Novel calamitic side-chain metallomesogenic polymers with ferrocene in the backbone: synthesis and properties of thermotropic liquid-crystalline poly(ferrocenylsilanes)

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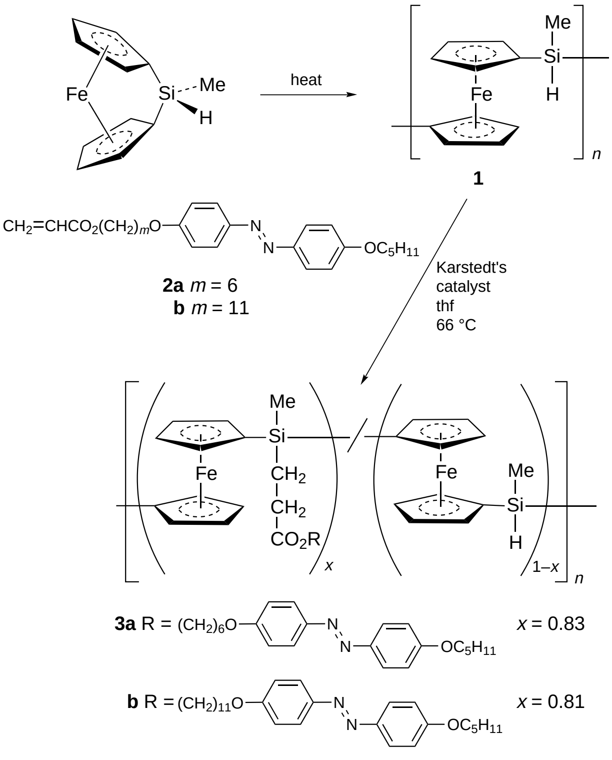
Novel thermotropic, metallomesogenic polymers with a poly(ferrocenylsilane) main chain and 4-pentoxy-4′-hydroxyhexanoxyazobenzene or 4-pentoxy-4′-hydroxyundecyloxyazobenzene acrylate side chains have been prepared; each material displays a nematic mesophase.

The study of the incorporation of metals into the structures of low molar mass liquid crystals with the aim of accessing novel physical properties is now a well established area of materials chemistry.[1,2] Metallomesogenic polymers 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.* colour, polarizability, magnetic characteristics).[3,4] Ferrocene units are of considerable interest as components of liquid-crystalline (LC) materials due to their high thermal stability, tunable redox characteristics and their structural variability which might lead to intriguing effects on mesophase morphology.[5] A range of low molecular mass 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] For example, thermotropic ferrocene-containing side-chain LC polymers have been prepared from ferrocene-containing monomers.[7a,b] Ferrocene-containing side chain LC polymers where the liquid crystallinity is derived from the organic mesomorphic monomers have also been reported.[7c] Although main-chain, LC polymers with ferrocene in the backbone are more common (*e.g.* main-chain polyester incorporating ferrocene units substituted at 1,1′-positions[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 difficult. Here, we report on the synthesis and thermal properties of the first side-chain metallomesogenic polymers with ferrocene units in the main chain. These materials were prepared by the functionalization of poly(ferrocenylmethylhydrosilane) and represent the first well characterized, liquid-crystalline poly(ferrocenylsilanes).

Recent work has shown that high molar mass poly(ferrocenylsilanes) are accessible *via* the ring-opening polymerization of silicon-bridged [1]ferrocenophane precursors.[9] To prepare side-chain LC poly(ferrocenylsilanes) a hydrosilylation strategy was used. First, poly(ferrocenylmethylsilane) **1** was synthesized by thermal ring-opening polymerization of the appropriate [1]ferrocenophane precursor.[10] Secondly, azobenzene-based mesogens, **2a** and **2b**,† were then attached to the backbone of polymer **1** *via* a platinum-catalysed hydrosilylation reaction (Scheme 1). Analysis of the orange polymers **3a** and **3b** by ^{1}H NMR gave a hydrosilylation yield of $>80\%$ for both polymers, although a significant amount of unreacted Si–H bonds was present in the resulting polymers, as indicated by IR and by ^{29}Si and ^{1}H NMR spectroscopy.‡

The mesomorphic behaviour of the azobenzene derivatives and the polymers was investigated by a combination of differential scanning calorimetry (DSC) and polarized optical microscopy. Thus, on heating, polymer **3b** underwent a glass transition at 35 °C followed by melting at 53 °C; polymer **3a** underwent a coincident glass transition and melting event at 36 °C (Fig. 1). Following melting, a birefringent phase was found which was readily identified as corresponding to a



