

Synthesis and Characterization of Liquid Crystalline Polymers Containing Aromatic Ester Mesogen and a Nonmesogenic Ferrocene Unit in the Spacer

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ABSTRACT: A new series of liquid crystalline polymers containing aromatic triad ester mesogen and 1,1'-disubstituted ferrocene as a nonmesogenic unit along with polymethylene spacer was synthesized. The polymer was synthesized by a room temperature polycondensation reaction between bis(4-chloroformyl phenoxy alkyl ferrocene dicarboxylate) and quinol. The alkyl groups have been varied by an even number of methylene groups with a range from two to ten groups. All the polymers were found to possess liquid crystalline properties. The identification of the mesophase is more transparent with an increase in the spacer. The thermal characteristics were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The results reveal that the thermal stability of the polymers was decreased with increasing spacer length. The T_g , T_m , and T_i of the polymers decreased with increasing methylene groups. The incorporation of the ferrocene moiety also has a considerable effect on the glass transition temperature. The char yield of the polymer decreases with an increasing methylene chain length. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3494–3501, 2002

Key words: liquid crystalline polymers; ferrocene polymers; spectral studies; thermal stability; char yield

INTRODUCTION

Liquid crystals are quintessential molecular electronics materials for the modern optical display technologies.^{1–3} Aromatic polyesters offer attractive possibilities for technological innovation, and recent research has been devoted to the exploration of their use in blends,⁴ fibers,⁵ composite system,⁶ and opto-electronic applications.¹ The structure–property relationship with regard to semiflexible aromatic liquid crystalline polymers is well established and was reported.⁷ Attaching a liquid crystalline backbone system and an organometallic nonmesogenic system to the chain may lead to the development of new multifunctional organic materials potentially capable of having novel electro-optical, thermal, and fire retardant properties.⁸ Indeed, various substituted ferrocene esters have been found to possess liquid crystalline properties.^{9–12} However, the said property is imparted when the sandwich compound is combined with other linear components such as ester or azomethane linked aromatic systems.^{13,14} Lenz et al.¹⁵ proved that ferrocene, as an individual is a nonmesogenic molecule; further more, the incorporation of ferrocene is expected to impart a metallic character and to enhance the polarization caused by the presence of a metal atom.¹⁶

Because of the polarization arise due to metallic iron to get high-order liquid crystalline phase. In our early work in this domain we reported several ferrocene-containing liquid crystalline polyphosphates/phosphonates with a high char content.^{17–19} This investigation includes the incorporation of ferrocene as a nonmesogenic unit in a liquid crystalline polymer system composed of aromatic triad ester mesogen and polymethylene spacers.

