Novel Phosphorus-Containing Dicyclopentadiene-Modified Phenolic Resins for Flame-Retardancy Applications

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ABSTRACT: 2-[4-(2-hydroxyphenyl)tricyclo[5.2.1.0^{2,6}]dec-8-yl]phenol (HPTCDP) were prepared from dicyclopentadiene (DCPD) and phenol via Friedel-Crafts alkylation. DCPD-containing phenolic resin (DPR) was also synthesized by incorporating the DCPD-containing monomer HPTCDP with formaldehyde. DPR was further modified by grafting the phosphate group. The phosphorylation was confirmed by a Fourier transform infrared, ^{31}P-NMR spectroscopy, and an element analysis. The phosphorus content in the DPR could be successfully tailored to give values of 3.46 to 7.79 wt % by varying the feeding ratios of the phosphorus group. The thermal stabilities of the phosphorus-containing polymers were identified by differential scanning calorimeter and thermogravimetric analysis. The glass transition temperature values were decreased as the content of phosphorus increased. High char yield 39–47 wt % in thermogravimetric analysis evaluation and limiting oxygen index values of 27 to 34 were found for all the phosphorylated phenolic resins. Such properties make these polymers highly promising for flame-retardant applications. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 342–349, 2001

Key words: flame-retardant; phosphorus-containing phenolic resin; dicyclopentadiene

INTRODUCTION

Organic polymeric materials are limited in many applications because of their flammability. Thus, the demand for flame-retardant polymeric materials has steadily increased with the increasing use of polymers. Flame retardation is a process by which adding certain chemicals alters the normal degradation or combustion processes of polymers. Some plastic materials are inherently fire retardant or smoke retardant and their fire performance is acceptable for certain applications. However, for many plastic materials, their fire resistance must be improved by incorporating commercially available flame retardants. As expected, retardants have to improve fire resistance without excessive loss of other important performance characteristics.

A conventional means of preparing flame-retardant polymers involves blending flame-retardant additives with polymeric materials. However, compatibility between the polymer and the additives restricts application of the blended flame-retardant. Covalently incorporating flame-retardant chemicals onto polymer backbones, i.e., using a reactive flame retardant, has attracted

much attention recently.[1–4] This method creates a more compatible product than the blended systems do that can also obtain excellent flame retardancy.[1,2] Nonhalogenated flame retardants such as phosphorus-containing flame retardant are currently used to avoid the generation of toxic, corrosive, or halogenated gases.[1–4] Currently, phosphorus-containing flame retardants are mainly burned through a condensed-phase mechanism that leads to the production of incombustible carbonaceous char.[1] Consequently, fewer toxic gases are released into the atmosphere. Furthermore, the flame-retardant efficiency of phosphorus compounds was reported to be better than equal-weighted halogenated compounds and could be further enhanced when phosphorus is covalently bound to the polymers.[1–4]

Thermosets are promising candidates for flame retardants because their three-dimensional network prefers to generate less decomposition gaseous products than thermoplastics. When heating, the surface will char, thus preventing ignition. Phenolic resins, a thermosets resin, have been used extensively because of their thermal stability and moderate char yield.[5–7] However, in some instances, they may have less than desired moisture and flame retardancy. At least one unsaturated hydrocarbon, for example, cyclopentene, 1,5-cyclooctadiene, dipentene, or dicyclopentadiene can be utilized to improve the desired moisture.[8,9] However, a flame retardant or an improvement of the polymer itself is needed to increase the phenolic resin's flame retardancy.

Cyclopentadiene (CPD) is a byproduct of C_5 streams in oil refineries. The CPD monomer usually exists in the form of dicyclopentadiene (DCPD), which is a dimeric adduct through the Diels Alder reaction at ambient temperature.[10] In this work, a series of DCPD-modified phenolic resins (DPR) with and without phosphorus groups was synthesized. The systematic investigation of flame-retardation included a differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) thermogram, index of the flame resistance, and the limiting oxygen index (LOI) study.

