

This article was downloaded by:

On: 26 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Liquid crystalline phase transitions in hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene

K. Moriya^a; H. Mizusaki^a; M. Kato^a; S. Yano^a; M. Kajiwara^b

^a Department of Chemistry, Faculty of Engineering, Gifu University, Gifu, Japan ^b Department of Applied Chemistry, School of Engineering, Nagoya University, Nagoya, Japan

To cite this Article Moriya, K. , Mizusaki, H. , Kato, M. , Yano, S. and Kajiwara, M.(1995) 'Liquid crystalline phase transitions in hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene', *Liquid Crystals*, 18: 5, 795 – 800

To link to this Article: DOI: 10.1080/02678299508036692

URL: <http://dx.doi.org/10.1080/02678299508036692>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Liquid crystalline phase transitions in hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene

by K. MORIYA*, H. MIZUSAKI, M. KATO, S. YANO and M. KAJIWARA†

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

† Department of Applied Chemistry, School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan

(Received 12 August 1994; accepted 20 September 1994)

Hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene (HHCP) was synthesized from hexachlorocyclotriphosphazene and 4-heptyloxy-4'-hydroxybiphenyl. The mesogenicity of HHCP was studied by DSC, FTIR spectroscopy and polarizing microscopy. Enantiotropic smectic C and nematic phases were observed between 450 and 455 K and 455 and 456 K, respectively, on heating, and between 456 and 455 K (nematic) and 455 and 440 K (smectic C) on cooling from the isotropic liquid phase. The introduction of the heptyloxybiphenoxy groups as side chains into cyclotriphosphazene has generated the liquid crystalline phase. FTIR spectroscopy showed that the P=N and P-O-(C) stretching vibrations converted to lower frequencies from 1224 to 1210 cm^{-1} and from 920 to 910 cm^{-1} , respectively, at the crystalline (C)-S_C phase transition. This result suggests that the state of the cyclotriphosphazene ring dramatically changes near the C-S_C phase transition.

1. Introduction

Hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene [PN(OC₆H₄C₆H₄OC₇H₁₅)₂]₃ (HHCP) has a central six-membered cyclotriphosphazene ring and six 4-(4'-heptyloxy)biphenoxy side groups as shown in figure 1. The cyclotriphosphazene ring contains three -P=N= bonds, and each P atom is connected to two 4-(4'-heptyloxy)biphenoxy side chains via phosphoether linkage.

Much attention has been paid to the synthesis of cyclotriphosphazene derivatives in order to find functional properties [1-6]. The alkyloxycyclotriphosphazenes are mesomorphic and are important as precursors of poly-

meric liquid crystals, but only a few systems have been studied so far [7-10]. The existence of long ether linked alkyl chains as spacers between the phosphorus atoms and the mesogenic groups enhanced the mobility of the mesogenic groups, and this frequently produced liquid crystalline states. However, we and also Allcock *et al.*, recently found that a monotropic mesomorphic phase exists even for hexakis(4-(4'-cyano)biphenoxy)cyclotriphosphazene (HCCP), which has no spacer such as an alkyloxy chain [10-12]. The side group of HCCP is a part of a 4-alkyloxy-4'-cyanobiphenyl, a series of stable liquid crystalline forming materials [13, 14]. On the question of design of our mesomorphic liquid crystalline compounds, we decided to introduce the 4-(4'-heptyloxy)biphenoxy groups as side chains in cyclotriphosphazene so as to increase the liquid crystallinity by weakening the intermolecular interactions along the long axes of the side groups. This compound is much more complicated compared with the usual simple mesomorphic compounds consisting of only one linear, hard, central core and soft terminal groups. Another motivation for studying mesomorphic cyclotriphosphazenes was therefore to clarify how these phosphazene derivatives with such a peculiar molecular shape manage to form a liquid crystalline phase. We think that the cyclophosphazene ring plays an important role in the liquid crystalline phase transition, because the ring is located at the centre of six mesogenic side chains.

