

Preparation and Characterization of Novel Flame Retardant (Aliphatic phosphate)Cyclotriphosphazene-Containing Polyurethanes

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ABSTRACT: A novel reactive flame retardant, (4-diethoxyphosphoryloxyphenoxy)(4-hydroxyphenoxy)cyclotriphosphazene (EPPZ), was prepared and characterized by FTIR, ³¹P-NMR, and ¹H-NMR analyses. Polyurethanes that contain (aliphatic phosphate)cyclotriphosphazene, with various phosphorus contents, were prepared from EPPZ, poly(propylene glycol), 1,4-butanediol, and 2,4-toluene diisocyanate. The polyurethanes were characterized by measurements of FTIR, TGA, DSC, limiting oxygen index (LOI), and tensile testing. The results indicated that the EPPZ-containing polyurethanes prepared in this study have higher glass-transition temperature, higher tensile strength, lower temperature of degradation, and

higher char yield residues than those of the pure polyurethane. The activation energies at various degradation stages for the polyurethanes were calculated by Ozawa's method. The LOI of the EPPZ-containing polyurethane was increased with increasing EPPZ content and the polyurethanes showed flame-extinguishable behavior. Moreover, it was found that the effect of the flame retardancy of the polyurethanes took place primarily in the condensed phase. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1357–1364, 2003

Key words: polyurethanes; flame retardance; cyclotriphosphazenes; chain; limiting oxygen index (LOI)

INTRODUCTION

Polyurethanes are particularly versatile polymeric materials and have been extensively applied in various areas, such as construction, automobiles, and biomaterials.¹ They are synthesized in reactions of polyether-based or polyester-based diols and diisocyanates, followed by the introduction of chain extenders to form macromolecules.

Generally, polyurethanes do not exhibit sufficient flame retardancy and are easily burned. Therefore, emphasis on the development of technologies to promote flame retardancy and create flame-retardant materials has recently increased.^{2–4} Among these materials, organophosphorus compounds, which generate negligible amounts of toxic gas and smoke, have demonstrated high efficiency as flame retardants for polyurethane.

The flame retardancy of polyurethane can be improved by adding flame retardants, which are divided into two groups: additive type and reactive type. The additive approach may be simple, although the

reactive approach, which incorporates flame-retardant-containing chemical units directly into a polymer backbone, is considered more effective. The main advantage of using the reactive-type flame retardants is the ability to confer permanent flame retardancy and, simultaneously, to maintain the original physical and mechanical properties of the polymer in a better way. Therefore, the study of incorporating phosphorus-containing groups onto the polymer backbone has attracted much attention recently.^{5–11}

Organocyclotriphosphazene materials,^{12–14} with phosphorus and nitrogen atoms in a ring, are known to exhibit good flame retardancy. Therefore, it is anticipated that the incorporation of both phosphate groups and cyclotriphosphazene rings into the polyurethane will increase its phosphorus content and improve the flame retardancy more effectively.

In this study, a novel reactive flame retardant aliphatic phosphate-containing cyclotriphosphazene, (4-diethoxyphosphoryloxyphenoxy)(4-hydroxyphenoxy)cyclotriphosphazene (EPPZ), was synthesized. The EPPZ-containing polyurethanes, EPPZ-PU, were then prepared from EPPZ, poly(propylene glycol) (PPG-3000), 1,4-butanediol (1,4-BD), and 2,4-toluene diisocyanate (TDI). All the polymers prepared were characterized by FTIR, TGA, DSC, limiting oxygen index (LOI), and tensile testing, and compared to the pure polyurethane.

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TABLE I
Composition of the EPPZ-PU Samples^a

| Sample | PPG-3000 | EPPZ | 1,4-BD | TDI |
|------------|----------|-------|--------|-------|
| PPG-PU | 61.35 | 0.00 | 11.69 | 26.96 |
| EPPZ-PU-10 | 54.35 | 6.04 | 11.68 | 27.93 |
| EPPZ-PU-20 | 47.55 | 11.89 | 11.68 | 28.89 |
| EPPZ-PU-30 | 40.97 | 17.56 | 11.68 | 29.79 |
| EPPZ-PU-40 | 34.58 | 23.05 | 11.70 | 30.66 |
| EPPZ-PU-50 | 28.38 | 28.38 | 11.69 | 31.54 |

^a In weight percentage.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) was kindly provided by Nippon Fine Chemical Co. (Tokyo, Japan). Poly(propylene glycol) with $M_w = 3000$ (PPG-3000) was kindly supplied by Arco Chemical Co. TDI and 1,4-BD were purchased from Aldrich Chemical (Milwaukee, WI). Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from Merck (Darmstadt, Germany). Triethylamine (TEA) was purchased from R.D.H. Chemical Co. THF was dried and distilled before use.

