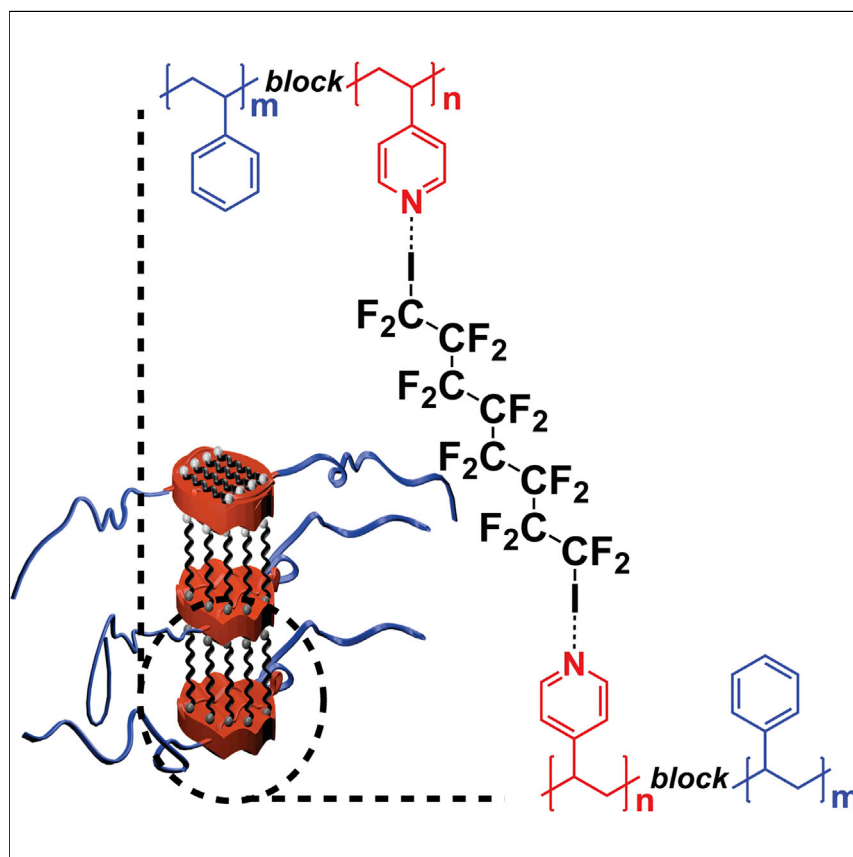


Article

Hierarchical Self-Assembly of Halogen-Bonded Block Copolymer Complexes into Upright Cylindrical Domains



Halogen bonding drives the hierarchical self-assembly of low-molecular-weight perfluorinated molecules and diblock copolymers. Specifically, binding of the ditopic halogen-bond donor 1,8-diiodoperfluorooctane to pyridine nitrogens of poly(styrene)-*block*-poly(4-vinylpyridine) results in lamellar-*within*-cylindrical self-assembly and promotes upright cylindrical alignment in films. This feature, along with the reversible nature of the halogen bond, provides a robust and modular approach for nanofabrication. Thanks to the robust halogen-bond-based crosslinks, separated segmented cylindrical micelles can be obtained by solvent treatment of bulk films.

Roberto Milani, Nikolay Houbenov, Francisco Fernandez-Palacio, ..., Arri Priimagi, Pierangelo Metrangolo, Olli Ikkala

pierangelo.metrangolo@polimi.it (P.M.)
olli.ikkala@aalto.fi (O.I.)

HIGHLIGHTS

Halogen bonding small molecules to block copolymers yields hierarchical self-assembly

Fluorinated additives increase block repulsion χ and enhance microphase separation

Upright cylinder structure alignment is favored by fluorocarbon low surface energy

Segmented cylindrical micelles can be obtained by solvent treatment of bulk films

Article

Hierarchical Self-Assembly of Halogen-Bonded Block Copolymer Complexes into Upright Cylindrical Domains

Roberto Milani,¹ Nikolay Houbenov,² Francisco Fernandez-Palacio,³ Gabriella Cavallo,³ Alessandro Luzio,⁴ Johannes Haataja,² Gabriele Giancane,⁵ Marco Saccone,⁶ Arri Priimagi,⁶ Pierangelo Metrangolo,^{1,2,3,4,7,*} and Olli Ikkala^{2,*}

