Flame-Retarding Materials. II. Synthesis and Flame-Retarding Properties of Phosphorus-on-Pendent and Phosphorus-on-Skeleton Polyols and the Corresponding Polyurethanes

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ABSTRACT: A phosphorus-on-skeleton compound was synthesized by reacting phenyl dichlorophosphate (PDCP) with 2-hydroxyethyl methacrylate (HEMA). This monomer was then copolymerized with other acrylic monomers to form a hydroxy-containing copolymer, which was then used as the polyol in the synthesis of a polyurethane. Phosphorus-on-pendent copolymers and phosphorus-free copolymers and their corresponding polyurethanes were also prepared for comparison with the phosphorus-on-skeleton material in terms of their flame-retardant properties. The flame retardancy and degradation mechanism of these copolymers and polyurethanes were analyzed with thermogravimetric analysis (TGA) and infrared spectroscopy. Although those phosphorus-on-skeleton copolymer polyols have less flame-retarding ability than that of the phosphorus-on-pendent copolymer polyol because of less phosphorus content, it was evident that the phosphorus-on-skeleton polyurethanes were more effective flame retardants than the phosphorus-on-pendent polyurethanes. This was attributed to the fact that the crosslinking arising from the phosphorus-on-skeleton copolymer polyols has a tremendous effect on the flame-retarding ability of the corresponding polyurethanes. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 343–357, 2001

Key words: phosphorus-on-pendent copolymers; phosphorus-on-skeleton copolymers; flame-retarding ability

INTRODUCTION

Phosphorus compounds have been widely used as flame-retardant materials, which function differently from other retardants such as inorganic materials and halogenated compounds. Phosphorus compounds function either in terms of a gas state or via a solid-state fire-protection mechanism.[1–4] For the former, phosphorus can quench flammable particles such as H· or HO·.[5] For the latter mechanism, these compounds can form glasslike polyphosphoric acid on heating, to protect the burning surface,[6–8] or can form inflammable phosphorus–carbon char by reacting with organic components.

Polyols are important intermediates for polyurethanes, which are the major component in polyurethane foams and artificial leathers, where

inflammability is required for many applications. The organic or inorganic phosphorus compounds are used as typical flame retardants either by blending with polymers or by reacting onto polymers.

In our previous work, alkyl phosphate types of polyols were prepared.[9] In this present study, two acrylic types of polyols were synthesized where (1) the phosphate group is built on the polymer backbone (P1), and (2) the phosphate group is pendent to the polymer chain (P2). P1 and P2 are prepared by copolymerizing hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), and butyl methacrylate (BMA) with di2-methyl-2-[(phenoxyphosphinyl)oxy]ethyl ester (DMPE) and commercial product 2-methyl-2-[(diphenoxyphosphinyl)oxy]ethyl ester (MDPE), respectively. P1 and P2 are then cured by 4,4′-diphenylmethane diisocyanate (MDI) to prepare polyurethane PU1 and PU2, respectively. It was found that the difference in flame-retarding ability between P1 and P2 is small; however, that between PU1 and PU2 is significant.

EXPERIMENTAL

Materials

Phosphorus oxychloride (EP grade; Lancaster Chemicals Ltd., UK), phenol (EP grade; Wako Pure Chemicals, Tokyo, Japan), 2-hydroxyethyl methacrylate (HEMA, EP grade; Acros), methyl methacrylate (MMA, EP grade; Ishizu), butyl methacrylate (BMA, EP grade; Merck, Darmstadt, Germany), 4,4′-diphenylmethane diisocyanate (MDI, EP grade; TCI), toluene (HPLC grade; Tedia), dimethyl sulfoxide (DMSO, HPLC grade; Tedia), benzoyl peroxide (BPO, EP grade; Kanto), sodium hydrogen carbonate (EP grade; Kanto), and anhydrous magnesium sulfate (EP grade; Kanto) were used without further purification.

Methods

Synthesis (Scheme 1)

Synthesis of di2-Methyl-2-[(phenoxyphosphinyl)oxy]ethyl Ester (DMPE). Phosphorus oxychloride (0.33 mol) was placed in a 250-mL four-neck reactor and stirred. Phenol (0.3 mol) in 30 mL of toluene was then added dropwise at 5°C over a period of 1 h. After addition of the phenol solution, the reaction was run for 24 h. Unreacted phosphorus oxychloride and solvent were vacuum
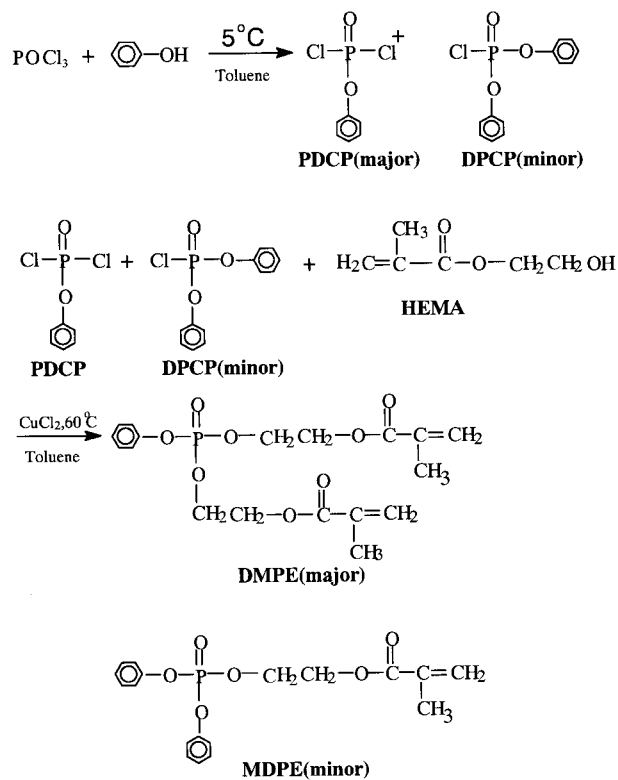
Scheme 1

distilled at 8 mmHg and 110°C. The pot residue contained a major product of phenyl dichlorophosphate (PDCP) and a minor product of diphenyl chlorophosphate (DPCP). A 23-g sample of the pot residue was then placed in another reaction kettle and 0.2 g of CuCl$_2$ was added. After raising the temperature to 60°C, 30 g (0.23 mol) of HEMA in 30 mL of toluene was added dropwise to the reactor over a period of 1 h. After 12 h, the solution was placed in a rotary evaporator to remove any unreacted reactants. The solution was then neutralized with sodium hydrogen carbonate and dried with anhydrous magnesium sulfate.[10,11] The final product was a mixture of DMPE (major product) and MDPE (minor product). This mixture was designated as MDMPE.

Copolymerization. Copolymerization was carried out in a four-neck reactor, with different ratios of MDMPE, MDPE, HEMA, MMA, and BMA under a nitrogen atmosphere. After raising the temperature to 90°C, 1 wt % of BPO in dioxane was added dropwise into the reactor. The reaction was continued for 1 h and then poured into cyclohexane to precipitate the polymer. The designation and composition of these copolymers are shown in Tables I to III.

