Studies on the Mesomorphic Properties of Ferrocenylene-Based Organophosphorous Liquid-Crystalline Polymers Containing Phenyl and Biphenyl Pendant Units

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ABSTRACT: The synthesis, mesomorphic character, and effect of spacers in ferrocene-containing main-chain liquid-crystalline polymers are reported in this article. Two different monomers containing ferrocene and phenyl/biphenyl phosphate groups possessing even numbers of spacers from 2 to 10 were prepared and polymerized by polycondensation at room temperature. All the polymers gave birefringent melt except one. The identification of the mesophase was transparent with an increase in spacers. The effect of substitution in the side chain with regard to bulkiness and spacers were studied with thermogravimetric analysis and differential scanning calorimetry. The results reveal that the thermal stability of the polymers increased with the increasing bulkiness of the side chain and decreased with increasing spacer length. The incorporation of the phosphorous moiety also had a considerable effect on the glass-transition temperature. Char yield of the polymer decreased with increasing methylene chain length, and it did not vary much with the size of the pendent groups. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 831–841, 2002

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

INTRODUCTION

Metal-containing liquid-crystalline polymers have emerged as an important category of polymeric materials.[1] The impetus for the development of these materials is based on the premise that polymers contain metals are expected to possess properties significantly different from those of conventional fully organic liquid-crystalline polymers. Examples of these properties include electrical conductivity, magnetic behavior, thermal stability, non-linear effects, and possibly superconductivity.[2] After the report of Vorlander in 1910,[3] motivation was directed toward the use of the potential advantages of the incorporation of ferrocene, a unique sandwich compound, in a polymer. Initially, it was incorporated in the chain for the promotion of thermal stability. Later, it was proven that it could be used as a part of mesogen in liquid-crystalline polymers. This thought has contributed to many research articles using the ferrocene moiety as a part of mesogen.[4–11] On the other hand, phosphate esters, a potential fire retardant,[12–17] is a flexible molecule, and reports on liquid-crystalline polymers containing phosphorus are very scarce.[18–20] Keeping these two moieties in the polymer backbone should give interesting properties, such as high thermal stability and low processing temperatures due to ferrocene and the phosphate esters, respectively. In our

early work, we reported on ferrocene-containing liquid-crystalline polyphosphates with high thermal stability and char yield.[21] This work deals with the synthesis and characterization of ferrocene-containing liquid-crystalline polyphosphates with phenyl and biphenyl pendant groups.

EXPERIMENTAL

Dichloromethane, methanol, and tetrahydrofuran (THF; SRL, India) were purified by the usual procedure[22] and dried before use. Phosphorous oxychloride was purchased (SD Fine, India) and distilled before use. Ferrocenedicarbonyl chloride was prepared with a method from the literature.[23] 4-Benzyloxy phenol was purchased from Aldrich (Switzerland) and was used without further purification. n-Bromoalkanol and n-hydroxyalkyloxy benzoic acid (n = 2, 4, 6, 8, and 10) were prepared with a procedure reported elsewhere.[21] Phenylphosphorodichloridate and biphenylphosphorodichloridates were prepared as per a procedure reported elsewhere.[24]

1,1′-Bis(*p*-benzyloxy phenyl ferrocene dicarboxylate)

Ferrocene dicarbonyl chloride (0.1 mol) was refluxed for 24 h with p-benzyloxy phenol (0.2 mol) and triethylamine (0.2 mol) in 300 mL of dry dichloromethane. The reaction mixture was cooled and washed successfully with diluted HCl, water, sodium bicarbonate, brine, and water. The organic layer was dried over fused calcium chloride, and the solvent was removed under vacuum. The residue was recrystallized from THF/n-hexane mixtures to get bright orange crystals (yield = 88%).

IR (KBr, cm^{-1}): 1735 (ester carbonyl), 3106 (1,1′-disubstituted ferrocene ring). NMR (CDCl$_3$, δ): 5.026 (s, 4H, cyclopentadienyl ring proton), 4.5 (s, 4H, —O—CH_2—Ph), 7.3 (s, 10H, aromatic proton benzyl), 7.07 (t, 8H, aromatic attached to ferrocene).

1,1′-Bis(*p*-hydroxyphenylferrocene dicarboxylate)

1,1′-Bis(p-benzyloxyphenylferrocene dicarboxylate) (0.1 mol) was dissolved in 1 : 1 THF/methanol, and cyclohexene (0.2 mol) refluxed with 5 wt % of 10% Pd/C for 6 h. The course of the reaction was monitored by thin layer chromatography. After complete reductive cleavage, the solution was filtered and dried under vacuum with a rotary

vacuum evaporator. The residue obtained was dissolved in a minimum amount of THF and precipitated with pet ether (40–60°C) to get yellow precipitate (yield = 75%).

IR (KBr, cm^{-1}): 3450 (phenolic OH), 3100 (1,1′-disubstituted ferrocene ring) 1735 (ester carbonyl). ^{1}H-NMR (CDCl$_3$, δ): 5.026 (s, 4H, cyclopentadienyl ring proton), 6.87 (t, 8H, aromatic, ortho to OH).

Bis[4-chloroformylphenyloxy-*n*-alkyl(aryl phosphate ester)] (*n* = 2, 4, 6, 8, and 10; aryl = phenyl, biphenyl)

The typical procedure used for the preparation of bis[4-chloroformylphenyloxyethyl(phenylphosphate ester)] was as follows: 2-hydroxyethoxy benzoic acid (0.01 mol) was dissolved in dry THF (20 mL), and dry triethylamine (TEA; 0.01 mol) was added under nitrogen with stirring to get a homogeneous mixture. Phenylphosphorodichloridate (0.005 mol) dissolved in dry THF (5 mL) was added dropwise, and this was stirred for 12 h at ambient temperature followed by refluxing conditions for 3 h. The amine hydrochloride formed was filtered, and THF evaporated to dryness under reduced pressure. The waxy compound obtained was triturated with dry benzene to remove unreacted TEA and phenylphosphorodichloridate. The product was purified by flash column chromatography over silica gel with a chloroform–methanol (95 : 5) mixture as an eluent (yield = 90%). A similar procedure was adopted for the synthesis of the remaining monomers.

