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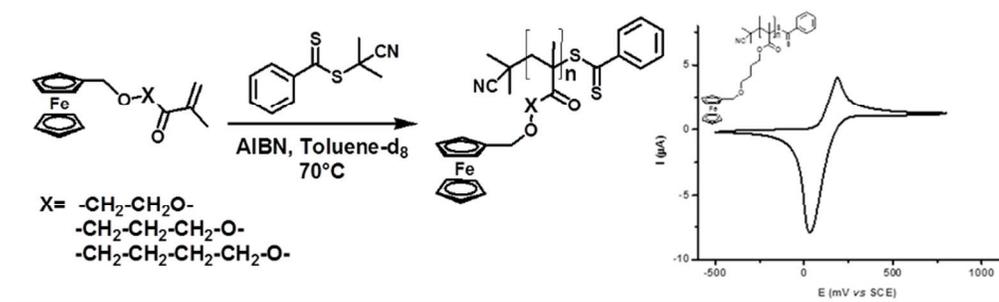


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A series of new alkoxy-ferrocene methacrylates was polymerized by the RAFT process leading to redox polymers with low T_g values.

80x24mm (300 x 300 DPI)



RAFT-synthesized polymers based on new ferrocenyl methacrylates and electrochemical properties

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Herein are reported the synthesis and the full characterization of three new ferrocenyl monomers, namely 2-(ferrocenylmethoxy)ethyl methacrylate (FMOEMA), 3-(ferrocenylmethoxy)propyl methacrylate (FMOPMA) and 4-(ferrocenylmethoxy)butyl methacrylate (FMOBMA), synthesized from ferrocenemethanol. Homopolymers were prepared by reversible addition-fragmentation chain transfer (RAFT) polymerization in toluene at 70°C using 2-cyanoprop-2-yl dithiobenzoate (CPDB) as chain transfer agent. Polymerization kinetics were compared to those of the well-known 1-ferrocenylmethyl methacrylate (FMMA). The ferrocenyl containing monomers with alkoxy linkers were found to be as reactive as FMMA in RAFT polymerization. Polymers with controlled molar masses with dispersities lower than 1.5 were obtained. The chemical structure of monomers and polymers were fully characterized by NMR and size exclusion chromatography. Glass transition temperatures of these methacrylic polymers ranged from 36°C to 2°C controlling the length of the alkoxy linker between the ferrocene unit and the backbone. The electrochemical properties of the monomers and the homopolymers were demonstrated using cyclic voltammetry.

Introduction

The incorporation of metallic redox centers into macromolecules has led to materials that combine the catalytic, magnetic, and electronic properties of metals with the desirable mechanical and processing properties of polymers. The research interest in this area has increased over the last three decades, affording the so-called class of organometallic polymers which have been used as active materials for a variety of applications such as sensing, catalysis and/or media storage.¹⁻⁴ Recent advances in polymerization techniques have provided ample new opportunities to prepare polymers with tunable chemistry and composition, associated with predetermined molar masses and low dispersity values (D_M). Furthermore, well-defined polymers with distinct microstructures including gradient, graft, and block copolymers are easy and readily prepared.^{5,6,7}

Among the main applications, there is a great demand on the elaboration of smart surfaces or coatings for a wide range of applications from material science to biological and environmental concerns. For instance, biofilms could easily grow on medical equipments, biosensors, food manufacturing,

water cooling systems or on marine submerged structures. Indeed, the accumulation of microorganisms (bacteria) and macroorganisms (algae, invertebrates) on surfaces causes adverse effects such as the biocontamination of medical equipments or the increase of the fuel consumption for ships. Several solutions are currently developed to prevent biofilm formation onto surfaces.^{8,9} For instance, although not widely reported, electrochemical polymerization or electrodeposition of polymers can be used as alternatives for making smart surfaces.¹⁰ In addition, the use of ferrocene units was reported to considerably reduce fouling on an electrode surface under electrical potential.^{11,12}

As the ferrocene oxidation/reduction cycles could switch the surface wettability from hydrophobic to hydrophilic surfaces,^{13,14} we turned our attention to the use of ferrocenyl-based polymers to prevent the adhesion of bacteria on surfaces by applying a potential. Vinylferrocene and acrylic ferrocene are known since decades and useful applications in the recent past have shown that homopolymers and block copolymers could be prepared in a controlled manner via anionic polymerization¹⁵⁻¹⁹, ring-opening metathesis polymerization (ROMP)^{20,21} and reversible deactivation radical polymerizations²² including atom transfer radical polymerization (ATRP)^{14,23} and reversible addition-fragmentation chain transfer polymerization (RAFT).^{19,24}

Herfurth et al. successfully polymerized alkyl-ferrocenyl methacrylic monomers in solution by conventional radical polymerization as well as by the RAFT process.²⁵ The authors demonstrate for the first time that the ferrocene moiety

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compatible with the sulfur functionalities typically used in the RAFT process.

Herein, we report the synthesis of a series of new ferrocene-containing methacrylates and their controlled homopolymerization by the RAFT process. Different alkoxy linkers were placed between the ferrocene unit and the methacrylic group, hoping that these linkers can alter significantly the glass transition temperature of the resulting polymers in reference to the well-known poly(1-ferrocenylmethyl methacrylate) (pFMMA). Kinetics studies were carried out to characterize the controlled behaviour of the polymerization process. The thermal properties of polymers were studied using differential scanning calorimetry (DSC). The electrochemical properties of these homopolymers were investigated and will be discussed.

Experimental section

Materials

Anhydrous tetrahydrofuran (THF), basic alumina, and crown ether were used as received from Acros. Cyclohexane and ethyl acetate were used as received from VWR. Methacryloyl chloride, 2-cyanoprop-2-yl-dithiobenzoate (CPDB), tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆), anhydrous dichloromethane (DCM), allyl bromide, ferrocenecarboxaldehyde, sodium hydride (NaH 60% dispersion in mineral oil), (2-bromoethoxy)-*tert*-butyldimethylsilane, ammonium chloride, magnesium sulfate (MgSO₄), hexane, toluene, tetrabutylammonium fluoride solution (TBAF, 1M in THF), hydrogen peroxide (H₂O₂), sodium hydroxide (NaOH), ethyl acetate, triethylamine (Et₃N), methacryloyl chloride, potassium carbonate (K₂CO₃), toluene-d₈, *tert*-butyl(4-iodobutoxy)dimethylsilane, and borane (BH₃, THF complex solution, 1 M) were used as received from Aldrich. 2,2-Azobis(isobutyronitrile) (AIBN, Aldrich) was recrystallized from methanol prior to use.

