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Synthesis and characterization of poly(organophosphazenes) bearing Schiff's base linkages

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Summary

Two new classes of Schiff's base poly(organophosphazene)s have been synthesized and characterized. The substitution degree of the Schiff's base linkage was found for the products of the form, $[NP(O\text{-}Ph\text{-}CHO)_x(O\text{-}Ph\text{-}CH{=}N\text{-}Ph\text{-}R)_y]_n$(polymer **II** series), where R are H, OCH_3, OH(p), OH(m) and -N=N-Ph, was less than 35%, while the products of the second class, $[NP(OCH2CH_2OCH_2CH_2O\text{-}Ph\text{-}CHO)_x(OCH_2CH_2OCH_2\text{-}CH_2O\text{-}Ph\text{-}CH{=}N\text{-}Ph\text{-}R)_y]_n$ (polymer **III** series), where R are H, COOH(m), COOH(p), NO_2, and OCH_3, marked 65% on the average. The solubility of the polymers in the common organic solvents was found very poor, except such strong polar or aprotic solvents at elevated temperature. The existence of flexible spacer group connected to the Schiff's base linkage has greatly influenced the thermal properties of the polymers. DSC measurements revealed about 100°C of melting transition for the polymer **II** series, while 214°C for the polymer **III** series with exhibiting multistage of thermal transition. The DSC results gave some evidences that the products of polymer **III** series have potentials for the thermotropic liquid crystalline polymers.

Introduction

The polyphosphazene is perhaps the most promising polymer because of its potentiality to provide various properties that can be tailored. The fact that this type of polymers can combine the advantages of inorganic backbone chain and organic side chain can possibly lead to the formation of a material having new functions and properties. The inorganic backbone elements can provide heat, fire, or radiation resistances, or electrical conductivity, while the organic side groups control properties such as solubility or resistance to solvent, liquid crystallinity or nonlinear optical behavior, refractive index, and surface properties such as hydrophobicity, hyrophilicity, adhesion, and biological compatibility (1-6).

The Schiff's base linkages are known to form easily by a condensation reaction of aromatic or aliphatic amine with an aldehydic group at the terminus of an organic compound. Those compounds containing this type of linkages usually reveal properties such as high thermal stability, ability to form metal chelates, easy hydrolyzability, liquid crystals, and semiconducting properties. Therefore, the synthesis of inorganic polymers bearing the Schiff's base side unit may allow to produce a new class of functional material (7-10). This leads us to attempt to prepare two different classes of poly(organophosphazene)s comprising Schiff's base units that are connected to phosphazene backbone through p-formylphenoxide and p-formylpheoxyethoxyethoxide groups.

This paper describes the synthesis of the poly(organophosphazene) bearing Schiff's base units and the effect of different spacer groups on the thermal transition behaviors of the products. Particularly, efforts are given to the evaluation of the possibility whether the products can assume side chain liquid crystallinity or not.

Experiment

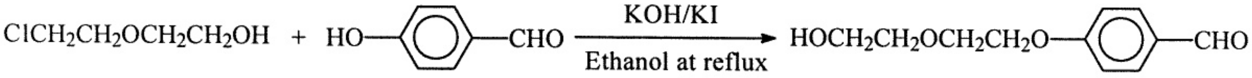
Materials

Hexachlorocyclotriphosphazene(HCTP) was purified as described elsewhere (11-12). THF, 1,4-dioxane, and 2-(2-chloroethoxy)ethanol were fractionally distilled under nitrogen before use. *p*-Hydroxybenzaldehyde was recrystallized from distilled water. All other reagents were used as received. All the synthetic procedures were carried out by the standard Schlenk technique.

