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Phase Transition in Cyclotriphosphazene Derivatives:The Effect of Side Chains on Mesomorphism

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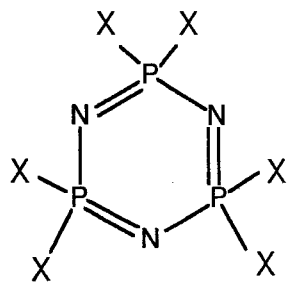
New cyclotriphosphazene derivatives with five different mesogenic moieties have been synthesized and their mesomorphic phase transitions have been studied using polarizing microscopy and differential scanning calorimetry. The difference in the side chains strongly affects on the appearance of the mesomorphic phase.
Key words: cyclotriphosphazenes, liquid crystals, phase transition, smectic phase

1. INTRODUCTION

Cyclotriphosphazenes are cyclic compounds of the general formula $(PNX_2)_3$ in which four-coordinated phosphorus atoms regularly alternate with nitrogen atoms in a ring. They are illustrated in Fig.1. Much concern has been paid to the synthesis of variety of cyclotriphosphaznes to provide functional properties to the compounds.[1-6] For the mesomorphic cyclotriphosphazenes, several papers have been reported as precursors of polyphosphazenes.[7-9] Recently, we synthesized several cyclotriphosphazene derivatives with mesomorphic side chains and found the existence of calamitic liquid crystalline phases.[10-17] In this paper, four cyclotriphosphazenes with side chains having a different hard central groups and similar flexible long end alkyl or alkoxy groups and a different type of cyclotriphosphazene, in which only three chlorine atoms are substituted by the side chains, were newly synthesized and their mesomorphic property was studied by use of polarizing microscopy and differential scanning calorimetry. We were concerned with the effect of different central groups and end groups on the cyclotriphosphazene into mesomorphic phase transition.



X=Aryloxy groups

Fig. 1 Chemical formula of cyclotriphosphazenes.

2. EXPERIMENTAL

2.1 Synthesis

2.1.1 Synthesis of hexakis(4-(4'-decyloxy)biphenoxy)cyclotriphosphazene(Compound 1)

Compound 1 was synthesized from hexachlorocyclotriphosphazene(HClCP)(supplied by Nihon Pure Chemicals Co., Ltd.) and 4-decyloxy(4'-hydroxy)biphenyl.[17] mp 430 K, cp 457 K; IR (KBr) 2921, 1608, 1500, 1241, 1178, 977, 827 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9(t, 3H), 1.3-1.8(m, 16H), 4.0(t, 2H), 6.8-7.3(m, 8H); ^{31}P NMR δ 10.7(s); Calcd. for $C_{132}H_{174}N_3O_{12}P_3$: C, 75.94; H, 8.40; N, 2.01 %, Anal. found: C, 75.87; H, 8.40; N, 2.05 %.

2.1.2 Synthesis of hexakis(4-(4'-decyl)biphenoxy)cyclotriphosphazene(Compound 2)

Compound 2 was synthesized from 4-decyl(4'-hydroxy)biphenyl(9.00 g, 29.0 mmol)(supplied from Chisso Petrochemicals Co.), NaH(1.16 g, 29.0 mmol) and HClCP (1.12g, 3.22 mmol) in THF(60 ml) solution under reflux for 12 h. The obtained crude products were purified by column chromatography (silica gel, chloroform), followed by the recrystallization twice from hexane/THF(20:1) mixed solvent. The samples were judged to be thoroughly purified by TLC(SiO_2, CCl_4), ^1H and ^{31}P NMR, and elemental analyses. The analytical results for compound 2 are as follows: mp 410 K, cp 430 K; IR (KBr) 2921, 1604, 1468, 1256, 1208, 1180, 1167, 970, 815 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9(t, 7.0 Hz, 3H), 1.2-1.7(m, 16H), 2.6(t, 7.7 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 $C_{132}H_{174}N_3O_6P_3$: C, 79.63; H, 8.81; N, 2.15 %, Anal. found: C, 79.24; H, 8.75; N, 2.11 %.

