Thermotropic Liquid Crystalline Polyphenylphosphates Containing Aryl Ester Mesogens

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ABSTRACT: A series of main-chain liquid crystalline polyphosphate esters with varying center core in a triad ester mesogen were prepared. The phosphorus is incorporated in the middle of the spacer unit. All the monomers and polymers were characterized by spectral and thermal techniques. Thermogravimetric analysis shows that these polymers were stable up to 295–340°C. The char yields of the polymer were in range of 11–31%. Differential scanning calorimetry (DSC) thermal analysis confirms the mesophase formation of the polymers. Some of the polymers exhibited micro-grainy textures with low glass transition. The DSC and microscopic analysis reveal that the polymer containing central unit which increases the aspect ratio shows liquid crystalline properties, whereas the unit that decreases the aspect ratio failed to show the mesophase formation. Energy minimized structures for the mesogenic units reveal that the polymers containing phenyl, pyridazine, diphenyl ester, and biphenyl unit shows high aspect ratio compared to nonmesogenic phenolphthalein, bisphenol-A, and bisphenol-S units. It revealed that increasing the length of the mesogen and incorporating heteroatoms in the aromatic moiety increased the mesophase stability. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 3924–3930, 2007

Key words: liquid crystalline polymers; structure property relationship; thermal analysis; optical microscopy studies

INTRODUCTION

Thermotropic liquid crystalline behavior of polymeric materials are of considerable current interest, not only because of their potential application as high strength fibers, plastics, moldings[1–3] but also because of their unique position in the theoretical scheme of structural order in fluid phases.[4] The commercial usage of phosphorus containing polymers is increasing year by year. Polyphosphate are generally used as heat resistant, fire retardant, adhesives, ion-exchange resins, and dental composites.[5–9] Many reports have appeared in the literature on para-linked aromatic crystalline polyesters with aliphatic liquid crystalline polyesters with aliphatic methyl spacers.[10]

The effect of introduction of lateral substitution in the spacer group in both conformational characteristic and transition temperatures has been studied.[11] Different structural factors influence the properties of the mesophases of these polymers by influencing dipolarity, planarity, rigidity of the mesogenic unit, and length-to-width ratio.[12–15] The effect of inclusion of smaller substituents on the central aromatic ring has also been investigated. It was found that LC behavior was modified because of the change in polarizability and steric attractions within the molecule.[10] The spacer containing hetero-atoms-like Si, P, O, and N along with or without methylene chain is interesting because of its unusual mesomorphic and thermal properties.[16–19] In particular, organophosphorus compounds function as flame retardants in the condensed phase by increasing the amount of carbonaceous residue or char.[6] We have demonstrated several liquid crystalline polyphosphate systems as fire retardant polymeric additives to common polymers.[20–23] In continuation of our research in this domain, the present work deals with synthesis and characterization of LCPs containing phenylphosphate segment in the main chain along with varying central units in a triad ester mesogen.

EXPERIMENTAL

Reagents and solvents

p-Hydroxybenzoic acid, bisphenol-A, bisphenol-S, 3,6-dihydroxy pyridazine, phenolphthalein, and quinol were purchased from Spectrochem, India, and recrystallized before use. Tetrahydrofuran (THF), ethanol, methanol chloroform, and triethylamine (SRL, India) were purified by the usual procedure and dried before use.[24] Phosphorus oxychloride (Merck) was used as received. 6-hydroxy hexyloxy-4-benzoicacid, phenylphosphorodichloridate, and 4,4′-dihydroxydiphenyl esters were prepared as per the procedure reported elsewhere.[20–23]

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Measurements

Infrared spectra were recorded on a Nicolet Impact 440 spectrophotometer using KBr pellets. High-resolution ^{1}H NMR spectra were recorded on a Bruker spectrometer using TMS as an internal reference. In general, $CDCl_3$ was used as solvent for NMR spectra. The inherent viscosity was measured in Ubbelohde viscometer using $CHCl_3$ as solvent. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymers were carried out on a Seiko thermal analyzer (SSC/5200H) under nitrogen atmosphere. The heating rate for TGA and DSC analysis was fixed at 10°C min^{-1}. All the DSC thermograms mentioned in the text were taken during first cooling cycle. The polarizing microscopic studies were performed using Euromex polarizing microscope equipped with Linkam HFS 91 heating stage and a TP-93 temperature programmer. Samples were prepared by melting a small quantity of the material between two thin glass cover slips to get uniform film with heating and cooling rate at 2–5°C min^{-1}. Photographs were taken using Nikon FM10 camera and exposed on Konica film. The energy minimization studies are carried out using MM2 molecular modeling package.