EXPERIMENTAL

Materials

DCPD, phenol, and formalin were purchased from TEDIA Co. The DCPD was extracted by 5% NaOH solution twice to remove any inhibitors, and was then dried over calcium hydride and distilled before use. The boron trifluoride diethylether ($BF_3 \cdot Et_2O$) from the Lancaster Company, copper(I) chloride, diethylphosphoryl chloride (DEPC), and hydrochloric acid (HCl) from the ACROS Company, were all used as received. Tetrahydrofuran (THF) was dried over sodium with benzophenone as an indicator and distilled under nitrogen. Finally, the triethylamine (TEA) was distilled over potassium hydroxide before use.

Syntheses of 2-[4-(2-Hydroxyphenyl)tricyclo[5.2.1.0²,⁶]dec-8-yl]phenol (HPTCDP)

The dicyclopentadiene and phenol adducts were prepared according to the literature.[8] Phenol (420 g) and 4 mL of $BF_3 \cdot Et_2O$ were added to a 500-mL three-necked flask equipped with a stirrer, condenser, and heater. The mixture was heated to 70°C, stirred for 1 h, and then cooled to 40°C. DCPD (30 mL) was added. The temperature was then heated to 120°C for another 3 h. The product mixture was extracted with 5% NaOH aqueous solution followed by distilled water to remove $BF_3 \cdot Et_2O$ and phenol after cooling to room temperature. The extract was dried over $MgSO_4$ and then concentrated. The final product was obtained in a 70% yield: IR (KBr): 3200 cm^{-1} (—OH), 1239 cm^{-1} (C—O); ^{1}H-NMR (CDCl$_3$): δ = 1.23–2.12 ppm (saturated protons for phenyl group and DCPD), δ = 2.26–4.18 ppm (—CH$_2$— for DCPD), δ = 5.61 ppm (—OH for phenyl), δ = 6.79–7.33 ppm (aromatic proton). Anal. Calcd for $C_{22}H_{23}O_2$: C, 82.76%; H: 7.21%; O, 10.03%. Found: C, 78.92%; H, 7.66%; O, 13.42%.

Syntheses of DCPD-Modified Phenolic Resin (DPR)

Twenty grams of HPTCDP, 3.2 mL of formalin, and three drops of HCl were added to a 100-mL round-bottom flask equipped with a stirrer and reflux condenser. The solution was then refluxed at 85°C for 30 min. A large amount of cool water was added when the reaction was completed. The crude product was condensed and dried under vacuum at 50°C. Using similar processes, this adducts of HPTCDP (20 g)/formalin (2.0 mL) (mol ratio 1:0.5) and HPTCDP (20 g)/formalin (4.0 mL) (mol ratio 1:1) were also prepared. IR (KBr): 922 cm^{-1} (aromatic proton with three substitutes), 1070 cm^{-1} (the end —C—OH), 3200 cm^{-1} (—OH).

Anal. Calcd for $C_{23}H_{24}O_2$ (mol ratio of HPTCDP/ formalin = 1:0.85): C, 83.13%; H: 7.23%; O: 9.64%. Found: C, 83,28%; H, 7.69%; O, 9.03%.

Syntheses of Phosphorus-Containing DCPD-Modified Phenolic Resin (PCDPR)

Ten grams of DPR (0.03 mol) was dissolved in 100 mL of dry THF in a 500-mL round-bottom flask fitted with a magnetic stirrer under nitrogen atmosphere. Distilled dry triethylamine (20 mL) was added, and the system was then cooled to 0°C. A solution of 3 mL of DEPC (0.15 mol) in 20 mL of THF was added dropwise over a period of 10 min after adding 0.5 g of Cu_2Cl_2. The reaction system was maintained at 0°C for 2 h and then kept at room temperature overnight. The precipitant was filtered and washed with THF. The filtrate was concentrated and precipitated from methanol. The obtained product was dried under vacuum at 50°C. The adducts of DPR (10 g)/DEPC (6 mL) (mol ratio 1:1) and DPR (10 g)/DEPC (12 mL) (mol ratio 1:2) were also prepared using similar processes. IR (KBr): 970 cm^{-1} (—P—OPh), 1295 cm^{-1} (—P=O). ^{31}P NMR ($CDCl_3$): $\delta = -18$ ppm (Ph—O—P) and $\delta = -26$ ppm (—CH$_2$O—P).

