Mesomorphic phase transition of a cyclotetraphosphazene containing Schiff base moieties: comparison with the corresponding cyclotriphosphazene

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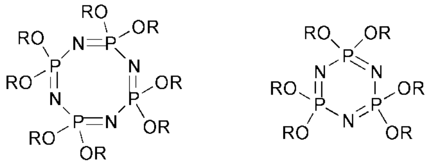
Newly prepared octakis{4-[*N*-(4′-heptyloxyphenyl)iminomethyl]phenoxy}cyclotetraphosphazene, consisting of a cyclotetraphosphazene ring backbone and Schiff base side-chain groups has been found to generate an enantiotropic smectic A phase; this is a first example of a mesomorphic cyclotetraphosphazene.

Cyclotetraphosphazenes are cyclic compounds of general formula $(PNX_2)_4$, in which tetracoordinated phosphorus atoms alternate regularly with the nitrogen atoms (Fig. 1). Several cyclotetraphosphazenes have been synthesized by introducing functional side chains into them.[1,2] Although some examples of mesomorphic transitions in cyclotriphosphazenes have been described[3–7] no liquid crystalline phases of cyclotetraphosphazenes have been observed.[5,7] In particular, in a previous paper, we reported our studies on phase transitions of cyclotetraphosphazenes and cyclotriphosphazenes with the same 4-octyloxybiphenyl mesogenic side groups.[5] We found no liquid crystalline phase for octakis[4-(4′-octyloxy)biphenoxy]cyclotetraphosphazene **1** but an enantiotropic smectic C phase was observed for hexakis[4-(4′-octyloxy)biphenoxy]cyclotriphosphazene **2**. These results were interpreted in terms of the X-ray single crystal structure analyses of octakis(4-biphenoxy)cyclotetraphosphazene (OBCP) and hexakis(4-biphenoxy)cyclotriphosphazene (HBCP), which have shown the side chains lining-up randomly in the former but in a relatively regular fashion for the latter.[8] A similar situation might be assumed for compounds **1** and **2**. In tetramer **1**, the eight side chains are directed essentially randomly so preventing the formation of a mesomorphic layer structure. However, in trimer **2**, each of the three side chains of the cyclotriphosphazene molecules point almost perpendicularly upwards and downwards from the cyclotriphosphazene ring plane, which aids in the formation of a mesomorphic layer structure. The molecular structure of compound **2** assuming an all *trans* conformation for the octyloxy side chains based on the crystal structure of HBOP.[4] The architecture of the mesomorphic phase is reminiscent of arrangements of the mesomorphic phase in a cyclotetrasiloxane,[9] a dendric octasilsesquioxane,[10] and a fullerene derivative.[11]



1, **3** **2**, **4**

1, **2** $R = C_6H_4C_6H_4OC_8H_{17}$

3, **4** $R = C_6H_4CH{=}NC_6H_4OC_7H_{15}$

Fig. 1 Chemical formulae of octakis{4-[*N*-(4′-heptyloxyphenyl)iminomethyl]phenoxy}cyclotetraphosphazene **3** and hexakis{4-[*N*-(4′-heptyloxyphenyl)iminomethyl]phenoxy}cyclotriposphazene **4**, octakis[4-(4′-octyloxy)biphenoxy]cyclotetraphosphazene **1** and hexakis[4-(4′-octyloxy)biphenoxy]cyclotriphosphazene **2**.

Schiff bases have a strong tendency to produce mesomophic phases.[6,12,13] Therefore, for attempted generation of liquid crystalline behavior, we synthesized octakis{4-[*N*-(4′-heptyloxyphenyl)iminomethyl]phenoxy}cyclotetraphosphazene **3** (Fig. 1), with side chains containing Schiff bases with long alkoxy tails, laterally linked to the cyclotetraphosphazene ring. We studied its phase transitions and mesogenicity using polarizing microscopy and DSC measurements, and the obtained results were compared with those for the cyclotriphosphazene, hexakis{4-[*N*-(4′-heptyloxyphenyl)iminomethyl]phenoxy}cyclotriphosphazene **4** with similar mesogenic side groups (Fig. 1). This paper presents the first evidence for the formation of a mesophase in cyclotetraphosphazenes.

