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Ferrocene-Containing Thermotropic Side-Chain Liquid-Crystalline Polymethacrylate from a Mesomorphic Trisubstituted Ferrocene Monomer

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ABSTRACT: The synthesis and mesomorphic properties of a methacrylate-containing ferrocene monomer bearing two flexible chains at the 1,1′-positions and the corresponding side-chain homopolymer are described. Both polymer and monomer showed enantiotropic smectic C and smectic A phases. The liquid-crystalline phases were fully characterized by means of X-ray diffraction experiments. Dilatometric measurements pointed to a head-to-tail molecular arrangement of the monomeric units within the smectic A phase. The results described in this report confirm that ferrocene-containing thermotropic side-chain liquid-crystalline polymethacrylates respresent a valuable family of metallomesogenic polymers.

Introduction

Ferrocene-containing thermotropic side-chain liquid-crystalline polysiloxanes[1] and polymethacrylates[2] obtained from either 1,1′- or 1,3-disubstituted ferrocene derivatives form a valuable class of metallomesogenic polymers (metal-containing liquid-crystalline polymers):[3] both structures showed good thermal stability, good solubility in common organic solvents, and pronounced mesomorphic character (enantiotropic smectic C and/or smectic A phases). The above polysiloxanes represented the first metallomesogenic polymers with appended mesogenic organometallic units. The corresponding mesomorphic vinyl (→polysiloxanes) and methacrylate (→polymethacrylates) ferrocene monomers, comprising two aromatic rings at each substitution position, were synthesized following a stepwise procedure we developed for preparing unsymmetrically disubstituted low molar mass liquid-crystalline ferrocene derivatives.[4] Grafting of the vinyl-containing monomer onto commercially available polyhydrosiloxanes and free-radical polymerization of the methacrylate-containing monomer were performed following conventional, well-established, literature procedures.[1,2]

Liquid-crystalline behavior has also been observed for polyacrylates prepared from monosubstituted ferrocene monomers containing a biphenyl system as a rigid rod.[5] Direct comparison with our own compounds is not straightforward because very different structures have been investigated in these studies. However, narrower mesomorphic ranges were observed for homopolymers prepared from the monosubstituted ferrocene monomers.[5] This behavior is in agreement with results obtained with low-molar-mass compounds which showed that large organic rods are required for generating favorable intermolecular interactions to thwart the steric repulsions resulting from the presence of the bulky ferrocene core.[6]

Owing to its unique electrochemical properties,[7] ferrocene represents a unit of choice for developing electroactive mesomorphic polymers. Interestingly, we have recently shown that electron transfer can be used to induce mesomorphism in the ferrocene−ferrocenium redox system.[8]

The three-dimensional structure[9] of ferrocene offers multiple possibilities for forming monomeric derivatives. Structural modifications of the ferrocene core could be used for tuning the liquid-crystalline properties of the polymers. To reach this goal, a better undestanding of the *structure* (of monomers and polymers)−*mesomorphic behavior* relationship has to be provided. In other words, further structures should be prepared and studied.

The purpose of this report is to present the synthesis and characterization of a new methacrylate-based liquid-crystalline ferrocene monomer **1** and the corresponding homopolymer **I** (Chart 1). The 1,1′,3-substitution pattern was selected to explore the influence of polysubstitution on the thermal and mesomorphic properties of side-chain polymers. Compounds **1** and **I** represent the first trisubstituted ferrocene-containing monomer and polymer reported so far.

Results and Discussion

Monomer Synthesis. The synthesis of monomer **1** is outlined in Scheme 1. The key intermediate, the trisubstituted ferrocene derivative **5**, was prepared in three steps from ferrocene (**2**). Acylation of **2** with octanoyl chloride gave diacyl **3**, the reduction of which led to dialkyl **4**. Treatment of the latter with $POCl_3$ and DMF furnished aldehyde **5**, which was transformed into the carboxylic acid derivative **6** by reaction with malonic acid. Esterification of **6** with hydroquinone monobenzyl ether gave ester **7**. Hydrogenation of the latter under standard conditions led to phenol intermediate **8**, which was condensed with 4-(benzyloxy)benzoic acid to give benzyl derivative **9**. Removal of the benzyl protective group under standard hydrogenation conditions yielded phenol **10**. Finally, esterification of **10** with methacrylate derivative **11**[10] gave the targeted monomer **1**. The latter was purified by column chromatography (silica gel; eluent, CH_2Cl_2/AcOEt 50:1). Its purity and structure were confirmed by ^1H NMR spectroscopy, mass spectrometry, and elemental analysis.

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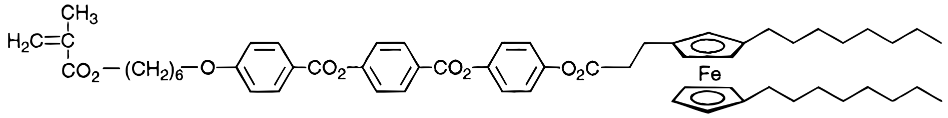
Chart 1



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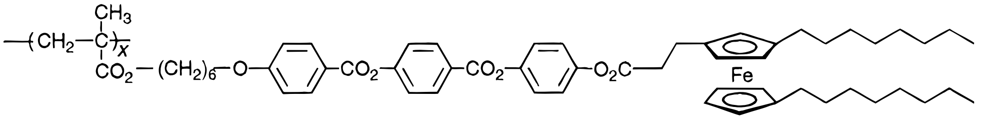


I

During the preparation of **5**, the 1,1′,2-trisubstituted derivative (see Chart 2) also formed in *ca*. 10% yield. The two isomers could be easily separated by column chromatography (silica gel; eluent, CH_2Cl_2/AcOEt 100:1): the 1,1′,2-trisubstituted ferrocene derivative eluted first followed by **5**. Their structures were identified by ^1H NMR spectroscopy (see Experimental Section) by analyzing the resonances of the three protons located on the disubstituted Cp ring. In the case of the 1,1′,3-isomer, protons $H_{2,4}$, which are *ortho* to the aldehyde function, are deshielded with respect to the one in the *meta* position (H_5). For the 1,1′,2-isomer, proton H_3, which is *ortho* to the aldehyde function, is deshielded with respect to the ones in *meta* positions ($H_{4,5}$). Additional proof was provided from NOESY experiments. For the 1,1′,2-isomer, a spatial coupling was observed between the proton of the aldehyde function and one proton of the CH_2 group connected to the Cp ring in position 1; as expected, this coupling was absent in the case of the 1,1′,3-isomer.

