Chem. Mater. **1997,** *9,* 255−263

Thermal and Structural Study on Liquid-Crystalline Phase Transition in Hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazene

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Received June 11, 1996. Revised Manuscript Received October 2, 1996⊗

A series of hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazene $[PN(OC_6H_4C_6H_4OC)_nH_{2n+1})_2]_3$ (HACP, $n = 6-12$) compounds was synthesized from sodium salts of 4-alkyloxy-4′-hydroxybiphenyl and hexachlorocyclotriphosphazene. The phase transition and mesogenicity of these substances were studied by FT-IR, X-ray diffraction, and DSC measurements and polarizing microscope observations. In the crystalline-to-smectic C phase transition of HACP with $n = 8$, the infrared bands of P═N and P−O−(C) stretching vibrations were found to shift to the lower frequency, indicating the weakening of the cyclotriphosphazene ring in the liquid-crystalline phase. The X-ray analyzed interlayer spacing 36 Å is smaller than the value expected for the fully extended molecular model, indicating that the tilt angle of the molecules is about 35° from the normal to the layer plane. For HACP with $n = 6$, monotropic nematic and smectic C phases were found to appear only in the cooling process. Enantiotropic N and Sc phases were found for the $n = 7$ member. For the HACP with the $n = 8-12$, only an enantiotropic Sc phase was detected. In the series of HACP, the temperature range of the mesomorphic phase increased with an increase in n. The odd−even effect was not clear, originating from the peculiar shape of the hexakis(4-(4′-alkyloxy)-biphenoxy)cyclotriphosphazene with three side chains pointing three upward and three downward in both sides of the cyclotriphosphazene ring.

Introduction

Cyclotriphosphazenes are composed of cyclotriphosphazene rings and side chains connected to phosphorus atom. The ring is built of alternating nitrogen and phosphorus atoms. These molecules are of interest because the rings are inorganic whereas the side chains are pure organic. From this point of view the phosphazene chemistry combines both organic and inorganic concepts.

Many functional cyclotriphosphazenes have been synthesized, and their physical properties were thoroughly studied.[1−6] In relation to the functionality, the liquid-crystalline phase is very important because it is the intermediate state having orientational disorder remained and positional disorder between the liquid and solid. This phase provides new information on physical properties different from those of the crystal and liquid.

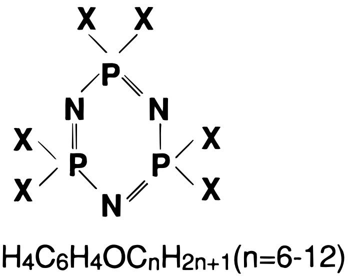

Figure 1. Chemical structure of hexakis(4-(4′-alkyloxy)-biphenoxy)cyclotriphosphazene $[(C_nH_{2n+1}OC_6H_4C_6H_4O)_2PN]_3$ (HACP, $n = 6-12$).

As shown in Figure 1, aryloxycyclotriphosphazenes have a peculiar shape with two aryloxy groups linked to each phosphorus atom of the six-membered cyclotriphosphazene rings, which seems to make them different from the usual liquid crystals. The problem to be solved is to clarify how such cyclotriphosphazene molecules form a liquid-crystalline phase.

Another point to mention here is the chemical structure of side chains. A few works have been published on the mesomorphic state of alkyloxycyclotriphosphazenes as the precursors of polymers.[9−12] However,

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[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

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S0897-4756(96)00333-X CCC: $14.00

they may show in general the "normal" liquid-crystalline behavior because the mesogen is able to move relatively easily due to the presence of long alkyl ether chains between the O and P atoms in the phosphoether linkage and can be rearranged to form the liquid-crystalline structure. On the contrary, the cyclotriphosphazenes without any alkyl ether chain between the O and P atoms have the possibility to form a new group of liquid crystals, because the motion of the mesogen is limited by its linking directly to the cyclotriphosphazene ring via the P–O bond combined and the packing of the side chains. The mesomorphic state of such a cyclotriphosphazene was observed first for hexakis(4-(4′-cyano)-biphenoxy)cyclotriphosphazene (HCCP) where a monotropic nematic phase was found in the cooling process from melting between 484 and 470 K.[13–15] Recently, we found the enantiotropic Sc and N phases in hexakis-(4-(4′-heptyloxy)biphenoxy)cyclotriphosphazene which was designed so as to increase the liquid crystallinity over the HCCP.[16]

In this paper we report on investigation of the liquid-crystalline phase transition of cyclotriphosphazene derivatives on the basis of X-ray diffraction and vibrational spectral data. The effect of the chain length of alkyloxy end groups on the liquid-crystalline phase transitional behavior in a series of aryloxycyclotriphosphazenes has also been studied. To check the thus-obtained empirical rules, we synthesized a series of hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazenes $[PN(OC_6H_4C_6H_4OC_nH_{2n+1})_2]_3$ (HACP, $n = 6–12$) compounds and studied their phase transition and liquid crystallinity using polarizing microscope observations and DSC measurements. We paid particular attention to the mesomorphism of the $n = 8$ member by using the X-ray diffraction and FT-IR techniques.

Results and Discussion

General Considerations. In this section, the liquid-crystalline phase transitions of the series of HACP are described from calorimetric, spectroscopic, and structural standpoints. The relation between the molecular shape and the liquid-crystalline phase transitions and effects of the length of end alkyloxy groups on the phase transition in the HACP series are discussed.

Liquid-Crystalline Phase Transition of HOCP (*n* = 8). 4-Hydroxy-4′-octyloxybiphenyl (HOB) shows two endothermic peaks in the DSC thermograms at 384 and 427 K in the first heating process. No mesomorphic phase was found for HOB by the polarizing microscope observation: the field in the eyepiece turned black above 427 K, suggesting a direct transition from the crystalline to the isotropic liquid phase at this temperature. The thermal anomaly at 384 K is considered to be a crystalline–crystalline phase transition. The corresponding two exothermic peaks were observed at 422 and 380 K in the cooling process, which are due to freezing and a crystalline–crystalline phase transition, respectively.

