

## Formation of a Miscible Supramolecular Polymer Blend through Self-Assembly Mediated by a Quadruply Hydrogen-Bonded Heterocomplex

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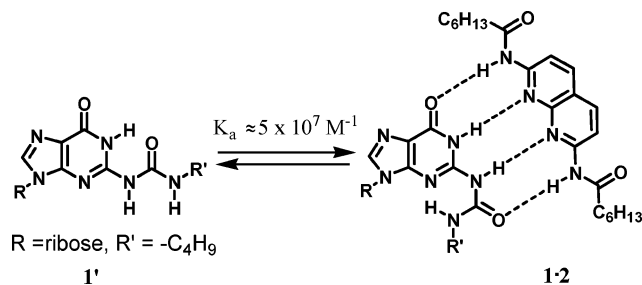
**Abstract:** A supramolecular network polymer consisting of a pair of immiscible polymers, poly(butyl)-methacrylate (PBMA) and polystyrene (PS), is described. A urea of guanosine (**1**, UG) and 2,7-diamido-1,8-naphthyridine (**2**, DAN), which form an exceptionally strong quadruply hydrogen-bonding complex, are displayed at 1–10 mol % along the main backbone of PBMA and PS, respectively. <sup>1</sup>H NMR studies show heterocomplexation between UG and DAN exclusively. This high-fidelity, high-affinity supramolecular connection of two different polymer coils at the molecular level produces a polymer blend. Blends containing different weight ratios of the polymers and mole percent of the recognition units were characterized by AFM and DSC experiments with no isolated domains observed and a single glass-transition temperature ( $T_g$ ). The  $T_g$  is tunable by varying the weight ratio of the polymers in the blend. In addition, viscosity measurements, size-exclusion chromatography (SEC), and dynamic light-scattering (DLS) studies demonstrate the formation of a supramolecular network structure.

Self-assembly mediated by hydrogen bonding is a well-documented approach to creating structures with nanometer dimensions.<sup>1</sup> Beyond the efficiency that such a building block approach affords in the production of oligomeric or polymeric structures, there are significant practical consequences as a result of the suprastructures being formed reversibly. The ability to form and break bonds in response to temperature or stress can confer properties that are not achievable in covalently bonded systems. Specific examples of unique macroscopic properties arising in such reversible supramolecular polymers have been reported recently. In particular, the self-associating unit 2-ureido-4[1H]-pyrimidinone<sup>2</sup> has been displayed along polymer backbones<sup>3</sup> or on their ends<sup>4</sup> to produce more complex polymeric structures.

New materials with tunable properties have also been prepared through the formulation of two or more immiscible polymers. Indeed, polymer blends have been a central topic in material science.<sup>5</sup> Numerous efforts have been made to minimize interfacial energy and reduce the propensity for phase separation

of the polymers, including the use of compatibilizers such as block or grafted copolymers.<sup>6</sup> Another approach has been the introduction of reactive groups to covalently connect individual polymers within the blend.<sup>7</sup> The use of hydrogen bonding to improve interfacial properties and favor blending is particularly appealing because of the potential for relatively low process temperature (reversibility), and because it may lead to mixing at the molecular level.<sup>8</sup> To achieve desired blends, monomers possessing weak hydrogen-bonding moieties such as hydroxyl, carboxyl, pyridyl, and amino groups have been employed. This method has been limited to only a few polymer pairs; the weak intermolecular contacts means that a high mole percent of

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**Figure 1.** Formation of a strong complex from UG and DAN.

comonomers is required. As a result, the properties of polymers can become quite different from those lacking the hydrogen-bonding groups. Lower mole percentage incorporation of recognition units has successfully reduced interfacial energies between two immiscible phases without blend formation.<sup>9</sup>

Heterocomplexes that form with high stability and fidelity might overcome the disadvantages of these simpler modules.<sup>10</sup> For example, even at a low mole percent incorporation of such modules along the polymer backbones, the assembly process would be thermodynamically driven, leading to efficient reversible, intermolecular cross-linking between immiscible polymeric chains and thus mixing at the molecular level.<sup>11</sup> Recently, we reported that guanosine urea **1'** (UG) weakly self-associates ( $K_a \approx 200 \text{ M}^{-1}$ ) but very strongly complexes with DAN **2**, (**1·2**,  $K_a \approx 5 \times 10^7 \text{ M}^{-1}$ ), thus representing a heterocomplex with unparalleled affinity and pairing fidelity (see Figure 1).<sup>12</sup> Indeed, the free energy of the quadruple hydrogen bonding is ca. 10% that of a C–C bond. Herein, we report polymer blends of poly-(butyl)methacrylate (PBMA) and polystyrene (PS) driven by appended UG and DAN recognition units. These two polymers were chosen because of their documented immiscibility.<sup>13</sup> Thus, the strong repulsive interactions between PS and PBMA

provides a significant challenge for molecular recognition-driven blend formation. Beyond determining if the highly stable UG·DAN heterocomplex could drive the formation of a miscible and reversible supramolecular network structure, it was of interest to see if the properties of such a blend might be tuned by varying the mole percent of the recognition units and the relative amounts of the two polymers within the mixture. Specifically, we describe the synthesis of UG-incorporated PBMA (UG-PBMA) **3** and DAN-incorporated PS (DAN-PS) **4** and detailed studies of the resulting suprastructure, its reversibility, the miscibility of the normally immiscible polymer pair, and the ability to tune the properties of the polymer blend.