Table I   Hydroxy-Containing Copolymers Prepared with Different Ratios of MDPE to MDMPE

Copolymer Code	cop1 (%)	cop2 (%)	cop3 (%)	cop4 (%)	cop5 (%)
MDPE	60	50	40	30	—
MDMPE	—	10.5	21	31	—
HEMA	15	15	15	15	15
MMA	12.5	12.25	12	12	42.5
BMA	12.5	12.25	12	12	42.5

Synthesis of the Corresponding Polyurethanes. To the solution of hydroxy-containing copolymer in dioxane described earlier, equal molal amounts of MDI were added and mixed at room temperature for 24 h to complete the reaction. The mixture was then poured into *n*-hexane, and the precipitate was filtered and dried in a vacuum oven at 60°C for 48 h. The actual amounts and sample code designations used in these reactions are tabulated in Table IV.

Characterization

Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR spectra of PDCP, DMPE, the copolymers, and the corresponding polyurethanes were recorded using a Nicolet Magna II 550 Fourier transform spectrometer (Nicolet Instruments, Madison, WI). The spectra were obtained for each sample by coating these materials on a potassium bromide (KBr) disc.

^{1}H–NMR Spectra. PDCP, MDMPE, and MDPE were dissolved in deuterium chloroform (CDCl$_3$) and then characterized with ^{1}H–NMR using a Bruker WP 1000 spectrometer (Bruker Instruments, Billerica, MA).

Determination of OH Value.[12] In a dry, 250-mL round-bottom flask, equipped with a stirrer, a condenser fitted with drying tube, and a ther-

mometer, was placed a measured amount of polymer sample and 25 mL of phthalating reagent (42.0 g of phthalic anhydride dissolved in 300 mL freshly distilled pyridine). A few millimeters of DMSO were also added to increase the solubility of the polymer sample. The mixture was then stirred and refluxed at 115 ± 2°C for 1 h. Upon cooling, the solution was titrated with 0.5*N* NaOH until a faint pink endpoint 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:

OH No.

$$= \frac{56.1N \text{ NaOH} \times (\text{mL blank} - \text{mL sample})}{\text{sample weight}}$$

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

Acid No.

$$= \frac{56.1N \text{ NaOH} \times (\text{mL sample} - \text{mL blank})}{\text{sample weight}}$$

Table II   Phosphorus-Containing Copolymers Prepared with Different Quantities of Hydroxyl Groups

Copolymer Code	cop3 (%)	cop6 (%)	cop7 (%)
MDPE	40	40	40
MDMPE	21	21	21
HEMA	15	30	7.5
MMA	12	4.5	15.75
BMA	12	4.5	15.75

Table III   Phosphorus-Free Copolymers Prepared with Different Quantities of Hydroxyl Groups

Copolymer Code	cop5 (%)	cop8 (%)
HEMA	15	30
MMA	42.5	35
BMA	42.5	35

Table IV   Data for Synthesis of Polyurethanes

Copolymer Code	cop1-di	cop2-di	cop3-di	cop4-di	cop5-di	cop6-di	cop7-di	cop8-di
Copolymer weight (g)	1.8343	1.7303	1.6249	2.0438	2.3344	2.0121	1.7431	2.1210
MDI weight (g)	0.1498	0.1564	0.1835	0.1829	0.2089	0.4544	0.0984	0.3796

After both values were obtained, the corrected OH number was calculated as follows:

$$OH\ No.\ (corrected) = OH\ No. + Acid\ No.$$

Phosphorus Content. The phosphorus content is an indication of flame retardancy. Procedures for measuring the phosphorus content are described below. The phosphorus-containing sample was oxidized with sulfuric acid and perchloric acid; then ammonium molybdate and phosphorus acid were added to react into phosphomolybdate. This compound was transformed into molybdenum blue after reduction with ammonium ferrous sul-

fate. Light absorbance of molybdenum blue was then measured with a Hach DR/2000 colorimeter at 700 nm.

Thermogravimetric Analysis (TGA). TGA of copolymers and the corresponding polyurethanes was carried out by using a Perkin–Elmer TGA-7 instrument (scan rate 20°C/min in nitrogen; Perkin–Elmer Cetus Instruments, Norwalk, CT).

Gel Permeation Chromatography (GPC). The number-average $(\overline{M}_n)$ and weight-average $(\overline{M}_w)$ molecular weights and molecular weight distribution (MWD; $\overline{M}_w/\overline{M}_n$) were determined by GPC
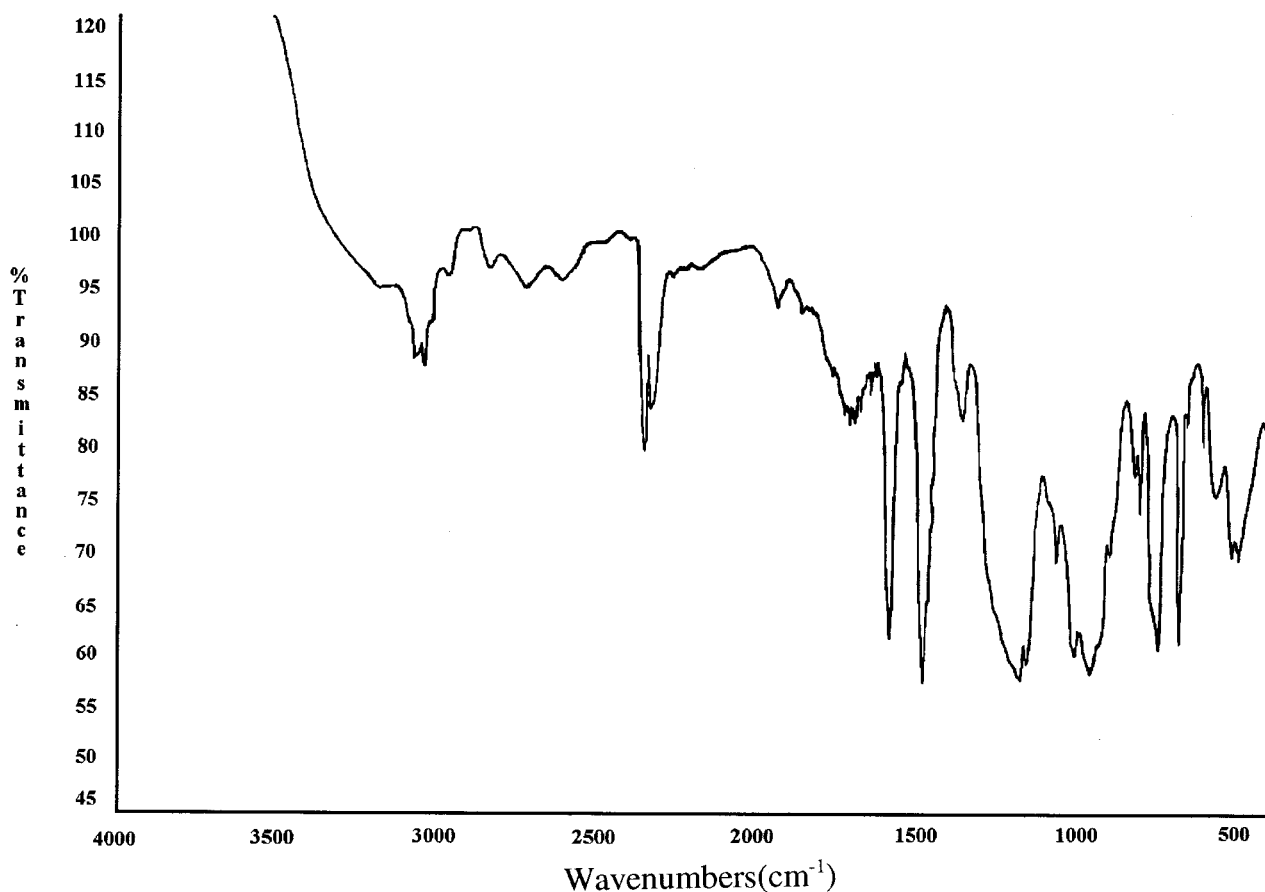