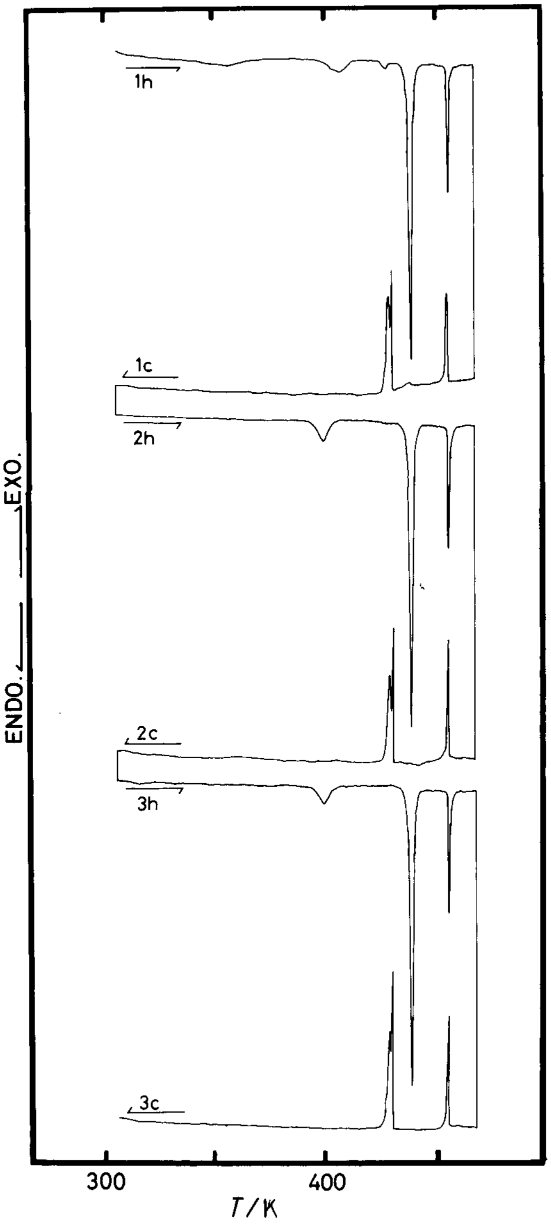

Figure 2. DSC thermograms of hexakis(4-(4′-octyloxy)biphenoxy)cyclotriphosphazene (HOCP, $n = 8$).

DSC thermograms of the hexakis(4-(4′-octyloxy)-biphenoxy)cyclotriphosphazene (HOCP, $n = 8$) are shown in Figure 2. In the first heating process, four endothermic peaks were observed at 409, 430, 440, and 457 K. In the first cooling process, three exothermic peaks are observed at 456, 432, and 429 K. In the polarizing microscope observation, the crystals melted at 440 K. Between 440 and 457 K, a texture pattern of the smectic C which exhibits a schlieren of disclination lines with $s = \pm 1$ and a broken fan was observed.[17] The smectic C phase changed to an isotropic liquid at 457 K. In the first cooling process, a similar Sc phase was observed between 456 and 432 K. The polarizing microscope photograph of the HOCP in the first cooling process at 454 K is shown in Figure 3. The thermal behavior of the second heating process is different from

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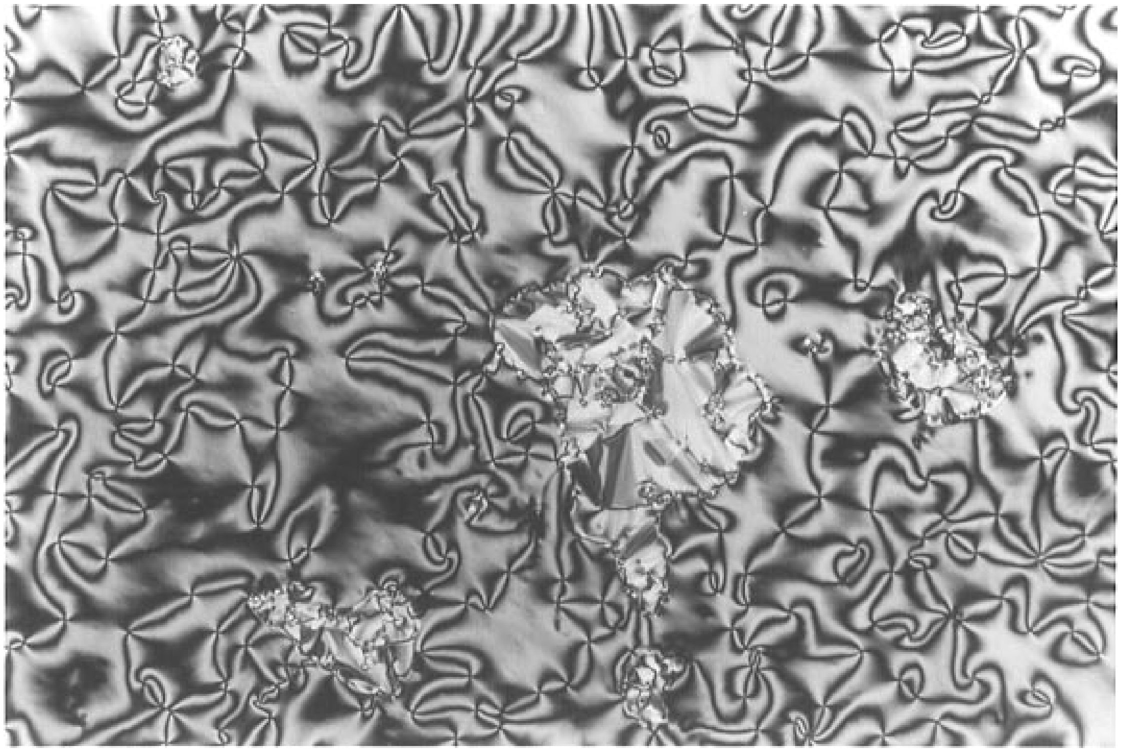

Figure 3. Polarizing microscope photograph of hexakis(4-(4′-octyloxy)biphenoxy)cyclotriphosphazene (HOCP, $n = 8$) at 453 K in the first cooling process.

that of the first heating process below the melting point but is similar to it about the melting point. Further repetition of the heating/cooling processes reproduces the second process.

The temperature dependence of the X-ray powder diffraction patterns of the HOCP between $2\theta = 2$ and 10° is shown in Figure 4. This scattering angle region correlates with an interlayer spacing. From the peaks at $2\theta = 4.1$ and 6.3°, the interlayer spacing is evaluated to be 41.6 Å (Figure 4a). These peaks shift to a lower 2θ direction above 323 K, reflecting a crystalline−crystalline phase transition deduced from the DSC curves. The diffraction intensity increased drastically above 380 K, and the peak position shifted to $2\theta = 2.4°$ as shown in Figure 4b. The lattice spacing is calculated to be 36.2 Å, an interlayer spacing of the Sc phase. The temperature dependence of the lattice spacing obtained from the X-ray diffraction data is shown in Figure 5. As stated above, the interlayer spacing decreases at the crystalline−smectic C phase transition temperature, $T_{\mathrm{K-Sc}}$ from 42 to 36 Å. The X-ray diffraction profile in the higher 2θ region between 10 and 30°, which corresponds to lattice spacings in the lateral direction of the liquid-crystalline molecules, is shown in Figure 6. In the two temperature regions the peaks shift to the low 2θ side due to the thermal expansion of the crystalline lattice. The diffraction pattern changes drastically at the crystalline−crystalline phase transition point. Above the transition temperature between the crystal and liquid crystal, the peaks become broad, reflecting a loss of packing regularity in the crystalline lattice.[18]

