Ferrocene- and Fullerene[60]-Containing Liquid-Crystalline Materials

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Abstract. This paper shows the versatility of ferrocene and fullerene for the design of thermotropic liquid-crystalline materials: *i*) the electrochemical properties of the ferrocene-ferrocenium system were exploited to design redox-active metallomesogens (**1** and **2**); *ii*) ferrocene-containing side-chain liquid-crystalline polysiloxane (**3**) and polymethacrylates (**5** and **6**) were synthesized by grafting a mesomorphic vinyl-ferrocene monomer (**4**) onto commercially available polysiloxane and by free-radical polymerization of mesomorphic methacrylate-ferrocene monomers (**7** and **8**), respectively; *iii*) a first-generation ferrocene-containing liquid-crystalline dendrimer (**9**) was synthesized; and *iv*) liquid-crystalline fullerene (**10**) and mixed fullerene-ferrocene (**11**) derivatives were obtained by functionalizing the C_{60} core with a twin cholesterol moiety.

Introduction

Organized molecular assemblies, referred to as supramolecular materials, resulting from the non-covalent association of molecular units, (*e.g.*, thermotropic and lyotropic liquid crystals, micelles, mono- and multi-layers and membranes) have generated enthusiastic studies at the frontiers of chemistry, physics, biology, and materials science [1]. These systems are of interest, firstly, to explore and understand better specific properties at the molecular level, and, secondly, to design efficient materials for advanced technologies, *i.e.*, the nanometer-scale technologies.

Among the above-mentioned organized molecular assemblies, thermotropic liquid crystals [2] play a crucial role in everyday life as they have found widespread applications in the manufacture of, *e.g.*, watches, calculators, mobile telephones, and notebook computers [3]. Further applications are expected in the future. Achievement of this goal requires the design of liquid-crystalline materials with novel properties. Incorporation of active subunits into liquid crystals should give rise to such new, highly efficient materials, which will combine the properties of

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the subunits with those of liquid crystals (organization, anisotropy). A family of materials illustrating this concept are metallomesogens (metal-containing liquid crystals) [4] and metallomesogenic polymers (metal-containing liquid-crystalline polymers) [5]: introduction of metals, acting as subunits, into mesogenic structures allows exploitation of the metal properties (electroactivity, color, polarizability, magnetism, catalytic behavior) within liquid-crystalline assemblies [4][5].

Our interest in organometallic and materials chemistry motivated us to design ferrocene-containing thermotropic liquid crystals [6]. Ferrocene is a candidate of choice to elaborate thermotropic liquid-crystals owing to its: *i*) three-dimensional structure which offers numerous possibilities for the synthesis of multiple derivatives by selecting the nature, number, and positions of the substituents (liquid-crystalline properties could be tuned by means of the synthesis), *ii*) good solubility in common organic solvents (making possible the use of usual techniques for the syntheses, purifications, and characterizations), *iii*) high thermal stability, and *iv*) electrochemical behavior (fast and reversible one-electron transfer process). Its redox activity may be used to develop switchable liquid-crystalline devices.

During the course of our activity devoted to thermotropic liquid crystals, fullerene[60] (C_{60}), which combines a most aesthetic structure associated with remarkable magnetic, optical, and redox proper-

ties, held our attention: the construction of mesomorphic materials from this compound is attractive in the light of the intense efforts currently focused on the design of fullerene-based materials [7]. Interestingly, fullerene derivatives were introduced into membranes [8] and organized into *Langmuir* and *Langmuir-Blodgett* films [9].

In this contribution, we present recent results on the design of ferrocene- and fullerene-containing thermotropic liquid crystals. In the case of ferrocene, we limit the description to material-related systems, *i.e.*, redox-active liquid crystals [10], side-chain liquid-crystalline polymers [11] [12], and liquid-crystalline dendrimers [13]. As for C_{60}, we present two examples: an organic-type fullerene-containing liquid crystal [14] and a mixed fullerene-ferrocene derivative [15].

Redox-Active Ferrocene-Containing Thermotropic Liquid Crystals

Ferrocene has found interesting applications as an electroactive building block for elaborating switchable molecular aggregates [16], redox-active receptors [17], redox-active polymeric ionomers [18], and conducting and magnetic materials [19]. With the aim of developing electroactive liquid-crystalline materials, we synthesized ferrocene derivative **1** [10]: a per-alkylated ferrocene unit was selected as an electron donor because of the ease of oxidation of such species in comparison with less substituted structures [19]. No liquid-crystalline behavior was detected for **1** (melting point: 154°). Ferrocenium derivative **2** was obtained by chemical oxidation of **1** with silver tosylate. Thermal analysis of **2** revealed an interesting behavior: when heated, **2** melted at 132° into an isotropic liquid. On cooling from the melt, a smectic A phase formed at 83°. No crystallization was observed for **2**; a glass transition temperature (Tg) was detected at *ca.* 37°.