Synthesis of bis[4-cholorocarbonylphenyloxyhexyl (phenylphosphate)]

6-Hydroxyhexyloxy-4-benzoic acid (0.025 mol) was dissolved in dry THF (60 mL) and dry triethylamine (TEA) (0.025 mol) was added under nitrogen with stirring to get homogeneous mixture. Phenylphosphorodichloridate (0.013 mol) dissolved in dry THF (5 mL) was added drop wise and stirred for 12 h at ambient temperature, followed by heating at refluxing condition for 3 h. The precipitated amine hydrochloride was filtered and THF was evaporated to dryness under reduced pressure. The precipitate thus obtained was triturated with dry benzene to remove unreacted phenylphosphorodichloridate and excess TEA. The crude product was crystallized in 50% aqueous ethanol (M.Pt. 75°C).

FTIR (KBR) cm^{-1}: 3340 (OH), 1704 (C=O), 2940 (methylene), 1257 (Ar—O—CH_2—), 1316 (P=O), 1168 (P—O—C_6H_5).

^{1}H NMR ($CDCl_3$) δ ppm: 1.4–2.0 (m, 8H, CH_2), 4.0 (t, 2H, P—O—CH_2), 4.3 (t, 2H, Ar—O—CH_2), 7.02–7.5 (d, 2H, aromatic phenyl moiety), 7.9–8.0 (d, 3H, P—O—C_6H_5), 9.5 (s, 1H, OH).

The dicarboxylic acid (0.025 mol) thus obtained was dispersed in benzene (25 mL) and thionyl chloride (0.125 mol) was added drop wise to it, followed by one drop of DMF. The mixture was stirred at room temperature for 2 h. The mixture was slowly heated to reflux and temperature was maintained for another 6 h. After the complete HCl evaluation ceased, excess thionyl chloride was removed under vacuum. The residual precipitate was connected to high vacuum for several hours to obtain bis[4-cholorocarbonylphenyloxyhexyl(phenylphosphate)]. A white pasty solid thus obtained was used as such without further purification.

Synthesis of polymers

All polymers were prepared by room temperature solution polycondensation method using various aromatic diols viz., quinol, 4,4′-dihydroxybiphenyl, 3,6-dihydroxy pyridazine, 4-hydroxy phenyl-1-carboxy-4-phenol, phenolphthalein, bisphenol-A, bisphenol-S with phosphorus containing monomer. A representative procedure for the preparation of poly [bis (4-phenyloxy carbonyl-4-phenyloxy hexyl (phenyl phosphate)] is as follows: Freshly recrystallized quinol (0.004 mol) was dissolved in dry THF (10 mL) and dry TEA (0.004 mol) was added under nitrogen atmosphere bis[(4-cholorocarbonylphenyloxyhexyl (phenylphosphate)] (0.004 mol) dissolved in dry THF (10 mL) was added drop wise at room temperature. It was further stirred for 12 h under the same condition. Finally, the mixture was heated to reflux for 2 h and the solution was concentrated to 10 mL, and poured into large excess of methanol to precipitate the product. The white powder thus obtained was purified by repeated precipitation using methanol and chloroform (Yield 70%).

FTIR (KBr) cm^{-1}: 2943 (aliphatic —CH_2), 1705 (ester —C=O), 1512–1608 cm^{-1} (aromatic ring breathing), 1316 (P=O— stretching), 957 (O—P—O— stretching), 1258 (Ar—O—C— stretching), 1171 (P—O—C_6H_5— stretching).