Liquid-Crystalline Phase Transition and Vibrational Spectra of HOCP. Figure 7 shows the temperature dependence of the IR spectra of HOCP in the second heating process. The bands characteristic of aryloxycyclotriphosphazene are detected in the wavenumber region between 800 and 1400 cm^{-1}. The P═N,[19] (P)−O−C and P−O−(C) stretching vibrations are located near 1227, 1168, and 968 cm^{-1}, respectively.[19−21] The temperature dependence of the peak frequency of these bands is shown in Figure 8. The P═N stretching vibration shifts to the lower frequency on increasing temperature. When the temperature reaches the crystalline (K)−Sc phase transition point at 442 K, the frequency decreases dramatically by about 13 cm^{-1}. In the temperature region above this transition point, the vibrational frequency decreases slowly. The P═N stretching vibration shifts from 1210 to 1208 cm^{-1} at 456 K, which corresponds to the Sc−I phase transition temperature. The P−O−(C) stretching vibration shows a temperature dependence similar to that of the P═N stretching mode. When increasing temperature, the P−O−(C) stretching vibration changes the position from 968 to 958 cm^{-1} at 442 K ($T_{\mathrm{K-Sc}}$) and to 954 cm^{-1} at 456 K ($T_{\mathrm{Sc-I}}$). On the other hand, the (P)−O−C stretching vibration shows only a slight change even at the crystal−Sc and Sc−I phase transition temperatures. There are two possible interpretations for the change of the P═N and P−O−(C) stretching vibrations at the K−Sc transition. It can be ascribed either to the change in the geometry of the cyclotriphosphazene ring and the P−O−(C) bond or to the decrease in the force constants of P═N and P−O bonds, in other words, to the softening of the rigidity of the cyclotriphosphazene ring. According to the ^{31}P NMR measurements, the local order parameter around the P atom is estimated ca. 0.44 in

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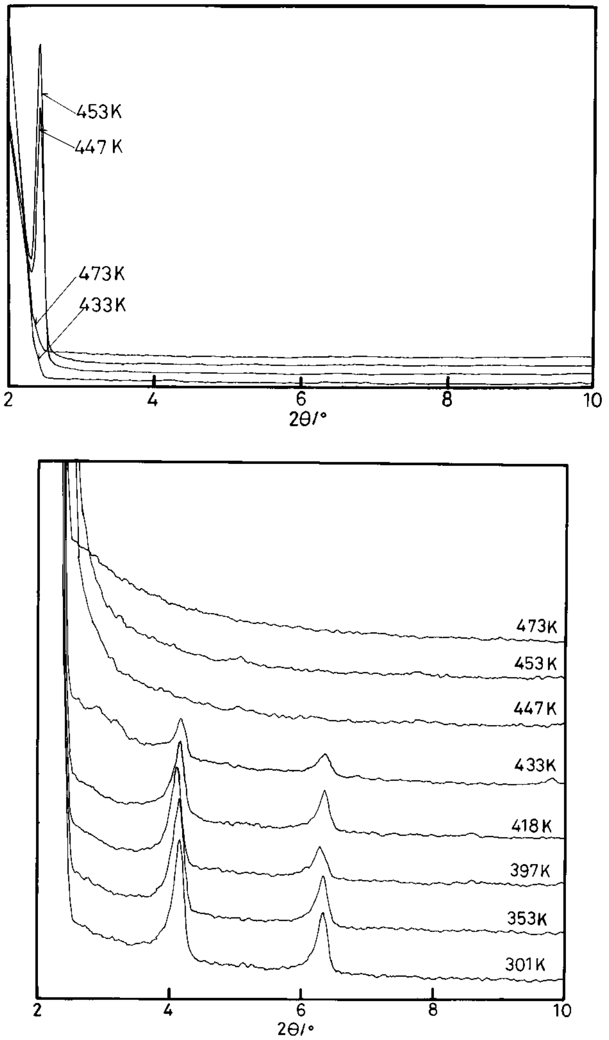

Figure 4. (a, top) Temperature dependence of X-ray diffraction patterns between 2θ is 2 and 20°. (b, bottom) X-ray diffraction patterns in the same region as (a) in an enlarged scale in HOCP.

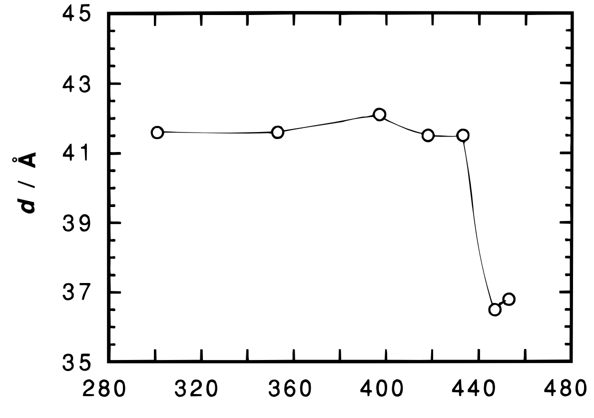

Figure 5. Temperature dependence of longest spacer length obtained from X-ray diffraction data in HOCP.

the smectic A phase of hexakis(4-(4′-dodecyl)biphenoxy)-cyclotriphosphazene.[22] This value is smaller than that found for the usual smectic A liquid crystals,[23,24] suggesting a relatively high disordering of the cyclotriphosphazene ring in the smectic A phase. The similar situation is considered to occur in the Sc phase of the HOCP. The disordering of the ring may relate to both the changes in the geometry and the force field of the cyclotriphosphazene ring. On the other hand, the band shifts in question could be interpreted as an effect of intermolecular interaction, which should change also in the phase transition region. But the 13 cm^{-1} shift of the P=N stretching mode seems to be too large in terms of this band to be correlated with the intramolecular vibration. In any case, however, the detailed analysis of the spectra by, for example, carrying out the normal modes treatment with an introduction of anharmonicity of the vibrations, will be needed in the future.

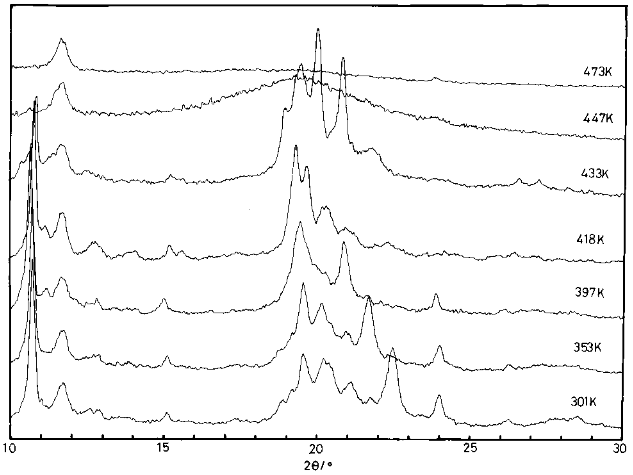

Figure 6. Temperature dependence of X-ray diffraction patterns between 2θ = 10 and 20° in HOCP.

