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공학석사학위논문

**A Study on Dielectric or Adsorption  
Properties of Network Polymers  
Containing Cyclotriphosphazene  
Rings**

Cyclotriphosphazene 고리를 함유한 네트워크  
고분자의 유전 특성 및 흡착 특성에 관한 연구

2018년 2월

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재료공학부

전희선

## **Abstract**

# **A Study on Dielectric or Adsorption Properties of Network Polymers Containing Cyclotriphosphazene Rings**

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Cyclotriphosphazenes are cyclic compounds having alternate nitrogen and phosphorus atoms. With a diverse combination of two substituent groups attached to the phosphorous atoms, they can have a broad range of chemical and physical properties. In this study, reactive cyclotriphosphazene derivatives were synthesized and used for the preparation of functional materials.

Firstly, flame retardant and low dielectric epoxy resins based on cyclotriphosphazene were studied. Cyclotriphosphazenes having epoxy

groups and 2'-biphenol (B-PE), 4-phenylphenol (P-PE), and 2-naphthol (N-PE) as co-substituents were synthesized. Highly cross-linked polymers were obtained by thermal polymerization with an active ester type hardener and dimethylaminopyridine. The resulting epoxy polymers showed good thermal stability. The temperatures of 5 % weight loss, measured by TGA, were above 300 °C. The polymers having B-PE, P-PE, and N-PE as co-substituents showed low dielectric constants of about 2.19, 2.39, and 2.18 and low dielectric losses of about  $6.08 \times 10^{-3}$ ,  $6.13 \times 10^{-3}$ , and  $4.97 \times 10^{-3}$  at 10 GHz, respectively. The flame-retardant property of the B-PE polymer was excellent, showing a very high LOI value of 31.

Secondly, porous cyclophosphazene-based polymers were prepared by Friedel-Crafts alkylation reaction of a biphenol substituted cyclophosphazene and dichloroethylene or bis(chloromethyl)biphenyl. Dichloroethylene and bis(chloromethyl)biphenyl acted as linkers and the microporosities of the polymers were tuned by adjusting their molar ratios to the cyclotriphosphazene monomer. All PCPs showed large Brunauer-Emmett-Teller surface areas, hierarchical pore size distributions, and good CO<sub>2</sub> uptake properties.

*Keywords:* Cyclotriphosphazene, epoxy, low dielectric, flame retardant, microporous polymer, carbon dioxide adsorption.

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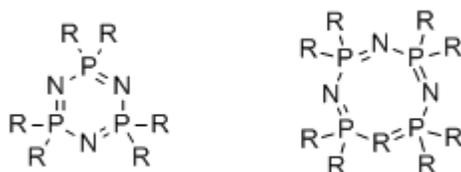
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# **Chapter I.**

## **Introduction**

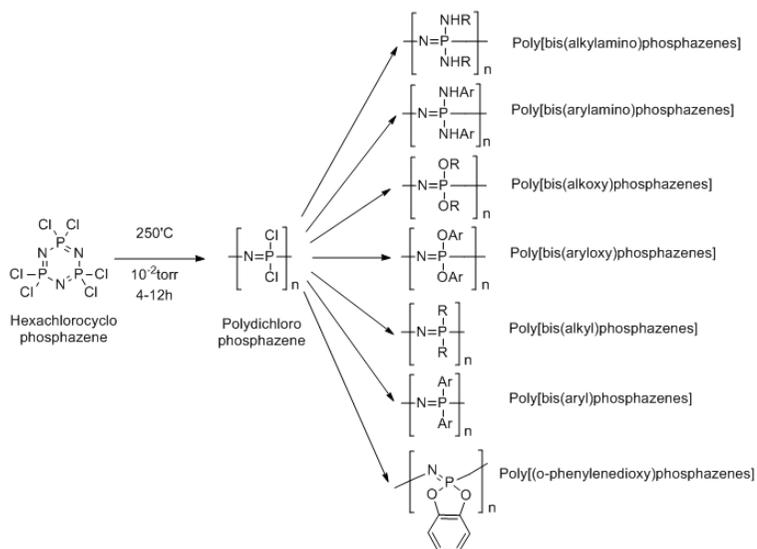
Cyclophosphazenes are inorganic heterocyclic compounds consisting of – P=N- repetitive units (Figure I-1). They have broad physical and chemical properties depending on substituent groups attached to the phosphorous atoms.<sup>[1,2]</sup>



**Figure I-1.** General structures of cyclophosphazenes.

Hexachlorocyclotriphosphazene is particularly interesting as a versatile starting material for the synthesis of cyclic organophosphazenes and poly(organophosphazene)s. In 1964, Allcock and co-workers firstly reported the synthesis of poly(dichlorophosphazene) from hexachlorocyclotriphosphazene. The chlorine atoms of poly(dichlorophosphazene) are easily replaced by nucleophiles to produce a variety of poly(organophosphazene)s with different chemical and physical characteristics (Figure I-2).<sup>[3-5]</sup> Cyclic organophosphazenes are obtained by

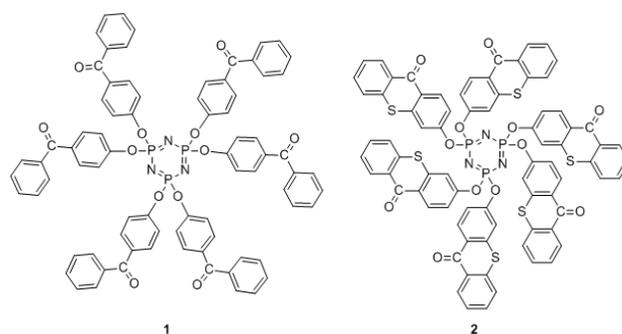
the similar substitution reactions of hexachlorocyclotriphosphazene (Figure I-3).<sup>[2]</sup>



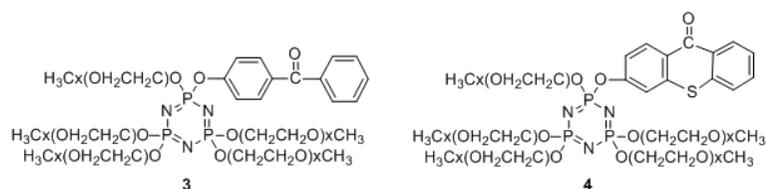
**Figure I-2.** Scheme for the general substitution reaction of poly(phosphazene).



Chromophoric substituents induce light absorption and exhibit photoreactivity. For example, low molecular weight cyclophosphazene derivatives (**1** and **2**) can be used as a photoinitiator for the free radical polymerization of vinyl monomers (Figure I-4).<sup>[6, 7]</sup> Cyclophosphazene-based photoinitiators **3** and **4** are water soluble due to the presence of ethylene oxide moieties (Figure I-5).<sup>[2]</sup>

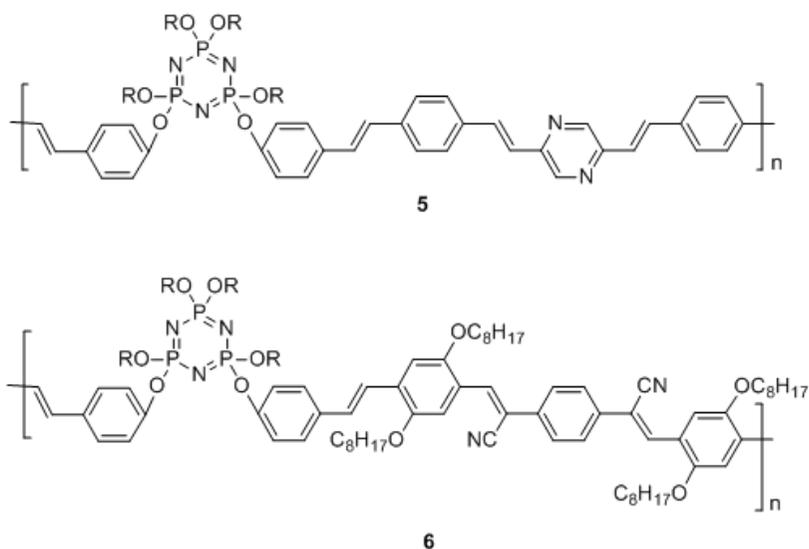


**Figure I-4.** Examples of cyclophosphazene-based photoinitiators containing benzophenone and thioxanthone groups.



**Figure I-5.** Examples of water-soluble cyclophosphazene photoinitiators.

Cyclotriphosphazene rings were incorporated into photoreactive conjugated polymer chains to improve solubility. Polymers **5** and **6** showed electroluminescent properties and excellent solubility (Figure II-6).<sup>[8]</sup>



