



# Diblock copolymers with an amorphous, high glass transition temperature, organometallic block: synthesis, characterisation and self-assembly of polystyrene-*b*-poly(ferrocenylisopropylmethylsilane) in the bulk state

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## ARTICLE INFO

### Article history:

Received 2 July 2009

Received in revised form

13 August 2009

Accepted 19 August 2009

Available online 6 September 2009

### Keywords:

Block copolymer

Metallopolymer

Ring-opening polymerisation

## ABSTRACT

Living anionic ring-opening polymerisation of isopropylmethylsila[1]ferrocenophane yields poly(ferrocenylisopropylmethylsilane) (PFiPMS) with controlled molecular weights and narrow polydispersities up to  $M_n = \text{ca. } 20,000$  Da. Polystyrene-*b*-poly(ferrocenylisopropylmethylsilane) (PS-*b*-PFiPMS) diblock copolymers have been prepared via sequential living anionic polymerisation. These materials are examples of diblock copolymers with an amorphous, organometallic block with a glass transition temperature ( $T_g$ ) above room temperature (60 °C). High molecular weight diblock copolymers ( $M_n = 42,000$ – $51,000$  Da) were targeted with low polydispersities (PDI = 1.1). As both blocks are amorphous, these materials self-assemble into predictable morphologies in the bulk state with well-ordered nanodomains.

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## 1. Introduction

The introduction of metal centres into block copolymers provides a means of increasing the functionality of these self-assembling materials, and is currently an area of growing interest [1–4]. Polyferrocenylsilane (PFS) block copolymers are known with a range of organic and inorganic coblocks [3,5,6]. These materials self-assemble in the bulk and in thin films to give ordered arrays of nanostructures containing iron and silicon [7–14]. The presence of a PFS block introduces redox activity [15–17], catalytic activity [18–22], resistance to reactive ion etching [11,14], and access to magnetic nanomaterials via pyrolysis [23]. As a result, PFS block copolymers have been investigated for a range of applications such as nanolithographic templates for surface-enhanced Raman spectroscopy (SERS) substrates [24] and high density data storage devices [25], and as catalysts for carbon nanotube growth for device fabrication [18–22,26].

The thermophysical properties of PFS can be tailored by changing the substituents at the silicon. PFS is semicrystalline when symmetrically substituted by short *n*-alkyl groups, but amorphous when asymmetrically substituted [6,27]. The vast majority of PFS block copolymers to date have used a PFS block with

two methyl groups at the silicon. However, the use of such a semicrystalline PFS block can introduce complications when trying to access nanoscale morphologies in the bulk and thin films, as crystallinity can compete with the incompatibility of constituent blocks, the driving force for regular self-assembly [28–32]. In order to eliminate this problem, an amorphous, asymmetrically substituted PFS with ethyl and methyl substituents at silicon (PFEMS) has been synthesised for use in PFS diblock copolymers where self-assembly in the solid state is required [9,10,33]. A disadvantage of using a PFEMS block, however, is the glass transition temperature ( $T_g$ ) is close to room temperature (ca. 25 °C) [9,10]. This means PFEMS-containing block copolymers, particularly with high PFEMS volume fractions, are difficult to use in many applications because of their low  $T_g$ . Therefore, access to an amorphous PFS block with a  $T_g$  sufficiently above room temperature has become desirable. Raising the  $T_g$  of the PFS block can be achieved by increasing the steric bulk of one of the groups at the silicon. In this paper, we report the preparation of a new strained [1]ferrocenophane monomer, with isopropyl and methyl groups at the silicon, and subsequent homopolymerisation via a living anionic mechanism to yield poly(ferrocenylisopropylmethylsilane) (PFiPMS). The preparation of PS-*b*-PFiPMS (PS = polystyrene) diblock copolymers and their morphological characterisation is also reported with a view to offering a high  $T_g$ , amorphous PFiPMS diblock copolymer for nanolithographic, nanoceramic, and catalyst precursor applications.

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## 2. Experimental

### 2.1. Equipment and materials

All reactions were carried out on a vacuum line under purified nitrogen or in a MBraun glove box in an inert purified argon atmosphere unless otherwise stated.

Ferrocene pellets purchased from Octel Germany were crushed to a fine powder before use. N,N,N',N'-tetramethylethylenediamine (tmeda) from Fisher was dried over CaH<sub>2</sub> and purified by distillation under reduced pressure. <sup>n</sup>Butyllithium (<sup>n</sup>BuLi) purchased from Acros (1.6 M in hexanes) was used as received. Dichloroisopropylmethylsilane from ABCR was distilled prior to use. THF was distilled under reduced pressure from Na/benzophenone. Hexanes and diethylether were purified using anhydrous engineering double alumina and alumina/copper catalyst drying columns. Methanol was deoxygenated by freeze, pump and thaw method. Cyclohexane was dried over CaH<sub>2</sub> before distillation. Styrene monomer from Acros Organics was dried over CaH<sub>2</sub> and subsequently distilled twice under reduced pressure. <sup>sec</sup>Butyllithium (<sup>sec</sup>BuLi) purchased from Aldrich (1.4 M in hexanes) was used as received.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained using Jeol Lambda 300 and ECP (Eclipse) 400 spectrometers.

