Self-Seeding Micelles

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Self-Seeding in One Dimension: An Approach To Control the Length of Fiberlike Polyisoprene–Polyferrocenylsilane Block Copolymer Micelles**

Jieshu Qian, Gerald Guerin, Yijie Lu, Graeme Cambridge, Ian Manners, and Mitchell A. Winnik**

Self-seeding is a phenomenon unique for polymer crystallization.[1] Polymers have difficulty in crystallizing and, in most cases, only part of each polymer chain can be accommodated in the crystal lattice. As a result, polymers form crystals with lamellar structures terminated by surfaces containing chain folds.[2] If long chains have to be integrated into the crystal in a short time, they will do so at the expense of lower crystallinity. As a consequence, polymer crystals inevitably consist of regions with different chain order and conformational entropy. Polymer crystals have a broad range of melting temperatures whose values depend upon the details of the crystallization process.[3] In a typical self-seeding experiment, a crystalline polymer in the bulk state or suspended in a solvent is heated slightly above its normal melting point (as determined, for example, by differential scanning calorimetry; DSC) so that no residual crystals can be detected optically or spectroscopically. Cooling this melt or solution leads to the formation of polymer single crystals, normally in the form of thin plates uniform in size and thickness, which can be ideally suited for further applications. These single crystals are thought to be initiated by submicroscopic nuclei that survived the dissolution procedure. Since the discovery of self-seeding in the 1960s[4] the process has attracted attention as a means of controlling the nucleation step of polymer crystallization without the need for external nucleating agents, to form uniform single crystals of homopolymers and block copolymers and also for materials applications.[5]

Polyferrocenyldimethylsilane (PFS) is a crystalline metal-containing polymer with a range of interesting properties.[6] PFS block copolymers and closely related materials self-assemble to form elongated micelles with a semicrystalline core.[7] They are the only currently known synthetic polymers to form fiberlike micelles by a mechanism resembling that for the formation of amyloid fibers from soluble protein. Thus soluble polymeric "monomers" consisting of block copolymer unimers condense onto both ends of seed structures present in, or intentionally added to, the solution.[8] PFS block copolymer fiber formation involves a conformation change driven by epitaxial crystallization of PFS moieties onto the open ends of the PFS core of existing micelles or seeds obtained by subjecting preformed fiberlike micelles to mild sonication. Thus, the number of micelles at the end of the growth process is determined by the number of seeds present at the beginning.[9] Moreover the seeded growth experiments permit exquisite control over the types of structures obtained. For example, one type of PFS block copolymer such as PI-PFS (PI = polyisoprene) can be used to form the seed structure, and a different type of PFS block copolymer such as PFS-PDMS (PDMS = polydimethylsiloxane) can be grown off the ends. In this way striking novel architectures referred to as "triblock co-micelles" can be prepared.[9,10] Our recent work targets a deeper understanding of the self-assembly process for PFS block copolymers in order to develop principles that can be extended to other coil-crystalline block copolymers. This may allow access to processable suspensions of semi-flexible nanowires with useful optical or electronic properties. With proper control over their length and dimensions, such structures could be incorporated into optoelectronic devices or used in other applications.

In 2009, Reiter and co-workers[1] examined the mechanism of self-seeding in the melt for PFS homopolymer single crystals and for single crystals formed by P2VP-PEO block copolymers. (P2VP = poly(2-vinylpyridine), PEO = poly(ethylene oxide)). They showed for these two systems that the number density of the regenerated crystals decreased exponentially with the increase of the dissolution temperature but did not vary with the dissolution time. They also found a correlation in molecular orientation between a starting single crystal and the regenerated crystal clones formed through the self-seeding process. Their experiments established that single-crystal growth by self-seeding operates under thermodynamic control, consistent with the idea that upon heating, the less perfect crystals will melt and more perfect crystallites will survive.[11] It is not a kinetic effect associated with polymer conformational memory effects.[12]

