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Novel thermotropic liquid crystalline polyphosphonates

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Abstract

Main chain liquid crystalline polyphosphonates containing semi-flexible phenylester mesogen with even number of methylene spacers (2–10) have been synthesized. The monomers and polymers were characterized by IR, ^{1}H, ^{13}C and ^{31}P NMR spectroscopy. The spectral details are in accordance with the structures. All the polymers were exhibited liquid crystalline property in the Hot stage optical polarized microscope (HOPM). DSC thermal analysis confirms the mesophase formation for all the polymers. The grain size of the liquid crystalline mesophase is increasing with increasing methylene chain. T_g, T_m and T_i of the polymers decreased with increase in spacer length. The T_g of these phosphorus-containing polymers is much lower than that of non-phosphorus polymers containing triad ester mesogens. Energy minimized structures for the molecules which mimic the polymer chain suggests that the reduction in T_g may be due to entanglement raised by incorporation of phosphorus heterogeneity.

Keywords: Polyphosphonate; Liquid crystalline; Thermotropic

1. Introduction

The commercial usage of phosphorus containing polymers is increasing year by year. Polyphosphates and polyphosphonates are generally used as heat resistant, fire retardant, adhesives, ion-exchange resins and dental composites [1–5]. On the other hand, research directed towards the study of mesomorphic properties of liquid crystals has gained tremendous impetus owing to their applications in hi-tech areas [6]. Several reports have been appeared in the literature on *para*-linked aromatic liquid crystalline polyesters with aliphatic methylene spacers [7–16]. The effect of methylene spacers and various substitutions in aromatic moiety with respect to physical properties have been well documented in main chain liquid crystalline polymers (LCPs) [1,13–16]. The effect of introduction of lateral substitution in the spacer group in both conformational characteristics and transition temperatures has been studied [17]. Any alteration in the length of methylene chain and incorporation of any polar group seriously affect the molecular parameter. Several reports have been appeared in the spacer containing heteroatoms like Si, P, O, and N along with or without methylene chain [17–21].

Studies on phosphorus containing LCPs are scarce [4,22–27]. Incorporation of phosphorus in the polymer backbone certainly increases the polarity and fire retardant characteristics. We have demonstrated several polyphosphate and polyphosphoramide systems as fire retardant polymeric additives to common polymers as well as photocross-linkable polymers [28–30]. In continuation of our research in this domain [31–33], the present work deals with synthesis and characterization of LCPs containing phenylphosphonate segment in the main chain along with varying methylene spacers and study the conformational characteristics of the polymeric structures.

2. Experimental

2.1. Materials

Dichloromethane, ethanol, methanol, acetic anhydride, acetonitrile, tetrahydrofuran (SRL) were purified by the usual procedure and dried before use [34]. Phosphorustrichloride, *p*-hydroxymethylbenzoate and 2-chloroethanol (Merck) were used as received. Dichlorophenylphosphine

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was prepared by the literature procedure reported elsewhere [35]. 4-bromobutylacetate, *n*-bromoalkanols and *n*-hydroxyalkyloxybenzoic acids ($n = 6$, 8, 10) were prepared by the reported methods [32]. Bis[4-carboxyphenyloxyethyl (phenylphosphonate)] was prepared as per the procedure reported elsewhere [33].

2.2. Measurements

GPC measurements were made on Waters GPC with styrogel column and THF used as eluent. High-resolution ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Brucker spectrometer of 300 and 75.4 MHz, respectively in $CDCl_3$. IR spectra were recorded on a Nicolet IR (Impact 440) spectrophotometer using KBr pellets. TGA and DSC studies were carried out on a Seiko thermal analyzer (SSC/5200H) under nitrogen atmosphere. The heating rate for TGA and DSC analysis was done at 20 °C min^{-1} with nitrogen flow of 20 ml min^{-1}. The second heating cycle was recorded for all the polymers in the DSC. The polarizing microscopic studies were performed using Euromax polarizing microscope equipped with Linkem HFS 91 heating stage and a TP-93 temperature programmer. Samples were made by melting a small quantity of the material between two thin glass cover slips to get uniform films with heating and cooling rate at 5 °C min^{-1}. The photographs were taken using Nikon FM10 camera and exposed on Konica film. X-ray diffraction measurement was performed with a Rigaku R axis IIC powder diffractometer. The monochromatized X-ray beam from nickel-filtered Cu K_α radiation with a wavelength of 0.15406 nm was used. A thermal controller was added to the X-ray for thermal measurement with a tolerance of ±0.5 °C. The molecular simulation studies have been done by CS Chem 3D Pro. The structures were initially minimized by MM2 (molecular mechanics 2) and the resultant structure was further refined by MOPAC (Molecular Orbital PACkage) using AM1 semi-empirical wave function. The minimization was stopped after reaching 0.100 RMS gradients.