Mass spectrometry (EI) was carried out using a VG Autospec spectrometer in Electron Ionisation (EI) mode.

Powder X-ray diffraction (XRD) was carried out on a Bruker D8 advance diffractometer.

Ultra-thin slices of bulk samples were prepared using an ultramicrotome and collected on carbon coated copper grids. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM 1200 EX microscope.

A Laurell WS-400B-6NPP/lite spin coater was used to prepare thin films which were subsequently plasma etched using a Harrick Plasma Cleaner. AFM was carried out using a Nanoscope 3D microscope.

Gel Permeation Chromatography (GPC) was carried out on a Viscotek GPCmax chromatograph equipped with a triple detector array. A flow rate of 1.0 ml/min was used with THF as the eluent. Differential scanning calorimetry was carried out on a TA Instruments DSC Q100 fitted with a DSC refrigerated cooling system.

Birefringence measurements were carried out on an Olympus BX50 optical microscope with crossed polarizers and a temperature controlled chamber.

### 2.2. Synthesis of Isopropylmethylsila[1]ferrocenophane (**1**)

Dilithioferrocene·tmeda was synthesised as described by Rider et al. [9]. Dilithioferrocene·tmeda (11.6 g, 36.9 mmol) was suspended in diethylether (300 ml) and cooled to -78 °C using dry ice and acetone. Distilled dichloroisopropylmethylsilane (7.0 ml, 46.0 mmol) was added dropwise and allowed to reach room temperature overnight whereby the reaction changed colour from orange to deep red. Diethylether was removed under vacuum and solids dried under dynamic vacuum for at least 5 h. Dissolution of the solids in hexanes (400 ml) followed by filtration and recrystallization yielded the isopropylmethylsila[1]ferrocenophane (**1**) (6.5 g, 65%) as deep red crystals. Subsequent recrystallization and sublimations under vacuum at 60 °C yielded monomer suitably pure for anionic polymerisation.

Characterisation of the monomer was carried out by mass spectrometry and <sup>1</sup>H NMR. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>) δ = 0.29 (3H, Si-CH<sub>3</sub>), 1.18 (7H, Si-CH(CH<sub>3</sub>)<sub>2</sub>), 3.95 (4H, Cp), 4.42 (4H, Cp). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) δ = -8.5 (Si-CH<sub>3</sub>), 11.4 (Si-CH(CH<sub>3</sub>)<sub>2</sub>), 16.6 (Si-CH(CH<sub>3</sub>)<sub>2</sub>), 33.0

(ipso-C Cp), 75.4 (Cp) 76.0 (Cp), 77.3 (Cp), 77.5 (Cp). MS (EI) *m/z* (%) 270 (100) [M<sup>+</sup>], 227 (52) [M<sup>+</sup>-iPr], 213 (58) [M<sup>+</sup>-iPr, -Me].

### 2.3. Synthesis and characterisation of PFiPMS homopolymer

The preparation of the representative homopolymer Sample 1 (Table 1) is described. In a glove box under inert argon atmosphere, isopropylmethylsila[1]ferrocenophane (**1**) (0.2 g, 0.7 mmol) was weighed into a glass vial and dissolved in THF (1 ml). To this <sup>n</sup>BuLi (25 μl, 0.04 mmol) was added using a microsyringe and the polymerisation allowed to proceed for 1.5 h. After this time the vial was fitted with a septum, removed from the glove box and the reaction rapidly terminated with a few drops of degassed methanol. The polymer solution was precipitated into rapidly stirring methanol to give an orange powder with a yield of 0.18 g (90%) followed by overnight drying in a vacuum oven (40 °C). GPC analysis: *M<sub>n</sub>* = 5,900 Da, PDI = 1.08.

<sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>) δ = 0.52(3H, Si-CH<sub>3</sub>), 1.05(6H, Si-CH(CH<sub>3</sub>)<sub>2</sub>), 1.22 (1H, Si-CH(CH<sub>3</sub>)<sub>2</sub>), 4.06(4H, Cp), 4.27(4H, Cp). <sup>13</sup>C NMR(CD<sub>2</sub>Cl<sub>2</sub>) δ = -4.6(Si-CH<sub>3</sub>), 14.8(Si-CH(CH<sub>3</sub>)<sub>2</sub>), 18.5(Si-CH(CH<sub>3</sub>)<sub>2</sub>), 68.3(ipso-C Cp), 69.5(ipso-C Cp), 71.1(Cp), 71.5(Cp), 73.8(Cp), 74.2(Cp).