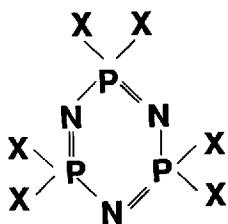


Figure 1. Structure of hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene (HHCP).

* Author for correspondence.

In the present paper we describe the synthesis of a new material, hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene (HHCP) and studies of its phase transitions and mesogenicity by polarizing microscopy, differential scanning calorimetry (DSC) and measurements of the temperature dependence of the infrared spectra.

2. Experimental

2.1. Preparation and characterization of hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene (HHCP)

4-Heptyloxy-4'-hydroxybiphenyl (HHB) was carefully prepared in order to obtain as pure HHCP as possible.

HHB was prepared from 1-bromoheptane (24.2 g, 0.43 mol), 4,4'-dihydroxybiphenyl (80 g, 0.43 mol) from the Tokyo Kasei Co., Ltd and KOH (51.2 g, 0.286 mol) in ethanol (1200 ml) solution, by heating under reflux for 5 h. The crude product was recrystallized twice from ethanol and once each from toluene and chloroform. The HHB crystals obtained were judged to be thoroughly purified by thin layer chromatography (TLC) (developing solvent: chloroform), IR, ^1H NMR and elemental analyses. The IR spectrum of HHB showed the presence of νOH (3300 cm^{-1}), $\nu_{\text{as}}\text{CH}_2$ (2929 cm^{-1}), $\nu_{\text{s}}\text{CH}_2$ (2857 cm^{-1}), δCH_3 (1348 cm^{-1}), C–C stretching of the biphenyl ring (1609 and 1496 cm^{-1}) and C–H out of plane deformation of the biphenyl ring (823 cm^{-1}). The ^1H NMR spectrum measured for a CDCl_3 solution showed the existence of the biphenyl ring system (7.15–7.80 ppm, m, Ar 8 H), methylene adjacent to oxygen (4.0 ppm, t, 2 H), other methylene groups (2.0–1.5 ppm, m, 10 H), the proton of OH (4.7 ppm, s, H) and the methyl (0.9 ppm, t, 3 H) protons. The results of elemental analysis of HHB are shown in table 1 and show good agreement with the calculated values within experimental error.

Hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene (HHCP) was synthesized from hexachlorocyclotriphosphazene (HCLCP) (2.7 g, 0.008 mol) from Nihon Seika Co., Ltd, and the sodium salt of HHB in THF (150 ml) solution in the presence of *n*-butylammonium bromide (1.4 g, 0.0043 mol). The sodium salt of HHB was prepared from HHB (20.0 g, 0.070 mol) and sodium

hydride (1.86 g, 0.077 mol). The crude product was purified by column chromatography (developing solvent: chloroform; substrate: silica gel) and then recrystallized from THF-cyclohexane (1:1). The HHCP crystals obtained were judged to be thoroughly purified by TLC (chloroform:hexane/7:3), IR, ^1H , ^{31}P NMR and elemental analysis. The IR spectrum of HHCP showed the presence of P=N (1225 cm^{-1}) [15], (P)–O–C (1170 cm^{-1}) [16] and P–O–C (970 cm^{-1}) [16] stretching vibrations in addition to those of HHB. The ^1H NMR spectrum (CDCl_3 solution) showed the existence of the biphenyl ring system (7.15–7.80 ppm, m, Ar 8 H), methylene adjacent to oxygen (4.0 ppm, t, 2 H), other methylene groups (2.0–1.5 ppm, m, 10 H) and the methyl (0.9 ppm, t, 3 H) protons in CDCl_3 . In the ^{31}P NMR spectrum only one singlet peak was found at 10.5 ppm, indicating that the chlorine atoms of HCLCP are completely substituted by HHB molecules. The elemental analytical data for HHCP are also shown in table 1, giving good agreement with the calculated values.

