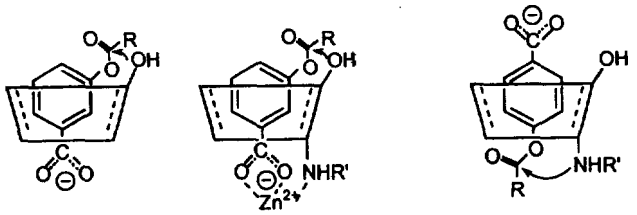

Scheme. Schematic representation of the major 'productive' complexes of carboxyphenyl acetates with β-CDs. The mode B complexes with native β-CD are non-productive and mode A complexes of the *p*-isomer are less reactive than those of *m*-isomer.

geometry for the reaction than the latter. Difference in affinity of the *p*-substituents to β-CD cavity might be responsible for this.

Table 1. also shows that the rate constant k_o^{CD} of the deacylation of the fully complexed substrate is greater for the *m*-isomer than for the *p*-isomer. This result is in line with the general trend known as '*meta selectivity*'.[2] The *meta* selectivity is biggest in β-CD and least in β-CDen. The less pronounced *meta* selectivity in β-CDen and β-CDdien can be explained in terms of the afore-mentioned mode B complexation. To be attacked by the amine groups, acetyl portion of the substrates should locate close proximity to the amine groups.[6] For the *m*-isomer, the mode B complexation results in positioning of the carboxylate anion deep in the hydrophobic cavity and considerable steric hindrance. Thus the mode B complexation is less plausible for the *m*-isomer than for the *p*-isomer and the reaction of the *m*-isomer proceeds mainly through mode A complexation, whereas the major reaction route for the *p*-isomer is *via* mode A complexation with β-CD and mode A and B complexations with β-CDen and β-CDdien.

Addition of zinc ion causes tighter binding of the substrates with β-CDen and β-CDdien except for the case between the *p*-isomer and β-CDen, and resulted in greater reactivity of all the complexed substrates with the aminated β-CDs. The effects of zinc ion on the binding constant is much more pronounced for the *m*-isomer. Zinc ion can form ternary complexes with carboxylate anion of the substrate and amine groups of the hosts.[10] This is possible only when the complexes are formed *via* mode A fashion. Little dependence of K values of the *p*-isomer on zinc ion and large enhancement in K values of *m*-isomer can be taken as a further evidence of involvement of mode A complexation for *m*-isomer and little contribution of mode A complexation for the *p*-isomer for the deacylation reaction.

In conclusion, this work demonstrates that the *p*-isomer of carboxyphenyl acetate shows enhanced binding affinity than the *m*-isomer to β-CD, β-CDen and β-CDdien, and addition of zinc ion increases the reactivity of the complexed substrates. The reaction of the *p*-isomer also proceeds *via* attack by amine groups of β-CDen and β-CDdien, whereas the attack by secondary hydroxyl group is the major reaction route for the m-isomer even in the presence of the amine-derivatized β-CD.

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7. In agreement with a previous study,[6] control experiments with ethylenediamine and diethylenetriamine in the absence of β-CDs did not show significant effects of the amines on the reaction rate. The observation of saturation kinetics (Figure 1) also indicates that the reactions proceed mainly via complexation with the hosts.
8. It was suggested[9] that both benzoic acid and sodium benzoate penetrate the cavity at the secondary hydroxyl side, carboxyl group first, on complexation with α-CD, although the sodium benzoate penetration is more random.
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A Melt Processable Ethynylphenoxy Group Substituted Cyclotriphosphazene: Synthesis and Thermal Polymerization