Characterizations

¹H- (400 MHz) and ¹³C- (100.6 MHz) NMR spectra were recorded on a Bruker Advance NMR spectrometer. Mass spectrometry was conducted on a Waters Micromass Q-ToF mass spectrometer, and the ionization source was a positive ion electrospray. The number average-molar mass (*M*_n) and dispersity (*D*_M) of polymers were determined by triple detection size exclusion chromatography (TD-SEC). Analyses were performed on a Viscotek apparatus, composed of a GPC Max (comprising a degasser, a pump and an autosampler) with a TDA-302 (refractive index detector, right and low angle light scattering detector at 670 nm and viscometer) and a UV detector ($\lambda = 303$ nm). The following columns were used: a Viscotek HHR-H precolumn and two Viscotek ViscoGel GMHHR-H columns. THF was used as the eluent with a flow rate of 1 mL.min⁻¹ at 30°C. For each precipitated polymer, the refractive index increment (*dn/dc*) was determined using the OmniSec software, from a solution of known concentration (ca. 10 mg.mL⁻¹) filtered through a 0.2 μ m PTFE filter.

Differential scanning calorimetry (DSC)

The glass transition temperatures (T_g) of the homopolymers were measured with a Q100 differential scanning calorimeter (TA Instruments). The samples were cooled down to -100°C and then scanned at a heating rate of 20°C.min⁻¹ from -100 to 165°C. The T_g values were determined as the midpoint between the onset and the end of a step transition on the second heating run using the TA Instruments Universal Analysis 2000 software.

Cyclic voltammetry (CV)

Cyclic voltammograms were acquired using a BioLogic VSP300 potentiostat and the EC-Lab® software. A three-electrode system based on a platinum working electrode (diameter 1.6 mm), a platinum counter electrode and a saturated calomel reference electrode were used. *n*-Bu₄NPF₆ was used as the supporting electrolyte (0.1 M). Electrochemical reduction/oxidation potential values vs SCE were determined from the cyclic voltammograms at a concentration of 1.10⁻³ M for monomers and 1.10⁻⁴ M for homopolymers with a scan rate of 10 mV.s⁻¹.

Monomers synthesis

Ferrocenemethanol (FcMeOH, 1).

Ferrocenemethanol **1** was prepared by reduction of a commercially available ferrocenylcarboxaldehyde following a published synthetic procedure.^{17,26} Mp: 78-80°C. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 1.60 (s, 1H, OH); 4.19 (s, 7H, C₅H₅+C₅H₄); 4.25 (s, 2H, C₅H₄); 4.31 (s, 2H, -CH₂OH). ¹³C-NMR (100.6 MHz, CDCl₃) δ (ppm): 60.9 (-CH₂OH); 68.1 (C₅H₄); 68.5 (C₅H₅+C₅H₄); 88.7 (C₅H₄).

Ferrocenyl methylmethacrylate (FMMA, 2).

Under an argon atmosphere, 1.80 g of compound **1** (8.33 mmol, 1 eq.) and 15 mL of Et₃N (104.70 mmol, 12.6 eq.) were dissolved in 100 mL of anhydrous DCM. To the ice-cooled solution (0°C) 1.80 mL of methacryloyl chloride (17.65 mmol, 2.12 eq.) were added dropwise over a period of 30 min. The reaction was kept at 0°C for 2 h then warmed up to room temperature overnight. The organic phase was washed twice with 150 mL of a saturated K₂CO₃ aqueous solution then with water. The combined organic phases were dried over MgSO₄, filtered and the solvent was removed under reduced pressure. The obtained residue was flashed over a pad of basic alumina affording the titled compound **2** as a yellow solid (2.15 g, 87% yield). Mp: 74-75°C. ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 1.94 (s, 3H, CH₃); 4.17 (m, 7H, Fc); 4.28 (s, 2H, Fc); 4.96 (s, 2H, CH₂-Fc); 5.54 (s, 1H, =CH₂); 6.10 (s, 1H, =CH₂).²³

tert-butyl(2-(ferrocenylmethoxy)ethoxy) dimethylsilane (FMOETBDMS, 3)

To a suspension of NaH (0.31 g, 7.87 mmol, 1.7 eq.) in dry THF (100 mL) was added a solution of crown ether (380 mg, 0.144 mmol) and FcMeOH (**1**) (1 g, 4.62 mmol, 1 eq.) in dry THF (50 mL). The reaction was stirred at room temperature for 2 h under an inert atmosphere. (2-bromoethoxy)-*tert*-butyldimethylsilane (1.7 mL, 7.87 mmol, 1.7 eq.) was added

dropwise. The resulting suspension was stirred overnight at room temperature. The solvent was partially removed under reduced pressure, and saturated ammonium chloride solution was added. The aqueous phase was extracted with ethyl acetate (3*100 mL) and the combined organic extracts were dried (MgSO₄) and concentrated under vacuum. The crude product was purified by flash column chromatography over SiO₂ using cyclohexane/ethyl acetate as eluent (8/2 V:V) leading compound **3** as an orange oil (1 g, 58 % yield). ¹H-NMR (400 MHz, CDCl₃) δ(ppm): 0.07 (s, 6H, -OSi(CH₃)₂); 0.91 (s, 9H, -OSi-C(CH₃)₃); 3.39 (t, 2H, -CH₂-OSi-C(CH₃)₃, ³J = 6.4 Hz); 3.89 (t, 2H, Fc-CH₂-O-CH₂-CH₂-OSi(-C(CH₃)₃), ³J = 6.4 Hz); 4.13 (m, 7H, C₅H₅ + C₅H₄); 4.20 (s, 2H, C₅H₄); 4.43 (s, 2H, -CH₂-Fc).