Polymer Synthesis. Polymer **I** was prepared in 61% yield by free-radical polymerization (THF, AIBN, 50 °C, 40 h, under argon) of monomer **1**. The polymer was purified by column chromatography (silica gel; eluent, CH_2Cl_2), as already described for other systems,[11] and precipitation in MeOH. The purity of **I** was confirmed by gel permeation chromatography (GPC), which revealed that unreacted monomer and oligomers were eliminated during the purification process. Polymer **I** was found to be soluble in common organic solvents such as THF, $CHCl_3$, and CH_2Cl_2. After purification, a polydispersity of 1.6 was obtained (Table 1).

Liquid-Crystalline Properties. The mesomorphic properties were investigated by a combination of polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction studies. The thermal and liquid-crystalline data of monomer **1** and polymer **I** are listed in Table 1.

Monomer. By DSC (second heating run), a T_g was obtained at −32 °C followed by an exotherm at 20 °C ($\Delta H = 22.9$ kJ mol^{-1}), indicating that cold crystallization occurred. Two endothermic peaks, indicative of mesomorphic behavior, were obtained at 32 and 88 °C.

Polarized optical miscroscopy supported the DSC data. Melting of the sample at 32 °C led to the formation of a smectic C phase, which transformed into a smectic A one at 55 °C. The transition at 88 °C corresponded to the isotropization temperature. No endotherm was detected by DSC at 55 °C, indicating a second-order character of the smectic C-to-smectic A transition. The mesophases were identified from their optical textures: the smectic C phase gave broken focal-conic and schlieren textures, and the smectic A phase presented a focal-conic texture and homeotropic areas.

The nature of the smectic C and smectic A phases was confirmed by X-ray diffraction analysis. Diffraction patterns typical of disordered smectic phases were recorded over the entire liquid-crystalline domain: a sharp diffraction peak was obtained at the small-angle region, and a diffuse one was detected at the wide-angle region.

Figure 1 shows the variation of the *d*-layer spacing as a function of temperature recorded on cooling the sample from the isotropic liquid. The *d*-layer spacing slightly increased from 52.0 (70 °C) to 52.5 Å (56 °C) and then decreased to 49.1 Å (30 °C). This behavior was in agreement with smectic A and smectic C phases.

From CPK molecular models, a molecular length L of *ca*. 49 Å was measured for **1** in the fully extended conformation. This value was significantly smaller than the *d*-layer spacing obtained within the smectic A phase (52.3 ± 0.2 Å at 60 °C).

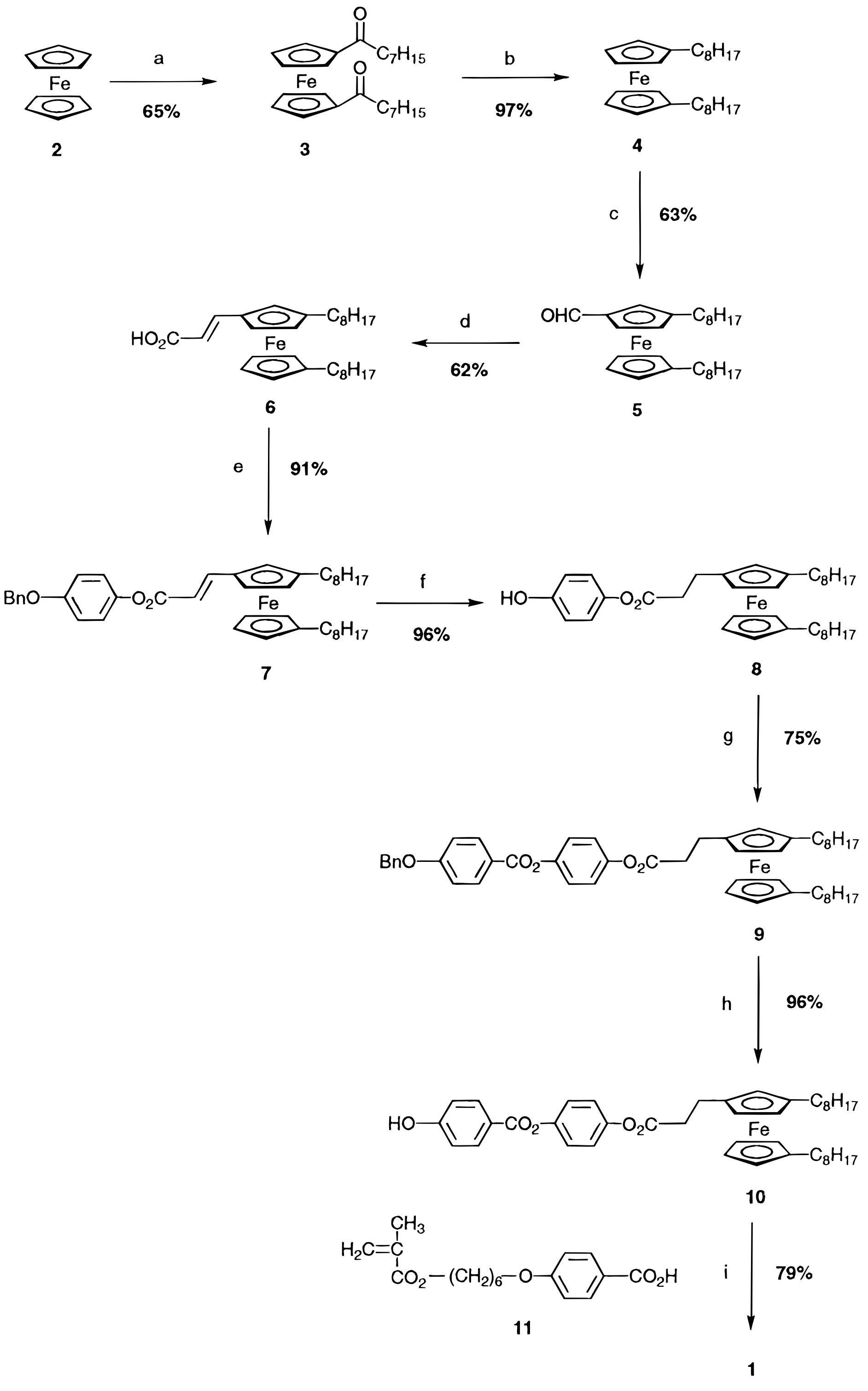
To explain the discrepancy between the two values (49 and 52.3 Å), high resolution dilatometric measurements[12] were carried out, and the molecular area S, which represents the ratio between the molecular volume and the *d*-layer spacing, was determined (Figure 2): a value of 28.0 Å^2 was obtained at 60 °C.

