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A Healable Supramolecular Polymer Blend Based on Aromatic $\pi-\pi$ Stacking and Hydrogen-Bonding Interactions

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Abstract: An elastomeric, healable, supramolecular polymer blend comprising a chain-folding polyimide and a telechelic polyurethane with pyrenyl end groups is compatibilized by aromatic $\pi-\pi$ stacking between the π-electron-deficient diimide groups and the π-electron-rich pyrenyl units. This interpolymer interaction is the key to forming a tough, healable, elastomeric material. Variable-temperature FTIR analysis of the bulk material also conclusively demonstrates the presence of hydrogen bonding, which complements the $\pi-\pi$ stacking interactions. Variable-temperature SAXS analysis shows that the healable polymeric blend has a nanophase-separated morphology and that the X-ray contrast between the two types of domain *increases* with increasing temperature, a feature that is repeatable over several heating and cooling cycles. A fractured sample of this material reproducibly regains more than 95% of the tensile modulus, 91% of the elongation to break, and 77% of the modulus of toughness of the pristine material.

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1. Introduction

Self-assembled polymeric materials have been developed and studied intensively over the past decade.[1] Such materials typically comprise low- to medium-molecular-weight species capable of strong, directed, supramolecular interactions[2] that impart physical properties, such as high solution viscosity and tensile strength, that are more traditionally associated with covalently bonded, high-molecular-weight polymers.[3] Self-assembled polymers are typically stimuli-responsive,[4] and the strength of the supramolecular interactions between the constitu-

ent monomers in the system can often be precisely controlled by application of a suitable external stimulus such as heat[5] or light.[6] This may in turn enable a specific physical property of the polymer, such as its tensile strength, to be modulated rapidly. Upon removal of the external stimulus, the properties of the material can return to those it possessed in its original state. This "switchable" behavior of supramolecular polymers has been demonstrated in applications as diverse as adhesives, coatings, and most recently, healable materials.[7]

The large and still-growing range of areas in which supramolecular materials may find application is driven by the wide range of molecular components from which they may be constructed. In recent years, supramolecular polymers that exploit hydrogen bonding,[2,4,8] nucleobase stacking,[3b] metal−ligand interactions,[2,9] and hydrophobic effects,[10] among others, have

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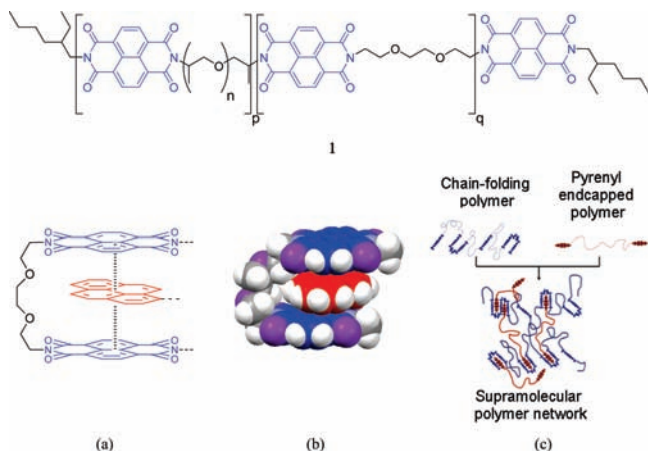
Figure 1. Top: Structure of chain-folding polyimide **1**. The average value of *n* is 6 and those of *p* and *q* are ~7. Bottom: (a) Proposed structure and (b) energy-minimized model of the electronically complementary $\pi-\pi$ stacking interaction between a bis(diimide) chain fold in polyimide **1** (represented by segment *q*) and a pyrenyl residue. (c) Schematic of a supramolecular network formed between polyimide **1** and a bis(pyrenyl) end-capped polymer.

Scheme 1. Synthesis of Pyrenemethyl End-Capped Hydrogen-Bonding Polymer **2** and Benzyl End-Capped Polymer **6**

been synthesized. The diverse nature of these supramolecular motifs offers an immense scope for tailoring the physical, chemical, and stimuli-responsive nature of the materials produced.

We recently introduced electronically complementary aromatic $\pi-\pi$ stacking as a noncovalent binding motif through which supramolecular polymers can be synthesized. Specifically, we reported a π-electron-deficient bis(diimide) motif that is capable of encapsulating π-electron-rich species such as pyrene and its derivatives through induced chain folding of a polyimide (Figure 1).[11] By positioning pyrenyl residues at the chain ends of a low-molecular-weight polyamide ($M_n < 6000$ g mol^{-1}) and blending the resulting telechelic material with a polyimide component ($M_n \approx 16\,000$ g mol^{-1}) containing a series of designed chain-folding residues within its backbone, we were able to generate novel, highly thermoresponsive supramolecular blends.[5,12] Tailoring the composition of the blend enabled us to produce a supramolecular material capable of very rapid healing at temperatures above 50 °C, with a healing efficiency, in terms of tensile modulus, of 100%.[5]

In other work, we reported a simple hydrogen-bonding (urea/ urethane-based) motif that can be appended to hydroxy- or amine-terminated oligomers.[13] The robust, one-pot, two-step synthesis involves addition of diphenylmethane-4,4′-diisocyanate (MDI) to the telechelic oligomer, with the resulting isocyanate-terminated prepolymer being subsequently end-capped by an amine or alcohol to give a polymer with a final $M_n \approx 17\,000$ g mol^{-1} having terminal residues capable of intermolecular hydrogen bonding.

