Review

Hydrogen bond-mediated self-assembly and supramolecular structures of diblock copolymer mixtures

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Abstract

This review summarizes recent advances in the preparation of hydrogen bonding block copolymer mixtures and the supramolecular structures they form through multiple hydrogen bonding interactions. Hydrogen bonding in block copolymer mixtures that form nanostructures and have unusual electronic, photonic and magnetic properties is a topic of great interest in polymer science. Combining the self-assembly of block copolymers with supramolecular structures offers unique possibilities to create new materials with tunable and responsive properties. The self-assembly of structures from diblock copolymer mixtures in the bulk state is readily controlled by varying the weight fraction of the block copolymer mixture and the copolymer composition; in solution, the morphologies are dependent on the copolymer composition, the copolymer concentration, the nature of the common solvent, the amount of the selective solvent and, most importantly, the hydrogen bonding strength.
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Keywords: self-assembly; block copolymer; hydrogen bonding; supramolecule

INTRODUCTION

Materials prepared on the nanoscale are usually obtained using 'top-down' and 'bottom-up' methods. The 'top-down' method is a traditional fabrication technique offering arbitrary geometrical designs and superior nanometre-level precision, accuracy and registration; it employs the two-dimensional etching, deposition and layer-by-layer manufacturing processes that constitute the foundation of current microelectronic technologies. Nevertheless, with the continuous requirements for higher performance and cheaper devices, this approach will soon reach its resolution limit because of diffraction of light at nanometre scales; it is also inefficient in terms of energy and materials. Self-organizing materials make the 'bottom-up' method a relatively simple and low-cost process to fabricate large-area periodic nanostructures from diblock copolymers or other materials (e.g. low molecular weight compounds) by controlling their self-assembly behaviour. The driving forces for producing nanostructures through the self-assembly of diblock copolymers are the combination of: (i) repulsive and attractive interactions within and between the blocks; and (ii) their covalent linkage. The repulsion effect between blocks A and B in the bulk state arises from their immiscibility; in solution, it results from one block segment being immiscible with a selective solvent. To control the degree of microphase separation down to the nanoscale requires attractive forces to exist within blocks A and B. The covalent bonds between blocks A and B confine the polymer to the nanoscale. Diblock copolymers can form many different well-defined self-assembled nanostructures in the bulk state, including lamellar, hexagonally packed cylindrical and body-centred cubic micellar structures, as a result of the presence of two immiscible polymer chains connected by covalent bonds and depending on the relative volume fractions of the blocks, the total degree of polymerization and the Flory–Huggins interaction parameter.[1–4] Block copolymers that have well-defined structures, such as known molecular weights, molecular weight distributions, compositions, architectures and end-group functionalities, are in high demand.

Block copolymers in solution can also spontaneously self-assemble into well-defined micelles or aggregates in the presence of a selective solvent for one of blocks. Many morphologies have been obtained through the self-assembly of synthesized diblock copolymers in selective solvents.[5–15] Eisenberg and co-workers, pioneers in this field, have reported various morphologies for micelles prepared from linear block copolymers, including spheres, rods, vesicles and large compound micelles.[16–18] Many other groups have prepared new copolymers with special structures to obtain novel self-assembled objects possessing particular morphologies.[19–23] The composition of the block copolymer can be tuned to effect the formation of micelles or aggregates of shapes other than spheres in block-selective solvents.[16,24] Block copolymer micelles or aggregates, which can be either thermodynamically or kinetically stable under a given set of conditions, have many potential applications in such diverse fields as cosmetics, drug delivery, electronics, pollution control, advanced materials and separation.[25–28] The equilibrium aggregate morphologies can be controlled by altering the influence exerted by a given parameter on the interplay of the three major components of the free energy of the aggregates: the stretching of core-forming blocks, intercorona interactions and the interfacial free energy between the solvent and the micellar

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core.[29,30] Changing any of these components disturbs the balance between the forces governing the aggregates, leading to the transformation of one morphology into another. There are many factors that influence these three components; by varying one or more of them, the morphologies can, in principle, be fine-tuned. Examples of such factors that have been studied previously are the relative block lengths of the copolymer, the initial copolymer concentration in solution, the choice of the common solvent, the use of a precipitant, the temperature and the types and amounts of added ions (salts, acids or bases).[31]

In addition to diblock copolymers, more complex macro-molecules, such as ABC triblock copolymers, have attracted much interest in recent years.[1] Because the synthesis of ABC triblock copolymers is relatively complex, mixing A–B with B–C or C–D diblock copolymers is a somewhat simpler approach towards exploring the morphological behaviour of these systems. The simplest case involves mixing an A-*block*-B diblock copolymer with a C homopolymer or a C-*block*-D diblock copolymer. If specific complementary interactions exist between the C block and one of the blocks in the A-*block*-B copolymer, inter-polymer complex micelles can be formed from their mixture.[32–36] The assembly of such non-covalently bonded micelles can be mediated by inter-polymer hydrogen bonding,[37–46] electrostatic interactions[47–50] and metal–ligand coordinative bonds.[51,52] This review discusses the influences of these kinds of non-covalent bonding interactions (especially hydrogen bonding) on the morphologies of diblock copolymer mixtures.