Within the smectic A phase, the molecular area S is equal to σ (average molecular area in a plane perpendicular to the director) and corresponds to the bulkiness of the rigid core. A reasonable assumption for the molecular organization within the smectic A phase is to consider an alernate up and down packing (Figure 3). Thus, the area occupied by two aromatic cores should be the same as the one occupied by three aliphatic chains. Therefore, the experimentally determined σ value has to be compared to the transverse area of 1.5 fully stretched molten aliphatic chains leading to a σ value of $1.5 \times 21.9 = 32.9$ Å^2 (the value $\sigma = 21.9$ Å^2 was obtained at 60 °C from specific volume measurements in liquid paraffins[12−14] and verified for terephthal-bis(4-n-decylaniline)[15]). The discrepancy between the two areas (28.0 and 32.9 Å^2) means that the actual aliphatic sublayer thickness is larger than the length of the stretched chains, which implies that the position of neighboring rigid cores is shifted along the director. Such an organization leads to a calculated overall layer thickness of 53.2 Å,[16] which is in good agreement with the experimental value (see above).

The presence in the X-ray patterns of a diffuse reflection centered at *ca*. 10.0−10.5 Å, in addition to the one centered at *ca*. 4.5−5.0 Å, indicated the presence of a repetition distance which corresponded to two molecular rows within the layers; this result confirms the alternate up and down packing presented in Figure 3.

X-ray patterns (Figure 4) of a sample which could be oriented by crossing the isotropic-to-smectic A transition

Scheme 1[a]



[a] (a) Octanoyl chloride, AlCl$_3$, CH$_2$Cl$_2$, reflux, 2 h. (b) LiAlH$_4$, AlCl$_3$, diethyl ether, 0 °C, 15 min. (c) DMF, POCl$_3$, CH$_2$Cl$_2$, reflux, 18 h. (d) Malonic acid, piperidine, pyridine, heat, 5.5 h. (e) Hydroquinone monobenzyl ether, *N*,*N'*-dicyclohexylcarbodiimide (DCC), 4-pyrrolidinopyridine (4-ppy), CH$_2$Cl$_2$, rt, 3 h. (f) H$_2$, Pd/C, CH$_2$Cl$_2$, rt, 10 h. (g) 4-(Benzyloxy)benzoic acid, DCC, 4-ppy, CH$_2$Cl$_2$, rt, 3 h. (h) H$_2$, Pd/C, CH$_2$Cl$_2$, rt, 20 h. (i) DCC, 4-ppy, CH$_2$Cl$_2$, rt, 3 h.

in a magnetic field of 1.4 T confirmed that both diffuse reflections corresponded to repetition distances within the layers (the arcs and circles being respectively the 4.5−5.0 and 10.0−10.5 Å reflections described above). By crossing the smectic A-to-smectic C transition, the director remained aligned in the field direction and the layer normal tilted from it. The tilt angles (ψ) could be determined from the X-ray pattern of the oriented sample; the values obtained were in agreement with those determined through the relation $\cos \psi = d_C/d_A$, d_C and d_A being the layer spacings in the smectic C and smectic A phases obtained from a powder sample. The variation of ψ as a function of temperature is given in Figure 5.

Polymer. By DSC (second heating run), two endotherms were detected at 154 and 185 °C. On cooling, reversible transitions were obtained.

Observation of **I** by POM supported the DSC data. A birefringent and viscous melt appeared above *ca.* 100 °C, the optical texture of which transformed at 154 °C, leading to homeotropic areas. The transition at 185 °C

Table 1. Properties of the Investigated Monomer and Polymer

Monomer **1**

phase transitions[a] (°C)			
T_g	K/S_C	S_C/S_A[b]	S_A/I
−32	32 (22.6)	55	88 (3.6)

Polymer **I**

analytical data[c]			phase transitions[a] (°C)		
M_w	M_n	M_w/M_n	T_g	S_C/S_A	S_A/I
100 000	63 000	1.6	*d*	154 (2.9)	185 (1.2)

[a] T_g = glass transition temperature, K = crystalline state, S_C = smectic C phase, S_A = smectic A phase, I = isotropic liquid; onset values taken from the second heating run; enthalpy changes of the monomer (in kJ mol^{-1}) and the polymer in J g^{-1}) are given in parentheses. [b] Determined by polarized optical microscopy. [c] Determined by gel permeation chromatography. [d] Not detected.

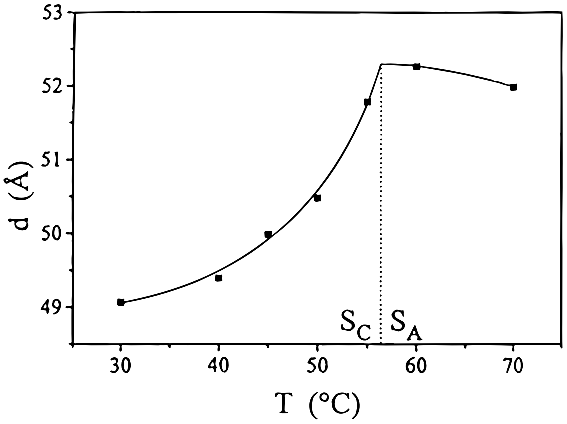


Figure 1. Variation of the *d*-layer spacing as a function of the temperature of monomer **1**.