The resulting supramolecular elastomers show interesting rheological properties, including a dramatic reduction in storage modulus above a critical temperature.[13] The temperature at
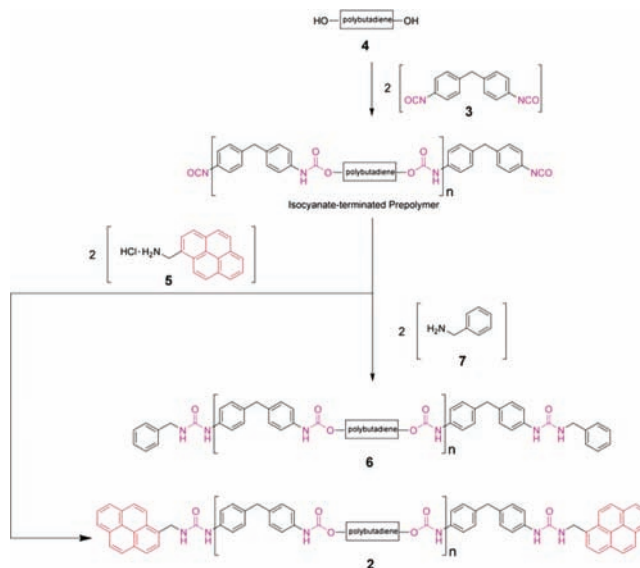
which this occurs can be predictively tuned by varying the chemical structure of either the oligomeric core component or the hydrogen-bonding end group added in the second step of the reaction.

In the present work, we investigated whether it is possible to combine the two supramolecular bonding modes of (i) electronically complementary $\pi-\pi$ stacking and (ii) interpolymer hydrogen bonding into a hybrid polymer system in which the structural integrity of the bulk supramolecular blend is maintained by a designed *combination* of these interactions. On the basis of previous studies, we envisaged that such a system might also afford a high degree of thermal healability, and this has indeed been demonstrated.

2. Results and Discussion

Synthesis and Characterization. The synthesis of pyrenyl end-capped polymer **2** was achieved using a one-pot, two-step reaction (Scheme 1) analogous to that described previously for purely hydrogen-bonded supramolecular systems.[13] Accordingly, MDI (**3**) was added to bis(hydroxy)-terminated polybutadiene **4** ($M_w = 2000$ g mol^{-1}; NCO/OH ratio = 2:1). The resulting isocyanate-terminated prepolymer was end-capped with 2-aminomethylpyrene (**5**) to yield a hydrogen-bonding polymer with π-electron-rich end groups as a pale-yellow elastomer. For control purposes, the benzyl end-capped polyurethane **6**, which lacks the π-electron-rich pyrenyl residues of **2**, was also synthesized by addition of excess benzylamine to the isocyanate-terminated prepolymer (Scheme 1). The pyrenyl end-capped polymer **2** and benzyl end-capped polymer **6** had almost identical number-average molecular weights ($M_n = 8400$ and 8500 g mol^{-1}, respectively).

Formation of a supramolecular $\pi-\pi$ stacked complex between **1** and **2** was readily accomplished by mixing an essentially colorless solution of the pyrenyl end-capped polymer **2** in 6:1 (v/v) chloroform/hexafluoropropan-2-ol with the pale-yellow solution of chain-folding polyimide **1** in the same solvent. The polymers were combined respectively in a 4:1 weight ratio, corresponding to an equimolar ratio of end-capping pyrenyl units and chain-folding bis(diimide) units (*q* in Figure 1), and instantly generated a deep-red solution. This dramatic color change

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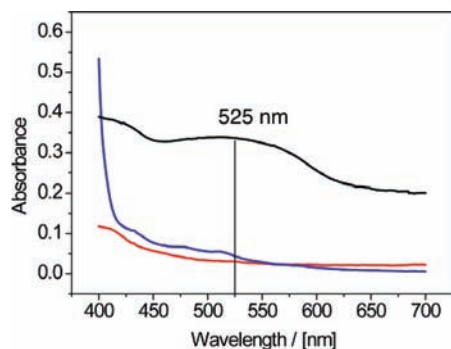
Figure 2. UV−vis spectra of the polymeric complex [**1**+**2**] (black), polyimide **1** (blue), and pyrenyl end-capped polyurethane **2** (red). The broad absorption centered at 525 nm represents a $\pi-\pi^*$ charge-transfer transition between the electron-rich pyrenyl and electron-poor diimide residues. The solution in 6:1 (v/v) chloroform/hexafluoropropan-2-ol was 10^{-3} M in pyrenyl units.
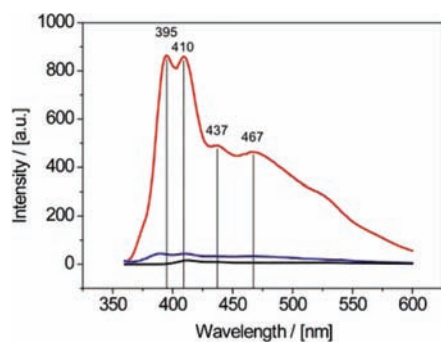

