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Synthesis, Thin-Film Self-Assembly, and Pyrolysis of Ruthenium-containing Polyferrocenylsilane Block Copolymers

Huda Nasser Al-Kharusi, Lipeng Wu, George Whittell, Robert Harniman and Ian Manners*

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Polyferrocenylsilane (PFS)-containing block copolymers have previously been shown to self-assemble into metal-rich nanodomains in thin films or the bulk phase. This patterning of the metalloblock can enable the fabrication of arrays of Fe nanoparticles for applications in catalytic carbon nanotube growth. Herein, we report the preparation of block copolymers with a ruthenium-containing polyferrocenylsilane (RuPFMEtS) segment from a polystyrene-*block*-polyferrocenylmethyl(trimethylsilyl)ethynylsilane (PS-*b*-PFMEt(TMS)S) precursor. The latter was prepared *via* the photocontrolled ring-opening polymerisation of methyl(trimethylsilyl)ethynylsila[1]ferrocenophane and a cyclopentadienyl-terminated polystyrene homopolymer. Deprotection of the Si(CH₃)₃ groups from the ethynyl substituents on the PFS block was carried out by using NaOMe. Incorporation of Ru₃(CO)₉H clusters into the block copolymer was achieved by reaction with Ru₃(CO)₁₂ to obtain PS-*b*-RuPFMEtS. This afforded two block copolymers high-metallised ruthenium-based segments; PS₂₆₅-*b*-RuPFMEtS₁₀ and PS₁₉₆-*b*-RuPFMEtS₃₁, containing 9 and 21 % Ru by mass, respectively. Phase-separation of the resulting block copolymers was investigated in the bulk and thin films and was found to yield spherical or cylindrical domains of RuPFMEtS in a PS matrix, respectively. Pyrolysis of PS₂₆₅-*b*-RuPFMEtS₁₀ and PS₁₉₆-*b*-RuPFMEtS₃₁ block copolymers at 500 or 800 °C for 2 h led to formation of either amorphous (ca. 2 nm in diameter at 500 °C) or polycrystalline (ca. 14 nm in diameter at 800 °C) Fe/Ru nanoparticles in a carbonaceous matrix. These NP composites are promising candidates for use as heterogeneous hydrogenation catalysts. The pyrolysed materials were characterised by high resolution transmission electron microscopy, energy-dispersive X-ray spectroscopy, selected area electron diffraction, scanning electron microscopy and powder X-ray diffraction.

Introduction

Metallopolymers have become of growing importance, as a result of their beneficial electronic, magnetic, optical, and catalytic properties.^{1–13} Using metallopolymers as precursors to metal nanoparticles (NPs) is key to some of these applications and this may be achieved by either radiation or thermal treatment.^{7, 8, 14–32} Polyferrocenylsilanes (PFSs) are a well-known class of metallopolymers,^{33–37} which contain both Fe and Si in the main chain. Due to the presence of these elements, these materials possess useful characteristics, such as high resistance to oxygen plasma etching and redox activity.^{38–41} In addition, PFSs have been used as precursors to Fe NPs with 35 – 91 % ceramic yields, upon pyrolysis at 700 – 1000 °C.^{16, 18, 24, 27, 29, 42} The NPs can be formed in an amorphous SiC/C/Si₃N₄ matrix, that acts as a barrier against agglomeration of the NPs, and hinders the formation of larger particles.³¹ The pyrolysis temperature has a direct effect on the properties of the resulting NPs. For example, the pyrolysis

of PFS with pendent cobalt clusters (Co-PFS) produced Fe/Co alloy NPs in an amorphous SiC/C matrix.²² Upon pyrolysis of thin films of Co-PFS at lower temperatures (ca. 500 – 600 °C), small NPs with monomodal size distribution were observed, while pyrolysis at higher temperatures (ca. 700 – 900 °C) produced larger NPs with a broader size distribution. Furthermore, changing the pyrolysis temperatures changed the shape of particles and the magnetic properties.

In addition to their unique properties, PFS materials can be readily accessed in the form of block copolymers, which can self-assemble into a variety of different morphologies either in the bulk, thin films or in solution.^{40, 43–55} The self-assembly of PS-*b*-PFS (PS: polystyrene) in thin films yielded well-ordered nanostructures, such as spheres, cylinders, lamellae and gyroids.^{53, 56} These morphologies varied according to the volume fraction of the PFS (ϕ_{PFS}). With ϕ_{PFS} values of 0.36 and 0.25, both afforded hexagonally packed cylinders.²⁸ In thin films, these could then be stabilised by cross-linking the PS block with UV-light. Pyrolysis subsequently afforded hexagonally packed ceramic cylinders of iron-based NPs. Furthermore, the pyrolysis of self-assembled PS-*b*-PFS into hexagonally ordered cylindrical domains and cubic close packed spherical domains led to produce periodically spaced Fe NPs,^{57–59} which catalysed the generation of single-walled carbon nanotubes (SWNTs). A comparative investigation

School of Chemistry, University of Bristol, B58 1TS, U.K.

E-mail: ian.manners@bristol.ac.uk

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between the use of PFS homopolymer and PS-*b*-PFS block copolymer (BCP) for the catalytic formation of SWNTs growth has been performed.⁶⁰ Although the % Fe in the homopolymer was larger than in the BCP, the catalytic activity of thin films of the BCP was much higher. The PS matrix has been shown to influence the dispersion of the Fe NPs in the film of PS-*b*-PFS, and to hinder the aggregation of the NPs and a consequential reduction of surface area during the pyrolysis.⁶⁰ In addition, the pattern obtained by self-assembly of PS-*b*-PFS BCP has been used as a template for the fabrication of Ag nanostructures for surface-enhanced Raman scattering (SERS),⁶¹ and a dense array of tungsten capped magnetic cobalt dots.⁶² The latter by a combination of oxygen reactive ion and ion beam etching.