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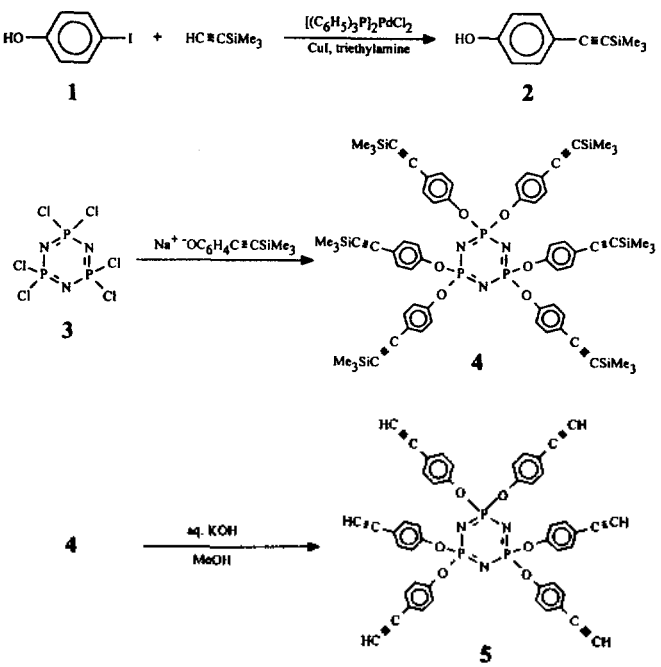
Cyclotriphosphazenes exhibit useful thermal properties such as self-extinguishibility and flame retardancy, which are imparted mainly by the presence of nitrogen and phosphorus atoms in the ring. Several research groups reported that cyclotriphosphazenes incorporated into organic polymeric systems as pendants improved thermal properties of the resulting polymers considerably.[1-10] The thermal polymerization of cyclotriphosphazenes containing thermally curable maleimido groups was also reported. The resulting polymers



Scheme 1.

showed excellent fire resistance as well as heat resistance.[9,10]

Recently we demonstrated the thermal polymerization of the ethynylanilino group substituted cyclotriphosphazene.[11] The ethynyl group terminated oligomers have been widely used as precursors of thermosetting heat resistant polymers for advanced composites since they are thermally curable under moderate conditions without the evolution of volatiles.[12~22] Melt processability as well as good solubility in common organic solvents are prerequisite properties to the precursors. However, the ethynylanilino group substituted cyclotriphosphazene did not melt before cross-linking occurred and was polymerized only in solid state under high pressure.

In this study, we prepared a melt processable and thermally curable cyclotriphosphazene. Ethynylphenoxy group substituted cyclotriphosphazene **5** has a distinctive melting point and exhibited a wide "processing window" between a melting temperature and a cure onset temperature. The cross-linked polymer showed excellent thermal stability and a high char yield.

Results and Discussion

Hexakis(4-ethynylphenoxy)cyclotriphosphazene (**5**) was prepared as described in Scheme 1. 4-Trimethylsilylethynylphenol (**2**) was prepared by coupling reaction of 4-iodophenol with trimethylsilylacetylene in the presence of a palladium catalyst.[23] We were concerned about the deterioration of the catalyst by the acidic phenolic proton but found the protection of the hydroxyl group of 4-iodophenol unnecessary under the reaction conditions. The addition of all reagents and the initial reaction was carried out below 0 ℃, otherwise coupling reaction between acetylenes to produce diacetylenic compounds was a major process. The trimethylsilyl group of compound **2** was removed easily under basic conditions. However, 4-ethynylphenol was very susceptible to hydration.

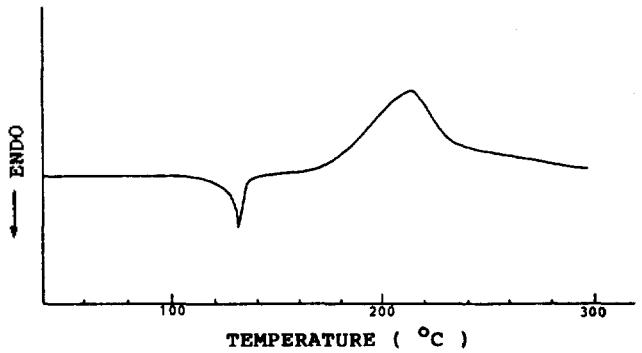


Figure 1. A DSC thermogram of compound **5** obtained with a heating rate of 10 ℃/min under nitrogen atmosphere.

