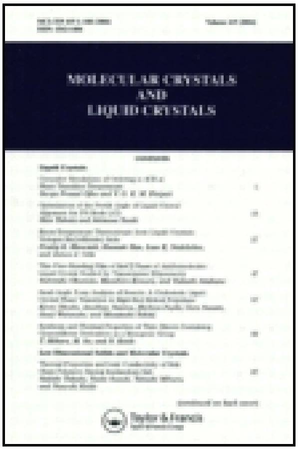

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Switchable Liquid-Crystalline Polymers Based on the Ferrocene-Ferrocenium Redox System

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Switchable Liquid-Crystalline Polymers Based on the Ferrocene-Ferrocenium Redox System*

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A ferrocene-containing side-chain liquid-crystalline polymethacrylate was oxidized with iodine into the corresponding ferrocenium polymeric species. The reduced polymer showed enantiotropic smectic C and smectic A phases. The oxidized polymer exhibited an enantiotropic nematic phase. The results described in this report confirm that ferrocene is a valuable redox-active unit for the design of switchable liquid-crystalline polymers.

Keywords: Metallomesogens; ferrocene; polymers; molecular switches

INTRODUCTION

Among the metallomesogenic polymers reported so far[1], ferrocene-containing side-chain liquid-crystalline polymers represent a valuable family of mesomorphic materials (i.e., multiple possibilities for synthesizing novel monomers from the three-dimensional structure of the ferrocene, tuneable thermal and liquid-crystalline properties depending on the number and position of the substituents, good thermal stability, good solubility in common organic solvents)[2,3]. The presence of the ferrocene unit is of interest for the development of

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[*] Dedicated to Dr Antoine Skoulios on the occasion of his 65th birthday

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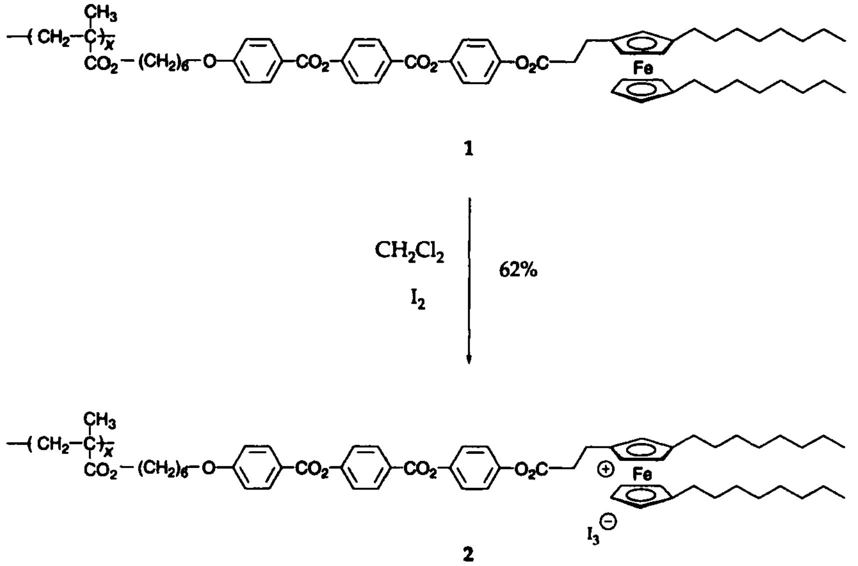
redox-active liquid-crystalline polymers. Indeed, we have shown in the case of low molar-mass compounds that electron transfer in the ferrocene-ferrocenium redox system can be used to generate mesomorphism: while the ferrocene derivatives did not show liquid-crystalline behavior, the oxidized form exhibited either smectic A[4] or columnar[5] phases. Such systems behave as switchable liquid crystals. Oxidation of ferrocene was also applied to prepare liquid-crystalline ionomers[6].

Recently, we reported polymer **1** ($M_w = 100\,000$, $M_n = 63\,000$, $M_w/M_n = 1.6$), which was prepared by free-radical polymerization of the corresponding mesomorphic methacrylate-containing ferrocene monomer[3a]. Polymer **1** showed enantiotropic smectic C and smectic A phases (T_g: not detected; smectic C-to-smectic A transition: 154 °C; smectic A-to-isotropic liquid transition: 185 °C). The ease of oxidation of alkylated ferrocene derivatives with iodine[7] makes structure **1** a candidate of choice for use as a redox-active metallomesogenic polymer.



We describe, herein, the preparation and mesomorphic properties of the ferrocenium-containing side-chain liquid-crystalline polymer **2**, which was obtained by oxidation of **1**. The elaboration of switchable anisotropic polymers motivated this study.

