

# Preparation of Phosphorous-Containing Poly(epichlorohydrin) and Polyurethane from a Novel Synthesis Route

CHUAN SHAO WU,<sup>1</sup> YING LING LIU,<sup>2</sup> YIE SHUN CHIU<sup>3</sup>

<sup>1</sup> Department of Textile Engineering, Nan Ya Institute of Technology, Chungli, Taoyuan 320, Republic of China

<sup>2</sup> Department of Chemical Engineering, Chung Yuan Christian University, Chungli, Taoyuan 320, Republic of China

<sup>3</sup> Chung San Institute of Science and Technology, Lungtan, Taoyuan 325, Taiwan, Republic of China

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**ABSTRACT:** Phosphorylation of poly(epichlorohydrin) (PECH) was successfully performed via reacting the P—H bond of 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with the pendent chloromethyl groups of PECH. From this reaction, phosphorus-containing PECH with hydroxyl terminal groups was obtained. This compound was further reacted with toluene-2,4-diisocyanate to form a phosphorous-containing polyurethane. The performance of the phosphorylation reaction and the structure of the resulting polymers were characterized by Fourier transform infrared spectroscopy, phosphorous-31 nuclear magnetic resonance (<sup>31</sup>P NMR) spectroscopy, and elemental analysis. The phosphorylated PECH and polyurethane were characterized by thermogravimetric analysis (TGA), which showed weight loss retardation behavior under air at high temperature at >500 °C and high char yield at 700 °C. Both of the synthesized polymers are potentially useful as multifunctional modifiers for epoxy resins and for improving the toughness and flame retardancy of the resins. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2254–2259, 2002

**Key words:** polyurethanes; thermal properties; modification

## INTRODUCTION

Polymer modification is a convenient way to prepare polymers with specialized functional groups for various applications. Polymer modification can be easily achieved via reacting simple chemicals with the reactive pendent groups of the polymer, such as hydroxyl, halomethyl, amino, vinyl groups, etc. Among these reactive groups, chloromethyl group is especially useful because it can be readily modified by a substitution reaction with various nucleophilic reactants under mild

reaction conditions. Therefore, polymers with chloromethyl pendent groups are very often used as starting materials for synthesizing functional polymers.

Poly(epichlorohydrin) (PECH) is one of the major useful polymers with reactive pendent chloromethyl groups for modification via nucleophilic substitution.<sup>1</sup> PECH can be conveniently prepared via a cationic ring-opening polymerization process.<sup>2</sup> Moreover, PECH with terminal hydroxyl groups can be prepared under a proper initiating system and reaction condition. This telechelic PECH can be used as a macromonomer or as a prepolymer for further reactions. Therefore, PECH, with its pendent chloromethyl groups and terminal hydroxyl groups, gives great versa-

Correspondence to: Ying-Ling Liu (ylliu@cycu.edu.tw).

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tility in polymer modifications and polymer reactions.<sup>1</sup> In this study, a telechelic PECH with terminal hydroxyl groups was initially prepared using a well-designed polymerization system. A phosphorus-containing group was then incorporated into the PECH molecular chain by substitution reaction of 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO) with the chloromethyl group. The phosphorus-containing PECH (possessing hydroxyl terminal groups) was further reacted with diisocyanates for preparing polyurethanes (PUs).

Phosphorus compounds and polymers are widely used as flame retardant materials.<sup>3</sup> Therefore, introducing phosphorous into PUs would improve its flame resistant property.<sup>4</sup> Because PECH<sup>5</sup> and PU<sup>6, 7</sup> have often been used as modifiers for toughening epoxy resins, the phosphorus-containing polymers of PECH and PU could be utilized as multifunctional modifiers for epoxy resins, simultaneously improving their toughness and flame retardancy.

## EXPERIMENTAL

### Materials

Epichlorohydrin (ECH, from Lancaster Company) was distilled prior to use. Boron trifluoride–ethylether complex,  $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$ , from TCI Company, was used as received. 9,10-Dihydro-oxa-10-phosphaphenanthrene-10-oxide (DOPO, from Aldrich Company) and toluene-2,4-diisocyanate (2,4-TDI, from TCI Company) were used as received. Glycerol from Aldrich Company was treated with activated charcoal and alumina. The treated glycerol was distilled at 15 mmHg under dry nitrogen and stored under  $\text{P}_2\text{O}_5$ . The solvents were purified according to standard procedures prior to use.

