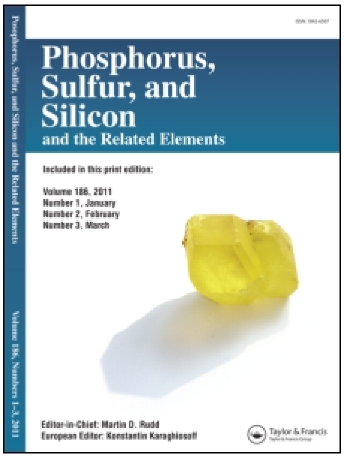

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MESOGENICITY OF ORGANOPHOSPHAZENES: THE EFFECT OF PHOSPHAZENE RINGS AND SIDE GROUPS ON THE PHASE TRANSITION

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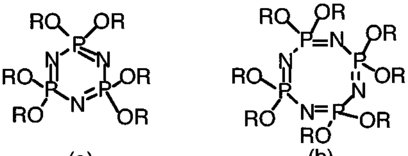
Cyclotriphosphazene and cyclotetraphosphazene derivatives with mesogenic 4-N-(4-alkoxyphenyl)iminomethyl)phenoxy and 4-(4′-alkoxy) biphenoxy moieties were synthesized. Schiff base moiety has higher mesomorphic stability than that in biphenyl moiety both in cyclotriphosphazene and cyclotetraphosphazene. Cyclotriphosphazenes possess higher thermal stability in the mesomorphic phase than the cyclotetraphosphazenes, suggesting the difference in the molecular structure.

Keywords: Cyclotetraphosphazene; cyclotriphosphazene; liquid crystals; organophosphazene; phase transition

INTRODUCTION

In the cyclotriphosphazene derivatives, several mesomorphic phases have been observed and discussed on the phase transition.[1–5]

In this study, the cyclotriphosphazenes and cyclotetraphosphazenes with mesomorphic 4-(N-(4-alkoxyphenyl)iminomethyl)phenoxy and 4-(4′-alkoxy)biphenoxy side groups (see Figure 1) were synthesized. The effect of the phosphazene nucleus and side groups on the mesomorphic phase transition in the organophosphazenes was studied based on the molecular shape and structure.


(a) (b)

$R = OC_6H_4C_6H_4OC_nH_{2n+1}$ (1)

$= OC_6H_4C{=}NC_6H_4OC_nH_{2n+1}$ (2)

FIGURE 1 Chemical formulas of hexakis(4-(4′-alkoxy)biphenoxy)cyclotriphosphazene (HBCTP-n)(a-1), hexakis(4-(N-(4-alkoxyphenyl)iminomethyl) phenoxy)cyclotriphosphazene (HSCTP-n)(a-2), octakis(4-(4′-alkoxy)biphenoxy) cyclotetraphosphazene (OBCTP-n)(b-1), and octakis(4-N-(4-alkoxyphenyl) iminomethyl)phenoxy)cyclotetraphosphazene(OSCTP-n)(b-2).

EXPERIMENTAL

Preparation of Cyclotriphosphazene and Cyclotetraphosphazene with 4-(4′-Alkoxy)biphenoxy Groups

4-Alkoxy-4′-biphenols were prepared from 4,4′-dihydroxybiphenyl, n-alkylbromide and KOH in ethanol under reflux for 8 h. The crude crystals were recrystallized from toluene once and chloroform twice. Cyclotriphosphazene and cyclotetraphosphazene were prepared from 4-alkoxy-4′-biphenols, sodium hydride and hexachlorocyclotriphosphazene or octachlorocyclotetraphosphazene in the presence of n-butylammonium bromide. The crude products were purified using column chromatography ($CHCl_3$, SiO_2) and recrystallized from THF-cyclohexane(1:1) mixed solution. The purified crystals were checked by TLC($CHCl_3$:hexane 7:3), IR, ^1H, and ^{31}P NMR and elemental analyses.

