

Synthesis and Characterization of Water-Dispersed Flame-Retardant Polyurethane Resin Using Phosphorus-Containing Chain Extender

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ABSTRACT: In this research, a flame-retardant water-dispersed polyurethane resin was synthesized through incorporating phosphonate groups into the polyurethane structure in the chain-extension step. A phosphorus-containing reactive flame-retardant compound was synthesized for this purpose. First, bis(4-nitrophenyl)phenyl phosphine oxide was synthesized and then converted to bis(4-amino phenyl)phenyl phosphine oxide (BAPPO) by reducing its nitro groups into amines. The obtained products were characterized by IR, ¹H-NMR, and ³¹P-NMR, and the thermal prop-

erties of the polymers were determined by DSC analysis. The BAPPO-containing polyurethane showed physical properties that were almost similar to those of phosphorus-free polyurethane and exhibited good flame resistance with a limiting oxygen index value of 27. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1314–1321, 2004

Key words: polyurethanes; thermal properties; phosphorus; flame retardance; resins

INTRODUCTION

High requirements for fire resistance and the increasing interest in using less organic solvents in polymer preparation because of the necessity of protecting the environment led to the development of fire-resistant waterborne polymer resins in coating technology. Aqueous polyurethane dispersions are one of the most rapidly developing branches of the waterborne polymers in the coating industry because of their high performance properties, such as high abrasion and weather resistance, tensile and impact strength, good gloss properties, and low temperature flexibility.^{1–10} This widespread use of water-based polyurethanes has necessitated enhancement of their flame resistance by incorporating flame-retardant compounds into their structure.^{11,12}

A simpler technique for preparing fire-resistant polymers is to blend flame-retardant compounds with polymeric materials. This process requires using large amounts of flame-retardant compound that may migrate toward the surface of the film after application, leading to the deterioration in the film properties of the polymer.^{13–15} Consequently, using reactive flame-retardant compounds has recently garnered much interest.^{11,12,16–21}

In the selection of the type of flame-retardant compound, the burning mechanism should be considered. Among most of the flame-retardant compounds, those containing phosphorus are known to produce incom- bustible char during combustion mainly through a condensed-phase mechanism, which leads to less toxic gas evolution into the atmosphere. In addition, the flame-retardant efficiency of phosphorus compounds is known to be higher than that of halogenated compounds.^{17,22–24}

In this investigation, a phosphorus-containing flame-retardant compound containing reactive groups was first synthesized and then characterized. A further process includes the introduction of this flame-retardant compound onto the polyurethane main chain in the chain-extension step. Physical, mechanical, thermal, and flame-retardant properties of the resulting polymers were then investigated.

EXPERIMENTAL

Materials

Phenyl phosphonic dichloride (PPDC), *p*-nitrophenol sodium salt (Aldrich Chemical, Milwaukee, WI), tetrahydrofuran (THF), tin(II) chloride, fuming hydrochloric acid, chloroform (Merck AG, Darmstadt, Germany) were used as received. Poly(propylene-co-ethylene) polyol (average functionality of 2.9 and MW of 3066) was supplied from Aksan Company and dehydrated before use. Toluene diisocyanate (TDI), triethylamine (TEA), and ethylene diamine (EDA) were

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supplied by Merck AG and used as received. Methyl ethyl ketone (MEK) and methyl ethyl ketoxime (MEKO) were dehydrated over molecular sieves. Tartaric acid (TA) was supplied by Merck AG and heated to 120°C for 2 h before use.

Synthesis of bis(4-nitrophenoxy)phenyl phosphine oxide (BNPPO)

Dehydrated *p*-nitrophenol sodium salt (17 g) was dissolved in 100 mL of dry THF in a 500-mL round-bottom flask fitted with a magnetic stirrer, condenser, thermometer, and a dropping funnel. A solution of a phenyl phosphonic dichloride (8.2 g) in 25 mL dry THF was added dropwise to the solution within a 15-min time period. The solution temperature was then increased to 45°C and maintained at this temperature for 6 h followed by stirring at room temperature for another 24 h. After removing THF, the precipitant was extracted two times with ethyl acetate and distilled water. The extract was then dried over MgSO₄ and the solvent was evaporated to obtain a final product having a yield of 90%.