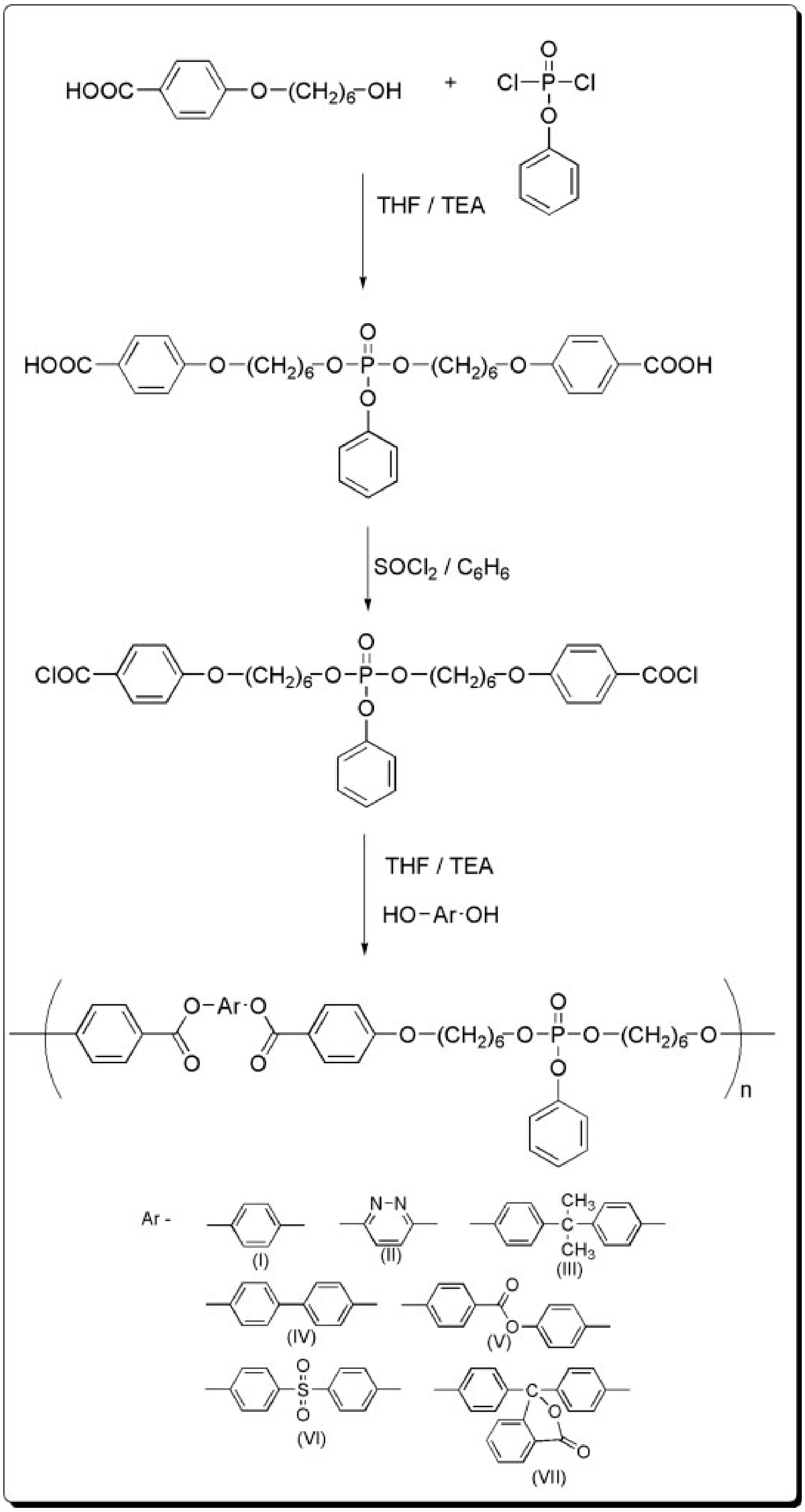
^{1}H NMR ($CDCl_3$) δ ppm: 1.34–1.81 (m, 8H, —CH_2), 3.94–4.02 (t, 2H, P—O—CH_2), 4.27–4.37 (t, 2H, Ar—O—CH_2), 7.0–7.26 (m, quinol moiety), 7.22–7.26 (d, 2H, aromatic ortho to ether), δ 7.87–6.89 (d, 2H, aromatic meta to ether), 7.95–7.98 (d, 3H, P—O—C_6H_5).

Similarly all the remaining polymers (II–VII) were prepared using respective aromatic diols.

RESULTS AND DISCUSSION

Synthesis of polymers

The phosphorus incorporation in the monomer was achieved by a room temperature condensation reaction of 6-hydroxyhexyloxy-4-benzoic acid and phenyl phosphorodichloridate. Further the compound was chloro-functionalized and polymerized with various aromatic diols to get the targeted polymers. All the polymers were obtained in good yield (70–75%). The synthesized polymers were further purified by repeated precipitation using chloroform and methanol



Scheme 1 Synthesis of polyphosphates.

