

Flame-Retarding Materials—I. Syntheses and Flame-Retarding Property of Alkylphosphate-Type Polyols and Corresponding Polyurethanes

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ABSTRACT: In this research, oligomeric polyalkyl phosphate-type polyols (P% = 14–17) were synthesized from ethylene glycol or 1,4-butanediol (PBE or PBB) by means of butyl phosphorodichloridate, which was prepared from phosphorus oxychloride and butanol. These polyols were then reacted with isocyanate to form the corresponding polyurethanes (PETD and PBTU). These polyols were characterized by FTIR, ¹H-NMR, and ³¹P-NMR, and the thermal stabilities were measured by thermogravimetry analysis. The degradation phenomena were traced by FTIR and interpreted in terms of the degradation and formation of bonds. The corresponding polyurethanes were also characterized by FTIR and ¹H-NMR, and their thermal stability was also studied by thermogravimetry analysis. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1635–1643, 1998

Key words: alkylphosphate-type polyols; polyurethanes; flame-retarding properties

INTRODUCTION

Flame retardants have been widely used for plastics, rubbers, coatings, and fibers in the industries for electronics, architecture, transportation, and components.¹ These flame retardants can be divided into organic materials like phosphorus compounds and halogenated compounds, or inorganic materials like metal oxides,² metal hydroxides,³ and metal borates.^{4,5} Recently, nonhalogenated flame retardants have been desired in many countries; thus, the phosphorus type of flame retardant have attracted a lot of attention both for academic and industrial purposes.

The organic or inorganic phosphorus compounds for flame retardants are used either by blending with polymers or by reacting onto polymers. Phosphorus compounds exhibit their function in the gas state and/or in solid-state fire protection.^{6,7} For the former, it can quench flammable particles like H[•] and HO[•].⁸ For the latter, it can form a polyphosphoric acid-like glass upon heating to protect the burning surface,^{9–11} or it can form inflammable P-C char by reacting with organic components.

Polyols are important intermediates for polyurethane, which are used for PU foam^{12,13} and artificial leathers, where inflammability is requested for many applications. Thus, to synthesize an effective and economic phosphorus-containing polyol is meaningful to industry.

In our laboratory, phosphorus-containing co-

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polymers were synthesized for antiwear purposes,¹⁴ and silica-containing copolymers were prepared as flame-retarding materials.¹⁵ In this study, phosphorus-containing polyols were synthesized from economic starting materials (phosphorus oxychloride, ethylene glycol, and 1,4-butanediol). These polyols were characterized by FTIR, ¹H-NMR, and ³¹P-NMR. Their molecular weights were estimated from ³¹P-NMR^{16,17} and OH values.¹⁸ Their thermal properties were investigated by TGA, and interpreted by the degradation of the polymer chains and by the formation of phosphorus bonds in the char that were monitored by the change in FTIR absorptions. Finally, their flame-retarding abilities were evaluated in terms of the oxygen index, which is calculated from the phosphorus content and the temperature of 50% degradation.

EXPERIMENTAL

Materials

Phosphorus oxychloride (Lancaster, EP grade), ethylene glycol (Merck, EP grade), 1,4-butanediol (Merck, EP grade), 2,4-Tolylene diisocyanate (Merck, ~ 80%), chloroform (Lab-sran, HPLC grade), acetone (Alps, EP grade), dichloromethane (Alps, LC grade). Aluminum chloride (Aldrich, 99%), and dimethyl sulfoxide (Tedia, HPLC grade) were used without further purification.

METHODS

Synthesis

Synthesis of Butyl Phosphorodichloridate^{19,20}

Butanol 37.5 g was added dropwise to 13.0 g of phosphorus oxychloride, agitated by a mechanical stirring bar at -5°C, and the produced HCl was chased out with N₂ gas. The colorless solution stood for a further 10 h at room temperature to complete the reaction. The butyl phosphorodichloridate was purified by vacuum distillation at b.p. 38°C/3 mmHg, with a yield of 80%.

Synthesis of the Alkyl Phosphate Type of Polyol (PBE and PBB)

10.0 g of ethylene glycol and 0.1 g of aluminum chloride in 40 mL of chloroform was refluxed with 26.8 g of butyl phosphorodichloridate under dry conditions for 15 h with constant stirring; then

the solvent was removed with a Rotavapor. About 12 g of polyphosphate (PBE) was obtained by removing the impurities with acetone. The product was a viscous liquid.

The PBB was similarly prepared by using 14.4 g of 1,4-butanediol to replace ethylene glycol and using dichloromethane as the solvent. About 16 g of the colorless powder product (PBB) was obtained.

