

Ferrocene-Containing Thermotropic Side-Chain Liquid-Crystalline Polysiloxanes

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ABSTRACT: The synthesis, purification, characterization, and liquid-crystalline properties of side-chain polysiloxanes bearing mesomorphic 1,1'- or 1,3-disubstituted ferrocene units are reported. The polymers were prepared by grafting the appropriate vinyl-containing ferrocene monomer onto commercially available poly(hydrosiloxane)s following a standard procedure. The monomers gave smectic A or smectic A and smectic C phases depending on the length of the flexible chains connected to the ferrocene unit. X-ray diffraction indicated that the polysiloxanes exhibited disordered smectic phases. Variation of the *d*-layer spacing determined for the polymers containing either 100% or 15–18% of the 1,1'-disubstituted ferrocene monomer (with the longest terminal alkyl chain) revealed the presence of smectic A and smectic C phases. Thermogravimetry showed a good thermal stability for the polymers.

Introduction

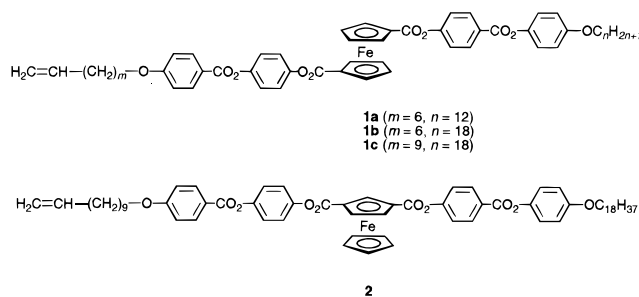
Side-chain liquid-crystalline polysiloxanes represent a class of interesting materials¹ which have found important applications in modern technology such as in the construction of information storage and ferroelectric devices^{1,2} and in nonlinear optics.³ These studies were made using organic homo- or copolymers. New developments may be expected by the introduction of a metal center into side-chain liquid-crystalline polysiloxanes. The combination of the properties of metals (color, polarizability, redox properties) with those of mesomorphic polymers (anisotropy, organization) seems particularly attractive for elaborating novel electrooptical devices.

If specific properties are to be exploited, the choice of the metal, and how it is connected to the polymeric structure, are of prime importance. Our interest in the search for new metallomesogens⁴ based on organometallic frameworks^{5–7} motivated us to consider ferrocene as a unit of choice for designing new metallomesogenic polymers.⁸ Indeed, ferrocene-containing liquid crystals show good thermal stability, good solubility in common organic solvents, and, if appropriately substituted, high liquid-crystalline tendency.⁵ Furthermore, the study of new metallomesogenic polymers will lead to important fundamental information to further explore and better understand the *structure–mesomorphic properties* relationship for such materials which are still in their infancy.

The successful development of unsymmetrically 1,1'- and 1,3-disubstituted mesomorphic ferrocene derivatives⁹ provided an access to the synthesis of vinyl-containing ferrocene monomers. Grafting of these onto poly(hydrosiloxane)s following conventional and well-established procedures was expected to lead to the targeted polymers.

We report, herein, the synthesis, characterization and mesomorphic properties of vinyl-containing ferrocene monomers **1** and **2** (Chart 1) and of their corresponding

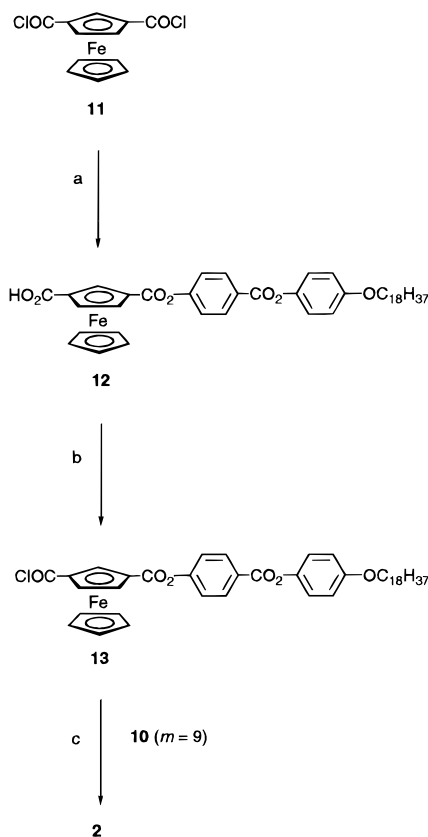
Chart 1



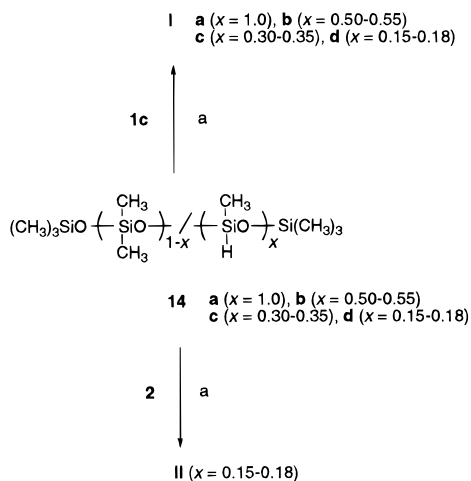
side-chain polysiloxanes **I** and **II** (Chart 2). Preliminary results have already been communicated.¹⁰ Prior to this report,¹⁰ no side-chain liquid-crystalline polymers with appended mesomorphic organometallic units had been described.⁸ Ferrocene derivative **1c** was selected to functionalize the poly(hydrosiloxane)s as it showed the highest liquid-crystalline tendency among the investigated monomers **1** (see below). As for monomer **2**, which led to higher melting and clearing points compared to the 1,1'-isomeric structure (see below), only a copolymer with a low ferrocene monomer content (15–18%) was synthesized; polymers with higher contents of the ferrocene moieties may exhibit too high clearing points and, consequently, decompose before reaching the isotropic liquid.