Table 1. Elemental analysis results for 4-heptyloxy-4'-hydroxybiphenyl (HHB) and hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene (HHCP).

	HHB		HHCP	
	Calculated (wt %)	Observed (wt %)	Calculated (wt %)	Observed (wt %)
C	80.25	80.15	74.61	74.62
H	8.51	8.61	7.58	7.54
N	—	—	2.29	2.28

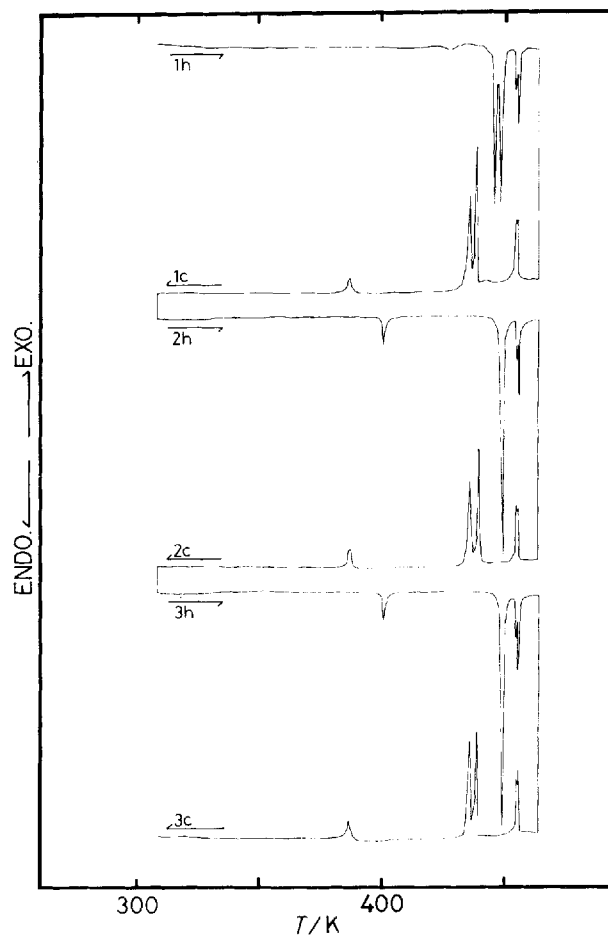


Figure 2. DSC thermograms of hexakis(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene (HHCP)—heating/cooling rates 5 K min^{-1} .

2.2. Analytical techniques and instruments

^1H and ^{31}P NMR spectra were measured by use of JEOL JNM-GX 270 spectrometer for CDCl_3 solutions with an internal standard of TMS, and for THF solutions locked by D_2O outside with an external standard of H_3PO_4 , respectively. The phase transitions and mesomorphism were investigated by DSC and polarizing microscopy. DSC scans were obtained using a Seiko Instruments DSC 210 at a heating/cooling rate of 5 K min^{-1} in a temperature range from 300 K to above the clearing point. The textures of the liquid crystalline phases were observed using a Nikon Optiphot-pol XTP-11 polarizing microscope, equipped with a Mettler hot stage FP82, at a heating/cooling rate of 5 K min^{-1} with 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 HT 32 heater with an Omron E5T temperature controller) in a temperature range from room temperature to above the clearing point in the heating process. The temperature of the sample was monitored by an iron-constantan thermocouple.

3. Results and discussion

3.1. Liquid crystalline phase transitions and optical textures of HHCP

In the DSC measurements for HHB, three endothermic peaks are observed at 368, 389 and 429 K in the first heating process. No mesomorphic state was found for HHB by polarizing microscopy. The peaks at 368 and 389 K may be attributed to phase transitions in the crystalline state, and the peak at 429 K corresponds to the melting point into the isotropic liquid. Three exothermic peaks are shown at 426, 385 and 320 K in

the first cooling process, and the peaks correspond to freezing and the crystalline-crystalline phase transitions, respectively.