IR (KBr, cm^{-1}): 1695 (carbonyl), 1250 (Ar—O—C), 1160 (P=O), 955 (P—O—phenyl). ^{1}H-NMR (DMSO-d_6, δ) 10.05 (*s*, 2*H*, —CO OH), 6.89 (d, 4H, aromatic, ortho to ether), 7.23 (d, 4H, aromatic, meta to ether), 3.45 (t, 2H, Ar—O—CH_2), 3.18 (t, 2H, P—O—CH_2), 6.58 (m, 5H, P—Ph).

We converted all the dicarboxylic acids to their corresponding title compounds by refluxing with thionyl chloride before use.

Polymerization

Poly{bis-1,1′-ferrocenedicarboxy[4-phenyloxy carbonyl-4-phenyloxy-n-alkyl (aryl phosphate ester)]} (n = 2, 4, 6, 8, and 10; aryl = phenyl, biphenyl)

The typical procedure used for the preparation of poly{bis-1,1′-ferrocene dicarboxy[4-phenyloxy carbonyl-4-phenyloxyethyl (phenylphosphate ester)]} was as follows: 1,1′-bis(p-hydroxyphenyl ferrocene
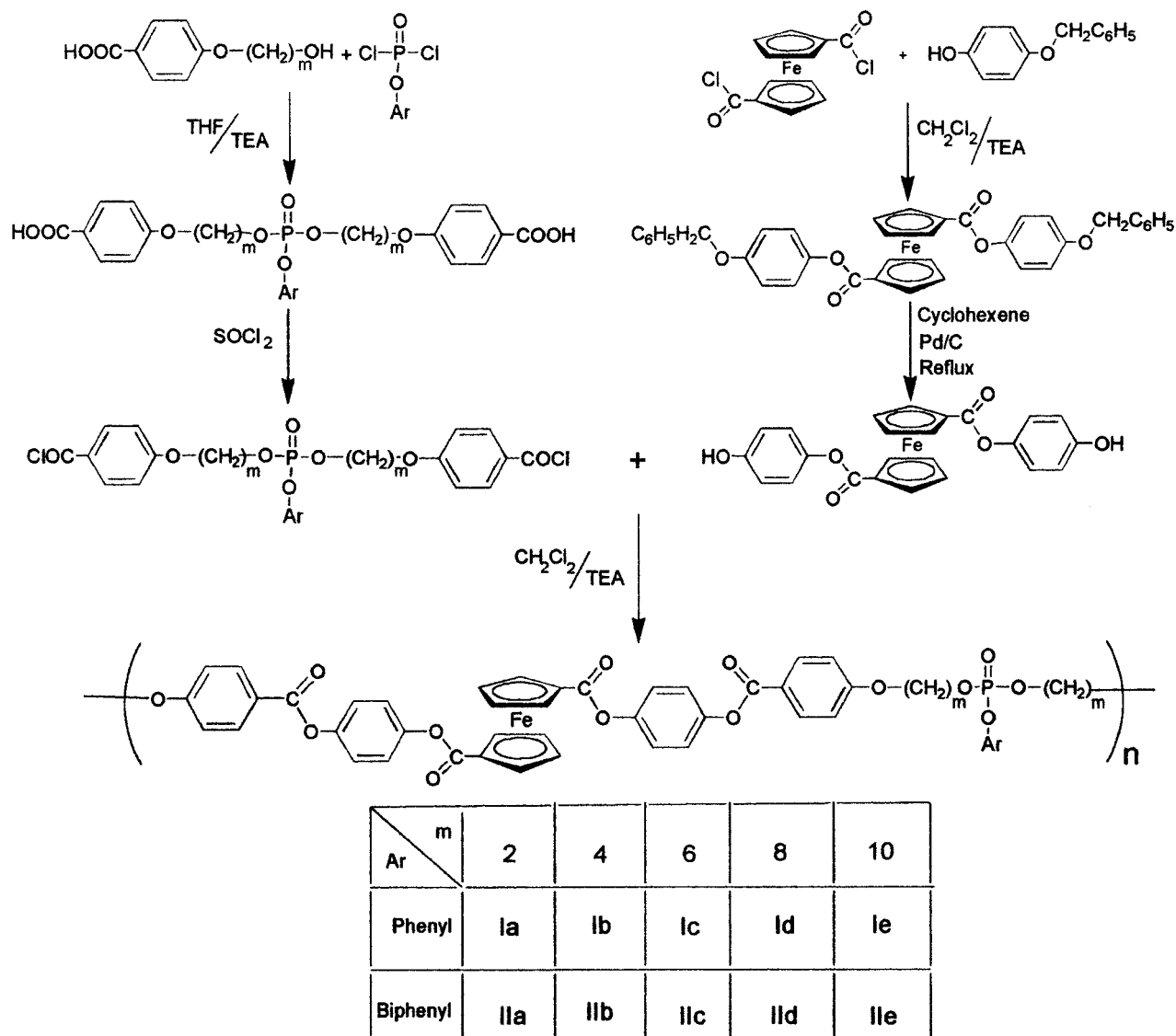
Scheme 1 Synthesis of polymers **Ia–Ie** and **IIa–IIe**.

dicarboxylate) (0.01 mol) was dissolved in dry dichloromethane (25 mL). Dry TEA (0.01 mol) was added under a nitrogen atmosphere. The bis[chloroformyl phenyloxy ethyl (phenylphosphate ester)] (0.01 mol) in dichloromethane (25 mL) was added dropwise at room temperature. During this addition, the solution became homogeneous. It was stirred further for 12 h under the same conditions. The solution was concentrated to 10 mL and poured into methanol. A orange precipitate formed and was purified by reprecipitation with methanol and dichloromethane (yield = 68%). A similar procedure was adopted for the preparation of poly{bis-1,1′-ferrocenedicarboxy[4-phenyloxy carbonyl-4-phenyloxybutyl (phenylphosphate ester)]}