Non-covalent interactions are being used increasingly in the molecular self-assembly of well-defined supramolecular structures and materials.[53–55] Such interactions are important in polymer science, where hydrogen bonding and other weak reversible interactions determine a polymer's properties and allow the design of new polymer architectures. In traditional polymers, these properties arise through the cooperative phenomenon of many weak interactions, which lack directionality, providing microphase-separated structures or gelation through network formation. A prerequisite for linear supramolecular polymers is that the non-covalent interactions are strong, highly directional and reversible, thereby allowing materials to be constructed without the need to form new covalent bonds. Although this concept has been known for many years, supramolecular polymers possessing appreciably high degrees of polymerization in the amorphous state or even in dilute solution were not previously available because it was not known how to incorporate such sufficiently strong, but still reversible, interactions into these systems. Efforts to use highly directional multiple hydrogen bonds have been hampered by: (i) the insufficient stability of single, double or triple hydrogen bonds; (ii) the difficulty in preparing strongly coupling systems; and (iii) the limited reversibility and tunability of the coordination of metal ions. Non-covalent interactions enable the development of novel supramolecular structures from functional polymeric precursors. Hydrogen bonding interactions exhibit greater thermoreversibility and specificity, allowing reversible attachment of guest molecules. In addition, the strength of hydrogen bonding associations is further tunable via variation of structural parameters and molecular design of the hydrogen bonding sites. If strong non-covalent interactions are present, block copolymers will exhibit microphase separation even when their outer blocks are short. These non-covalently interacting block copolymers have potential applications in elastomers and as ion-conducting materials for fuel cells and water purification membranes.
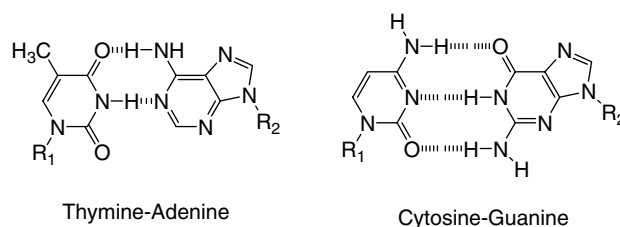
**Figure 1.** Chemical structures and hydrogen bonding interactions of DNA nucleobases.

Nevertheless, the intermolecular association equilibrium constant between commercial polymers is usually *ca* 100, which makes it difficult to prepare regular self-assembled structures. In contrast, the intermolecular association equilibrium constants between adenine (A)–thymine (T) and guanine (G)–cytosine (C) base pairs in the DNA double helical structure are *ca* 10^4–10^5 and significantly larger than those in commercial hydrogen bonding polymers.[56] Fig. 1 displays the intermolecular hydrogen bonds formed by the A–T and G–C base pairs and the supramolecular structures that can be formed after incorporating these functional groups into commercial polymers. This review also discusses recent approaches towards forming supramolecular structures from diblock copolymer mixtures featuring such strong multiple hydrogen bonding interactions.

## DIBLOCK COPOLYMER MIXTURES FEATURING HYDROGEN BONDING IN THE BULK STATE
Diblock copolymer/homopolymer mixtures

Blending diblock (A-*block*-B) copolymers with homopolymers (C) has attracted much interest in polymer science during the last few years because of the unusual phase behaviour of such systems.[57–63] Most studies have concentrated on blending an immiscible A-*block*-B diblock copolymer with a homopolymer A. Another major system that has been investigated is the blending of a homopolymer C with an immiscible A-*block*-B diblock copolymer, where C is immiscible with block A but interacts favourably with block B. Zhao *et al*. first investigated the blending of immiscible polystyrene-*block*-poly(vinyl phenol) (PS-*block*-PVPh) diblock copolymers with various hydrogen bond-acceptor polymers, such as poly(ethylene oxide) (PEO), poly(4-vinyl pyridine) (P4VP) and poly(butyl methacrylate) (PBMA), which can form hydrogen bonds with PVPh, yet are immiscible with the PS block; although microphase separation plays a dominant role in the development of morphologies from such systems, the self-assembly of nanostructures was not reported.[55] Recently, it was found that (PS-*block*-PVPh)-*blend*-P4VP = 1/1 can form a gyroid structure that differs from the lamellar structure of the pure PS-*block*-PVPh diblock copolymer (Fig. 2) (Kuo SW and Chang FC, unpublished results). Ikkala and co-workers reported the blending of immiscible polyisoprene-*block*-poly(2-vinyl pyridine) (PI-*block*-P2VP) diblock copolymer with novolac resin. The hydrogen bonding interactions between the hydroxyl groups of novolac with the pyridine groups of P2VP can result in a miscible phase, even through novalac is immiscible with PI. As a result, a separate glass transition temperature can be observed for the PI block.[64]

Several systems comprising an immiscible A-*block*-B diblock copolymer and a homopolymer C, where C is miscible with both A and B, have been reported. For example, Zhao *et al*. investigated blends of (PS-*block*-PVPh)-*blend*-poly(vinyl methyl ether), where
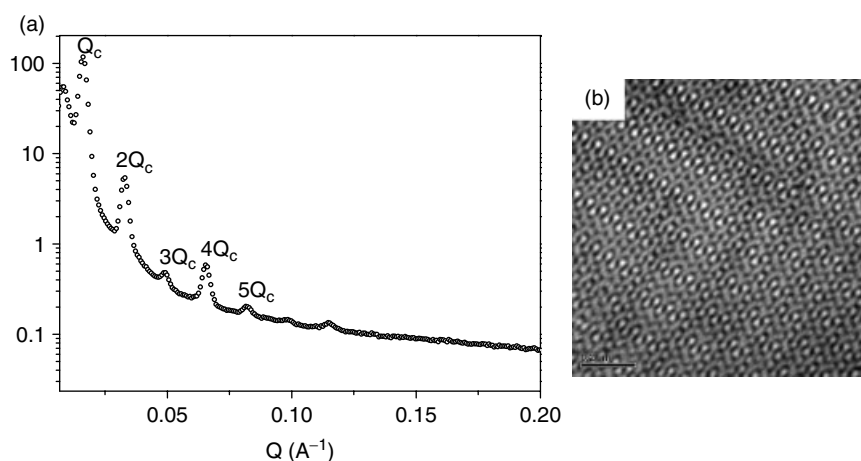
Figure 2. (a) Small-angle X-ray scattering of PVPh-*block*-PS and (b) a transmission electron microscopy image of (PVPh-*block*-PS)-*blend*-P4VP = 1/1 blend.
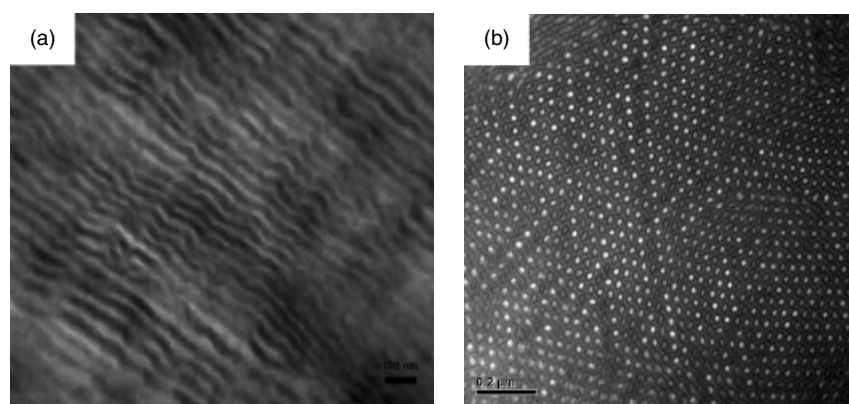