Preparation of Cyclotriphosphazene and Cyclotetraphosphazene with 4-(N-(4-alkoxyphenyl)iminomethyl)phenoxy Groups

4-Alkoxyacetanilide was prepared from n-alkylbromide and KOH in ethanol under reflux for 6 h. 4-alkoxyaniline was prepared from 4-alkoxyacetanilide and KOH in ethanol under reflux for 12 h. Hexakis-(4-formylphenoxy)cyclotriphosphazene or octakis(4-formylphenoxy)-cyclotetraphosphazene was prepared from 4-hydroxybenzaldehyde, sodium hydride and hexachlorocyclotriphosphazene or octachlorocyclotetraphosphazene in THF at ambient temperature for 6 h. Crude products were recrystallized from a hexane-THF(10:1) solution. Cyclotriphosphazene and cyclotetraphosphazene were prepared by the reaction of hexakis(4-formylphenoxy)cyclotriphosphazene or octakis(4-formylphenoxy)cyclotetraphosphazene and 4-alkoxyaniline in benzene under reflux for 6 h. The crystals purified were checked by IR, ^{1}H, and ^{31}P NMR and elemental analyses.

Analytical Techniques and Instruments

Phase transitions were studied using a differential scanning calorimeter (Seiko Instruments DSC 210) in the temperature range from room temperature to over the melting point at heating/cooling rates of 5 K min^{-1}. The apparatus was calibrated using the melting of indium (T_m; 429.6 K, ΔH; 28.5 Jg^{-1}) and tin (T_m; 505.1 K, ΔH; 59.5 Jg^{-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-82) at the heating/cooling rates of 5 K min^{-1} under crossed polarizers. Powder X-ray measurements were done with a Rigaku, Rint 2000, and a homemade cell using CuKα beams. ^{1}H NMR (solvent $CDCl_3$) and ^{31}P NMR (solvent $CDCl_3$) spectra were recorded on a JEOL JNM-A400 spectrometer using TMS as the internal standard for the former and 85% H_3PO_4 as the external standard for the latter. IR spectra were measured with KBr disks using a Perkin-Elmer FT-IR 1640.

RESULTS AND DISCUSSION

The phase transitions of cyclotriphosphazenes and cyclotetraphosphazenes with biphenyl and Schiff base moities with an end carbon number of 12 were compared.

In the first cooling process of HSCTP-12 DSC thermograms, 5 exopthermic peaks were observed at 499, 485, 446, 429, and 365 K, respectively. On the polarizing microscope observation, SmA fan and SmC schlieren textures were observed between 499 and 485 K and 485 and 446 K. A mosaic texture was observed between 446 and 426 K, suggesting the presence of a higher ordered smectic phase(Sm1), but this has not been identified at present. At 446 K, HSCTP-12 froze to a crystal(Cr), and the exothermic peak at 365 K corresponds to a crystal-crystal phase transition. In the second heating process, five endothermic peaks were observed at 378, 435, 453, 486, and 500 K, respectively. From the polarizing microscope observation these temperatures correspond to a Cr-Cr, Cr-Sm1, Sm1-SmC, SmC-SmA, and SmA-I phase transitions. Thus, an enantiotropic Cr-Sm1-SmC-SmA-I phase transition was observed in HSCTP-12.

In the first cooling process of OSCTP-12 DSC thermograms, four exothermic peaks were observed at 431, 403, 384, and 320 K. On the polarizing microscope observation, between 431 and 403 K, the SmA fan texture was observed. OSCTP froze to a crystal at 403 K and the exothermic peaks at 431 and 403 K correspond to crystal-crystal phase transitions. In the second heating process, four endothermic peaks were observed at 320, 384, 403, and 431 K. The crystal melted at 403 K and a similar SmA fan texture was observed between 403 and 431 K. Therefore an enantiotropic Cr-SmA-I phase transition was observed in OSCTP-12.

