

# Synthesis and Properties of Intumescent, Phosphorus-Containing, Flame-Retardant Polyesters

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**ABSTRACT:** Phosphate–polyester copolymers were synthesized from spirocyclic pentaerythritol di(phosphate acid monochloride)s (SPDPC), which is an intumescent, phosphate flame retardant. Because of the new monomer being introduced, the structure and properties of the polyester were altered. The effects of the phosphate on the properties of flame retardance oxygen index, (OI), glass-transition temperature ( $T_g$ ), and solubility parameters ( $\delta$ ) were studied. It was found that the OI,  $T_g$ , and  $\delta$  increase with increasing SPDPC content in the copolymers. The flame-retardant mechanism was found to possibly be the solid phase intumescence found by analysis of the SEM photos of the copolymer chars. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1511–1515, 1997

## INTRODUCTION

According to the flame-retardant mechanism, flame-retardant materials can be classified into intumescent and nonintumescent. The intumescent system has attracted more and more attention from many researchers.<sup>1–3</sup> Because intumescent materials can be formed by heating, a charred layer of cellular foam on their surface provides resistance to heat and mass transfer, producing good heat insulation so that the underlying materials are protected from flame.

Generally speaking, the intumescent system consists of three main substances: the acid source, carbon source, and gas source. Although it has been known for a long time that intumescent systems have high fire retardance as coatings for combustible materials, it has only been known in recent years that its particular components could be added to general polymers to give specific intumescent properties. The intumescent fire retardant/polymer system has the advantages of low smoke, low toxicity, low corrosion, long life, no molten dropping, and being halogen free, so

the technology is considered to be a revolution in flame retardant technologies.<sup>4</sup> However, until now intumescent technology has been mainly applied to the flame retardance of polypropylene, polyurethane, polyethylene, etc.

Polyesters are raw materials for synthetic fibers, engineering plastics, and coatings. They have the advantages of being low priced and easily obtained and are used in various applications. So studies on developing polyesters into flame retardant materials have practical significance. Various methods could be used, but each method has its own advantages and disadvantages. Because copolymerization could fix the fire retardant monomer completely, ooze (or sublimation), dissolution, or extraction cannot take place in its application and it possesses permanent fire retardance properties. In addition it is not harmful to the human body. Copolymerization has the potential to become a popular flame retardant technique. Because of new monomer being introduced, the structure of polyesters is altered, thus altering their properties as well.

Spirocyclic pentaerythritol di(phosphoric acid monochloride)s (SPDPC) are flame retardant intumescent phosphates of 3,9-dichloride-2,4,6,8-tetraoxa-3.9-diphosphaspiro[5,5] undecane-3.9 dioxide. They contain an acid source and a carbon source in one molecule, and are formed by heating

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a charred layer of cellular foam. Furthermore, a group of phosphates, phosphate amides, polyphosphates, and polyphosphate amides were synthesized from SPDPC, which are very effective as additives for flame retardants<sup>4,5</sup> and are used for the flame retardation of polyolefin and polyesters. If SPDPC could be converted into polyesters, the phosphate polyesters could be synthesized, which is one type of intumescent flame retardant material.

In this study phosphate–polymalic ethanol ester copolymer and phosphate–polyphthalic ethanol ester copolymer were synthesized and the effects of these phosphates on the properties of polyesters were studied, emphasizing practical applications.

## EXPERIMENTAL

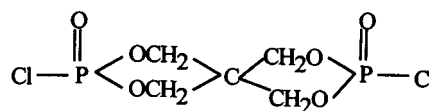
### Equipment and Characterization Procedures

IR measurements were recorded with KBr pellets using a TFS-40 IR spectrometer. <sup>1</sup>H-NMR spectra were recorded with a Varian XL-200 MHz NMR spectrometer using D<sub>2</sub>O as the solvent for SPDPC and DCl<sub>3</sub>C as the solvent for the polymers, with tetramethyl silane as the internal standard. Phosphorus was analyzed by a 3080EII X-ray flurometer, and the element chlorine was analyzed by the Schoniger combustion flask method. All the glass-transition temperatures (*T<sub>g</sub>*) values were determined with a Shimadzu DT-40 instrument in nitrogen at a flow rate of 40 mL/min, operating at temperatures of −50 to +80°C at a 20°C/min heating rate. The scanning microscopic image was observed on an Ammry 1000B. The limiting oxygen index (LOI) data were obtained on an HC-1 apparatus, fabricated in accordance with the GB-

2406-80 standard. The cloudiness method was used for determining the solubility parameters.

