Using Aromatic Donor Acceptor Interactions to Affect Macromolecular Assembly

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The molecular structure and unique functions of many natural polymers result from extensive noncovalent interactions between chains. Coded information in the DNA double helix, the tensile strength and elasticity of spider silk, the quaternary structures of protein assemblies, and RNA recognition all utilize some combination of hydrogen bonding, complementary electrostatics, hydrophobic contacts, and aromatic−aromatic interactions to achieve their amazing functions.[1] These interactions also play a critical role in defining the properties of many synthetic polymers such as nylons and the aromatic polyamides used for bulletproof vests.[2]

Recent advances in supramolecular chemistry have yielded a variety of tools for the rational design and utilization of directed noncovalent interactions in polymers.[3] This includes the self-complementary donor−acceptor (and derivatives thereof) hydrogen bonding units such as the UPy unit of Meijer and co-workers[4,5] which interact with a high dimerization constant in organic solvent. Extensive work by Rotello and co-workers has explored hydrogen bonding directed self-assembly in various polymer systems including their "plug and play" design.[6] A second major class of noncovalent interactions utilizes metal-coordination, including palladium "pincer" ligands, to direct interaction and assembly.[7] Weck and co-workers have exploited the orthogonal assembly modes of metal-coordination and hydrogen bonding by using both simultaneously in recent work,[8] and these along with similar designs have been utilized to form supramolecular architectures that have recently been incorporated into covalent polymers and polymer blends to modulate solution and solid-state properties.[9]

A third type of noncovalent interaction, namely aromatic−aromatic interactions, has also been used to affect molecular assemblies in solution.[10,11] In contrast to hydrogen bonding and metal-coordination systems, the solvophobic driving force of this interaction allows for enhanced assembly in water.[12] We have utilized aromatic donor−acceptor interactions, specifically electron rich 1,5-dialkoxynaphthalene (Dan) with electron poor 1,4,5,8-naphthalene-tetracarboxylic diimide (Ndi), to promote directed folding of linear molecules in water.[13] Recently, we have shown that short oligomers of independent Dan and Ndi can form discrete hetero duplexes with high affinity in water,[14] while Li and co-workers as well as Ramakrishnan and co-workers have carried out similar studies in organic solvent.[15,16] In this communication, we extend the use of the Dan−Ndi interaction to preliminary results in affecting solid-state structures from aqueous polymer chains.

Synthesis of the independent Dan and Ndi polymers was achieved by functionalization of polyethylene-*alt*-maleic anhydride with previously reported Dan and Ndi monomers[13d] to yield P1 and P2 (Figure 1) according to Scheme 1. This approach generates a relatively large number of negative charges on each polymer chain, which are intended to provide for solubility in water as well as keep the chains elongated in solution to facilitate interactions between complementary polymer strands.

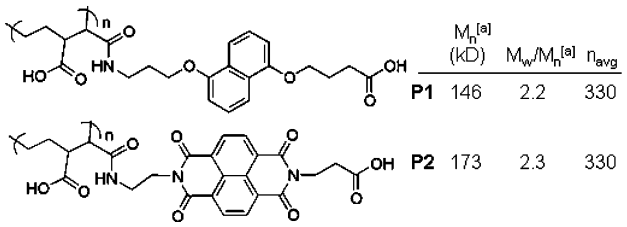
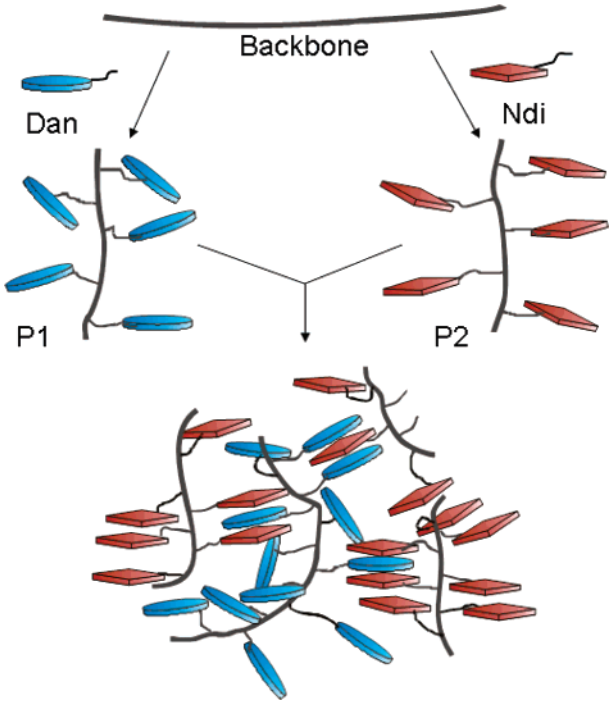