**Figure I-6.** Soluble electroluminescent polymers containing cyclotriphosphazene.

Bifunctional cyclotriphosphazenes have been used for the synthesis of linear organic-inorganic hybrid polymers *via* a condensation reaction.<sup>[9]</sup> The polymers having cyclotriphosphazene units exhibited improved thermal stability.<sup>[10, 11]</sup> In particular, cyclotriphosphazene-containing compounds demonstrated flame retardancy because phosphorous could form foam char

layers while on burning, and nitrogen could release inert gases to reduce oxygen concentration. Owing to these thermal properties of cyclotriphosphazenes, they draw considerable attention as eco-friendly heat resistant material in electronic industry.<sup>[12-16]</sup>

Organo-substituted cyclotriphosphazenes have paddle-wheel structures, resulting in unusual molecular packing.<sup>[17]</sup> Taking advantage of this characteristic, a porous crystalline solid of a cyclotriphosphazene was prepared.<sup>[18]</sup> It is well known that three-dimensional rigid paddle-wheel structures can produce highly porous materials.<sup>[19]</sup> Recently, several studies reported cyclotriphosphazene-based porous polymers for CO<sub>2</sub> capture. Porous inorganic-organic hybrid polymers containing cyclotriphosphazene rings could be good candidate materials for CO<sub>2</sub> adsorption because of the presence of many nitrogen atoms with a lone pair of electrons. Nitrogen-rich aminated linked inorganic-organic hybrid nanoporous materials with cyclotriphosphazene moieties were reported to show relatively high specific surface areas and CO<sub>2</sub> capture ability.<sup>[20]</sup>

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## **Chapter II.**

### **Flame Retardant and Low Dielectric Epoxy Resin**

#### **Based on Cyclotriphosphazenes**

## II-1. Introduction

With the rapid development of communication technology, an integrated circuit (IC) has become complex and working frequency of an electronic device has increased. In the high-frequency region, the performance of IC is heavily dependent on the interconnect signal delay and the dissipation of energy between wires. The replacement of conventional Al technology with Cu and the introduction of low dielectric materials have been considered as solutions to reduce both resistivity of and the capacitance between wires, so the development of low dielectric materials is very demanding.<sup>[1-4]</sup> Since the interconnect capacitance, cross-talk, and power dissipation are strongly related to the reduction in dielectric properties of the insulator, low dielectric insulating materials become more and more significant in future technology.

Dielectric properties of materials are influenced by two main factors. One is porosity and the other is the polarity.<sup>[5]</sup> Various approaches have been attempted to develop low dielectric materials; introducing fluoro groups,<sup>[6-10]</sup> increasing free volume,<sup>[6, 8, 11]</sup> or controlling the polarity.<sup>[12, 13]</sup> But commercially viable materials with all other suitable properties such as thermal, mechanical, adhesive, and environmental, are still rare. Epoxy resins, one of the most useful commercial materials, have been used in diverse electronic areas as advanced thermosetting polymers due to their attractive

properties such as high mechanical strength, good adhesion, good electrical properties, and low shrinkage.<sup>[14-16]</sup> For the next generation applications, however, they should have lower dielectric properties in a high-frequency range. There have been several approaches to this end including the modification of polymer structures<sup>[14, 17, 18]</sup> and the introduction of new inorganic fillers,<sup>[19]</sup> but the development of low dielectric epoxy resins is an ongoing issue.

In this study, we prepared three types of epoxy monomers based on cyclotriphosphazenes having 2,2'-biphenoxy (B-PE), 4-phenylphenoxy (P-PE) and 2-naphthoxy (N-PE) groups as co-substituents. Cyclotriphosphazenes possess unique structural characteristics. Their paddle wheel structures with curable groups can produce highly cross-linked porous matrices with mechanical stability, low density, and low dielectric properties.<sup>[20]</sup> Moreover, phosphorus-containing cyclotriphosphazene rings show flame retardancy and self-extinguishability.<sup>[19, 21-24]</sup> The epoxy monomers were cured using an active ester hardener to produce cross-linked matrices with low dielectric constants and loss values, and good thermal properties.

## II-2. Experiment

**Materials.** 4-Vinylphenyl Acetate (> 98%) was purchased from TCI. Hexachlorocyclophosphazene (HCCP) (99%), 4-phenylphenol, 4-(dimethylamino)pyridine (DMAP) (99%) and sodium hydride (dry, 95%) were purchased from Sigma-Aldrich. *m*-Chloroperbenzoic acid (*m*-CPBA) (70-75% in water), 2,2'-biphenol (99%) were obtained from ACROS Organics. Sodium hydroxide (NaOH), sodium chloride (NaCl), cesium carbonate (CsCO<sub>3</sub>), magnesium sulfate (MgSO<sub>4</sub>) and sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) were purchased from Daejung Chemical & Metals Co. 2-Naphtol was purchased from Yakuri Pure Chemicals. EPICLON HPC-8000-65T was purchased from DIC color & comfort. Silica gel (Merck 60) was used for column chromatography. Tetrahydrofuran (THF) was purchased from Duksan Pure Chemical and distilled with sodium before use.

**Synthesis of 4-Hydroxystyrene (1).** Compound **1** was synthesized according to the literature with a minor modification.<sup>[25]</sup> 4-Acetoxy acetate (10.0 g, 61.7 mmol) and sodium hydroxide (2.71 g, 67.9 mmol) were dissolved in methanol (50 ml). The mixture was stirred at room temperature for 24 h. After methanol was evaporated, the residue was dissolved in ethyl acetate (50 ml). The solution was extracted with a sodium chloride aqueous

solution (50 ml) several times and dried over anhydrous magnesium sulfate. After filtration and evaporation, the product was isolated by column chromatography on silica gel. (10% ethyl acetate in *n*-hexane). White powder was obtained by vacuum filtration. Yield: 5.70 g, 77 %. <sup>1</sup>H NMR (DMSO) : δ 9.51 (s, 1H, -OH), 7.26-7.29 (d, 2H, Ar), 6.72-6.76 (d, 2H, Ar), 6.56-6.66 (q, 1H, Vinyl), 5.54-5.61 (d, 1H, Vinyl), 5.01-5.06 (d, 1H, Vinyl).

**Synthesis of [N<sub>3</sub>P<sub>3</sub>Cl<sub>4</sub>(O<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)] (2).** This compound was synthesized according to the literature with a minor modification.<sup>[26]</sup> 2,2'-Biphenol (2.68 g, 14.4 mmol) and cesium carbonate (23.9 g, 72.4 mmol) were dissolved in distilled THF (200 ml). Hexachlorocyclophosphazene (HCCP) (5.00 g, 14.4 mmol) was added to the solution and the mixture was stirred at room temperature for 30 min. After THF was evaporated, the residue was dissolved in dichloromethane (200 ml) and the solution was washed with water (200 ml). White powder was obtained by vacuum filtration. Yield: 5.9 g, 89 % <sup>1</sup>H NMR (CDCl<sub>3</sub>) : δ 7.54-7.58 (d, 2H, Ar), 7.45-7.51 (t, 2H, Ar), 7.36-7.42 (t, 2H, Ar), 7.29-7.32 (d, 2H, Ar) <sup>31</sup>P NMR (CDCl<sub>3</sub>) : δ 25.03-25.38 (d, 1P, P(O<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)), 12.95-13.65 (t, 2P, PCl<sub>2</sub>).

**Synthesis of N<sub>3</sub>P<sub>3</sub>(O<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)(OC<sub>8</sub>H<sub>7</sub>)<sub>4</sub> (3).** This compound was synthesized according to the literature with a minor modification.<sup>[27]</sup> Dry THF

(200 ml) was added to a flame dried flask which was evacuated and refilled with nitrogen gas. 4-Hydroxystyrene (6.75 g, 56.2 mmol) and sodium hydride (1.35 g, 56.2 mmol) were added. After stirring 1 h at room temperature, compound **2** (5.00 g, 10.8 mmol) was added and refluxed for 24 h. After filtration, the product was purified by recrystallization from methanol. Yield: 8.63 g, 73 % <sup>1</sup>H NMR (DMSO) : δ 7.45-7.49 (q, 2H, Ar), 7.30-7.34 (d, 8H, Ar), 7.29-7.32 (q, 2H, Ar), 7.05-7.07 (q, 4H, Ar), 6.70-6.85 (d, 8H, Ar), 6.60-6.64 (q, 4H, vinyl), 5.69-5.66 (d, 4H, vinyl), 5.26-5.23 (d, 4H, vinyl).