EXPERIMENTAL

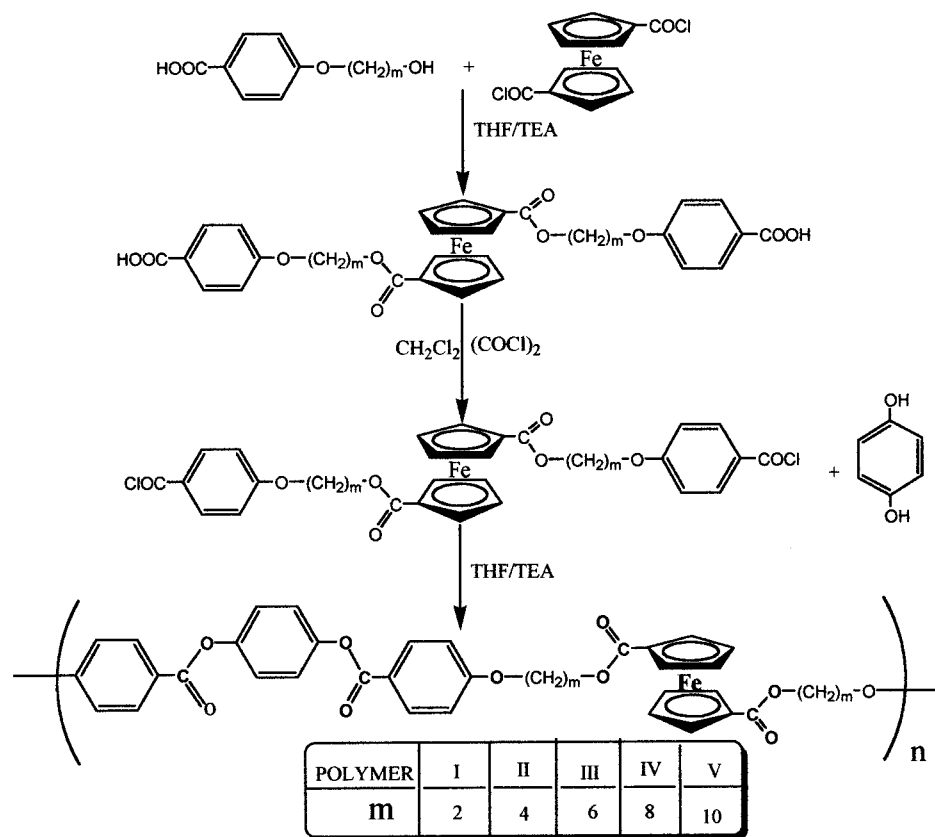
Materials

Dichloromethane, methanol, and tetrahydrofuran (THF) were purified by the usual procedure²⁰ and dried before use. Oxalylchloride was purchased (Spectrochem, India) and distilled before use. Ferrocene dicarbonyl chloride was prepared using a literature method from the literature.²¹ N-bromo alkanol and n-hydroxy alkyloxy benzoic acid ($n = 2,4,6,8,10$) were prepared using a reported procedure.¹⁷

Bis(4-carboxy phenoxy alkyl ferrocene dicarboxylate)

A typical procedure for the preparation of bis(4-carboxy phenoxy ethyl ferrocene dicarboxylate) is as follows: 2-hydroxy ethyloxy benzoic acid (0.01 mol) was dissolved in dry THF (20 mL) and dry triethylamine (TEA) (0.01 mol) was added under nitrogen,

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Scheme 1 Synthesis of Polymer I-V.

stirring to get a homogeneous mixture. 1,1'-ferrocenedicarbonylchloride (0.005 mol) dissolved in dry THF (10 mL) was added drop by drop and stirred for 12 h at the ambient temperature and then at the refluxing condition for 3 h. The amine hydrochloride formed was filtered, and THF was evaporated to dryness under reduced pressure. The product was purified by flash column chromatography over silica gel using a chloroform and methanol (95 : 5) mixture as eluent. Similarly other compounds, such as bis(4-carboxy phenoxy butyl ferrocene dicarboxylate), bis(4-carboxy phenoxy hexyl ferrocene dicarboxylate), bis(4-carboxy phenoxy octyl ferrocene dicarboxylate), and bis(4-carboxy phenoxy decyl ferrocene dicarboxylate) were prepared by adopting similar procedures.

IR (KBr): 3424 cm^{-1} (carboxylic acid -OH), 1692 cm^{-1} (carbonyl), 1251 cm^{-1} (Ar-O-C), 3100 cm^{-1} (1,1'-disubstituted ferrocene ring), 2939 cm^{-1} (methylene), ^1H NMR (DMSO- d_6) δ : 10.02 (s, 2H, -COOH), δ 6.90 (d, 4H, aromatic, ortho to ether), δ 7.25 (d, 4H, aromatic, meta to ether), δ 4.6, 5.04 (s, 8H, cyclopentadiene proton), δ 3.53 (t, 2H, Ar-O-CH₂), δ 3.32 (t, 4H, Fc-COO-CH₂).

Bis(4-chloroformyl phenoxy alkyl ferrocene dicarboxylate)

A typical procedure for the preparation of bis(4-chloroformyl phenoxy ethyl ferrocene dicarboxylate) is

as follows: bis(carboxy phenoxy ethyl ferrocene dicarboxylate) (0.01 mol) was dispersed in dry dichloromethane (15 mL). Freshly distilled oxalyl chloride (0.04 mL) was added drop by drop and stirred at room temperature for 3 h. During stirring, two drops of dry pyridine were added. The mixture was slowly brought to gentle reflux for 3 h. The excess oxalyl chloride and dichloromethane were removed under vacuum. The residue was connected to high vacuum at 50°C for several hours to remove the traces of oxalyl chloride. Bisacid chloride thus obtained was used without further purification. Other homologues were prepared by a similar method.

Polymerization

Poly(4-phenyl ester-4-phenoxy alkyl-1,1'-ferrocene dicarboxylate)

A typical procedure for the synthesis of poly(4-phenyl ester-4-phenoxy ethyl-1,1'-ferrocene dicarboxylate) (I) is as follows: recrystallized quinol (0.01 mol) was dissolved in dry THF (25 mL). To this mixture, dry TEA (0.01 mol) was added under a nitrogen atmosphere. Bis(chloro carboxy phenoxy ethyl ferrocene dicarboxylate) was added drop by drop at room temperature, and the mixture was stirred for 12 h. The reaction mixture was poured into excess methanol. An orange color precipitate formed was filtered and re-

