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Interplay of Fidelity, Binding Strength, and Structure in Supramolecular Polymers

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The foundation of modern polymer chemistry rests to a large degree on structure−property relationships, which are just now being worked out for supramolecular polymers.[1] For example, we recently compared[2] polymer blends of polystyrene (PS) and poly(butyl methacrylate) (PBMA) driven by two related quadruply hydrogen bonded complexes, UG·DAN[3] and UPy·DAN[4] (see Figure 1a). The supramolecular network in **1·3** grew significantly faster with concentration than in **1·2**, as measured by the increased specific viscosity (η_{SP}), a result attributed to the greater fidelity of assembly of the UG·DAN complex.

Herein we report a more extensive structure−property investigation of these blends, using the increase in η_{SP} with concentration to measure the growth of the supramolecular network. The study was prompted by two unexpected observations. The first came in examining the self-association of **2** and **3** in chloroform.[5] Both PBMA **2b** (20 kD) and **3b** (16 kD) have similar M_w and 10 mol % of recognition units UPy and UG, respectively. Given that the UPy dimerization constant ($K_{dimer} \approx 6 \times 10^7$ M^{-1})[6] is orders of magnitude higher than that for UG ($K_{dimer} \approx 200$ M^{-1}),[3] interchain aggregation should be significantly stronger. Indeed, the stability of the UPy dimer led it to be incorporated into similar supramolecular networks.[7] Thus, it was surprising that **3b** gives a steeper η_{SP} plot than does **2b** (Figure 1b, see bottom three curves).

Second, it was expected that increasing the number of recognition units along the polymer backbone would cause the onset of increased viscosity to occur at a lower concentration. In examining blends of polystyrene (PS) **1** (M_w = 23 kD) with 4 mol % of DAN and PBMA **2**, as the mol % of UPy in **2** is increased **2a** (4 mol %, 32 kD) → **2b** (10 mol %, 20 kD) → **2c** (16 mol %, 17 kD), the η_{SP} minimally changed (Figure 1b, top three curves). The picture was complicated because along the same series the polymer M_w decreased. Nonetheless, similar studies with **3** (vide infra) suggested that the M_w differences alone were insufficient to account for the similar viscosity plots.[2b]

Both results could potentially be explained by intramolecular dimerization of UPy. Indeed, the earlier increase in η_{SP} with concentration seen with **1·3** relative to **1·2** was previously attributed to the higher fidelity in the UG·DAN versus UPy·DAN complex;[2] that is, it was hypothesized that strong intramolecular dimerization led the UPy unit being tied up in intramolecular dimers and unavailable for blend formation.[8] To examine whether this is indeed the case and whether intramolecular dimerization increased along the series **2a** → **2b** → **2c**, the ^{1}H NMR of the blends was examined and compared to that of the UPy dimer and the UPy·DAN heterocomplex (Figure 2).

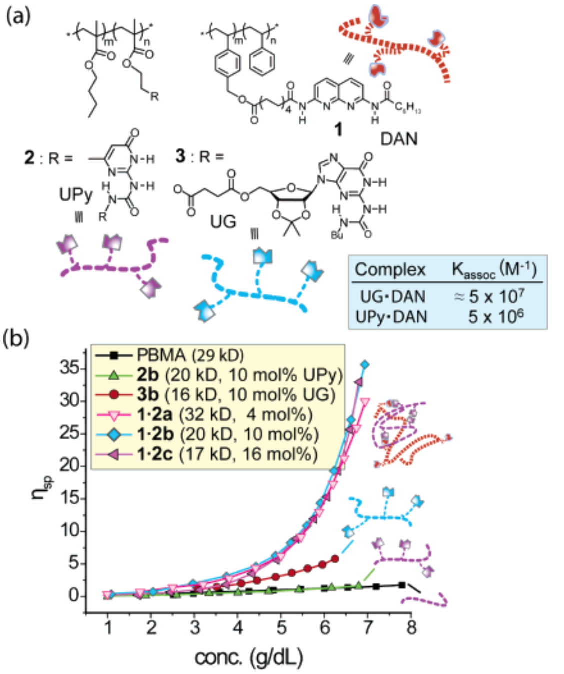

Figure 1. (a) Structure of polymers used in this study. (b) Specific viscosity (CHCl$_3$) versus concentration plots for polymers and blends. Legend indicates polymer properties. For **1**, M_w = 23 kD, M_n = 13 kD, 4 mol % of DAN. See Supporting Information for details.

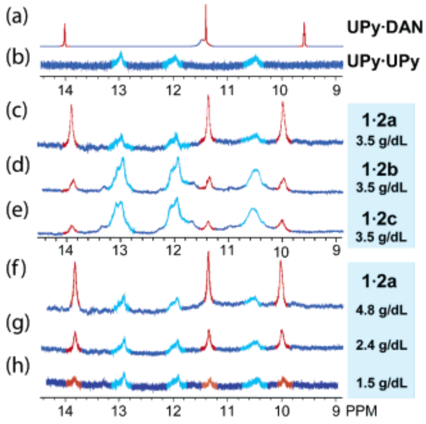

Figure 2. ^{1}H NMR spectra in CDCl$_3$. (a) UPy·DAN complex; (b) UPy dimer (**2a**); (c−e) increase in mol % of UPy; (f−h) dilution of **1·2a**. See Supporting Information for details, including additional NMR comparison data for **1·3a**.

