Ferrocenyl dendronized polymers†‡

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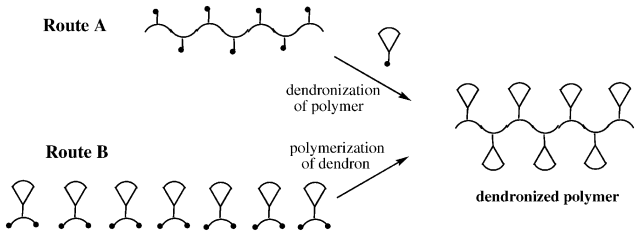
Styrenic dendrons functionalized with ferrocenyl and chloromethylsilyl termini were synthesized and polymerized by the AIBN-initiated radical polymerization procedure yielding a ferrocenyl dendronized polymer and a chloromethylsilyl dendronized polymer, respectively. The latter polymer was functionalized with ferrocenyl groups using "click" chemistry. The ferrocenyl dendronized polymers are soluble in common organic solvents such as tetrahydrofuran, dichloromethane, and chloroform. They show a reversible ferrocenyl wave in cyclic voltammetry (CV) and form derivatized Pt electrodes. Their sizes and shapes were examined by size exclusion chromatography (SEC), atomic force microscopy (AFM), dynamic light scattering (DLS) and DOSY ^{1}H NMR spectroscopy.

Introduction

Dendronized polymers[1] are large nano-objects that can be synthesized either by the dendronization of a functional polymer (Scheme 1, route A) or the macromonomer route involving polymerization of a pre-formed dendron (Scheme 1, route B).[1–5] Their size, shape and functionalities bring about specific potential applications, for instance in materials science[3,4] and nanomedicine.[5] It has been shown that dendronized polymers are either spherical or cylindrical depending on the size of the dendronic side chains.[4] Given their large size, the visualization of the shape of dendronized polymers can be carried out by microscopy techniques such as atomic force microscopy (AFM).

Metal-containing polymers are of great interest for their materials properties including catalysis, molecular electronics, sensors and semi-conductors.[6] Although ferrocene-containing polymers are well known for such applications,[6] only one example of dendronized polyferrocene is known: Manners and co-workers recently reported substitution of the chloro group in poly(ferrocenylchloromethylsilane),[7] with a Percec-type dendron[4] containing a benzylate focal point (*i.e.* Scheme 1, route A), as well as several physico-chemical studies including AFM observation of spherical cocoons for the single chains of the dendronized polymer and elongated single-chain structures.[3,8]

Continuing our interest in redox-robust systems in nano-objects,[9] we wished to investigate the synthesis of ferrocenyl dendronized polymers including their redox properties and functions.



Scheme 1 Two routes to dendronized polymers.

In this paper, we report an alternative method to synthesize a ferrocene-containing dendronized polymer, *i.e.* the polymerization of new triferrocenylsilyl and tris-(chloromethylsilyl) dendrons containing a styrenyl group at the focal point (*i.e.* Scheme 1, route B). In recent work, we reported the attachment of triferrocenylsilyl dendrons containing other focal groups to the termini of dendrimers including gold nanoparticle (AuNP)-centered dendrimers as sensors for inorganic anions including ATP.[10] Thus, modification of this family of dendrons by the introduction of a styrenyl group now brings about the key entry to ferrocenyl dendronized polymers.

Experimental

1. General data

All operations were performed under a nitrogen atmosphere using standard Schlenk techniques. Prior to use, THF was dried over sodium benzophenone ketyl and freshly distilled under a nitrogen atmosphere. CH_2Cl_2 was dried over calcium hydride and freshly distilled under a nitrogen atmosphere. All other reagents were obtained from commercial sources and used without further purification. All glassware was previously dried in an oven and cooled under a nitrogen flow. Ferrocenyldimethylsilane was synthesized according to ref. 11.

2. Physical measurements

The ^{1}H NMR spectra were recorded at 25 °C on a Bruker AC 250 (250 MHz), a Bruker Advance 300 (300 MHz), and a Bruker

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‡ This article is dedicated to our distinguished colleague Dr Jean-Pierre Sauvage, on the occasion of his 65th birthday.

DPX 400 (400 MHz) spectrometer. ^{13}C NMR spectra were recorded in the pulse FT mode on a Bruker AC 300 spectrometer at 75.50 MHz. ^{29}Si NMR spectra were recorded on a Bruker AC 300 spectrometer at 59.6 MHz. All chemical shifts are reported in parts per million (δ, ppm) with reference to $SiMe_4$ (TMS). Mass spectra were obtained at the CESAMO, Université Bordeaux 1, on a PerSeptive Biosystems Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. This instrument was equipped with a nitrogen laser (337 nm), a delayed extraction, and a reflector. It was operated at an accelerating potential of 20 kV in both linear and reflection modes. The mass spectra shown represent an average over 256 consecutive laser shots (3 Hz repetition rate). Peptides were used to calibrate the mass scale using the two points calibration software 3.07.1 from PerSeptive Biosystems. Elemental analyses were performed at the Center of Microanalysis of the CNRS, Lyon Villeurbanne, France. All electrochemical measurements were recorded in degassed CH_2Cl_2 at 20 °C. Supporting electrolyte: [*n*-Bu_4N][PF_6] 0.1 M; working and counter electrodes: Pt, quasi-reference electrode: Ag; internal reference: $[Fe(\eta^5\text{-}C_5Me_5)_2]^{+/0}$;[15] scan rate: 0.200 V s^{-1}.