## Results and Discussion

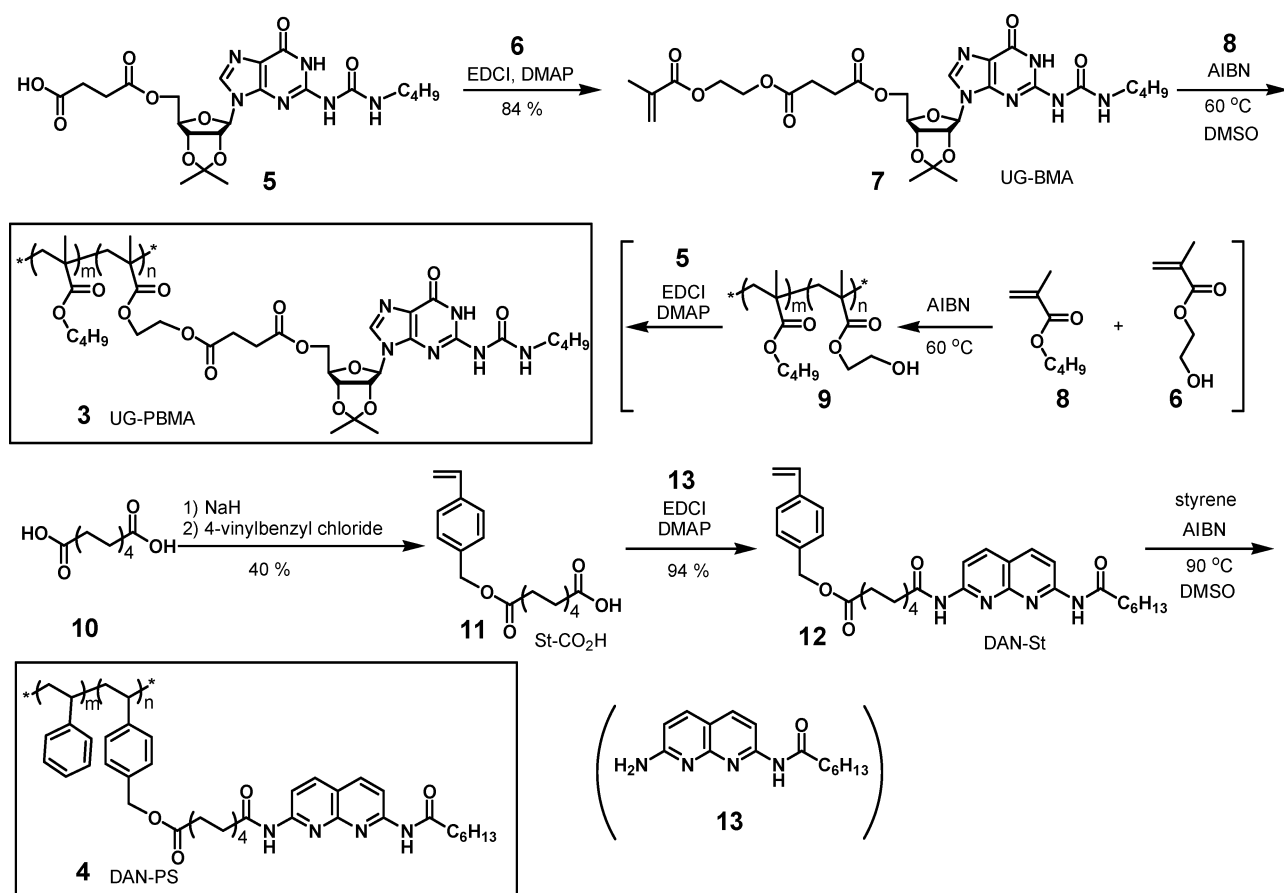
**Monomer Synthesis and Copolymerization.** To obtain a random copolymer, we chose UG-BMA **7** and BMA **8**, because their radical propagation sites are similar; this means that their copolymerization reactivities ( $r_7 = k_{77}/k_{78}$  and  $r_8 = k_{88}/k_{87}$ ) would also be similar.<sup>14</sup> UG-PBMA **3** was prepared by radical copolymerization<sup>4g,h</sup> of **7** and **8** in DMSO at 60 °C with AIBN, as outlined in Scheme 1. The esterification reaction of the carboxylated UG **5**<sup>12a</sup> and **6** using EDCI and DMAP activation produced UG-BMA **7** in 84% yield. Monomer **7** was very soluble in methanol; thus, the remaining **7** was easily removed by precipitating the copolymer in methanol. Alternatively, UG-PBMA **3** could be prepared from prepolymer **9** with hydroxyl groups where the carboxylated UG **5** could be attached. Likewise, DAN-PS **4** was obtained by the radical polymerization of styrene (St) and DAN-St **12** in DMSO at 90 °C, with AIBN used as the initiator. DAN-St **12** was synthesized by treating carboxylated styrene (St-CO<sub>2</sub>H) **11** with amino naphthyridine **13**<sup>12a</sup> and EDCI. Styrene **11**, in turn, was synthesized by the substitution reaction of 4-vinylbenzyl chloride with 2 equiv of sebacic acid in the presence of K<sub>2</sub>CO<sub>3</sub> and 18-crown-6 in DMF.

The properties of a representative group of copolymers prepared in this study are summarized in Table 1. Mole ratios of recognition units in a copolymer were varied by varying the monomer feed. The molecular weights of the copolymers were kept relatively low to minimize physical entanglement of polymer coils in semidilute solutions. The molecular weights and the polydispersity indices (PDI) were determined by gel permeation chromatography (GPC) in THF with standard polystyrene calibration. The PDI values are typical for these types of polymerization reactions. The mole percentage of recognition unit in **4** was estimated from the <sup>1</sup>H NMR integration ratio of aromatic *H* (6.62 ppm) and benzyl CH<sub>2</sub> (5.05 ppm) in chloroform-*d*. Vinylic hydrogens in **12**, observed at 5.25, 5.75, and 6.70 ppm, were not detected in **4** (Figure 2), indicating that the starting monomers were completely removed. In case of **3**, DMSO-*d*<sub>6</sub> was used as a result of the peak broadness observed in chloroform-*d*. Two peaks at 5.97 and 5.63 ppm, assigned as the vinylic hydrogen atoms in **7**, disappeared in copolymer **3**, for which the mole percentage of recognition unit was estimated

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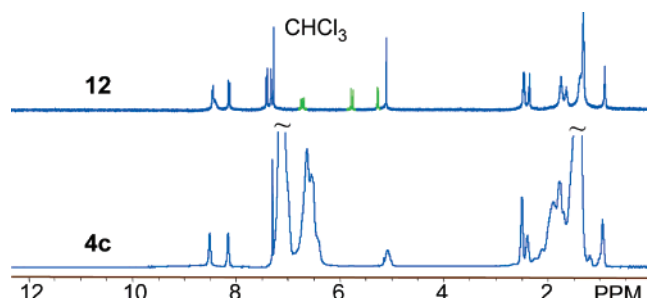
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Scheme 1



from <sup>1</sup>H NMR integration ratio of aromatic *H* (8.00 ppm) and OCH<sub>2</sub> (4.22–3.82 ppm). The copolymer composition determined by NMR was in good agreement with the monomer feed ratios. Thus, functional monomers were randomly incorporated into the resulting copolymers, as expected from the structural similarity of radical propagation sites in BMA **8** and UG-BMA **7**, and St and DAN-St **12**. The average number of functional group (*F*) per chain was calculated from the experimentally determined monomer mole ratios and the number averaged molecular weights (*M<sub>n</sub>*) of the polymers.

**<sup>1</sup>H NMR Evidence for Intermolecular Heterocomplexation of UG and DAN Units Attached to Polymers.** Intermolecular heterocomplexation of UG and DAN units was readily observed by <sup>1</sup>H NMR in chloroform-*d* (Figure 3). Unlike the very clean spectrum of UG **1'** that weakly self-associated, that of **3a**, in which UG units were attached to PBMA, exhibited multiple



**Figure 2.** <sup>1</sup>H NMR of **12** and polystyrene **4c** containing DAN in chloroform-*d* at room temperature. Vinylic hydrogens (marked as green) in **12** were not detected in **4c**.

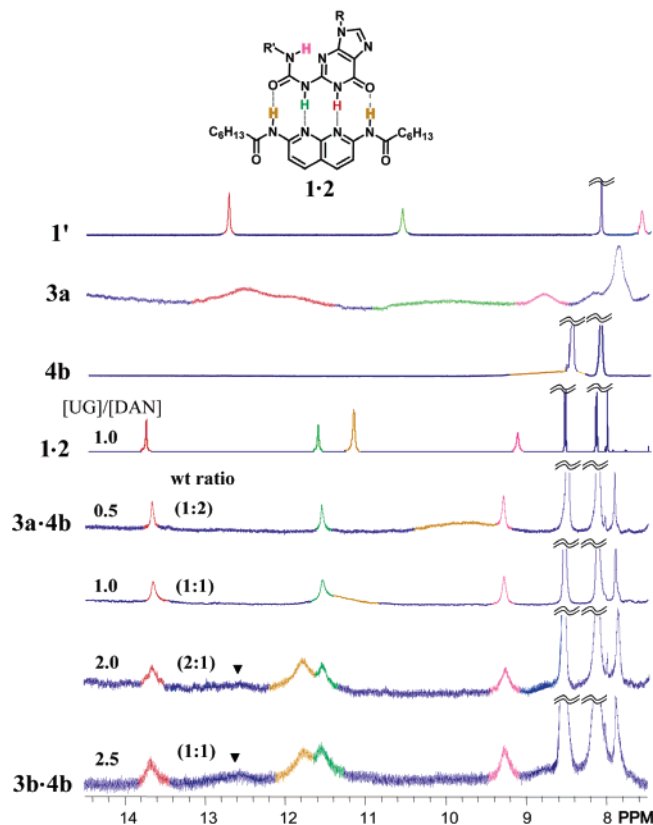
**Table 1.** Characterization Results of Copolymers Containing Recognition Units UG or DAN