Interestingly, in some cases bimetallic NPs have been shown to exhibit improved catalytic activity and/or selectivity compared to monometallic NPs.⁶³⁻⁶⁷ Ruthenium NPs have shown a remarkable catalytic activity for hydrogenation of unsaturated and functional compounds,⁶⁷⁻⁷⁰ alloying other metal with ruthenium in NPs enhanced the catalytic properties.^{65, 71} It was found that selectivity of the Ru catalyst for the hydrogenation of unsaturated aldehydes to unsaturated alcohols was enhanced by the addition of iron.⁷² Furthermore, the thermally stable silica-supported Fe/Ru bimetallic NPs have been reported to catalyse growth of small SWNTs.⁷³ Recently, Luska *et al.* demonstrated improved catalytic activities and selectivities for the hydrogenation of multifunctional aromatics and heteroaromatics using bimetallic Fe/Ru NPs immobilized on a supported ionic liquid phase, relative to monometallic NPs.⁷⁴

The work herein describes the synthesis of two ruthenium-containing polyferrocenylsilane-containing BCPs (PS₂₆₅-*b*-RuPFMEtS₁₀ and PS₁₉₆-*b*-RuPFMEtS₃₁, PFMEtS: polyferrocenylmethyl(ethynyl)silane) by incorporation of triruthenium clusters into PS-*b*-PFMEtS. We also demonstrate the self-assembly of the BCPs in bulk and thin films, and report the pyrolysis of these structures to fabricate **bimetallic** Fe/Ru NPs. The catalytic activity of these species will be investigated as part of a future project.

Experimental Section

Materials

Styrene was acquired from Acros, dried over CaH₂ and distilled under reduced pressure. Methyltrichlorosilane, dichlorodimethylsilane and chlorotrimethylsilane, all purchased from Aldrich, were distilled over CaH₂ twice and degassed by three freeze, pump and thaw cycles. Magnesocene, obtained from STREM was purified by sublimation. *n*-BuLi (1.6 M solution in hexane) and *sec*-BuLi (1.4 M solution in cyclohexane) were purchased from Acros Organics and used as received. Ethynyltrimethylsilane, purchased from Aldrich, was degassed by three freeze, pump and thaw cycles. Sodium hexamethyldisilazide solution (1M in THF) was purchased from Sigma-Aldrich and used as received. THF was dried over Na/benzophenone and distilled under a dinitrogen atmosphere. Dry diethyl ether was purified with a

Grubbs-type solvent system. Cyclohexane was purified and dried over several steps: it was washed several times by 95 mol % sulphuric acid until colourless solution was observed, it then with 5 M NaOH solution and de-ionised water several times until neutral; dried over MgSO₄ before being distilled from CaH₂ and *n*-BuLi.

Characterization

UV lamp. The photocontrolled ROP experiments were carried out with medium pressure mercury lamp purchased from *Photochemical Reactors Ltd.* Polymerisations were carried out in Pyrex tubes, which filter out wavelengths at $\lambda < 310$ nm.

NMR Spectroscopy. ¹H-, ¹³C- and ²⁹Si-NMR spectroscopy were obtained using JEOL ECP300, Varian400 and Varian500 spectrometers. ¹H and ¹³C resonances were referenced internally to residual protonated solvent resonances (C₆H₆: 7.16 ppm; CD₂Cl₂: 5.32 ppm and C₆H₆: 128.06 ppm; CD₂Cl₂: 53.84 ppm respectively). ²⁹Si resonances were referenced externally to tetramethylsilane.

Gel Permeation Chromatography (GPC). Absolute molecular weights and molecular weight distributions of polymers were obtained by GPC using a *Viscotek VE 2001 Triple-Detector GPC* equipped with automatic sampler, pump, injector, inline degasser, column oven (30 °C), styrene/divinylbenzene columns with pore sizes of 500 Å and 100,000 Å, VE 3580 refractometer, four-capillary differential viscometer and 90° angle laser and low angle laser (7°) light scattering detector (VE 3210 & VE 270). THF, stabilised with 0.025% butylated hydroxytoluene (*Fisher*), was used as the eluent at a flow rate of 1.0 mL/min. Conventional calibration GPC was performed on a Viscotek RI max, using a flow rate of 1.0 mL/min of THF with 0.1 wt% [*n*-Bu₄N]Br and calibrated monodisperse polystyrene standards from *Aldrich*. Molecular weights of diblock copolymers were calculated from the absolute molecular weight of the first block, as determined by multi-detection GPC, and the block ratio as determined by ¹H-NMR spectroscopy.

Powder X-ray Diffraction Microscopy (PXRD). Samples were collected from TGA experiments and placed on silicon sample holders. Experiments were performed with Cu-K α radiation ($\lambda = 1.5418$ Å) on a *Bruker D8 Advance* powder diffractometer.

Transmission Electron Microscopy (TEM). TEM samples were prepared by casting a single drop onto carbon-coated copper grids and analysis was carried out on either a *JEOL 1200EX Mk2* with a standard tungsten filament at an acceleration voltage of 120 kV, or a *JEOL TEM 2010* with a LaB₆ filament operating at 200 kV. The images were recorded with a *MegaViewII* digital camera.

Energy-dispersive X-ray analysis (EDX). EDX analysis was performed on an *Oxford Instruments ISIS 310* system with a silicon detector and *Atmospheric Thin Window ATW*.

Selected Area Electron Diffraction (SAED). SAED images were recorded using a *Kodak Electron Image Film SO-163*.

Synthesis of cyclopentadiene-terminated polystyrenes (5)

Styrene (3.0 mL, 0.026 mol) in cyclohexane (20 mL) was initiated by addition of *sec*-BuLi (75.0 μ L, 0.104 mmol, 1.4 M in

cyclohexane) and the colour of the solution changed immediately to orange due to the formation of living polymer. The reaction was allowed to stir for 1 h and quenched with an excess of Me_2SiCl_2 (2 mL). The colour of the solution changed to colourless and the reaction was allowed to stir for 3 h. The solvent and excess silane were removed under vacuum and the residue dried under vacuum at 60 °C for 24 h to obtain BCP 4A. A solution of MgCp_2 (64.0 mg, 0.416 mmol) in dry THF (20 mL) was prepared and added to a greaseless Schlenk tube containing BCP 4A. The reaction was stirred for 16 h and quenched by addition of excess Me_3SiCl (1 mL). After 2 h of stirring, the volatiles were removed under vacuum, the product redissolved in dry THF and precipitated in dry hexane under inert condition. This process was repeated three times. The polymer was dried under vacuum at 70 °C for 48 h. The yield of the colourless BCP 5A was 2.5 g (93 %).

