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Thermotropic main chain liquid crystalline polyesters containing ferrocene and phosphate units: synthesis and characterization

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A new series of liquid crystalline main chain copolyesters were prepared, having ferrocene in the mesogenic segment and a methyl phosphate group along with a methylene spacer. The even numbered methylene groups were varied from two to ten. Liquid crystalline behaviour was investigated on a hot stage optical polarized microscope. Thermal properties of the polymers were analysed by TGA and DSC, revealing that the polymers yield high char products, probably caused by the formation of phosphorus and iron oxides. The glass transition (T_g) temperatures of the polymers were found to be fairly low, the result of the incorporation of bulky phosphorus and ferrocene moieties in the chain. The phase behaviour was analysed and correlated with the structure of the polymers. The liquid crystalline textures of the polymers became more transparent with increasing spacer length. Energy minimized structures for the polymer repeating units reveal that both the ferrocene and phosphorus moieties produce more molecular entanglement, thus reducing the T_g and T_m of the polymers.

1. Introduction

Aromatic liquid crystalline copolyesters of commercial importance are mostly produced with compositionally heterogeneous chemical sequences along the polymer chain [1]. Such chemical heterogeneity is responsible for a number of interesting properties in thermotropic liquid crystalline polymers (LCPs), such as tailoring of the transition temperature, thermal stability and crystal morphology. Changing the molecular structure of the mesogenic moiety and/or the flexible spacer may affect many molecular parameters [2]. LCPs with an aromatic ester mesogen group and spacers of different length have been under investigation with regard to chemical nature by several research groups since the early 1980s [3–14].

The shape and aspect ratio of the mesogens are the key factors affecting the properties of the polymers. The introduction of a bulky ferrocene unit into an aromatic triad ester mesogen is expected to give interesting property changes due to this alteration of the aspect ratio; this will in turn affect the packing possibilities and type of liquid crystalline texture. Transition metal-containing organometallic compounds are known to impart an interesting metallic character and enhance the thermal stabiliy of an LCP [15]. The first liquid crystal prepared from a sandwich compound was a ferrocene ester compound [16]; the selection of ferrocene was justified by its excellent aromatic character and thermal stability over 500°C [17–23]. On the other hand, phosphorus being a non-metal provides its own distinguishing characteristics (e.g. fire resistance [24–28] and adhesive properties [19]) when it is incorporated in the polymer chain. The introduction of a polar phosphate ester group in the spacer will also affect the polymer properties with its polarity and by increasing the molecular entanglement [30].

We have previously demonstrated several polyphosphate esters as fire retardant materials and reported the structure–property relationship of lateral substitution in a main chain liquid crystalline polymer containing ferrocene and phosphorus [31]. The objective of the present work is to incorporate the ferrocene moiety in the centre core of the mesogen, and include various substituted phosphate esters as part of the spacer. It also includes the study of the effect of substitution over the phosphorus group on thermal and mesomorphic properties.

2. Experimental

2.1. *Synthesis*

The synthesis of the polymers is shown in the scheme. 4-Hydroxy-*n*-alkyloxybenzoic acids were prepared from *n*-bromoalkanols and hydroxybenzoic acid using Williamson ether syntheses. The phosphorus-containing monomer was prepared by condensation between 2 moles of a 4-hydroxy-*n*-alkyloxybenzoic acid and one mole of methyl phosphorodichloridate using triethylamine as an acid scavenger. The dicarboxylic acid thus obtained was converted to the corresponding bisacid chloride by