(**Ib**), poly{bis-1,1′-ferrocene dicarboxy[4-phenyloxycarbonyl-4-phenyloxyhexyl (phenyl phosphate ester)]} (**Ic**), poly{bis-1,1′-ferrocene dicarboxy[4-phenyloxycarbonyl-4-phenyloxyoctyl (phenyl phosphate ester)]} (**Id**), poly{bis-1,1′-ferrocenedicarboxy[4-phenyloxycarbonyl-4-phenyloxy decyl (phenylphosphate ester)]} (**Ie**), poly{bis-1,1′-ferrocenedicarboxy[4-phenyloxy carbonyl-4-phenyloxyethyl(biphenylphosphate ester)]} (**IIa**), poly{bis-1,1′-ferrocenedicarboxy[4-phenyloxycarbonyl-4-phenyloxybutyl (biphenyl phosphate ester)]} (**IIb**), poly{bis-1,1′-ferrocene dicarboxy[4-phenyloxycarbonyl-4-phenyloxy hexyl (biphenylphosphate ester)]} (**IIc**), poly{bis-1,1′-ferrocenedicarboxy[4-phenyloxycarbonyl-4-pheny-

Table I GPC and TGA Data of Polymers Ia–Ie and IIa–IIe

| Polymer | M_n | M_w | M_w/M_n | Weight Loss Corresponds to | | Weight Loss at 600°C | Char Yield (%) |
				2%	50%		
Ia	5043	5346	1.06	240	400	56	44
Ib	5412	5683	1.05	220	380	59	41
Ic	5573	6019	1.08	220	410	62	38
Id	5192	5296	1.02	208	400	65	35
Ie	6373	6692	1.05	180	400	70	30
IIa	5537	5814	1.05	320	399	52	48
IIb	6002	6183	1.03	320	405	55	45
IIc	6017	6499	1.08	290	410	59	41
IId	5976	6156	1.03	275	405	62	38
IIe	6784	7192	1.06	220	400	65	35

M_n = number-average molecular weight; M_w = weight-average molecular weight.

loxyoctyl (biphenyl phosphate ester)]} (**IId**), and poly{bis-1,1′-ferrocenedicarboxy[4-phenyloxycar-bonyl-4-phenyloxydecyl (biphenyl phosphate ester)]} (**IIe**).

IR (KBr, cm^{-1}): 3100 (1,1′-disubstituted ferrocene ring), 2939 (CH$_2$), 1731 (ester carbonyl), 1606 (aromatic ring breathing), 1170, and 955 (P—O—phenyl), 1271 (Ar—O—C), 1375 (P=O), 2350 (—P(O)—OH). ^{1}H-NMR (CDCl$_3$, δ): 4.6 and 5.04 (S, 8H, cyclopentadiene proton), 7.09 (d, 11H, aromatic, ortho to —OCO—, attached to ferrocene and phenyl protons), 7.40 (d, 2H, aromatic, meta to —OCO—, attached to ferrocene),

8.13 (d, 2H, aromatic, ortho to —COO—), 8.00 (d, 2H, aromatic, meta to —COO—), 4.6 (t, 2H, Ar—O—CH$_2$—). ^{31}P-NMR (CDCl$_3$, δ): −11.369, −18.810. ^{13}C-NMR (CDCl$_3$, δ): 68.12 and 70.45 (two unsubstituted ring carbons in ferrocene), 73.24 (tertiary carbon in ferrocene), 166 (ferrocene attached to carbonyl carbon), 115.51 (aromatic, tertiary carbon attached to ferrocene through —OCO—), 122.53 (two unsubstituted aromatic carbons), 127.90 (aromatic, tertiary fourth-position carbon attached to ferrocene), 156 (carbonyl carbon attached to phenyl ring), 120.93 (aromatic, tertiary fourth-position carbon from aryl alkyl linkage), 132.32 and 131.82 (ar-
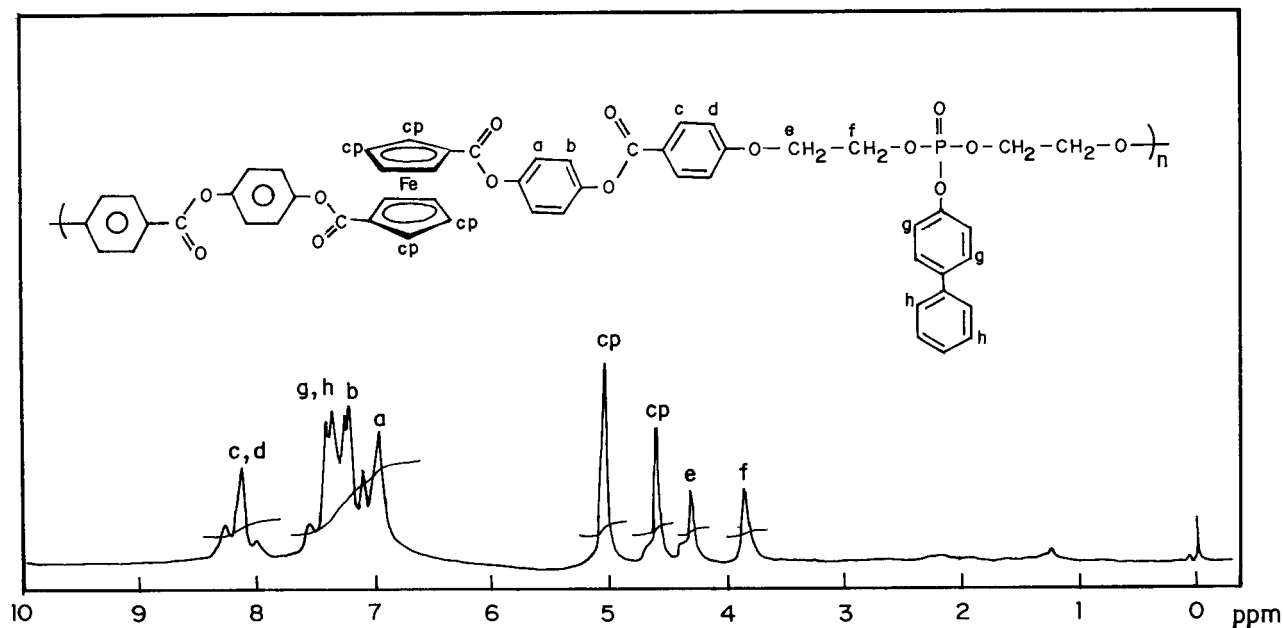
Figure 1 ^{1}H-NMR spectrum of polymer **IIa**.

