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Influence of the Interplay of Crystallization and Chain Stretching on Micellar Morphologies: Solution Self-Assembly of Coil−Crystalline Poly(isoprene-*block*-ferrocenylsilane)

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The self-assembly of amphiphilic block copolymers in block selective solvents is of considerable interest as the resulting supramolecular micellar aggregates have a variety of potential applications.[1] As the chemical composition of the insoluble block and the lengths of the individual blocks can be varied, one can investigate systematically how these changes affect the size and structure of the micelles that are formed. Most diblock copolymers form spherical micelles in a selective solvent. For this case, there is a rich body of theory to help us understand how the dominant interactions, the interplay of interfacial energy with the stretching entropies of the core and corona blocks, determine micelle size.[1] We have a poorer understanding of the formation of other structures, such as cylinders and vesicles.[2]

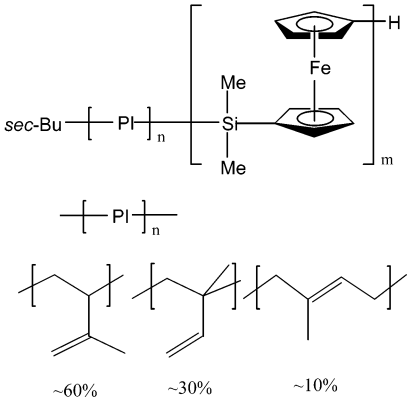
When the insoluble block is crystalline, one would imagine that the energy of crystallization is so large that this block must pack in a folded structure. As a result, these diblock copolymers should form platelet structures consisting of a thin crystalline lamellar domain sandwiched between solvent-swollen coronas of the soluble block protruding from both faces.[3] Experimental studies of micellar aggregates formed by semicrystalline diblock copolymers in dilute solution are rare. The first experiments, by Lotz et al.,[4] examined poly(styrene-*block*-ethylene oxide) (PS-*b*-PEO) diblock copolymers (with a crystalline PEO block) in ethylbenzene. They observed platelet micellar structures by transmission electron microscopy (TEM). Gast et al.[5] subsequently reported the coexistence of spherical and large lamellar aggregates from a PS-*b*-PEO diblock copolymer sample in cyclopentane. They also found some cylindrical aggregates protruding from the edge of the platelets. The authors attributed the multiple morphologies to different water content in the aggregates. More recently, Lin and Gast[6] used small-angle X-ray scattering and small-angle neutron scattering to study the platelet structures formed by PS-*b*-PEO in cyclopentane and by poly(ethylene-*block*-ethylpropylene) (PE-*b*-PEP, crystalline PE block) in decane. The latter system was also examined independently by Richter et al.[7]

In this communication we describe a remarkable change in morphology in the micelle-like structures formed by a coil−crystalline diblock copolymer in a selective solvent as the ratio of the lengths of the soluble and crystalline blocks is varied. We describe experiments with poly(isoprene-*block*-ferrocenyldimethylsilane) (PI-*b*-PFS) in hexane containing a small amount of tetrahydrofuran (THF). Hexane is a good solvent for the PI block but a poor solvent for the crystalline PFS block.[8] When the PI block is short, the polymer forms tapelike structures with high aspect ratios. When this block is long, the polymer forms dense cylinders. At intermediate chain lengths, one sees that both types of structures coexist in solution.

Table 1. Characteristics of PI_n-*b*-PFS_m

	PI block[a]	PI_n-*b*-PFS_m[a]		
samples	M_n (g/mol)	M_n (g/mol)	PDI	$n{:}m$[b]
PI_{30}-*b*-PFS_{60}	2 000	17 400	1.03	1:2
PI_{70}-*b*-PFS_{70}	4 800	23 600	1.03	1:1
PI_{320}-*b*-PFS_{53}	22 000	30 700	1.05	6:1
PI_{340}-*b*-PFS_{30}	23 000	29 300	1.05	11.5:1

[a] Apparent values based on SEC measurements. [b] Calculated from ^{1}H NMR integration.