2.3. Polymerization

All the polymers were prepared by room temperature solution polycondensation method. A representative synthetic procedure for the preparation of poly[4-phenyloxycarbonyl-4-phenyloxyethyl(phenylphosphonate)] (I) is as follows:

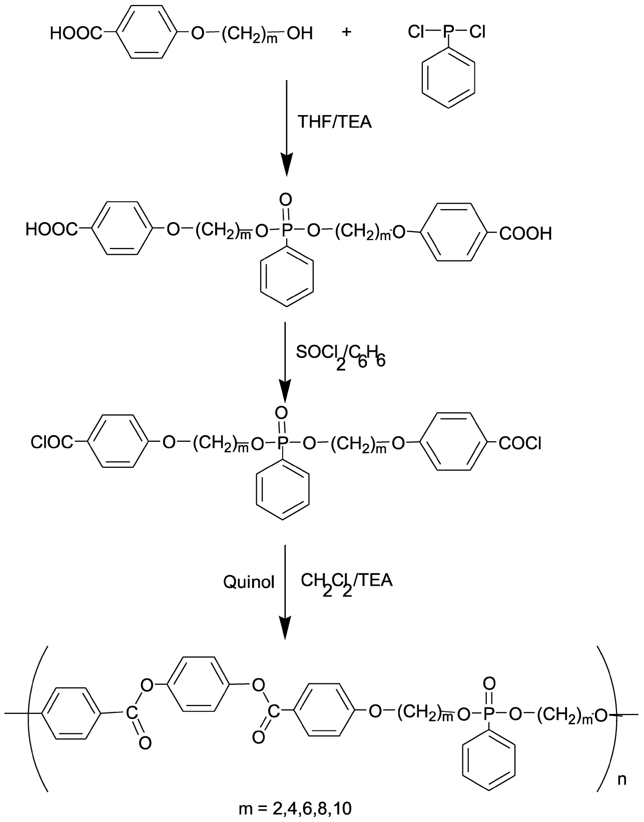
Recrystallized quinol (0.01 mol) was dispersed in dry dichloromethane (25 ml). To this dry TEA (0.01 mol) was added under nitrogen atmosphere. The bis[4-chlorocarbonylphenyloxyethyl(phenylphosphonate)] (0.01 mol) in dichloromethane (25 ml) was added drop wise at room temperature. During addition the solution becomes homogeneous. It was further stirred for 12 h under the same condition. The solution was concentrated to 10 ml and poured into methanol. A white precipitate thus formed was reprecipitated in methanol (yield 70%). All other homologues (II–V) were prepared by adopting the similar procedure using corresponding acid chlorides and quinol.

IR (KBr): 2930 cm^{-1} (aliphatic $-CH-$), 1730 cm^{-1} (ester $C{=}O$), 1600 and 1510 cm^{-1} (aromatic ring breathing), 1050 and 920 cm^{-1} ($P{=}O$ stretching). ^{1}H NMR ($CDCl_3$) δ : 3.16 (t, 2H, $-C\,H_2-O-P$), δ 4.28 (t, 2H, $-C\,H_2-O\text{-}Ar$), δ 6.9 (d, 2H,aromatic, *ortho* to $-OCO-$), δ 7.13 (d, 2H, aromatic, *ortho* to ether), δ 7.29 (m, 5H, aromatic, pendant phenyl), δ 8.15 (d, 2H, aromatic, *meta* to ether) ^{31}P NMR: δ 12.487. ^{13}C NMR ($CDCl_3$) δ : 122.26 (aromatic carbon-O attached), 132.47 (aromatic, *ortho* to ether), 133.62 (aromatic, *meta* to ether), 30.10 ($C\ H_2-O-P$), 42.00 ($Ar\text{-}O-C\ H_2-$), 29.61 ($Ar\text{-}O-CH_2-C\ H_2-$), 114.54 (aromatic, pendant phenyl), 121.13 (aromatic, P-attached pendant phenyl), 165.07 (carbonyl), 116.45 (aromatic carbon, $-CO-$ attached), 114.82 (aromatic carbon, $-OCO-$ attached).