Even during storage as solids at room temperature, 4-acetylphenol was found to be formed. For this reason, compound **2** was employed in substitution reaction of hexachlorocyclotriphosphazene. Hexachlorocyclotriphosphazene was reacted with sodium salt of 4-trimethylsilylethynylphenol obtained by using sodium hydride in 1,4-dioxane. Compound **4** was isolated by column chromatography on silica gel. ^{1}H NMR spectroscopy showed that trimethylsilyl groups were intact during the reaction.

Deprotection of ethynyl groups was carried out in a solution of aqueous KOH and methanol. Compound **5** was isolated as white solids by column chromatography on silica gel. In the ^{31}P NMR spectra, both compound **4** and **5** showed singlet peaks at 9.07 and 8.70 ppm, respectively. In the ^{1}H NMR spectra, compound **4** showed a singlet peak at 0.25 ppm for methyl protons and two doublet peaks with a AB spin system centered at 6.72 and 7.38 ppm for benzene ring protons, while compound **5** exhibited two doublet peaks with a AB spin system centered at 6.82 and 7.38 ppm for benzene ring protons and a singlet peak at 3.10 ppm corresponding to ethynyl protons.

The cross-linking reaction of ethynyl groups was examined by DSC. In the thermogram of compound **5**, a sharp endotherm for melting transition at 132 ℃ and a strong exotherm between 180 ℃ and 240 ℃ due to inter- and intramolecular reactions of the ethynyl groups were observed in the first scan (Figure 1). No significant endotherm or exotherm appeared in the 2nd scan, which indicated that most ethynyl groups had been reacted during the 1st scan. Compound **5** was placed on a glass plate and heated up to 250 ℃ with a heating rate of 10 ℃/min. It became liquid above the melting point and then cross-linked near 200 ℃ to yield a yellow film. The film was brittle and insoluble in organic solvents such as alcohols, N,N-dimethylformamide, and dimethyl sulfoxide.

In the IR spectrum of compound **5** (KBr pellet), the characteristic bands for C-H stretching and C-C triple bond stretching of the ethynyl groups appeared at 3370 cm^{-1} and 2060 cm^{-1}, respectively. A thin film was prepared by heating compound **5** between two NaCl plates at 220 ℃ under vacuum and employed in IR analysis. IR spectroscopy showed that intensity of C-H stretching band of ethynyl groups at 3370 cm^{-1} decreased gradually as curing reaction proceeded, but the band with reduced intensity was still observed even after heating for 1 h at 220 ℃. New bands near 3090 cm^{-1} appear-

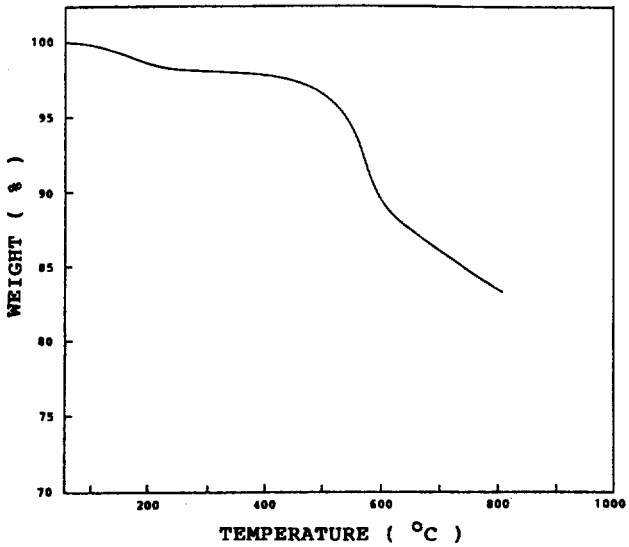


Figure 2. A TGA thermogram of compound **5** obtained with a heating rate of 10 ℃/min under nitrogen atmosphere.

ed, which was attributed to olefinic C-H stretching vibrations.

Figure 2 shows the thermogravimetric analysis result of compound **5**. About 2% weight loss was observed between 140-220 ℃ where the curing reaction occurred. The causes for this result are not clear but volatiles including moisture in the sample are primarily suspected. The cured material exhibited excellent thermal stability. The onset temperature of decomposition was 400 ℃ and the total weight loss at 600 ℃ was about 10%. The compound had a char yield of 83% at 800 ℃.