^1H NMR (400 MHz, C_6D_6): δ = 7.32 – 6.88 (overlap br m, 795 H, C_6H_5), 6.75 – 6.34 (overlap br m, 530 H, C_6H_5), 1.84 (br m, 265 H, CH), 1.47 (br m, 530 H, CH_2). GPC: M_n = 27,600 g/mol, PDI = 1.04. GPC analysis: 5A: M_n = 27,600 g/mol (PDI = 1.04); 5B: M_n = 20,400 g/mol (PDI = 1.01).

Synthesis of PS-*b*-PFMEt(TMS)S (7)

An excess of $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ (45 μL , 1.0 M in THF) was added to a solution of Cp-capped PS macroinitiator (5A) (M_n = 27,600 g/mol, 1.00 g, 36.2 μmol) in dry THF (6 mL). The light yellow solution was allowed to stir for 1 h at 25 °C in the glovebox. A solution of monomer 3 (153 mg, 0.471 mmol) in THF (2 mL) was then added to form a red solution that was irradiated with UV light at 5 °C for 17 h. The resulting light amber solution was quenched with Me_3SiCl (0.1 mL) and stirred for 1 h. The solvent and Me_3SiCl were removed under vacuum. The product was dissolved in THF and precipitated in methanol. After two additional precipitations in methanol, the obtained polymer was dried under vacuum at 40 °C for 48 h. The obtained diblock copolymer 7A was a light orange powder with a yield of 1.1 g (93%).

^1H -NMR (CD_2Cl_2 , 400 MHz): δ = 7.26 – 6.90 (overlap br m, 3x H, C_6H_5), 6.75 – 6.34 (overlap br m, 2x H, C_6H_5), 4.43 (m, 4y H, Cp), 4.22 (m, 2y H, Cp), 4.13 (m, 2y H, Cp), 1.82 (br m, 1x H, CH), 1.47 (br m, 2x H, CH_2), 0.63 (s, 3y H, $\text{Si}(\text{CH}_3)$), 0.28 (s, 9y H, $\text{Si}(\text{CH}_3)_3$). ^{13}C -NMR (CD_2Cl_2 , 400 MHz): δ = 146.5, 146.2, 145.8, 145.4, 128.4, 128.0 (C_6H_5), 115.2 ($\text{SiC}\equiv\text{C}$), 112.2 ($\text{SiC}\equiv\text{C}$), 74.4, 74.3, 74.0, 73.9, 73.0 (Cp), 68.7 (Cp $\text{C}_{\text{ipso}}\text{-Si}$), 40.8 (CHCH_2), 0.2 ($\text{Si}(\text{CH}_3)_3$), -1.2 ($\text{Si}(\text{CH}_3)$ ppm. ^{29}Si -NMR (CD_2Cl_2 , 99.3 MHz): δ = -19.3 ($\text{Si}(\text{CH}_3)_3$), -25.3 ppm ($\text{Si}(\text{CH}_3)$). GPC analysis: 7A: M_n = 39,400 g/mol (PDI = 1.09); 7B: M_n = 31,100 g/mol (PDI = 1.16). NMR integration: 7A: M_n = 30,800 g/mol; 7B: M_n = 30,400 g/mol.

Synthesis of PS-*b*-PFMEtS (8)

An excess of NaOMe (120 mg, 2.22 mmol) was added to $\text{PS}_{265}\text{-}b\text{-PFMEt}(\text{TMS})\text{S}_{10}$ (7A) (500 mg, 16.4 μmol) dissolved in 30 mL THF and 10 mL methanol. The solution was stirred for 5 h at 0 °C, then a spatula of $[\text{NH}_4]\text{Cl}$ was added and the solution was stirred for another 5 min. The solution was filtered and the

solvents were removed under vacuum. The orange residue was dissolved in THF and precipitated into methanol and this procedure repeated a further two times. The polymer 8A was dried under vacuum at 40 °C for 71 h. The yield of the light orange polymers for 8A and 8B was 0.34 g (70%) and 0.40 (80%), respectively.

^1H -NMR (CD_2Cl_2 , 400 MHz): δ = 7.38 – 6.89 (overlap br m, 3x H, C_6H_5), 6.73 – 6.28 (overlap br m, 2x H, C_6H_5), 4.43 (m, 4y H, Cp), 4.23 (m, 2y H, Cp), 4.13 (m, 2y H, Cp), 2.69 (s, 1y H, $\text{C}\equiv\text{CH}$), 1.84 (br m, 1x H, CH), 1.46 (br m, 2y H, CH_2), 0.65 (s, 3y H, $\text{Si}(\text{CH}_3)$). ^{13}C -NMR (CD_2Cl_2 , 400 MHz): δ = 147.0, 146.4, 145.6, 145.0, 128.4, 126.1 (C_6H_5), 94.7 ($\text{C}\equiv\text{CH}$), 88.6 ($\text{C}\equiv\text{CH}$), 74.4, 74.3, 74.1, 74.0, 73.0 (Cp), 68.4 (s, $\text{C}_{\text{ipso}}\text{-Cp}$), 46.9 (CHCH_2CH), -1.2 (CH_3). ^{29}Si -NMR (CD_2Cl_2 , 99.3 MHz): δ = -23.3 ($\text{Si}(\text{CH}_3)$). ^1H -NMR for 8B showed almost same resonance peaks as 8A. GPC analysis: 8A: M_n = 34,800 g/mol (PDI = 1.09); 8B: M_n = 31,700 g/mol (PDI = 1.16). NMR integration: 8A: M_n = 30,100 g/mol; 8B: M_n = 28,200 g/mol.