Spectroscopy and Measurements

^{31}P NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 101.27 MHz. ^{1}H NMR spectra were also recorded on a Bruker AM-300 spectrometer operating at 250.13 MHz. The chemical shifts of ^{31}P and ^{1}H NMR spectra are relative to 85% H_3PO_4 at 0 ppm and tetramethylsilane(TMS) at $\delta = 0$ in DMSO-d or $CDCl_3$, respectively. The data were processed by the use of integral computer of the spectrometer. Infrared spectra were obtained with the use of a FT-IR spectrophotometer, FTS-40 BIO-Rad Digilab Division Instrument. A DuPont 2100 thermal analyzer was used to obtain DSC thermograms. The heating rate was 10°C/min under nitrogen atmosphere and sample sizes were about 30 mg. A Perkin Elmer 240 C was used for the elemental analysis.

Scheme 1. Synthetic Pathway of Compound **I**



Compound **I**

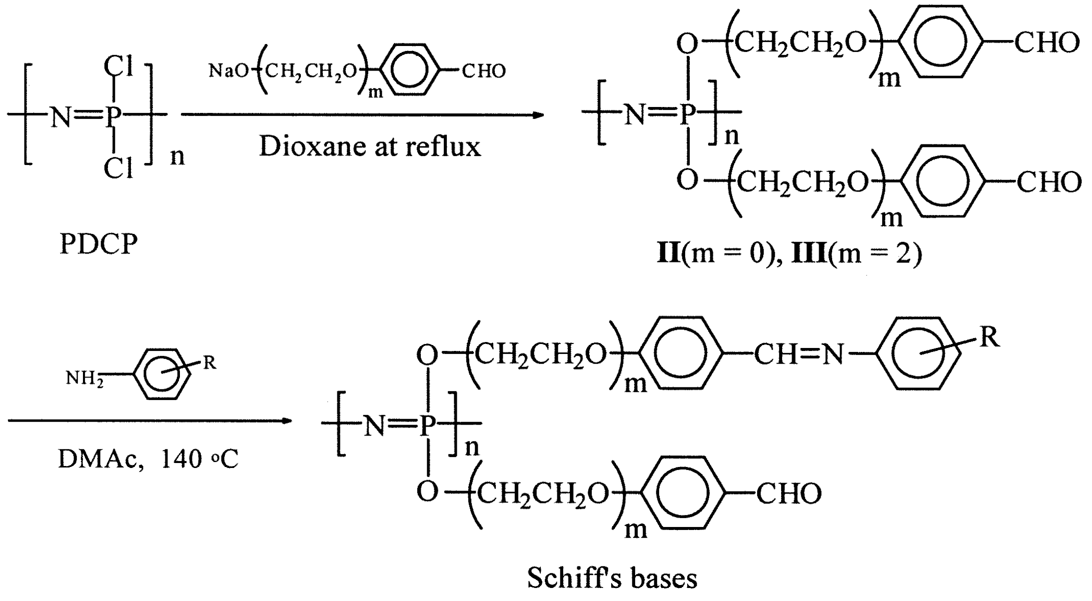
Synthesis of 2-[2-(p-formylphenoxy)ethoxy]ethanol(I)

The synthetic pathway used to prepare compound (I), being employed as the side group containing flexible diethyleneoxy unit, is illustrated in Scheme 1. A typical reaction procedure is as follows: to an ethanol(300 mL) solution of 4-hydroxybenzaldehyde (35.64 g, 0.3 mol), potassium hydroxide(16.83 g, 0.3 mol), and potassium iodide(4.98 g, 0.03 mol) were added 100 mL of ethanol solution of 2-(2-chloroethoxy)ethanol (36.13g, 0.29 mol) with stirring. The reaction mixture was stirred at 78°C for 24 hr, cooled to room temperature, and neutralized with dilute HCl. Being evaporated, the crude residue was redissolved in 250 mL of methylene chloride, washed with water, and dried over magnesium sulfate. The product was isolated by column chromatography to give compound **I**. n-Hexane and ethyl acetate were used as the eluents.

