

## **Ferrocene containing liquid crystalline copolyesters**

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### Summary

Iron-containing aromatic copolyesters were synthesized from 1,1'-bis-(chlorocarbonyl)ferrocene, terephthaloyl chloride, isophthaloyl chloride and methylhydroquinone. The copolymers obtained were characterized for their liquid crystalline properties by a variety of methods, and all of the copolyesters synthesized were nematic.

### Introduction

Thermotropic liquid crystalline polymers (LCP) form ordered mesophases in the molten state above the melting point and below the temperature for formation of an isotropic melt (1). When properly processed, these polymers produce materials with high degrees of molecular orientations, resulting in exceptional tensile strength and stiffness (2) because a high degree of parallel molecular orientation can be achieved on a molecular level on processing LCP. That is, the rigidity of the polymer backbone forces the chains to align spontaneously. However, completely rigid systems are difficult to process because of their low solubilities in common solvents and their high melting points. For example, poly(hydroquinone terephthalate) melts above 600°C and cannot be melt-processed (3). Thus, the introduction of various elements of dissymmetry and/or branching in the chain is required to reduce the melting transition temperatures to a processable range, and many such rigid disordered systems have been studied(4).

Ferrocenecarboxaldehyde has been reported to exhibit thermotropic behavior (5,6), and certain ferrocene-containing Schiff bases are mesomorphic and have found utility in Mossbauer spectroscopy (7). The ferrocene unit inserted into the backbone of a polymer chain could also impart enhanced weatherability to materials based on these polymers, since some ferrocene derivatives are known to be excellent UV light absorbers and have been utilized to stabilize polymers against the degrading effects of ultraviolet radiation (8,9). Likewise, ferrocene-containing polymers would be expected to exhibit low smoke and flame characteristics on burning, because ferrocene derivatives in small amounts are exceptional smoke and soot retardants when incorporated into fuels, waxes and polymers (10).

For copolymers, the molecular shape of ferrocene can be considered 3-dimensional as compared to a 2-dimensional benzene ring, and this feature could provide enough irregularity in the system to achieve the desired transition temperatures. Also, from the geometry requirements of the various types of mesophases known, ferrocene-containing systems should be of interest because this molecule has the capability of forming both a condense and a plastic crystal. Indeed, it is also possible that the ferrocene ring would be able to assume the proper conformation and may have the proper

shape to be a component of a mesogen unit itself; that is, to contribute directly to the formation of an LC state. However, when it is present as part of a repeating unit in a rigid chain, some of the characteristic transitions may have a higher activation barrier. For these reasons, the incorporation of the ferrocene unit into a copolyester which should show liquid crystalline behavior was investigated.

### Experimental

All the polymer preparations were carried out under prepurified nitrogen. Methylene chloride was distilled from calcium hydride under argon. Microanalyses were performed by the Microanalytical Laboratory, University of Massachusetts, Amherst. TGA thermograms were obtained with a Perkin-Elmer TGS-2 analyzer interfaced with a system-4-microprocessor controller, and DSC analyses were carried out with a Perkin-Elmer DSC-2 calorimeter interfaced with a thermal analysis data station. X-ray diffraction was conducted on a Statton diffractometer using a pinhole camera.  $^1\text{H}$  NMR spectra were recorded on Varian A-60, Varian XLR-200 and Varian XLR-300 spectrometers. The nitrogen and argon gases used were dried over  $\text{P}_2\text{O}_5$ , and trace amounts of oxygen were removed with BTS catalyst.

Terephthaloyl chloride was purchased from Aldrich Chemical Co. and was purified by vacuum sublimation. Ferrocene, isophthaloyl chloride and methylhydroquinone were purchased from Aldrich and used without any further purification. Oxalyl chloride was purchased from Aldrich and purified by flash chromatography on a 2" x 2" plug of activated alumina.

#### Low temperature solution polymerization for ferrocene-containing polymers (6-15)

Example: A solution of methylhydroquinone (1.55 g, 12.5 mmol) and pyridine (2.0 ml, 25 mmol) in 50 ml of methylene chloride was added to a stirred solution of 1,1'-bis(chlorocarbonyl)ferrocene (2.33 g, 7.5 mmol), terephthaloyl chloride (0.71 g, 3.5 mmol), and isophthaloyl chloride (0.31 g, 1.5 mmol) in methylene chloride. The reaction mixture was heated at reflux for 14 h. The warm solution was poured into methanol, stirred for 30 min and filtered. The orange polymer was dissolved in methylene chloride, reprecipitated with methanol and filtered. The powder (11) was dried in a vacuum oven at 40°C. Yield 36%. IR(KBr):  $\nu(\text{CO})$  1750  $\text{cm}^{-1}$ . Monomer feed data and elemental analyses are shown in Tables 1 and 2, respectively.