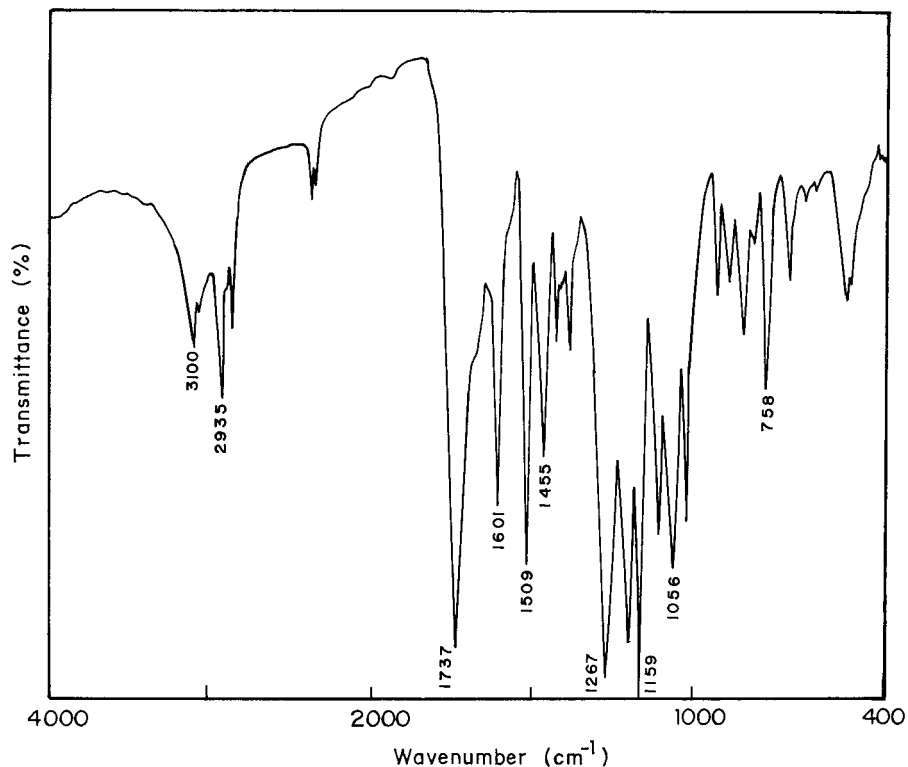


Figure 1 IR spectrum of Polymer V.

precipitated using THF and methanol. Similarly other polymers, such as poly(4-phenyl ester-4-phenyloxy butyl-1,1'-ferrocene dicarboxylate) (II), poly(4-phenyl ester-4-phenyloxy hexyl-1,1'-ferrocene dicarboxylate) (III), poly(4-phenyl ester-4-phenyloxy octyl-1,1'-ferro-

cene dicarboxylate) (IV), and poly(4-phenyl ester-4-phenyloxy decyl-1,1'-ferrocene dicarboxylate) (V), have also been prepared by a similar method.

IR (KBr): 1737 cm^{-1} (ester carbonyl), 1267 cm^{-1} (Ar-O-C), 3098 cm^{-1} (1,1'-disubstituted ferrocene ring), 2934

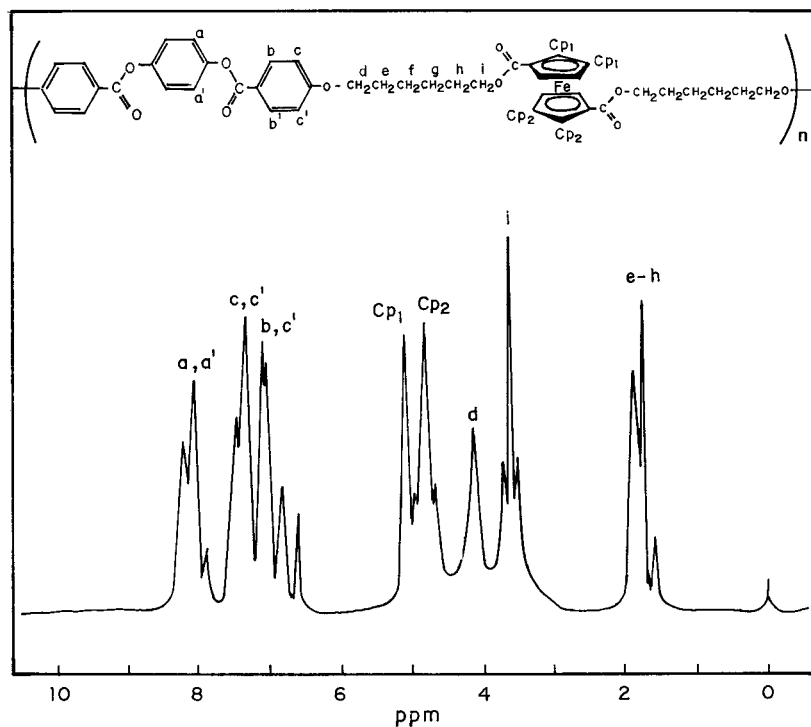


Figure 2 $^1\text{H-NMR}$ spectrum of Polymer III.