Synthesis of the Corresponding Polyurethanes (PETD and PBTD)

To the solution of 0.75 g PBE dissolved in 10 g of DMSO, 0.17 g of TDI was added and mixed. The mixture was kept at room temperature for 24 h to complete the reaction. Then the mixture was poured into chloroform, and the precipitate (PETD) was filtered and dried in a vacuum oven for 24 h.

With a similar procedure, 2.45 g PBB and 0.13 g TDI were mixed and purified to obtain PBTD.

Characterization

Fourier Transform Infrared (FTIR) Spectra

The FTIR spectra of PBE, PBB, PETD, and PBTD were recorded using a Nicolet Magna II 550 Fourier transform infrared spectrometer. Each sample was measured by mixing with potassium bromide (KBr) pellet.

³¹P-NMR Spectra

The ³¹P-NMR spectra of 2-HEMA (using D₂O as solvent) was recorded using a Bruker AMX-400 spectrometer.

Elemental Analysis

The elemental analysis of PBE and PBB were conducted by using a Heraeus CHN-O-RAPID element analyzer.

Determination of OH Value

In a dry, 250-mL round-bottomed flask equipped with a stirrer, a condenser fitted with a drying tube and a thermometer was placed a measured amount of polymer sample and 25 mL of a phthalating reagent (42.0 g of phthalic anhydride dissolved in 300 mL of freshly distilled pyridine). A few millimeters of dimethyl sulfoxide (DMSO) were also added to increase the solubility of the polymer sample. The mixture was then stirred

and refluxed at $115 \pm 2^\circ\text{C}$ for 1 h. Upon cooling, the solution was titrated with 0.5 *N* NaOH until a faint pink end point was reached, with 1% of phenolphthalein in pyridine as an indicator. A blank was run on the phthalating reagent to determine the amount of anhydride consumed. The OH number was calculated as follows

$$\text{OH No.} = \frac{56.1 \times N \cdot \text{NaOH} \times (\text{mL} \cdot \text{blank} - \text{mL} \cdot \text{sample})}{\text{sample weight}}$$

To obtain the corrected OH number, the procedure for the measurement of the acid number is described below. The polymer sample was dissolved in a 6/1 of DMSO (or pyridine)/water solution, then titrated with 0.5 *N* NaOH. A blank is run on the phthalating reagent in a similar manner. The acid number was calculated as follows:

$$\text{Acid No.} = \frac{56.1 \times N \cdot \text{NaOH} \times (\text{mL} \cdot \text{sample} - \text{mL} \cdot \text{blank})}{\text{sample weight}}$$

After both values were obtained, the corrected OH number was calculated as shown below.

$$\text{OH No. (corrected)} = \text{OH No.} + \text{Acid No.}$$

Phosphorus Content

The phosphorus content is an indication of flame retardancy. The procedure for measuring the phosphorus content are described below. The phosphorus-containing sample was oxidized with sulfuric acid and perchloric acid, then combined with ammonium molybdate and phosphoric acid to react into phosphomolybdate. This compound turned into molybdenum blue after reduction with ammonium ferrous sulfate. Light absorbance of molybdenum blue was then measured with a Hach DR/2000 colorimeter at 700 μm .

Thermogravimetric Analysis

The thermogravimetric analysis of PBE, PBB, PETD, and PBDT was carried out using a Du Pont SDT 2960 instrument (scan rate $20^\circ/\text{min}$ in nitrogen).

RESULTS AND DISCUSSION

Alkyl phosphate can be obtained by transesterification from triethyl phosphate and alkyl alcohol.

If the alkyl alcohol is a difunctional alcohol like ethylene glycol or 1,4-butanediol, the transesterification is difficult because of steric hindrance where two ends of the ethylene or butylene groups connect to the bulky phosphate groups. Thus, this type of reaction occurs more easily if the triethyl phosphate is changed to a more reactive phosphorus compound like phosphorus oxychloride. Therefore, in this study, the polyphosphates of ethylene glycol and of 1,4-butanediol (PBE and PBB) were synthesized by reacting the ethylene glycol or 1,4-butanediol with butyl phosphorodichloridate (BPC), which in turn was obtained by reacting phosphorus oxychloride with butanol. PBE and PBB were terminated with hydroxyl groups so that they can be used as polyols to react with isocyanates to prepare polyurethanes.

The synthesized BPC was characterized by $^1\text{H-NMR}$. The existence of the butyl groups in BPC was evidenced by the following peaks: $\delta = 0.9$ for CH_3- , $\delta = 4.3$ for the methylene groups next to oxygen, and $\delta = 1.4-1.7$ for other methylene groups. BPC was also characterized by FTIR with the absorption of 1300 cm^{-1} for $\text{P}=\text{O}$, $1000-1100\text{ cm}^{-1}$ for $\text{P}-\text{O}-\text{C}$, $2900-3000\text{ cm}^{-1}$ for $-\text{CH}_2-$ and CH_3- , and 580 cm^{-1} for $\text{P}-\text{Cl}$.

