Polymer Chemistry

Supramolecular AB Diblock Copolymers**

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Coupling incompatible oligomeric or polymeric chains at their ends leads to the formation of block copolymers. Block copolymers have a fascinating tendency to attain, through self-assembly and microphase separation, various ordered morphologies that have characteristic dimensions on the nanometer scale.[1] In recent years, efforts to develop supramolecular polymers, that is, macromolecules which consist of monomeric building blocks that are linked together by noncovalent forces, have generated great enthusiasm.[2] A successful design of supramolecular polymers relies on the availability of noncovalent association units that can link various structural modules together. Although strategies that lead to a variety of chains or networks have been reported, association units with reasonable affinity and specificity have only recently become available. The groups of Zimmerman[3] and Meijer[4] have developed self-complementary, quadruply hydrogen-bonded complexes that serve as associating end groups for the construction of supramolecular polymers of high molecular weights. Other polymeric systems that involve supramolecular interactions are also known.[5] Despite the progress made, few hydrogen-bonded supramolecular block copolymers have been reported so far.[5i] Owing to the unavailability of heterodimeric hydrogen-bonded units of sufficient strength and specificity, supramolecular block copolymers that display microphase separation have not been reported. Lohmeijer and Schubert recently reported an exciting example of supramolecular block copolymers by using unsymmetrical metal complexes which were obtained with 30–50 % yield after purification (column chromatography).[6]

To ensure microphase separation of designed supramolecular block copolymers and to couple different blocks, ideally, association units that link the different blocks together should exhibit both high stability and high non-self-complementary specificity, and at the same time the linkages should be kinetically reversible. Indeed, this is an unsolved problem. Many metal complexes are highly stable but are kinetically inert, whereas most hydrogen-bonded complexes lack high binding affinities and specificities.

We report herein a new class of supramolecular, AB-type diblock copolymers that rely on hydrogen-bond-enforced association of incompatible polymer chains. In the general structures **1** and **2**, hydroxyl-terminated polystyrene (PS) and poly(ethylene glycol) monomethyl ether (PEG) chains were coupled to two different oligoamide strands. We previously showed that oligoamide strands such as **1'** and **2'** paired into a hexa-hydrogen-bonded heteroduplex with an association constant $K_a > 10^9\,\text{M}^{-1}$ in chloroform.[7] Thus, mixing the modified PS with the PEG chains in a ratio of 1:1 in a common solvent (chloroform) should also lead to hydrogen-bonded supramolecular diblock copolymers. We also reported that the pairing of oligoamides similar to **1'** and **2'** was accompanied by significant downfield shifts of the signals for the protons of the amide groups: *g* (*g'*), *m* (*m'*), and *t* (*t'*; see structures **1** and **2** for atom labels).[7b] Here, the 1D ^{1}H NMR spectra of **1'·2a**, **1a·2a**, and **1c·2c** exhibited similar downfield shifts of N–H protons to those of the duplex **1'·2'**[8] which indicates that the PEG and PS strands are linked by intermolecular hydrogen bonds. Results from 2D ^{1}H NMR (NOESY) studies on **1a·2a** and **1c·2c** revealed interstrand NOEs that are also consistent with the formation of hydrogen-bonded duplexes, that is, the noncovalent coupling of PEG and PS strands.[8]

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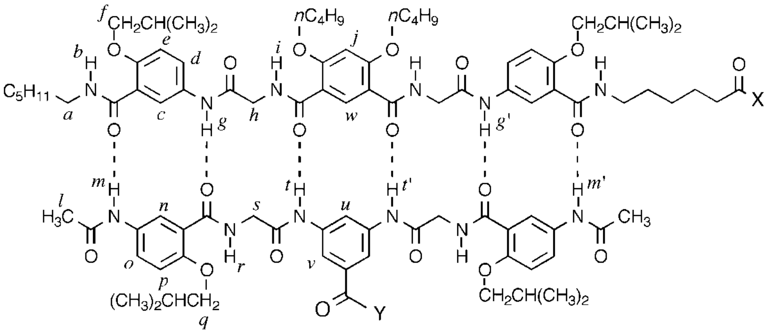
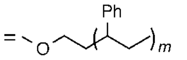