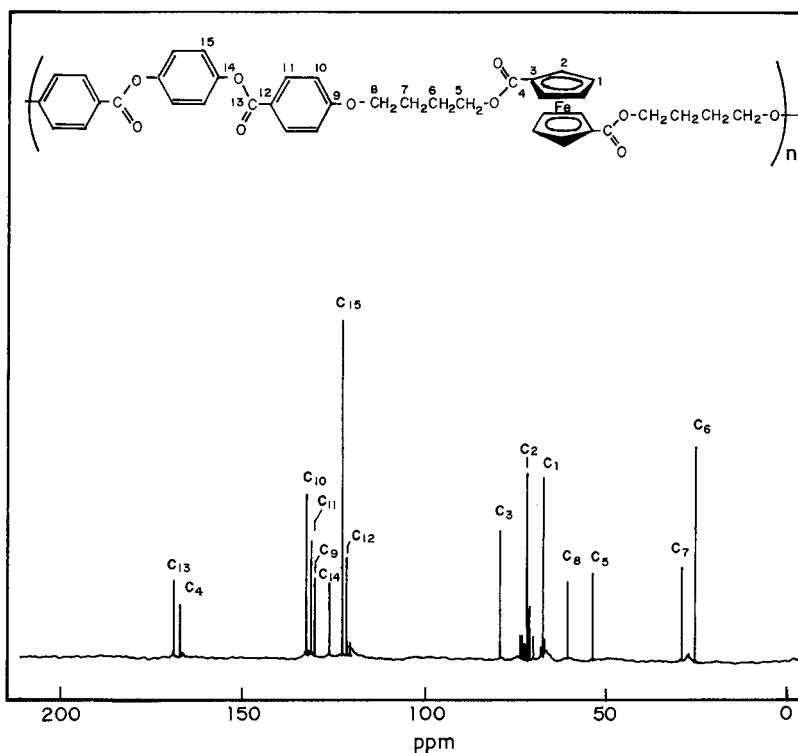


Figure 3 ^{13}C NMR spectrum of Polymer II.

cm^{-1} (methylene), ^1H NMR (DMSO- d_6) δ : $\delta 7.01$ (d, 2H, aromatic, *ortho* to ether), $\delta 7.35$ (d, 2H, aromatic, *meta* to ether), $\delta 8.05$ (d, 2H, aromatic, *ortho* to OCO-), $\delta 4.89$, 5.18 (s, 8H, cyclopentadiene proton), $\delta 4.10$ (t, 2H, Ar-O-CH $_2$), $\delta 3.48$ (t, 4H, Fc-COO-CH $_2$). ^{13}C -NMR(C- DCl_3): $\delta 67.00$, 72.07 (two unsubstituted ring carbon in ferrocene), $\delta 79.23$ (tertiary carbon in ferrocene), $\delta 164.16$ (ferrocene attached carbonyl carbon), $\delta 122.30$ (aromatic, tertiary fourth position carbon from aryl alkyl linkage), $\delta 131.81$ (aromatic phenyl carbon, *ortho* to aryl alkyl linkage), $\delta 131.54$ (aromatic phenyl carbon, *meta* to aryl alkyl linkage), $\delta 131.16$ (aromatic, tertiary carbon attached to aryl alkyl linkage), $\delta 60.13$ (methylene carbon attached to ether linkage), $\delta 53.32$ (methylene carbon attached ester linkage).

Characterization

Infrared (IR) spectra were recorded on a Nicolet IR (Impact 440) spectrophotometer using KBr pellets.

GPC measurements were done on a Waters GPC with a styrogel column and a using THF as the solvent. High-resolution ^1H and ^{13}C nuclear magnetic resonance-(NMR) spectra were recorded on a Bruker spectrometer (300 and 75.4 MHz, respectively). In general, deuterated chloroform was used as a solvent for NMR spectra unless otherwise specified. TGA and DSC studies were carried out on a Mettler Toledo STAR^e system under nitrogen atmosphere. The heating rate of TGA analysis was done at $20^\circ\text{C min}^{-1}$, with a nitrogen flow of 20 mL min^{-1} .