2-(ferrocenylmethoxy)ethanol (FMOE, 4).

To a solution of compound **3** (1 g, 2.67 mmol, 1 eq.) in dry THF was carefully added TBAF at 0°C under a N₂ atmosphere (1 M in THF, 2.93 mmol, 2.93 mL), then warmed up to room temperature for 2 h. The solvent was partially removed in vacuum. The combined organic extracts were washed with water then dried over MgSO₄ and concentrated under reduced pressure. The product was purified by flash column chromatography over SiO₂ using cyclohexane/ethyl acetate (7/3 V:V) affording compound **4** as an orange solid (0.60 g, 86% yield). Mp: 41°C. ¹H-NMR (400 MHz, CDCl₃) δ(ppm): 1.97 (s, 1H, OH); 3.53 (t, 2H, Fc-CH₂O-CH₂-, ³J = 4.4 Hz); 3.68 (q, 2H, -CH₂-OH, ³J=4.8 Hz); 4.14 (m, 7H, C₅H₅+C₅H₄); 4.24 (s, 2H, C₅H₄); 4.32 (s, 2H, Fc-CH₂-O-). ¹³C-NMR (100.6 MHz, CDCl₃) δ(ppm): 61.8 (Fc-CH₂O-CH₂-CH₂O-); 68.6 (C₅H₅); 69.5 (C₅H₄); 70.8 (C₅H₄); 83.1 (C₅H₄).

2-(ferrocenylmethoxy)ethyl methacrylate (FMOEMA, 5).

This compound was prepared like compound **2** from compound **4** (0.36 g, 1.38 mmol, 1 eq.), anhydrous DCM, Et₃N (2.34 mL, 17.35 mmol, 12.6 eq.), methacryloyl chloride (0.29 mL, 2.93 mmol, 2.12 eq.) following a similar procedure used for FMMA (**2**) giving compound **5** as an orange oil (0.40 g, 89 % yield). ¹H-NMR (400 MHz, CDCl₃) δ(ppm): 1.87 (s, 3H, CH₃); 3.66 (t, 2H, Fc-CH₂O-CH₂-CH₂-, ³J = 4.8 Hz); 4.02 (m, 7H, C₅H₅+C₅H₄); 4.11 (s, 2H, C₅H₄); 4.13 (s, 2H, -OCH₂-Fc); 4.18 (t, 2H, Fc-CH₂O-CH₂-CH₂-O-C=O, ³J = 5.2 Hz); 5.29 (s, 1H); 6.14 (s, 1H). ¹³C-NMR (100.6 MHz, CDCl₃) δ(ppm): 18.2 (-CH₃); 63.8 (-CH₂-O-CH₂-CH₂-O-); 67.3 (C₅H₅); 68.4 (C₅H₄); 69.3 (C₅H₄); 83.0 (C₅H₄); 125.7 (-CH₂=C-); 136.0 (-C=CH₂-); 167.3 (-C=O). MS (EI), m/z calcd for C₁₇H₂₀FeO₃ 328.08; found 328 [M]⁺.

1-(allyloxymethyl)ferrocene (AMF, 6).

This compound was prepared from FcMeOH (**1**) (1 g, 4.63 mmol, 1 eq.) with anhydrous THF, allyl bromide and NaH (200 mg, 50.90 mmol, 1.1 eq.) following a similar procedure used for compound **6** to give an orange oil (1.09 g, 92 % yield). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 4.00 (d, 2H, -OCH₂-CH-, ³J = 4.8 Hz); 4.15 (s, 7H, C₅H₅+C₅H₄); 4.26 (s, 2H, C₅H₄); 4.3 (s, 2H, -OCH₂-Fc); 5.19 (d, 1H, CH₂=CH-, ²J = 10.4 Hz trans); 5.29 (d, 1H, CH₂=CH-, ²J = 17.2 Hz cis); 5.92 (m, 1H, -CH=CH₂). ¹³C-NMR (100.6 MHz, CDCl₃) δ (ppm): 68.2 (Fc-CH₂O-CH₂-); 68.3 (C₅H₅); 69.3 (C₅H₄); 70.6 (C₅H₄); 83.3 (C₅H₄); 116.7 (CH₂=CH-); 134.8 (-CH=CH₂).

3-(ferrocenylmethoxy)propanol (FMOP-1-ol, 7).

To a solution of compound **6** (1 g, 3.90 mmol, 1 eq.) in dry THF (35 mL) was added dropwise 4 mL of BH₃ (1M solution in THF) at 0°C over a period of 1 h. After 1 h at room temperature, ice pellets were added to hydrolyse the excess of borane. The reaction mixture was cooled with an ice-bath before the addition of 0.9 mL of NaOH (3 M) followed by 0.5 mL of 30 % H₂O₂, over a period of 1 h. After stirring 1 h at room temperature, the combined organic phases were dried over MgSO₄. The crude product was purified by column chromatography over SiO₂ with cyclohexane/ethyl acetate (8/2 V:V) affording compound **7** (0.53 g, 47 % yield) as orange solids. Mp: 32°C, ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 1.81 (q, 2H, -OCH₂-CH₂-CH₂OH, ³J = 5.6 Hz); 2.41 (s, 1H, OH); 3.63 (t, 2H, OCH₂-CH₂-, ³J = 6 Hz); 3.74 (q, 2H, -CH₂OH, ³J = 4.8 Hz); 4.13 (m, 7H, C₅H₅+C₅H₄); 4.21 (s, 2H, C₅H₄); 4.28 (s, 2H, Fc-CH₂-O-). ¹³C-NMR (100.6 MHz, CDCl₃) δ (ppm): 31.9 (HO-CH₂-CH₂-CH₂O-CH₂-Fc); 61.8 (-CH₂-CH₂-OH); 68.4 (Fc-CH₂-O-CH₂-); 69.0 (C₅H₅); 69.1 (C₅H₄); 69.3 (C₅H₄); 83.2 (C₅H₄). MS (EI), m/z calcd for C₁₄H₁₈FeO₂ 274.07, found 274 [M]⁺.

3-(ferrocenylmethoxy)propyl methacrylate (FMOPMA, 8).