3. Synthesis and polymerization

Synthesis of the monomeric triferrocenyl dendron 3. The phenol triferrocenyl dendron **3** (0.562 g; 5.4 × 10^{-4} mol), *p*-iodomethylstyrene (0.152 g, 6.23 × 10^{-4} mol), and potassium carbonate (0.436 g; 3.15 × 10^{-4} mol) were successively introduced into a Schlenk tube. DMF (30 mL) was then added into the Schlenk tube in the dry lab. This reaction mixture was stirred for one day at ambient temperature. DMF was then evaporated under reduced pressure, and the crude residue was dissolved in dichloromethane, potassium carbonate was then filtered, and the concentrated solution was chromatographed over a silica gel column using dichloromethane as the eluant. Removal of dichloromethane under reduced pressure yielded 0.420 g of **3** as an orange–red solid (67%).

^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm}: 0.6 (s, 6H, Si-C*H*$_3$); 0.6 (t, 2H, Si-C*H*$_2$); 1.12 (m, C*H*$_2$); 1.58 (t, 2H, Cq-C*H*$_2$); 4.11 (s, 2H, Cp, Si-C-C*H*); 4.15 (s, 5H, Cp); 4.36 (s, 2H, Si-C-CH-C*H*); 5.04 (s, 2H, C*H*$_2$O); 5.28 (m, 1H, vinyl); 5.76 (d, 1H, vinyl); 6.92 (q, 1H, vinyl); 7.16 (d, 2H, arom.); 7.19 (d, 2H, arom.); 7.19 (d, 2H, arom.); 7.42 (s, 4H, arom.).

^{13}C NMR ($CDCl_3$, 75.47 MHz), δ_{ppm}: 0.00 (Si-*C*H$_3$); 19.49 (*C*H$_2$); 20.06 (*C*H$_2$); 44.13 (*C*H$_2$); 45.26 (*C*q); 70.79–75.63 (Cp); 78.59 (*C*H$_2$-O); 116 (*C*H$_2$ vinyl); 128.39 and 129.73 (*C*H, arom.); 133.51 (*C*q arom.); 138.94 (*C*q arom.); 153.27 (*C*q arom.).

^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: −2.67 (s, Si).

Anal. calc. for $(C_{61}H_{76}Fe_3OSi_3)_n$: C 68.02, H 7.11; found: C 67.61, H 7.21.

MALDI TOF mass spectrum (*m*/*z*): calc.: 1077.05; found: 1044.34 $(M - CH_3)^+$; 1076.38 $(M)^+$.

Polymerization of the dendron 3. Radical polymerization was carried out using a 0.013 molar THF solution of AIBN[11] that was prepared by introducing 20 mg of AIBN in 10 µL of THF. The dendron **3** (0.146 g; 1.36 × 10^{-4} mol) was introduced into a Schlenk flask containing a side entry. The THF solution of AIBN (101 µL) was then added, the solution was degassed under vacuum, and the reaction mixture was stirred for 15 h in the closed Schlenk tube under a nitrogen atmosphere at 100 °C (pressure was kept with caution using the specially equipped Schlenk tube). The solvent was removed under vacuum, and the orange solid residue was partly dissolved in dichloromethane. The orange solid residue (37 mg) was insoluble in all solvents. The soluble fraction was concentrated to 2 mL and precipitated using 20 mL methanol, yielding an orange waxy product that was then reprecipitated twice from dichloromethane solutions with methanol, leaving a waxy orange product (44 mg, 30% yield).

^{1}H NMR ($CDCl_3$, 300 MHz), δ_{ppm} (broad signals): 0.5 (Si-CH_3); 0.6 (Si-CH_2); 1.13 (CH_2); 1.56 (Cq-CH_2); 3.99 (2H, Cp Si-C-CH); 4.05 (5H, Cp); 4.26 (2H, Cp, Si-C-CH); 5.3 (CH_2-O); 6.83 (H vinyl); 7.13 (H arom.).

^{13}C NMR ($CDCl_3$, 75.47 MHz), δ_{ppm}: −1.35 (Si-*C*H$_3$); 18.01 (*C*H$_2$); 18.51 (*C*H$_2$); 42.54 (*C*H$_2$); 43.63 (*C*q); 68.88–73.73 (Cp); 77.61 (*C*H$_2$-O); 127.87 and 128.18 (*C*H arom.); 156.94 (*C*q arom.).

^{29}Si NMR ($CDCl_3$, 59.62 MHz), δ_{ppm}: −2.658 (s, Si).

Size exclusion chromatography (SEC): M = 160 kDa; PDI = 1.9.

Synthesis of the tris(chloromethylsilyl) dendron 7. The triallyl phenol dendron **2** (100 mg, 0.18 mmol) and iodomethylstyrene (66 mg, 0.271 mmol) were introduced into a Schlenk flask, and dry DMF (20 mL), then K_2CO_3 (125 mg, 0.904 mmol) were added to the solution. The mixture was stirred for 3 days at ambient temperature. At the end of the reaction, DMF was removed, and the product was extracted with CH_2Cl_2, washed with water, and purified by chromatography (CH_2Cl_2 100%), which gave 86 mg of **7** as a yellow oil (70% yield).

