

Thermotropic Liquid-Crystalline Polyphosphate Esters Containing Phenolphthalein Moiety

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ABSTRACT: A new series of thermotropic liquid-crystalline (LC) polyphosphate esters containing phenolphthalein as a part of their mesogen has been synthesized by a solution polycondensation method. The even-numbered methylene spacers were varied from 2–10, and ethyl phosphate was used as a phosphorus heterogeneity. Thermal analysis showed that these polymers are stable up to 275–342°C with high char yield. All of the polymers exhibited liquid-crystalline properties except for Polymers I and VI. Differential scanning calorimetry (DSC) confirmed the mesophase formation of the polymers. The glass transition temperature (T_g) and melting temperature (T_m) of the polymers were considerably low. A polymer containing phenolphthalein

alone as a rigid segment with decamethylene spacers was also synthesized, but it did not show birefringent melt properties. These results reveal that phenolphthalein alone cannot act as a mesogen, whereas phenolphthalein phenylester can. Molecular modeling studies and conformational analysis confirmed that the steric hindrance of phenylester and the conjugation effect could explain the promotion of mesogenic behavior by phenolphthalein phenylester. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 194–200, 2004

Key words: liquid-crystalline polymers; conformational analysis; molecular modeling

INTRODUCTION

Phenolphthalein-based polyphosphates were studied because they promote extinction and suppress smoke production by accelerated char formation.^{1,2} This type of polymer normally promotes higher glass transition temperatures due to its rigid structure.³ Phenolphthalein-based polyaryl-ethers and arylether-ketones were investigated to determine whether they increase the toughness of composites and blends due to their excellent mechanical and thermal stability.⁴ The introduction of the bulky and polarizable phenolphthalein group in place of an aromatic ring results in increased rigidity of the molecular chain, raising the glass transition temperature.⁴ Phosphorus-containing polymers have received considerable attention in recent decades owing to their effectiveness as flame retardants.⁵ Incorporation of organophosphorus into the chain leads to an increase in polarity and thereby seriously affects molecular parameters.^{6–9} Organophosphorus compounds function as flame retardants in the condensed phase by increasing the amount of carbonaceous residue or char.¹⁰ Liquid-crystalline (LC) polymers attracted researchers because of the potential successful applications of liquid crystals, particularly in displays, optical and electro-optical applications, blends and composites, and fibers and films.^{11–14} Different struc-

tural factors influence the properties of the mesophase of these polymers by influencing dipolarity, planarity, rigidity of the mesogenic unit and length-to-width ratio.^{15–18} The effect of the inclusion of smaller substituents on the central aromatic ring, called central substituents, has also been investigated. It was found that LC behavior was modified due to changes in polarizability and steric attractions within the molecule.¹⁹ Phenolphthalein containing LC polymers have hitherto been unreported in the literature. This article deals with the synthesis, characterization and conformational analysis of phenolphthalein based LC polymers containing ethyl phosphate groups in the main chain along with an even number of methylene spacers. An attempt has also been made to assess the influence of phenolphthalein and phosphorus-containing units on mesomorphic behavior and transition temperatures.

EXPERIMENTAL

All of the solvents were obtained from Sisco Research Laboratory (Chennai, India) and purified before use by standard methods. *n*-Hydroxyalkoxybenzoic acid ($n = 2, 4, 6, 8, 10$) and ethylphosphorodichloridate were prepared as per a procedure reported elsewhere.^{20–23}

Monomer synthesis

Bis[4-chlorocarbonylphenoxyalkyl(ethylphosphate)]s (where alkyl = ethyl, butyl, hexyl, octyl, and decyl) were prepared as described previously.⁷