The different thermal behavior observed between **1** (neutral species) and **2** (ionic compound) can be explained in terms of structural considerations. The absence of mesomorphic properties for **1** is due to the presence of the bulky ferrocene unit which makes intermolecular interactions too weak to generate mesomorphism. This behavior is in agreement with literature data obtained for other ferrocene derivatives [6], and, in a general sense, for materials incorporating a bulky unit in their structure [4]. In the case of **2**, favorable electrostatic interactions can

compensate, at least in part (the mesophase is monotropic), the unfavorable influence of the bulky ferrocene core, resulting in the formation of a liquid-crystalline phase.

The above example shows that electron transfer can be exploited in the ferrocene-ferrocenium redox system to design electroactive metallomesogens. The possibility of inducing and controlling mesomorphism is attractive for the elaboration of switchable anisotropic materials.

Ferrocene-Containing Thermotropic Side-Chain Liquid-Crystalline Polymers

Prior to our first publication on ferrocene-based metallomesogenic polymers [11a], only one report on ferrocene-containing liquid-crystalline polymers was known [20]. These materials (main-chain polyesters incorporating the ferrocene unit in their backbone) showed limited proper-

ties: a nematic melt was observed at elevated temperatures (isotropization temperatures were not reported because of thermal degradation); furthermore, these compounds were found to be insoluble in most solvents. The low solubility and poor thermal stability of these polymers is most likely due to the presence of a large number of unreacted end groups (carboxylic-acid chlorides and phenols) because of their oligomeric nature.

We turned our attention to side-chain polysiloxanes [11] and polymethacrylates [12] in which the ferrocene units are appended to the polymer backbone. We anticipated that such polymers could be prepared from vinyl- and methacrylate-containing ferrocene monomers, respectively, following well-established procedures developed for organic monomers. Two synthetic strategies can be applied to prepare ferrocene-containing side-chain liquid-crystalline polymers: *i*) by copolymerizing a non-mesomorphic ferrocene
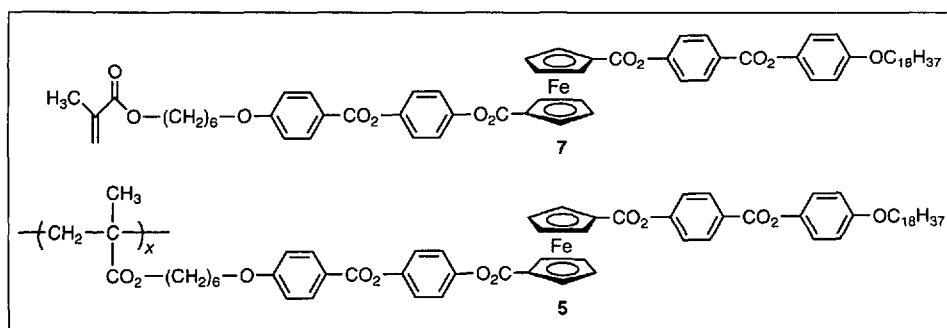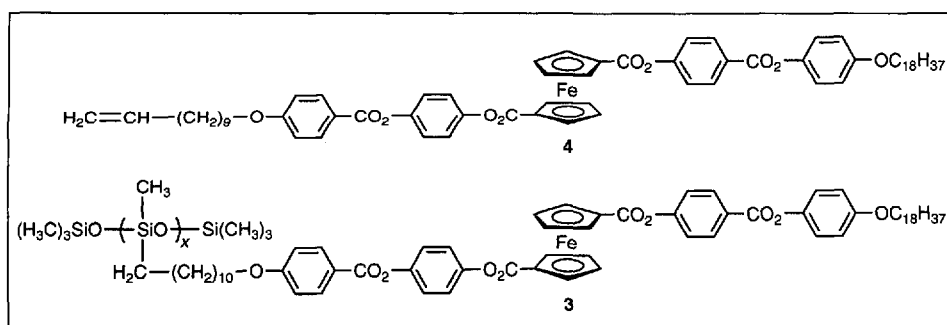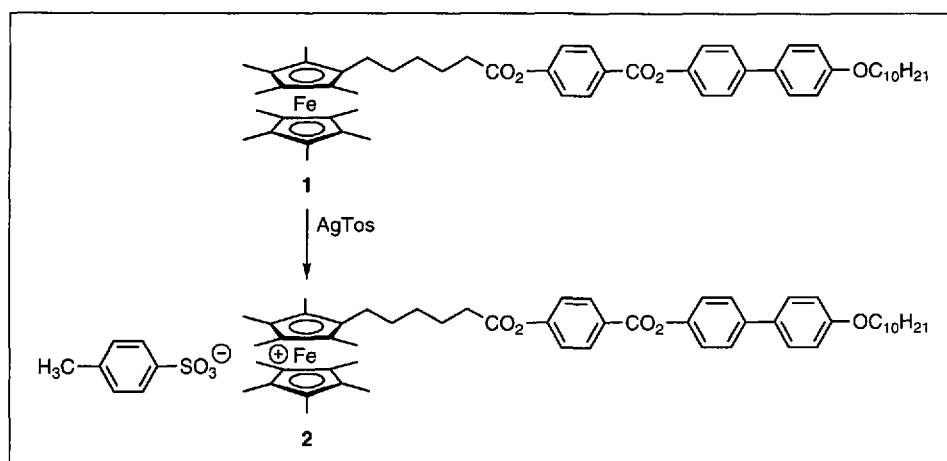
monomer with a liquid-crystalline comonomer, or *ii*) by polymerizing a mesomorphic ferrocene monomer. In the latter case, copolymers can be prepared using either non-mesomorphic or mesomorphic comonomers. We decided to apply the second, more elegant, strategy. Properties of polymers and monomers are reported in the *Table*.