**Synthesis of N<sub>3</sub>P<sub>3</sub>(O<sub>2</sub>C<sub>12</sub>H<sub>8</sub>)(O<sub>2</sub>C<sub>8</sub>H<sub>7</sub>)<sub>4</sub> (B-PE).** This compound was synthesized according to the literature with a minor modification.<sup>[28]</sup> The compound **3** (5.00 g, 6.28 mmol) and *m*-CPBA (8.60 g, 34.9 mmol) were dissolved in methylene chloride (200 mL). The mixture was stirred at room temperature for 24 hr. The solution was washed with sodium hydroxide solution twice (200 mL 2 M) and dried over anhydrous sodium sulfate. After filtration and evaporation, white powder was obtained. Yield: 5.31 g, 95 % <sup>1</sup>H NMR (DMSO) : δ 7.62 (s, 2H, Ar), 7.54 (s, 2H, Ar), 7.51 (s, 2H, Ar), 7.31-7.34 (d, 8H, Ar), 7.05 (s, 8H, Ar), 6.58 (s, 2H, Ar), 3.96 (s, 4H, epoxy), 3.14 (s, 4H, epoxy), 2.87 (s, 4H, epoxy).

**Synthesis of N<sub>3</sub>P<sub>3</sub>(OC<sub>8</sub>H<sub>7</sub>)<sub>3</sub>(OC<sub>12</sub>H<sub>9</sub>)<sub>3</sub> (4).** The compound was prepared

by following the procedure for the preparation of compound **3**. Dry THF (100 ml) was added to a flame dried flask which was evacuated and refilled with nitrogen gas. 4-hydroxystyrene (3.00 g, 25.0 mmol), 4-phenylphenol (4.24 g, 25.0 mmol) and sodium hydride (1.20 g, 50.0 mmol) were added. After stirring for 1 h at room temperature, HCCP (2.22 g, 4.80 mmol) was added and refluxed for 24 h. After filtration, the product was purified by recrystallization from methanol. Yield: 3.97 g, 73 %  $^1\text{H}$  NMR (DMSO) :  $\delta$  6.61-7.62 (broad peak, Ar), 5.79-5.85 (d, 3H, vinyl), 5.26-5.30 (d, 3H, vinyl).

**Synthesis of  $\text{N}_3\text{P}_3(\text{O}_2\text{C}_8\text{H}_7)_3(\text{OC}_{12}\text{H}_9)_3$  (P-PE).** This compound was prepared by following the procedure for the preparation of B-PE. The compound **4** (2.50 g, 2.50 mmol) and *m*-CPBA (3.70 g, 15.0 mmol) were dissolved in methylene chloride (100 mL). The mixture was stirred at room temperature for 3hr. The solution was washed with Sodium hydroxide solution twice (100 mL 2 M) and dried over anhydrous sodium sulfate. After filtration and evaporation, Yellow powder was obtained. Yield: 1.81 g, 72 %  $^1\text{H}$  NMR (DMSO) :  $\delta$  6.85-7.64 (broad peak, Ar), 3.86-3.87 (t, 3H, epoxy), 2.97-3.07 (t, 3H, epoxy), 2.50-2.52 (t, 3H, epoxy).

**Synthesis of  $\text{N}_3\text{P}_3(\text{OC}_8\text{H}_7)_3(\text{OC}_{10}\text{H}_8)_3$  (5).** This compound was prepared by following the procedure for the preparation of compound **3**. Dry THF (100

ml) was added to a flame dried flask which was evacuated and refilled with nitrogen gas. 4-hydroxystyrene (3.00 g, 25.0 mmol), 2-naphtol (3.60 g, 25.0 mmol) and sodium hydride (1.20 g, 50.0 mmol) were added. After stirring 1 h at room temperature, HCCP (2.22 g, 4.80 mmol) was added and refluxed for 24 h. After filtration, the product was purified by recrystallization from methanol. Yield: 5.56 g, 93 %  $^1\text{H}$  NMR (DMSO) :  $\delta$  6.58-7.94 (broad peak, Ar), 5.61-5.81 (q, 3H, vinyl), 5.20-5.30 (q, 3H, vinyl).

**Synthesis of  $\text{N}_3\text{P}_3(\text{O}_2\text{C}_8\text{H}_7)_3(\text{OC}_{10}\text{H}_8)_3$  (N-PE).** This compound was prepared by following the procedure for the preparation of B-PE. The compound **5** (2.50 g, 2.67 mmol) and *m*-CPBA (4.00 g, 16.2 mmol) were dissolved in methylene chloride (100 mL). The mixture was stirred at room temperature for 3 hr. The solution was washed with sodium hydroxide solution twice (100mL 2M) and dried over anhydrous sodium sulfate. After filtration and evaporation, Brown powder was obtained. Yield: 2.45 g, 93 %  $^1\text{H}$  NMR (DMSO) :  $\delta$  6.67-7.94 (broad peak, Ar), 3.36-3.83 (t, 3H, epoxy), 3.05-3.11 (t, 3H, epoxy), 2.50-2.73 (t, 3H, epoxy).

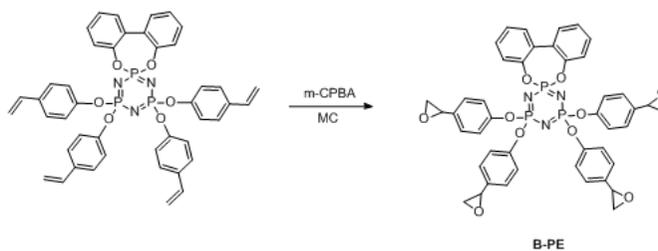
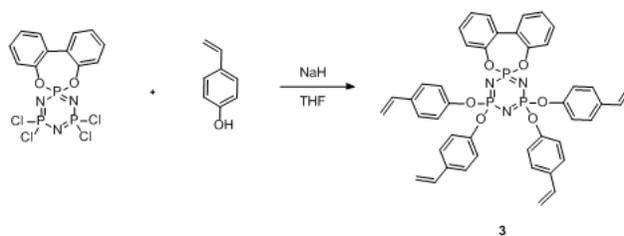
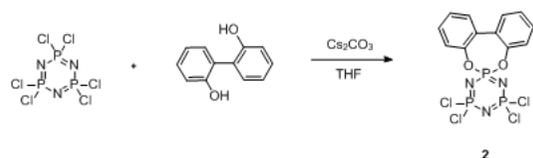
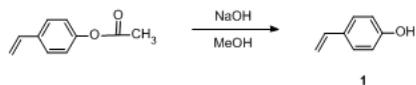
**Polymerization.** A cyclotriphosphazene based compound was dissolved in a hardener solution (33.3 wt% in methyl ethyl ketone) with a mole ratio of 1:1 and 1 wt% of DMAP was added as an initiator. The resulting solution was

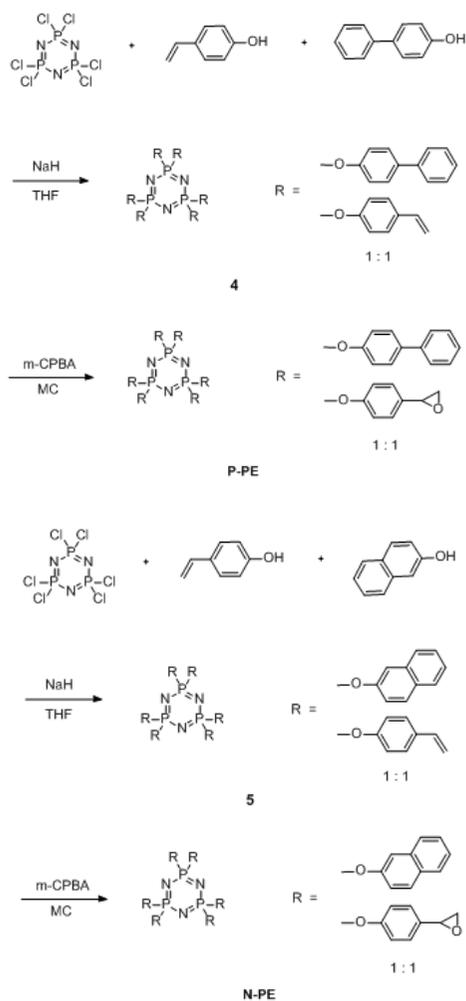
mixed by ultrasonication for 1 min. After evaporation for 5 min, the resin was placed in a copper foil by bar coating and heated at 200 °C for 2h under gentle pressure.