### SPDPC Synthesis and Characterization

SPDPC was synthesized by the reaction of phosphorus oxychloride and pentary threitol as reported elsewhere.<sup>6</sup> The SPDPC is a white powder. Elemental analysis showed 20.8% P and 24% Cl (calcd: 20.9% P and 23.9% Cl). IR spectra were 3000 cm<sup>−1</sup> (CH<sub>2</sub>), 1300 cm<sup>−1</sup> (P=O), 1000 cm<sup>−1</sup> (P—O—C), 790 cm<sup>−1</sup> (P(OCH<sub>2</sub>)<sub>2</sub>C). The NMR was carried out with the solution made from that hydrolyzed with D<sub>2</sub>O in boiling water. Its spectrum showed, due to the coincidence of P—H, that the <sup>1</sup>H of —OCH<sub>2</sub>— resonated in the δ = 4.4 and 4.1 ppm area and the proton signals appeared equal in intensity, confirming that the structure of SPDPC is



### Synthesis of Polymers

#### Synthesis of 1a and 1b

Acid anhydride and ethylene alcohol were mixed together and heated to 165°C, refluxed 1 h. Then distillation was begun by raising the temperature slowly to 200°C over 3 h to drive off the water. When the acid value reached the demand point, the reaction was stopped and the product was ready for use.

#### Synthesis of 2a, 3a, 4a, 2b, and 3b

Heating the ethylene alcohol to 120°C, the SPDPC was added in batches and the deacidifying agent

**Table I** Components of Polymers

Polymer	Raw Materials (mol)			
	SPDPC	Phthalic Anhydride	Maleic Anhydride	Ethylene Alcohol
<b>1a</b>	0.00	4.00		4.00
<b>2a</b>	0.25	3.75		4.00
<b>3a</b>	0.50	3.50		4.00
<b>4a</b>	0.75	3.25		4.00
<b>1b</b>	0.00		4.00	4.00
<b>2b</b>	0.20		3.80	4.00
<b>3b</b>	0.40		3.60	4.00

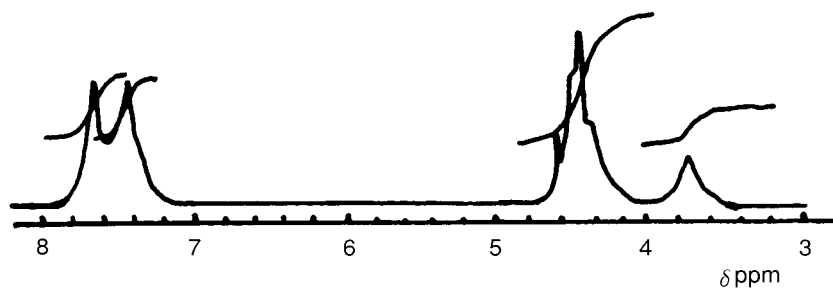


Figure 1  $^1\text{H-NMR}$  of **3a**.

was added to remove the HCl. Then the acid anhydride was introduced into the mixture at  $160^\circ\text{C}$  for 1 h. Distillation was begun and gradually the temperature was raised to  $200^\circ\text{C}$  in 3 h to drive off the water. When the acid value attained the demand point, we stopped the reaction. The product was solved in acetone and precipitated by pouring it into water. Then it was dried in a vacuum at  $60^\circ\text{C}$  (Table I).

## RESULTS AND DISCUSSION

### Characterization of Copolymers

In the IR spectra of copolymers, the band at  $1000\text{ cm}^{-1}$  implies the presence of the phosphate in the

copolymers, because the band corresponds to the appearance of the deforming vibration of  $\text{P-O-C}$ .

As can be seen from the  $^1\text{H-NMR}$  spectra of **3a** (Fig. 1), the peak in the region of  $\delta = 7.3\text{--}7.8$  ppm is attributed to the aromatic protons of the phthalic acid of the copolymer. The peaks corresponding to  $(\text{CH}_2\text{O})_2\text{-PO-CH}_2\text{O}$  protons were in the region of  $\delta = 4.3\text{--}4.7$  ppm and the peaks corresponding to  $\text{-COOCH}_2\text{-}$  protons were  $3.5\text{--}3.9$  ppm. The  $^1\text{H-NMR}$  spectra of **2b** (Fig. 2) shows that the peak in the  $\delta = 6.9$  ppm region is attributed to the double bond protons of the maleic acid of the copolymer. The peaks corresponding to  $(\text{CH}_2\text{O})_2\text{-PO-OCH}_2$  protons were  $\delta = 4.2\text{--}4.6$  ppm, and the peaks corresponding to maleic acid-