Scheme 1. Intrinsic viscosity measurements showed the values in between 0.80 and 0.86 g dL^{-1} Table I, which indicate that the molecular weights of the polymers are in moderate molecular weight category. The products were characterized by FTIR, ^1H NMR spectroscopy. The differential scanning calorimetric

TABLE I
Viscosity and Thermogravimetric Analysis of Polymers I–VII

Polymer	$[\eta]$ (g dL^{-1})	Weight loss corresponds to 5% (°C)	Weight loss corresponds to 50% (°C)	Wt. loss at 600°C (%)	Char yield at 600°C (%)
I	0.87	310	390	83	17
II	0.89	312	400	87	13
III	0.85	360	445	89	11
IV	0.89	335	404	84	16
V	0.84	340	410	96	10
VI	0.86	295	380	69	31
VII	0.88	338	406	84	16

studies and thermo gravimetric studies were accomplished to verify the presence of mesophase and thermal stability and decomposition investigations, respectively.

The FTIR spectra exhibit the characteristic bands of different groups of the molecule e.g., P=O, —P—O—C_6H_5, aliphatic chain, and phenyl groups. In the ^{1}H NMR spectra, the signals corresponding to both aromatic and aliphatic parts of the molecule are observed. In addition two-triplet type resonance signal corresponding to aryl-alkyl ether methylene and phosphate ester linked methylene are observed. The methylene proton near the phosphate ester group experienced more deshielding than the aryl linked methylene proton and it appears around 3.8–4.0 δ. This splitting of two different triplets confirmed the incorporation of phosphorus moiety in the polymer chain (Fig. 1).

Thermal analysis

Thermogravimetric analysis

In the present study, thermal stability is evaluated by 5% weight loss occurred at the minimum temperature. Thermogravimetric data of various polymers are tabulated in Table I. The pattern of the TGA analysis is summarized in Figure 2(a,b). The TGA data of all the polymers (I–VII) showed single stage decomposition pattern and all the polymers were stable between 295 and 340°C. The char yield of all the polymers were almost equal (10–17%) except for polymer VI (31%) at 600°C. The sulfur group present in the polymer backbone could be the reason for high char yield because of the thermal cross-linking reaction leading to formation of vulcanized product. The 50% weight loss of all the polymers occurs at the similar temperature range 390–410°C except for

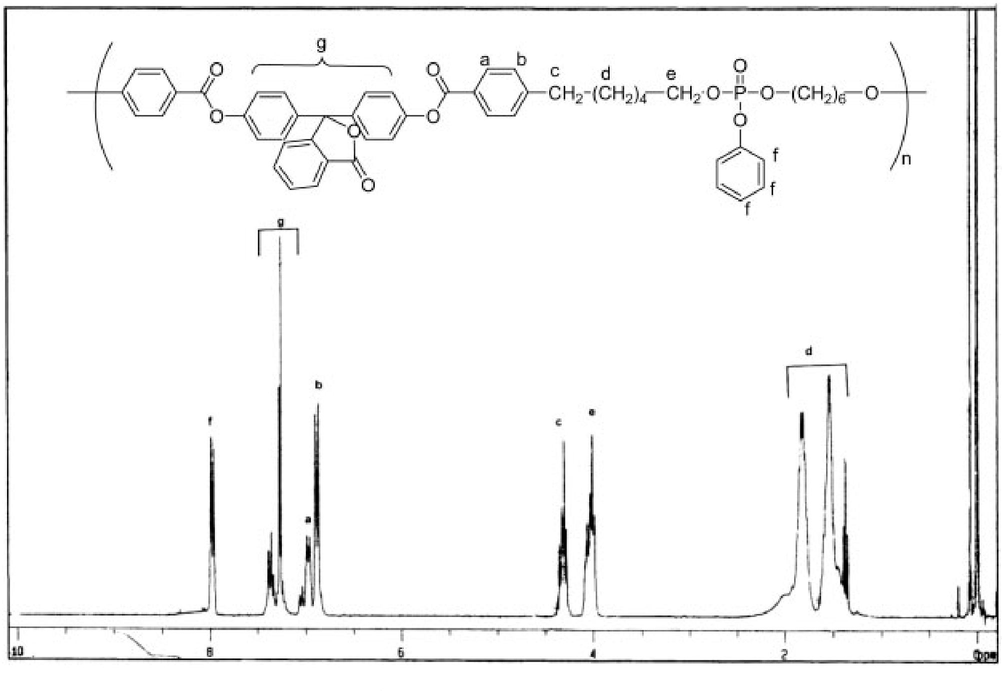


Figure 1 ^{1}H NMR spectrum of polymer VII.

