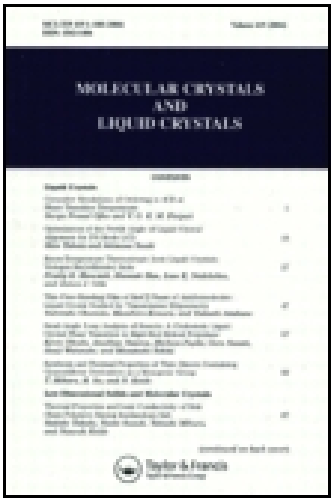

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Phase Transition in Cyclic Organophosphazenes: The Effect of Side Chains on Mesomorphism

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Phase Transition in Cyclic Organophosphazenes: the Effect of Side Chains on Mesomorphism

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Mesogenicity of five cyclotriphosphazenes and two cyclotetraphosphazenes with a similar dodecyl or dodecyloxy end and different central hard groups was studied. In the four cyclotriphosphazenes except for a cyclotriphosphazene with phenyl derivative side chains, enantiotropic mesomorphic phases were observed. The order of the thermal stability in mesophase is phenylazobenzene > phenyliminomethylphenyl > biphenyl groups for the side chains. The cyclotetraphosphazenes with biphenyl and Schiff base derivatives have lower mesomorphic thermal stability than cyclotriphosphazenes with the same side groups.

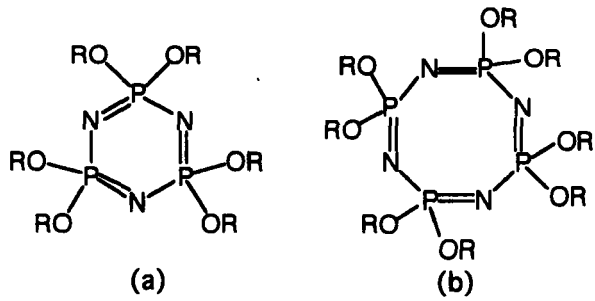
Keywords: liquid crystals; mesomorphic phase transition; cyclotriphosphazenes; cyclotetraphosphazenes

I. INTRODUCTION

Cyclotri- or cyclotetraphosphazenes are constituted of side chains and the hexa- or octa-membered organophosphazene ring, made of alternating P and N atoms.(See Fig. 1) For the mesomorphic cyclotriphosphazenes, several compounds have been prepared as precursors of the polyphosphazenes.[1-3] However, their physical properties were not studied in detail. The mesomorphic cyclotetraphosphazenes have not been studied.

Recently, we synthesized several cyclotriphosphazene and cyclotetraphosphazene derivatives with mesogenic side groups and studied their phase transition and mesogenicity. We found mesomorphic phases in some of the cyclotriphosphazenes[4-12] and also found a SmA phase in the cyclotetraphosphazene with a Schiff base derivative side chain.[13]

In this paper, we describe the synthesis of the five cyclotriphosphazenes and two cyclotetraphosphazenes with different hard groups and similar end groups in the side chains and studied the effects of side chains on the mesomophic phase transition in such cyclic organophosphazenes. The described cyclotriphosphazenes and cyclotetraphosphazenes are shown in Fig. 1.



(a) (b)

R = $C_6H_4OC_{12}H_{25}$(c), $C_6H_4C_6H_4OC_{12}H_{25}$(d), $C_6H_4C_6H_4C_{12}H_{25}$(e), $C_6H_4N{=}NC_6H_4OC_{12}H_{25}$(f), $C_6H_4CH{=}NC_6H_4OC_{12}H_{25}$(g)

Figure 1 Chemical formulae of hexakis(4-(4'-dodecyloxy)phenoxy)-cyclotriphosphazene (1)(a-c), hexakis(4-(4'-dodecyloxy)biphenoxy)-cyclotriphosphazene (2)(a-d), hexakis(4-(4'-dodecyl)biphenoxy)cyclotri-phosphazene (3)(a-e), hexakis(4-(4'-dodecyloxyphenylazo)phenoxy)-cyclotriphosphazene (4)(a-f), hexakis(4-(N-(4'-dodecyloxyphenyl)-iminomethyl)phenoxy)cyclotriphosphazene (5)(a-g), octakis(4-(4'-dodecyloxy)biphenoxy)cyclotetraphosphazene (6)(b-d), octakis(4-(N-(4'-dodecyloxyphenyl)iminomethyl)phenoxy)cyclotetraphosphazene (7)(b-g).