The PI-*b*-PFS diblock copolymers were synthesized by sequential living anionic polymerization in THF as described previously[9,10] and possessed a narrow size distribution (Table 1).[11] To prepare micelle solutions, diblock copolymers were first dissolved in a small amount of THF, a common solvent for both blocks. Hexane, a precipitant for PFS, was added dropwise with gentle stirring, and the solutions were monitored in a light scattering apparatus. When a strong increase in light scattering intensity indicated the onset of the aggregate formation, the addition of hexane was stopped. The solution was left to stir for 3 days at 23 °C to equilibrate the micellar structures. All micelle solutions had a final polymer concentration of 1 mg/mL.

We employed TEM measurements to investigate the morphology of the aggregates. Figure 1 shows representative TEM micrographs of the micellar structures derived from these diblock copolymers in the THF/hexane mixture. No staining is necessary to visualize the Fe-rich PFS core.[9,12] Because of the low contrast between PI and the supporting carbon film, the objects on the TEM micrograph represent only the PFS domains. From Figure 1A,B, we see that PI_{320}-*b*-PFS_{53} and PI_{340}-*b*-PFS_{30} form cylindrical micellar aggregates consisting of a PFS core surrounded by a corona of PI chains. The cylinders seem stiff, with persistence lengths on the order of at least several hundred nanometers. The aggregates formed by PI_{30}-*b*-PFS_{60} are very different. They appear as long strips of various sizes (Figure 1C). The uniform electron density seen in the TEM image, even when the aggregate is folded or when two structures overlap, is indicative of thin tapelike structures. They have a high aspect ratio with straight edges and right angle corners. These features may indicate that each structure is a single crystal. These structures

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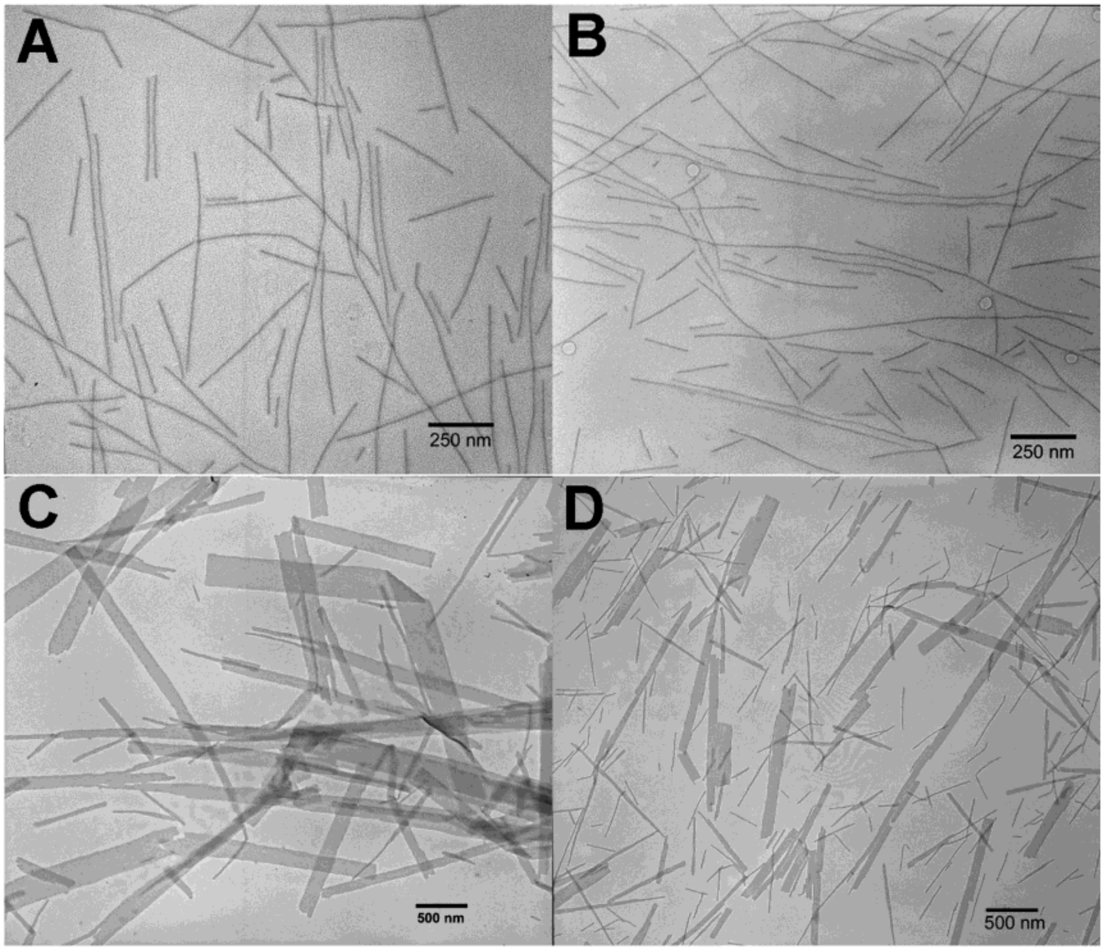