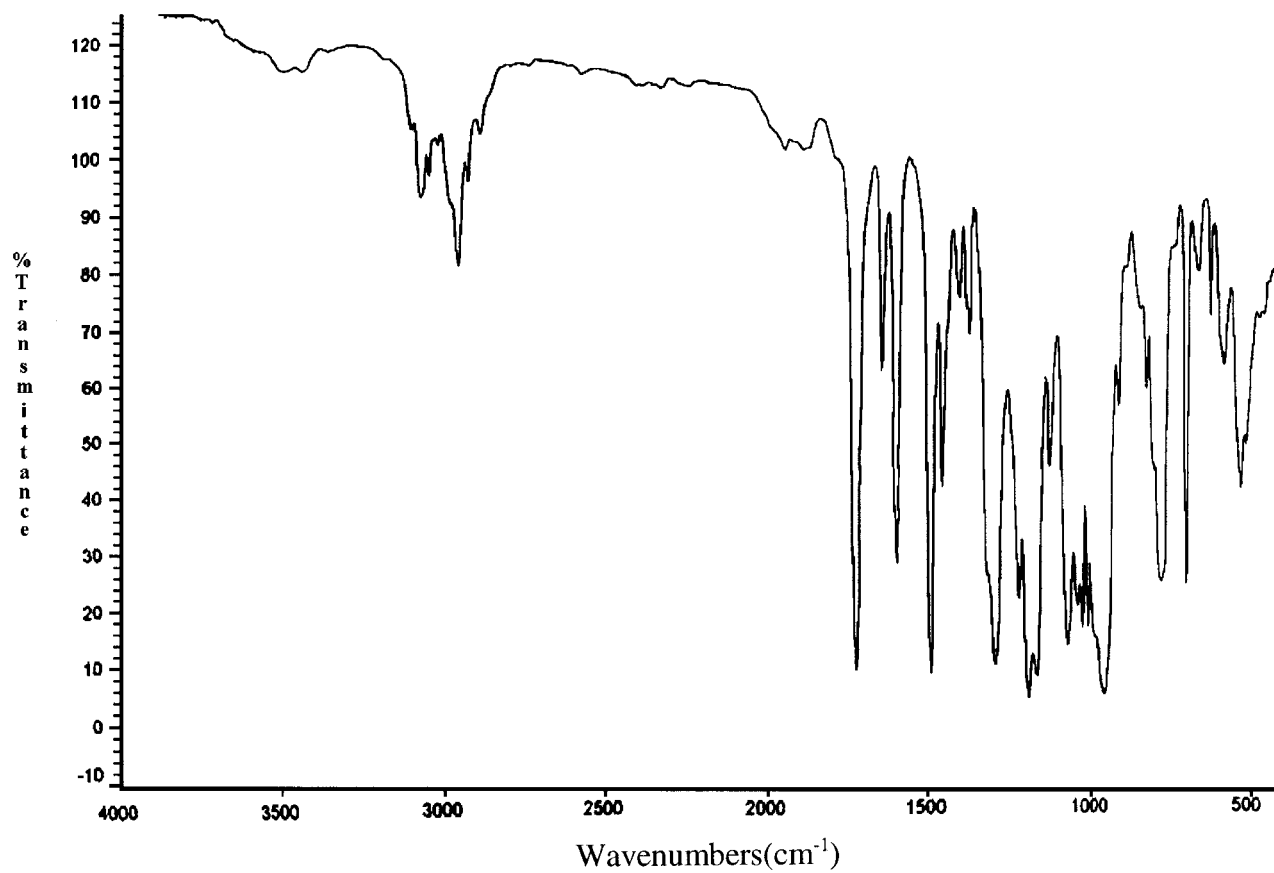**Figure 1**   The infrared spectrum of PDCP intermediate (with minor DPCP).
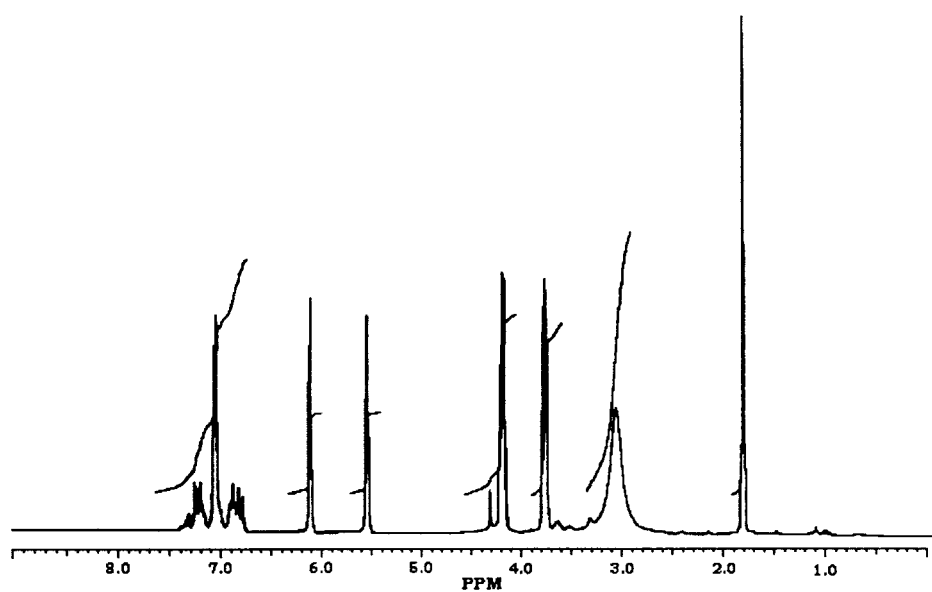
Figure 2 The infrared spectrum of MDMPE.
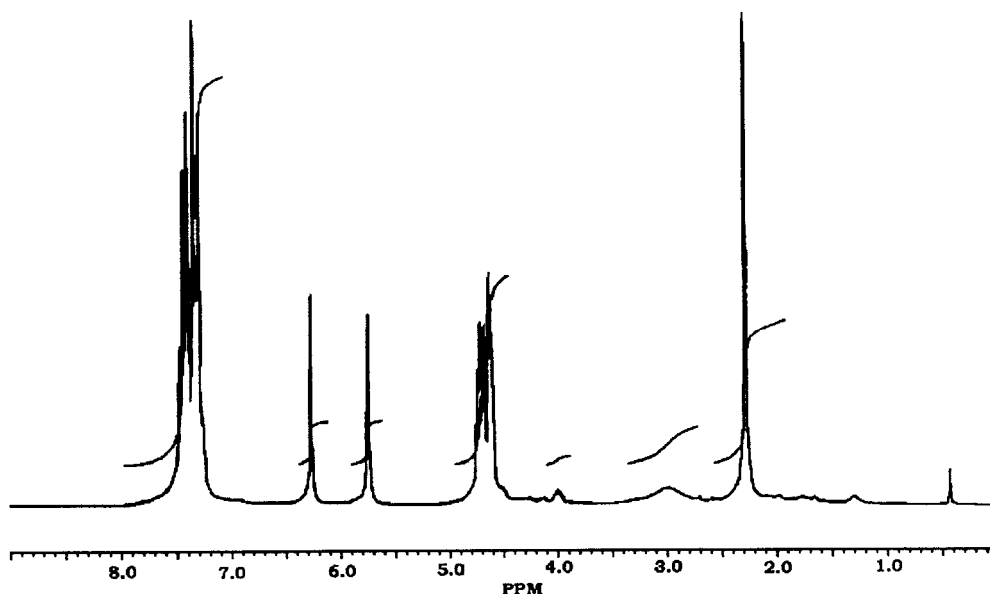

Figure 3 ^{1}H–NMR spectrum of MDMPE.