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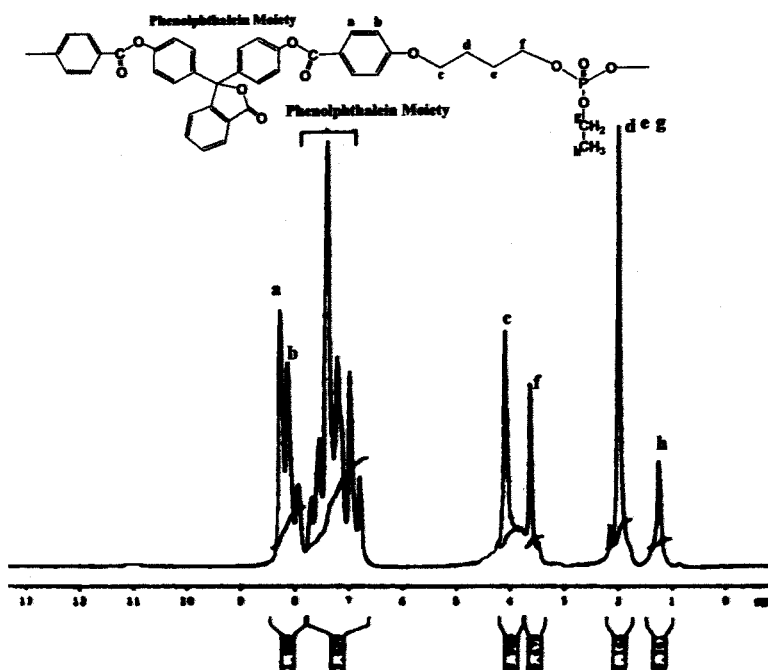


Figure 1 $^1\text{H-NMR}$ spectrum of Polymer II.

Bis(10-hydroxydecyloxy-4,4'-phenolphthalein)

Phenolphthalein (0.05 mol, 15.9 g) was dissolved in ethanol (100 mL). KOH (0.11 mol, 6.1 g) and KI (100 mg) were dissolved in water (10 mL) and then added to the above ethanol solution of phenolphthalein. The mixture was refluxed and 10-bromodecanol (0.1 mol, 23.8 g) was added dropwise. Reflux was continued for 15 h. The solution was concentrated by distilling the excess ethanol under reduced pressure. The remaining solution was poured into ice-cold dilute HCl (10%) with stirring. A waxy mass thus obtained was purified by column chromatography using chloroform and methanol gradient mixtures to get the title compound. The IR and $^1\text{H-NMR}$ results were as follows:

IR (Nujal): 3400 cm^{-1} (OH), 1750 cm^{-1} (lactone ring), 2935 cm^{-1} (methylene), 1601 and 1508 cm^{-1} (aromatic ring breathing)

$^1\text{H-NMR}$ (CDCl_3): $\delta 6.7$ - 7.8 (m, 8H, aromatic, phenolphthalein moiety); $\delta 4.7$ (s, 1H, OH); $\delta 4.6$ (t, 2H, Ar—O—CH₂); $\delta 1.5$ - 2.0 (m, 16H, CH₂)

Polymerization

Poly[bis-4-phenolphthaleinoxycarbonyl-4-phenyloxyethyl(ethylphosphate)]

Phenolphthalein (0.01 mol, 3.18 g) was dissolved in dry tetrahydrofuran (THF) (25 mL). To this mixture, dry triethyl amine (TEA) (0.02 mol, 2.02 g) was added under a nitrogen atmosphere. The bis[4-chlorocarbonylphenyloxyethyl(ethylphosphate)] (0.01 mol, 4.6 g) in dry THF (25 mL) was added dropwise at room tem-

perature. The reaction mixture was further stirred for 12 h, followed by refluxing for 6 h. The solution was concentrated to 10 mL and poured into methanol. A white precipitate thusly obtained was re-precipitated using THF and methanol (yield 60%, Polymer I). All of the other homologues (Polymers II–V) were prepared by a similar procedure using corresponding acid chlorides and phenolphthalein. The IR and NMR data for Polymer I were as follows:

IR (KBr): 2931 cm^{-1} (methylene), 1732 cm^{-1} (lactone carbonyl), 1200 cm^{-1} (Ar—O—C), 1301 cm^{-1} (P=O), 950 cm^{-1} (P—O—C), 1055 , 1465 cm^{-1} (P—O—CH₂—CH₃)

$^1\text{H-NMR}$ (CDCl_3): $\delta 8.14$ (d, 2H, aromatic, ortho to ether); $\delta 8.27$ (d, 2H, aromatic, meta to ether); $\delta 6.79$ - 7.93 (m, 8H, phenolphthalein moiety); $\delta 4.09$ (t, 2H, Ar—O—CH₂—CH₂); $\delta 3.87$ (t, 2H, P—O—CH₂—CH₂); $\delta 4.42$ (q, 2H, P—O—CH₂—CH₃); $\delta 1.25$ (brs, 3H, CH₂—CH₃); $\delta 1.99$ (m, 4H, CH₂) (Fig. 1)