Figure 1. Representative TEM micrographs of the aggregates formed by (A) PI_{320}-*b*-PFS_{53} in THF/hexane (2/8, v/v), (B) PI_{340}-*b*-PFS_{30} in THF/hexane (1/9, v/v), (C) PI_{30}-*b*-PFS_{60} in THF/hexane (3/7, v/v), and (D) PI_{70}-*b*-PFS_{70} in THF/hexane (3/7, v/v).

are expected to consist of a chain-folded PFS lamellar domain between solvated PI chains. For PI_{70}-*b*-PFS_{70}, we observed the coexistence of cylindrical and lamellar aggregates, as shown in Figure 1D.

Bragg peaks are seen in the wide-angle X-ray scattering (WAXS) spectra of films formed from both the cylindrical and platelet structures. Both show a strong reflection at 6.4 Å similar to that seen in PFS homopolymer.[8]

The scaling model of Vilgis and Halperin (VH) provides a theoretical framework to help us understand aspects of our observations.[13] VH consider a chain-folded crystalline core in which each chain experiences an integral number of chain folds. Thicker cores have fewer folds, and this brings the junctions closer together. Overlap of the solvent-swollen coils of the soluble block leads to stretching of these chains. The equilibrium structure represents a balance between thick cores, which minimize the interfacial energy, and thin cores, which minimize the entropy penalty of stretching the corona chains. The formation of lamellar aggregates for PI_{30}-*b*-PFS_{60} agrees very well with this theoretical predication. For semicrystalline diblock copolymers with long coil blocks, VH predicted that cylindrical aggregates of finite length would be possible by the adjustment of the crystalline block in the micellar core. The core dimensions are truncated to accommodate the space-filling requirements of the soluble block.

PI_{30}-*b*-PFS_{60} and PI_{320}-*b*-PFS_{53} have similar PFS block lengths but differ significantly in the PI block length. The formation of cylindrical aggregates for PI_{320}-*b*-PFS_{53} is consistent with a strong competition between chain stretching of the PI corona and the energy of the crystalline PFS core. While crystallization of the PFS block would favor a lamellar morphology, the free energy cost for stretching of the long corona chains will be substantial. Although the system could minimize the energy penalty from the stretching of PI chains by making more folds in the lamellar domain (i.e., a thinner lamellar region), every chain fold is energetically costly. A cylindrical structure provides the best balance between these effects. We also observe cylindrical aggregates for PI_{340}-*b*-PFS_{30}. This type of highly asymmetric diblock copolymer would form starlike spherical micelles if the PFS block were not crystalline.[10] The soluble block is stretched to a greater degree in a cylindrical structure than in a sphere. We see that the energy of crystallization is sufficient to overcome entropy of stretching associated with this shape transition.