Liquid Crystallinity and Molecular Shape of HOCP. An introduction of the 4-octyloxy-4′-hydroxybiphenyl group to the cyclotriphosphazene ring via a P−O linkage results in the formation of the enantiotropic mesomorphic smectic C phase. The free motion of the mesogen is restricted by the cyclotriphosphazene ring and the mesogenic side chains are closely packed one to each other. Furthermore, the aromatic ring of the mesogen and the phosphazene ring in the HOCP may not be coplanar as in the case of other organocyclophosphazenes.[25] Recently, the crystal structure of hexakis(4-biphenoxy)cyclotriphosphazene (HBCP) was determined by X-ray structural analysis of the single crystal.[26] In the molecular structure of the HBCP, the biphenoxy groups are linked almost perpendicularly to the phosphazene ring. As a result, three biphenoxy groups are almost perpendicular to the phosphazene ring upward and the other three biphenoxy groups slightly bend downward to the ring. By assuming that the structure of HOCP is similar to that of HBCP and assuming the octyloxy groups of the all-trans conformation along the molecular long axis, the molecular length perpendicular to the phosphazene ring is estimated to be about 44 Å and the length of the short axis about 13 Å. The thus-constructed molecular model of the HOCP is shown in Figure 9. The X-ray powder diffraction data

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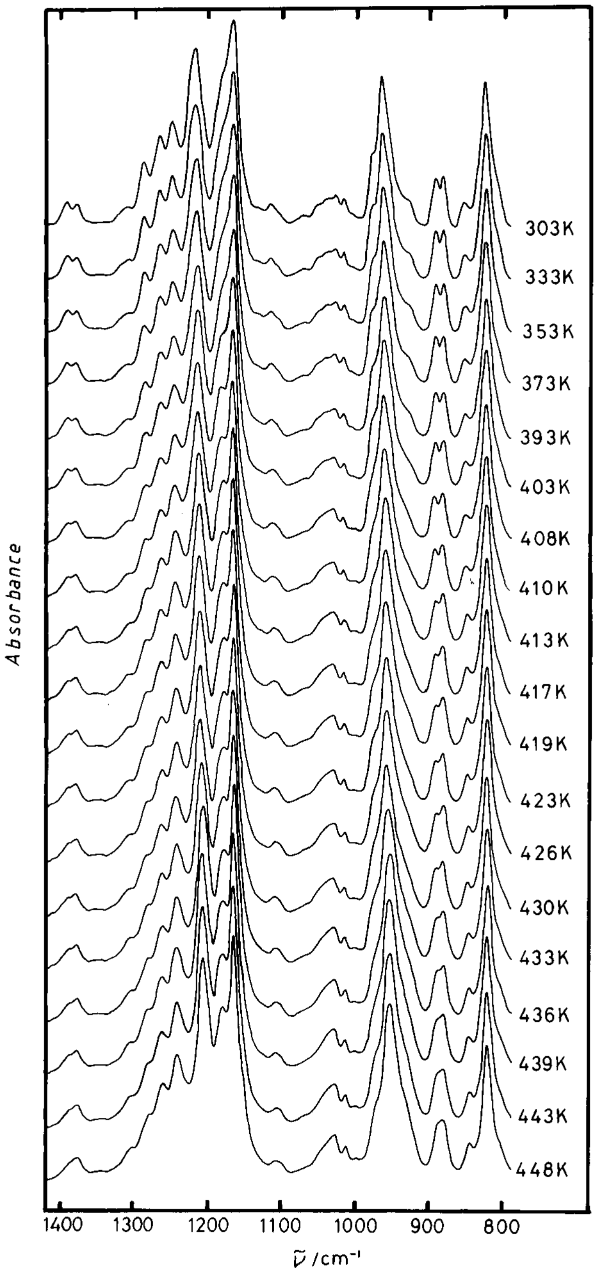

Figure 7. Temperature dependence of IR spectra between 800 and 1400 cm^{-1} of HOCP.

indicate a layer structure of 42 Å in the crystalline phase at 313 K and 36 Å for the smectic C phase at 432 K in the HOCP. These values are slightly shorter than 44 Å. The molecular long axes are tilted to the normal of the smectic layer at about 35°. This model might be applied to the structure of the smectic C phase.

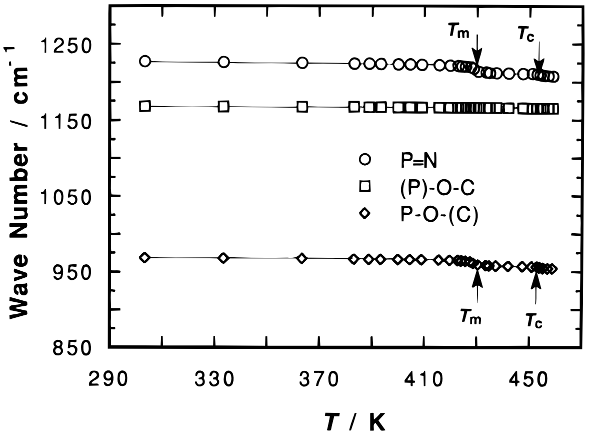

Figure 8. Temperature dependence of P=N:, P−O−(C):, and (P)−O−C: stretching vibrational frequencies in HOCP.

