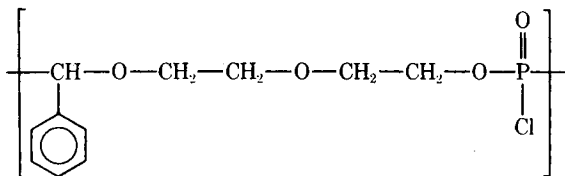


Copolymerization of Ethylene Chlorophosphonite with 2-Phenyl-1,3-Dioxolane and Its Flame-Retardant Effect on Polyester Fabric

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Synopsis

Copolymerization of ethylene chlorophosphonite (ECP) with 2-phenyl-1,3-dioxolane (PhD) and the flame-retardant effect of the copolymer on polyester fabric were investigated. (1) Copolymerization occurred without added catalyzer. The number-average molecular weight ranged from 600 to 1000. ^1H -nmr and ir spectra for the copolymers showed that their structures varied depending on feed composition (ECP/PhD ratio): ECP/PhD less than or equal to 1 yielded an alternating copolymer having the structure



and at ECP/PhD ratios greater than 1, some insertion reaction of ECP into polymer I occurred. (2) Selectivity of flame retardation could be observed. The copolymer with structure I was an effective flame retardant for polyester fabric but useless for cotton fabric. Its effectiveness in polyester fabric was superior to that of TBPP.

INTRODUCTION

This paper describes the copolymerization of ethylene chlorophosphonite with 2-phenyl-1,3-dioxolane and the flame-retardant effect of the copolymer on polyester fabric.

A number of workers have investigated the flame retardation of polyester/cotton blend fabric, but no effective retardant could be found. The flammability behavior of the fabric blends cannot be predicted from a knowledge of the flammability of the component fibers.^{1,2} Miller et al.³ have reported that the cotton component in the blended fabrics plays a dominant role in determining the flammability behavior of the fabric. From this finding an especially effective flame retardant for the cotton component was added to the polyester/cotton fabric, but this was not successful in decreasing the flammability. Therefore, it was concluded that an effective flame-retardant treatment for polyester/cotton fabric blends must include the modification of the flammability of both components.

Halogen-containing phosphates such as Tris(2,3-dibromopropyl)phosphate (TBPP) are well-known effective flame retardants for polyester. When the phosphates were applied to polyester/cotton fabrics, their flame-retardant effect operated predominantly on the cotton component and less so on the polyester component.⁴ A transfer of the flame retardant from the polyester to the cotton component was observed.^{5,6} A flame retardant that is effective on a simple fiber does not always operate predominantly on the corresponding component in a fabric blend.

We considered the reason why the phosphate does not operate on polyester component in the fabric blend. The following was inferred. At low temperature (near 200°C), the phosphate is degraded to yield phosphoric acid. The phosphoric acid interacts strongly with the cotton component before temperatures where the interaction with polyester occurs. If the transformation of phosphate to phosphoric acid occurred near 350°C, where phosphate could interact with polyester, a powerful flame retardation for the polyester component could be expected. A copolymer of ethylene chlorophosphonite with 2-phenyl-1,3-dioxolane was chosen as such a new flame retardant.

EXPERIMENTAL

Materials. *Ethylene chlorophosphonite* (ECP) was prepared from the reaction of trichlorophosphine and ethylene glycol.⁷ The product was distilled under vacuum: bp 72°C/50 Torr, yield 70%, NMR (CCl₄) δ 4.43 ppm. *2-Phenyl-1,3-dioxolane* (PhD) was prepared from the reaction of benzaldehyde and ethylene glycol according to the literature.⁸ The product was distilled under vacuum: bp 121°C/25 Torr, NMR (CCl₄) δ 3.80 (4H), 5.65 (1H), 7.25 ppm(5H). *Polyester fabric* was commercial grade (Kuraray Co. Ltd., 75 denier, 120 × 90, plain weave, weight 94 g/m²). *Cotton fabric* was a bleached and mercerized broad cloth (120 g/m²).