Polysiloxane 3 [11] was obtained by grafting vinyl monomer 4 onto commercially available polyhydrosiloxane following a standard procedure (toluene, 70°, 24 h, $PtCl_2(1,5-C_8H_{12})$). Polymethacrylates 5 [12a] and 6 [12b] were prepared by free-radical polymerization (THF, AIBN, 50°) of methacrylate-containing ferrocene monomers 7 and 8, respectively. Polymers 3, 5, and 6 showed good solubility in common organic solvents (CH_2Cl_2, $CHCl_3$, THF), good thermal stability (no decomposition was detected up to 250°), and a narrow molecular-weight distribution (M_w/M_n: 1.4–1.6).

Enantiotropic smectic C and/or smectic A phases were observed for polymers 3, 5, and 6, as well as for monomers 4, 7, and 8. Stabilization of the liquid-crystalline domain was observed upon grafting or polymerization. This result is the consequence of stronger interactions between the mesomorphic units within the polymeric structure. Finally, in 4 and 7, the ferrocene unit is included within the rigid rod; both compounds melt above 100°. In 8, the ferrocene unit is functionalized by two flexible chains, the tendency of which is to destabilize the crystalline state. As a consequence, 8 melts near room temperature. This result shows that structural modification at the ferrocene level can be used to engineer the thermal and mesomorphic behavior of liquid-crystalline ferrocene derivatives.

Ferrocene-Containing Liquid-Crystalline Dendrimers

To explore further the capability of mesogenic ferrocene derivatives to act as mesomorphic building blocks for the construction of liquid-crystalline macromolecules, we extended our interest to ferrocene-containing thermotropic dendrimers. Such structures are of interest with the aim of elaborating mesomorphic receptors capable of encapsulating different guest molecules. Desired properties (depending on the guest) could be introduced into liquid-crystalline materials. As a first example, prototype 9 [13], which represents a first-generation dendrimer, was synthesized. A smectic A phase was ob-

served from 47 to 150°; no decomposition was detected up to 250°. The broad mesomorphic range of **9** is an indication that higher-generation dendrimers should be able to encapsulate guest molecules and retain liquid-crystalline properties.

Fullerene-Containing Thermotropic Liquid Crystals

Compound **10** [14] represents the first fullerene-containing thermotropic liquid crystal. The following structural requirements were applied for the successful design of a mesomorphic C_{60} derivative: *i*) to generate strong intermolecular interactions between the mesogenic units, a twin cholesterol derivative was selected for the formation of a C_{60} derivative; *ii*) a flexible chain was used to decouple the mesomorphic cholesterol framework from the bulky C_{60} moiety (this allows the cholesterol units to position such as to interact favorably with the neighbors); and *iii*) owing to the well-established synthetic procedure [21], the formation of a methano-fullerene was chosen to connect the cholesterol fragment to the C_{60}. Fullerene derivative **10** gave a monotropic smectic A phase from 190 to 146°.