Figure 3. Transmission electron microscopy images of (a) PCL-*block*-P4VP copolymer and (b) (PCL-*block*-P4VP)-*blend*-PVPh = 4/1 blend.

poly(vinyl methyl ether) (PVME) is miscible with both PS and PVPh blocks and serves as a common solvent; this system results in a single phase when the PVME content is higher than 50 wt%.[58] Hameed and Guo reported an immiscible A-*block*-B diblock copolymer, where C is miscible with both blocks A and B, but the hydrogen bonding interactions between the B and C segments are stronger than those of the A and C segments ($\chi_{BC} \gg \chi_{AC}$). They investigated the selective hydrogen bonding in poly(ε-caprolactone)-*block*-poly(2-vinyl pyridine) (PCL-*block*-P2VP) with phenoxy resin, where both the blocks are miscible with the phenoxy resin and the value of χ_{AB} is positive (A and B are immiscible) and χ_{AC} and χ_{BC} are negative, but χ_{BC} is more negative than χ_{AC}.[65] The selective hydrogen bonding interaction leads to the formation of a variety of composition-dependent microphase separations. Kuo *et al*. also investigated the blending of PCL-*block*-P4VP with PVPh, where the hydrogen bonding interaction of the miscible PVPh-*blend*-P4VP blend ($K_A = 598$)[66] is much stronger than that of the miscible PVPh-*blend*-PCL blend ($K_A = 90$),[67,68] based on the Painter–Coleman association model,[69,70] but where the PCL-*blend*-P4VP blend is immiscible. The morphology changes from lamellar to cylinder structures upon increasing the PVPh content (Fig. 3) (Kuo SW and Chang FC, unpublished results).

Recently, we focused our attention on (A-*block*-B)-*blend*-C systems featuring all negative, but different, values of the interaction parameters χ_{AB}, χ_{BC} and χ_{AC} (i.e. all binary blends are miscible). Because of the inherent flexibility and long-chain nature

of most synthetic polymers, specific interactions in polymer blends usually occur in an uncontrollable manner and consequently lead to irregular structures.[45] Therefore, it is a great challenge to construct regular self-assembled structures from polymeric building blocks through specific interactions in the bulk state. When all three binary pairs (B-*blend*-A, B-*blend*-C and A-*blend*-C) are individually miscible in a ternary polymer blend system, a closed immiscibility loop phase separation diagram can form in ternary polymer blends because of $\Delta\chi$ and ΔK effects.[71–78] Nonetheless, these ternary blend systems exhibit only irregular macroscopic phase separation; regular self-assembled structures have rarely been observed. The design of a miscible diblock copolymer blended with a third homopolymer that confines the phase separation to the nanometre scale is an interesting challenge. We first reported a new type of (A-*block*-B)-*blend*-C system, formed from (PMMA-*block*-PVP)-*blend*-PVPh (where PMMA is poly(methyl methacrylate)), that displays unusual phase behavior.[79] In this blend, the PMMA (A) and PVP (B) blocks within the PMMA-*block*-PVP (A-*block*-B) copolymer are miscible; although PVPh (C) experiences attractive interactions through hydrogen bonding with both the PVP and PMMA blocks, its interaction with the former block is significantly stronger than that with the latter. The proton spin–lattice relaxation time in the rotating frame indicated that phase separation occurred for blends containing *ca* 20–60 wt% PVPh. Transmission electron microscopy (TEM) images indicated clearly that the morphology
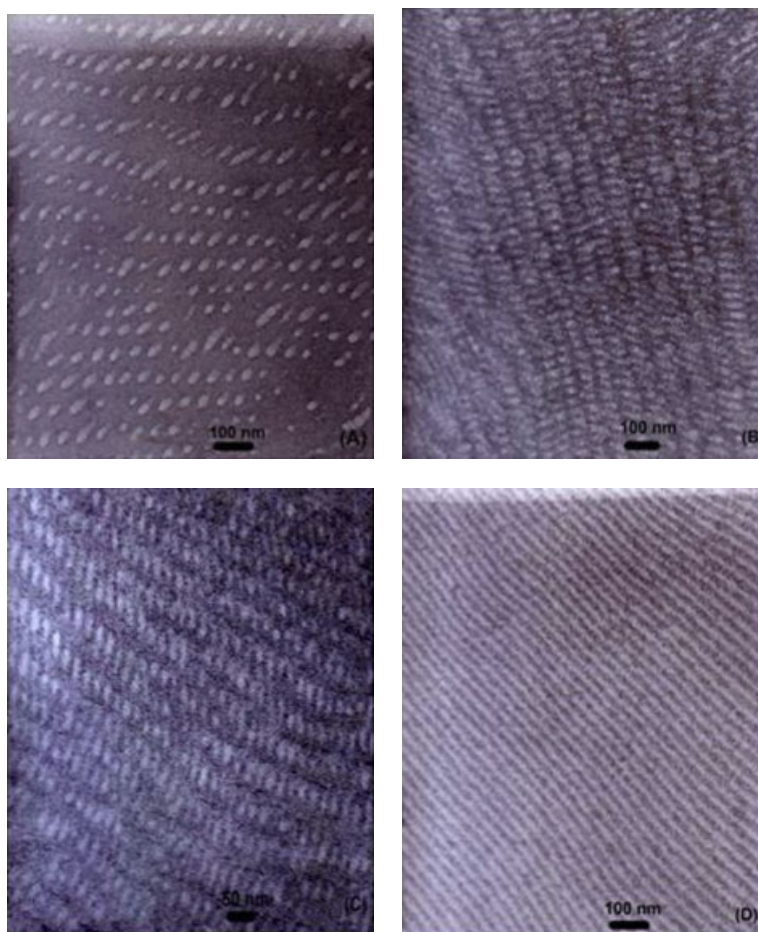
Figure 4. TEM images of solution-cast films of (A) 27, (B) 42, (C) 48 and (D) 56 wt% PMMA in (PVPh-*block*-PMMA)-*blend*-PVP stained with RuO$_4$.

