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Versatile and Controlled Functionalisation of Polyferrocenyldimethylsilane-*b*-Polyvinylsiloxane Block Copolymers using a *N*-hydroxysuccinimidyl (NHS) Ester Strategy

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Additional Supporting Information may be found in the online version of this article.

ABSTRACT

A general route for the *N*-hydroxysuccinimidyl ester functionalisation of poly(ferrocenyldimethyl)silane-*b*-polyvinylsiloxane copolymers, which should be readily transferrable to other vinyl containing polymers, has been developed using a simple two step approach. Facile reaction of the *N*-hydroxysuccinimidyl (NHS) ester functionalised polymers with primary amines enables the incorporation of a range of functionalities previously inaccessible using standard thiol-ene “click” reactions.

KEYWORDS: block copolymers, functionalisation of polymers, polysiloxanes, synthesis, inorganic polymers

INTRODUCTION

Block copolymers (BCPs) are comprised of chemically distinct segments that are generally attached through covalent bonds. Upon addition of a selective solvent for one of these blocks, core-shell nanoparticles are formed which have an insoluble core and solvated corona.¹ The solution self-assembly of BCPs has enabled the preparation of different micelle morphologies, including spherical^{2,3}, vesicles^{2,4}, cylinders⁵⁻⁷, and platelets^{8,9}. These self-assembled materials are of interest for a range of applications from drug delivery¹⁰⁻¹³ to composite reinforcement.^{14,15}

Polyferrocenyldimethylsilane block copolymers have attracted widespread attention with respect to their self-assembly in the solid state to form metal-rich nanodomains.¹⁶⁻²³ In addition, solution self-assembly of BCPs containing a solvophobic poly(ferrocenyldimethylsilane) (PFS) block have also been well-studied and

have been found to favour the formation of morphologies with low interfacial curvature such as cylinders and platelets due to core crystallization.²⁴⁻²⁶ Significantly, the core termini of the micelles remain active to further growth on addition of further molecularly dissolved BCP. This process, termed living crystallisation-driven self-assembly (CDSA), is analogous to a living covalent chain growth polymerisation where the sequential addition of BCPs with a common crystallisable core block, or different core blocks with a small lattice mismatch, results in the formation of a range of multicompartiment block co-micelles with nanosegregated functionality.^{9,27-30} Using this approach has led to a range of different micelle architectures and synthetic routes that are able to increase the number of functional groups that can be incorporated into these materials are highly desirable. Such methods may be of broader significance if they are also transferable to other polymer systems.

One strategy that has been successfully applied to introduce functionality to macromolecular systems is post-polymerisation functionalisation. The development of the azide-alkyne and thiol-ene click reactions^{31–36} has been particularly important in this regard by providing quantitative functionalisation approaches. Recent work by our group has illustrated the utility of the thiol-ene click reaction in modifying the corona forming segment of BCPs.^{29,37,38} Our group has focussed on the use of the thiol-ene click reaction for post-polymerisation functionalisation due to the ease with which vinyl groups can be incorporated into the polymers. However, the range of functionalities that can be introduced with this approach is restricted as there is a limited number of commercially available thiols and side reactions can occur. In addition, as the reaction is intolerant to certain functional groups and others are unstable to the photoirradiation conditions required, new synthetic routes are desirable.

Herein we report a simple two-step process to introduce *N*-hydroxysuccinimidyl (NHS) ester groups onto polymethylvinylsiloxane (PMVS) segments, which can then selectively react with primary amines under mild conditions to produce the amide functionalised polymer. This method should be useful for the modification of a broad range of polymers containing pendant vinyl groups.

EXPERIMENTAL

General Experimental

Anionic polymerisations were carried out in an argon atmosphere glovebox. All other manipulations were carried out under an open atmosphere unless otherwise stated. All reagents were purchased from Sigma-Aldrich unless otherwise stated. Dimethylsila[1]ferrocenophane³⁹ and *N*¹-(2-aminoethyl)thymine⁴⁰ were prepared via literature procedures. Monomer purifications were performed under an atmosphere of purified N₂. THF was distilled from

Na/benzophenone immediately before use. Photoirradiation experiments were carried out with Pyrex-glass filtered emission from a 125 W medium-pressure mercury lamp (Photochemical Reactors Ltd.). An ethylene glycol/water bath in conjunction with a thermostat was used to maintain constant temperatures of 20 °C during the photoirradiation experiments. ¹H and ¹³C NMR spectra were recorded using Jeol Eclipse 400 MHz, Varian VNMR 400 MHz or Varian VNMR S500a spectrometers.

Polymer Characterisation

Matrix-assisted laser desorption/ionisation time of flight (MALDI-TOF) mass spectrometry measurements of poly(ferrocenyldimethyl)silane (PFDMS) were performed using a Bruker Ultraflextreme running in linear mode. Samples were prepared using a *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malonitrile matrix (20 mg mL⁻¹ in THF) and the polymer sample (2 mg mL⁻¹ in THF), mixed in a 10:1 (v/v) ratio. Approximately 1 μL of the mixed solution was deposited onto a MALDI sample plate and allowed to dry in air.

The molecular weights (*M_n*) of the block copolymers were determined from the molecular weights of the first block (PFDMS), by MALDI-TOF mass spectrometry, and the block ratios obtained by ¹H NMR spectroscopy integration of the vinyl protons (3H) of poly(methylvinylsiloxane) (PMVS) and the methyl protons (6H) of PFDMS. The absolute molecular weights of the PFDMS homopolymers obtained by multi-detection GPC corresponded well with those obtained by MALDI-TOF mass spectrometry. Polydispersity indices (PDI = *M_w*/*M_n*) of all the polymers were obtained by Gel Permeation Chromatography (GPC) using a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph equipped with automatic sampler, pump, injector, inline degasser, column oven (30 °C), styrene/divinylbenzene columns (pore sizes of between 500 Å and 100,000 Å), VE 3580

refractometer, four-capillary differential viscometer, VE 3210 UV/Vis detector ($\lambda = 450$ nm) and VE 270 dual angle laser light scattering detector (7° and 90°). THF stabilized with 0.025% butylated hydroxytoluene (Fisher) was used as the chromatography eluent, at a flow rate of 1.0 mL min^{-1} . Samples were dissolved in the eluent (2 mg mL^{-1}) and filtered with a Ministart SRP 15 filter (polytetrafluoroethylene membrane of $0.45 \mu\text{m}$ pore size) before analysis. Calibration of all three detectors (refractive index, laser light scattering and viscometry) was performed using polystyrene standards (Viscotek). Theoretical molecular weights for the functionalised block copolymers were used for yield calculations, assuming quantitative functionalisation.

