

# Functionalization of poly(metallocenes) via hydrosilylation: synthesis and properties of thermotropic liquid crystalline poly(ferrocenylsilanes)

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## Abstract

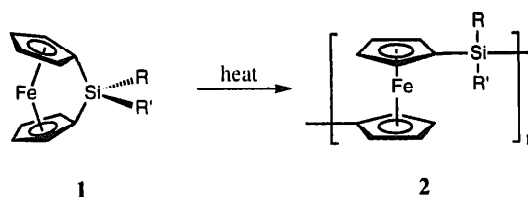
Hydrosilylation of poly(ferrocenylmethylhydrosilane)  $[\text{Fe}(\eta\text{-C}_5\text{H}_4)_2\text{SiMeH}]_n$  with 1-hexene and ethyl acrylate was achieved using Karstedt's catalyst with degrees of functionalization of ca 80%. Using a similar strategy, 4-pentoxy-4'-hydroxyhexanoyazobenzene or 4-pentoxy-4'-hydroxyundecyloxyazo-benzene acrylate side chains were successfully attached to the poly(metallocene) main chain. The resulting functionalized poly(ferrocenylsilanes) represent the first examples of calamitic thermotropic side chain liquid crystal polymers with ferrocene groups in the backbone. © 1997 Elsevier Science B.V.

## 1. Introduction

Metallomesogenic macromolecules are particularly attractive as they have the potential to combine the advantageous properties of polymers (e.g. excellent mechanical properties, low thermal expansion, and excellent processability) with those of transition metal complexes (e.g. color, polarizability, magnetic characteristics) [1–4]. Ferrocene units are of considerable interest as components of liquid-crystalline (LC) materials owing to their high thermal stability, novel redox characteristics and their structural variability which might lead to intriguing effects on mesophase morphology [5]. A range of low molecular weight calamitic (rod-like) systems can be prepared by monosubstitution or by 1,2-, 1,3-, or 1,1'-disubstitution of the ferrocene nucleus [6]. Several examples of calamitic side-chain metallomesogenic polymers with ferrocene in the side group structure are known [7]. Although main-chain, LC polymers with ferrocene in the backbone are more common [8], these are limited to materials in which the ferrocene units are a significant distance apart making the exploitation of cooperative interactions between the iron atoms impossible.

Poly(ferrocenylsilanes) **2** are an interesting class of

transition metal-based polymers which were recently prepared in high molecular weight form via a thermal ring-opening polymerization (ROP) route [9]. These and related ROP-derived materials have attracted recent attention with respect to their interesting physical properties [10–13]. A novel feature of these polymers is that the skeletal iron atoms interact with one another as has been shown by cyclic voltammetric studies [10].



The ability to functionalize polymers permits the tailoring of physical properties and is particularly well-established for inorganic polymers such as polyphosphazenes [14], polysiloxanes [15], and more recently polycarbosilanes [16] but is virtually unknown for transition metal-based polymeric materials. With this in mind, we recently reported the synthesis of poly(ferrocenylsilanes) with chlorine substituents at silicon, **2** (R and/or R' = Cl). These materials are tunable and permit the introduction of different functional substituents (e.g. acetylenic groups) via nucleophilic substitution reactions [17]. In this paper, we explore an alternative

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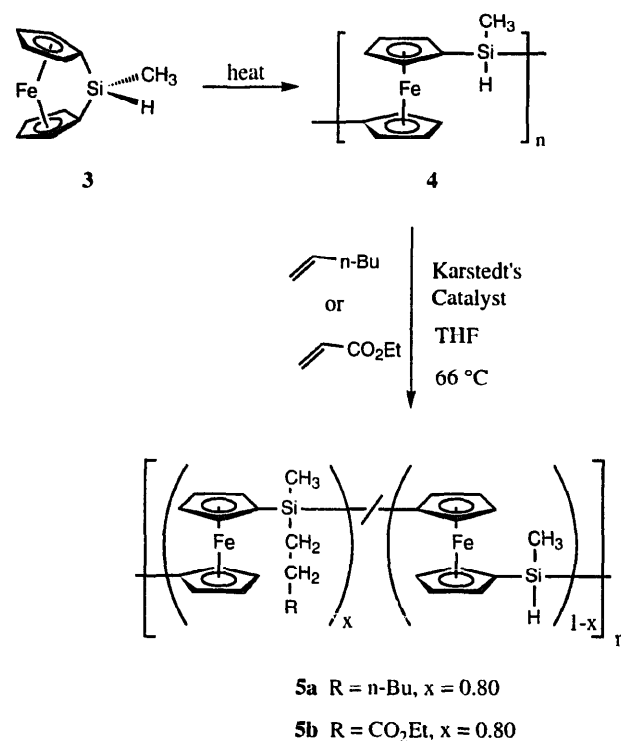
hydrosilylation strategy for the functionalization of a poly(ferrocenylsilane) with Si–H substituents. We describe the use of this methodology to allow the synthesis of the first side chain metallomesogenic polymers with ferrocene units in the main chain. These materials represent the first well-characterized, liquid-crystalline poly(ferrocenylsilanes) [18].

## 2. Results and discussion

### 2.1. Hydrosilylation reactions of 4 with simple $\alpha$ -olefins

Hydrosilylation of polysiloxanes with Si–H groups provides a well-established method of functionalizing these materials [15]. The introduction of mesogenic groups to yield side chain LC materials has been studied in particular detail [15,19]. In order to determine whether a similar strategy might permit access to LC poly(ferrocenylsilanes) we initially explored two model reactions of the poly(ferrocenylmethylhydrosilane) (4) with simple vinyl-terminated species. Polymer 4 was prepared via the previously reported thermal ROP of the strained monomer 3 at 150°C [20]. Reaction of 4 with the  $\alpha$ -olefins 1-hexene and ethyl acrylate in the presence of Karstedt's catalyst in refluxing THF was found to yield poly(ferrocenylsilanes) 5a and 5b, respectively Scheme 1.