Synthesis of hexakis(4-methylphenoxy)cyclotriphosphazene (MPP) and hexakis(4-hydroxyphenoxy)cyclotriphosphazene (HPP)¹⁵

A suspension of sodium 4-methoxyphenoxide in dry THF (250 mL) was prepared from 4-methoxyphenol (106.9 g, 0.86 mol) and sodium hydride (20.7 g, 0.86 mol) under a dry nitrogen atmosphere. A THF solution (100 mL) of $N_3P_3Cl_6$ (50 g, 0.14 mol) was added dropwise, and the reaction mixture was maintained at reflux for 24 h with vigorous stirring. The product was isolated by precipitation into methanol. It was washed several times to remove NaCl and oven-dried overnight at 80°C. The yield of MPP was 95.6 g (76.2%).

A solution of boron tribromide (0.1 mol, 9.8 mL) in CH_2Cl_2 (50 mL) was added dropwise to a solution of 15 g (0.017 mol) of MPP in CH_2Cl_2 (50 mL). The reaction mixture was stirred at room temperature for 3 h and then poured into 100 mL of water. A white solid was collected by filtration, washed several times with water, and dried by vacuum distillation to obtain 13.2 g (97.1%) of HPP.

Synthesis of EPPZ¹⁵

A solution of HPP (6.7 mmol) in 100 mL of dry THF was prepared in a flask with a stirrer, reflux condenser, and a nitrogen inlet. To this solution, 3.68 mL of distilled dry TEA and a small amount of CuCl was added. The flask was kept in an ice bath, and a 3-equiv ratio solution of diethylchlorophosphate (22.8 mmol)

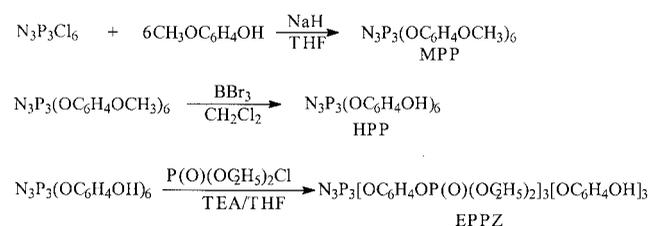
in 50 mL of dry THF was added dropwise over a period of 30 min. The system then became increasingly viscous because of the precipitation of amine hydrochloride. After the system had been maintained at 0°C for 2 h, it was further reacted at room temperature for another 24 h. The produced amine hydrochloride salt was separated by filtration and the solvent was removed under distillation. The residue obtained was then dissolved in CH_2Cl_2 , washed several times in water, and dried over magnesium sulfate. Finally, this solution was vacuum-distilled and EPPZ was obtained and identified as $N_3P_3[OC_6H_4OP(O)(OC_2H_5)_2]_{2.94}(OC_6H_4OH)_{3.06}$ (yield: ~ 67%).

Preparation of the polyurethanes

The polyurethanes that contained EPPZ (EPPZ-PU) were prepared from various ratios of TDI, PPG-3000, 1,4-BD, and EPPZ in three-neck flasks, using DMF as a solvent. Table I lists the recipes of all the PU samples. The mixtures were refluxed at 80°C under a nitrogen atmosphere and stirred for 6 h. The reaction solution was subsequently poured into water. The polyurethanes were obtained, then washed with water and dried overnight in a vacuum oven at 80°C. To make film samples, the polyurethanes were dissolved in THF and placed carefully into Teflon molds, after which the solvent was removed at 100°C for 24 h.

Measurements

¹H, ¹³C, and ³¹P nuclear magnetic resonance (NMR) spectra were obtained using a Bruker AC 200 spectrometer (Bruker Instruments, Billerica, MA). An 85% H_3PO_4 aqueous solution assigned to 0 ppm was used as an external reference for the ³¹P-NMR spectra. By convention, the ¹H- and the ¹³C-NMR spectra were referenced to tetramethylsilane. FTIR spectra were recorded by a Bio-Rad FTS-7 FTIR spectrometer (Bio-Rad, Hercules, CA). Elemental analysis was performed for C, H, and N using a Perkin-Elmer elemental analyzer (Perkin Elmer Cetus Instruments, Norwalk, CT) with acetanilide as a standard. A Seiko TG/DTA-220 thermal analyzer (TGA; Seiko Instruments, Japan) was used to measure thermal stability at a heating rate of 10°C/min from 30 to 600°C both in



Scheme 1 Synthesis of EPPZ.