**Instrumental Characterization.** <sup>1</sup>H NMR, <sup>31</sup>P NMR spectra were recorded by a Bruker Avance 300 (300 MHz for <sup>1</sup>H NMR) spectrometer and a Bruker Avance 500 (500 MHz for <sup>31</sup>P NMR) spectrometer. The FT-IR spectra were measured by a PERKIN ELMER Spectrum GX I spectrometer using KBr pellets. Field emission scanning electron microscopy (FE-SEM) images were obtained by JEOL JSM-6700F microscope. Thermogravimetric analyses (TGA) were performed on a TA modulated TGA 2050 with a heating rate of 10 °C/min under nitrogen. Differential scanning calorimeter (DSC) measurement was performed on a TA modulated DSC-Q1000 with a scanning rate of 10 °C/min under nitrogen. Dielectric constant and dielectric loss measured by a resonant cavity method with Agilent E8364B network analyzer according to a JIS C2565 standard at a frequency of 10 GHz with test specimen bars of 100 mm in length, 3.5 mm in width and about 60 μm in thickness. LOI (Limiting oxygen index) values measured by a Fire Testing Technology instrument according to ISO 4589 with test specimen bars of 80 mm in length, 10 mm in width and about 4.0 mm in thickness.

## II-3. Results and Discussion

### II-3-1. Monomer Synthesis



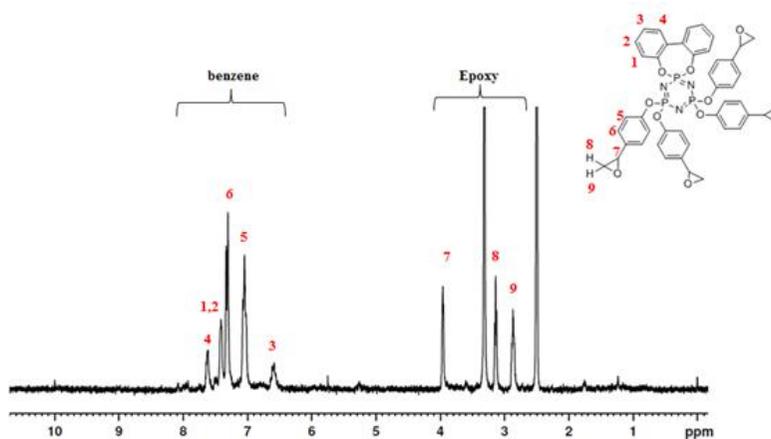


**Scheme II-1.** Synthesis of the epoxy monomer B-PE, P-PE and N-PE.

Cyclotriphosphazenes having epoxy groups were synthesized according to Scheme II-1. 4-Hydroxystyrene were prepared by the reaction of 4-vinylphenyl acetate with sodium hydroxide. Two chloro groups of HCCP were replaced by the reaction with the cesium salt of 2,2'-biphenol to give a

compound (2). Other chloro groups of compound 2 were substituted by the sodium salt of 4-hydroxystyrene to result in the formation of a vinyl phosphazene (3). Other heterosubstituted cyclotriphosphazene compounds (4 and 5) were synthesized in the same manner using 4-hydroxystyrene and 4-phenylphenol or 2-naphtol as a cosubstituents. 3 – 5 were reacted with *m*-CPBA to produce epoxy groups on the rings.

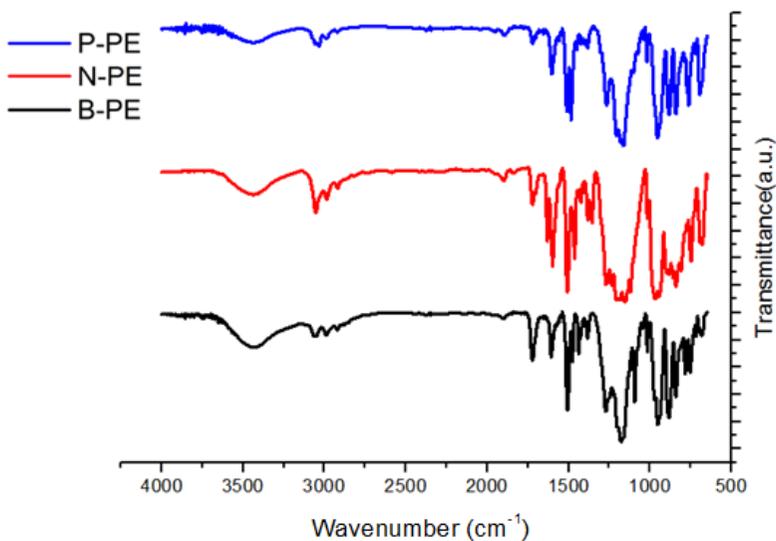
The structures of compounds 3 – 5 were examined by <sup>1</sup>H NMR and FT-IR spectroscopy. In the <sup>1</sup>H NMR spectra (Figure II-1), the peaks for epoxy groups were observed around 2.9, 3.2 and 4.0 ppm.



**Figure II-1.** <sup>1</sup>H NMR spectrum of the epoxy monomer B-PE.

The IR spectra of B-PE, P-PE and N-PE were almost similar (Figure II-2). The characteristic stretching vibrations of P-O-Ph, P-N-P and P-O-C were observed at 1269, 1171 and 949 cm<sup>-1</sup>, respectively. The peaks for the epoxy

ring appeared at  $880\text{ cm}^{-1}$ , which was attributed to the C-O deformation vibration. <sup>[19]</sup>

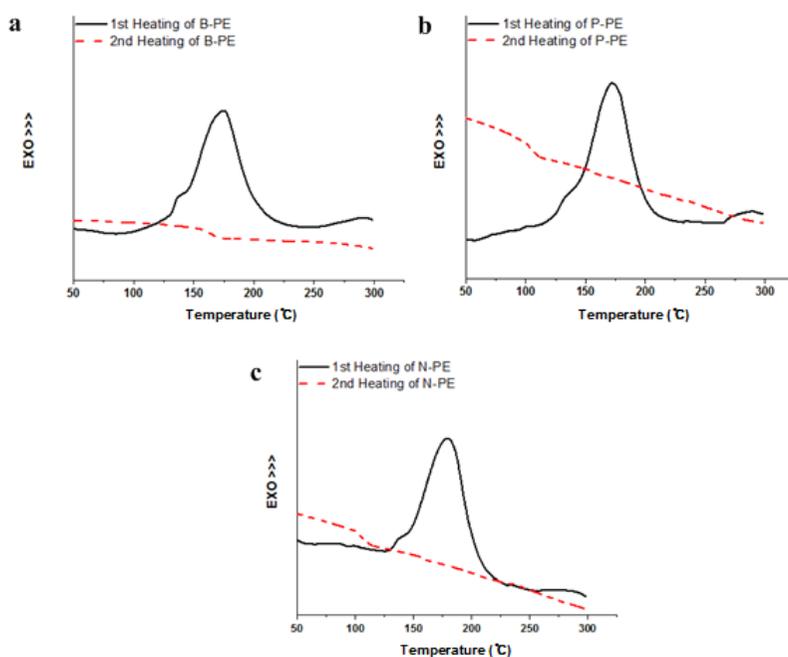


**Figure II-2.** FT-IR spectra of the epoxy monomer B-PE, P-PE and N-PE.

### II-3-2. Thermal Polymerization

The thermal behaviors of B-PE, P-PE and N-PE were examined by DSC. An active mater and DMAP were used for the curing reaction. Thermo grams obtained by scanning the samples twice from  $50\text{ }^{\circ}\text{C}$  to  $300\text{ }^{\circ}\text{C}$  with a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$  under nitrogen atmosphere are shown in

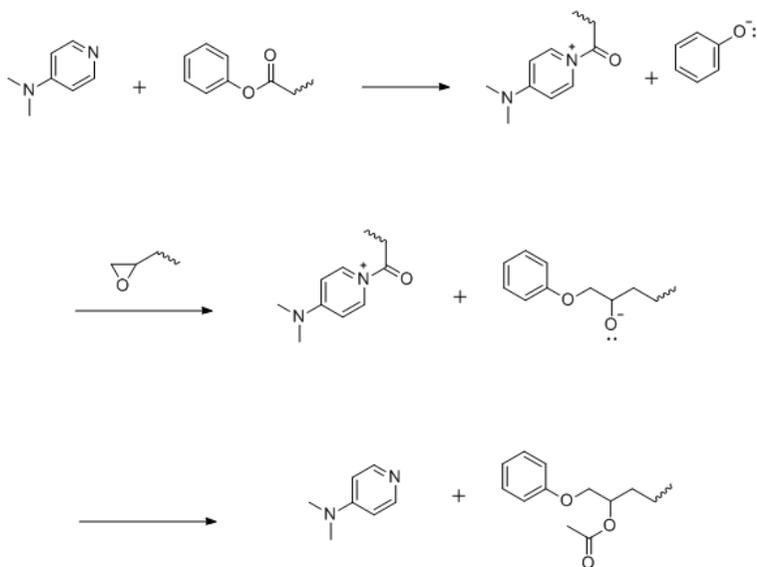
Figure II-3. All of the compounds showed strong exotherms for the thermal reaction of epoxy functional groups above 170 °C. In the second scan, no significant exothermic peaks appeared, indicating that most epoxy groups were thermally reacted in the first scan.