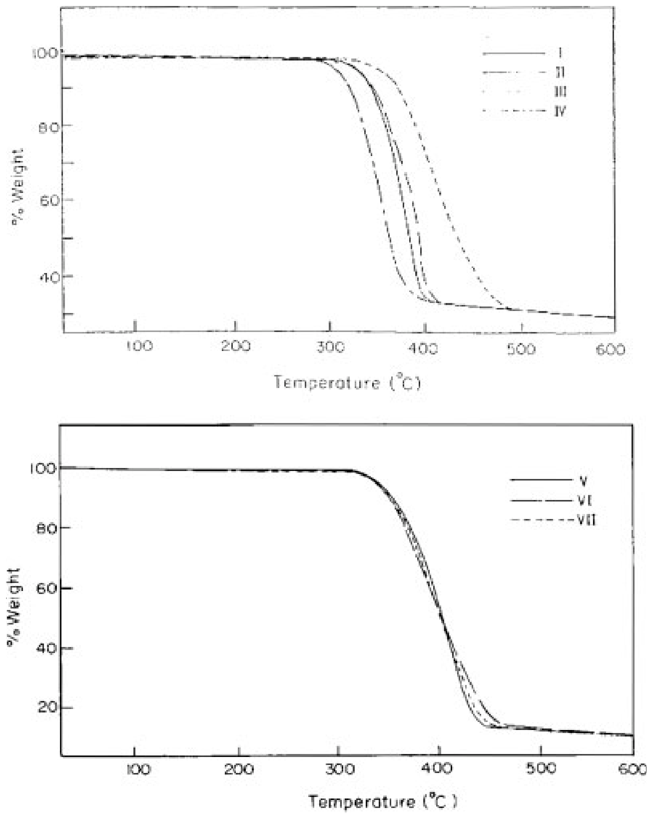


Figure 2 TGA thermograms of the polymers I–VII.

polymer III (445°C). This observation suggests that the first breakage may be at bond between phenyl and different mesogenic ester and the second possibility of the breakage could be happened at phosphate ester linkage yielding phosphoric acid as the end product.[22] Thermal stability and high char yield are very much related to fire retardancy of the polymers.[25] Indeed, the reasonable thermal stability with high char yield provided by these polymers indicates that they can be explored as fire retardant polymeric materials.

Differential scanning calorimetric analysis

Figure 3 shows the DSC thermograms of the polymers. The data are listed in Table II. It shows that the polymers I, II and IV, V were exhibiting two melting endotherm whereas for the polymer III, VI, and VII show simple melting behavior. Peaks at temperature above the melting point are observed in some of the polymers (polymer I, II and IV, V) suggesting the presence of mesophase in these polymers. These evidence indicates that the polymers having bisphenol-A (III), bisphenol-S (VI), and phenolphthalein (VII) residue in the center core of triad ester mesogen is unable to sustain an order in the melt state, therefore fail to generate the mesophase observed in other cases. The former case (polymer III, VI, VII) destroys the linearity by virtue of its structure and the latter case (polymer I, II, V, IV) promotes the aspect ratio with increasing the linearity of the mesogen.