The polymeric products were characterized by NMR spectroscopy and gel permeation chromatography to provide an estimate of the molecular weight (Table 1). The  $^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{29}\text{Si}$ -NMR spectra were consistent with the assigned structures. Significantly, the  $^1\text{H}$ - and  $^{29}\text{Si}$ -NMR spectra of 5a and 5b indicated incomplete substitution of the Si–H groups. For example, the  $^{29}\text{Si}$ -NMR spectra showed the presence of  $\text{fcSiR}_2\text{fc}$  and  $\text{fcSiMeHfc}$  environments at  $-5$  and  $-20$  ppm, respectively (see, for example, Fig. 1). The integrable  $^1\text{H}$ -NMR spectra gave the degree of substitution as ca. 80%.



Scheme 1.

Interestingly, even when longer reaction times were used the degree of substitution was comparable and was generally in the range of 80–86%. When different solvents (e.g. toluene) were used as an alternative solvent to THF, the degree of hydrosilylation over comparable reaction times was less (ca. 50%). GPC showed that the polymers 5a and 5b were of comparable molecular weight and polydispersity as the starting material 4 which indicated that hydrosilylation proceeds with minimal chain cleavage. Studies of the poly(ferrocenylsilanes) 5a and 5b by DSC showed the presence of glass transitions ( $T_g$ 's) at 9°C and 20°C, respectively.

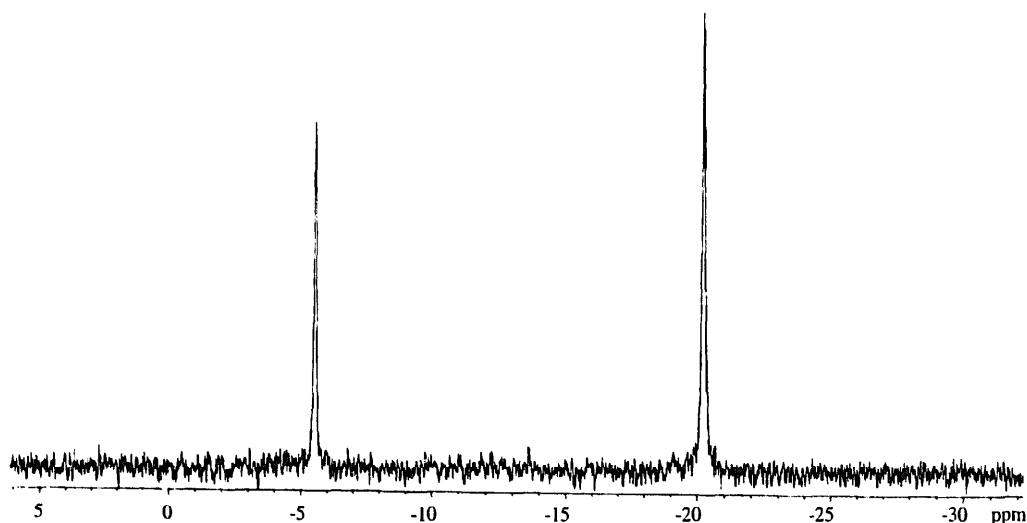


Fig. 1.  $^{29}\text{Si}$ -NMR (79.8 MHz,  $\text{CDCl}_3$ ) spectrum of poly(ferrocenylsilane) (5a).

Although no clear reason for the apparent maximum degree of hydrosilylation is apparent at this time, similar degrees of hydrosilylation have recently been achieved using poly(carbosilanes) with Si–H bonds [16]c.

Attempts to derivatize the [1] ferrocenophane **3** via hydrosilylation with the aim of subsequently performing a ROP process to yield a completely derivatized polymer have, to date, been unsuccessful. Thus, reaction of **3** with  $\alpha$ -olefins in the presence of Karstedt's catalyst in refluxing THF yielded the targeted hydrosilylated derivatives of **3**. However, also formed were polymer **4**, via transition metal catalyzed ROP of **3** [21,22], and the derivatized polymer **5a** with a similar degree of substitution via hydrosilylation as found above.

## 2.2. Synthesis and characterization of LC poly(ferrocenylsilanes) **11a** and **11b**

The azo-benzene based mesogens **10a** and **10b** were prepared by the reaction sequence in Scheme 2. To