of the phase separation consisted of a matrix of homogeneous mixed PVP-*blend*-PVPh and micellar domains of excluded PMMA. In addition, we also investigated the polymer blending of PVPh-*block*-PMMA with PVP.[80] This miscible PVPh-*block*-PMMA copolymer becomes immiscible upon blending with 20–60 wt% PVP (27–56 wt% PMMA in the blend system) and forms unusual self-assembled morphologies because of the significant difference in the strengths of the hydrogen bonds. TEM images indicated that different compositions of (PVPh-*block*-PMMA)-*blend*-PVP blends induced different microphase-separated structures mediated by hydrogen bonding interactions. Figure 4 illustrates the various morphologies of (PVPh-*block*-PMMA)-*blend*-PVP blends prepared at different compositions. At a lower PMMA fraction (27 wt%) in the blend system, small PMMA microdomains were finely dispersed and confined within the matrix of the miscible PVPh-*blend*-PVP phase (Fig. 4(A)). Most of these PMMA-rich microdomains were nearly spherical. Increasing the PMMA content to *ca* 42–48 wt% led to short PMMA cylinders dispersed within a miscible phase of PVPh and PVP (Figs 4(B) and (C)). On further increasing the PMMA content to 56 wt%, the blend adopted a lamellar morphology (Fig. 4(D)). Clearly, self-assembled nanostructures of miscible diblocks can be obtained through hydrogen bonding.

Diblock copolymer mixtures

Because the synthesis of ABC triblock copolymers is relatively complex, mixing AB with BC or CD diblock copolymers is a
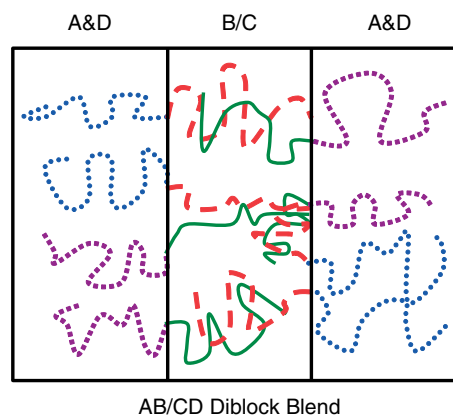
Figure 5. Schematic representation of (A-*block*-B)-*blend*-(C-*block*-D) diblock copolymer mixture.

somewhat simpler approach towards exploring these systems' morphological behaviour. The simplest case involves mixing an A-*block*-B copolymer with a C-*block*-D copolymer in the bulk state (Fig. 5).[81]

Abezt and co-workers reported the blending of polystyrene-*block*-poly(1,2-butadiene)-*block*-poly(*tert*-butyl methacrylate) (SBT) triblock copolymers (with different degrees of saponification of poly(*tert*-butyl methacrylate) blocks)
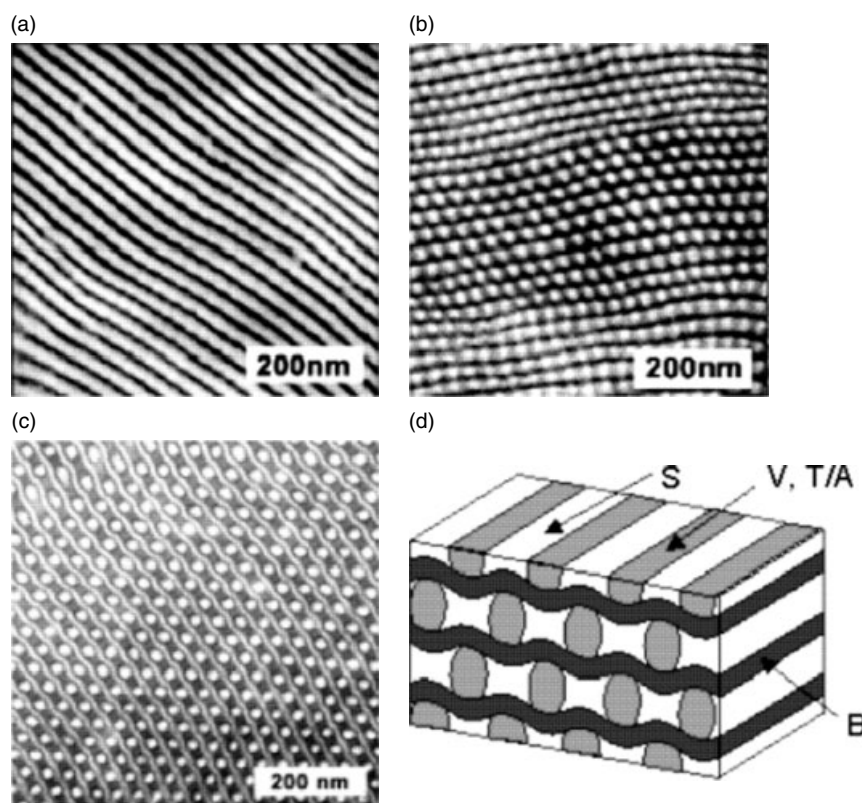
Figure 6. (a–c) TEM micrographs of SB(T82/A18) blended with S45V55: (a) stained with OsO$_4$; (b) stained with OsO$_4$ and CH$_3$I; (c) stained with RuO$_4$. (d) Schematic representation of the microphases in (a–c). (Reprinted with permission from Jiang et al.[82] 2006 American Chemical Society).