Experimental Section

Materials and Instrumentation. Hexachlorocyclotriphosphazene (Aldrich) was purified by fractional vacuum sublimation at 60 ℃ in 0.5 mmHg. Reagent grade solvents were dried and purified as follows: Triethylamine was distilled over BaO. Tetrahydrofuran and 1,4-dioxane were distilled over sodium-potassium alloy. Toluene was distilled over CaH_2. All the other reagents were used as received. Melting points were obtained by a Fisher-Johns melting point apparatus. Proton-decoupled ^{31}P NMR spectra were obtained with the use of a Bruker AM-300 spectrometer. Chemical shifts were reported in ppm relative to 85% H_3PO_4 at 0 ppm. ^1H NMR spectra were recorded on a Varian Gemini 200 or a Jeol PMX60 spectrometer. IR spectra were obtained with the use of a Perkin-Elmer 240 spectrometer. Thermal analyses were performed by a Du Pont DSC-910 and a Perkin-Elmer TGA-7. Elemental analyses were performed by a Carlo Erba 1108 or Perkin Elmer 240C elemental analyzer at Korea Research Institute of Chemical Technology and Korea Basic Research Center.

Synthesis of 4-Trimethylsilylethynylphenol (2). To a solution of 4-iodophenol (10 g, 45.4 mmol) and (trimethylsilyl)acetylene (9.1 mL, 68.1 mmol) in triethylamine (200 mL) under nitrogen were added dichlorobis(triphenylphosphine) palladium (1.8 g, 2.52 mmol) and copper iodide (0.3 g, 1.50 mmol) at −4 ℃. The reaction mixture was stirred at the same temperature for 2 h. After stirring at room temperature for additional 10 h, the reaction mixture was concentrated to dryness by evaporation under reduced pressure. The crude product was isolated by sublimation (35-45 ℃, 0.1 mmHg) and further purified by column chromatography on silica gel (20% ethyl acetate in hexane) to yield 6.6 g (76%), mp 60-62 ℃. Anal. Calcd for $C_{11}H_{14}OSi$: C, 69.42; H, 7.41. Found: C, 69.19; H, 7.42. ^1H NMR ($CDCl_3$): δ 7.37 and 6.75 (dd, 4H, C_6H_4), 5.15 (s, 1H, OH), 0.25 (s, 9H, $SiCH_3$). IR (KBr): 3345, 2966, 2164, 1612, 1515 cm^{-1}.

Synthesis of Hexakis(4-trimethylsilylethynylphenoxy)cyclotriphosphazene (4). To a solution of 4-trimethylsilylethynylphenol (6.60 g, 34.6 mmol) in 1,4-dioxane (100 mL) was added NaH (0.83 g, 34.6 mmol). The mixture was stirred for 4 h at room temperature and then a solution of hexachlorocyclotriphosphazene (1.0 g, 2.87 mmol) in 1,4-dioxane (20 mL) was added dropwise to the mixture. The mixture was stirred at refluxing temperature for 3 days and passed through a silica gel column. After evaporation, the product was isolated by column chromatography on silica gel (5% ethyl acetate in hexane) to yield 1.8 g (50%), mp 139-141 ℃. Calcd for $C_{66}H_{78}N_3O_6P_3Si_6$: C, 62.40; H, 3.30; N, 6.20. Found: C, 62.72; H, 3.15; N, 6.52. ^1H NMR ($CDCl_3$): δ 6.72 and 7.38 (dd, 24H, C_6H_4), 0.25 (s, 54H, $SiCH_3$). ^{31}P NMR ($CDCl_3$): δ 9.07. IR (KBr): 2966, 2159, 1498, 1255 cm^{-1}.