The compound **8** was obtained as an orange oil after purification from the reaction of compound **7** (0.35 g, 1 eq.), Et₃N (1.63 g, 12.6 eq.), and methacryloyl chloride (0.28 g, 2.12 eq.) in dry DCM (15 mL) (0.38 g, 88 % yield). ¹H-NMR (400 MHz, CDCl₃) δ (ppm): 1.92 (m, 5H, -OCH₂-CH₂-CH₂O- and -CH₃); 3.51 (t, 2H, ³J = 6.4 Hz, Fc-CH₂O-CH₂-); 4.12 (m, 7H, C₅H₅+C₅H₄); 4.21 (m, 4H, -OCH₂-Fc and -OCH₂-CH₂-); 4.26 (s, 2H, C₅H₄); 5.53 (s, 1H); 6.07 (s, 1H). ¹³C-NMR (100.6 MHz, CDCl₃) δ (ppm): 18.2 (-CH₃); 28.9 (-OCH₂-CH₂-CH₂-O-); 61.7 (-CH₂-O-C=O); 66.1 (Fc-CH₂O-CH₂-); 68.3 (C₅H₅); 69.0 (C₅H₄); 69.2 (C₅H₄); 83.4 (C₅H₄); 125.1 (CH₂=CH-); 136.2 (-C=CH₂); 167.1 (-C=O). MS (EI), m/z calcd for C₁₈H₂₂FeO₃ 342.09; found 342 [M]⁺.

tert-butyl(4-(ferrocenylmethoxy)butoxy)dimethylsilane (FMOBTBMS, 9)

The compound **9** was prepared from compound **1** (6 g, 1 eq.), tert-butyl(4-iodobutoxy)dimethylsilane (9.6 g, 1.1 eq.), NaH (60% in mineral oil) (1.22 g, 1.1 eq.), crown ether (70 mg, 0.01 eq.) in dry THF (250 mL) following a similar procedure used for compound **3**, affording **9** as an orange oil (3.90 g, 35 % yield). ¹H-NMR (400 MHz, CDCl₃) δ(ppm): 0.06 (s, 6H, -OSi(CH₃)₂); 0.91 (s, 9H, -OSi-C(CH₃)₃); 1.59 (m, 4H, -CH₂-CH₂-CH₂-CH₂-); 3.44 (t, 2H, ³J = 6.4 Hz, -CH₂-OSi-); 3.62 (t, 2H, ³J = 6.4 Hz, Fc-CH₂O-CH₂-); 4.14 (m, 7H, C₅H₅+C₅H₄); 4.24 (s, 2H, C₅H₄); 4.27 (s, 2H, Fc-CH₂-O-).

4-(ferrocenyl methoxy)butan-1-ol (FMOB, 10).

This compound was prepared from compound **9** (3.9 g, 1 eq.) and TBAF (21 mL, 2.1 eq.) solution in dry THF following a similar procedure used for compound **4** leading to **10** as an orange oil (1.80 g, 65 % yield). ¹H-NMR (400 MHz, CDCl₃) δ(ppm): 1.62 (m, 4H, -CH₂-CH₂-); 2.03 (s, 1H, OH); 3.45 (t, 2H, ³J = 5.6 Hz, Fc-CH₂O-CH₂-); 3.58 (t, 2H, ³J = 5.6 Hz, -CH₂OH); 4.13 (m, 7H, C₅H₅+ C₅H₄); 4.21 (s, 2H, C₅H₄); 4.27 (s, 2H, C₅H₄). ¹³C-NMR (100.6 MHz, CDCl₃) δ(ppm): 26.8 (-CH₂-CH₂-CH₂-OH); 30.7 (-CH₂-CH₂-OH); 62.5 (-CH₂-OH); 68.5 (Fc-CH₂O-CH₂-, 2C); 69.1

(C₅H₅); 69.4 (C₅H₄, 1C); 69.9 (C₅H₄, 1C); 83.2 (C₅H₄). MS (EI), m/z calcd for C₁₅H₂₀FeO₂ 288.08; found 288 [M]⁺.

4-(ferrocenylmethoxy)butyl methacrylate (FMOBMA, **11**)

This compound was prepared from compound **10** (1.7 g, 1 eq.), Et₃N (7.5 g, 12.60 eq.), and methacryloyl chloride (1.3 g, 2.12 eq.) in dry DCM (100 mL) following a similar procedure used for compound **2** giving compound **11** as an orange oil (1.80 g, 86 % yield). ¹H-NMR (400 MHz, CDCl₃) δ(ppm): 1.62 (q, 2H, -O-CH₂-CH₂-CH₂-CH₂-O-, ³J = 7.2 Hz); 1.67 (q, 2H, -O-CH₂-CH₂-CH₂-CH₂-O-, J = 6.4 Hz); 1.91 (s, 3H, -CH₃); 3.42 (t, 2H, -O-CH₂-C=O, ³J = 6.4 Hz); 4.10 (m, 9H, C₅H₅+C₅H₄); 4.20 (s, 2H, Fc-CH₂-O-); 4.24 (s, 2H, -CH₂-OC=O); 5.52 (s, 1H); 6.07 (s, 1H). ¹³C-NMR (100.6 MHz, CDCl₃) δ(ppm): 18.1 (-CH₃); 25.3 (Fc-CH₂-O-CH₂-CH₂-); 26.1 (-CH₂-CH₂-O-C=O); 64.3 (-CH₂-O-CO); 68.3 (Fc-CH₂-O-CH₂-); 68.9 (C₅H₅); 69.1 (C₅H₄); 69.2 (C₅H₄); 83.4 (C₅H₄); 125.1 (CH₂=C-); 136.2 (-C=CH₂); 167.2 (-C=O). MS (EI), m/z calcd for C₁₉H₂₄FeO₃ 356.10; found 356 [M]⁺.