Polyferrocenylsilane₆₈-b-[(polydimethylsiloxane)₆₅₂-r-(polymethylvinylsiloxane₆₇)] (PFS₆₈-b-(PDMS₆₅₂-r-PMVS₆₇) (1)

In a glove box under an argon atmosphere 1.6 M *n*-butyllithium ($21 \mu\text{L}$, 0.03 mmol) was added in one portion to a vigorously stirring solution of dimethylsila[1]ferrocenophane (400 mg , 1.65 mmol) in dry THF (10 mL) in a greaseless Schlenk flask. The reaction mixture was stirred for 1 h over which time the colour changed from red to orange. An aliquot (0.2 mL) for later analysis was removed, diluted with THF (1 mL) and quenched with 3,5-di-*tert*-butyl-4-hydroxytoluene. To the remaining reaction mixture, a solution of 1,3,3,5,5-pentamethyl-1-vinylcyclotrisiloxane (385 mg , 1.64 mmol) and 1,1,3,3,5,5-hexamethylcyclotrisiloxane (856 mg , 3.85 mmol) in dry THF (2 mL) was added in one portion. After 2 h the flask was removed from the glove box, set up under a nitrogen atmosphere and the reaction quenched with a few drops of chlorotrimethylsilane. The product was precipitated once in methanol with 10% triethylamine and twice more in methanol. To remove the homopolymer the crude product was dissolved in a minimum amount of THF and ethyl acetate was added with stirring until the solution became cloudy. The suspension was

centrifuged at 6000 rpm for 15 minutes and the supernatant concentrated *in vacuo*. This process was repeated twice more, then the resulting solid was dried *in vacuo* at 40°C to afford the pure block copolymer (1.09 g , 63% , $\text{PDI} = 1.09$) as an orange solid. (See Table S1). **¹H NMR (400 MHz; CD₂Cl₂):** δ_{H} 6.07-5.90 (m, 134H, CHCH₂), 5.86-5.77 (m, 67H, SiCHCH₂), 4.23 (t, $J = 1.7 \text{ Hz}$, 272H, CpH), 4.03 (t, $J = 1.7 \text{ Hz}$, 272H, CpH), 0.48 (s, 408H, FcSi(CH₃)₂), 0.15 (s, 201H, Si(CH₃)), 0.08 (s, 3912H, Si(CH₃)₂) ppm. **¹³C NMR (101 MHz; CD₂Cl₂):** δ_{C} 137.7 (CHCH₂), 133.3 (CHCH₂), 73.7 (CpC), 72.2 (CpCSi), 71.8 (CpC), 1.3 (OSi(CH₃)₂), -0.3 (Si(CH₃)CHCH₂) -0.8 (SiCH₃)₂ ppm. The BCPs PFS₄₉-b-PMVS₃₁₆ and PFS₅₄-b-(PDMS₄₂₄-r-PMVS₂₁₂) were synthesised using the same method but with 100% of the monomers V₃ and VD₂ respectively.

Hydrothiolation of PFS₆₈-b-(PDMS₆₅₂-r-PMVS₆₇) with 3-mercaptopropionic acid (2)

To a solution of PFS₆₈-b-(PDMS₆₅₂-r-PMVS₆₇) (200 mg , $2.8 \times 10^{-3} \text{ mmol}$, 0.19 mmol vinyl groups) in dry THF (2 mL) was added 3-mercaptopropionic acid ($50 \mu\text{L}$, 0.57 mmol , 3 equiv.) and the photo-initiator 2,2-dimethoxy-2-phenylacetophenone (5 mg , 0.02 mmol). The orange solution was sealed under an argon atmosphere and irradiated 3 cm away from a mercury lamp for 1.5 h . The mixture was then precipitated in methanol three times, then dried *in vacuo* to afford the pure block copolymer (202 mg , 92% , $M_n = 77,700 \text{ g mol}^{-1}$). **¹H NMR (400 MHz; CD₂Cl₂):** δ_{H} 4.23 (t, $J = 1.7 \text{ Hz}$, 272H, CpH), 4.02 (t, $J = 1.7 \text{ Hz}$, 272H, CpH), 2.77 (t, $J = 7.3 \text{ Hz}$, 134H, CH₂COOH), 2.68-2.57 (m, 268H, CH₂SCH₂), 0.94-0.82 (m, 134H, SiCH₂CH₂S), 0.48 (s, 408H, Si(CH₃)₂), 0.19--0.01 (m, 4113H, Si(CH₃) and OSi(CH₃)₂) ppm. **¹³C NMR (101 MHz; CD₂Cl₂):** δ_{C} 73.5 (CpC), 72.0 (CpCSi), 71.7 (CpC), 35.0 (CH₂CO), 26.9 (SCH₂), 26.7 (SiCH₂CH₂), 18.6 (SiCH₂), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm. **GPC:** This polymer interacts with the stationary phase in the above-described GPC equipment, and was used without further characterisation.

Synthesis of PFS₆₈-b-(PDMS₆₅₂-r-PMVS₆₇) functionalised with NHS ester (3)

