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## The Reaction of Chlorophosphazenes with Chitosan

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### ABSTRACT

A new type of fire-retardant polymer has been formed by modification of dispersions of chitosan [(1,4)-2-amino-2-deoxy- $\beta$ -D-glucan] in inert organic liquids using hexachlorocyclotriphosphazene or octachlorocyclotetraphosphazene as well as mixtures thereof in the presence of an acid acceptor. The reaction products are essentially insoluble and infusible, contain up to 8% phosphorus, and have IR spectra indicative of exclusive reaction at the amino groups of the aminopolysaccharide. The influence of reaction conditions on the characteristics of the products is discussed.

### INTRODUCTION

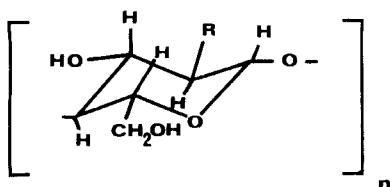
Phosphazenes have been the subject of much interest as potential fire retardants for cellulosic textiles [1]. The usual approach has been to react chlorophosphazenes with the accessible cellulose macromolecules on the fiber surface in order to covalently attach the

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fire retardant [2]. This attachment is intended to reduce loss of the fire-retardancy properties when the textile is repeatedly laundered. However, it is not easy to react chlorophosphazenes with cellulose under simple practical conditions to achieve a degree of substitution adequate to ensure that the textile has useful fire-retardant characteristics. One possible approach to the circumvention of this difficulty would be to treat the cellulosic textile fiber with a strongly adherent polymer which would be more reactive toward the chlorophosphazenes than cellulose itself. One candidate for the reactive adhesive polymer role is chitosan (I, R = NH<sub>2</sub>), a naturally occurring linear aminopolysaccharide consisting of 1,4-linked 2-amino-2-deoxy-β-D-glucose units [3].

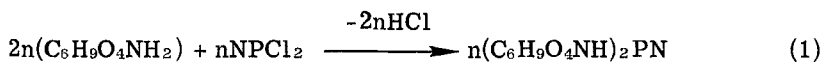


I

This easily acid-soluble polymer is closely related in structure and stereochemistry to cellulose (I, R = OH) to which it adheres with great tenacity [4]. The amino group content of chitosan is another asset in this application because it is established that chlorophosphazenes can be readily reacted with amines [1]. Therefore, as a prelude to a detailed investigation of this new approach to making textile, nonwoven, and paper fire-retardants, a study of the reaction of chitosan with chlorophosphazenes has been undertaken and is now described.

## RESULTS AND DISCUSSION

Reactions between the aminopolysaccharide and the various chlorophosphazenes were heterogeneous and were attempted using dispersions of the chitosan in inert liquid organic media containing optionally an acceptor for evolved HCl. An idealized empirical representation of the metathesis desired is given by



In the absence of an acceptor for HCl, this reaction occurred to only an insignificant extent since the product had a phosphorus content

of only 0.34%. In contrast, the presence of pyridine increased the degree of substitution (D.S.) almost twentyfold to 6.20% (Table 1). The D.S. attained when the molar ratio of glucosamine units to chlorophosphazene entities ( $\text{NPCl}_2$ ) was 2:1 was also augmented by elevation of the temperature through the range 80–120°C. At the reflux temperature of the 1,1,2,2-tetrachloroethane-based dispersion, the reaction achieved was appreciably less as measured by the amount of phosphorus incorporated into the polysaccharide. The nature of the dispersion media also influenced the extent of reaction in the order 1,1,2,2-tetrachloroethane > nitrobenzene > toluene > acetone although the contribution of temperature is comingled to some extent (Table 2).

Prolongation of the reaction time from 2 to 10 h also served to increase the degree of substitution considerably. However, beyond this period of time the phosphorus content of the product tended to diminish (Table 1).