Synthesis of Hexakis(4-ethynylphenoxy)cyclotriphosphazene (5). To a solution of compound **4** (0.68 g, 0.53 mmol) in 5% tetrahydrofuran in methanol (100 mL) was added 1 N aqueous KOH (3.2 mL). The solution was stirred at room temperature for 10 h. The solvent was removed by evaporation under reduced pressure. The product was isolated by column chromatography on silica gel (5% ethyl acetate in hexane) to yield 0.38 g (85%), mp 130-132 ℃. Calcd for $C_{48}H_{30}N_3O_6P_3$: C, 69.42; H, 3.60; N 5.00. Found: C, 68.80; H, 4.21; N, 4.61. ^1H NMR ($CDCl_3$): δ 6.82 and 7.38 (dd, 24H, C_6H_4), 3.10 (s, 6H, CH). ^{31}P NMR ($CDCl_3$): δ 8.70. IR (KBr): 3297, 2925, 2854, 2105, 1606, 1505, 1280 cm^{-1}.

Acknowledgment. This work was supported by the Ajou University and Korea Science and Engineering Foundation.

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Isolation and Structure Determination of a New Bastadin from an Indonesian Sponge *Ianthella basta*

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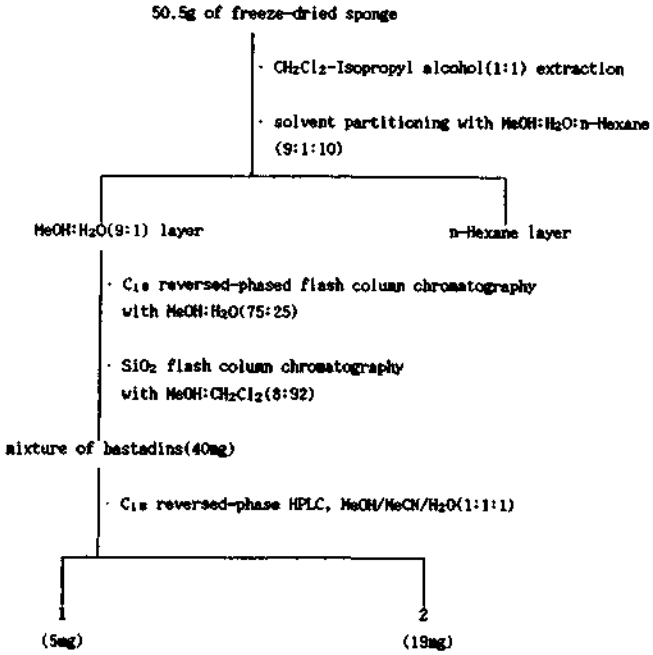
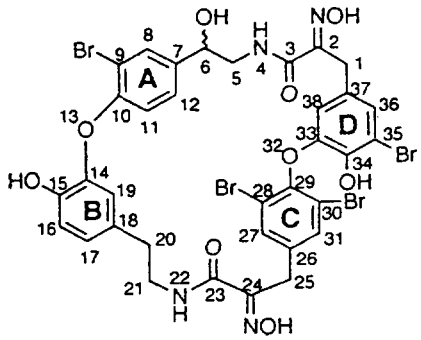
The bastadins are series of predominantly macrocyclic sponge metabolites, which are biogenetically derived from four tyrosines by oxidative phenolic coupling of two tyramine-tyrosine units.[1~8] We now report the isolation and structure determination of a new bastadin 17 and the previously reported compound, bastadin 3,[4] from the Marine sponge *Ianthella basta* Pallas collected in October, 1992 at Manado Bay, Sulawesi Indonesia.



Scheme 1.

The *Ianthella basta* extract was partitioned between MeOH/H_2O (9 : 1) and *n*-hexane and the MeOH/H_2O (9 : 1) layer residue was subjected to C_{18} reversed-phase followed by Silica gel normal-phase flash column chromatography to yield a fraction whose ^1H NMR spectrum revealed structural features of bastadins. The mixture of bastadins was sepa-



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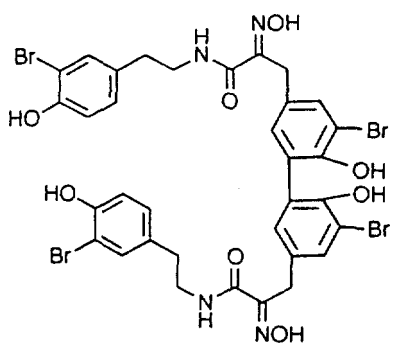

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