Synthesis of bis(4-aminophenoxy)phenyl phosphine oxide (BAPPO)

Tin(II) chloride (45 g) was dissolved in a solution of fuming hydrochloric acid (50 mL) and 100 mL ethanol at room temperature in a 500-mL round-bottom flask. BNPPO (6.25 mL) was then added to the solution and the reaction temperature was maintained at 40°C for 5 h under agitation. The temperature was cooled to room temperature and stirred for a further 24 h. The mixture was then neutralized by a 25% NaOH aqueous solution and extracted with chloroform. After concentrating the extract, BAPPO was obtained with 50% efficiency.²⁰

Synthesis of water-dispersed polyurethane resins

Hydrophilic monomer (L-tartaric acid, 1.05 g) was dissolved in a cosolvent (MEK, 5 mL) under nitrogen atmosphere at room temperature in a 500-mL flask. Copolymer polyol (23.809 g), of which the hydroxyl number and molecular weight were determined by using ASTM D-4274 test method, was added to the system and the solution temperature was increased to 70°C. After keeping the solution at that temperature for 30 min, TDI (4.229 g) was added and the solution was stirred until the completion of the reaction controlled by a dibutylamine back titration method. The system was then cooled to 50°C and the NCO groups of the prepolymer were blocked with MEKO (0.296 g). After stirring the solution at that temperature, carboxyl groups of the prepolymer were neutralized with TEA (0.708 g) dissolved in MEK over a period of 30

min. Dispersion was accomplished by adding demineralised water to the solution at room temperature. Ethylene diamine (0.204 g) was then added to the dispersion for a period of 10 min, and chain extension was performed for the next 2 h.

For the preparation of flame-retardant water-dispersed polyurethane resin, BAPPO (1.16 g) was used as a chain extender instead of ethylene diamine.

Preparation of test panels

A sufficient number of test panels were prepared, which allowed us to repeat the measurements. For the abrasion, impact, and mandrel bending test methods, metal plates were used and the resins were applied to the surface of the test panels with a thickness of 50 μm by using a film-casting knife. For the pendulum hardness test, glass panels [70 × 37 × 3 mm (length × width × thickness)] were filled with subsequent applications of the resin after alternate drying periods. Gloss measurements were carried out on glass sheets that were coated in the same way as the metal plates. The samples [125 × 6.5 × 3.0 mm (length × width × thickness)] were prepared to perform the experiments for determining limiting oxygen index (LOI) values of the resins. All of the samples were first predried at room temperature and then heated to 125°C for a period of 60 min to perform chain extension.

Instrumental analysis

IR spectra were recorded with KBr powder using a Nicolet 510 FTIR spectrophotometer (Nicolet Analytical Instruments, Madison, WI). A Bruker Spectrospin Advance Series DPX 400 NMR spectrometer (Bruker Instruments, Billerica, MA) was used to obtain ¹H-NMR and ³¹P-NMR spectra for which CDCl₃ and DMSO-*d*₆ were used as solvents. Thermal properties of the samples were measured using differential scanning calorimetry (Perkin-Elmer DSC-4; Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10°C/min under a nitrogen atmosphere. LOI values were measured on a Stanton Redcroft flame meter according to ASTM D2863 testing method. Perzox pendulum hardness was measured by a Braive-Instruments Persoz/Koning Pendulum (No. 3034) according to ASTM D4366. The impact resistance of the cured resins was determined with a Gardner impact tester (Model 5510) by following ASTM D2794. The resistance of the coatings to cracking along the increasing radius of the conical mandrel was measured according to ASTM D522 by using a conical mandrel bender tester (Braive-Instruments, No. 1510). ASTM D523 was followed to determine 20, 60, and 80° specular gloss and ASTM D968-81 to determine the resistance of the coated surface to abrasion produced by sand falling onto the coated test panels from an 80-cm height.