Polymers synthesis

In situ ¹H-NMR RAFT polymerizations were carried out in toluene-d₈ at 70°C using CPDB as chain transfer agent (CTA) and AIBN as initiator at a molar ratio [CPDB]/[AIBN] = 5. The concentration of CPDB was adjusted to the targeted number-average molar mass (M_n^{tg}), taking into account a full conversion of monomers and the theoretical number-average molar mass M_n^{th} , calculated with Eq. 1:

$$M_n^{th} = \frac{[M]_0}{[CTA]_0 + df[A]_0(1 - e^{-k_d t})} \times M_{mon} \times conv. + M_{CTA} \quad (1)$$

where [M]₀ and [CTA]₀ are the initial concentrations of monomer and CTA respectively, M_{mon} and M_{CTA} the molar mass of monomer and CTA respectively, *conv.* the monomer conversion, *d* the average number of chains that are formed in a termination reaction, *f* the initiator efficiency, *k_d* the constant of initiator decomposition, *t* the half-live of the initiator and [A]₀ the initiator concentration. Considering that each polymer chain contains one CTA, a simplified version of Eq. 1 was used:

$$M_n^{th} = \frac{[M]_0}{[CTA]_0} * M_{mon} * conv. + M_{CTA} \quad (2)$$

In a typical experiment, 160 mg of monomer **11** (FMOBMA) (0.45 mmol), 3.62 mg of CPDB (0.0164 mmol) and 0.54 mg of AIBN (0.00328 mmol) were dissolved in 0.3 mL of dry toluene-d₈ in a high pressure/vacuum Wilmad NMR tube, then degassed by three cycles of freeze-pump-thaw. The polymerization occurred into the NMR apparatus, heated at 70°C during 15 h, and followed by ¹H-NMR analysis at regular times. After cooling down to room temperature, the reaction mixture was precipitated in hexane. The obtained precipitate was redissolved in toluene and reprecipitated into hexane twice. The obtained purified polymer was vacuum-dried for 24 h (30 mg, 19% yield).

Polymers from monomers **2**, **5**, and **8** were prepared following a similar procedure as for monomer **11** with yield values after precipitation of 20 %, 20 % and 23 %, respectively.

The conversion of FMOBMA **11** is determined from *in situ* ¹H-NMR analysis of the reaction mixture by comparing the integration area of peaks at 5.0 (one vinylic protons of monomer) and the peak between 3.6 at 3.0 ppm corresponding to the methylene protons (-C(O)-O-CH₂-) of both monomer and polymer. The conversion of FMOBMA **11** and M_n^{NMR} were determined using Eq. 3 and Eq. 4, respectively:

$$conv. (\%) = \frac{I_{pol}}{I_{mon+pol}} \times 100 = \frac{I_{2H,3.6-3.0\text{ ppm}}/2 - I_{1H,5.0\text{ ppm}}}{I_{2H,3.6-3.0\text{ ppm}}/2} \times 100 \quad (3)$$

$$M_n^{NMR} = X_n^{NMR} * M_{mon} + M_{CTA} \quad (4)$$

where X_n^{NMR} is the number of repeating unit, determined from ¹H-NMR spectra by integrating the two aromatic protons of CPDB (in ortho position) that are shifted from 7.9 to 8.1 ppm when inserted at the end of the polymer chains (Eq. 5).

$$X_n^{NMR} = \frac{I_{pol}}{I_{CTA}} = \frac{I_{2H,3.6-3.0\text{ ppm}}/2 - I_{1H,5.0\text{ ppm}}}{I_{2H,8.1\text{ ppm}}/2} \quad (5)$$

The conversion, M_n^{NMR} , and X_n^{NMR} of all the monomers **2**, **5**, and **8** were determined using similar equations as Eq. 3, 4, and 5.

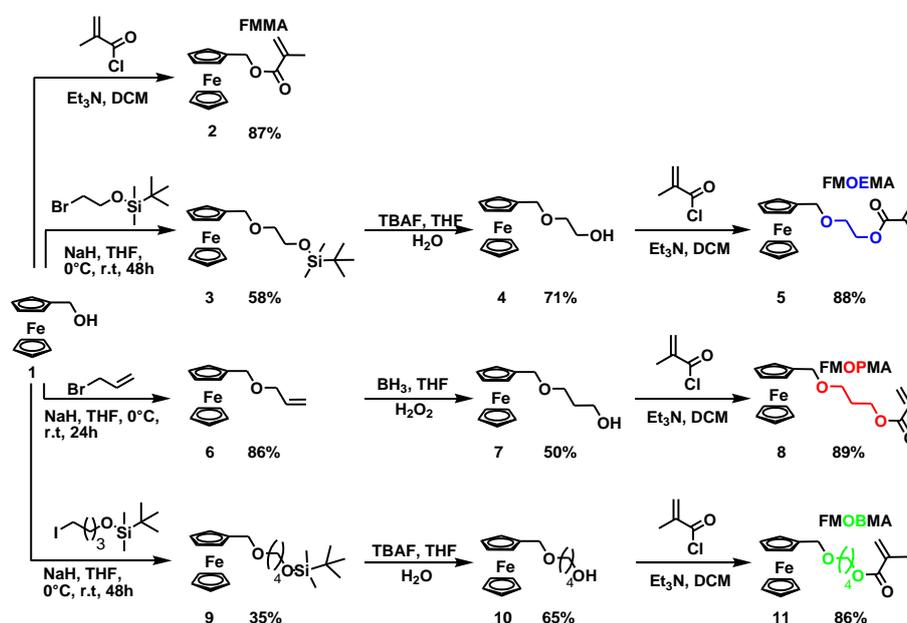
Results and discussion

Synthesis of monomers

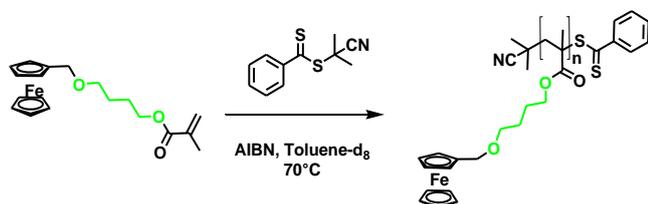
The synthesis of monomers **2**, **5**, **8** and **11** is outlined in Scheme 1. All monomers were readily obtained from ferrocenemethanol **1**. Subsequent reaction of **1** with methacryloyl chloride in dry DCM in presence of Et₃N affords FMMA **2** in 87 % yield. Monomer **5** was prepared in three steps from **1** as follows: compound **1** was first reacted with ethyl (7-bromoethoxy-*tert*-butyl)dimethylsilane in dry THF in the presence of NaH affording **3** in 58 % yield, followed by deprotection with TBAF in dry THF at room temperature (**4**, 71 %) and subsequent condensation with methacryloyl chloride to give monomer **5** in 88 % yield. Compound **1** was further reacted with bromoallyl in anhydrous THF in the presence of NaH affording the intermediate **6** in 92 % yield. Hydroboration of the later with BH₃ in THF led to the alcohol **7** in 50 % yield, after column chromatography purification. Reaction between **7** and methacryloyl chloride in dry DCM in the presence of Et₃N led to monomer **8** in 89 % yield. The corresponding monomers structurally differ from each other by the length of the linker between the ferrocenyl moiety and the methacrylate end-group. FMOBMA **11** has the longest linker and FMOEMA **5** the shortest one.