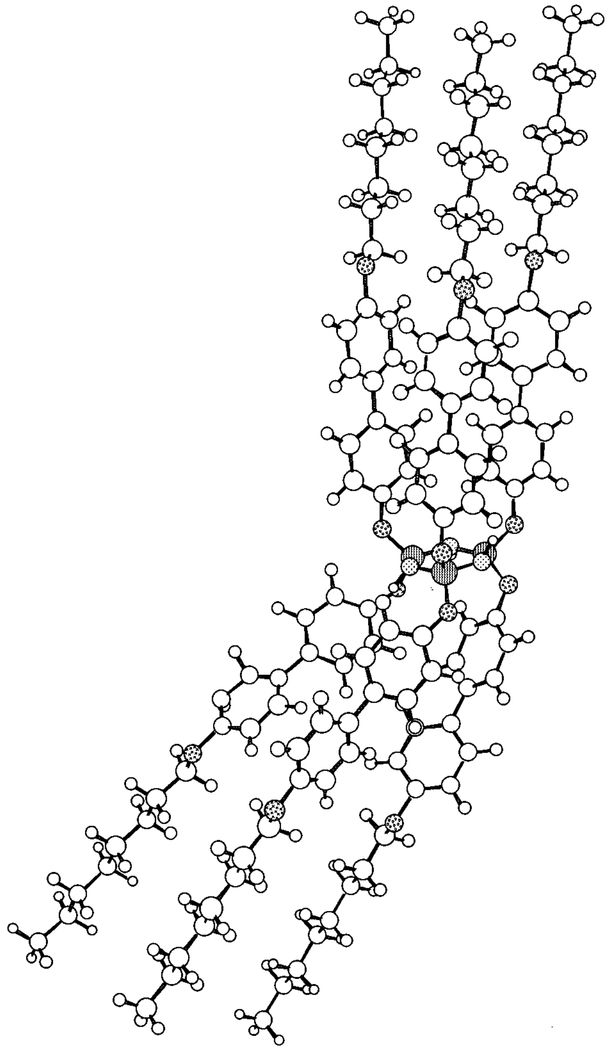

Figure 9. Assumed molecular structure of hexakis(4-(4′-octyloxy)biphenoxy)cyclotriphosphazene (HOCP).

In the benzene hexa-*n*-alkanoates, benzene rings, and side groups are coplanar, and this planarity reflects on the appearance of a columnar phase.[27] In the columnar phase, the optic axis is perpendicular to the director of the liquid-crystalline molecules. In the HOCP, on the other hand, the biphenyl ring is not parallel to the phosphazene ring; rather, it is perpendicular to the ring due to the bending of the (P)−O−C bond. As a result, the phosphazene ring in the mesomorphic state may be parallel to the normal of the Sc phase layer as mentioned above. As discussed here, in a liquid crystalline smectic C phase of this large molecules with a molecular weight of more than 2000 layer structure was formed, although the shape of the HOCP molecule differs greatly from that of the usual calamitic liquid crystals. The latter is composed of simple rodlike molecules having a rigid core of the mesogenic groups.[7,8] A conoscopic observation using a polarizing microscope for the nematic phase of hexakis(4-(4′-heptyloxy)biphenoxy)cyclo-

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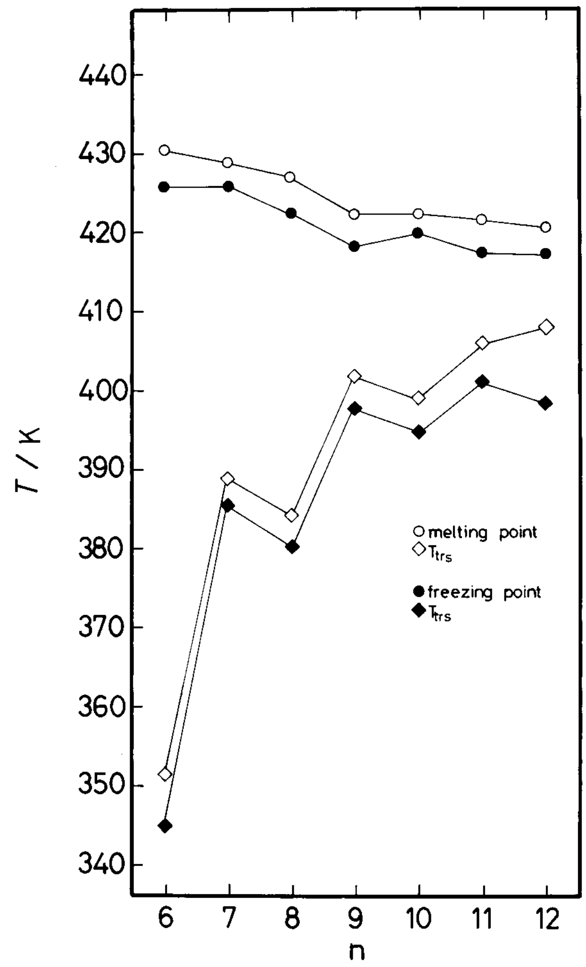

Figure 10. Phase transition temperature of 4-alkyloxy-4′-hydroxybiphenyl ($C_nH_{2n+1}OC_6H_4C_6H_4OH$, AB, $n = 6-12$).

triphosphazene ($n = 7$) indicates that the optic axis is parallel to the director of the liquid-crystalline molecules (optically positive uniaxial material) because the first and third quadrants are blue and the second and fourth quadrants are red in the eyepiece field when a gypsum first-order-red plate is inserted.[28] This result shows that the optical axis is parallel to the director of the cyclotriphosphazene molecule, and, as a result, the nematic phase is not a discotic liquid crystal but a normal one formed by rodlike molecules.

Effect of End Alkyloxy Groups on the Phase Transition and Mesomorphism of HACP. In the DSC thermograms measured for 4-alkyloxy-4′-hydroxybiphenyl ($C_nH_{2n+1}OC_6H_4C_6H_4OH$, AHB, $n = 6-12$), two endothermic peaks are observed between 350 and 430 K in the first heating process; the transition temperatures slightly differ for a different carbon number, n, of the end alkyloxy groups. No mesomorphic phase was found for the AHB in the polarizing microscope observation under crossed polarizers, but the crystal transformed directly to the isotropic liquid phase. The lower transition point corresponds to a crystalline–crystalline phase transition. In the cooling process, two exothermic peaks were detected between 345 and 426 K which correspond to the freezing and the crystalline–crystalline phase transition temperatures, respectively. The phase transition temperatures obtained from DSC measurements are plotted against the number of carbon in the alkyloxy groups in Figure 10, where a so-called odd–even effect can be clearly seen.