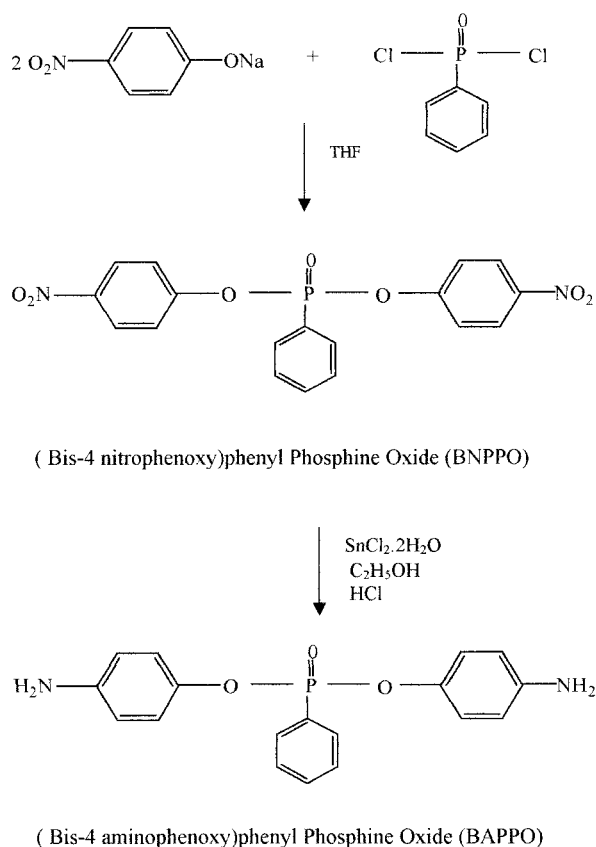


Figure 1 Synthesis of BNPPO and BAPPO.

RESULTS AND DISCUSSION

The synthesis of phosphorus-containing polyurethane was achieved by reacting BAPPO with the prepolymer. The phosphorus-containing nitro compound (BNPPO) was first synthesized and was then converted to the amine-containing compound, which is BAPPO. Figure 1 illustrates the steps followed to obtain a flame-retardant compound.

Chemical structures of the resulting compounds were characterized by IR, $^1\text{H-NMR}$, and $^{31}\text{P-NMR}$ and the related data are summarized in Tables I and II. The IR spectra of BNPPO and BAPPO are given in Figures 2 and 3, respectively. The formation of the phosphonate structure was revealed by the peaks observed at 1250 cm^{-1} for $\text{P}=\text{O}$, 1218 cm^{-1} for $\text{P}-\text{O}-\text{Ph}$, and $1437\text{--}1442\text{ cm}^{-1}$ for $\text{P}-\text{Ph}$. The spectrum shows strong absorption bands at 827 , 1354 , and 1515 cm^{-1} , indicating the existence of nitro groups (Fig. 2). The formation of BAPPO from BNPPO was confirmed by absorption bands appearing at 3361 and 3464 cm^{-1} , indicating the existence of NH_2 groups in the structure (Fig. 3). The formation of BNPPO and BAPPO was further verified by $^1\text{H-NMR}$ and $^{31}\text{P-NMR}$, which are illustrated in Figures 4 and 5, respectively. In Figure 4(A) the aromatic protons of BNPPO may be observed at $\delta = 7.40$ and 8.23 ppm ($\text{C}_6\text{H}_4-\text{NO}_2$) and at $\delta = 7.60$,

TABLE I
Absorption Band Assignments for BNPPO, BAPPO, and Polyurethane Resins

Wavenumber (cm^{-1})	Assignment ^a
1233–1250	ν ($\text{P}=\text{O}$)
1218	ν ($\text{P}-\text{O}-\text{Ph}$)
1437–1442	ν ($\text{P}-\text{Ph}$)
827	ν ($\text{N}-\text{O}$)
1354	ν_s (NO_2)
1515	ν_a (NO_2)
3361–3464	ν ($\text{N}-\text{H}$) in BAPPO
1730	ν ($\text{C}=\text{O}$) in urethane bond
3400	ν ($\text{N}-\text{H}$) urethane nonbonded
1530	δ ($\text{N}-\text{H}$)
2800	ν_s ($\text{C}-\text{H}$) in CH_2
2900	ν_a ($\text{C}-\text{H}$) in CH_2
1600	ν ($\text{C}=\text{C}$) in aromatic ring

^a ν , stretching; δ , bending; ν_a , asymmetric stretching; ν_s , symmetric stretching.

7.71, and 8.0 ppm ($\text{P}-\text{C}_6\text{H}_5$); the aromatic protons of BAPPO displayed peaks at $\delta = 6.56$ and 6.95 ppm ($\text{C}_6\text{H}_4-\text{NO}_2$) and at $\delta = 7.47$, 7.92 , and 7.57 ppm ($\text{P}-\text{C}_6\text{H}_5$) in Figure 5(A). The broad peak appearing at $\delta = 3.60\text{ ppm}$ in the $^1\text{H-NMR}$ spectrum of BAPPO corresponds to the $\text{C}_6\text{H}_4-\text{NH}_2$ protons. Furthermore, in Figure 4(B) and Figure 5(B) the $^{31}\text{P-NMR}$ spectra of BNPPO and BAPPO gave peaks at $\delta = 13.70$ and 13.20 ppm , respectively, confirming the formation of phosphonate structure.