1·2

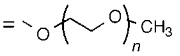
1': X = -OCH$_3$
1a: X = -O-PS (M_w = 1.7×10^3)
1b: X = -O-PS (M_w = 3.2×10^3)
1c: X = -O-PS (M_w = 20×10^3)

2': Y = -OC(CH$_3$)$_3$
2a: Y = -O-PEG (M_w = 350×10^3)
2b: Y = -O-PEG (M_w = 2.0×10^3)
2c: Y = -O-PEG (M_w = 5.0×10^3)

-O-PS =



-O-PEG =



Hydrogen-bond-mediated association of the modified PS and PEG chains was further confirmed by gel permeation chromatography (GPC). The **1c·2c** pair, relative to **1c** or **2c** alone, had the fastest elution time (23.00 min), followed by **1c** (23.45 min), and then **2c** (24.99 min; Figure 1 a). Upon elution with the polar solvent DMF (Figure 1 b), **1c·2c** appeared as two peaks that coincided with the positions of **1c** and **2c** which again confirmed the hydrogen-bonded nature of **1c·2c**. Similar results were obtained from GPC analyses of another duplex, **1b·2b**, and its corresponding constituent blocks **1b** and **2b**.[8]

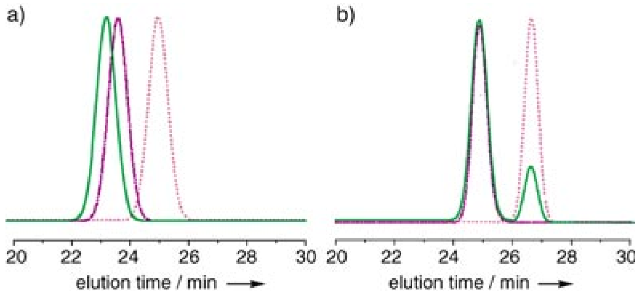


Figure 1. GPC traces of **1c·2c** (green), **1c** (–•–•, purple), and **2c** (——, pink) eluted with a) DMF/toluene (10:90, v/v) and b) DMF, both at 60 °C. DMF = *N*,*N*-Dimethylformamide.

The above NMR and GPC results clearly establish that PS and PEG strands can indeed be linked through hydrogen bonding. In the bulk phase, under conditions that favor the formation of intermolecular hydrogen bonds, these supramolecular block copolymers may demonstrate properties that are characteristic of typical covalent block copolymers. On the other hand, under conditions that disrupt intermolecular hydrogen bonds, these supramolecular diblock copolymers may dissociate and behave like A/B polymer blends. One of the most important properties of block copolymers involves microphase separation, which depends on the incompatibility or immiscibility of the two constituent polymer blocks and the volume fraction of the blocks.[1] If the molecular weights of the blocks are low, the constituent blocks are miscible and the corresponding block copolymers will be disordered and therefore not show microphase separation. As their molecular weights increase, the constituent blocks will eventually become immiscible and the corresponding block copolymers will show microphase separation.

According to the method described by Cheng and co-workers,[9] the interaction parameters (χN; 60 °C) of the PS and PEG chains in the diblock copolymer architecture were estimated to have values of 2.8, 4.5, 17.3, and 19.8 for **1b·2a**, **1b·2b**, **1c·2b**, and **1c·2c**, respectively. In terms of polymer–polymer interactions in the phase diagram of diblock copolymers,[10] these χN values mean that 1) **1b·2a** and **1b·2b** should exist as disordered hydrogen-bonded block copolymers, which do not exhibit PS/PEG microphase separation owing to their low χN values, 2) **1c·2b** may still be disordered owing to its low PEG volume fraction (9.5 %), although it has a reasonably large χN value, and 3) **1c·2c** with its χN value of 19.8 and PEG volume fraction of 20.9 % should show microphase separation, which would lead to discontinuous nanoscale PEG domains embedded in the PS matrix. These predictions based on the χN values are fully consistent with results from differential scanning calorimetry (DSC) studies.

