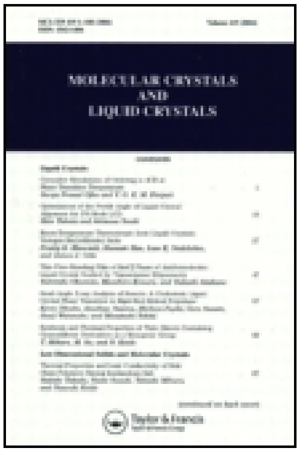

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Keiichi Moriya [a] , Tsuyoshi Masuda [a] , Toshiya Suzuki [a] , Shinichi Yano [a] & Meisetsu Kajiwara [b]

[a] Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu, 501-11, Japan

[b] School of Dentistry, Aichigakuin University, Kusumoto-cho, 1-100, Chikusa-ku, 464, Japan

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Liquid Crystalline Phase Transition in Hexakis(4-(N-(4'-alkoxyphenyl)iminomethyl)phenoxy)cyclotriphosphazene

KEIICHI MORIYA[a†], TSUYOSHI MASUDA[a], TOSHIYA SUZUKI[a],
SHINICHI YANO[a], and MEISETSU KAJIWARA[b]
[a]Department of Chemistry, Faculty of Engineering, Gifu University,
Yanagido Gifu 501-11, Japan; [b]School of Dentistry, Aichigakuin University,
Kusumoto-cho, 1-100, Chikusa-ku, 464, Japan

A new series of cyclotriphosphazenes bearing Schiff bases with different carbon number alkoxy end groups(HAICP) in the side chains were synthesized and their phase transitions and liquid crystallinity were studied using DSC measurements and polarizing microscope observations. We found a monotropic Sm1 phase for n = 3 and an enantiotropic Sm1 phase for n = 4 - 5, enantiotropic Sm1, SmC and SmA phases for n= 6 - 7, enantiotropic SmC and SmA phases for n = 8 - 10, and enantiotropic Sm2, SmC and SmA phases for n=11 and 12 in the HAICP series. The Sm1 phase is a low-order uniaxial smectic phase and Sm2 phase is a low-order biaxial smectic phase. The melting point decreased with an increase in the end alkoxy carbon number, n, of the cyclotriphosphazenes, but the clearing point decreased with an increase in n. As a result, the mesomophic region expands with an increase in n. The melting and clearing points do not show clear odd-even effects, which is caused by the peculiar shape of the cyclotriphosphazenes.

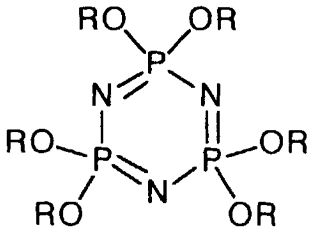
Keywords: liquid crystals; cyclotriphosphazene; phase transition; smectic polymorphism

INTRODUCTION

Much attention has been paid to the synthesis of several cyclotriphosphazenes with different side chains because different physical properties are produced by the introduction of functional side chains to the cyclotriphosphazenes.[1-6]

For the liquid crystalline cyclotriphosphazenes, several compounds have been synthesized as the precursor of the polyphosphazenes.[7-9] Recently, we found a liquid crystalline phase transition in the cyclotriphosphazenes bearing alkoxybiphenoxy groups in the side chains. They show nematic, smectic C and C*, respectively.[10-17]

In this report, we discuss a series of cyclotriphosphazenes having Schiff base side chains because molecules bearing Schiff bases in the central groups sometimes have different types of smectic phases.[18, 19] Based on this premise we synthesized a series of hexakis(4-(N-(4'-alkoxyphenyl)iminomethyl)phenoxy)cyclotriphosphazenes$[PN(OC_6H_4CH{=}NC_6H_4OC_nH_{2n+1})_2]_3$ (HAICP, n=3-12) and studied their phase transition and mesogenicity and the effects of the length of the end alkoxy chains on the liquid crystalline phase transition using polarizing microscope observations and differential scanning calorimetry(DSC). In Fig. 1, the chemical structure of HAICP is shown.



$R{=}C_6H_4CH{=}NC_6H_4OC_nH_{2n+1}$, n=3-12

FIGURE 1 Chemical structure of the cyclotriphosphazenes.

EXPERIMENTAL SECTION

Preparation of a series of hexakis(4-(N-(4'- alkoxyphenyl)iminomethyl)phenoxy)cyclotriphosphazene (HAICP)(n=3-12)

The synthesis of the n=3 compound is presented as a representative example of the HAICP series.