Copolymerization. A sealed tube (Pyrex, 13 mm i.d. × 350 mm) containing a serum-type stopper was used. An ethylene chloride solution of PhD (0.006–0.036 mol) was placed in the tube. The tube was sealed under vacuum and then the ethylene chloride solution of ECP (0.036–0.006 mol) was introduced into the tube from the stopper using a syringe. The copolymerization was carried out at 20°C for 2–5 hr. The product was dissolved in acetone and precipitated with petroleum ether. This procedure was repeated at least five times. The arabic number used in the description of samples refers to feed composition (ECP/PhD), e.g., 1/3 corresponds to a molar ratio of ECP to PhD of 1:3.

Fabric Treatment with Copolymer. The polyester or cotton fabrics (10 × 16 cm) were scoured in methanol to remove all residual spinning oils and then immersed in acetone solution of the polymer(1/1) sample. The fabrics were squeezed using a nip roll of a laboratory pad and dried under reduced pressure.

Infrared Spectra. Samples were cast from acetone solution of copolymers on sodium chloride plates. Infrared spectra were obtained using a Nihon-Bunko spectrometer IRA-II.

NMR Spectra. The NMR spectra were obtained using tetrachloromethane or *d*-chloroform as solvent and tetramethylsilane as internal standard on a Nihon-Denshi spectrometer JNM-100M and a Hitachi spectrometer R-24.

Gel-Permeation Chromatography. A Toyo Soda model HLC-801A chromatograph was used. The separation system consisted of two columns (Toyo Soda TGK-Gel 200H8, 4000H8; 7.5 mm i.d. \times 610 mm) connected in series. The flow of solvent, tetrahydrofuran (THF), was maintained at 1 ml/min at 40°.

Thermogravimetric Analysis. A Shinku-Riko thermogravimetric analyzer DGC-3 was used. All analyses were run in air at a programmed rate of 4.0°C/min.

Flame-Retardant Test. The oxygen index test (ASTM D-2863-70) was used to evaluate a limiting index of the treated fabrics.

RESULTS AND DISCUSSION

Copolymerization of ECP with PhD

Without added catalyst the copolymerization of ECP with PhD occurred at 20°C. Results of the copolymerization are shown in Table I. Resulting polymers were soluble in solvents such as acetone, chloroform, ethylene chloride, benzene, and THF. Their number-average molecular weight was not large, being in the range 600–1000. Their appearance depended on a feed composition (ECP/PhD); when the ECP/PhD ratio was below unity, colorless, hard polymer was obtained; with ratios above unity, light yellow, viscous polymer resulted. The GPC chromatograms for all polymers showed only one peak. Four fractionated polymers from acetone solution gave similar NMR spectra. These findings indicate that the resulting polymer is not a mixture of homopolymers of ECP and PhD, but a copolymer of ECP with PhD.

The structure of the copolymer was determined by spectroscopy, taking into consideration that the appearance of the copolymer depended on the feed composition. Copolymers with ECP/PhD \leq 1 gave similar ir spectra. One such spectrum is shown in Fig. 1. The spectrum consists of absorptions due to CH₂ (2925, 2850, 1450 cm⁻¹),

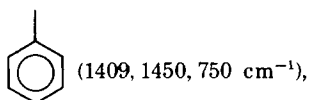


TABLE I
Copolymerization of ECP with PhD

Copolymer	Feed composition, ECP/PhD	Temperature, °C	Time, hr	Yield, %	P, %
Polymer 1/6	1/6	20	5	21	
Polymer 1/3	1/3	20	2	19	11.3
Polymer 1/1	1/1	20	2	54	11.2
Polymer 3/1	3/1	20	2		11.5
Polymer 4/1	4/1	20	5	52	12.1
Polymer 5/1	5/1	20	5	18	13.6
Polymer 6/1	6/1	20	5	35	14.6
Polymer 1/0 ^a	1/0	110	24	60	

^a Homopolymer of ECP.