A chloroform-*d* spectrum of a model UPy·DAN complex and UPy dimer is shown in Figure 2a and b, respectively, for comparison. As the UPy content in the blend is increased along the series **2a** → **2b** → **2c**, the signals for the UPy dimer grow in intensity (Figure 2c−e). However, this observation does not provide information about whether the pairings are intra- or interchain. As seen in Figure 2f−h, when a 1:1 mixture (in recognition units) of **1** and **2a** is diluted, the resonances corresponding to the UPy·DAN contacts diminish more rapidly despite the fact that the equilibrium

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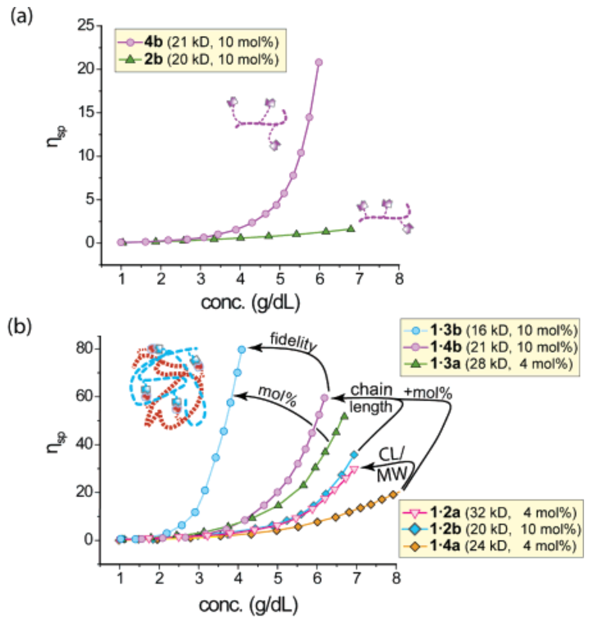
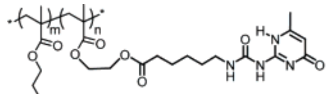


Figure 3. Specific viscosity (η_{SP}, $CHCl_3$) versus concentration plots for individual polymers and blends. CL = chain length. Legends indicate polymer properties. See Supporting Information for details.

constant for 2DAN + $UPy_2 \rightleftharpoons$ 2UPy·DAN has been measured to be quite large ($K = 4 \times 10^5$ M^{-1}).[4a] These data indicate that intramolecular dimerization of UPy is indeed competing with the interchain UPy·DAN interactions.[5] These data may further explain why unfunctionalized PBMA (M_w = 29 kD) exhibits a viscosity plot superimposable on that for **2b** (M_w = 20 kD, Figure 1). In principle, the UG unit in **3** is also capable of intramolecular dimerization so its higher viscosity may be attributed to the longer chain linking it to the PBMA backbone.[5]



4a (24 kD, 4 mol%)
4b (21 kD, 10 mol%)

To address the importance of the linker chain length, PBMA **4a** and 4**b** were synthesized.[7] In **4**, the chain linking the UPy unit and the PBMA backbone approximates the length of that in **2**. As seen in Figure 3a, the longer linker in **4b** has a marked effect on the viscosity plot, and the stronger dimerization constant of the UPy unit now manifests itself in more rapid network growth. The longer linker chain may reduce the likelihood of intramolecular dimerization while at the same time favoring interpolymer contacts by requiring less interpenetration of the random coils.

The viscosity plots for several PBMA polymers blended with PS-DAN **1** are overlaid in Figure 3, including, for comparison, the plots for **1·2a**−**b** from Figure 1b. The linking chain effect seen in the self-association of **2**−**4** in Figure 3a is also observed in the polymer blends; for example, compare **1·2b** and **1·4b** in Figure 3b. Indeed, whereas increasing the mol % of UPy in **2** minimally affected its self-assembly, with the longer linker in **4** increasing, the UPy mol % from **4a** (4 mol %) to **4b** (10 mol %) leads to a more rapid onset in viscosity with concentration. The onset of higher viscosity in **1·3b** occurs at significantly lower concentration than for **1·4b**, indicating that the difference observed earlier cannot be attributed solely to the length of the linker chain, rather it is a reflection of the higher fidelity with which the UG·DAN complex forms. Another key factor is the absolute number of recognition units presented by the macromolecule, which is a function of the molecular weight (M_w) and mol % of the recognition unit. In comparing blend **1·4a** and **1·2a** (Figure 3b), increasing the linker length **2a** → **4a** actually leads to a lower viscosity because the M_w of **2a** is higher than that for **4a** (32 vs 24 kD), meaning that, although both polymers have UPy mol % = 4, **2a** on average presents 6.8 UPy units versus 4.6 for **4a**.[5]

In conclusion, we have provided ^1H NMR evidence that UPy units displayed along the backbone of PBMA are able to pair intramolecularly. The intra- versus intermolecular balance can be tilted by varying the length of the chain linking the recognition unit to the polymer backbone. Indeed, the UG unit in **3**, whose dimerization constant is orders of magnitude lower than that for UPy, can be a better promoter of assembly (i.e., **3b** vs **2b**). We imagine this finding can be extended to explain the performance of other systems, such as the Coates' polyolefin elastomers,[7b] whose 10 carbon chain linker makes it well suited for assembly. Beyond the linker chain length effect, the results described herein show that an interplay of fidelity, recognition unit mol %, and M_w controls the formation of polymeric supramolecular assemblies. These types of design rules have the potential to facilitate the development of new materials.

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Supporting Information Available: Longer list of citations to relevant literature, detailed synthetic procedures, characterization, NMR and viscosity data for polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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