II. EXPERIMENTAL

1. Preparation of hexakis(4-(4'-dodecyloxy)phenoxy)-cyclotriphosphazene (1)

4-Dodecyloxyphenol (PO12) was synthesized from hydroquinone (50.0 g, 0.454 mol), 1-bromododecane (94.2 g, 0.378 mol) and KOH (29.0 g, 0.454 mol) in ethanol (500 ml) under reflux for 12 h. The sodium salt of PO12 was prepared from PO12 (7.00 g, 25.2 mmol) and NaH (1.00 g, 25.0 mmol) in THF(50 ml) under reflux for 2 h. Compound 1 was prepared from the sodium salt of PO12 and hexachlorocyclotriphosphazene (HClCP)(1.00 g, 2.88 mmol) in THF (70 ml) under reflux for 15 h. The obtained crude products were column chromatographed (SiO_2, $CHCl_3$), followed by recrystallization three times from ethanol. Compound 1 was recognized as thoroughly purified using TLC (SiO_2, $CHCl_3$), IR, ^1H and ^{31}P NMR, and elemental analyses. mp 346 K; IR (KBr) 1506, 1476, 1253, 1197, 1171, 956, 834 cm^{-1}; ^1H NMR δ 0.9(t, 6.6 Hz, 3H), 1.3-1.8(m, 20H), 3.9(t, 6.6 Hz, 2H), 6.7(d, 9.2 Hz, 2H), 6.8(d, 9.2 Hz, 2H); ^{31}P NMR δ 11.1(s); Calcd. for $C_{108}H_{174}O_{12}N_3P_3$: C, 72.11; H, 9.75; N, 2.34 %, Found: C, 71.96; H, 9.84; N, 2.38 %.

2. Preparation of hexakis(4-(4'-dodecyloxy)biphenoxy)cyclotri-phosphazene (2)

Compound 2 was prepared by a method similar to that in a previous paper.[9] mp 425 K, cp 453 K; IR (KBr) 2956, 1608, 1500, 1242, 1178, 977, 826 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9(t, 7.3 Hz, 3H), 1.3-1.8(m, 20H), 4.0(t, 7.3 Hz, 2H), 6.8~7.3(m, 8H); ^{31}P NMR δ 10.6(s); Calcd. for $C_{144}H_{198}O_{12}N_3P_3$: C, 76.66; H, 8.85; N, 1.86 %, Found: C, 76.52; H, 8.88; N, 1.90 %.

3. Preparation of hexakis(4-(4'-dodecyl)biphenoxy)cyclotriphosphazene (3)

Compound 3 was prepared from 4-octylbiphenyl-4'-ol (supplied by Chisso Co., Ltd.)(5.00 g, 14.7 mmol) using a suspension of sodium hydride (0.630 g, 15.7 mmol) in THF (60 ml) and HClCP (0.710 g, 2.04 mmol) in THF (10 ml) under reflux for 12 h. The obtained crude products were isolated using column chromatography(SiO_2, $CHCl_3$), followed by recrystallization from ethyl acetate. The crystals were recognized as thoroughly purified by TLC(SiO_2, CCl_4), ^1H and ^{31}P NMR, IR and elemental analyses. mp 406 K, cp 426 K; IR (KBr) 2920, 1604, 1468, 1241, 1207, 1180, 982, 972, 813 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9(t, 7.3 Hz, 3H), 1.3-1.7(m, 12H), 2.6(t, 7.9 Hz, 2H), 7.0(d, 8.4 Hz, 2H), 7.1(d, 8.4 Hz, 2H), 7.3(d, 8.4 Hz, 4H); ^{31}P NMR δ 10.6 (s); Calcd. for $C_{144}H_{198}O_6N_3P_3$: C, 80.10; H, 9.24; N, 1.95 %, Found: C, 79.95; H, 9.34; N, 1.99 %.