Figure 4 ^{1}H–NMR spectrum of MDPE.

using a Waters Liquid chromatograph (Waters Instruments, Rochester, MN) equipped with a 410 RI Detector and 3-μ Styragel columns.

RESULTS AND DISCUSSION

Synthesis and Characterization of Monomer and Copolymers

MDPE is a phosphorylate-containing acrylate. It can copolymerize with other acrylate monomers to form a phosphorus-containing acrylate polymer. In view of the location of phosphorus, polymers of this type can be regarded as phosphorus-on-pendent polymers.

On the other hand, DMPE consists of two acrylate monomers and can be copolymerized into a type of phosphorus-on-skeleton polymer.

In the synthesis of phosphorus-on-skeleton polymers, the phenyl dichlorophosphate (PDCP)

intermediate was first prepared. However, the by-product diphenyl chlorophosphate (DPCP) was also produced. Hence, after copolymerization of HEMA, the unwanted product MDPE was also present (**Scheme 1**).

The intermediate PDCP product and the final acrylate monomer DMPE were characterized and their structure confirmed by FTIR and ^{1}H–NMR. As the FTIR spectrum given in Figure 1 shows, the band at 3050 cm^{-1} is ascribed to the hydrogen stretch of the benzene ring. Two peaks at 1488 and 1595 cm^{-1} are attributed to C=C aromatic ring breathing. Evidence for the condensation of phenol with phosphorus oxychloride was clearly confirmed with the formation of P—O—C bonds, with absorptions present at 1185 and 975 cm^{-1}.[13,14]

The infrared spectrum of MDMPE is shown in Figure 2. The C—H stretch of the aromatic ring appears at 3070 cm^{-1}. The C—H stretch of the

Table V   Actual and Theoretical OH Content and OH Value of Phosphorus-Containing and Phosphorus-Free Copolymers

Copolymer Code	cop1	cop2	cop3	cop4	cop5	cop6	cop7	cop8
OH content (%)								
Theoretical	1.96	1.96	1.96	1.96	1.96	3.92	0.98	3.92
Measured	2.22	2.34	2.43	2.40	2.21	4.28	1.27	4.01
OH value	73.22	77.08	80.26	79.26	72.84	141.26	41.92	132.36

Table VI   Phosphorus Content of Phosphorus-Containing Copolymers

Copolymer Code	cop1	cop2	cop3	cop4	cop6	cop7
Phosphorus content (%)						
Theoretical	5.01	5.02	5.04	5.01	5.04	5.04
Measured	5.81	5.54	5.29	5.20	5.15	5.32

aliphatic CH_2 occurs at 2957 cm^{--1}. The absorption at 1295 cm^{-1} is assigned to P=O. Confirmation of the structure of the DMPE monomer was ascertained by the carbonyl absorption peak at 1720 cm^{-1} and the P—O—C peak of aliphatic carbon at 1070 cm^{-1}.[15,16]

However, to determine the fractions of DMPE and MDPE in the mixture MDMPE that was synthesized, the ^{1}H–NMR spectra of the MDMPE and MDPE monomers must be used (Figs. 3 and 4). The fraction of DMPE can be quantified by comparing the ^{1}H–NMR spectrum of MDMPE to the spectrum of pure MDPE (commercial product). Given that the ratios of the resonance peak areas for hydrogen atoms on the benzene ring to the hydrogen atoms on the double bond are 5/4 and 10/2 for pure DMPE and MDPE, the calculated ratios of synthesized DMPE and MDPE are 89 and 11%, respectively.

Two types of copolymers were then synthesized by MDMPE and MDPE with other acrylate monomers (HEMA, MMA, and BMA): phosphorus-containing copolymers and phosphorus-free copolymers (Tables I–III). The phosphorus-containing copolymers were further divided into copolymers with constant hydroxyl-group content (i.e., a constant ratio of HEMA) and copolymers with different hydroxyl-group contents.

The theoretical and actual contents of hydroxyl groups obtained for these copolymers are shown in Table V. In addition, the theoretical and actual phosphorus contents of the phosphorus-containing copolymers are shown in Table VI. It is evident that the higher the content of MDMPE (i.e., DMPE), the lower the content of phosphorus re-

sulting from the higher molecular weight of DMPE.

Table VII shows $\overline{M_n}$ and $\overline{M_w}$ for representative copolymers. It is obvious that, except for cop3, higher MDMPE to MDPE ratios reduce the molecular weights ($\overline{M_n}$ and $\overline{M_w}$) of the copolymers and increase their polydispersities. Alternatively, there is a tendency that, if no MDMPE and MDPE are contained in these copolymers (i.e., cop5 and cop8), the molecular weights of the copolymers increase (except for cop1 and cop3) and their polydispersities decrease. This may be attributed to the higher steric hindrance of the large DMPE molecule.

Thermal Analysis of Copolymers

Copolymers Containing Different Ratios of the Phosphorus-on-Skeleton Compound DMPE (MDMPE in Table I)

The effect of phosphorus content on the stability of these copolymers under a nitrogen atmosphere is illustrated in Figure 5 and Table VIII. As shown in Figure 5, all TGA curves display a rapid degradation process between 300 and 450°C. However, cop5 completely degraded before reaching 450°C, whereas cop1 through cop4 still exhibit char residues until 900°C, indicating the flame-retarding ability of these phosphorus-containing copolymers.