Figure 3. Fluorescence spectra of polyurethane **2** (red), polyimide **1** (blue), and supramolecular polymeric network [**1**+**2**] (black) in 6:1 (v/v) chloroform/hexafluoropropan-2-ol solution at 20 °C, showing essentially complete quenching of the pyrene emission bands upon complexation. Excitation was at 345 nm; the concentration was 10^{-7} M in pyrenyl units.

resulted from the presence of a new absorption band at 525 nm in the visible spectrum of the blend (Figure 2). Absorption at this wavelength is indicative of charge-transfer between the π-electron-rich (pyrene) and π-electron-deficient (diimide) species.[11] The absorption is entirely analogous to the one at 530 nm reported previously for the complex formed between discrete compounds designed to model this interaction.[11]

Irradiation of a solution of the pyrenyl end-capped polymer **2** under a standard laboratory UV source (310 nm) revealed the familiar blue fluorescence response originating from the pyrenyl residues on polymer **2**, as shown in Figure 3.[12,14] However, this fluorescence is almost completely quenched in the solution blend [**1**+**2**], confirming the occurrence of complementary $\pi-\pi$ stacking [see p S12 in the Supporting Information (SI)].[12] Moreover, the emission spectrum of the pyrenyl end-capped polyurethane **2** shows characteristic emission bands for the monomeric pyrenyl group at 395, 410, and 437 nm as well as the excimer emission at 467 nm originating from the association of two pyrenyl moieties.[12,14] These emission bands are completely absent in the fluorescence spectrum of the blend of the complementary polymers **1** and **2**.

The UV−vis and fluorescence data for both the individual components **1** and **2** and their blend [**1**+**2**] are consistent with those previously obtained for structurally related polymer blends that lacked urea and urethane hydrogen-bonding residues in close proximity to the pyrenyl end group.[5a] Thus, in solution, the formation of a $\pi-\pi$ stacked complex between the pyrenyl end groups of **2** and the chain folds in **1** (Figure 1) is unaffected by the incorporation of the urea-based hydrogen-bonding motif. Computational modeling of this interaction suggests that such $\pi-\pi$ stacking interactions are reinforced by multiple hydrogen bonding between the urea and diimide residues, as discussed below.

While these solution studies were encouraging, it was also necessary to verify the formation of $\pi-\pi$ stacked interpolymer complexes in the solid state. Films cast from a 1:4 (w/w) blend of polymers **1** and **2** by evaporation of a solution in 2,2,2-trichloroethanol indeed produced dark-red elastomeric materials, clearly demonstrating that complementary $\pi-\pi$ stacking is also retained in the solid state.

The IR spectrum of the solid blend of **1** and **2** showed absorption bands at 3375, 1660, and 1730 cm^{-1} assigned to hydrogen-bonded ν(N−H), hydrogen-bonded ν(C=O), and non-H-bonded ν(C=O) (urethane) vibrations, respectively (Figure 4).[15] This suggests that not all of the urethane linkages within the bulk material are able participate in hydrogen bonding.[3b] When the sample was heated from 25 to 120 °C, the absorptions due to the hydrogen-bonded N−H and C=O residues were appreciably reduced in intensity while those corresponding to the free carbonyl stretch increased in intensity, as shown in Figure 4, demonstrating the thermally responsive nature of the hydrogen bonds in this novel, supramolecular polymer blend.

To investigate the morphology of the supramolecular polymer blend, variable-temperature small-angle X-ray scattering (SAXS) analysis of the material was carried out. The sample was initially held at −20 °C and then cycled sequentially to 80 °C, back to −20 °C, and finally to 80 °C again at a ramp rate of 5 °C min^{-1} with a 2 min isothermal hold between successive steps in the temperature cycle. At all temperatures within the range studied, the blend showed a single scattering signal at $q = 0.08$ Å^{-1} that is indicative of a phase-separated morphology with a domain spacing on a 10 nm length scale. While the size of the domain spacing was essentially invariant within the temperature range studied, the X-ray contrast between the different domains increased with increasing temperature. This is demonstrated in Figure 5 by a plot of the intensity of the scattering signal at $q = 0.08$ Å^{-1} as a function of temperature, where the reversible nature of this relationship becomes apparent.

We previously demonstrated that a driving force for producing a stable, homogeneous blend is the formation of complementary $\pi-\pi$ stacking complexes between two polymers.[5] In the present system, the SAXS data suggest that supramolecular complexation is reduced at elevated temperatures, with the result that the polymers become less miscible, thereby driving phase separation, most probably into polyimide-rich and polybutadiene-rich domains.[16] This conclusion was supported by com-