### Instrumental Analysis and Measurements

Fourier transform infrared spectra (FT-IR) were obtained with a Perkin Elmer 2000 FT-IR. The proton and phosphorus-31 nuclear magnetic resonance ( $^1\text{H}$  NMR and  $^{31}\text{P}$  NMR, respectively) spectra were recorded with a Bruker MSL-300 (300 MHz) NMR spectrometer with  $\text{CDCl}_3$  as a solvent. Elemental analysis (EA) was performed with a Heraeus CHN-O rapid elementary analyzer with benzoic acid as a standard. The phosphorous content was determined by elemental analysis with a Micro Digestion Apparatus with a

spectrophotometer. Differential scanning calorimetry (DSC) thermograms were recorded with a thermal analysis (TA) DSC-2900 at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed with a Perkin Elmer TGA 7 at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen or air atmosphere.

### Synthesis of Poly(epichlorohydrin)

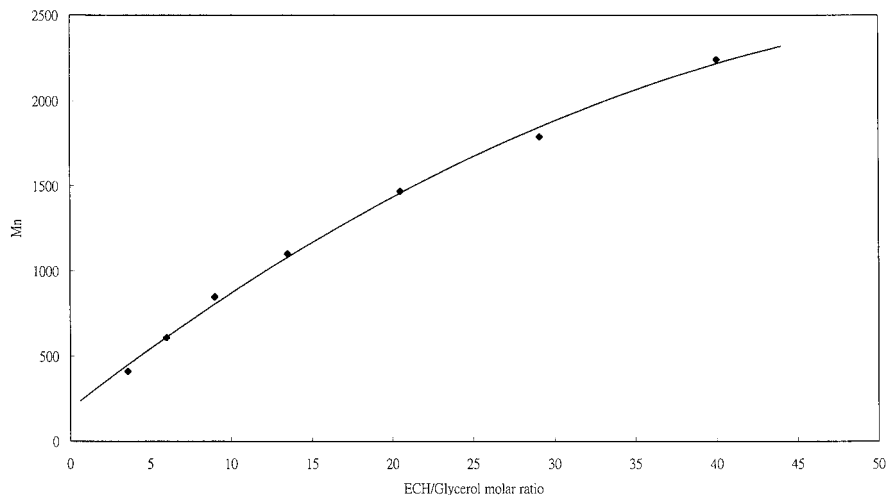
First, 90 mL of dichloromethane and 0.92 g of glycerol (10 mmol) were put into a three-necked round-bottomed flask equipped with a nitrogen stream, a thermometer, and a stirrer. Then, 1.98 g of boron trifluoride–ethylether complex (10 mmol) was introduced into the flask with a syringe. The reaction system was kept at  $\sim 32\text{--}35^\circ\text{C}$  with a water bath. The solution of 12.5 g of epichlorohydrin (135 mmol) in 20 mL of dichloromethane was slowly added into the reaction mixture for 1 h. The reaction mixture was then heated to reflux for 0.5 h. After being cooled to room temperature, 10 mL of 0.5 N ammonia aqueous solution was added to the mixture while stirring. The mixture was then washed with distilled water, a 50/50 wt % methanol/water mixture, and an 80/20 wt % methanol/water solution. The organic layer was then separated. The solvent was removed with a rotary evaporator under reduced pressure. A transparent, viscous product was obtained: product yield, 85 %;  $M_n = 1100$  (measured by GPC), polydispersity index = 1.19.

### Synthesis of DOPO–PECH

First, 8 g of PECH ( $M_n = 1100$ ), 20.5 g of DOPO, and 3 mL of triethylamine were charged into a 250-mL three-necked round-bottomed flask equipped with a nitrogen stream and condenser. The mixture was stirred at  $170^\circ\text{C}$  for 6 h. The reaction mixture was then cooled to room temperature and washed with 150 mL of water. Next, 150 mL of toluene was introduced into the flask, and the mixture was refluxed for 0.5 h and cooled to room temperature. The precipitant was collected and dried at  $80^\circ\text{C}$  under vacuum for 3 h to obtain the white solid product: product yield, 75%;  $M_n = 3280$ ; polydispersity index = 1.26.