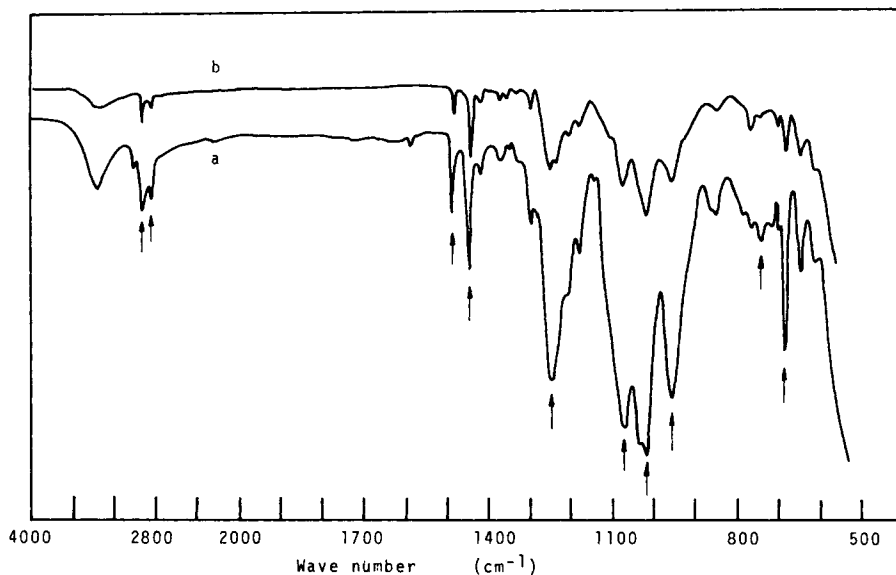


Fig. 1. Infrared spectra of copolymers of ECP with PhD: (a) copolymer 1/3 and (b) copolymer 3/1.

P=O (1250 cm^{-1}), P-O-C ($1070, 1020, 960\text{ cm}^{-1}$) and P-C groups (690 cm^{-1}). The $^1\text{H-NMR}$ spectrum afforded more useful information. Four peaks appeared at δ 7.5 (5H), 4.8 (1H), 4.2 (4H), and 3.7 ppm (4H) (Fig. 2).

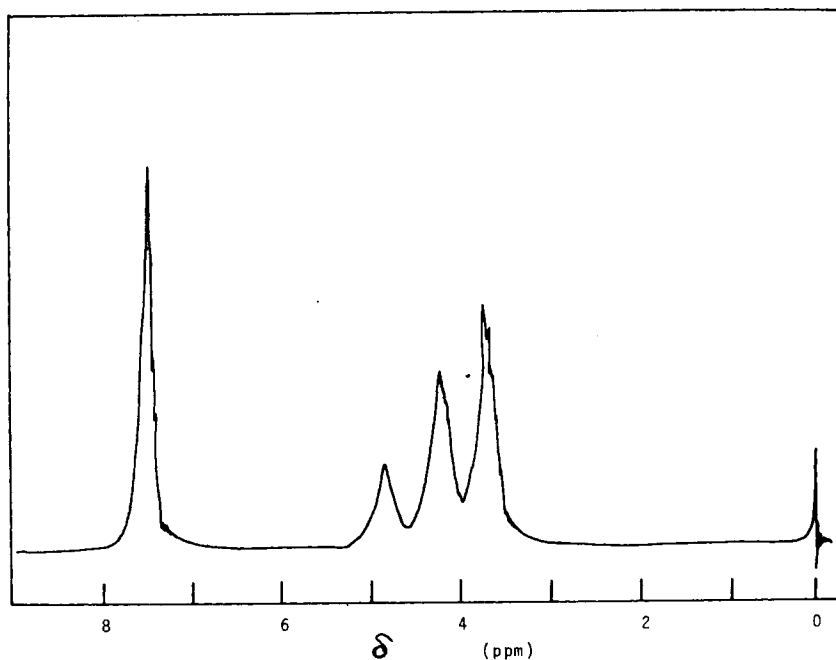
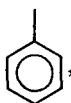


Fig. 2. $^1\text{H-NMR}$ spectra of copolymer 1/3 in CDCl_3 at 90°C .

Peak (ppm)	Assignment
7.5 (5H)	a
4.8 (1H)	b
4.2 (4H)	c,f
3.7 (4H)	d,e

Phosphorus analytical data (Table I) were in agreement with the calculated value, 11.3 wt %, for a 1:1 composition. It was established that the copolymer produced with $ECP/PhD > 1$ was the alternating copolymer I. In the case of $ECP/PhD > 1$, the ir spectra showed only absorptions due to the CH_2 ,



P-O-C, and P-C groups (Fig. 1). The NMR spectra showed new peaks (Fig. 3). The peak at δ 4.8 ppm (CH) became less intense; new peaks at δ 5.2 and 2.0–1.4 ppm appeared. With increasing ratios of ECP/PhD , the two peak areas increased and the peak at δ 5.2 ppm shifted to a low magnetic field. For example, when the ratio was varied from 3/1 to 6/1, the peak at δ 5.2 ppm shifted to at δ

