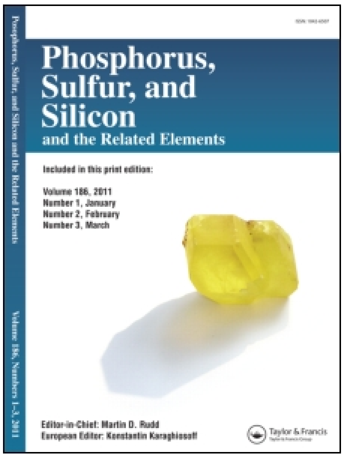

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Spectroscopic and Thermal Characterization of Trimeric to Octameric Phenoxycyclophosphazenes

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SPECTROSCOPIC AND THERMAL CHARACTERIZATION OF TRIMERIC TO OCTAMERIC PHENOXYCYCLOPHOSPHAZENES

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Trimeric to octameric phenoxycyclophosphazenes, $[NP(OPh)_2]_n$ (n = 3 to 8), were isolated and characterized for the compilation of the spectroscopic and thermal analytical data. The NMR and absorption spectra showed similar behavior, except for ^{31}P NMR of the trimer. In thermal analysis, the hexamer has the lowest melting point among these phosphazenes, and nonvolatile residues were observed in the hexamers, heptamers, and octamers. The melting points of oligomers were re-evaluated and compared with the values in the literature.

Keywords Cyclophosphazene oligomer; flame retardant; phenoxycyclophosphazenes; spectroscopy; thermal analysis

INTRODUCTION

Cyclophosphazenes have been investigated and proposed as non-halogenated alternatives to halogenated flame retardants due to the high phosphorous content and the ease of the synthesis of various derivatives.[1] In particular, phenoxycyclophosphazenes $[NP(OPh)_2]_n$ (Figure 1), which can be easily synthesized by the nucleophilic substitution of the Cl atoms in chlorocyclophosphazenes, $(NPCl_2)_n$, with phenoxy groups,[2] have excellent hydrolysis resistance and proper thermal stability.[1,3] In recent decades, phenoxycyclophosphazenes have attracted much attention because of the launch of their commercial production.[4,5] Industrially, phenoxyphosphazenes have been produced as an oligomeric mixture,[4–6] because the starting material, chlorophosphazene, is obtained as an oligomeric mixture from phosphorus pentachloride and ammonium chloride. Among them, cyclic trimer (n = 3) and tetramer (n = 4) have been synthesized in pure form and characterized.[2] On the other hand, the pentamer and higher oligomers are rarely mentioned in the literature.[7] To our knowledge, no literature that compiles data on this series of oligomers has been published. In this article, we report comprehensive data on the thermal and spectroscopic properties of phenoxyphosphazene oligomers up to the octamer.

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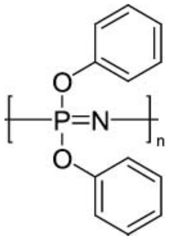

Figure 1 Chemical structures of the oligophenoxycyclophosphazenes.

RESULTS AND DISCUSSION

In the ^{1}H, ^{13}C, and ^{31}P NMR spectra (Table I), the most significant difference appeared between ^{31}P NMR spectra of the trimer and the other oligomers. It is known that the chemical shift of the trimer[8] is higher than that of the tetramer.[9] The signals of the pentamer and the higher oligomers appeared near the signal of the tetramer. A similar tendency was seen in the case of chlorocyclophosphazenes.[10] On the other hand, ^{1}H and ^{13}C NMR spectra did not show any significant variation, because the signals are derived from the phenyl groups, whose chemical structures are not affected by the size of the phosphazene ring. In the ^{1}H NMR spectra, the signals of the phenoxy groups shifted slightly toward the higher field as the ring size increased from the trimer to the octamer. This phenomenon suggests conformational flexibility in the higher oligomers, which allows spreading of the distance between two phenyl groups attached to the adjacent phosphorus atoms. The deshielding of a proton in a phenoxy group by the other phenoxy group becomes weaker as the distance increases. This is supported by the fact that this tendency is not observed in alkoxy-substituted phosphazenes.[7]

The absorption spectra of the oligomers were also similar to each other. The absorption maxima of the trimer[11] and the tetramer were slightly blue-shifted compared to those of

Table I Summary of spectroscopic and thermal properties of $[NP(OPh)_2]_n$

	Trimer	Tetramer	Pentamer	Hexamer	Heptamer	Octamer
^{1}H NMR/δ^a	6.89–6.95	6.90–6.96	6.87–6.94	6.85–6.91	6.83–6.87	6.80–6.85
	7.06–7.20	7.03–7.17	6.98–7.11	6.97–7.05	6.92–7.01	6.89–6.98
^{13}C NMR/δ^a	150.7	151.4	151.6	151.8	151.8	151.8
	121.1	121.1	121.1	121.2	121.3	121.3
	129.5	129.2	129.1	130.0	128.9	128.8
	124.9	124.4	124.1	123.9	123.7	125.4
^{31}P NMR/δ^a	9.8	−11.4	−16.9	−17.0	−18.3	−19.3
λ_{max}/nm^b	261	262	263	263	263	263
mp (DSC)/°C^c	113.4	86.3	72.7	50.8	69.3	111.8
mp (lit.)	110–111^d	85–86^d	129–130^e	320–324^e	340–344^e	338–342^e
$T_{10\%}{}^c$	346	390	399	435	438	445
residue (600°C)/%^{c}	0	0	0	8	11	16

[a] In $CDCl_3$ at 300 MHz.