Following the structural requirements applied for the preparation of **10**, we synthesized the mixed fullerene-ferrocene derivative **11** [15]. This latter compound gave an enantiotropic smectic A phase from 66 to 118°. Structure **11** is interesting to investigate photoinduced electron transfer in organized molecular assemblies as recently demonstrated in solution for non-mesomorphic fullerene-ferrocene dyads [22]. Such studies may lead to optical devices with new properties.

Conclusion

Careful functionalization of the ferrocene and fullerene units gave rise to liquid-crystalline materials showing a rich mesomorphism. Structural engineering at the ferrocene level allowed the control and tuning of the mesomorphic and thermal behavior of side-chain liquid-crystalline polymers. The presence of the ferrocene units in macromolecular structures is interesting with a view to the development of switchable materials. Indeed, in the case of low-molar mass materials, we showed that electron transfer can be used in the ferrocene-ferrocenium redox system to induce mesomorphism. A mixed fullerene-ferrocene liquid-crystalline material was synthesized. Such a structure is of interest for the development of new optical devices. Future activities will be focused on the exploitation of the redox activity of the ferrocene in liquid-crystalline polymers and dendrimers, and emphasis of the *structure-mesomorphic properties* relationship of liquid-crystalline fullerenes.
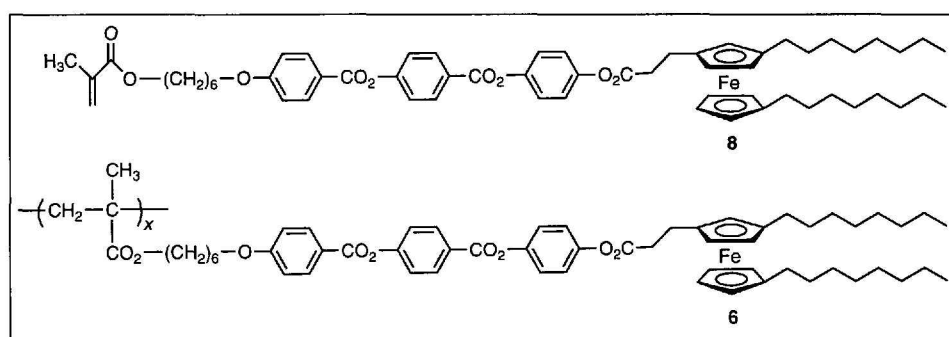

Table. *Phase-Transition Temperatures* [°]ᵃ) *of Monomers* **4**, **7**, *and* **8**, *and Selected Analytical Data and Phase-Transition Temperatures* [°]ᵃ) *of Polymers* **3**, **5**, *and* **6**

Monomer	Cr/S_C	Cr/S_A	S_C/S_A	S_A/I			
4	124	–	134	149			
7	–	117	–	130			
8	32	–	55	88			
Polymer	M_w	M_n	M_w/M_n	T_g	Cr/S_C	S_C/S_A	S_C/I	S_A/I
3	31 300	23 100	1.4	ᵇ)	136	140	–	183
5	111 300	74 800	1.5	30	–	–	210	–
6	100 000	63 000	1.6	ᵇ)	–	154	–	185