In summary, we have shown that a change in block length for coil−crystalline PI-*b*-PFS leads to a change in micelle structure. While the VH model provides separate scaling relationships for lamellar and cylindrical coil−crystalline aggregates in selective solvents, it cannot describe the requirements for a crossover between the two types of structures. The coexistence of both cylindrical and lamellar aggregates for PI_{70}-*b*-PFS_{70} identifies a crossover composition. Whether the crossover occurs when the two blocks have similar lengths or when the degree of polymerization of the PI block exceeds 70 is a topic for future investigation. Our observations suggest that the use of crystalline blocks represents a potentially powerful approach to systematically control micellar morphology. We hope that these results help stimulate the development of a more detailed theory of coil−crystalline block copolymer self-assembly from which one can predict the crossover from lamellar to cylindrical and spherical structures.

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Supporting Information Available: Experimental details of the polymer characterization and TEM sample preparation. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Halperin, A.; Tirrell, M.; Lodge, T. P. *Adv. Polym. Sci.* **1992**, *100*, 31. (b) Halperin, A. *Macromolecules* **1987**, *20*, 2943. (c) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195. (d) Liu, G. J. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 200. (e) Wooley, K. L. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 1397. (f) Liu, S.; Armes, S. P. *J. Am. Chem. Soc.* **2001**, *123*, 9910. (g) Gohy, J.-F.; Lohmeijer, B. G. G.; Schubert, U. S. *Macromolecules* **2002**, *35*, 4560.

(2) (a) Won, Y.; Davis, H. T.; Bates, F. S. *Science* **1999**, *283*, 960. (b) Cameron, N. S.; Corbierre, M. K.; Eisenberg, A. *Can. J. Chem.* **1999**, *77*, 1311. (c) Luo, L.; Eisenberg, A. *J. Am. Chem. Soc.* **2001**, *123*, 1012. (d) Luo, L.; Eisenberg, A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1001.

(3) Hamley, I. W. *Adv. Polym. Sci.* **1999**, *148*, 113.

(4) (a) Lotz, B.; Kovacs, A. J. *Kolloid-Z. Z. Polym.* **1966**, *209*, 97. (b) Lotz, B.; Kovacs, A. J.; Bassett, G. A.; Keller, A. *Kolloid-Z. Z. Polym.* **1966**, *209*, 115.

(5) Gast, A. P.; Vinson, P. K.; Cogan-Harinas, K. A. *Macromolecules* **1993**, *26*, 1774.

(6) Lin, E. K.; Gast, A. P. *Macromolecules* **1996**, *29*, 4432.

(7) Richter, D.; Schneiders, D.; Monkenbusch, M.; Willner, L.; Fetters, L. J.; Huang, J. S.; Lin, M.; Mortenson, K.; Farago, B. *Macromolecules* **1997**, *30*, 1053.

(8) For references to the crystallinity of the PFS homopolymer, see the recent review: Kulbaba, K.; Manners, I. *Macromol. Rapid Commun.* **2001**, *22*, 711.

(9) (a) Ni, Y.; Rulkens, R.; Manners, I. *J. Am. Chem. Soc.* **1996**, *118*, 4102. (b) Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 797.

(10) Massey, J. A.; Temple, K.; Cao, L.; Rharbi, Y.; Raez, J.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 11577.

(11) Refer to the block copolymers as PI_n-*b*-PFS_m, where n represents the number average degree of polymerization of the PI block determined from the size exclusion chromatography measurements and m represents the number average degree of polymerization for PFS block calculated from the ^{1}H NMR integration ratio of PI to PFS.

(12) Massey, J. A.; Power, K. N.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 9533.

(13) Vilgis, T.; Halperin, A. *Macromolecules* **1991**, *24*, 2090.

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