On the other hand, large changes in the ratio of chlorophosphazene to chitosan did not yield a substantially different product (Table 1) and the phosphorus content was only incrementally increased. Augmentation of the phosphorus content of the modified chitosan was also only achieved to a limited extent by the transition from the trimeric to the use of the tetrameric phosphazene (Table 3). The higher phosphorus values obtained with the commercial grade chlorophosphazene may be a reflection of some content of linear oligomers which are commonly present in this type of material and which could become attached to the aminopolysaccharide backbone.

All of these chlorophosphazene reactions are presumed to occur predominantly at the amino groups of chitosan because the IR spectra of the products (Fig. 1) do not exhibit any absorption bands characteristic of the P–O–C moiety. In support of this viewpoint, it was noted that microcrystalline cellulose subjected to the same reaction conditions gave a product having a phosphorus content of less than 1%. However, the IR spectra did contain typically an absorption band in the range of 1270–1225  $\text{cm}^{-1}$ . These correspond to the asymmetric stretching vibrations of the P=N moiety which in the cyclic trimers is located at 1218  $\text{cm}^{-1}$ . For a particular phosphazenyated polysaccharide it is noteworthy that the frequency of this band varies with the degree of substitution of the chitosan. The symmetric stretching vibrations, on the other hand, are manifested both in the chlorophosphazene and the products by absorption bands at 870–860  $\text{cm}^{-1}$ . The specific absorption band ascribed to the presence of the P–N–C sequence of atoms appears in the region of 960–910  $\text{cm}^{-1}$ . This assignment is supported by previous studies of the IR spectra of phenylaminocyclophosphazenes [5]. Although the P–N–C absorption band was then located at the frequency of 940  $\text{cm}^{-1}$ , Kajiwara and Saito [6] found it at 850–650  $\text{cm}^{-1}$  in the polycondensation product of tetrachlorodiphenylcyclotriphosphazene and p-phenylenediamine.

The solubilities of each of the various products in various solvents are summarized in Table 4. From the solubility data it is clear that

TABLE 1. The Effect of the Reaction Conditions on the Properties of the Products from the Reactions of Chitosan with Chlorophosphazene Oligomers

Reaction conditions <sup>a</sup>		Properties of solid reaction product			Infrared absorption frequency of units (cm <sup>-1</sup> )	
Temperature (°C)	Time (h)	Molar ratio of NPCl <sub>2</sub> to glucosamine unit	Yield (g)	P content (%)	P-N-C	
					Color	P=N
120	2	2:1	6.88	3.21	1255	955
			Light yellow			
120	6	2:1	7.90	5.77	1265	960
120	10	2:1	7.87	7.17	1245	960
120	12	2:1	7.50	6.20	1270	960
120	14	2:1	7.90	5.80	1260	910
80	10	2:1	7.28	2.82	1250 <sup>b</sup>	910 <sup>b</sup>
			Yellow-grey			
100	10	2:1	7.96	4.11	1250	950
			Yellow			
Reflux	10	2:1	7.96	5.31	1250	965
120	10	1:3	8.70	8.44	1225	955
			Grey-yellow			

<sup>a</sup> All reactions were carried out at 120°C for 10 h on chitosan (6.97 g) dispersed in 1,1,2,2-tetrachloroethane.

<sup>b</sup> Very weak.

TABLE 2. The Effect of the Dispersion Medium on the Properties of the Reaction Products of Chitosan with Chlorophosphazene Cyclic Oligomers<sup>a</sup>

Dispersion medium	Temperature of reaction (°C)	Properties of solid reaction product			Infrared absorption frequency of units (cm <sup>-1</sup> )	
		Color	Yield (g)	P content (%)	P=N	P-N-C
Acetone	Reflux	Grey	7.08	1.34	1240 <sup>b</sup>	-
Toluene	Reflux	Light brown	7.15	2.89	1270	-
Nitrobenzene	120	Black	8.09	4.01	1250	945
Tetrachloroethane	120	Brown	7.90	5.80	1260	910

<sup>a</sup>All reactions were carried on chitosan (6.97 g) for 14 h at a chlorophosphazene-to-glucosamine unit molar ratio of 1:2.

