

# Intumescent Polyurethane Coatings with Reduced Flammability Based on Spirocyclic Phosphate-Containing Polyols

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**ABSTRACT:** Polyurethane coatings (PUC) with reduced flammability based on spirocyclic phosphate-containing polyols were synthesized from spirocyclic pentaerythritol di(phosphate acid monochlorides) (SPDPC). Some characteristic properties of the polyols and PUC were examined. The effects of the structure and the amount of contained phosphate on the properties of the polyols and PUC, especially on their resistance to combustion were studied. The spirocyclic phosphate-containing polyols are effective flame retardants for improving the resistance to combustion of PUC. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 471–475, 1997

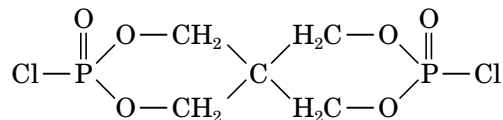
**Key words:** spirocyclic phosphate containing polyols; intumescent polyurethane coatings; thermal analysis; flammability; flame-resistance mechanism

## INTRODUCTION

According to the flame-retardant mechanism, flame-retardant coatings can be classified into intumescent and nonintumescent. Intumescent systems have attracted more and more attention from many researchers.<sup>1–4</sup> Because intumescent materials can form, by heating, a charred layer of cellular foam on their surface to provide resistance to both heat and mass transfer, giving good heat insulation, so that the underlying material is protected from a flame. Generally speaking, the intumescent system consists of three main substances: an acid source (e.g., phosphorus-containing substance), a carbon source (e.g., polybasic alcohol), and a gas source (nitrogen-containing substance). Many organophosphorous compounds of various types have been synthesized for this purpose and some of them are com-

mercially available. It has been found that among the most suitable flame retardants is reactive phosphorus-containing compounds, mainly polyols.<sup>5,6</sup> An important advantage in this case is the inclusion of the phosphorus-containing polyols in the chemical structure of the polyurethane. For this reason, unlike the nonreactive additives, they do not diffuse toward the surface of the polymeric material and remain more effectively resistant to combustion for longer periods.

Spirocyclic pentaerythritol di(phosphoric acid monochlorides) (SPDPC), a phosphate of 3,9-dichloride-2,4,6,8-tetraoxa-3,9-diphosphaspiro-(5,5)undecane-3,9-dioxide, is an intumescent flame retardant. Its structure is



Because it contains an acid source and a carbon source in one molecule, SPDPC forms, on heating, a charred layer of cellular foam. Furthermore, a

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**Table I** Components of Polyols

Polyols	Raw Materials (mol)						Acid No. (mg KOH/g)
	SPDPC	Phthalic Anhydride	Sebacic Acid	Diethylene Glycol	Trimethanol Propane		
P0 <sup>a</sup>	0	0.05	0.25	0.3	0.07	19	
P1	0.024	0.05	0.225	0.3	0.07	65.2	
P2	0.050	0.05	0.200	0.3	0.07	86.3	
P3	0.050	0.15	0.100	0.3	0.07	117.8	

<sup>a</sup> P0, P1, P2, and P3 indicate polyol 0, polyol 1, polyol 2, and polyol 3, respectively.

group of phosphates, phosphate amides, polyphosphates, and poly(phosphate amide)s were synthesized from SPDPC; these are very effective as additives for flame retardants<sup>7,8</sup> and have been used for the flame retardation of polyolefins and polyesters.

The isocyanate-containing component of polyurethane contains nitrogen, which can be used as gas source of an intumescent system. The aim of the present work was to prepare polyurethane coatings (PUC) and to study the effect of the structure and amount of the phosphate on some properties of polyols and PUC, mainly on the resistance to combustion.

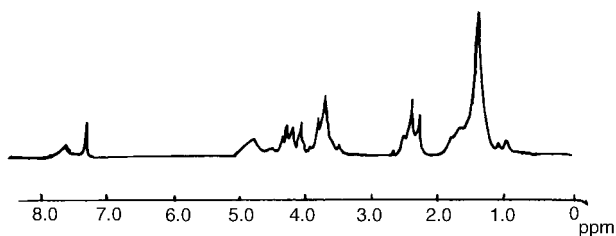
## EXPERIMENTAL

### Materials

SPDPC was synthesized by the reaction of phosphorus oxychloride with pentaerythritol as reported.<sup>9</sup> The isocyanate-containing component (solidifying) of polyurethane was obtained from the Beijing Academy of Building Materials Science. The NCO % was 8–10, which was prepared from TDI and trimethanolpropane.