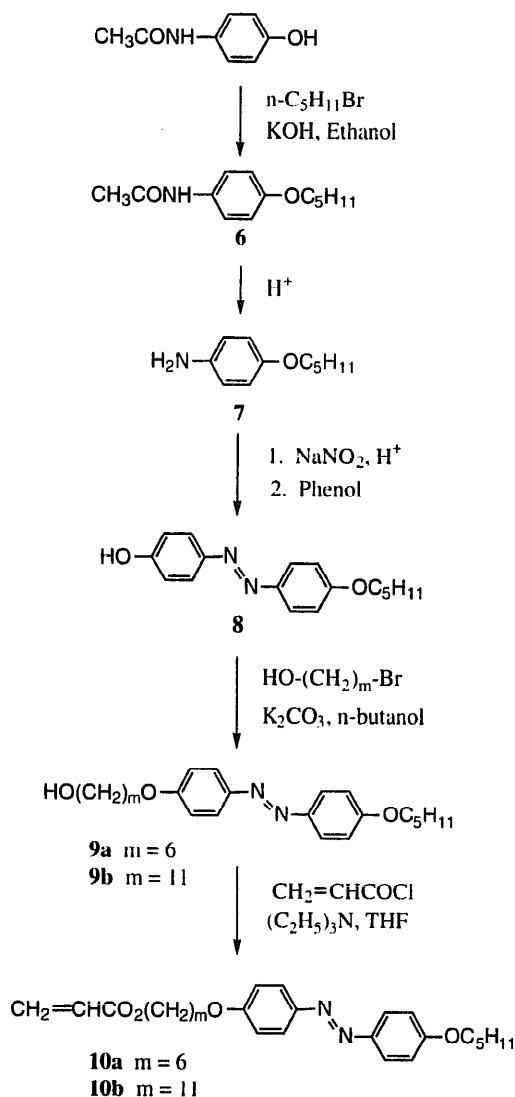


Table 1  
Molecular weight,  $^{29}\text{Si}$ -NMR, thermal transition temperatures and assignments for **4**, **5a**, **5b**, **10a**, **10b**, and the metallomesogenic polymers **11a** and **11b**

Com- pound	$M_w^a$	$M_n^a$	PDI <sup>a</sup>	$\delta(^{29}\text{Si})^b$ (ppm)	Transition <sup>c</sup>	$T$ (°C)
<b>4</b>	$2.1 \times 10^5$	$9.6 \times 10^4$	2.2	-20.3	$T_g$	9
<b>5a</b>	$3.7 \times 10^4$	$1.8 \times 10^4$	2.1	-20.3 -5.6	$T_g$	9
<b>5b</b>	$8.7 \times 10^4$	$4.1 \times 10^4$	2.1	-20.3 -4.5	$T_g$	20
<b>10a</b>					C-I	89
<b>10b</b>					C-I I-N N-SmA	96 (84) (82)
<b>11a</b>	$3.8 \times 10^4$	$1.4 \times 10^4$	2.7	-20.3 -4.5	$T_g$ C-N	$\sim 30^d$ $\sim 36^d$
<b>11b</b>	$4.2 \times 10^4$	$1.7 \times 10^4$	2.5	-20.3 -4.5	N-D $T_g$ C-N N-D	$> 250^e$ $\sim 35$ 53 $> 250^e$

<sup>a</sup> Estimated by gel permeation chromatography (GPC) in THF using polystyrene standards.

<sup>b</sup>  $^{29}\text{Si}$ -NMR spectra were recorded in  $\text{CDCl}_3$ .

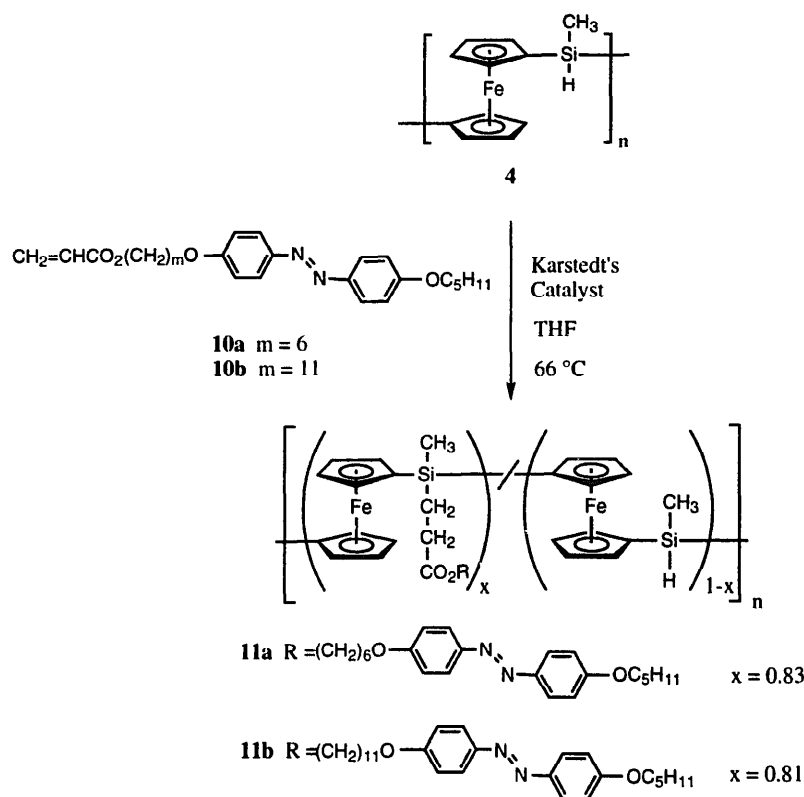
<sup>c</sup> The transition temperatures were measured by DSC at  $10^\circ\text{C}/\text{min}$ . Notation: glass transition ( $T_g$ ), smectic A (SmA), nematic (N), and isotropic (I) phases, and decomposition temperature (D).

<sup>d</sup> One broad peak was observed at  $\sim 36^\circ\text{C}$  during the first heating scan by DSC, and during the second heating scan only a  $T_g$  was observed at  $\sim 30^\circ\text{C}$ . This suggests the  $T_g$  and melting point are almost coincident.

<sup>e</sup> DSC suggests that decomposition begins around  $185^\circ\text{C}$  for **11a** and around  $170^\circ\text{C}$  for **11b**, although  $250^\circ\text{C}$  represents a temperature at which it becomes rapid.

prepare LC poly(ferrocenylsilanes) platinum-catalyzed hydrosilylation of **4** with **10a** and **10b** was explored (Scheme 3). Analysis of the orange polymers **11a** and **11b** by  $^1\text{H}$ -NMR again gave a hydrosilylation yield of around 80% for both polymers. The unreacted Si–H bonds were present in the resulting polymers, as indicated by infrared spectroscopy and by  $^{29}\text{Si}$  and  $^1\text{H}$ -NMR spectroscopy. The  $^1\text{H}$ -NMR spectrum of **11b** is shown in Fig. 2: the small resonance at ca. 5 ppm is assigned to unreacted Si–H groups.