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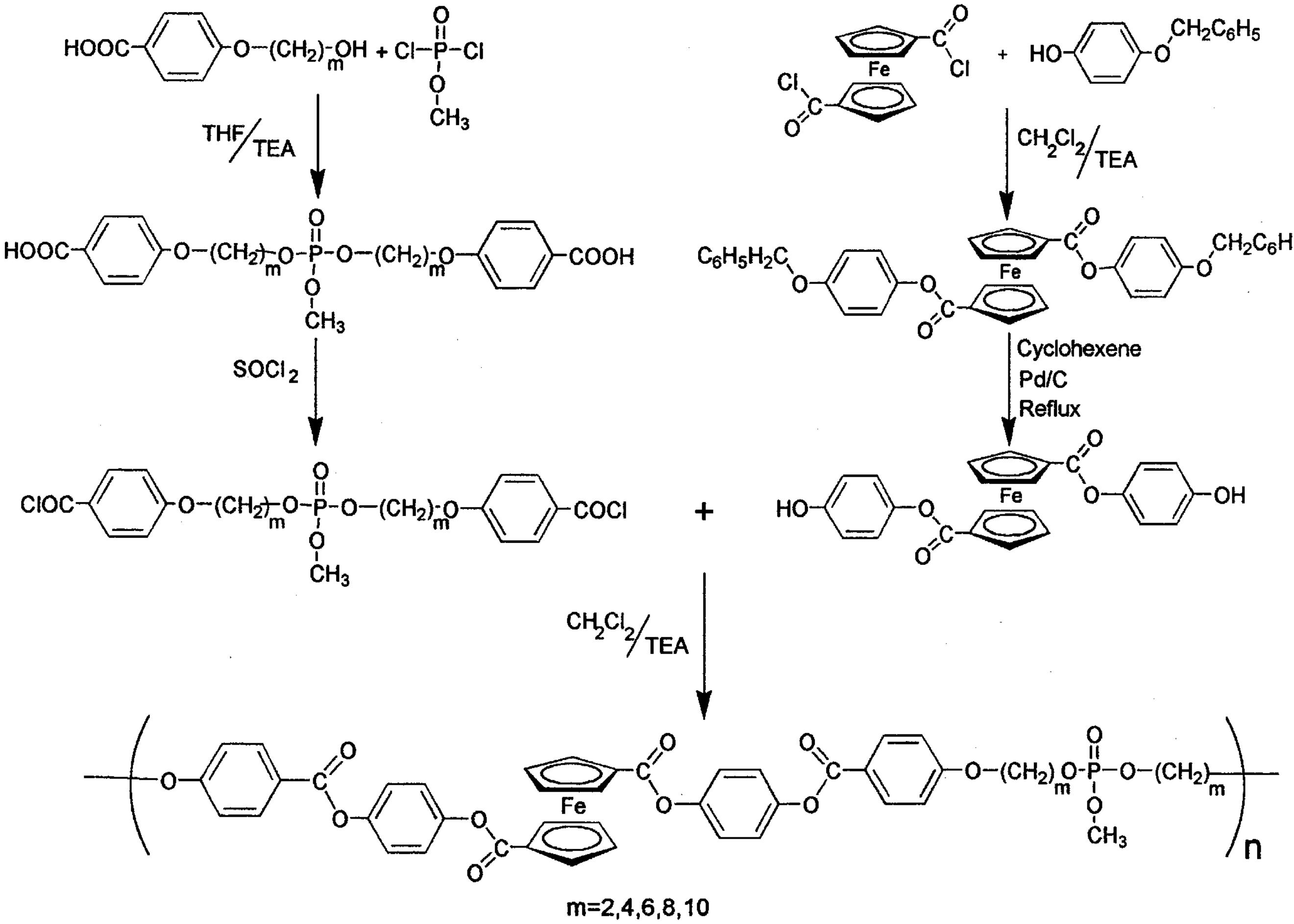

Scheme. Scheme of the synthesis of polymers **Ia**–**Ie**.

heating under reflux with thionyl chloride. The ferrocene-containing monomer was prepared by reacting benzyl-protected quinol with 1,1′-ferrocenedicarbonyl chloride. Deprotection was achieved by reductive cleavage of the benzyloxy group using Pd/C and hydrogen. Cyclohexene was used for *in situ* generation of hydrogen, by heating the reactants in THF/methanol at reflux. During heating, the cyclohexene was converted to benzene with release of two molecules of hydrogen which effected the reductive cleavage of the benzyloxy group. The polymers were prepared by a room temperature solution polycondensation method using the ferrocene-containing bisphenol and the phosphorus-containing bisacid chloride in dichloromethane under nitrogen. GPC analysis showed a weight average molecular mass of 4970–6320 daltons with reference to polystyrene standards. The values obtained are summarized in table 1.

Dichloromethane, methanol and tetrahydrofuran (SRL) were purified by the usual procedure [32] and dried before use. Phosphorus oxychloride was purchased (SD

Table 1. Thermogravimetric analysis of polymer **Ia**–**Ie**.

Polymer	M_n	M_w	M_n/M_w	Temperature for weight loss corresponding to 2%	Temperature for weight loss corresponding to 50%	Char yield at 600°C/%
Ia	4520	4870	1.10	225	580	40
Ib	4870	5310	1.09	210	490	32
Ic	5183	5650	1.09	200	480	29
Id	4620	4990	1.08	185	440	25
Ie	5745	6320	1.10	170	400	22

Fine, India) and distilled before use. Ferrocenedicarbonyl chloride was prepared using a literature method [33]. 4-Benzyloxyphenyl was purchased from Aldrich and used without further purification. *n*-Bromo alkanols and 4-hydroxy-*n*-alkyloxybenzoic acid ($n = 2, 4, 6, 8, 10$) were prepared using a reported procedure [31].