To a solution acid-functionalised PFS₆₈-b-(PDMS₆₅₂-r-PMVS₆₇) (190 mg, 2.4×10^{-3} mmol, 0.16 mmol acid groups) in dry THF (15 mL) was added *N*-hydroxysuccinimide (57 mg, 0.49 mmol, 3 equiv.), *N,N'*-dicyclohexylcarbodiimide (101 mg, 0.49 mmol, 3 equiv.) and 4-dimethylaminopyridine (12 mg, 0.10 mmol, 0.6 equiv.). The reaction was stirred under an argon atmosphere at room temperature for 24 h, then precipitated three times into methanol and dried *in vacuo* to afford the pure block copolymer (178 mg, 86 %, $M_n = 84,200 \text{ g mol}^{-1}$). ¹H NMR analysis showed quantitative functionalisation of the acid functional groups with *N*-hydroxysuccinimide. ¹H NMR (400 MHz; CD₂Cl₂): δ_H 4.23 (t, J = 1.7 Hz, 272H, CpH), 4.02 (t, J = 1.7 Hz, 272H, CpH), 2.96-2.73 (m, 536H, SCH₂CH₂COOH and H_a and H_b), 2.70-2.56 (m, 134H, SiCH₂CH₂S), 0.94-0.82 (m, 134H, SiCH₂CH₂S), 0.48 (s, 408H, Si(CH₃)₂), 0.18--0.01 (m, 4113H, Si(CH₃) and OSi(CH₃)₂) ppm; ¹³C NMR (101 MHz; CD₂Cl₂): δ_C 169.4 (2CO), 167.8 (CO), 73.5 (CpC), 72.1 (CpCSi), 71.7 (CpC), 32.3 (CH₂CO), 27.2 (SCH₂), 26.5 (SiCH₂CH₂), 26.0 (C_a and C_b), 18.6 (SiCH₂), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm (see Supporting Information for labelled structures). GPC: PDI = 1.12.

Amine reaction of NHS ester functionalised PFS₆₈-b-(PDMS₆₅₂-r-PMVS₆₇)

General Procedure:

To a solution NHS ester-functionalised PFS₆₈-b-(PDMS₆₅₂-r-PMVS₆₇) (25 mg, 3.0×10^{-4} mmol, 0.02 mmol NHS ester groups) in THF (2 mL) was added benzylamine (7 μL, 6 mg, 0.06 mmol, 3 equiv.) The reaction was stirred at room temperature for 16 h, then precipitated three times into methanol and dried *in vacuo* to afford the pure BCP 4a (19 mg, 77 %, $M_n = 83,700 \text{ g mol}^{-1}$). ¹H NMR (400 MHz; CD₂Cl₂): δ_H 7.43-7.16 (m, 335H, 2ArH_d, 2ArH_e and H_f), 4.37 (br s, 134H, H_c), 4.23 (t, J = 1.7 Hz, 272H, CpH),

4.03 (t, J = 1.7 Hz, 272H, CpH), 2.92-2.69 (m, 134H, H_b), 2.68-2.54 (m, 134H, H_a) 2.51-2.37 (m, 134H, SiCH₂CH₂S), 0.97-0.81 (m, 134H, SiCH₂CH₂S), 0.48 (s, 408H, Si(CH₃)₂), 0.18--0.09 (m, 4113H, Si(CH₃) and OSi(CH₃)₂) ppm;

¹³C NMR (101 MHz; CD₂Cl₂): δ_C 139.1 (ArC_{ipso}), 128.9 (2C_e), 128.0 (2C_d), 127.7 (C_f), 73.5 (CpC), 72.1 (CpCSi), 71.7 (CpC), 43.7 (C_c), 37.0 (C_b), 27.9 (C_a), 27.2 (SiCH₂CH₂), 18.7 (SiCH₂), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm (see Supporting Information for labelled structures). GPC: PDI = 1.17 (see Supporting Information Figure S3).

BCP 4b

Precipitated into methanol and dried *in vacuo* to afford the pure block copolymer (20 mg, 81 %, $M_n = 83,700 \text{ g mol}^{-1}$). ¹H NMR (400 MHz; CD₂Cl₂): δ_H 8.62-8.39 (m, 134H, 2ArH_e), 7.31-7.10 (m, 134H, 2ArH_d), 4.50-4.28 (m, 134H, H_c), 4.23 (t, J = 1.7 Hz, 272H, CpH), 4.02 (t, J = 1.7 Hz, 272H, CpH), 2.93-2.71 (m, 134H, H_b), 2.65-2.56 (m, 134H, H_a) 2.54-2.46 (m, 134H, SiCH₂CH₂S), 0.94-0.82 (m, 134H, SiCH₂CH₂S), 0.48 (s, 408H, Si(CH₃)₂), 0.18--0.09 (m, 4113H, Si(CH₃) and OSi(CH₃)₂) ppm; ¹³C NMR (101 MHz; CD₂Cl₂): δ_C 150.1 (ArC_e), 122.5 (ArC_d), 73.5 (CpC), 72.0 (CpCSi), 71.7 (CpC), 42.6 (C_c), 36.8 (C_b), 27.9 (C_a), 27.2 (SiCH₂CH₂), 18.7 (SiCH₂), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm (see Supporting Information for labelled structures). GPC: PDI = 1.65 (see Supporting Information Figure S3).

BCP 4c

Precipitated into methanol and dried *in vacuo* to afford the pure block copolymer (22 mg, 84 %, $M_n = 86,800 \text{ g mol}^{-1}$). ¹H NMR (400 MHz; CD₂Cl₂): δ_H 6.88-6.16 (m, 134 3ArH), 4.23 (t, J = 1.7 Hz, 272H, CpH), 4.02 (t, J = 1.7 Hz, 272H, CpH), 3.39 (app. s, 134H, H_c), 2.90-2.25 (m, 536H, H_a, H_b, H_d and SiCH₂CH₂S), 0.94-0.82 (m, 134H, SiCH₂CH₂S), 0.48 (s, 408H, Si(CH₃)₂), 0.18--0.09 (m, 4113H, Si(CH₃) and OSi(CH₃)₂) ppm. ¹³C NMR (101 MHz; CD₂Cl₂): δ_C 172.7 (CO), 145.1 (ArCOH), 136.7 (ArCOH), 128.8 (ArC_{ipso}), 125.8 (ArC), 120.6 (ArC), 115.5 (ArC), 73.6 (CpC), 72.1 (CpCSi), 71.7 (CpC), 34.6 (C_c), 30.4 (C_b and C_d),

27.1 (C_a), 26.7 (SiCH₂CH₂), 18.6 (SiCH₂), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm (see Supporting Information for labelled structures). **GPC:** PDI could not be determined due to interactions of the block copolymer with the column