Instrumental Analysis

The ^{1}H-NMR and ^{31}P-NMR spectra were obtained from a Bruker AM-400 NMR Spectrometer. The Fourier transform infrared (FTIR) spectra were measured by a Bio-Rad FTS-155 spectrometer. Samples were cast onto a KBr tablet for the measurement. Inherent viscosities were measured in THF using an Ostwald viscometer at 25°C. DSC thermograms were recorded with a Seiko SSC 5200 at a heating rate of 10°C/min under nitrogen atmosphere. The elemental analysis was performed with a F002 HERAEUS CHN-O rapid element analyzer using acetanilides as a standard. Gel permeation chromatographic (GPC) analysis was performed with polystyrene standards with a Shimadzu LC-9A liquid chromatographic and a Shimadzu RID-6A refractive index detector using TSK gel columns (eluent THF). TGA was performed with a Seiko EXSTAR 6000 Thermogravimetric Analyzer at a heating rate of 10°C/min under nitrogen atmosphere. The LOI values were measured on a Stanton Redcroft flame meter by a modified method.[11,12] The percentage of the O_2-N_2 mixture just sufficient to sustain the flame was taken as the LOI.
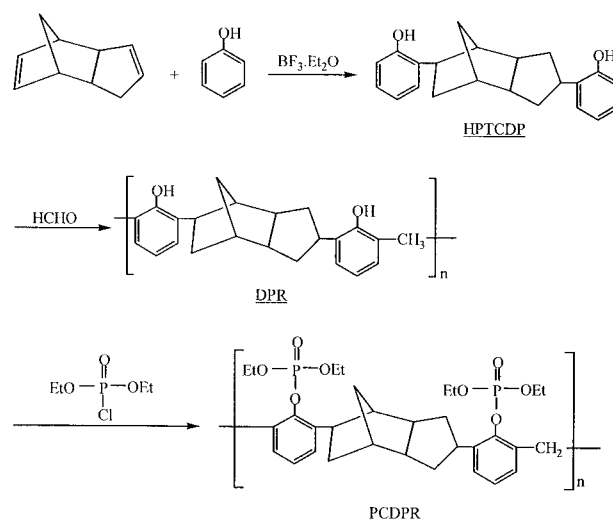
Scheme 1   Synthesis scheme of phosphorus-containing dicyclopentadiene-modified phenolic resin.

RESULTS AND DISCUSSION

Monomer (HPTCDP) Synthesis and Characterization

Scheme 1 depicts the synthesis routes of the HPTCDP. The HPTCDP synthesis reaction was performed in the presence of a Friedel-Crafts catalyst such as hydrofluoric acid, aluminum chloride, boron trifluoride etherate, and acid complexes. Boron trifluoride etherate and its acid complexes are the preferred catalysts.[13] The amount of catalyst required is that amount sufficient to cause the reaction to complete a product with a desirably low molecular weight, i.e., lower than 600, and will generally be less than about 1% of weight of the reactants, exclusive of the weight of the catalyst.

The chemical structure of the HPTCDP was identified by an FTIR, ^{1}H-NMR, and an element analysis. Figure 1 displays the FTIR spectra of HPTCDP and its precursor DCPD. The aliphatic stretching characteristic of the DCPD segment was located at $2800 \sim 3000$ cm^{-1}. The absorption peak appearing at 1590 cm^{-1} can be attributed to the aromatic stretching band from the phenol group. Moreover, the characteristic band of the ethylene groups contributed from DCPD is discovered from the monomer HPTCDP. The monomer HPTCDP was further characterized by ^{1}H-NMR (Fig. 2). Chemical shifts appearing at 3.57 and 4.20 ppm can be ascribed to the protons of Ph—
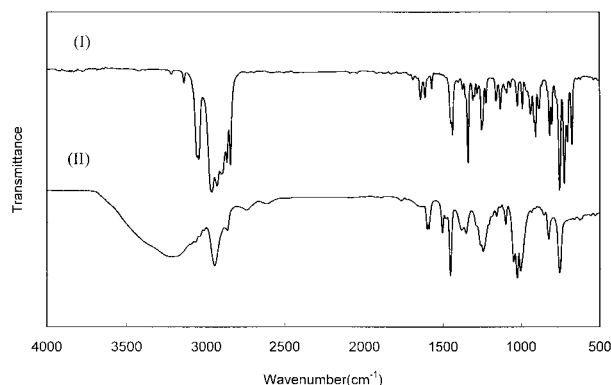
Figure 1 FTIR spectra of (I) HPTCDP and (II) DCPD.