The DSC curves of HHCP are shown in figure 2. The thermodynamic parameters of the heating and cooling processes are summarized in tables 2 and 3, respectively. In the first heating process, five endothermic peaks are observed at 428, 447, 449, 455.3 and 456.1 K. In the first cooling process, six exothermic peaks are observed at 387, 436, 440, 442.4, 454.7 and 455.4 K. In the second heating process, four endothermic peaks are observed at 401, 450, 455.3 and 456.1 K. In the second cooling process, five exothermic peaks are seen at 387, 436, 440, 454.9 and 455.7 K. The third heating/cooling processes are similar to the second heating/cooling processes.

It was found by polarizing microscopy that HHCP melted at 449 K in the heating process and froze at 439 K in the cooling process. The field became black above 456.1 K in the heating process, indicating formation of the isotropic liquid. A schlieren texture having disclinations with strengths $s = \pm 1/2$ and $s = \pm 1$ was observed between 449 and 455.3 K in the heating processes. This texture indicates that the mesophase is nematic [17]. A schlieren texture having disclinations with strength $s = \pm 1$ and a broken-fan texture were simultaneously found between 449 and 455.3 K in the heating processes. This result shows that the phase is smectic C [17]. Only in the first cooling process, was another metastable mesophase observed between 442.4 and 440 K. In this metastable state, the broken-fan texture observed in the smectic C phase was retained, but the schlieren areas became black. This result suggests that this texture is optically uniaxial and that this phase might be attributed to smectic B. The textures at 456 and 454 K are shown in

Table 2. Thermodynamic parameters for HHCP in the heating process. (T in K; ΔH in kJ mol^{-1} ; ΔS in J K mol^{-1}).

	T_{t1}	T_{t2}	T_{t3}	T_m	T_{S_C-N}	T_C^\dagger	ΔH_{t1}	ΔH_{t2}	ΔH_{t3}	ΔH_m	ΔH_{S_C-N}	ΔH_c	ΔS_{t1}	ΔS_{t2}	ΔS_{t3}	ΔS_m	ΔS_{S_C-N}	ΔS_c
1 h	428	447	—	449	455	456	2.4	37	—	41	3.9	10.2	5.6	82	—	91	8.6	22
2 h	—	—	401	450	455	456	—	—	6.6	62	3.6	11.7	—	—	16	137	8.0	26
3 h	—	—	401	450	455	456	—	—	6.5	60	4.1	11.1	—	—	16	133	9.0	24

Subscripts t_1 , t_2 and t_3 denote crystal-crystal transitions, m, the melting transition, S_C-N the smectic C to nematic transition, and c the clearing transition.

Table 3. Thermodynamic parameters of HHCP in the cooling process. (T in K; ΔH in kJ mol^{-1} ; ΔS in $\text{J K}^{-1} \text{mol}^{-1}$).

	T_{I-N}	T_{N-S_C}	T_f	T_{t4}	T_{t5}	ΔH_{I-N}	ΔH_{N-S_C}	ΔH_f	ΔH_{t4}	ΔH_{t5}	ΔS_{I-N}	ΔS_{N-S_C}	ΔS_f	ΔS_{t4}	ΔS_{t5}
1 c	456	455	439	436	387	5.0	8.2	22	33	6.5	11	18	50	76	17
2 c	456	455	440	436	387	5.3	7.4	24	32	6.9	12	16	54	73	18
3 c	456	455	439	436	387	5.5	7.5	22	34	6.0	12	17	50	79	16

Subscripts t_4 and t_5 denote crystal-crystal transitions, I-N the isotropic to nematic phase transition, N- S_C the smectic C to nematic phase transition and f the freezing transition.