Chemical structures of phosphorus-free and phosphorus-containing polyurethanes were identified by IR spectra, depicted in Figures 6 and 7, respectively. Both spectra showed strong absorptions at around 3400 cm^{-1} corresponding to the urethane NH stretching; at 1530 cm^{-1} referring to NH deformation; and at 1730 cm^{-1} , indicating the presence of the $\text{C}=\text{O}$ group in the urethane structure. The peak shoulders appearing around 2800 and 2900 cm^{-1} were assigned to the symmetric and asymmetric stretching absorptions for $\text{C}-\text{H}$ in CH_2 groups, respectively. Aromatic groups were detected around 1600 cm^{-1} in the spectra. In addition to these characteristic absorptions, in the IR spectrum of BAPPO-containing polyurethane (Fig. 7)

TABLE II
NMR Characterization of Phosphorus-Containing Compounds

Compound	Chemical shift (δ , ppm)	
	$^1\text{H-NMR}$	$^{31}\text{P-NMR}$
BNPPO	7.40–8.23 ($\text{C}_6\text{H}_4-\text{NO}_2$) 7.60–8.00 ($\text{P}-\text{C}_6\text{H}_5$)	13.70
BAPPO	6.56–6.95 ($\text{C}_6\text{H}_4-\text{NO}_2$) 7.47–7.92 ($\text{P}-\text{C}_6\text{H}_5$) 3.60 ($\text{C}_6\text{H}_4-\text{NH}_2$)	13.20

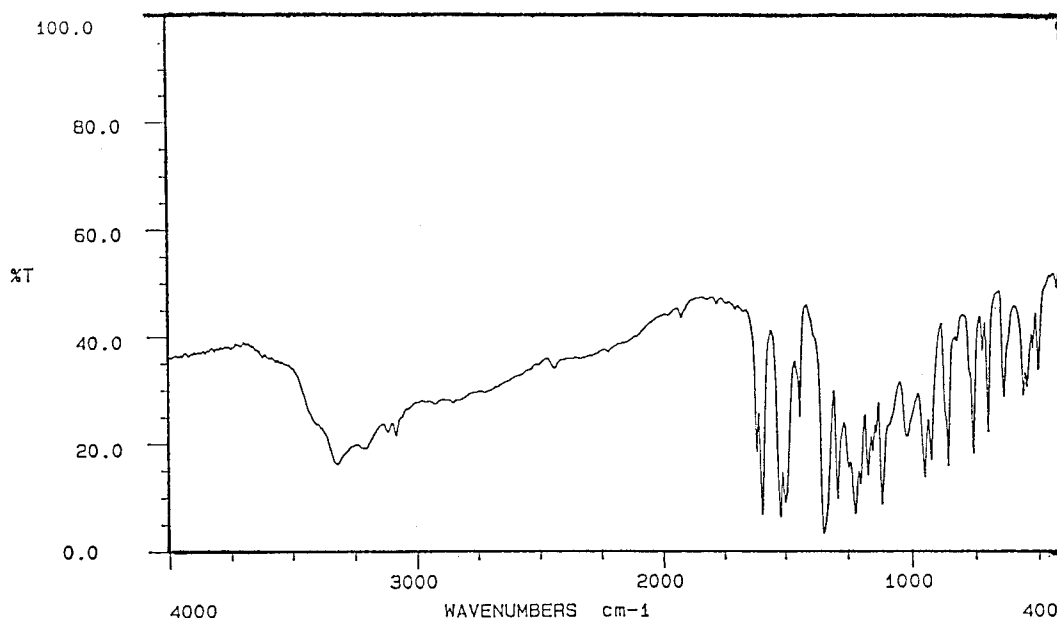


Figure 2 IR spectrum of BNPPPO.

the phosphonate structure was characterized by the peaks at 1218 cm^{-1} (P—O—Ph stretching), at 1233 cm^{-1} (P=O stretching), and at 1438 cm^{-1} (P—Ph stretching).