Powder XRD of both a sample thermally annealed above the *T<sub>g</sub>* of the homopolymer (70 °C for 24 h under vacuum) and an unannealed sample displayed a broad halo centred at *d* = 3.08 Å with no distinguishable peaks.

### 2.4. Synthesis and characterisation of PS-*b*-PFiPMS diblock copolymers

The preparation of the diblock copolymer PS<sub>346</sub>-*b*-PFiPMS<sub>57</sub> (Table 2) is described as a representative example where subscripts denote the degree of polymerisation. In an inert atmosphere glove box styrene (0.8 g, 7.7 mmol) was stirred in cyclohexane (4.2 ml) in a glass vial and initiated with <sup>sec</sup>BuLi (16.8 μl, 0.02 mmol). After 1 h, half of the living polystyrene solution was removed and quenched with degassed methanol. The molecular weight of the PS aliquot was determined by PS calibrated GPC. To the remaining living polystyrene solution, isopropylmethylsila[1]ferrocenophane (**1**) (0.2 g, 0.7 mmol) in THF (1 ml) was rapidly added. Following stirring for 4 h, the reaction was quenched with degassed methanol. The diblock copolymer was precipitated into rapidly stirring methanol and dried overnight in a vacuum oven at 40 °C to yield an orange powder 0.57 g (95%).

GPC analysis: *M<sub>n</sub>* = 51,000, PDI = 1.09. <sup>1</sup>H NMR(CD<sub>2</sub>Cl<sub>2</sub>) δ = 0.52 (3H, Si-CH<sub>3</sub>), 1.05(6H, Si-CH(CH<sub>3</sub>)<sub>2</sub>), 1.24(1H, Si-CH(CH<sub>3</sub>)<sub>2</sub>), 1.58 (2H, CH<sub>2</sub>CH(Ph)), 1.87(1H, CH<sub>2</sub>CH(Ph)), 4.06(4H, Cp), 4.27(4H, Cp), 6.57–7.11(5H, CH<sub>2</sub>CH(Ph)).

Block volume fractions were calculated by GPC and integration of <sup>1</sup>H NMR peaks representing the PS phenyl ring and PFiPMS cyclopentadienyl rings. A calculated density of 1.26 g/ml was used

**Table 1**  
Characterisation of PFiPMS homopolymers.

Sample	Monomer: initiator ratio	<i>M<sub>n</sub></i> Th/Da <sup>a</sup>	<i>M<sub>n</sub></i> Exp/Da	Polym'n time/h	PDI	Yield/%	<i>T<sub>g</sub></i> /°C
1	17.5	5,000	5,900	1.5	1.08	90	45
2	55.5	15,000	16,000	4.0	1.13	97	50
3	92.5	25,000	25,000	4.0	1.26	90	58
4	128.5	35,000	29,000	5.5	1.30	69	60
5	128.5	35,000	31,000	7.0	1.40	46	60

<sup>a</sup> Assuming 100% conversion of monomer **1**.

**Table 2**  
Characterisation of PS-*b*-PFiPMS diblock copolymers.

Polymer	$\phi_{\text{PFiPMS}}$	$M_{n\text{Tot}}/\text{Da}$	PDI	Yield/%
PS <sub>346</sub> - <i>b</i> -PFiPMS <sub>57</sub>	0.26	51,000	1.09	95
PS <sub>247</sub> - <i>b</i> -PFiPMS <sub>71</sub>	0.38	45,000	1.14	92
PS <sub>82</sub> - <i>b</i> -PFiPMS <sub>124</sub>	0.77	42,000	1.10	93

for the PFiPMS block using the molar mass and molar volume from constituent atoms [34].

### 2.5. Bulk self-assembly

Bulk samples were prepared by slow casting of a concentrated toluene solution (~30 mg/ml) onto a glass slide over two days. The resulting films were solvent annealed in a toluene vapour chamber overnight. Thermal annealing was carried out at 150 °C under vacuum for 4 days followed by subsequent quenching with liquid nitrogen. Ultra-thin sections (~50 nm) of the bulk films were microtomed and imaged by TEM.

### 2.6. Thin film self-assembly

Thin films were prepared by spin coating 0.25 w/t% toluene solutions on to Si wafers followed by solvent annealing in a toluene chamber for 3 h. The films were then treated with O<sub>2</sub> plasma for 30 s before being imaged by AFM.