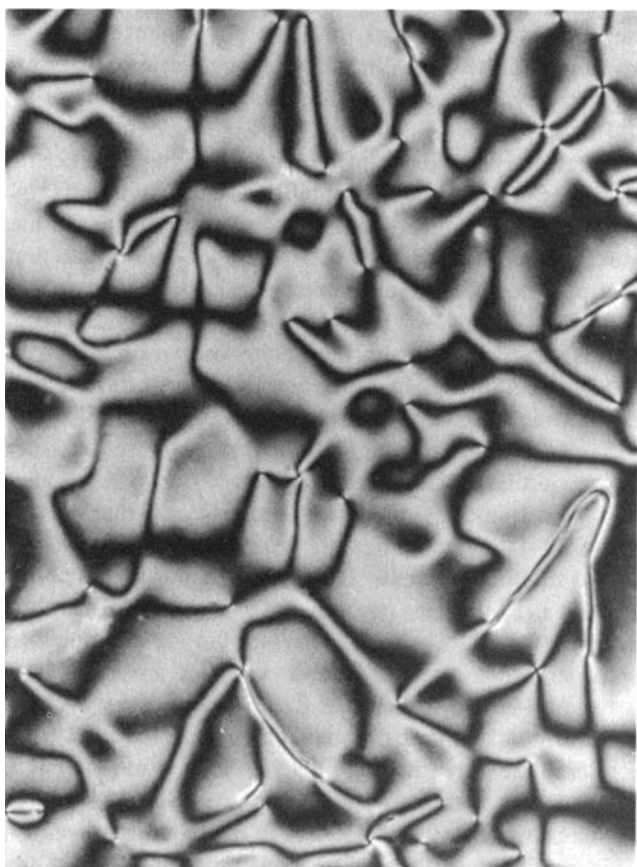


Figure 3. Polarizing microscope photograph of hexakis-(4-heptoxy(4'-biphenoxy))cyclotriphosphazene (HHCP) in the nematic phase at 456 K in the first cooling process.

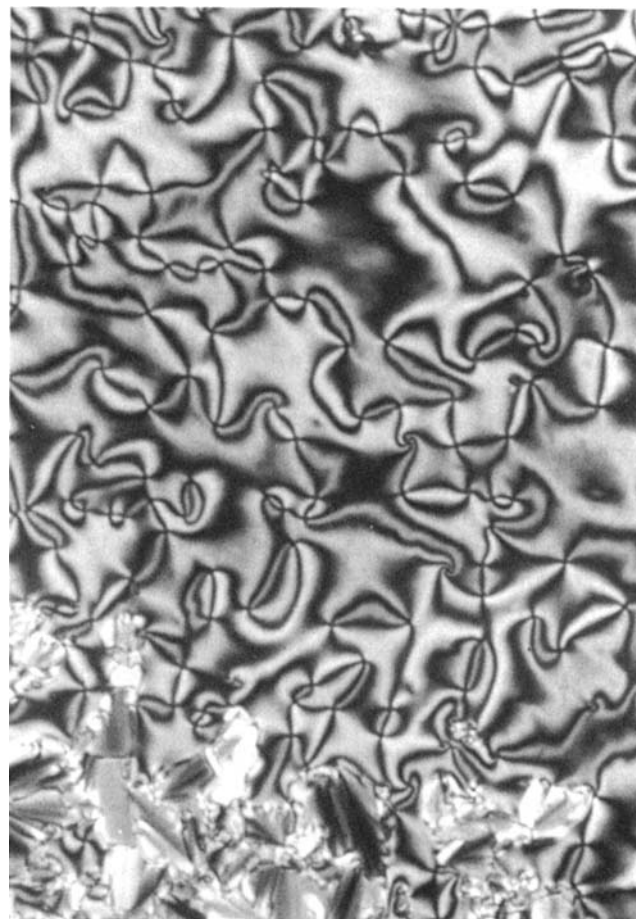


Figure 4. Polarizing microscope photograph of hexakis-(4-(4'-heptyloxy)biphenoxy)cyclotriphosphazene (HHCP) in the smectic C phase at 454 K in the first cooling process.

figures 3 and 4, respectively. In figure 3 the nematic texture is shown, and in figure 4 the schlieren and broken-fan textures of the smectic C phase can be seen.

