

Preparation and Characterization of Phosphorus-Nitrogen Polymers for Flameproofing Cellulose. I. Polymers of THPC and Amines

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Synopsis

Polymers from tetrakis(hydroxymethyl)phosphonium chloride (THPC) or tris(hydroxymethyl)phosphine (THP) with ammonia show similar thermal degradation, but appear to be of different chemical structure. Solution reaction of THPC with urea or melamine or by solid-phase reaction with urea gives products ranging from water-soluble liquids to hard, brittle, insoluble polymers. Reaction of THPC with piperazine yields products of low thermal stability.

INTRODUCTION

During the past decade, and the last five years in particular, the growing interest in flameproofing of materials such as fabrics and plastics has been phenomenal. This has been international and is reflected in the research effort, the numerous meetings and committees, and the legislation in several countries¹ aimed to reduce burn injuries and especially fabric burn injuries. The majority of fabric burn injuries are due to ignition of cotton or rayon fabrics which normally ignite easily and burn readily. These cellulose fabrics may be made flame resistant by treatment with various compounds, the usual method being the formation of a phosphorus-nitrogen polymer in the fabric by the reaction of tetrakis(hydroxymethyl)phosphonium chloride (THPC), or a derivative of THPC, with an amine. Unfortunately, most of the commercial treatments adversely affect the fabric properties, and there has been only marginal improvements in these treatments since they were introduced about twenty years ago.² Although many papers appear each year, dealing with the application of compounds to fabrics and the subsequent flammability properties of the treated fabrics, little work has been reported on the syntheses and characterization of the phosphorus-nitrogen polymers per se.

The characteristics of some polymers can be altered appreciably by the environment in which the polymerization occurs. Hence, the polymer which is precipitated in, or on, a fabric may be different from that produced

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in solution or by intimate contact of the reactants. Despite this, it is very desirable to synthesize and characterize polymers in environments other than that of the fabric for which the polymer may act as a flameproofing agent. First, the fully polymerized polymer, in powder form, may be dispersed in a solution (e.g., viscose or acetate) or melt before being converted to fibers, so that each fiber contains the agent. Second, it is very difficult to produce some polymers, e.g., THPC-ammonia, in fabrics whereas the reaction occurs rapidly in solution. Therefore, although lack of success in polymerizing a compound directly onto fabrics may indicate failure of a given process, successful polymerization of the same reactants in other media may indicate potential methods for application to fabrics. The main objective of the work reported was to investigate the factors involved in the production of very inert polymers with high phosphorus and nitrogen contents. Such materials, in finely dispersed form, should be good flameproofing agents for regenerated cellulose fibers.

Much of the original and subsequent work on THPC and its derivatives has been carried out at the Southern Regional Research Laboratories of the U. S. Department of Agriculture. An account of THPC and some of its reactions with amines and phenol has been given by Reeves and Guthrie,³ and recently⁴ it has been shown that THPC and THPOH react with primary and secondary amines to produce compounds with the phosphine structure, which can be oxidized to the corresponding phosphine oxide. In these reactions, the THPC or its derivatives lose one of the hydroxymethyl groups as formaldehyde, and it has been proposed that the formaldehyde forms an adduct or zwitterion.⁵

EXPERIMENTAL

Materials

Tetrakis(hydroxymethyl)phosphonium chloride (THPC) from Hooker Chemical Corporation was crystallized twice from *n*-propanol to give a melting point of 149°–151°C. Tris(hydroxymethyl)phosphine (THP) was prepared by the method of Petrov et al.⁶ and characterized by infrared and elemental analysis, oxidation to tris(hydroxymethyl) phosphine oxide (THPO), and preparation of the THPO trilaurate. Commercially available hexahydropyrazine (piperazine) was crystallized twice from ethanol to give a melting point of 108°C, and melamine, urea, and the solvents were obtained in analytical grades, while ammonia gas was obtained from a cylinder.