SUMMARY

Self-assembly of block copolymers into well-defined, ordered arrangements of chemically distinct domains is a reliable strategy for preparing tailored nanostructures. Microphase separation results from the system, minimizing repulsive interactions between dissimilar blocks and maximizing attractive interactions between similar blocks. Supramolecular methods have also achieved this separation by introducing small-molecule additives binding specifically to one block by noncovalent interactions. Here, we use halogen bonding as a supramolecular tool that directs the hierarchical self-assembly of low-molecular-weight perfluorinated molecules and diblock copolymers. Microphase separation results in a lamellar-within-cylindrical arrangement and promotes upright cylindrical alignment in films upon rapid casting and without further annealing. Such cylindrical domains with internal lamellar self-assemblies can be cleaved by solvent treatment of bulk films, resulting in separated and segmented cylindrical micelles stabilized by halogen-bond-based supramolecular crosslinks. These features, alongside the reversible nature of halogen bonding, provide a robust modular approach for nanofabrication.

INTRODUCTION

Block copolymers (BCPs) can self-assemble in a series of well-defined, ordered arrangements of the chemically distinct domains, providing a reliable strategy for the preparation of tailored nanostructures. This strategy is widely exploited in the semiconductor industry with directed self-assembly (DSA) techniques, which combine self-assembling materials and lithographic nanopatterning to achieve large-area manufacturing of periodic nanostructures on the scale of a few tens of nanometers.

Microphase separation arises from the immiscibility of dissimilar blocks, which try to minimize repulsive interactions. Immiscibility of the blocks can be promoted with supramolecular methods by the block-specific complexation of low-molecular-weight additives.^{1–7} Therein, a wide variety of additives ranging from amphiphilic molecules to mesogens incorporating chemical groups that mediate supramolecular interactions with polymer chains can be chosen. Several kinds of noncovalent interactions are useful for binding these additives to polymers, such as ionic interactions, metal coordination, hydrogen bonding, or their combinations.^{8–12} However, to the best of our knowledge, there have been no examples of using halogen bonding.

The Bigger Picture

Directed self-assembly (DSA) is probably the most promising strategy for high-volume cost-effective manufacturing at the nanoscale to support the ever-growing needs of the semiconductor market. DSA exploits the spontaneous self-assembly of block copolymers onto lithographically nanopatterned surfaces, resulting in large-area fabrication of periodic nanostructures on the scale of a few tens of nanometers. Tailoring the structure, periodicity, and orientation of the block copolymer is crucial and requires control over features such as block volume fraction, immiscibility, and surface energy. Here, we use fluorocarbon additives that specifically form halogen bonds with only one of the blocks, promoting microphase separation even upon rapid casting and without subsequent solvent annealing, which, along with the reversible nature of the halogen bond, could pave the way for new self-assembly routes toward the alignment and periodicity of block copolymers and nanostructures.

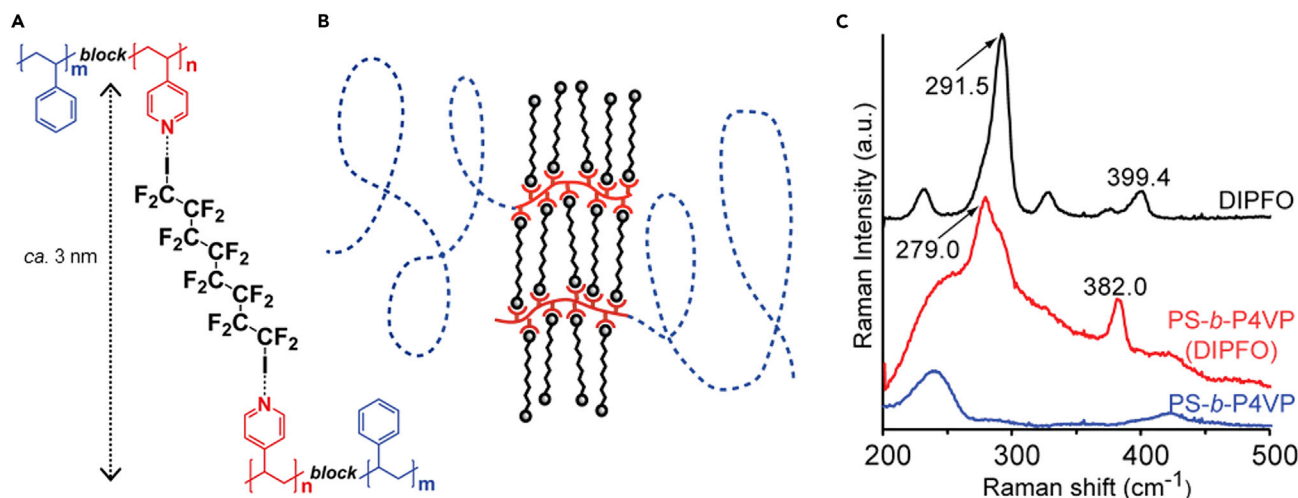


Figure 1. System Design and Proof of Halogen Bonding

(A) Molecular design of the target PS-*b*-P4VP(DIPFO) complex.