$^{31}\text{P-NMR}$ (CDCl_3): $\delta -19.559$, -12.920

$^{13}\text{C-NMR}$ (CDCl_3): $\delta 134.37$ (aromatic tertiary carbon, attached to ether linkage); $\delta 128.86$ (aromatic, ortho to ether); $\delta 129.32$ (aromatic, meta to ether); $\delta 120.75$ (aromatic tertiary carbon, attached to -COO linkage); $\delta 164.16$ (ester carbonyl carbon); $\delta 157.1$ (aromatic tertiary carbon, attached to -OCO linkage); $\delta 114.42$ (aromatic, ortho to -OCO linkage); $\delta 128.21$ (aromatic, meta to -OCO linkage); $\delta 134.10$ (aromatic tertiary carbon, para to -OCO linkage); $\delta 151.8$ (aromatic tertiary carbon, attached to -C—O—CO of lactone ring); $\delta 125.96$ (aromatic, ortho to -C—O—CO of lactone ring);

δ 128.21 (aromatic, meta to -C—O—CO of lactone ring); δ 128.46 (aromatic, meta to -CO—O—C- of lactone ring); 131.86 (aromatic, ortho to -CO—O—C- of lactone ring); δ 125.49 (aromatic tertiary carbon, attached to -CO—O—C- of lactone ring); δ 170.12 (carbonyl carbon of lactone ring); δ 67.38 (Ar—O—CH₂); δ 66.12 (P—O—CH₂); δ 66.35 (P—O—CH₂—CH₃); δ 44.49 (P—O—CH₂—CH₃); δ 26.16, 26.48 (CH₂)

Poly{bis[4,4'-phenolphthaleinoxydecyl-(ethylphosphate)]} (VI)

Bis(10-hydroxydecyloxy-4,4'-phenolphthalein) (0.01 mol, 4.75 g) was dissolved in dry chloroform (25 mL), and dry TEA (0.01 mol, 1.1 g) was added to it. The mixture was refluxed under a nitrogen atmosphere in an oil bath. Ethylphosphorodichloridate (0.01 mol, 1.4 g) in dry chloroform was added dropwise under the same conditions, and the reaction continued for 12 h. The reaction mixture was poured into large excess of methanol. The white precipitate formed was filtered. The polymer thusly obtained was purified by re-precipitation using chloroform and methanol to get a pure, white polymer (yield 68%). The IR and NMR for the polymer were as follows:

IR (Nujal): 3400 cm⁻¹ (OH), 1750 cm⁻¹ (lactone ring), 2931 cm⁻¹ (methylene), 1605 and 1510 cm⁻¹ (aromatic ring breathing)

¹H-NMR (CDCl₃): δ 6.7-7.9 (m, 8H, aromatic, phenolphthalein moiety); δ 1.25 (t, 3H, P—O—CH₂—CH₃); δ 4.3 (q, 2H, P—O—CH₂—CH₃); δ 4.56 (t, 2H, Ar—O—CH₂); δ 3.8 (t, 2H, P—O—CH₂); δ 1.5-2.0 (m, 16H, CH₂)

Characterization

GPC measurements were completed on a Waters GPC with a styrogel column using THF as a solvent. High-resolution ¹H, ³¹P and ¹³C-NMR spectra were recorded on a Bruker spectrometer at 300 MHz and 75.4 MHz for proton and carbon-13, respectively. IR spectra were recorded on a Nicolet IR (Impact 440) spectrophotometer using KBr pellets. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies were carried out on a Mettler Toledo STAR^e system under a nitrogen atmosphere. TGA was conducted at 20°C min⁻¹ with nitrogen flow of 20 mL/min. The polarizing microscopic studies were performed using a Euromax polarizing microscope equipped with a Linkem HFS 91 heating stage and a TP-93 temperature programmer. The photographs were taken using a Nikon FM10 camera and exposed on Kodak 200 film. The energy minimization tests initially used Molecular Mechanics 2 (MM2) followed by Molecular Orbital PACKage (MOPAC) calculations using an AM1 semiempirical wave function.