## 3. Results and discussion

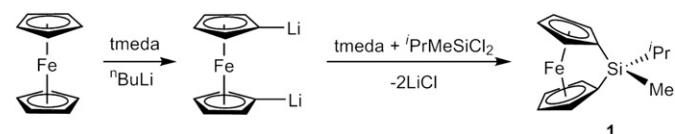
### 3.1. Synthesis of isopropylmethylsila[1]ferrocenophane monomer (**1**)

The preparation of isopropylmethylsila[1]ferrocenophane **1** was carried out as described in Scheme 1. The synthesis of the ferrocenophane monomer was achieved by a 2 step process. Firstly, ferrocene was dilithiated using butyllithium (BuLi) in the presence of the amine catalyst tetramethylethylenediamine (tmeda) to give an orange pyrophoric powder in high yields. Secondly, a salt metathesis reaction between dilithioferrocene·tmeda and dichloroisopropylmethylsilane at subambient temperature was carried out to yield the ferrocenophane monomer **1** (yield 65%). Subsequent recrystallizations and sublimations were carried out to achieve material sufficiently pure for anionic polymerisation.

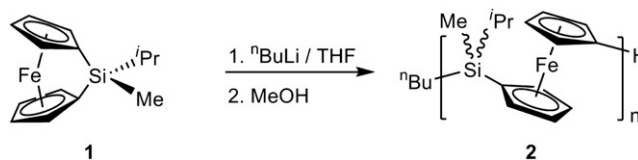
### 3.2. Synthesis and characterisation of PFiPMS homopolymer

The ring-opening polymerisation of the strained ferrocenophane monomer **1** was carried out as described in Scheme 2. Monomer **1** was initiated by <sup>n</sup>BuLi in THF at room temperature. Living chain ends were terminated with methanol to afford orange polymers in high yields. Results are displayed in Table 1.

Molecular weights were accurately controlled by varying monomer: initiator ratios. A plot of molecular weight versus monomer: initiator ratios (Fig. 1) was linear, which is consistent with a living polymerisation. However, the polydispersities



**Scheme 1.** Synthesis of isopropylmethylsila[1]ferrocenophane **1**.

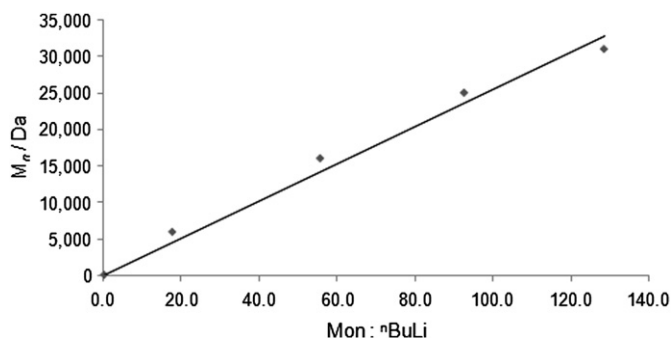


**Scheme 2.** Anionic polymerisation of ferrocenophane **1**.

observed for the polymers with molecular weights above 5,900 Da increased to >1.1 with increased polymerisation times required to consume all of the monomer. The polymerisation times reported in Table 1 are significantly longer than those required for the synthesis of PFEMS with comparable molecular weights, which was reported to be 30 min [9]. This is likely to be due to the steric bulk of the isopropyl group at the silicon which decreases the rate of propagation. Long reaction times are likely to increase the probability of competing chain transfer and chain termination steps, which broaden the molecular weight distribution. The polymerisation appears to behave ideally, with no significant chain transfer or termination, only up to molecular weights of ca. 20,000 Da.

The tacticity of PFiPMS homopolymer was investigated by <sup>13</sup>C NMR and the morphology was analysed by powder XRD. Firstly, the <sup>13</sup>C NMR spectrum of the PFiPMS showed two peaks for the ipso-carbon environments. Previously, asymmetrical polyferrocenylsilanes with different substituents on silicon have been shown to exhibit more than one peak for the ipso-carbon environments in their <sup>13</sup>C NMR spectra, which is indicative of their atacticity [35]. Secondly, the XRD trace of the PFiPMS homopolymer displayed a broad halo with no distinguishable peaks. These results indicate that PFiPMS homopolymer does not possess any significant stereoregularity and is an atactic, amorphous polymer.