ᵃ) Cr = crystal, S_C = smectic C phase, S_A = smectic A phase, I = isotropic liquid, T_g = glass transition temperature. ᵇ) Not detected.
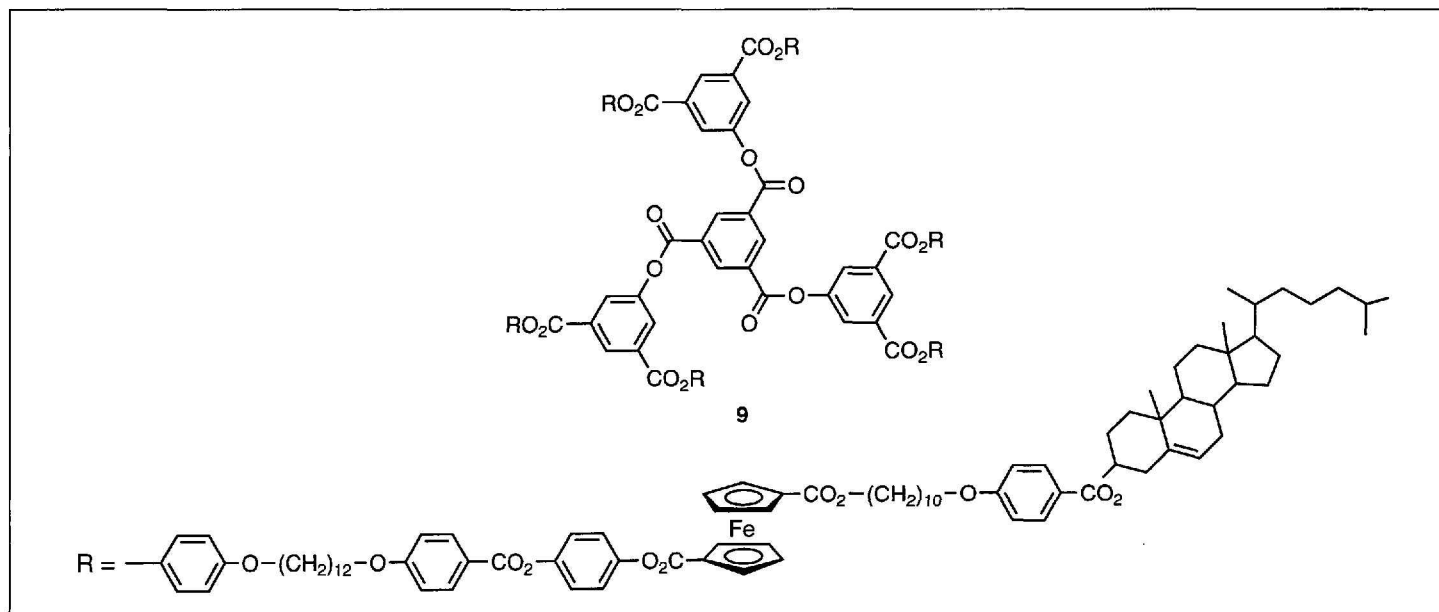
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[2] A thermotropic liquid crystal is a compound that, on heating the crystal or on cooling the isotropic liquid, gives rise to mesomorphism. Liquid crystallinity occurs between the crystal and the isotropic liquid states. The intermediate phases, or mesophases, can be either enantiotropic, *i.e.*, thermodynamically stable, or monotropic, *i.e.*, thermodynamically unstable. The solid-to-mesophase transition is referred to as the melting point, while the mesophase-to-isotropic-liquid transition is referred to as the clearing point. The *Fig.* shows the molecular organization whithin nematic, smectic A, and smectic C phases. In the nematic phase, the molecules align parallel to an axis, the director. In the smectic A phase, the molecules are organized into layers and are perpendicular to the planes; in the smectic C phase, the molecules are organized into layers and are tilted.

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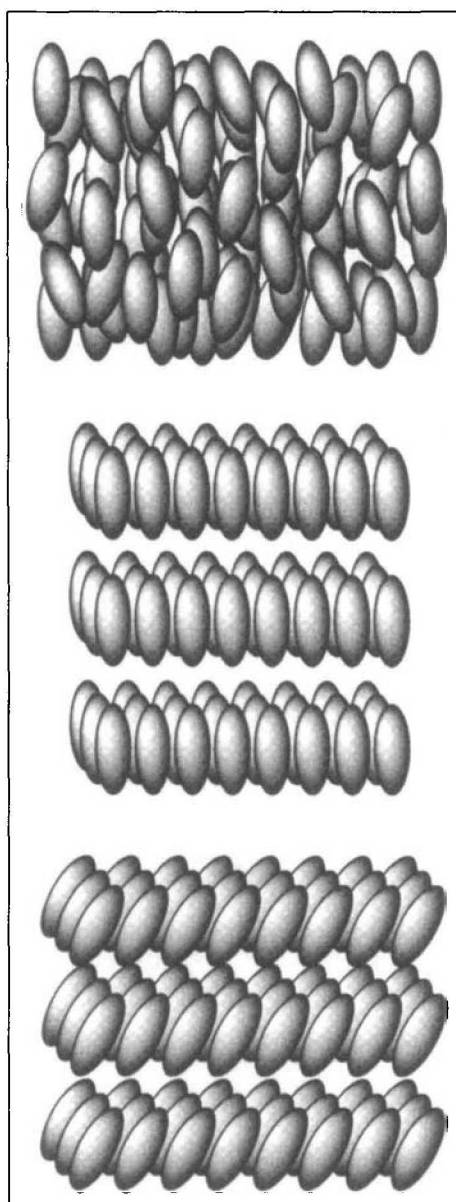
Figure. *Schematic representation of nematic* (top), *smectic A* (middle), *and smectic C* (bottom) *phases*

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