TABLE II
Characterization Data for Compounds MPP and HPP

| Compound | Elemental analysis | | | | NMR (ppm) | | | IR (cm ⁻¹) | |
|----------|--------------------|------|-----|-----|-----------|-----------------|---------------------------------|--|---|
| | | %C | %H | %N | %O | ³¹ P | ¹ H | | ¹³ C |
| MPP | Calcd | 57.7 | 4.8 | 4.8 | 22.0 | 10.62 | 3.72 (s, 3H, OCH ₃) | 55.4 (CH ₃) | 1507 (C=C) |
| | Found | 57.5 | 4.8 | 4.8 | 22.0 | | 6.6–6.8 (4H, aromatic) | 114.2 (aromatic) 121.8 (aromatic) 144.3 (aromatic) 156.6 (aromatic) | 1260 (P=N) 1180 (P=N) 1035 (Ph—O—C) 972 (P—O—Ph) |
| HPP | Calcd | 54.8 | 3.8 | 5.3 | 24.3 | 16.09 | 6.71 (s, aromatic) | 116.5 (aromatic) | 3321 (OH) |
| | Found | 54.1 | 3.8 | 5.3 | 25.0 | | | 122.5 (aromatic) 144.1 (aromatic) 155.2 (aromatic) | 1505 (C=C) 1255 (P=N) 1182 (P=N) 960 (P—O—Ph) |

nitrogen and in air. DSC measurements were obtained using a Seiko SSC-5200 calorimeter (Seiko Instruments, Japan), at a heating rate of 10°C/min under nitrogen atmosphere. The mechanical properties were determined using a Bionix 850 material testing system (MTS Systems Corp., Eden Prairie, MN). Tensile tests of the polyurethanes were measured according to ASTM-D638. The LOI values were used to evaluate the flammability of the polyurethane samples according to ASTM-D2863.

RESULTS AND DISCUSSION

Characterization of MPP, HPP, and EPPZ

The aliphatic phosphate- and hydroxyl-containing cyclotriphosphazene, EPPZ, was synthesized according to **Scheme 1**. Hence, the hydroxyl group-containing cyclotriphosphazene, HPP, was prepared by reaction of N₃P₃Cl₆ with 4-methoxyphenol to obtain MPP and followed by reduction with an excess of BBr₃.¹⁶ Then, HPP was reacted with diethylchlorophosphate, through partial phosphorylation, to give EPPZ.

The structures of both cyclotriphosphazenes, MPP and HPP, were confirmed by FTIR and NMR (¹H, ¹³C, and ³¹P) spectroscopies. The corresponding data are listed in Table II. The only sharp singlets at δ values of

10.62 and 10.07 ppm in the ³¹P-NMR spectra of the two compounds indicate complete and equivalent substitution of the chlorines in the parent N₃P₃Cl₆.

The ¹H- and ¹³C-NMR spectra unambiguously identified the various functional groups attached to the cyclotriphosphazene ring. The singlets in ¹H-NMR at δ = 3.72 ppm and in ¹³C-NMR at δ = 55.4 ppm are the characteristic peaks of the methoxy group in MPP. These peaks disappeared from the spectrum of HPP, thus verifying the structure. The results are similar to those reported elsewhere.¹⁵

The functionalized cyclotriphosphazene EPPZ was also characterized by FTIR and ¹H- and ³¹P-NMR spectra. Table III presents the corresponding data. As shown in the FTIR spectrum of EPPZ (Fig. 1), the strong absorption peaks between 1262 and 1185 cm⁻¹ correspond to P=N stretching in the cyclotriphosphazene ring and the strong absorption peak at 3272 cm⁻¹ corresponds to the free -OH stretching in the hydroxyphenoxy (-OC₆H₄OH) group. The absorption at 1033 cm⁻¹ for the P(O)—O—CH₂— linkage and the strong absorption peaks at 953 cm⁻¹ for -P—O—Ph support the phosphate and the phenoxy-substituted cyclotriphosphazene ring structure.

TABLE III
Characterization Data for the Compound EPPZ

| Sample | Elemental analysis | | | | NMR (ppm) | | | IR (cm ⁻¹) | |
|--------|--------------------|------|------|------|-----------|-----------------|--|--|---|
| | | %C | %H | %N | %O | ³¹ P | ¹ H | | ¹³ C |
| EPPZ | Calcd | 48.2 | 4.79 | 3.53 | 28.0 | 9–10 (P=N) | 4.1–4.3 (m, 2H, OCH ₂ CH ₃) | 15.9 (OCH ₂ CH ₃) | 3272 (OH) |
| | Found | 48.5 | 4.78 | 3.51 | 28.4 | -5.7 (P=O) | 1.3–1.4 (t, 3H, OCH ₂ CH ₃) 6.8–7.0 (4H, aromatic) | 64.4 (OCH ₂ CH ₃) 115.7 (OC ₆ H ₄ OH) 121.4 (OC ₆ H ₄ OH) 142.1 (OC ₆ H ₄ OH) 154.6 (OC ₆ H ₄ OH) 121.0 [OC ₆ H ₄ OP(O)] 121.7 [OC ₆ H ₄ OP(O)] 146.7 [OC ₆ H ₄ OP(O)] 147.2 [OC ₆ H ₄ OP(O)] | 1505 (C=C) 1260~1185 (P=N) 1170 (P=N) 1033 [P(O)—O—CH ₂] 953 (P—O—Ph) |