As noted above, block copolymers with amorphous, asymmetrically substituted PFS blocks are potentially advantageous for solid state self-assembly as crystallization of the PFS block is eliminated as a driving force for self-assembly. PFEMS blocks, with ethyl and methyl substituents at the silicon, have been successfully prepared and employed in a number of applications, however the glass transition temperature (*T*<sub>g</sub>) of this polymer is close to room temperature. By increasing the steric bulk of substituents at the silicon, as for this isopropyl methyl substituted PFiPMS, the *T*<sub>g</sub> can be increased. Thermal analysis of PFiPMS homopolymers was carried out by differential scanning calorimetry (DSC) (Table 1). At low molecular weights (*M*<sub>n</sub> = 5,900 Da) a *T*<sub>g</sub> of 45 °C was observed. This increased with increasing molecular weight reaching a plateau of ~60 °C above



**Fig. 1.** Monomer: initiator ratio versus molecular weight plot for the living anionic polymerisation of **1**.

a molecular weight of ca. 25,000 Da. A DSC trace of Sample 5 is shown in the Supporting information (Fig. S1).

### 3.3. Synthesis and characterisation of PS-*b*-PFiPMS diblock copolymers

PS-*b*-PFiPMS diblock copolymers with targeted molecular weights and volume fractions were prepared as described in Scheme 3. Styrene was initiated by <sup>sec</sup>BuLi in cyclohexane at room temperature. After 1 h, an aliquot of the living polystyrene solution was removed and terminated with degassed methanol. Molecular weights were determined by GPC calibrated using PS standards. To the remaining living PS aliquot, monomer **1** in THF was added and propagation allowed to proceed for a further 4 h before quenching with degassed methanol. The diblocks were precipitated into rapidly stirring methanol to give orange powders. Results are presented in Table 2.

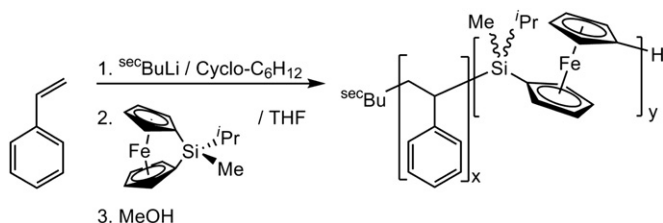
All diblock copolymers were characterised by <sup>1</sup>H NMR and GPC. Molecular weight values obtained from PS aliquots allowed the number of styrene repeat units in the PS block to be determined. Integration of the <sup>1</sup>H NMR peaks representing the PS phenyl ring and PFiPMS cyclopentadienyl rings allowed the number of PFiPMS repeat units to be determined and thus absolute molecular weights of the diblocks to be calculated. Figs. 2 and 3 show a GPC trace of a PS-*b*-PFiPMS peak and precursor PS aliquot, and a <sup>1</sup>H NMR spectrum of a PS-*b*-PFiPMS diblock copolymer, respectively. A DSC trace of PS<sub>247</sub>-*b*-PFiPMS<sub>71</sub> is shown in the Supporting information (Fig. S2) where the *T*<sub>g</sub>s of both constituent blocks are displayed.

The molecular weights and volume fractions of the diblock copolymers presented in Table 2 were well-controlled with high yields obtained. Additionally, the PDIs for all of the diblock copolymers were significantly lower (~1.1) than that of the PFiPMS homopolymers of comparable molecular weights (see Table 1).

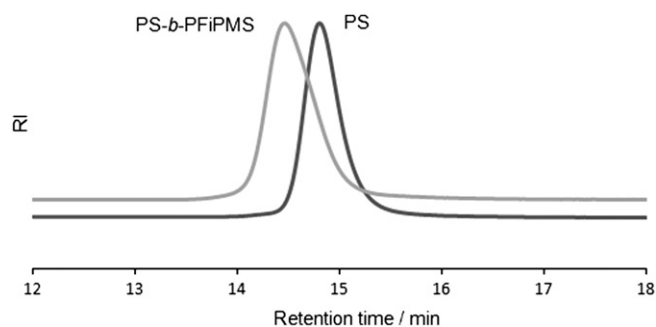
The order-disorder transition temperature of PS<sub>247</sub>-*b*-PFiPMS<sub>71</sub> was found to be 235 °C ± 5 °C by birefringence measurements using polarizing optical microscopy [36–39].

### 3.4. Self-assembly of PS-*b*-PFiPMS diblock copolymers in the bulk

In order to study the ability of the diblock copolymers to self-assemble in bulk, concentrated solutions of each polymer (~30 mg/ml) in toluene were slow cast on to glass slides over several days. The resulting films (~1 mm in thickness) were then solvent annealed in a toluene chamber overnight before thermal annealing at 150 °C under vacuum for 4 days. Rapid quenching with liquid nitrogen gave brittle orange films. Bulk samples were mounted on a cured acrylate-based resin, microtomed at a thickness of ~50 nm and subsequently transferred to a carbon-coated TEM grid. Microtomed sections of the bulk films were imaged by bright field TEM. The high electron density of the iron-containing PFiPMS block provides sufficient contrast for TEM