If the criterion for stability is taken as the temperature at which 10% weight loss occurred (i.e., $T_{10\%}$), it can be seen that $T_{10\%}$ decreases in the order: cop1 > cop5 > cop2 > cop3 > cop4. The

Table VII   Number-Average ($\overline{M_n}$) and Weight-Average ($\overline{M_w}$) Molecular Weights of Representative Copolymers

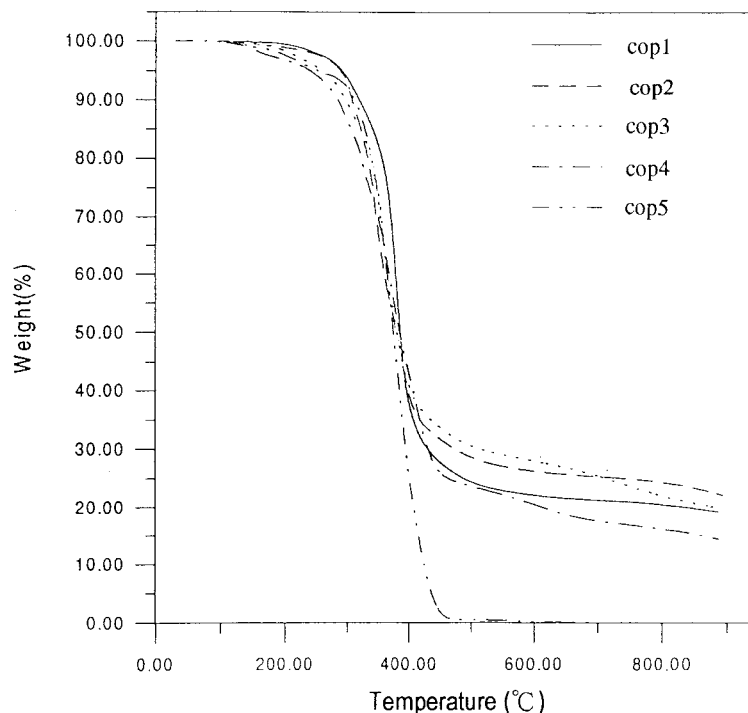| Copolymer Code	cop1	cop2	cop3	cop4	cop5	cop8
$\overline{M_w}$ (g/mol)	69,720	46,604	78,734	27,749	60,988	58,977
$\overline{M_n}$ (g/mol)	17,061	14,137	8313	8866	30,717	24,545
Polydispersity	4.09	3.30	9.47	3.13	1.99	2.40

Figure 5 TGA curves of hydroxy-containing copolymers with different ratios of MDPE to MDMPE.

earlier degradation most likely results from cleavage of the P—O—C (aliphatic) bonds and hydroxyl groups, which is confirmed by IR spectra (see Figs. 8 and 9 below). Therefore, the higher the ratio of P—O—C (aliphatic) bonds (i.e., a higher DMPE content), the lower the degradation temperature of the copolymer. In contrast, the better thermal stability of cop1 over that of cop5 is probably caused by the longer branch of MDPE in cop1, which has a protection effect on its hydroxy groups. Moreover, it is found that the char residue at 900°C decreases in the order: cop2 > cop3 > cop4.

Some important results can be derived from these observations. First, the presence of MDMPE (i.e., DMPE) will increase the crosslinking density of the copolymers. Second, as seen from Table VI, the higher the content of DMPE, the lower the content of phosphorus. It seems that the cross-

linking density may be low in the copolymers of cop2 through cop4. Hence, the higher char residues are mainly caused by the higher phosphorus contents. On the other hand, crosslinking is really helpful for flame-retarding ability. Hence, although the cop1 has the highest phosphorus content, the char yield for cop1 is higher than that for cop4 only because no crosslinking is present.

Copolymers Containing Constant Ratios of Phosphorus Compounds and Different Ratios of Hydroxyl Groups (Table II)

When copolymers have the same phosphorus content, that is, the same ratio of MDMPE to MDPE, the degradation process as inferred from the TGA curves exhibits similar trends (Fig. 6). As seen in the figure, the char residues and degradation temperatures of the three copolymers are almost

Table VIII   TGA Results of Copolymers Prepared with Different Ratios of MDPE to MDMPE

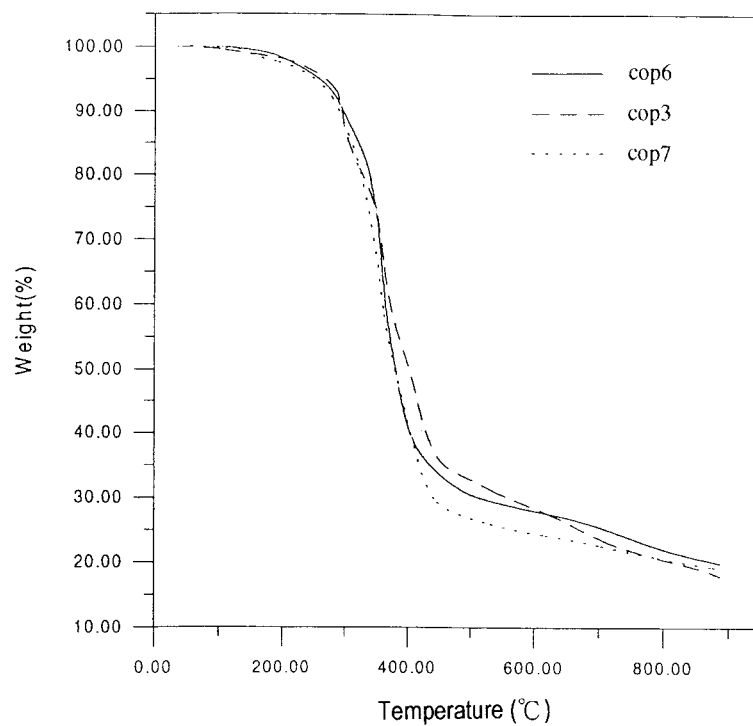| Copolymer Code	cop1	cop2	cop3	cop4	cop5
$T_{10\%}$ (10% weight loss)	319°C	306°C	296°C	283°C	311°C
Char residue at 900°C (%)	19.17	22.08	19.88	14.38	0

Figure 6 TGA curves of phosphorus-containing copolymers with different quantities of hydroxyl groups.
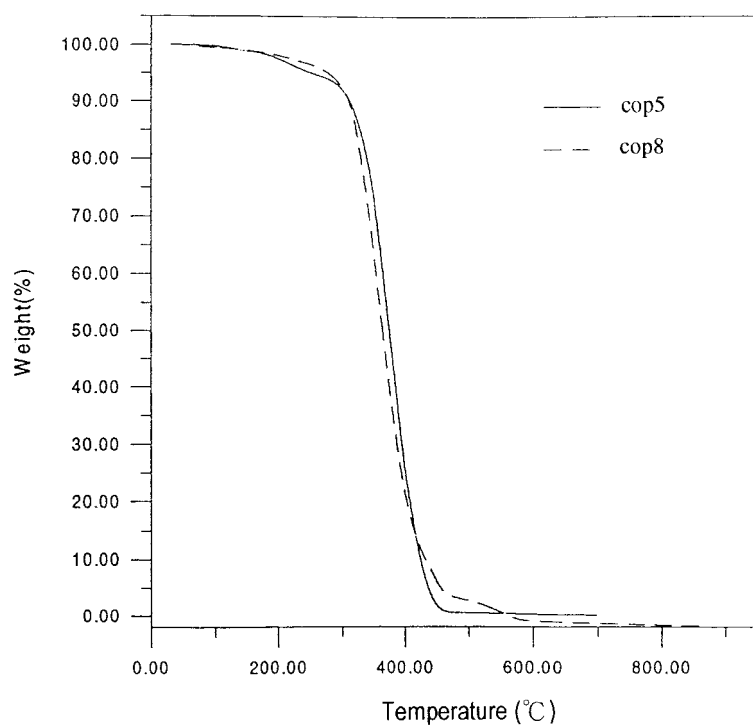