Table I Reaction Condition for HPTCDP Adduct

Sample Code	Reaction Temperature (°C)	Reaction Time (h)	Yield (%)[a]	η_{inh} (dlg^{-1})[b]
I	120	1	72	0.0856
II	120	3	74	0.0994
III	120	5	78	0.0796
IV	150	1	74	0.0979
V	150	3	70	0.1085
VI	150	5	72	0.0703

[a] Yield of adduct HPTCDP.
[b] Measure at 25°C in THF.

C$\underline{H}$—. The chemical shifts of aromatic protons (—C$_6\underline{H}_4$) are found at 6.79–7.33 ppm.

Effect of Reaction Condition for Monomer (HPTCDP) Synthesis

Generally, the molecular weight of the monomer heavily depends on the monomer concentration, reaction temperature, and reaction time. According to Nelson et al.,[8] the optimized monomer concentration is the mol ratio of phenol to DCPD higher than 20:1. The effects of reaction temperature and reaction time were determined to find the optimized reaction condition to prepare HPTCDP. Table I confirms that the reaction conditions for sample III are ideal. Chemical modification of some dienes will occur when temperatures rise above 135°C.[13] Therefore, temperatures markedly exceeding 135°C should be avoided. Herein, 120°C was the optimized reaction temperature and reaction completion was achieved within 2–4 h.
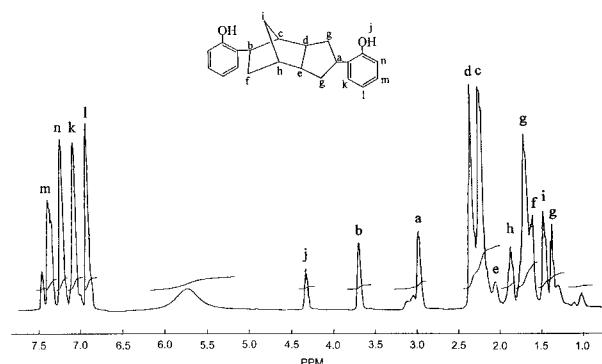
Synthesis and Characterization of DCPD-Modified Phenolic Resin (DPR)

A red semisolid phenolic resin DPR was acquired using HCl as a catalyst by incorporating HPTCDP with formaldehyde. Scheme 1 illustrates the reactions. Several feed ratios were performed to obtain an optimized composition for flame-retardation. Table II shows the elemental analyses of DCPD-modified phenolic resins DPR-0.50, DPR-0.85, and DPR-1.00. The composition of DPR-0.85 obtained from the elemental analyses correlated with that of the theoretical calculated value. However, the composition of DPR-0.5 and DPR-1.0 deviated from the calculated value, probably because of the network formation. The network restricts the phosphorus graft. Thus, the composition of DPR is chosen as the molar ratio of HPTCDP/formaldehyde = 1:0.85 for flame retardation. Figure 3 depicts the FTIR spectra of DPR-0.85. Peaks appearing at 922 cm^{-1} for the IR spectra verify that the phenyl group possesses three substitute sites. The characteristic absorp-

Figure 2 ^{1}H-NMR spectra of adduct HPTCDP.

Table II Element Analysis of DCPD-Modified Phenolic Resins

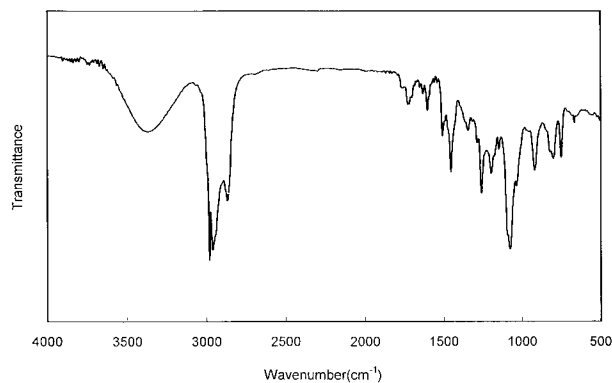|	Elemental Analyses			
	Calculated		Found	
Sample	C %	H %	C %	H %
DPR-0.50	83.13	7.23	80.08	7.69
DPR-0.85	83.13	7.23	83.28	9.03
DPR-1.00	83.13	7.23	80.04	12.20

Figure 3 FTIR spectra of DPR-0.85.

tion band of the hydroxy group on the aliphatic chain was found at 1070 cm^{-1}. The stretching band of the hydroxy group appears at 3200 cm^{-1}.