BCP 4d

DMF (1 mL) was added to the reaction mixture to help solubilise amine. Precipitated into water and dried *in vacuo* to afford the pure block copolymer (17 mg, 65 %, $M_n = 87,800 \text{ g mol}^{-1}$). **¹H NMR (400 MHz; CD₂Cl₂):** δ_H 7.17 (s, 67H, CH)4.23 (t, J = 1.7 Hz, 272H, CpH), 4.02 (t, J = 1.7 Hz, 272H, CpH), 3.78 (app. s, 134H, H_c), 3.42 (app. s, 134H, H_d), 2.74 (t, J = 7.2 Hz, 134H, H_b) 2.66-2.50 (m, 134H, H_a), 2.46-2.35 (m, 134H, SiCH₂CH₂S), 1.38 (s, 201H, CH₃), 0.96-0.79 (m, 134H, SiCH₂CH₂S), 0.48 (s, 408H, Si(CH₃)₂), 0.18--0.09 (m, 4113H, Si(CH₃) and OSi(CH₃)₂) ppm. **¹³C NMR (101 MHz; CD₂Cl₂):** δ_C 173.4 (CO), 165.8 (CO), 152.2 (CO), 142.3 (CH), 73.7 (CpC), 72.2 (CpCSi), 71.8 (CpC), 38.6 (C_c), 36.6 (C_b), 27.9 (C_a), 27.3 (SiCH₂CH₂), 18.8 (SiCH₂), 12.2 (CH₃), 1.2 (OSi(CH₃)₂), -0.8 (SiCH₃)₂ ppm. Note - a drop of *d*⁴-methanol was added to the NMR sample to break up the intramolecular hydrogen bonding between the thymine units and aid dissolution (see Supporting Information for labelled structures). **GPC:** PDI could not be determined due to interactions of the block copolymer with the column.

BCP 4e

Precipitated into water and dried *in vacuo* to afford the pure block copolymer (39 mg, 65 %, $M_n = 198,800 \text{ g mol}^{-1}$). **¹H NMR (400 MHz; CD₂Cl₂):** δ_H 4.23 (t, J = 1.7 Hz, 272H, CpH), 4.02 (t, J = 1.7 Hz, 272H, CpH), 3.80-3.38 (m, 12328H, H_c, H_d, H_e, H_f), 3.34 (s, 201H, OCH₃), 2.77 (t, J = 7.1 Hz, 134H, H_b), 2.64-2.55 (m, 134H, H_a) 2.48-2.37 (m, 134H, SiCH₂CH₂S), 0.94-0.79 (m, 134H, SiCH₂CH₂S), 0.48 (s, 408H, Si(CH₃)₂), 0.19--0.09 (m, 4113H, Si(CH₃) and OSi(CH₃)₂) ppm. **¹³C NMR (101 MHz; CD₂Cl₂):** δ_C 73.5 (CpC), 72.1 (CpCSi), 70.9 (CpC and C_d, C_e and C_f), 59.0 (OCH₃), 39.7 (C_c), 36.9 (C_b), 27.9 (C_a), 27.2 (SiCH₂CH₂), 18.7 (SiCH₂), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm (see

Supporting Information for labelled structures). **GPC:** PDI = 1.20 (see Supporting Information Figure S3).

Mixed amine reaction of NHS ester functionalised PFS_{68-b}-(PDMS_{652-r}-PMVS₆₇) (5)

To a solution NHS ester-functionalised PFS_{68-b}-(PDMS_{652-r}-PMVS₆₇) (25 mg, $3.0 \times 10^{-4} \text{ mmol}$, 0.02 mmol NHS ester groups) in THF (2 mL) was added benzylamine (1.2 μL, 1.2 mg, 0.01 mmol, 0.55 equiv.) and 1-hexylamine (1.5 μL, 1.1 mg, 0.01 mmol, 0.55 equiv.) The reaction was stirred at room temperature for 16 h, then precipitated three times into methanol and dried *in vacuo* to afford the pure block copolymer (19 mg, 77 % $M_n = 83,500 \text{ g mol}^{-1}$). **¹H NMR (400 MHz; CD₂Cl₂):** δ_H 7.39-7.2.0 (m, 170H, 2ArH_d, 2ArH_e and H_f), 4.40 (br s, 68H, H_c), 4.23 (t, J = 1.7 Hz, 272H, CpH), 4.03 (t, J = 1.7 Hz, 272H, CpH), 3.25-3.10 (m, 66H, H_i), 2.86-2.70 (m, 134H, H_b and H_h), 2.67-2.54 (m, 134H, H_a and H_g), 2.52-2.30 (m, 134H, SiCH₂CH₂S), 1.37-1.20 (m, 134H, H_k, H_l and H_m), 0.96-0.79 (m, 200H, SiCH₂CH₂S and H_n), 0.48 (s, 408H, Si(CH₃)₂), 0.20--0.11 (m, 4113H, Si(CH₃) and OSi(CH₃)₂) ppm; **¹³C NMR (101 MHz; CD₂Cl₂):** δ_C 128.9 (2ArC_e), 128.0 (2ArC_d), 127.7 (ArC_f), 73.5 (CpC), 72.0 (CpCSi), 71.7 (CpC), 43.7 (C_c), 39.9 (C_i), 37.0 (C_b and C_h), 31.9 (C_l), 30.0 (C_j), 27.9 (C_a and C_g), 27.2 (SiCH₂CH₂), 27.0 (C_k), 23.0 (C_m), 18.7 (SiCH₂), 14.2 (C_n), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm (see Supporting Information for labelled structures). **GPC:** PDI = 1.16 (see Supporting Information Figure S3).

Hydrothiolation of PFS_{54-b}-(PDMS_{424-r}-PMVS₂₁₂) with 3-mercaptopropionic acid

To a solution of PFS_{54-b}-(PDMS_{424-r}-PMVS₂₁₂) (100 mg, $1.6 \times 10^{-3} \text{ mmol}$, 0.34 mmol vinyl groups) in dry THF (2 mL) was added 3-mercaptopropionic acid (88 μL, 1.02 mmol, 3 equiv.) and the photo-initiator 2,2-dimethoxy-2-phenylacetophenone (5 mg, 0.02 mmol). The orange solution was sealed under an argon atmosphere and irradiated 3 cm away from a mercury lamp for 1.5 h. The mixture was then precipitated in hexanes three times, then dried

in vacuo to afford the pure block copolymer (130 mg, 96%, $M_n = 85,300 \text{ g mol}^{-1}$). This polymer is only sparingly soluble in THF and interacts with the stationary phase in the above-described GPC equipment, and was used without characterisation.