(B) Supramolecular scheme of the target PS-*b*-P4VP(DIPFO) system.

(C) Raman spectra of pure components and the complex indicating the occurrence of halogen bonding manifested in the C–I stretching-band redshift.

Halogen bonding has only recently been developed as a supramolecular tool in the design of functional materials.¹³ A halogen bond occurs as a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.¹⁴ Despite their many similarities, halogen and hydrogen bonds differ mainly in aspects such as directionality, hydrophilicity of the involved functional groups, and robustness in various solvent environments. Despite its established role in small-molecule self-assembly,^{15,16} halogen bonding has seldom been applied to directing polymer self-assemblies. Examples include molecularly imprinted polymers,¹⁷ liquid crystalline supramolecular polymers,¹⁸ layer-by-layer assemblies,¹⁹ light-responsive polymers,²⁰ and long-range alignment of polymer self-assemblies.²¹ Solution-phase self-assembly of complementary halogen-bonding polymers has been reported only recently.²²

Here, we show that halogen bonding directs the supramolecular binding of low-molecular-weight additives to block copolymers to form hierarchical self-assemblies in bulk samples and films and allows a route to complex micellar nanostructures. In particular, a perfluorinated halogen-bond donor selectively binds its iodines to pyridine nitrogens of a poly(4-vinyl pyridine) block copolymer and promotes microphase separation even upon rapid casting and without subsequent annealing, thus indicating the robustness of the approach. This occurs thanks to the tendency of perfluorocarbons to segregate into separate phases,^{21,23} which increases the immiscibility of the two polymer blocks described by the Flory-Huggins χ parameter. High- χ block copolymers are important for preparing assemblies with low periodicity, useful in nanolithography.²⁴ In films, selective incorporation of perfluorinated compounds allows microdomain alignment in upright cylinders to be controlled by tuning interfacial energies.

Some of us previously reported that 1,8-diiodoperfluorooctane (DIPFO) halogen bonds to low-molecular-weight poly(4-vinylpyridine) (P4VP) in a 1:2 molar ratio, pairing all iodine atoms with nitrogens.²⁵ In the present work, poly(styrene)-*block*-poly(4-vinylpyridine) diblock copolymer (PS-*b*-P4VP; Figure 1) with $M_n = 41.3$ kDa

¹VTT Technical Research Centre of Finland Ltd., 02044 VTT Espoo, Finland

²Department of Applied Physics, HYBER Centre of Excellence, Aalto University, 02150 Espoo, Finland

³Laboratory of Nanostructured Fluorinated Materials (NFMLab), Department of Chemistry, Materials, and Chemical Engineering “Giulio Natta”, Politecnico di Milano, 20131 Milano, Italy

⁴Center for Nano Science and Technology@PoliMi, Istituto Italiano di Tecnologia, 20131 Milano, Italy

⁵Dipartimento Beni Culturali, Università del Salento, 73100 Lecce, Italy

⁶Department of Chemistry and Bioengineering, Tampere University of Technology, 33101 Tampere, Finland

⁷Lead Contact

*Correspondence:

pierangelo.metrangolo@polimi.it (P.M.),
olli.ikkala@aalto.fi (O.I.)

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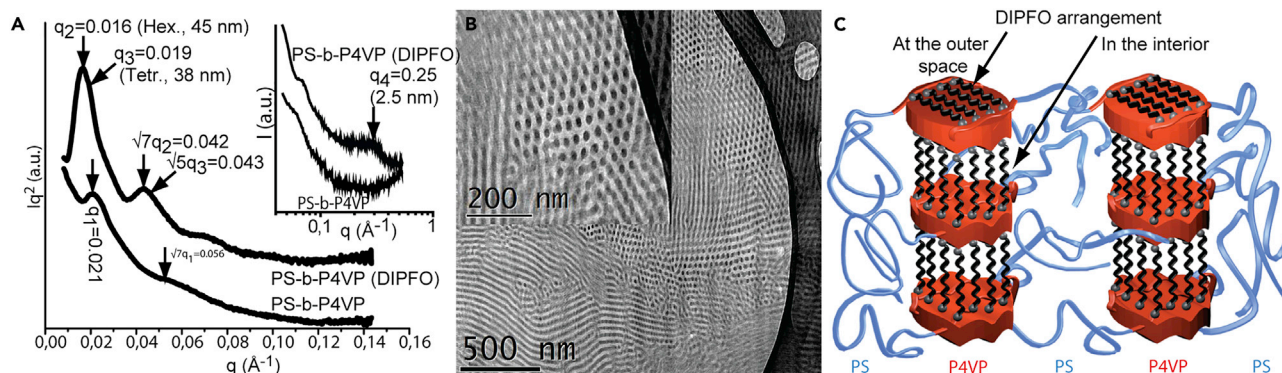