[b] In $CHCl_3$.

[c] Heating rate: 10 °C/min in N_2.

[d] Reported values in ref. [2].

[e] Reported values in ref. [7].

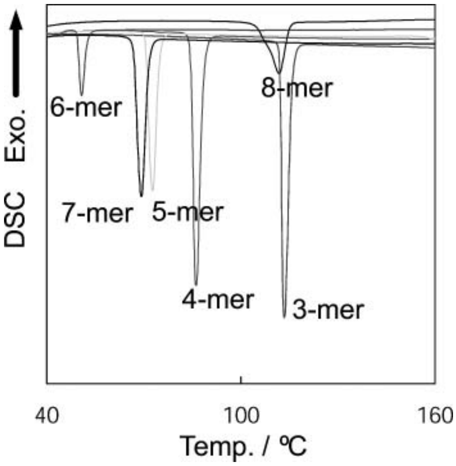

Figure 2 DSC thermograms of $[NP(OPh)_2]_n$.

the other oligomers. This shift is explained by the flexibility of the molecule. The rigidity of the trimer and the tetramer prevents the phenyl ring and the adjacent oxygen atom from being in a mutual configuration suitable for the conjugation. The weak electron-donating effects of the oxygen atoms in the trimer are supported by the DFT calculations.[12]

The melting points were determined by DSC analysis (Figure 2, Table I). The melting points of the trimer and the tetramer were in agreement with the values in the literature,[2] although the values of the pentamer to octamer were different from those values in the literature.[7] The melting point descended as the size of the ring increased, showing a minimum at the hexamer, and then ascended. This tendency is probably due to two opposing factors: flexibility and molecular weight. The loss in conformational entropy upon crystallization is larger for flexible molecules, and causes a drop in their melting points. As seen in the ^1H NMR spectra, the change in flexibility as the ring size increases seems larger for the lower oligomers such as the trimer. The contribution from the change in flexibility overcomes

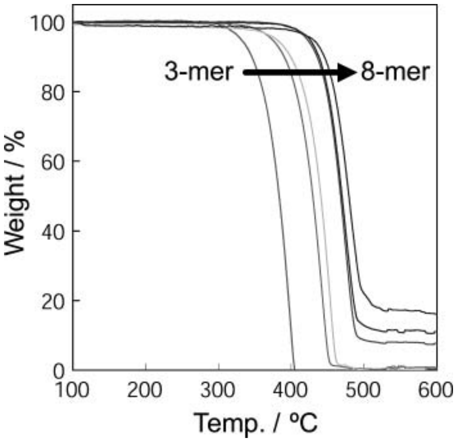

Figure 3 TGA profiles of $[NP(OPh)_2]_n$.

the opposing contribution from the change in molecular weight when the size of the ring is small, causing a drop in the melting point as the size of the ring increases. On the other hand, the contribution from the molecular weight becomes dominant when the size of the ring is large enough not to influence the flexibility, causing rise in the melting point. A similar tendency is seen in cyclic siloxanes.[13,14]

Figure 3 shows the thermogravimetric analysis (TGA) in N_2 for the oligomers. Oligomers lower than the hexamer showed one-step drop in weight to zero. This behavior indicates complete evaporation before the formation of char. The larger oligomers also showed one-step drop in weight, but left 8–15% of its original weight as nonvolatile residue. This difference probably originates from the larger molecular weight. The higher oligomers remain in the condensed phase at a temperature high enough for the formation of char to compete with the evaporation. The formation of char, consisting of the nonvolatile residue, is a major factor in flame retardancy attributed to phosphorus atoms,[15–17] therefore, the contents of the hexamer and higher oligomers in the phenoxyphosphazene mixture would affect its flame retardant properties.

CONCLUSION

Trimers to octamers of phenoxycyclophosphazenes have been isolated from the mixture of the oligomers. These absorption and NMR spectra have a similar shape. The thermal analysis showed that the hexamer has the lowest melting point among these oligomers, and char formation was found for hexamer and higher oligomers.

EXPERIMENTAL

The phenoxyphosphazene mixture was prepared by the method reported in the literature.[2] Each oligomer from the tetramer to the octamer was isolated by reverse-phase HPLC equipped with an ODS column and using acetonitrile as the eluent, followed by recrystallization from methanol.

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