Results and Discussion

Monomer Synthesis. Monomers **1a–c** were prepared following the synthetic strategy described in Scheme 1. Ferrocene-1,1'-dicarboxylic acid chloride (**3**) was reacted with benzyl alcohol to give monoester **4**. Treatment of the latter with oxalyl chloride (**5**) followed by condensation with phenol derivatives **6** ($n = 12, 18$) led to **7** ($n = 12, 18$). Removal of the benzyl protective group under standard hydrogenation conditions gave acids **8** ($n = 12, 18$), which were transformed with oxalyl chloride into the corresponding acid chlo-

Scheme 2^a

^a Key: (a) benzene, **6** ($n = 18$, see Scheme 1), pyridine, reflux, 26%; (b) oxalyl chloride, pyridine, CH_2Cl_2 , reflux, 84%; (c) CH_2Cl_2 , **10** ($m = 9$, see Scheme 1), triethylamine, reflux, 62%.

Scheme 3^a

^a Key: (a) toluene, $\text{PtCl}_2(1,5\text{-C}_8\text{H}_{12})$, 70 °C, 32% (for **Ia**).

of the crude material in CH_2Cl_2 , precipitation with MeOH, and recovery by centrifugation led to pure polymers: Gel permeation chromatography (GPC) revealed that unreacted monomers and low-molecular weight oligomers were removed during the purification process.

The molecular weights (Table 1) of polymers **I** and **II** were determined, on one hand, by GPC and, on the other hand, by ^1H NMR spectroscopy taking into account the percent of substitution present in the starting polymer¹² (calculated by comparing the signal intensity of the methyl groups anchored onto the polymer backbone with

Table 1. Molecular Weights and Molecular Weight Distributions of Investigated Polymers

polymer	molecular weight of starting polysiloxanes ^a	calcd molecular weight	% grafting ^b	M_w^c	M_n^c	M_w/M_n
Ia	2270	37 500	90	31 300	23 100	1.4
Ib	900–1000	max: 8800 min: 6400	100	26 100	18 600	1.4
Ic	2000–2100	max: 13 100 min: 10 800	100	29 700	20 400	1.5
Id	2000–2500	max: 9100 min: 6400	100	24 800	17 900	1.4
II	2000–2500	max: 9100 min: 6400	100	33 300	22 900	1.6

^a Given by the supplier. ^b By ^1H NMR spectroscopy (see main text). ^c Data obtained by gel permeation chromatography.

Table 2. Phase Transition Temperatures and Enthalpy Changes of Investigated Monomers

monomer	transition ^a	T (°C) ^b	ΔH (kJ/mol)
1a	K → I	144	57.3
	(I → S_A) ^c	137	<i>d</i>
1b	K → S_A	135	55.0
	(S_C → S_A) ^{c,e}	117	
	S_A → I	145	10.8
1c	K → S_C	124	44.3
	S_C → S_A ^e	134	
	S_A → I	149	12.6
2	K → S_A	164	38.8
	(S_C → S_A) ^{c,e}	161	
	S_A → I	198	11.0

^a K = crystalline state, S_C = smectic C phase, S_A = smectic A phase, I = isotropic liquid. ^b Note that the transition temperatures reported in our preliminary communication¹⁰ (*i.e.* for **1c** and **2**) were determined on a Mettler DSC 30 calorimeter connected to a Mettler TA 3000 processor and corresponded to the peak transitions (see Experimental Section: Techniques). ^c Monotropic transition. ^d Not determined (peak overlap with the crystallization transition). ^e Determined by polarized optical microscopy.

that of the terminal CH_3 in the ferrocene-containing monomeric units) and the number of methylhydrosiloxane units (CH_3SiH).

The percentage of monomer grafting determined revealed that the reaction occurred with a good yield (90%) for homopolymer **Ia** and quantitatively for copolymers **Ib–d** and **II**. With the exception of homopolymer **Ia**, the molecular weights calculated by NMR are smaller than those determined by GPC. This discrepancy arises from the fact that polystyrene standards were used to calibrate the GPC columns. The molecular weights obtained from both techniques cannot be compared.

Molecular weights distribution (M_w/M_n) (Table 1) ranging from 1.4 to 1.6 were obtained after purification.

Mesomorphic Properties. The mesomorphic properties were investigated by a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). The thermal and liquid-crystalline data of the monomers (**1** and **2**) and polymers (**I** and **II**) are listed in Tables 2 and 3, respectively.