Thermal Properties of the DCPD-Modified Phenolic Resin (DPR)

The molecular weight and thermal properties of phenolic resin with and without DCPD-modified are listed in Table III, to help study the effect of DCPD in the phenolic resin. The weight-average molecular weight of the phenolic resin and the DCPD-modified phenolic resin (DPR-0.85) were found with 500–800 and 18000, respectively. The degradation temperature at 5% weight loss was found at 144°C and 274°C for phenolic resin and DPR-0.85, respectively. These results indicated that the reactivity and thermal stability could be effectively improved by introducing DCPD into the phenolic backbone. Figure 4 shows the DSC thermograms of the phenolic resins' DPRs. The phenolic resin DPR-0.85 possesses the highest glass transition temperature (T_g = 118°C). This can also prove that the DPR-0.85 has the best linear structure.

Synthesis and Characterization of Phosphorus-Containing DCPD-Modified Phenolic Resin (PCDPR)

A series of phosphorus-containing phenolic resins, PCDPRs, were synthesized to increase flame

Table III   Thermal Properties of DPR and PR

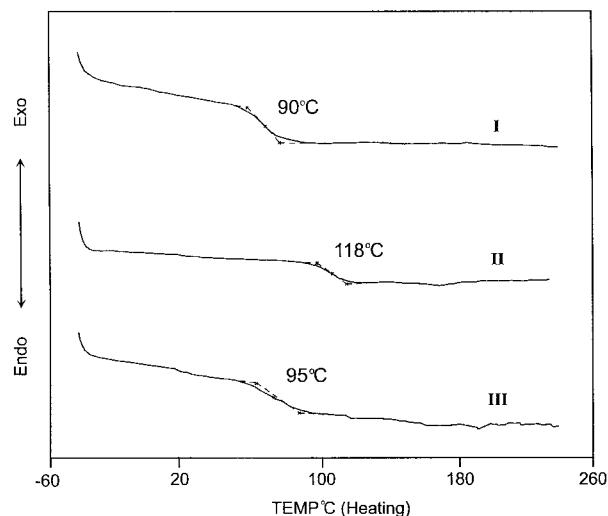| Sample	MW	T_g (°C)	T_d (°C)
Phenolic resin	500–800	112	144
DPR-0.50	—	90	314
DPR-0.85	18,000	118	292
DPR-1.00	—	95	304

Figure 4 DSC thermogram of (I) DPR-0.5, (II) DPR-0.85, and (III) DPR-1.00.

retardancy of the phenolic resin. The phosphorus-containing phenolic resins PCDPR21, PCDPR11, and PCDPR12 were obtained by incorporating the phenolic resin DPR-0.85 with the phosphonic compound DEPC at the compositions of 2:1, 1:1, and 1:2 by mol ratio, respectively. Figure 5 illustrates the FTIR spectra of the phosphorus-containing phenolic resins PCDPRs. The characteristic absorption peaks of the functional groups of P—OPh and (EtO)$_3$P=O for the phosphorus-containing phenolic resin PCDPR21 were assigned at 968 and 1291 cm^{-1}, respectively. These three compounds were further identified by ^{31}P-NMR. Figure 6 demonstrates the ^{31}P-NMR spectra of the phosphorus-containing phenolic resins. A
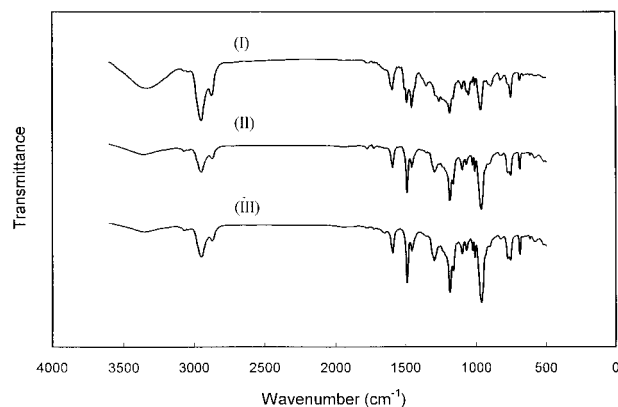