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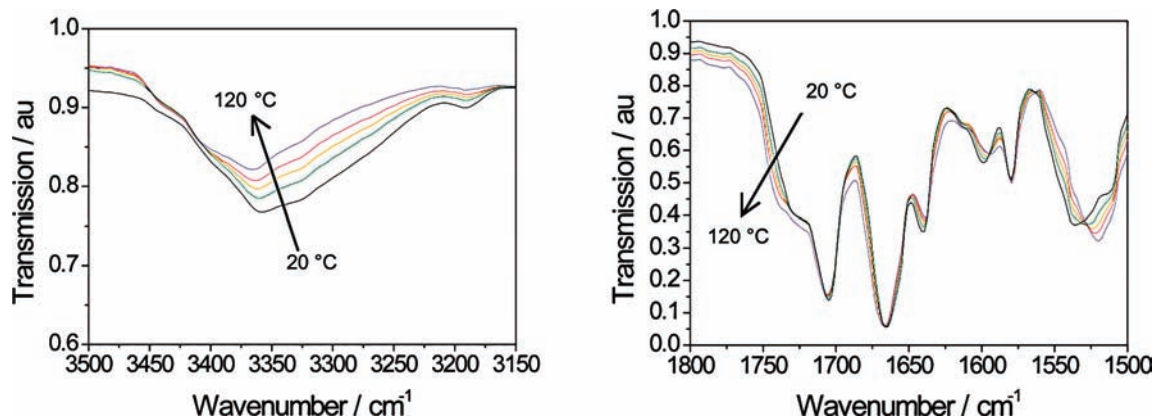
Figure 4. Variable-temperature FTIR spectroscopic analysis of the supramolecular network formed by **1** and **2**.
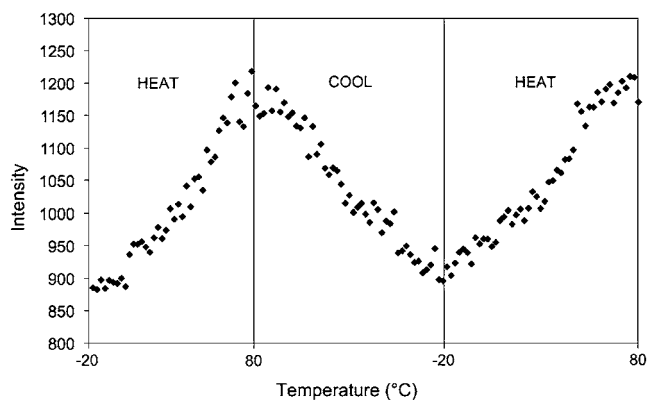

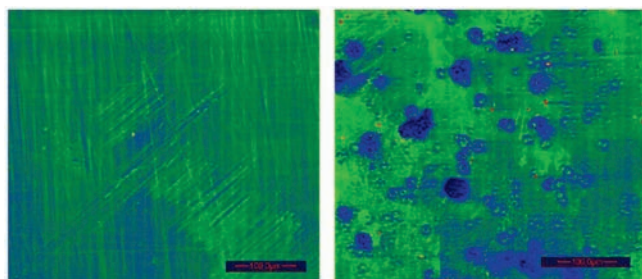**Figure 5.** Intensity of the SAXS scattering signal at $q = 0.08$ Å^{-1} as a function of temperature.

Figure 6. False-color ESEM images of (left) the $\pi-\pi$ stacked network [**1**+**2**] and (right) the non-π-stacking blend [**1**+**6**] at 20 °C. The fine, parallel lines visible in the left-hand image reflect the texture of the PTFE substrate on which the films were cast.

parison of environmental scanning electron microscopy (ESEM) images of the 1:4 (w/w) supramolecular polymer blend [**1**+**2**] and an analogous control material produced from benzyl end-capped polyurethane **6** and chain-folding polyimide **1** (Figure 6). It can be seen that the film cast from the electronically complementary components [**1**+**2**] is homogeneous at the micrometer scale, whereas the material comprising the chain-folding polyimide and the benzyl end-capped polyurethane is very clearly phase-separated at this length scale. This demonstrates the necessity of $\pi-\pi$ complexation to drive miscibility of the polymers and thus enable the formation of stable elastomeric films, in agreement with our studies on related polymer blends.[5]

Wide-angle X-ray scattering (WAXS) analysis of the polymer film [**1**+**2**] was carried out at 25 °C to investigate the local

packing of the self-assembled blend. Several peaks were observed, corresponding to d spacings of 15.4, 9.2, 5.1, and 3.4 Å. The 5.1 Å peak is in close agreement with that previously measured for the urea−urethane separation in hydrogen-bonded elastomers.[17] The smallest spacing, $d = 3.4$ Å, has been previously attributed to $\pi-\pi$ stacking within supramolecular polymers.[3b] It may also be compared to the distance predicted[11] from energy-minimized models (e.g., Figure 1b) in which pyrenyl groups are bound within the designed chain fold in polymer **1** (3.4−3.5 Å) as well as the interplanar distances measured by single-crystal X-ray analysis of related $\pi-\pi$-stacked model complexes.[18]

We previously showed that $\pi-\pi$ stacking and hydrogen bonding between polymer chains can be successfully modeled using molecular mechanics simulations with charge equilibration.[11] In the present work, this approach enabled a detailed, atomistic analysis of the interaction between the pyrenemethylurea end groups of polymer **1** and the designed bis(diimide) chain folds of polyimide **2**. Thus, Cerius2 (v.3.5, Accelrys Inc., San Diego, CA) was used to construct a model based on segment q of polyimide **1**, which contains two naphthalenediimide residues linked by a triethylenedioxy chain (see Figure 1). This unit was designed specifically to generate a chain fold that would be complementary to an electron-rich pyrenyl unit.[11] A model compound representing a pyrenemethylurea end group was inserted into the chain fold and, after calculation of the atomic charge distribution, the system was energy-minimized using the Dreiding2 force field.[19] After initial minimization, the position of each atom was disordered by 0.1 Å and the system reminimized. The minimize−disorder−reminimize cycle was repeated until a consistent structure was obtained. This approach provided some reassurance that a deep (though not necessarily global) energy minimum had been identified.