PBE and PBB, synthesized from the condensation of BPC with ethylene glycol and 1,4-butanediol, respectively, were characterized by $^1\text{H-NMR}$ and FTIR. In $^1\text{H-NMR}$ spectra, for both PBE and PBB, peaks are observed at $\delta = 0.86$ for CH_3 , $\delta = 3.3-4.2$ ppm for the methylene groups next to an oxygen atom, and $\delta = 1.2-1.7$ ppm for the other methylene groups [Fig. 1(a) for PBB]. In $^{31}\text{P-NMR}$ spectra, the peaks are at $\delta = -3.6$ to -4.1 ppm for PBE, and at $\delta = -3.6$ to -4.0 ppm for PBB (Fig. 2 for PBB). The peak at $\delta = -3.6$ and at $\delta = -4.1$ corresponds to the P atom at the terminals for which only one side is neighbored by alkylene phosphate and the P atom other other than that at the terminals, respectively.

In FTIR spectra, for both PBE and PBB, the absorptions are observed at 3400 cm^{-1} for $-\text{OH}$, $2850-3000\text{ cm}^{-1}$ for $-\text{CH}_2-$ and $-\text{CH}_3$, $1250-1300\text{ cm}^{-1}$ for $\text{P}=\text{O}$, and $1000-1100\text{ cm}^{-1}$ for $\text{P}-\text{O}-\text{C}$. PBB, as an example, is shown in Figure 1(b).

PBE and PBB are polyols of a polyalkyl phosphate-type polyol, and can react with isocyanates to form polyurethanes. In this study, TDI (toluene diisocyanate) was used to react with PBE and PBB, respectively, at room temperature for 24 h to form the corresponding polyurethanes of PETD and PBDT. In the $^1\text{H-NMR}$ spectra of both PETD

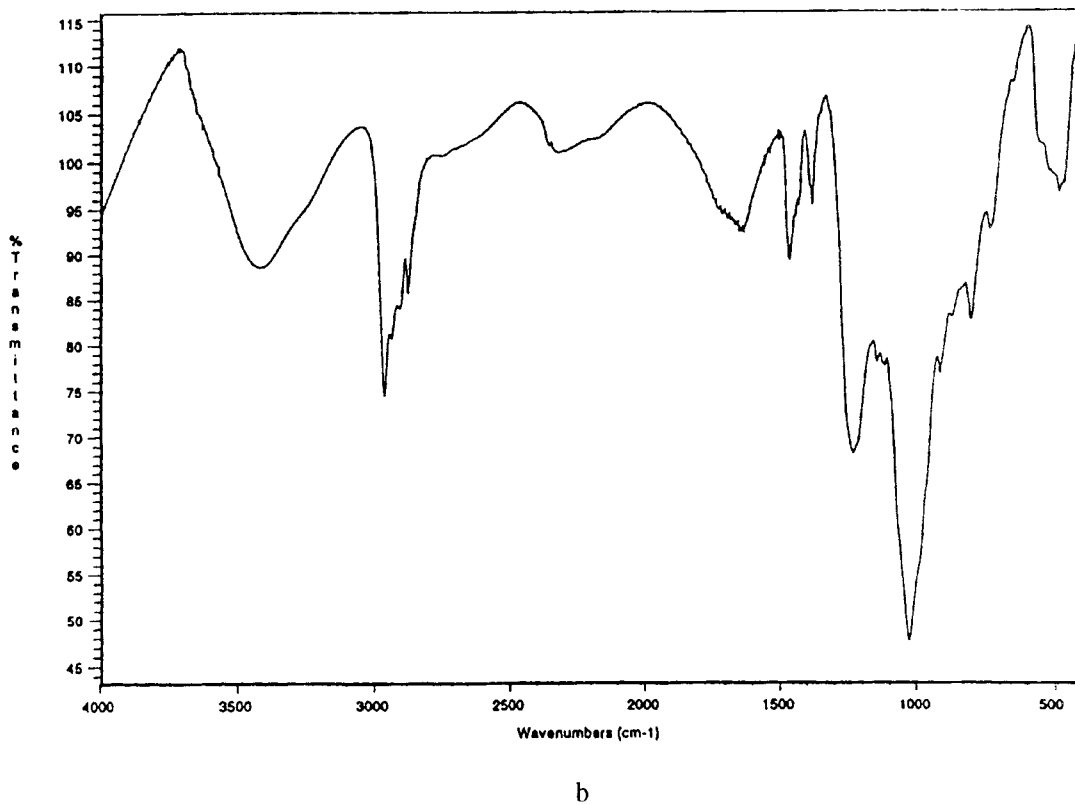
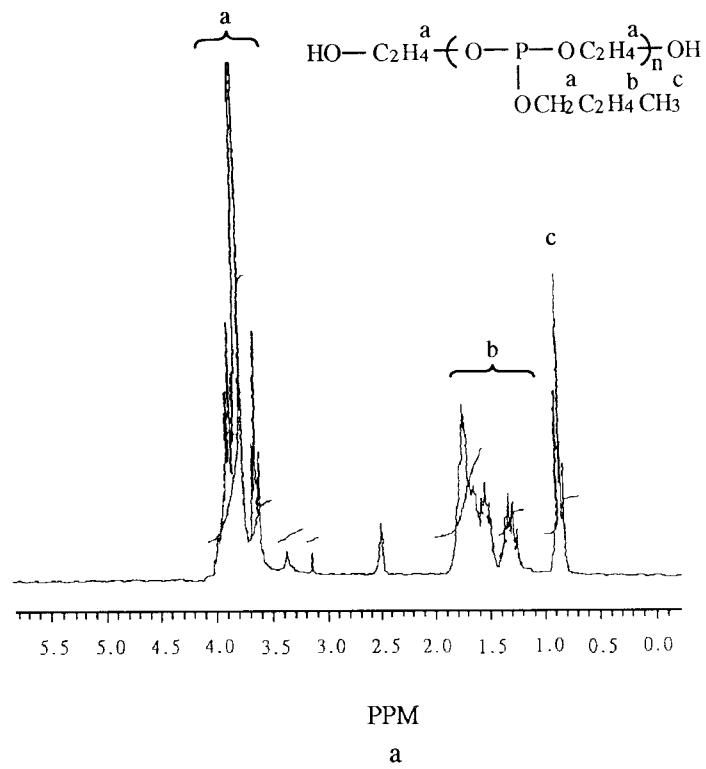


