Ferrocene-containing thermotropic side-chain liquid-crystalline polymethacrylates

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The synthesis and mesomorphic properties of the title compounds, prepared by free-radical polymerization (or copolymerization) of a ferrocene-containing methacrylate monomer (with methylmethacrylate), are reported.

Metallomesogenic polymers represent an important field of current interest:[1] the combination of the properties of metals (polarisability, colour, magnetism) with those of polymers (processability) is expected to lead to anisotropic materials possessing unique characteristics which would be of particular interest for the design of new electro-optical devices.[1]

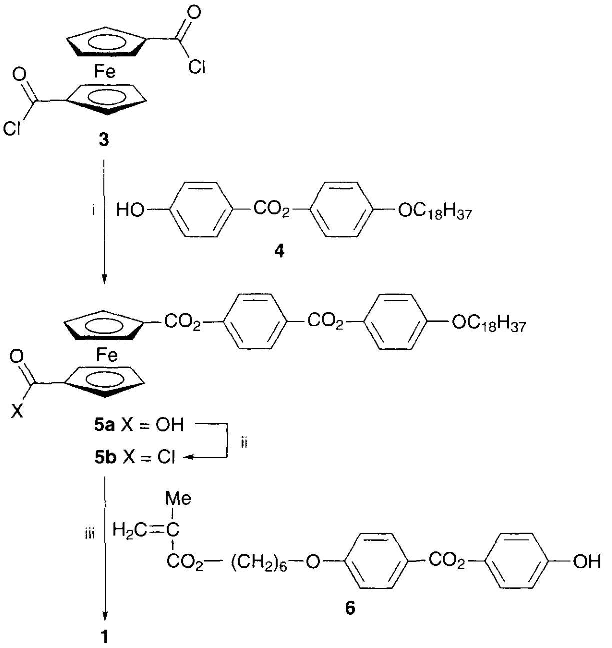
Recently we reported the first ferrocene-containing side-chain liquid-crystalline polymers which were synthesized by grafting vinyl-containing ferrocene momomers onto commercially available polyhydrosiloxanes.[2] The latter structures, which constituted the first liquid-crystalline polymers with appended organometallic units, showed high thermal stability, good solubility in organic solvents and broad enantiotropic mesophases. The observed results clearly demonstrated the great potential of ferrocene for elaborating polymeric architectures with essential properties.[1]

Obviously, better understanding and rationalization of the structure-mesomorphic properties relationship for ferrocene-containing liquid-crystalline polymers, and for metallomesogenic polymers in general, require the design and study of new systems.

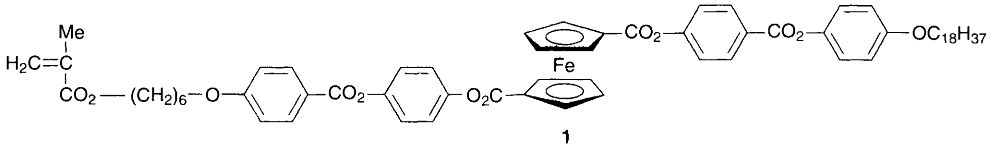
Here we report the synthesis and thermal properties of the methacrylate-containing monomer **1** and of side-chain polymethacrylates **2a–f**, which were prepared by polymerization of **1** (→ **2a**) or by copolymerization of **1** with methylmethacrylate (MMA) (→ **2b–f**).

Monomer **1** was prepared following a step-wise procedure we developed for synthesizing unsymmetrically disubstituted ferrocene derivatives[3] (Scheme 1). Treatment of ferrocene-1,1′-dicarboxylic acid chloride **3**,[4] with phenol intermediate **4**[5] gave the mono-acid **5a** [purified by column chromatography (silicagel, CH_2Cl_2/AcOEt 10 : 1 and then CH_2Cl_2/AcOEt/AcOH 100 : 10 : 1) and crystallization (EtOH/CH_2Cl_2); mp = 176–178 °C], which was subsequently converted into the carboxylic acid chloride **5b** [purified by extraction of the solid residue with hot light petroleum (bp 90–120 °C); mp = 104–105 °C]. Esterification of **5b** with the methacrylate derivative **6**[6] furnished the targeted monomer **1** [purified by column chromatography (silicagel, CH_2Cl_2) and crystallization (EtOH/CH_2Cl_2)]. The structure and purity of compounds **1** and **3–6** were confirmed by elemental analysis and ^1H NMR spectroscopy.

Homopolymer **2a** and statistical copolymers **2b–f** were prepared by free radical polymerization of the appropriate monomer(s) [degassed THF, AIBN (1 mol% with respect to the overall monomeric concentration), 50 °C, 60 h, Ar], and were purified by column chromatography[7] (silicagel, CH_2Cl_2), precipitated by adding the concentrated CH_2Cl_2 solution to



Scheme 1 *Reagents and conditions*: i, pyridine, benzene, reflux, 48%; ii, oxalyl chloride, pyridine, CH_2Cl_2, reflux, 98%; iii, Et_3N, CH_2Cl_2, reflux, 60%



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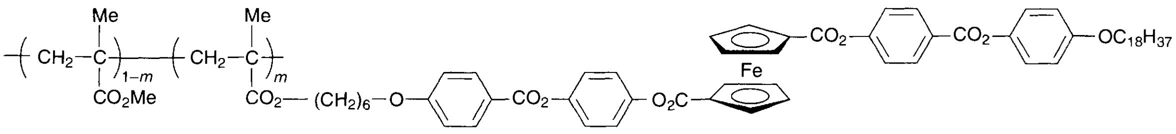

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MeOH and finally recovered by centrifugation (60% yield). Removal of unreacted monomers and oligomers was confirmed by gel permeation chromatography (GPC) (see note *c* in Table 1).