2.1.1. *1,1′-Bis(4-benzyloxyphenyl) ferrocenedicarboxylate*

Ferrocenedicarbonyl chloride (0.1 mol) was heated under reflux for 24 h with 4-benzyloxyphenol (0.2 mol) and triethylamine (0.2 mol) (TEA) in 300 ml of dry dichloromethane. The reaction mixture was cooled and washed successively with dil. HCl, water, sodium bicarbonate, brine, and water. The organic layer was dried over fused calcium chloride, and the solvent removed under vaccum. The residue was recrystallized from THF/hexane mixtures to give bright orange crystals; yield 88%. IR (KBr): 1735 cm^{-1} (ester carbonyl), 3106 cm^{-1} (1,1′-disubstituted ferrocene ring). ^{1}H NMR (CDCl$_3$): δ 5.026 (s, 4H, cyclopentadienyl ring H), 4.5 (s, 4H, –O–CH$_2$–Ph), 7.3 (s, 10H, ar H benzyl), 7.70 (t, 8H, ar attached to ferrocene).

2.1.2. *1,2′-Bis(4-hydroxyphenyl) ferrocenedicarboxylate*

1,1′-Bis(4-benzyloxyphenyl) ferrocenedicarboxylate (0.1 mol) was dissolved in 1/1 THF/methanol, cyclohexene (0.2 mol) added, and the mixture heated under reflux with 5 wt % of 10% Pd/C for 6 h. The course of the reaction was monitored by TLC. After complete reductive cleavage, the solution was filtered and evaporated to dryness under vacuum using a rotary evaporator. The residue obtained was dissolved in a minimum amount of THF and precipitated using petroleum ether (40–60°C) to give a yellow precipitate; yield 75%. IR (KBr): 3450 cm^{-1} (ar OH), 3100 cm^{-1} (1,1′-disubstituted ferrocene ring), 1735 cm^{-1} (ester CO). ^{1}H NMR (CDCl$_3$): δ 5.026 (s, 4H, cyclopentadienyl ring H), 6.87 (t, 8H, ar, *ortho* to OH).

2.1.3. *Bis(4-carboxyphenoxyethyl) methyl phosphate*

2-Hydroxyethoxybenzoic acid (0.01 mol) was dissolved in dry THF (20 ml) and dry TEA (0.01 mol) was added under nitrogen with stirring. Methylphosphorodichloridate (0.005 mol) dissolved in dry THF (5 ml) was added dropwise and the mixture stirred for 12 h at ambient temperature, followed by heating under reflux for 3 h. The amine hydrochloride thus formed was filtered and the THF evaporated off under reduced pressure. The waxy compound obtained was triturated with dry benzene to remove unreacted TEA and methylphosphorodichloridate. The product was purified by flash column chromatography over silica gel using chloroform/methanol (95/5) mixture as eluent; yield 92%. The other homologues were prepared by a similar procedure. IR (KBr): 3300 cm^{-1} (carboxylic OH), 1250 cm^{-1} (Ar–O–C), 1290 cm^{-1} (P=O), 1695 cm^{-1} (C=O), 2960 cm^{-1} (CH$_2$), 950 cm^{-1} (P–O–C). ^{1}H NMR (DMSO-d$_6$) δ: 11.05 (S, 2H, –COOH), 6.78 (d, 4H, ar, *ortho* to ether), 7.6 (d, 4H, ar, *meta* to ether), 3.7 (t, 2H, Ar–O–CH$_2$), 3.2 (t, 2H, P–O–CH$_2$), 4.05 (S, 3H, P–O–CH$_3$).

2.1.4. *Bis(4-chloroformylphenoxy-n-alkyl) methyl phosphate*

Bis(4-carboxyphenoxyethyl) methyl phosphate (0.01 mol) was dispersed in dry benzene (15 ml). Distilled thionyl chloride (0.04 mol) was added dropwise and the mixture stirred at room temperature for 3 h. During the stirring two drops of dry DMF were added as catalyst. The mixture was slowly brought to gentle reflux for 3 h. Excess of thionyl chloride and benzene was removed under vacuum, and the residue was connected to high vacuum at 50°C for several hours to remove final traces of thionyl chloride. The bisacid chloride thus obtained was used without further purification. A similar procedure was adopted for the preparation of the remaining monomers.