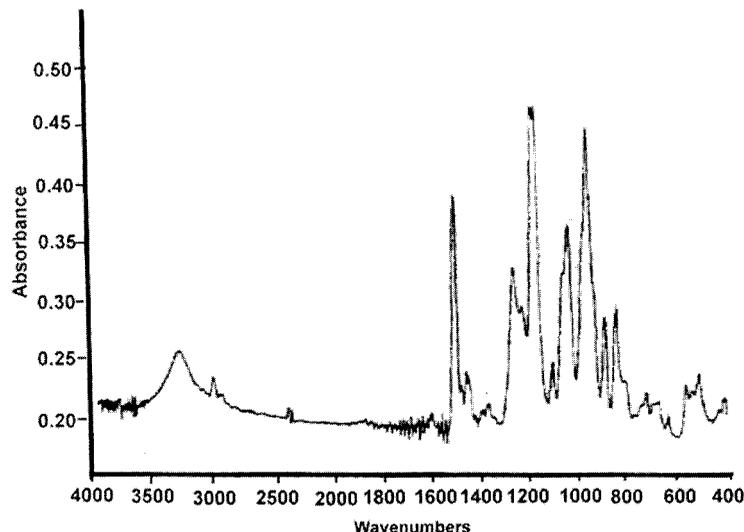


Figure 1 FTIR spectrum of EPPZ.

As expected, the $^1\text{H-NMR}$ spectrum of EPPZ showed a multiplet between 7.01 and 6.83 ppm associated with the aromatic phenoxy protons ($-\text{OC}_6\text{H}_5$), a multiplet between 4.24 and 4.09 ppm ($-\text{OCH}_2\text{CH}_3$), and a triplet between 1.37 and 1.26 ppm ($-\text{OCH}_2\text{CH}_3$) associated with the ethoxy group of the phosphate.

Because the (4-diethoxyphosphoryloxyphenoxy) $[(\text{OC}_2\text{H}_5)_2\text{OC}_6\text{H}_4\text{OP}(\text{O})]$ and 4-hydroxyphenoxy ($\text{HOC}_6\text{H}_4\text{O}$) groups have similar shielding effects on the phosphorus atoms of the cyclotriphosphazene ring, the $^{31}\text{P-NMR}$ spectrum of EPPZ showed an overlapping multiplet peak between 9 and 10 ppm that was difficult to resolve, whereas a singlet peak at -6.26 ppm was assigned to the phosphorus of the diethyl phosphate group. This result confirms the occurrence of phosphorylation and supports the structure of EPPZ.

Synthesis and characterization of the EPPZ-PU

The polyurethane that contains aliphatic phosphate and cyclotriphosphazene, EPPZ-PU, was prepared by reacting PPG-3000, 1,4-BD, and EPPZ with TDI, according to the recipe of Table I. The reaction was monitored by FTIR measurements of the reaction solution and was considered completed when the strong absorption band near 2270 cm^{-1} assigned to the diisocyanate group disappeared completely. The reaction conditions for preparing EPPZ-PU samples were examined by DSC thermogram of the mixture of the reactants and compared to that for preparing PPG-PU, the pure polyurethane without EPPZ. The reactivity of these systems was determined as the starting temperatures of the exothermic peaks. As shown in Figure 2, the maximum exothermic peak for the reac-

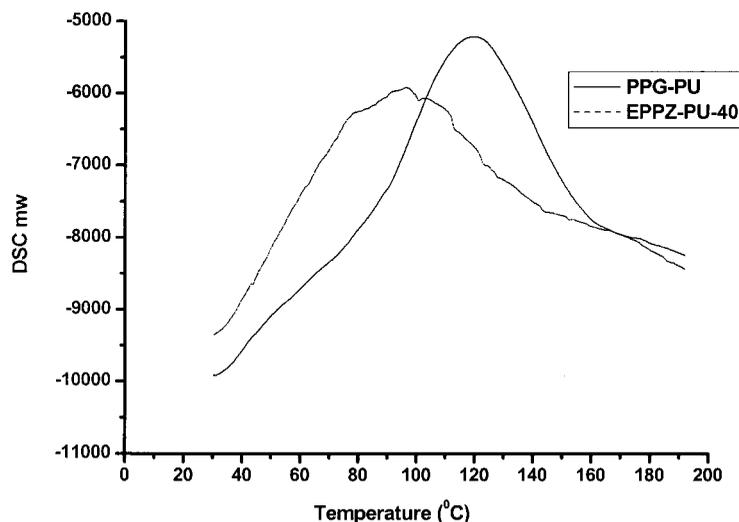


Figure 2 DSC thermograms of the reactants of EPPZ-PU-40 and PPG-PU.