Synthesis of PFS₅₄-*b*-(PDMS₄₂₄-*r*-PMVS₂₁₂) functionalised with NHS ester

To a solution acid-functionalised PFS₅₄-*b*-(PDMS₄₂₄-*r*-PMVS₂₁₂) (130 mg, 1.5×10^{-3} mmol, 0.32 mmol acid groups) in dry THF (15 mL) was added *N*-hydroxysuccinimide (112 mg, 0.97 mmol, 3 equiv.), *N,N'*-dicyclohexylcarbodiimide (200 mg, 0.97 mmol, 3 equiv.) and 4-dimethylaminopyridine (24 mg, 0.19 mmol, 0.6 equiv.). The reaction was stirred under an argon atmosphere at room temperature for 24 h, then precipitated three times into hexanes and dried *in vacuo* to afford the pure block copolymer (138 mg, 86 %, $M_n = 105,900 \text{ g mol}^{-1}$). ¹H NMR analysis showed quantitative functionalization of the acid functional groups with *N*-hydroxysuccinimide. ¹H NMR (400 MHz; CD₂Cl₂): δ_H 4.23 (t, J = 1.7 Hz, 216H, CpH), 4.02 (t, J = 1.7 Hz, 216H, CpH), 2.99-2.70 (m, 1696H, SCH₂CH₂COOH and H_a and H_b), 2.70-2.56 (m, 424H, SiCH₂CH₂S), 0.94-0.81 (m, 424H, SiCH₂CH₂S), 0.48 (s, 324H, Si(CH₃)₂), 0.21--0.01 (m, 3180H, Si(CH₃) and OSi(CH₃)₂) ppm; ¹³C NMR (101 MHz; CD₂Cl₂): δ_C 169.4 (2CO), 167.8 (CO), 73.5 (CpC), 72.1 (CpCSi), 71.7 (CpC), 32.3 (CH₂CO), 27.2 (SCH₂), 26.5 (SiCH₂CH₂), 26.0 (C_a and C_b), 18.6 (SiCH₂), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm (see Supporting Information for labelled structures). GPC: PDI = 2.1. We believe this higher than expected PDI is that despite the average vinyl group incorporation being 33% the range is probably 33±5% which once functionalized results in a broadening of M_w range and hydrodynamic radii which in turn produces a much higher PDI. This is magnified further due to the apparent interaction of the BCP with the GPC columns.

Benzylamine reaction of NHS ester functionalised PFS₅₄-*b*-(PDMS₄₂₄-*r*-PMVS₂₁₂)

To a solution NHS ester-functionalised PFS₅₄-*b*-(PDMS₄₂₄-*r*-PMVS₂₁₂) (25 mg, 2.4×10^{-4} mmol, 0.05 mmol NHS ester groups) in THF (2 mL) was added benzylamine (17 μL, 17 mg, 0.15 mmol, 3 equiv.) The reaction was stirred at room temperature for 16 h, then precipitated three times into hexanes and dried *in vacuo* to afford the pure block copolymer (20 mg, 81%, $M_n = 104,200 \text{ g mol}^{-1}$). ¹H NMR (400 MHz; CD₂Cl₂): δ_H 7.50-7.14 (m, 1060H, 2ArH_d, 2ArH_e and H_f), 4.33 (br s, 424H, H_c), 4.23 (t, J = 1.7 Hz, 216H, CpH), 4.03 (t, J = 1.7 Hz, 216H, CpH), 2.78 (t, J = 7.3 Hz, 424H, H_b), 2.69-2.53 (m, 424H, H_a) 2.44 (t, J = 7.3 Hz, 424H, SiCH₂CH₂S), 0.99-0.79 (m, 424H, SiCH₂CH₂S), 0.48 (s, 324H, Si(CH₃)₂), 0.19--0.01 (m, 3180H, Si(CH₃) and OSi(CH₃)₂) ppm; ¹³C NMR (101 MHz; CD₂Cl₂): δ_C 139.1 (ArC_{ipso}), 128.9 (2C_e), 128.0 (2C_d), 127.7 (C_i), 73.5 (CpC), 72.1 (CpCSi), 71.7 (CpC), 43.7 (C_c), 37.0 (C_b), 27.9 (C_a), 27.2 (SiCH₂CH₂), 18.7 (SiCH₂), 1.2 (OSi(CH₃)₂), -0.9 (SiCH₃)₂ ppm (see Supporting Information for labelled structures). GPC: PDI = 1.65

Hydrothiolation of PFS₄₉-*b*-PMVS₃₁₆ with 3-mercaptopropionic acid

To a solution of PFS₄₉-*b*-PMVS₃₁₆ (50 mg, 1.2×10^{-3} mmol, 0.39 mmol vinyl groups) in dry THF (2 mL) was added 3-mercaptopropionic acid (101 μL, 1.17 mmol, 3 equiv.) and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (5 mg, 0.02 mmol). The orange solution was sealed under an argon atmosphere and irradiated 3 cm away from a mercury lamp for 1.5 h. The mixture was then precipitated in hexanes three times, then dried *in vacuo* to afford the pure block copolymer (87 mg, 94%, $M_n = 72,600 \text{ g mol}^{-1}$). This polymer is only sparingly soluble in THF and interacts with the stationary phase in the above-described GPC equipment, and was used without characterisation.

Synthesis of PFS₄₉-*b*-PMVS₃₁₆ functionalised with NHS ester

To a solution acid-functionalised PFS₄₉-*b*-PMVS₃₁₆ (87 mg, 1.2×10^{-3} mmol, 0.38 mmol