### Synthesis of DOPO–PU

First, 10 g of DOPO–PECH and 0.45 g of toluene-2,4-diisocyanate (2,4-TDI) were introduced into a 250-mL three-necked flask with 150 mL of tetrahydrofuran (THF) as a solvent. The mixture was refluxed at  $75^\circ\text{C}$  under nitrogen atmosphere for



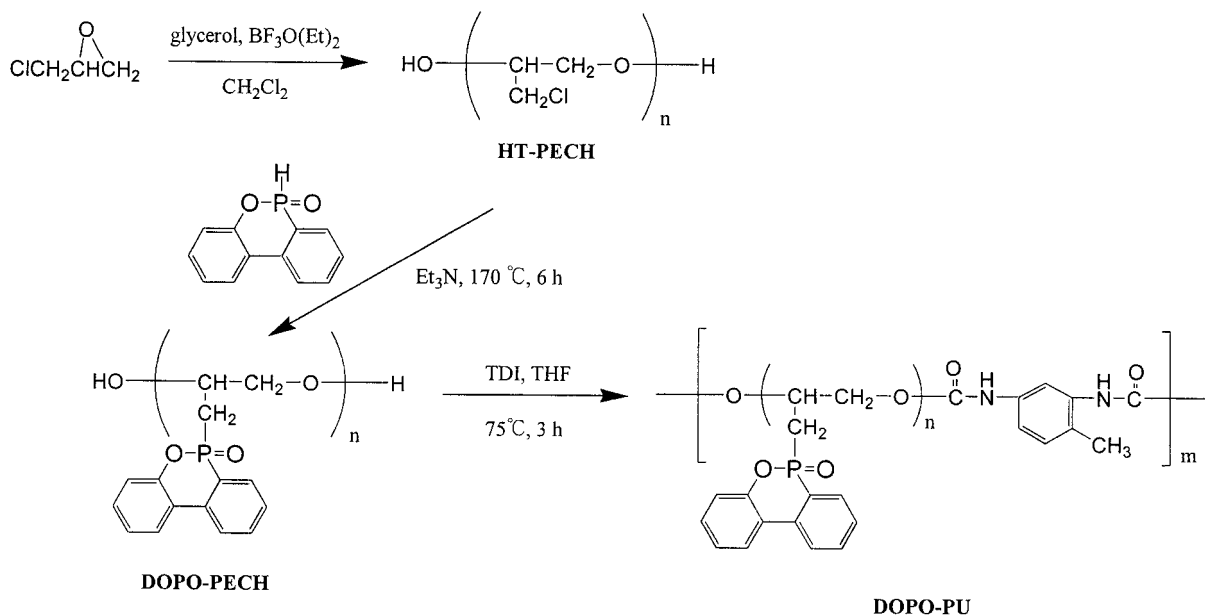
**Figure 1** Synthesis of polyepichlorohydrin: the plot of the  $M_n$  of PECH versus the ECH/glycerol mole ratio.

3 h. The reaction solution was subsequently poured into water. The obtained solid was filtered, washed with water, and dried in a vacuum oven at 70°C for 24 h.

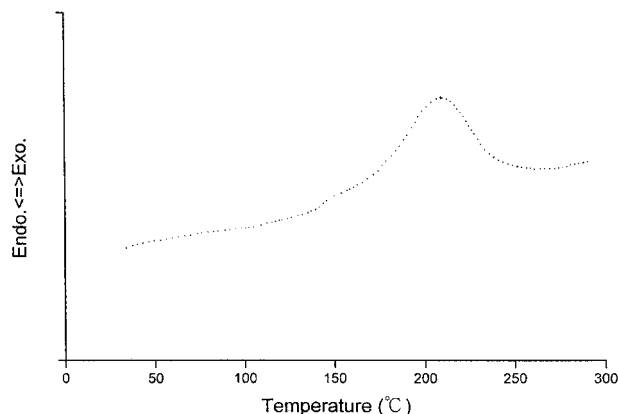
## RESULTS AND DISCUSSION

Hydroxyl-terminated poly(epichlorohydrin) (HT-PECH) was obtained by a cationic ring-opening polymerization reaction, with glycerol as an initiator and  $\text{BF}_3\text{-O}(\text{C}_2\text{H}_5)_2$  as a catalyst. With various

feeding ratios of monomer to glycerol initiator, polymers with different molecular weight were obtained (Figure 1). It was found that the molecular weight of HT-PECH increased and hydroxyl functionality decreased with increasing monomer/initiator ratios. When used as monomers for PU preparation, the molecular weight of the HT-PECH should not be high. Moreover, a hydroxyl functionality of near 2.0 is proper for preparing linear PU with diisocyanates. Based on the experimental results, the molar ratio of monomer/initiator was taken as 13.5, resulting in a HT-PECH