**Figure II-3.** DSC thermograms of epoxy matrixes containing (a) B-PE (b) P-PE, (c) N-PE.

The curing mechanism of the epoxy is shown in Scheme II-2. The curing reaction is initiated by the attack of DMAP on an active ester type hardener to

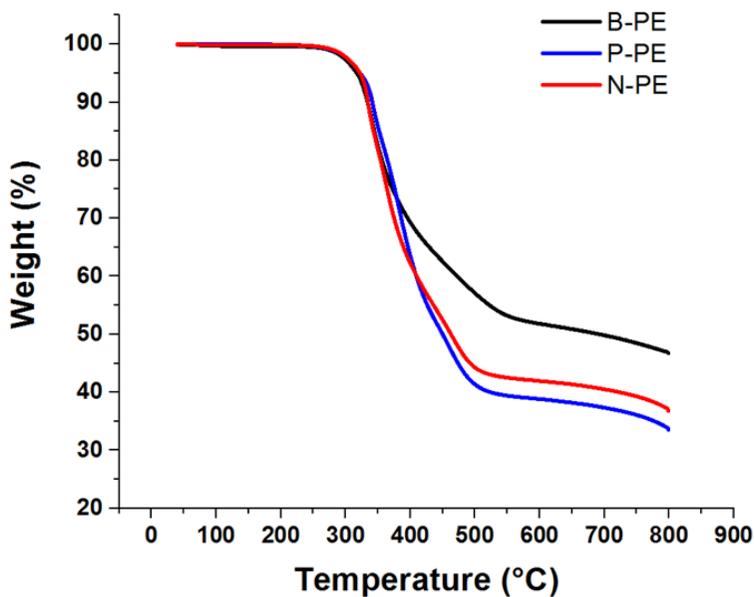
form a phenolate anion and a pyridinium cation. The phenolate anion causes epoxy ring opening to generate another alkoxy anion. When the alkoxy anion reacts with the pyridinium cation, an acetate and an initial DMAP are formed.



**Scheme II-2.** Curing mechanism of the epoxy matrix with an active ester type hardener and a DMAP initiator.

Highly cross-linked polymers were obtained by thermal curing at 200 °C for 2 h and showed excellent thermal stability. The 5 % weight loss temperatures (Td<sub>5</sub>) of the cross-linked polymers of B-PE, P-PE and N-PE, measured by TGA under nitrogen, were 317, 318 and 322 °C, respectively.

Their char yields were 46.1, 33.3 and 36.0 % at 800 °C, respectively (Figure II-4).

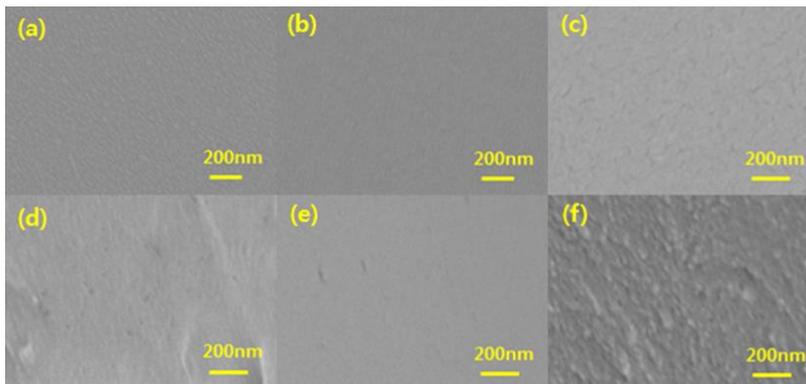


**Figure II-4.** TGA thermograms of high cross-linked polymers B-PE, P-PE and N-PE under nitrogen.

### II-3-3. Dielectric Properties

The Dielectric properties of the polymers were measured by the resonant cavity method with an Agilent E8364B network analyzer according to a JIS C2565 standard. Films with 3.5 mm of width, 100 mm in length and about 60

um thickness were prepared by the dielectric property measurement. Coating the epoxy resins on a copper foil. After curing, the copper foil was removed by a nitric acid solution and the polymer samples were washed with water several times. The surface and cross-section morphology was measured by SEM and no macro pores were observed (Figure II-5).



**Figure II-5.** SEM images of surface and cross-section of the specimen prepared by polymerization of (a, d) B-PE, (b, e) P-PE and (c, f) N-PE.

The dielectric constants of B-PE, P-PE and N-PE were 2.19, 2.39 and 2.18 and dielectric losses were about  $6.08 \times 10^{-3}$ ,  $6.13 \times 10^{-3}$  and  $4.97 \times 10^{-3}$ , respectively, at 10 GHz (Table II-1). These values were lower than those of other epoxy-type polymer networks, by about 3.0 in dielectric constant and about 0.015 in dielectric loss.<sup>[29]</sup> We presumed that the low dielectric properties of the epoxy resins containing cyclotriph

osphazenes came from their structural uniqueness. The paddle wheel structure of a cyclotriphosphazene could generate more free volume in the network structure decrease the dielectric constant. Moreover, multi-epoxy groups produced a highly cross-linked network structure, leading to low dielectric loss by restricting the orientation and relaxation of dipoles in the matrix.<sup>[19]</sup>

Monomer	Dielectric Constant (@ 10 GHz)	Dielectric Loss (@ 10 GHz)	T <sub>g</sub> /°C	T <sub>d5</sub> /°C	Char yield (%)	LOI (%)
B-PE	2.19	6.08 * 10 <sup>-3</sup>	163	317	46.1	31
P-PE	2.39	6.13 * 10 <sup>-3</sup>	109	318	33.3	-
N-PE	2.18	4.97 * 10 <sup>-3</sup>	112	321	36.0	-

**Table II-1.** The dielectric and thermal properties of the polymers.

### II-3-4. Flame Retardant Property

The flame retardant property of B-PE was evaluated by measuring an LOI (limiting oxygen index) value according to an ISO 4589 method. The polymer

showed a high LOI value of 31. The LOI can be estimated by Van Krevelen and Hoftyzer equation.<sup>[30]</sup>

$$\text{LOI} = 17.5 + 0.4 Y_c$$

where  $Y_c$  = char yield

Because the char yield of B-PE was 46.06, the calculated LOI value was about 36, which was similar to the measured value. Thermal properties of the polymers are summarized in Table 1. The flame retardant property of cyclotriphosphazenes is well known. The thermooxidative reaction of cyclotriphosphazenes yields the dense and rigid char during combustion. The protective char layer on the surface of the network disturbs heat and oxygen diffusion. Simultaneously, the nonflammable gasses such as  $\text{CO}_2$ ,  $\text{NH}_3$  and  $\text{N}_2$  from the cyclotriphosphazene moieties disrupt combustion.<sup>[24]</sup>

## **II-4. Conclusions**

In this study, we synthesized and characterized cyclotriphosphazene based epoxy resins as low dielectric materials. All of these polymers showed low dielectric constants of 2.18 ~ 2.39 and dielectric losses of  $4.97 * 10^{-3}$  ~  $6.13 * 10^{-3}$ . The polymers also had excellent thermal properties, showing a high LOI value and high char yields. The cyclotriphosphazene based epoxy polymers with good thermal properties and low di

electric properties could be used as advanced insulating materials in high frequency and large scale integration.