Compound **1** was synthesized as follows. 4-Heptyloxyacetanilide **5** was prepared from 4-hydroxyacetanilide (25 g, 0.16 mol), bromoheptane (28.5 g, 0.16 mol) and KOH (11 g, 0.17 mol) in ethanol (200 ml) under reflux for 6 h. 4-Heptyloxyaniline **6** was synthesized from **5** (20 g, 83 mmol) and KOH (15 g, 0.23 mol) in ethanol (200 ml) under reflux for 24 h. Hexakis(4-formylphenoxy)cyclotetraphosphazene **7** was prepared from hexachlorocyclotetraphosphazene (5.0 g, 10.6 mmol) (Nihon Soda Co., Ltd.) and the sodium salt of 4-hydroxybenzaldehyde in THF (125 ml) under reflux for 3 h. The sodium salt was prepared from 4-hydroxybenzaldehyde (17.5 g, 0.143 mol) and NaH (5.73 g, 0.143 mol) in THF under reflux for 2 h. Finally, compound **3** was prepared by the reaction of **6** (2.7 g, 13 mmol) and **7** (1.0 g, 0.87 mmol) in benzene (50 ml) under reflux for 6 h. Water produced in the solution was removed by molecular sieves in a Dean–Stark tube. The obtained crude products were separated by filtration and recrystallized three times from benzene and once from THF–cyclohexane (1 : 1) after being separated by filtration. Compound **3** was characterized by ^1H and ^{31}P NMR, IR spectroscopy and elemental analysis.[14] Phase transitions were studied using Seiko DSC 210 and SSC 5500 systems from room temperature to above the melting point at heating/cooling rates of 5 K min^{-1}. The textures of the mesophase were observed using a polarizing microscope (Nikon, Optiphot-pol XTP-11) with a temperature controlled hot stage (Mettler, FP-80) at heating/cooling rates of 5 K min^{-1}.

The DSC thermograms of octakis{4-[*N*-(4′-heptyloxyphenyl)iminomethyl]phenoxy}cyclotetraphosphazene **3** for the first cooling (1c) and second heating (2h) processes are shown in Fig. 2. For the first cooling process, two exothermic peaks were observed at 429 and 422 K. According to polarizing microscopy, upon cooling from an isotropic liquid, batonnets were observed at 429 K which grew into a fan texture at *ca.* 428.8 K, suggesting the presence of a smectic A phase.[15] In the first heating process, two endothermic peaks were observed at 428 and 430 K. According to polarizing microscopy, melting of compound **3** was observed at 428 K and between 428 and 430 K a fan texture similar to that in the first cooling process was seen, which establishes the existence of the smectic A phase. The view become black at 430 K, which corresponds to the SmA–I phase transition. This is the first case of a mesomorphic phase in cyclotetraphosphazenes.

Table 1 Phase transition temperatures (*T*/K) and (in parentheses) phase transition enthalpies (ΔH/kJ mol^{-1}) and entropies (ΔS/J K^{-1} mol^{-1}) of compound **1**–**4**

Compound	Side chain	Backbone	Cr		Sm1		SmC		SmA		I
1	$C_8H_{17}OC_6H_4C_6H_4O$	P_4N_4	·	411(76,185)	—		—		—		·
2	$C_8H_{17}OC_6H_4C_6H_4O$	P_3N_3	·	440(79,180)	—		·	457(15,33)	—		·
3	$C_7H_{15}OC_6H_4N{=}CC_6H_4O$	P_4N_4	·	428(77,180)	—		—		·	430(28,66)	·
4	$C_7H_{15}OC_6H_4N{=}CC_6H_4O$	P_3N_3	·	460(74,161)	·	482(1,3)	·	499(0.5,1)	·	512(18,35)	·

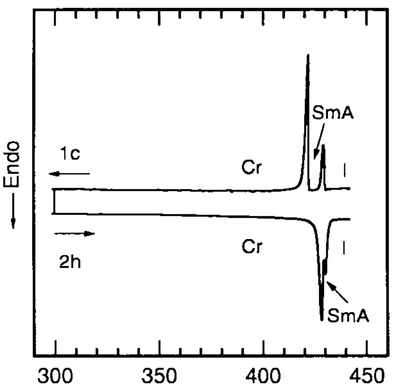


Fig. 2 DSC thermograms of octakis{4-[*N*-(4′-heptyloxyphenyl)iminomethyl]phenoxy}cyclotetraphosphazene **3** for the first cooling (1c) and second heating (2h) processes.