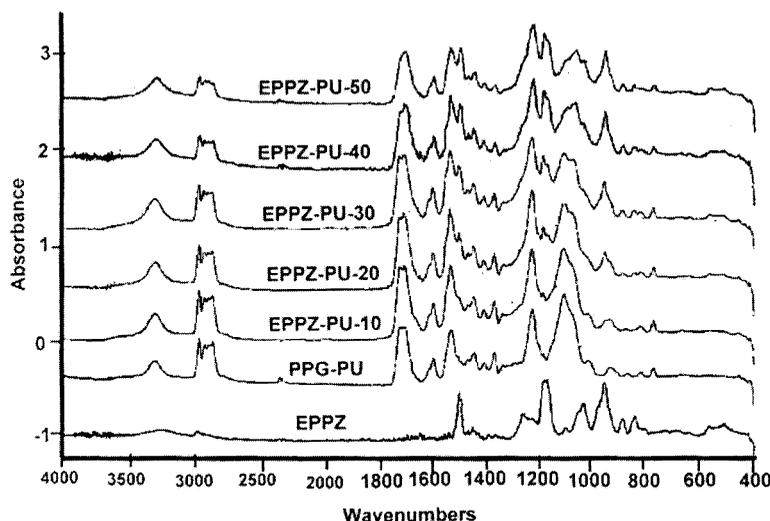


Figure 3 FTIR spectra of the polyurethanes.

tants of PPG-PU is at 119°C, which decreased when EPPZ was added. For EPPZ-PU-40, the maximum peak temperature decreased to 93°C. This reveals that EPPZ is more reactive than PPG-3000 toward isocyanate. Restated, EPPZ accelerated the polymerization of the polyurethane. This acceleration is ascribed to the electronic effect caused by the phenyl group of EPPZ. The polymerization of the polyurethane is considered to occur by nucleophilic attack of the hydroxy group on the diisocyanate of TDI. Hence, the electron-donating effect by the phenyl group in EPPZ increases the electron density of the hydroxyl group and promotes the reaction between the diisocyanate and the hydroxy group.

The FTIR spectroscopies characterize all the synthesized polyurethanes. As shown in Figure 3 the absorption bands at 3340–3250 cm^{-1} for NH stretching, 1540 cm^{-1} for NH deformation, and 1740–1708 cm^{-1} for C=O stretching all relate to the urethane structure. As may be observed, when the EPPZ content in the polyurethane increases, the intensities of the characteristic bands peaked at around 1260 and 1182 cm^{-1} for P=N, 953 cm^{-1} for P—O—Ph, 1033 cm^{-1} for P(O)—O—CH₂, and 1500 and 1600 cm^{-1} for the aromatic ring in the EPPZ increase significantly, relative to the intensity of the C=O bands in the 1747–1708 cm^{-1} region. These results confirm the formation of the urethane units between EPPZ and TDI.

Thermal and mechanical properties of the polyurethanes

The thermal properties of the polyurethanes were investigated by DSC thermograms measured in a nitrogen atmosphere.

As shown in Figure 4, the polyurethanes with various EPPZ contents exhibit different thermal properties. A reproducible, endothermic baseline shift for

PPG-PU corresponding to the glass-transition temperature (T_g) is observed, but was not apparent with the increase of EPPZ. Table IV indicates that EPPZ-PU displays higher T_g values than that of PPG-PU and the T_g values of these polymers increase from -56.5°C to about -35.8°C , when the content of EPPZ was increased to 50%. This is reasonable given that PPG-PU contains C—C—O linkages in the backbone that render the polymer more flexible than EPPZ-PU, which contains more rigid cyclotriphosphazene and phenyl rings.

The mechanical properties of the polyurethanes are typically determined by intermolecular bonding, the domain size of the hard-segment region, and the capacity of strain-induced crystallization of the soft segment. Figure 5 presents the stress-strain curves of the prepared polyurethanes. As may be noticed, when the content of EPPZ gradually increases, the tensile strength increases and the elongation decreases. This

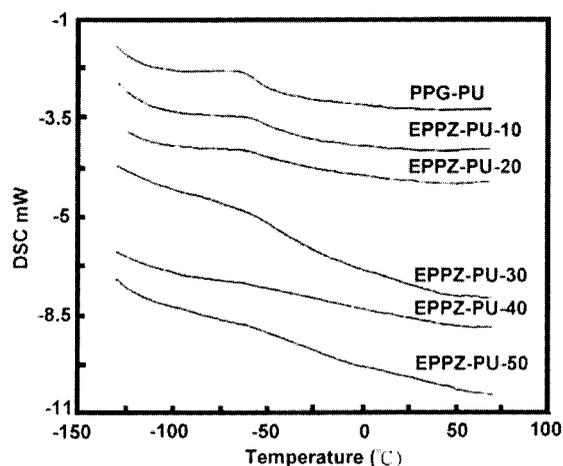


Figure 4 DSC thermograms of the polyurethanes.