The polarizing microscopic studies were performed using a Euromax polarizing microscope equipped with a Linken HFS 91 heating stage and TP-93 temperature programmer. Samples were made by melting a small quantity of the material between two thin glass cover slips to get a uniform film with heating and cooling rates of 5°C min^{-1} . The photographs were taken using a Nikon FM10 camera and were exposed

TABLE I
GPC and TGA Data of Polymers I-V

| Polymer | M_n | M_w | M_w/M_n | Weight loss corresponds to ($^\circ\text{C}$) | | Weight Loss at 600°C (%) | Char yield (%) |
|---------|-------|-------|-----------|---|-----|--|----------------|
| | | | | 2% | 50% | | |
| I | 5026 | 5377 | 1.07 | 305 | 390 | 87 | 13 |
| II | 5472 | 5800 | 1.06 | 301 | 389 | 89 | 11 |
| III | 5582 | 6084 | 1.09 | 298 | 385 | 91 | 9 |
| IV | 5220 | 5742 | 1.10 | 289 | 385 | 93 | 7 |
| V | 6400 | 6912 | 1.08 | 260 | 382 | 95 | 5 |

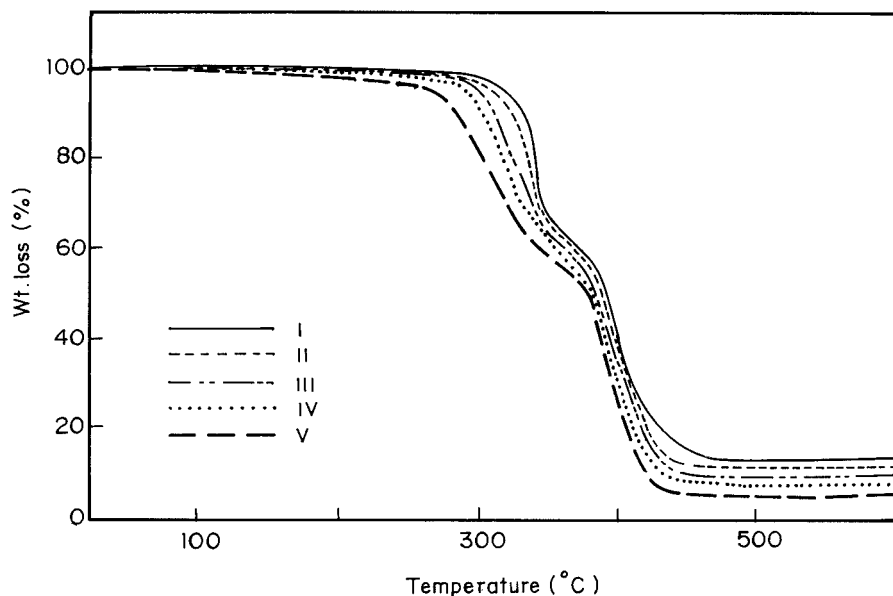


Figure 4 TGA traces of Polymer I-V.

on Konica film. Molecular modeling studies were performed using computer program Chem 3D Pro. The structures were initially minimized with molecular mechanics (MM2) to minimum RMS gradient of 0.100, and they were further refined by the MOPAC (Molecular Orbital package) program using Semiempirical Hamiltonian AM1 unrestricted wave function.

RESULTS AND DISCUSSION

Synthesis

The synthesis of the polymers is shown Scheme 1. The starting material *n*-bromoalkanol ($n = 2,6,8,10$) were prepared from their corresponding diols with 47% HBr²². The Williamson aryl alkyl ether synthesis of *p*-hydroxy benzoic acid with *n*-bromoalkanol yielded *n*-hydroxy alkoxy benzoic acid ($n = 2,6,8,10$)¹⁷. The yield of the product is drastically diminished if 4-hydroxy butyloxy benzoic acid is prepared using 4-bromobutanol, because 4-bromobutanol is cyclized at normal conditions to give THF. To overcome this problem, 4-bromobutyl acetate was prepared instead of 4-bromobutanol for the preparation of the polymer containing a four-methylene spacer. Then the acetyl-protected bromo alkanol is allowed to react with the methyl ester of hydroxy benzoic acid to give a corresponding diester. Methyl-protected hydroxy acid was used to prevent self-polymerization. The diester was easily deprotected, using alcoholic sodium hydroxide to yield 4-hydroxy butyloxy benzoic acid in amounts that were high in comparison unprotected 4-bromobutanol.²³ The incorporation of ferrocene group in the chain is achieved by the reaction of 2 *M* of *n*-hydroxy alkoxy benzoic acid with 1 *M* of 1,1'-ferrocene di-

carbonyl chloride, using triethylamine as an acid scavenger. The biscarboxylic acid was purified by the flash column chromatography over silica gel, using chloroform-methanol mixtures as eluent. The dicarboxylic acid was converted to corresponding acid chloride by gentle reflux with oxalyl chloride. The polymers were prepared by the solution polycondensation method, using quinol and various acid chlorides in THF at room temperature. GPC measurements show that the average molecular weight is in the range of 5026–6400. Representative IR, ¹H-NMR and ¹³C-NMR spectra were given in Figures 1–3, respectively.