RAFT polymerization of ferrocenyl methacrylate monomers

We wanted to explore the use of the RAFT process for the controlled radical polymerization of these new ferrocenyl monomers.



Scheme 1. Synthetic pathways for ferrocenyl-methacrylate monomers.



Scheme 2. Synthesis of p(FMOBMA) by the RAFT process.

The RAFT process is a reversible deactivation radical polymerization, which is arguably the most robust, tolerates the largest variety of monomers, and is less demanding in terms of experimental set-up, compared to other controlled polymerization processes. The key difference from a conventional free radical polymerization is the addition of a chain transfer agent (CTA) to control the polymerization.^{27,28,29}

Importantly, the reactivity of the CTA must be adjusted to the reactivity of the monomer to obtain a good control over the polymerization while maintaining an ideally unaltered rate of polymerization. Consequently, CTAs best suited for the polymerization of methacrylates bear different R and Z groups^{30,31} from CTAs used for the polymerization of acrylates.³² 2-Cyanoprop-2-yl-dithiobenzoate (CPDB) and 2,2-azobis(isobutyronitrile) were used as CTA and initiator, respectively (Scheme 2). The homopolymerizations were carried out in toluene-*d*₈ with a molar ratio [CPDB]/[AIBN] of 5/1 at 70°C.

To demonstrate that the RAFT polymerization of these ferrocenyl monomers follows a controlled process, kinetics were investigated. The polymerization conditions were kept constant for all monomers in order to compare the monomers reactivities. The targeted molar mass was 10 000 g.mol⁻¹. The disappearance of the vinyl protons from the methacrylate group, around 5.6 and 5.0 ppm, and the appearance of broad peaks assigned to the main chain around 2.0 ppm (-CH₂-) and 0.8-1.2 ppm (-CH₃) and to the -OCH₂- directly linked to the ferrocene group around 3.5 ppm except for FMMA (4.3 ppm) suggested the successful polymerization for all monomers (Figure 1).

The semilogarithmic plots are shown in Figure 2. Each polymerization showed a linear kinetic plot, indicating the control of the growth of the polymer chains with time, up to ca. 77 % of monomer conversion.

All ferrocenyl monomers including FMMA were found to be highly reactive in RAFT polymerization, leading to monomer conversion values up to at least 90 % (supporting information). These results were reported for monomers with longer spacer groups ((4-Ferrocenylbutyl methacrylate) with 4 atoms between the polymerizable and the ferrocene moiety) which polymerized under standard conditions (AIBN, 60°C) using dodecyl-4-cyanovaleric acid trithiocarbonate (DoCVAT) as CTA.²⁵ Figure 2 shows that the length of the alkoxy linker affects the polymerization rate of monomers.

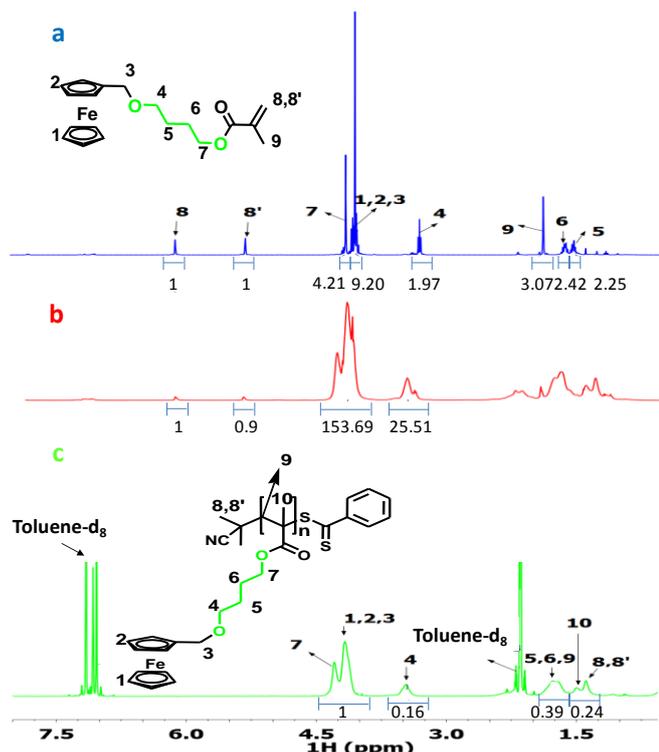


Figure 1. $^1\text{H-NMR}$ spectra of (a) FMOBMA **11**, (b) the polymerization media after 15h of reaction in toluene- d_8 at 70°C , and (c) the purified pFMOBMA homopolymer.

The global polymerization constant value (k_p) is ranging from 7 to $13 \text{ mol}^{-1/2} \cdot \text{L}^{1/2} \cdot \text{s}^{-1}$ (Table 1).

A linear molar mass growth with monomer conversion and low dispersities (less than 1.4) were obtained for all the polymers (Figure 3, Table 2, and supporting information), indicating the control of the RAFT polymerization of FMMA **2**, and the three new ferrocenyl monomers FMOEMA **5**, FMOPMA **8**, and FMOBMA **11**.