### Synthesis of P0

The raw materials were mixed together (Table I) and heated to 165°C, refluxing for 1 h; then the



**Figure 1** <sup>1</sup>H-NMR spectra of P2.

apparatus was changed to distillation, increasing the temperature slowly to 200°C in 3 h to remove the water. When the acid value could not be decreased, the reaction was stopped. The product was ready to be used.

### Synthesis of P1, P2, and P3

After heating the diethylene glycol to 120°C, the SPDPC was added in batches, and the nitrogen was inlet to drive off the HCl. Then, the phthalic anhydride, sebacic acid, and trimethanol propane was introduced into the mixture at 160°C for 1 h. Next, the device was changed to distillation and the temperature was gradually increased to 200°C in 3 h to drive off the water. When the acid value could not be decreased, the reaction was stopped and the product was ready to be used.

### Preparation of the PUC

The PUC were prepared by dissolving the polyols in a miscible solvent of xylene and *n*-butyl acetate and then it was manually mixed by solidifying and laid aside in air until completely dry.

### Equipment and Characterization Procedures

Thermal analysis was performed on a Shimadzu DT-40 instrument at a heating rate of 10°C min<sup>-1</sup>. The 60 MHz <sup>1</sup>H-NMR spectra were recorded on a Kitachi R-24B spectrometer in a 5 mm o.d. sample tube (tetramethylsilane served as the internal standard) using CDCl<sub>3</sub> as the solvent. Infrared spectra were recorded on a TFS-40 spectrophotometer as a KBr disc. The scanning microscopic image was observed on an AMMRY-1000B. Elemental analyses were performed on a PE-2400 analyzer. The cloudiness method was used for determining the solubility parameters.

**Table II Results of Titration Using Acetone as the Solvent**

Polyols	Concn g (50 mL) <sup>-1</sup>	Water		<i>n</i> -pentane		$\delta$ (Jm <sup>-3</sup> ) <sup>1/2</sup>
		ml	$\delta$ mh	ml	$\delta$ ml	
P0	0.2	3.0	26.48	12.9	17.45	21.97
P1	0.2	3.9	27.80	11.1	17.65	22.72
P2	0.2	4.2	28.20	7.0	18.25	23.22
P3	0.2	4.4	28.46	3.0	19.19	23.83

### Resistance to Combustion

The ease of ignition of the PUC was studied by the oxygen index (OI) method (GB-2406-80) and by the coating flame-resistance standard experiment method (ASTM D-1360-79). The OI was determined on an HC-1 apparatus, using samples with dimensions of 120 × 6 × 3 mm. Samples with dimensions 300 × 150 × 0.2 mm were employed in the flame-resistance experiment.

## RESULTS AND DISCUSSION

### Characterization of Polyols

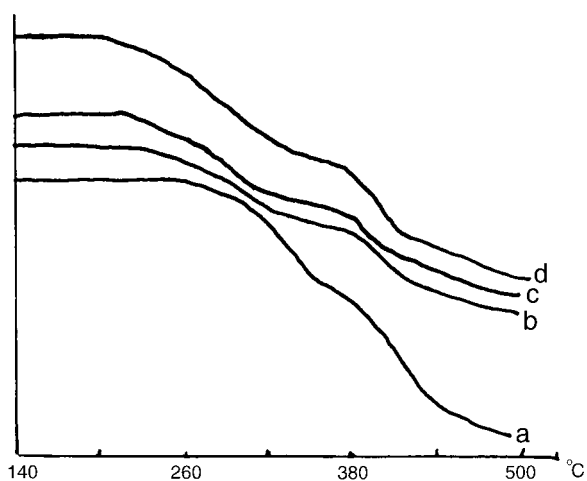
In the IR spectra of P1, P2, and P3, the band at 980 cm<sup>-1</sup> implies the presence of the phosphate in the polyols, because the band corresponds to the appearance of the deforming vibration of P—O—C. Figure 1 shows the <sup>1</sup>H-NMR spectra of P2. The polymer was purified by solvating the polyol in acetone and precipitated by pouring it into water; then it was dried in a vacuum at 100°C for 72 h. As can be seen from Figure 1, the peak in the region of  $\delta$