Propyloxyacetanilide was prepared from 4-hydroxyacetanilide(30 g, 0.20 mol), bromopropane(29.6 g, 0.12 mol) and KOH(16 g, 0.24 mol) in ethanol(200 ml) under reflux for 6 h. Obtained crude products were recrystallized three times from a water-ethanol(1:3) mixed solvent. The purity of the sample was recognized by TLC(ethyl acetate). 4-Propyloxyaniline was prepared from 4-propyloxyacetanilide(20g, 0.10 mol) and KOH(20 g, 0.30 mol) in ethanol(200 ml) under reflux for 24 h. Crude products were extracted by benzene and then distilled(114 °C/6 mmHg). The purity was determined by TLC(ethyl acetate), ^{1}H NMR and IR spectra.

Hexakis(4-formylphenoxy)cyclotriphosphazene was synthesized from 4-hydroxybenzaldehyde(30.0 g, 0.247mol), NaH(6.00 g, 0.25 mol) and hexachlorocyclotriphosphazene (supplied by Nihon Pure Chemicals Co., Ltd.)(12.1 g, 34.3mol) in THF(200 ml) under reflux for 2 h. Crude products were recrystallized from a hexane-THF solution. The samples were characterized by TLC(ethyl acetate), IR, ^{1}H and ^{31}P NMR.

Hexakis(4-(N-(4'-propyloxyphenyl)iminomethyl)phenoxy)-cyclotriphosphazene(n=3) was prepared by the reaction of hexakis(4-formylphenoxy)cyclotriphosphazene(1.06 g, 12.0 mmol) and 4-propyloxyaniline(1.81 g, 12.0 mmol) in benzene under reflux for 6 h. The obtained crude products were three times recrystallized from absolute THF. The products were characterized as being thoroughly purified by ^{1}H and ^{31}P NMR, and elemental analysis. The analytical results for n=3 are as follows. mp 516 K; IR (KBr) 2935, 2878, 1625, 1604, 1578, 1249, 1216, 1175, 1161, 983 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.1(t, 7.3 Hz, 3H), 1.3-1.8(m, 2H), 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 $C_{96}H_{96}N_9O_{12}P_3$: C, 69.42; H, 5.83; N, 7.59 %, Anal. found: C, 68.88; H, 5.72; N, 7.49 %.

Other members of the hexakis(4-(N-(4'-alkoxyphenyl)iminomethyl)-phenoxy)cyclotriphosphazene($4 \leq n \leq 12$) series were prepared by a method similar to that mentioned above. However in the case of alkoxyanilines in which the end alkoxy carbon number, n, is greater than 6, they are solids and are purified by two recrystallizations from water-ethanol(1:3) mixed solvent.

Analytical techniques and instruments

^1H and ^{31}P NMR spectra were measured using a JEOL JNM-GX 270 spectrometer in $CDCl_3$ solution with an internal standard of TMS and in THF solution locked by D_2O outside with an external standard of H_3PO_4. The phase transitions and mesogenicity were investigated using DSC(Differential Scanning Calorimetry) measurements and polarizing microscope observations. DSC were measured using a Seiko Instruments DSC 210 at a heating/cooling rate of 5 $Kmin^{-1}$ in a temperature range from 300 K to over the clearing point. The textures of the liquid crystalline phase were observed using a polarizing microscope, Nikon Optiphot-pol XTP-11 equipped with a Mettler hot stage FP-82, at a heating/cooling rate of 5 K min^{-1} under crossed polarizers. The IR spectra were measured with KBr disks using a Perkin Elmer FT-IR 1600.

RESULTS AND DISCUSSION

Phase transion and mesomorphism of hexakis(4-(N-(4'-alkoxyphenyl)iminomethyl)phenoxy)cyclotriphosphazene (HAICP, n=3 - 12)

The DSC thermograms of the series of n=3, 7 and 11 in the HAICP series are shown in Fig. 2. The thermodynamic parameters obtained from the DSC thermograms are shown in Table I. In the first cooling process of n=3, four exothermic peaks were observed at 511, 507, 439 and 386 K in the first cooling process. In the polarizing microsope observation upon cooling from an isotropic liquid, a mosaic texture was observed between 511 and 507 K. This phase is optically uniaxial and the phase seems to be smectic B, but has not been determined. This phase is called the smectic 1(Sm1) phase. In the