The final model is shown in Figure 7, which reveals not only close, electronically complementary $\pi-\pi$ stacking between the pyrenyl end group and the two naphthalenediimide residues of the chain fold but also, less predictably, a pair of strong, convergent hydrogen bonds from the urea NH groups to a single diimide carbonyl group. The hydrogen-bond parameters are

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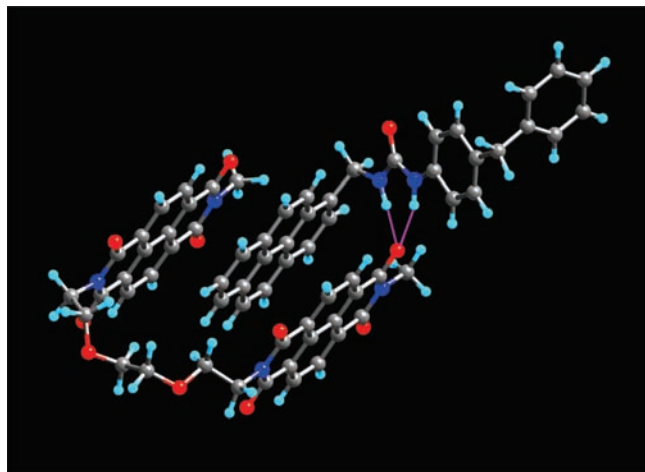
Figure 7. Minimized computational model of the interaction between a pyrenemethylurea end group of polyurethane **2** and a designed chain fold of polyimide **1**. Key binding features are the electronically complementary triple π-stack (with mean interplanar spacings of 3.45 and 3.41 Å) and a pair of strong, convergent hydrogen bonds (shown in magenta) from the urea unit to a diimide carbonyl group ($N{\cdots}O$ = 2.95, 2.84 Å; $H{\cdots}O$ = 2.03, 1.91 Å; $N{-}H{\cdots}O$ = 160, 161°).

Scheme 2. Model Chain Fold **8**[11] and Synthesis of the End-Group Model Compound **9**
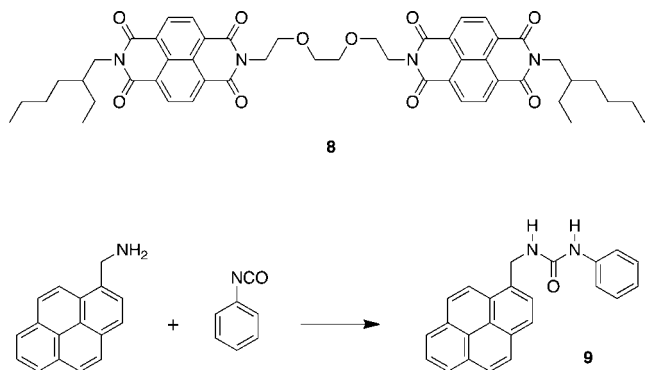
$N{\cdots}O$ = 2.95, 2.84 Å; $H{\cdots}O$ = 2.03, 1.91 Å; and $N{-}H{\cdots}O$ = 160, 161°.

Experimental support for this binding mode was provided by Job analysis using the $\pi{-}\pi^*$ charge-transfer band at 530 nm resulting from complexation of model chain fold **8** with pyrenylurea compound **9** (Scheme 2). The Job plot peaks at 0.50 (see p S7 in the SI), confirming the 1:1 complexation predicted by the simulation shown in Figure 7. Moreover, ^{1}H spectra of an equimolar mixture of **8** and **9** over a range of concentrations (2−14 mg mL^{-1}) show progressive downfield shifts of both NH protons ($\Delta\delta$ = 0.42 and 0.21 ppm) with increasing concentration, consistent with the hydrogen-bonding pattern shown in Figure 7. The diimide aromatic proton resonance shows a corresponding upfield shift ($\Delta\delta$ = 0.30 ppm) under these conditions, as a consequence of increasing ring-current shielding by the associating pyrenyl residue, again in good agreement with the proposed bonding model (see p S8 in the SI).

Analysis of the supramolecular blend [**1**+**2**] using both spectroscopic (UV−vis/IR) and X-ray scattering (SAXS/WAXS) techniques has demonstrated that the material is phase-separated on the nanoscale and that there is clear evidence for hydrogen bonding and $\pi{-}\pi$ stacking interactions, as proposed. Computational simulation based on molecular mechanics has provided
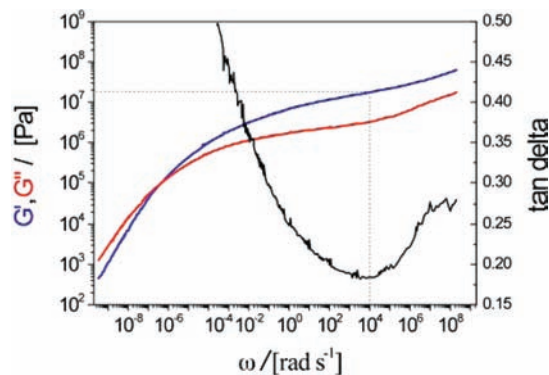

Figure 8. Master curve for the supramolecular network [**1**+**2**], with a reference temperature of 30 °C. The storage modulus profile is shown in blue, the loss modulus profile in red, and tan δ in black.

a good atomistic model for such interactions that is supported by spectroscopic studies in solution. With these data in hand, our attention turned to the physical properties of the new material.