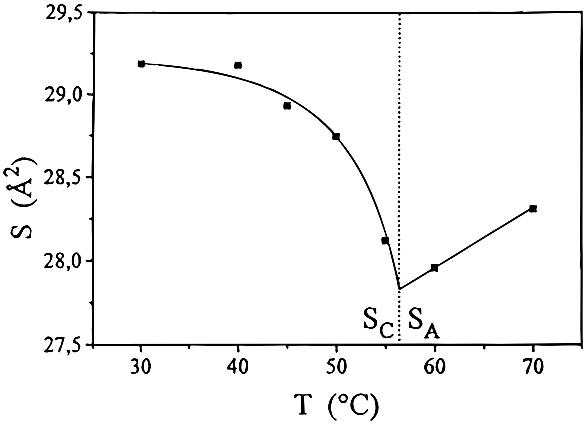


Figure 2. Variation of the molecular area as a function of the temperature of monomer **1**.

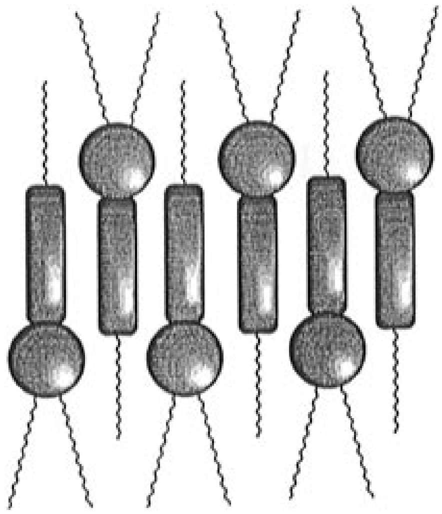


Figure 3. Schematic representation of the head-to-tail organization of monomer **1** within the smectic A phase.

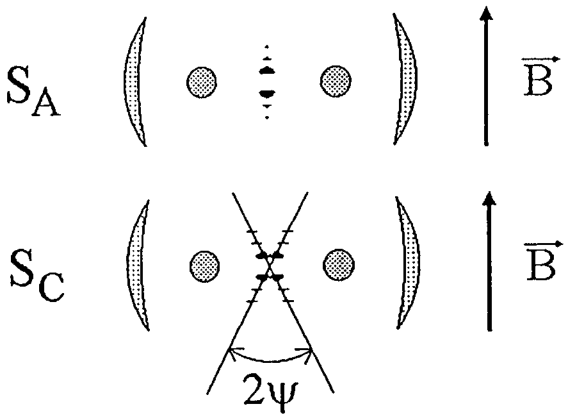


Figure 4. Schematics of the X-ray patterns obtained with an oriented sample of monomer **1** in the smectic A and smectic C phases ($\vec{B}$ is the direction of the magnetic field); see text for details.

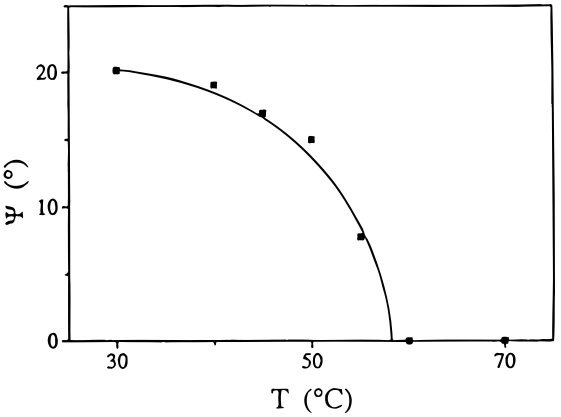


Figure 5. Variation of the tilt angle as a function of the temperature of monomer **1**.

corresponded to the clearing point. Therefore, POM indicated the formation of two liquid-crystalline phases (referred to as low- and high-temperature liquid-crystalline phase). When the sample was slowly cooled from the isotropic fluid, homeotropic and focal-conic textures were observed for the high-temperature liquid-crystalline phase, which was identified as a smectic A phase. Modification of the focal-conic texture was noticed on further cooling. However, the exact nature of the low-temperature liquid-crystalline phase could not be identified on the basis of POM examinations. This is often the case for viscous materials which do not allow typical liquid-crystalline textures to form.[17]

X-ray diffraction studies revealed a disordered smectic character for both mesophases: diffractograms consisting of two sharp peaks in the low-angle region and a diffuse one in the wide-angle region were recorded from 180 °C to room temperature. Therefore, the polymer retained the layered smectic organization at room temperature.

The variation of the *d*-layer spacing as a function of temperature was recorded on cooling the sample from the isotropic liquid (Figure 6). Two distinct regions were observed: the first one from the isotropic fluid to *ca.* 160 °C, in which the *d*-layer spacing increased to reach a maximum value of 67.5 Å, and a second one from 160

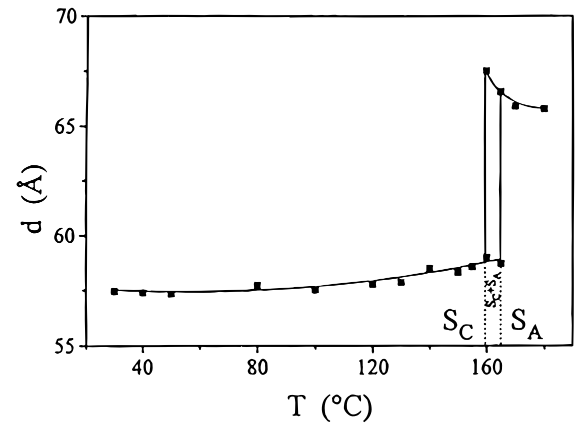


Figure 6. Variation of the *d*-layer spacing as a function of the temperature of polymer **I**.