RESULTS AND DISCUSSION

Synthesis

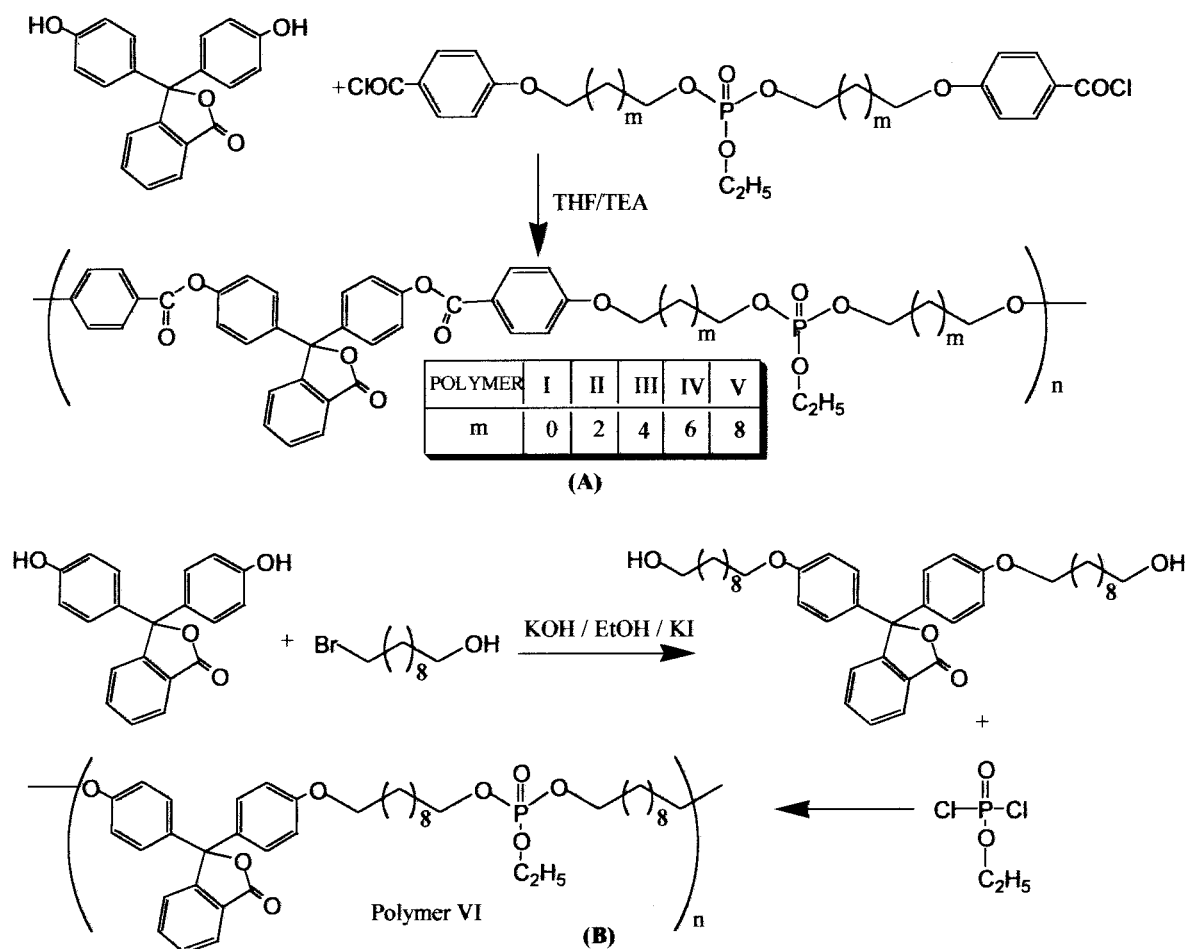
n-Hydroxyalkyloxybenzoic acid was prepared from *n*-bromoalkanol and hydroxybenzoic acid using the Williamson ether synthesis. The phosphorus-containing monomer was prepared by a condensation reaction between two moles of *n*-hydroxyalkyloxy benzoic acid and one mole of ethylphosphorodichloridate, using triethyl amine as an acid scavenger. The dicarboxylic acid thus obtained was converted to the corresponding bisacid chloride by refluxing with thionyl chloride. The polymers (I–V) were prepared with a room temperature solution polycondensation method using phenolphthalein and phosphorus-containing bisacid chloride in THF. Polymer VI was prepared by a solution polycondensation method using

bis(10-hydroxydecyloxy-4,4'-phenolphthalein) and ethylphosphorodichloridate. Polymer VI was prepared in order to investigate the mesogenic activity of the phenolphthalein moiety. GPC measurements show the number average molecular weight is in the range of 5076–7230, as given in Table I.