Thermal properties of phosphorus-free polyurethane and BAPPO-containing polyurethane were investigated by DSC under nitrogen atmosphere and the corresponding thermograms are illustrated in Figures 8 and 9, respectively. In the thermograms, endotherms appearing above 250°C were assigned to the melting temperature of the hard-segment microcrystalline

structure.^{25,26} Both resins decomposed at around 375°C . It is known that only above 350°C , does polyol begin to decompose at a significant rate.²⁷ The increase in the melting temperature of the hard-segment microcrystalline structure (Fig. 9) indicates that the polyurethane with BAPPO chain extender exhibited a higher hard-segment crystallinity than that of the polyurethane with aliphatic chain extender (EDA) (Fig. 8). The longer chain length and the presence of rigid aromatic groups in BAPPO-containing polyurethane may contribute to the higher packing ability of

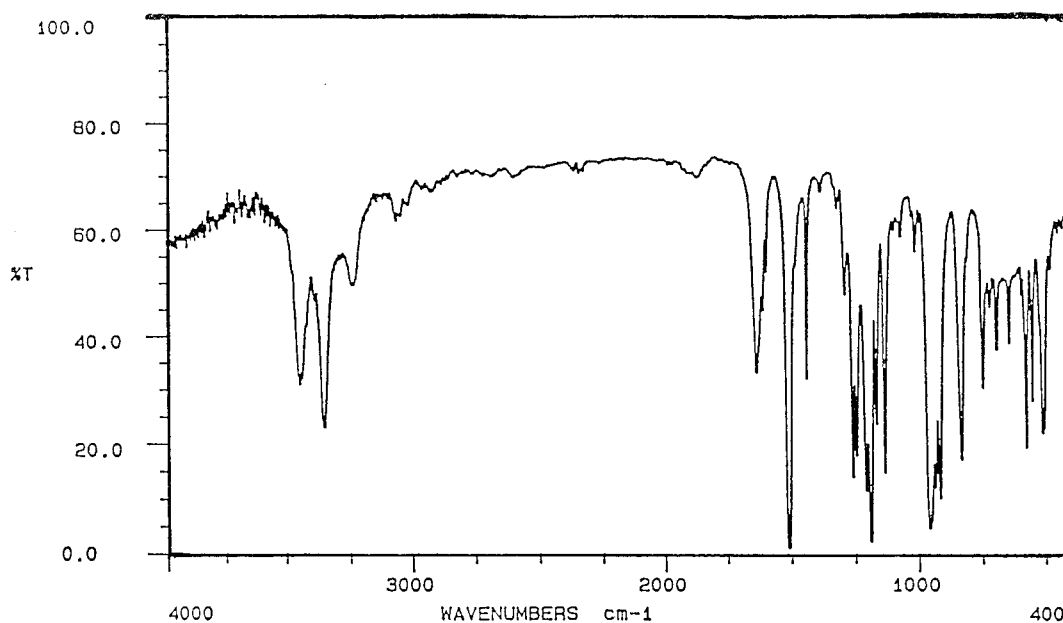


Figure 3 IR spectrum of BAPPO.

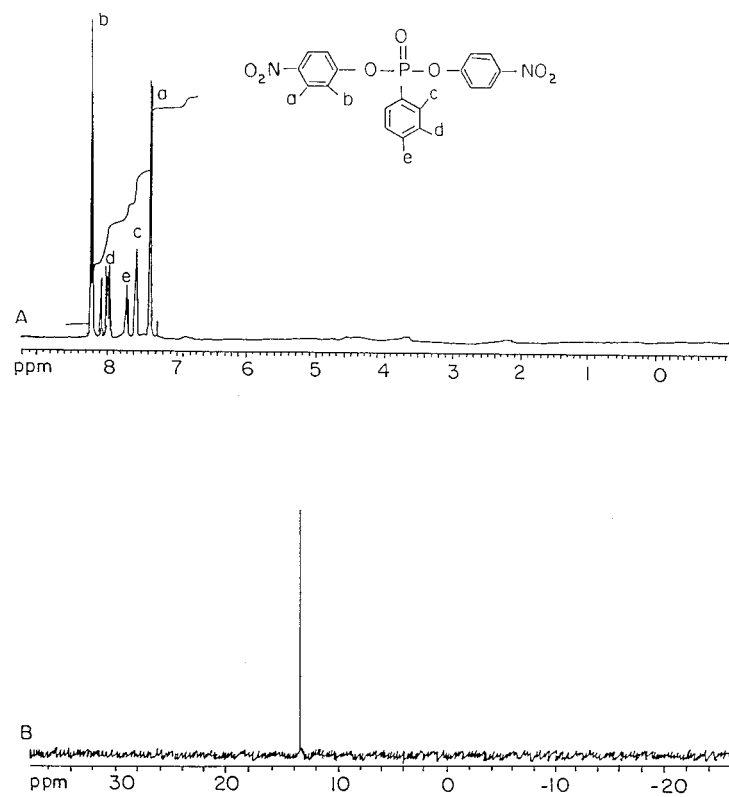


Figure 4 (A) $^1\text{H-NMR}$ and (B) $^{31}\text{P-NMR}$ spectra of BNPPO.

