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Large Area Ordering at Room Temperature in Thin Films of Poly(isoprene-*block*-ferrocenylsilane)s for Nanofabrication

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Block copolymer thin films have attracted significant interest in nanofabrication as self-assembled templates.[1,2] As the glass transition temperature T_g of one (or both) of the block copolymer constituents is often above room temperature, prolonged heating at high temperatures is often required to perfect the order of the patterns. This slows down the manufacturing process of block-copolymer-based microphase-separated platforms and enhances the chance of introducing structural errors. Block copolymers with poly(ferrocenylsilane)[3] (PFS) blocks have been used by us, and others, to fabricate nanoscale platforms in a variety of applications, including nanoperiodic dots and pillars in Si and Si_3N_4,[4,5] magnetic nanodots,[6] core−shell micelles for nanowires,[7] and nanopatterned surfaces for catalytic growth of carbon nanotubes.[8] PFS's[9,10] owe many of their useful and unique characteristics to the presence of ferrocene and alkylsilane units in the main chain. Their high resistance to reactive ion etching, for example, allows pattern transfer into Si or Si_3N_4, as we showed for asymmetric block copolymers composed of polyisoprene (PI)[4,11] or polystyrene (PS)[12] and poly(ferrocenyldimethylsilane) (PFDMS) blocks.

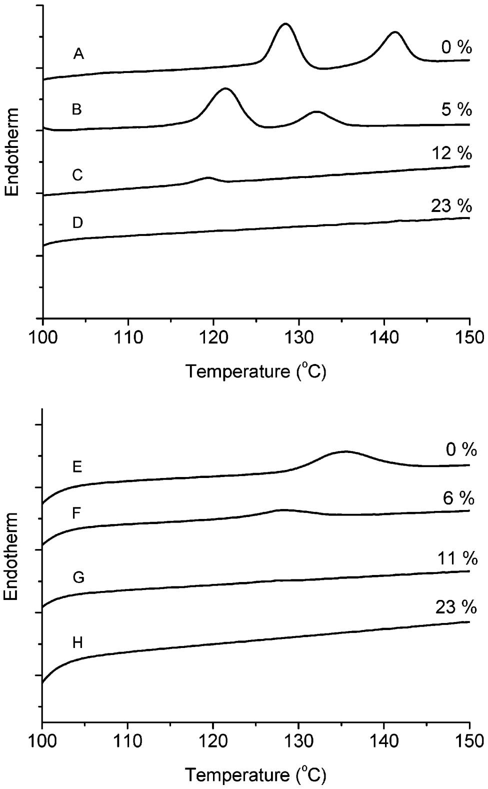

Figure 1. DSC heating scans of PFS copolymers (top) with increasing amounts of EM: (A) PFDMS, (B) F 13($DM_{95}EM_5$), (C) F 16($DM_{88}EM_{12}$), and (D) F 15($DM_{77}EM_{23}$). DSC heating scans of PI-*b*-PFS block copolymers (bottom) with increasing amounts of EM: (E) IF 58/22 [EM = 0%], (F) IF 54/18($DM_{94}EM_6$), (G) IF 52/20($DM_{89}EM_{11}$), and (H) IF 56/21($DM_{77}EM_{23}$). All samples were kept at 95 °C for 2 h, prior to heating.

PI-*b*-PFDMS thin films do not require annealing to obtain regular, phase-separated patterns as the T_g's of the constituents are near room temperature.[4,11,13] Over longer periods of time, however, PFDMS crystallizes at room temperature. Hedrite-like structures form, destroying the microdomain morphology.[11] To obtain stable, well-ordered nanostructures, crystallization of the organometallic constituent must be suppressed. Amorphous poly(ferrocenylsilane)s are in principle obtained by polymerizing unsymmetrically substituted, silicon-bridged ferrocenophanes.[14] Living anionic polymerization, a method of choice for preparing well-defined PFS homo- and block copolymers,[10,15] however, has led in the case of the unsymmetrical ethylmethylsila[1]ferrocenophane or methylphenylsila[1]ferrocenophane to corresponding amorphous PFS's with higher polydispersities ($\bar{M}_w/\bar{M}_n = 1.2-1.3$)[16] than typically found for the dimethylsila[1]ferrocenophane monomer ($\bar{M}_w/\bar{M}_n = 1.05-1.1$), likely due to the remaining impurities in the former monomers.[17]