2.1.5. *Poly[1,1′-ferrocenyl-bis{4-(4-carbonyloxyphenoxy)-carbonylphenoxyethyl} methyl phosphate]*

1,1′-Bis(4-hydroxyphenyl) ferrocenedicarboxylate (0.01 mol) was dissolved in dry dichloromethane (25 ml). To this, dry TEA (0.01 mol) was added under a nitrogen atmosphere. The bis(4-chloroformylphenoxyethyl) methyl phosphate ester (0.01 mol) in dichloromethane (25 ml) was added dropwise at room temperature. During addition the solution became homogeneous; stirring was continued for 12 h under the same condition. The solution was concentrated to 10 ml and poured into methanol, giving an orange precipitate which was reprecipitated with methanol; yield 68%. IR (KBr); 3080 cm^{-1} (1,1′-disubstituted ferrocene ring), 2930 cm^{-1} (CH$_2$), 1731 cm^{-1} (ester CO), 1268 cm^{-1} (Ar–O–C), 1290 cm^{-1} (P=O), 1605 cm^{-1} (C=O), 990 cm^{-1} (P–O–C). ^{1}H NMR (CDCl$_3$): δ 58, 5.03 (S, 8H, cyclopentadiene proton), 6.97 (d, 2H, ar, *ortho* to –OCO–, attached to ferrocene), 7.23 (d, 2H, ar, *meta* to –OCO–, attached to ferrocene), 8.13 (d, 2H, ar, *ortho* to –COO–), 3.84 (t, 2H, Ar–O–CH$_2$–), 4.27 (S, 3H, –O–CH$_3$), 1.77 (t, 2H, CH$_2$–O–P). ^{31}P NMR (CDCl$_3$): δ −10.17. ^{13}C NMR (CDCl$_3$): δ 68.05, 72.23 (two unsubstituted ring carbon in ferrocene), 73.26 (tertiary carbon in ferrocene), 163 (ferrocene attached carbonyl carbon), 115.4 (ar, tertiary carbon attached to ferrocene through –OCO–), 122.52 (two unsubstituted ar carbon), 128.52 (ar, tertiary 4th position carbon attached to ferrocene), 156 (carbonyl carbon, attached to phenyl ring), 120.8 (ar, tertiary 4th position carbon from aryl alkyl linkage), 132.49 (ar unsubstituted phenyl carbon attached to aryl alkyl linkage), 132.32 (ar, tertiary carbon attached to aryl alkyl linkage), 77.42 (methylene carbon attached to ether linkage), 77 (methylene carbon attached to phosphate ester), 41.55 (methoxy carbon).

All other polymers were prepared by adopting a similar procedure.

2.2. *Characterization*

GPC measurements were made using a styrogel column and THF as solvent. The column was calibrated with polystyrene standards of molecular mass 5000–25 000. High resolution ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker spectrometer (300 MHz and 75.4 MHz). In general, deuteriated chloroform was used as a solvent for NMR spectra unless otherwise specified. IR spectra were recorded using a Nicolet IR (Impact 440) spectrophotometer with KBr pellets. TGA and DSC studies were carried out on a Mettler Toledo STAR^{e} system under nitrogen; the heating rate for TGA analysis was 20°C min^{-1} with a nitrogen flow of 20 ml min^{-1}. The POM studies were performed using a Euromax polarizing microscope equipped with a Linkam 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 obtain a uniform film, with heating and cooling rates of 5°C min^{-1}. The photographs were taken using a Nikon FM10 camera and exposed on Konica film. Molecular modelling studies were performed using computer program Chem 3D Pro. The structures were initially minimized with Molecular Mechanics (MM2) to a minimum RMS gradient of 0.100; further refining was by MOPAC (Molecular Orbital PACkage) program using Semi-empirical Hamiltonian AM1 unrestricted wave function.