Figure 7 TGA curves of phosphorus-free copolymers with different quantities of hydroxyl groups.
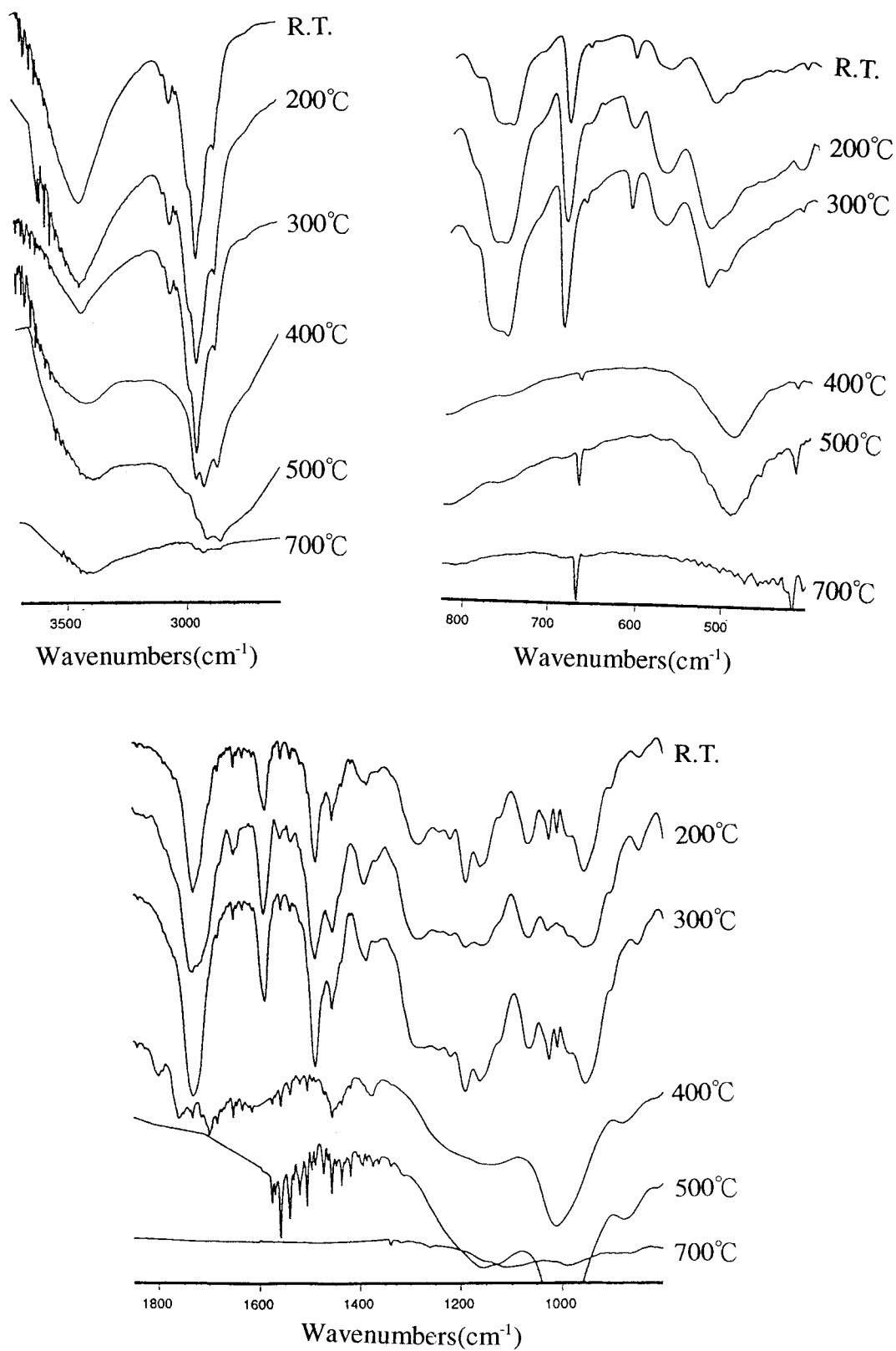
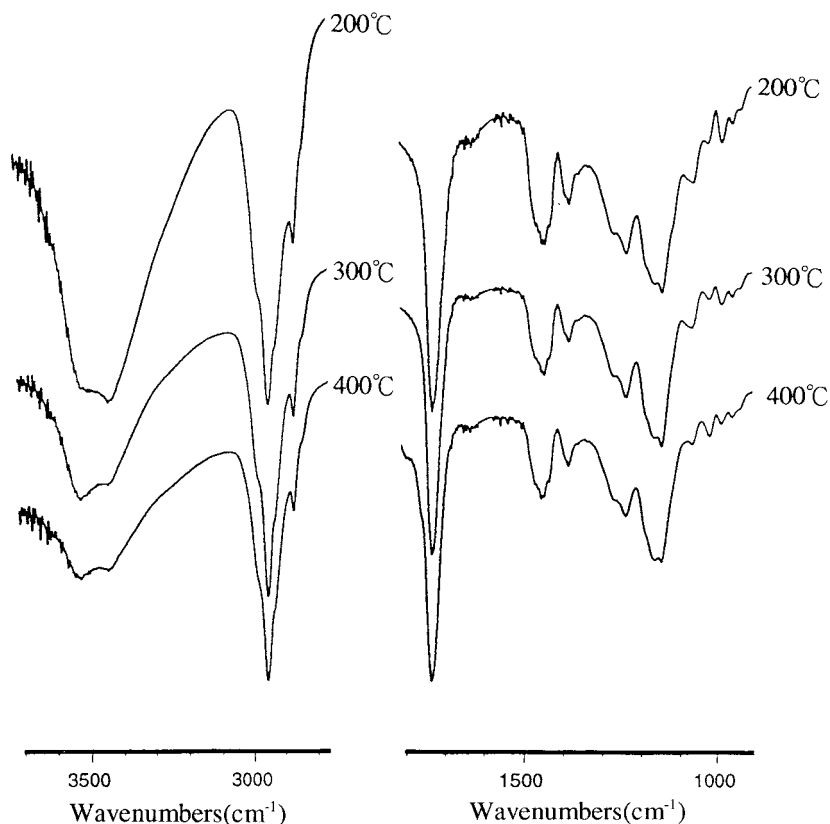**Figure 8** The infrared spectra of cop1 at different temperatures.

Figure 9 The infrared spectra of cop5 at different temperatures.

the same, indicating that the hydroxyl group content has no obvious effect on the flame retardancy of the copolymers.

Phosphorus-Free Copolymers Containing Different Ratios of Hydroxyl Groups (Table III)

As Figure 7 shows, phosphorus-free copolymers completely degrade when reaching approximately 450°C. In addition, no significant difference in degradation temperature was found for these two copolymers.