polymer <sup>a</sup>	recognition unit ( <i>F</i> )	mol % unit ( <i>F</i> ) <sup>b</sup>	<i>M<sub>n</sub></i> <sup>c</sup>	<i>M<sub>w</sub></i> <sup>c</sup>	avg no. of <i>F</i> per chain <sup>d</sup>
<b>3a</b>	UG	4	17	28	4.2
<b>3b</b>	UG	10	11	16	5.7
<b>4a</b>	DAN	1	15	29	1.4
<b>4b</b>	DAN	4	13	23	4.2
<b>4c</b>	DAN	7	16	33	8.2
<b>PBMA</b>			22	29	
<b>PS</b>			10	21	

<sup>a</sup> Polymerization was carried out in DMSO at 60 °C (24 h) for **3** or at 90 °C (48 h) for **4**. <sup>b</sup> Estimated from the <sup>1</sup>H NMR spectrum. <sup>c</sup> Relative molecular weights against polystyrene standards calculated from GPC in THF. <sup>d</sup> Calculated from the number average molecular weight (*M<sub>n</sub>*) and mol % recognition unit of polymer.

broad peaks; these probably resulted from a slow exchange rate between the self-associated and free UG units.<sup>12a</sup> The addition of **4b** to a solution of **3a** entirely converted the broad downfield peaks to sharp resonances similar to those seen in the intermolecular UG·DAN heterocomplex. Thus, the <sup>1</sup>H NMR signals of a mixture of **3a**·**4b** with a 1:1 mole ratio shifted significantly downfield from their position in the individual components.<sup>15</sup> It is notable that the resonances of the amido NHs are broad and that their chemical shift depended on the mole ratio of DAN and UG units, indicating a fast exchange rate between free and

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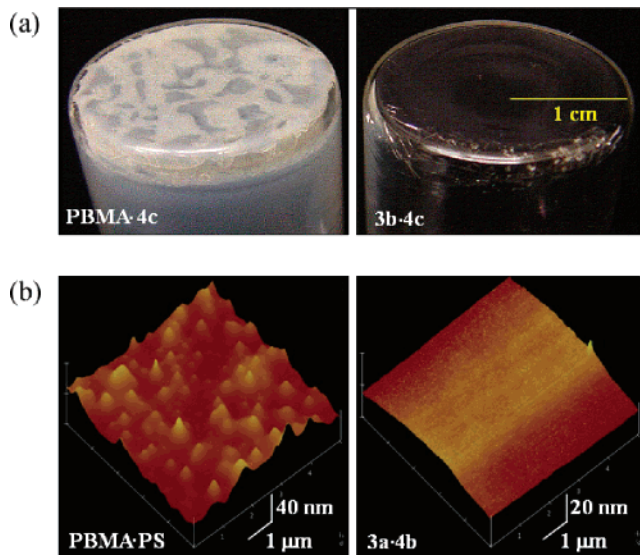


**Figure 3.**  $^1\text{H}$  NMR spectra in chloroform-*d* at various [UG]/[DAN] ratios (room temperature). **3a** exhibited unidentified, weak self-association of UG, which appeared in polymeric systems containing excess UG moiety (▼). Concentration of mixtures: 3.5 g/dL for **3a-4b**, 1.5 g/dL for **3b-4b**.

complexed DAN on the NMR time scale. In addition, there is no self-association of DAN (**4b** in Figure 3), consistent with previous observations.<sup>12a</sup> As a result, the excess (uncomplexed) DAN units appear to be involved in the intermolecular hetero-complexation of UG units through fast exchange with complexed units. In contrast, when UG is in excess, the exchange between free and complexed UG was slow on the NMR time scale, as evidenced by the lack of change in the peak positions of the complexed UG and the appearance of a weakly self-associated species (▼ in Figure 3).

#### Morphology Study of a Supramolecular Polymer Blend.

Figure 4a shows films of **PBMA-4c** and **3b-4c** prepared from the slow drying of a chloroform solution (4 g/dL, 1:1 w/w). The **3b-4c** film was homogeneous, colorless, and transparent.<sup>13a,16</sup> In contrast, a mixture of **PBMA** and **4c** gave a solid with thick, white domains (millimeter dimensions) that likely contain mostly **4c**. AFM images provide nanoscopic evidence for the homogeneous mixing without phase separation (Figure 4b).<sup>13,17</sup> The thin film prepared by casting a 1.0 g/dL solution of **PBMA** and **PS** in chloroform on mica exhibited islands with lateral dimensions ranging from ca. 100 to 40 nm (Figure 4b).



**Figure 4.** (a) Photographs of **PBMA-4c** and **3b-4c** films prepared from slow drying of a chloroform solution. (b) Tapping mode AFM images of **PBMA-PS** and **3a-4b** thin films prepared from solution-casting on mica.

However, the thin film of a mixture of **3a** and **4b** both having 4 mol % recognition unit, prepared in the same way as that above, was smooth, with no features evident on the nanometer scale. These observations are consistent with the formation of a miscible blend driven by the DAN-UG recognition. Although the structure of the polymer assembly is not known, it is likely that a supramolecular network is formed.

Differential scanning calorimetry (DSC) was performed on mixtures of **3b** and **4c**, which were prepared by manual melt mixing on glass for ~5 min at 120 °C. To erase any thermal history, we took the sample through a 10 min isothermal stage before the first cooling step. A control study was carried out using a mixture of **3b** and **PS** prepared identically to the **3b-4c** mixture. The DSC of the **3b-PS** mixture exhibited two endothermic relaxation peaks at 43 and 104 °C, indicating phase separation.<sup>18</sup> The two glass-transition temperatures ( $T_g$ ) for the mixture corresponded to those observed for the individual polymers. Consistent with the formation of homogeneous blends,<sup>18</sup> 1:1 and 1:2 w/w mixtures of **3b-4c** exhibited one endothermic peak that corresponded to the enthalpic relaxation of a homogeneous, glassy amorphous material. The glass-transition temperatures ( $T_g$ ), 73 and 80 °C, respectively, are located between those of **3b** (43 °C) and **4c** (104 °C) and depend on the ratio of the polymers.<sup>18,19</sup> It is noticeable that no clear transition was observed for the 2:1 w/w mixture of **3b** and **4c**.