Rheological Studies. Initial studies of the rheological behavior of the supramolecular polymer blend [**1**+**2**] were carried on a parallel-plate rheometer. The Boltzmann time−temperature superposition (TTS) technique was used to create a master curve with a reference temperature of 30 °C; the curve exhibited a plateau modulus of 2×10^7 Pa as determined by the MIN method,[20] which considers the plateau modulus to be the value of the storage modulus when tan δ reaches a minimum (Figure 8).[20c] The storage modulus (G') and the loss modulus (G'') appear to be essentially parallel in the low-frequency region and slow to achieve their limiting power laws of 2 and 1, respectively, with frequency.[21] This behavior is in contrast to that observed for isotropic covalent and noncovalent polymers, which are known to exhibit slopes of 2 and 1, respectively, for G' and G'' in this region.[20a,21] This result is consistent with a structural model for [**1**+**2**] in which multiple chain-fold receptors within the backbone of each polyimide lead to formation of a noncovalently cross-linked network rather than extended linear chains in the solid state.

However, as one considers the very low frequency region, the complex viscosity approaches a constant value (see p S14 in the SI). The zero-shear (i.e., terminal) viscosity η_0 was obtained from a Carreau−Yasuda fit, which converted the dynamic data to a steady-shear model using the Cox−Merz rule,[20b] resulting in an extrapolated value of η_0 greater than 3.5×10^{13} Pa s. The material appears to be an extremely viscous liquid, with a relaxation time in excess of 10^{10} s ($\sim$300 years) at 30 °C. We note that the magnitude of the viscosity is larger than that frequently associated with the glassy state (10^{12} Pa s),[22] although this value is disputed[23] and may not be applicable to our case.

Figure 9a shows a plot of the rheometric shift factor a_T, a parameter related to melt viscosity, as a function of temperature for the noncovalent network [**1**+**2**]. It can be seen that a_T

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(22) Barlow, A. J.; Lamb, J.; Matheson, A. J. *Proc. R. Soc. London, Ser. A* **1966**, *292*, 322–342.
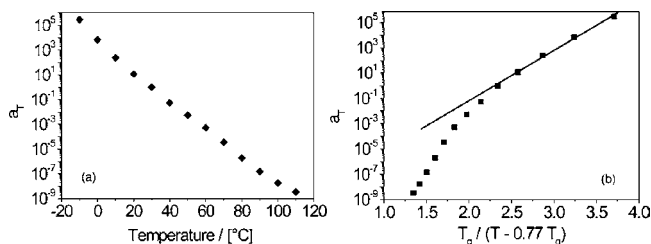(23) Soesanto, T.; Williams, M. C. *J. Phys. Chem.* **1981**, *85*, 3338–3341.

Figure 9. (a) Shift factor a_T of the supramolecular network [**1**+**2**] as a function of temperature. (b) Plot of a_T for [**1**+**2**] as a function of temperature normalized to T_g.

changes by some 14 orders of magnitude between -10 and $+110\ °C$. This is approximately the same rate of change of a_T with temperature as observed in previous healable supramolecular blends, though it is seen here over a much wider temperature range.[5a] The very large change in a_T over a small, readily accessible temperature range is consistent with dissociation of the supramolecular network, resulting in a large drop in viscosity that thereby facilitates healing.

It has recently been postulated[24] that for all amorphous, covalently bonded polymers there is a linear relationship between a_T and temperature (normalized to the glass transition temperature T_g). However, this relationship has also been shown[25] to break down for supramolecular polymers such as telechelic ionomers, where the plot of a_T as a function of temperature deviates significantly from linearity at high temperature.

Figure 9b shows a shift factor plot for the supramolecular polymer network [**1**+**2**]. At low temperatures the plot is essentially linear, whereas at higher temperatures the plot gradient increases dramatically, in line with results for other supramolecular polymer systems.[25] This deviation is attributed[25] to disengagement of the supramolecular ($\pi-\pi$ stacking and hydrogen-bonding) interactions, leading to a change in the apparent molecular weight of the noncovalent polymer blend and thus resulting in a rapid change in viscosity with temperature.

Healing Studies. In an initial investigation of the healing potential of the polymer blend [**1**+**2**], a strip of film (0.4 mm in thickness and 2.6 mm in width) was analyzed to break by tensometry. The pristine elastomer exhibited a tensile modulus of $\sim 3 \times 10^5$ Pa. The two ruptured portions of the film were then positioned with their broken edges in contact, but not overlapped, on a preheated PTFE plate at 100 °C and then placed in an oven at 100 °C for varying periods of time (20–1000 min), after which the tensile modulus was measured again. The resulting data are displayed in Figure 10, which shows the tensile modulus and associated healing efficiency for the healed material as function of healing time. From these data it is evident that the material achieves its maximum healing efficiency (95%) after

a healing time of ~ 240 min, as shown in Figure 10a. This healing efficiency relative to the pristine material was maintained over five break–heal cycles of a single sample, as shown in Figure 10b.