Analyses

The following commercially available instruments were used for analyses: Beckman IR-8 and Perkin Elmer 521 spectrophotometers, Perkin Elmer CHN 240 analyzer, F & M CHN 185 analyzer, Coleman Junior spectrophotometer model 6A, Bausch and Lomb Spectronic 505, and a thermogravi-

metric analyzer with a Cahn electrobalance and F & M Model 240M temperature programmer.

Polymerization

Unless otherwise stated, all polymerizations were carried out in a three-necked flask of 100-ml or 250-ml capacity, fitted with a stirrer, a thermometer and a reflux condenser, and placed in an oil bath at the desired temperature.

THPC-Ammonia. Because of the rapidity of the reaction of THPC with ammonia, these reactions were carried out at room temperature, 25°–28°C. Also, the reflux condenser was replaced by an inlet-outlet for ammonia. THPC, 5 g, in 50 ml water, ethanol, dimethyl sulphoxide (DMSO), or dimethyl formamide (DMF) was placed in the flask and ammonia slowly bubbled through. In each case, the temperature rose to 50°–55°C after about 5 min and a white precipitate formed, the mixture becoming a viscous slurry. Stirring was continued for a further 15 min, after which time the precipitate was filtered, washed several times with distilled water, and dried in a vacuum desiccator. The yield was 1.7 g from water, 1.8 g from ethanol, and 2.3 g from DMSO and DMF. Each of the products was a soft, white powder with a yellow tinge, insoluble in water, the common organic solvents, dilute hydrochloric and sulfuric acids, and 10% sodium hydroxide solution. Further analysis of the product prepared in DMF gave P, 24.0%; N, 17.8%, and C, 38.3%; IR spectrum by the potassium disc technique is shown in Figure 1. Differential thermal analysis (DTA) of this product showed a small exotherm at 58°C and a large endotherm at 87°C, while thermogravimetric analysis (TGA) under nitrogen, at 5°C/min, gave a 5% weight loss at 244°C and 48% loss at 550°C. Products similar to those described above were obtained by

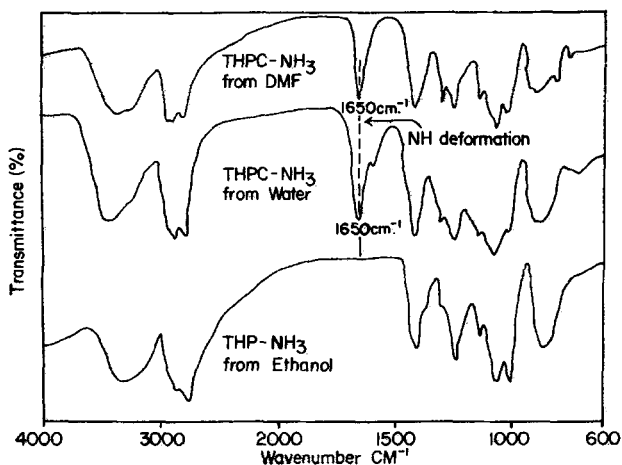


Fig. 1. Infrared spectra of polymers.

addition of ammonia solution to THPC solution. Addition of 10% ammonia solution to 10% THPC solution gives an immediate white precipitate which, when examined under the microscope, appears to consist of small particles, each about 10^{-4} cm in diameter.

THP-Ammonia. As with THPC, gaseous ammonia was slowly bubbled through a solution of 1.2 g THP in 12 ml water, ethanol, or DMF at 27°C. In each case, the temperature rose to 50°–55°C, and, after 1 min in the case of ethanol and after 5 min for the reactions in water and in DMF, the products in the flask turned into a highly viscous slurry. This was filtered, washed, and dried in a vacuum desiccator to give 0.6 g of product from water, 0.5 g from ethanol, and 0.8 g from DMF. As with THPC, the products from ethanol and DMF were soft, white solids, but that from water was a hard, white solid; and these THP-NH₃ products were insoluble in the common solvents or in dilute acids and alkalis. The product from ethanol was examined further and gave an IR curve similar in many respects to that obtained for the THPC-NH₃ product from ethanol, as can be seen in Figure 1. Although the IR curves for the THPC-NH₃ and THP-NH₃ products are similar, small differences are apparent, which also depend on the solvent used. Also, the DTA and TGA curves for the products from THPC or THP with NH₃ were nearly identical and virtually independent of the solvent used. Elemental analysis gave P, 24.4%; N, 10.9%, and C, 42.5%.