^{1}H NMR spectrum of the dendron **7** ($CDCl_3$, 250 MHz): 7.43 (C*H* arom. core), 7.17 and 6.79 (C*H* arom. dendron), 6.73 (C*H*═CH_2), 5.74 and 5.24 (CH═C*H*$_2$), 5.06 (C*H*$_2$O), 2.74 (C*H*$_2$Cl), 1.63 (C*H*$_2$$CH_2$$CH_2$Si), 1.09 ($CH_2$C*H*$_2$$CH_2$Si), 0.59 ($CH_2$$CH_2$C*H*$_2$Si), 0.07 (Si(C*H*$_3$)$_2$).

^{13}C NMR ($CDCl_3$, 62 MHz): 153.35 (*C*q-O-CH_2), 139.96 (*C*q arom. and *C*H═CH_2), 127.86 (*C*H arom. dendron), 115.13 (*C*H arom. styrene), 70.26 (O-*C*H$_2$, arom.), 43.42 (*C*q arom. and *C*H$_2$$CH_2$$CH_2$Si), 30.85 (*C*H$_2$Cl), 17.95 ($CH_2$*C*H$_2$$CH_2$Si), 14.79 ($CH_2$$CH_2$*C*H$_2$Si), −4.10 (Si(*C*H$_3$)$_2$).

Polymerization of the tris(chloromethylsilyl) monomer 7. The monomeric dendron **7** (140 mg, 0.205 mmol) was dried in a Schlenk tube. A solution of azobisisobutyronitrile (AIBN) was prepared with 36 mg of AIBN in 10 mL of distilled THF. 100 µL of this solution (0.36 mg, 2.05 × 10^{-6} mol, 1% molar) were added to the monomer. The mixture was stirred for 15 h at 100 °C under a nitrogen atmosphere. At the end of the reaction, the product was extracted with CH_2Cl_2 and purified by precipitation with methanol. The precipitate was filtered and recovered with dichloromethane, and reprecipitated three times using methanol, yielding **8** as a yellow oil (70 mg, 50% yield).

^{1}H NMR of **8** ($CDCl_3$, 250 MHz): 7.17 and 6.89 (C*H* arom.), 4.87 (C*H*$_2$O), 2.71 (C*H*$_2$Cl), 1.93 (C*H*$_2$I), 1.62 (C*H*$_2$$CH_2$$CH_2$Si), 1.09 ($CH_2$C*H*$_2$$CH_2$Si), 0.58 ($CH_2$$CH_2$C*H*$_2$Si), 0.05 (Si(C*H*$_3$)$_2$).

^{13}C NMR of **8** ($CDCl_3$, 62 MHz): 157.00 (*C*q-O-CH_2), 139.93 (*C*q arom.), 134.61 (*C*HCH$_2$), 127.77 (*C*H arom.), 70.26 (O-H_2 arom.), 46.85 (*C*qCH$_2$), 42.28 (*C*H$_2$CH$_2$CH$_2$Si), 30.79 (*C*H$_2$Cl), 17.92 (CH$_2$*C*H$_2$CH$_2$Si), 13.93 (CH$_2$CH$_2$*C*H$_2$Si), −4.40 (Si(*C*H$_3$)$_2$). SEC: M = 33.6 kDa g mol^{-1}. Polydispersity: PDI = 1.58.

Functionalization of the polymer 8 and "click" reaction. The polymer **8** (0.06 g, 87.8 μmol) was dissolved in DMF (8 mL), and an excess of NaN_3 (0.068 mg, 1.05 mmol) was added. The reaction mixture was stirred at 60 °C for 12 h. DMF was removed, the crude product was dissolved in 10 mL of dichloromethane, and the salts were filtered. Dichloromethane was removed under vacuum, and the dendronized polymer **9** was obtained as a yellow oil in 85% yield.

^{1}H NMR ($CDCl_3$, 250 MHz): 7.16 and 6.89 (8H arom.), 6.50 (1H, C*H* arom.), 5.42 (2H, CH_2 CH arom.), 4.86 (2H, CH_2O), 2.7 (2H, CH_2N$_3$), 1.62 (2H, CH_2CH$_2$CH$_2$Si), 1.11 (2H, CH$_2$CH_2CH$_2$Si), 0.55 (2H, CH$_2$CH$_2$CH_2Si), 0.03 (6H, Si(CH_3)$_2$).

^{13}C NMR ($CDCl_3$, 62 MHz): 157.04 (*C*q-O-CH_2), 139.84 (*C*q arom.), 134.61 (*C*HCH$_2$), 127.68 (*C*H arom.), 70.31 (O-*C*H$_2$ arom.), 43.47 (*C*qCH$_2$), 42.27 (*C*H$_2$CH$_2$CH$_2$Si), 41.40 (*C*H$_2$N$_3$), 17.93 (CH$_2$*C*H$_2$CH$_2$Si), 15.26 (CH$_2$CH$_2$*C*H$_2$Si), −3.67 (Si(*C*H$_3$)$_2$). Infrared ν_{C-N3}: 2094 cm^{-1}. SEC: M = 34 600 g mol^{-1}.