TABLE IV
Thermal Analysis Data and LOI Values of the Polyurethanes^a

| Sample | $T_{5\%}$ (°C) | $T_{\max 1}$ (°C) | $T_{\max 2}$ (°C) | Y_c at 600°C (%) | T_g | LOI |
|------------|-------------------|----------------------|----------------------|--------------------|---------|------|
| EPPZ | 264.4 | 268.7 | 505.1 | 44.9 | — | — |
| PPG-PU | 279.4 | 327.9 | 372.6 | 0.0 | -56.1 | 23 |
| EPPZ-PU-10 | 275.9 | 302.8 | 380.1 | 4.2 | -50.7 | 23.5 |
| EPPZ-PU-20 | 261.7 | 283.1 | 379.2 | 7.9 | -47.5 | 24 |
| EPPZ-PU-30 | 258.0 | 279.4 | 379.0 | 10.2 | ~ -43.7 | 24 |
| EPPZ-PU-40 | 256.2 | 277.8 | 379.0 | 16.1 | ~ -38.2 | 25 |
| EPPZ-PU-50 | 256.0 | 277.6 | 379.0 | 19.1 | ~ -35.8 | 25.5 |

^a Under nitrogen atmosphere.

is attributed to an increase of the crosslink density caused by the formation of urethane units between multifunctional EPPZ and TDI and the rigid structure of the backbone resulting from the rigid rings of the cyclotriphosphazene and phenyl groups at the crosslink junctions.

Thermal decomposition of the polyurethanes

The thermal decomposition properties of the polyurethanes were investigated by TGA in both nitrogen and air. Figure 6 presents the TGA thermograms of the polyurethanes and EPPZ in nitrogen. As one may observe, the decomposition of EPPZ is a two-stage degradation. The first stage of the degradation at around 250–270°C is considered to be the decomposition of the phosphate groups that caused formation of the phosphorus-rich residues to inhibit further decomposition,¹⁷ and the second stage degraded at around 500°C is ascribed to the cleavage of the phenoxy groups, as found in other phenoxycyclotriphosphazene compounds.¹⁸ The high char yield found is as high as 57%, implying that EPPZ is an effective flame retardant. On the other hand, a one-stage degradation occurring at 347°C is observed for PPG-PU, whereas a

two-stage degradation behavior is obtained for EPPZ-PU samples as observed for EPPZ. Therefore, as the concentration of EPPZ increases, the initial degradation temperature of EPPZ-PU decreases accordingly and the two-stage degradation behavior becomes more obvious. Table IV indicates that for EPPZ-PU the maximum degradation temperature of the first stage ($T_{\max 1}$) decreases as the concentration of EPPZ increases, whereas that of the second stage ($T_{\max 2}$) increases slightly. The behavior has been found in most phosphorylated polymers and is attributed to the relatively easy thermal degradation of the phosphate segments of the EPPZ contents.^{19–21} In addition, at 600°C the EPPZ-PU samples show higher char yields than those of PPG-PU. This is attributed to formation of the thermally stable polyphosphate in the condensed phase at a high-temperature range. The increase in char yield with EPPZ content also implies that the flame retardancy of the EPPZ-PU materials may be increased accordingly.

Figure 7 shows the TGA curves of the various PU samples measured in air. As noticed, the 5% weight loss temperature ($T_{5\%}$) is almost the same as that ob-

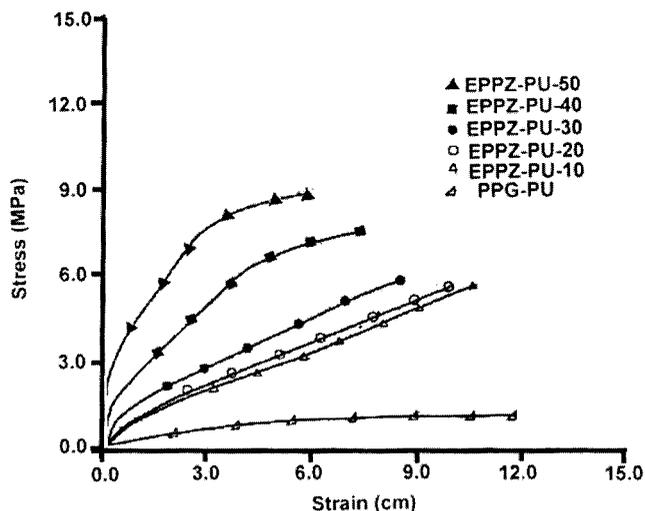


Figure 5 Stress-strain curves of the polyurethanes.