**Scheme 1** Synthesis of phosphorylated poly(epichlorohydrin) and polyurethane.



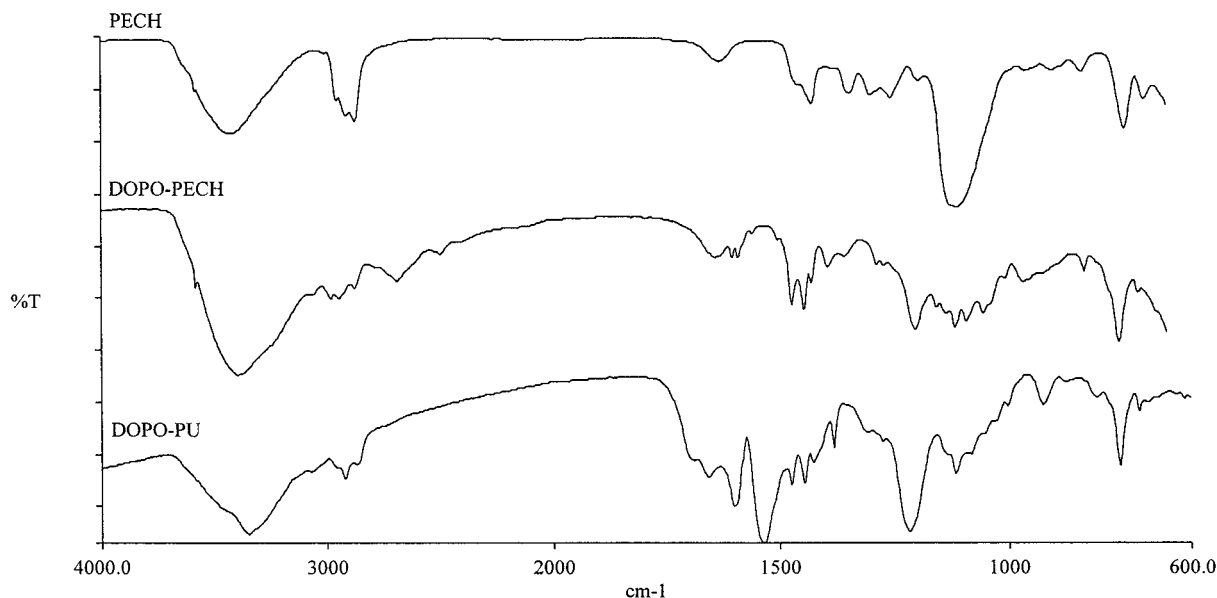
**Figure 2** DSC thermogram of the reaction between PECH and DOPO.

with an  $M_n = 1100$  and a hydroxyl functionality of 2.08.

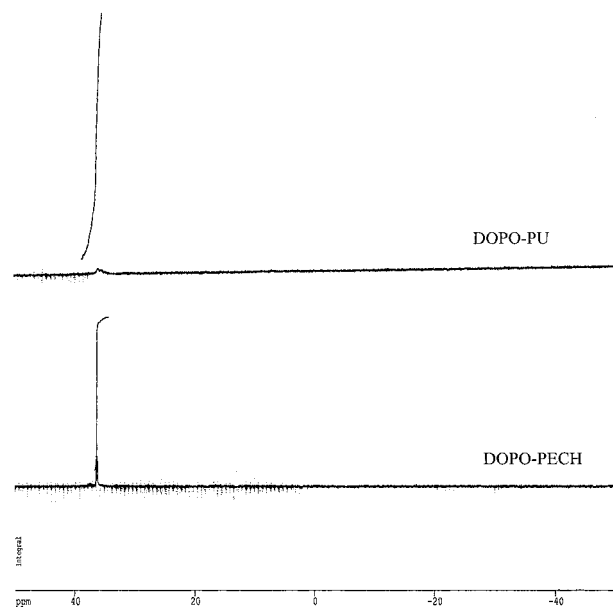
The phosphorylation on HT-PECH was performed by reacting the P—H group of DOPO with the chloromethyl groups of HT-PECH (Scheme 1). The P—H group of DOPO has been demonstrated to be reactive with the vinyl group,<sup>8</sup> carbonyl group,<sup>9</sup> and oxirane ring.<sup>10</sup> The reactivity of the P—H group with the chloromethyl group was probed by DSC in this work. As shown in Figure 2, an exothermic peak at  $\sim 218^\circ\text{C}$  was observed in the DSC heating scan thermogram of the mixture of HT-PECH and DOPO. This exothermic peak revealed the occurrence of the reaction between