3. Thermal analysis

Thermogravimetric data of the polymers are summarized in table 1. The pattern of the TGA analysis is shown in figure 1. Thermal stability is evaluated by the minimum temperature for 2% weight loss. The polymers were stable up to 170–225°C; TGA thermograms show that the stability of the polymer decreases with increasing spacer length. The 50% weight loss of the polymers takes place in the range 400–580°C; the temperature for 50% weight loss decreases with increasing methylene chain. Decomposition of the polymer is almost complete at 600°C; after that no weight loss is observed. The char yield of the polymers at 600°C starts at 40% (**Ia**) and decreases regularly to 22% (**Ie**) with increase in spacer length. The high char formation may be due to

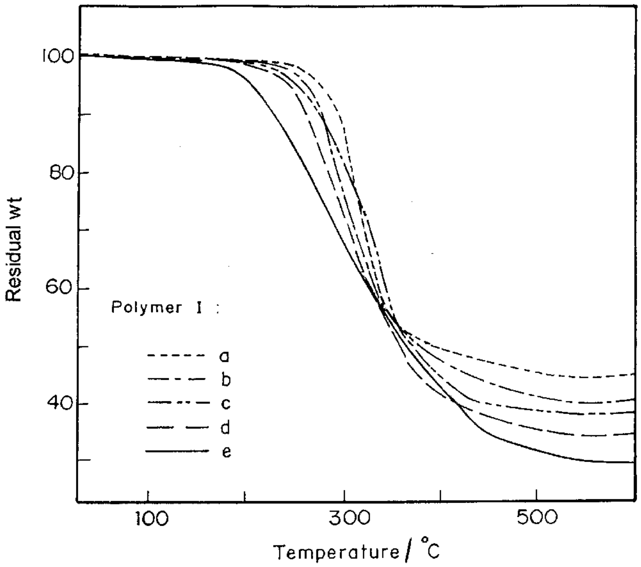

Figure 1. TGA traces for polymers **Ia**–**Ie**.

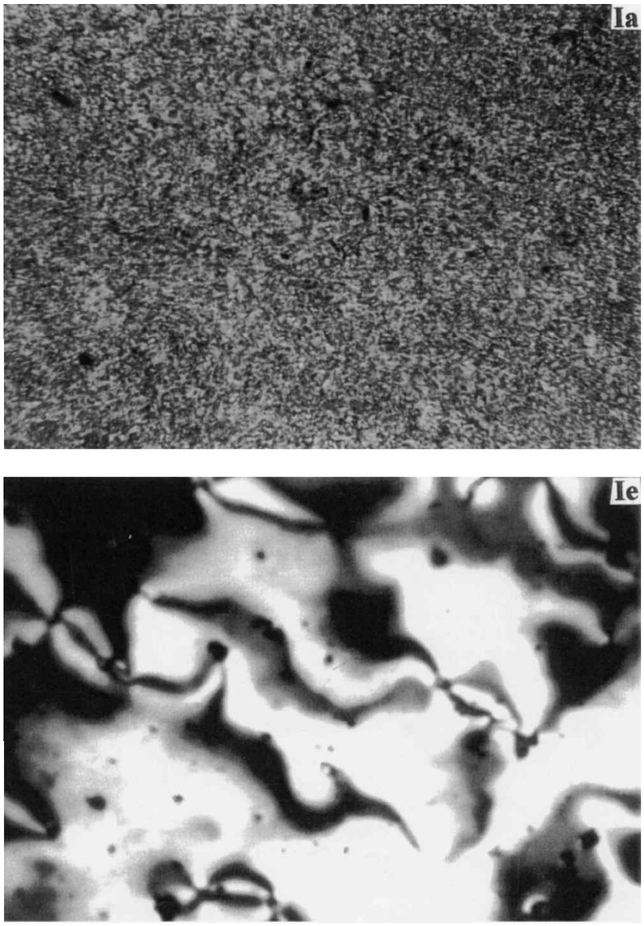

Figure 2. Representative liquid crystalline photographs of polymer **Ia** and **Ie**: photographs were taken at 1st cooling cycle (20 ×).