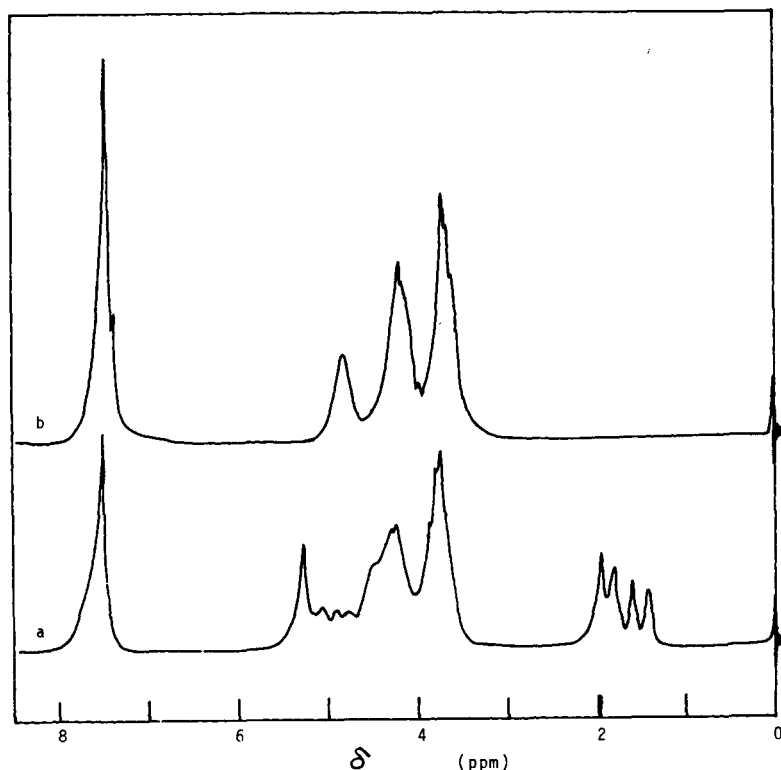


Fig. 4. 1H -NMR spectrum of product of copolymer 1/1 with ECP: (a) product of copolymer 1/1 with ECP, and (b) copolymer 1/1.

5.9 ppm. In order to reveal their structures, an additional experiment was carried out. The 1/1 polymer sample was treated with ECP in ethylene chloride at 20°C, and the NMR spectrum of the product was compared with that of the untreated sample.

Flame-Retardant Effect of the 1/1 Polymer

We have investigated how halogen-containing phosphates such as TBPP act as flame retardants in polyester fabric.¹⁴ A tentative mechanism has been proposed: Before an interaction with polyester occurs, the halogen atoms in the phosphates are eliminated and phosphoric acid is yielded. The resulting phosphoric acid acts as an acidic catalyzer of Aldol condensation of flammable aldehydes and ketones, which are main degradation products of polyester fabric. The condensation contributes to diminishing the flammability of polyester fabric. Before using the 1/1 polymer as a flame retardant, its behavior at high temperature was examined. A thermogravimetric curve for the polymer is shown in Fig. 5, together with that of the homopolymer of ECP. The copolymer has higher thermal stability compared with the homopolymer: the initial weight loss occurred at a relatively low temperature (200°C); the weight loss at 400°C was less (20 wt %). These thermogravimetric data indicate that there is a possibility that the 1/1 polymer could have a selective flame-retardant effect on polyester fabric.

The polymer was used as a flame retardant for polyester fabric. The flame-retardant effect was compared with that of TBPP (Table II). The table shows that the polymer is effective as a flame retardant for polyester fabric and that its efficiency is superior to that of TBPP. The polymer is independent of the flammability of cotton fabric. TBPP acts as a flame retardant on both polyester and cotton fabrics.