The thermal and liquid crystal properties of monomer **1** and polymers **2a–f** were investigated by polarized optical microscopy, differential scanning calorimetry (DSC) and X-ray diffraction studies. The molecular weight and molecular weights distribution of **2a–f** were determined by GPC (see note *c* in Table 1). The data are listed in Table 1.

The ferrocene derivative **1** exhibited an enantiotropic smectic A phase (C·117·S_A·130·I) which was identified by polarized optical microscopy from the formation of a focal-conic fan texture and homeotropic areas. This was confirmed by X-ray diffraction analysis which revealed two sharp reflections (in a 2 : 1 ratio) in the small angle region and a diffuse band in the wide angle region.

Polymers characterized by a narrow molecular weights distribution (M_w/M_n ranged from 1.3 to 1.5) were obtained after purification. This is of particular interest in view of developing processable materials. All of the polymers showed good solubility in organic solvents such as $CHCl_3$, CH_2Cl_2, THF and toluene. The monomer content within the copolymers, analysed by ^1H NMR spectroscopy, was in agreement with the initial monomeric ratio in solution.

With the exception of **2f**, all of the polymers showed mesomorphic behaviour when examined by polarized optical microscopy. However, no typical textures were observed, either on heating or on cooling from the isotropic state. This is often the case for polymers due to their high viscosity.[8]

By DSC, the isotropization temperature could be determined for **2a–e**; reversible transitions were obtained from successive heating–cooling cycles. However, during the first heating run, the temperature at which the mesomorphic state formed (T_{LC}) was not apparent from the thermograms and, therefore, required X-ray diffraction investigations.

Table 1 Phase transition temperatures[a] and analytical data of polymers **2**

Polymer	x^b	m^b	M_n^c	M_w^c	M_w/M_n	T_g^d/°C	T_{LC}^e/°C	T_i^d/°C
2a	1.00	1.00	74 800	111 300	1.5	30	100	210
b	0.90	0.88	63 400	81 700	1.3	40	105	201
c	0.80	0.78	47 500	60 500	1.3	40	105	192
d	0.60	0.58	57 000	75 800	1.3	40	105	176
e	0.40	0.38	42 000	53 000	1.3	40	105	143
f	0.10	0.12	64 300	99 500	1.5	80	101[f]	—

[a] *Tg* = glass transition temperature; T_{LC} = liquid-crystalline state formation; T_i = isotropization temperature. [b] *x* and *m* = molar fraction of monomer **1** in the feed and in the copolymers, respectively. [c] GPC data (THF, Ultrastyragel 10^3–10^4 Å, polystyrene standards). [d] DSC data (Mettler DSC 30 connected to a Mettler-TA 4000 processor; rate: 5 °C min^{-1}; under N_2; second heating run). [e] X-Ray data (transition obtained from the diffraction pattern registered with a curved counter 'Inel CPS 120' equipped with a bent quartz monochromator [Cu-$K\alpha_1$]; first heating run; approximate values). [f] Melting point (see text), determined by DSC from the first heating run.

X-Ray diffraction studies confirmed: (i) the liquid-crystalline character of polymers **2a–e**, (ii) the non-mesomorphic behavior of **2f** and (iii) revealed an amorphous character of **2a–e** below the liquid crystalline state during the first heating run.

In the case of **2a–e**, X-ray diffraction patterns gave two sharp peaks in the low-angle region (in a 2 : 1 ratio) and a diffuse peak in the wide-angle one. These data were consistent with the formation of disordered smectic phases (smectic C or smectic A phases). In order to gain further information about the nature of the mesophase(s), the *d*-layer spacing was determined as a function of temperature for **2a**: the *d*-layer spacing remained constant from 120 to 170 °C with an average value of 84.1 Å and then increased up to 89.5 Å near the clearing point. This behavior is an indication that **2a** might exhibit a smectic C phase. When cooled from the mesomorphic state to room temperature, **2a–e** solidified retaining the layered structure of the smectic phase. Therefore, the glass transition temperatures (*Tg*), which could be determined during the second heating run, corresponded to the transition between the glassy state and the liquid-crystalline phase.

The data reported in Table 1 emphasizes the role played by the MMA content in the polymeric structures. At low concentration, the MMA did not markedly influence the thermal properties of the polymers (compare **2a** and **2b**). An increase of the MMA concentration had no influence on the *Tg* and T_{LC} (compare **2b** and **2c–e**) but reduced the isotropization transition, the consequence of which was a reduction of the liquid-crystalline domain. This result was in agreement with the fact that **2f**, which contains 90% of MMA monomer, *i.e.* the highest percent of MMA of the described polymers, was found to be non-mesomorphic. Finally, polymers **2a–e** showed good thermal stability; no decomposition was observed in the liquid-crystalline state under the applied measurement conditions.

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