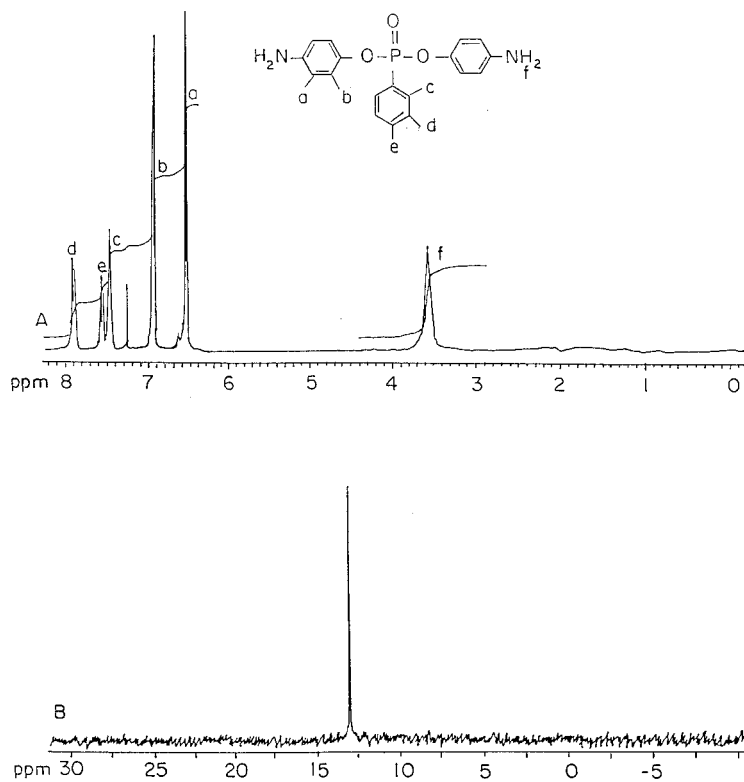


Figure 5 (A) $^1\text{H-NMR}$ and (B) $^{31}\text{P-NMR}$ spectra of BAPPO.

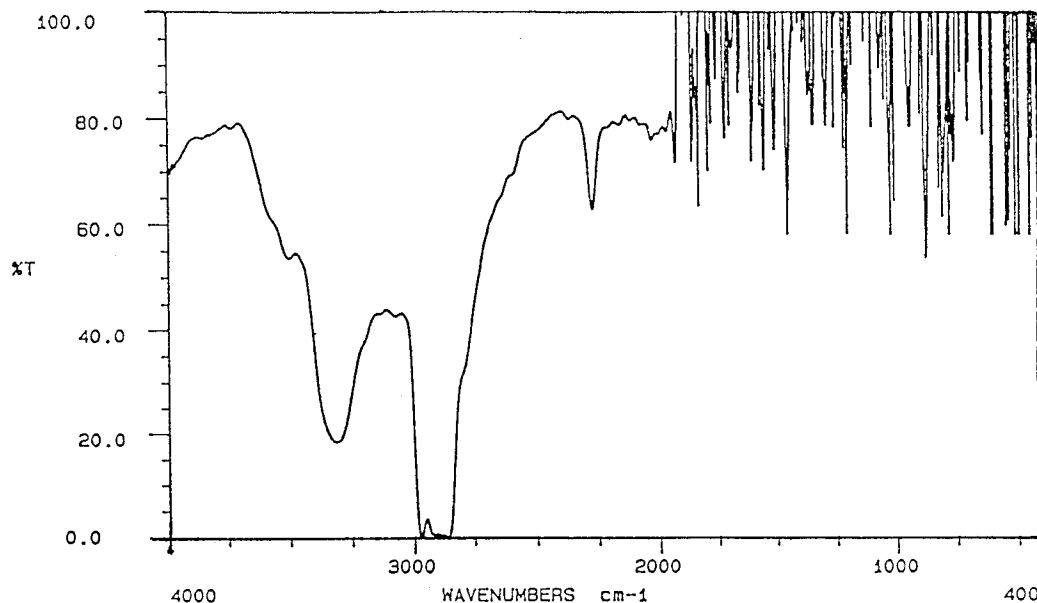


Figure 6 IR spectrum of polyurethane with EDA chain extender.