2.1.3 Synthesis of hexakis(4-(4'-decyloxyphenylazo)phenoxy)cyclotriphosphazene(Compound 3)

4-Decyloxy(4'-hydroxy)phenylazobenzene(DHPA) was synthesized from 4, 4'-dihydroxyazobenzene

(HAZ)(4.00g, 18.7 mmol), decylbromide(9.15 g, 41.5mmol) and KOH(1.50 g, 31.0 mmol) in ethanol(80 ml) solution at 50 °C for 24 h. The crude products were recrystallized three times from a water/ethanol(1:2) mixed solvent. HAZ was prepared from 4-nitrophenol(5.00 g, 36.0 mmol) and KOH(25.0 g, 450 mmol) at 200 °C for 5 h in a water solution. The crystals were recrystallized from 70 % aqueous ethanol solution after extracting from diethylether.

Compound 3 was synthesized from DHPA(7.00 g, 19.8 mmol), NaH(0.79 g, 19.8 mmol) and HClCP(1.78 g, 5.12mmol) in THF(140 mml) under reflux for 12 h. The crude products were separated by column chromatography(silica gel, chloroform), followed by recrystallization from a THF/hexane(1:10) mixed solvent. The obtained crystals were judged to be thoroughly purified by TLC(SiO_2, chloroform and CCl_4), ^1H and ^{31}P NMR and elemental analysis. The analytical results for Compound3 are as follows: mp 431 K, cp 439 K; IR (KBr) 2921, 1604, 1473, 1419, 1257, 1227, 1207, 964, 851 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9(t, 7.0 Hz, 3H), 1.3-1.8(m, 16H), 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 9.8(s); Calcd. for $C_{132}H_{174}N_{15}O_{12}P_3$: C, 70.30; H, 7.78; N, 9.32 %, Anal. found: C, 69.99; H, 7.67; N, 9.23 %.

2.1.4 Synthesis of hexakis(4-(N-(4'-decyloxyphenyl)iminomethyl)phenoxy)cyclotriphosphazene (Compound 4)

4-Decyloxyacetanilide was prepared from 4-hydroxyacetanilide(19.6 g, 0.13 mol), bromodecane (28.5 g, 0.13 mol) and KOH(9 g, 0.13 mol) in ethanol (200 ml) under reflux for 6 h. The obtained crude products were recrystallized three times from a water-ethanol(1:3) mixed solvent. The purity of the sample was recognized by TLC(SiO_2, ethyl acetate). 4-Decyloxyaniline was prepared from 4-decyloxyanilide(21g, 72 mmol) and KOH(10 g, 0.15 mol) in ethanol(200 ml) under reflux for 24 h. The crude products were recrystallized from water-ethanol(1:3). Hexakis(4-formylphenoxy)cyclotriphosphazene(HFCP) was synthesized from 4-hydroxybenzaldehyde (30.0 g, 0.247mol), NaH (6.00 g, 0.25 mol) and HClCP(12.1 g, 34.3mol) in THF(200 ml) under reflux for 2 h. The crude products were recrystallized from a hexane-THF 1:1 solution.

Compound 4 was prepared by the reaction of HFCP(1.06 g, 12 mmol) and 4-decyloxyaniline(2.99 g, 12 mmol) in benzene under reflux for 6 h. The obtained crude products were recrystallized three times from absolute THF. The products were characterized as thoroughly purified by ^1H and ^{31}P NMR, and elemental analysis. The analytical results for compound 4 are as follows: mp 445 K, cp 507 K; IR (KBr) 2935, 2878, 1625, 1604, 1578, 1249, 1216, 1175, 1161, 983 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.1(t, 7.3 Hz, 3H), 1.3-1.8(m, 16H), 3.9(t, 7.3 Hz, 2H), 6.8(d, 8.8 Hz, 2H), 7.0(d, 8.8 Hz, 2H), 7.1(d, 8.8 Hz, 2H), 7.7(d, 8.4 Hz, 2H), 8.4(s, 1H); ^{31}P NMR δ 9.7(s); Calcd. for $C_{138}H_{180}N_9O_{12}P_3$: C, 73.67; H, 8.06; N, 5.60 %, Anal. found: C, 73.89; H, 8.22; N, 7.89 %.