Table 1 shows a comparison of the phase transition temperatures, phase transition enthalpies and entropies for the pairs of tetramers (**1**, **3**) and trimers (**2**, **4**) bearing the same mesogenic substituents: octyloxybiphenoxy (**1**, **2**) and 4-{*N*-[4′-heptyloxyphenyl]iminomethyl}phenoxy groups (**3**, **4**). The thermodynamic values were obtained from the second heating process *via* DSC measurements. For the tetramers, the derivative **3** with substituents containing the Schiff base (compound **3**) has a narrow enantiotropic liquid crystalline phase with a temperature range of only 2 K, while no mesomorphic phase was observed for the derivative with octyloxybiphenoxy side chains (compound **1**).[5] The trimer with the Schiff base substituents (compound **4**) shows the enantiotropic mesomorphic phase transition sequence Cr–Sm1–SmC–SmA–I.[6] It displays a high SmA–I transition temperature (512 K) and wide mesomorphic phase transition region (ΔT = 52 K). By contrast, the trimer with octyloxybiphenoxy side chains (compound **2**) undergoes an enantiotropic mesomorphic phase transition, Cr–SmC–I.[3–5] The SmC phase was confirmed by X-ray photography under a magnetic field.[3] The SmC–I transition temperature (457 K) is lower, and the mesomorphic phase transition region (ΔT = 17 K) is narrower than those for the trimer with the Schiff base substituents (compound **4**). The compounds with the Schiff base side chains appear to have a higher thermal stability in the mesomorphic phase and higher mesomorphic phase generation ability than those with 4-octyloxybiphenoxy side chains. Two possible interpretations for the observed differences may be considered. In the first, the molecular structure of the tetramer with Schiff base side chains is assumed to differ significantly from that of the tetramer with octyloxybiphenoxy side chains. The other possible interpretation is that the intermolecular interactions might be much stronger for the Schiff base derivative **3** than for the octyloxybiphenoxy derivative **1** even if the molecular structures do not differ very much from each other. Based on this assumption, the mesomorphic ability of the compounds with Schiff base side chains would be high. Assuming this, and that compound **3** retains this molecular structure after melting, it would appear to be difficult to form a mesomorphic phase because of the random orientation of the side groups. Probably, the cyclotetraphosphazene rings would soften and the Schiff base side chains can form a smectic A layer structure. This behavior was observed in the SmA phase of the cyclotriphosphazene with dodecylbiphenoxy side groups, in which the local order parameter around the P atom obtained by ^{31}P NMR spectroscopy was *ca.* 0.44.[4] This value is lower than that in a typical sectic A phase and suggests the presence of disorder in the cyclotriphosphazene. The difference in the mesogenicity of tetramers and trimers is a result of their differing molecular structure.

In conclusion, we have introduced mesogenic side groups containing Schiff base functionalities onto the cyclotetraphosphazene ring and obtained the first N_4P_4 derivative capable of generating a mesomorphic smectic A phase. The liquid crystalline behavior results from assistance from the Schiff base to the formation of a layer structure due to the favorable intermolecular interactions of the laterally linked mesogenic units, which may override the formation of random orientations of the side chains typical in cyclotetraphosphazenes.

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14 *Characterization data* for compound **3**: mp 425 K; IR (KBr) 2932, 2856, 1625, 1604, 1578, 1251, 1220, 1174, 1161, 985, 846 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.9 (t, *J* 7.0 Hz, 3H), 1.3–1.8 (m, 10H), 3.9 (t, *J* 6.6 Hz, 2H), 6.8 (d, *J* 9.0 Hz, 2H), 7.0 (d, *J* 9.0 Hz, 2H), 7.1 (d, *J* 9.0 Hz, 2H), 7.7 (d, *J* 8.8 Hz, 2H), 8.4 (s, 1H); ^{31}P NMR δ −12.7 (s). Anal. Calc. for $C_{160}H_{192}O_{16}N_4P_4$: C, 72.16; H, 7.27; N, 6.31 Found: C, 71.94; H, 7.08; N, 6.25%. ^{1}H NMR (solvent CDCl$_3$) and ^{31}P NMR (solvent CDCl$_3$) spectra were recorded on a JEOL A-400 spectrometer using TMS as the internal standard for the former and 85% H_3PO_4 as the external standard for the latter.
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