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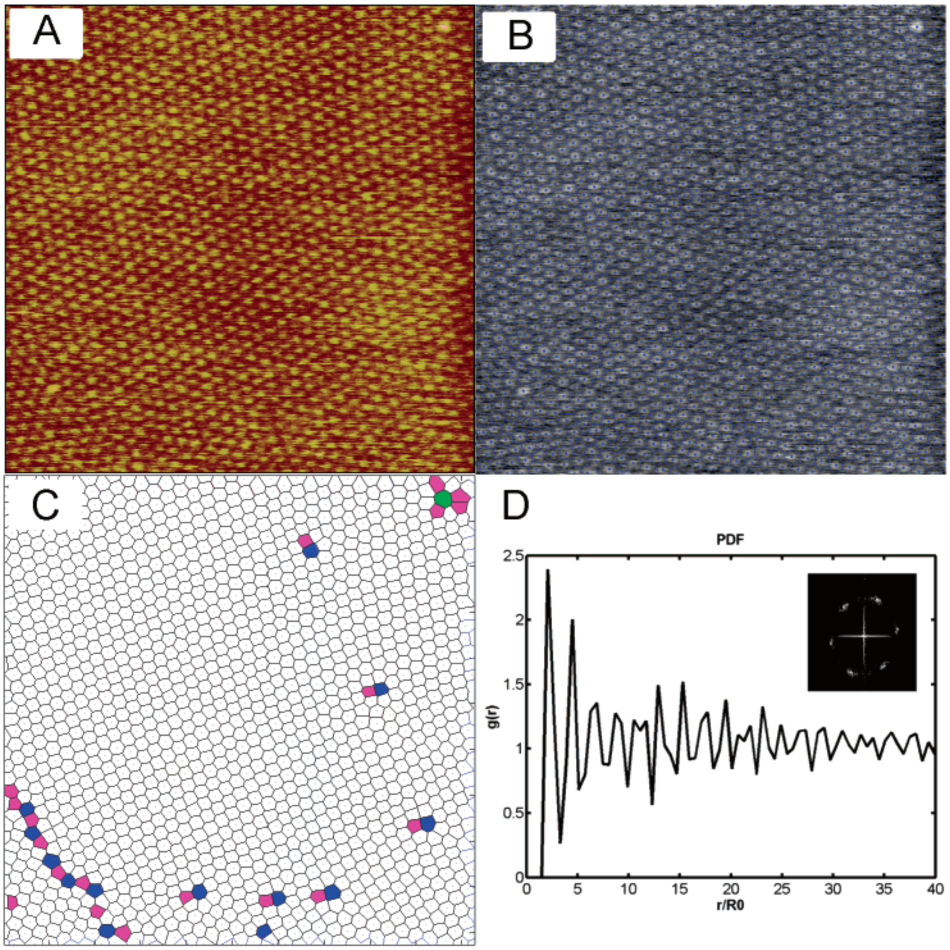
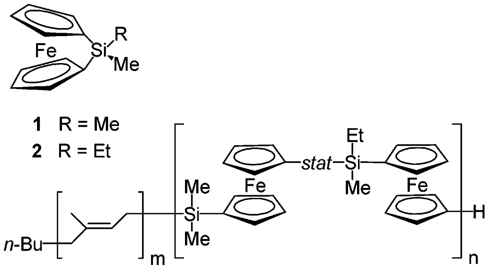


Figure 2. (A) AFM TM height image of a IF 35/10($DM_{89}EM_{11}$) block copolymer thin film, scan size 1 μm × 1 μm. (B) Voronoi diagram of image 2A, projected on top of the image. (C) Voronoi diagram, where sites surrounded by 6 neighbors are unshaded, 5-fold-coordinated sites are magenta, and 7-fold-coordinated sites are blue. (D) Pair distribution function and Fourier transform of image 2A.

Scheme 1. Organic−Organometallic Block Copolymer Featuring an Amorphous Organometallic Block



Here we present a route to amorphous, low-T_g organic−organometallic block copolymers with narrow molar mass distributions. Living anionic copolymerizations of dimethylsila[1]ferrocenophane **1** and ethylmethylsila[1]ferrocenophane **2** were employed to form amorphous PFS blocks. We demonstrate significant improvements in block copolymer ordering using amorphous PI-*b*-PFS as compared with PI-*b*-PFDMS and PS-*b*-PFDMS structures (Scheme 1).