Synthesis of Poly[bis(p-formylphenoxy)phosphazene](II)

Poly(dicholorophosphazene)(PDCP) was prepared by thermal polymerization of HCTP according to well-known procedures. PDCP (10.65 g, 0.092 mol) dissolved in dioxane(500 mL) was added slowly to a stirred solution of sodium p-formylphenoxide prepared from p-hydroxybenzaldehyde (22.42 g, 0.18 mol) and sodium hydride(4.60 g, 0.19 mol) in dioxane(200 mL). The solution was stirred at reflux temperature for 3 days, and completed the substitution reaction by addition of small amount of tetrabutyl-ammonium bromide. The polymer was recovered by precipitation into large excess of methanol and purified by successive washing with hexane, methanol, and water to remove sodium chloride, excess sodium hydride, and mineral oil. After final wash with methanol, the polymer was dried under reduced pressure.

Scheme 2. Synthetic Pathway of Polymers



IIa R = H, **IIb** R = OCH_3(para), **IIc** R = OH(para), **IId** R = OH(meta), **IIe** R = N=N-C_6H_5(para)
IIIa R = H, **IIIb** R = COOH(meta), **IIIc** R = COOH(para), **IIId** R = NO_2(para), **IIIe** R = OCH_3(para)

Synthesis of Poly[bis(2-(2-(p-formylphenoxy)ethoxy)ethoxy)phosphazene] (III)

A solution of PDCP(10 g, 0.086 mol) in dioxane(500 mL) was added slowly to a stirred dioxane solution of sodium 2-[2-(p-formylphenoxy)ethoxy]ethoxide prepared from the reaction of 2-[2-(p-formylphenoxy)ethoxy]ethanol(36.12 g, 0.172 mol) and sodium hydride(4.15 g, 0.173 mol). The reaction mixture was stirred for 3 days at reflux temperature and then cooled to room temperature. The polymer was recovered by precipitation into hexane and purified by means of dialysis against water and methanol for 4 days, respectively.

Synthesis of Polymeric Schiff Bases IIa ~ IIe and IIIa ~ IIIe

The polymer **II**(1.43 g, 0.005 mol) and **III**(2.32 g, 0.005 mol) were dissolved in 50mL of hot N,N-dimethylacetamide(DMAc) and DMSO, respectively. The following procedure is typical for the preparation of polymeric Schiff's base. The polymer **III** (2.32 g, 0.005 mol) in 50 mL of DMSO was treated with aromatic amines(0.015 mol) having various structures as illustrated in Scheme 2. The solution containing aromatic amine was stirred for 24 hours at 25°C, added catalytic amounts of concentrated HCl, and then maintained at 80°C for 12 hours. Cooling to room temperature, the polymer was obtained by precipitation into methanol. The polymer was separated, washed with methanol twice, and dried under reduced pressure.

Results and Discussion

Synthesis and Structural Characterization

The compound **I** containing flexible spacer group was prepared by treating the 4-hydroxybenzaldehyde with 2-(2-chloroethoxy)ethanol. The final product was viscous liquid having purity of 98% by HPLC. The structure of this compound was characterized by ^{1}H NMR analysis. The spectra show those sharp resonances at δ =9.75 ppm(C**H**O), δ =7.71, 7.69, 6.92, and 6.89 ppm(Ar**H**), δ =4.12, 4.10, and 3.77 ppm(OC**H**$_2$) and δ =2.5 ppm(O**H**). All these proton resonances give evidences that the compound **I** has been successfully synthesized with high purity.