Thermal and polarizing microscopic analysis

The polymer's thermogravimetric data are shown in Table I. The pattern of the TGA analysis is summarized in Figure 4. Thermal stability is evaluated by 1% weight loss at the minimum temperature. The polymer containing two-methylene spacer (I) is stable up to 305°C, whereas the 10-methylene spacer-containing polymer (V) is stable up to 260°C. The TGA thermograms reveal that the stability of the polymer decreases with increasing spacer length. The char yield of the polymers at 600°C is increased to 13% and it is reduced by up to 5% with an increase in spacer (polymer V). The char yield follows the regular order by decrease with increase in methylene spacer. [V < IV < III < II < I]. The data suggest that the char yield decreases when the ratio between the spacer and the mesogenic content of a single monomeric unit increases. The 50% weight loss of the polymers occurred around 382–390°C for all polymers. The TGA thermograms show two-stage decomposition for all the polymers. The second decomposition of the polymers oc-

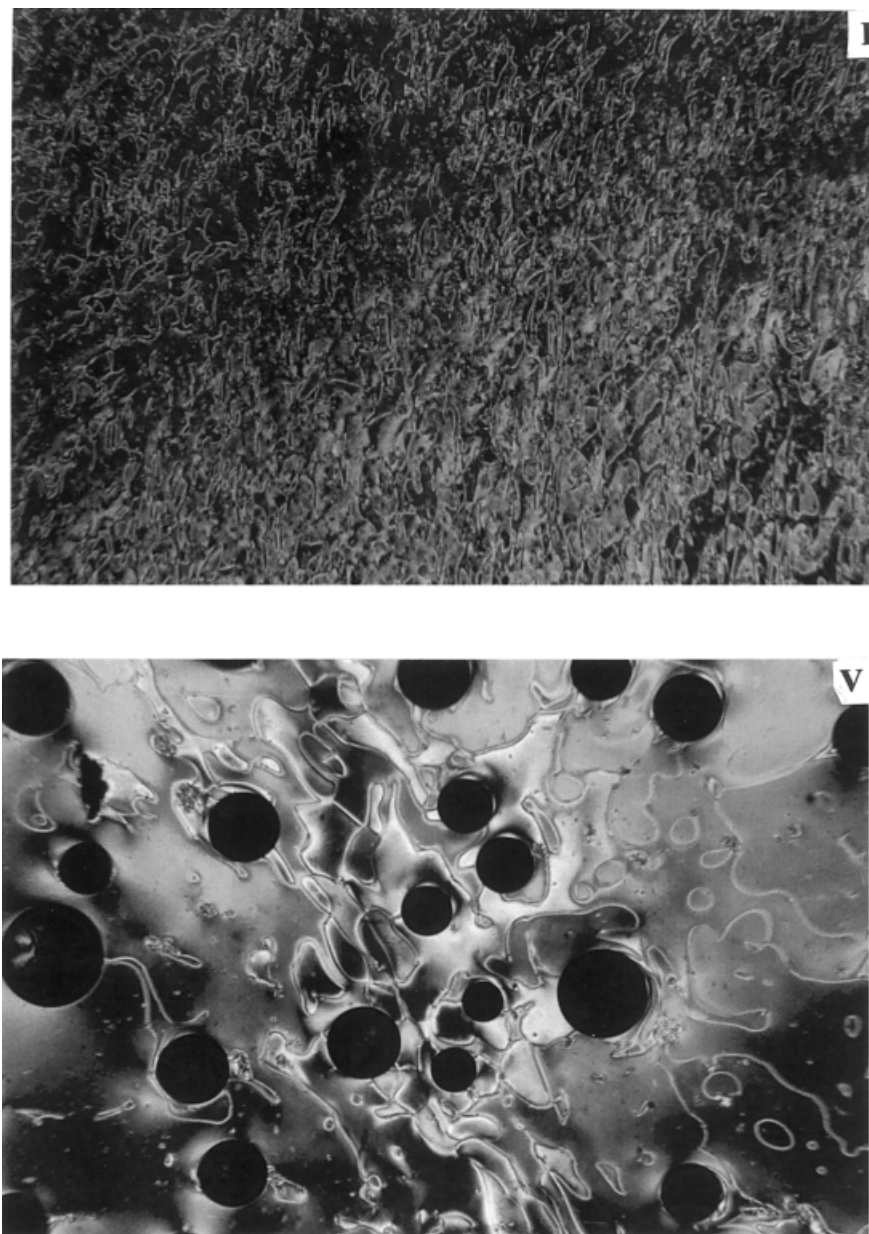


Figure 5 Liquid crystalline pictures of polymer I and V

curs at almost the same temperature for all of the polymers, but the first decomposition of the polymers was undergone at different temperatures and the decomposition temperature increased with a decrease in