THPC-Urea. Reaction of THPC with urea was examined in both the solid state and in solution. In a dry box, under a nitrogen atmosphere, 0.01 mole THPC and 0.01 mole anhydrous urea were ground in a mortar to a smooth paste. This was transferred to a dry test tube, fitted with a stopper and glass tube, and placed in an oil bath at 105°C. The effluent vapor was passed through a Dry-Ice trap, and the liquid condensed was confirmed to be water. The vapor passing the cold trap was bubbled through Schiff's reagent, turning it red and indicating formaldehyde. Depending on the time of heating the THPC-urea mixture, products were obtained ranging from water-soluble syrups to hard, brittle solids. To determine whether more than one of the methylol groups of THPC yield formaldehyde, tris(hydroxymethyl)phosphine oxide (THPO) was prepared,⁷ and 0.01 mole THPO was ground with 0.01 mole urea and heated at 105°C as before. Water was condensed in the cold trap, but formaldehyde could not be detected in the vapor, indicating that only one of the methylol groups of THPC yields formaldehyde during reaction with urea at 105°C.

Solution reaction of THPC with urea was carried out in DMSO under nitrogen by adding 0.01 mole urea in 6 ml DMSO to 0.01 mole THPC in 20 ml DMSO in the flask. The mixture was heated rapidly to 95°C and kept at this temperature for 30 min, during which time the mixture became turbid and a granular precipitate formed which absorbed most of the solvent. A further 25 ml DMSO was added to produce a slurry which was cooled and filtered, and the clear filtrate was again heated at 95°C for 30

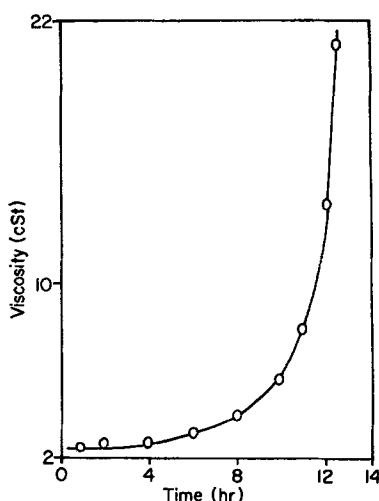


Fig. 2. Viscosity of THPC-melamine in DMSO at 65°C.

min. A further small amount of precipitate formed, which was filtered and added to the initial yield. The total was ground, washed thoroughly with hot water, and dried in a vacuum desiccator to yield 0.82 g powdery, white solid which yellowed on prolonged heating in air at 100°C. The white powder was not soluble in water, DMF, ethyl alcohol, or 10% sodium hydroxide solution, and analysis gave P, 14.5%; N, 20.8%, and C, 32.3%, with traces of sulfur which further washing with hot water failed to remove. The IR spectrum of the product is shown in Figure 1; TGA gave 3% weight loss at 250°C and 43% loss at 450°C.

THPC-Melamine. When equimolecular proportions of purified THPC were ground in a mortar with melamine, no apparent reaction occurred at room temperature. However, when crude, dry THPC was ground with melamine, the dry mixture became a slurry after a few minutes, and, after 10–15 min, a white precipitate formed. After being washed thoroughly with water, filtered, and dried, the white solid was found to be insoluble in the usual solvents and resistant to heat.

To follow the reaction of THPC and melamine in solution, 0.05 mole THPC and 0.05 mole melamine were stirred in 100 ml DMSO at 65°C and the viscosity of the solution was followed. Results are shown in Figure 2, which indicate little polymerization in less than 12 hr. Only after 20 hr is a product formed which is insoluble in both DMSO and water. However, after 10 hr a white water-soluble product was obtained on pouring the reaction mixture into excess ethanol. Elemental analysis of the water-soluble or water-insoluble precipitates showed about 1–1.5% sulfur but no chlorine. To remove the sulfur from the water-soluble products, the product was thrice dissolved in water followed by precipitation with ethanol, but the product still contained nearly 1% sulfur. To determine whether DMSO

reacts with either THPC or melamine, 0.01 mole THPC was stirred in 20 ml DMSO for 10 hr at 65°C, as was 0.01 mole melamine in 20 ml DMSO. After pouring either product into excess ethanol, no precipitate formed, indicating that, with the THPC-melamine product, DMSO is being occluded in the polymer, rather than reacting.