acid groups) in dry THF (15 mL) was added *N*-hydroxysuccinimide (131 mg, 1.14 mmol, 3 equiv.), *N,N'*-dicyclohexylcarbodiimide (234 mg, 1.14 mmol, 3 equiv.) and 4-dimethylaminopyridine (28 mg, 0.28 mmol, 0.6 equiv.). The reaction was stirred under an argon atmosphere at room temperature for 24 h, then precipitated three times into hexanes and dried *in vacuo* to afford the pure block copolymer (87 mg, 70 %, $M_n = 103,300 \text{ g mol}^{-1}$). $^1\text{H NMR}$ (400 MHz; CD_2Cl_2): δ_{H} 4.24 (t, $J = 1.7 \text{ Hz}$, 196H, CpH), 4.03 (t, $J = 1.7 \text{ Hz}$, 196H, CpH), 3.02-2.73 (m, 2528H, $\text{SCH}_2\text{CH}_2\text{COOH}$ and H_a and H_b), 2.73-2.59 (m, 632H, $\text{SiCH}_2\text{CH}_2\text{S}$), 1.02-0.88 (m, 632H, $\text{SiCH}_2\text{CH}_2\text{S}$), 0.48 (s, 294H, $\text{Si}(\text{CH}_3)_2$), 0.20 (s, 948H, $\text{Si}(\text{CH}_3)$) ppm; $^{13}\text{C NMR}$ (101 MHz; CD_2Cl_2): δ_{C} 169.4 (2CO), 167.8 (CO), 73.5 (CpC), 72.1 (CpCSi), 71.7 (CpC), 32.3 (CH_2CO), 27.2 (SCH_2), 26.5 (SiCH_2CH_2), 26.0 (C_a and C_b), 18.6 (SiCH_2), 1.2 ($\text{OSi}(\text{CH}_3)_2$), -0.9 (SiCH_3) ppm (see Supporting Information for labelled structures). GPC: PDI = 1.44.

Benzylamine reaction of *N*-hydroxysuccinimidyl (NHS) ester functionalised PFS₄₉-*b*-PMVS₃₁₆

To a solution NHS ester-functionalised PFS₄₉-*b*-PMVS₃₁₆ (25 mg, $2.4 \times 10^{-4} \text{ mmol}$, 0.08 mmol NHS ester groups) in THF (2 mL) was added benzylamine (26 μL , 26 mg, 0.24 mmol, 3 equiv.) The reaction was stirred at room temperature for 16 h, then precipitated three times into hexanes and dried *in vacuo* to afford the pure block copolymer (21 mg, 86%, $M_n = 100,800 \text{ g mol}^{-1}$). $^1\text{H NMR}$ (400 MHz; CD_2Cl_2): δ_{H} 7.28-7.10 (m, 1580H, 2ArH_d , 2ArH_e and H_f), 4.36-4.14 (m, 828H, H_c and CpH), 4.03 (t, $J = 1.7 \text{ Hz}$, 196H, CpH), 2.76 (t, $J = 7.5 \text{ Hz}$, 632H, H_b), 2.67-2.52 (m, 632H, H_a) 2.44 (t, $J = 7.5 \text{ Hz}$, 632H, $\text{SiCH}_2\text{CH}_2\text{S}$), 1.00-0.79 (m, 632H, $\text{SiCH}_2\text{CH}_2\text{S}$), 0.48 (s, 294H, $\text{FcSi}(\text{CH}_3)_2$), 0.17 (m, 948H, $\text{Si}(\text{CH}_3)$) ppm; $^{13}\text{C NMR}$ (101 MHz; CD_2Cl_2): δ_{C} 139.1 (ArC_{ipso}), 128.9 (2C_e), 128.0 (2C_d), 127.7 (C_f), 73.5 (CpC), 72.1 (CpCSi), 71.7 (CpC), 43.7 (C_c), 37.0 (C_b), 27.9 (C_a), 27.2 (SiCH_2CH_2), 18.7

(SiCH_2), 1.2 ($\text{OSi}(\text{CH}_3)_2$), -0.9 (SiCH_3) ppm (see Supporting Information for labelled structures).

GPC: PDI = 1.11

RESULTS AND DISCUSSION

Synthesis of NHS Functionalised PFDMS₆₈-*b*-PDMS₆₅₂/PMVS₆₇

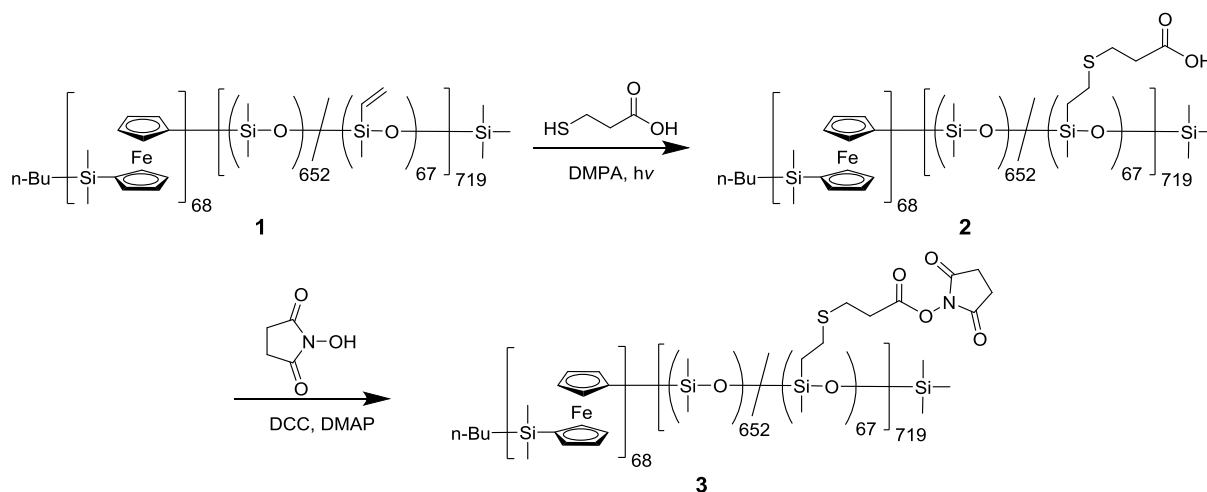
The block copolymer PFS₆₈-*b*-PDMS₆₅₂/PMVS₆₇ **1** was synthesised by the sequential living anionic polymerisation of dimethylsila[1]ferrocenophane and a mixture of hexamethylcyclotrisiloxane (D_3) and 1,3,3,5,5-pentamethyl-1-vinylcyclotrisiloxane (VD_2). An initiator amount of *n*-butyllithium was added to the dimethylsila[1]ferrocenophane monomer in THF, the reaction mixture stirred at room temperature. After 1 h a mixture of D_3 and VD_2 in THF was added and the reaction stirred for a further 2 h and then quenched with trimethylchlorosilane. The PFS homopolymer was removed by selective precipitation into ethyl acetate. The purified block copolymer was obtained in 63% yield as an orange solid after several precipitations in methanol ($M_n = 70,700 \text{ g mol}^{-1}$, PDI 1.09, Table S1 Supporting Information).