Thermal Properties

The thermal properties of the homopolymers were characterized by DSC. Thermal behaviours of these homopolymers exhibited a strong relationship with the alkoxy linkers. As shown in supporting information, pFMOBMA, which

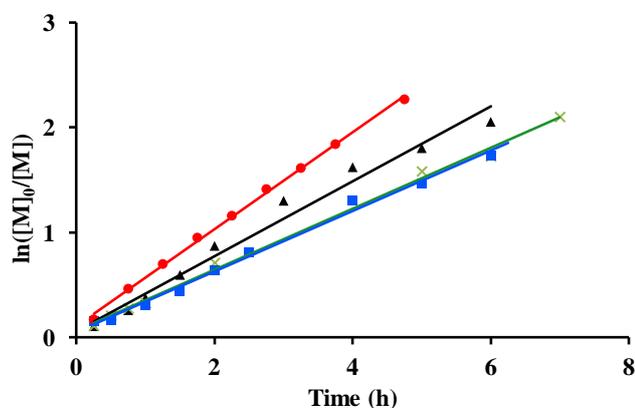


Figure 2. $\ln([M]_0/[M])$ vs time during the RAFT polymerization of FMMA (\blacktriangle , **2**), FMOEMA (\blacksquare , **5**), FMOPMA (\bullet , **8**), and FMOBMA (\times , **11**). $[M]=1.5 \text{ mol} \cdot \text{L}^{-1}$, CTA/initiator=5/1.

Table 1. The global polymerization constant k_p of monomers

Polymers	k_p ($10^{-4} \text{ mol}^{-1/2} \cdot \text{L}^{1/2} \cdot \text{s}^{-1}$)
pFMMA	13
pFMOEMA	8
pFMOPMA	13
pFMOBMA	7

Table 2. Characteristics of ferrocenyl methacrylic homopolymers prepared by the RAFT process

Polymers	conv. ^a (%)	M_n ^b ($\text{g} \cdot \text{mol}^{-1}$)	M_n^{NMR} ^c ($\text{g} \cdot \text{mol}^{-1}$)	$M_n^{\text{TD-SEC}}$ ^d ($\text{g} \cdot \text{mol}^{-1}$)	\bar{D}_M ^d
pFMMA	97	9 600	15 000	20 400	1.3
pFMOEMA	99	9 900	14 400	19 400	1.2
pFMOPMA ^e	99	9 900	18 000	13 800	1.2
pFMOBMA	89	8 900	16 800	15 700	1.4

^a calculated from Eq. 3, ^b calculated from Eq. 2, ^c calculated from Eq. 4, ^d determined by TD-SEC, ^e additional peaks corresponding to some uncontrolled chains observed on TD-SEC chromatogram.

contains the longest alkoxy linker, showed the lowest T_g around 2°C , whereas pFMOPMA and pFMOEMA with shorter alkoxy linkers exhibited T_g at 6 and 36°C , respectively. The T_g of pFMMA, which contains no alkoxy linker was at 106°C . Clearly, the longer the linker between the bulky ferrocene unit and the polymer backbone, the lower the T_g of the polymers. This is in agreement with variations encountered for methacrylate polymers having alkylester side chains.³³ Compared to alkyl-ferrocene methacrylic polymers with butyl linker, namely the poly(4-Ferrocenylbutyl methacrylate), which exhibited T_g at 40°C ,²⁵ pFMOPMA and pFMOBMA exhibited expected and noticeable lower T_g s due to the alkoxy group. In addition, pFMOBMA and pFMOPMA exhibited a lower T_g than the poly(4-(acryloyloxy)butyl ferrocenecarboxylate)²³ (T_g at 20°C). The ether linkage is known to strongly decrease the T_g of ferrocenyl homopolymers when localized in the main chain such as poly(ferrocenyl glycidyl ether) homopolymers with a T_g value of -8°C .³⁴ The presence of the ether linkage in lateral groups decreases the T_g of methacrylic homopolymers to a level close to acrylic polymers and suitable for forming coatings with good film properties.

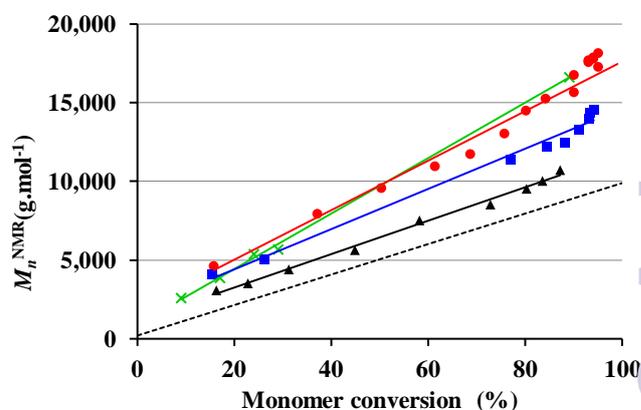


Figure 3. Evolution of M_n^{NMR} vs monomer conversion during the RAFT polymerization of FMMA (\blacktriangle , **2**), FMOEMA (\blacksquare , **5**), FMOPMA (\bullet , **8**), and FMOBMA (\times , **11**). $[M]=1.5 \text{ mol} \cdot \text{L}^{-1}$, CTA/initiator=5/1. $M_n^{\text{th}}=10\,000 \text{ g} \cdot \text{mol}^{-1}$. Solid lines are linear fits to the data. The dashed line is corresponding to the theoretical line.



Electrochemical Properties

Cyclic voltammetry (CV) of the ferrocenyl methacrylate monomers and of their corresponding homopolymers was carried out in DCM and *n*-Bu₄NPF₆ as supporting electrolyte. As expected for all monomers a reversible redox behaviour attributed to the ferrocene/ferricenium (Fc/Fc⁺) couple appears within the range of 448–525 mV vs SCE (Figure 4, Table 3 and supporting information).

All *E*_{1/2} redox potentials of monomers were slightly higher than the corresponding value of ferrocene (440 mV vs SCE) in the same conditions of electrolyte and solvent (Table 3). It is in good agreement with the electron-withdrawing effect of the methacrylate group.³⁵ The direct link of the ferrocenyl group to the ester function of methacrylate in FMMA leads to a significant increase of *E*_{1/2}. The increase of the length of the alkoxy linker between the cyclopentadienyle ring and the methacrylate group leads to a negative shift of *E*_{1/2} potential in comparison with FMMA. This last result is in good correlation with a decrease of electron-withdrawing effect of the methacrylate group, coming back to the *E*_{1/2} potential of the ferrocene. As for monomers, cyclic voltammetry of homopolymers revealed a negative shift of *E*_{1/2} with the increase of the linker length between the cyclopentadienyle ring and the ester function.