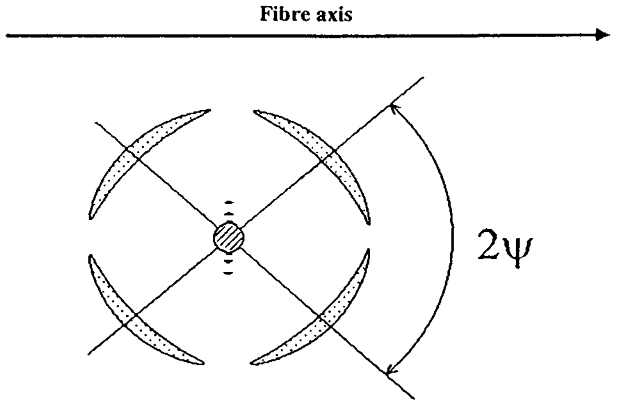


Figure 7. X-ray diffraction pattern of the smectic C phase of an oriented fiber polymer sample.

°C (59 Å) to 30 °C (57.5 Å), in which the *d*-layer spacing slightly decreased. The variation of the *d*-layer spacing indicated the presence of two smectic phases and confirmed the POM observations. Two *d*-values were obtained between 160 and 165 °C, revealing the coexistence of the two mesophases.

The temperature dependence of the *d*-layer spacing as a function of temperature strongly suggested that the low-temperature phase was smectic C in nature and the high-temperature phase was smectic A in nature. Contrary to monomer **1**, polymer **I** gave a first-order smectic C-to-smectic A transition.

The tilted nature of the low-temperature phase was confirmed from X-ray diffraction patterns recorded at room temperature for fibers pulled from the isotropic melt (near the clearing temperature) (Figure 7). The preferential stretching direction is parallel to the fiber axis and the layer normal perpendicular to the fiber axis. Consequently, the layer stacking reflections lie on a line perpendicular to the fiber axis and the diffuse reflections at *ca.* 4.5 Å lie on two lines tilted with respect to the fiber axis by the tilt angle between the director and the layer normal. Unfortunately, because of disorientation phenomena, no fiber patterns could be obtained above 80 °C.

Finally, the thermal stability of **I** was investigated by thermogravimetry. No decomposition was detected up to *ca.* 300 °C. Weight loss of 1, 5, and 10% was determined at 325, 345, and 352 °C, respectively.

The results described in the present report are of particular interest considering the current attention devoted to metallomesogenic polymers[3] and, in a more general sense, metallomesogens.[6,18] Firstly, a simple and efficient synthetic route was developed to synthesize 1,1′,3-trisubstituted ferrocene-containing liquid-crystalline monomers. Owing to the numerous substituents which can be used to derivatize the ferrocene unit,[6] such a substitution pattern leads the way to novel and most promising structures. Secondly, as compared to a previously published 1,1′-disubstituted methacrylate-containing ferrocene monomer (K/S_A, 117 °C; S_A/I, 130 °C),[2] compound **1** shows mesomorphic behavior near room temperature and a broad anisotropic range. This interesting combination of thermal and liquid-crytalline behavior is a consequence of the association of two flexible alkyl chains, which decrease the crystallization tendency, with a large organic rod, the presence of which is indispensable to thwart the steric repulsions of the bulky, three-dimensional, ferrocene core. Depression of transition temperatures consequent to the attachment of an alkyl chain to a ferrocene nucleus bearing a rigid organic rod was already observed (compare the thermal properties of monosubstituted ferrocene derivative **32** with those of corresponding alkyl derivatives **33** and **34** in ref 19) and is therefore in agreement with our own observations.

Polymer **I** has essential properties (good solubility in common organic media, good thermal stability, pronounced mesomorphic tendency) and makes such a structure an interesting material. The incorporation of **1** into a polymeric stucture strongly stabilized the liquid-crystalline phases (compare the clearing points of **1** and **I**). This result is in agreement with literature data.[20]

The results obtained for monomer **1** and polymer **I** and those we already reported[2] clearly prove that structural engineering can be used for tuning thermal and mesomorphic properties of ferrocene-containing monomers and related polymers. Finally, taking into account that the redox behavior of substituted ferrocene derivatives strongly depends on the nature and number of substitutents,[7] structural modifications can also be used to design mesomorphic polymers with tailor-made electroactive properties.

Conclusions

A trisubstituted methacrylate-containing mesogenic ferrocene monomer and the related side-chain liquid-crystalline homopolymer have been synthesized and their thermal and mesomorphic properties investigated by a combination of differential scanning calorimetry, polarized optical microscopy, thermogravimetry, and X-ray diffraction studies. Both monomer and polymer showed enantiotropic smectic C and smectic A phases. Owing to its three-dimensional structure, which offers multiple possibilities for forming derivatives by changing the nature, number, and position of the substituents, ferrocene is a promising organometallic unit for designing metallomesogenic polymers with tailor-made mesomorphic properties.

Experimental Section

Materials. Diethyl ether ($LiAlH_4$, under N_2), CH_2Cl_2 (P_2O_5, under N_2), and THF (sodium, benzophenone, under N_2) were distilled prior to use. Hydroquinone monobenzyl ether (Fluka, 99%), malonic acid (Fluka, 98%), *N*,*N*′-dicyclohexylcarbodiimide (Fluka, 99%), 4-pyrrolidinopyridine (Aldrich, 98%), anhydrous $AlCl_3$ (Fluka, 99%, puriss p.a.), $LiAlH_4$ (Fluka, 97%), DMF (SDS, analytical grade, 99.8%), $POCl_3$ (Fluka, 98%), octanoyl chloride (Fluka, 99%), and ferrocene (Chemische Betriebe Pluto/Veba Oel) were used as received. Pyridine (Fluka, 99.8%) and piperidine (Fluka, 99%) were stored on 4 Å molecular sieves. α,α′-Azoisobutyronitrile (Fluka, 98%) was crystallized from CH_3OH prior to use. 4-(Benzyloxy)benzoic acid was synthesized in two steps from methyl 4-hydroxybenzoate and benzyl bromide [(1) K_2CO_3, DMF, 120 °C for 3 h; crystallization from EtOH/THF. (2) Treatment in alkaline solution (KOH, EtOH/H_2O/THF), reflux, cooled to room temperature, acidified with HCl (5 N); crystallization from EtOH/hexane]. Methacrylate derivative **11** was synthesized following a literature procedure.[10]