Synthesis of PS-*b*-RuPFMEtS (9)

$\text{PS}_{265}\text{-}b\text{-PFMEtS}_{10}$ (8A) (300 mg, 0.996 mmol of FcSiMe_2 units) and $[\text{Ru}_3(\text{CO})_{12}]$ (38 mg, 0.060 mmol) were dissolved in dry benzene (ca. 10 mL) in a greaseless Schlenk tube. The reaction was covered with aluminum foil and heated at 78 °C for 3 h. The resulting clear orange solution was allowed to cool to 25 °C, filtered, and then precipitated into rapid stirred hexane. The solid was redissolved in toluene and repeatedly precipitated into hexane to remove the unreacted $\text{Ru}_3(\text{CO})_{12}$. The resulting polymer 9A was dried under vacuum for 48 h to afford a light brown solid. Polymers 9A and 9B yielded 200 mg (56%) and 110 mg (55%), respectively.

^1H -NMR (CD_2Cl_2 , 400 MHz): δ = 7.41 – 6.91 (overlap br m, 3x H, C_6H_5), 6.78 – 6.30 (overlap br m, 2x H, C_6H_5), 4.52 – 3.97 (br m, 8y H, Cp), 1.82 (br m, 1x H, CH), 1.46 (br m, 2x H, CH_2), 0.89 (s, 3y H, $\text{Si}(\text{CH}_3)$), -21.10 (s, 0.1y H, $\text{Si-C}\equiv\text{C}(\text{Ru}_3[\text{CO}]_9\text{H})$). ^{29}Si -NMR (CD_2Cl_2 , 99.3 MHz): δ = -7.4 ($\text{Si-C}\equiv\text{C}(\text{Ru}_3[\text{CO}]_9\text{H})$), -23.7 ($\text{SiC}\equiv\text{CH}$). FTIR (25 °C, solid state) ν = 2097 (w), 2068 (s), 2049 (s), 2011 (vs), 1981 (vs) (CO) cm^{-1} . In addition to these resonance peaks in ^1H -NMR, 9B showed a resonance at 2.69 ppm (s, 1y H, $\text{C}\equiv\text{CH}$). GPC analysis: 9A: M_n = 42,600 g/mol (PDI = 1.16); 9B: M_n = 84,600 g/mol (PDI = 1.10). NMR integration: 9A: M_n = 35,700 g/mol; 9B: M_n = 45,400 g/mol.

Preparation of bulk and thin films of PS-*b*-RuPFMEtS (9)

Bulk samples were prepared by slow casting of a concentrated toluene solution (50 mg/mL) onto a glass slide over two days. The resulting films were thermally annealed at 140 °C under vacuum for 72 h, followed by subsequent quenching with liquid nitrogen. Ultra-thin sections (80 nm) of the bulk films were microtomed and imaged by TEM.

Thin films were prepared by spin coating a 2 wt% toluene solution on silicon wafer followed by solvent annealing in THF/toluene (1:1), for 1 h or thermal annealing at 120 °C for 24 h. The films were then treated with O_2 plasma for 30 s before being imaged by AFM.

Results and Discussion

Synthesis of block copolymers

A promising method for the preparation of patterned metal NP, is *via* BCP self-assembly in thin films as the particles formed can be localised in specific nanodomains, limiting aggregation. PFS-containing BCPs with a variety of different organic coblocks have been reported.^{48, 53, 75-77} Anionic and photolytic ring-opening polymerisation have been successfully used as methods for the preparation BCPs containing PFS, and with control of block ratio and molecular weight and low polydispersity indices (PDI). Following on from our work on metallocopolymers in which Co,^{22, 34, 75} Au,⁷⁵ Mo³⁴ and Ni³⁴ moieties were incorporated into PFS we have targeted the clusterisation of acetylide-substituted PFS by reaction with Ru₃(CO)₁₂ to obtain highly metallised materials containing both Fe and Ru. Reaction of Ru₃(CO)₁₂ and trimethylsilylacetylene afforded [(μ-H)Ru₃(CO)₉(C≡CR)], R = SiMe₃ (Scheme 1),⁷⁸ and this model reaction has been extended to form BCPs of PFS clusterised with Ru as precursor for Fe/Ru NPs. This pathway was previously reported to be effective in obtaining highly metallised PFS blocks with Co and Au.⁷⁵

In this project, [1]ferrocenophane monomers **3** were synthesised as reported in the literature from monomer **1** (Scheme 2).^{75, 79} Thus, methyltrichlorosilane (MeSiCl₃) was added dropwise to a solution of dilithioferrocene.tmeda (tmeda = *N,N,N',N'*-tetramethylethylenediamine) in diethyl ether yielding red crystals of monomer **1**.⁷⁹ Reaction of monomer **1** with lithium trimethylsilylacetylide (**2**) then afforded **3** as a red crystalline solid.⁷⁵

Next, cyclopentadiene-terminated polystyrene, **5**, (Scheme 3) was synthesised following the published procedure.⁷⁵ Styrene was reacted with the initiator *sec*-BuLi and the resulting anionic polymer was quenched with Me₂SiCl₂, to obtain chlorosilane-terminated polystyrene (**4**). To the same reaction flask, bis(cyclopentadienyl)magnesium(II) (MgCp₂) was then added followed by Me₃SiCl to afford polymer **5**. Two different cyclopentadienyl-terminated polystyrenes were synthesised with different molecular weights, which were measured by GPC (triple detector) relative to monodisperse PS standards; **5A** (*M*_n = 27,600 g/mol, PDI = 1.04) and **5B** (*M*_n = 20,400 g/mol, PDI = 1.01).