with PS-*block*-P2VP (SV) and poly(2-vinyl pyridine)-*block*-poly(cyclohexyl methacrylate) (VC) diblock copolymers.[82] Varying the content of hydrogen bond donors via controlled saponification of the SBT triblock copolymer led to various self-assembled morphologies in its blends with SV and VC diblock copolymers (Fig. 6).[82]

Matsushita and co-workers investigated blends of PI-*block*-P2VP and PS-*block*-PVPh.[83] The strong hydrogen bonding between the pyridine groups of P2VP and the hydroxyl groups of PVPh groups forces the corresponding blocks together, creating self-assembled three-phase hierarchical structures (Fig. 7). In a subsequent paper, the AB diblock copolymer was replaced with a BAB triblock copolymer, P2VP-*block*-PI-*block*-P2VP, and blended with PS-*block*-PVPh.[84] Again the PVPh blocks and the P2VP blocks segregate together because of hydrogen bonding. Matsushita and co-workers extended the concept by employing tiling as a skeleton and demonstrated the existence of the complex. These examples demonstrate that blending of block copolymers that associate intermolecularly via hydrogen bonding is a very promising route towards hierarchical two-dimensional nanostructures.

We have also investigated the blending of PMMA-*block*-P4VP and PS-*block*-PVPh, where strong hydrogen bonding exists between the P4VP and PVPh blocks (Kuo SW and Chang FC, unpublished results). Figure 8 shows selected TEM images of these two blended diblock copolymers. Clearly, controlling the blend composition and the fraction of each block in the copolymers allows the hierarchical nanostructure to change from a three-phase lamellar structure to a core/shell cylinder structure.

DIBLOCK COPOLYMER MIXTURES FEATURING HYDROGEN BONDING IN SOLUTION
Diblock copolymer/homopolymer mixtures

The self-assembly of block copolymer/homopolymer blends in solution has been studied extensively for decades. When specific interactions, such as electrostatic or hydrogen bonding interactions, exist between complementary bonding sites on different polymers or blocks, inter-polymer complexation can facilitate co-aggregation in blend solutions. In these systems, the solvent plays an important role in affecting or controlling the type of complex that forms.[85] For example, PVPh-*blend*-poly(N,N-dimethylacrylamide) (PDMA) yields a complex precipitate in dioxane, but causes no precipitation in dimethylformamide (DMF). Because solvent molecules can also participate in hydrogen bonding interactions, they compete with PDMA for the hydroxyl groups in PVPh. The affinity of the hydrogen bond acceptor can be estimated by comparing the difference in the frequencies of the infrared signals ($\Delta\nu$) of the hydrogen bonded and free hydroxyl groups of phenol (a model compound for PVPh). This approach confirms that dioxane is a weaker hydrogen bond acceptor ($\Delta\nu = 235$ cm^{-1}) than DMF ($\Delta\nu = 340$ cm^{-1}). Similarly, PVPh-*blend*-P4VP blends also can form inter-polymer complexes in both methanol and ethanol. In DMF solution, however, the solvent disrupts hydrogen bonding to such an extent that the system cannot form an inter-polymer complex.[86] Furthermore, the glass transition temperature (T_g) of PVPh-*blend*-P4VP complex obtained from ethanol solution is always higher than that of the miscible PVPh-*blend*-P4VP blend obtained from casting the DMF solution. Therefore, the supramolecular chemistry of hydrogen bonded polymers is mostly examined in non-polar solvents,
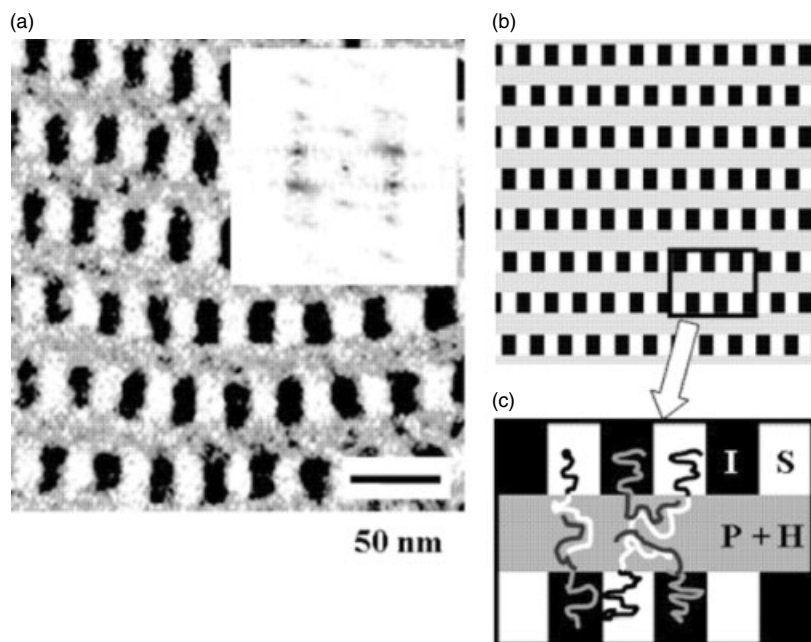
Figure 7. (a) TEM image of (IP-55)-*blend*-(SH-55) = 50/50 blend. Inset: fast Fourier transform pattern for all areas in the TEM image. (b) Schematic representation of the microdomain arrangement for the blend observed in (a). (c) Enlarged domain assembly and possible molecular arrangement in this structure. (Reprinted with permission from Asari *et al*.[83] 2006 American Chemical Society).
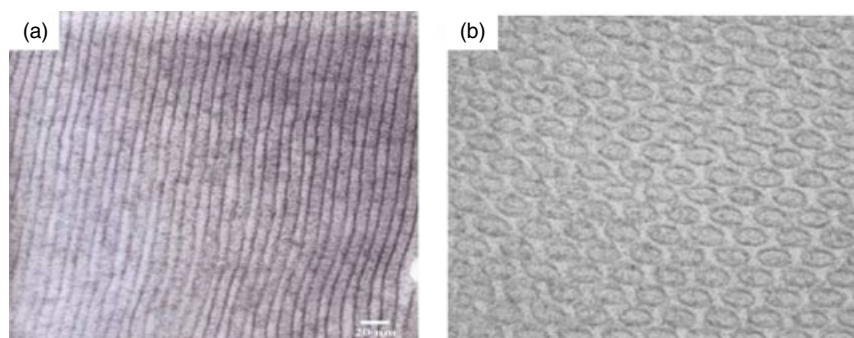