The dendronized polymer **9** (0.028 g, 45.2 μmol, 1 eq.) and ethynylferrocene (0.019 g, 90.5 μmol, 2 eq. per branch) were dissolved in THF. $CuSO_4$ was added at 0 °C (4 eq. per branch, 1 M water solution), followed by dropwise addition of a freshly prepared solution of sodium ascorbate (8 eq. per branch, 1 M water solution) in order to obtain a ratio of solvent equal to 1 : 1 (THF–water). The solution was stirred for 12 h at 25 °C under nitrogen. After removing THF under vacuum, CH_2Cl_2 and an aqueous ammonia solution were added. The mixture was stirred for 10 min in order to remove all the Cu^I trapped inside the dendrimer as $Cu(NH_3)_6^+$. The organic phase was washed twice with water, dried with sodium sulfate and the solvent was removed under vacuum. The product was precipitated with CH_2Cl_2–pentane, and then with CH_2Cl_2–ether in order to remove excess ethynylferrocene (yield = 70%).

^{1}H NMR ($CDCl_3$, 250 MHz): 7.42 (C*H* triazole), 7.14 and 6.89 (C*H* arom.), 4.69 (C*H*, CH_2O), 4.69, 4.26, 4.04 (9H, Cp), 3.81 (2H, SiCH_2N), 1.58 (2H, CH_2CH$_2$CH$_2$Si), 1.11 (2H, CH$_2$CH_2CH$_2$Si), 0.58 (2H, CH$_2$CH$_2$CH_2Si), 0.06 (6H, Si(CH_3)$_2$).

^{13}C NMR ($CDCl_3$, 62 MHz): 157.0 (*C*qO), 146.1 (*C*q of triazole), 139.9 (*C*q arom.), 134.6 (*C*H arom.), 126.7 (*C*H$_2$CH arom.), 120.0 (*C*H of triazole), 114.5 (*C*H arom.), 73.4 (*C*q of Cp), 70.9 (*C*H$_2$O), 69.9, 68.9 and 66.9 (*C*H of Cp), 41.2 (*C*H$_2$CH$_2$CH$_2$Si), 40.8 (*C*H$_2$N), 15.2 (CH$_2$*C*H$_2$CH$_2$), 14.6 (CH$_2$CH$_2$*C*H$_2$Si), −3.5 (SiMe$_2$).

Infrared ν_{C-N3}: disappearance of the band at 2094 cm^{-1}.

DOSY ^{1}H NMR: D = 6.65 (±0.6) × 10^{-11} m^2 s^{-1}; r_h = 8.6 (±0.8) nm; (D: diffusion coefficient; r_h: hydrodynamic radius). Dynamic light scattering: r_h = 9.25 (±0.9) nm.

Derivatization of the Pt electrodes with the ferrocenyl dendronized polymers 5 and 10. A platinum electrode (Sodimel, Pt 30) was dipped into 10% aqueous HNO_3 for 3 h, then rinsed with distillated water, dried in air, and polished using cerium oxide powder (5 MU). The dendronized polymer **5** was electrodeposited onto the platinum-disk electrodes (A = 0.0078 cm^2) from degassed CH_2Cl_2 solutions (9.3 × 10^{-6} M) and [n-Bu$_4$N][PF$_6$] (0.1 M) by continuous scanning (0.20 V s^{-1}) up to 50 cycles between 0.0 and 0.9 V *vs.* [Fe(η^5-C$_5$Me$_5$)$_2$]$^{+/0}$. The coated electrode was washed with CH_2Cl_2 in order to remove the solution from material and dried in air. This modified electrode was characterized by cyclic voltammetry (CV) using freshly distilled CH_2Cl_2 as solvent containing only the supporting electrolyte. It showed a single symmetrical CV wave, and the linear relationship of the peak current with potential sweep rate was verified. The surface coverage Γ (mol cm^{-2}) by the ferrocenyl dendronized polymer **5** was determined from integrated charge of the CV wave. $\Gamma = Q/nFA$, where Q is the charge, n is the number of electrons transferred, F is the Faraday constant, and A is the area. Thus, the surface coverage for the electrode modified with **5** was 8.3 × 10^{-9} mol cm^{-2} (ferrocenyl sites), corresponding to 1.34 × 10^{-10} mol cm^{-2} of **5**. The dendronized polymer **10** was electrodeposited in the same way as **5**, and the surface coverage Γ for the electrode modified with **10** was 7. 4 × 10^{-10} mol cm^{-2} (ferrocenyl sites).

4. Dynamic light scattering measurements (DLS)

The DLS measurements were made using a Malvern Zetasizer 3000 HSA instrument at an angle of 90°, in dichloromethane solution at 25 °C. Measurements were carried out at different concentrations until the hydrodynamic diameter was found to be constant at three different concentrations (for high concentration, higher hydrodynamic diameter values were found, due to aggregation).