The acid functionalised polymer **2** was prepared by the thiol-ene "click" reaction of PFS₆₈-*b*-PDMS₆₅₂/PMVS₆₇ (**1**) with 3-mercaptopropionic acid. PFS₆₈-*b*-PDMS₆₅₂/PMVS₆₇, the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) and 3-mercaptopropionic acid were dissolved in THF under an inert atmosphere. The reaction was sealed and irradiated with a UV lamp for 1.5 h. The functionalised polymer was obtained in 92% as a gummy, orange solid after several precipitations into methanol. Analysis by $^1\text{H NMR}$ spectroscopy showed complete loss of vinyl group protons and the appearance of peaks corresponding to the quantitative incorporation of 3-mercaptopropionic acid ($M_n = 77,700 \text{ g mol}^{-1}$). PDI could not be determined by GPC due to the interaction of

oxygen lone pairs from the pendant acid groups of the BCP with the column.⁴¹

The NHS ester functionalised block polymer **3** was synthesised by the amide coupling of the acid functionalised PFS₆₈-b-PDMS₆₅₂/PMVS₆₇ and

Scheme 1: Synthetic Method to Introduce an NHS Ester Group onto PFS₆₈-b-PDMS₆₅₂/PMVS₆₇



NHS. The acid functionalised PFS₆₈-b-PDMS₆₅₂/PMVS₆₇, NHS, *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were dissolved in THF. The reaction was sealed under an inert atmosphere and stirred at room temperature for 24 h. The pure NHS ester functionalised polymer was obtained in 86% yield as an orange solid after several precipitations into methanol ($M_n = 84,200 \text{ gmol}^{-1}$, PDI 1.12). Analysis by ¹H NMR spectroscopy confirmed the incorporation of NHS ester with integrations consistent with quantitative functionalisation (Scheme 1). The appearance of a singlet peak at 2.80 ppm was assigned to the methylene groups of NHS (assigned as a multiplet in experimental due to overlap of signals).

Functionalisation of NHS Ester Functionalised PFS₆₈-b-PDMS₆₅₂/PMVS₆₇ with Primary Amines

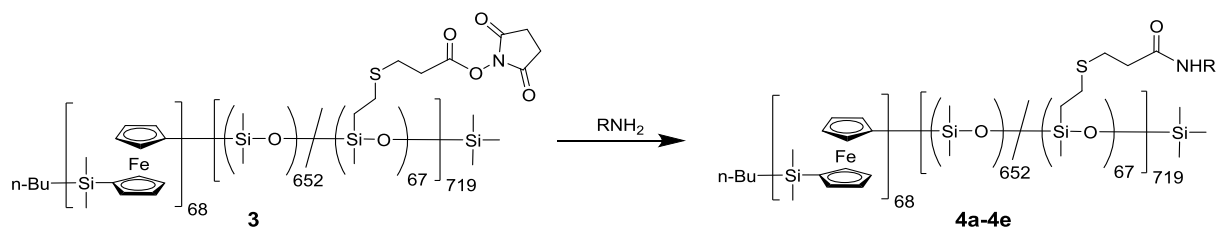
A variety of functional groups can be introduced into polymers using the thiol-ene click reaction.^{29,37,38} However, not all functional groups are suitable for this approach due to their instability under the radical reaction conditions. Additionally, for electron deficient thiols the rate of proton abstraction is too slow resulting in the loss of vinyl groups due to undesired cross-linking, preventing complete conversion to the thioether.³⁸ Also, there are fewer commercially available thiols compared

to functional groups such as primary amines and alcohols. Therefore a synthetic route which is able to introduce a range of more complex functionalities using mild conditions and readily available starting materials into siloxane containing polymers is desirable.

A functionalisation strategy applied in bioconjugate chemistry is the reaction between *N*-hydroxysuccinimidyl esters and primary amines to form the corresponding amide. The use of this approach for the functionalisation of BCPs would enable the incorporation of a wide range of different functionalities. For example the incorporation of biological molecules into BCPs to enhance their material properties has already been demonstrated to be a successful approach.^{42,43} To explore this methodology the NHS ester functionalised PFS₆₈-b-PDMS₆₅₂/PMVS₆₇ and benzylamine were dissolved in THF and stirred at room temperature for 16 h. The polymer was precipitated into methanol several times and dried in vacuo to give a gummy orange solid **4a**. ¹H NMR analysis showed complete loss of the signals associated with the NHS ester group as well as the presence of signals consistent with the quantitative incorporation of the benzylamine ($M_n 83,700 \text{ gmol}^{-1}$, PDI = 1.17)

To test the generality of this approach a range of different primary amines including biorelevant

Table 1: Reaction of NHS Ester Functionalised PFS₆₈-b-PDMS₆₅₂/PMVS₆₇ with Primary Amines



Amine (RNH ₂)	Product	Isolated Yield	M _n / gmol ^{-1a)}	PDI ^{b)}
	4a	77	83,700	1.17
	4b	81	83,700	1.65 ^{c)}
	4c	84	86,800	- ^{d)}
	4d	65	87,800	- ^{d)}
	4e	65	198,800	1.20

^{a)} Determined by ¹H NMR spectroscopy integration of the vinyl protons (3H) of PMVS and the methyl protons (6H) of PFDMS and PDMS ^{b)}Determined by GPC with conventional calibration of polystyrene standards; ^{c)}High PDI was obtained by GPC due to interaction of the block copolymer with the column; ^{d)}PDI could not be determined by GPC due to strong interaction of the block copolymer with the column which led to a broad peak (see Supporting Information Figure S3).

nucleotide analogues and amine terminated polymers were subjected to the same reaction conditions as **4a** (Table 1). In all cases, ¹H NMR analysis showed complete loss of the NHS ester protons and the quantitative incorporation of the amine protons. The non-quantitative yields of polymers **4a-e** was attributed to the loss of material during the precipitation steps to remove the excess amine, this was accentuated by the small scale of the reactions and the high polarity of the materials which made purification difficult.