The difference between the first and subsequent heating processes observed by DSC is considered to show that the as-grown crystal of HHCP is different from that grown from the melt. Tables 2 and 3 give the entropies of the S_C -N phase transition, ΔS_{S_C-N} , and the N-I phase transition, ΔS_{N-I} as $9 \text{ J K}^{-1} \text{ mol}^{-1}$ and 24 J K mol^{-1} , respectively. These values are smaller than the entropy of the C- S_C transition, ΔS_{C-S_C} , of $135 \text{ J K}^{-1} \text{ mol}^{-1}$. This shows that the intermediate mesophases are disordered, with a disorder close to that of the isotropic liquid. However, the values of ΔS_{S_C-N} and ΔS_{N-I} are much larger than those of more usual liquid crystal materials having single mesogenic molecules [18, 19], especially, the value of ΔS_{N-I} for HHCP is almost ten times larger than for more usual liquid crystals, suggesting that structural change of the complicated and large molecular shape affects the N-I phase transition of HHCP.

3.2. Liquid crystalline phase transitions and vibrational spectra of HHCP

Figure 5 shows the temperature dependence of the IR spectra of HHCP in the second heating process. The specific bands characteristic of an aryloxycyclotriphosphazene appear between 700 and 1400 cm^{-1} . The symmetric deformation mode of the methyl group is seen at about 1375 cm^{-1} at 313 K . This band broadens near C- S_C phase transition at 446 K , suggesting that the thermal motion of the methyl groups increases at this phase transition. This may correlate with the high fluidity of HHCP in the mesomorphic phase. The P=N, (P)-O-C and P-O-(C) stretching vibrations are seen near 1230 , 1170 and 970 cm^{-1} , at 313 K , respectively. The temperature dependences of peak-top frequencies of these bands are shown in figure 6. The P=N stretching vibration shifts to the lower frequency side with increasing temperature. At 400 K , the crystalline-crystalline phase transition temperature (T_i), the band shifts to lower frequency by 2 cm^{-1} . When the temperature reaches the crystal- S_C phase

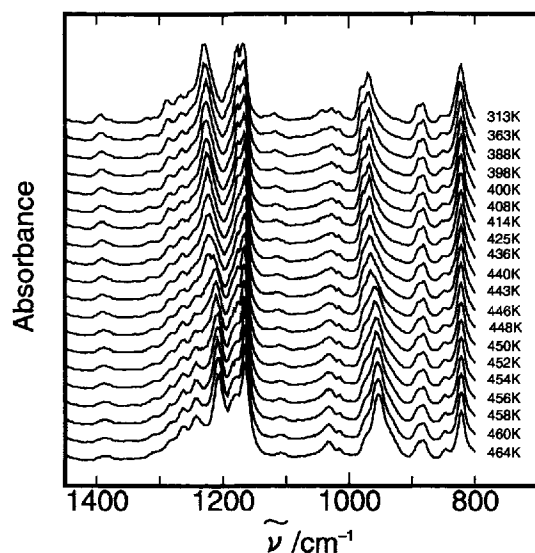


Figure 5. Temperature dependence of the IR spectra of HHCP between 700 and 1400 cm^{-1} .