3. Results and discussion

n-Bromoalkanols ($n = 2$, 6, 8, 10) were synthesized from their corresponding diols with 47% HBr. *n*-Hydroxyalkoxy benzoic acids ($n = 2$, 6, 8, 10) were synthesized from *p*-hydroxybenzoic acid and corresponding *n*-bromoalkanols using Williamson aryl–alkyl ether synthesis method. The yield of the product was drastically diminished when 4-hydroxybutyloxybenzoic acid prepared using 4-bromobutanol, because of cyclization reaction leading to THF. Hence, 4-bromobutylacetate was used to get 4-hydroxybutyloxybenzoic acid followed by alkaline hydrolysis. The incorporation of phenylphosphonate group in the chain is achieved by the reaction of 2 mol of *n*-hydroxyalkyloxybenzoic acids with 1 mol of dichlorophenylphosphine using triethylamine as an acid scavenger. The dicarboxylic acids were purified by the flash column chromatography over silica gel using chloroform–methanol mixtures as eluent. During the reaction and purification the trivalent phosphorus atom is oxidized to more stable pentavalent phosphonate group and the structure of the later was confirmed by IR spectroscopy. The dicarboxylic acid was converted to corresponding acid chloride by gentle reflux with thionyl chloride and benzene. The polymers were prepared by solution polycondensation method using quinol and various acid chlorides in dichloromethane at room temperature. ^{31}P NMR of the polymers shows a peak at $\delta \sim 12.487$, which confirms the successful incorporation of phosphonate group in the main chain of the polymer. The GPC measurements show the number average molecular weight is in the range of 4210–5900 (Scheme 1).

Thermogravimetric data of the polymer is shown in Table 1. The pattern of the TGA analysis is summarized in Fig. 1. Thermal stability is evaluated by 1% weight loss at the minimum temperature. The polymer containing two-methylene spacer (I) is stable up to 320 °C. whereas the



Polymer	I	II	III	IV	V
m	2	4	6	8	10

Scheme 1. Synthesis of polymer I–V.

ten-methylene spacer-containing polymer (V) is stable up to 225 °C. Close inspection of the TGA thermograms reveal that the stability of the polymer is decreasing with increasing spacer length. The char yield of the polymers at 600 °C is increased to 38% and it is reduced up to 8% with 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 suggests that the char yield is decreases with increase in the ratio between hydrocarbons and phosphorus content of single monomeric unit. The initial decomposition temperature and char yield reveal that the polymers were not decomposed via an ester bond breakage mechanism because such degradation route would give about the same decomposition temperature for all the polymers [36]. The decomposition of the polymers would occur probably through the pyrolytic cleavage of the phosphonate ester group and breaking the linkage between the mesogenic groups with different methylene units.

Table 1
Thermogravimetric data of the polymers I–V

Polymer	Weight loss corresponds to (°C)		Char yield at 600 °C (%)
	2%	50%	
I	330	420	38
II	300	390	32
III	285	450	25
IV	225	310	15
V	220	300	8

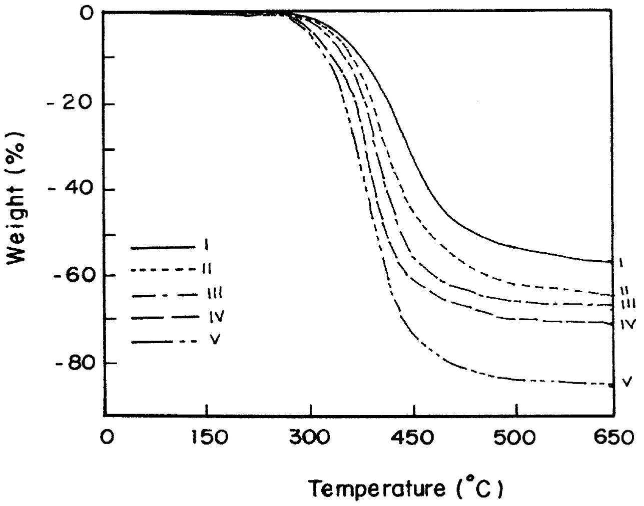


Fig. 1. TGA traces of polymers I–V.