2.1.5 Synthesis of 1,3,5-trichloro-tris(4-(4'-decyl)-biphenoxy)cyclotriphosphazene(compound 5)

Compound 5 was synthesized from 4-decyl(4'-hydroxy)biphenyl(10.0 g, 32.3 mmol), NaH(1.26 g, 31.5 mmol) and HClCP (1.12g, 3.22 mmol) in THF(220 ml) solution under reflux for 24 h. The crude products obtained were purified by column chromatography(SiO_2, $CHCl_3$), followed by recrystallization twice from a hexane/THF(10:1) mixed solvent. The samples were judged to be thoroughly purified by TLC(SiO_2, $CHCl_3$ and CCl_4), ^1H and ^{31}P NMR, and elemental analyses. The analytical results for compound 5 are as follows: mp 455 K; IR (KBr) 2924, 1604, 1497, 1232, 1207, 1175, 1160, 994 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.9(t, 7.0 Hz, 3H), 1.2-1.7(m, 16H), 2.6(t, 7.9 Hz, 2H), 7.0(d, 8.8 Hz, 2H), 7.1(d, 8.1 Hz, 2H), 7.3(d, 8.1 Hz, 2H), 7.4(d, 8.8 Hz, 2H); ^{31}P NMR δ 20.6(s); Calcd. for $C_{66}H_{87}N_3O_3P_3Cl_3$: C, 67.77; H, 7.50; N, 3.59 %, Anal. found: C, 67.94; H, 7.50; N, 3.53 %.

2.2 Analytical techniques and instruments

Phase transition temperatures were measured using a differential scanning calorimeter (Seiko Instruments DSC 210) and texture observations were performed using an optical polarizing microscope (Nikon Optiphot-pol XTP-11) equipped with a Mettler FP 82 hot stage at a heating/cooling rate of 5 K min^{-1} between room temperature and to over the clearing point. ^1H NMR (solvent $CDCl_3$) and ^{31}P NMR (solvent THF) were recorded on a JEOL JNM-GX 270 spectrometer using TMS as the internal standard for the former and 85% H_3PO_4 as the external standard for the latter. The lock signal for ^{31}P NMR was provided by external D_2O inserts. IR was measured in KBr disks using a Perkin Elmer FT-IR 1600.

3. RESULTS AND DISCUSSION

The phase transition of five different cyclotriphosphazenes, which have similar end alkoxy and alkyl groups, were compared. The chemical

Table 1 Phase transition temperature and chemical shift of ^{31}P NMR in $(PNX_2)_3$

Compound	X	Liquid crystalline phase transition temperature / K								^{31}P NMR chemical shift / ppm
		Cr		SmC		SmA		I		
1	$H_{21}C_{10}O$-⟨⟩-⟨⟩-O-	■	430	■	457	—		■		10.6
2	$H_{21}C_{10}$-⟨⟩-⟨⟩-O-	■	410	■	428	■	430	■		10.6
3	$H_{21}C_{10}O$-⟨⟩-N=N-⟨⟩-O-	■	431	■	439	—		■		9.8
4	$H_{21}C_{10}O$-⟨⟩-N=CH-⟨⟩-O-	■	445	■	493	■	507	■		9.7
5	$H_{21}C_{10}$-⟨⟩-⟨⟩-O-, Cl	■	455	■		—		■		20.6

structures of the mesogenic side chains in the cyclotriphosphazene derivatives are shown in Table 1 with their phase transition temperatures in the second heating process and chemical shift of the ^{31}P NMR. Chemical shifts of the ^{31}P NMR are different for the cyclotriphosphazenes having different mesogenic side chains, suggesting that they have different electron and steric configurations. All the ^{31}P spectra of these samples showed only one singlet, indicating that the chlorine atoms of hexachlorocyclotriphosphazene are completely substituted by the correct side chains except for compound 5. In compound 5, three chlorine atoms were substituted by the side chains bnased on the elemental analysis. For the substitution of the chlorine atoms by side chains, there are two methods, geminal and non-geminal. In the geminal type substitution, the second attack on the side chain occurs to the chlorine atoms of the same P atoms attacked first by the side chains. On the other hand, non-geminal type substitution occurs at the chlorine atoms attached to adjacent P atoms. The ^{31}P NMR of compound 5 shows the singlet at 20.6 ppm and this indicates that the electronic and steric configurations of the all P atoms are the same. This result suggests that the side groups are attached to the adjacent P atoms of the cyclotriphosphazenes, so the introducing of the side groups into the cyclotriphosphazene is non-geminal.