#### Polymerization of terephthaloyl chloride (45%) and isophthaloyl chloride (55%) with methylhydroquinone (polymer 16)

A mixture of terephthaloyl chloride (0.91 g, 4.5 mmol), isophthaloyl chloride (1.12 g, 5.5 mmol) and methylhydroquinone (1.24 g, 10 mmol) was refluxed for 14 h in methylene chloride in the presence of a few drops of pyridine. The warm mixture was poured into excess methanol. The precipitated polymer was filtered and washed with methanol. The product was purified by dissolution in methylene chloride and precipitated in methanol. The polymer (16) was filtered and dried in a vacuum oven at 40°C.

### Results and discussion

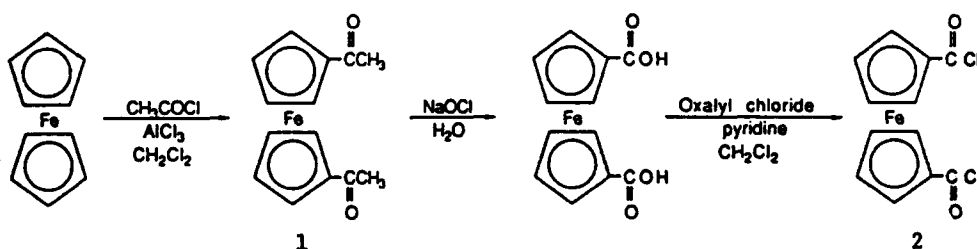
1,1'-Bis(chlorocarbonyl)ferrocene (2) was synthesized from 1,1'-bis(acetyl)ferrocene (1) according to the procedure of Knobloch and Rauscher (11):

Table 1. Data for synthesis of ferrocene-containing aromatic polymers

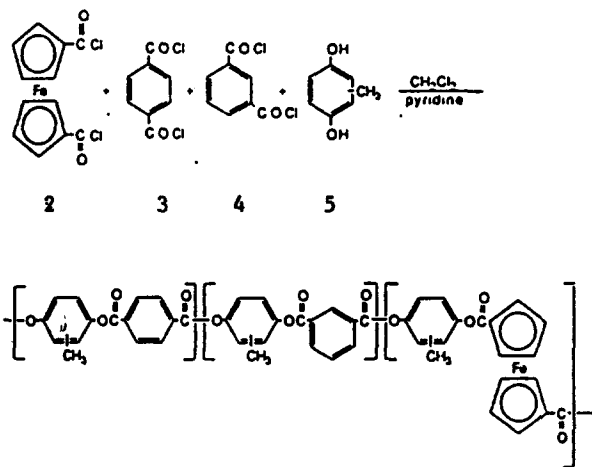
Polymer	Ferrocene Monomer	Ferrocene Dicarboxyl Chloride		Terephthaloyl Chloride		Isophthaloyl Chloride		Methyl Hydroquinone	
	mol %	g	mmol	g	mmol	g	mmol	g	mmol
6	0	0	0	1.42	7	0.61	3	1.24	10
7	18	0.62	2	1.34	6.6	0.49	2.4	1.36	11
8	30	0.93	3	0.99	4.9	0.43	2.1	1.24	10
9	40	1.12	3.6	0.77	3.8	0.33	1.6	1.12	9
10	50	1.38	4.4	0.71	3.5	0.3	1.5	1.17	9.4
11	60	2.33	7.5	0.71	3.5	0.31	1.5	1.55	12.5
12	70	2.72	8.7	0.53	2.6	0.23	1.1	1.55	12.5
13	80	1.66	5.3	0.19	0.9	0.08	0.4	0.83	6.6
14	90	2.8	9	0.14	0.7	0.06	0.3	1.24	10
15	100	3.11	10	0	0	0	0	1.24	10

Table 2. Results of C, H, Fe analyses of ferrocene-containing polymers

Polymer	%C, calcd.	%C, found	%H, calcd.	%H, found	%Fe, calcd.	%Fe, found
7	68.80	68.07	3.95	4.43	4.05	0.76
8	67.89	66.29	3.94	3.76	5.85	2.57
10	66.25	59.02	3.92	3.93	9.06	3.66
11	65.52	64.08	3.92	3.97	10.50	9.14
12	64.83	63.50	3.91	4.22	11.85	11.14
13	64.18	62.38	3.91	4.0	13.12	11.95
14	63.58	62.31	3.90	4.32	14.30	13.42
15	63.01	61.41	3.89	4.02	15.42	14.00



The copolymers were prepared by solution polymerization procedures. A series of polymers were prepared with terephthaloyl chloride (3) and isophthaloyl chloride (4), in which the amount of 2 in the feed was varied while maintaining a constant ratio of 7:3 for 3 and 4. The three acid chlorides were polymerized with methylhydroquinone (5) in methylene chloride solution as shown on the next page:



## 6-15

Pyridine was used as the hydrogen chloride acceptor. The polymers (6-15) were precipitated in methanol, purified by reprecipitation and dried in a vacuum oven at 40°C. Some post-polymerization increase in the molecular weight may have occurred in the drying process.