Thermal analysis

The TGA traces of the polymers are summarized in Table I. TGA thermograms are shown in Figure 2. The thermal stability of the polymers was evaluated by 2% weight loss at the minimum temperature. The initial decomposition temperatures of the polymers were decreased as the length of the methylene chain increased. The polymers were stable up to 342°C (Polymer I) and 275°C (Polymer V). The second decomposition takes place between 403 and 415°C for all of the polymers except Polymer VI. This observation suggests that the first bond breakage could occur at the phosphate ester linkage.²⁰ The second decomposition suggests the breakage of the bond between the terminal phenyl group and the phenolphthalein moiety in the mesogen, because of the narrow range of temperature over which this decomposition occurs for all polymers studied.

A useful indication of fire retardancy at the research and development stage is a polymer's char yield, obtained from TGA under either air or nitrogen atmosphere. Thick char becomes a better thermal insulating layer, which undergoes slow oxidative degradation and prevents heat from reaching the remaining polymers.²¹ The char yield of the polymers studied at 600°C follows a similar trend. Polymer I exhibited a high char yield (40%), and the char yield decreased with increasing methylene chains. This trend is obvious because polymers with longer alkyl spacers have more carbon per repeated unit and thus should experience greater mass loss by the degradation of C—C bonds at 600°C. The high char yield may be attributed



Scheme 1 (A) Synthesis of Polymers I-V and (B) synthesis of model Polymer VI.

to the formation of phosphoric acid as the end product.²²

Polarizing microscope studies indicate the LC behavior of Polymers II-V but not Polymers I or VI. The representative LC photographs are shown in Figure 3. Polymers II-IV exhibit grainy textures, whereas Polymer V shows a nematic schlieren texture. The grain size of the textures increases with an increasing number of methylene spacers. Polymers I and VI show normal melting behavior. The rigid segment of Polymer VI contains only phenolphthalein, which did not

show LC properties. This may be ascribed to the insufficient aspect ratio of the rigid segment to act as a mesogen. On the other hand, Polymer I had only two methylene units in the spacer, which may not be sufficient for the alignment of the mesogen even though the aspect ratio of the rigid segment is higher than that of Polymer VI.

DSC thermograms are shown in Figure 4. The transition temperature data obtained from DSC thermograms are consolidated in Table II. Glass transitions of the polymers are between 50 and 75°C. It is noteworthy

TABLE I
GPC and TGA Data of Polymers I-V

Polymer	M_n	Temperature of Wt. Loss		Wt. Loss at 600°C (%)	Char Yield at 600°C (%)
		2% (°C)	50% (°C)		
I	5076	342	413	60	40
II	5900	318	412	61.4	38.6
III	5563	308	403	66.5	33.5
IV	7230	295	415	69.7	30.3
V	5534	275	410	69.7	30.3

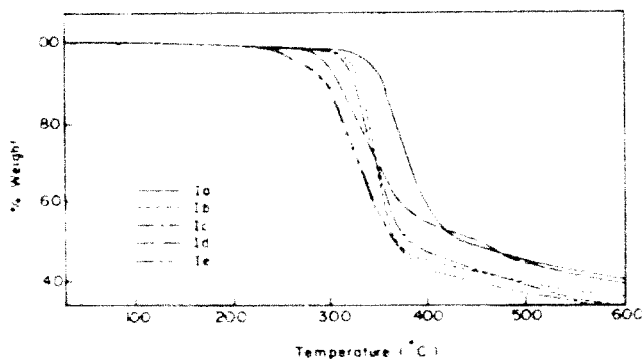


Figure 2 TGA thermograms of Polymers I-V.

thy that the T_g values of the polymers were considerably lower than those of a similar class of polymers already reported without phosphorus segments. The T_g values also decreased as the chain length increased due to higher allowance for segmental motion rendered by the increased spacer lengths.²⁴ The DSC thermograms for Polymers I and VI show single melting endotherms, whereas those for Polymers II-V show two transition peaks, attributed to the melting (T_m) and isotropic (T_i) transitions, suggesting mesophase formation for Polymers II-V. The T_m and T_i also decreased with increasing spacer length.