Table 1. PFS Statistical Copolymer and PI-*b*-PFS Block Copolymer Characteristics[a]

polymer	$\bar{M}_n$ [kg/mol]	$\bar{M}_w$ [kg/mol]	$\bar{M}_w/\bar{M}_n$	EM [mol %]	PFS [vol %]
F 13($DM_{95}EM_5$)	12.8	13.5	1.05	5	
F 16($DM_{88}EM_{12}$)	15.9	17.7	1.11	12	
F 15($DM_{77}EM_{23}$)	15.3	16.7	1.09	23	
IF 58/22	79.8	83.3	1.04	0	22
IF 54/18($DM_{94}EM_6$)	71.8	74.2	1.03	6	19
IF 35/10($DM_{89}EM_{11}$)	45.1	46.7	1.04	11	18
IF 52/20($DM_{89}EM_{11}$)	71.5	74.8	1.04	11	22
IF 56/21($DM_{77}EM_{23}$)	76.7	80.8	1.05	23	22

[a] Compositions measured by ^{1}H NMR spectroscopy. Molar masses obtained by GPC in THF, relative to polystyrene standards. The notation used to identify the diblock copolymers includes the corresponding molar masses (M_n, in 10^3 g/mol) of the two blocks, i.e., IF 58/22 is a 58000 g/mol polyisoprene-*b*-22000 g/mol poly(ferrocenylsilane) diblock. DM denotes incorporated **1**; EM denotes incorporated **2**.

A series of statistical copolymers of **1** and **2** with varying compositions (Table 1) were synthesized and characterized by ^{1}H and ^{13}C NMR spectroscopy and gel permeation chromatography (GPC). The amounts of **2** incorporated in the PFS chains, as gauged by ^{1}H NMR, agreed well with the monomer ratios used. Clearly, polydispersity values did not increase by copolymerizing **1** with **2**. The copolymers constitute orange, gummy substances, with T_g's in the range of 11−20 °C, depending on molar mass and composition. Their thermal behavior was studied by allowing isothermal crystallization at 95 °C, followed by DSC heating scans (Figure 1, top). For poly(ferrocenyldimethylsilane) (M_n = 15200 g/mol, M_w/M_n = 1.05), trace A, two endothermic peaks associated with the melting-recrystallization behavior of PFDMS were observed.[18] Upon introducing ferrocenyl-

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ethylmethylsilane (EM) units in the chains, the melting transitions shift to lower temperatures as anticipated for statistical copolymers. At 12 mol % EM the high-temperature melting transition disappeared. Melting transitions were no longer observed upon increasing the EM percentage to 23%. A similar trend of decreasing, and subsequently disappearing, melting transitions was found for the corresponding PI-*b*-PFS block copolymers (Figure 1, bottom).[19]

Thin films of the amorphous block copolymers on silicon were imaged by tapping mode AFM (Figure 2A), showing a relatively well-ordered monolayer of PFS spheres. To establish the degree of ordering more quantitatively, a Voronoi construction was employed, which aids in the visualization of packing defects and grain boundaries occurring in the block copolymer thin film.[20] Spheres surrounded by 6 neighbors appear as hexagons while 5- and 7-fold-coordinated sites are displayed as pentagons and heptagons, respectively. A dislocation core is seen as a bound 5−7 pair; a grain boundary appears as a row of dislocations.[21,22] A simple sphere-finding algorithm was used to identify the sphere centers, enabling the construction of a Voronoi diagram which was superimposed on the original image (Figure 2B). A perfect match between the domains and the polygons was found. Defects are shaded in the Voronoi diagram in Figure 2C. The amorphous block copolymer self-organized at room temperature to a well-ordered monolayer of organometallic spheres, with a single hexagonal grain extending over almost the whole scanned area of 1 μm × 1 μm. A pair-distribution function[20] associated with the AFM image (Figure 2D) confirmed the ordering quality and the relatively large single grain size. In comparison, the average grain size found in the PS-*b*-PFDMS diblock copolymer thin films is typically around 280 nm.[23] Similar correlation length values were observed for PI-*b*-PFDMS diblock copolymers. PS−P2VP diblock copolymer thin films on flat silicon substrates showed single-grain sizes of about 400 nm.[24] The increased correlation length for the amorphous PI-*b*-PFS block copolymer monolayers likely is a result of the high molecular mobility, allowing for the removal of point defects and grain boundaries by sphere rearrangement. The high molecular mobility is due to both the low-T_g polyisoprene block and a lowered T_g of the PFS block[11,25] combined with the suppression of crystallization of the PFS domains.