#### SEC Study of the Aggregation of an Immiscible Polymer Pair through Molecular Recognition.

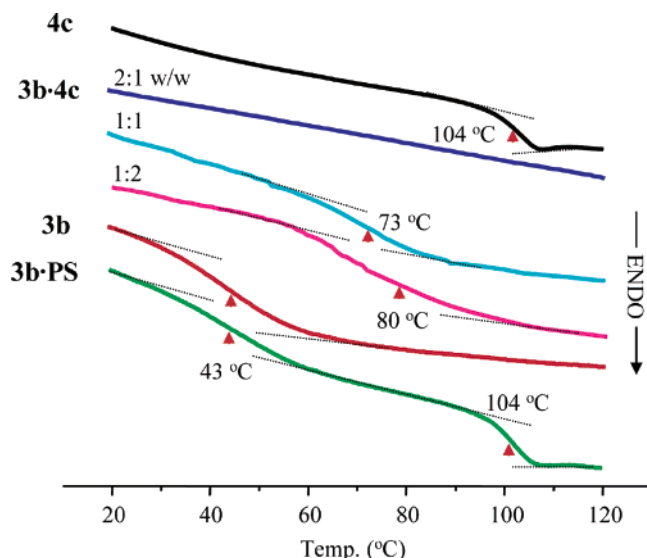
The aggregation of UG-PBMA and DAN-PS in toluene solution was examined using size-exclusion chromatography (SEC) with a UV detector set to 345 nm, a wavelength specific to the DAN moiety (Figure 6). Tailing of supramolecular assemblies can be caused by at

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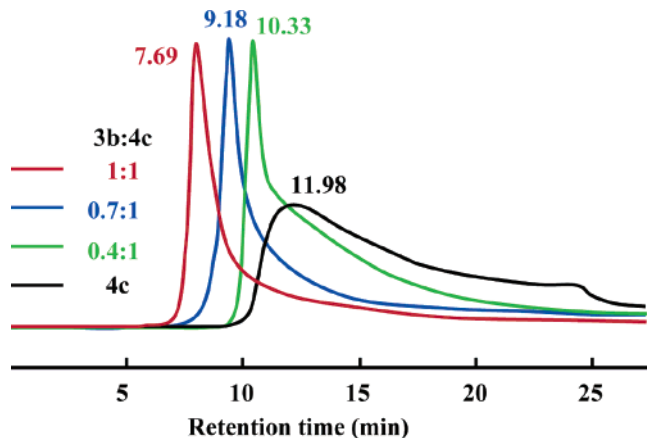
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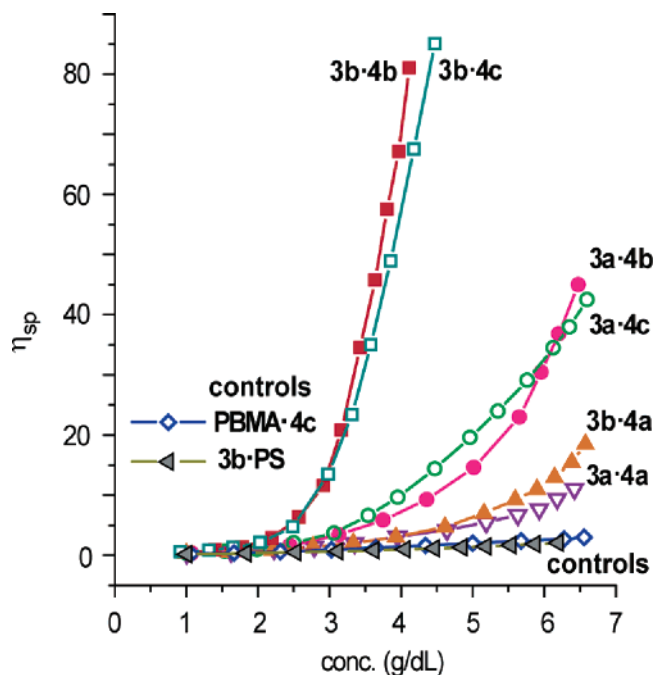


**Figure 5.** DSC thermograms (2nd heating) of three mixtures of **3b** and **4c** (2:1, 1:1, and 1:2 w/w) and three controls (**4c**, **3b**, and a mixture of **3b** and **PS**). Experimental conditions: melt mixing for the mixtures, 20 °C/min (1st heating) → 10 min of isothermal stage at 130 °C → 20 °C/min (cooling) → 20 °C/min (2nd heating). Baseline was not corrected.



**Figure 6.** SEC of **4c** and various weight ratios of **3b** and **4c** in toluene on a single column (HR4E). Ten microliters of the solution (~2.3 g/dL) were injected. A UV detector was used to detect DAN at 345 nm.

least two phenomena.<sup>20,21</sup> First, polar hydrogen-bond donor and acceptor groups may cause absorption of the materials to the cross-linked polystyrene packing in SEC columns. Secondary dissociation of units in dynamic equilibrium may become physically separated because of the flow and thus lose the chance to re-form a complex. Indeed, significant tailing due to the interaction with the solid phase was observed in **4c** containing DAN. However, with increasing amounts of **3b** added, the retention time and the tailing were progressively reduced, giving a sharp and narrow peak, as the strong complexation of UG and DAN minimized the interaction between DAN units and the packing material. The result is both consistent with the formation of a supramolecular polymer and multivalence pairings of PS and PBMA chains. The highest degree of aggregation was observed in a 1:1 wt % mixture of **3b** and **4c**



**Figure 7.** Plots of specific viscosity ( $\eta_{sp}$ ) of mixtures (1:1 w/w) of various DAN-PS **4** and UG-PBMA **3** with two control polymer mixtures (**PBMA-4c** and **3b-PS**) vs concentration.

at a concentration of ~2.3 g/dL. Larger assemblies could not be observed because of the high viscosity at higher concentration.

**Solution Viscosity Behavior and Aggregate Growth.** The blends were further characterized by measuring the solution viscosity of mixtures of PS-DAN and UG-PBMA in chloroform, using an Ubbelohde viscometer (Figure 7). Plots of specific viscosities ( $\eta_{sp}$ ) of two control polymer mixtures (**PBMA-4c** and **3b-PS**) vs concentration were linear over the concentration range 1–7 g/dL, indicating that there were no significant physical entanglements or noncovalent interactions between the random polymer coils at least within the range of molecular weights of the polymers used in this study.<sup>21</sup> However, consistent with the formation of suprastructures,<sup>3,4</sup> 1:1 (w/w) mixtures of DAN-PS **4** and UG-PBMA **3** exhibited large increases in  $\eta_{sp}$  with increasing concentration.

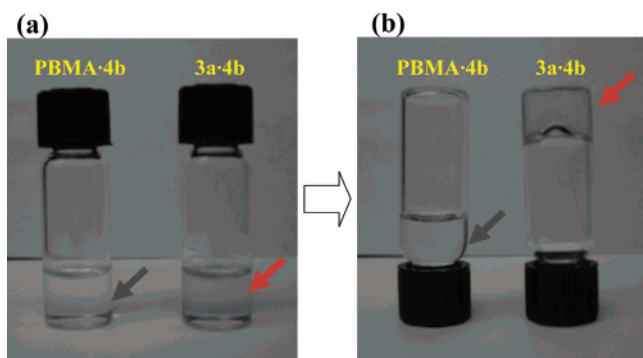
The increase in viscosity observed in Figure 7 depended on the mole ratio of recognition unit within the polymer and the molecular weight of the polymer. In general, the viscosity of a polymer solution depends on the size of the macromolecule, according to the Mark–Houwink equation. The aggregation of macromolecular chains in dilute solution driven by hydrogen bonding might lead to an unentangled reversible supramolecular polymer network, because entanglement of low-molecular-weight macromolecular chains would not be expected.<sup>23</sup> Thus, the viscosity increase may result from the altered dynamic motion of the polymer coil, which is constrained and slowed by reversible hydrogen bonding between neighboring polymer coils. The extent of this effect would likely depend on the lifetime or the binding constant of the hydrogen-bonding interactions and the number of interactions between polymer

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**Figure 8.** Photographs of a control (**PBMA-4b**) and a supramolecular polymer (**3a-4b**) solution in chloroform at the same concentration (15 g/dL).

chains. A number of factors can lead to a higher-viscosity polymer solution. For example, higher MWs generally correlate with higher viscosities. It was anticipated that a higher density of recognition units would be a critical parameter in obtaining high viscosity increases when comparing polymers of similar molecular weights. Indeed, the viscosity increases observed for chloroform solutions of **3b-4b** or **3b-4c** were much larger than those of **3a-4b** or **3a-4c**, even though the molecular weight of **3b** (16 kD) is smaller than that of **3a** (28 kD). Polymer **4a**, with an average of 1.4 recognition units per chain, showed only a modest increase in viscosity with concentration. Thus, it appears that more than a single connection between polymer chains is required.