Fig. 2 shows the DSC thermograms of the polymers I–V. The transition temperatures for all the polymers obtained in DSC and optical polarized microscope (HOPM) is shown in Table 2. It shows that the T_g of the polymers decreases as the flexible chain length increases. Moreover, the phase duration is increased with increase in chain length as expected. The regular insertion of the flexible molecules in

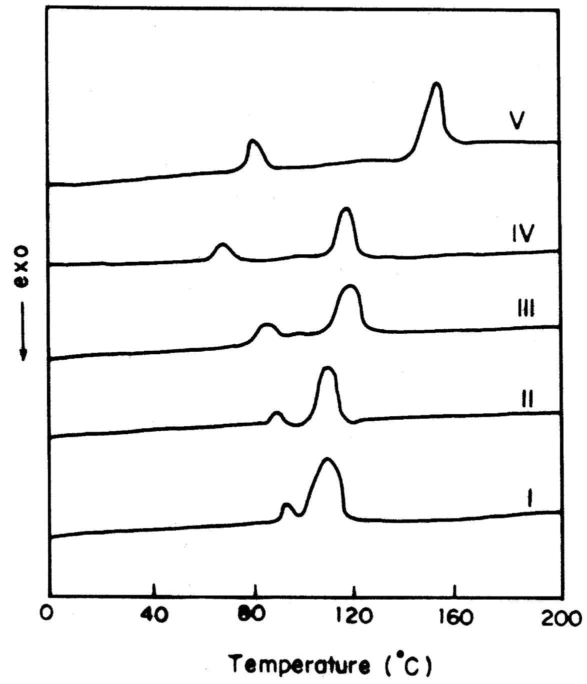


Fig. 2. DSC thermograms of second heating cycle of polymer I–V.

Table 2
Transition temperatures observed in DSC and HOPM for the polymers I–V

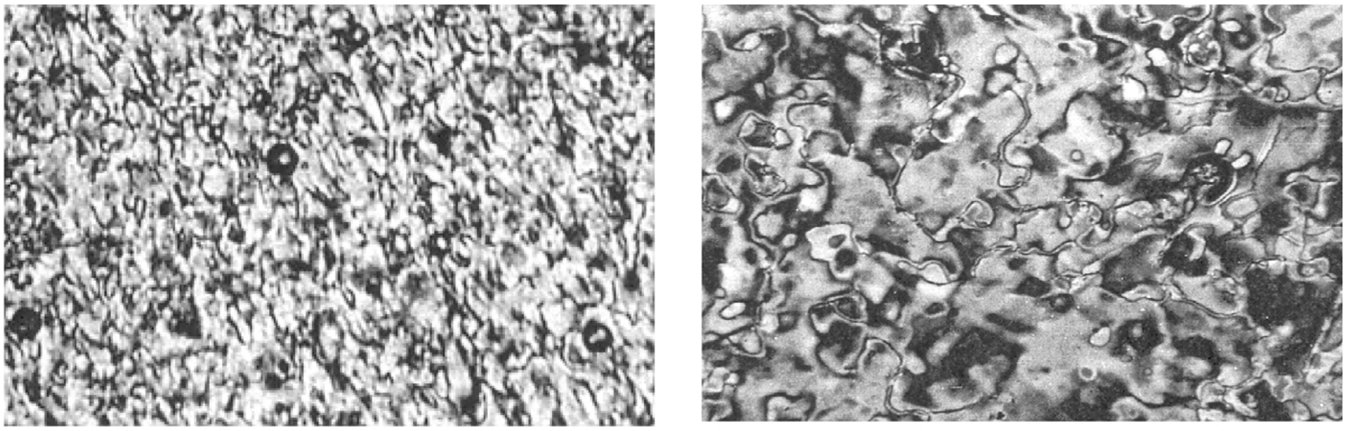
Polymer	T_g (°C)	T_{smc} (°C)		T_n (°C)		T_i (°C)	
		DSC	HOPM	DSC	HOPM	DSC	HOPM
I	87	–	–	95	97	110	108
II	67.6	–	–	90	92	105.2	106
III	61.4	–	–	85.3	85	116.3	116
IV	58.9			67.6	71	114.7	118
V	55	74	76	81	80	152	155

T_g, glass transition temperature; T_{smc}, smectic transition temperature; T_n, nematic transition temperature; T_i, isotropic liquid transition temperature.

the chain separates the mesogen along the molecular chain provide extra flexibility to the polymer backbone and leads to reduction in transition temperatures.