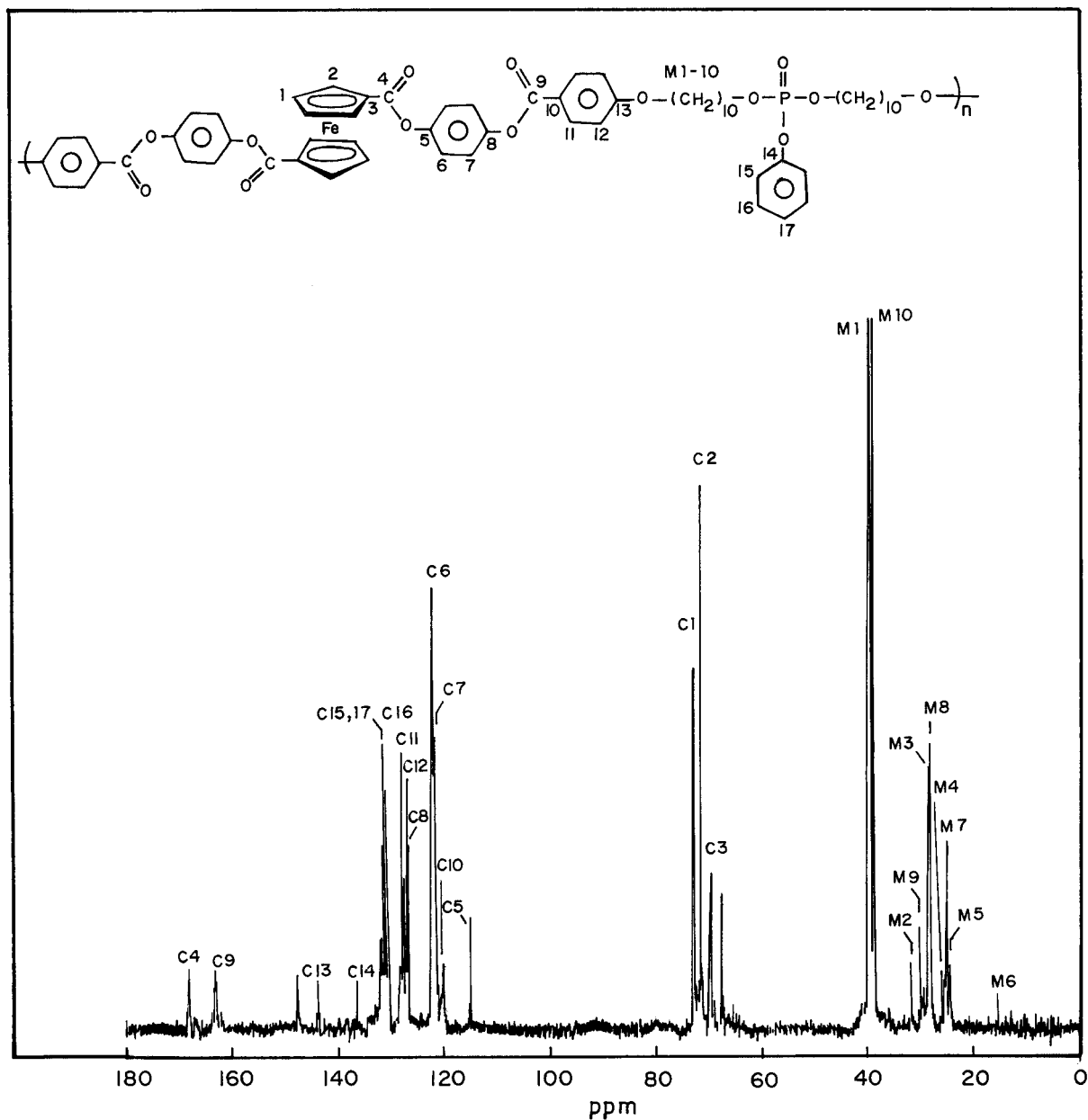**Figure 2** ^{13}C-NMR spectrum of polymer **Ie.**

omatic unsubstituted phenyl carbon attached to aryl alkyl linkage), 131.30 (aromatic, tertiary carbon attached to aryl alkyl linkage), 72.24 (methylene carbon attached to ether linkage), 66.22 (methylene carbon attached to phosphate ester), 128–132 (aromatic, P-attached aromatic carbon).