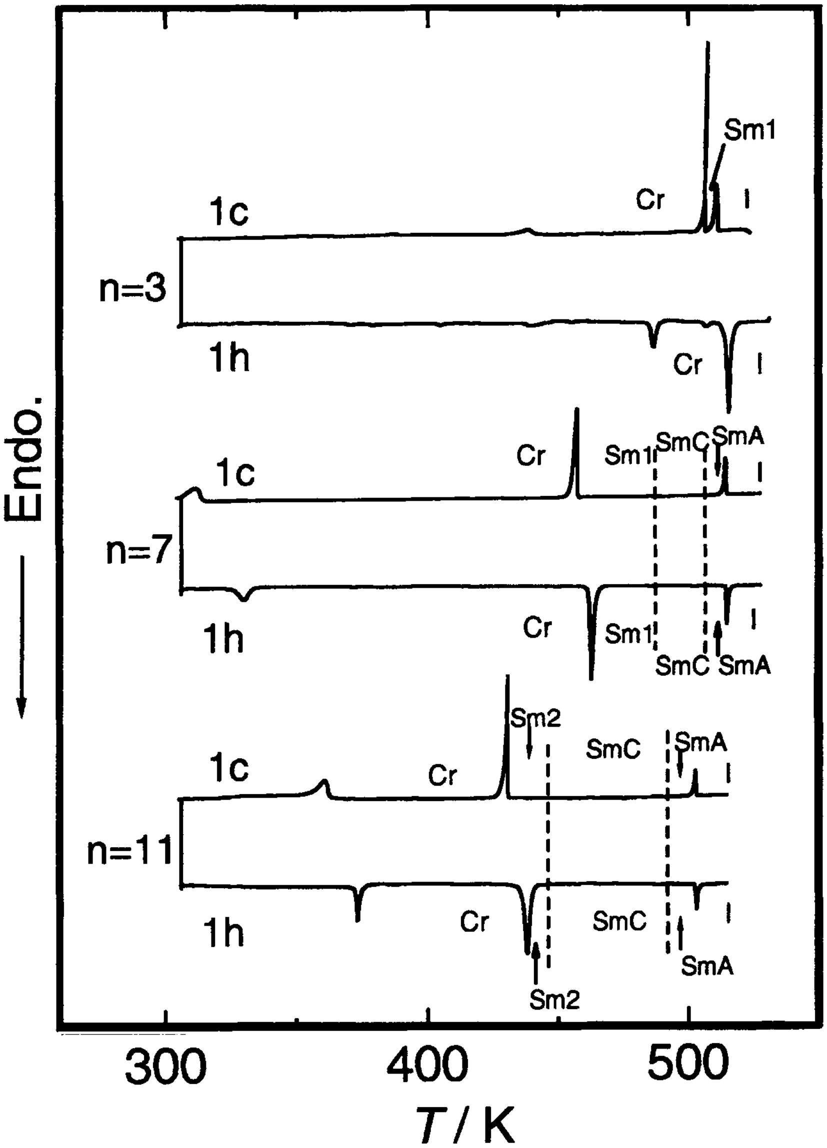


FIGURE 2 DSC thermograms of n = 3, 7 and 11 in the hexakis(4-(N-(4'-alkoxyphenyl)iminomethyl)phenoxy)cyclotriphosphazene(HAICP) series.

ABLE I Phase transition temperature (T / K) and liquid crystalline phase transition entropy (ΔS / $JK^{-1}mol^{-1}$) of a series of hexakis(4-(N-(4'-alkoxyphenyl)iminomethyl)phenoxy)cyclotriphosphazene $[(C_nH_{2n+1}OC_6H_4N{=}CHC_6H_4O)_2PN]_3$ (HAICP, n=3-12) in the second heating process.

n	K	•	Sm1	•	Sm2	•	SmC	•	SmA	•	I
3		516/121		•		•		•		$(511/43)^a$	
4		507/99		•		•		•		521/45	
5		488/67		•		•		•		517/44	
6		474/81		•		502/1.9		507/0.4		516/32	
7		463/166		•		486/1.6		503/0.5		515/33	
8		•		•		458/190		500/0.4		513/32	
9		•		•		443/204		496/0.4		510/31	
10		•		•		445/204		493/0.5		507/28	
11		•		438/208		445/1.2		489/0.5		503/28	
12		•		435/241		452/1.1		486/0.5		500/28	

[a] parentheses show the values for the monotropic phase transition.

polarizing microsope observation, the peak at 511 K is the clearing point and the peak at 507 K is the freezing point. In the second heating process, five endothermic peaks were observed at 406, 441, 487, 508 and 516 K. On the polarizing microsope observation, no mesomorphic phase was observed in the heating process. Therefore, the mesomorphic Sm1 phase is monotropic for n=3. The 516 K peak is the melting.