The flame-retardant action of the polymer was investigated from the point of view of thermal degradation. A thermogravimetric curve for the treated

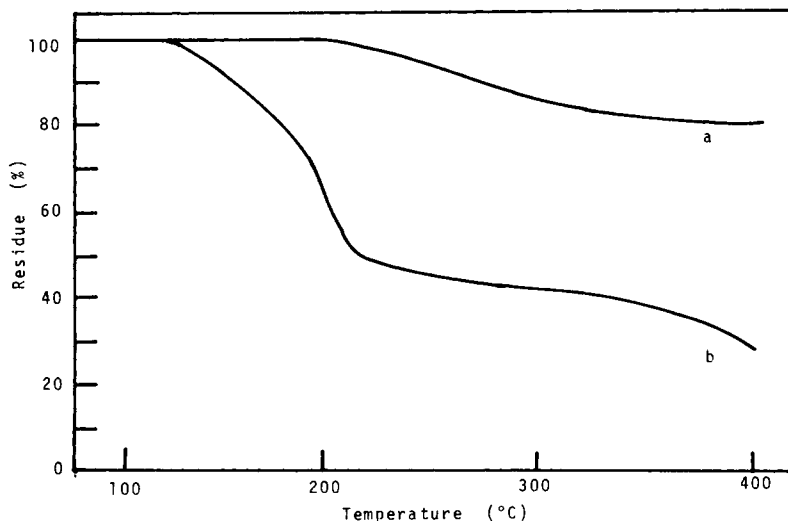


Fig. 5. Thermogravimetric curve for copolymer: (a) copolymer 1/1 and (b) homopolymer of ECP.

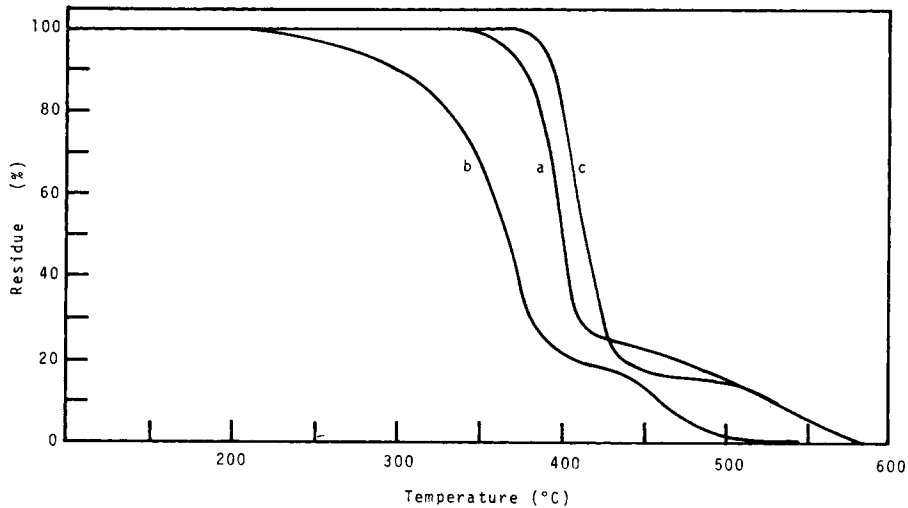


Fig. 6. Thermogravimetric curves for treated polyester fabrics: (a) polyester fabric treated with copolymer 1/1, (b) polyester fabric treated with TBPP, and (c) original polyester fabric.

TABLE II
Oxygen Index Test for Treated Polyester and Cotton Fabrics

Flame retardant	Add-on, %	Oxygen index, %	
		Polyester	Cotton
Polymer 1/1	1.7	30.0	—
	5.0	33.0	20.0
	10	35.0	21.0
(CH ₂ CHCH ₂ O) ₃ PO	5.0	26.2	21.8
Br Br	7.5	28.2	23.8
(TBPP)	10	30.0	25.7
Original		22.4	17.8

polyester fabric with the polymer is shown in Fig. 6, together with a fabric treated with TBPP. Thermogravimetric behavior of the fabric with TBPP has been investigated.¹⁴ Thermal degradation proceeded in one stage; the degradation occurred at 210°C, and the rate of weight loss was slow. The figure shows that the fabric with the polymer has a different thermogravimetric behavior from the fabric with TBPP. The initial temperature for weight loss is higher, near 350°C. The shape of the curve is similar to that of original fabric rather than to that of the fabric with TBPP. It is not unreasonable that the 1/1 polymer could operate in a different mode of flame retardation from TBPP. In addition to its selective flame-retardant effect, it is important to note that the polymer can minimize the decrease in thermal stability brought about by flame retardant finish.

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