**Scheme 3.** Schematic procedure for the preparation of PS-*b*-PFiPMS diblock copolymers.



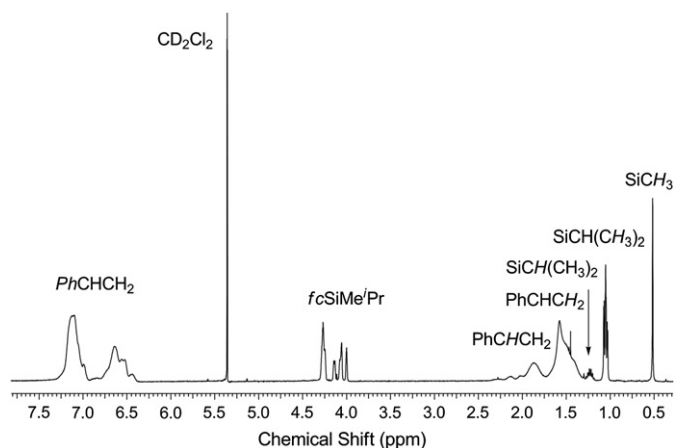
**Fig. 2.** GPC trace of PS<sub>346</sub>-*b*-PFiPMS<sub>57</sub> diblock copolymer and precursor PS block.

imaging without the necessity of staining. The organic PS blocks were therefore bright compared with the more electron dense PFiPMS block.

The theoretical diblock copolymer phase diagram [40] displays adopted morphologies as a function of volume fraction and the product of the Flory–Huggins interaction parameter  $\chi$ , with degree of polymerisation, *N*. For the diblock copolymer PS<sub>346</sub>-*b*-PFiPMS<sub>57</sub> ( $\phi_{\text{PFiPMS}} = 0.26$ ) a morphology of hexagonally packed PFiPMS cylinders in a PS matrix is predicted. Fig. 4 (a and b) show the TEM images of PS<sub>346</sub>-*b*-PFiPMS<sub>57</sub> illustrating that this is the morphology observed, with a centre-to-centre distance between each PS cylinder of ~25 nm.

The potential use of PFiPMS-containing diblock copolymers in thin film applications, such as nanolithography, was investigated by spin coating a 0.25 w/t% toluene solution of PS<sub>346</sub>-*b*-PFiPMS<sub>57</sub> on to Si wafer, solvent annealing for 3 h and etching with O<sub>2</sub> plasma to remove the organic PS block. The resulting PFiPMS morphology was imaged by AFM (Fig. 5 a–d) where PFiPMS cylinders can be seen to align perpendicular to the substrate at the surface, which is consistent with the bulk morphology shown in Fig. 4 (a and b).

The PFiPMS volume fraction was higher ( $\phi_{\text{PFiPMS}} = 0.38$ ) for PS<sub>247</sub>-*b*-PFiPMS<sub>71</sub> which displayed a gyroid morphology in the bulk, as shown in Fig. 6 (a–b). In some regions of the sample a lamella morphology was observed (Fig. 7). This is likely to be due to the gyroid morphology only being stable within a very small window of the phase diagram, and this particular polymer being located at a phase transition threshold.



**Fig. 3.** <sup>1</sup>H NMR spectrum of PS<sub>346</sub>-*b*-PFiPMS<sub>57</sub> diblock copolymer in CD<sub>2</sub>Cl<sub>2</sub> (*f*<sub>c</sub> = Fe( $\eta$ -C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>).

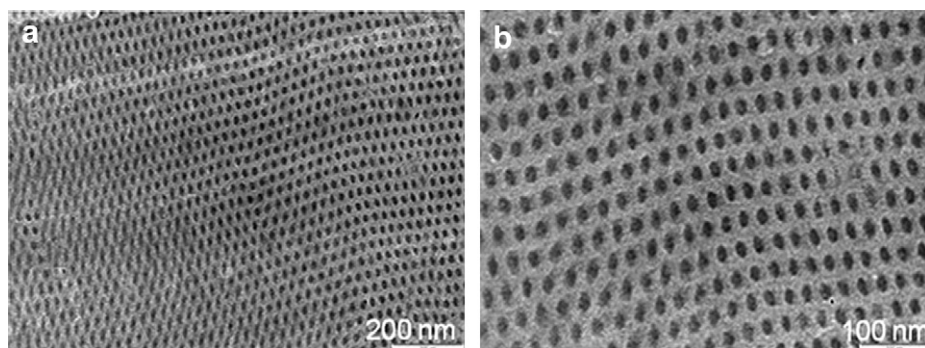


Fig. 4. (a and b) TEM images of diblock copolymer PS<sub>346</sub>-*b*-PFiPMS<sub>57</sub> ( $\phi_{\text{PFiPMS}} = 0.26$ ).