Monomers. Ferrocene derivative **1a** having the shortest flexible chains gave a monotropic smectic A phase. Monomer **1b** led to an enantiotropic smectic A phase and a monotropic smectic C one. As for **1c**, bearing the longest alkyl chains, it showed enantiotropic smectic C and smectic A phases. Ferrocene derivative **2** gave an enantiotropic smectic A phase and a monotropic smectic C one. Higher melting and clearing

Table 3. Phase Transition Temperatures of Investigated Polymers

polymer	transition ^a	T (°C) ^b	ΔH (J/g)	liq-crystalline behavior ^a
Ia	T_m	136	11.0	$S_C \rightarrow S_A$: 140 °C
	T_c	183	9.7	(by X-ray diffr)
Ib	T_m	127	9.4	smectic A phase (by X-ray diffr)
	T_c	173	8.4	
Ic	T_m	118	7.3	smectic A phase (by X-ray diffr)
	T_c	163	7.4	
Id	T_m	120	14.4	$S_C \rightarrow S_A$: 151 °C (1.4 J/g)
	T_c	159	1.4	(by DSC, polarized optical microscopy and X-ray diffr)
II	T_m	139	6.9	smectic A and/or smectic C
	T_c	200	1.2	phase(s) (by X-ray diffr)

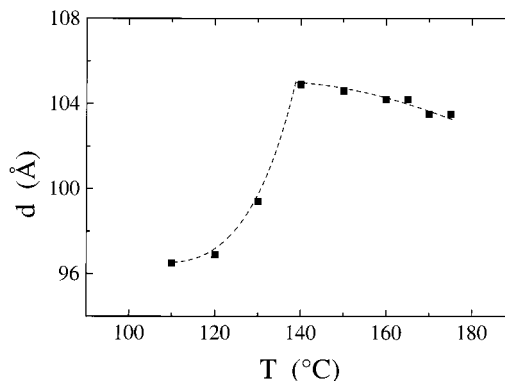
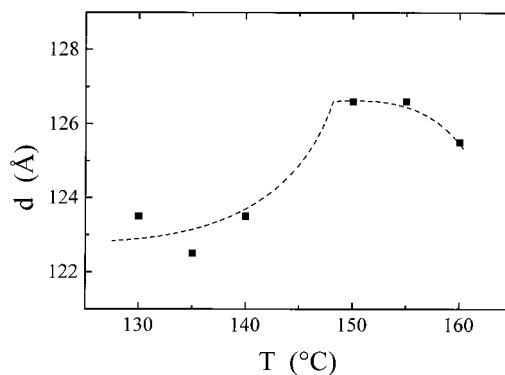
^a T_m = melting point, T_c = clearing point, S_C = smectic C phase, S_A = smectic A phase. ^b Note that the transition temperatures reported in our preliminary communication¹⁰ (i.e. for **Ia** and **II**) were determined on a Mettler DSC 30 calorimeter connected to a Mettler TA 3000 processor (see Experimental Section: Techniques).

points were observed for **2** than for its isomeric analogue **1c**. The influence of the substitution pattern on the thermal properties can be explained from the X-ray crystal structure obtained for a 1,3-disubstituted ferrocene derivative,¹³ which revealed that such a substitution pattern leads to a highly anisotropic structure compared to the “step” structure of ferrocene derivatives substituted in the 1,1'-positions.¹⁴

The liquid-crystalline phases were identified by POM. On cooling of the samples from the isotropic melt, textures typical of smectic A (focal conic fan texture and homeotropic areas) (for **1a–c** and **2**) and smectic C (broken focal conic fan and schlieren textures) (for **1b,c** and **2**) phases were observed.

The liquid-crystalline phases of **1c** and **2**, which were used for preparing the side-chain polysiloxanes **I** and **II**, were characterized by XRD. For both monomers, diffraction patterns typical of disordered smectic phases were recorded and showed two sharp reflection peaks (1:2 ratio) in the small-angle region and a diffuse band in the wide-angle region. The d -layer spacing was calculated for both monomers in the smectic A phase and was found to be 59.8 Å (at 135 °C) for **1c** and 57.1 Å (at 175 °C) for **2**. From CPK molecular models, a molecular length L of ca. 68.5 Å was measured for **1c** and **2** in their fully extended conformation. From these values, d/L ratios of 0.87 and 0.83 were obtained for **1c** and **2**, respectively. The discrepancy between the d and L values suggested a monomolecular organization of **1c** and **2** within the smectic A phase with a pronounced disorganization of the alkyl chains. Such an arrangement is in agreement with low-molar mass ferrocene-containing thermotropic liquid crystals we previously investigated.¹⁵

Polymers. All the polymers exhibited liquid-crystalline properties. Their melting and clearing points were determined by DSC and POM. Interestingly, polymer **Id** gave an additional endotherm which was indicative of the presence of two liquid-crystalline phases. Crystal-to-crystal transitions were detected for **Ia–c**. In the case of **Ia–c** and **II**, the liquid-crystalline phases could not be identified by POM. This is often the case for polymers owing to their viscosity which prevents the development of typical textures. In some cases, a focal-conic texture was observed and indicated a smectic nature of the liquid-crystalline phase(s). For **Id**, on cooling slowly the sample from the isotropic fluid, the

**Figure 1.** Variation of the d -layer spacing of polymer **Ia** as a function of temperature.¹⁶**Figure 2.** Variation of the d -layer spacing of polymer **Id** as a function of temperature.

formation of *bâtonnets*, which then transformed into a focal-conic fan texture, was clearly noticed. Homeotropic areas were also observed. On further cooling (i.e. after the second transition), a schlieren texture formed from the previous homeotropic areas, and the focal-conic fan texture transformed into a broken focal-conic fan texture. From these observations, the liquid-crystalline phases of **Id** were identified as smectic A (high-temperature mesophase) and smectic C (low-temperature mesophase) phases.