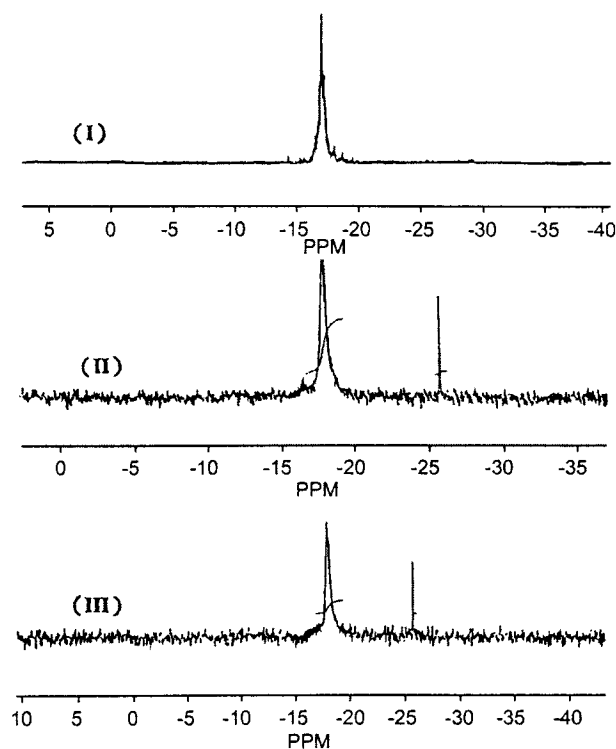**Figure 5** FTIR spectra of (I) PCDPR21, (II) PCDPR11, and (III) PCDPR12.

Figure 6 ^{31}P-NMR spectra of (I) PCDPR21, (II) PC-DPR11, and (III) PCDPR12.

Figure 7 DSC thermogram of (I) PCDPR12, (II) PC-DPR11, (III) PCDPR21, and (IV) DPR-0.85.

chemical shift that appeared at -18 ppm exhibit DEPC was incorporated onto the phenolic resin DPR-0.85. The integration of a new chemical shift ($\delta = -26$ ppm) appeared as the content of the phosphorus-containing compound increased. The peak that appears at $\delta = -26$ ppm may be ascribed as the phosphorus-containing group bonded on the terminal hydroxy methylene of the DCPD-modified phenolic resin DPR-0.85. In Figure 6(I), DECP was covalently grafted onto the phenolic resin DPR-0.85 and the peak at $\delta = -26$ ppm was not observed when its concentration was low. Table IV summarizes the chemical charac-
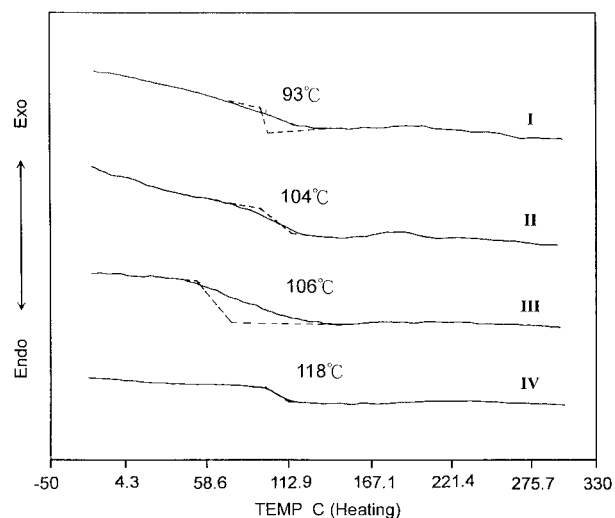
teristics of the phosphorus-containing DCPD-modified phenolic resin PCDPR. The phosphorus content can be obtained from element analysis.