Figure 1 (a) NMR spectrum for PBB, and (b) FTIR spectrum for PBB.

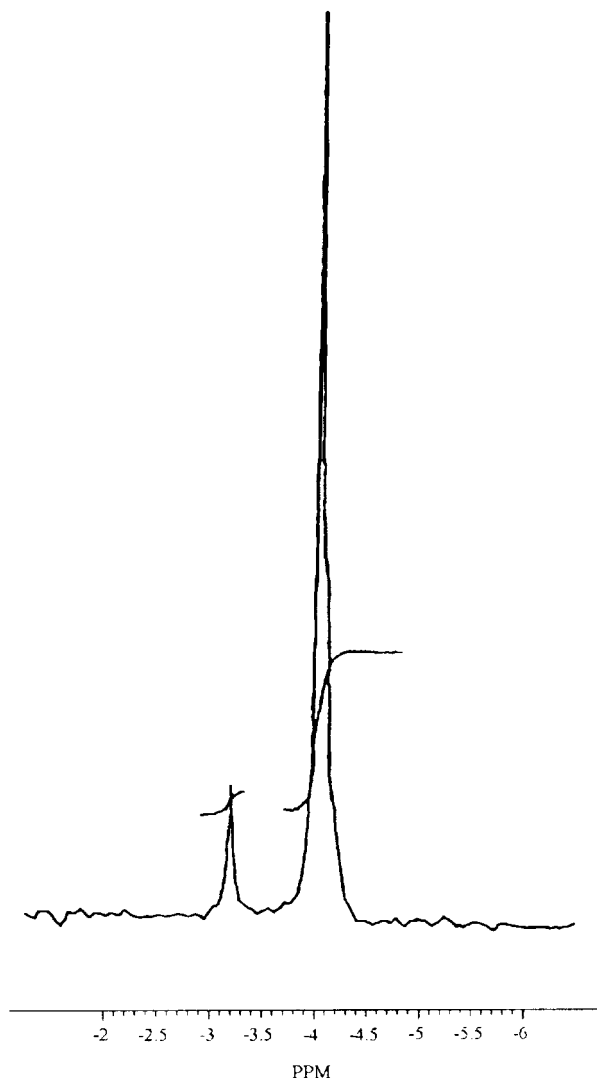


Figure 2 ^{31}P -NMR spectrum for PBB.

and PBTD, the resonances dedicated to PBE and PBB [$\delta = 0.86$, $\delta = 3.3\text{--}4.2$, and $\delta = 1.2\text{--}1.7$ ppm, as shown in Fig. 1(a) for PBB] are observed. Except for these, the peaks from TDI are also seen in the spectra, i.e., $\delta = 2.2$ ppm for CH_3 , and $\delta = 7.0$ ppm for the aromatic ring. [^1H -NMR for PBTD, as an example, is shown in Fig. 3(a)]. In the FTIR spectrum, the peaks of $\text{P}=\text{O}$, $\text{P}-\text{O}-\text{C}$, and $\text{C}-\text{O}$ for PBB in Figure 1(b) also can be observed for PETD and PBTD. Other than those peaks, the peak for NH ($3300\text{--}3400\text{ cm}^{-1}$) can be observed. Figure 3(b) is the FTIR spectrum of PBTD.