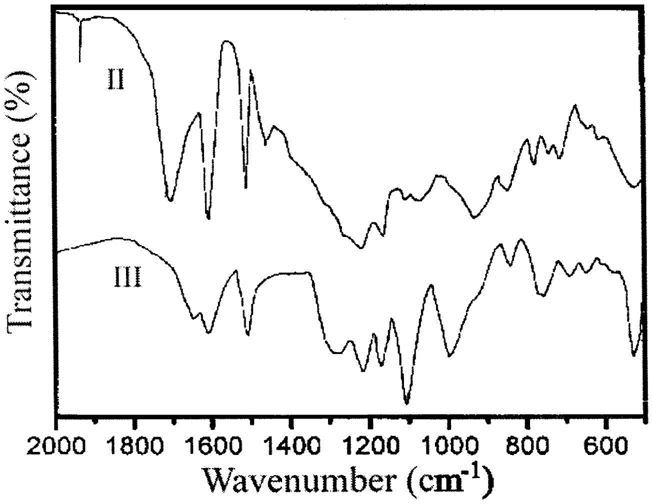


Fig. 1. IR spectra of polymers **II** and **III**.

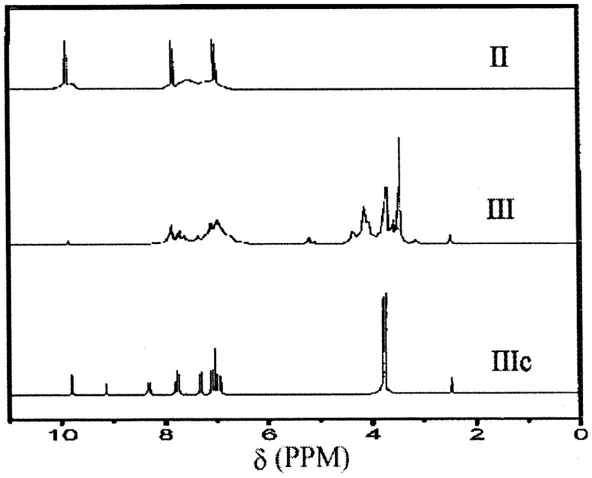


Fig. 2. ^{1}H NMR spectra of polymers **II**, **III**, and **IIIc**.

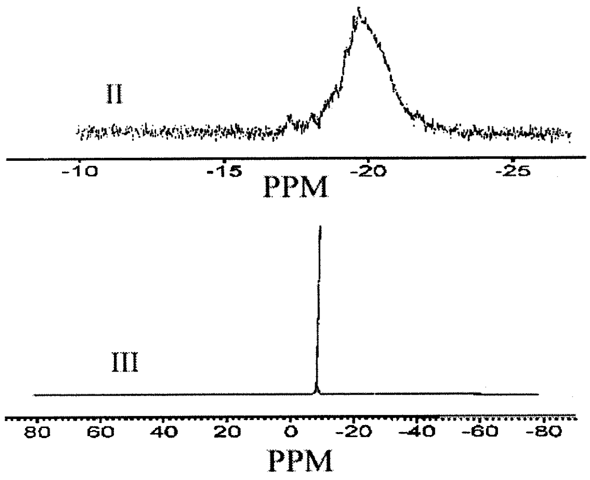


Fig. 3. ^{31}P NMR spectra of polymers **II** and **III**.

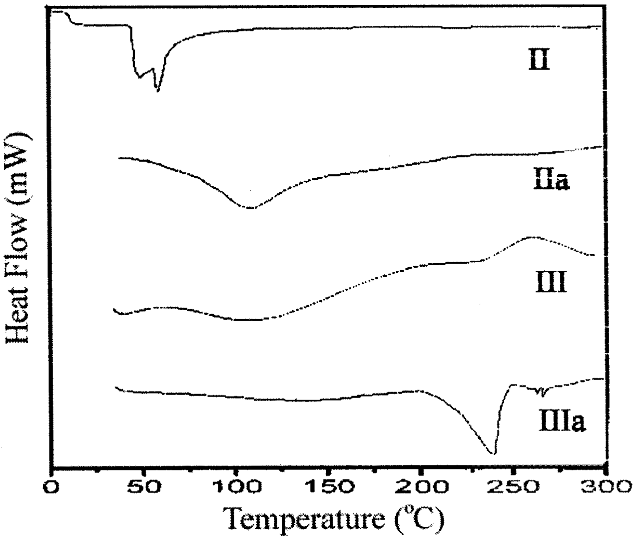


Fig. 4. DSC curves of polymer **II**, **IIa**, **III**, and **IIIa**.