Figure 1. PolyDan (P1) and PolyNdi (P2). Footnote a: calculated from characterization data of polymer backbone and monomer incorporation.

Scheme 1[a]



[a] Representation of PolyDan and PolyNdi synthesis and their combination to form supramolecular structures.

Solubility in water is a major challenge for polymers containing multiple large aromatic groups. While P2 was soluble up to 3% weight in 0.2 M NaOH, isolated P1 was not soluble in basic water without the addition of detergent. However, adding an equal aromatic equivalent of P2 to P1 (3% weight total polymer in 0.2 M NaOH) resulted in a very viscous, purple liquid. The visible absorbance spectrum of the mixture revealed the presence of a charge-transfer absorbance band at 560 nm and hypochromism of the Ndi absorbance, both consistent with Dan−Ndi stacking interactions.[17] Viscosity measurements at 3% total weight of polymer in 0.2 M NaOH for P1 + SDS detergent, P2, and equal aromatic equivalents of P1 and P2 yielded viscosities of 2.5cP, 1.7cP, and 11.9 cP, respectively. The significant increase in viscosity of the mixed polymers verifies a high degree of interchain interaction in the P1 + P2 mixture.[18] Addition of SDS detergent to the P1 + P2 mixture has no observable effect on the viscosity of the mixed solution, indicating that Dan−Ndi face-centered stacking interactions,