Characterization

IR spectra were recorded on a Nicolet IR (Impact 440) spectrophotometer (USA) with KBr pellets. Gel permeation chromatography (GPC) measurements were done on a styrogel column with THF as the solvent. High-resolution ^{1}H, ^{31}P- and ^{13}C-NMR spectra were recorded on a Brucker spectrometer (USA) (300 and 75.4 MHz, respectively). Generally, deutrated chloroform was used as a solvent for NMR spectra unless otherwise specified. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies were carried out on a Metler Toledo STAR^{e} system (Germany) under a nitrogen atmosphere. The heating rate of TGA analysis was 20°C/min with a
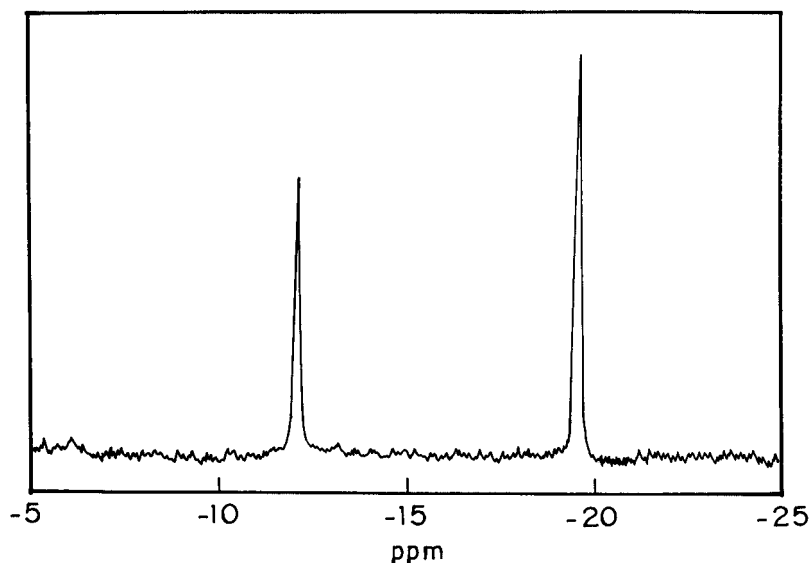
Figure 3 ^{31}P-NMR spectrum of polymer **Ic.**

nitrogen flow of 20 mL/min. The polarizing microscopic studies were performed with a Euromax polarizing microscope (Holland) equipped with a Linkem HFS 91 heating stage and a TP-93 temperature programmer (London, UK). We made samples by melting a small quantity of the material between two thin glass cover slips to get a uniform film with a heating and cooling rate of 5°C/min. The photographs were taken with a Nikon FM10 camera and exposed on Konica film.

RESULTS AND DISCUSSION

4-(*n*-Hydroxyalkyloxy benzoic acid) was prepared from corresponding *n*-bromoalkanol and *p*-hydroxybenzoic acid with the Williamson aryl-alkyl ether synthesis method. The previously mentioned precursor was condensed with phenyl/biphenylphosphorodichloridate. The dicarboxylicacid thus obtained was converted to the corresponding bisacid chloride by reflux with thionyl chloride. We prepared the ferrocene-containing monomer by reacting benzyl-protected quinol and 1,1′-ferrocenedicarbonyl chloride. Deprotection was done by the reductive cleavage of the benzyloxy group with Pd/C and cyclohexene. The polymers were prepared by room temperature solution polycondensation with 1,1′-bis(*p*-hydroxyphenylferrocene dicarboxylate) and bis[chloroformylphenyloxy alkyl (biphenyl/phenylphosphate)] in dichloromethane. The polymers were soluble in all polar organic solvents such as dichloromethane, THF, dioxane,

dimethylformamide (DMF), dimethylacetamide (DMAc), and dimethylsulphoxide (DMSO) and were insoluble in benzene, toluene, methanol, and acetone. GPC analyses are shown in Table I. The polymers were characterized by various spectral techniques. Figures 1, 2, and 3 show the ^{1}H-NMR of polymer **IIa,** the ^{13}C-NMR of polymer **Ie,** and the ^{31}P-NMR of polymer **Ic,** respectively.

Thermogravimetric data of the polymers are summarized in Table I. The pattern of the TGA analysis is shown in Figures 4 and 5. Thermal stability was evaluated by 2% weight loss at the
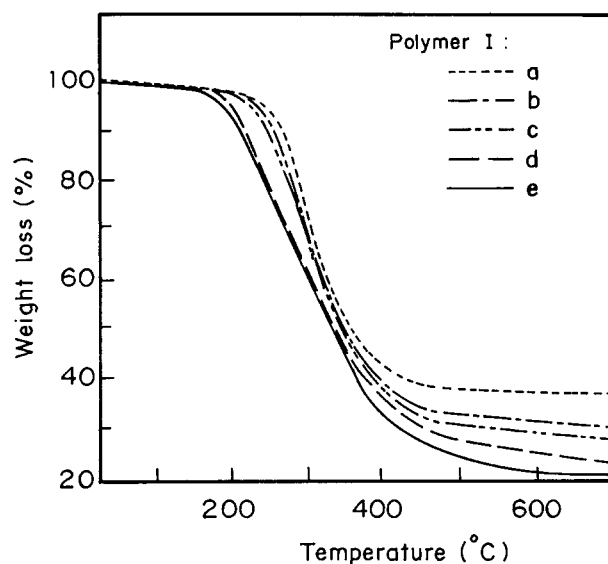