4. Preparation of hexakis(4-(4'-dodecyloxyphenylazo)phenoxy)-cyclotriphosphazene (4)

4,4'-Hydroxyazobenzene(AZ) was prepared from 4-nitrophenol (5.00 g, 36.0 mmol) and KOH (25.0 g, 450 mmol) in water (20 ml) at 200 ℃ for 5 h. 4-Dodecyloxy-phenylazophenyl-4'-ol (AZO12) was prepared from AZ (5.00 g, 23.4 mol), KOH (2.20 g, 32.8 mmol) and 1-bromododecane (12.9 g, 51.8 mmol) in ethanol (80 ml) by reacting at 50 ℃ for 24 h. Compound 4 was synthesized from AZO12 (5.00 g, 13.0 mmol), the suspension of NaH (0.560 g, 14.0 mmol) in THF (20 ml) and HClCP (0.501 g, 1.14 mmol) in THF (70 ml) under reflux for 12 h. The obtained crude crystals were column chromatographed (SiO_2, $CHCl_3$) and recrystallized three times from a THF-hexane(1:10) mixed solvent. The purity of the samples was recognized using TLC(SiO_2, $CHCl_3$), IR, ^1H and ^{31}P NMR and elemental analyses. mp 416 K, cp 443 K; IR (KBr) 2919, 1604, 1474, 1420, 1252, 1240, 1215, 1171, 1150, 986, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9(t, 7.0 Hz, 3H), 1.3-1.8(m, 20H), 4.0(t, 6.6 Hz, 2H), 6.9(d, 8.8 Hz, 2H), 7.1(d, 8.8 Hz, 2H), 7.7(d, 8.8 Hz, 2H), 7.8(d, 8.8 Hz, 2H); ^{31}P NMR δ 9.7(s); Calcd. for $C_{144}H_{198}O_{12}N_{15}P_3$: C, 71.35; H, 8.23; N, 8.67 %, Found: C, 70.70; H, 8.33; N, 8.57 %.

5. Preparation of hexakis(4-(N-(4-dodecyloxyphenyl)iminomethyl)-phenoxy)cyclotriphosphazene (5)

4-Dodecyloxyacetanilide (AA-12) was prepared from 4-acetaminophenol (60.5 g, 0.430 mol), KOH (33.0 g, 0.500 mol) and 1-bromododecane (110 g, 0.440 mol) in ethanol (200 ml) under reflux for 1.5 h. 4-Dodecyloxyaniline (A-12) was prepared from (AA-12) (69.3 g, 0.25

mol) and KOH (71.3 g, 1.27 mol) in ethanol (350 ml) under reflux for 12 h. Hexakis(4-formylphenoxy)cyclotriphosphazene (HFCP) was prepared from 4-hydroxybenzaldehyde (10.0 g, 8.20 mmol) with a suspension of NaH (3.77 g, 9.43 mmol) in THF (100 ml) and HClCP (3.80 g, 1.09 mmol) in THF (50 ml) under reflux for 6 h. The obtained crude products of HFCP were purified by reprecipitation of the THF solution into hexane. Compound 5 was synthesized from A-12 (3.86 g, 13.9 mmol) and HFCP (1.50 g, 1.74 mmol) in benzene (100 ml) under reflux for 6 h. The obtained crude products were recrystallized three times from THF. The purity of the sample was recognized by ^{1}H and ^{31}P NMR, IR and elemental analyses. mp 435 K, cp 500 K; IR (KBr) 2919, 1625, 1465, 1252, 1223, 1174, 1162, 988, 839 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9(t, 6.6 Hz, 3H), 1.3-1.9(m, 20H), 4.0(t, 6.6 Hz, 2H), 6.8(d, 8.8 Hz, 2H), 7.0(d, 9.2 Hz, 2H), 7.1(d, 8.6 Hz, 2H), 7.7(d, 8.6 Hz, 2H), 8.4(s, 1H); ^{31}P NMR δ 9.6(s); Calcd. for $C_{142}H_{204}O_{12}N_9P_3$: C, 74.50; H, 8.50; N, 5.21 %, Found: C, 74.38; H, 8.57; N, 5.19 %.