The supramolecular polymer could be visualized macroscopically with a 2:1 (w/w) mixture of **3a** and **4b** in chloroform forming a gel, whereas at the same concentration (15 g/dL), a solution of **PBMA** and **4b** lacking any specific interpolymer interaction flowed freely (Figure 8). The molecular weight of **PBMA** (29 kD) is similar to that of **3a** (28 kD), so that the difference in properties qualitatively indicates that intermolecular recognitions of UG and DAN units on the polymers **3a** and **4b**, respectively, are responsible for the significant increases in viscosity.

More details of the aggregation driven by strong complexation of UG and DAN are found in the double logarithmic plots of  $\eta_{sp}$  and concentration (g/dL), as shown in Figure 9a. The slopes for mixtures of **3b-4b** (1:1 w/w) and **3a-4b** (2:1 to 1:2 w/w) over a certain concentration range from 3.98 to 5.68, values that are higher than that ( $\sim 3.6$ ) predicted<sup>4a,c,21</sup> from the reptation model of a telechelic type of living polymer ( $F = 2$ ).<sup>24</sup> The larger slopes are due to the higher mole percent of the recognition units ( $F > 4$ ) in the polymers used in this study. The data are consistent with the <sup>1</sup>H NMR results described above, both sets of data indicating that the UG and DAN units on the polymers fully participate in intermolecular interactions. Interestingly, the slope for a 1:1 (w/w) mixture of **3b-4b** ([UG]/[DAN] = 2.5) is higher than that of **3a-4b** ([UG]/[DAN] = 1.0) despite the fact that the molecular weight of **3a** (28 kD) is higher than that of **3b** (16 kD). As observed in the <sup>1</sup>H NMR experiments (Figure 3), the excess UG units on **3b** are not involved in the heterocomplexation of DAN units on **4b**, but rather increase viscosity through weak self-association.

To examine this issue in more detail, additional viscometric measurements were carried out on blend of **3a-4b** with different

weight ratios of the polymers. These two polymers each have 4 mol % recognition units and similar molecular weights. As seen in Figure 9a, when the amount of **3a** is increased (more UG units) the viscosities are higher and the slope of the log–log plot is higher. This is fully consistent with the conclusion above that excess UG units participate by weakly self-associating. Indeed, in examining **PBMA**, **3a**, and **3b** alone, we find that the weak self-association of UG units produces slopes in the viscosity plot of 1.09, 1.65, and 1.98, respectively (Figure 9b).

Aggregation driven by the weak self-association of UG units occurs even in dilute concentrations. Thus, the hydrodynamic radius ( $R_h$ ) of **3b**, measured by dynamic light scattering (DLS), at the overlap concentration<sup>26</sup>  $C^*$  ( $\sim 0.8$  g/dL) in chloroform was 6.4 nm, which is almost 3-fold bigger than that in THF (2.3 nm), where UG self-association is minimal. In addition, with increasing concentration over  $C^*$ , formation of very large particles was observed (Figure 10a). In contrast, the  $R_h$  values of **PBMA** as controls were 3.1 and 2.7 nm at the overlap concentration ( $C^* \approx 0.7$  g/dL) in THF and chloroform, respectively. Furthermore, the  $R_h$  of **PBMA** in chloroform decreased with increasing concentration, a typical behavior for noninteracting polymer coils.<sup>26</sup>

In looking at the viscosity increases in Figure 9a, it was interesting to note the presence of a universal transition viscosity, characterized by a change in slope in the  $\log(\eta_{sp})$  vs  $\log(c)$  plots. This transition viscosity is dependent on concentration, occurring at  $\log(\eta_{sp}) = 0.25$ – $0.50$  with the slope increasing from 1.52–1.99 to more than 3.79 (Figure 9a). Occurring at relatively constant  $\eta_{sp}$ , and therefore similarly rigid aggregates, the transition may represent the concentration at which supramolecular aggregates start to overlap. This concentration can be defined as  $C_{supra}^* = 3M_{w,supra}/N_A 4\pi R_{g,supra}^3$ , where  $M_{w,supra}$  and  $R_{g,supra}$  are the molecular weight and radius of gyration for supramolecular aggregates, respectively, and  $N_A$  is Avogadro's number.<sup>27</sup> Therefore, the higher  $C_{supra}^*$  values would correspond to denser supramolecular structures at dilute concentration (and vice versa). For example, the excess DAN units in the 1:2 weight ratio of **3b-4b** are involved in the heterocomplexation of UG units within the same aggregate, whereas excess UG units (2:1 w/w) weakly link the less-dense supramolecular aggregates, creating interparticle connections.

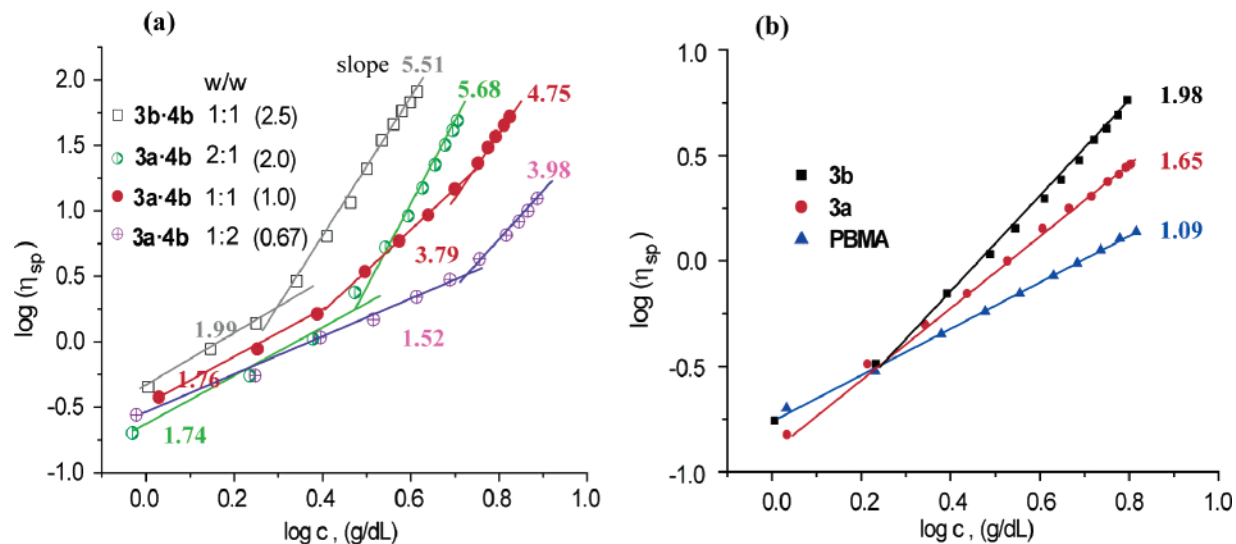
The DLS data in panels b and c of Figure 10 show the growth of aggregates as well as their distribution. Polymer **3b** fixed at two concentrations (0.56 and 1.13 g/dL) was titrated with **4b**. At the lower concentration of **3b** (0.56 g/dL), the degree of aggregation was lower and the distribution of the aggregates was more homogeneous. This result suggests a dynamic process whereby most of the aggregates have sufficient freedom to exchange polymers and form uniform particles. On the other