Figure 8. TEM images of (P4VP-*block*-PMMA)-*blend*-(PS-*block*-PVPh) blended at ratios of (a) 5 : 5 and (b) 7 : 3.

such as linear and cyclic alkanes, toluene, CH_2Cl_2 and $CHCl_3$. For example, in toluene, which is inert to hydrogen bonding, the complexation between poly[(styrene-*co*-(4-vinyl phenol)] and poly(ethyl methacrylate) occurs spontaneously upon mixing the two polymer solutions.[87] Because the morphology of the resultant inter-polymer complex is very different from those of the individual polymers, aggregation of the preformed complex may generate different types of aggregates in terms of morphology and structure.[88,89]

Shi and co-workers investigated the co-micellization of a PEO-*block*-poly(acrylic acid) (PEO-*block*-PAA) copolymer with P4VP in ethanol solution. Because the hydrogen bonding interaction in the PAA-*blend*-P4VP complex is stronger than that in the PAA-*blend*-PEO complex, the resultant micellar complexes are core (PAA/P4VP)/corona (PEO block) spheres.[42] Chen and co-workers reported vesicle formation mediated by inter-polymer hydrogen bonding complexation between PEO-*block*-polybutadiene (PEO-*block*-PB) and PAA in a mixed solvent of tetrahydrofuran (THF) and *n*-dodecane. The formation of the self-assembled structure was driven by hydrogen bonding complexation between the PAA and PEO sites (Fig. 9).[41]

Lee *et al*. studied the pH-induced reversible complexation of PEO with a PCL-*block*-PMAA diblock copolymer in aqueous solution. Because PEO can form long-range-interconnected micelles via hydrogen bonding interactions with the PMAA segment, the micelle structure can be controlled by adjusting the pH of the medium.[39] Matejicek *et al*. reported the inter-polymer complexes of core/shell micelles formed from blended solutions of PS-*block*-PMAA and P2VP in dioxane/water mixtures. Because of the strong hydrogen bonding between the P2VP and PMAA segments, complex structures based on the core/shell micelles form in mixed selective solvents.[90] Gohy and co-workers investigated the morphologies formed from mixtures of PS-*block*-P4VP copolymers with PAA in organic solvents.[36,38] Complexation occurred via hydrogen bonding between the P4VP and PAA blocks; these insoluble complexes aggregated to form the cores of micelles surrounded by coronas of PS chains. The addition of water at a controlled pH led to the disintegration of the initial complexes and to the formation of other types of aggregates.
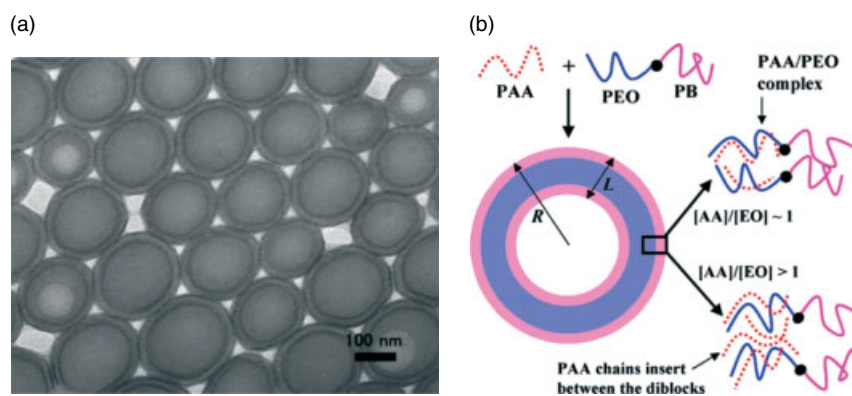
Figure 9. (a) Typical TEM image of a PAA-*blend*-(PEO-*block*-PB) blend (OsO$_4$-stained sample of W_A/W_{EB} = 2.0). (b) Schematic representation of a bilayer ULV of PAA-*blend*-(PEO-*block*-PB). When [AA]/[EO] >1, the excess PAA chains are uniformly inserted into the membrane core between the diblocks. (Reprinted with permission from Gao *et al.*[41] 2006 American Chemical Society).

Diblock copolymer mixtures

If specific interactions exist between a C-*block*-D copolymer and one of the blocks in an A-*block*-B copolymer, inter-polymer complex micelles can form. The assembly of such non-covalently bonded micelles can be mediated by inter-polymer hydrogen bonding, electrostatic interactions and metal–ligand coordinative bonds. The shapes of these supramolecular structures can be classified into three general types: (i) core/shell spherical micelles having an insoluble complex core and a soluble block as the corona;[37–39] (ii) onion-type (core/shell/corona (CSC)) micelles having an insoluble core A, a shell composed of a B–C inter-polymer complex and a corona formed by a soluble block D;[40,41] and (iii) vesicles formed from A-*block*-B and C-*block*-D copolymers featuring two insoluble segments (A and D) and mutually interacting B and C blocks.[91] If the two blocks composing the core are sufficiently large and mutually immiscible, they will most likely segregate into different phases, forming two separate compartments in the core of the micelle. Nevertheless, depending upon the molecular structure of the segments, diverse morphologies can be expected for a multi-compartmentalized core.[92,93] Micelles displaying a compartmentalized corona have been observed also for systems possessing two immiscible coronal blocks.[37–39]