In the first cooling process of HBCTP-12, three exothermic peaks were observed at 425, 418, and 378 K. Between 425 and 418 K, a SmC schlieren texture was observed. At 418 K, HBCTP-12 froze and the peak at 378 K corresponds to a Cr-Cr phase transition. In the second heating process, three endothermic peaks corresponding to Cr-Cr, Cr-SmC, and SmC-I phase transitions were observed at 392, 425, and 453 K. Thus an enantiotropic Cr-SmC-I phase transition was observed in HBCTP-12.

In the cooling process of OBCTP-12, exothermic peaks were observed at 394 and 387 K. Between these temperatures, a SmA fan texture was observed. In the second heating process, only one endothermic peak, which corresponds to melting, was observed at 398 K. Only a monotropic SmA phase was observed at OBCTP-12.

Comparing these results, the biphenyl circumstances are very low mesogenicity compared to that in Schiff base moiety. In these compounds, the tetrameric nucleus is much less mesomorphic stability than that in trimeric nucleus. These results suggest that the molecular structure in cyclotriphosphazene stabilizes the mesomorphic structure compared to that in cyclotetraphosphazene.

In Figure 2, the alkyl spacer dependence of the phase transition in the series of HSCTP-n(closed circles) and OSCTP-n(open circles) was shown. In the series of the tetramer with an increase in the end alkoxy carbon number, the clearing points increased and the melting points decrease with an increase in the carbon number. As a result, the mesomorphic temperature region in OSCTP-n increased with the increasing carbon number. In the cyclotriphosphazenes with similar mesomorphic side chains, this tendency in which the mesomorphic temperature region increased with the increasing carbon number was also shown. However, the difference between cyclotriphosphazene and cyclotetraphosphazene is that the mesomorphic phase in cyclotetraphosphazene is much less thermally stable than those of the cyclobreak triphosphazenes because both the melting and clearing points in the cyclotetraphosphazenes are lower than those in the cyclotriphosphazenes.

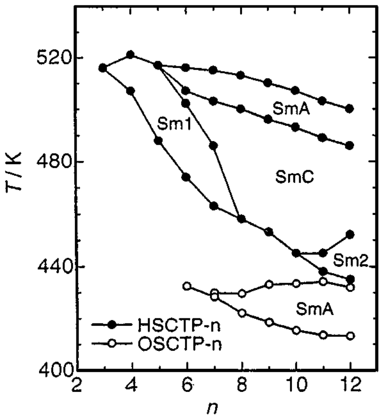


FIGURE 2 Alkoxy carbon number dependence of phase transition temperature in the series of HSCTP-n and OSCTP-n.

In Figure 3, the alkyl spacer dependence of the phase transition in the series of HBCTP-n(closed circles) and OBCTP-n(open circles) was shown. In the series of the trimer with an increase in the end alkoxy carbon number, the clearing points increased and the melting points decrease with an increase in the carbon number. As a result, the mesomorphic temperature region in HBCTP-n increased with the increasing carbon number. In the OBCTP-n series, only monotropic SmA phase was observed at $n=11$ and $n=12$ in the cooling process. Therefore for biphenoxy moieties cyclotriphosphazene has higher mesomorphic

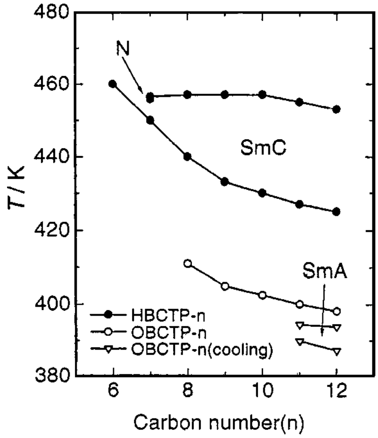


FIGURE 3 Alkoxy carbon number dependence of phase transition temperature in the series of HBCTP-n and OBCTP-n.

stability than that in cyclotetraphosphazene. This is probably caused by the difference in the molecular structure of the cyclotriphosphazenes and cyclotetraphosphazenes.

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