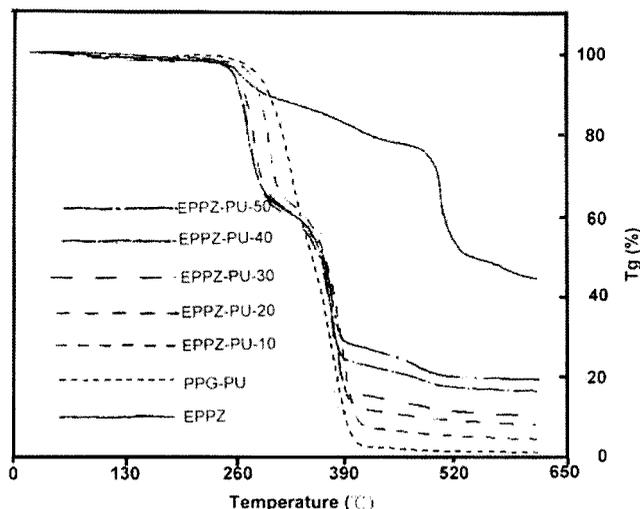


Figure 6 TGA thermograms of the polyurethanes under nitrogen atmosphere.

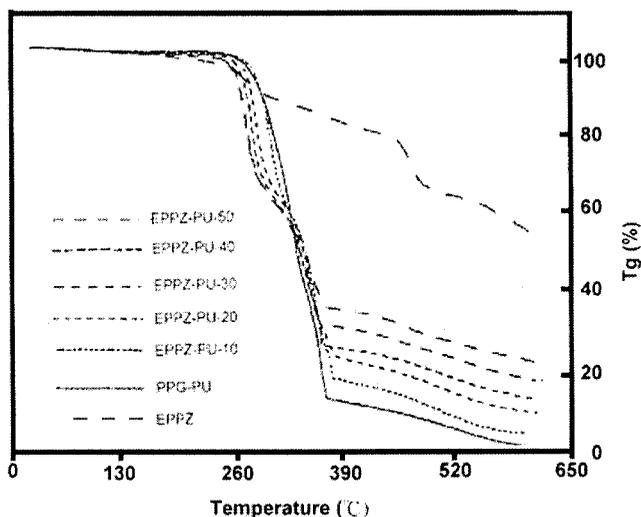


Figure 7 TGA thermograms of the polyurethanes under air atmosphere.

tained in N_2 , indicating that the EPPZ-PU polymers have similar thermal stabilities in air and in nitrogen. Nevertheless, the char yields at 600°C measured in air are higher than those measured in nitrogen.

Flame retardancy of the polyurethanes

As indicated by the char yields obtained from the TGA analysis, the flame retardancy of the EPPZ-PU polymer is predicted to be improved as EPPZ is increased. To confirm this, the flame retardancy of the polyurethanes was evaluated by the LOI values measured according to ASTM-D2863. However, because a dripping phenomenon was found during the measurements, the LOI values obtained were expected to be underestimated. Nevertheless, as listed in Table IV, the LOI values of the EPPZ-PU polymers are greater than that of PPG-PU and increase with an increase of EPPZ concentration. As shown in Figure 8, the LOI value increases with phosphorus content, indicating that the flame retardancy of the EPPZ-PU polymer is attributed to the presence of the

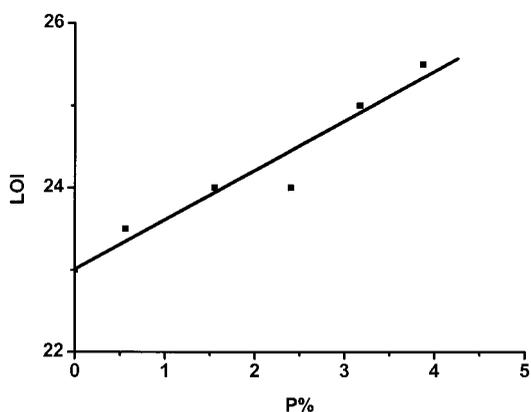


Figure 8 Effect of phosphorus content on the LOI value.

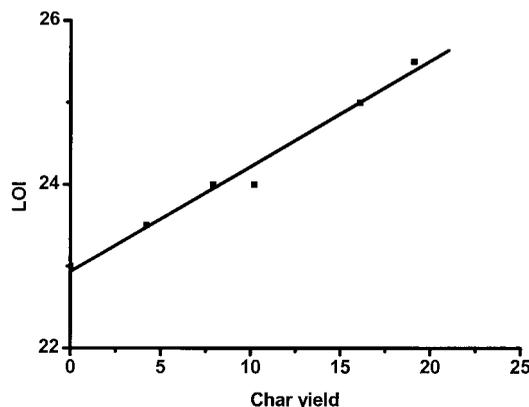


Figure 9 Effect of char yield on the LOI value.

phosphorus element in EPPZ. Besides, Figure 9 shows that the LOI value linearly increases with the char yield, as proposed by Van Krevelen,²² suggesting that the effect of the flame retardancy of the polyurethane takes place primarily in the condensed phase.