Shi and co-workers prepared complex micelles with tunable channels through the self-assembly of poly(*tert*-butyl acrylate)-*block*-poly(*N*-isopropylacrylamide) (PtBA-*block*-PNIPAM) with PtBA-*block*-P4VP.[43] The size and permeability of the channels could be regulated through manipulation of the composition of the diblock copolymers or by changing the environmental conditions (e.g. the temperature or pH of the solution). Those authors also prepared multilayered micelles comprising a PS cores, swollen PAA-*blend*-P4VP complex shells and PNIPAM coronas from the (PS-*block*-PAA)-*blend*-(P4VP-*block*-PNIPAM) copolymer mixture in ethanol because of the hydrogen bonding interactions between the PAA and P4VP blocks.[94] The temperature-sensitive PNIPAM block corona collapsed onto the PAA/P4VP shell and the excessive P4VP shell extended into the acidic solution to form corona-reversed micelles when the aqueous solution was heated to 45 °C. In addition, worm-like aggregates possessing a PAA/P4VP complex and a PEG/PNIPAM mixed shell were also prepared from the hydrogen bonding of mixtures of PEO-*block*-PAA and PNIPAM-*block*-P4VP in ethanol solution. The lengths of these worm-like aggregates varied from 100 nm to several micrometres

upon changing the weight ratio of the diblock copolymer mixture, although the diameter remained constant at *ca* 15 nm.[95]

Similarly, Han and co-workers also obtained a fibre-like aggregate from the self-assembly of a (PS-*block*-P4VP)-*blend*-(PS-*block*-PAA) mixture mediated by intermolecular hydrogen bonding of the PAA/P4VP complex in non-selective solvents.[96] They found that kinetic factors play an important role in the formation of fibre-like aggregates. Such nanofibre-like aggregates have been formed from low molecular weight compounds via hydrogen bonding interactions.[97] Han and co-workers also investigated the solvent-induced crystallization of spherical micelles obtained from (PS-*block*-PAA)-*blend*-(PS-*block*-P2VP-*block*-PEO) blends (formed through hydrogen bonding of PAA/P2VP complexes) via treatment with DMF vapour. Phase separation between the PS and PEO blocks in the coronas of the initial micelles played an important role in the morphological change.[98]

Zhang and co-workers studied the blending of PS-*block*-PAA and PS-*block*-PEO, obtaining mixed micellar clusters with hydrogen bond-mediated complexation of PAA and PEO blocks as the core and repulsion between the PS chains in the corona.[99] They also investigated the formation of (PS-*block*-PAA)-*blend*-(PMMA-*block*-PEO) mixed micelles as a function of the PAA-to-PEO molar ratio. The complexation between the PAA and PEO blocks in the core and the segregation between the PS and PMMA blocks in the corona led slowly to the development of a hyper-branched structure.[100]

We have also reported a new approach towards preparing self-assembled hydrogen bonded complexes having vesicle and patched spherical structures from two species of block copolymers in non-selective solvents. Two diblock copolymers, PS-*block*-PVPh and PMMA-*block*-P4VP, were synthesized through anionic polymerization. The assembly of vesicles from the intermolecular complex formed after mixing PS-*block*-PVPh with PMMA-*block*-P4VP in THF was driven by strong hydrogen bonding between the complementary binding sites on the PVPh and P4VP blocks. In contrast, well-defined patched spherical micelles formed after blending PS-*block*-PVPh with PMMA-*block*-P4VP in DMF; the weaker hydrogen bonds that formed between the PVPh and P4VP blocks in DMF, relative to those in THF, resulted in the formation of spherical micelles having compartmentalized coronas consisting of PS and PMMA blocks (Fig. 10).[44] In addition, well-defined micelles formed through hydrogen bonding were also prepared by mixing PMMA-*block*-P4VP diblock copolymers with PS-*ran*-PVPh random copolymers in single solvents.[101]
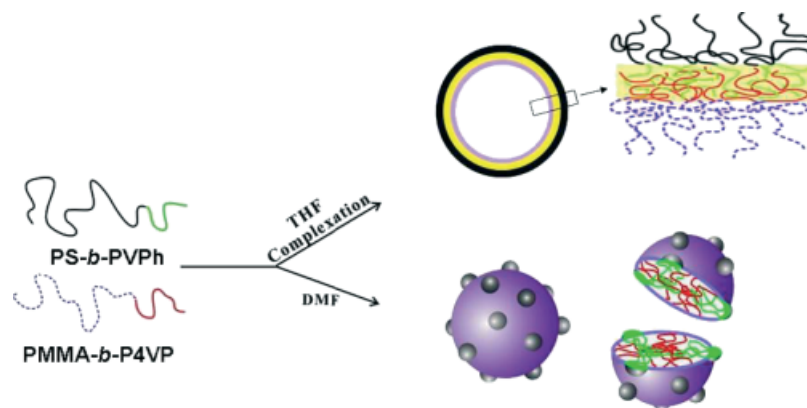
Figure 10. Schematic representation of micelle formation, mediated by hydrogen bonding interactions, from SVPh/MVP diblock copolymer mixtures.
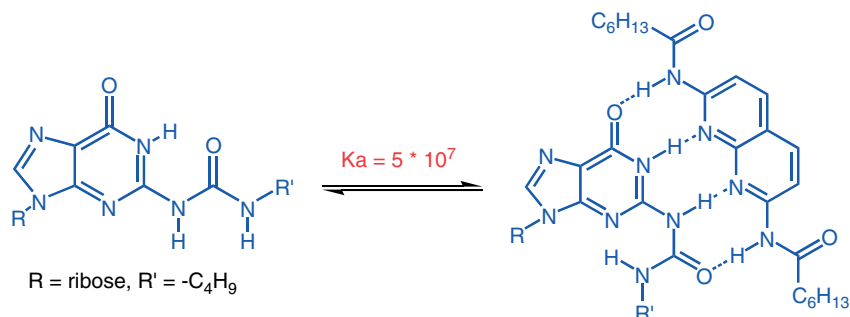
Figure 11. Formation of a strong complex between DAN and UG.