In addition to recovery of the tensile modulus (stiffness) of the material, it is important from an application-driven point of view to recover the modulus of toughness.[26] The modulus of toughness is a measure of the energy required to break the material and is readily calculated from the area under the stress–strain curve. The elastomeric nature of the pristine supramolecular blend [**1**+**2**] allows it to be stretched to 2.7 times its original length before breaking, i.e., it shows 170% elongation (Figure 11a), and the blend has a modulus of toughness of 510 MPa. This can be compared with an elongation to break of 22% and modulus of toughness of 59 MPa for the pyrenyl end-capped polymer **2** alone and with a value of 18 MPa measured here (see p S15 in the SI) for a previously reported healable π-stacking blend based on a polyamide rather than polybutadiene backbone.[5a]

After one break–heal cycle, the present supramolecular blend [**1**+**2**] regained 91% of the original elongation to break and 70% of its original modulus of toughness (360 MPa). As shown in Figure 11b, the modulus of toughness remained in the range 10^8-10^9 Pa over five break–heal cycles. In these repeat experiments, fracture was generally observed at or near the site of the original break. Several attempts were made to heal the pyrenyl end-capped polymer **2** in the *absence* of the polyimide component **1** (100 °C for up to 24 h), but these were completely unsuccessful. The polyimide itself is not film-forming, so its mechanical properties could not be evaluated.[5]

Analysis of rheometry scans for the supramolecular polymer blend [**1**+**2**] and for the pyrenyl end-capped polyurethane **2** showed very disparate responses to the healing conditions (Figure 12). For blend [**1**+**2**], the storage modulus G' and loss modulus G'' converge as temperature increases and cross at 93 °C (i.e., just below the observed healing temperature). Thus, above 93 °C, the viscous properties of the material dominate over the elastic properties, allowing reorganization of the polymer chains and rapid re-engagement of the supramolecular interactions, facilitating healing. This is in contrast to G' and G'' for the pyrenyl end-capped polymer **2** alone, which *diverge* over the temperature range studied, showing that the elastic properties dominate at all temperatures accessed.

In a final demonstration of the importance of $\pi-\pi$ stacking interactions in maintaining the stiffness, elongation, and toughness of material [**1**+**2**] and in enabling it to heal, the "control" blend of benzyl end-capped polyurethane **6** with chain-folding polyimide **1** was subjected to the same tensile tests (Figure 13). The pristine blend [**1**+**6**] exhibited an elongation of 40% before breaking (cf. 170% for [**1**+**2**]) and a modulus of toughness of
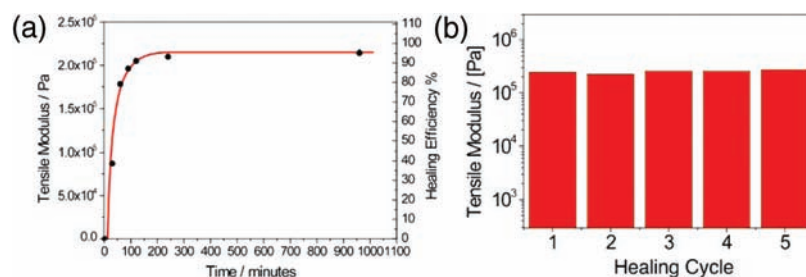

Figure 10. (a) Recovery of tensile modulus as a function of healing time for a sample of [**1**+**2**]. (b) Recovery of the tensile modulus for the network [**1**+**2**] sample over five break–heal cycles.
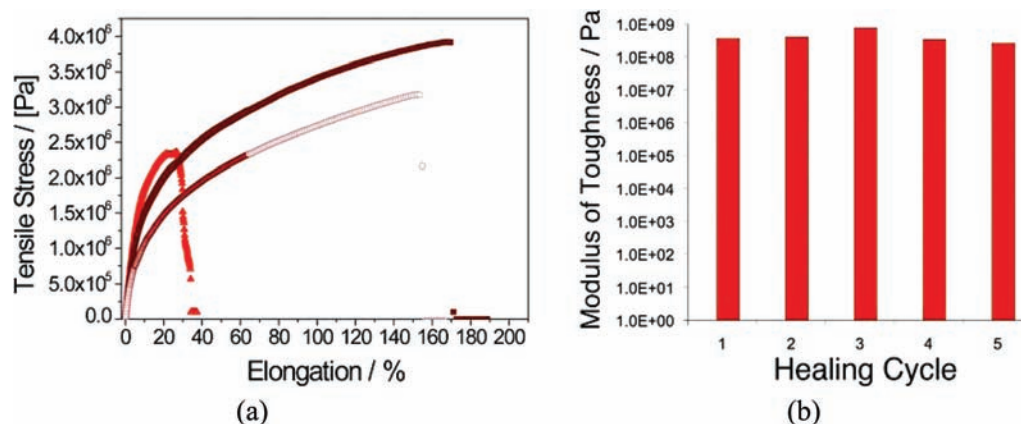
Figure 11. (a) Stress−strain curves for elastomer **2** (▲), the pristine network [**1**+**2**] (■), and the healed network [**1**+**2**] after annealing at 100 °C for 4 h (○). (b) Recovery of the modulus of toughness for the network [**1**+**2**] over five break−heal cycles.
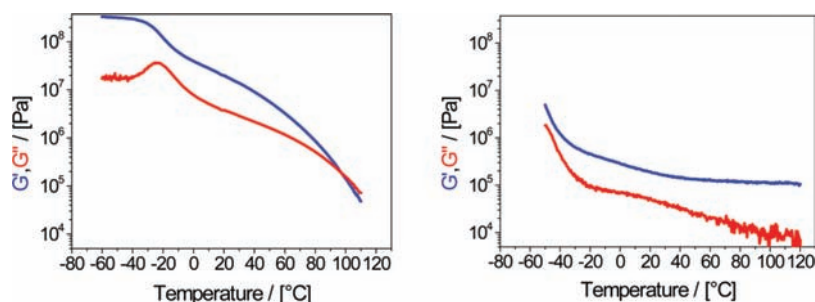