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[*] J. S. Qian, Dr. G. Guerin, Y. J. Lu, G. Cambridge, Prof. M. A. Winnik
Department of Chemistry, University of Toronto
80 St. George Street Toronto, Ontario, M5S 3H6 (Canada)
Fax: (+1) 416-978-0541
E-mail: mwinnik@chem.utoronto.ca

Prof. I. Manners
School of Chemistry, University of Bristol
Bristol BS8 1TS (United Kingdom)
Fax: (+44) 117-929-0509
E-mail: ian.manners@bristol.ac.uk

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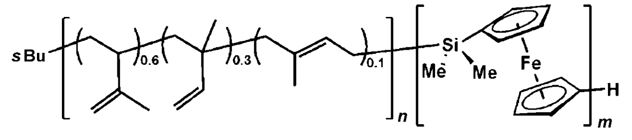
Here, we describe an approach to control the length of rodlike micelles formed by PFS block copolymers by taking advantage of the concept of "self-seeding." Specifically we describe experiments in which sonication-shortened fiberlike micelles of a PFS block copolymer in decane, (PI_{1000}-PFS_{50};[13,14] the subscripts refer to the number average degree of polymerization, the structure is shown in Scheme 1) were subjected to typical self-seeding conditions: heating the solutions to temperatures at which the micelles start to disappear, followed by slow cooling to room temperature, where the dissolved polymer crystallizes at the ends of the remaining fragments. As a result, we obtained longer micelles with a very narrow length distribution in which the length was very sensitive to the dissolution temperature.



Scheme 1. Structure of PI_{1000}-PFS_{50}, $n=1000$, $m=50$.

Micelles of PI_{1000}-PFS_{50} in decane were prepared at 0.1 mg mL^{-1} by heating the polymer–solvent mixture to 90 °C for 0.5 h, and then cooling it slowly (ca. 1.5 °C min^{-1}) to room temperature. In this way we obtained fiberlike micelles with a PFS core of uniform width (ca. 20 nm), as seen in unstained TEM images (see Figure S1 in the Supporting Information), with lengths on the order of 10 μm. Previous experiments established that the mass per unit length of these micelles (M_L) corresponds to 1.9 polymer molecules per nm.[13] When these solutions were subjected to sonication at 23 °C for two 10 min periods using a 70 W ultrasonic cleaning bath, much shorter micelles were obtained. When long PFS block copolymer micelles are sonicated, they fracture to form shorter micelles of uniform width, and with a fracture rate that decreases strongly as the micelles become shorter.[15] Intense or prolonged sonication can lead to very small structures.[16] In Figure 1 a, we show a TEM image of the micelle fragments obtained here. From the histogram of their length distribution (Figure 1 b), we calculated the number- and weight-average length (L_n, L_w, respectively), and the standard deviation σ of the length distribution ($L_n = 52$ nm, $L_w = 59$ nm, $L_w/L_n = 1.13$, $\sigma/L_n = 0.365$).

We then annealed aliquots of the solutions of micelle fragments in an oil bath at different dissolution temperatures for 30 min and then allowed these solutions to cool slowly in air back to room temperature. Experimental details are provided in the Supporting Information. As shown in the TEM images in Figure 1 c and d for samples annealed at 70, and 80 °C, we obtained longer micelles with a narrow length distribution. The PFS core remained uniform in width with a diameter essentially identical to that of the initially prepared micelles. The results of all these experiments are summarized in Figure 1 e, where we plot L_n versus dissolution temperature and find that for solutions heated above 60 °C, there was drastic increase in length. The micelle fragments that were approximately 50 nm long were transformed into micelles that could be greater than 1 μm long. For these samples, the size distribution remains very narrow, as shown by the error bars (σ) for each point. The values of L_n, L_w, L_w/L_n, and σ/L_n for all of these samples are presented in Table S1 in the Supporting Information.