Techniques. Column chromatography: silica gel 60 (0.060−0.200 mm, SDS). Transition temperatures (onset point) and enthalpies were determined with a differential scanning Mettler DSC 30 calorimeter connected to a Mettler TA 4000 processor, under N_2, at a rate of 10 °C min^{-1}; data treatment used Mettler TA72.2/.5 GRAPHWARE; for **1** and **I**, second heating run; for **3**, **7**, **9**, and **10**, first heating run. 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 conducted using a Zeiss-Axioscop polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage, under N_2. Gel permeation chromatography (GPC) was performed with a WATERS 510 instrument connected to a WATERS 410 differential refractometer (Ultrastyragel 10^3−10^4 columns calibrated with polystyrene standards; eluent, THF, 1 mL min^{-1}; $T = 35$ °C; treatment of data used Baseline 510 software). ^1H NMR spectra were recorded on a Varian GEMINI 200 spectrometer or a Bruker AMX 400 spectrometer, with the solvent as an internal standard. Mass spectra (chemical ionization, NH_3) were recorded on a Nermag R 30.10 spectrometer. Elemental analyses were done by Mikroelementaranalytisches Laboratorium ETH-Zurich or Ciba (Marly, Switzerland). Polymerization reactions were performed using Schlenk techniques under an inert Ar atmosphere.

X-ray Diffraction Studies. (a) Powder Samples. The crude powder was placed in Lindemann capillaries, and a linear monochromatic Cu-Kα 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.

(b) Oriented Samples. Fibers of the molten polymer were drawn (at a temperature close to the clearing point), bundled, and placed in a Lindemann capillary. For the monomer, the filled capillary was introduced into a magnetic field of 1.4 T and the sample was oriented by crossing many times the isotropic liquid-to-smectic A transition. The samples were illuminated by a pinhole Cu-Kα beam passing through a Ni-filter from a GX-20 Eliott rotating anode X-ray generator. The patterns were registered photographically, and the temperature was controlled within ±0.3 °C. Dilatometric measurements were performed with a high-precision home-made apparatus with an automatic computer-controlled operation, including data acquisition and temperature control within ±0.03 °C; relative variations of the specific volume could be detected with a resolution of 10^{-2}%, and its absolute value could be determined with an accuracy of 10^{-1}%.

Abbreviations. *N*,*N*′-Dicyclohexylcarbodiimide = DCC; 4-pyrrolidinopyridine = 4-ppy; dimethylformamide = DMF; α,α′-azoisobutyronitrile = AIBN.

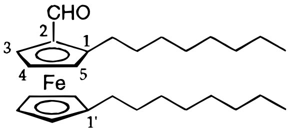
Synthesis. 1,1′-Dioctanoylferrocene (3). A mixture of $AlCl_3$ (53.2 g, 0.40 mol) and octanoyl chloride (63.5 g, 0.39 mol) in CH_2Cl_2 (500 mL) was added to a stirred solution of ferrocene (**2**) (37.2 g, 0.20 mol) in CH_2Cl_2 (750 mL). The mixture was stirred under reflux for 2 h, cooled to room temperature, and poured onto ice. The organic layer was separated, dried ($MgSO_4$), and evaporated to dryness. Purification of the residue by column chromatography (hexane/AcOEt 10:1) and crystallization from hexane gave pure **3** (57.0 g, 65%). $M_p =$ 60 °C. ^1H NMR (200 MHz, $CDCl_3$) δ 4.77 (t, 4 H, HCp), 4.48 (t, 4 H, HCp), 2.65 (t, 4 H, CH_2CO), 1.73−1.65 (m, 4 H, $C\mathit{H}_2$-CH_2CO), 1.59−1.31 (m, 16 H, aliphatic CH_2), 0.90 (t, 6 H, CH_3). Anal. Calcd for $C_{26}H_{38}O_2Fe$ (438.43): C, 71.23; H, 8.74. Found: C, 70.96; H, 8.62.

1,1′-Dioctylferrocene (4). To a suspension of $LiAlH_4$ (5.8 g, 0.15 mol) and diethyl ether (400 mL) cooled to 0 °C and kept under N_2 was added portionwise $AlCl_3$ (20.4 g, 0.15 mol). A solution of **3** (30.0 g, 0.068 mol) in diethyl ether (200 mL) was added. The mixture was stirred for 15 min and cautiously poured onto ice. The organic layer was separated and the aqueous phase extracted with diethyl ether. The organic layers were combined, washed successively with a saturated aqueous $NaHCO_3$ solution and a saturated aqueous NaCl solution, dried ($MgSO_4$), and evaporated to dryness. Purification of the residue by column chromatography (hexane) gave pure **4** (27.0 g, 97%, oil). ^1H NMR (200 MHz, acetone-d_6) δ 3.97 (s, 8 H, HCp), 2.35 (t, 4 H, CH_2Cp), 1.55−1.47 (m, 4 H, $C\mathit{H}_2CH_2Cp$), 1.30 (br s, 20 H, aliphatic CH_2), 0.89 (t, 6 H, CH_3).