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## **Chapter III.**

# **Porous Cyclotriphosphazene-Based Polymers for CO<sub>2</sub> Capture**

### III-1. Introduction

Since CO<sub>2</sub> is considered as the prime contributor to global warming, there are great interests in the CO<sub>2</sub> capture and storage as well as the reduction of CO<sub>2</sub> emissions from fossil fuel combustion.<sup>[1, 2]</sup> Several classes of microporous materials are under investigation for the CO<sub>2</sub> capture such as porous organic frameworks (POFs),<sup>[3-8]</sup> metal-organic frameworks (MOFs)<sup>[9-13]</sup> and activated carbons.<sup>[14-16]</sup>

High cross-linked polymers (HCPs) are another important class of porous materials, which have high surface areas and good physicochemical stability. HCPs have been synthesized by various coupling reactions of rigid multifunctional monomers. For example, a series of porous networks were synthesized by the Friedel-Crafts alkylation reaction of dichloroethylene (DCX), bis(chloromethyl)biphenyl (BCMBP).<sup>[17]</sup>

In this study, cyclotriphosphazene-based porous polymers (PCPs) were synthesized as potential sorbents for CO<sub>2</sub> capture. The polymers showed microporosity and high surface areas. They were expected to have enhanced CO<sub>2</sub> adsorption ability because of the Lewis-acid /base interactions between the electron-rich heterocycles and the electron-poorer carbon dioxide molecules.<sup>[18-20]</sup>

## III-2. Experiment

**Materials.** Hexachlorocyclophosphazene (HCCP) (99%), 2,2'-biphenol (99%) were obtained from ACROS Organics. Sodium hydride (dry, 95%), *a,a'*-dichloro-*p*-xylene (DCX), 4,4'-bis(chloromethyl)-1,1'-biphenyl (BCMBP) and iron(III) chloride (97%) were purchased from Sigma-Aldrich. Dichloroethane (DCE) was purchased from Junsei. Tetrahydrofuran (THF) was purchased from Duksan Pure Chemical and distilled with sodium before use.

**Synthesis of  $[\text{N}_3\text{P}_3(\text{O}_2\text{C}_{12}\text{H}_8)_3]$  (1).** This compound was synthesized according to the literature with a minor modification.<sup>[21]</sup> A mixture of 2,2'-biphenol (0.81 g, 4.32 mmol), NaH (0.25 g, 10.4 mmol) in dry THF (40 mL) was stirred for 90 min at room temperature. HCCP (0.50 g, 1.44 mmol) was added to the mixture and stirred at room temperature for 24 h. The volatiles were evaporated in vacuo, and the residue was stirred in water for 1 h. The solution was washed with methanol. White powder was obtained by vacuum filtration.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) :  $\delta$  7.52-7.56 (d, 4H, Ph), 7.43-7.48 (t, 6H, Ph), 7.25-7.38 (t, 12H, Ph)

**Synthesis of PCP-1.** This compound was synthesized according to the

literature with a minor modification.<sup>[22]</sup> Compound **1** (0.69 g, 1.00 mmol) and DCX (1.05 g, 6.00 mmol) were dissolved in DCE (15 mL). FeCl<sub>3</sub> (1.95 g, 12.0 mmol) was added and stirred 24 h at 80 °C. The product was filtered and washed with methanol and purified by Soxhlet extraction in methanol for 24 h. Brown powder was obtained by vacuum filtration. <sup>13</sup>C NMR: δ 136.75-129.01 (d, Ph), 36.24 (s, methylene).

**Synthesis of PCP-2.** This compound was prepared by following the procedure for the preparation of PCP-1. Compound **1** (0.69 g, 1.00 mmol) and DCX (0.70 g, 4.00 mmol) were added in DCE (15 mL). FeCl<sub>3</sub> (1.30 g, 8.00 mmol) was added and stirred 24 h at 80 °C. The product was filtered and washed with methanol and purified by Soxhlet extraction in methanol for 24 h. Brown powder was obtained by vacuum filtration. <sup>13</sup>C NMR: δ 136.69-128.77 (d, Ph), 35.58 (s, methylene).

**Synthesis of PCP-3.** This compound was prepared by following the procedure for the preparation of PCP-1. Compound **1** (0.69 g, 1.00 mmol) and DCX (1.40 g, 8.00 mmol) were dissolved in DCE (20 mL). FeCl<sub>3</sub> (2.59 g, 16.0 mmol) was added and stirred 24 h at 80 °C. The product was filtered and washed with methanol and purified by soxhlet extraction in methanol for 24 h. Brown powder was obtained by vacuum filtration. <sup>13</sup>C NMR: δ 136.55-128.85

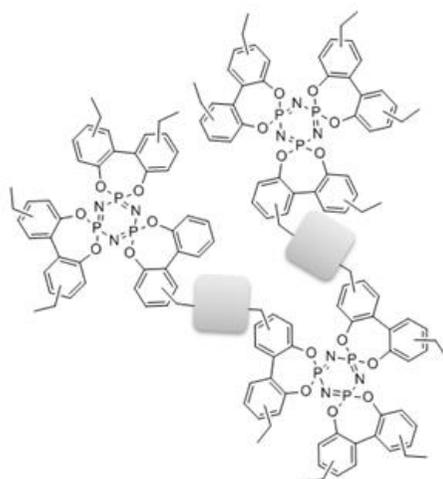
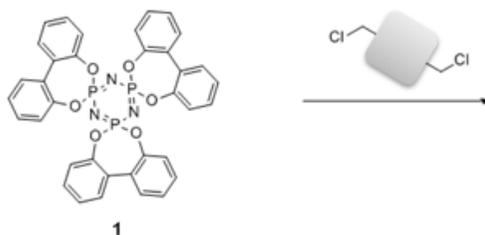
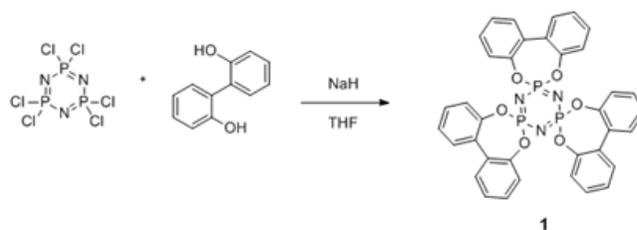
(d, Ph), 35.12 (s, methylene).

**Synthesis of PCP-4.** This compound was prepared by following the procedure for the preparation of PCP-1. Compound **1** (0.69 g, 1.00 mmol) and BCMBP (1.51 g, 6.00 mmol) were dissolved in DCE (15 mL). FeCl<sub>3</sub> (1.95 g, 12.0 mmol) was added and stirred 24 h at 80 °C. The product was filtered and washed with methanol and purified by soxhlet extraction in methanol for 24 h. Brown powder was obtained by vacuum filtration. <sup>13</sup>C NMR: δ 136.71-128.59 (d, Ph), 37.61 (s, methylene).

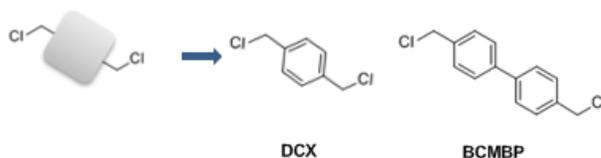
**Instrumental Characterization.** <sup>1</sup>H NMR spectra were recorded by a Bruker Avance 300 (300 MHz) spectrometer. <sup>13</sup>C solid NMR spectra were recorded by Bruker Avance II spectrometer (125 MHz). The FT-IR spectra were measured by a Nicolet 6700 (Thermo Scientific, USA) using ATR Acc. N<sub>2</sub> adsorption-desorption isotherms, pore size distribution and CO<sub>2</sub> uptake properties were investigated by a Belsorp-Max (BEL Japan, Inc.) apparatus. Elemental analysis was performed by a Vision-EA (Isoprime, UK).

### III-3. Results and Discussion

#### III-3-1. Monomer Synthesis and Polymerization



PCP



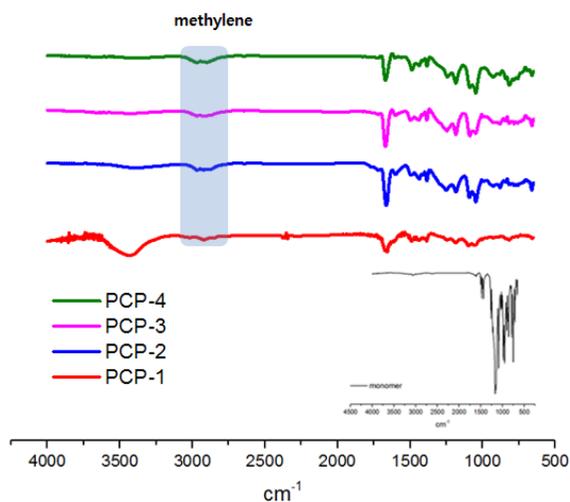
**Scheme III-1.** Scheme presentation for the synthesis of PCP-1,2,3 and 4.