= 7.5–7.7 ppm is attributed to the aromatic protons of the phthalic acid of the polymer. The peaks in the region of  $\delta$  = 4.65–5.0 ppm are attributed to the proton of —OH, the peaks corresponding to (CH<sub>2</sub>O)<sub>2</sub> —PO—CH<sub>2</sub>O protons are shown in the region of  $\delta$  = 4.0–4.4 ppm, and the peaks corresponding to —COOCH<sub>2</sub>— protons are shown in the region of  $\delta$  = 3.5–3.9 ppm. The peaks in the region of  $\delta$  = 2.2–2.5 ppm are attributed to the —CH<sub>2</sub>—COO— protons of sebacic acid, and the peaks in the region of  $\delta$  = 1.2–1.9 ppm correspond to the —CH<sub>2</sub>—CH<sub>3</sub>— of trimethanol propane and the —C—(CH<sub>2</sub>)<sub>6</sub>—C— of sebacic acid. These facts confirm the formation of the phosphate–polyester copolymers.

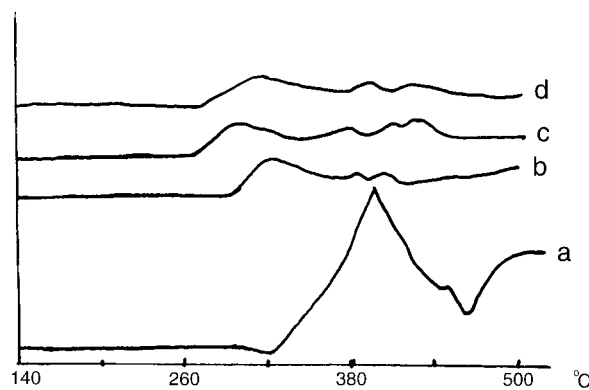
### Solubility Parameter of Polyols

Because of the phosphate introduced, the structure of polyol was altered; thus, its properties were altered as well. The solubility parameters of copolyols have practical significance for the solvent selection of a coating component.

For a binary miscible system, if the polymer solubility parameter  $\delta$  is between the  $\delta_s$  values of components 1 and 2, it can conveniently make a



**Figure 2** TG traces of (a) P0PU, (b) P1PU, (c) P2PU, and (d) P3PU.



**Figure 3** DTA traces of (a) P0PU, (b) P1PU, (c) P2PU, and (d) P3PU.

**Table III Thermal Analysis Data of Polyurethanes**

Sample	P% Calcd	N% Determined	TG		DTA		
			On-set (°C)	W loss at 500°C (%)	Temperature (°C)	Heat (mJ/mg)	Total Heat (mJ/mg)
P0PU	0	5.58	216.9	85.34	322–442.8 450–493.4	+3926.91 –42.79	+3884.12
P1PU	0.79	7.78	220.8	69.91	275.1–295.1 295.1–375.1 375.1–426.1	+30.25 +1036.02 +180.25	+1246.52
P2PU	1.57	6.78	210.5	62.32	251.7–327.6 354.1–381.6 394.8–446.4	+636.54 +44.49 +213.2	+894.23
P3PU	1.58	8.42	205.3	62.98	257.1–339.1 377.2–399.0 407.1–455	+650.5 +67.2 +103.47	+821.17

P0PU, P1PU, P2PU, and P3PU are polyurethane coatings prepared from P0, P1, P2, and P3, respectively.

miscible solvent, so that the parameter  $\delta sm$  value of the miscible solvent is close to the solubility parameter of the polymer's  $\delta$ . The turbidity titration method was used to dissolve a polymer in a solvent; then, the solution was titrated by a precipitating agent which can be miscible with the solvent. The titration is then stopped until the solution is turbid. In this way, the cloud point can be obtained; the solubility parameter of the miscible solvent  $\delta sm$  is

$$\delta sm = \Phi_1\delta_1 + \Phi_2\delta_a$$

where  $\Phi_1$  and  $\Phi_2$  are the volume fractions of components 1 and 2 in the solution. The polymer dissolved in a binary miscible solvent system permits the solubility parameter of the system to have a range. When the polymer was dissolved in acetone [ $\delta = 20.4 (\text{Jm}^{-3})^{1/2}$ ], the solution was titrated by

using water [ $\delta = 47.7 (\text{Jm}^{-3})^{1/2}$ ] and *n*-pentane [ $\delta = 15.17 (\text{Jm}^{-3})^{1/2}$ ]. The solubility parameter's upper limit and lower limit of the miscible solvent could also be obtained. Then, the average value of the solubility parameter of the polymer is