The molecular weights of PBE and PBB, can be estimated from OH values that were obtained from the titration of excess phthalic anhydride reacted with PBE and PBB. The OH value is 140–

150 mg KOH/g for PBE and 30–50 mg KOH/g for PBB. Assuming that all of the OH groups are at the terminal sites of PBE and PBB, then the molecular weights for PBE and PBB can be calculated to be 750–800 for PBE and 2240–3700 for PBB. This value can be obtained by ^{31}P -NMR, for example, for PBB, the area ratio of the peak at $\delta = -3.7$ (the P atom at the terminal) to that at $\delta = -4.1$ (the P atom not at the terminal) is 1 : 7 (Fig. 2), and the molecular weight of PBB can be calculated to be 3400. This value is close to that obtained for the OH value. The molecular weight for PBB is higher than that from PBE. This result is reasonable, because ethylene glycol is shorter than 1,4-butanediol and is more crowded for the two hydroxyl groups at the two ends to react with BPC to form the condensate (PBE).

The thermogravimetry degradation analysis (TGA) of PBB and PBE was investigated using a DuPont SDT 2960, with the temperature increasing rate of $20^\circ\text{C}/\text{min}$ under nitrogen (Fig. 4). The residue at 700°C is 17.3% for PBE and 14.6% for PBB. The higher residue for PBE is due to its higher phosphorus content (Table I). For both PBE and PBB, there are two sharp decreases in wt % at 250 and 550°C , corresponding to their first degradation stage and second degradation stage, respectively.²² $T_{0.1}$ for PBE is lower than that of PBB, indicating that the higher phosphorus content for PBE shows lower thermal stability. For PBE the combination of the lower $T_{0.1}$ and the higher residue at 700°C result in a higher $T_{0.5}$ (498°C for PBE and 249°C for PBB). For both PBB and PBE, the wt % keeps constant above 650°C .

The above-mentioned degradation phenomena were further investigated by observing the bond degradation and bond formation at different temperatures using FTIR. The change in the absorptions of PBB for the peaks at around 800 cm^{-1} , 1500 cm^{-1} , and 3000 cm^{-1} was traced at different temperatures, i.e., 200 , 400 , 500 , and 800°C , with the temperature increasing rate of $20^\circ\text{C}/\text{min}$ under nitrogen (Fig. 5). In FTIR spectra, the intensities of the absorptions of PBB at 2960 cm^{-1} and at 1450 cm^{-1} that correspond to the absorptions of methylene groups, decrease as temperature increases from 200 to 800°C . It describes the degradation phenomena of alkylene groups on the backbone or the butyl groups on the side chains of PBE. The absorption at 850 cm^{-1} corresponding to $\text{P}-\text{O}-\text{C}$ decreases as temperature increases from 200 to 500°C , but the peak around 700 cm^{-1} increases sharply at 800°C . The decrease indi-