Comparison of the melting and clearing points in series **I** and between **Id** and **II** showed the influence of the monomer content and structural isomerism on the thermal properties. First, decreasing the content of the mesogenic ferrocene monomer lowered both the melting and clearing points. Second, as expected from the results obtained for monomers **1c** and **2** (see above), incorporation of the 1,3-disubstituted ferrocene units onto the polymer led to a broadening of the liquid-crystalline domain.

The liquid-crystalline phases exhibited by **I** and **II** were investigated by XRD. Diffractograms typical of disordered smectic A and/or smectic C phases, characterized by two sharp diffraction peaks (1:2 ratio) in the low-angle region and a diffuse one in the wide-angle region, were recorded. The d -layer spacing was determined as a function of temperature for **I** on cooling the sample from the isotropic melt. For **Ia** (Figure 1) and **Id** (Figure 2), the variation of the layer thickness showed two regimes typical of smectic A (high-temperature liquid-crystalline phase) and smectic C (low-temperature liquid-crystalline phase) phases. These data supported the POM observations in case of **Id**. For **Ib,c**, the layer spacing was found to be nearly independent of temperature (not shown here) indicating that

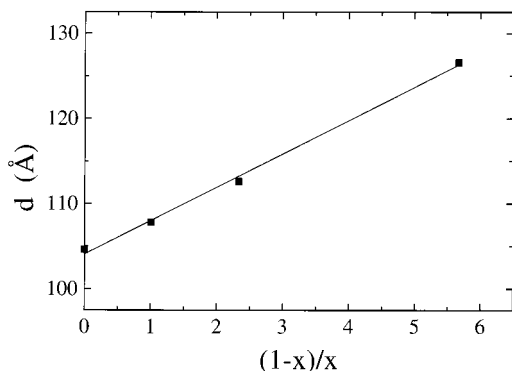


Figure 3. Variation of the d -layer spacing of polymers **Ia–d** as a function of the monomeric molar ratio at 150 °C.

the mesophase observed for these two copolymers was smectic A in nature.

The molecular organization of the mesomorphic units in the polymeric structure can be deduced by taking into account the above X-ray data and the structure of the ferrocene core. First, because of the bulkiness of the latter, the mesomorphic ferrocene units are, most likely, organized in an alternating way leading to a double layer (herringbone organization). Second, the ratio of the d -layer spacing obtained for polymer **Ia** (105 Å at 140 °C)¹⁶ and the one of monomer **1c** (59.8 Å at 135 °C) within the smectic A phase gives a value of $d_{\text{polymer}}/d_{\text{monomer}} = 1.75$, suggesting an interdigitation of the layers and a disorganized state (folding, curling) of the flexible chains.

The influence of the monomeric ratio on the interlamellar distance was investigated by determining the d -layer spacing of **Ia–d** at 150 °C (Figure 3). Clearly, the layer thickness increased with the content of dimethylsiloxane units. This behavior was in agreement with literature data¹⁷ obtained for other polysiloxanes and could be explained in terms of microphase separations: the amphipatic character between the different constituent parts of the polymer leads to a microsegregation in space of the polysiloxane backbone, the aromatic units, and the aliphatic chains, respectively. The overall layer thickness is the sum of the siloxane and mesogenic sublayers; since the smectic order is kept with dilution (i.e., there is no significant change in the lateral order of the side groups), it can be assumed that the increase of the smectic layer thickness corresponds mainly to the increase of the polysiloxane sublayer, as already reported for other types of liquid-crystalline polymers.¹⁸ If such, the layer thickness should increase linearly as a function of $(1 - x)/x$, where x is the percentage of the ferrocene units. Thus, the slope of this linear variation can be estimated to be equal to V_{DMS}/S , where V_{DMS} is the volume of one dimethylsiloxane unit (ca. 145 Å³ at 170 °C)¹⁹ and S the molecular area of one mesogenic unit. The value found for this slope in the present work is about 4 Å and leads to an S value of about 36 Å². This value can be understood from the proposed structural model given in Figure 4. Indeed, due to the bulkiness of the ferrocene group (ca. 44 Å²),²⁰ which is about twice that of the classical calamitic mesogenic part (ca. 23–26 Å²), two successive side groups along the same side of the polymer backbone should be shifted along the normal to the smectic layers to fill the space efficiently. In such a description, the effective molecular area of each side group is about 33 Å² (see ref 21) a value which is compatible with the

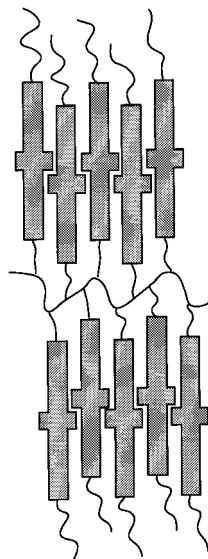


Figure 4. Proposed organization of the appended ferrocene units anchored onto the polymer within the smectic A phase.

distance (6.2 Å) between the corresponding two silicon atoms along the polymer backbone. Finally, it is worth noting that such a molecular organization implies that the aliphatic chains (spacer and terminal chains) be highly disorganized and thus rather spread laterally, which is again in agreement with the values of the layer spacing observed (smaller than twice the molecular length of the monomer in the case of the homopolymer).