We were able to successfully increase the PFiPMS volume fraction to 77% for PS<sub>82</sub>-*b*-PFiPMS<sub>124</sub> thereby demonstrating that block copolymers with a majority PFiPMS volume fraction could be prepared. Fig. 8 shows an inverse PFiPMS cylinder morphology in the bulk, as predicted at this composition.

#### 4. Summary

We have demonstrated that the strained isopropylmethylsila[1]ferrocenophane monomer **1** undergoes ring-opening

polymerisation via an anionic mechanism to give an amorphous PFiPMS with a  $T_g$  well above room temperature. The polymerisation shows living character up to molecular weights of ca. 20,000 Da. In addition, PS-*b*-PFiPMS diblock copolymers were prepared via a sequential living anionic polymerisation, with targeted molecular weights and low PDI's, and with predicted nanoscale morphologies observed in the bulk and thin films. Due to the relatively high  $T_g$  of the PFiPMS block, these materials are excellent candidates for use in solid state self-assembly with a variety of potential applications in nanoscience.

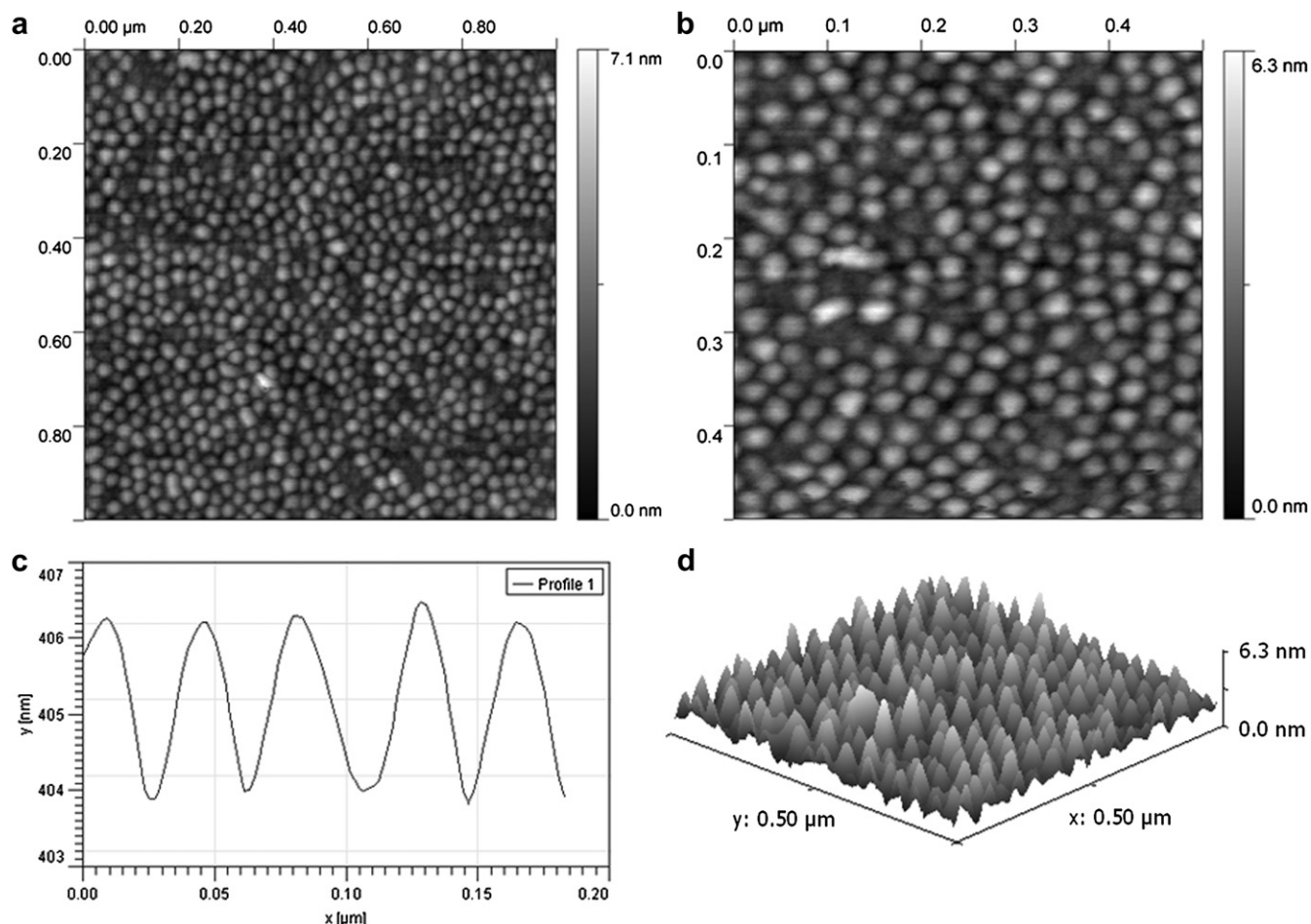


Fig. 5. (a–d) AFM height images of PS<sub>346</sub>-*b*-PFiPMS<sub>57</sub> ( $\phi_{\text{PFiPMS}} = 0.26$ ) thin films etched with an O<sub>2</sub> plasma.