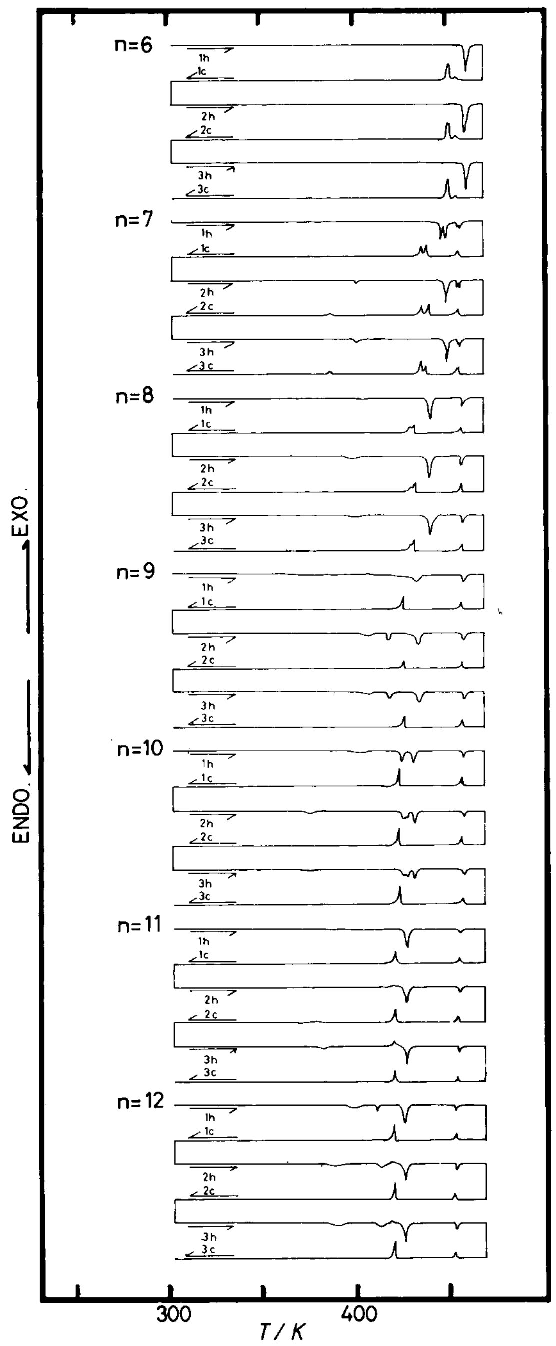

Figure 11. DSC thermograms of hexakis(4-(4′-alkyloxy)-biphenoxy)cyclotriphosphazene [$(C_nH_{2n+1}OC_6H_4C_6H_4O)_2PN]_3$ (HACP, $n = 6-12$).

The DSC thermograms measured for a series of HACP are shown in Figure 11 and obtained thermodynamic parameters in the second heating process are shown in Tables 1 and 2. For the number of $n = 6$, only one endothermic peak was observed at 460 K in the first heating process, corresponding to the melting to an isotropic liquid. In the cooling process, three exothermic peaks were detected 455, 452, and 451 K. Between 455 and 452 K, a schlieren texture having disclination lines with $s = \pm 1$ and $s = \pm 1/2$ was observed under the polarizing microscope, suggesting a typical nematic phase.[17] Between 452 and 451 K, a schlieren texture of disclination lines of $s = \pm 1$ and a broken fan was

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Table 1. Thermodynamic Parameters of HACP in the Liquid-Crystalline Phase Transition in the Heating Process[a]

n		T_m/ K	ΔH_m/ kJ mol^{-1}	ΔS_m/ J K^{-1} mol^{-1}	T_{Sc-N}/ K	ΔH_{Sc-N}/ kJ mol^{-1}	ΔS_{Sc-N}/ J K^{-1} mol^{-1}	T_{Sc-I}/ K	ΔH_{Sc-I}/ kJ mol^{-1}	ΔS_{Sc-I}/ kJ mol^{-1}	T_{N-I}/ K	ΔH_{N-I}/ kJ mol^{-1}	ΔS_{N-I}/ kJ mol^{-1}
6	1h	460	89.8	195									
	2h	460	90.4	196									
	3h	460	90.4	196									
7	1h	449	40.8	90.8	455.7	3.90	8.56				456.5	10.2	22.4
	2h	450	61.7	137	455.8	3.62	7.95				456.5	11.7	25.5
	3h	450	59.6	133	455.7	4.11	9.02				456.5	11.1	24.4
8	1h	440	80.8	184				457	15.2	33.2			
	2h	440	81.0	184				457	15.4	33.6			
	3h	440	81.2	185				457	15.0	32.8			
9	1h	434	50.4	110				457	16.0	35.0			
	2h	433	47.5	110				457	15.6	34.2			
	3h	433	47.8	110				457	15.6	34.2			
10	1h	431	47.4	110				457	16.7	36.6			
	2h	430	51.4	119				457	16.1	35.2			
	3h	430	50.3	117				457	16.1	35.2			
11	1h	427	67.8	159				455	16.3	35.8			
	2h	427	73.2	171				455	16.5	36.3			
	3h	427	70.6	165				455	15.9	34.8			
12	1h	425	64.8	152				453	16.7	40.4			
	2h	425	57.8	136				453	15.9	37.3			
	3h	425	57.8	136				453	17.1	37.8			

[a] T_m: melting temperature. ΔH_m: enthalpy of melting. ΔS_m: entropy of melting. T_{Sc-N}: transition temperature from Sc to N. ΔH_{Sc-N}: enthalpy of transition from Sc to N. ΔS_{Sc-N}: entropy from Sc to N. T_{Sc-I}: transition temperature from Sc to isotropic liquid. ΔH_{Sc-I}: enthalpy of transition from Sc to isotropic liquid. ΔS_{Sc-I}: entropy from Sc to isotropic liquid. T_{N-I}: transition temperature from N to isotropic liquid. ΔH_{N-I}: enthalpy of transition from N to isotropic liquid. ΔS_{N-I}: entropy from N to isotropic liquid.

Table 2. Thermodynamic Parameters of HACP in the Liquid-Crystalline Phase Transition in the Cooling Process[a]

n		T_{I-N}/ K	ΔH_{I-N}/ kJ mol^{-1}	ΔS_{I-N}/ J K^{-1} mol^{-1}	T_{I-Sc}/ K	ΔHI_{I-Sc}/ kJ mol^{-1}	ΔS_{I-Sc}/ J K^{-1} mol^{-1}	T_{N-Sc}/ K	ΔH_{N-Sc}/ kJ mol^{-1}	ΔS_{N-Sc}/ kJ mol^{-1}	T_f/ K	ΔH_f/ kJ mol^{-1}	ΔS_f/ kJ mol^{-1}
6	1c	455	7.00	15.4				452	7.58	16.9	451	32.4	71.9
	2c	454	7.05	15.5				452	7.53	16.8	451	28.1	62.4
	3c	455	7.13	15.7				452	7.62	17.0	451	25.9	57.6
7	1c	456	5.01	11.0				455	8.17	17.9	439	21.9	50.0
	2c	456	5.33	11.7				455	7.43	16.3	440	23.9	54.4
	3c	456	5.50	12.1				455	7.54	16.6	439	22.1	50.3
8	1c				456	14.2	31.1				432	23.1	53.5
	2c				456	14.6	32.0				432	22.2	51.3
	3c				456	15.4	33.6				432	21.2	49.1
9	1c				457	14.2	31.1				426	45.7	107
	2c				457	15.2	33.3				426	46.3	109
	3c				457	15.4	33.8				426	45.7	107
10	1c				456	15.9	34.8				423	50.7	120
	2c				456	15.9	34.8				423	50.9	121
	3c				456	16.1	35.3				423	50.9	121
11	1c				455	15.9	34.9				422	70.6	167
	2c				455	16.1	35.3				421	64.5	153
	3c				455	15.4	33.9				421	59.5	141
12	1c				453	15.6	34.4				418	51.7	124
	2c				453	15.8	34.9				418	52.6	126
	3c				453	15.3	33.9				418	52.3	125