For the n=4 and 5, similar mesomophic textures as n=3 were observed on the polarizing microscope observations both in the heating and cooling processes. Their thermal behavior was obtained by DSC.

As shown in Fig. 2, in the first cooling process of the DSC thermogram of n=7, two large and two small peaks are seen at 514, 457 and 503, 486 K, respectively. On the polarizing microscope observation upon cooling from an isotropic liquid, at 514 K a SmA texture with a fan texture[20] was observed. Below 503 K, the fan texture changed to a broken-fan and schlieren textures, showing the presence of the SmC[20]. Below 486 K, broken-fan texture changed to a mosaic texture, which is similar to the mesomorphic mosaic texture of n=3. For the identification of the phase, the mixing test of the n=5 and 7 was done between the cover slide on the polarizing microscope observations. The mesorphic phase of the n=5 and the lowest temperature mesomorphic phase of the n=7 completely mixed, indicating that these phases were the same Sm1 phases. At 457 K, the mesomorphic phase changed to a crystalline phase. In the second heating process, three large endothermic peaks were observed at 340, 463 and 515 K and two small endothermic peaks were observed at 486 and 503 K. From the polarizing microscope observation, the peak at 463 K corresponds to melting. The small peaks at 486 and 503 K correspond to the Sm1-SmC and SmC-SmA phase transitions, respectively. Above 515 K, the eye-field becomes black, suggesting an isotropic liquid. The small entropy of the Sm1-SmC and SmC-SmA suggests that the structure of Sm1, SmC and SmA phases are very close together.

For n=6, similar mesomorphic textures and a similar thermal behavior to n=7 were observed. For n=8, 9 and 10, only the enantiotropic SmC and SmA phases were observed in DSC measurements and polarizing microscope observations.

As shown in Fig. 2, in the first cooling process of n=11, three large exothermic peaks at 503, 431 and 361 K and two'small exothermic peaks at 489 and 435 K are seen in the DSC thermograms. On the polarizing microscope observations, upon cooling from the isotropic liquid, at 503 K, a smectic A fan texture and at 489 K, SmC with shlieren and broken-fan textures are observed and then at 435 K, it changed to fan and shlieren(Sm2) and finally at 431 K it changed to a cystalline phase. The Sm2 phase was optically biaxial and seems to be a higher order smectic phase. It appears to us that the phase is possibly the smectic F and G ones. To determine the mesomorphic phase, a more precise experiment of structure in the liquid crystalline phase will be needed. In the second heating process, three large and two small peaks were observed at 373, 438 and 503 K, and at 445 and 489 K, respectively. From the polarizing microscope observations, the peaks at 438 and 503 K are the melting point and the clearing point and the small peaks at 445 and 489 K are the Sm2-SmC and SmC-SmA phase transition temperatures, respectively. The themal behavior of n=12 is close to that of n=11 and the presence of a higher order smectic Sm2 phase was also observed. The phase treansition entropy of the Sm2-SmC phase transition is 2-3 times that of tthe transition entropy of the SmC-SmA phase transition.

In Figure 3, the phase transition temperatures of HAICP(n=3-12) are shown versus the carbon number of the alkoxy group, n. The melting point, T_m, suddenly decreases with an increase in the carbon number, n, having a slight odd-even effect. The clearing point, T_c, shows slight decrease with an increase in the carbon number, n. As a result the mesomorphic range expands with an increase in n in a series of HAICP. The Sm1 phase is monotropic at n=3, changes to enantiotropic at n=4 and then the appearance temperature of Sm1 slightly decreases by maintaining a similar mesomorphic range between n=5-7. The Sm1 phase disappeares at n=8 when increasing carbon number, n. The SmC phase appeares at n=6 as n increases, and the mesomorphic temperature range of SmC phase rapidly increases with an increase in the number n till n reaches 10, but rapidly decreases at n =11 where the Sm2