<sup>b</sup>Very weak.

TABLE 3. The Effect of the Type of Chlorophosphazene Oligomers Used on the Properties of Their Reaction Products with Chitosan

NPCl <sub>2</sub> oligomers used	Molar ratio of NPCl <sub>2</sub> to glucosamine unit	Properties of solid reaction product <sup>a</sup>			Infrared absorption frequency of units (cm <sup>-1</sup> )	
		Color	Yield (g)	P content (%)	P=N	P-N-C
Hexachlorocyclo-triphosphazene	1:2	Yellow-grey	7.46	1.99	1225	930
Octachlorocyclo-tetraphosphazene	1:3	Grey	7.20	2.77	1230	930
	3:1	Light brown	7.42	3.62	1260	-
Cyclic-linear mixture	1:2	Brown	7.87	7.17	1245	960

<sup>a</sup>All reactions were carried out at 120°C for 10 h on chitosan (6.97 g) dispersed in 1,1,2,2-tetrachloroethane.

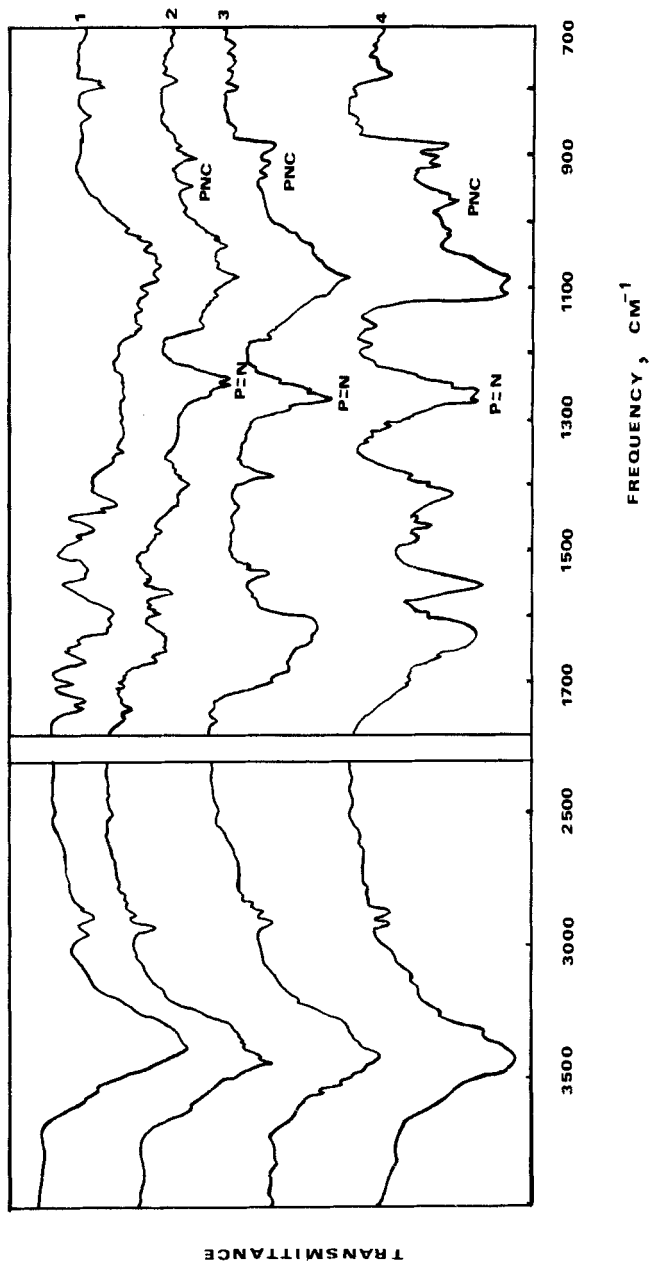


FIG. 1. Infrared spectra of chitosan (1), the products formed by modification of chitosan with hexachlorotriphosphazene (2) or octachlorocyclotetraphosphazene (3), and the mixture of cyclic and linear chlorophosphazene oligomers (4).