5. Atomic force microscopy (AFM) experiments

The AFM samples were prepared by spin coating of a suitable solution (1 mg mL^{-1}) (adjusted on a trial and error basis) of dendronized polymer in CH_2Cl_2. Before spin coating, the mica surface was cleaved with Scotch tape. The freshly cleaved highly oriented mica surface was covered with the solution and spinned at 1000 rpm with subsequent 10–15 second extra spinning at 3000 rpm for complete drying in air. The AFM apparatus is a Thermomicroscope CP Research capable of obtaining measurements in multiple modes, and the sample imaging is achieved in air immediately after spin coating. The tapping mode was used giving the weakest interaction with the surface and therefore the less chance of alteration. The cantilever–tip systems used were nanosensors (PPPNCL, spring constant = 40 N m^{-1}), with typical tip (silicon tip) radius of curvature of 6 nm. For each sample, the images of topography, amplitude and phase were obtained using the software Image Processing and Data Analysis 20.0. A sample was considered as good when a monolayer of ferrocenyl dendronized polymer was measured by AFM. In order to estimate the size of the polymers, it is necessary to consider the radius of curvature of the tip only if the measured nano-object is smaller than the tip. In the present case, the tip (6 nm) is much smaller than the measured object (22 nm), thus one does not need to eliminate the tip-shape induced impact by deconvolution.

6. Size exclusion chromatography

Size exclusion chromatography (SEC) or gel permeation chromatography (GPC) was performed using THF as eluant at 40 °C and a flow rate of 1 mL min^{-1} through 4 columns (TSK G5000HXL (9 μm), G4000HXL (6 μm), G3000HXL (6 μm), and G2000HXL (5 μm)) and connected to Varian refractometer and UV-visible spectrophotometer calibrated against linear polystyrene standards.

Results and discussion

Synthesis of the triferrocenyl dendron 4

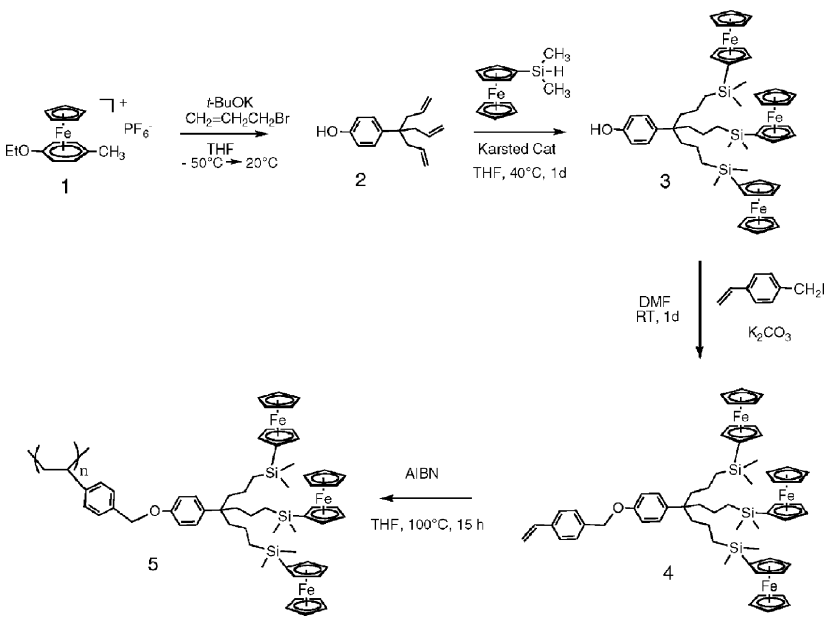
The new triferrocenyl dendron **4** containing a styrenyl group was synthesized by Williamson reaction of the triferrocenyl dendron **3**[10b] with *p*-iodomethylstyrene, as shown in Scheme 2. The precursor triferrocenyl dendron **3** was synthesized according to a previously reported procedure by hydrosilylation of the triallylphenol dendron **2** using ferrocenyldimethylsilane[11] (Scheme 2). The substantial advantage of the catalyzed hydrosilylation reaction in the present chemistry is that it is compatible with the phenol group and thus does not require a tedious protection–deprotection procedure. Likewise, the ferrocenyl dendronic branch termini do not prevent the Williamson reaction to attach the styrenyl group, and this reaction proceeds smoothly in 67% yield.

Polymerization of the dendron 4 to the dendronized polymer 5

The best working procedure in our hands turned out to be the AIBN-initiated radical polymerization of the styrenyl derivative bearing the dendronic group as a *para* substituent.[12] A possible problem of the dendron polymerization is the bulk around the reactive focal point, as with any convergent molecular construction.[13] When the generation increases, the bulk becomes large around the focal point, which inhibits further coupling. Therefore, the structure of this dendron was designed to be located far enough from the bulky termini, and the number of ferrocenyl termini was kept low at the first generation although higher generations are known.[10] The radical polymerization, carried out using the standard procedure,[12] yielded an insoluble red powder (25% of the total mass that could be a high-molecular-weight polymer) and a polymer soluble in dichloromethane that was reprecipitated three times from dichloromethane solutions using methanol. This soluble polymer was analyzed using ^{1}H and ^{13}C NMR (see Experimental section) including DOSY NMR, dynamic light scattering (DLS), size exclusion chromatography (SEC) and AFM. The DOSY experiment was not successful, because the polymer was too large, and this technique does not work with very large nano-objects. DLS measurements reproducibly provided an apparent diameter size of 28 ± 2 nm. A large size was expected from the failure of the DOSY NMR experiment, but this latter value appears to be very large, presumably because of the solvent sphere around the polymer and the non-spherical shape of the polymer. Even larger values were observed for the other ferrocenyl dendronized polymers by Manners *et al.*[3] SEC provided a molecular weight of 160 kDa with a polydispersity index (PDI) of 1.9 (Fig. 1).