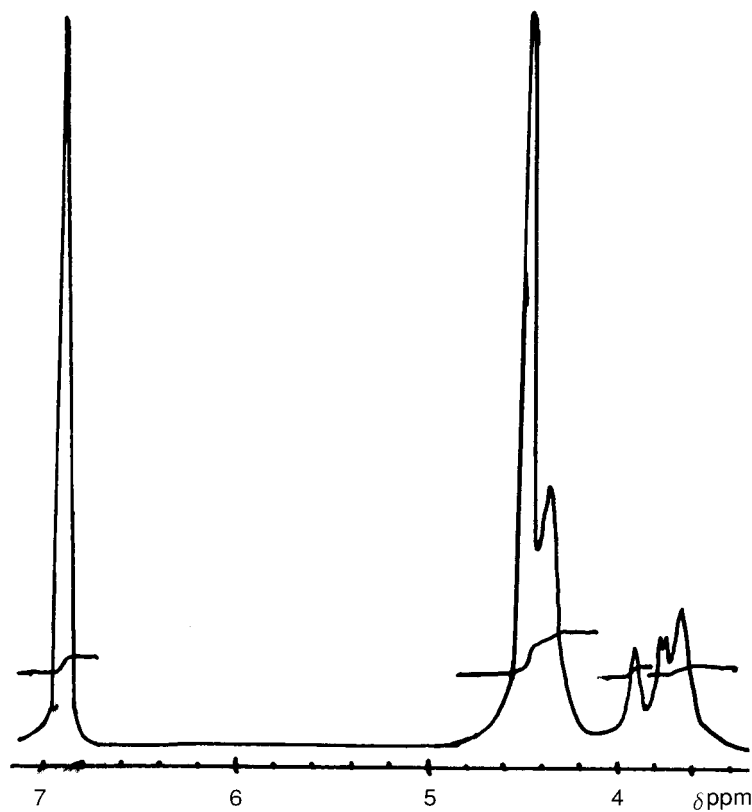


Figure 2  $^1\text{H-NMR}$  of **2b**.

**Table II** Oxide Index and Glass-Transition Temperature of Copolymers

Polymers	OI	$T_g$ (°C)
<b>1a</b>	17	18.1
<b>2a</b>	20	32.15
<b>3a</b>	24	36.75
<b>4a</b>	30	29.2
<b>1b</b>	18	-9.45
<b>2b</b>	23	-4.05
<b>3b</b>	27	-1.3

ethylene alcohol ester  $-\text{COOCH}_2$  proton were 3.5–3.9 ppm. These facts confirm the formation of phosphate–polyester copolymers.

### Properties of Copolymers

Because of the phosphate introduced, the structure of the polyester was altered, thus altering its properties as well. So the flame retardance, glass-transition temperature, and solubility parameters of the copolymers were studied and found to have practical significance.

As can be seen from Table II, the OI of the copolymer increases with increasing phosphate content. Figure 3 is a SEM photo of chars that were made by degrading **1a** and **3a** in a muffle furnace at 400°C for 10 min. The photo shows that the char of **1a** has a large empty hole and a thin slice framework. The SEM photo shows that the char of the degraded **3a** has a thick framework, high strength (having many granular carbons in the hole of the char), and a 12-fold intumescence. These imply that the copolymer formed by heating forms a tight charred layer of cellular foam. This structure of the char provides resistances of bath mass and heat transfer and retards the degradation of underlying materials to form a combustible substance, so that they function as flame retardant by both mechanisms. Thus, as the phosphate content of the copolymer increases, the OI of the copolymer increases rapidly. It complies with the flame-retardant mechanism of the intumescent solid phase.

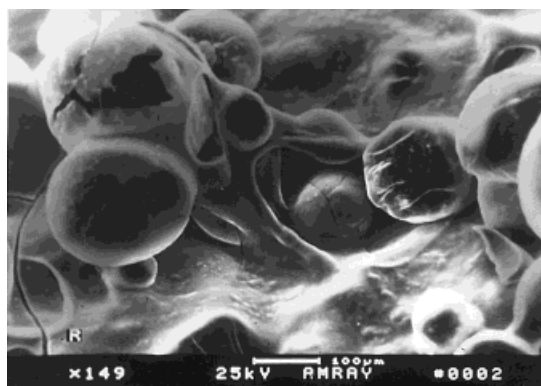
As can be seen from Table II also, as the phosphate content increases, the  $T_g$  increases but the  $T_g$  of **4a** is lower than **2a** and **3a** but higher than **1a**. This phenomenon is not yet understood.