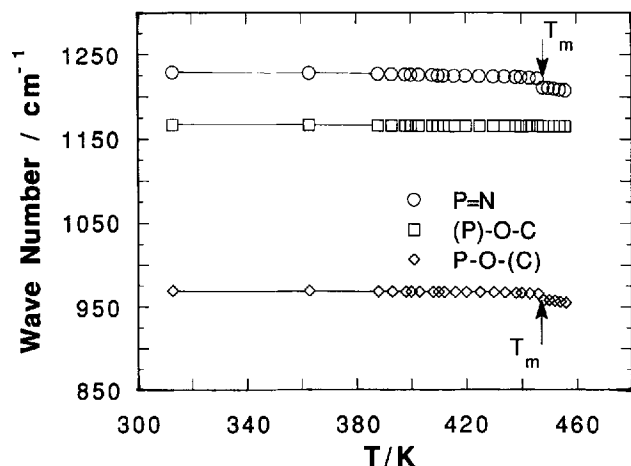


Figure 6. Temperature dependence of the P=N; \circ , P-O-(C); \diamond and (P)-O-C; \square stretching vibrational frequencies in HHCP.

transition point of 446 K, the frequency decreases dramatically by about 14 cm^{-1} from 1224 to 1210 cm^{-1} . In the temperature region higher than this transition, the vibrational frequency decreases with a steep slope. In the vicinity of the S_C -N phase transition temperature (T_{S_C-N}) at about 455 K, the shift is detected only slightly to about 1 cm^{-1} . Lastly, the P=N stretching vibration shifts from 1209 to 1206 cm^{-1} at 456 K, which corresponds to the N-I phase transition temperature (T_{N-I}). The P-O-(C) stretching vibration shows a temperature dependence similar to that of the P=N stretching mode. With increasing temperature, the P-O-(C) stretching vibration converts from 967 to 958 cm^{-1} at 446 K (T_{C-S_C}) and from 957 to 955 cm^{-1} at 456 K (T_{N-I}). However, the (P)-O-C

stretching vibration shows no prominent temperature dependence at T_I and T_{S_C-N} . There are two interpretations for the dramatic change of the P=P and P-O-(C) stretching vibrations at the C-S_C transition. One is due to a change in the geometry of the phosphazene ring and the P-O-(C) bond. The other is due to a decrease in the force constants of the P=N and P-O bonds. The latter correlates with a weakening of the bond of the cyclotriphosphazene ring in aryloxy cyclotriphosphazenes at the C-S_C transition. It is not clear which interpretation is more reasonable at present.

3.3. Liquid crystallinity and the molecular shape of HHCP

Hexa-acyloxybenzenes show a discotic mesophase because of their planarity [20]. However, from the X-ray structural analysis of Allcock *et al.*, the biphenyl rings are comparatively perpendicular to the phosphazene ring due to the bend of the (P)-O-C bonds in hexa(4-biphenoxy)cyclotriphosphazenes [21]. In HHCP, the biphenyl rings are also not coplanar with the phosphazene ring. As a result, the phosphazene ring may also be parallel to the line normal to the layer plane in the S_C phase. Also, conoscopic observation by polarizing microscopy shows that the nematic phase is not discotic and simply a common nematic.

Although 4-heptyloxy-4'-hydroxybiphenyl does not show any mesomorphic state, direct introduction of this group without an alkyl ether spacer into cyclotriphosphazene via the P-O linkage induces the formation of an enantiotropic mesomorphic phase in HHCP. Moreover, introduction of 4-heptyloxybiphenyl as side groups into cyclotriphosphazene enhances the liquid crystallinity of HHCP compared with that of HCCP, where only a monotropic nematic phase is observed. This may be due to the reduction in the dipole moment at the ends of the side groups of the cyclotriphosphazene ring, perpendicular to the plane of cyclotriphosphazene ring, an effect which may stabilize the liquid crystalline phase in HHCP because the neighbouring end groups along the side group long axes are heptyloxy for HHCP and cyano for HCCP. This interpretation also implies that the intermolecular interactions along these long axes decrease and that this decrease enhances the liquid crystallinity.