For all homopolymers, the peak current ratios, *I*_{pa}/*I*_{pc} were less than one which indicates an adsorption of the oxidized species followed by cathodic desorption from the electrode surface (Figure 4 (down), Table 3 and supporting information).^{36,37}

The number of electrons transferred during the oxidation of the polymers (*n*_e) can be determined with the Bard-Anson electrochemical method³⁴ using the empirical Eq. 6 where *I*_d, *M*, and *C* are the CV wave intensities of the diffusion current, molar mass, and concentration of the monomer (*I*_{d,mon}, *M*_{mon}, *C*_{mon}) and polymer (*I*_{d,pol}, *M*_{pol}, *C*_{pol}), respectively:

$$n_e = \frac{\left(\frac{I_{d,pol}}{C_{pol}}\right)}{\left(\frac{I_{d,mon}}{C_{mon}}\right)} \left(\frac{M_{pol}}{M_{mon}}\right)^{0.275} \quad (6)$$

Table 3. Anodic and cathodic potentials for monomers and homopolymers recorded in *n*-Bu₄NPF₆/CH₂Cl₂ at 1.10⁻³ M and 1.10⁻⁴ M, respectively

	Monomer (mV vs SCE)			Homopolymer (mV vs SCE)		
	<i>E</i> _{pa}	<i>E</i> _{pc}	<i>E</i> _{1/2}	<i>E</i> _{pa}	<i>E</i> _{pc}	<i>E</i> _{1/2}
FMMA	593	456	525	576	327	452
FMOEMA	540	399	470	504	346	425
FMOPMA	523	396	460	485	361	423
FMOBMA	499	397	448	191	33	112

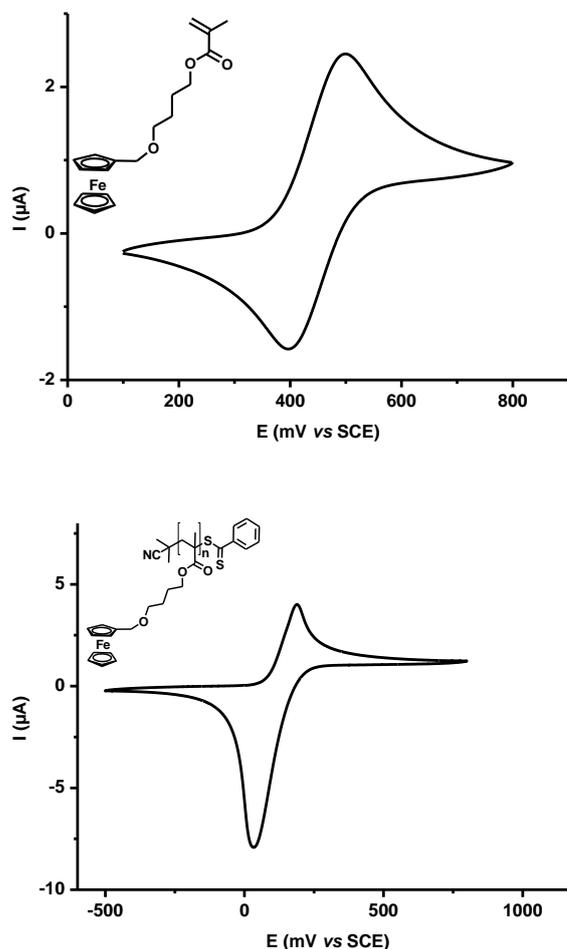


Figure 4. Cyclic voltammograms of (up) FMOBMA **11** at 1.10⁻³ M and (down) pFMOBMA at 1.10⁻⁴ M in 0.1M *n*-Bu₄NPF₆/CH₂Cl₂ in both cases. Scan rate: 10 mV/s, Pt working electrode, SCE reference.

Table 4. Comparison of the number of transferred electrons *n*_e and the polymerization degree *X*_n for the ferrocenyl homopolymers

Polymers	<i>I</i> _{d, mon} ^a (μA)	<i>I</i> _{d, pol} ^a (μA)	<i>n</i> _e ^b	<i>X</i> _n ^{TD-SEC c}
pFMMA	2.66	6.84	79.5	71.8
pFMOEMA	2.23	4.64	58.6	59.1
pFMOPMA	2.37	7.07	82.2	40.4
pFMOBMA	2.42	4.00	46.1	44.1

^a determined by cyclic voltammetry, ^b calculated with Eq. 6 and ^c determined by TD-SEC.

By assuming that the oxidation process of ferrocene is the same for monomers alone and for monomer units in the polymer, the total number of electrons transferred during the oxidation of polymers can be compared with the polymerization degree X_n obtained from TD-SEC to evaluate the oxidation ability of the ferrocenyl groups in the polymers. As shown in Table 4, the estimated values of electrons (n_e) and X_n are in good agreement for all the polymers except for pFMOPMA for which small proportions of uncontrolled polymer chains are present as indicated in Table 2. The good correlation between n_e and X_n values demonstrates the electroactivity of all ferrocenyl groups in homopolymers, i.e. all the ferrocenyl groups present in the homopolymers can be oxidized.

Conclusions

In this paper, a series of new electroactive monomers based on ferrocenyl unit was synthesized with several alkoxy linkers between the ferrocene and the methacrylate groups. These new monomers were well characterized by conventional techniques (NMR, MS, etc.). The polymerization of these ferrocenyl methacrylate monomers was successfully carried out by the RAFT process. Homopolymers with controlled molar masses and low molar mass dispersities values were obtained. Electrochemical investigations on monomers and homopolymers by cyclic voltammetry showed that all ferrocenyl groups present in polymers can be oxidized. DSC investigations showed that the ether linkage reduced the T_g values to a level suitable for further forming well-ordered microphase separated nanostructures in block copolymers. Further electrochemical investigations on polymers, and potential marine bacterial anti-adhesion properties upon redox control are now under progress.

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