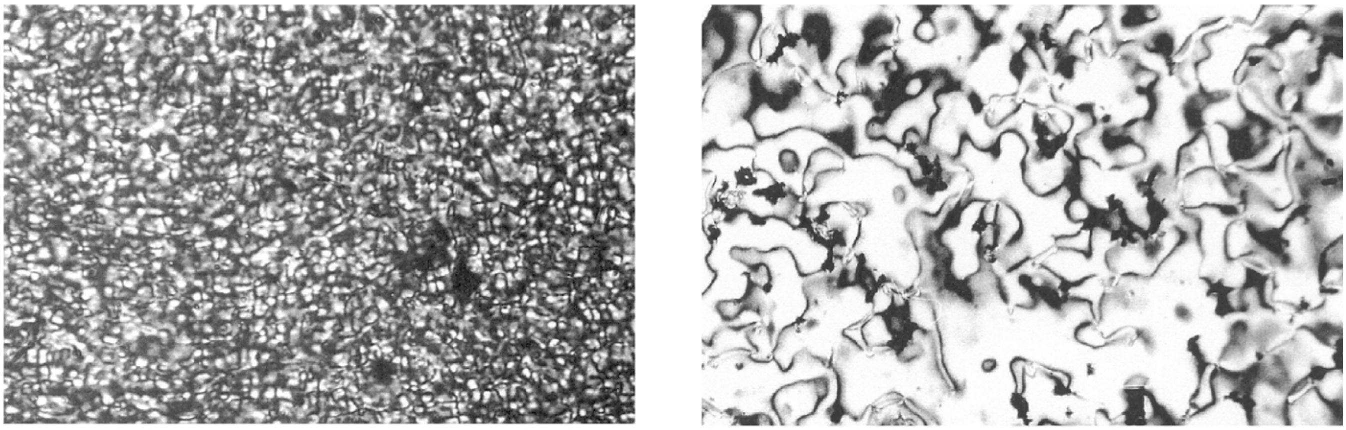
The liquid crystalline properties of the polymers (I–V) were studied under polarizing microscope. All the polymers were exhibited anisotropic behavior. Representative polarizing microscope photographs for the polymer II, IV and V were shown in Fig. 3. The liquid crystalline phases were identified and compared with previously observed mesophases reported in the literature [1]. Polymer I, II, III and IV exhibiting grainy texture and nematic texture respectively. Good reproducibility of the formation of liquid crystalline phases was observed. The grain size of the LCPs was improved with increasing methylene spacer. The increase in grain size may be ascribed to the more and more segmental mobility on increasing the content of spacer segment. Polymer V melts at 76 °C and it forms smectic C structure, and changed to threaded nematic texture at 80 °C. The isotropization was taking place at 155 °C. The above observation was confirmed by DSC. It gives a transition at 74 °C (melting), 81 °C (smectic–nematic) and 152 °C (nematic–isotropic).

XRD pattern at different temperatures for the polymer V is shown in Fig. 4. Temperature dependant X-ray diffraction diagrams at 30, 75, 90, 150 and 170 °C, respectively for polymer V was taken. A sharp reflection at low angle (associated with smectic layer) and a broad reflection at wide angle (associated to lateral packing) were observed at 75 °C. This indicates the presence of smectic liquid crystal phase [37]. Upon cooling from isotropic liquid phase into nematic phase, polymer V exhibited with a threaded nematic texture. The X-ray diffraction diagram at 150 °C



Polymer II (20X magnification) at 100°C

Polymer IV (20X magnification) at 109°C



Polymer V (20X magnification) at 80°C

Polymer V (20X magnification) at 148°C

Fig. 3. HOPM Photographs for the polymer I–V.