Finally, the thermal stability of polymers **Ia–d** and **II** was examined by thermogravimetry. No decomposition was detected up to 250 °C, which indicated good thermal resistance of the investigated polymeric materials.

Conclusion

The above results and those obtained for ferrocene-containing thermotropic side-chain liquid-crystalline polymethacrylates²² and thermotropic liquid-crystalline polyferrocenylsilanes²³ demonstrate that ferrocene is a valuable unit for designing ferrocene-based metallomesogenic polymers. Considering the numerous possibilities for functionalizing the ferrocene core,⁵ the choice and positions of substituents may be used for tuning and controlling both the thermal and mesomorphic properties of such polymeric materials. Furthermore, our recent studies devoted to the design and study of chiral ferrocene-containing liquid crystals with planar chirality^{9a} and ferrocenium-containing thermotropic liquid crystals²⁴ open the doors toward the development of new polymeric materials presenting interesting properties.

Experimental Section

Materials. CH₂Cl₂ (P₂O₅, under N₂) and toluene (sodium, benzophenone, under N₂) were distilled prior to use. Benzene (Fluka, puriss pa), benzyl alcohol (Fluka, puriss pa), pyridine (Fluka, puriss pa), oxalyl chloride (Fluka, purum), and triethylamine (Fluka, puriss pa) were used as received. Pyridine and triethylamine were stored on 4 Å molecular sieves. Compounds **3**²⁵ (from ferrocene-1,1'-dicarboxylic acid), **6** ($n = 12, 18$),²⁶ **10** ($m = 6, 9$),²⁷ and **11**^{25,28} (from ferrocene) were synthesized by following literature procedures. Poly(hydrosiloxane)s **14a–d** [$x = 1.0$ (PS 120); $x = 0.50–0.55$ (PS 122.5); $x = 0.30–0.35$ (PS 123); $x = 0.15–0.18$ (PS 123.5)] were Hüls America Inc. products. Dichloro(1,5-cyclooctadiene)-

platinum(II) (PtCl₂(1,5-C₈H₁₂)) was purchased from Strem Chemicals Inc. All reactions were carried out under N₂.

Techniques. Column chromatography used silica gel 60 (0.060–0.200 mm, SDS). Melting points (uncorrected) were determined on a Büchi 530 instrument. Transition temperatures (onset point for monomers; peak transition for polymers) and enthalpies were determined with a differential scanning Mettler DSC 30 calorimeter connected to a Mettler TA 4000 processor, under N₂, at a rate of 10 °C min⁻¹ (for **1b**, 2 °C min⁻¹) (second heating run); Mettler TA72.2/0.5 GRAPHWARE was used for data treatment. Thermogravimetry analyses were performed with a Mettler TG 50 thermobalance connected to a Mettler TA 4000 processor at a rate of 10 °C min⁻¹. Optical studies were made using a Zeiss-Axiocrop polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N₂. Gel permeation chromatography (GPC) was made with a Waters 510 instrument connected to a Waters 410 differential refractometer. Ultrastayragel 10³–10⁴ columns were calibrated with polystyrene standards (eluent, THF, 1 mL min⁻¹; T = 35 °C; Baseline 510 software used for data treatment). ¹H NMR spectra were recorded in CDCl₃ on a Varian Gemini 200 spectrometer or a Bruker AMX 400 spectrometer, with the solvent as an internal standard. IR spectra were recorded on a Perkin-Elmer 1720 FTIR spectrometer. Elemental analyses were done by Mikroelementaranalytisches Laboratorium ETH-Zurich or Ciba (Marly, Switzerland).

X-ray Diffraction Studies. The crude powder was filled in Lindemann capillaries, and a linear monochromatic Cu K α beam obtained with a sealed-tube generator and a bent quartz monochromator was used. The diffraction patterns were registered either with a curved proportional detector "Inel CPS 120" or photographically. In general, the position of the second-order reflection in the small-angle region was used to determine the layer spacing. The temperature was controlled within ± 0.05 °C.