Figure 2. Structural Characterization of Sub-millimeter Bulk Samples

(A) SAXS patterns of PS-*b*-P4VP and PS-*b*-P4VP(DIPFO) prepared by drop casting.

(B) TEM micrograph of a microtomed PS-*b*-P4VP(DIPFO) bulk sample.

(C) Schematic representation of the observed lamellae-*within*-cylinder structure of the PS-*b*-P4VP(DIPFO) complex for the used block lengths. The suggested arrangement of DIPFO molecules within the interior illustrates the 2.5 nm periodicity, whereas the very low surface energy of the perfluorinated compounds is suggested to direct the upright cylindrical alignment at the outer surface of the films.

(PS) and 8.2 kDa (P4VP) was selected to form microphase-separated P4VP(DIPFO) complexes with a lamellae-*within*-cylinder structure. Cylindrical structures are particularly interesting for nanolithography and membranes.^{2,26,27} The ditopic additive, i.e., DIPFO, was chosen in order to provide supramolecular crosslinking by simultaneous involvement of the two halogen-bond donor sites at either end of the DIPFO.

RESULTS

Sub-millimetric Bulk Samples

We obtained PS-*b*-P4VP(DIPFO) supramolecular assemblies by mixing PS-*b*-P4VP with DIPFO in a 1:1 I/N atomic ratio (corresponding to an overall DIPFO weight fraction of ca. 34%) in chloroform and evaporating the solvent in open air until it dried. Binding through halogen bonding was demonstrated by the typical redshift of the C–I stretching band in the Raman spectrum, from 291.5 cm^{−1} in pure DIPFO to 279.0 cm^{−1} in the complex (Figure 1C), and by several shifts in the 1,000–1,250 cm^{−1} region of the Fourier transform infrared (FTIR) spectrum, where C–F stretching vibrations are located (Figure S1).²⁸ The thermogravimetric analysis (TGA) thermogram of the complex demonstrated the full complexation of the DIPFO because no significant weight loss was observed between 40°C and 85°C (Figure S2). Instead, a 34% weight loss occurred between 90°C and 190°C, indicating that the DIPFO was quantitatively bound to the polymer.

The complexation between PS-*b*-P4VP and DIPFO was also obtained by a solvent-free process, i.e., grinding the two components in a ball mill to reach a maximum pyridine complexation of about 75% after 4 hr of milling at a 1:1 I/N atomic ratio, as demonstrated by TGA and infrared spectra (Figure S3 and Table S1).

To investigate the structure of the PS-*b*-P4VP(DIPFO) supramolecular complex, we first prepared sub-millimeter-thick samples from chloroform by drop casting in air without any annealing. Small-angle X-ray scattering (SAXS) showed that the reflections were distinct but broad. We observed two closely located peaks at scattering-vector magnitudes of $q_2 = 0.016 \text{ Å}^{-1}$, plus a partially hidden reflection at $q_3 = 0.019 \text{ Å}^{-1}$ and a pronounced higher-order reflection between 0.04 and 0.05 Å^{−1} (Figure 2A). This indicates order at the block copolymer length scale.

A maximum at ca. 0.042 \AA^{-1} with a tiny shoulder at 0.043 \AA^{-1} corresponds to the higher-order composite reflections $\sqrt{7}q_2$ and $\sqrt{5}q_3$, suggesting hexagonal and tetragonal packing, respectively. Despite the absence of the expected $\sqrt{3}q_2$ and $\sqrt{2}q_3$ secondary reflections (note the weak scattering between 0.02 \AA^{-1} and 0.03 \AA^{-1} , where reflections are most likely screened by the intense main peaks), we suggest a coexistence of regions of hexagonal and tetragonal cylindrical packings at the block copolymer length scale with spacing between the adjacent P4VP(DIPFO) domains of ca. 45 nm ($q_2 = 0.016 \text{ \AA}^{-1}$) and 38 nm (0.019 \AA^{-1}), respectively. The coexistence of tetragonal and hexagonal phases has been reported previously.²⁹