Scheme 1

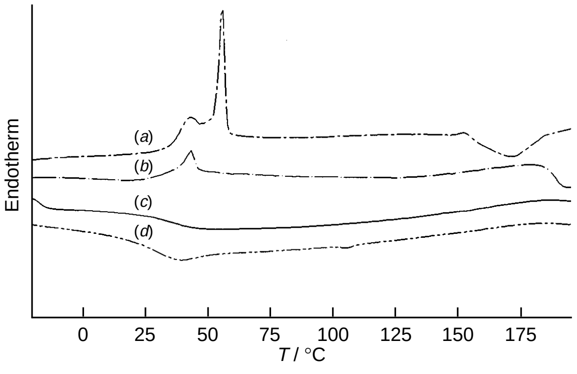


Fig. 1 Differential scanning calorimetry thermograms of polymers **3a** and **3b** (10 °C min^{-1}); (*a*) the first heating of **3b**, (*b*) the first heating of **3a**, (*c*) the first cooling of **3a**, (*d*) the first cooling of **3b**

nematic phase on account of the characteristic ‘flashing’ seen when the sample was subject to mechanical stress (although the ‘flashing’ was, of course, much slower than that normally observed in low molar mass systems on account of the much higher viscosity of the polymer). Thus, the polymers melted at much lower temperature than the free azobenzene groups and by comparing the transition temperature of the two liquid-crystal polymers **3a** and **3b**, 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, **3a** and **3b** 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. On cooling, **3a** and **3b** did not recrystallize. Table 1 shows the transition types, temperatures, molecular mass data and ^{29}Si NMR chemical shifts.

In conclusion, we have reported the synthesis and mesogenic properties of two novel calamitic thermotropic side-chain LC polymers containing ferrocene in the backbone. The optical microscopy showed a well defined texture for the nematic phase. These functionalized poly(ferrocenylmethylsilanes) represent the first examples of calamitic thermotropic side-chain LC polymers with ferrocene units in the backbone, and in particular, it is interesting to note that whereas the precursor mesogen **2a** is not liquid-crystalline, mesophase stabilization is apparent in polymer **3a**. 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[11] is the study of the liquid-crystal properties in the three oxidation states accessible for these materials (neutral, oxidised at alternate iron sites, and fully oxidised).[9]

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Table 1 Molecular masses, ^{29}Si NMR, thermal transition temperatures and assignments for **1**, **2a**, **2b** and the metallomesogenic polymers **3a** and **3b**

Compound	M_w[a]	M_n[a]	PDI[a]	$\delta(^{29}\text{Si})$[b]	Transition[c]	T/°C
1	2.1×10^5	9.6×10^4	2.2	−20.3	T_g	9
2a					K–I	89
2b					K–I	96
					(I–N)	(84)
					$(\text{N–S})_\text{A}$	(82)
3a	3.8×10^4	1.4×10^4	2.7	−20.3	T_g	*ca.* 30
				−4.5	K–N	*ca.* 36
					N–d	> 250[d]
3b	4.2×10^4	1.7×10^4	2.5	−20.3	T_g	35
				−4.5	K–N	53
					N–d	> 250[d]

[a] Estimated by gel permeation chromatography (GPC) in thf using polystyrene standards, PDI = M_w/M_n. [b] ^{29}Si NMR spectra were recorded in $CDCl_3$. [c] The transition temperatures were measured by DSC at 10 °C min^{-1}. Notation: crystal (K), glass transition (T_g), smectic A (S_A), nematic (N), and isotropic (I) phases, and decomposition temperature (d). [d] DSC suggests that decomposition begins around 185 °C for **3a** and around 153 °C for **3b**, although 250 °C represents a temperature at which it becomes rapid.

Footnotes

† The synthesis of **2a** and **2b** was achieved in five steps from *p*-acetamidophenol. The steps involved reaction with i, $n\text{-}C_5H_{11}Br$; ii, $H^+–H_2O$; iii, phenol, HCl and $NaNO_2$; iv, $HO(CH_2)_mBr$ and v, $CH_2CHCOCl$. Both compounds gave satisfactory IR, ^{1}H and ^{13}C NMR and mass spectra.

‡ **3a**: The catalyst $[Pt_2\{(\eta\text{-}CH_2{=}CHSiMe_2)O\}_3]$ (4 mg) in xylenes (20 μl) was added to a mixture of polymer **1** (0.3 g, 1.32 mmol) and compound **2a** (0.58 g, 1.32 mmol) in dry thf (100 ml). The reaction mixture was heated to reflux and ^{1}H NMR was used to follow the hydrosilylation reaction. After three days ^{1}H NMR showed that a small amount of unreacted Si–H bonds still existed. The product was purified by precipitation into hexanes twice. An orange coloured polymer was obtained. Yield 0.55 g (63%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.4–0.65 (br m, 6 H, CH_3SiCH_2 and CH_3SiH), 0.85–1.1 (m, 5 H, CH_3CH_2 and $SiCH_2$), 1.25 −1.95 [br m, 14 H, $(CH_2)_7$], 2.34 (br s, 2 H, CH_2CO_2), 4.0–4.2 (br m, 22 H, C_5H_4, CH_2OPh and CO_2CH_2), 4.9 (br s, 1 H, SiH), 6.95–7.1 (d, 4 H, Ph), 7.85–8.0 (d, 4 H, Ph). ^{13}C NMR (50 MHz, $CDCl_3$): 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. ^{29}Si NMR (79 MHz, $CDCl_3$) δ 4.5 ($SiCH_2$), −20.3 (SiH, $^1J_{SiH}$ 51 Hz). The hydrosilylation yield was confirmed by ^{1}H NMR.

3b was synthesised by using the same method as **3a**. Similar analytical data were obtained.

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