TABLE II
Differential Scanning Calorimetry Transition
Temperatures of Polymers I-V

| Polymer | T_g (°C) | T_m (°C) | T_i (°C) | ΔT (°C) | Type of texture |
|---------|------------|------------|------------|-----------------|-----------------|
| I | 99 | 130 | 258 | 128 | Grainy |
| II | 82 | 120 | 226 | 106 | Grainy |
| III | 78 | 112 | 208 | 96 | Grainy |
| IV | 62 | 100 | 195 | 95 | Nematic |
| V | 48 | 92 | 175 | 83 | Nematic |

spacer length. Hence, the polymers may have not decomposed via phenylester bond breakage mechanism, because such a degradation route would give about the same decomposition temperature values for all the polymers. The decomposition of the polymers is probably by the pyrolytic cleavage of the ferrocene ester bond, cutting of the linkages between the mesogenic groups and methylene spacers.²⁴

The liquid crystalline properties of the polymers (I-V) were studied under a polarizing microscope. All five polymers exhibit anisotropic behavior. The representative liquid crystalline photographs are shown in Figure 5. The liquid crystalline phases were identified and compared with previously observed phases reported in the literature.² The transition temperature

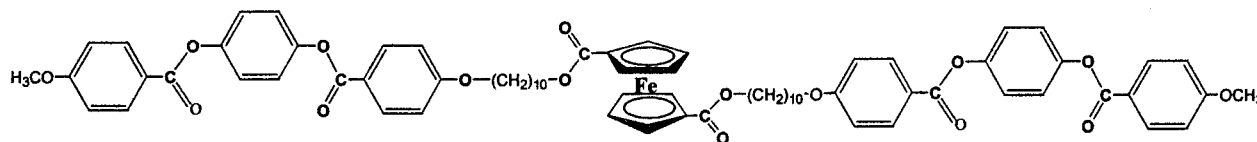


Figure 6 Model compound which mimics the polymer backbone.

for all the polymers observed in DSC is shown in Table II. All the polymers exhibit normal melting and clearing behavior. Good reproducibility of the formation of liquid crystalline phases was observed. Polymers I–III showed grainy texture, whereas polymers IV and V showed nematic schlieren texture. The order of the liquid crystalline monodomain was improved while comparing the textures of polymers I–V. This result reveals that, as the spacer increases, they tend to grow as large monodomains possibly ascribed to much segmental mobility and that the alignment of mesogens takes maximum unidirectional in a melt condition, thereby forming nematics. In contrast, the spacers containing two, four, and six (polymers I, II, and III) show micrograin, which may be the result of restricted mesogenic movement. Close observation of the photographs for these polymers implied that there is an increase in the size of the domains on moving two to six methylene groups from the spacer. The decrease in transparency with decreasing methylene chains seen in observing liquid crystalline textures may be attributed to bulky nonmesogenic ferrocene units, which form a step structure that hinders the packing possibility to align maximum.² An energy-

minimized structure was obtained for model compound 1 (Fig. 6), which mimics the polymer structure using a computer modeling program. The structure was shown in Figure 7, which shows the step-like alignment of the ferrocene ester in the polymer chain. This may hinder the molecular alignment to maximum. This could be one of the reasons for getting a grainy texture for polymer I–III, and the flexibility might be increased if the methylene chain increases and produces the nematic textures.

Figure 8 shows the DSC thermograms of polymers I–V. It shows that the T_g of the polymers decreases as the flexible chain length increases. Moreover, the phase duration is decreased with an increase in chain length, as expected. The regular insertion of the flexible molecules in the chain separates the mesogen along the molecular chain and thereby gives the chemical periodicity to the molecules. Also, these molecules provide extra flexibility to the polymer backbone. This facilitates the segmental motion more favorably and imparts high order to the liquid crystalline structure. But they tend to decrease the overall aspect ratio of the chain, thereby losing its crystallinity while increasing the methylene chain.