Synthesis. 1'-[(Benzyloxy)carbonyl]ferrocene-1-carboxylic acid (**4**). A solution of benzyl alcohol (3.71 g, 34.3 mmol) in CH₂Cl₂ (29 mL) was added dropwise to a stirred solution of **3** (10.6 g, 34.1 mmol) and triethylamine (6.89 g, 68.1 mmol) in CH₂Cl₂ (1430 mL); the addition was done in three times: 50% first, followed by twice 25% at 15 min intervals. The mixture was stirred at room temperature for a further 4 h and evaporated to dryness. Purification of the residue by column chromatography (first with 8:2 CH₂Cl₂/AcOEt to recover the diester and then with 8:2:0.1 CH₂Cl₂/AcOEt/AcOH) gave pure **4** (5.26 g, 42%). Mp = 154 °C. ¹H NMR (200 MHz): δ 7.50–7.34 (m, 5 H, aromatic protons, benzyloxy), 5.29 (s, 2 H, CH₂Ph), 4.91 (t, 2 H, HCp), 4.83 (t, 2 H, HCp), 4.47 (t, 2 H, HCp), 4.35 (t, 2 H, HCp).

1-(Chlorocarbonyl)-1'-[(benzyloxy)carbonyl]ferrocene (**5**). A solution of **4** (2.00 g, 5.50 mmol), oxalyl chloride (3.36 g, 26.5 mmol), and pyridine (20 drops) in CH₂Cl₂ (20 mL) was stirred under reflux for 7 h and evaporated to dryness. The solid residue was extracted with hot light petroleum until the extracts remained colorless. Evaporation of the solvent gave **5** (2.10 g, 100%), which was used in the next step without further purification. Mp = 70 °C. ¹H NMR (200 MHz): δ 7.50–7.38 (m, 5 H, aromatic protons, benzyloxy), 5.29 (s, 2 H, CH₂-Ph), 4.96 (t, 2 H, HCp), 4.87 (t, 2 H, HCp), 4.54 (t, 2 H, HCp), 4.48 (s, 2 H, HCp).

1-[(Benzyloxy)carbonyl]-1'-[p'-p'-[(octadecyloxy)phenyl]oxy]carbonyl] [(phenyloxy)carbonyl] ferrocene (**7**) (*n* = 18). A solution of **5** (2.10 g, 5.49 mmol), **6** (*n* = 18) (2.65 g, 5.49 mmol), and triethylamine (0.53 g, 5.2 mmol) in CH₂Cl₂ (40 mL) was heated under reflux overnight and evaporated to dryness. Purification of the residue by column chromatography (50:1 CH₂Cl₂/AcOEt) and crystallization (CH₂Cl₂/EtOH) gave pure **7** (*n* = 18) (4.0 g, 88%). Mp = 91–92 °C. ¹H NMR (400 MHz): δ 8.23 (d, 2 H, aromatic protons), 7.42–7.33 (m, 7 H, aromatic protons), 7.13 (d, 2 H, aromatic protons), 6.94 (d, 2 H, aromatic protons), 5.25 (s, 2 H, CH₂Ph), 4.95 (t, 2 H, HCp), 4.91 (t, 2 H, HCp), 4.52 (t, 2 H, HCp), 4.44 (t, 2 H, HCp), 3.97 (t, 2 H, CH₂O), 1.79 (m, 2 H, CH₂CH₂O), 1.46 (m, 2 H, CH₂CH₂CH₂O), 1.26 (m, 28 H, aliphatic protons), 0.88 (t,

3 H, CH₃). Anal. Calcd for C₅₀H₆₀O₇Fe (828.87): C, 72.45; H, 7.30. Found: C, 72.48; H, 7.35.

Compound **7** (*n* = 12) was prepared from **6** (*n* = 12) by following the above synthetic procedure and gave analytical data which were in agreement with its structure.

1'-[p'-p'-[(octadecyloxy)phenyl]oxy]carbonyl] [(phenyloxy)carbonyl] ferrocene-1-carboxylic acid (**8**) (*n* = 18). A mixture of **7** (*n* = 18) (6.04 g, 7.29 mmol), Pd (10%)/C (0.6 g) and 2:3 CH₂Cl₂/EtOH (500 mL) was stirred overnight at room temperature under 4 bar of H₂. The mixture was filtered and the solvent evaporated to dryness. Purification of the residue by crystallization (EtOH) gave pure **8** (*n* = 18) (4.71 g, 87%). Mp = 176–178 °C. ¹H NMR (400 MHz): δ 8.27 (d, 2 H, aromatic protons), 7.39 (d, 2 H, aromatic protons), 7.12 (d, 2 H, aromatic protons), 6.93 (d, 2 H, aromatic protons), 5.01 (s, 2 H, HCp), 4.95 (s, 2 H, HCp), 4.57 (d, 4 H, HCp), 3.96 (t, 2 H, CH₂O), 1.78 (m, 2 H, CH₂CH₂O), 1.46 (m, 2 H, CH₂CH₂CH₂O), 1.26 (m, 28 H, aliphatic protons), 0.88 (t, 3 H, CH₃). Anal. Calcd for C₄₃H₅₄O₇Fe (738.74): C, 69.91; H, 7.37. Found: C, 69.89; H, 7.32.

Compound **8** (*n* = 12) was prepared from **7** (*n* = 12) by following the above synthetic procedure and gave analytical data which were in agreement with its structure.