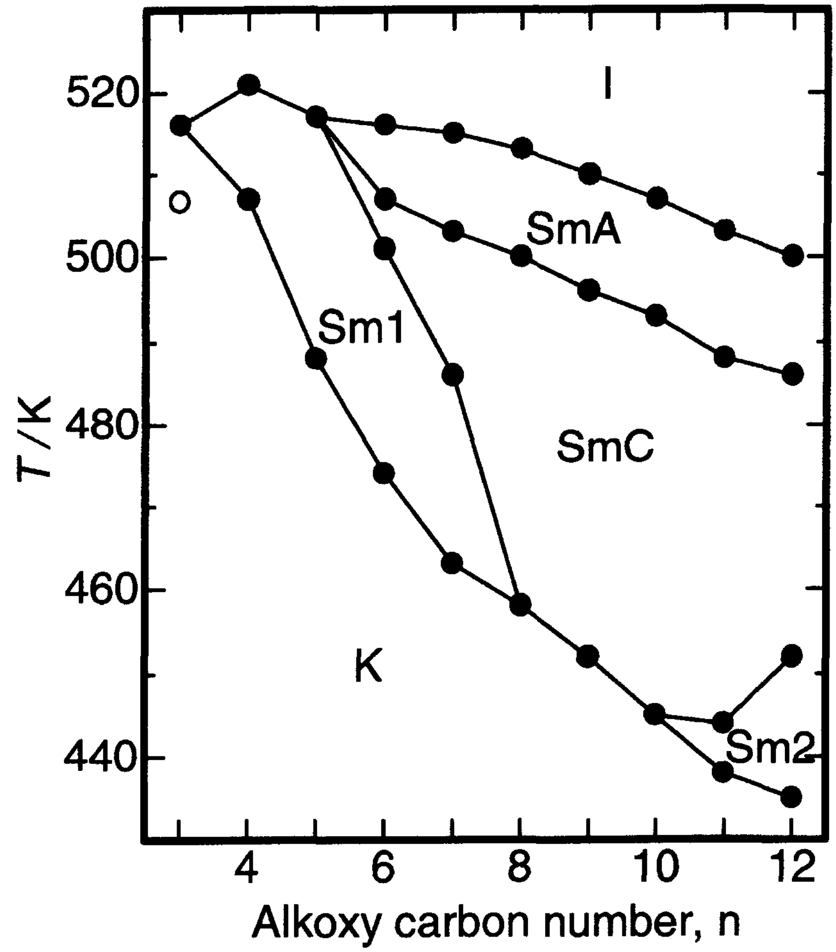


FIGURE 3 Phase transition temperature of hexakis(4-(N-(4'-alkoxyphenyl)iminomethyl)phenoxy)cyclotriphosphazene(HAICP, n=3-12); the closed circles show enantiotropic phase transitions and an open circle shows a monotopic one.

phase appeared. The SmA phase also appeared at n=6, and the mesomorphic range of SmC is almost 14 K between n=8 and 12, and then the mesomorphic temperature decreases with an increase in n. In the HAICP series, alkoxy carbon numbers n=4, 6, 8, 11 are the turning points of the mesomorphic transition.

Especially the occurrence of the higher-order smectic Sm1 has a good advantage in the short alkoxy end groups of the cyclotriphosphazenes. Usually in the low-molecular weight calamitic liquid crystals which consist of hard central groups and long soft end groups, an occurrence of lower-order liquid crystalline phase(for example, nematic) has a good advantage in the compounds with a short carbon number because the dipolar energy along the molecular long axis becomes larger rather than that of the lateral. The Sm1 phase is a higher-order liquid crystalline phase than the SmC phase because the Sm1 phase appeared at a temperature lower than the SmC phase. The occurrence of the higher-order smectic phase seems to be an artifact of the molecular packing of the cyclotriphosphazene derivatives. The entropy of melting increased with an increase in the carbon number, n, till n = 11 and almost constant at n=11.

The odd-even effect to the carbon number of the end alkoxy groups is not clear in the HAICP series. Usually, the odd-even effect is prominent in a series of calamitic liquid crystals having hard central groups and soft end alkyl or alkoxy groups corresponding to the end groups positioned at a straight line or deviated from that position. The vagueness of the odd-even effect in the cyclotriphosphazenes caused by the three mesogenic side chains of cyclotriphosphazenes which are not able to be exactly regularly aligned.

Acknowledgement

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