In compound 1, based on the polarizing microscope observations, a texture having simultaneous a schlieren with s = ±1 and a broken fan was found between 435 and 457 K, suggesting the existence of the smectic C(SmC) phase[18]. In compound 2, on the polarizing microscope observations, a texture similar to compound 1 was observed between 418 and 428 K, and a fan texture and simultaneous black(homeotropic region) texture was observed between 428 and 430 K, suggesting the existence of enantiotropic smectic C and smectic A(SmA) phases. In compound 3, a texture similar to compound 1 was found between 431 and 439 K, suggestng the presence of an enantiotropic SmC phase. In compound 4, textures similar to SmA and SmC phases of compound 2 were observed between 445 and 493 K and 493 and 507 K, respectively. In compound 5, no mesomorphic phase was observed and the compound only melted from the crystalline phase to the isotropic liquid phase at 455 K.

The crystal structure of hexakis(4-biphenoxy)-cyclotriphosphazene(HBCP) was studied by X-ray single crystal analysis.[19] The molecular structure based on this structure assuming an all trans conformation alkoxy chain is shown in Fig. 2. In this structure each of the three side chains line up perpendicular to the cyclotriphosphjazene rings upwards and downwards and this large molecule forms a layer structure of the smectic phase of compound 1

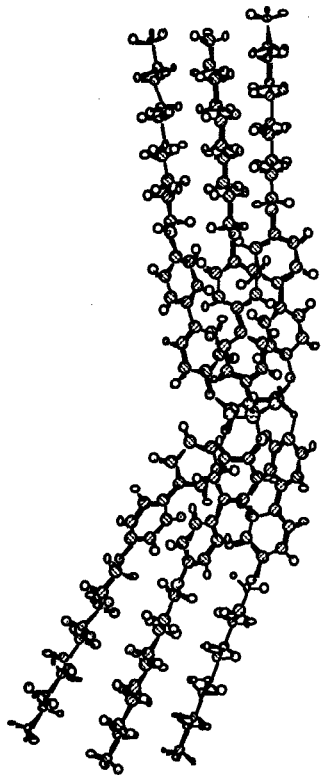


Fig. 2 Assumed molecular structure of compound 1.

and 2. When comparing the compounds having alkyl and alkoxy groups at the end of the side chains, the alkoxy compound 1 has about 20 K higher melting and clearing points than alkyl ompound 2. This result is due to the fact that alkoxy end groups stabilize the smectic phase by an interaction in the lateral direction of the molecules. This explanation is supported by the above molecular structure. This is also found in normal calamitic mesogenic compounds.[20]

Compound 4, which includes phenyliminomethylphenyl side groups possesses a high melting point and wide liquid crystalline temperature range compared with compounds 1, 2 and 3, which include biphenyl or phenylazobenzene groups in the side chains. This result may be due to the fact that the phenyliminomethylphenyl groups have a dipole moment in the lateral direction of the mesogens. This explanation is also supported by the above molecular structure by assuming similar molecular structures for the cyclotriphos-phazenes with phenyliminomethylphenyl and phenylazobenzene side chains. The order of thermal stability of mesomorphic phase is phenyliminomethylphenyl > phenylazobenzene > biphenyl. This order of the thermal stability is similar to that usually found in calamitic liquid crystals having two side chains.[21] In compound 5, no mesomophic phase transition was found. This may caused from the fact that the chlorine atoms with strong interaction are present at the end of cyclotriphosphazenes and the existence of chlorine atoms prevents the appearance of the mesomorphic phase.

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