The structures are further confirmed here by transmission electron microscopy (TEM) on bulk samples and atomic force microscopy (AFM) on films. At the smaller DIPFO length scale, a broad but pronounced reflection at $q_4 = 0.25 \text{ \AA}^{-1}$ was observed, which indicates structures of ca. 2.5 nm periodicity (Figure 2A, inset). This value was not detected for the pure PS-*b*-P4VP (Figure 2A, inset) and is close to the expected spacing of ca. 3 nm for two P4VP chains halogen bonded by a DIPFO molecule (Figure 1A). In fact, the directionality of halogen bonds and the supramolecular crosslinking within the P4VP(DIPFO) domains caused by the ditopic nature of the DIPFO molecules are expected to cause packing frustration, and the broad peak at q_4 does not come as a surprise. In conclusion, SAXS supports the hierarchical self-assembly at the two-length scale (Figure 2C).

As a reference, pure PS-*b*-P4VP in bulk showed only a main broad reflection at $q_1 = 0.021 \text{ \AA}^{-1}$ and a secondary weak reflection at ca. 0.056 \AA^{-1} with a ratio of $1:\sqrt{7}$, indicating poor hexagonal local order and a cylinder spacing of ca. 34 nm. Therefore, upon halogen bonding the DIPFO, the order in bulk improved significantly.

For TEM, a sub-millimeter-thick sample of the complex PS-*b*-P4VP(DIPFO) was prepared by drop casting. The sample was microtomed orthogonally to the sample surface to 50–150 nm sections and imaged by TEM. The images showed cylindrical microphases mostly arranged in a hexagonal pattern, although a tetragonal arrangement was also observed (Figure 2B), in agreement with the SAXS analysis. The local inhomogeneous orientation of the cylindrical phases in millimeter-thick bulk samples is expected and differs significantly from thin film behavior as a result of interfacial and chain confinement effects.

Spin-Coated Films

Films were next explored. Films of the PS-*b*-P4VP(DIPFO) complex with ca. 1 μm thickness were prepared by spin coating on glass substrates from chloroform. AFM showed self-assembled regions of hexagonal P4VP(DIPFO) patterns with an average diameter of $27.2 \pm 5.7 \text{ nm}$ and an average center-to-center distance of $45.3 \pm 5.8 \text{ nm}$, as well as regions with tetragonal order with a center-to-center distance of $39.7 \pm 2.8 \text{ nm}$ (see Figure 3B). Therefore, the patterns and dimensions in the films agree well with those observed in thick samples by SAXS and TEM, providing the evidence that the patterns in the films consist of cylinders that are upright aligned. No clear structuring occurred for pure PS-*b*-P4VP in films prepared similarly (Figure 3A), as also shown by the profile section and the very small root-mean-square roughness (R_{RMS}) of 0.2 nm. In comparison, PS-*b*-P4VP(DIPFO) films showed a feature height of about 4 nm and an increased R_{RMS} of 1.2 nm (Figures 3B, S4, and S5).