Conformational analysis

A model compound that mimics the repeating unit of Polymer III [Fig. 5(a)] was generated for conforma-

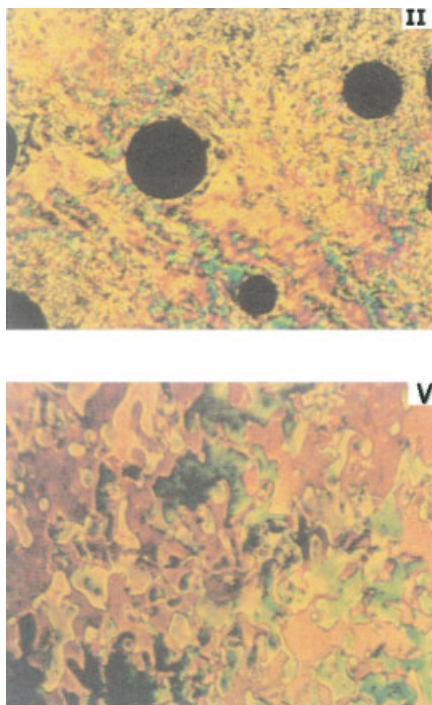


Figure 3 DSC curves of Polymers I-V.

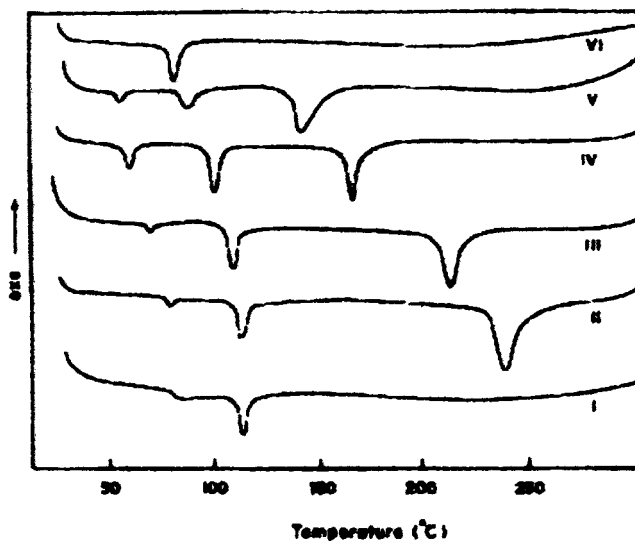


Figure 4 Representative photographs of Polymers II and V. Photos taken during first cooling at 20X.

tional analysis. Studies of the lowest-energy conformations for the model compound were obtained initially using MM2 and further refined by the semi-empirical quantum mechanical program MOPAC. The energy-minimized structure is shown in Figure 5(b).

The structure reveals that the bond angle between phosphorus and the three oxygen atoms in the phosphate ester is 109.4° in the minimized energy state. This indicates that the bond angle of the phosphate ester group destroys the linearity of the spacer group and leads to more entanglement. The increased entanglement may be one of the reasons for the reduction of the T_g values of the polymers. It is evident in liquid crystal science that any substitution, either in the mesogenic segment or in the spacer segment, will lower the T_g . Furthermore, from the energy-minimized calculations, it was demonstrated that sp^3 -hybridized phosphorus adopts 109° angles, which could also explain the increased entanglement. In addition, the T_g values of the polymers were affected by the lateral substitution of the ethyl group with phosphorus.²⁵

On the other hand, investigation of the rigid segment showed that the mesogeneity was promoted by the steric hindrance of the *ortho* hydrogen in relation to the terminal phenyl group and the carbonyl oxygen of the ester linkage in the mesogen. The data (bond length and angle) obtained from conformational energy calculations are given in Figure 5(c). Based on the measurements, the distance between the ester carbonyl and the *ortho* hydrogen of the central phenyl ring was calculated to be approximately 1.6\AA . In addition, the ester linkage gave a sideways displacement of 1.2\AA , which is slightly less than the reported value (1.34\AA).²⁶ These results reveal that there is a possibility of overlapping between two atoms, the carbonyl