the hard segments and this may result in a more-ordered structure compared to that of the polyurethane resin with EDA chain extender.⁷

The main objective of this study was to enhance the flame retardancy of the polyurethane resin. The LOI test method was used to evaluate the flame-retardant properties of both resins. Whereas the LOI value for water-dispersed polyurethane resin was found to be 24, it increased to 27 when BAPPO was incorporated into the polymer structure.

The physical properties of the obtained polymers are summarized in Table III. In general, phosphorus-

free polyurethane resin showed better abrasion resistance. This may be attributed to the presence of more flexible units in the EDA chain extender, which is replaced by BAPPO in the case of phosphorus-containing polyurethane. The Persoz hardness value of BAPPO-containing resin was slightly higher than that of EDA-containing resin, again because of the presence of more rigid groups and higher hard-segment crystallinity of BAPPO-containing resin.²⁸ All the samples passed the mandrel bending and impact resistance tests without any crack formation on the coating surface. Incorporating BAPPO into the structure dete-

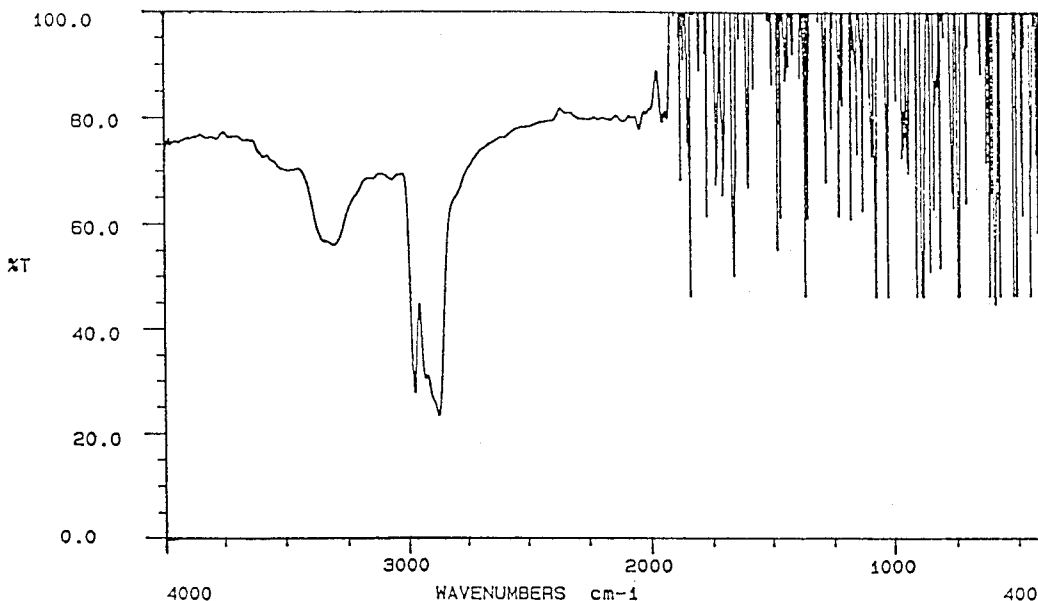


Figure 7 IR spectrum of polyurethane with BAPPO chain extender.