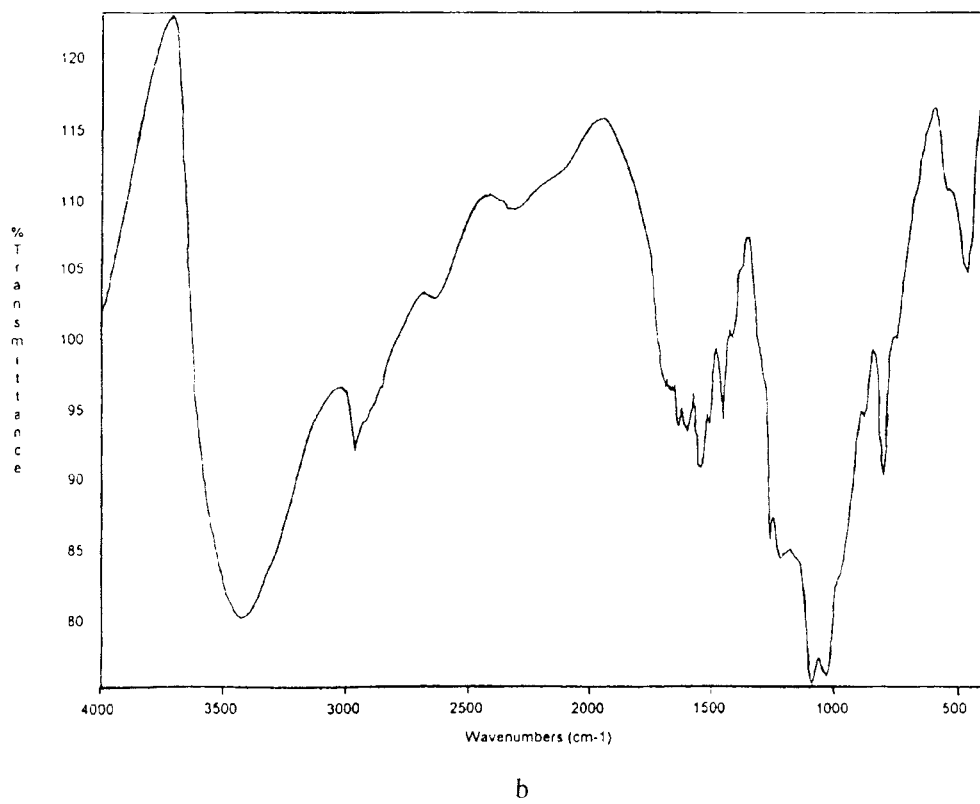
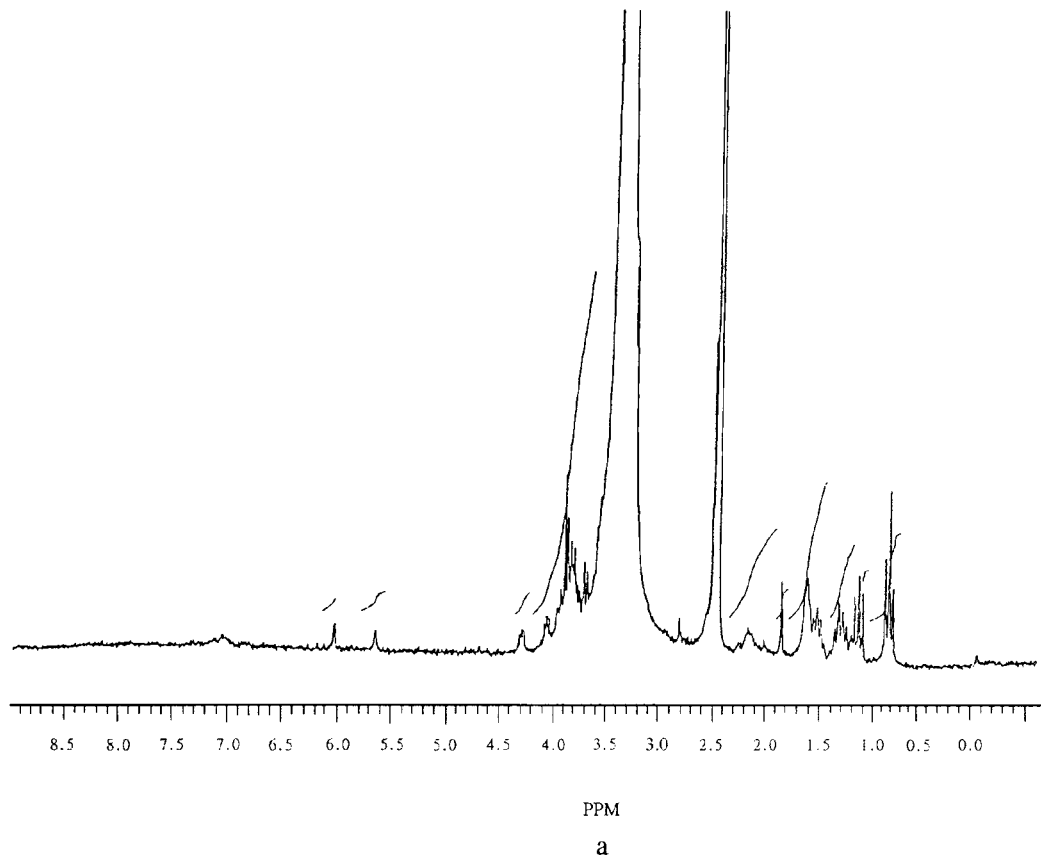


Figure 3 (a) NMR spectra for PBTD, and (b) FTIR spectra for PBTD.