Synthesis and polymerization of a tris(chloromethylsilyl) dendron and "click" ferrocenylation

An alternative synthesis of a ferrocenyl dendronized polymer involves the synthesis of a tris(chloromethylsilyl) dendron that might be functionalized with ferrocenyl termini subsequent to polymerization. This strategy is a variant of the former one also starting with the polymerization of a dendron, but the latter method adds an additional series of two reactions after polymerization (Scheme 3).



Scheme 2 Synthesis and AIBN-induced radical polymerization of the triferrocenyl styrenyl dendron **4**. The triallyl phenol dendron **2** and the triferrocenyl phenol dendron **3** were synthesized according to ref. 10*a*,*e* and 10*b*, respectively.

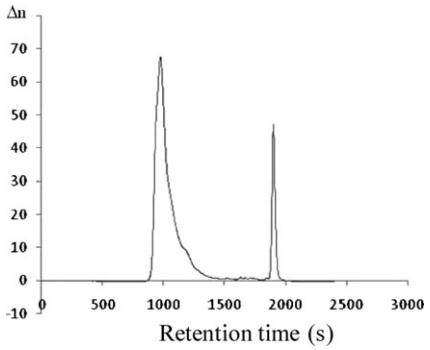
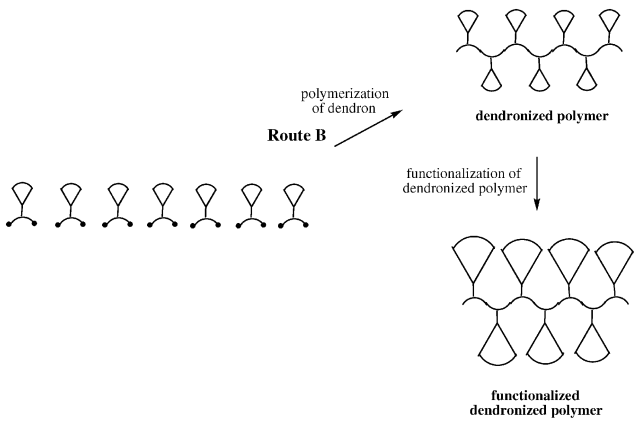


Fig. 1 Size exclusion chromatogram (SEC) of **5** (left) using polystyrene as the reference and 1,3,5-trichlorobenzene as a marker (shown on the right). The SEC was carried out using a refractometer. Δn is the variation of the refraction index as a function of time (seconds).

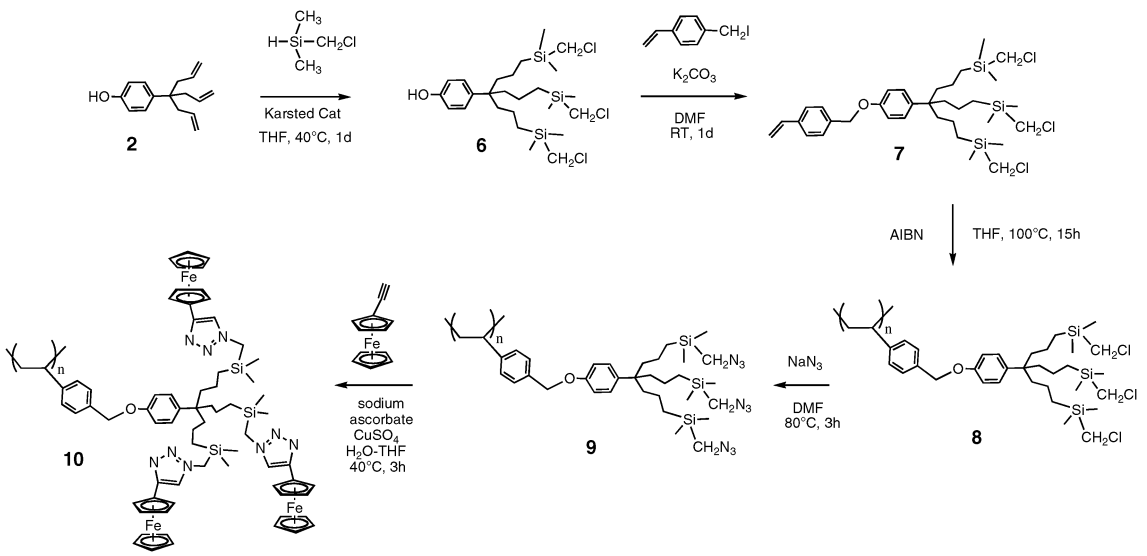


Scheme 3 Modification of route B (Scheme 1) with the functionalization of a dendronized polymer applied to the ferrocenylation reaction by "click" chemistry (Scheme 4).