Degradation Mechanism

The degradation mechanism of phosphorus-containing copolymers is analyzed by FTIR. As seen in Figure 8, the hydroxyl group absorption (around 3400 cm^{-1}) of cop1 disappears before 300°C. It is also clear that the intensity of the P—O—C bonds at 1080 cm^{-1} decreases before 300°C. Hence, the P—O—C bonds of aliphatic carbon (at 1080 cm^{-1}) are less stable than the P—O—C bonds of aromatic carbon (at 1180 and 950 cm^{-1}). At 300 to 500°C, the disappearance of absorption peaks around 1180, 1080, and 950 cm^{-1} indicate the breakage of the O—C bond of P—O—C in the copolymer. At 700°C, the IR spectrum indicates that the char residue consists of undissociated polymer segments with partial P—O—C and P=O bonds. For the phosphorus-free copolymer cop5, the IR spectrum (Fig. 9) also shows that hydroxyl groups dissociate first before reaching 400°C. The other absorption peaks decrease rapidly after reaching 400°C, and com-

Table IX   TGA Results of Polyurethanes Prepared with Different Ratios of MDPE to MDMPE

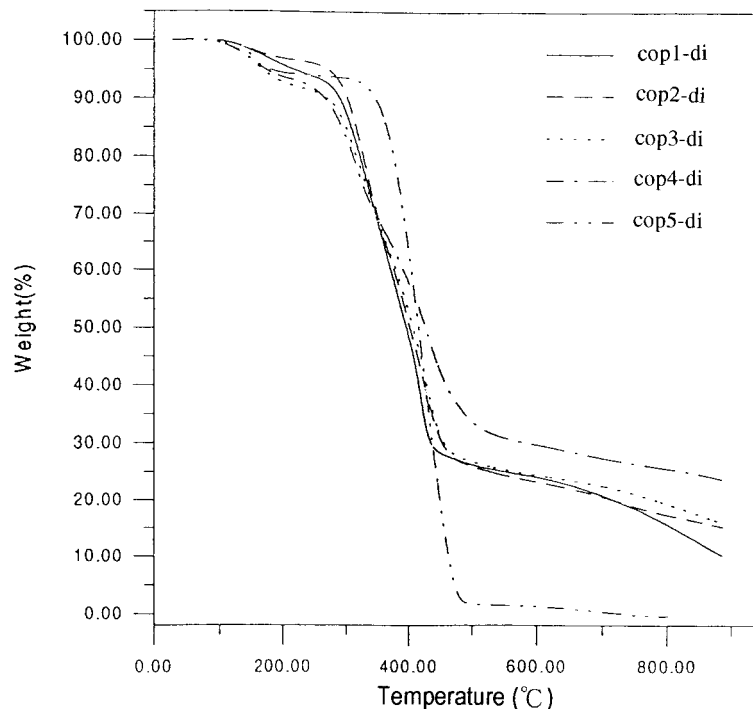| Polymer Code	cop1-di	cop2-di	cop3-di	cop4-di	cop5-di
$T_{10\%}$ (10% weight loss)	289°C	302°C	271°C	266°C	347°C
Char residue at 900°C (%)	10.18	15.15	15.92	23.69	0

Figure 10 TGA curves of hydroxy-containing polyurethanes with different ratios of MDPE to MDMPE.

pletely disappear around 500°C, indicating that no char residue was left, in line with the observations from TGA analysis.

Thermal Analysis of Polyurethanes

Polyurethanes Synthesized from Different Ratios of the Phosphorus-on-Skeleton Compound DMPE (MDMPE in Table I)

Table IX and Figure 10 show the thermal stability and char residues of polyurethanes synthesized from cop1 through cop5. From the TGA curves, it was also found that all phosphorus-containing polyurethanes degrade at low temperatures, which most likely results from cleavage of the P—O—C bonds and hydroxyl groups. Additionally, it can be seen that $T_{10\%}$ decreases in the order: cop5-di > cop2-di > cop1-di > cop3-di > cop4-di. This can be attributed to the earlier observation that the higher content of phosphorus-on-skeleton (i.e., more MDMPE) may cause the earlier decomposition of the polyurethanes. Given that the cop5-di is a phosphorus-free polyurethane, it has a lower initial degradation compared to that of the other polyurethanes. However, the higher $T_{10\%}$ for cop2-di than that for cop1-di may be attributed to the higher molecular weight of this polyurethane. Consequently, the degradation amount is lower relative to its molecular weight.

Subsequently, it is observed that in all phosphorus-containing polyurethanes a considerable amount of residue is present at 900°C. The char residues at 900°C increase in the order: cop1-di < cop2-di < cop3-di < cop4-di. The lower initial degradation temperature and correspondingly higher amount of char yield may indicate that all of the phosphorylated samples are effective flame retardants.

It is noteworthy to observe that the higher the content of the phosphorus-on-skeleton compound (DMPE), the better the flame retardancy of the polyurethane. Because there are two double bonds present in the DMPE compound, it has been suggested that crosslinking involving the

Table X   TGA Results for Polyurethanes with Constant Phosphorus Content and Different Quantities of Hydroxyl Groups

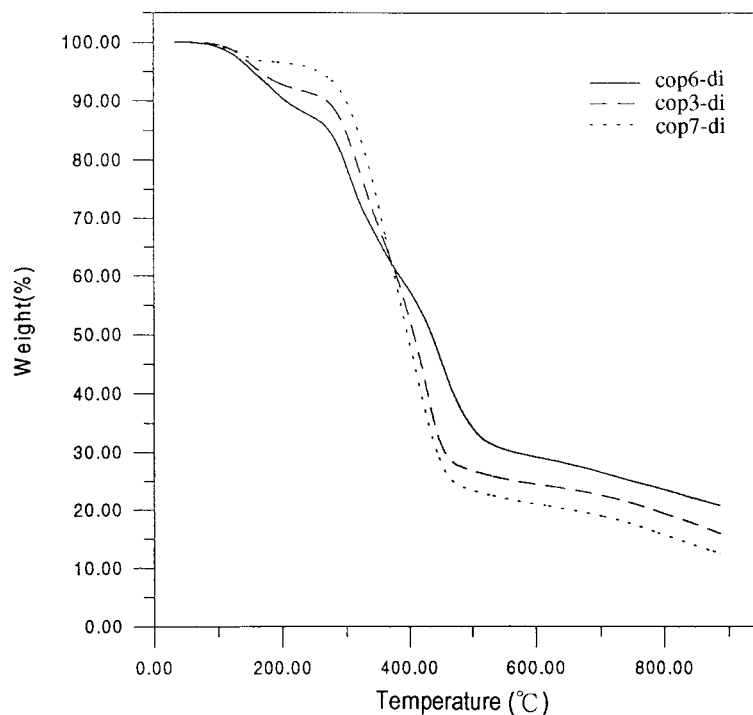| Polymer Code	cop3-di	cop6-di	cop7-di
$T_{10\%}$ (10% weight loss)	271°C	207°C	301°C
Char residue at 900°C (%)	15.92	20.79	12.50

Figure 11   TGA curves of phosphorus-containing polyurethanes with different quantities of hydroxyl groups.
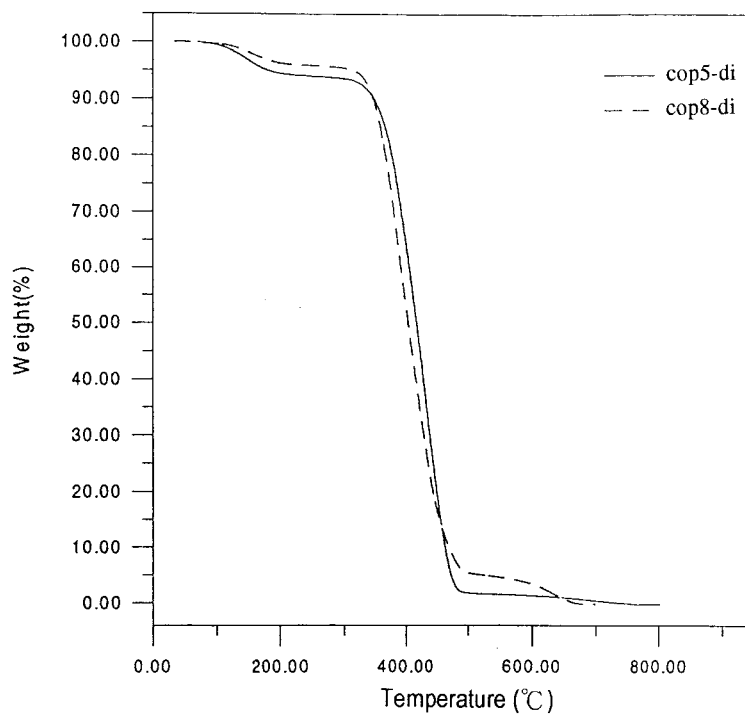