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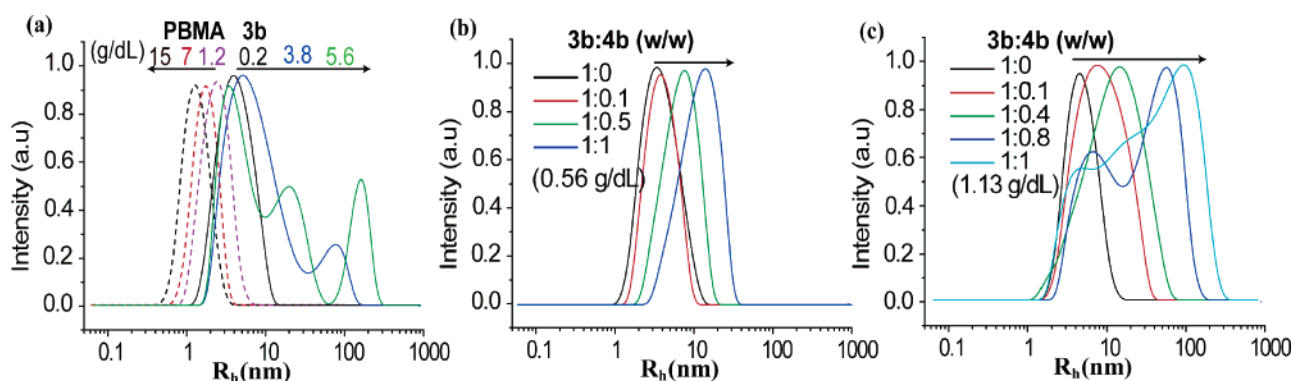
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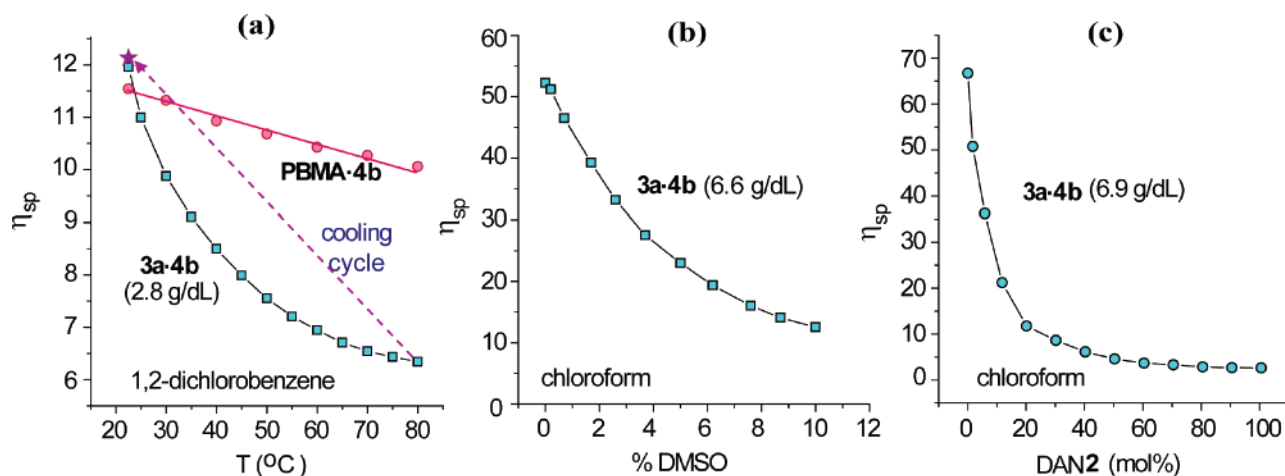
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**Figure 9.** Double logarithmic plots of  $\eta_{sp}$  and concentration (g/dL): (a) Effect of recognition unit ratios, [UG]/[DAN], on the slopes; 1:1 w/w for 3b:4b (2.5) and 3a:4b (1.0), 2:1 for 3a:4b (2.0), 1:2 for 3a:4b (0.67). The values in parentheses indicate recognition unit ratios, [UG]/[DAN], on polymers. (b) Comparison of slopes in PBMA and UG-PBMA (3a and 3b).



**Figure 10.** Distribution of the hydrodynamic radius ( $R_h$ ) of PBMA, 3b, and reversible supramolecular network polymers, measured by DLS in chloroform at room temperature. (a) Concentration dependence of noninteractive (PBMA) and interactive polymer (3b). (b) Titration of 3b with 4b at a concentration of 0.56 g/dL. (c) Titration of 3b with 4b at a concentration of 1.13 g/dL. Plots are normalized with an arbitrary scattered intensity.



**Figure 11.** Dependences of specific viscosities ( $\eta_{sp}$ ) of supramolecular network polymers on external stimuli. (a) Temperature: ( $\blacksquare$ ) 2.8 g/dL of 3a and 4b (2:1 w/w) in 1,2-dichlorobenzene, ( $\square$ ) recovered viscosity of a supramolecule after cooling from 80 °C, ( $\bullet$ ) a mixture of PBMA and 4b as control. (b) % DMSO: 6.6 g/dL of 3a and 4b (2:1 w/w) in chloroform. (c) Mole percent DAN added to a solution of 3a and 4b (6.6 g/dL, 2:1 w/w) in chloroform.

hand, larger aggregates lead to viscous solutions where larger heterogeneous particle distribution results from a slow dynamic exchange (Figure 10c).

**Reversibility of Supramolecular Polymer Formation.** The reversibility of supramolecular polymer formation was inves-

tigated because the ability to form or break the hydrogen bonds by external stimuli is a key reason for the interest in these materials. Panels a and b of Figure 11 show the dependence of viscosities on temperature and solvent polarity, respectively. The viscosity of a mixture of 3a and 4b (2.8 g/dL, 2:1 w/w) in 1,2-

dichlorobenzene exhibited an exponential decrease in  $\eta_{sp}$  with increasing temperature, in contrast to the results of the control mixture (**PBMA** and **4b**). In the latter case, the dynamic motion of a polymer coil is faster at higher temperatures, leading to the decreased viscosity, whereas for **3a-4b**, the rapid decrease in  $\eta_{sp}$  can be ascribed to weakened hydrogen bonding, resulting in network disassembly. Upon being cooled to 26 from 80 °C, the aggregates spontaneously re-formed, returning to the original, higher viscosity.

A similar result was observed upon the addition of DMSO to a chloroform solution of a mixture of **3a** and **4b** (6.6 g/dL, 1:1 w/w), in which the viscosity decreased progressively. The addition of ca. 20% v/v DMSO resulted in the loss of viscosity obtained by hydrogen bonding, indicating complete disassembly of the aggregates. In addition to heat and solvent polarity, it was anticipated that the aggregates might be disassembled by the addition of **2**. Thus, free DAN would compete with DAN linked to PS and displace it, resulting in breaking the intermolecular contacts between polymer coils. Indeed, a dramatic decrease in viscosity was observed upon addition of DAN (Figure 11c). As the concentration of free DAN reached the point where it was 20–40% that of polymer-bound DAN, the  $\eta_{sp}$  dropped to ca. 5–10% of its original value.