These reactions are the substitution of the chloro group by the azido group followed by click reaction with ethynylferrocene. The initial polychloro polymer **8** was purified by reprecipitation from a dichloromethane solution using methanol, and this same type of purification was carried out for the "clicked" polyferrocenyl dendronized polymer. Using this method, a ferrocenyl dendronized polymer of dispersity PDI = 1.2 was obtained, which is satisfactory given the type of polymerization reaction that was used (Scheme 4). This good PDI value was obtained, because the polymer was purified by reprecipitation three times. The virtually quantitative conversion **8** → **9** → **10** (Scheme 4) is verified by ^{1}H NMR, because the CH_2Cl (and CH_2N_3) signal completely disappears upon "click" reaction of **9**.

The DOSY ^{1}H NMR experiments provided a mean diameter of 17.2 nm, whereas the dynamic light scattering (DLS) experiments yielded a diameter value of 18.5 nm, which is a reasonably good agreement consistent with the relatively low PDI value (Table 1).

Cyclic voltammetry shows the reversible behavior of the ferrocenyl oxidation wave in both **5** and **10** as with ferrocenyl-terminated dendrimers.[14] It is also a good means of determining the average number of ferrocenyl units in a polymer using the Bard–Anson equation.[15] This equation only applies in the absence of adsorption, however, because adsorption increases the peak intensity value, and the number of redox units would be provided in excess. In dichloromethane, the ferrocene oxidation wave of **10** at 0.69 V *vs.* decamethylferrocene–decamethylferrocenium[16] on a Pt anode indeed appears reversible without adsorption as indicated by a $E_{p,ox}-E_{p,red}$ value of 50 mV and a ratio between the anodic and cathodic peak current that is about unity (Fig. 2). The number of ferrocenyl units calculated for **10** with this equation yields an average value of 153 ferrocenyl units (51 triferrocenyl dendrons, corresponding to 67 kDa). This method could not be applied to the other ferrocenyl dendronized polymer **5**, because adsorption was too strong, even in dichloromethane. This is due to the larger size of ferrocenyl dendronized polymer **5** compared to **10**. Scanning around the ferrocenyl potential value easily led to the formation of fully derivatized Pt electrodes[17] for both **5** and **10** (Fig. 3 and S1, ESI†).



Scheme 4 Synthesis of a ferrocenyl dendronized polymer by functionalization of a poly(chloromethylsilyl) dendronized polymer.

Table 1 Compared physico-chemical data for the ferrocenyl dendronized polymers **5** and **10**

	SEC PDI	DOSY ^{1}H NMR Diffusion coefficient/m^2 s^{-1}	DOSY ^{1}H NMR Diameter/nm	DLS Diameter/nm	AFM Height/nm	AFM Width/nm
Fc-dendronized polymer **10**	1.2	6.65 (±0.6) × 10^{-11}	17.2 (±1.7)	18.5 (±1.8)	2.4 (±0.2)	22.5 (±2.2)
Fc-dendronized polymer **5**	1.9	Not applicable		28 (±2.8)	5 (±0.5)	100 (±10)

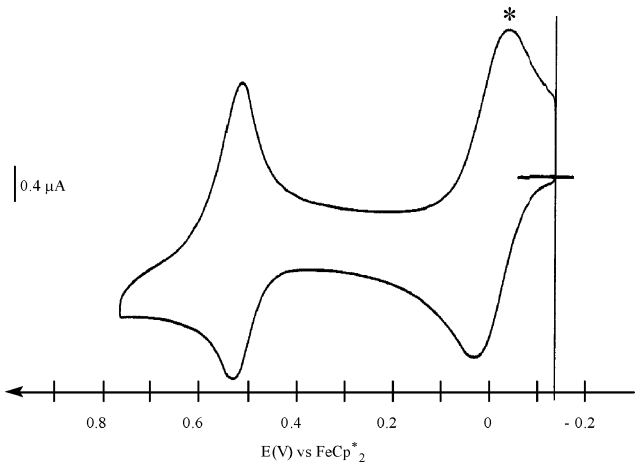


Fig. 2 Cyclic voltammetry of the ferrocenyl dendronized polymer **10** using decamethylferrocene as the internal reference (right wave). $E_{1/2}$ = 0.47 V. Solvent: CH_2Cl_2; temperature: 20 °C; supporting electrolyte: [*n*-Bu_4N][PF_6] 0.1 M; working and counter electrodes: Pt; reference electrode: Ag; scan rate: 0.400 V s^{-1}.

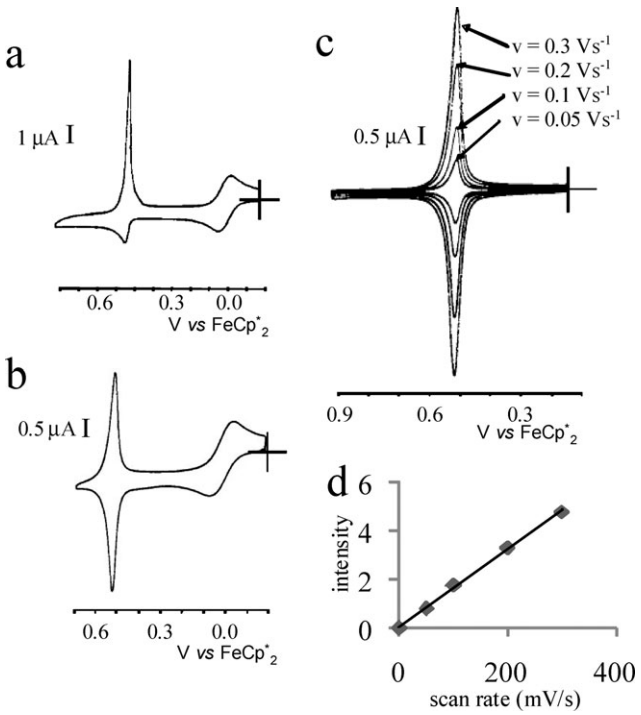


Fig. 3 Cyclic voltammograms of the ferrocenyl dendronized polymer **5** using decamethylferrocene as a reference (a and b): (a) in dichloromethane solution; (b) of an electrode modified with **5**; (c) of an electrode modified with **5** at various scan rates.