To prepare copolymers PS-*b*-PFMeT(TMS)S (**7A** and **7B**), polymer **5A** and **5B** were treated with an excess of sodium hexamethyldisilazane (Na[N(SiMe₃)₂]) to deprotonate the cyclopentadiene end-group of the PS and afford polymers **6**. Monomer **3** was then added to the reaction and the vessel exposed to taken as Pyrex-filtered UV light for 16 h at 5 °C. A change in the reaction colour from red to amber was an indication that ring-opening of **3** had occurred. After quenching with an excess of Me₃SiCl, BCPs PS-*b*-PFMeT(TMS)S

(**7A** and **7B**) were obtained (Scheme 4).⁷⁵ The observation of a resonance at 0.28 ppm in ¹H-NMR spectrum confirmed the presence of the Si(CH₃)₃ group in BCPs **7**. Using the degree of polymerisation of the precursor **5**, integration of the phenyl protons of the PS segment and the Cp protons in the PFS block revealed the number of PFS units in the BCPs **7**. This was established as ca.

Scheme 1. Reaction of Ru₃(CO)₁₂ and terminal alkynes.

Scheme 2. Synthesis of monomers **1** and **3**.

Scheme 3. Synthesis of cyclopentadiene-terminated polystyrenes (**5**).

Scheme 4. Synthesis of PS-*b*-RuPFMeTs (**9**).

10 for **7A** (PS₂₆₅-*b*-PFMeT(TMS)S₁₀) and **31** for **7B** (PS₁₉₆-*b*-PFMeT(TMS)S₃₁). The absolute molecular weights of BCPs **7A** and **7B** were found to be 30,800 and 30,400 g/mol, respectively, and were calculated from the molecular weights of the cyclopentadiene-terminated polystyrene **5** (*M*_n (**5A**) = 27,600 g/mol and *M*_n (**5B**) = 20,400 g/mol) and the molecular weights of protected PFS blocks (*M*_n (10 PFS units) = 3,244 g/mol and *M*_n (31 PFS units) = 10,056 g/mol) (Table 1).

In the next step BCPs **7** were desilylated by reaction with NaOMe in a mixture of THF/MeOH to afford BCPs **8**. ¹H-NMR spectroscopic analysis of BCPs **8** revealed the presence of the

alkynyl proton at $\delta = 2.69$ ppm. Integration of the phenyl protons in the PS and the Cp protons in PFS confirmed that the block ratio in the diblock copolymers remained the same as in

Table 1: Molecular masses and polydispersity indices of the synthesized polymers.

Polymer	5A	5B	7A	7B	8A	8B	9A	9B
M_n (g/mol)	27,600 ^a	20,400 ^a	30,800 ^b	30,400 ^b	30,100 ^b	28,200 ^b	35,700 ^b	45,400 ^b
PDI ^a	1.04	1.01	1.09	1.16	1.09	1.19	1.16	1.10

^a M_n was determined by GPC relative to monodisperse PS standards. ^b M_n was determined by NMR.

Figure 1: ¹H NMR spectrum (C_6D_6 , 500 MHz) of PS_{265} - b - $RuPFMEtS_{10}$ (**9B**). g: THF, h: grease

the deprotection step. ¹³C-NMR spectroscopy revealed the disappearance of the $Si(CH_3)_3$ signal (at 0.2 ppm for BCPs **7**) and signals of the alkynyl carbons shifted upfield from 94.4 and 88.5 ppm for BCPs **7** to 115.2 and 112.2 ppm for BCPs **8**, as a result of alkyne deprotection. The calculated absolute molecular weights of BCPs **8** based on a similar integration of ¹H NMR peaks used for BCPs **7** were found to be $M_n = 30,100$ g/mol (PS_{265} - b - $PFMEtS_{10}$, **8A**) and $M_n = 28,200$ g/mol (PS_{196} - b - $PFMEtS_{31}$, **8B**) and the polydispersity indices (PDIs) were 1.09 and 1.19, respectively, according to the GPC analysis (Table 1).

The reactivity of the alkyne groups was then exploited to incorporate ruthenium clusters into BCPs **8** using known derivatisation chemistry^{80–82} to yield highly metallised BCPs **9**. This was achieved by refluxing PS - b - $PFMEtS$ (**8**) and $Ru_3(CO)_{12}$ in dry benzene at 78 °C for 3 h. The resulting orange BCPs **9** were characterised by ¹H-NMR spectroscopic and GPC techniques. The appearance of a signal at $\delta = -21.10$ ppm in the ¹H-NMR spectrum (Figure 1) indicated the formation of a metal hydride (polymer **9**) and this value in agreement to the literature ($\delta = -21.16$ ppm) for the model compound (Scheme 1).⁷⁸ The integration of the ¹H-NMR spectrum of phenyl (PS), Cp (PFS) and the alkynyl proton showed ca. 10 units of PFS in the BCP with ca. 100 % of them clusterised with Ru for **9A**

BCPs **7**, which indicated that no chain cleavage took place during

(PS_{265} - b - $RuPFMEtS_{10}$) and ca. 31 units of PFS in the BCP with an average of ca. 58% of them clusterised with Ru for **9B** (PS_{196} - b - $RuPFMEtS_{31}$) (Figure 1). Fourier transform infrared (FT-IR) spectroscopy of BCPs **9** showed multiple signals corresponding to CO vibrations ($\nu = 2097$ (w), 2068 (s), 2049 (s), 2011 (vs) 1981 (vs) cm^{-1}). These peaks are similar to the reported values for $[(\mu-H)Ru_3(CO)_9(C\equiv CSiMe_3)]$.⁷⁸ The calculated absolute molecular weights of clusterised BCPs **9A** and **9B** were $M_n = 35,700$ and 45,400 g/mol, respectively. GPC analysis in THF of BCP **9A** (PDI 1.16) showed a slightly broader molecular weight distribution compared to that of BCPs precursor **8A** (PDI 1.09) which is not unexpected as a distribution in terms of the degree of clusterisation would be expected. In addition, molecular weight distributions for **8B** and **9B** are 1.19 and 1.10, respectively.