1-(Chlorocarbonyl)-1'-[p'-p'-[(octadecyloxy)phenyl]oxy]carbonyl] [(phenyloxy)carbonyl] ferrocene (**9**) (*n* = 18). A solution of **8** (*n* = 18) (1.57 g, 2.13 mmol), oxalyl chloride (1.40 g, 11.0 mmol), and pyridine (6 drops) in CH₂Cl₂ (90 mL) was heated under reflux for 7 h and evaporated to dryness. The solid residue was extracted with hot light petroleum until the extracts remained colorless. Evaporation of the solvent gave **9** (*n* = 18) (1.41 g, 87%), which was used in the next step without further purification. Mp = 103–105 °C. ¹H NMR (400 MHz): δ 8.27 (d, 2 H, aromatic protons), 7.38 (d, 2 H, aromatic protons), 7.12 (d, 2 H, aromatic protons), 6.93 (d, 2 H, aromatic protons), 5.10 (t, 2 H, HCp), 5.03 (t, 2 H, HCp), 4.74 (t, 2 H, HCp), 4.68 (t, 2 H, HCp), 3.96 (t, 2 H, CH₂O), 1.79 (m, 2 H, CH₂CH₂O), 1.47 (m, 2 H, CH₂CH₂CH₂O), 1.26 (m, 28 H, aliphatic protons), 0.88 (t, 3 H, CH₃).

Compound **9** (*n* = 12) was prepared from **8** (*n* = 12) by following the above synthetic procedure and gave analytical data which were in agreement with its structure.

1-[p'-p'-[(Undec-10-enyloxy)benzoyl]oxy] [(phenyloxy)carbonyl]-1'-[p'-p'-[(octadecyloxy)phenyl]oxy]carbonyl] [(phenyloxy)carbonyl] ferrocene (**1c**). A solution of **9** (*n* = 18) (1.02 g, 1.35 mmol), **10** (*m* = 9) (0.57 g, 1.49 mmol), and triethylamine (0.14 g, 1.38 mmol) in CH₂Cl₂ (35 mL) was heated under reflux overnight and evaporated to dryness. Purification of the residue by column chromatography (100:1 CH₂Cl₂/AcOEt) and crystallization (CH₂Cl₂/EtOH) gave pure **1c** (1.04 g, 70%). ¹H NMR (400 MHz): δ 8.22 (d, 2 H, aromatic protons), 8.12 (d, 2 H, aromatic protons), 7.34 (d, 2 H, aromatic protons), 7.22 (d, 4 H, aromatic protons), 7.11 (d, 2 H, aromatic protons), 6.96 (d, 2 H, aromatic protons), 6.91 (d, 2 H, aromatic protons), 5.82 (m, 1 H, CH=CH₂), 5.09 (m, 4 H, HCp), 5.03–4.92 (m, 2 H, CH=CH₂), 4.64 (m, 4 H, HCp), 4.04 (t, 2 H, CH₂O), 3.95 (t, 2 H, CH₂O), 2.06 (m, 2 H, CH₂CH=CH₂), 1.80 (m, 4 H, CH₂CH₂O), 1.46 (m, 4 H, CH₂CH₂CH₂O), 1.41–1.26 (m, 38 H, aliphatic protons), 0.88 (t, 3 H, CH₃). IR (KBr): 3126, 3077, 2920, 2850, 1739, 1722, 1642, 1606, 1510, 1471, 1454 cm⁻¹. Anal. Calcd for C₆₇H₈₂O₁₀Fe (1103.23): C, 72.94; H, 7.49. Found: C, 72.96; H, 7.55.

Monomers **1a** [from **9** (*n* = 12) and **10** (*m* = 6)] and **1b** [from **9** (*n* = 18) and **10** (*m* = 6)] were prepared by following the above synthetic procedure and gave analytical data which were in agreement with their structures.

3-[p'-p'-[(Octadecyloxy)phenyl]oxy]carbonyl] [(phenyloxy)carbonyl] ferrocene-1-carboxylic acid (**12**). A solution of **11** (0.31 g, 1.0 mmol), **6** (*n* = 18) (0.48 g, 1.0 mmol), and pyridine (a few drops) in benzene (70 mL) was heated under reflux for 36 h and evaporated to dryness. Purification of the residue by column chromatography (first with CH₂Cl₂, then with 10:1 CH₂Cl₂/AcOEt, and finally with 10:1:0.1 CH₂Cl₂/AcOEt/AcOH) and crystallization (CH₂Cl₂/hexane) gave pure **12** (0.19 g, 26%). Mp = 180 °C. ¹H NMR

(400 MHz): δ 8.29 (d, 2 H, aromatic protons), 7.33 (d, 2 H, aromatic protons), 7.12 (d, 2 H, aromatic protons), 6.94 (d, 2 H, aromatic protons), 5.73 (s, 1 H, HCp), 5.34 (s, 1 H, HCp), 5.20 (s, 1 H, HCp), 4.49 (s, 5 H, HCp), 3.97 (t, 2 H, CH₂O), 1.79 (m, 2 H, CH₂CH₂O), 1.46 (m, 2 H, CH₂CH₂CH₂O), 1.26 (m, 28 H, aliphatic protons), 0.88 (t, 3 H, CH₃). Anal. Calcd for C₄₃H₅₄O₇Fe (738.74): C, 69.91; H, 7.37. Found: C, 70.05; H, 7.22.