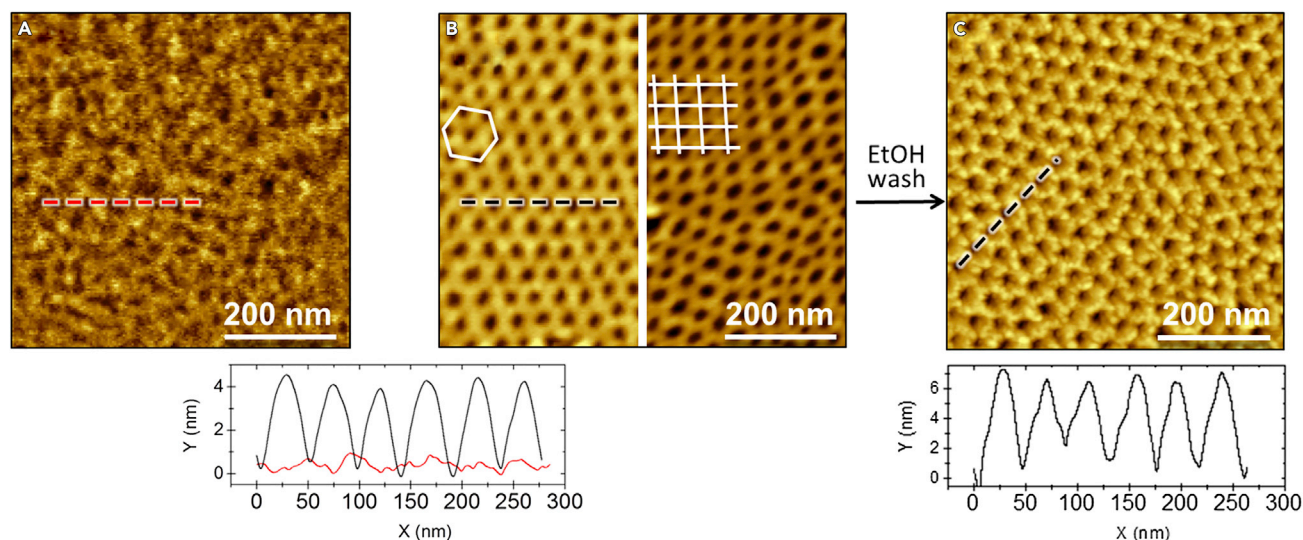


Figure 3. Structural Characterization of Spin-Coated Films

AFM topographic micrographs of films prepared by spin coating. Profile sections taken along the dashed lines are reported below the images. Scale bars, 200 nm. Large-scale AFM micrographs and analysis of the diameter and center-to-center distance of the P4VP/DIPFO domain are available in the [Supplemental Information](#) and [Figures S4 and S5](#).

(A) Pure PS-*b*-P4VP.

(B) Complex PS-*b*-P4VP(DIPFO) showing the presence of regions with hexagonal and tetragonal order.

(C) PS-*b*-P4VP(DIPFO) film after ethanol washing.

We obtained further evidence that the patterns observed in the films are upright cylinders rather than spherical domains by studying the removal of DIPFO from the PS-*b*-P4VP(DIPFO) films by solvent treatment. Upon washing with ethanol, the film retained its periodic structure ([Figures 3C and S4](#)), such that P4VP resided in the cylinders and was surrounded by the intact PS matrix. On the other hand, ethanol displaced DIPFO through the formation of hydrogen bonds with the pyridine nitrogens, allowing its complete removal as evident by the loss of its FTIR absorption bands ([Figure 4](#)). This suggests that there has to be phase continuity of the P4VP(DIPFO) domains throughout the film, given that ethanol does not swell PS, and DIPFO and PS are immiscible.³⁰ Furthermore, this confirms that the patterns in the films are upright cylinders. The feature height of the top surface layer in AFM (ca. 6 nm) and the overall roughness of the surface ($R_{\text{RMS}} = 1.5$ nm) were slightly increased, as would be expected upon extraction of DIPFO.³¹ Finally, an ethanol-washed film was exposed to gold vapors, and the PS-*b*-P4VP polymer template was subsequently extracted in acetone. This allowed deposition of gold nanostructures on the underlying glass substrate with heights typically ranging from 3 to 9 nm ([Figure S6](#)).

DISCUSSION

The specific binding of DIPFO by PS-*b*-P4VP thus enhanced the tendency for microphase separation and ordering in bulk and in films. In the latter case, upright alignment of the cylindrical microdomains was obtained in a robust way. Achieving upright cylindrical alignment typically requires subtle solvent treatment, surface functionalization, or application of external stimuli, as reviewed recently.³² Two main factors affect the observed structure formation in the reported system. First, halogen bonding of DIPFO promotes self-assembly by effectively and modularly increasing the Flory-Huggins parameter χ as a result of the omniphobicity of perfluorocarbons and their ensuing tendency toward

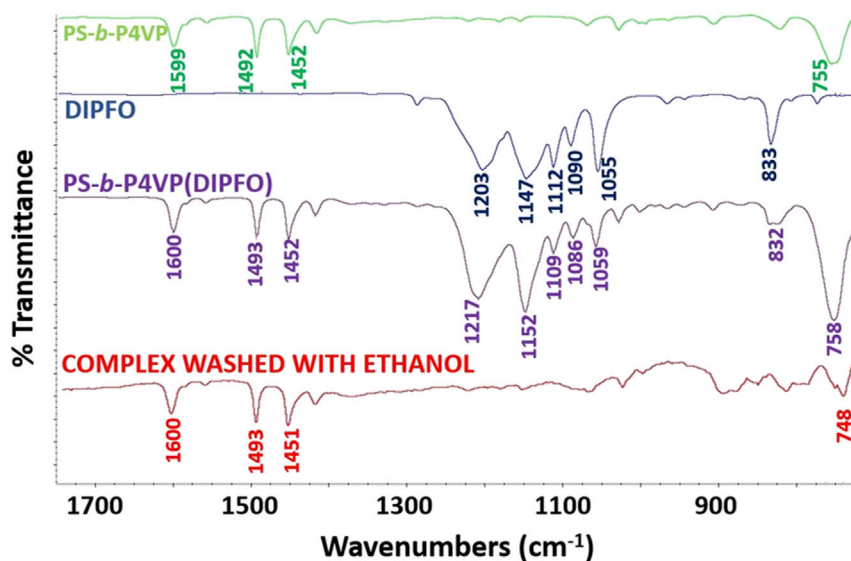


Figure 4. FTIR Proof of DIPFO Removal

ATR-FTIR spectra of PS-*b*-P4VP, DIPFO, and a PS-*b*-P4VP(DIPFO) film as prepared and after ethanol washing show that DIPFO can be completely removed.