Figure 12. Rheology of (left) supramolecular network [**1**+**2**] and (right) elastomer **2**, showing the temperature dependence of the dynamic shear moduli. Scan rate = 1 °C min^{-1}.
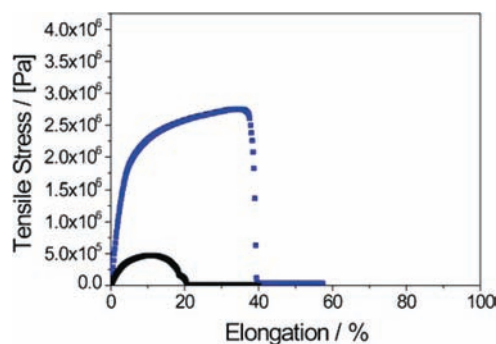

Figure 13. Stress−strain curves for the pristine blend of benzyl end-capped polyurethane and polyimide [**1**+**6**] (blue) and the healed blend, annealed at 100 °C for 24 h (black). The recovery of the modulus of toughness (area under the curve) for this blend was no more than 8%.

91 MPa (cf. 510 MPa for [**1**+**2**]). Even after an extended annealing time (24 h), the healed material exhibited a greatly reduced elongation to break (20%) and a modulus of toughness of only 7 MPa (cf. 360 MPa for [**1**+**2**]), resulting in a healing efficiency of 8% (cf. 77% for [**1**+**2**]).

3. Conclusions

A novel pyrenemethylurea end-capped polymer (**2**) that forms a thermally healable material when blended with a chain-folding polyimide (**1**) has been designed and synthesized. Pristine

samples of the blend [**1**+**2**] exhibit a tensile modulus of 3 × 10^5 Pa, are elastomeric in nature (170% elongation), and have a high modulus of toughness (510 MPa) when compared with previously reported supramolecular healable materials.[5] When it was broken and rehealed, the present material repeatedly regained 95% of its tensile modulus, 91% of its elongation to break, and 77% of its modulus of toughness after annealing for 240 min at 100 °C. In contrast, control experiments on a pure sample of the pyrene end-capped polymer (**2**) failed to show significant healing even after extended periods at 100 °C, a result that is consistent with the very disparate temperature dependence of G' and G'' for polymer **2** and the blend [**1**+**2**]. Analysis of a second control material, a blend of a benzyl end-capped polymer **6** and chain-folding polyimide **1** (essentially identical to the healing blend [**1**+**2**] but lacking the π-electron-rich pyrenyl groups), demonstrated the importance of interpolymer π−π stacking in producing a tough, coherent, and healable material. Pristine samples of the control blend [**1**+**6**] exhibited a low modulus of toughness (91 MPa) and a healing efficiency of only 8% even under forcing conditions. Computational modeling of the interaction between a polyimide chain fold and a pyrenemethylurea end group confirmed the stability of the proposed triple π-stack and showed that this is reinforced by a pair of strong, convergent hydrogen bonds between the adjacent urea unit and a diimide carbonyl group.

The supramolecular polymer [**1**+**2**] shows a significant enhancement of tensile modulus over that of the purely hydrogen-bonded system described by Leibler and co-workers (3 × 10^5 vs 1 × 10^4 Pa),[4] though the elongation to break of the

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latter material (400%) is considerably greater than the 170% shown by [**1**+**2**]. Conversely, the thermally healable networks described by Wudl and co-workers[27] based on reversible covalent (Diels−Alder) chemistry show very much higher tensile moduli (typically in the region of 10^9 Pa) but relatively low degrees of strain to failure.

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Supporting Information Available: Full experimental details of materials synthesis and characterization and rheology, X-ray scattering, and healing studies; raw scattering data for the variable-temperature SAXS experiments; Job plot and ^{1}H NMR spectra for complexation of **8** with **9**; WAXS data; unprocessed ESEM images and photographs of the healing polymer blend in solution under visible light and UV irradiation; photograph of a sample of the healable material [**1**+**2**]; plot of the complex viscosity η^* of [**1**+**2**] as a function of frequency; and a stress−strain plot for the supramolecular π-stacking polymer blend reported in ref 5a. This material is available free of charge via the Internet at http://pubs.acs.org.

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