TABLE II
DSC Transition Temperatures of Polymers I–V

Name	T_g (°C)	T_m (°C)	T_i (°C)	ΔT (°C)	Type of Mesophase
Polymer I	84	114	—	—	—
Polymer II	78	110	242	132	Grainy
Polymer III	70	103	215	102	Grainy
Polymer IV	58	96	165	75	Grainy
Polymer V	50	82	135	53	Nematic
Polymer VI	Not observed	74	—	—	—

oxygen and the *ortho* hydrogen of the phenyl group, when the groups are coplanar. It was also observed that the three phenyl rings attached to the sp^3 -carbon were noncollinear. Moreover, the phthalic anhydride ring in the phenolphthalein was hindered from rotation. The prevention of rotation makes the molecule highly rigid and promotes mesogeneity. The central sp^3 -hybridized carbon in the phenolphthalein moiety causes a bend in the mesogen, making it banana shaped. The mesogeneity is also promoted by the conjugation resulting from the electron delocalization of the oxygen of the alkoxy chain. This conjugation arises from the fact that the ether oxygen gives a double bond character to the bond between itself and the benzenoid carbon. A similar situation exists for the ester carbonyl carbon and the benzenoid carbon. Otherwise it can be said that the outer core of the mesogen attains quinonoid structure. Accordingly, from the energy minimization studies, the steric hindrance between the carbonyl carbon and the *ortho* hydrogen of the benzene ring in phenolphthalein made the unit rigid within the inner core of the mesogen, and conjugation arising from the ether oxygen caused the outer core to take on a quinonoid structure. Collectively, both effects generated a rigid rod-like structure

and promoted the mesogeneity of the liquid crystal system. In addition, Polymer VI did not show birefringent melt, implying that the aspect ratio of the phenolphthalein moiety alone was not sufficient to act as a mesogen. The addition of two more phenyl rings on both sides of the phenolphthalein increased the aspect ratio and promoted mesogeneity.

CONCLUSIONS

An even series of phenolphthalein-containing polyphosphates was prepared from phenolphthalein and various phosphorus-containing monomers. 1H , ^{13}C and ^{31}P NMR and IR spectroscopy of the polymers confirmed their structures. Thermal analysis showed that these polymers were stable up to 275–342°C in nitrogen with high char yield. Polarizing microscopic studies show LC properties for the polymers except for Polymers I and VI. DSC confirmed the mesophase formation of Polymers II–V. T_g and T_m values of the polymers were considerably low. Molecular modeling studies and conformational analysis showed that the steric hindrance of phenylester and the conjugation effect, respectively, could account for the promotion of mesogenic behavior in phenolphthalein phenylester.

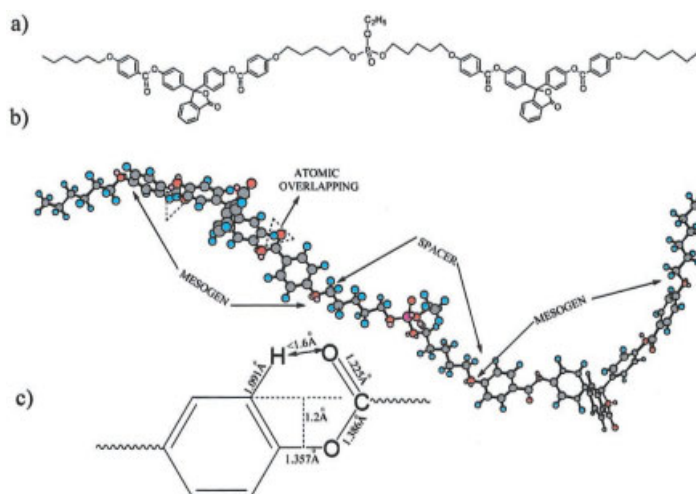


Figure 5 (a) Model compound that mimics the backbone of Polymer III, (b) energy-minimized structure of model compound and (c) bond length and sidewise displacement value of phenylester unit in mesogen.

These results reveal that phenolphthalein alone could not act as a mesogen, whereas phenolphthalein phenylester could.

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