The mesomorphic behavior of the azobenzene derivatives and the polymers was investigated by a combination of differential scanning calorimetry and polarized optical microscopy. Thus, on heating, polymer **11b** underwent a glass transition at  $35^\circ\text{C}$  followed by melting at  $53^\circ\text{C}$ ; polymer **11a** underwent a coincident glass transition and melting event at  $36^\circ\text{C}$  (Fig. 3). Following melting, a birefringent phase was found (Fig. 4) which was readily identified as a nematic phase on account of the characteristic flashing seen when the sample was subject to mechanical stress. Thus, the polymers melted at much lower temperatures than the free azobenzene groups and by comparing the transition temperature of



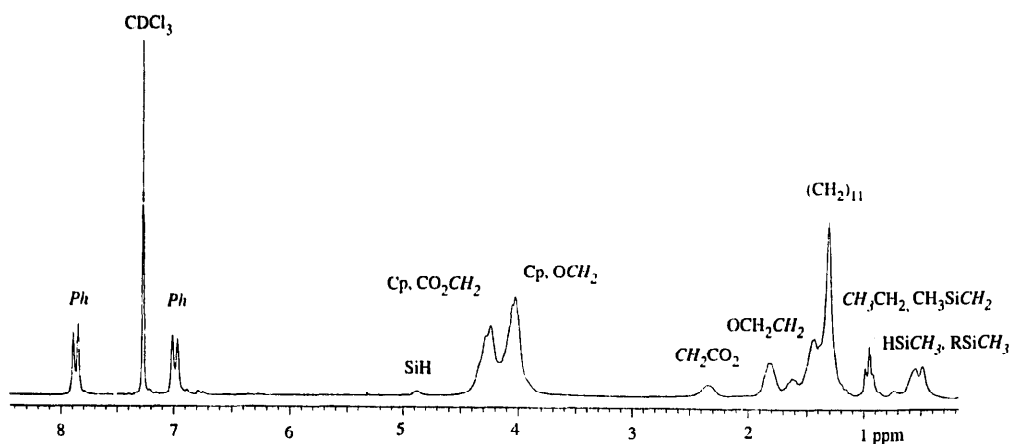
Scheme 3.

the two LC polymers **11a** and **11b**, it is apparent that as the number of carbon atoms in the flexible spacer is increased, the melting point increases. On further heating, the nematic phase was found to persist above 250°C, by which time decomposition of the sample was becoming rapid. By DSC, **11a** and **11b** showed broad exothermic transitions at 185 and 153°C, which did not correspond to any event observable by microscopy, and which we therefore suppose represented the onset of decomposition. The nature of the decomposition is,

however, unclear at present, as neither the parent, unfunctionalized polymer, nor the free azobenzene fragments, decomposed below 300°C. Table 1 shows the transition types, temperatures, and molecular weight and  $^{29}\text{Si}$ -NMR data.

### 2.3. Summary

We have reported the synthesis and mesogenic properties of two novel calamitic thermotropic side chain LC

Fig. 2.  $^1\text{H}$ -NMR spectrum (200 MHz,  $\text{CDCl}_3$ ) of poly(ferrocenylsilane) (**11b**).

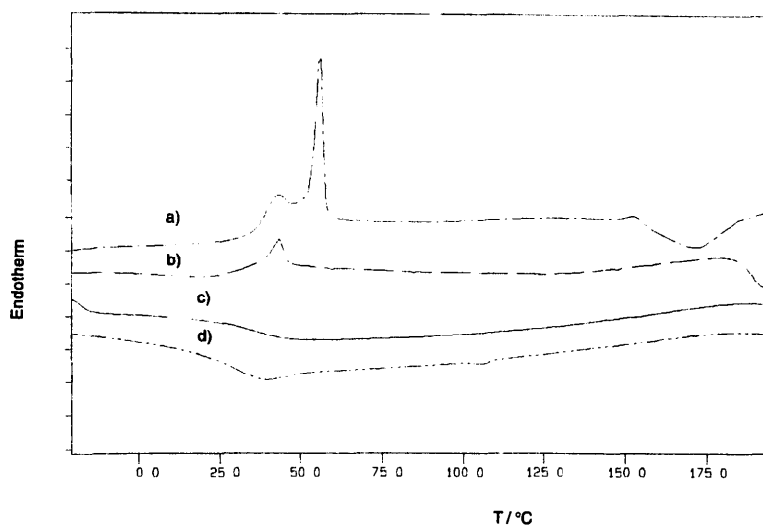


Fig. 3. Differential scanning calorimetry thermograms of polymers **11a** and **11b** (10°C/min): (a) the first heating of **11b**, (b) the first heating of **11a**, (c) the first cooling of **11a**, (d) the first cooling of **11b**.

polymers containing ferrocene in the backbone. The optical microscopy showed well-defined texture for the nematic phase. These functionalized poly(ferrocenylmethylsilanes) represent the first examples of calamitic thermotropic side chain LC polymers with ferrocene unit in the backbone. This synthetic route offers ample opportunities for structural variations and we are exploring these and the properties of the materials in detail. Of particular interest [23] is the detailed study of the LC properties in the three oxidation states accessible for

these materials (neutral, oxidized at alternate iron sites, and fully oxidized) [10].