HT-PECH and DOPO. The temperature of  $170^\circ\text{C}$  at the left mid-slope of the exothermic peak was taken as the reaction temperature for preparing DOPO-modified HT-PECH (DOPO-PECH). The resulting product was characterized by FT-IR (Figure 3). The disappearance of the absorption peak of the P—H bond of DOPO ( $2389\text{ cm}^{-1}$ ) and the absorption peak of the  $-\text{CH}_2-\text{Cl}$  bond of HT-PECH ( $746\text{ cm}^{-1}$ ) confirmed the reaction between the P—H group and chloromethyl group. As a result of this reaction, the DOPO group was incorporated into the chain of HT-PECH to form DOPO-PECH. Characteristic absorption peaks for the P=O bond ( $1206\text{ cm}^{-1}$ ), P—Ph bond ( $1593\text{ cm}^{-1}$ ), and P—O—Ph bonds ( $926$  and  $757\text{ cm}^{-1}$ ) were also found for DOPO-PECH, demonstrating the DOPO incorporation reaction.

Furthermore, the performance of DOPO phosphorylating into PECH was demonstrated by  $^{31}\text{P}$  NMR analysis. DOPO-PECH showed a single absorption peak at  $\delta = 35.7\text{ ppm}$  in the  $^{31}\text{P}$  NMR analysis (Figure 4). The chemical shift of this absorption peak is coincident with the peak position of DOPO- $\text{CH}_2$  structure. The single peak in the  $^{31}\text{P}$  NMR spectrum also implied that there was no unreacted DOPO in the DOPO-PECH product because DOPO exhibits absorption peaks at  $\delta = 12.5$  and  $17.5\text{ ppm}$  in the  $^{31}\text{P}$  NMR spectrum. Moreover, the results of elemental analysis on phosphorous (Table I) gave further evidence of the phosphorylation and the chemical structures of the products.



**Figure 3** FT-IR spectra of PECH, DOPO-PECH, and DOPO-PU.



**Figure 4**  $^{31}\text{P}$  NMR spectra of DOPO-PECH and DOPO-PU.

DOPO-PECH was further reacted with toluene-2,4-diisocyanate (2,4-TDI) to form PU. This reaction was observed by FT-IR (Figure 2). The consumption of the isocyanate groups of 2,4-TDI was confirmed by the disappearance of the absorption peak at  $2271\text{ cm}^{-1}$ . Moreover, the urethane structure was characterized by absorption bands at  $3479\text{ cm}^{-1}$  ( $\text{—N—H}$  stretching),  $1538\text{ cm}^{-1}$  ( $\text{—N—H}$  deformation), and  $1700\text{ cm}^{-1}$  ( $\text{—C=O}$ ).<sup>11</sup> Absorption peaks for  $\text{P=O}$  bond ( $1219\text{ cm}^{-1}$ ),  $\text{P—Ph}$  bond ( $1598\text{ cm}^{-1}$ ), and  $\text{P—O—Ph}$  ( $926$  and  $757\text{ cm}^{-1}$ ) were also found for DOPO-PU. In addition, a single peak at  $\delta = 35.9$  ppm was observed in the  $^{31}\text{P}$  NMR spectrum of DOPO-PU (Figure 3), implying the existence of DOPO structure in DOPO-PU.

Thermal analysis of the DOPO-containing polymers was performed by DSC and TGA (see Table II). Endothermic peaks at  $85$  and  $181\text{ }^\circ\text{C}$  were found in the DSC thermograms of DOPO-PECH and DOPO-PU, respectively. The endo-