Figure 2 shows the DSC heating diagrams of four PS–PEG pairs, **1b·2a**, **1b·2b**, **1c·2b**, and **1c·2c**. The similar results obtained during the first heating scans for **1b·2a**, **1b·2b**, and **1c·2b** indicate the absence of ordered PEG domains, which suggests that these three duplexes are disordered block copolymers. This is consistent with the above theoretical predictions on **1b·2a**, **1b·2b**, and **1c·2b**. In contrast, the first DSC heating diagram of **1c·2c** revealed a sharp melting peak for PEG near 60 °C and a glass transition of PS near 100 °C. This heating diagram is very similar to those of ordered, covalent PS–PEG diblock copolymers[9] and suggests that **1c·2c** self-assembles into an ordered morphology. The endothermic peaks observed for **1b·2a** (175 °C), **1b·2b** (174 °C), and **1c·2b** (190 °C) during the first heating scans are likely brought about by the dissociation of the hydrogen-bonded duplex units because a similar peak (192 °C) was also observed in the heating diagram of duplex **1'·2'**, which does not carry a polymer chain. The first heating scans of **1c·2c** revealed a broad exothermic peak centered around 179 °C, which indicates that the hydrogen-bonded duplex unit of **1c·2c** is in an environment that is very different from those in the three supramolecular pairs that exist in the disordered state. The endothermic peaks were reproduced in the second heating of **1b·2a** (172 °C) and **1b·2b** (174 °C). The corresponding endo- or exothermic peak was absent in the diagram of **1c·2b** or **1c·2c** during the second heating cycle. Instead, melting peaks of PEG were observed for both **1c·2b** and **1c·2c**, which suggests that the blocks of **1b·2a** and **1b·2b** remain as miscible blends after the hydrogen-bonded duplex unit dissociates at high temperatures. Upon cooling, the two

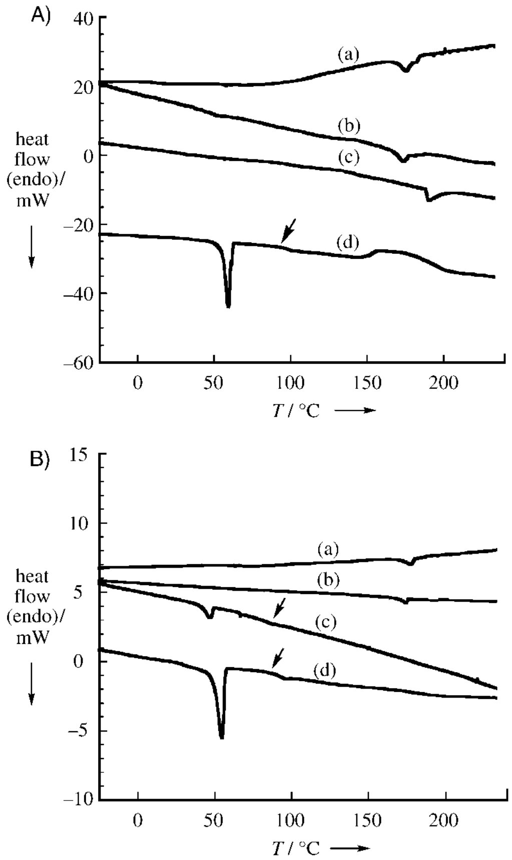


Figure 2. DSC profiles from the A) first and B) second heating at 5 °C min^{-1} of a) **1b**·**2a**, b) **1b**·**2b**, c) **1c**·**2b**, and d) **1c**·**2c**. Prior to the second heating, the samples were cooled from 250 °C to −50 °C at 5 °C min^{-1}. Arrows are used to indicate the glass transition from the PS domains of either ordered or macrophase-separated PS/PEG.