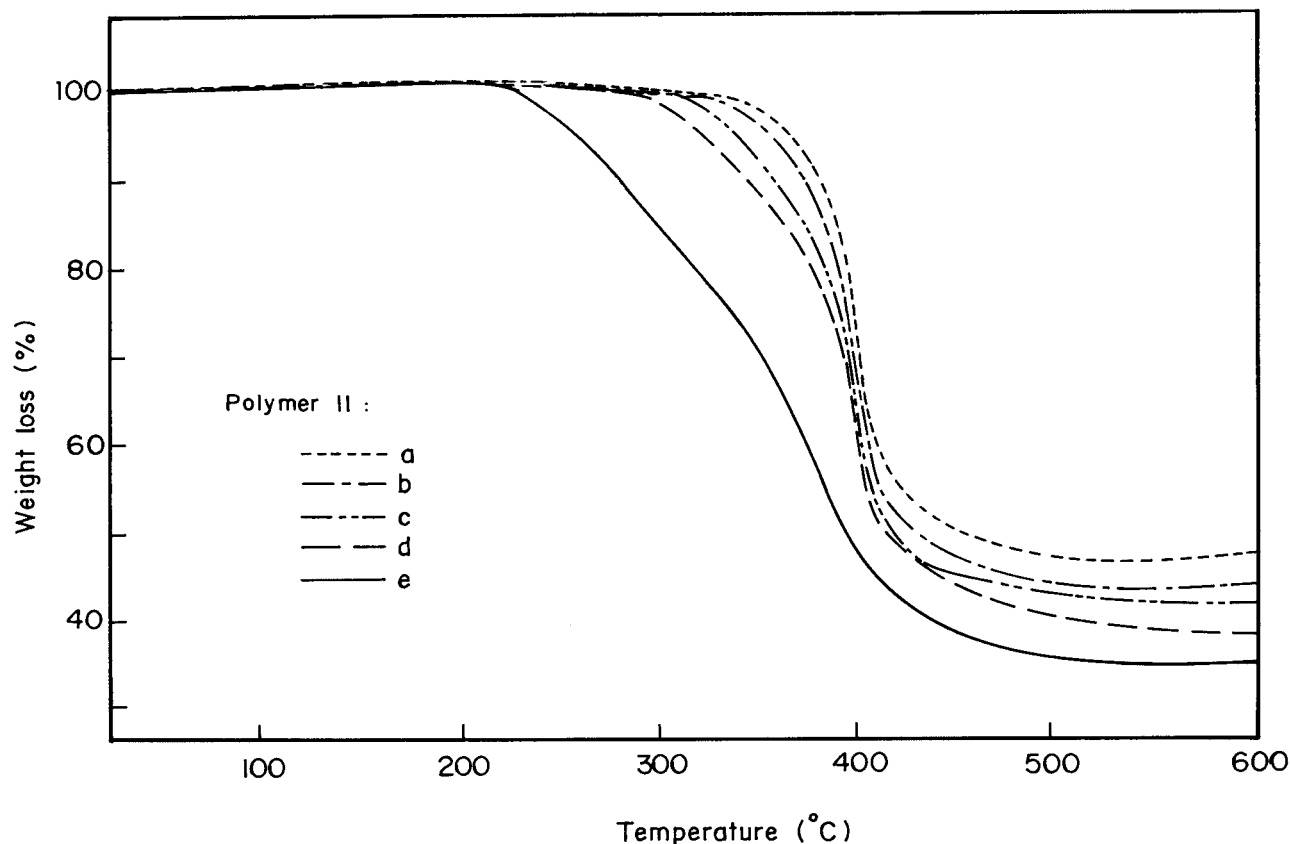**Figure 4**   TGA traces of polymers **Ia–Ie.**

Figure 5 TGA traces of polymers **IIa–IIe.**

minimum temperature. Close inspection of the TGA thermograms of the two series of the polymers revealed that the stability of the polymer decreased with increasing spacer length. It also showed that polymers with biphenyl groups in the side chain were more stable than the polymers with pendant phenyl groups with same number of methylene groups. The char yield fell between 30 and 48% for all the polymers. The data suggests that the char yield was in decreasing order, when the ratio between hydrocarbons and the phosphorous content of a single monomeric unit increased. The 50% weight loss of the polymers occurred at around 400°C. Decomposition of the polymer was almost completed at 600°C, after which no weight loss was observed. The char yield of the polymers at 600°C increased to 48%, and it was reduced up to 30% with an increase in spacers. The decomposition of the polymers probably occurred by the pyrolytic cleavage of the phosphate ester group and the breakage of the link between the mesogenic groups with different methylene units. The high char yield may be ascribed to the decomposition of phenyl esters and

the cyclopentadiene of ferrocene ring, and thus would produce finally iron oxide and phosphoric acid.[21]

The liquid-crystalline properties of the polymers were studied under a polarized microscope. Representative photographs are shown in Figure 6, and the type of the mesophase is tabulated in Table II. All the polymers exhibited liquid-crystalline behavior except for polymer **Ia.** The phases were identified and compared with previously observed phases reported in literature.[25] The transition temperature for all the polymers observed in DSC are shown in Table II. All the polymers exhibited normal melting and clearing behavior and showed micrograin structure for polymers **Ib–Ic.** The reproducibility of the formation of the liquid-crystalline phases was satisfactory. Polymers that contained 8- and 10-methylene spacers showed similar transition behavior with the formation of a clear nematic texture (polymers **Id–Ie**). Whereas polymers **IIa–IIc** showed a grainy texture, a nematic texture was observed for polymers **IId** and **IIe.** In general, the size of the liquid-crystalline monodomain was im-
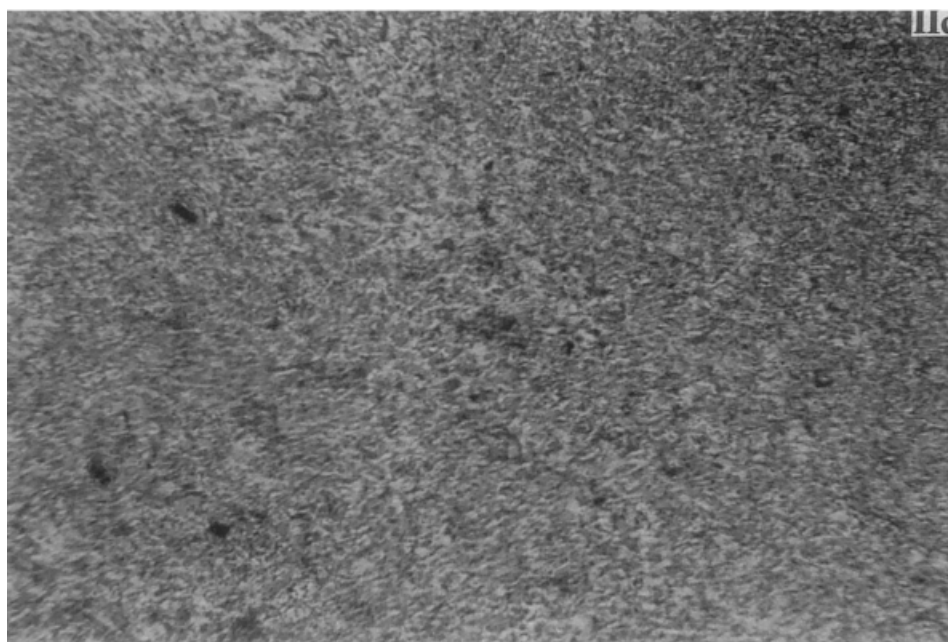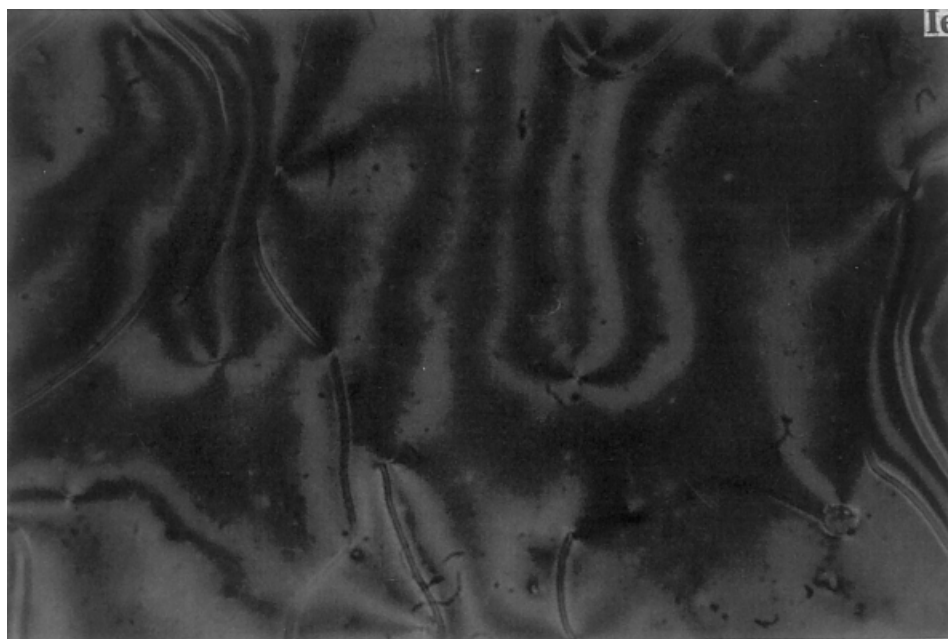
Figure 6 Representative photographs of polymer **Ie** and **IIc** (the photos were taken during the first cooling at a magnification of 20×).