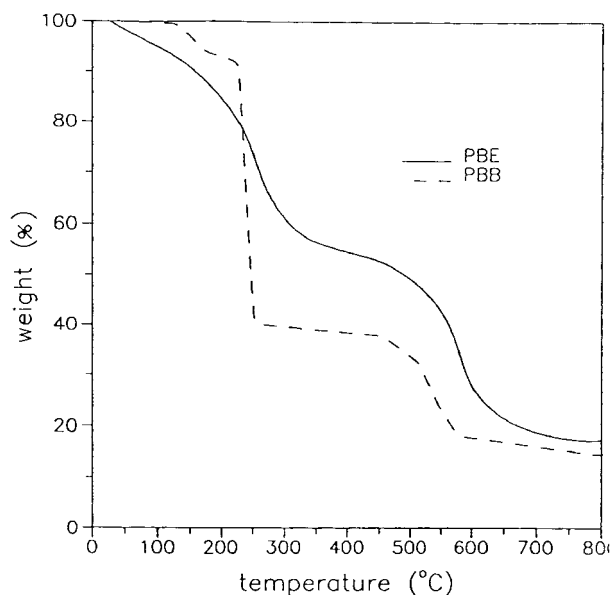


Figure 4 The thermogravimetry analysis (TGA) of PBE and PBB.

icates the degradation of O—C bonds, and the increase probably indicates the formation of P—O—P bonds. The absorptions at 700 cm^{-1} and below 500 cm^{-1} [Fig. 5(a)] correspond to the formation of P=O, P—O—C, and P—O—P bonds and the fragments of methyl or methylene groups.

Figure 6 shows the TGA curves of the corresponding polyurethanes of PBE and PBB (PETD and PBTd, respectively). The residue at 700°C is 39.2% for PETD and 26.3% for PBTd. $T_{0.1}$ for PETD (200°C) is lower than that of PBTd (263°C). The higher residue at 700°C and the lower $T_{0.1}$ for PETD is again due to the higher phosphorus content (Table I). Combination of the fact of higher residue at 700°C and of the lower $T_{0.1}$ show that PETD has a higher $T_{0.5}$ than PBTd (460 vs. 340°C).

Oxygen index (OI)²³ is a good parameter to predict the flame-retarding ability of a material.

It is defined as the oxygen ratio in mixture of N_2/O_2 , under which the sample can just keep burning after it is ignited. For the polyphosphate, the $(\text{OI})_m$ value was reported to be calculated as follows by Annakutty and Kishore in 1988²⁴:

$$(\text{OI})_m = 3.0(\text{TS})^{1/3}(\text{PC})^{1/2}$$

where $(\text{OI})_m$ is defined as the minimum percentage of oxygen required in a nitrogen–oxygen atmosphere, surrounding the sample to maintain its combustion for at least 30 s after ignition. PC is the phosphorus content and TS is the percentage stability defined as “100 – percentage of instability,” i.e., $T_{0.5}/10$ ($T_{0.5}$ is the temperature of 50% weight loss). By using the data in Table I, the $(\text{OI})_m$ value was calculated as 46.3 for PBE and 33.8 for PBB. Material that has an OI value higher than 26 can be regarded as having flame-retarding ability. Comparing this OI value, it shows that both PBE and PBB have very high OI value and can be regarded as effective flame-retarding materials. From $(\text{OI})_m$, PBE has a better flame-retarding ability than PBB. This result coincides with that obtained from char residue data at 800°C , as mentioned above (also see Table I).

Similarly, the $(\text{OI})_m$ values for PETD and PBTd were calculated by the above-mentioned method, i.e., to be 34.6 for PETD and 16.3 for PBTd. Again, PETD has the higher $(\text{OI})_m$ value than PBTd. Compared with PBE and PBB, the corresponding polyurethanes PETD and PBTd have lower $(\text{OI})_m$ values. Even though PETD and PBTd have lower phosphorus contents, they result in rather high $(\text{OI})_m$ values and the accompanying good flame-retarding ability.

CONCLUSIONS

The synthesized BPC was characterized by $^1\text{H-NMR}$, with the peaks: $\delta = 0.9$ for CH_3 —, $\delta = 4.3$

Table I Phosphorous Content, Thermal Degradation Properties, and Oxygen Index of PBE and PBB

Sample	P-content (%)	$T_{0.1}$ ($^\circ\text{C}$) ^a	$T_{0.5}$ ($^\circ\text{C}$) ^b	Char Residue at 800°C (%)	$(\text{OI})_m$
PBE	17.6	156	498	17.3	46.3
PBB	14.9	230	249	14.6	33.8
PETD	10.4	200	460	39.2	34.6
PBTd	2.8	263	340	26.3	16.3

^a Temperature of 10% weight loss.