The synthetic pathways of poly(organophosphazene) bearing Schiff's base are outlined in Scheme 2. The PDCP, prepared by the thermal polymerization of the cyclic trimer(HCTP), was allowed to react with either sodium salts of p -formylphenoxide or sodium salts of 2-[2-(p-formylphenoxy)ethoxy]ethanol to give polymer **II** or **III**, respectively. An aldehyde group at the terminus of the aryloxy side groups attached at the polymer **II** or **III** was allowed to form a Schiff's base linkage by reactions with various aromatic amines. All the final products bearing Schiff's base linkage were powder showing colors of yellow to dark brown according to the kinds of functional groups attached to those aromatic amines used.

They were found to be insoluble in common organic solvents, but showed partial solubility to those hot solvents like DMAc, DMSO, and DMF. This poor solubility is, in the main, a consequence of the formation of microcrystallinity, which can usually observable from the poly(organophosphazene) containing bulky side group (10-12).

Table 1. Substitution Percentage and Spectral Data for the Synthesized Polymers

Polymer	Substitution Percentage	IR(KBr) (cm^{-1})	^1H NMR(δ, ppm)
II		1701(CHO), 1302, 1212(P-N-P), 1598, 1503(Ar C-C), 931(P-O-C)	9.78(CHO), 6.90~7.77(Ar H)
IIa	34.3	1601(CH=N), 1270, 1213, 1166 (P-N-P), 935(P-O-C)	9.77(CHO), 6.93~7.75(Ar H), 8.27(CH=N)
IIb	42.6	1707(CHO, w),1603(CH=N), 1211, 1166(P-N-P), 1603(Ar C-C), 931(P-O-C), 1030(OCH_3)	9.79(CHO), 6.87~7.66(Ar H), 3.72(OCH_3), 8.25(CH=N)
IIc	43.0	1600(CH=N), 1692(CHO, w), 1213, 1164(P-N-P), 932(P-O-C), 1600, 1506(Ar C-C)	9.76(CHO), 6.61~7.68(Ar H), 8.30(CH=N)
IId	17.2	1599(CH=N), 1208, 1162(P-N-P), 927(P-O-C), 1599(Ar C-C)	9.78(CHO), 6.91~7.77(Ar H), 8.25(CH=N)
IIe	34.3	1602(CH=N), 1212, 1166(P-N-P), 1602, 1510(Ar C-C), 933(P-O-C)	9.79(CHO), 6.83~7.89(Ar H), 8.31(CH=N)
III		1710(CHO), 1604, 1512(Ar C-C), 1170, 1254(P-N-P)	9.86(CHO), 6.5~7.87(Ar H), 3.48~4.44(CH2O)
IIIa	-	1603(CH=N), 1507, 1602(Ar C-C), 1210, 1170(P-N-P)	9.8(CHO, trace), 6.93~7.90(Ar H)
IIIb	44.4	1667(CHO), 1603(CH=N), 1583(Ar C-C), 1309, 1170(P-N-P)	9.78(CHO), 8.26, 8.29(CH=N, m), 6.92~7.78(Ar H), 3.76~3.82 (CH_2O), 10.5(COOH)
IIIc	65.0	1654(CH=N), 1603, 1518(Ar C-C), 1299, 1260, 1171(P-N-P)	9.78(CHO), 8.30~8.33(CH=N), 6.92~7.81(Ar H), 3.76~3.82(CH_2O), 10.5(COOH)
IIId	68.9	1689(CHO), 1658(CH=N), 1611, 1583(Ar C-C), 1260, 1179(P-N-P)	9.77(CHO), 8.23, 8.26,8.29(CH=N), 6.92~7.92(Ar H), 3.76~3.82(CH_2O)
IIIe	82.7	1605(CH=N), 1550(Ar C-C), 1249, 1150(P-N-P)	9.77(CHO), 8.18, 8.22, 8.45(CH=N), 6.92~8.04(Ar H), 3.38~3.46(OCH_3)