## Conclusion

Several recently reported, multiply hydrogen-bonded complexes have created an important toolkit for chemists interested in creating supramolecular polymers. For the formation of supramolecular blends from an immiscible polymer pair, where strong repulsive forces exist, UG and DAN have been found to be quite useful as a result of the high stability and fidelity of their heterocomplex. Specifically, DAN and UG units were displayed along the backbone of immiscible polymers, PS and PBMA (DAN-PS and UG-PBMA), respectively. Both polymers were readily prepared via radical copolymerization. It was found that intermolecular recognition between two different polymer coils occurred, connecting PS and PBMA coils at the molecular level. The mixture of UG-PBMA and DAN-PS formed colorless and transparent films with no evidence of phase separation on either the nano- or macroscopic scale. A differential scanning calorimetry study further demonstrated the formation of a homogeneous blend with a single endothermic peak, corresponding to the enthalpy relaxation of an amorphous material with one major composition. SEC, viscosity, and DLS studies also demonstrated the formation of a supramolecular polymer. The properties of the resulting supramolecular blends are tunable as well as thermoreversible. The key finding is that miscible blends were formed even though a low mol % of the recognition units was incorporated into the polymers. This result underscores the importance of high-affinity and high-fidelity heterocomplexation in the creating of new supramolecular polymer architectures.

## Experimental Section

**General Experimental.** All reactions were carried out under a dry nitrogen atmosphere. Reaction temperatures reported are the temperatures of the heating medium. DMF was distilled from sodium hydride under a vacuum prior to use. DMSO was distilled from calcium hydride under a vacuum prior to use. Butyl methacrylate and styrene were passed over aluminum oxide (activated, basic) and then distilled from calcium hydride at reduced pressure prior to use. All other chemicals

and reagents were of reagent grade and were used as received without further purification.

Melting points were measured on a Thomas–Hoover melting point apparatus and are uncorrected. Brine refers to a saturated aqueous solution of NaCl. All NMR spectra were acquired in the VOICE laboratory, University of Illinois, Urbana-Champaign, with Varian Unity 500 MHz instrument. Chemical shifts are in parts per million and coupling constants ( $J$ ) are in Hertz. For  $^1\text{H}$  spectra, chemical shifts are referenced to the residual protio solvent peak: 7.26 ppm for chloroform- $d$ , 2.50 ppm for DMSO- $d_6$ . For  $^{13}\text{C}$  spectra, chemical shifts are referenced to the solvent peak at 77.5 ppm in chloroform- $d$  and 39.5 ppm in DMSO- $d_6$ .

Molecular weights against polystyrene standards were estimated at 30 °C in THF at a flow rate of 1.0 mL/min using a Viscotek SEC (TDA model 300) equipped with a Hitachi autosampler (L-7250), a Hitachi pump (L-7100), and a Viscotek refractive index detector (300 RI). SEC experiment for study of the formation of aggregates was carried out at room temperature in toluene at a flow rate of 1.0 mL/min using SEC (single column, HR4E) equipped with a Hitachi pump (L-6000) and a Hitachi UV detector (L-4000L). Viscosity was measured in chloroform using an Ubbelohde viscometer (Cannon, 75L50) at 26 °C. Hydrodynamic radius ( $R_h$ ) and distribution were collected at room temperature using a protein solution DLS (DynaPro) and analyzed with Dynamics V6 software. For the DLS and viscometry experiments, solutions of polymers and solvents were filtered using a 0.2  $\mu\text{m}$  PTFE filter (Millipore). The filtrate was precipitated into methanol, collected, and dried. Glass-transition temperatures ( $T_g$ ) were determined at heating and cooling rates of 20 °C/min under nitrogen using a Pyris Perkin–Elmer DSC and reported as the midpoint of the second heating. Surface topography was examined at a scan rate of 1.969 Hz using a Digital Instrument atomic force microscope (multimode AMF) in tapping mode with a TappingMode silicon probe (NanoDevices Metrology tip, type TAP300). The collected images were flattened using Nanoscope III software (Digital Instrument).

**Succinic Acid 6-[2-(3-Butyl-ureido)-6-oxo-1,6-dihydro-purin-9-yl]-2,2-dimethyl-tetrahydro-furo[3,4-d][1,3]dioxol-4-ylmethyl Ester 2-(2-Methyl-acryloyloxy)-ethyl Ester (UG-BMA, **7**).** A mixture of 780 mg (6.0 mmol) of 2-hydroxyethyl methacrylate, 2.1 g (4.0 mmol) of carboxylated UG **5**,<sup>12a</sup> 866 mg (4.4 mmol) of EDCI, and 66 mg (0.6 mmol) of DMAP in 30 mL of DMF was stirred overnight at room temperature. The solvent was removed using a rotary evaporator equipped with a high vacuum. The crude gel was dissolved in 50 mL of chloroform, and 30 mL of water was poured into the solution. The organic layer was collected, and the aqueous layer was extracted three times with 30 mL of chloroform. The combined organic layers were washed with 30 mL of brine, dried over  $\text{MgSO}_4$ , filtered, and reduced. The crude material was purified by column chromatography ( $\text{SiO}_2$ ,  $R_f$  = 0.25, 9:1 chloroform:methanol) to give 1.78 g (71%) of **7** as a white solid. Mp: 69.0–71.5 °C (chloroform/methanol).  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ):  $\delta$  11.95 (1H, s), 9.91 (1H, s), 8.00 (1H, s), 7.17 (1H, s), 6.03 (1H, d,  $J$  = 1.8), 5.97 (1H, s), 5.63 (1H, s), 5.25 (1H, dd,  $J$  = 2.1, 6.3), 5.02 (1H, dd,  $J$  = 3.4, 5.8), 4.33 (1H, q,  $J$  = 2.1, 6.3), 4.22 (5H, m), 4.13 (1H, m), 3.14 (2H, m), 2.46–2.40 (4H, m), 1.81 (3H, s), 1.51 (3H, s), 1.46–1.40 (2H, m), 1.31–1.26 (5H, m), 0.88 (6H, t,  $J$  = 6.8).  $^{13}\text{C}$  NMR (125 MHz, DMSO- $d_6$ ):  $\delta$  172.4, 172.3, 167.0, 155.5, 149.1, 137.8, 136.2, 126.7, 120.1, 114.1, 89.8, 84.7, 84.6, 81.6, 64.7, 63.0, 62.6, 39.4, 32.3, 32.0, 29.0, 28.9, 27.6, 26.0, 25.8, 25.0, 20.1, 18.5, and 14.2.  $m/z$  (ESI): 635.2650 [(M + H) $^+$ ];  $\text{C}_{28}\text{H}_{39}\text{N}_6\text{O}_{11}$  requires  $M$ , 635.2677.