Porous cyclotriphosphazene-based polymers (PCPs) were prepared according to Scheme III-1. Six chlorines of HCCP were replaced by the reaction with sodium salts of 2,2'-biphenol to give compound **1**. The Friedel-Craft reaction of compound **1** with DCX or BCMBP in the presence of a Lewis acid was carried and to yield a cross-linked polymer. We chose DCE as a reaction solvent because the oxygenated solvent interacted with the iron active species, preventing them to react with the alkyl chloride.<sup>[23]</sup> The polymers were isolated by filtration and washed with methanol. Further purification was conducted by Soxhlet extraction using methanol for 24 h. Four polymers (PCP-1 – PCP-4) were prepared with changing a molar ratio of compound **1** and DCX or replacing DCX by BCMBP. (Table III-1)

Sample code	Monomer : DCX ( mol : mol )	Monomer : BCMBP ( mol : mol )
PCP-1	1 : 6	-
PCP-2	1 : 4	-
PCP-3	1 : 8	-
PCP-4	-	1 : 6

**Table III-1.** Molar ratios of the monomer and linkers for the synthesis of PCPs.

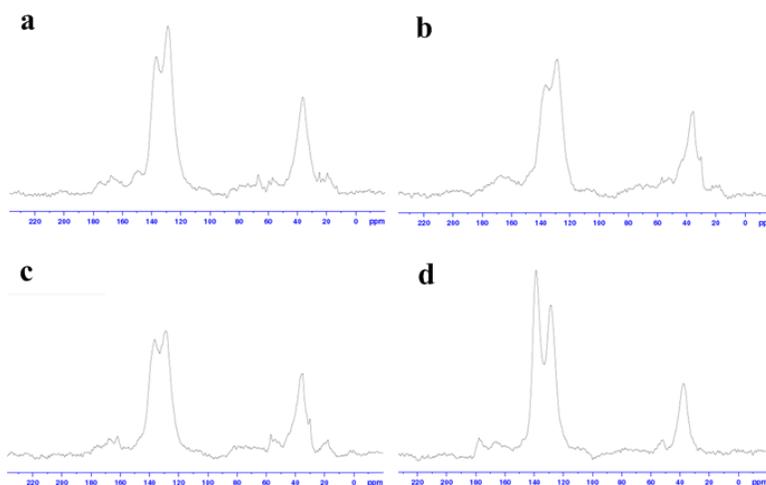
The structures of PCPs were conformed by solid-state  $^{13}\text{C}$  NMR and FT-IR spectroscopy.



**Figure III-1.** FT-IR spectra of PCP-1 - 4 and the monomer  $\text{N}_3\text{P}_3(\text{O}_2\text{C}_{12}\text{H}_8)_3$ .

In the FT-IR spectra, of the polymers, the characteristic stretching vibrations of P-O-Ph, P-N-P and P-O-C were observed at 1270, 1173 and 953  $\text{cm}^{-1}$ , respectively. The peak at about 2920  $\text{cm}^{-1}$  was assigned to the C-H stretching vibrations of methylene groups, indicating that the aromatic rings were linked by methylene groups. (Figure III-1).

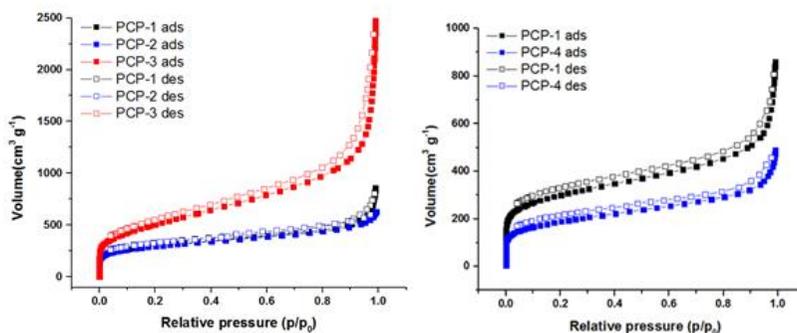
In the solid-state  $^{13}\text{C}$  NMR spectra, the carbon peaks at around 38 ppm were assigned to the methylene linkers. The peaks at about 136 ppm and 130 ppm corresponded to the substituted phenyl carbons (Figure III-2).



**Figure III-2.** Solid-state  $^{13}\text{C}$  CP/MAS NMR spectra of (a) PCP-1, (b) PCP-2, (c) PCP-3 and (d) PCP-4.

### III-3-2. Properties of PCPs

Nitrogen adsorption-desorption isotherms of PCPs measured at 77K are shown in Figure III-3. All the nitrogen adsorption-desorption isotherms showed rapid uptake at low relative pressures. With changing of a linker ratio, the Brunauer-Emmett-Teller (BET) surface areas of the polymers also changed. PCP-3 showed the highest BET surface area of  $1322.9 \text{ m}^2\text{g}^{-1}$ . PCP-1 and PCP-2 had surface areas of  $1090.6 \text{ m}^2\text{g}^{-1}$  and  $1056.8 \text{ m}^2\text{g}^{-1}$ , respectively. PCP-4 prepared using BCMBP as a longer linker showed a lower BET surface area of  $671.4 \text{ m}^2\text{g}^{-1}$  than those from DCX. (Table III-2)

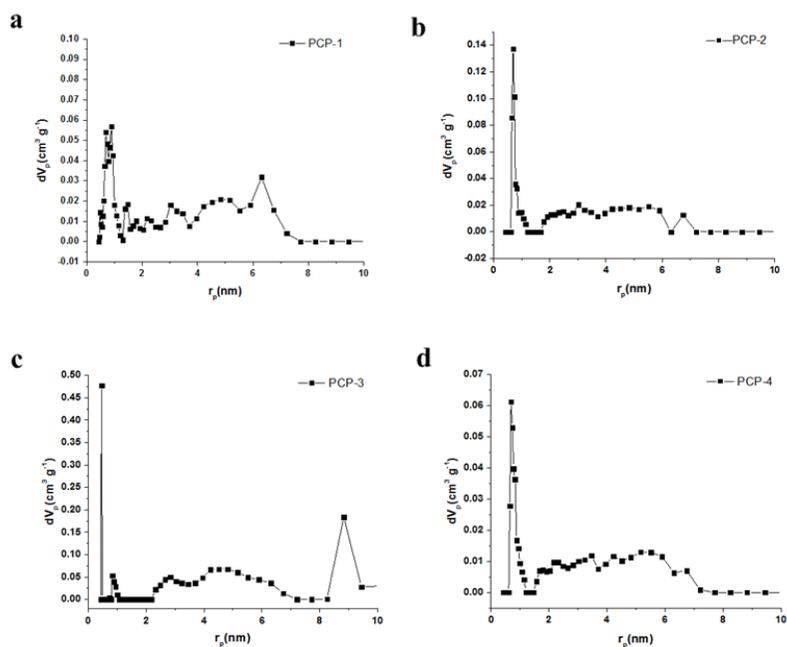


**Figure III-3.** Nitrogen adsorption/desorption isotherms for PCP-1,- 2, -3 and -4 at 77 K. (Adsorption : filled symbols; desorption : open symbols)

Polymer	Surface area / m <sup>2</sup> g <sup>-1</sup>	Mean pore diameter (nm)	CO <sub>2</sub> uptake (wt%)
PCP-1	1090.6	5.13	14.0
PCP-2	1056.8	3.84	12.0
PCP-3	1322.9	4.60	12.4
PCP-4	671.4	4.71	8.08

**Table III-2.** Porosity properties and gas uptake capacities of the polymers.

Figure III-4 shows the pore size distribution (PSD) calculated by nonlocal density functional theory (NL-DFT). Table III-2 summarizes the porosity properties and gas uptake capacities of the resultant polymers.



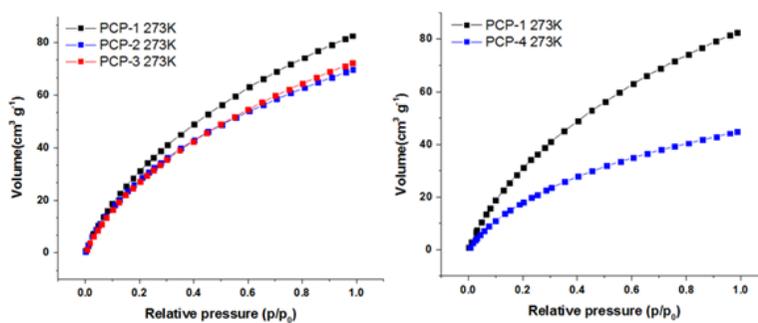
**Figure III-4.** Pore size distribution curves of (a) PCP-1 (b) PCP-2 (c) PCP-3 and (d) PCP-4 calculated by NL-DFT method.