6. Preparation of octakis(4-(4'-dodecyloxy)biphenoxy)cyclotetraphosphazene (6)

Compound 6 was prepared from the sodium salt of octachlorocyclotetraphosphazene (OClCP)(3.00 g, 8.46 mmol) in THF (40 ml) and 4-dodecyloxy(4'-hydroxy)biphenyl (3.00, 8.46 mmol) with a suspension of NaH(0.203 g, 8.46 mmol) under reflux for 15 h. The obtained crude products were column chromato-graphed (SiO_2, $CHCl_3$), followed by recrystallization three times from THF. Compound 6 was recognized as thoroughly purified using TLC (SiO_2, $CHCl_3$), IR, ^{1}H and ^{31}P NMR, and elemental analyses. mp 398 K; IR (KBr) 1502, 1474, 1246, 1240, 1218, 1171, 979, 824 cm^{-1}; ^{1}H NMR δ 0.9(t, 6.6 Hz, 3H), 1.2-1.8(m, 20H), 4.0(t, 6.2 Hz, 2H), 6.8(d, 8.8 Hz, 2H), 7.0(d, 8.4 Hz, 2H), 7.3(d, 5.6 Hz, 2H), 7.3(d, 6.8 Hz, 2H); ^{31}P NMR δ -11.4(s).

7. Preparation of octakis(4-(N-(4'-dodecyloxyphenyl)iminomethyl)-phenoxy)cyclotetraphosphazene (7)

Octakis(4-formylphenoxy)cyclotetraphosphazene (OFCP) was prepared from the sodium salt of 4-hydroxybenzaldehyde (17.7 g, 0.145 mol) with a suspension of NaH (5.75 g, 0.144 mol) in THF (100 ml) and OClCP(5.05 g, 10.9 mmol) in THF (50 ml) under reflux for 6 h. Compound 7 was synthesized by the reaction of A-12 (2.45 g, 8.79 mmol) and OFCP (0.800 g, 0.696 mmol) in benzene (60 ml) under reflux for 4 h. Water produced in the solution was removed by molecular sieves in a Dien-Stark tube. The obtained crude products were recrystallized three times from benzene and once from 1:1 THF-cyclohexane after being separated by filtration. Compound 7 was characterized by ^{1}H and ^{31}P NMR, IR and elemental analysis. mp 413 K, 432 K; IR (KBr) 2954, 2871, 2852, 1625, 1604, 1252 1227, 1163, 981, 841 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.9(t, 7.0 Hz, 3H), 1.2-1.9(m, 20H), 3.9(t, 6.6 Hz, 2H), 6.8(d, 8.8 Hz, 2H), 7.0(d, 8.4 Hz, 2H), 7.1(d, 8.8 Hz, 2H), 7.7(d, 8.8 Hz, 2H), 8.4(s, 1H); ^{31}P NMR δ -12.7 (s); Calcd.

for $C_{200}H_{272}O_{16}N_4P_4$: C, 74.50; H, 8.50; N, 5.21; P, 3.84; Anal. found: C, 74.22; H, 8.31; N, 4.99; P, 3.81 %.