**Decanedioic Acid Mono-(4-vinyl-benzyl) Ester (St-CO<sub>2</sub>H, **11**).** A mixture of 2.64 g (17.3 mmol) of 4-vinylbenzyl chloride, 7.0 g (34.6 mmol) of sebacic acid, 7.2 g (51.9 mmol) of  $\text{K}_2\text{CO}_3$ , and 53 mg (0.2 mmol) of 18-crown-6 in 150 mL of DMF was stirred overnight at 110 °C. Water (10 mL) was added to the mixture, and the solvent was removed using a rotary evaporator equipped with high vacuum. Ethyl acetate (200 mL) was poured into the remaining solid, and the resulting



slurry was stirred. The insoluble solid was filtered off. The filtrate was washed three times with 40 mL of water. The organic layer was collected, dried over  $\text{MgSO}_4$ , filtered, and reduced. The crude material was purified by column chromatography ( $\text{SiO}_2$ ,  $R_f = 0.55$ , ethyl acetate) to give 2.2 g (40%) of **11** as a white solid. Mp: 62.5–64.0 °C (chloroform/methanol).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.44 (1H, br s), 7.40 (2H, d,  $J = 8.2$ ), 7.31 (2H, d,  $J = 8.2$ ), 6.72 (H, dd,  $J = 10.8$ , 17.6), 5.76 (H, d,  $J = 17.6$ ), 5.26 (H, d,  $J = 10.8$ ), 5.10 (2H, s), 2.36–2.32 (4H, m), 1.66–1.59 (4H, m), 1.33–1.29 (4H, m).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  179.9, 173.9, 136.6, 128.7, 128.6, 126.6, 125.9, 114.5, 66.1, 65.9, 65.7, 34.5, 34.1, 29.1, 25.1 and 24.8.  $m/z$  (ESI): 319.1897 [(M + H) $^+$ ];  $\text{C}_{19}\text{H}_{27}\text{O}_4$  requires  $M$ , 319.1909.

**9-(7-Heptanoylamino-[1,8]naphthyridin-2-ylcarbamoyl)-nonanoic Acid 4-Vinyl-benzyl Ester (DAN-St, 12).** A mixture of 1.57 g (4.93 mmol) of St- $\text{CO}_2\text{H}$  **10**, 1.34 g (4.93 mmol) of amino naphthyridine **13**,<sup>12a</sup> 0.95 g (4.9 mmol) of EDCI, and 60 mg (0.5 mmol) of DMAP in 30 mL of DMF was stirred overnight at room temperature. The solvent was removed using a rotary evaporator equipped with a high vacuum. The crude gel was dissolved in 100 mL of chloroform, and 50 mL of water was poured into the solution. The organic layer was collected, and the aqueous layer was extracted three times with 30 mL of  $\text{CHCl}_3$ . The combined organic layers were washed with 30 mL of brine, dried over  $\text{MgSO}_4$ , filtered, and reduced. The crude material was purified by column chromatography ( $\text{SiO}_2$ ,  $R_f = 0.33$ , 95:5 chloroform:methanol) to give 2.65 g (94%) of **12** as a white solid. Mp: 135–137 °C (chloroform/methanol).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.43 (2H, d,  $J = 8.8$ ), 8.40 (2H, br s), 8.12 (2H, d,  $J = 8.8$ ), 7.39 (2H, d,  $J = 8.2$ ), 7.30 (2H, d,  $J = 8.2$ ), 6.70 (H, dd,  $J = 10.8$ , 17.6), 5.75 (H, d,  $J = 17.6$ ), 5.25 (H, d,  $J = 10.8$ ), 5.08 (2H, s), 2.44 (4H, q,  $J = 7.0$  and 13.9), 2.33 (2H, t,  $J = 7.8$ ), 1.78–1.69 (4H, m), 1.62 (2H, t,  $J = 7.0$ ), 1.39–1.26 (10H, m), 0.88 (3H, t,  $J = 6.8$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  173.9, 173.0, 172.9, 154.4, 153.8, 139.3, 137.7, 136.6, 135.8, 128.7, 126.6, 118.4, 114.5, 113.8, 66.0, 38.0, 37.9, 34.5, 31.7, 29.3, 29.2, 29.0, 25.4, 25.1, 22.7 and 14.2.  $m/z$  (ESI) 573.3421 [(M + H) $^+$ ];  $\text{C}_{34}\text{H}_{45}\text{N}_4\text{O}_4$  requires  $M$ , 573.3441.

**UG-Attached Poly(butyl)methacrylate (UG-PBMA, 3).** The radical copolymerization under a nitrogen atmosphere in a 50 mL round-bottom flask sealed with a rubber septum followed a general procedure as outlined below. A solution of UG-BMA **7**, BMA, and AIBN in DMSO was stirred for 24 h at 60 °C. The reaction generated gel inside the flask. The solvent was decanted, and the resulting gel was then dissolved in chloroform followed by precipitation into methanol. The unreacted UG-BMA **7** was soluble in methanol. The precipitated gel was collected, redissolved in chloroform, and reprecipitated into

methanol. This process was done again. The collected gel was dried under a vacuum at 40 °C. **3a:** The general procedure for the radical polymerization using 253.7 mg (0.4 mmol) of UG-BMA **7**, 1.42 g (10 mmol) of BMA, and 32.8 mg (0.2 mmol) of AIBN in 42 mL of DMSO provided **3a**. **3b:** The general procedure for the radical polymerization using 634.3 mg (1.0 mmol) of UG-BMA **7**, 1.42 g (10 mmol) of BMA, and 32.8 mg (0.2 mmol) of AIBN in 42 mL of DMSO provided **3b**.  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  11.96 (s, NH), 9.92 (s, NH), 8.00 (s, CH), 7.16 (s, NH), 6.01 (s, CH), 5.25 (s, CH), 5.02 (s, CH), 4.30 (s, CH), 4.22–3.82 (br m, CH and  $\text{OCH}_2$ ), 3.14 (s,  $\text{CH}_2$ ), 2.00–0.88 (br m,  $\text{CH}_2$  and  $\text{CH}_3$ ).

**DAN-Attached Polystyrene (DAN-PS, 4).** The radical copolymerization under a nitrogen atmosphere in a 50 mL round-bottom flask sealed with a rubber septum followed a general procedure as outlined below. A solution of DAN-St **12**, styrene, and AIBN in DMSO was stirred for 48 h at 90 °C and then precipitated into methanol. The resulting solid was collected, redissolved in chloroform, and reprecipitated into methanol. This process was done again. The collected solid was dried under a vacuum at 40 °C. **4a:** The general procedure for the radical polymerization using 100 mg (0.17 mmol) of DAN-St **12**, 1.8 g (17.3 mmol) of styrene, and 12 mg (0.073 mmol) of AIBN in 20 mL of DMSO provided **4a**. **4b:** The general procedure for the radical polymerization using 790 mg (1.38 mmol) of DAN-St **12**, 3.44 g (33.1 mmol) of styrene, and 23 mg (0.14 mmol) of AIBN in 50 mL of DMSO provided **4b**. **4c:** The general procedure for the radical polymerization using 367 mg (0.64 mmol) of DAN-St **12**, 752 mg (7.23 mmol) of styrene, and 5.2 mg (0.031 mmol) of AIBN in 10 mL of DMSO provided **4c**.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.52 (d,  $J = 8.5$ , Ar-H in the naphthyridine), 8.35 (s, NH), 8.16 (d,  $J = 8.5$ , Ar-H in the naphthyridine), 7.35–7.00 (br s, Ar-H in styrene unit), 6.80–6.45 (br s, Ar-H in styrene unit), 5.10 (s, Ar- $\text{CH}_2\text{O}$ ), 2.44 (br s,  $\text{CH}_2$ ), 2.33 (br s,  $\text{CH}_2$ ), 2.14–1.79 (br s, H in styrene unit overlapped with  $\text{CH}_2$ ), 1.74–1.36 (br s, H in styrene unit overlapped with  $\text{CH}_2$ ), 1.23–1.15 (m,  $\text{CH}_2$ ), 1.04–0.96 (m,  $\text{CH}_3$ ).

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