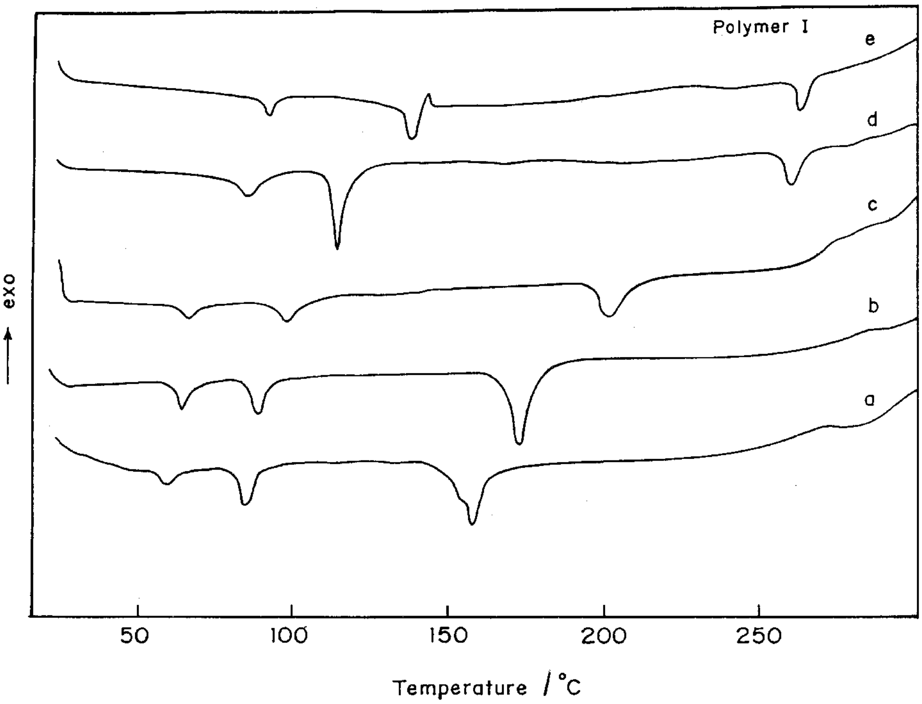

Figure 3. DSC curves for polymers **Ia**–**Ie**.

pyrolytic decomposition of the phosphate ester group and ferrocene moiety into phosphoric acid and iron oxide [31].

The liquid crystalline properties of the polymers **Ia**–**Ie** were studied under polarizing optical microscopy (POM). All the polymers exhibit liquid crystalline behaviour; the phases were identified and compared with previously observed phases reported in literature [14]. The transition temperatures for the polymers observed by DSC are given in table 2. Polymers **Ia** and **Ib** exhibit normal melting and clearing behaviour and show grainy texture. Polymers **Ic**–**Ie** show similar transition behaviour with the formation of clear nematic schlieren texture. The reproducibility of the liquid crystalline phases was satisfactory. The size of the liquid crystalline monodomain was improved in polymer **Ie** over that for polymers **Ia** (figure 2). The lengthy spacer unit allows the mesogen to move freely, with the maximum possibility for alignment to form large monodomains. This leads to the formation of nematic texture in polymers containing longer methylene chains. In the case of polymers **Ia** and **Ib**, the restricted mesogenic movement due to limited spacer size would disturb the mesogenic alignment, resulting in small microdomains [34].

DSC results (figure 3) show that the T_g of the polymers decreases as the flexible chain length increases. Moreover, the phase range (ΔT) increases with decrease in chain length. The glass transition temperature of the polymers was found to be fairly low; this may be attributed to the incorporation of the phosphate ester group and the pendant methyl group, disturbing the molecular close packing and resulting in poor crystallinity and thermal stability [2]. The abnormal bond angle of the sp^3 hybridized phosphorus (107°) could lead to more molecular entanglement, the effect being enhanced by lateral substitution of the methyl group over the phosphorus atom [28]. Moreover the dilution of the mesogen by alkyl chains tends to decrease the overall aspect ratio of the chain. The T_m and T_g of the polymers were therefore much decreased.

Table 2. DSC transition temperatures of polymers **Ia**–**Ie**.

Polymer	T_g/°C	T_m/°C	T_i/°C	ΔT/°C	Type of mesophase
Ia	87	130	255	125	Grainy
Ib	80	110	210	100	Grainy
Ic	70	97	200	103	Schlieren
Id	62	92	170	78	Schlieren
Ie	60	87	155	68	Schlieren