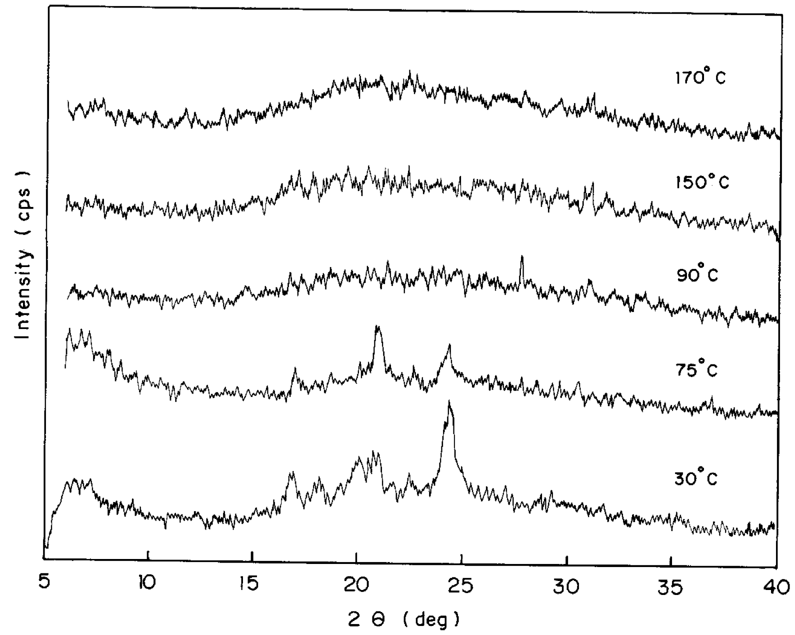


Fig. 4. XRD pattern of the polymer V at different temperatures.

exhibits diffused refluxion at wide angle, which corresponds to nematic texture. On further cooling of the polymer results more crystalline peaks at 75 °C and give some sharp crystalline refluxion at wide angle suggests the formation of smectic mesophase. Sharp distinguished crystalline peaks appeared at small angle and a broad crystalline peak at 25 degree is disappearing in the X-ray pattern at 90 °C. These observations confirmed the polymorphism exhibited in the polymer V.

The energy minimized structure for bis(decamethylenephenylphosphonate) a model compound which mimic the polymer chain with its lowest energy conformation was first generated using computer modeling program MM2 force field (molecular mechanics). The structures were further refined by using the semi-empirical SCF quantum mechanical program MOPAC is shown in Fig. 5. This data obtained from the calculations showed that the phosphorus takes the –O–P(O)–O– bond angle of 125.99°. This abnormal bond angle may destroy the persistent ratio of the polymer chain [38]. The insertion of sp^3 hybridized phosphorus will link the *trans* configured methylene spacer with an abnormal angle of 104–107°, which destroy the packing possibility of the methylene and increasing entanglement thereby the T_g of the polymers are greatly reduced [39]. It is already evident that the lateral substituent in the flexible spacer decreases the steric packing efficiency of the chain in the liquid crystalline state [1]. The lateral substituent through phosphonate linkage may produce disturbance to the packing of the polymer chain and there by it greatly reduce the melting and glass transition of the polymer. The T_g and T_m of the polymers are greatly reduced because of the phosphorus entanglement, compared to polymers having same triad mesogens and homogeneous methylene spacers [39].

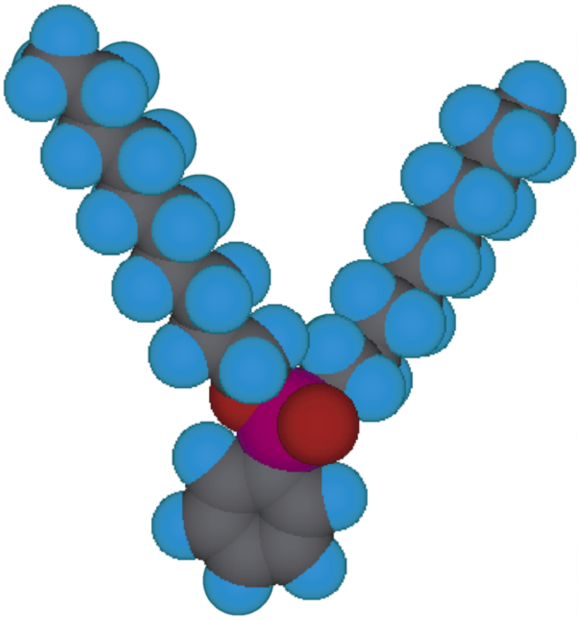


Fig. 5. Energy minimized model for bis(decamethylenephenylphosphonate).