[a] T_{I-N}: transition temperature from isotropic liquid to N. ΔH_{I-N}: enthalpy of transition from isotropic liquid to N. ΔS_{I-N}: entropy from isotropic liquid to N. T_{I-Sc}: transition temperature from isotropic liquid to Sc. ΔH_{I-Sc}: enthalpy of transition from isotropic liquid to Sc. ΔS_{I-Sc}: entropy from isotropic liquid to Sc. T_{N-Sc}: transition temperature from N to Sc. ΔH_{N-Sc}: enthalpy of transition from N to Sc. ΔS_{N-Sc}: entropy from N to Sc. T_f: freezing temperature. ΔH_f: enthalpy of freezing. ΔS_f: entropy of freezing.

observed, suggesting a smectic C phase. For $n = 7$,[16] five endothermic peaks were observed in the first heating process at 428, 446, 449, 455.3, and 456.1 K. In the first cooling process, six exothermic peaks were observed at 387, 436, 440, 442.4, 454.7, and 455.4 K. In the polarizing microscope observation under the crossed polarizers, between endothermic peaks at 449 and 455.3 K, a smectic C phase was observed with a schlieren texture of disclination lines of $s = \pm 1$ and a broken fan. Between endothermic peaks at 455.3 and 456.1 K, a nematic phase was observed with a schlieren texture of disclination lines of $s = \pm{}^{1}/_{2}$ and ± 1.[16,17] For $n = 8$, only one liquid-crystalline phase, the Sc phase, was detected by DSC and polarizing microscope observation as mentioned above. Similar enantiotropic Sc phases were found for $n = 8$ and 12 between two temperatures in the range 419−457 K, in which transition temperatures are slightly different depending on the carbon number n of the end alkyloxy groups. Between $n = 8$ and 12, no mesomorphic phase other than smectic phase was observed in the series of the HACP.

In the polarizing microscope examination of $n = 9$ and 11, a new schlieren texture with a disclination having $s = \pm 2$ and ± 3 was found in the Sc phase, and the disclination lines formed a characteristic pattern close to each other. Usually, in the smectic C phase, the textures observed in the polarizing microscope have disclination lines of $s = \pm 1$.[17] The disclination lines are relaxed by point disclinations for the stability of energies and are diversed without close contact with each other.[29,30] For the formation of higher-order disclination ($|s| \geq 2$), relatively large orientational strain energy is

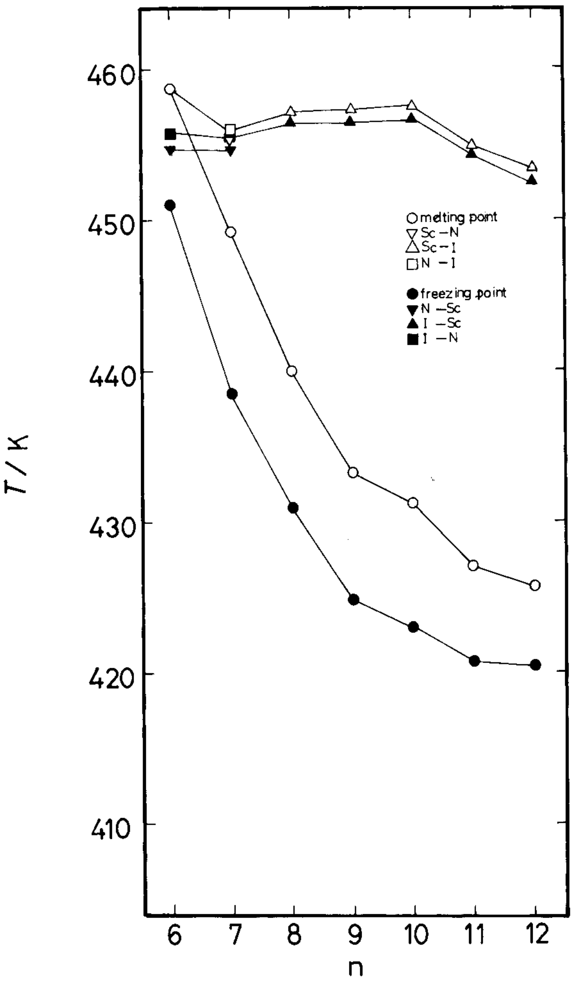

Figure 12. Dependence of phase transition temperatures on carbon number, *n*, in the end alkyloxy groups in the series of hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazene (HACP, *n* = 6–12).

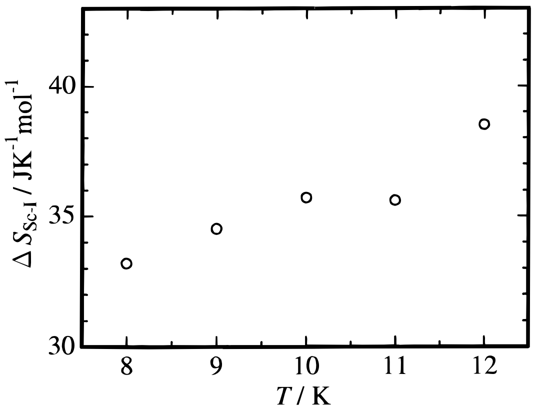

Figure 13. Sc–I phase transition entropies of hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazene (HACP, *n* = 6–12).

needed. These new disclinations ($s = \pm 2$, 3) may be generated from a large orientational strain energy in the liquid-crystalline phase because of the high viscosity of the hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazenes, but more detailed observation is needed for the interpretation of these defects.

In Figure 12, the phase transition temperatures were plotted against the number of end alkyloxy carbon atoms, *n*, of the side chains in the series of HACP (n = 6–12). As the *n* of alkyloxy groups is increased, the melting point, T_m, is lowered with a slight odd–even effect, but the clearing point, T_c, does not change. As a result, the temperature range of the mesomorphic phases becomes wider with an increase in *n* in the series of HACP. The odd–even effect of T_m and T_c is not clear in the series of HACP. The odd–even effect of the melting and clearing temperatures is prominent in a series of usual liquid crystals having monomesogenic unit because end alkyl or alkyloxy groups are positioned in a straight line or deviate from that corresponding to the odd or even carbon number of the end groups.[31–33] The vagueness of the odd–even effect in this cyclotriphosphazene series perhaps originates from the peculiar shape in which three mesogenic side groups point upward and downward from the cyclotriphosphazene ring. Therefore, the side chains of the cyclotriphosphazenes cannot be regularly aligned because of their packing and the hindrance of the bond between the side chain and the cyclotriphosphazene ring.

The dependence of Sc–I phase transition entropies on the end alkyloxy carbon number, *n*, in the HACP is shown in Figure 13. The values of the Sc–I phase transition entropies, ΔS_{Sc-I} are 33 J K^{-1} mol^{-1} at $n = 8$ and slightly increase with an increase in the carbon number of the terminal group in the series of the HACP. This result suggests that the disorder in the smectic C phase is not dependent on the carbon number and that the structure in the Sc phase is similar in the series of the HACP.