TABLE 4. The Solubility and Flame Retardancy of the Reaction Products of Chitosan with Chlorophosphazenes

NPCl <sub>2</sub> oligomers used	Phosphorus content (%)	Solubility characteristics <sup>a</sup> in					Flame retardancy <sup>b</sup>
		Formic acid	50%		1,2-Dichloropropanol		
			Aqueous formic acid	Acetic acid		Aqueous acetic acid	
Hexachlorocyclo-triphosphazene	2.77	V.Sl.	P, Sw	P, Sw	P, Sw	I	S.E.
Octachlorocyclo-tetraphosphazene	3.64	V.Sl.	P, Sw	P, Sw	P, Sw	I	S.E.
Cyclic-linear mixture	7.17	V.Sl.	P, Sw	P, Sw	P, Sw	I	N.F.

<sup>a</sup>V.Sl., very slightly soluble; P, partly soluble; I, insoluble; Sw, swelling.

<sup>b</sup>S.E., self-extinguishing; N.F., nonflammable.

none of the modifications of chitosan possess its original solubility in acidic solvents. However, some swelling was observed. These observations are consistent with the conclusion that the reaction products are cross-linked. This view is supported by the chlorine content of the products which was less than 2% in all cases.

Table 4 also contains a summary of the qualitative fire resistance testing which was carried out. Although pure chitosan ignited and sustained a flame, the modified aminopolysaccharides did not under the same conditions. The application of this fire-retardant system to textiles will be the subject of a future report.

## EXPERIMENTAL

### Materials

Hexachlorocyclotriphosphazene (mp 113-114°C,  $^{31}\text{P}$ , NMR, -19.0 ppm) and octachlorocyclotetraphosphazene (mp 123-124°C,  $^{31}\text{P}$ , NMR, +7.1 ppm) were prepared by the reaction of  $\text{PCl}_5$  with  $\text{NH}_4\text{Cl}$  using a new patented procedure [7]. A commercial grade of "phosphonitrilic chloride" (mp 89-90°C), donated by the Millmaster Chemical Co., (New York, New York) and consisting of a mixture of cyclic and linear chlorophosphazene oligomers, was used as supplied. The chitosan employed was a commercial grade ( $M_w$ ,  $1.3 \times 10^5$ ) prepared from crabshells and provided by the Kypro Co. (Seattle, Washington). The microcrystalline cellulose (Avicel) was a gift from the FMC Corp. (Philadelphia, Pennsylvania).

### Methods

Standard analytical procedures were used to measure the phosphorus [8] and chlorine [9] contents of the products. Their IR spectra (in KBr disks) were obtained by using a Beckman IR-10 spectrophotometer while a Jeol PS spectrometer was employed to record the  $^{31}\text{P}$  NMR spectra of the chlorophosphazenes. The flammability of polymers was qualitatively tested by holding powdered material (50 mg) in a Bunsen flame for 5 s on a spatula.

### Modification of Polysaccharides with Chlorophosphazenes

A dispersion of chitosan (6.97 g) or microcrystalline cellulose in acetone, nitrobenzene, toluene, or 1,1,2,2-tetrachloroethane (100 mL) at 50°C was stirred for 1 h and then treated with pyridine equivalent to the amount of chlorophosphazene subsequently added. Thereafter a solution of the chlorophosphazene, in the appropriate molar ratio

desired, in the dispersion medium (100 mL) was added dropwise during 30 min with a continued stirring. After a period (2-14 h) of heating at a specified temperature, the product was collected by filtration, successively washed with the dispersion medium, with acetone and water, and then finally dried at 45°C under reduced pressure.

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