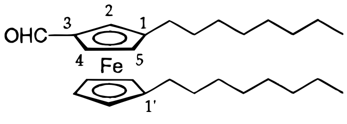
1,1′-Dioctylferrocene-3-carboxaldehyde (5). To a solution of **4** (22.0 g, 0.054 mol) in CH_2Cl_2 (150 mL) heated under reflux was added dropwise a solution of $POCl_3$ (20.5 g, 0.134 mol) and DMF (17.4 g, 0.238 mol) in CH_2Cl_2 (50 mL). The solution was stirred under reflux for 18 h, cooled to room temperature, and poured onto ice. K_2CO_3 (80 g) was added portionwise, and the mixture was stirred for 1 h. Diethyl ether (100 mL) was added and the organic layer separated. The aqueous phase was extracted with diethyl ether (2 × 50 mL). The organic layers were combined, washed with water, dried (Na_2SO_4), filtered, and evaporated to dryness. Purification of the residue by column chromatography (CH_2Cl_2/AcOEt 100:1) gave pure **5** (15.0 g, 63%, oil). ^1H NMR (400 MHz, $CDCl_3$) δ 9.87 (s, 1 H, CHO), 4.61 (dd, $J_o = 2.6$ Hz, $J_m = 1.3$ Hz, 1 H, H_4), 4.58 (t, $J_m = 1.3$ Hz, 1 H, H_2), 4.42 (dd, $J_o = 2.5$ Hz, $J_m =$ 1.5 Hz, 1 H, H_5), 4.09−4.04 (m, 4 H, HCp), 2.42−2.30 (m, 2 H, $C\mathit{H}_2Cp(CHO)$), 2.23 (m, 2 H, CH_2Cp), 1.56−1.48 (m, 2 H, $C\mathit{H}_2$-$CH_2Cp(CHO)$), 1.45−1.39 (m, 2 H, $C\mathit{H}_2CH_2Cp$), 1.37−1.25 (m, 20 H, aliphatic CH_2), 0.89 (t, 3 H, CH_3), 0.88 (t, 3 H, CH_3). MS: 439 (MH^+).

The 1,1′,2-isomeric compound (first fraction) was isolated in *ca.* 10% yield (oil). ^1H NMR (400 MHz, $CDCl_3$) δ 10.03 (s, 1 H, CHO), 4.63 (m, 1 H, H_3), 4.42 (m, 1 H, H_4), 4.40 (m, 1 H, H_5), 4.08−4.05 (m, 4 H, HCp), 2.76−2.68 (m, 1 H, $CH\mathit{H}Cp$-(CHO)), 2.51−2.44 (m, 1 H, $C\mathit{H}HCp(CHO)$), 2.21 (m, 2 H, CH_2-Cp), 1.54−1.26 (m, 24 H, aliphatic CH_2), 0.88 (t, 6 H, CH_3). MS: 439 (MH^+).

Chart 2



1,1',2-isomer



5

1,1',3-isomer

1,1′-Dioctylferrocene-3-*trans*-propenoic acid (6). A solution of **5** (12.0 g, 0.027 mol), malonic acid (4.2 g, 0.04 mol), and piperidine (25 drops) in pyridine (25 mL) was stirred at 55 °C for 4 h and at 110−120 °C for 1.5 h. The solution was poured onto a mixture of ice and water, and acidified with HCl (2 N). AcOEt was added and the organic layer separated, washed with H_2O, dried ($MgSO_4$), and evaporated to dryness. Purification of the residue by column chromatography (AcOEt) gave pure **6** (8.0 g, 62%, oil). ^1H NMR (200 MHz, $CDCl_3$) δ 7.62 (d, 1 H, vinylic proton), 5.96 (d, 1 H, vinylic proton), 4.32 (m, 2 H, HCp), 4.29 (m, 1 H, HCp), 4.01−3.94 (m, 4 H, HCp), 2.34 (m, 2 H, CH_2Cp(substituted by the vinylic function)), 2.22 (m, 2 H, CH_2Cp), 1.51−1.27 (m and br s, 24 H, aliphatic CH_2), 0.89 (t, 3 H, CH_3), 0.88 (t, 3 H, CH_3). MS: 481 (MH^+). Anal. Calcd for $C_{29}H_{44}O_2Fe$ (480.51): C, 72.49; H, 9.23. Found: C, 72.46; H, 9.40.

4-(Benzyloxy)phenyl 1,1′-Dioctylferrocene-3-*trans*-propenoate (7). A solution of **6** (4.0 g, 8.3 mmol), hydroquinone monobenzyl ether (2.0 g, 10 mmol), DCC (1.85 g, 8.96 mmol), and 4-ppy (0.13 g, 0.88 mmol) in CH_2Cl_2 (35 mL) was stirred at room temperature for 3 h. The mixture was filtered and evaporated to dryness. Purification of the residue by column chromatography (CH_2Cl_2) gave pure **7** (5.0 g, 91%). An analytically pure sample was obtained by crystallization from hexane. $M_p = 63$ °C. ^{1}H NMR (200 MHz, acetone-d_6) δ 7.67 (d, 1 H, vinylic proton), 7.53−7.33 (m, 5 H, aromatic protons, benzyl), 7.07 (m, 4 H, aromatic protons), 6.20 (d, 1 H, vinylic proton), 5.14 (s, 2 H, CH_2Ph), 4.56 (m, 2 H, HCp), 4.40 (m, 1 H, HCp), 4.09−3.98 (m, 4 H, HCp), 2.43 (m, 2 H, CH_2Cp-(substituted by the vinylic function)), 2.29 (m, 2 H, CH_2Cp), 1.61−1.30 (m and br s, 24 H, aliphatic CH_2), 0.89 (t, 3 H, CH_3), 0.87 (t, 3 H, CH_3). MS: 663 (MH^+). Anal. Calcd for $C_{42}H_{54}O_3Fe$ (662.73): C, 76.12; H, 8.21. Found: C, 76.28; H, 8.17.

4-Hydroxyphenyl 1,1′-Dioctylferrocene-3-propanoate (8). A mixture of **7** (4.8 g, 7.24 mmol), Pd(10%)/C (0.5 g), and CH_2Cl_2 (200 mL) was stirred at room temperature under 4.8 bar of H_2 for 10 h. The mixture was filtered and the solvent evaporated to dryness. Purification of the residue by column chromatography (AcOEt) gave pure **8** (4.0 g, 96%, oil). ^{1}H NMR (200 MHz, acetone-d_6) δ 8.40 (s, 1 H, OH), 6.94−6.80 (m, 4 H, aromatic protons), 3.99−3.94 (m, 7 H, HCp), 2.73 (m, 4 H, $CH_2CH_2CO_2$), 2.36 (t, 2 H, CH_2Cp), 2.32 (t, 2 H, CH_2Cp), 1.55−1.30 (m and br s, 24 H, aliphatic CH_2), 0.89 (t, 6 H, CH_3). MS: 575 (MH^+). Anal. Calcd for $C_{35}H_{50}O_3Fe$ (574.62): C, 73.16; H, 8.77. Found: C, 73.17; H, 8.85.