### 3. Experimental details

#### 3.1. Materials

1.6 M butyllithium in hexanes, 1-hexene, ethyl acrylate, *p*-acetamidophenol, 1-bromopentane 6-chlorohexanol, 11-bromo-1-undecanol and acryloyl chloride

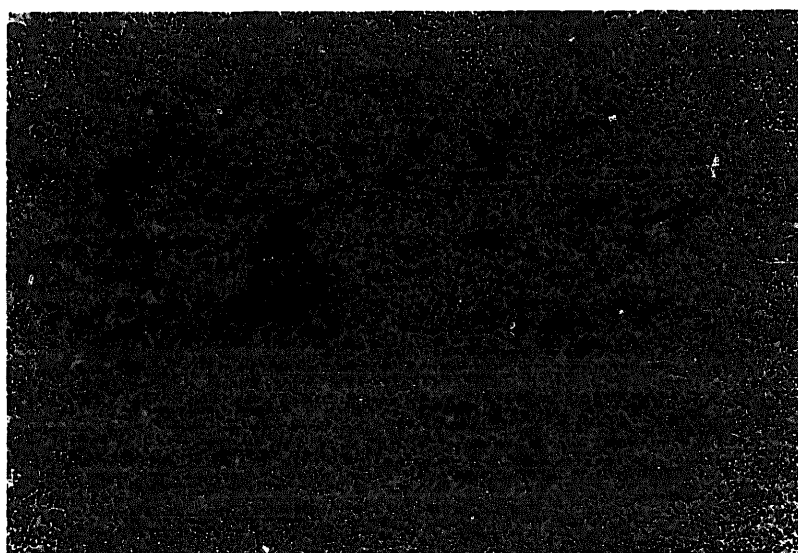


Fig. 4. Polarizing optical micrograph of poly(ferrocenylsilane) (**11b**) at 155°C.

were purchased from Aldrich. Dichloromethylsilane and platinum-divinyltetramethyldisiloxane complex 3% irxylene, 'Karstedt's catalyst', were obtained from United Chemical Technologies. Poly(ferrocenylmethylhydrosilane) was prepared as described previously [20].

### 3.2. Equipment

All reactions and manipulations were carried out under an atmosphere of prepurified nitrogen using either Schlenk techniques or an inert-atmosphere glove box (Vacuum Atmospheres) except for the purification of the polymers which was carried out in air. Solvents were dried by standard methods, distilled, and then stored under nitrogen over activated molecular sieves. The 200 or 400 MHz  $^1\text{H-NMR}$  spectra and 50.3 or 100.5 MHz  $^{13}\text{C-NMR}$  spectra were recorded on a Varian Gemini 200. NMR chemical shifts were referenced to residual protonated solvent peaks. Mass spectra were obtained with the use of a VG 70-250S mass spectrometer operating in an Electron Impact (EI) mode. Elemental analyses were performed by Quantitative Technologies, Whitehouse, NJ. Molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, ultrastraygel columns with a pore size between  $10^3$ – $10^5$  Å, and a Waters 410 differential refractometer. A flow rate of 1.0 ml/min was used and samples were dissolved in a solution of 0.1% tetra-*n*-butylammonium bromide in THF. Ten samples of monodisperse polystyrene in the range  $M_w = 10^3$ – $10^6$  were used as standards for calibration purposes. A Perkin-Elmer DSC-7 Differential Scanning Calorimeter equipped with a TAC 7 instrument controller was used to study the thermal behavior. The thermograms were calibrated with the melting transitions of decane and indium and were obtained at a heating rate of  $10^\circ\text{C}/\text{min}$  under dinitrogen. Polarizing microscopy was carried out with a polarizing microscope equipped with a Mettler FP82 hot stage and FP80 central processor.

### 3.3. Synthesis of poly(ferrocenylsilanes) **5a** and **5b**

Sample of poly(ferrocenylmethylhydrosilane) **4** (GPC:  $M_w = 2.1 \times 10^5$ ,  $M_n = 9.6 \times 10^4$ , PDI = 2.1).

**5a:** Dry THF (100 ml) was added to a two necked round bottom flask containing poly(ferrocenylmethylhydrosilane) (0.45 g, 2.0 mmol) and 1-hexene (0.22 g, 2.6 mmol). Karstedt's catalyst (5 mg, 25  $\mu\text{l}$ ) was then added by syringe. The mixture was refluxed under nitrogen for 8 d.  $^1\text{H-NMR}$  was used to follow the hydrosilylation reaction. After 3 d only a small amount of unreacted Si–H still existed. After a further 8 d no further decrease in the amount of unreacted Si–H bonds was apparent. The polymer product **5a** was purified by

precipitation from THF into dry hexanes twice and was isolated as deep-orange colored material. Yield 0.4 g (65%).

Polymer **5b** was prepared analogously in 68% yield using ethyl acrylate.