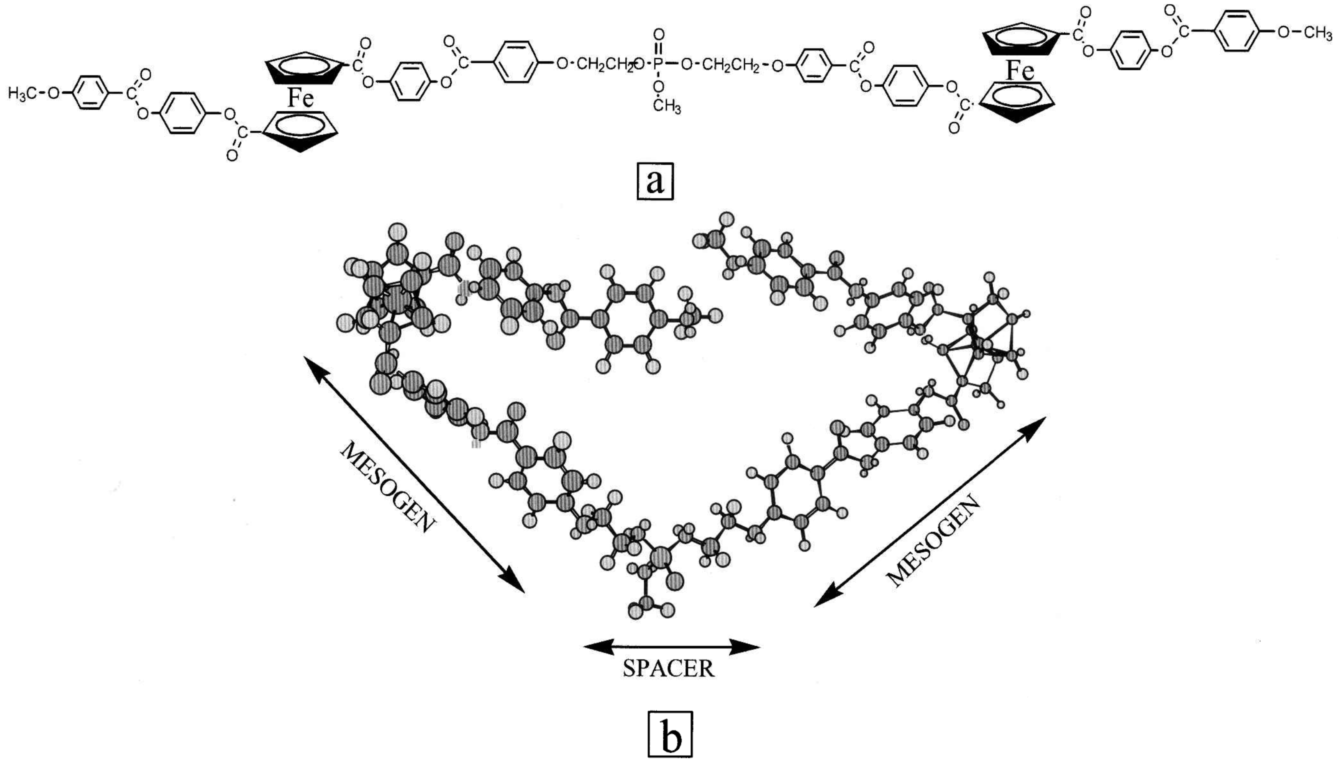

Figure 4. Energy minimized structure of polymer repeating unit containing mesogenic and spacer segment.

Energy minimized structures of the mesogen (figure 4) reveal that, the 1,1′-disubstituted ferrocene unit in the mesogen produces a step-like structure to the mesogen. In addition, the bulky ion atom may disturb the packing of the mesogen and/or polymer chain: it thereby causes reduction in T_g and T_m of the polymers. Conformational analysis of the phosphorus-containing spacer segment (figure 4) shows that the lateral substitution of the methyl group close to the phosphorus atom and the abnormal bond angle of the methyl phosphate ester will collectively result in more entanglement of polymer chain. This causes reduction in the glass transition temperature in comparison with other ferrocene-containing liquid crystalline polymers [35–37].

4. Conclusions

A new series of ferrocene- and phosphorus-containing main chain polymers with varying methylene chain length was synthesized, all of them exhibiting liquid crystalline behaviour. The size of the monodomain increased with increase in length of the methylene groups. The polymers demonstrated high thermal stability with good char yield, which is a criterion for the polymers to act as fire retardant materials. The T_g and T_m of the polymers were much reduced, due to incorporation of ferrocene and methyl phosphate groups in the main chain, in comparison with other ferrocene-containing liquid crystalline polymers. The energy minimized structure of the polymers supports this reason for the reduction in T_g and T_m of the polymers.

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References

[1] DESCHENAUX, R., and GOODBY, J. W., 1995, *Ferrocenes*, edited by A. Togni and T. Hayashi (New York: VCH), p. 471.
[2] OBER, C. K., JIN, J., and LENZ, R. W., 1984, *Liquid Crystals* in Advances in Polymer Science-59, p. 103.
[3] JIN, J. I., AUTOUN, S., OBER, C. K., and LENZ, R. W., 1980, *Br. polym. J.*, **12,** 132.
[4] GALLI, G., LAUS, M., CHIELLINI, E., OBER, C. K., and LENZ, R. W., 1982, *Makromol. Chem.*, **183,** 2693.
[5] CHIELLINI, E., GALLI, G., CARROZZINO, S., and GALLOT, B., 1990, *Macromolecules*, **23,** 2106.
[6] ASRAR, J., TORIUMI, H., WATANABE, J., KRIGBAUM, W. R., and CIFERRI, A., 1983, *J. polym. Sci. polym. Phys. Ed.*, **21,** 1119.
[7] KRIGBAUM, W. R., and WATANABE, J., 1983, *Polymer*, **24,** 1299.
[8] MOORE, J. S., and STUPP, S. I., 1988, *Macromolecules*, **21,** 1217.