Characterisation of bulk films of PS - b - $RuPFMEtS$ (**9**)

According to previous studies, the self-assembly of PS - b - $PFEMS$ (PDEMS: polyferrocenylethylmethylsilane) in the bulk and thin films was reported to afford different morphologies as the volume fraction of PFEMS (ϕ_{PFEMS}) was varied.⁵³ Spherical and cylindrical morphologies were observed by using ϕ_{PFEMS} values of 0.10 and 0.36, respectively. By increasing the volume fraction

Figure 2: (a, c) TEM images of the bulk film prepared by drop-casting of toluene solution (50 mg/ml) of **9A** (a) and **9B** (c) and followed by annealing at 140 °C for 72 h (scale bar = 40 nm); (b) diameter distribution histogram for 200 domains in (a); (d) diameter distribution histogram for 200 domains in (c).

of the PFEMS segment to 0.52, a highly ordered lamellar morphology was observed. Similarly, PS-*b*-PFiPMS (PFiPMS: poly(ferrocenylisopropylmethylsilane)) was shown to form cylinders ($\phi_{\text{PFiPMS}} = 0.26$) and gyroids ($\phi_{\text{PFiPMS}} = 0.38$) within a PS matrix, and inverse PFiPMS cylinders ($\phi_{\text{PFiPMS}} = 0.77$).⁵⁶ The phase-separation of BCPs of PS and clusterised PFS with cobalt- and gold-containing segments in the bulk has also been reported,⁷⁵ and these results motivated the investigation of the self-assembly of PS₂₆₅-*b*-RuPFMEtS₁₀ (**9A**) and PS₁₉₆-*b*-RuPFMEtS₃₁ (**9B**). By using the density of PDEMS (1.29 g/mL), the volume fraction of PFMEtS in BCPs **8A** and **8B** was calculated to be 0.10 and 0.30, respectively.

In order to study the bulk morphologies of the **9A** and **9B** BCPs, concentrated solutions of the polymers in toluene (50 mg/ml) were drop-cast onto glass slides and were then left to dry over two days. The resulting films were then thermally annealed at 140 °C under vacuum for 72 h. Samples of **9A** and **9B** were then microtomed and thin sections (~80 nm) were

transferred to carbon-coated copper grids for analysis by TEM (Figure 2a, c). Interestingly, samples **9A** and **9B** revealed the presence of phase-separated spherical and cylindrical domains of RuPFMEtS, respectively, within a PS matrix. Measuring diameters of 200 domains afforded mean values of 4.2 nm with a standard deviation (σ) of 1.3 nm for sample **9A** and 12.7 nm with a standard deviation of 1.6 nm for sample **9B** (Figure 2b, d). Some areas of **9B** showed the hexagonal packing characteristic of cylinders. We attribute the presence of disorder to the relatively rigid polymer main chain which would make the removal of kinetically-trapped defects a challenge. It is also possible that the BCP composition corresponds to a boundary between morphologies or a disordered region in the phase diagram.

Pyrolysis of bulk PS-*b*-RuPFMEtS (**9**)

The potential applications of metallic NPs⁸³⁻⁸⁶ motivated an investigation into the pyrolysis of polymers **9A** and **9B**.

Powdered samples were heated under N₂ at 10 °C/min to either 500 or 800 °C and held at these temperatures for 2 h. In all cases, black powders were afforded. The resulting materials

Figure 3: TGA thermogram of **8B_{800-2h}** (yellow), **9A_{800-2h}** (gray), **9B_{500-2h}** (orange) and **9B_{800-2h}** (blue).

from the pyrolysis of **9A** at 500 and 800 °C were **9A_{500-2h}** and **9A_{800-2h}**, respectively. Analogously, those from the pyrolysis of **9B** were **9B_{500-2h}** and **9B_{800-2h}**. Figure 3 shows the thermograms of the pyrolysed samples. The ceramic yields of **9B_{500-2h}** and **9B_{800-2h}** were anticipated to be higher than those of **9A_{500-2h}** and **9A_{800-2h}** due to the higher % of clusterisation with Ru in **9B**. As expected, the ceramic yield of **9B_{500-2h}** was 55% with significant weight loss starting at 400 °C. The ceramic yields of the pyrolysed samples **9A_{800-2h}** and **9B_{800-2h}** were 12% and 40%, respectively, at 800 °C. It is clear that as the number of RuPFMEtS units increased in the diblock copolymers, the ceramic yield increased. Sample **9B** (precursor of **9B_{500-2h}** and **9B_{800-2h}**) was also pyrolysed under same conditions at 800 °C to investigate its thermal behaviour and a comparison with that of **9B_{800-2h}**. Sample **8B** was heated at 800 °C to obtain ceramic material of **8B_{800-2h}** in 20% yield. The ceramic yield of **9B_{800-2h}** was higher than that of **8B_{800-2h}** and this was due to the incorporation of the Ru in **9B_{800-2h}**.

High resolution TEM analysis (Figures 4-6) of the pyrolysed samples showed NPs embedded in the matrix with average diameters of 1.8 nm with an estimated standard deviation (σ) of 0.8 for sample **9A_{500-2h}** (Figure 4a, b), 13.8 nm ($\sigma = 7.3$) for sample **9A_{800-2h}** (Figure 5a-c), 2.4 nm ($\sigma = 0.7$) for sample **9B_{500-2h}** (Figure S1a), and 14.6 nm ($\sigma = 6.5$) for sample **9B_{800-2h}** (Figure 6a-c). NP diameters for sample **9A_{500-2h}** and **9B_{500-2h}** were smaller than those of **9A_{800-2h}** and **9B_{800-2h}** presumably as a result of Ostwald ripening and agglomeration of the NPs at the higher temperature (800 °C). Figures 4d, 5e, S1c and 6d indicate the diameter distribution of NPs in the pyrolysed samples. Selected area electron diffraction pattern (SAED) indicated that samples **9A_{500-2h}** and **9B_{500-2h}** were amorphous (Figures 4c and S1b), while samples **9A_{800-2h}** and **9B_{500-2h}** were polycrystalline and were consistent with the presence of nano crystallites (Figures 5d and 6d).