For **5a**:  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.45–0.6 (6H,  $\text{CH}_3$ –Si– $\text{CH}_2$  and  $\text{CH}_3$ –Si–H), 0.9 (5H, Si– $\text{CH}_2$  and  $\text{CH}_2\text{CH}_2$ ), 1.3–1.5 (8H,  $\text{CH}_2$ ), 4.0–4.4 (16H, Cp), 4.9 (1H, Si–H) ppm.  $^{13}\text{C-NMR}$  (50.3 MHz,  $\text{CDCl}_3$ )  $\delta$ : –3.8 ( $\text{CH}_3$ –Si–H), –2.2 ( $\text{CH}_3$ –Si– $\text{CH}_2$ ), 14.9 ( $\text{CH}_2\text{CH}_2$ ), 16.9 (Si– $\text{CH}_2$ ), 23.3 ( $\text{CH}_2\text{CH}_2$ ), 24.9 ( $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 32.3 (Si $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 34.1 (Si $\text{CH}_2\text{CH}_2\text{CH}_2$ ), 67.9 (C–Si–H), 68.2 (C–Si– $\text{CH}_2$ ), 71.8 (Cp), 71.96 (Cp), 71.99 (Cp), 72.2 (Cp), 72.4 (Cp), 72.6 (Cp), 74.1 (Cp), 74.3 (Cp), 74.9 (Cp) ppm.  $^{29}\text{Si-NMR}$  (79.8 MHz,  $\text{CDCl}_3$ )  $\delta$ : –5.6 (Si– $\text{CH}_2$ ), –20.3 (Si–H,  $^1J = 51$  Hz) ppm. IR (film) Si–H ( $2112\text{ cm}^{-1}$ ).

For **5b**:  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ )  $\delta$ : 0.46 (3H,  $\text{CH}_3$ –Si– $\text{CH}_2$ ), 0.55 (3H,  $\text{CH}_3$ –Si–H), 1.25 (5H, Si– $\text{CH}_2$  and  $\text{CH}_2\text{CH}_2$ ), 2.34 (2H,  $\text{CH}_2\text{CO}_2$ ), 4.0–4.2 (18H, Cp and  $\text{CO}_2\text{CH}_2$ ), 4.9 (1H, Si–H) ppm.  $^{13}\text{C-NMR}$  (50.3 MHz,  $\text{CDCl}_3$ )  $\delta$ : –3.9 ( $\text{CH}_3$ –Si–H), –2.7 ( $\text{CH}_3$ –Si– $\text{CH}_2$ ), 12.0 ( $\text{CH}_2\text{CH}_2$ ), 14.9 (Si– $\text{CH}_2$ ), 29.8 ( $\text{CH}_2\text{CO}_2$ ), 60.9 ( $\text{CO}_2\text{CH}_2$ ), 68.0 (C–Si–H), 70.3 (C–Si– $\text{CH}_2$ ), 72.2 (Cp), 72.3 (Cp), 72.4 (Cp), 73.9 (Cp), 74.1 (Cp), 74.2 (Cp), 74.6 (Cp), 74.8 (Cp), 74.9 (Cp), 175.3 ( $\text{CO}_2$ ) ppm.  $^{29}\text{Si-NMR}$  (79.8 MHz,  $\text{CDCl}_3$ )  $\delta$ : –4.5 (Si– $\text{CH}_2$ ), –20.3 (Si–H,  $^1J = 51$  Hz) ppm. IR (film) Si–H ( $2113\text{ cm}^{-1}$ ), C=O ( $1734\text{ cm}^{-1}$ ).

### 3.4. Synthesis of **10a** and **10b**

#### 3.4.1. *p*-Acetamidophenyl pentyl ether **6**: $\text{C}_5\text{H}_{11}\text{OC}_6\text{H}_4\text{NHCOCH}_3$

*p*-Acetamidophenol (35 g, 0.23 mol) and potassium hydroxide (25.76 g, 0.46 mol) were dissolved in a solution of water (233 ml) and absolute alcohol (467 ml) and stirred. 1-bromopentane (32 ml) was added to the solution and the resulting mixture was refluxed for 6 h. After cooling to room temperature, the alcohol and water were removed under vacuum and the residue was extracted with diethyl ether and washed with water, and then dried over solid  $\text{MgSO}_4$ . Diethyl ether was removed under vacuum. The crude product was recrystallized in absolute alcohol. A white crystalline product was obtained. Yield 23.4 g (64%), m.p.  $87$ – $89^\circ\text{C}$ .

#### 3.4.2. *p*-Aminophenyl pentyl ether **7**: $\text{C}_5\text{H}_{11}\text{OC}_6\text{H}_4\text{NH}_2$

To a solution of *p*-acetamidophenyl pentyl ether (3.02 g, 13.7 mmol) in ethanol was added 20% (dilute) sulphuric acid (60 ml) very slowly. The mixture was refluxed for overnight. The cold mixture was brought to pH  $\approx 10$ – $11$  by addition of dilute of sodium hydroxide solution (0.1 M). The mixture was extracted with diethyl ether and washed three times with water and dried with  $\text{CaCl}_2$ . The desired product was obtained as a

light-yellow oil by distillation at 130–132°C (0.05 mmHg). Yield 1.66 g (68%).

**3.4.3. 4-Hydroxy-4'-pentyloxyazobenzene 8:**  
 $C_5H_{11}OC_6H_4N_2C_6H_4OH$

*p*-Aminophenyl pentyl ether (12 g, 67 mmol) was dissolved in a solution of dilute hydrochloric acid. The solution was stirred and cooled to 0°C. Sodium nitrite (6.1 g, 3.4 M) water solution was added dropwise over period of 30 min to form the diazonium salt. A solution of phenol (9.3 g, 67.0 mmol) in sodium hydroxide (0.1 M) was prepared and cooled to 5°C in ice bath. The diazonium salt was added very slowly to the phenol solution. A red-brown colored solid precipitated out. The precipitate was filtered and recrystallized from glacial acetic acid to give deep red-brown crystals, m.p. 92–94°C. Yield 11.6 g (61%).