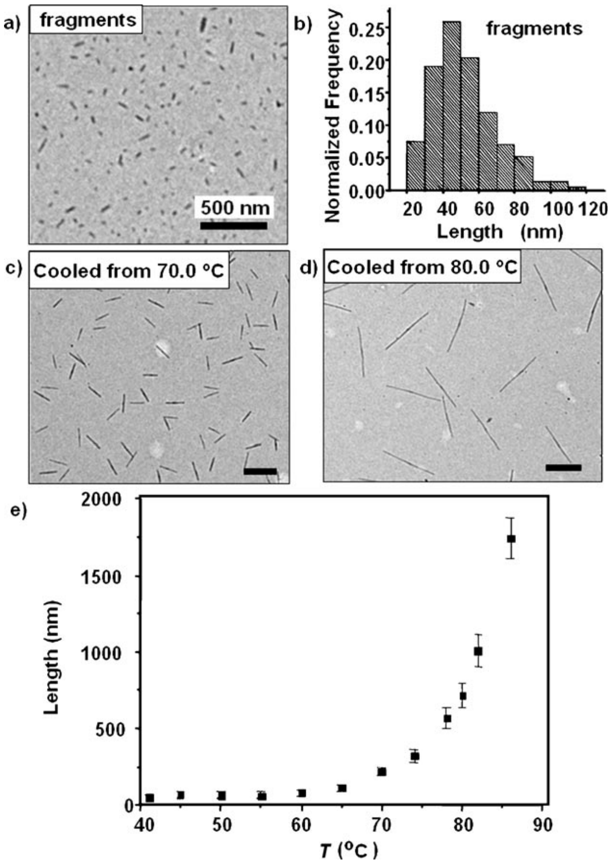


Figure 1. Micelles of PI_{1000}-PFS_{50} in decane at 23 °C. a) TEM images of micelles after sonication. b) Histogram of the length distribution of the sonicated micelles. c,d) TEM images of micelles formed after annealing decane solutions for 30 min at 70 and 80 °C, respectively, and cooling. Scale bar: 500 nm. e) Mean micelle length L_n vs dissolution temperature for solutions annealed for 30 min (the error bars are the standard deviations σ of the length distribution). For the micelles sample shown in (c) $L_n = 168$ nm, $L_w/L_n = 1.02$, $\sigma/L_n = 0.155$; for (d) $L_n = 718$ nm, $L_w/L_n = 1.01$, $\sigma/L_n = 0.116$.

Some other features of this process are also important. To demonstrate that micelle growth occurs upon cooling, we placed a drop of hot solution, annealed at 80 °C, on a TEM grid. Images of this sample (Figure S2) show a mixture of short cylinders ($L_n \approx 120$ nm) and amorphous material, very different from the result in Figure 1 d. Reference [1] points out that crystal growth by self-seeding under thermodynamic control should yield crystals whose size depends only upon the annealing temperature and not on the annealing time. We tested the effect of annealing time on micelle length for two temperatures, 70 and 80 °C. Samples annealed for 10, 120, and 1440 min were examined by TEM after cooling back to room temperature. Neither L_n nor σ varied with annealing time (see Figure S3, Table S2 and S3). When the dissolution temperature was too high (≥ 95 °C), the micelles formed were too long to get accurate length information from TEM image analysis, and the structures seen on these TEM grids resembled those shown in Figure S1 for the initially prepared micelle samples. These results suggest that virtually all of the polymer contained in the micelle fragments dissolved at these high temperatures.

Elongation of the micelles through dissolution of the fragments in solution strongly resembles a self-seeding event. To test this idea, we examine these results in more detail. First, we note that each solution contains an equal mass of polymer, M. Second, the critical micelle concentration for this polymer in decane at room temperature is undetectably small.[14] Thus, there is a negligible amount of free polymer in solution at room temperature, and we can assume that all of the polymer present in each sample is incorporated into the micelles. As a consequence, the length of the micelles is connected to the number N of micelles present as given in Equation (1).

$$L_n = (1/M_L)(M/N) \qquad (1)$$

The thermodynamic argument for self-seeding supposes that it is the polymer less perfectly incorporated into the semicrystalline PFS core that dissolves at a given dissolution temperature, and that higher temperatures lead to dissolution and disappearance of a greater fraction of the remaining micelle fragments. As these fragments dissolve, they form free polymer in solution. The surviving fragments serve as seed crystals. As the solution is cooled, the polymer molecules in solution condense epitaxially onto the ends of these seed crystals, and the length of the micelles formed is determined by the number of seed crystals that survive the dissolution process.