Activation energy of degradation

To study the possible mechanism of degradation and the possible behavior of the flame retardancy of the EPPZ-PU polymers during pyrolysis, the activation energies of the degradation (E_a) were calculated by following the isoconversional method proposed by Ozawa.²³ Accordingly, several TGA curves at different heating rates (β) were measured and the relationships of $\log \beta$ versus $1/T$ for each value of the degree of conversion ($\alpha =$ weight loss at a given temperature/total weight loss of degradation) were plotted as shown in Figure 10. The E_a value was then calculated for each conversion from these isoconversional curves

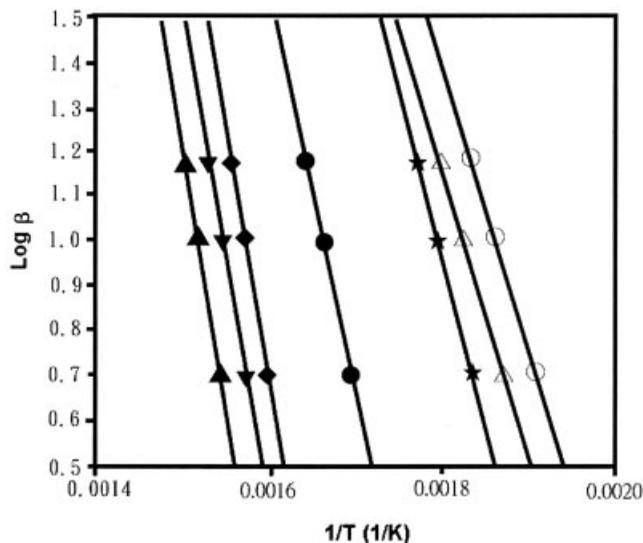


Figure 10 Dependency of logarithm of the heating rate ($\log B$) versus the $1/T$ of EPPZ-PU-40 measured in nitrogen.

TABLE V
Apparent Activation Energies at Different Conversions for Polyurethanes Under Thermal Degradation in N₂

| Sample | Activation energy, E_a | | | | | | | |
|------------|--------------------------|--------|--------|--------|--------|--------|--------|--------|
| | Conversion, α^a | | | | | | | |
| | 0.1 | 0.2 | 0.3 | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 |
| PPG-PU | 143.63 | 157.75 | 161.2 | 195.55 | 191.6 | 192.1 | 198.32 | 191.19 |
| EPPZ-PU-10 | 137.22 | 142.58 | 146.16 | 193.51 | 204.99 | 204.12 | 207.94 | 206.16 |
| EPPZ-PU-20 | 143.59 | 148.58 | 152.36 | 194.42 | 213.98 | 200.99 | 205.7 | 213.56 |
| EPPZ-PU-30 | 128.71 | 145.94 | 138.98 | 185.51 | 207.41 | 208.4 | 205.19 | 201.86 |
| EPPZ-PU-40 | 135.66 | 130.54 | 136.19 | 164.53 | 204.99 | 208.63 | 209.03 | |
| EPPZ-PU-50 | 114.06 | 118.1 | 135.45 | 158.62 | 208.56 | 205.03 | 209.05 | |

^a $\alpha = [100 - \text{wt \% of TGA}]/100$.

and was averaged over the whole range of conversion (80%) for each degradation stage. Because these straight lines display excellent linearity for the polyurethanes as shown in Figure 10 for EPPZ-PU-40, the E_a values were calculated from the slopes of the lines according to the following equation:

$$E_a = -(\text{slope} \times R)/0.457$$

where R is the gas constant.²³

The E_a values of the samples at various degradation stages are listed in Table V, from which one may observe that the activation energies of the EPPZ-PU are smaller than those of PPG-PU, and decrease with increasing EPPZ content in the first stage of degradation ($0.1 \leq \text{conversion} \leq 0.4$), whereas it tends to increase in the second stage of degradation ($0.5 \leq \text{conversion} \leq 0.8$). The finding supports the result reported by Grassie and Scott²⁴, that is, in the first stage, the thermal degradation was accelerated by the dehydration caused by the degraded products of the phosphate segment in EPPZ, and in the second stage, the activation energies were increased because of the formation of thermally stable compounds produced from the reaction of carbodiimide with polyphosphoric acid produced from the first stage of EPPZ's degradation. Such residues retarded the flammability of the EPPZ-PU polymers. The results indicate that the effect of flame retardancy of the EPPZ-PU polymers takes place primarily in the condensed phase and is in agreement with the result of LOI values discussed above.

CONCLUSIONS

The cyclotriphosphazene that contains aliphatic-phosphate and free-hydroxy groups, EPPZ, was successfully synthesized. It was used as a reactive flame retardant to incorporate with PPG, 1,4-butanediol to react with TDI to synthesize a series of the EPPZ-containing polyurethanes. Compared with the pure polyurethane PPG-PU, the EPPZ-containing polyurethanes prepared in this study had higher T_g and tensile strength. These polyurethanes show lower thermal stability than that of PPG-PU, but are still thermally stable up to 250°C. The LOI

values show that with sufficient amounts of EPPZ the polyurethanes are flame extinguishable. In addition, it is believed that the effect of the flame retardancy of the EPPZ-containing PU polymers occurs in the condensed phase.

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