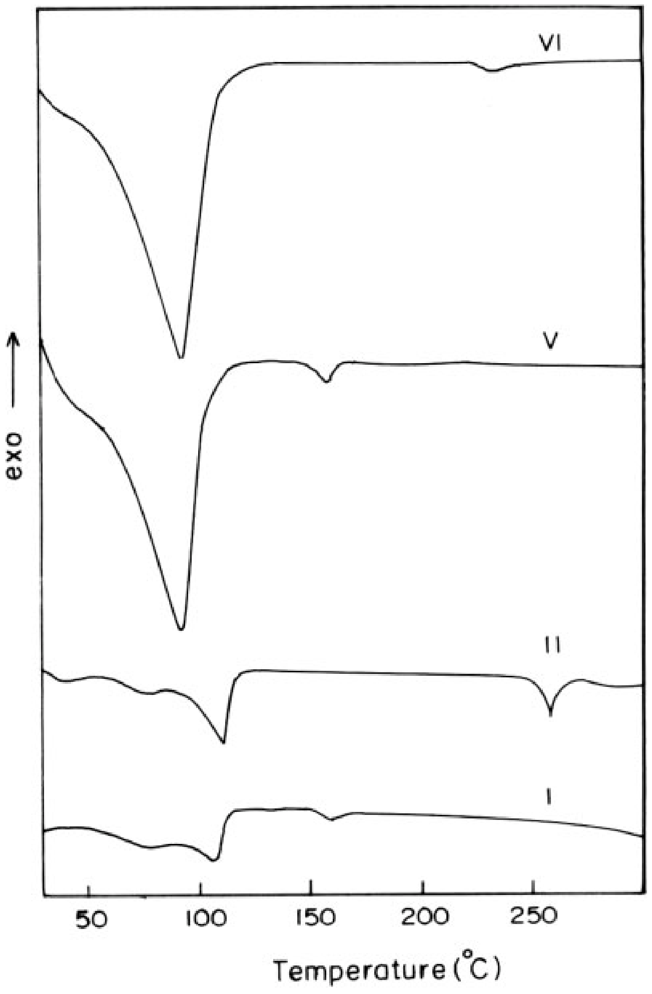


Figure 3 DSC thermograms of polymers.

Polarizing microscopic studies

The hot stage optical polarizing microscope pictures of the polymers I and II are shown in Figure 4. The transition temperature observed is in accordance with DSC thermal data type. All the polymers are

TABLE II
DSC Transition Temperatures of Polymers I–VII

Polymer	Temperature (°C)			
	T_g	T_m	T_i	ΔT
I	75	105	157	52
II	73	107	260	153
III	–	75	–	–
IV	–	90	160	70
V	–	91	262	171
VI	–	80	–	–
VII	–	78	–	–

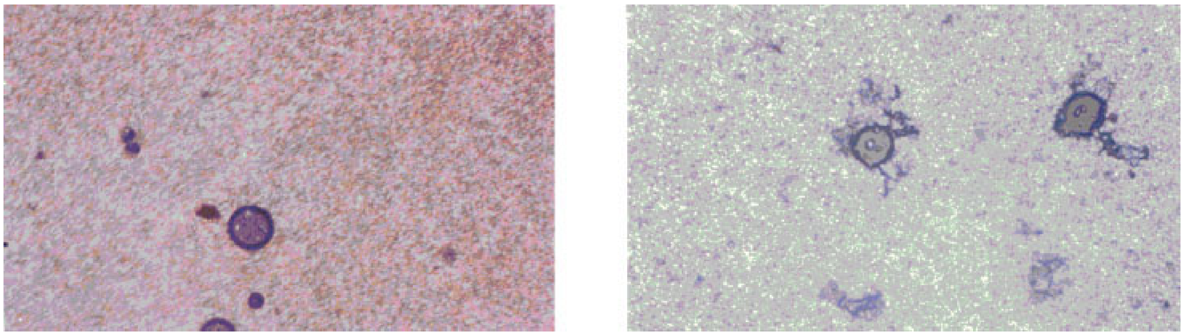


Figure 4 Optical polarized microscopic pictures of polymers I and II. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

show enantiotropic liquid crystalline behavior except for polymer III, VI, and VII. Photographs were taken during first cooling cycle at 10× magnification. The formations of liquid crystalline phases were satisfactory after cooling from isotropic transition temperature. Polymer I, II and V, IV were exhibiting grainy texture. Very small grainy domain formation nematic texture may be due to the phenyl pendant group, which disturbs the alignment of the mesogens. Comparing the transition temperatures of the polymer I and II, IV and V both the polymers are showing same melting temperature (T_m) but mesophase duration was increased considerably to 100°C possibly ascribed to the hetero atoms and ester carbonyl present in the central aromatic ring, respectively.