segregation.^{21,23} On the other hand, we used ditopic DIPFO ligands with halogen-bond donor sites at either end to ascertain reliable binding within the P4VP blocks and suppress the excessive volatility of fluorocarbons. This leads to a nanoconfined supramolecular crosslinking of the P4VP chains within the P4VP(DIPFO) microdomains.

We suggest that the upright alignment of the P4VP(DIPFO) cylinders in films be promoted by the very low surface energy of DIPFO, i.e., 20.9 dyn/cm³³ (see Figure 2C for its suggested arrangement on the outer surface of the cylinders). This can be compared with a method for upright alignment with the use of poly(styrene)-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP) with trioctylphosphine (TOPO)-decorated nanoparticles confined in the P2VP-containing cylinders, where the octyl chains of TOPO reduce the air-interface energy of the P2VP-TOPO cylinders.³⁴

Finally, we demonstrate the robustness of the ditopic halogen bonding of DIPFO to physically crosslink (see Figure 1) the smaller-length-scale P4VP nanodomains within P4VP(DIPFO) cylinders to stabilize nanostructures. Because toluene is a selective solvent for PS and a poor solvent for P4VP(DIPFO), we aimed to disassemble the larger length-scale structure of the block copolymer and preserve only the P4VP(DIPFO) cylinders incorporating their internal smaller-length-scale lamellar structure. For that purpose, a bulk sample of PS-*b*-P4VP(DIPFO) was immersed in toluene. After evaporation of the solvent, AFM (Figures 5A and S7) indeed revealed a disordered set of nanofibrils of micrometer length and uniform diameter, fully consistent with those of P4VP(DIPFO) cylinders within the original PS-*b*-P4VP(DIPFO) self-assemblies. This suggests that the fibrillar nanostructures consist of cores that are composed of alternating nanoconfined lamellae of P4VP and DIPFO connected by DIPFO-mediated halogen bonds and a corona consisting of PS brushes (Figure 5B). As a result, segmented cylindrical micelles are obtained, as visualized in the dried state. Complex cylindrical micelles with patterned cores have previously been achieved from block copolymer solutions by solvent mixtures

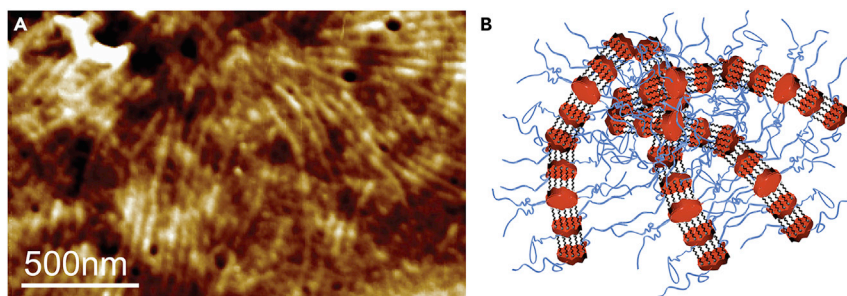


Figure 5. Segmented Cylindrical Micelles Stabilized by Halogen Bonding

(A) AFM of cylindrical micelles consisting of PS brush coronas and cores of alternating layers of P4VP and DIPFO. They were prepared by cleaving the P4VP(DIPFO) cylinders from the PS matrix by a PS-selective solvent. Scale bar, 500 nm. See also [Figure S7](#) for larger-scale images.

(B) Representative scheme of the segmented cylindrical micelles.

and solvent exchanges.^{35–39} By contrast, the present concept leads to segmented cylindrical micelles from larger-scale self-assemblies by solvent-induced cleavage. The resulting objects, which are stabilized by halogen-bonded supramolecular crosslinks, are relatively rod-like, probably as a result of the lateral packing of the rod-like DIPFO molecules.

It is worth noting that the formation of these structures is exclusively favored by the hydrophobic nature of halogen bonding, which allows easy processing of ditopic additives such as DIPFO in relatively low-polarity solvents such as chloroform. This would be clearly more difficult or impossible to accomplish with related ditopic hydrogen-bond donors by relying, for example, on highly polar moieties such as carboxylic groups,⁴⁰ which are not soluble in non-polar solvents.