The Effect of Phosphorus on the Thermal and Flame-Retardant Properties of Phenolic Resin

TGA and DSC were used to investigate the thermal properties of the phosphorus-containing phenolic resins. Figure 7 illustrates the DSC thermograms of the phenolic resin DPR-0.85 and the phosphorus-modified phenolic resin PCDPR. The crystallinity and T_gs slightly decreased when diethylphosphoryl chloride was grafted onto the phenolic resin. Thus, when the phosphorus content increased, the decrease in the T_g value may be attributed to plasticization of the phosphorus-containing side groups.

Figure 8 depicts the TG and DTG thermograms of the phenolic resin DPR-0.85 and the phospho-

Table IV   FTIR Characteristic Absorptions and Elemental Analysis of PCDPR

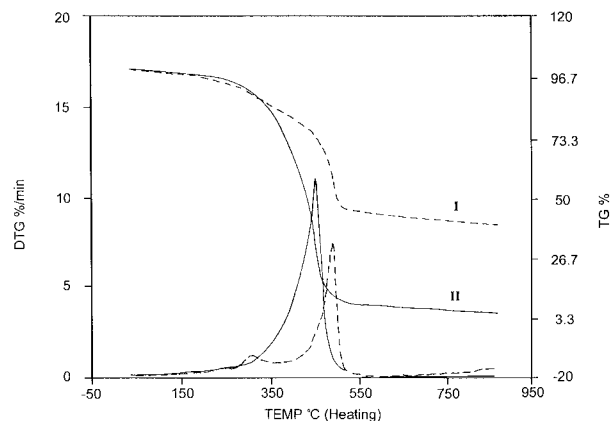| | | IR (cm^{-1}) | | Elemental Analysis | | | |
| | | | | Calculated | | Found | |
Sample	P % (wt %)	Ph—O—P	P=O	C %	H %	C%	H%
PCDPR21	3.46	968	1291	77.72	6.96	77.68	6.36
PCDPR11	5.50	965	1294	74.81	6.06	74.47	5.85
PCDPR12	7.79	964	1297	70.91	5.92	70.85	5.28

Figure 8 TG and DTG thermograms of (I) PCDPR12 and (II) DPR-0.85.

rus-modified phenolic resin PCDPR12. Despite that introducing phosphorus group onto the phenolic resin DPR-0.85 slightly diminished the thermal stability of DPR-0.85, the phosphorus-containing phenolic resin PCDPR12 still exhibits relatively good stability in heating resistance. In Figure 8, one stage degradation behavior was observed under nitrogen atmosphere. The degradation may be due to the cracking of the polymer backbones. However, two-stage degradation behavior was found for the phosphorus-containing resin PCDPR12 under nitrogen when the temperature increased. The first-stage degradation at 299°C for PCDPR12 may be caused by the decomposition of the graft phosphate groups. Similar degradation behavior was also observed for the other phosphate-containing polymer.[14] With an increasing temperature, the phosphate groups were aggregated and a solid polyphosphoric acid formed. The covered polyphosphoric acid retards heat penetration and protects the polymer backbone from further degradation. Thus, the decomposition temperature of the PCDPR12 (503°C) backbone was higher than DPR-0.85 (449°C).

The TGA thermograms of DPR-0.85 and PC-DPR with various phosphorus contents are illustrated in Figure 9 and are listed in Table V. PCDPRs with various phosphorus contents presented a similar weight loss behavior. The first-stage weight loss temperature decreased as the phosphorus content increased. Whereas the second degradation stage became gentler and the char yield ratios increased. As the phosphorus content increased, a more phosphorus-rich residue formed during the first-stage decomposition.

Because the phosphorus-rich residue prevents the degradation of the phenolic polymer backbone, a condensed-phase mechanism was involved in the flame-retardant mechanism for PC-DPR.[3] Alternatively, flame-retardation can be gauged by the weight of flame residue up to 700°C.[15] The char yield for DPR-0.85 was 7% whereas the phosphorus-containing phenolic resins PCDPRs were higher than 23% char yield at 700°C under nitrogen. Thus, the PCDPRs possesses more flame retardancy than the phenolic resin DPR-0.85. Furthermore, the LOI values of PCDPR (LOI ≥ 27) were higher than the phenolic resin DPR-0.85 (LOI ≤ 17). The LOI values increase as the phosphorus content increases, confirming that the thermal stability at higher temperatures and the flame retardancy of the polymer can be improved by grafting phosphorus onto the backbone.