SUPRAMOLECULAR STRUCTURES FORMED THROUGH MULTIPLE HYDROGEN BONDING INTERACTIONS

Multiply hydrogen bonded arrays play a fundamental role in complex biological systems (e.g. DNA complexation). DNA is a very influential structure in polymer science, where it is often presented as a defined macromolecule possessing a nearly perfect molecular structure. As a result, the preparation of synthetic polymers that mimic DNA remains a very important challenge in polymer science.[102] The self-assembly of pairs of DNA strands is mediated by intermolecular hydrogen bonding between complementary purine (A and G) and pyrimidine (T and C) bases attached to a phosphate sugar backbone: G binds selectively to C and A binds selectively to T.[103] Taking this cue from nature, supramolecular structures can be prepared from synthetic polymers possessing nucleotide bases on their side chains.

Liu and co-workers investigated the co-aggregation of PtBA-*block*-poly(2-cinnamyloxyethyl methacrylate) (PCEMA) and PS-*block*-PCEMA in a mixture of $CHCl_3$ and hexane. To ensure co-aggregation, the PCEMA block was tagged with the hydrogen bonding DNA base pairs T and A.[46,104] Lutz *et al*. demonstrated that the adenine-functionalized copolymer self-assembles with its thymine-functionalized counterpart into supramolecular aggregates, which show a temperature-dependent 'melting' behaviour in non-polar solvents.[105–107] Rotello and co-workers demonstrated the thermally reversible formation of micrometre-size gel-like spherical aggregates through non-covalent polymer cross-linking. This cross-linking occurred as a direct result of specific three-point hydrogen bonding between thymine and diacyldiamidopyridine functionalities.[108–110] The spherical aggregates are stable indef-

initely at ambient temperature, dissociate at 50 °C and reform upon cooling; this heating–cooling cycle can be repeated many times with no decomposition.[108]

Long and co-workers synthesized a nucleobase-functionalized triblock copolymer featuring A- and T-containing blocks through nitroxide-mediated radical polymerization.[111] The blending of complementary polymers led to dramatic increases in viscosities and glass transition temperatures as a result of hydrogen bonding interactions between the A and T units.[112,113] Bazzi and Sleiman used ring-opening metathesis polymerization to synthesize A-containing block copolymers that self-assembled into cylindrical morphologies through self-complementary hydrogen bonding of the adenine units in the molecular core.[114] Park and Zimmerman reported a supramolecular polymer blend consisting of a pair of immiscible polymers, PBMA and PS. A urea derivative of guanosine (UG) and 2,7-diamido-1,8-naphthyridine (DAN) form an exceptionally strong quadruply hydrogen bonding complex (Fig. 11).

SEC, dynamic light scattering (DLS) and viscosity analyses have been used to provide evidence for the formation of supramolecular network structures in these binary blend systems.[115] We have investigated the miscibility behaviour, specific interactions and supramolecular structures of blends of the DNA-like copolymers poly[vinylbenzylthymine-*co*-(butyl methacrylate)] (T-PBMA) and poly(vinylbenzyladenine-*co*-styrene) (A-PS) with respect to their vinylbenzylthymine (VBT) and vinylbenzyladenine (VBA) contents. ^{1}H NMR spectroscopy and one- and two-dimensional Fourier transform infrared spectroscopy revealed that hydrogen bonding occurred exclusively between the VBA and VBT units.[116] In addition, SEC, DLS and viscosity analyses provided evidence for the formation of supramolecular network structures in these
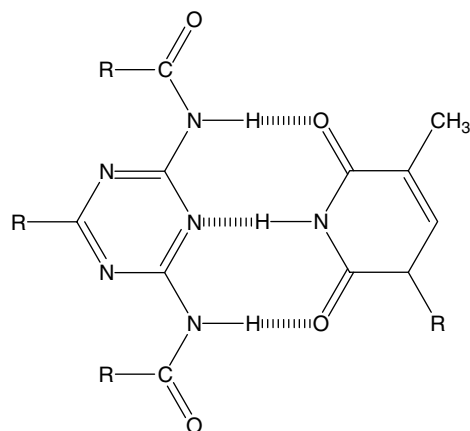
Figure 12. Hydrogen bonding interactions between DAT and T.

binary blend systems. A miscibility window existed in the A-PS-*blend*-T-PBMA system when the VBT and VBA fractions in the copolymers were greater than 11 mol%, as predicted using the Painter–Coleman association model.

Weck and co-workers synthesized random copolymers containing cyanuric acid recognition units via ring-opening metathesis polymerization and studied their cross-linking behaviour through complementary hydrogen bonding in a non-polar solvent.[117–119] Celiz and Scherman performed controlled anionic ring-opening polymerization of PCL in toluene using self-complementary quadruply hydrogen bonding 2-ureido-4[1H]-pyrimidinone (UPy)-functionalized initiators, which led to a marked increase in viscosity.[120] Komiyama and co-workers used free radical polymerization to prepare a series of homopolymers based on 2-vinyl-4,6-diamino-1,3,5-triazine (VDAT), which can form triply hydrogen bonded complexes with thymine adducts in non-polar solvents (Fig. 12).[121] The inter-association equilibrium constant between DAT and T is *ca* 890 $(mol\,L^{-1})^{-1}$, based on a ^{1}H NMR titration experiment.[122]

CONCLUSIONS

This review summarizes the recent results obtained from studies of hydrogen bonding in diblock copolymer mixtures in the bulk and in solution. The self-assembly of structures from diblock copolymer mixtures in the bulk state is readily controlled by varying the weight fraction of the block copolymer mixture and the copolymer composition; in solution, the morphologies are dependent on the copolymer composition, the copolymer concentration, the nature of the common solvent, the amount of the selective solvent and, most importantly, the hydrogen bonding strength. In addition, significant increases in the viscosities can be observed for solutions containing supramolecular structures stabilized through multiple hydrogen bonding interactions.

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