proved with an increase in spacer length when the textures of the two series of polymers were compared. Meanwhile, the transparency in the liquid-crystalline structure was less with an increase in the bulkiness of the side chain. Polymer **Ia** did not show anisotropic behavior, whereas all other polymers, including **IIa,** showed birefrin-

gent melt. This indicates that the biphenyl group in the side chain of the polymer was also individually acting as a mesogen; hence, the series containing the biphenyl group in the pendant showed liquid-crystalline behavior. However, in the case of the phenyl group, it did not act as mesogen although it acted as nonmesogenic rigid moiety in

**Table II   DSC Transition Temperatures of Polymers Ia–Ie and IIa–IIe**

Polymer	T_g (°C)	T_m (°C)	T_i (°C)	ΔT (°C)	Type of Texture
Ia	50	100	—	—	—
Ib	48	92	220	128	Grainy
Ic	Not observed	85	175	90	Grainy
Id	Not observed	79	140	61	Nematic
Ie	Not observed	72	115	43	Nematic
IIa	72	82	250	168	Grainy
IIb	70	80	223	143	Grainy
IIc	50	76	198	122	Grainy
IId	46	70	154	84	Nematic
IIe	Not observed	60	122	62	Nematic

T_m = melting temperature.

the side chain. So in polymer **Ia,** the mesogen and nonmesogens were arranged alternatively with only a 2-methylene spacer. Moreover, the ferrocene moiety in the mesogen imparted a step-like structure, which also caused more disorder, rather than imparting order for showing liquid-crystalline behavior. However, this effect was diluted on the increase of the methylene chain and favored mesogenic alignment in the case of other polymers in the same series (**Ib–Ie**).