CONCLUSIONS

HPTCDP was synthesized via the Friedel-Crafts reaction. DPR was also synthesized by HPTCDP and formaldehyde. The molecular weight could be increased by introducing DCPD into the phenolic resin. When the phosphorus group incorporated into the DPR, the thermal stability was slightly diminished. The char yield and LOI studies verified that the flame retardance of DPR could be improved by phosphorylation. TGA investigation confirmed that a condensed-phase mechanism
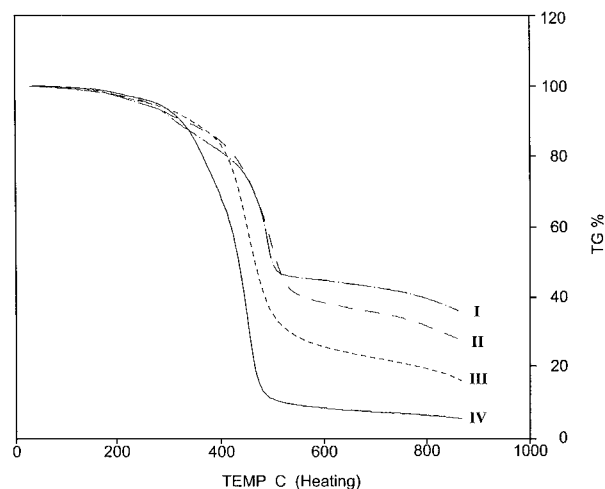

Figure 9 TGA thermogram of (I) PCDPR12, (II) PCDPR11, (III) PCDPR21, and (IV) DPR-0.85.

Table V   DSC, TGA Data, and LOI Values of DPR and PCDPR

Samples	T_g (°C)	Specific Temperature of Weight Loss from TGA (°C)			Char % at 700°C	LOI
		5% Loss	Step 1	Step 2		
DPR-0.85	118	292	—	449	12	<17
PCDPR21	106	218	308	453	39	27
PCDPR11	104	298	299	489	43	31
PCDPR12	93	285	281	503	47	34

prevents the phenolic resin from further degradation. The above results prove that DCPD, a low-valued byproduct obtained from petroleum refinery, can be incorporated with phosphorus-containing compounds to generate high-valued materials with high flame-retardant characteristics. They can have extensive potential application on flame-retardant industrial products.

REFERENCES

1. Banks, M.; Ebdon, J. R.; Johnson, M. Polymer 1994, 35, 3470.
2. Banks, M.; Ebdon, J. R.; Johnson, M. Polymer 1993, 35, 4547.
3. Banerjee, S.; Palit, S. K.; Maiti, S. J Polym Sci Polym Chem 1994, 32, 219.
4. Horrocks, A. R.; Zhang, J.; Hall, M. E. Polym Int 1994, 33, 303.
5. Zupancic, J. J.; Conrad, J. P.; Wrezel, J. A.; Zweig, A. M.; Frechet, J. M. U. S. Pat. 4,824,920, 1989.
6. Curvin, D. R. U. S. Pat. 5,587,007, 1996.
7. Bogan, G. W.; Monnerat, G. A. U. S. Pat. 4,806,625, 1989.
8. Nelson, D. L. U. S. Pat. 4,390,680, 1983.
9. Mori, S.; Fujimoto, K.; Tonoki, S. U. S. Pat. 5, 270, 104, 1993.
10. John, M. U. S. Pat. 5,877,366, 1999.
11. Nair, C. P. R.; Glouet, G.; Guilbert, Y. Polym Degrad Stab 1989, 26, 305.
12. Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S.; Jeng, R. J.; Perng, L. H. J Appl Polym Sci 1996, 61, 613.
13. Gobran; Ramsis. U. S. Pat. 3,944,523, 1976.
14. Liu, Y. L.; Hsiue, G. H.; Chiu, Y. S.; Jeng, R. J.; Ma, C. J Appl Polym Sci 1996, 59, 1619.
15. Krevelen, D. W. Polymer 1975, 16, 615.