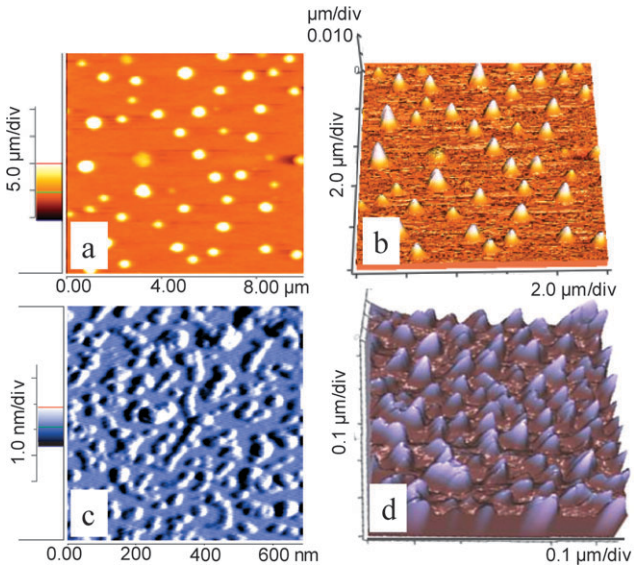


Fig. 4 AFM image of **5** and **10** on mica surface. (a) Topographic 2D AFM image of **5**. (b) Topographic 3D AFM image of **5**. (c) Amplitude mode 2D AFM image of **10**. (d) Topographic mode 3D AFM image of **10**.

AFM of the ferrocenyl dendronized polymers

Both ferrocenyl dendronized polymers **5** and **10** were examined by AFM on mica surfaces.[18] The largest dendronized polymer **5** gave pictures containing spots that were typically 5 nm high and 100 nm wide whereas pictures of **10** gave spots that were 22 nm wide and 2.5 nm high (Fig. 4). The spots of both dendronized polymers look globular as for classic polymers, *i.e.* like if polymers did not aggregate among one another. It does not appear that the dendronized polymer **10** agglomerates in its condensed state on the mica surface, because the width of 22 nm is close to the height measured by DOSY ^{1}H NMR and DLS (in deuterated chloroform and dichloromethane solution, respectively). On the other hand, the size of the spots obtained for **10** corresponds to clusters of aggregated dendronized polymers. One could observe by AFM that elongated shapes were not found, as expected with dendronized polymers in which the dendrons are not bulky. Elongated dendrimers are observed by AFM when dendrons of several generations are constructed, whereas no dendritic construction was elaborated in the present study. At some places in **10**, however, it can be seen that several polymeric units seem to stick together to form a chain fragment.

Concluding remarks

Two closely related routes to ferrocenyl dendronized polymers were conducted *via* AIBN-initiated radical polymerization of

functionalized styrenyl dendrons in this work: a direct polymerization of a triferrocenyl dendron and a ferrocenylation of a dendronized polymer using "click" chemistry.

The first route yielded a larger dendronized polymer than the former. A possible explanation is that the chlorine atoms located on the tris(chloromethylsilyl) dendrons could be responsible for radical reactions terminating the chains, thus shortening the polymer. The sizes and shapes of both materials have been analyzed using a variety of physico-chemical techniques.

The polydispersities (from SEC) were found to be larger for the directly polymerized ferrocenyl dendron (PDI = 1.9) than for the ferrocenylized dendronic polymer (PDI = 1.2), which is presumably due to their size difference.

DLS was an excellent technique to evaluate the size of these dendronized polymers (diameter: 28 nm for **5** *vs.* 18.5 nm for **10**), confirmed by DOSY ^{1}H NMR in the case of the smaller dendronized polymer **10**), whereas AFM shows that they are rather globular, *i.e.* the dendrons are not large enough to cause a sufficient rigidity of the materials.

AFM also shows the flattening of these materials on a mica surface in the condensed state[18] (height: 5 nm for **5** and 2.5 nm for **10**). The diameter found is not significantly different for **10** (22.5 nm) from that determined by DLS (18.5 nm), suggesting that the dendronic polymeric units of **10** do not aggregate on mica, whereas they do with the larger dendronized polymer **5** (100 nm width spots).

Both ferrocenyl dendronized polymers show a reversible ferrocene oxidation wave (which indicates that the ferrocenyl units are located at the periphery of the dendronized polymers)[19] and form stable derivatized Pt electrodes. The Bard–Anson equation can be used for **10** to determine the number of ferrocenyl groups (153) given the absence of adsorption in dichloromethane, but not for **5** due to adsorption.

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