Based upon these ideas, we used Equation (1) to calculate the fraction of seed micelles remaining after annealing at each temperature. This calculation took account of the initial length of the seed micelles before annealing and the final length after annealing at different temperatures. As shown in Figure 2a, we see that, as the dissolution temperature was increased in the range of 70 to 90 °C, the fraction of surviving seed decreased exponentially. This is one of the key characteristics of the self-seeding phenomenon as reported in reference [1].

The data in Figure 2a suggest that the length of the micelles should increase exponentially with the increase in dissolution temperature. To test this idea, we replot the data of Figure 1e in Figure 2b as $\ln(L_n)$ versus $1000/T$. In the range of 70 to 90 °C, the data fit well to this Arrhenius-type plot. Setting the slope of the plot equal to $-E/RT$, where R is the gas constant, we calculate an E value of 148 kJ mol^{-1}. Since micelle elongation operates under thermodynamic rather than kinetic control, this E value must be related to thermodynamic factors, for example, the enthalpy of dissolution of the micelles in decane.

In summary, short fragments of rodlike PFS block copolymer micelles in decane, approximately 50 nm in length, rearrange when the solutions are heated above a characteristic temperature (60 °C) and then cooled to room temperature. The net result is fewer micelles of increased length, of a similar uniform width, and a narrow length distribution. The overall process appears to involve selective dissolution of the micelle fragments of the lowest degree of crystallinity, with the surviving submicroscopic seeds serving as nuclei for the growth of micelles upon cooling. This process is irreversible. A cartoon illustrating the proposed mechanism is presented in Figure 3.

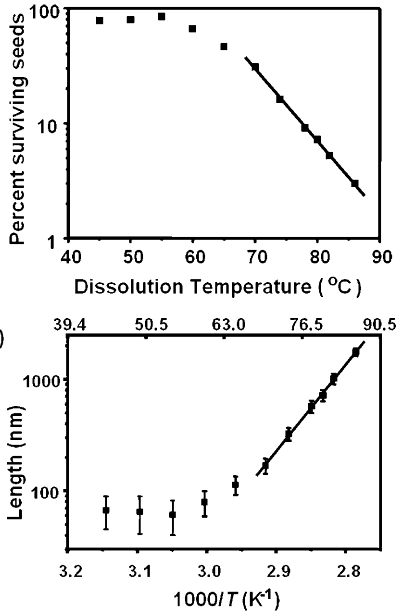


Figure 2. a) Semilogarithmic plot of fraction of surviving seeds in solutions of PI_{1000}-PFS_{50} micelle fragments in decane vs dissolution temperature. The solid line represents the linear best fit for the six points of highest T. b) Semilogarithmic plots of micelle length L_n versus $1000/T$ [K^{-1}], where T is the dissolution temperature. The error bars are as defined in Figure 1. The straight line represents the best fit for the six points of highest T to $\ln(L_n) = A - E/RT$, where A is a constant.

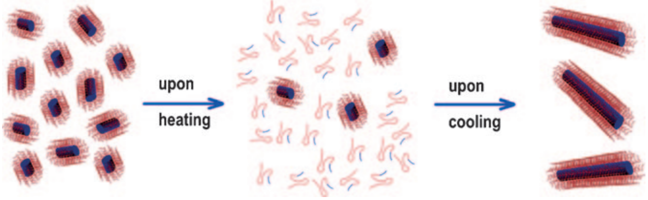


Figure 3. The proposed mechanism for the irreversible self-seeding process for PI-PFS micelles in decane solution.