4-((4-(Benzyloxy)benzoyl)oxy)phenyl 1,1′-Dioctylferrocene-3-propanoate (9). A solution of **8** (4.0 g, 7.0 mmol), 4-(benzyloxy)benzoic acid (1.7 g, 7.4 mmol), DCC (1.54 g, 7.46 mmol), and 4-ppy (0.11 g, 0.74 mmol) in CH_2Cl_2 (100 mL) was stirred at room temperature for 3 h. The mixture was filtered and evaporated to dryness. Purification of the residue by column chromatography (CH_2Cl_2) and crystallization from CH_2Cl_2/EtOH gave pure **9** (4.1 g, 75%). $M_p = 73$ °C. ^{1}H NMR (200 MHz, acetone-d_6) δ 8.15 (d, 2 H, aromatic protons), 7.55−7.17 (series of m, 11 H, aromatic protons), 5.29 (s, 2 H, CH_2-Ph), 4.02−3.94 (m, 7 H, HCp), 2.78−2.72 (m, 4 H, $CH_2CH_2CO_2$), 2.38 (t, 2 H, CH_2Cp), 2.37 (t, 2 H, CH_2Cp), 1.55−1.31 (m and br s, 24 H, aliphatic CH_2), 0.88 (t, 6 H, CH_3). MS: 785 (MH^+). Anal. Calcd for $C_{49}H_{60}O_5Fe$ (784.86): C, 74.99; H, 7.71. Found: C, 75.02; H, 7.63.

4-((4-Hydroxybenzoyl)oxy)phenyl 1,1′-dioctylferrocene-3-propanoate (10). A mixture of **9** (4.0 g, 5.1 mmol) and Pd-(10%)/C (0.4 g) in CH_2Cl_2 (150 mL) was stirred at room temperature under 4.8 bar of H_2 for 20 h. The mixture was filtered and evaporated to dryness. Purification of the residue by column chromatography (CH_2Cl_2/AcOEt 10:1) and crystallization from hexane/EtOH gave pure **10** (3.4 g, 96%). $M_p = 55$ °C. ^{1}H NMR (200 MHz, acetone-d_6) δ 8.06 (d, 2 H, aromatic protons), 7.30 (d, 2 H, aromatic protons), 7.19 (d, 2 H, aromatic protons), 7.01 (d, 2 H, aromatic protons), 4.02−3.94 (m, 7 H, HCp), 2.90−2.72 (m, 4 H, $CH_2CH_2CO_2$), 2.38 (t, 2 H, CH_2Cp), 2.34 (t, 2 H, CH_2Cp), 1.55−1.31 (m and br s, 24 H, aliphatic CH_2), 0.88 (t, 6 H, CH_3). MS: 694 (M^+). Anal. Calcd for $C_{42}H_{54}O_5Fe$ (694.73): C, 72.61; H, 7.83. Found: C, 72.58; H, 7.82.

4-[[4-[[4-[[6-[(2-methyl-1-oxo-2-propenyl)oxy]hexyl]oxy]-benzoyl]oxy]benzoyl]oxy]phenyl 1,1′-Dioctylferrocene-3-propanoate (1). A solution of **10** (3.1 g, 4.5 mmol), **11** (1.5 g, 4.9 mmol), DCC (1.03 g, 5.0 mmol), and 4-ppy (75 mg, 0.5 mmol) in CH_2Cl_2 (40 mL) was stirred at room temperature for 3 h. The mixture was filtered and evaporated to dryness. Purification of the residue by column chromatography (CH_2Cl_2/AcOEt 50:1) gave pure **1** (3.5 g, 79%). ^{1}H NMR (200 MHz, acetone-d_6) δ 8.29 (d, 2 H, aromatic protons), 8.16 (d, 2 H, aromatic protons), 7.53 (d, 2 H, aromatic protons), 7.38 (d, 2 H, aromatic protons), 7.22 (d, 2 H, aromatic protons), 7.14 (d, 2 H, aromatic protons), 6.07 (m, 1 H, vinylic proton), 5.61 (m, 1 H, vinylic proton), 4.18 (t, 2 H, CH_2O_2C or CH_2OPh), 4.16 (t, 2 H, CH_2O_2C or CH_2OPh), 4.02−3.94 (m, 7 H, HCp), 2.81−2.73 (m, 4 H, $CH_2CH_2CO_2$), 2.38 (t, 2 H, CH_2Cp), 2.34 (t, 2 H, CH_2Cp), 1.92 (m, 3 H, $CH_3C{=}C$), 1.91−1.71 (2 m, 4 H, CH_2-CH_2OPh and C$H_2CH_2O_2C$), 1.59−1.31 (m and br s, 28 H, aliphatic CH_2), 0.89 (t, 6 H, CH_3). MS: 982 (M^+), 983 (MH^+). Anal. Calcd for $C_{59}H_{74}O_9Fe$ (983.07): C, 72.08; H, 7.59. Found: C, 71.98; H, 7.51.

Preparation of Polymer I. A solution of monomer **1** (0.983 g, 1.0 mmol) and AIBN (1.64 mg, 0.01 mmol) in THF (5 mL) was stirred for 40 h at 50 °C in a thermostated bath. The solution was evaporated to dryness. Purification of the residue by column chromatography (CH_2Cl_2) and by precipitation from MeOH gave pure **I** (0.60 g, 61%), as a yellow solid. Anal. Calcd for $(C_{59}H_{74}O_9Fe)_n$: C, 72.08; H, 7.59. Found: C, 72.07; H, 7.59.

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