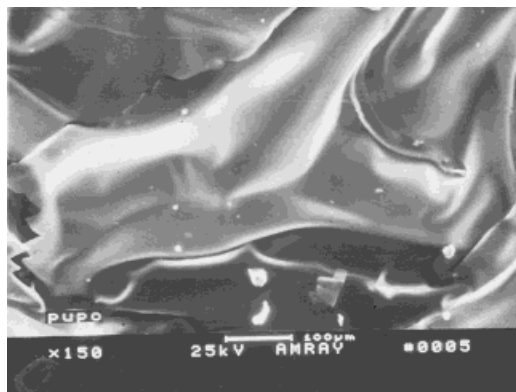
$$\delta = \frac{1}{2}(\delta mh + \delta ml)$$

Here,  $\delta mh$  and  $\delta ml$  are the higher and lower solubility parameters, respectively.

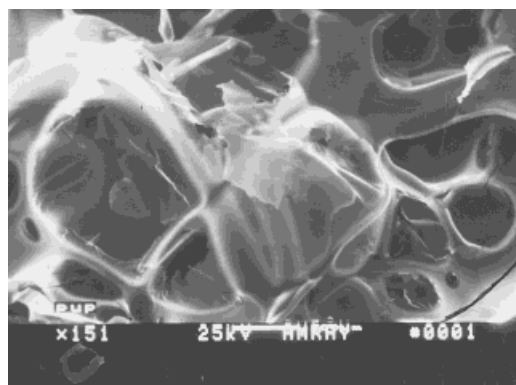
The experimental results are listed in Table II, which shows that when phosphate is introduced into the polyol molecule the solubility parameters tend to increase because of the action of the polar function. So, lower phosphate-containing polyols can be dissolved in the miscible solvent of xylene and *n*-butyl acetate, but higher phosphate-containing polyols cannot be dissolved in the preced-

**Table IV Flammability Behavior of Polyurethanes (PUs)**

Sample	OI	Combustion Behavior	Standard Experiment		
			Wt Lost %	Carbonized Area	Intumescent Height
P0PU	21	Dropping	28.5	26 × 12 cm <sup>2</sup>	0 cm
P1PU	24.5	Dropping			
P2PU	29	Intumescent	3.8	13 × 8 cm <sup>2</sup>	1 cm
P3PU	29	Intumescent			



(a)



(b)

**Figure 4** (a) SEM photo of P0PU char at 400°C. (b) SEM photo of P<sub>2</sub>PU char at 400°C.

ing solvent. A higher solubility parameter solvent (e.g., cyclohexanone) must be added.

### Flammability and Flame-retardant Mechanism

Figures 2 and 3 show typical TG traces and typical DTA traces of all the polyurethanes. The initial decomposition temperature, the maximum polymer decomposition at 500°C, and the thermal results are summarized in Table III. The results show that the polymers' initial decomposition temperatures decrease and the maximum polymer decomposition at 500°C decreases at higher phosphorus concentrations. DTA results show that P0PU has a larger exothermic peak, but all phosphorus-containing polymers have smaller exothermic peaks. The total exothermic heat of 1 mg of the polymer from the decomposition temperature to 500°C decreases. Obviously, the intervention of SPDPC expedites the decomposition of

PUC, leading to a deceleration of the decomposition within the temperature range of combustion (250–400°C) and a reduction of heat release. These are of momentous significance for the decrease of the flammability of PUC.

As can be seen from Table IV, the polymers at higher phosphorus concentrations have greater OI values and no dropping of combustion behavior and are intumescent. Standard experimental results show that P2PU has less weight lost, a smaller carbonized area, and a higher intumescent height. Figure 4 is a photo of chars from an SEM, which was made by degrading P0PU and P2PU in a muffle furnace at 400°C for 10 min. The SEM photo shows that the char of the degraded P0PU has a thin slice framework and also that the char of the degraded P2PU has a three-dimensional-thick framework and high strength. This implies that the phosphorus-containing polyurethane, by heating, forms the tight charred layer of cellular foam. This structure of the char provides resistance to both mass and heat transfer and retards the degradation of the underlying materials, which could form a combustible substance by degradation, thus the function of a flame retardant by both mechanisms. Thus, as the phosphate content of the polymer increases, obviously the thermooxidative exothermic heat decreases and the maximum polymer decomposition at 500°C decreases and char yield increases. This complies with the flame-retardant mechanism of the intumescent solid phase.

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