thermic peak should be the melting behavior of the polymers. However, a baseline shift was not observed for the DSC thermograms, indicating no glass transition temperatures ( $T_g$ ) for the polymers. Therefore, the  $T_g$  of the polymers might be lower than room temperature. The TGA thermograms of the obtained polymers are shown in Figure 5. DOPO-PECH showed a two-stage weight loss behavior under heating in nitrogen at  $220$  and  $350\text{ }^\circ\text{C}$ . The first weight loss was due to bond breaking of the DOPO groups, and the second weight loss was from the decomposition of the PECH chain, as indicated by the TGA results that PECH demonstrates rapid weight loss at  $348\text{ }^\circ\text{C}$ .<sup>12</sup> Moreover, when heated in air, DOPO-PECH showed a weight loss pattern similar to that of nitrogen at temperatures  $< 450\text{ }^\circ\text{C}$ . In the high temperature region, the weight loss rate of the polymer was retarded in air. However, this retardation of weight loss was not observed for the polymer heated in nitrogen. When heated in air, oxidation occurred in high temperature region, with involvement of phosphorus. This oxidation resulted in some phosphorus-containing char with high heat resistance and weight loss retardation. On the other hand, the bond-breaking temperature of the DOPO group in DOPO-PECH was leveled up to  $\sim 280\text{ }^\circ\text{C}$  after polymerizing with TDI (DOPO-PU), implying that the long polymer chain and crosslinking structure enhanced the thermal stability of the pendent DOPO groups. Moreover, the temperature of the second-stage weight loss for DOPO-PU ( $400\text{ }^\circ\text{C}$ ) was also observed to be higher than that of DOPO-PECH ( $350\text{ }^\circ\text{C}$ ). From these results, it was concluded that the decomposition behaviors of the pendent DOPO groups and the polymer chains were independent for DOPO-PECH and DOPO-PU. This enhancement of the thermal stability of DOPO-PU resulted from the long polymer chain, crosslinking structure, and the urethane linkage. Finally, it is noteworthy that the weight loss retardation was also observed for DOPO-PU when heated in air (Figure 5, curve d). Oxidation and

**Table I** The Phosphorus Content of the Obtained Polymers

Polymer	C	H	P
	Found % (Calc. %)	Found % (Calc. %)	Found % (Calc. %)
PECH	39.01 (38.92)	5.32 (5.40)	0.0 (0.0)
DOPO-PECH	66.94 (66.18)	4.21 (4.78)	11.0 (11.4)
DOPO-PU	66.71 (66.00)	4.12 (4.57)	10.4 (10.9)

**Table II Thermal Analysis Data of the Polymers**

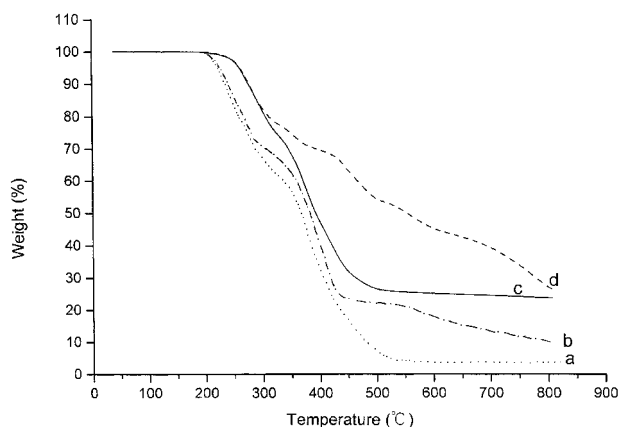
Polymer	DSC Analysis Data		TGA Analysis Data: Temperature (°C) at							
	$T_g$ (°C)	$T_m$ (°C)	5% Weight Loss		1st Rapid Weight Loss		2nd Rapid Weight Loss		Char Yield at 700°C (%)	
			In N <sub>2</sub>	In air	In N <sub>2</sub>	In air	In N <sub>2</sub>	In air	In N <sub>2</sub>	In air
PECH	— <sup>a</sup>	—	281	275	348	352	—	—	0	0
DOPO-PECH	—	85	212	213	220	223	350	360	5	13
DOPO-PU	—	181	258	258	280	280	400	460	25	37

<sup>a</sup> Not observed for DSC measurement at the temperature range of 30–250°C.

phosphorus carbonization resulted in a weight loss retardation and led to the complicated multistep weight loss pattern.

## CONCLUSIONS

It has been demonstrated that PECH can be modified with the phosphorous-containing compound DOPO by reacting the chloromethyl group with the P—H bond. This phosphorylation reaction was utilized to obtain phosphorous-containing PECH with hydroxyl terminal groups (DOPO-PECH). Subsequent reaction with TDI resulted in phosphorous-containing PU (DOPO-PU). A novel route for obtaining phosphorous polymers was performed.



**Figure 5** TGA thermograms of (a) DOPO-PECH in nitrogen, (b) DOPO-PECH in air, (c) DOPO-PU in nitrogen, and (d) DOPO-PU in air.

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