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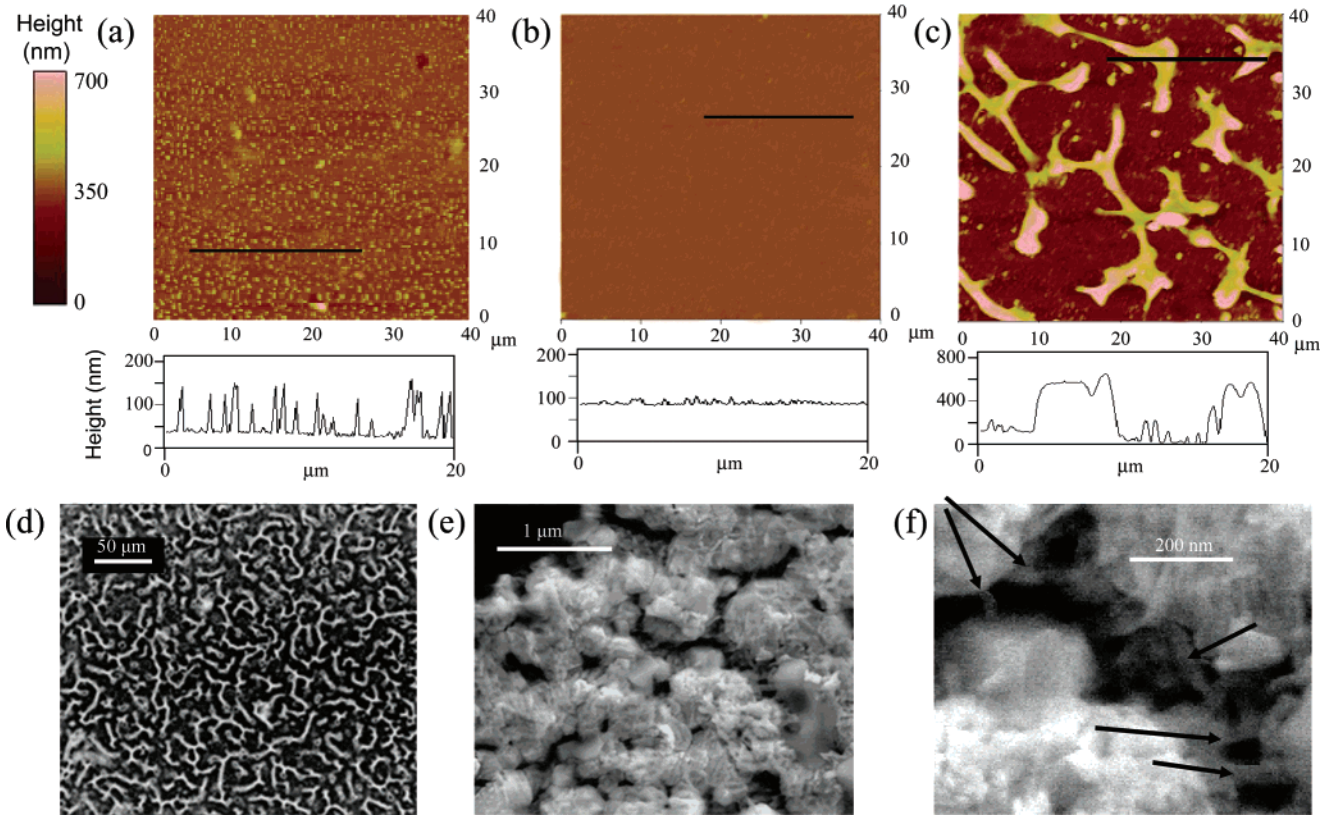

Figure 2. Tapping mode AFM (a, b, c). optical microscopy (d), and SEM images (e, f) of polymer films made from 0.2 M NaOH solutions (3% total weight polymer). Key: (a) P1 + 0.2 wt % sodium dodecyl sulfate surfactant (SDS), (b) P2, (c) equal aromatic equivalents of P1 and P2, (d) network of structures from equal aromatic equivalents of P1 and P2, (e) amorphous surface of the P1 and P2 structures seen in Figure 2c, and (f) threads spanning gaps between dense domains of P1 + P2 structures seen in Figure 2e.

perhaps in concert with some other mode of interaction that is not yet characterized, apparently drive association of the P1 and P2 chains to create a viscous and thus aggregated aqueous mixture in which the P1 polymer has been solubilized by P2. It should be noted that a comparison of the UV−Visible spectrum to those of model systems[13] indicates a relatively small fraction of the Dan and Ndi units are involved in interactions between P1 and P2 chains in the mixture. Although the reasons for this are not clear at this time, the extent of association present is sufficient to promote the desired assembly of the polymer chains and dramatically alter physical properties.

AFM was used to evaluate the solid-state structures of the polymers and their mixture. Thin films were spun from P1 solubilized with SDS, P2, and a mixture of P1 and P2. The solutions were spun onto glass supports and allowed to dry. Films were washed with 0.5 M HCl followed by water to remove sodium salts, and annealed at 180 °C for 24 h. AFM imaging carried out in tapping mode verified that films formed from the solution of P1 + SDS yielded roughly circular deposits with average widths and heights of 500 nm and 75 nm, respectively (Figure 2a). This texture is characteristic of micelles deposited on a surface.[19] Films made from solutions of P2 were smooth and uniform, displaying a thickness of about 100 nm (Figure 2b). The viscous, purple mixture of polymers P1 and P2 yielded structures approximately 700 nm high, 1.6 μm across and averaging 14 μm in length (Figure 2c). Optical microscopy shows these features uniformly over the film (Figure 2d). The macrostructure of the film from the combined polymers is quite distinct from either of the two films made with individual components, further indicating that the structures are the result of interactions between the unlike polymer chains. The Dan−Ndi stacking interaction drives the association of P1 and P2 into an integrated polymer network that results in large elongated structures upon film formation.