The amounts of Schiff's base linkage introduced into the polymer **II** or **III** are determined by calculating the integration ratio of aldehydic proton(-C**H**O, δ = 9.8 ppm) and imine proton(-C**H**=N-, δ = 8.5 ppm) of those ^1H NMR spectra obtained from each of the polymeric Schiff's bases prepared. The yields of mother polymers(polymer **II** and **III**) were in the range of 49% to 56%. These relatively low values of yield are tentatively ascribed to the bulkiness of the substituents to be introduced, which can prevent the geminal replacement patterns due mainly to the steric hindrances. Table 1 shows the substitution degree of Schiff's base linkages being introduced into the polymer **II** and **III**. The substitution degrees of polymeric Schiff's bases derived from polymer **II** marked lower values(34 % average) than those of polymer **III** series(65 % average). This difference can be explained in part by the fact that the polymer **II** which contains side chains of very bulky but no flexible spacer group cannot assume a random structure, which leads to a molecule having less freedom of side chain motion, and hence less Schiff’s base linkages can be formed.

The structural characterizations for the mother polymers(polymer **II** and **III**) and their Schiff's base side group units were carried out by IR, ^{1}H NMR, ^{31}P NMR, and elemental microanalysis. Table 1 summarized spectral data obtained by IR and ^{1}H NMR. Fig. 1 is the representative IR spectra showing absorption bands of polymer **II** and **III**. The absorption bands, in Table 1, at 1650 ~ 1599 cm^{-1} observed from all of the polymeric Schiff's bases are the characteristic absorptions due to the azomethine stretching, which confirms the formations of Schiff's base linkages in the side chain units of mother polymers.

The formation of Schiff's base linkage can also be confirmed by the ^{1}H NMR data. The typical ^{1}H NMR spectra obtained from the polymer **II**, **III** and its Schiff's base product are illustrated in Fig. 2. Table 1 shows that all the final products including polymer **II** and **III** revealed aldehydic proton resonance at around $\delta = 9.7$, which is an indication that those mother polymers are prepared correctly. Furthermore, the Schiff’s base products derived from polymer **II** show azomethine proton resonances at $\delta = 8.25 \sim 8.31$, and those products from polymer **III** also reveal resonances at $\delta = 8.18 \sim 8.45$, which is a strong evidence for the formation of poly(organophospazene) bearing Schiff's base linkage.

The replacement of chlorine atoms in PDCP by nucleophilic substituents was confirmed by ^{31}P NMR. A singlet broad resonance at $\delta = -19.7$ ppm from polymer **II** and resonance (narrow) at $\delta = -8.8$ ppm from polymer **III** can be found from Fig. 3, which implies the complete chlorine replacement (10-11,13). The values of elemental analysis for the polymer **II** were C: 58.04 (58.54), H: 3.49 (3.52), N: 4.83 (4.88), P: 10.68 (10.78), and Cl: 0.14%(the values in parenthesis are the calculated values). Also the chlorine content of the polymer **III** was 0.01%. All these values of chlorine contents of both the mother polymers confirmed the complete removal of chlorine atoms.

Thermal Characterization

The thermal transition behaviors were characterized by DSC measurements. Representative DSC thermograrns for polymer **II**, **IIa**, **III**, and **IIIa** are shown in Fig. 4, and those thermal analysis results obtained from the mother polymers and their Schiff’s base derivatives are summarized in Table 2.

The molecular origin of the glass transition is in cooperative chain motions involving main chain bond rotation, and hence the glass transition temperature(Tg) is believed to be a measure of the reorientational freedom of the macromolecular chain. The most important molecular structural feature that influences the motion of polymer chain is the intrinsic flexibility of the main chain. Undoubtedly, the chain flexibility is depended largely on the amounts of potential energy barriers to rotation around the backbone chain. Low potential energy generally leads to a flexible chain polymer and gives usually low values of Tg's. However, multiatomic side groups containing rigid constituent atomic grouping in a highly flexible backbone chains can generate high Tg values, due mainly to the steric hindrance or polar interactions between rigid side groups.