It may be concluded that the introduction of 4-heptyloxybiphenoxy groups as side groups in cyclotriphosphazenes produces enantiotropic liquid crystals by helping the alignment of the mesogenic side groups when the geometry or the bond strength of the cyclotriphosphazene ring in HHCP changes. Consequently the large molecules of HHCP, composed of six mesogenic groups and a cyclotriphosphazene ring and having a large molecular weight of more than 2000, form a liquid crystalline structure.

The present work was supported partly by a Grant-in-Aid for Scientific Research (C03650650) from the Ministry of Education, Science and Culture, Japan and partly by the Iketani Science and Technology Foundation. The authors wish to thank Nihon Seika Co., Ltd., for supplying the hexachlorocyclotriphosphazene. We are grateful to Dr Kohji Tashiro of the Faculty of Science, Osaka University for fruitful discussions.

References

- [1] HAIDUC, I., 1970, *Chemistry of Inorganic Ring Systems, Part 2* (Wiley-Interscience), p. 624.
- [2] ALLCOCK, H. R., 1972, *Chem. Rev.*, **72**, 319.
- [3] ALLCOCK, H. R., 1972, *Phosphorus-Nitrogen Compounds* (Academic Press).
- [4] HEAL, H. G., 1980, *The Inorganic Heterocyclic Chemistry of Sulphur, Nitrogen and Phosphorus* (Academic Press), p. 214.
- [5] ALLEN, C. W., 1987, *The Chemistry of Inorganic Homo- and Hetero-cycles*, edited by I. Haiduc and D. B. Sowerby (Academic Press), p. 501.
- [6] ALLEN, C. W., 1990, *Organophosphorus Chem.*, **21**, 368.
- [7] SINGLAR, R. E., WILLIAMS, R. A., LENZ, R. W., FURUKAWA, A., and FINKELMANN, H., 1987, *Macromolecules*, **20**, 1727.
- [8] KIM, C., and ALLCOCK, H. R., 1987, *Macromolecules*, **20**, 1726.
- [9] ALLCOCK, H. R., and KIM, C., 1989, *Macromolecules*, **22**, 2596.
- [10] MORIYA, K., YANO, S., and KAJIWARA, M., 1990, *Chemistry Lett.*, 1039.
- [11] ALLCOCK, H. R., and KIM, C., 1990, *Macromolecules*, **23**, 3881.
- [12] MORIYA, K., MIYATA, S., YANO, S., and KAJIWARA, M., 1992, *J. Inorg. Organomet. Polym.*, **2**, 443.
- [13] HULME, D. S., and RAYNES, E. P., 1974, *J. chem. Soc. chem. Commun.*, 98.
- [14] GRAY, G. W., and McDONNELL, D. G., 1976, *Molec. Crystals liq. Crystals*, **37**, 189.
- [15] FITZSIMMONS, B. W., and SHAW, R. A., 1964, *J. chem. Soc.*, 1735.
- [16] CORBRIDGE, D. E. C., 1969, *The Infrared Spectra of Phosphorus Compounds*. In *Topics in Phosphorus Chemistry*, Vol. 6, edited by M. Grayson and E. J. Griffith (Interscience), p. 235.
- [17] DEMUS, D., and RICHTER, D., 1978, *Textures of Liquid Crystals* (Verlag Chemie), p. 32.
- [18] BARRALL, II, E. M., and JOHNSON, J. F., 1974, *Liquid Crystals and Plastic Crystals*, Vol. 2, edited by G. W. Gray and P. A. Winsor (John Wiley), p. 259.
- [19] ARNOLD, H. Z., 1964, *Z. phys. Chem.*, **226**, 146.
- [20] CHANDRASEKHAR, S., 1982, *Advances in Liquid Crystals*, Vol. 5, edited by G. H. Brown (Academic Press), p. 47.
- [21] ALLCOCK, H. R., NGO, D. C., PARVEZ, M., WHITTLE, R. R., and BIRDSALL, W. J., 1991, *J. Am. chem. Soc.*, **113**, 2628.