[9] Bilibin, A. Yu., Tenkovtsev, A. V., Piraner, O. N., Pashkovsky, E. E., and Skorokhodov, S. S., 1985, *Makromol. Chem.*, **186,** 1575.

[10] Antoun, S., Lenz, R. W., and Jin, J. I., 1981, *J. polym. Sci. polym. Chem. Ed.*, **19,** 1901.

[11] Percec, V., Navara, H., and Johnson, H., 1987, *J. polym. Sci. polym. Chem. Ed.*, **25,** 1943.

[12] Mormann, W., and Brahm, M., 1991, *Macromolecules*, **24,** 1096.

[13] Blumstein, A., and Thomas, O., 1982, *Macromolecules*, **15,** 1264.

[14] Demus, D., Goodby, J., Gray, G. W., Spieces, H. W., Vill, V. (editors), 1998, *Handbook of Liquid Crystals*, Vol. 3 (New York: Wiley-VCH), p. 26.

[15] Deschenaux, R., Marendaz, J., and Santiago, J., 1993, *Helv. Chim. Acta.*, **76,** 865.

[16] Malthete, J., Billard, J., and Jacques, J., 1975, *C. R. Acad, Sci. Ser. C.*, **281,** 333.

[17] Singh, P., Rausch, M. D., and Lenz, R. W., 1989, *Polym. Bull.*, **22,** 247.

[18] Deschenaux, R., Turpin, F., and Guillon, D., 1997, *Macromolecules*, **30,** 3759.

[19] Deschenaux, R., Rama, M., and Santiago, J., 1993, *Tetrahedron Lett.*, **34,** 3293.

[20] Bhatt, J., Fung, B. M., and Nicolas, K. M., 1992, *Liq. Cryst.*, **12,** 263.

[21] Wilbert, G., Traud, S., and Zentel, R., 1997, *Macromol. Chem. Phys.*, **198,** 3769.

[22] Reddy, K. P., and Brown, T. L., 1992, *Liq. Cryst.*, **12,** 369.

[23] Thompson, N. J., Goodby, J. W., and Toyne, K. J., 1993, *Liq. Cryst.*, **13,** 381.

[24] Annakutty, K. S., and Kishore, K., 1989, *J. Sci. Ind. Res.*, **48,** 479.

[25] Kishore, K., Kannan, P., and Iyanar, K., 1991, *J. polym. Sci. A: polym. Chem.*, **29,** 1039.

[26] Varbanov, S., and Borisov, G., 1988, *Acta Polym.*, **39,** 507.

[27] Kishore, K., and Rajalinkam, P., 1986, *J. polym. Sci. polym. Lett. Ed.*, **24,** 471.

[28] Kricheldorf, H., 1992, *J. polym. Sci. A: polym. Chem.*, **30,** 337.

[29] Jalowski, A. J., Singler, R. E., and Atkins, E. D. T., 1995, *Macromolecules*, **28,** 1668.

[30] Shimasaki, C., and Kitano, H., 1996, *Encyclopedia of Polymeric Materials* (CRC), p. 5084.

[31] Senthil, S., and Kannan, P., 2001, *J. polym. Sci. A: polym. Chem.*, **39,** 2396.

[32] Perrin, D. D., and Armarigo, W. L. F., 1988, *Purification of Laboratory Chemicals* (New York: Pergamon).

[33] Knowbloch, F. W., and Rauscher, W. H., 1961, *J. polym. Sci.*, **54,** 651.

[34] Craig, A. A., and Imrie, C. T., 1995, *Macromolecules*, **28,** 3617.

[35] Cochin, D., Passmann, M., Wilbert, G., Zentel, R., Wischerhoff, E., and Laschewsky, A., 1997, *Macromolecules*, **30,** 4775.

[36] Wilbert, W., Wiesemann, A., and Zentel, R., 1995 *Macromol. Chem. Phys.*, **196,** 3771.

[37] Paβmann, M., Wilbert, G., Cochin, D., and Zentel, R., 1998, *Macromol. Chem. Phys.*, **199,** 179.