4. Conclusion

A series of phosphorus containing thermotropic main chain liquid crystal polymers with varying methylene chain lengths were synthesized by a solution polycondensation method. The structures of the polymers were confirmed using various spectroscopy techniques. ^{31}P NMR of the polymer shows successful incorporation of phosphorus in the polymer backbone. HOPM analysis indicated that all the polymers possessing liquid crystalline property. Thermogravimetric analysis revealed that the polymers are stable from 225–320 °C. The effect of methylene chain, the incorporation of polar phosphorus moiety with regard to phase duration, T_g and order of the liquid crystalline phase has also been discussed. The conformational analysis revealed that the reduction in T_g is due to the phosphorus entanglement.

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References

[1] Annakutty KS, Kishore K. Polymer 1988;29:756.
[2] Annakutty KS, Kishore K. J Sci Ind Res 1989;48:479.
[3] Kishore K, Annakutty KS, Mallik IM. Polymer 1988;29:762.
[4] Kricheldorf H. J Polym Sci Part A: Polym Chem 1992;30:337.
[5] Varbanov S, Borisov G. Acta Polym 1988;39:507.
[6] Demus D, Goodby J, Gray GW, Spieces HW, Vill V, editors. Hand book of liquid crystal. New York: Wiley-VCH; 1998.
[7] Vanluter D, Strzelecki L. Eur Polym J 1980;16:303.
[8] Meurisse P, Noel C, Monner L, Fayolle B. Br Polym J 1981;13:55.
[9] Jin JI, Autoun S, Ober CK, Lenz RW. Br Polym J 1980;12:132.
[10] Chiellini E, Galli G, Carrozzino S, Gallot B. Macromolecules 1990; 23:2106.
[11] Asrar J, Toriumi H, Watanabe J. J Polym Sci Polym Phys Ed 1983;21: 1119.
[12] Krigbaum WR, Watanabe J. Polymer 1983;24:1299.
[13] Moore JS, Stupp SI. Macromolecules 1988;21:1217.
[14] Krigbaum WR, Kotek R, Ishikawa T, Hakemi H. Eur Polym J 1984; 20:225.
[15] Craig AA, Imrie CT. Macromolecules 1995;28:3617.
[16] Griffin AC, Havens SJ. J Polym Sci Polym Phys Ed 1981;19:951.
[17] Aharoni SM. Macromolecules 1988;21:1941.
[18] Aquilera C, Bartulin J, Hisgen B, Ringsdorh H. Makromol Chem 1983;184:253.
[19] Galli G, Laus M, Chiellini E, Ober CK, Lenz RW. Makromol Chem 1982;183:2693.
[20] Angeloni AS, Caretti D, Laus M, Chiellini E. Polym J 1988;20:1157.
[21] Angeloni AS, Laus M, Burgin E, Galli G, Chiellini E. Polym Bull 1985;13:131.
[22] Senthil S, Kannan P. J Polym Sci Part A: Polym Chem 2001;39:2396.
[23] Jaglowski AJ, Singler RE, Atkins EDT. Macromolecules 1995;28: 1668.
[24] Allcock HR, Kim C. Macromolecules 1989;22:2596.
[25] Singler RE, Willingham RA, Noel C, Friedich C, Atkins E. Macromolecules 1987;20:1727.
[26] Allcock HR, Kim C. Macromolecules 1990;23:3881.
[27] Singler RE, Willingham RA, Lenz RW, Furukza A, Finkelman H. Macromolecules 1987;20:1727.
[28] Kishore K, Kannan P. J Polym Sci Part A: Polym Chem 1990;28: 3481.
[29] Kishore K, Kannan P, Iyanar K. J Polym Sci Part A: Polym Chem 1991;29:1039.
[30] Kannan P, Murugavel SC. J Polym Sci Part A: Polym Chem 1999;37: 3285.
[31] Senthil S, Kannan P. J Polym Sci Part A: Polym Chem 2002;40:2256.
[32] Senthil S, Kannan P. J Appl Polym Sci 2002;85:831.
[33] Senthil S, Kannan P. Liq Cryst 2002;29:1297.
[34] Perrin DD, Armarigo WLF. Purification of laboratory chemicals. New York: Pergamon; 1988.
[35] Gefter YL. Organophosphorus monomers and polymers. New York: Pergamon press; 1962.
[36] Craig AA, Imrie CT. Macromolecules 1995;28:3617.
[37] Hsiue GH, Sha YA, Jeng RJ. Macromol Chem Phys 2001;202:287.
[38] Donald AM, Windle AH. Liquid crystalline polymers. Cambridge: Cambridge University Press; 1995.
[39] Lenz RW. Polym J 1985;17:105.