EDX analysis confirmed the presence of Ru and Fe, in addition to Si, C and O in all pyrolysed samples. EDX spot analyses are shown in Figure S2 for samples **9A_{500-2h}**, **9A_{800-2h}**

and **9B_{800-2h}**. The pyrolysed materials were also analysed by PXRD. The PXRD

Figure 4: Characterisation of sample **9A_{500-2h}** (a, b) high resolution TEM images; (c) SAED pattern and (d) diameter distribution of NPs in (b).

pattern of samples **9A_{500-2h}** and **9B_{500-2h}** (Figures 7a, c) showed no reflections, and these results are consistent with the SAED analysis (Figure 4c and Figure S1b, respectively) that indicated that these samples were amorphous. In contrast, several Bragg reflections were observed for sample **9A_{800-2h}** and **9B_{800-2h}** with

d-spacings of 2.33, 2.13, 2.04, 1.57, 1.34, 1.21, 1.17 and 1.13 Å (Figure 7b), and 2.29, 2.08, 2.03, 1.54 and 1.33 Å **Figure 5:** Characterisation of sample **9A_{800-2h}** (a, b) High Resolution TEM images; (c) SAED pattern; scale bar = 5 nm for inset; (d) diameter distribution of NPs in (a).

(Figure 7d), respectively, which were also consistent with SAED data (Figures 5d, c and 6b) suggesting that these samples were crystalline. The Bragg reflections for sample **9A_{800-2h}** could be indexed to those reported for Ru, FeRu and RuO₂ (Table 2.2).⁸⁷⁻⁸⁹ The d-spacings for FeRu (110), Ru (002) and FeRu (202) lattice planes correspond to those observed in the high resolution TEM images at 2.02, 2.14 and 1.56 Å, respectively (Figure 5b, c). The presence of RuO₂ crystallites was unexpected since the pyrolysis was carried out under nitrogen. This may be due to the presence of oxygen in the polymer scaffold or oxidation that occurred during sample handling and storage. Sample **9B_{800-2h}** exhibited Bragg reflections corresponding to only FeRu, while no reflections appeared for Ru and RuO₂. The d-spacings of 2.03, 1.33 and 1.18 Å correspond to the lattice planes FeRu (110) and (211) observed **Figure 6:** Characterisation of sample **9B_{800-2h}** (a, b) High Resolution TEM images; (c) SAED pattern; scale bar = 2 nm for inset (d) diameter distribution of NPs in (a).

in the High resolution TEM image (Figure 6b). Sample **9A_{800-2h}** contained Ru NPs, whereas, sample **9B_{800-2h}** did not. This may be consequences of the high ceramic yield of **9B_{800-2h}**, which led to a lower degree of loss of Fe-containing molecular fragments.

Figure S3 shows SEM images of samples **9A_{800-2h}** and **9B_{800-2h}** and the EDX elemental maps of Fe and Ru for the same region. The elemental maps of both samples revealed heterogeneous distribution of Ru and Fe in both samples and these materials correspond to alloy NPs rather than a mix of Fe and Ru NPs. This was confirmed by the previous characterisation on samples **9A_{800-2h}** and **9B_{800-2h}** by high resolution TEM and PXRD, which revealed the presence of Fe/Ru as an alloy in both samples

and the size of the NPs in both samples were *ca.* 14 nm. Whilst, sample **9A**_{800-2h} also contained Ru and RuO₂, based on PXRD and high resolution TEM, and resolution in SEM-EDX mapping images were not sufficient to confirm this.

Self-assembly and pyrolysis of thin films of PS₂₆₅-*b*-RuPFMEtS₁₀ (**9A**)

Thin films of **9A** were prepared by spin coating 2 wt% of **9A** solution in toluene on silicon wafers. These were then thermally annealed at 120 °C for 24 h before the organic components (in particular the PS domains) were removed by oxygen plasma.^{40, 90-95} This procedure left regions of oxidised Ru and Fe and therefore enabled improved AFM images to be obtained, due to the increased height contrast. These indicated a spherical morphology for the residual metal-rich nanodomains (Figure S4a) which were relatively low dispersity, with an average diameter of 9.8 nm ($\sigma = 1.7$) (Figure S4b). The average diameters of the domains from AFM were larger than those determined by TEM. This is probably due to a combination of the additional (oxidative plasma) processing

step, and tip convolution effects common to AFM. When solvent annealing with a mixture of toluene and THF (1:1) was performed for 1 h, the diblock copolymer self-assembled into spheres with average sizes of 10.0 nm and a standard deviation of 2.3 (Figure 8a).

Further thin films were prepared by spin coating the sample solution (2 wt%) in toluene, but this time with thermal annealing at 120 °C for 24 h prior to pyrolysis. The resultant thin films of **9A** were pyrolysed at 500 °C and 800 °C for 2 h with heating rate of 10 °C/min under nitrogen. The AFM images of pyrolysed thin films are shown in Figure S5 (a, c). The average diameter of the domains was 8.1 nm with a standard deviation of 2.7 for the film that was pyrolysed at 500 °C (Figure S5b).

Figure 7: PXRD spectra for samples: (a) **9A**_{500-2h}, (b) **9A**_{800-2h}, (c) **9B**_{500-2h} and (d) **9B**_{800-2h}. (*Artifact)

Table 2: Structure types and d-spacings of PXRD reflections from samples **9A**_{800-2h}^a and **9B**_{800-2h}^b.