THPC-Piperazine. THPC, 0.005 mole, in 9.5 ml water was added to 0.01 mole piperazine in 8.6 ml water at 25°C and stirred under nitrogen. Within 5 min the temperature rose to 37°C and the viscosity of the solution had increased appreciably. In another experiment, this clear, viscous solution remained stable for over one month. Water, 25 ml, was added to lower the viscosity, followed by 0.005 mole triethylamine in 5 ml water. The latter addition caused immediate gelation, and a further 25 ml water was added and stirring continued for 30 min. To further polymerize the product, the temperature was raised to 50°C for 30 min and the fine white precipitate formed was filtered, washed thoroughly with water, and again filtered. The product was dried in a vacuum desiccator to yield 1.1 g of a white powder. The product was not soluble in the common solvents including DMF, DMSO, and 10% sodium hydroxide; elemental analysis gave P, 11.0%; N, 21.3%, and C, 51.9%. TGA analysis gave 2.2% weight loss at 200°C, 50% loss at 310°C, and total loss at 400°C. After 1 hr in air at 100°C, the product appeared heterogeneous and more resistant to some chemicals such as concentrated nitric acid, which reacts violently, producing brown fumes, with most of the phosphorus-nitrogen polymers described above.

DISCUSSION

Most commercial durable flameproofing treatments for cotton and rayon fabrics involve the formation of a THPC-melamine or THPC-urea polymer in the fibers or a partial polymerization followed by after-treatment with ammonia. Alternatively, a finely divided phosphorus-nitrogen polymer can be dispersed in viscose solution to give flame-resistant rayon, hence the interest in most of the products studied in the present work. As is normal with many phosphorus-containing organic compounds, analysis by combustion methods lead to considerable difficulties in the determination of P and C, due to the formation of a small amount of heat-resistant, P-containing char. Because of the inconsistent results obtained by combustion methods for P and C in the polymers obtained, the P was determined by nitric acid decomposition, followed by phosphomolybdate color formation.

Although the THPC-ammonia and the THP-ammonia products appear physically similar and show similar thermal decomposition properties, the ratio of P to N indicates that THPC reacts with only two of the hydrogens of the ammonia to give a product containing $-\text{NH}-$ groups, whereas THP reacts with all three hydrogens. This is supported by the IR data in Figure 1, in which the THPC-ammonia gives a strong NH deformation

band at 1650 cm^{-1} for products prepared in DMF or water, whereas the THP-ammonia does not show this band. Presence of these NH groups may account for the hydrolytic instability of THPC-ammonia when it is dispersed in viscose solution.⁸ If the THP-ammonia has no free NH groups, it should be more stable to hydrolysis.

Solution reaction of THPC with both melamine and urea appears to be a simple condensation polymerization to give linear products which eventually crosslink to form hard, brittle products. This is supported by elemental analysis and by viscosity increase during reaction. Solid-phase reaction of THPC with urea follows a similar course, and similar products can be isolated. However, although such products can be obtained by reacting THPC with methylol melamines, the reaction of THPC with melamine in the solid phase does not appear to be quite as simple. Reaction with the difunctional piperazine yields a product of relatively low thermal stability, which would be expected due to the insertion, in the polymer structure, of this large molecule which is held by only one bond at each end.

Because chlorine could not be detected in any of the polymers produced, and because formaldehyde is evolved during the initial stages of the reaction, the THPC must form THP before or during reaction with amines. It is possible to oxidize the reacted THP to the phosphine oxide but not before reaction with amines, because THPO is unreactive with amines.⁹ These results are in agreement with those of Reeves and co-workers.⁴

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