The length of the micelles obtained (up to 1.5 μm) increased exponentially over the operative temperature range, implying that the number of surviving seeds decreased exponentially with temperature. The process operates under thermodynamic rather than kinetic control. These are the features of self-seeding of polymer crystals, and these experiments demonstrate that a typical self-seeding protocol can be used to generate one-dimensional nanostructures with controlled length.

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[1] J. J. Xu, Y. Ma, W. B. Hu, M. Rehahn, G. Reiter, *Nat. Mater.* **2009**, *8*, 348 – 353.

[2] B. Wunderlich, *Macromolecular Physics*, *Vol. 1*, Academic Press, New York, **1973**.

[3] G. Strobl, *Prog. Polym. Sci.* **2006**, *31*, 398 – 442.

[4] a) D. J. Blundell, A. Keller, A. J. Kovacs, *J. Polym. Sci. B.* **1966**, *4*, 481 – 486; b) D. J. Blundell, A. Keller, *J. Macromol. Sci. Part B* **1968**, *2*, 301 – 336.

[5] a) B. Lotz, A. J. Kovacs, *Kolloid Z. Z. Polym.* **1966**, *209*, 97 – 114; b) M. S. Hsiao, J. X. Zheng, R. M. V. Horn, R. P. Quirk, E. L. Thomas, H. L. Chen, B. Lotz, S. Z. D. Cheng, *Macromolecules* **2009**, *42*, 8343 – 8352; c) B. Li, C. Y. Li, *J. Am. Chem. Soc.* **2007**, *129*, 12 – 13.

[6] a) V. Bellas, M. Rehahn, *Angew. Chem.* **2007**, *119*, 5174 – 5197; *Angew. Chem. Int. Ed.* **2007**, *46*, 5082 – 5104; b) G. R. Whittell, I. Manners, *Adv. Mater.* **2007**, *19*, 3439 – 3468; c) I. Korczagin, R. G. H. Lammertink, M. A. Hempenius, S. Golze, G. J. Vancso, *Adv. Polym. Sci.* **2006**, *200*, 91 – 117.

[7] a) J. A. Massey, K. Temple, L. Cao, Y. Rharbi, J. Raez, M. A. Winnik, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 11577 – 11584; b) L. Cao, I. Manners, M. A. Winnik, *Macromolecules* **2002**, *35*, 8258 – 8260.

[8] J. S. Qian, M. Zhang, I. Manners, M. A. Winnik, *Trends Biotechnol.* **2010**, *28*, 84 – 92.

[9] X. S. Wang, G. Guerin, H. Wang, Y. S. Wang, I. Manners, M. A. Winnik, *Science* **2007**, *317*, 644 – 647.

[10] T. Gädt, N. S. Ieong, G. Cambridge, M. A. Winnik, I. Manners, *Nat. Mater.* **2009**, *8*, 144 – 150.

[11] A. T. Lorenzo, M. L. Arnal, J. J. Sanchez, A. J. Müller, *J. Polym. Sci. Part B* **2006**, *44*, 1738 – 1750.

[12] a) M. V. Massa, M. S. M. Lee, K. Dalnoki-Veress, *J. Polym. Sci. Part B* **2005**, *43*, 3438 – 3443; b) A. Maus, E. Hempel, T. Thurn-Albrecht, K. Saalwächter, *Eur. Phys. J. E* **2007**, *23*, 91 – 101.

[13] G. Cambridge, G. Guerin, I. Manners, M. A. Winnik, *Macromol. Rapid Commun.* **2010**, *31*, 934 – 938.

[14] J. S. Qian, G. Guerin, G. Cambridge, I. Manners, M. A. Winnik, *Macromol. Rapid Commun.* **2010**, *31*, 928 – 933.

[15] G. Guerin, H. Wang, I. Manners, M. A. Winnik, *J. Am. Chem. Soc.* **2008**, *130*, 14763 – 14771.

[16] J. B. Gilroy, T. Gädt, G. R. Whittell, L. Chabanne, J. M. Mitchels, R. M. Richardson, M. A. Winnik, I. Manners, *Nat. Chem.* **2010**, *2*, 566 – 570.