In conclusion, we have shown that the specific halogen bonding of low-molecular-weight perfluorocarbons to one block of a diblock copolymer directs hierarchical self-assemblies both in bulk and in films and allows a route to complex micelles. As a model system, we used ditopic, rod-like DIPFO molecules to form halogen bonds at either end with the pyridines of PS-*b*-P4VP, which leads to cylindrical self-assemblies at the block copolymer length scale and to nanoconfined lamellar halogen-bonded supramolecular networks within the P4VP(DIPFO) cylinders. This demonstrates that halogen bonding can be used to direct block copolymer self-assembly into nanostructured films and complex polymeric nanostructures. In particular, the design choice of a small fluorocarbon molecule as a halogen-bond donor allows for the synergistic use of this noncovalent interaction together with surface energy-reduction effects, ultimately providing a robust pathway to upright cylindrical arrangement even in relatively thick films. Significant film nanostructuring is obtained without any need for further thermal or solvent-based annealing. Furthermore, the more hydrophobic nature of halogen bonding than of hydrogen bonding allows for the use of ditopic additives in low-polarity solvents, which are often not compatible with multifunctional, highly polar hydrogen-bonding additives. This advantage can thus provide higher processing flexibility in the preparation of block copolymer films, for example, when relatively high volume fractions of non-polar polymer blocks are involved. Because block copolymers with different compositions can be selected for diverse self-assemblies, we foresee that our approach could be of general interest for modularly increasing the effective repulsion (the χ parameter) between copolymer blocks in bulk and in films and

for obtaining perpendicularly aligned self-assemblies in films and complex nanostructures in a facile way.

EXPERIMENTAL PROCEDURES

Solid-State Synthesis of the Complex

Solid-state synthesis of the complex between PS-*b*-P4VP and DIPFO was performed with a Retsch MM 400 ball mill with 5.0 mL stainless steel vessels operating at 30 Hz. PS-*b*-P4VP and DIPFO were mixed in either a 1:2 molar ratio of DIPFO/vinylpyridine (N/I atomic ratio of 1:1; 33 wt % DIPFO) or a 1:4 molar ratio of DIPFO/vinylpyridine (N/I atomic ratio of 2:1; 17 wt % DIPFO) for durations varying from 2 to 8 hr.

Preparation of Complex Bulk Samples from Solution

PS-*b*-P4VP and DIPFO were dissolved in CHCl₃ separately at 0.1 g.mL⁻¹ concentration. The PS-*b*-P4VP solution was added dropwise to the DIPFO solution during sonication in an ultrasonic bath to yield a final 1:2 molar ratio of DIPFO/vinylpyridine.

Thick films were prepared by drop casting on glass slides and allowing the solvent to evaporate at room conditions.

Preparation of Complex Films from Solution and Removal of the DIPFO by Washing

Thin films of the complex were prepared by spin coating on silicon and glass slides at 500 rpm. The films were placed in ethanol overnight for the removal of DIPFO. The thickness of the films was measured with a KLA Tencor Alpha-Step Surface Profiler.

Metalation Experiments

Ethanol-washed complex films as above were coated with a 5-nm-thick gold layer through physical vacuum deposition at an MB-ProVap-3 glovebox workstation (tungsten source). Evaporation was carried out at a pressure of 5×10^{-6} mbar at a constant rate of 0.2–0.3 Å/s.

Cleaving P4VP(DIPFO) Cylinders for Segmented Cylindrical Micelles

A bulk sample of PS-*b*-P4VP(DIPFO) was immersed in toluene (1 mg of PS-*b*-P4VP(DIPFO) in 1 mL of toluene overnight) and subsequently diluted by a factor of 10 with additional toluene. The resulting nanostructures were studied by AFM after the evaporation of toluene.

SUPPLEMENTAL INFORMATION

Supplemental Information includes Supplemental Experimental Procedures, seven figures, and one table and can be found with this article online at <http://dx.doi.org/10.1016/j.chempr.2017.02.003>.

AUTHOR CONTRIBUTIONS

Conceptualization, P.M. and O.I.; Methodology, P.M., O.I., R.M., and N.H.; Investigation, F.F.-P., N.H., G.C., A.L., J.H., G.G., and M.S.; Writing – Original Draft, R.M. and N.H.; Writing – Review and Editing, P.M., O.I., R.M., N.H., F.F.-P., G.C., A.L., and A.P.; Funding Acquisition, P.M. and O.I.; Supervision, P.M., O.I., and R.M.

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