Structure type	Lattice plane	d-spacing (Å)	Literature data
Ru	100	2.33 ^a	2.33
Ru	002	2.13 ^a	2.14
FeRu	100	2.29 ^b	2.28
FeRu	002	2.08 ^b	2.09
FeRu	110	2.03 ^b 2.04 ^a	2.05
FeRu	102	1.54 ^b 1.57 ^a	1.54
FeRu	200	1.46 ^b	1.45
FeRu	110	1.34 ^{a,b}	1.32
RuO ₂	400	1.21 ^a	1.21
FeRu	211	1.17 ^a	1.18
FeRu	200	1.14 ^a	1.14

The average diameter of the spheres for the sample before the pyrolysis was 9.8 nm and after the pyrolysis was 8.1 nm. The diameter reduction presumably resulted from the loss of the sample mass. The average diameters of the domains for the film which was pyrolysed at 800 °C was 20.4 nm with a standard deviation of 4.1 (Figure S5c). These domains were larger compared to the domains before the pyrolysis (10.0 nm). This was probably due to a thermal expansion during pyrolysis although the potential influence of AFM tip deconvolution effects on these measurements makes the conclusion less than definitive.

Self-assembly and pyrolysis of thin films of PS₁₉₂-*b*-RuPFMEtS₃₁ (**9B**)

Thin films of **9B** were prepared similarly to the case of **9A**. The thin films of **9B** exhibited cylindrical domains perpendicular to the substrate (Figure 9a). Some areas showed that the RuPFMEtS cylinders were hexagonally packed in matrix (e.g.

blue circles in Figure 9a). The average diameter of cylinders was 9.9 nm ($\sigma = 1.6$) (Figure 9b).

The thin films of **9B** with cylindrical morphology were pyrolysed at 500 °C and 800 °C for 2h with heating rate of 10 °C/min under nitrogen and analysed by AFM. The AFM images revealed that the cylindrical domains persist after the pyrolysis (Figure 10a-d). Presumably, Ru domains were thermally cross-linked through residual acetylene groups or as a consequence of CO loss during the early stage of the pyrolysis leading to

Figure 8: (a) AFM height image of thin film prepared by spin-coating of 2 wt% **9A** solution in toluene and followed by solvent annealing in toluene/THF (1:1) for 1 h; (b) size distribution histogram of 200 domains in (a).

Figure 9: (a) AFM height images of thin films prepared by spin coating of 2 wt% of **9B** solution in toluene, followed by annealing at 120 °C for 24 h and plasma etching for 30 s; (b) diameter distribution histogram for 200 domains in (a).

Figure 10: (a-d) AFM height images of thin films prepared by spin coating a 2 wt% **9B** solution in toluene and annealed thermally at 120 °C for 24 h prior to pyrolysis for 2 h at (a, b) 500 °C, (c, d) 800 °C; (e) diameter distribution histogram for 200 domains in (a); (f) diameter distribution histogram for 200 domains in (c).

significant preservation of the morphology. The average diameters of the domains for films that were pyrolysed at 500 and 800 °C (Figure 10e, f) were 27.8 nm ($\sigma = 4.3$) and 32 nm ($\sigma = 3.9$), respectively. The increase in the average diameters of the domains after the pyrolysis compared to those before (9.9 nm) was presumably due to the thermal expansion at high temperatures.

Thin films of **9A** and **9B** utilised in the future to study the catalytic activity of the fabricated bimetallic Fe/Ru NPs. Several studies have been conducted on the application of Fe/Ru alloy as heterogeneous catalyst. Li et al. reported the ability of a silica-supported Fe/Ru bimetallic catalyst to promote the growth of small SWNTs.⁷³ These NPs were thermally stable for producing small diameter (< 1.2 nm) SWNTs. Using Fe/Ru catalysts have shown improvement in activity and/or selectivity for the hydrogenation of unsaturated compounds comparing to the monometallic Ru catalyst.^{72, 74}

Conclusions

Block copolymers of PS₂₆₅-*b*-PFMeTS₁₀ (**8A**) and PS₁₉₆-*b*-PFMeTS₃₁ (**8B**) were synthesised by photolytic ring-opening polymerisation and the acetylide-substituted PFMeTS segment was clusterised with Ru₃(CO)₁₂ to obtain the corresponding PS-*b*-RuPFMeTS (**9A** and **9B**) BCPs. These metal-rich BCPs were targeted to fabricate bimetallic Fe/Ru NPs. Pyrolysis of the

bulk **9A** and **9B** at 500 and 800 °C afforded ceramic materials in 12-55% yields. The pyrolysed samples at 800 °C produced bimetallic Fe/Ru NPs embedded in the matrix. EDX analysis confirmed the presence of Fe and Ru in all pyrolysed samples. According to the high resolution TEM, SAED and PXRD, the NPs of samples **9A**_{500-2h} and **9B**_{500-2h} were amorphous with average diameter of ca. 2.0 nm and were polycrystalline for samples **9A**_{800-2h} and **9B**_{800-2h} with average diameters of ca. 14 nm. Sample **9A**_{800-2h} afforded the formation of FeRu, Ru and RuO₂ NPs, while, sample **9B**_{800-2h} produced only the FeRu NPs.

Based on previous work with phase-separated PFS-containing BCPs, the ability to prepare well-defined, small and potentially highly-active catalytic Fe/Ru NPs partially embedded in a ceramic film to promote resistance to Ostwald ripening should offer much potential. The polymeric materials **9A** and **9B** were spin-coated onto substrates to create thin films of metal rich copolymers and annealed thermally, or by solvent, to access the equilibrium self-assembled structures. Both bulk and thin films of **9A** revealed a spherical morphology for the RuPFMeTS domains in the PS matrix. However, bulk and thin films of **9B** exhibited cylindrical domains of RuPFMeTS. Interestingly, the morphologies showed a significant degree of preservation after the pyrolysis at 500 and 800 °C presumably as a result of the thermally-induced crosslinking of the Ru-containing nanodomains. The thin films containing Fe/Ru NPs are interesting candidates as heterogeneous catalysts. Future work on the project will involve the investigation of the

catalytic activity of the bimetallic Fe/Ru NPs. These NPs are thermally stable and therefore promising for potential applications such as heterogeneous catalysts for the hydrogenation of unsaturated olefins and multifunctional aromatics.^{72, 73}

Conflicts of interest

There are no conflicts to declare.

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