Conclusion

The HOCP has been found to exhibit an enantiotropic smectic C phase on the basis of the study with use of DSC and polarizing microscope analysis. In the smectic C phase of the HOCP, the 4-octyloxybiphenoxy groups and the mesomorphic side chains are regularly aligned with a molecular director almost perpendicular to the normal of the smectic C layer. As judged from the FT-IR and NMR data, the liquid-crystalline phase of the HOCP may be produced due to the softening of the cyclotriphosphazene ring and upward and downward arrangements of three separate side groups spreading out of the cyclotriphosphazene ring. In the series of HACP, mesomorphic temperature regions increased with an increase in the carbon number, *n*. Melting and clearing points of the HACP do not show a clear odd–even effect, reflecting a peculiar shape of the cyclotriphosphazenes.

Experimental Section

Preparation and Characterization of AHB (n = 6–12). The synthesis of 4-hydroxy-4′-octyloxybiphenyl (HOB), as a representative of a series of AHB, is presented below. HOB was prepared from octylbromide (55.2 g, 0.29 mol), 4,4′-dihydroxybiphenyl (80 g, 0.43 mol, Tokyo Kasei Co., Ltd.), and KOH (24.2 g, 0.43 mol) in ethanol (1200 mL) solution under

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Table 3. Elemental Analysis Results for Hexakis(4-(4′-alkyloxy)biphenoxy)cyclotriphosphazene (HACP, *n* = 6−12)

	n													
	6		7		8		9		10		11		12	
	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd	calcd	obsd
C	74.08	73.86	74.61	74.49	75.09	74.93	75.53	75.40	75.94	75.87	76.32	76.12	76.66	76.52
H	7.25	7.32	7.58	7.64	7.88	7.96	8.15	8.19	8.40	8.40	8.63	8.66	8.85	8.88
N	2.40	2.41	2.29	2.32	2.19	2.23	2.10	2.17	2.01	2.05	1.93	2.00	1.86	1.90

reflux (5 h). The crude products were recrystallized three times from ethanol and once each from toluene and chloroform. The obtained HOB were characterized by thin layer chromatography (TLC, developing solvent chloroform), IR, ^{1}H NMR, and elemental analyses. The IR spectrum of HOB shows the existence of ν(OH) (3300 cm^{-1}), $\nu_{as}(CH_2)$ (2958 cm^{-1}), $\nu_s(CH_2)$ (2857 cm^{-1}), $\delta_s(CH_3)$ (1349 cm^{-1}), the C−C ring stretching of the biphenyl ring (1609 and 1496 cm^{-1}) and the C−H out-of-plane deformation of the biphenyl ring (823 cm^{-1}). The ^{1}H NMR spectra of HOB measured for $CDCl_3$ show the existence of biphenyl (6.9−7.5 ppm, m-Ar 8H), a methylene adjacent to oxygen (4.0 ppm, t, 2H), other methylenes (2.0−1.5 ppm, m, 12H), OH (4.7 ppm, s, H), and methyl (0.9 ppm, t, 3H) protons. The series of AHB with other alkyloxy end spacers was synthesized and identified using the similar method.

Preparation and Characterization of HACP (*n* = 6−12). The exemplary synthesis of HOCP with *n* = 8 is shown below. HOCP was prepared by the reaction of hexachlorocyclotriphosphazene (HCCP, supplied by Nihon Seika Co., Ltd., 2.6 g, 7 mmol) and the sodium salt of HOB in dioxane solution (200 mL) in the presence of *n*-butylammonium bromide (1.3 g, 4 mmol).[16] The sodium salt of HOB was prepared from OHB (20 g, 67 mmol) and sodium hydride (1.6 g, 67 mmol, Tokyo Kasei Co., Ltd.). The solution was refluxed for 24 h. The crude products were purified using column chromatography (developing solvent chloroform, and substrate silica gel) and then recrystallized from THF−cyclohexane (1:1) mixed solution. The HOCP crystals purified were checked by TLC (chloroform: hexane 7:3), IR, ^{1}H and ^{31}P NMR, and elemental analyses. The IR spectrum of HOCP shows the existence of P═N (1227 cm^{-1}),[19] (P)−O−C (1168 cm^{-1})[20,21] and P−O−(C) (968 cm^{-1})[20,21] stretching vibration in addition to those of HOB. The ^{1}H NMR spectra of HOCP show the existence of biphenyl (6.8−7.3 ppm, *m*-Ar 8H), a methylene adjacent to oxygen (4.0 ppm, t, 2H), other methylenes (2.0−1.5 ppm, m, 12H), and methyl (0.9 ppm, t, Ar 8H) protons in $CDCl_3$. In the ^{31}P NMR spectra, only one singlet peak was found at 10.5 ppm,[17] indicating that the chlorine atoms of HClCP are completely substituted with HOB molecules. The series of the cyclophosphazenes having a different number of end alkyloxy groups were synthesized and then recognized as thoroughly purified by a similar method. The elemental analytical data for HHCP are also shown in Table 3, being in good agreement with the calculated values.

Analytical Techniques and Instruments. ^{1}H and ^{31}P NMR spectra were measured with a JEOL JNM-GX 270 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, respectively. The phase transitions and mesogenicity were studied by DSC measurements and polarizing microscope observations. DSC were measured using a Seiko Instruments DSC 210 at a heating/cooling rate of 5 K min^{-1} in a temperature range from 300 K to over the clearing point. The textures of the liquid-crystalline phase were observed with a polarizing microscope, Nikon Optiphoto-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 temperature dependence of the IR spectra was measured for KBr disks by a Perkin-Elmer FT-IR 1600 using a temperature-controlled optical cell (Omron E5T temperature controller and Omron HT-32 heater) in a temperature range from room temperature to over the clearing point in the heating process. The temperature of the sample in the FT-IR measurement was monitored by an iron−constantan thermocouple. Powder X-ray measurement was done with a Rigaku, Rinto 2000, and a homemade cell[34,35] using Cu Kα beams. The temperature of the sample was monitored by alumel−chromel thermocouple.

Acknowledgment. The present work was partly supported by a Grant-in-aid for Scientific Research (C03650650) from the Ministry of Education, Science, Culture and Sports, Japan, and partly by Iketani Science and Technology Foundation. The authors with to thank Professor Seiichi Miyajima of the Institute of Molecular Science for his fruitful discussion. The authors also with to thank Nihon Seika Co., Ltd. and Chisso Co., Ltd. for supplying us with hexachlorocyclotriphosphazene and for telling us how to synthesize 4-alkyloxy-4′-hydroxybiphenyl.

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