For a binary miscible system, if the polymer solubility parameter  $\delta$  is between the  $\delta_s$  values of the two miscible solvents, it can conveniently make a miscible solvent, so that the parameter

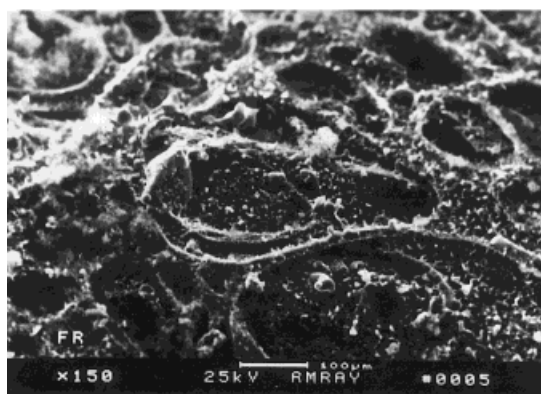
$\delta_{sm}$  value of the miscible solvent is close to the solubility parameter of the polymer  $\delta$ . The turbidity titration method is dissolving polymer with a solvent, then titrating the solution by a precipitating agent, which can be miscible with the solvent. The titration is stopped when the solution is turbid. In this way the cloud point can be obtained. The solubility parameter of the miscible solvent  $\delta_{sm}$  is

$$\delta_{sm} = \varphi_1\delta_1 + \varphi_2\delta_2$$

where  $\varphi_1$  and  $\varphi_2$  are the volume fraction of component 1 and 2 in the solution. The polymer dissolved in a binary miscible solvent system allows the solubility parameter of the system to have a range where the polymers were dissolved in ace-



(1)



(2)

**Figure 3** SEM photo of char at 400°C for (1) **1a** and (2) **3a**.

Table III Result of Titration with Acetone as Solvent

Polymer	Concn	Methyl Alcohol		Water		Diethyl Ether		<i>n</i> -Pentane		$\delta$
		<i>ml</i>	$\delta_{mh_1}$	<i>ml</i>	$\delta_{mh_2}$	<i>ml</i>	$\delta_{ml_1}$	<i>ml</i>	$\delta_{ml_2}$	
<b>1a</b>	0.2	19.0	26.43	4.7	29.13	38.2	16.20	8.0	18.07	22.46
<b>1a</b>	0.1	18.4	26.36	4.8	29.25	28.4	16.48	8.7	19.97	22.51
<b>2a</b>	0.2	21.6	26.69	5.8	30.42	4.9	18.66	1.5	19.72	23.87
<b>2a</b>	0.1	26.0	27.05	8.0	32.52	9.2	17.86	2.3	20.58	24.50
<b>3a</b>	0.2	9.0	24.77	4.3	28.61	4.6	18.74	0.95	19.95	23.02
<b>3a</b>	0.1	10.4	25.09	5.2	29.74	3.8	18.94	1.4	19.75	23.38
<b>4a</b>	0.2	9.5	24.88	3.8	27.91	5.25	18.58	2.0	19.53	22.73
<b>4a</b>	0.1	8.6	24.66	4.1	28.34	5.6	18.50	2.0	19.53	22.76
<b>1b</b>	0.2	8.2	24.55	4.0	28.20	6.5	18.32	2.4	19.39	22.61
<b>2b</b>	0.2	16.6	26.14	6.0	30.64	2.9	1.1	19.88	23.97	

tone ( $\delta = 20.4 \text{ (J m}^{-3}\text{)}^{1/2}$ ). Titrating the solution by using methyl alcohol ( $\delta = 29.6 \text{ (J m}^{-3}\text{)}^{1/2}$ ), water ( $\delta = 47.7 \text{ (J m}^{-3}\text{)}^{1/2}$ ), *n*-pentane ( $\delta = 15.17 \text{ (J m}^{-3}\text{)}^{1/2}$ ), and diethyl ether ( $\delta = 15.1 \text{ (J m}^{-3}\text{)}^{1/2}$ ), the solubility parameter's upper and lower limits of miscible solvents were obtained. Then the average value of the solubility parameter of the polymer  $\delta = (\delta_{mh_1} + \delta_{mh_2} + \delta_{ml_1} + \delta_{ml_2})/4$  was found. Here,  $\delta_{mh}$  and  $\delta_{ml}$  are the higher and lower solubility parameters, respectively.

The experimental results are listed in Table III. It can be seen from Table III, by introducing phosphate into the polyester molecule, the solubility parameters tend to increase because of the action of the polar function. At lower phosphate contents, the solubility parameters increased as phosphate content increased; but at higher phosphate contents, it decreased to some extent. These are the indications of a type **a** polymer. The solubility parameter of **2b** is higher than **1b**, because **3b** cannot dissolve in acetone. Its solubility pa-

rameter was not determined. Nevertheless, **3b** dissolved in the miscible solvent of acetone and tetrahydrofuran ( $\delta = 20.2 \text{ (J m}^{-3}\text{)}^{1/2}$ ). This also implied that the solubility parameter of **3b** is lower than that of **2b**. This is probably the result of the symmetry of molecular increase as the phosphate content increased.

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