To investigate any anisotropy in the P1 + P2 film, polarization NSOM (near-field scanning optical microscopy) was preformed. No difference in the optical rotation of light along the long axis compared to the short axis of the structures was observed, suggesting that the film features and thus polymer backbone orientations are uniform in all directions.[20]

SEM was performed on the P1 + P2 film to further analyze the surface morphology. The film structures are made of small densely packed domains, averaging 300 nm in diameter (Figure 2e). The surface image shows a rough amorphous morphology for these domains consistent with the absence of anisotropy shown by the polarization NSOM results. Closer inspection of the disperse regions between domains reveals the presence of discrete polymer threads traversing the gaps between dense domains (Figure 2f). These threads have an average width of 30 nm, lengths of up to 200 nm, and they appear to be connecting densely packed regions. This is consistent with a model in which several polymer chains interact via a few Dan−Ndi interactions to form individual threads in solution, inducing the noted viscosity increase, then aggregate together upon film formation to form the rough amorphous regions. Threads on the periphery of the domains interact with other regions, connecting them together and forming the structures of the film.

Preliminary attempts at aligning the proposed P1 + P2 threads by forming fibers from the complementary polymer mixtures were made by precipitating them after quickly passing through a small aperture. When an aqueous solution of P1 + P2 (0.2 M NaOH, 3% total weight polymer) was injected via a 30 gauge needle into 1 M HCl it yielded long, delicate fibers (Figure 3a) up to several centimeters in length. Similar solutions of either

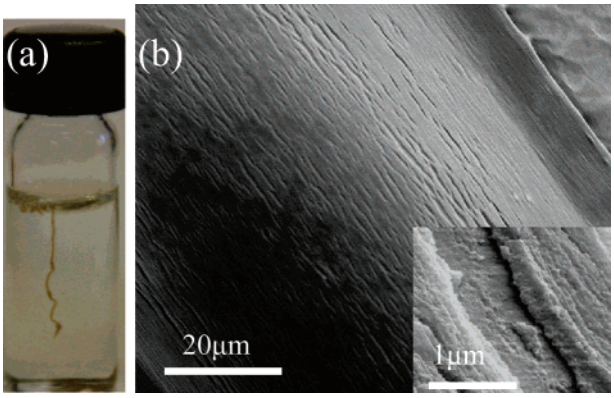

Figure 3. (a) Fiber formed from injection of a P1 + P2 mixture (0.2 M NaOH solution, 3% total weight polymer) into 1 M HCl. (b) SEM image of P1 + P2 fiber.

P1 solubilized with SDS, or P2 formed no fiber, but rather very fine precipitates. The P1 + P2 fiber was removed from aqueous solution and placed on a glass slide for analysis by SEM. Similar to the interpretation of the P1 + P2 films, the fiber appears to be made up of densely packed threads. However, the threads are now oriented in a uniform direction to form an elongated fiber (Figure 3b). With the small percentage of Dan/Ndi overlap the fiber is very easily broken, but remarkable in its assembly compared to the independent polymers.

The use of noncovalent aromatic donor acceptor interactions can be a useful tool in affecting solid-state macromolecular structure and assembly. It offers an orthogonal design element to both hydrogen bonding and metal coordination with the added benefit of enhanced stability coming from very polar solvents and water. Future work will be aimed at producing polymeric systems with increased aqueous solubility and in which greater numbers of aromatic units are designed to be involved in intermolecular aromatic donor acceptor interactions, along with the development of discrete units for more traditional supramolecular chemistry in multiple dimensions.

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Supporting Information Available: Text giving the experimental protocols, a scheme showing the reactions, and figures showing the NMR and UV−vis spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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