HCPs synthesized *via* Friedel-Craft alkylation showed has BET surface areas and microporous structures. Cyclotriphosphazene-containing porous organic frameworks were reported to have high  $\text{CO}_2$  adsorption ability due to the electron-rich structure.<sup>[18]</sup> It is known that through an Lewis acid/ base reaction, nitrogen atoms effectively catch  $\text{CO}_2$  molecules. The nitrogen contents of PCP-1, -2, -3, and PCP-4, measured by the elemental analysis, were 3.00, 3.05, 2.92 and 3.17 wt%, respectively (Table III-3). The  $\text{CO}_2$  uptake behaviors of the polymers were measured at 273K (Figure III-5). PCP-

1, 2, 3 and 4 showed the CO<sub>2</sub> adsorption of 14.0, 12.0, 12.4 and 8.08 wt%, respectively. PCP-1 showed the highest CO<sub>2</sub> adsorption.

Polymer	N (wt%)	C (wt%)	H (wt%)
PCP-1	3.00	71.9	5.45
PCP-2	3.05	69.5	4.96
PCP-3	2.92	71.9	5.40
PCP-4	3.17	70.9	5.41

**Table III-3.** Elemental compositions of the PCP-1,2,3 and 4 measured by elemental analysis.



**Figure III-5.** CO<sub>2</sub> adsorption isotherms of PCP-1,2,3 and 4 measured at 273 K.

### **III-4. Conclusions**

We synthesized cyclotriphosphazene-based porous polymers via a Friedel-Crafts alkylation. The polymer networks showed attractive BET specific surface areas up to  $1322.9 \text{ m}^2\text{g}^{-1}$  and good  $\text{CO}_2$  uptake properties due to the  $\text{CO}_2$ -philic nitrogen atoms. We demonstrated the possibility that the porosities and adsorption properties of the polymers could be controlled by adjusting the cross-linker length and the molar ratio of a cross-linker to the cyclotriphosphazene monomer.

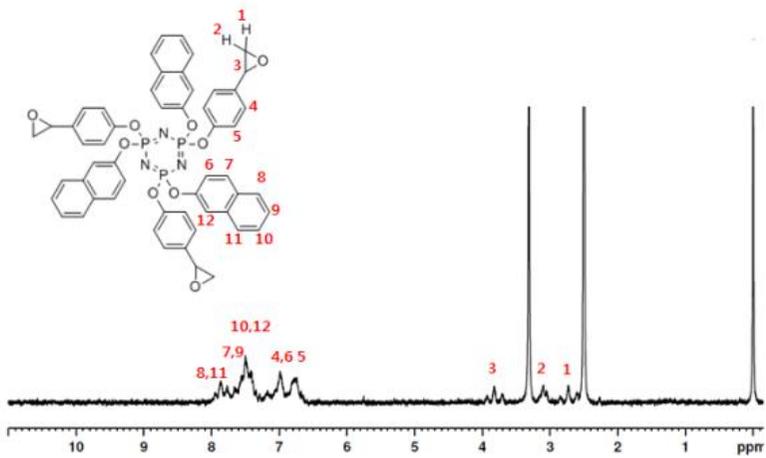
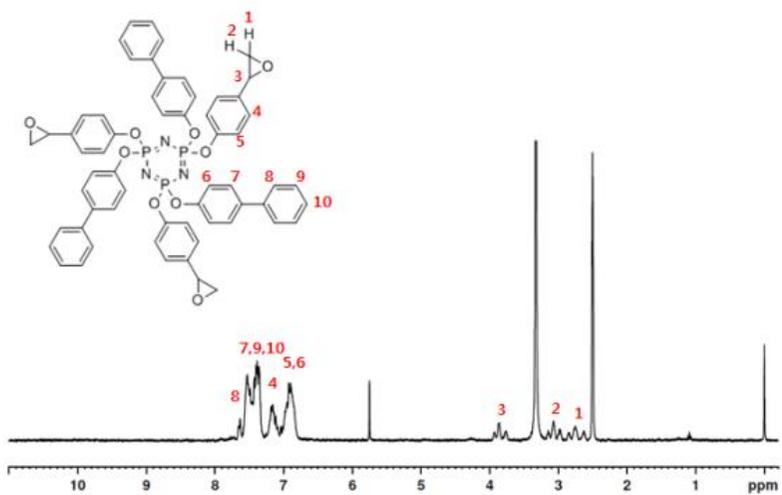
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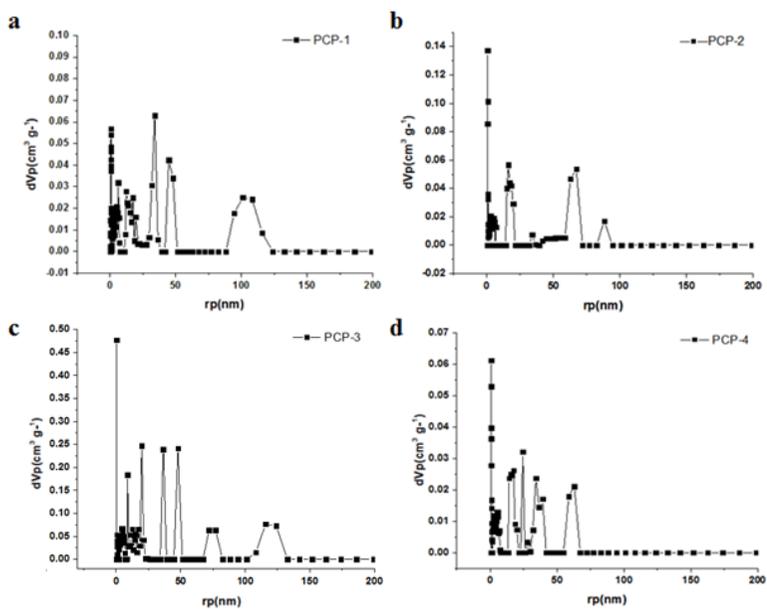
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# Appendix



**Appendix II-1.**  $^1\text{H}$  NMR spectrum of the epoxy monomer P-PE and N-PE.



**Appendix III-1.** Pore size distribution curves of (a) PCP-1 (b) PCP-2 (c) PCP-3 and (d) PCP-4 from micro-size to macro-size calculated by NL-DFT method.

## 국문요약

Cyclotriphosphazene은 인과 질소 원자로 구성된 고리형 구조를 갖는 화합물로, 인 원자에 연결된 두 개의 치환기에 따라 다양한 물리, 화학적 특성을 지닌다. 본 연구에서는 반응성 cyclotriphosphazene들을 합성하고 이를 기능성 재료의 제조에 이용하였다.

첫 번째로 저 유전 특성 및 난연 특성을 갖는 cyclotriphosphazene 기반 에폭시 고분자의 제조에 대해 연구하였다. Hexachlorocyclotriphosphazene 의 염소 일부를 에폭시 기능기로 치환하고 나머지 염소를 2,2'-biphenol (B-PE), 4-phenylphenol (P-PE), 또는 2-naphtol (N-PE)로 치환하여 cyclotriphosphazene 단량체를 합성하고, 이를 active ester 유형의 경화제와 반응시켜 가교된 에폭시 경화물을 얻었다. 이렇게 얻어진 에폭시 경화물은 5% 무게 감소 온도가 300도 이상인 높은 열적 안정성을 보였다. B-PE, P-PE 또는 N-PE 치환체를 함유한 고분자들은 10 GHz 측정 조건에서 각각 2.19, 2.39 및 2.18의 매우 낮은 유전 특성을 보였으며 유전 손실을 역시  $6.08 \times 10^{-3}$ ,  $6.13 \times 10^{-3}$  및  $4.97 \times 10^{-3}$ 로 매우 낮았다. B-PE 경화물의

난연성을 측정한 결과 LOI 지수 31 수준으로 매우 우수하였다.

두 번째로, cyclotriphosphazene을 활용한 다공성 고분자를 합성하였다. Biphenol로 치환된 cyclophosphazene과  $\alpha,\alpha'$ -dichloro-p-xylene 또는 4,4'-bis(chloromethyl)-1,1'-biphenyl의 Friedel-crafts alkylation 반응을 통하여 다공성 고분자를 합성하였다. 다공성 고분자들은  $671 \sim 1322 \text{ m}^2\text{g}^{-1}$  의 높은 BET 표면적을 가졌고 273 K, 1 bar 측정조건에서 8 ~ 13 wt%의 CO<sub>2</sub> 흡착 능력을 보였다.

**주요어:** Cyclotriphosphazene, 에폭시, 저 유전율, 난연 특성, 다공성 고분자, 이산화 탄소 흡착

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