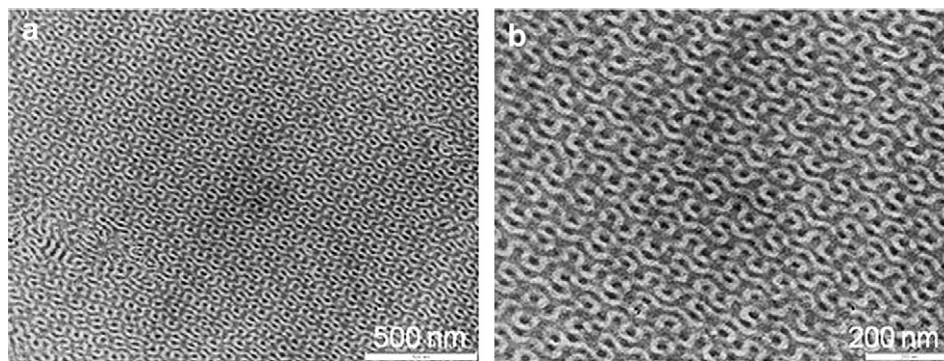


Fig. 6. (a and b) TEM images of diblock copolymer PS<sub>247</sub>-*b*-PFiPMS<sub>71</sub> ( $\phi_{\text{PFiPMS}} = 0.38$ ).

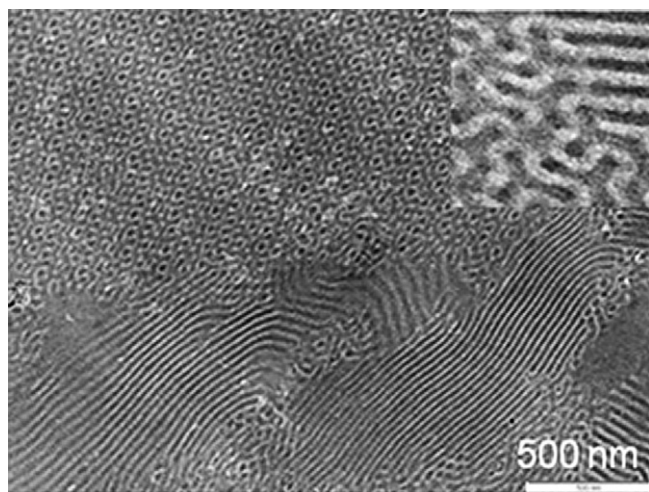


Fig. 7. TEM images of diblock copolymer PS<sub>247</sub>-*b*-PFiPMS<sub>71</sub> ( $\phi_{\text{PFiPMS}} = 0.38$ ) including high resolution view of phase boundary (inset).

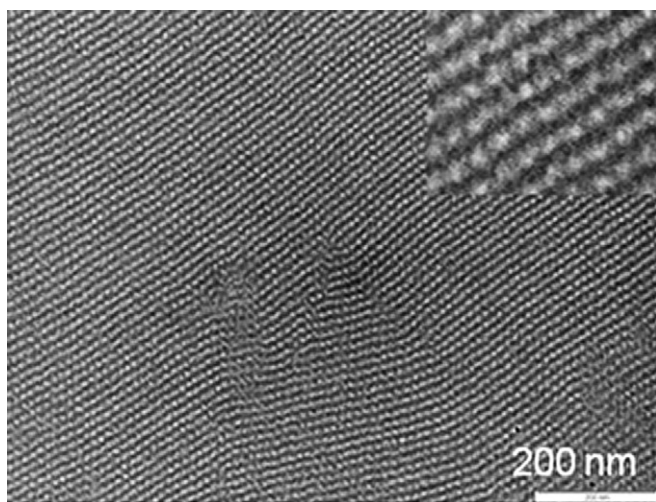


Fig. 8. TEM images of diblock copolymer PS<sub>82</sub>-*b*-PFiPMS<sub>124</sub> ( $\phi_{\text{PFiPMS}} = 0.77$ ) including high resolution view (inset).

## Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at [doi:10.1016/j.polymer.2009.08.041](https://doi.org/10.1016/j.polymer.2009.08.041).

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