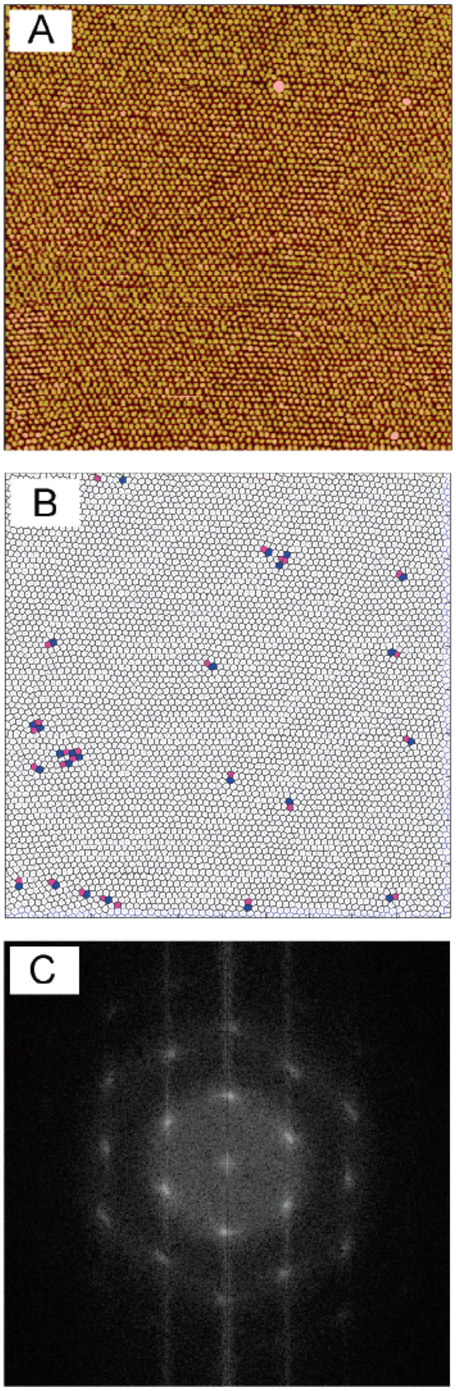

Figure 3. (A) AFM TM height image of a IF 35/10(DM$_{89}$EM$_{11}$) block copolymer thin film after an O_2 plasma treatment, scan size 2 μm × 2 μm. (B) Voronoi diagram, where sites surrounded by 6 neighbors are unshaded, 5-fold-coordinated sites are magenta, and 7-fold-coordinated sites are blue. (C) Fourier transform of image A, showing the high degree of order of the etched film.

Figure 3A shows an AFM TM image, scan size 2 μm × 2 μm, of an amorphous PI-*b*-PFS block copolymer thin film exposed to an O_2 plasma. In this treatment, the organic matrix is removed and arrays of Fe/Si/O domains remain. The relatively high degree of order of the etched film is demonstrated by the Voronoi diagram, which shows the scanned area to consist of a single grain containing approximately 5 defects/μm^2 (Figure 3B). The six sharp first-order Bragg peaks and twelve second-order peaks observed in the Fourier transform (Figure 3C) provide further evidence

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(19) Isothermal crystallization experiments performed for several days at larger undercoolings (at 40 °C) led to the same observations. Thin films of PI-*b*-PFS, containing 11 or 23 mol % of EM, showed no sign of crystallization after being kept at room temperature for several days.

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for the high degree of order. This image also demonstrates that large, well-ordered areas can be transferred to underlying substrates by reactive ion etching, using these block copolymer patterns as nanolithographic masks.

In conclusion, by incorporating unsymmetrically substituted ferrocenylsilane units in PFDMS blocks,[26] crystallization in PI-*b*-PFDMS block copolymer thin films can be effectively suppressed. In thin films, the amorphous low-T_g diblock copolymers self-assemble to form well-ordered monolayers of PFS spheres, with single-grain sizes larger than 1 μm × 1 μm, without thermal annealing. This significant increase in correlation length over previous crystallizable PS-*b*-PFDMS or PI-*b*-PFDMS block copolymers renders the amorphous diblock copolymers highly useful as self-assembling templates for nanolithography or other functional nanostructures. Topographically patterned substrates may induce order over even larger areas.

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(26) Monomers **1** and **2** were prepared as described in refs 15, 16, and 27. PFDMS and statistical copolymers of **1** and **2** were synthesized by anionic polymerization in THF, using *n*-BuLi as the initiator. PI-*b*-PFS block copolymers were synthesized by sequential anionic polymerization; see ref 4. Isoprene polymerizations in ethylbenzene were initiated by *n*-BuLi. After completion of the PI block, **1** and **2** were added, followed by THF, for the formation of the PFS block. Degassed methanol was added after 1 h. Polymers were precipitated in methanol and dried under vacuum. DSC measurements were performed on a Perkin-Elmer DSC-7 instrument. Samples were annealed above the melting temperature and quenched (300 K/min) to a holding temperature to allow isothermal crystallization, followed by heating (10 K/min) from this temperature to above the equilibrium melting temperature (143 °C); see ref 18. T_g values correspond to the midpoint of the heat capacity change. Thin films were spin-coated from 1 wt % PI-*b*-PFS solutions in toluene and left overnight at room temperature to phase-separate. Oxygen reactive ion etching experiments and AFM studies were performed as described in ref 4.

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