Polymer **II** showed a glass transition temperature(Tg) at 9.1°C and a melting transition temperature(Tm) at 56.4°C. The Tg value found is very high than -8°C of poly[bis(phenoxy)phosphazene] (8). This difference can be attributed in part to the further reduction of the reorientational freedom of backbone chain by the strong polar interactions between terminal aldehyde groups. However, in case of polymer **III**, Tg was not clearly detected by DSC measurements. This is tentatively ascribed to the alkyl ether alkoxy spacer unit, which apparently does allow sufficient flexibility to permit side group stacking or the formation of microcrystallinity.

Table 2. Results of Thermal Transitions of Polymers

	Polymer											
	II	IIa	IIb	IIc	IId	IIe	III	IIIa	IIIb	IIIc	IIId	IIIe
Tg (°C)	9.1						104.1					
Tm (°C)	56.4	102.5	115.5	110.9	126.4	88.5		102.7, 152.4	239.0, 263.0, 266.0	88.5	-	112.9, 136.4

The replacement of p-formyl groups of mother polymers with Schiff's base linkage by the reactions of various aromatic amines brings about a modest rise in Tm's of about 50°C for polymer **II** series and 100°C for polymer **III** series on the average than those of their mother polymers. This enhancement of Tm's may be responsible for the increased microcrystallinity formed by the rigidity of Schiff’s base units and polar interactions between azomethine groups. The lower value of Tm's for the Schiff's base polymers being derived from polymer **II** may be the consequences of the inability of the aryloxy spacer linkage to decouple the chain motions from those of the side groups, and the lack of organized or repetitive structure due to the low substitution degree of Schiff's base units which may be distributed randomly along the main chain.

On the contrary, the polymeric Schiff's bases containing phenoxyethoxyethoxy units show trends of steep rising in Tm's about 100°C on the average than that of their mother polymer **III**, and multistage of thermal transitions. For example, polymer **IIIb** reveals its Tm's as <266°C, and three steps of thermal transition. This effect is tentatively ascribed to the formation of higher microcrystalline order which can be established by the organization of side groups themselves in parallel arrays by the help of flexible spacer groups. Moreover, the fact that 65% (average degree of substitution of Schiff’s base polymer from polymer **III**) of the repeating unit in the backbone chain bearing Schiff's base linkage can influence the side chains to make increased organization due to their strong polar interactions between azomethine groups. In addition, the phenomena showing multistage of thermal transition, together with the result of higher crystalline order of side chain, would suggest that the polymer has potential for exhibiting thermotropic liquid crystalline behavior.

Conclusions

Two new classes of poly(organophosphazene) bearing Schiff's base linkages were prepared via the substitution reactions of PDCP. The first class of polymeric Schiff's bases contains the azomethine units that are connected to the p-formylphenoxy side groups(polymer **II** series). The second class comprises mixed-substituent polymers that contain Schiff's base groups separated from the main chain by 2-phenoxyethoxyethoxy spacer groups(polymer **III** series).

Polymer **II** series showed crystalline melting transitions in the range of 86-126°C, but in the case of polymer **III** series revealed not only much higher melting transition range 88-

266°C than those of polymer **II** series but also multistage of transition. The low degree of microcrystallinity of polymer **II** series may be the consequence of the structural absence for the requirements needed for crystallization. Conversely, the products from polymer **III** in which the rigid Schiff's base group was separated from the main chain by the flexible spacer groups established the microcrystallinity enhancement or liquid crystalline order because of those side groups organization in parallel arrays. It is reasonable therefore suggest that the products of polymer **III** series have potentials for use as a thermotropic side chain liquid crystalline polymer.

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