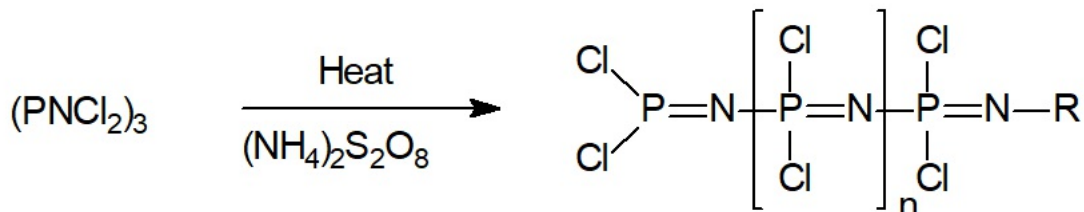


# Polyphosphonitrilic Chloride

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## 1. Procedure

**CAUTION!** The monomer is toxic and should be handled in a well-ventilated hood, while wearing protective clothing. Phosphonitrilic chloride trimer is ground in a mortar and pestle with ammonium persulfate in a ratio of 100 g of trimer to 2 g of persulfate (mole ratio = 2.87:0.0875, Note 1) to give an intimate mixture of the two compounds. Four grams of the mixture is sealed under vacuum in a 10 mm diameter glass tube 10-15 cm long (Note 2), and the tube is wrapped in a sheet of copper gauze and placed in an air oven at 210°.

After heating for 24 h (Note 3), the tube is allowed to cool, and the polymerized material is separated from the unchanged trimer by swelling the contents of the tube in 50 mL of sodium-dried benzene for 24 h. The insoluble  $(\text{PNCI}_2)_n$  rubber is removed by filtration on a sintered glass crucible (porosity No. 3). The swollen rubber is dried in a vacuum oven at 60-80° until a constant weight is obtained. The yield is 3-3.4 g, representing a conversion of 75-85%. The rubber is a pale yellow rubbery solid (Note 4) that hydrolyzes slowly in moist air. It should be stored in a dry atmosphere, preferably in a small stoppered vessel.

## 2. Notes

1. The trimer is also called hexachlorocyclotriphosphazene and may be obtained from Albright and Wilson, Birmingham, England, as a commercial grade melting at 111.5-112.5°. It may be purified by the following procedures:  
(a) recrystallized from isopropyl alcohol, mp 113-113.5°; ligroin may be preferred because it is quite inert with the trimer, whereas alcohols do react under certain conditions; (b) zone-refined using six passes at 1 in/h down a tube 12 mm in diameter, 15 cm long; mp 113.5°. The rate of conversion of trimer to polymer is not greatly affected by the purity of the trimer. Conversions of 75% were obtained after 24 h of heating with both crude and recrystallized trimer. Zone-refined material gave 83% polymer.
2. The polymerization is not seriously retarded by air, and conversions of 70-75% are obtained if the polymerization is done in tubes sealed under 1 atm of air. The vacuum used in the experimental procedure was 1 torr, obtained by using a vacuum pump. Although there is no pressure generated during polymerization, it is always considered good practice to enclose a sealed-tube reaction vessel in a protective sheath. The phosphonitrilic chloride will sublime at 210° if a sealed tube is not used.

3. The conversion-time curve for the polymerization reaction depends on the method of determining the polymer yield. If the benzene extraction technique is used, the low molecular weight oils that are present at low conversions are not isolated because they dissolve in the benzene with the trimer. If, however, the unchanged trimer is removed by vacuum sublimation, the total yield of polymer is obtained. When using the latter technique, it is important to re-evacuate the reaction tube, after heating at 210°, because the vapor pressure in the tube is too high to allow sublimation at a suitable temperature (140°). By using the sublimation method, it is shown that the polymerization is retarded during the first 4 h of heating. The conversion is linear with time, between 4 and 20 h, and a maximum is reached after approximately 24 h of heating.
4. The color of the final rubber is very dependent on the water content of the trimer. The trimer may be conveniently dried by heating it at 140° in an oven with a small amount of anhydrous silica gel or by zone refining. If the monomer is not dried, the polymer will have a dark brown to black appearance, perhaps due to dehydrochlorination, although this is not shown by elemental analysis.

### 3. Methods of Preparation

The polymerization of phosphonitrilic chloride trimer has been the subject of a considerable research. The polymerization can be divided into catalyzed and non-catalyzed reactions. The trimer polymerizes if heated alone at 250-350°, although the reaction is very slow if the materials are carefully purified. There are large in the rates of polymerization obtained for a purely thermal reaction at 350° depolymerization occurs. The tetramer is more expensive than the trimer and polymerizes at a much lower rate.

The advantage of using a catalyzed reaction is that polymerization is possible at lower temperatures, and the results are much more reproducible. Konecny and Douglas<sup>3</sup> reported the polymerization of both trimer and tetramer at 211° using a variety of catalysts such as benzoic acid and diethyl ether, and obtained results very similar to those given in the procedure above. Ammonium persulfate gives very consistent results and a lighter-colored product than most other catalyst systems. The reaction is now believed to be ionic in character.

### 4. Characterization of Phosphonitrilic Chloride Rubbers

Rubbers obtained at very low conversions (<10%) are low molecular weight oils that are benzene-soluble and have intrinsic viscosities in the range 0.05-0.15 dL/g. At higher conversions, insoluble rubbers are formed that have a swelling index (mL of benzene imbibed per gram of rubber) of 3.7-3.9. If the rubbers are allowed to stand in moist air, this value falls, as a result of hydrolysis of the phosphorus-chloride bonds, to 2.0-3.0. The insolubility and swelling of these polymers suggest that they possess highly cross-linked structures.

The analysis of the rubber is given below and compared with that of trimer; zone-refined trimer gave almost the same analysis.

	%P	%N	%Cl
$\text{PNCI}_2$ (theory)	26.72	12.09	61.19
$\text{PNCI}_2$ trimer	26.92	12.06	61.00
$\text{PNCI}_2$ rubber	27.35	11.98	61.00

## 5. Use of Phosphonitrilic Chloride Rubbers

This inorganic rubber is potentially stable at high temperature, but it has not been possible to develop it commercially because of the ease with which it undergoes hydrolysis. Early attempts to prepare derivatives and to graft non-polar side chains onto the rubber<sup>4</sup> were unsuccessful. More recent work has shown that soluble, high molecular weight polymer may be obtained under the right conditions, and a wide variety of groups bonded to the backbone phosphorous moieties.<sup>5</sup>

## 6. References

1. *Adhesive Tapes Ltd., Borehamwood, Herts, England.*
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