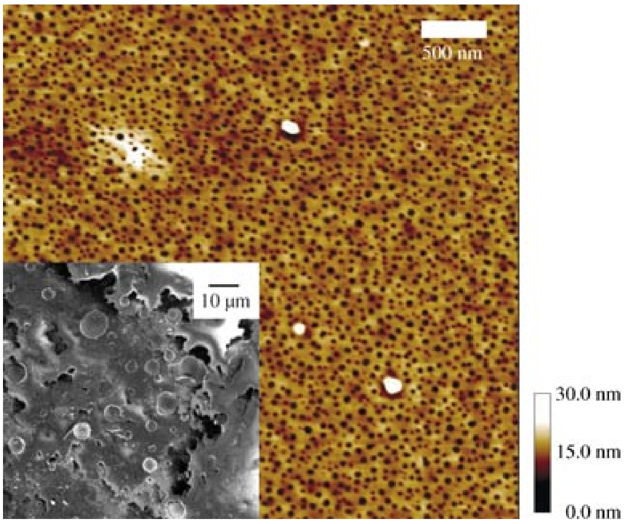


Figure 3. Tapping mode AFM image (height) of a film of **1c**·**2c** by spin-coating from benzene solution. Inset: SEM image of freeze-fractured surface of a sample of **1c**·**2c**, which had been heated to 250 °C and cooled to −50 °C at 5 °C min^{-1} (that is, after the DSC experiments).

blocks were linked through hydrogen bonds to form the diblock copolymers from the homogeneous mixtures of the melts. As for **1c**·**2b** and **1c**·**2c**, the separated PS and PEG macrophases did not allow the pairing of their hydrogen-bonded duplex units and thus the block copolymers within the timeframe of the cooling cycle. This conclusion is further supported by comparison of the behavior of **1c**·**2c** with that of a PS/PEG (M_M: 20000:5000) blend by DSC studies, which revealed significant differences between the two.[8] The first heating scan gave results that were consistent with microphase separation for **1c**·**2c** and macrophase separation for the PS/PEG blend. After cooling down from the first heating scan, the second heating scan on the same samples led to DSC results that indicated macrophase separation of both samples relative to the original **1c**·**2c** duplex and the PS/PEG blend.

The microphase separation of **1c**·**2c** was also confirmed by the AFM image of its spin-coated film from benzene (Figure 3). It was reported that PEG cylinders could be aligned normal to the substrate by spin-coating PS–PEG diblock copolymers from benzene.[11] From the AFM image (Figure 3), the well-dispersed discontinuous PEG domains (dark regions) with an average diameter of 24 nm indicate that the **1c**·**2c** sample has a typical PS–PEG diblock copolymer-like microphase separation,[11] although it is not clear at this moment whether the PEG domains are vertically oriented cylinders or dispersed spheres. The morphology of a cryogenically fractured surface of the **1c**·**2c** sample was examined by scanning electron microscopy (SEM) after the DSC experiments, which revealed that the sample had indeed undergone a macroscopic phase separation after the heating and cooling cycles in the DSC analyses. The AFM images of **1c**·**2c** before and after dipping into a mixture of methanol/water (1:1 v/v) at room temperature for one hour show that the methanol/water-treated sample contains nanoscale local swellings in the PEG domains, which is presumably due to the disruption of the six hydrogen-bonded association units and the swelling of PEG.[8] Furthermore, the AFM image of **1d**·**2d**, with its higher ratio of PEG relative to that for **1c**·**2c**, contains enlarged dark regions,[8] which supports our contention that the dark regions in the AFM image of **1c**·**2c** correspond to microphase-separated PEG domains.

In summary, the supramolecular diblock copolymers described here demonstrate the phase behavior that is typical of diblock copolymers. The perturbation of the hydrogen-bonded duplex units on the phase behavior of the diblock assemblies, such as **1c**·**2c** and **1d**·**2d**, with long PS and PEG blocks is surprisingly small. Relative to covalent block copolymers, these supramolecular block copolymers offer unique advantages such as 1) the rapid generation of numerous block combinations, 2) the preparation of block copolymers consisting of blocks that can only be prepared separately by using drastically different methods, 3) the hydrogen-bonded bridging units can be formed or cleaved under mild conditions, and 4) the ability of the designed system to undergo self-repair (or error-correcting). Coupled with the programmable sequence-specificity and high stability of our hydrogen-bonded duplexes, the described strategy can be easily extended to the creation of tri- and multiblock copolymers, which will greatly enhance the diversity of the corresponding self-assembled nanoarchitectures.

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