8. Analytical techniques and instruments

Phase transition temperatures were measured using a differential scanning calorimeter (Seiko Electronics DSC 210 and SSC 5500 system) at a heating/cooling rate of 5 K min^{-1} between room temperature and over the melting point. The apparatus was calibrated using the melting of indium (T_m; 429.6 K, ΔH; 28.5 Jg^{-1}) and tin (T_m; 505.1 K, ΔH; 59.5 Jg^{-1}). Texture observations were performed using an optical polarizing microscope (Nikon Optiphotopol XTP-11) equipped with a Mettler FP 82 hot stage at a heating/cooling rate of 5 K min^{-1} between room temperature and over the melting or clearing point under crossed polarizers. The ^1H NMR (solvent $CDCl_3$) spectra and ^1P NMR (solvent THF) were recorded on a JEOL JNM-A 400 spectrometer using TMS as the internal standard for the former and 85% H_3PO_4 as the external standard for the latter. IR spectra were measured for KBr discs using a Perkin-Elmer FT-IR 1640.

III. RESULTS AND DISCUSSION

1. The mesomorphic phase transition in cyclotriphosphazenes

The phase transition temperatures and phase transition entropies for cyclotriphosphazenes and cyclotetraphosphazenes obtained from the second heating process of the DSC measurements are shown in Table 1.

In compound 1 with dodecyloxyphenyl side groups, the melting point is 346 K and no mesomorphic phase was observed on the polarizing microscope observations. Probably, the phenyl ring is too short as a rigid part of the mesogenic side chains in the cyclotriphosphazene. Compound 2, which has dodecyloxybiphenyl side groups, melted at 425 K. Between 425 and 453 K, a schlieren texture with disclination lines having $s = \pm 1$ was observed on the polarizing microscope, suggesting the existence of the SmC phase.[14] Compound 2 changed from the SmC phase to an isotropic liquid at 453 K. Compound 3 with dodecylbiphenyl side chains melted at 406 K, and between 406 and 424 K, a schlieren texture similar to that of compound 2 was observed with the polarizing microscope, showing the existence of the SmC phase. Between 424 and 426 K, a typical SmA fan texture was observed. Compound 3 changed to an isotropic liquid at 426 K. In compound 4, which has dodecyloxyphenylazobenzene groups, an enantiotropic SmA phase was observed between 416 and 443 K. In compound 5, which has dodecyloxyphenyliminomethylphenyl side groups, enantiotropic Sm1, SmC and SmA phases were observed between 435 and 452, 452 and 486, and 486 and 500 K, respectively. Sm1 was a biaxial higher-order smectic phase which was confirmed by polarizing microscope observation; however, the Sm1 has not yet been identified. Compound 5, which includes dodecyloxyphenyliminomethylphenyl side groups, possesses a high melting point and a wide liquid crystalline temperature range compared with compounds 2 and 3, both which include biphenyl derivatives in the side chains. This result may be due to that the fact that dodecyloxyphenyliminomethylphenoxy groups have a relatively

Table 1 Phase transtion temperatures(T / K) / phase transition entropies (ΔS / $JK^{-1}mol^{-1}$) of compound 1-7.

Compound	Side chain	backbone	Cr	Sm1	SmC	SmA	I
1	$C_{12}H_{25}OC_6H_4O$	P_3N_3	• 348/393	—	—	—	•
2	$C_{12}H_{25}OC_6H_4C_6H_4O$	P_3N_3	• 425/136	—	• 453/37	—	•
3	$C_{12}H_{25}C_6H_4C_6H_4O$	P_3N_3	• 406/93	—	• 424/206	• 426/33	•
4	$C_{12}H_{25}OC_6H_4N{=}NC_6H_4O$	P_3N_3	• 416/215	—	• 443/55	—	•
5	$C_{12}H_{25}OC_6H_4N{=}CC_6H_4O$	P_3N_3	• 435/239	• 452/1	• 486/1	• 500/28	•
6	$C_{12}H_{25}OC_6H_4C_6H_4O$	P_4N_4	• 396/181	—	—	(•) (390/42)	•
7	$C_{12}H_{25}OC_6H_4N{=}CC_6H_4O$	P_4N_4	• 413/218	—	—	• 433/41	•

