative of complex formation[16] and may be compared to that observed at 539 nm during our studies on model systems[13] (Figure 1, structure **C**). An elastomeric film was cast from the novel blend [**1**+**3**] (1:3 w/w ratio, corresponding to 0.8:1 mol ratio of the chain-folding motif ["p"] in **1** to tweezer end-groups in **3**), and this also displayed a dark red color, confirming that the complementary $\pi-\pi$-stacked complexation between the π-electron-rich "tweezer" end-groups and π-electron poor naphthalene diimide systems is retained in the solid state.

The results of tensile tests on blend [**1**+**3**] are shown in Figure 4 and Table 1, together with results for the same tests conducted with the previously reported material [**1**+**2**], which is very closely related to [**1**+**3**] but contains only a single pyrenyl residue at either end of the polyamide.

Blends [**1**+**2**] and [**1**+**3**] (both at 1:3 w/w ratio) show similar tensile moduli (ca. 1.5 MPa). However, [**1**+**3**], containing tweezer-type end-groups, exhibits a far higher elongation to break and an increased ultimate tensile strength when compared to [**1**+**2**] with only simple pyrenyl end groups. The modulus of toughness, which defines the energy needed to break the material, is calculated from the area under the stress−strain curve and this increases by an order of magnitude as a result of the increased association constant between the two components of the blend.

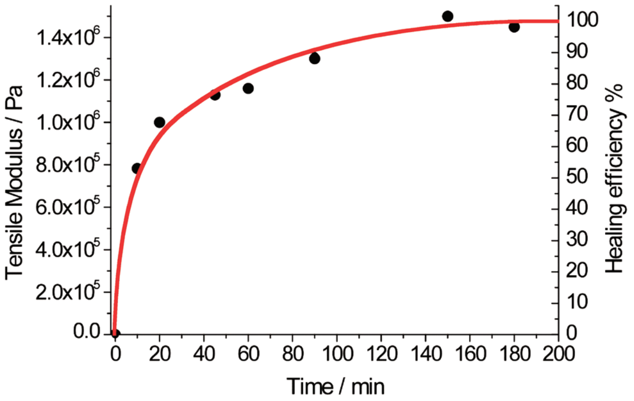

Figure 5. Recovery of tensile modulus as a function of healing time at 140 °C for samples of [**1**+**3**].

To evaluate the healing ability of the polymer blend, fractured samples of [**1**+**3**] were placed with their broken edges overlapped and heated at 140 °C for varying periods of time. The tensile strength of the sample was then remeasured. The curve in Figure 5 shows that the material regains essentially 100% of its original tensile modulus after ca. 160 min healing time.

In conclusion, a new polyamide with tweezer-type dipyrenyl end-groups (**3**) has been successfully synthesized. A blend of this polymer with the chain folding polydiimide **1** affords a novel supramolecular, $\pi-\pi$-stacked network both in solution and in the solid state. The new material, [**1**+**3**], differs from a related but mechanically much weaker blend[7b] ([**1**+**2**]) solely in the strength of specified supramolecular interactions between the components, rather than in the chain-structures of the polymers themselves. Blend [**1**+**3**] thus exhibits an enhanced ultimate tensile strength and greatly increased modulus of toughness and elongation to break compared to the previous system [**1**+**2**]. Time-dependent healing studies have shown that [**1**+**3**] regains essentially 100% of its original tensile modulus after 160 min healing time at 140 °C. As observed with some supramolecular hydrogen-bonded materials,[17] changing the strength of the supramolecular interactions has little impact on the initial tensile modulus, but it produces a marked change in the thermal response of the material: the new generation material ([**1**+**3**] requires substantially longer healing times at elevated temperatures compared to the previously studied supramolecular blend [**1**+**2**].

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Supporting Information Available: General experimental details; synthesis and characterization of polymer **3**; details of tensile testing and healing experiments; UV/vis spectra for polymers **1**, **3**, and the solution blend of [**1**+**3**]; expanded MALDI-ToF spectrum of polymer **3** (PDF)This material is available free of charge via the Internet at http://pubs.acs.org.

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