Figure 12   TGA curves of phosphorus-free polyurethanes with different quantities of hydroxyl groups.
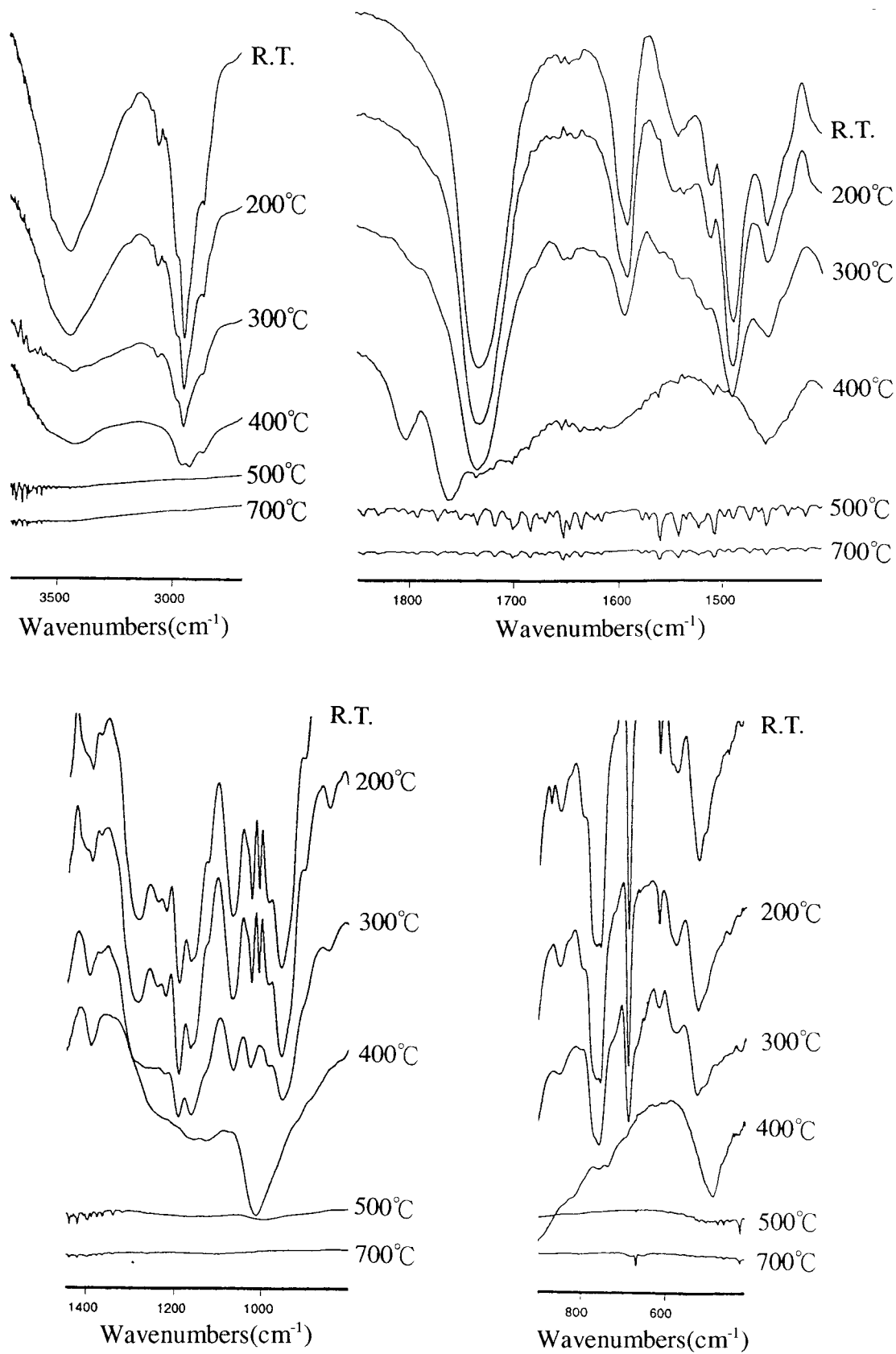
Figure 13   The infrared spectra of cop1-di at different temperatures.

phosphorus-containing chain occurs after initial chain cleavage, resulting in a higher char yield.

Polyurethanes Containing Constant Ratios of Phosphorus Compounds and Different Ratios of Hydroxyl Groups

As illustrated in Table X and Figure 11, it is found that incorporating higher contents of hydroxyl group in the polyurethanes lowers the initial degradation temperature and increases the char yield at 900°C. As noted previously, the hydroxyl group content has no obvious effect on the flame retardancy of the copolymers cop3, cop6, and cop7. The distinct difference in the flame retardancy for their corresponding polyurethanes may imply that the presence of a nitrogen atom, which was introduced after reaction with MDI, has a synergistic effect on the flame retardancy of the phosphorus-containing compound. Hence, the initial degradation temperature is lower, and the char yield is higher.

Phosphorus-Free Polyurethanes Containing Different Ratios of Hydroxyl Groups

For the phosphorus-free polyurethanes, complete degradation at about 640°C was found (Fig. 12). In addition, it can be seen that the higher content of hydroxyl groups lowers the initial degradation temperature, which is confirmed by the IR spectra.

Degradation Mechanism

The degradation mechanism of the corresponding polyurethanes has been ascertained by IR spectra. From the IR spectrum of cop1-di, it is evident that earlier degradation at 200°C results from the dissociation of OH bonds and P—O—C bonds. As seen in Figure 13, it is clear that the absorption at 3400 cm^{-1} ascribed to OH bonds and the absorptions around 1180, 1080, and 950 cm^{-1} attributed to P—O—C bonds start to disappear before 200°C. The other absorptions attributed to C=O bonds (1720 cm^{-1}) and aromatic ring breathing (1500 and 1600 cm^{-1}) are found to disappear around 300°C.

CONCLUSIONS

A phosphorus-on-skeleton acrylate monomer (DMPE) was successfully synthesized. After copolymerization with a variety of other acrylic monomers, these copolymers were used as a polyol for the subsequent synthesis of the corresponding polyurethane. It was found that all phosphorus-containing copolymers showed distinct flame-retardant behavior and that their corresponding polyurethanes are also effective flame retardants. It should be noted that a higher content of the phosphorus-on-skeleton compound, and a higher hydroxyl group content both resulted in the formation of the corresponding polyurethane with a lower initial degradation temperature and a correspondingly higher amount of char yield. This may be attributed to the occurrence of crosslinking, which involves the phosphorus-containing chain.

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