Polymer **4b** was prepared from the reaction of 4-(aminomethyl)pyridine with the NHS ester functionalised polymer **3**. Introducing this functionality provides the opportunity to quaternise the pyridine groups. Furthermore, this provides a polymer where the corona-forming block is not completely quaternised as a method to help modulate the solubility of the resulting material. Polymer **4c** contains the biologically relevant catechol group 3,4-dihydroxyphenethylamine. This moiety has been extensively employed in the formation of

polymeric hydrogels, metallic coatings, and to aid the surface adhesion of polymers.^{44,45} Polymer **4d** was synthesised using the primary amine *N*¹-(2-aminoethyl)thymine which contains the pyrimidine moiety found in the DNA base pair thymine and provides the potential for directional H-bonding interactions. To aid the dissolution of the 1-(2-aminoethyl)-5-methylpyrimidine-2,4(1H,3H)-dione starting material the reaction was carried out in a mixture of THF/DMF (2:1) and yielded the polymer product with a pendant thymine nucleotide as a pale orange, brittle solid. Due to the high reactivity of primary amines with NHS esters compared to other aromatic amines, phenols and alcohols no side reaction with the phenol groups of the catechol to form the corresponding ester or reaction of the secondary amine was observed by ¹H NMR.

Grafting polymers onto the backbone of BCPs is an attractive target and recent work in our group has demonstrated how having long alkyl chains attached to the polymer in this fashion produces interesting properties.²⁹ Extending this approach to use with polymeric side-chains of polyethylene oxide (PEO, $M_w = 2000 \text{ gmol}^{-1}$) produced polymer **4e**. The ability to graft homopolymers onto the polymer backbone using this approach is a significant result as attempting this reaction on the original PFS₆₈-b-PDMS₆₅₂/PMVS₆₇ BCP with thiol terminated PEO ($M_w = 2000 \text{ gmol}^{-1}$) resulted in only 26% incorporation of thiol determined by ¹H NMR spectroscopy. A reduction of the vinyl protons of 43% was also observed in the ¹H NMR spectrum which indicated that the radical abstraction process for this reaction is too slow.

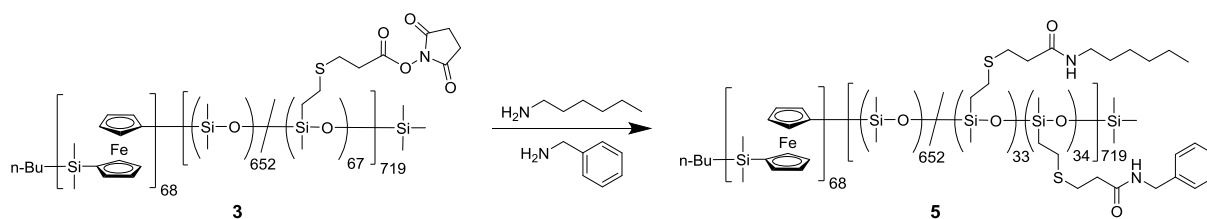
Derivatisation of NHS Ester Functionalised PFS₆₈-b-PDMS₆₅₂/PMVS₆₇ with a mixture of amines

Due to the vastly different reactivities of thiols in the thiol-ene reaction, the incorporation of more than one chemical functionality in a reaction using this approach is a challenge.³⁵ To explore whether using a mixture of amines resulted in their incorporation into the polymer a mixture of 1-aminohexane and benzylamine was added to the reaction in a 1:1 ratio (Scheme 2). The two amines were chosen due to their very different electronic properties and to therefore ascertain if there is preferential addition of one amine over the other. The resulting polymer by ¹H NMR showed complete loss of the NHS ester protons as well as the presence of signals corresponding to both amines. The ratio of the two amines present in polymer **5** was analysed by ¹H NMR spectroscopy and was determined to be 1:1, indicating that each were equally incorporated into the final material.

NHS Functionalisation of PFS₅₄-b-PDMS₄₂₄/PMVS₂₁₂ and PFS₄₉-b-PMVS₃₁₆

Introducing functionality into the corona of the block copolymer can alter the self-assembly behaviour of the resulting material. To prevent major changes, low loadings of 10% or less of the functional groups were used. However, in other situations higher levels of functionality are desirable. To investigate if this reaction could be utilised to functionalise BCPs with a larger proportion of vinyl groups it was applied to the following BCPs; PFS₅₄-b-PDMS₄₂₄/PMVS₂₁₂ and

Scheme 2: Reaction of NHS Ester Functionalised PFS₆₈-b-PDMS₆₅₂/PMVS₆₇ with a mixture of amines



PFS₄₉-b-PMVS₃₁₆, with 33% and 100% vinyl groups in the amorphous block, respectively. The acid functionalised version of both BCPs had very low solubility in THF, chloroform and dichloromethane which prevented accurate analysis by ¹H NMR. The material was therefore taken through to the NHS coupling step without further purification and characterisation. Analysis of the NHS ester functionalised BCPs by ¹H NMR showed their formation with total conversion and indicated that the thiol-ene click reactions had also gone to completion. Reaction with benzylamine for both BCPs resulted in quantitative conversion to the amide and exemplifies the generality of this approach to vinyl-containing BCPs.

CONCLUSION

We have demonstrated a general approach using mild conditions to incorporate a broad range of different functionalities into PFS-*b*-PMVS BCPs. This approach extends the widely established thiol-ene click functionalisation of vinyl containing BCPs such as polybutadiene and poly(allyl glycidyl ether) to enable a range of previously inaccessible moieties to be incorporated. The azide-alkyne and thiol-ene click reactions are also used to form BCPs from two functionalised homopolymers and therefore the NHS ester strategy could be employed as an alternative method when one of the functionalised homopolymers is incompatible with standard click reaction conditions.

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GRAPHICAL ABSTRACT

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Versatile and Controlled Functionalisation of Polyferrocenyldimethylsilane-*b*-Polyvinylsiloxane Block Copolymers using a *N*-hydroxysuccinimidyl (NHS) Ester Strategy

TEXT

This article reports the introduction of a *N*-hydroxysuccinimidyl ester group onto the pendant vinyl group of poly(ferrocenyldimethyl)silane-*b*-polyvinylsiloxane copolymers which provides a route to incorporate a range of functionalities previously inaccessible using reported methods.

GRAPHICAL ABSTRACT FIGURE