**3.4.4. 4-Pentoxy-4'-hydroxyhexyloxylazobenzene 9a:**  
 $C_5H_{11}OC_6H_4N_2C_6H_4O(CH_2)_6OH$

4-Hydroxy-4'-pentyloxyazobenzene (3.0 g, 11.0 mmol), 6-chlorohexanol (1.5 ml, 13.0 mmol) and potassium carbonate (3.1 g, 22.0 mmol) were dissolved in *n*-butanol (100 ml). The mixture was refluxed with vigorous stirring for 3 days. After cooling to room temperature the precipitate was filtered; the crude product was recrystallized from chloroform to give a orange-yellow needles, m.p. 114–116°C. Yield 3.04 g (75%). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 0.95 (t, 3H, -CH<sub>2</sub>CH<sub>3</sub>), 1.2–1.9 (m, 14H, alkyl), 3.6 (t, 2H, HOCH<sub>2</sub>), 4.0 (m, 4H, PhOCH<sub>2</sub>), 6.9 (d, 4H, pH) and 7.8 (d, 4H, pH) ppm. Anal. Calcd for C<sub>23</sub>H<sub>31</sub>N<sub>2</sub>O<sub>3</sub>: C 71.9, H 8.3, N 7.3; Found: C 71.7, H 8.1, N 7.4.

**3.4.5. 4-Pentoxy-4'-hydroxyundecyloxylazobenzene 9b:**  
 $C_5H_{11}OC_6H_4N_2C_6H_4O(CH_2)_{11}OH$

Compound **9b** was prepared by the same method of **9a** using 11-bromo-1-undecanol. Yield 5.79 g (58%), m.p. 114–116°C. <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ 0.9–1.84 (m, 27H, alkyl), 3.65 (t, 2H, HOCH<sub>2</sub>), 4.05 (m, 4H, OCH<sub>2</sub>), 7.0 (d, 4H, pH) and 7.86 (d, 4H, pH) ppm. Anal. Calcd for C<sub>28</sub>H<sub>42</sub>N<sub>2</sub>O<sub>3</sub>: C 74.0, H 9.3, N 7.3; Found: C 73.7, H 8.8, N 7.7.

**3.4.6. 4-Pentoxy-4'-(6-acryloyloxyhexyloxyl)azobenzene 10a:**  
 $C_5H_{11}OC_6H_4N_2C_6H_4O(CH_2)_6O_2CCH=CH_2$

To a well stirred solution of **9a** (3.0 g, 7.8 mmol) and triethylamine (0.79 g, 7.8 mmol) in THF under nitrogen cooled in a water-ice bath, was added acryloyl chloride (0.71 g, 24.8 mmol) was added very slowly. The mixture was refluxed for 6 h. After this time the solution was cooled to room temperature, THF was evaporated under vacuum, the residue was dissolved in dichloromethane, washed with water and with saturated NaCl solution and then dried with MgSO<sub>4</sub>. After recrystallization in dichloromethane, a yellow-orange powder was obtained. Yield 0.82 g (72%), m.p. 88.4–90.5°C.

For **10a**: IR:  $\nu_{max}$  1720 cm<sup>-1</sup> (C=O) and 1604 cm<sup>-1</sup> (CH<sub>2</sub>=CH). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ = 0.95 (t, 3H, *J* = 7.0, CH<sub>3</sub>), 1.3–1.56 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 1.67–1.83 (m, 6H, (CH<sub>2</sub>)<sub>3</sub>), 4.0 (t, 4H, *J* = 6.6 Hz, PhOCH<sub>2</sub>), 4.16 (t, 2H, *J* = 6.6 Hz, CO<sub>2</sub>CH<sub>2</sub>), 5.8 (dd, 1H, *J* = 1.8, 10.3, CH<sub>2</sub>=CH), 6.1 (dd, 1H, *J* = 10.3, 17.3 Hz, CH<sub>2</sub>=CH), 6.4 (dd, 1H, *J* = 1.7, 17.3 Hz, CH<sub>2</sub>=CH), 7.0 (m, 4H, Ph), 7.87 (m, 4H, Ph). <sup>13</sup>C-NMR (50.3 MHz, CDCl<sub>3</sub>) δ: 14.0, 22.5, 25.8, 28.2, 28.6, 29.0, 29.2, 64.5, 68.2, 68.4, 114.8, 124.4, 128.7, 130.5, 147.0, 161.2, 166.3 ppm. MS (EI): *m/e*: 438 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>26</sub>H<sub>34</sub>N<sub>2</sub>O<sub>4</sub>: C 71.2, H 7.8, N 6.4. Found: C 70.9, H 7.8, N 6.2.

**3.4.7. 4-Pentoxy-4'-(11-acryloyloxyundecyloxyl)azobenzene 10b:**  
 $C_5H_{11}OC_6H_4N_2C_6H_4O(CH_2)_{11}O_2CCH=CH_2$

Compound **10b** was prepared by using the same method of **10a**. Yield 0.84 g (75%), m.p. 94.5–96.1°C. IR:  $\nu_{max}$  1721 cm<sup>-1</sup> (C=O) and 1615 cm<sup>-1</sup> (C=C). <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ = 0.95 (t, 3H, *J* = 7.0 Hz, CH<sub>3</sub>), 1.42 (m, 18H, (CH<sub>2</sub>)<sub>9</sub>), 1.68 (m, 2H, CH<sub>2</sub>), 1.82 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>), 4.03 (t, 4H, *J* = 6.6 Hz, PhOCH<sub>2</sub>), 4.16 (t, 2H, *J* = 6.7 Hz, CO<sub>2</sub>CH<sub>2</sub>), 5.81 (dd, 1H, *J* = 1.8, 10.3, CH<sub>2</sub>=CH), 6.13 (dd, 1H, *J* = 10.3, 17.3 Hz, CH<sub>2</sub>=CH), 6.43 (dd, 1H, *J* = 1.7, 17.3 Hz, CH<sub>2</sub>=CH), 7.0 (m, 4H, Ph), 7.87 (m, 4H, Ph) ppm. <sup>13</sup>C-NMR (50.3 MHz, CDCl<sub>3</sub>) δ = 14.0, 22.5, 25.9, 26.1, 28.2, 28.7, 29.0, 29.2, 29.3, 29.4, 29.5, 64.7, 68.3, 114.6, 124.2, 128.6, 130.2, 146.9, 161.1, 166.2 ppm. MS (EI): *m/e*: 508 (M<sup>+</sup>, 100%). Anal. Calcd for C<sub>31</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>: C 73.2, H 8.7, N 5.5; Found: C 72.9, H 8.7, N 5.4.