strong interaction in the lateral direction of the mesogenic side chains, which aids the formation of the mesomorphic layer structure. In comparing the compounds having alkyl and alkoxy groups at the end of the side chains, alkoxy compound 2 has more than a 20 K higher melting and clearing points than alkyl compound 3. This result suggests that alkoxy end groups stabilize the smectic phase by the interaction of lateral direction. This is also found in normal meosgenic compounds.[15] Compound 5, which has phenylazobenzene mesogenic groups in the side chain, forms the enantiotropic smectic C phase with different schlieren textures than other compounds between 416 and 443 K, in which they have disclination lines with $n \geq 2$. The reason for the existence in different optical texture may be due to the high viscosity of the compound 5, but the reason must be studied more thoroughly. The order of the thermal stability in cyclotriphosphazene is phenylazobenzene > phenyliminomethylphenyl > biphenyl groups in the side chains. This order of themal stability of liquid crystalline phase is similar to that usually found in liquid crystals having mono mesogenic groups in the core.[16]

2. The mesomorphic phase transition in cyclotetraphosphazenes: comparison with cyclotriphosphazenes

In compound 6, which has dodecyloxybiphenyl side groups, in the second heating process the crystal melted at 398 K, and no mesomorphic texture was observed with the polarizing microscope. However, only in the cooling process, a SmA fan texture was observed between 390 and 386 K. In compound 7, which has 4-(N-(4'-dodecyloxyphenyl)-iminomethyl)phenyl side groups, the crystal melted at 413 K in the second heating process. Between 413 and 432 K, a SmA fan-texture was observed.

Comparing compound 2 with 6, which are cyclotriphosphazene and cyclotetraphosphazene with the same dodecyloxybiphenyl side groups, the former has higher melting points than the latter. Moreover, compound 6 has only a monotropic SmA phase, but compound 6 has an enantiotropic SmC phase. These results suggest that the cyclotriphosphazene has much higher mesomorphic thermal stability than that in cyclotetraphosphazene. Comparing compound 5 with 7, which are cyclotriphosphazene and cyclotetraphosphazene having the same 4-(N-(4'-dodecyloxyphenyl)iminomethyl)phenyl side groups, both of them have an enantiotropic mesomorphic phase. However, the melting and clearing points for the former are 435 and 500 K, and those for the latter are 413 and 432 K. These results show that melting and clearing points of the compound 5 are much higher than those of the compound 7. Therefore, the cylotriphospahzene has a much higher mesomorphic thermal stability than that in the cyclotetraphospahzene with the same Schiff base derivatives in the side chains.

In the X-ray single crystal structure analysis of hexakis(4-biphenoxy)cyclotriphosphazene(HBCP) and octakis(4-biphenoxy)-cyclotetraphosphazene (OBCP), side chains line up relatively regularly for the former and at random for the latter.[17] In the assumed molecular structure of compound 2 based on the structure of HBCP, each of the three mesogenic side chains direct upwards and downwards almost

perpendicularly to the cyclotriphosphazene ring. This molecular organization in compound 2 aids the formation of the smectic layer structure. However, the random orientation of the side chains in compound 6, where the situation may be similar to OBCP, prevents the formation of the smectic layer structure.

In conclusion, in the cyclic organophosphazenes, the chemical structures of the mesomorphic side chain affect the mesomorphic phase transition. Cylotetraphosphazenes have much lower thermal stability in the mesomorphic phase than that in cyclotriphosphazenes with the same side chains, which is probaly derived from the difference in their molecular structure.

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