^b Temperature of 50% weight loss.

for the methylene groups next to oxygen, and $\delta = 1.4\text{--}1.7$ for other methylene groups. Polyols PBE and PBB, and the corresponding polyurethanes PETD and PBTD, were successfully synthesized and characterized by $^1\text{H-NMR}$, $^{31}\text{P-NMR}$, and FTIR. The molecular weights of PBE and PBB were calculated from OH values to be 750–800 for PBE and 2240–3700 for PBB. The thermogravimetry analysis (TGA) of PBB and PBE showed that the higher residue for PBE is due to its higher phosphorus content (Table I). For both PBE and PBB, there are two sharp decreases in wt % at 250 and 550°C, corresponding to their first degradation stage and second degradation stage,

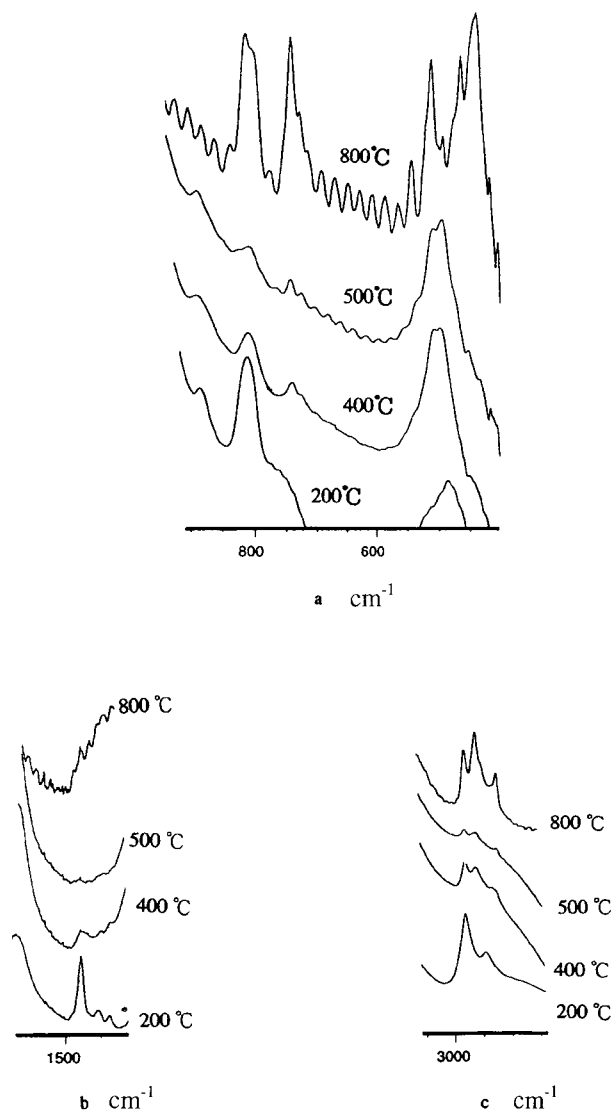


Figure 5 The change in the absorptions of PBB for the peaks at (a) around 800 cm^{-1} , (b) 1500 cm^{-1} , and (c) 3000 cm^{-1} .

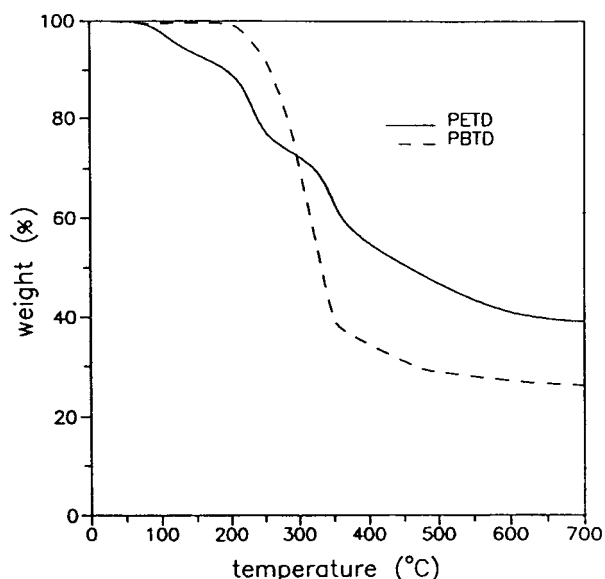


Figure 6 The thermogravimetry analysis (TGA) of PETD and PBTD.

respectively.²² But $T_{0.1}$ for PBE is lower than that of PBB. In FTIR spectra, the intensities of the absorptions of PBB at 2960 cm^{-1} and at 1450 cm^{-1} , as temperature increases from 200 to 800°C , describes the degradation phenomena of alkylene groups on the backbone or the butyl groups on the side chains of PBE. The absorptions at 700 cm^{-1} and below 500 cm^{-1} correspond to the formation of $\text{P}=\text{O}$, $\text{P}-\text{O}-\text{C}$, and $\text{P}-\text{O}-\text{P}$ bonds, and the fragments of the methyl or methylene groups. The $(\text{OI})_m$ values were calculated as 46.3 for PBE and 33.8 for PBB, showing that both PBE and PBB have very high OI values and can be regarded as effective flame-retarding materials. The $(\text{OI})_m$ values for PETD and PBTD were also calculated to be 34.6 for PETD and 16.3 for PBTD.

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