As the spacer length increased and the bulkiness of the side chain decreased, the easy segmental mobility and packing possibility of the polymers provided opportunity to align themselves to form a large monodomain. Whereas in the case of lower spacer length and a bulky side chain (**Ib, Ic,**
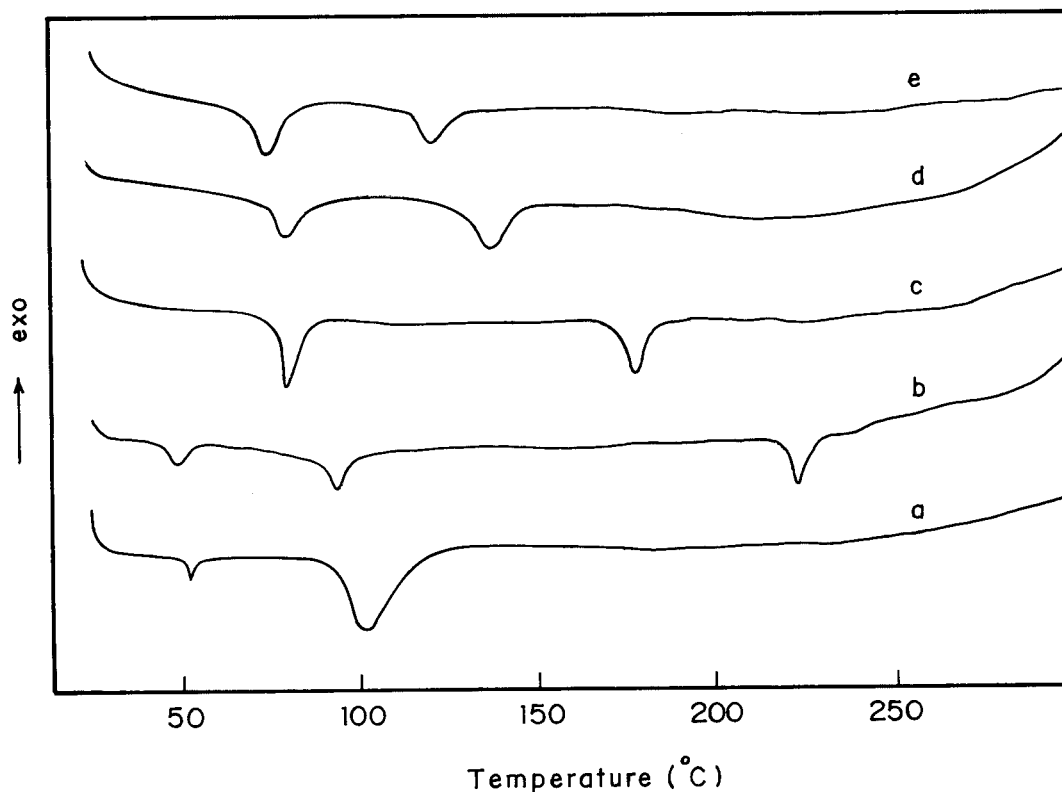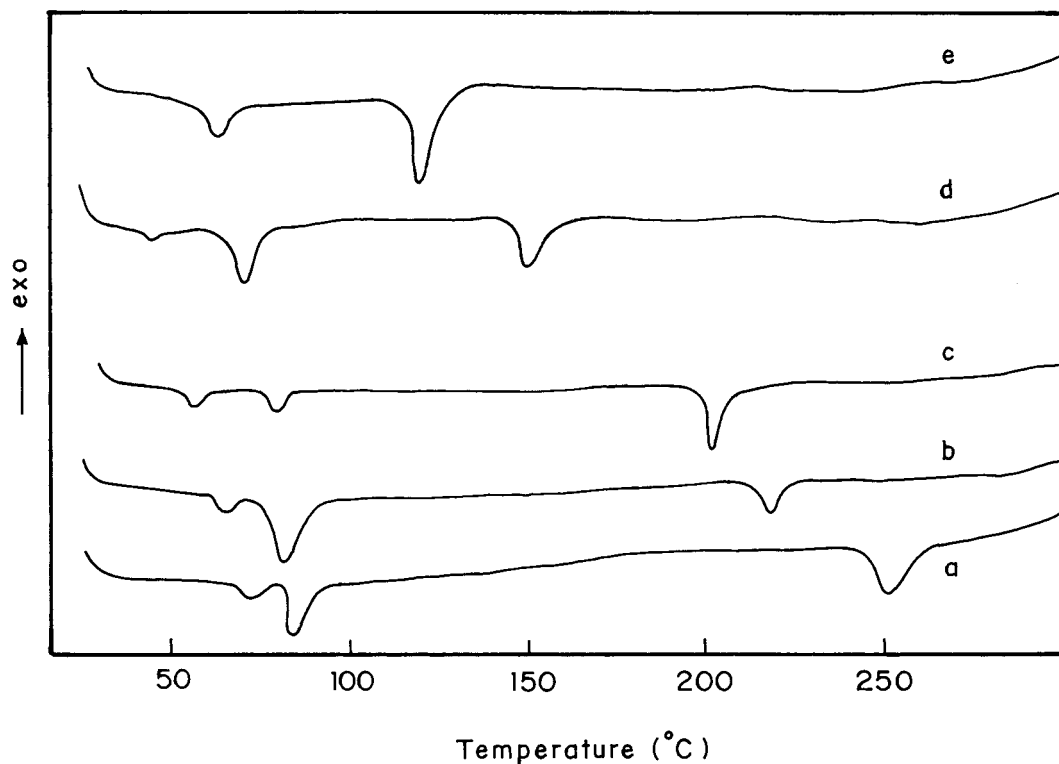

Figure 7   DSC curves of polymers **Ia–Ie.**

Figure 8 DSC curves of polymers **IIa–IIe.**

and **IIa–IIc**), restricted mesogenic movement due to limited spacer availability disturbed the structural alignment, and thereby, small microdomains resulted.

DSC results (Figs. 7 and 8) reveal that the glass-transition temperature (T_g) of the polymers decreased as the flexible chain length increased. The respective transition temperatures are tabulated in Table II. The T_g of the polymers was considerably low because of the incorporation of the phosphate group and because the lateral substitution of the aromatic groups disturbed the molecular close packing.[25] Moreover, the phase duration (ΔT) decreased with an increase in chain length. The polarity of the chain also definitely imparted considerable change in the physical properties. The high polarity of the phosphorus atom and the Sp^3-hybridized abnormal bond angle (107°) acting as a linear chain would be greatly hindered.[18] Thus, the packing of the chain was affected, which would lead to a decrease in the isotropic transition temperature and the liquid-crystalline transition temperature. Evidently, the isotropic transition temperature was greatly reduced compared to other similar nonphosphorus polymers.[26] The side groups phenyloxy and biphenyloxy, which disturbed the conformational distribution of the methylene chain, were linked by mesogenic moieties. This kind of uneven arrangement of spacers affected the order of the mesogen so as to give a lesser order micrograin structure. The consistency of the phase was observed even after three or more heating and cooling cycles. ΔT of polymers **Ib–Ie** was from 43 to 128°C and for polymers **IIa–IIe** was from 62 to 168°C. The data reveal that biphenyl pendant polymers had higher transition temperatures than phenyl pendant polymers. This may have been due to an increase in the aromaticity of the pendant and the mesogenic behavior of the biphenyl group. This indicates that the nonmesogen pendant phenyloxy group had less influence on the maintenance of the liquid-crystalline phase than the biphenyloxy pendant group.

CONCLUSIONS

A new series of ferrocene-containing liquid-crystalline polyphosphates containing an even series of methylene spacers from 2 to 10 were synthesized. Two types of lateral substitution, namely,

phenyl and biphenyl, over phosphate esters were studied. All the polymers were found to give birefringent melt. The T_g of the polymers decreased with increases in spacer length. The thermal stability of the polymers increased with increases in bulkiness and aromaticity of the pendant group through phosphate ester. DSC thermal analysis confirmed the formation of liquid-crystalline mesophases.

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