Energy minimized structures for all the mesogenic units were obtained using molecular modeling program (MM2). Total length of the mesogen between two-aryl-alkyl ether oxygen is also measured by the same method. Energy minimized structures and length of some of the mesogen in this study are represented in Figure 5. It reveals that, polymers having linear central aromatic substituents namely phenyl, hydrazine, biphenyl, and diphenyl esters are having length 18.392, 18.602, 23.098, 24.328 Å, respectively, whereas diphenylisopropylidine, diphenylsulphone, and phenolphthalein are having 17.839, 18.029, and 17.135, respectively. Although polymer III, VI, and VII are having four aromatic rings when compared with polymer I and II (having three aromatic rings) shows shorter length of the mesogen because of sp^3 hybridized central aliphatic carbon and sulfur, respectively. Again for this reason, all the former mesogens are adopting bent structures and experience the low aspect ratio and failed to show anisotropic behavior. On the other hand in phenyl phosphate unit produces more entanglement due to characteristic bond angle of around 105 degrees.[26] Because of the characteristic sp^3 hybridized phosphorus and bent structure of central unit collectively produces more entanglement and it reduces the glass transition for the entire polymers below room temperature except for polymer I and II.

CONCLUSIONS

A series of polymers with varying aromatic substituents containing central unit of triad ester mesogen with phosphorus heterogeneity in the spacer was synthesized. TGA analysis showed that polymer containing diphenylsulphone moiety exhibit high char

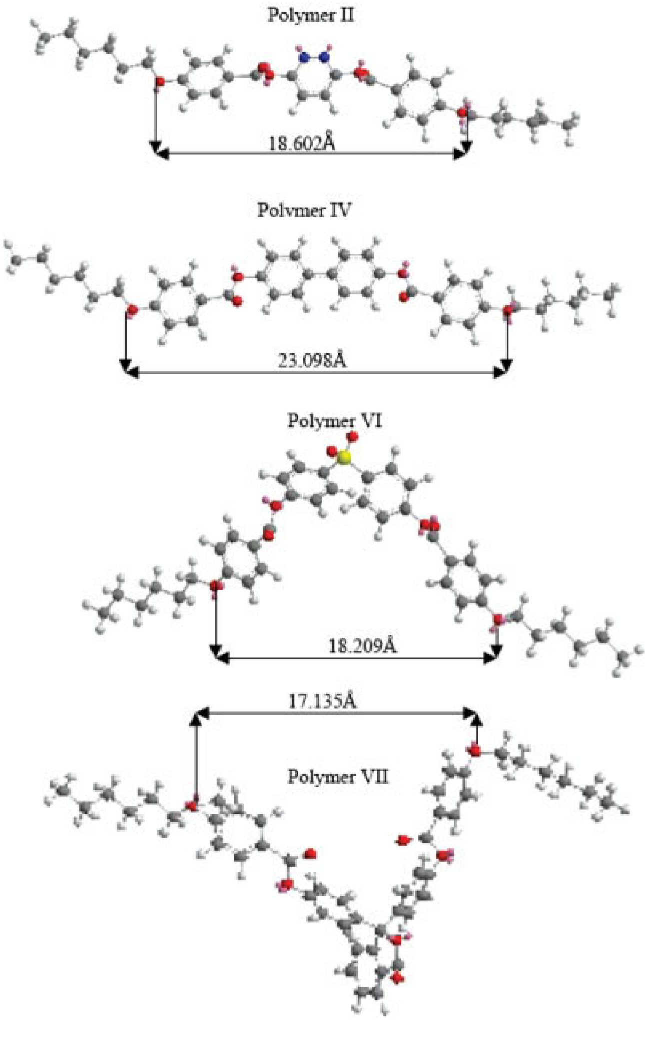


Figure 5 Energy minimized structures of mesogens and its lengths. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

content, possibly ascribed to the formation of sulfur crosslinked vulcanized product. Four polymers possessing linear structure of central unit exhibited mesophase formation, whereas other three polymers that contain bent structure failed to show liquid crystalline properties. DSC thermograms confirmed the presence of liquid crystallinity in the anticipated polymers. The mesophase was increased considerably by increasing the length of the mesogen and incorporation of heteroatoms. Energy minimized structures obtained using MM2 calculations reveal that, linear central aromatic substituents increase aspect ratio and promotes anisotropic character. The sp^3 hybridized central aliphatic carbon and sulfur imparts bent structures thereby produced more entanglement leads to reduction in glass transition.

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