RESULTS AND DISCUSSION

Synthesis

Polymer **2** was obtained by oxidation of **1** with iodine in CH_2Cl_2 (62 % yield). The composition and purity of **2** were confirmed by elemental analysis.

Liquid-Crystalline Properties

The mesomorphic properties of **2** were investigated by polarized optical microscopy (POM) and X-ray diffraction (XRD).

POM observations revealed the formation of a birefringent and viscous melt from about 70 °C, which indicated a mesomorphic character for **2**. The liquid-crystalline phase persisted up to about 160 °C, where decomposition started. The mesophase could not be identified as no typical texture developed, most likely as a consequence of the viscosity of the sample.

Diffraction patterns consisting of diffuse bands in the low- and wide-angle regions were recorded from room temperature to 160 °C. The birefringent fluid observed by POM combined with the XRD data indicated that the liquid-crystalline phase displayed by **2** is nematic in nature, characterized by the presence of cybotactic groups (i.e. groups of side-chains locally arranged in a smectic structure). A typical diffractogram is shown in Figure 1: the diffuse signal at about $2\theta = 5$–$7°$ was attributed to two adjacent side-groups. The lateral distance which is deduced, about 15 Å, corresponding to the lateral distance between ferocene moieties is larger than for the neutral polymer (10–11 Å[3a,8]), but can be explained by the presence of the iodine ions which increase the distance between side-groups. Moreover, this result is in agreement with an alternate up and down packing of the mesogenic ferrocene units. The second diffuse signal at about $2\theta = 20°$ is due to the disorganized aliphatic chains as usual.

The nematogenic character of **2** (ionic polymer) is due to a disruption of the layered organization observed for **1** (neutral polymer) as a consequence of electrostatic repulsions, and of the presence of the iodide counterions, which add bulkiness at the side group level and make lateral interactions less efficient.

The results reported above demonstrate that incorporation of the ferrocene unit into polymeric structures is a suitable means to elaborate redox-active liquid-crystalline polymers. Interestingly, the use of different counter-anions (tosylate was used in the case of low molar-mass materials[4,5]) could serve to tune the liquid-crystalline and thermal behavior of the oxidized polymers. This first example opens the doors for further studies devoted to the search of polyfunctional molecular switches.

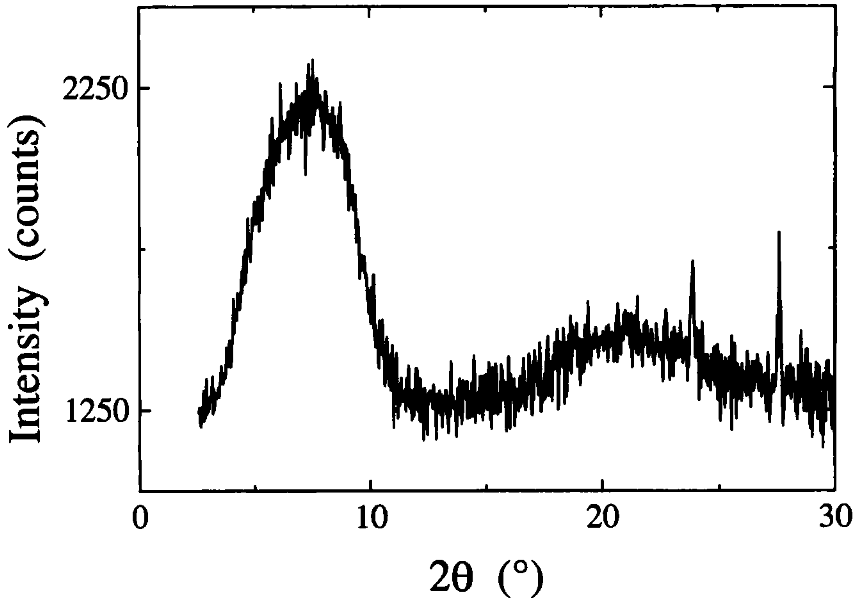


FIGURE 1 X-ray diffraction pattern of polymer **2** recorded in the nematic phase at 120 °C

EXPERIMENTAL

For instrumentation and techniques see ref. 3a.

Preparation of Polymer 2

A solution of **1** (190 mg, 0.2 mmol in ferrocene units) and iodide (100 mg, 0.4 mmol) in CH_2Cl_2 (100 mL) was sonicated for 20 min. The mixture was poured into diethyl ether. Polymer **2** was recovered by filtration, washed with diethyl ether and dried (170 mg, 62 %). Anal. Calcd for $(C_{59}H_{74}I_3FeO_9)_n$: C, 51.96; H, 5.47. Found: C, 51.72; H, 5.68.

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