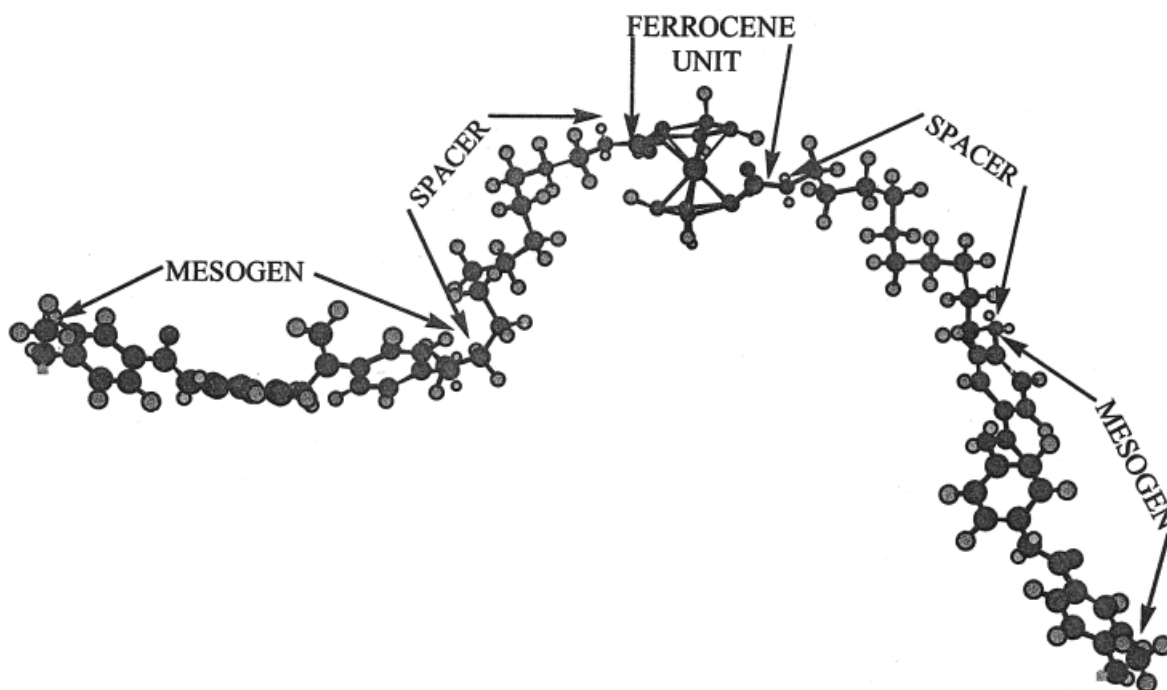


Figure 7 Energy minimized structure for model compound 1.

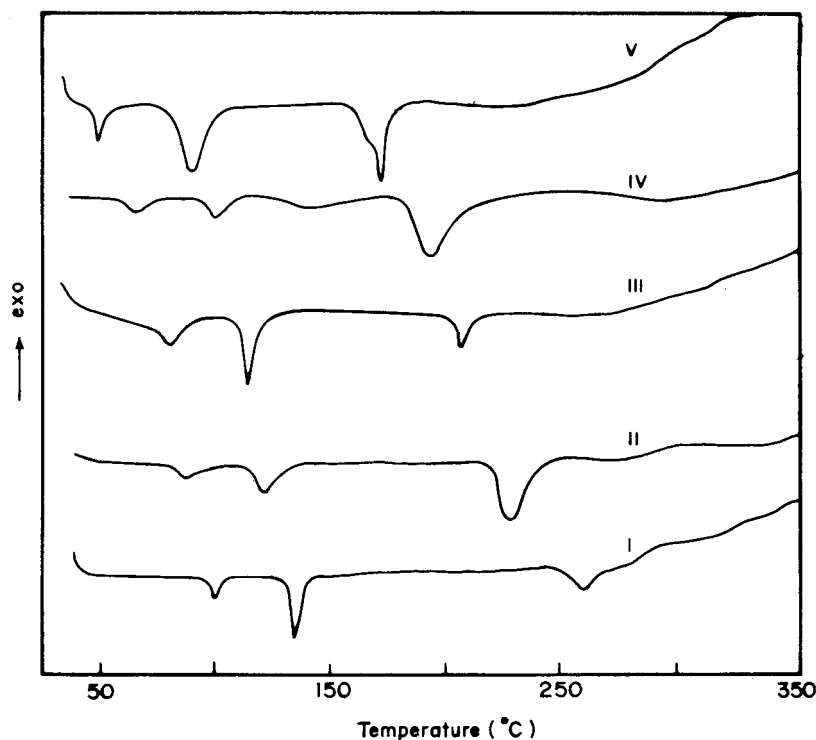


Figure 8 DSC curves of Polymer I-V.

CONCLUSION

A new series of ferrocene: containing aromatic polyesters with methylene spacers has been synthesized. The even number of flexible spacers has been varied from two to ten. All the polymers were found to possess a liquid crystalline property. Thermogravimetric analysis reveals that the polymers were moderately stable. The char yield of the polymers was very low, which was attributed to the flexible rotation of the cyclopentadiene rings of the ferrocene. DSC analysis confirms the formation of birefringent melt. The T_g of the polymer was found to low. The liquid crystalline phase duration of the polymers was decreased with increasing methylene spacers. The transparency of the liquid crystalline phases was increased with an increase in spacer length. An energy-minimized structure also supports the above conclusion.

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