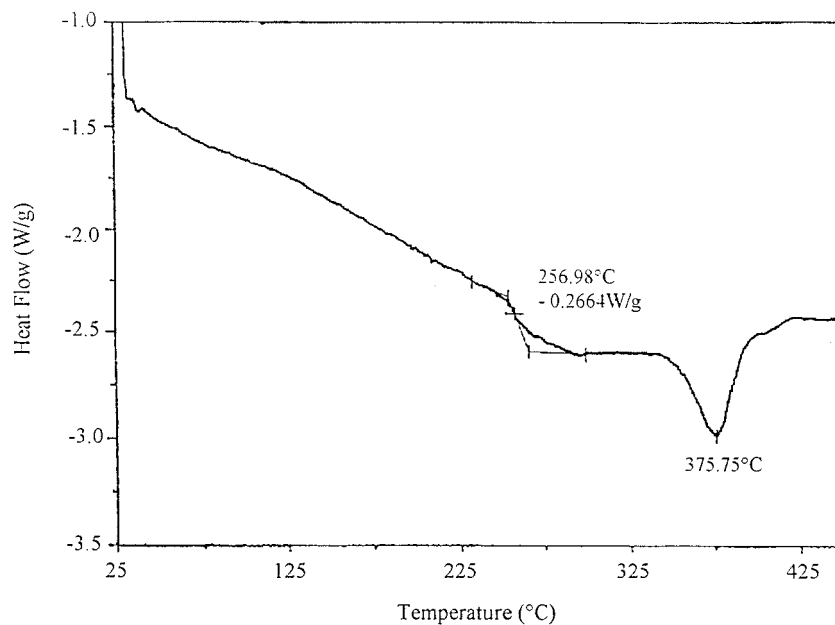


Figure 8 DSC thermograms of polyurethane with EDA chain extender.

riorated the gloss properties of the polyurethane, which should be attributable to the change in the chain conformation caused by the presence of different chain extenders in the structure.

CONCLUSIONS

A reactive phosphorus-containing compound was successfully obtained on the base of phenyl phosphonic dichloride and used as a chain extender in the

synthesis of flame-retardant polyurethane resin. The structural information of all the synthesized products was determined using IR, $^1\text{H-NMR}$, and $^{31}\text{P-NMR}$ techniques. Most of the physical properties of BAPPO containing polyurethane were compared with those of phosphorus-free polyurethane. No significant deterioration except in the gloss properties of the polymer was detected after BAPPO was incorporated into the structure. This difference is attributed to the change in the chain conformation of polyurethane with BAPPO.

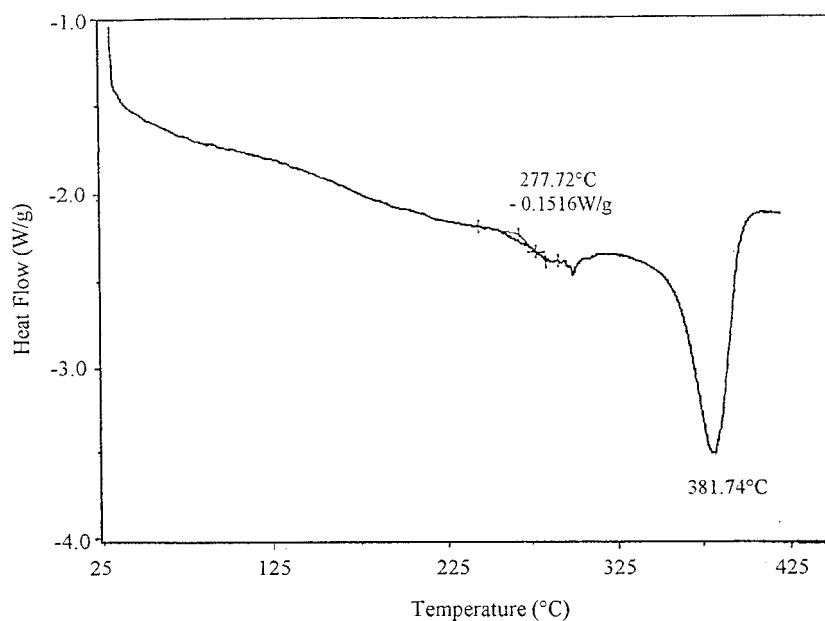


Figure 9 DSC thermograms of polyurethane with BAPPO chain extender.

TABLE III
Physical and Mechanical Properties of Polyurethanes

Test type	Sample	
	Phosphorus-free PU	Flame-retardant PU
Hardness (Persoz)	38.25	39.87
Specular gloss		
20°	6.5	1.8
60°	32.8	11.5
85°	50.4	18.1
Abrasion resistance (kg/ μ)	4.99	4.08
Impact resistance (J)	>19	>19
Mandrel bending	Pass	Pass

The DSC heating curves revealed that the presence of BAPPO affects the crystallizability of the hard segments of polyurethane and raises the melting temperature of the hard segment microcrystalline structure. It has been demonstrated by LOI testing that BAPPO is an effective flame-retardant compound in enhancing the flame resistance of polyurethane resins.

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