**3.5. Synthesis of LC poly(ferrocenylsilanes) 11a and 11b**

**11a**: Dry THF (100ml) was added to a two-neck flask containing polymer **4** (0.3 g, 1.32 mmol) and compound **10a** (0.58 g, 1.32 mmol). Karstedt's catalyst (4 mg, 20 μl) was added into the flask by syringe. The reaction mixture was refluxed under nitrogen for 3 days. <sup>1</sup>H-NMR was used to follow the hydrosilylation reaction. After 3 days <sup>1</sup>H-NMR showed small amount unreacted Si–H bonds still existed. The product was purified by precipitating into dry hexanes twice. An orange-colored polymer was obtained. Yield 0.55 g (71%). GPC:  $M_w = 3.8 \times 10^4$ ,  $M_n = 1.4 \times 10^4$ , PDI = 2.7,  $T_g = \sim 30^\circ\text{C}$ . <sup>1</sup>H-NMR (200 MHz, CDCl<sub>3</sub>): δ = 0.4–0.65 (br m, 6H, CH<sub>3</sub>-Si-CH<sub>2</sub> and CH<sub>3</sub>-Si-H), 0.85–1.1 (m, 5H, CH<sub>3</sub>CH<sub>2</sub> and Si-CH<sub>2</sub>), 1.25–1.95 (br m, 14H, (CH<sub>2</sub>)<sub>7</sub>), 2.34 (br s, 2H, CH<sub>2</sub>CO<sub>2</sub>), 4.0–4.2 (br m, 22H, Cp, PhOCH<sub>2</sub> and CO<sub>2</sub>CH<sub>2</sub>), 4.9 (br s, 1H, Si-H), 6.95–7.1 (d, 4H, Ph), 7.85–8.0 (d, 4H, Ph) ppm. <sup>13</sup>C-NMR (50.3 MHz, CDCl<sub>3</sub>): δ = -3.9, -2.7, 11.4, 14.1, 22.5, 25.6, 26.0, 28.2, 28.7, 28.9, 29.1, 29.3, 29.4, 29.5, 31.5, 64.6, 67.9, 68.3, 71.5, 72.9, 73.0, 114.6,

124.2, 146.9, 161.0, 174.8 ppm.  $^{29}\text{Si-NMR}$  (79.8 MHz,  $\text{CDCl}_3$ )  $\delta = -4.5$  (Si- $\text{CH}_2$ ),  $-20.3$  (Si-H,  $^1J = 51$  Hz) ppm. IR:  $\nu_{\text{max}}$  2113  $\text{cm}^{-1}$  (Si-H), 1734  $\text{cm}^{-1}$  (C=O). The hydrosilylation yield was confirmed by  $^1\text{H-NMR}$  integration of the SiH resonance vs. the  $\text{CO}_2\text{CH}_2$  resonance.

Polymer **11b** was synthesized by using the same method as **11a** using mesogen **10b**. Yield = 0.47g (50%) GPC:  $M_w = 4.2 \times 10^4$ ,  $M_n = 1.7 \times 10^4$ , PDI = 2.5,  $T_g = 35^\circ\text{C}$ .  $^1\text{H-NMR}$  (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.4$ – $0.65$  (br m, 6H,  $\text{CH}_3$ -Si- $\text{CH}_2$  and  $\text{CH}_3$ -Si-H), 0.85–1.1 (m, 5H,  $\text{CH}_2\text{CH}_2$  and Si- $\text{CH}_2$ ), 1.25–1.9 (br m, 24H,  $(\text{CH}_2)_{12}$ ), 2.34 (br s, 2H,  $\text{CH}_2\text{CO}_2$ ), 4.0–4.2 (br m, 22H, Cp,  $\text{PhOCH}_2$  and  $\text{CO}_2\text{CH}_2$ ), 4.9 (br s, 1H, Si-H), 6.95–7.1 (d, 4H, Ph), 7.85–8.0 (d, 4H, Ph) ppm.  $^{13}\text{C-NMR}$  (50.3 MHz,  $\text{CDCl}_3$ ):  $\delta = -3.9$ ,  $-2.7$ , 11.9, 14.0, 14.1, 22.4, 22.6, 25.6, 26.0, 28.2, 28.7, 28.9, 29.1, 29.3, 29.4, 29.5, 29.6, 31.5, 64.5, 68.0, 67.9, 68.3, 71.5, 71.6, 73.5, 114.6, 124.2, 146.9, 161.1, 174.7 ppm.  $^{29}\text{Si-NMR}$  (79.8 MHz,  $\text{CDCl}_3$ ):  $\delta = -4.5$  (Si- $\text{CH}_2$ ),  $-20.3$  (Si-H,  $^1J = 51$  Hz) ppm. IR:  $\nu_{\text{max}}$  2113  $\text{cm}^{-1}$  (Si-H), 1734  $\text{cm}^{-1}$  (C=O). The hydrosilylation yield was confirmed by  $^1\text{H-NMR}$ .

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