The polymers were found to be insoluble in most solvents, including tetrahydrofuran, toluene, methylene chloride, chloroform, tetrachloroethane, and p-chlorophenol, but they were soluble in pentafluorophenol. The solubility increased initially with increasing amounts of ferrocene unit incorporation, but decreased again at the higher ferrocene unit end of the series, presumably because the random copolymers were of low crystallinity. Solution viscosities could not be obtained since the polymers were not completely soluble in common organic solvents.

## Thermal analysis

Thermal gravimetric analyses (TGA) of the polymers 6-15 in the series gave similar characteristics. All of the samples were heated from 50°C to 700°C at a rate of 10°C per minute, and decomposition was observed to start between 250-300°C. The slope of the thermogram increased between 325-375°C and over this range approximately 20% weight loss occurred. The weight loss was about 50% at 700°C in all ferrocene-containing samples, while the sample without any ferrocene units (16) showed a 90% decrease in weight.

Table 3 summarizes the data obtained from analysis by differential scanning calorimetry (DSC) of the series. The samples were heated at 10° per min from 325°K to 550°K. Reproducible glass transition temperatures ( $T_g$ ) were observed in all heating and cooling cycles, but polymer 15 decomposed before melting. Melting was observed in all of the other samples in the first heating cycle, but was not observed in subsequent heating cycles of polymers 8, 9, 11 and 13.

## Optical microscopy

Observation of polymer samples on the hot stage of a polarizing microscope was conducted on the melts of the polymers. All the samples except 15 were birefringent in the melt and showed dense nematic textures. The melt viscosity appeared to increase as the amount of ferrocene units

Table 3. Results of thermal analyses of ferrocene-containing aromatic polymers

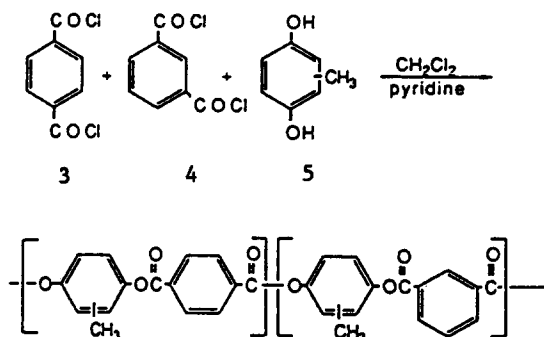
Polymer	Ferrocene Monomer %	T <sub>g</sub> (°C)	T <sub>m</sub> (°C)
6	0	90	240
7	20	75	260
8	30	80	225
10	50	80	180
11	60	70	225
12	70	90	250
13	80	90	190
14	90	80	270
15	100		

increased. This behavior resulted in thicker samples which required increased exposure times (25 sec) for obtaining photographs.

#### X-ray diffraction

X-ray diffraction studies were conducted on unoriented quenched samples. Sample preparation involved heating the polymer between mica sheets (ca. 10 μ) up to the desired temperature on a Fisher-Johns apparatus and subsequent quenching in liquid nitrogen. The X-ray diffraction pattern of polymer 12 contained a single diffuse ring at a spacing between 3.6 Å to 4.3 Å, as expected for nematic liquid crystals.

In order to confirm that the ferrocene units actually contributed to liquid crystallinity in the above polymers, the ferrocene monomer 2 was substituted by a known non-mesogenic monomer, isophthaloyl chloride 4. The resulting polymer 16 consisted of 45 mole percent of 3 and 55 mole percent of 4 together with methylhydroquinone 5, as shown below, and was not expected to be liquid crystalline:



16

Polymer 16 gave an isotropic melt without any evidence of mesophase formation when viewed on a polarizing microscope. In contrast, Polymers 11 to 14 all had terephthalate unit contents of less than 40 mole percent, and all of those polymers formed LC states above their T<sub>m</sub>. Hence, it can be concluded that the ferrocene dicarboxylate-methyl hydroquinone units were

themselves mesogenic, and these units contributed directly to the spontaneous formation of the nematic states observed for these copolyesters.

### Conclusions

Ferrocene-containing liquid crystalline polymers 6-15 were prepared by solution polymerization of 1,1'-bis(chlorocarbonyl)ferrocene, terephthaloyl chloride, isophthaloyl chloride and methylhydroquinone. The presence of liquid crystallinity was determined by DSC, polarized light microscopy and X-ray diffraction studies. All of the copolyesters except 15 produced birefringent melts. Polymer 16 was prepared to confirm that the presence of ferrocene units in the polymer was contributing to the liquid crystallinity of the ferrocene-containing polymers. This polymer was not observed to be liquid crystalline, which confirmed that the ferrocene units were mesogenic.

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