1-(Chlorocarbonyl-3-{*p*'-[(octadecyloxy)phenyl]oxy}-carbonyl}[(phenyloxy)carbonyl]ferrocene (13). A solution of **12** (0.45 g, 0.61 mmol), oxalyl chloride (0.38 g, 3.0 mmol), and pyridine (5 drops) in CH₂Cl₂ (15 mL) was heated under reflux for 7 h and evaporated to dryness. The solid residue was extracted with hot light petroleum until the extracts remained colorless. Evaporation of the solvent gave **13** (0.39 g, 84%), which was used in the next step without further purification. Mp = 120–125 °C. ¹H NMR (200 MHz): δ 8.29 (d, 2 H, aromatic protons), 7.33 (d, 2 H, aromatic protons), 7.13 (d, 2 H, aromatic protons), 6.94 (d, 2 H, aromatic protons), 5.74 (t, 1 H, HCp), 5.35 (m, 1 H, HCp), 5.21 (m, 1 H, HCp), 4.50 (s, 5 H, HCp), 3.97 (t, 2 H, CH₂O), 1.79 (m, 2 H, CH₂CH₂O), 1.26 (m, 30 H, aliphatic protons), 0.88 (t, 3 H, CH₃).

1-{*p*'-[(Undec-10-enyloxy)benzoyl]oxy}[(phenyloxy)carbonyl]-3-{*p*'-[(octadecyloxy)phenyl]oxy}carbonyl}[(phenyloxy)carbonyl]ferrocene (2). A solution of **13** (0.12 g, 0.16 mmol), **10** (*m* = 9) (0.080 g, 0.21 mmol), and triethylamine (16 mg, 0.16 mmol) in CH₂Cl₂ (15 mL) was heated under reflux overnight and evaporated to dryness. Purification of the residue by column chromatography (100:1 CH₂Cl₂/AcOEt) and crystallization (CH₂Cl₂/EtOH) gave pure **2** (0.11 g, 62%). ¹H NMR (400 MHz): δ 8.29 (d, 2 H, aromatic protons), 8.15 (d, 2 H, aromatic protons), 7.35 (d, 2 H, aromatic protons), 7.29 (d, 2 H, aromatic protons), 7.26 (d, 2 H, aromatic protons), 7.13 (d, 2 H, aromatic protons), 6.98 (d, 2 H, aromatic protons), 6.94 (d, 2 H, aromatic protons), 5.79 (t, 1 H, HCp), 5.83–5.78 (m, 1 H, CH=CH₂), 5.28–5.25 (m, 2 H, HCp), 5.02–4.92 (m, 2 H, CH=CH₂), 4.47 (s, 5 H, HCp), 4.05 (t, 2 H, CH₂O), 3.97 (t, 2 H, CH₂O), 2.05 (m, 2 H, CH₂CH=CH₂), 1.81 (m, 4 H, CH₂CH₂O), 1.46 (m, 4 H, CH₂CH₂CH₂O), 1.41–1.26 (m, 38 H, aliphatic protons), 0.88 (t, 3 H, CH₃). IR (KBr): 3131, 3079, 2920, 2851, 1733, 1722, 1641, 1606, 1510, 1466 cm⁻¹. Anal. Calcd for C₆₇H₈₂O₁₀Fe (1103.23): C, 72.94; H, 7.49. Found: C, 72.98; H, 7.20.

Synthesis of Polymer Ia. A solution of poly(methylhydroxysiloxane) **14a** (0.024 g, 0.41 mmol of SiH units) in toluene (5 mL) was added to a solution of monomer **1c** (0.5 g, 0.45 mmol) in toluene (13 mL). The mixture was heated to 70 °C, and PtCl₂(1,5-C₈H₁₂) (0.9 mg, 2.4 × 10⁻³ mmol) was then added. The solution was heated at 70 °C for 24 h and evaporated to dryness. Purification of the residue by dissolution in CH₂Cl₂ and precipitation with MeOH gave **Ia** (0.15 g, 32%). The purification process was repeated until no monomer was detected by GPC. ¹H NMR (400 MHz): δ 8.21 (br s, 2 H, aromatic protons), 8.10 (br s, 2 H, aromatic protons), 7.31 (br d, 2 H, aromatic protons), 7.21 (br s, 2 H, aromatic protons), 7.09 (br s, 2 H, aromatic protons), 6.90 (br d, 4 H, aromatic protons), 5.08 (br s, 4 H, HCp), 4.63 (br s, 4 H, HCp), 4.01 (br s, 2 H, CH₂O), 3.94 (br s, 2 H, CH₂O), 1.78 (br s, 4 H, CH₂-CH₂O), 1.45 (br s, 4 H, CH₂CH₂CH₂O), 1.25 (br m, 38 H, aliphatic protons), 0.86 (br s, 3 H, CH₃), 0.51 (br s, 2 H, CH₂-Si), 0.08 (br m, 123 H, CH₃Si). IR (KBr): 3126, 3078, 2921, 2851, 1738, 1606, 1580, 1510, 1456 cm⁻¹.

Polymers **Ib** (from **14b**), **Ic** (from **14c**), **Id** (from **14d**), and **II** (from **2** and **14d**) were prepared by following the above synthetic procedure and gave analytical data which were in agreement with their structures.

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