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Hydrolysis of Poly(dichlorophosphazene)

DOUGLAS G. GABLER AND JAMES F. HAW*

Department of Chemistry, Texas A&M University,
College Station, Texas 77843

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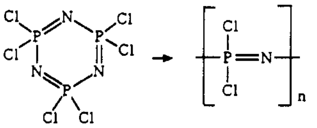
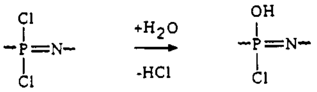
The usual synthesis of poly(chlorophosphazene) is via the melt polymerization of the cyclic trimer of phosphonitrilic chloride with an appropriate catalyst to form poly(dichlorophosphazene).

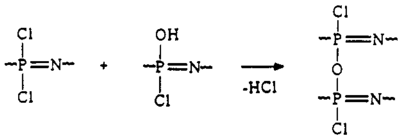


Soluble polymer can be formed under the conditions developed by Allcock[1] in the middle 1960s.[2] The chloropolymer is hydrolytically unstable



and must be converted to more hydrolytically stable organophosphazenes. Solubility of poly(dichlorophosphazene) is essential not only to remove unreacted trimer but also to derivitize the polymer through nucleophilic substitution reactions. The effects of water on solutions of the polymer are detrimental in that gel formation occurs due to hydrolytic cross-linking. The gels are not soluble and must be discarded, making this side reaction costly.

Gel formation from hydrolytic cross-linking is generally thought to occur through the reaction of a ClPOH with another PCl_2.



We have used ^{31}P NMR to probe the hydrolysis of poly(dichlorophosphazene) in solutions of THF up to the point of gel formation. Under the conditions used in our experiments, gel formation occurred when ca. 7% of the PCl_2 groups were hydrolyzed. On the basis of ^{31}P multiplicity patterns and nuclear Overhauser enhancement (NOE) data, the evidence suggests that gel formation is the result of hydrogen bonding between ClPOH groups rather than POP cross-linking.

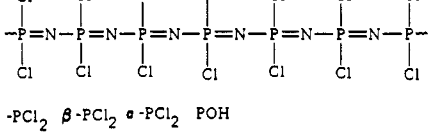
All steps were performed under anhydrous conditions either in a glovebox purged with liquid nitrogen boil off or with needles and septa. THF (Aldrich) was dried over and distilled from sodium benzophenone. Pyridine (Fischer) was dried over KOH and distilled from BaO.

Phosphonitrilic chloride cyclic trimer (Aldrich, 99.9+%) was sublimed once at 55 °C and 10^{-2} Torr and then loaded into heavy walled glass ampules. BCl_3 (Matheson), the polymerization catalyst, was condensed into the tube at a mole ratio of 50:1, trimer to catalyst. The tube was flamed sealed and baked at 200 °C for 5 h. The molecular weight of the resulting polymer was not determined. Under the conditions used in this synthesis, however, molecular weights of 10^6 could be expected.[2] After cooling, the rubbery contents of the tube were extracted, and most of the unreacted trimer was removed by sublimation. ^{31}P NMR was used to confirm the absence of cyclic oligomers and the presence of chloropolymer (−18 ppm; relative to phosphoric acid). No evidence of chain ends was observed in the NMR spectrum, an observation consistent with a high molecular weight.

Polymer (1.0 g) was loaded into a 10-mm NMR tube that had been dried in a vacuum oven prior to transfer to the glovebox. C_6D_6 (1-mL ampule, Aldrich, 99.5%) was added as an internal lock, and the tube was fitted with a septum. THF (4.0 mL) was injected through the septum to dissolve the sample, and a ^{31}P spectrum was obtained prior to the addition of water. Water (15.0 μL, 10 mol % on a PCl_2 basis) was introduced into the sample, and spectral acquisition was begun within 1 min. Additional spectra were obtained every 15 min thereafter to follow the course of the hydrolysis which was carried out at 25 °C.

The spectrometer employed was a Varian XL-400 NMR operating at a ^{31}P resonance frequency of 162 MHz and 25 °C. Spectra were acquired by using a 45° pulse, a 15-s recycle time, and 64K data points to characterize the FID. Poly(dichlorophosphazene) was used as an internal chemical shift reference (−18 ppm relative to phosphoric acid), and negative numbers denote an upfield chemical shift. For those spectra requiring quantitative peak intensities, the proton decoupler was left off to prevent buildup of NOE.

Hydrolysis of the polymer proceeded rapidly enough that multiplets appeared in the first spectrum immediately after the addition of water. Figure 1 is a set of ^{31}P NMR spectra from a typical hydrolysis experiment. The multiplets in Figure 1 were the only signals to appear, and they grew in intensity with time. No additional signals were observed even after gel formation. The most downfield signal, a triplet of triplets, is assigned to a ClPOH phosphorus resonance.



The splitting pattern is consistent with the A spin of an AM_2N_2 spin system. Such a pattern is to be expected for the nucleus of a ClPOH group. The coupling between the ClPOH and the phosphorus α to the ClPOH is 41.8 Hz. On the basis of previous studies[3] conducted in this laboratory on the ^{31}P NMR spectral properties of hydrolyzed chlorotrimer, this value is consistent with two-bond coupling between a ClPOH and a PCl_2. The long-range coupling between the hydrolyzed phosphorus (ClPOH) and the phosphorus β to the ClPOH has a coupling of 7.2 Hz. This value is consistent with four-bond coupling[4] and is probably transmitted via the delocalized π-electron cloud of the polymer.[5] The multiplicity pattern was unaffected when a continuous proton decoupling mode was employed.

The upfield signals at −22 and −20 ppm are assigned to the α-PCl_2 and β-PCl_2 groups, respectively. Four-bond coupling is exhibited in these signals as well. The γ-PCl_2 was observed as a broad hump at the base of the main polymer peak in most experiments. 2D-COSY (homo-

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* To whom correspondence should be addressed.

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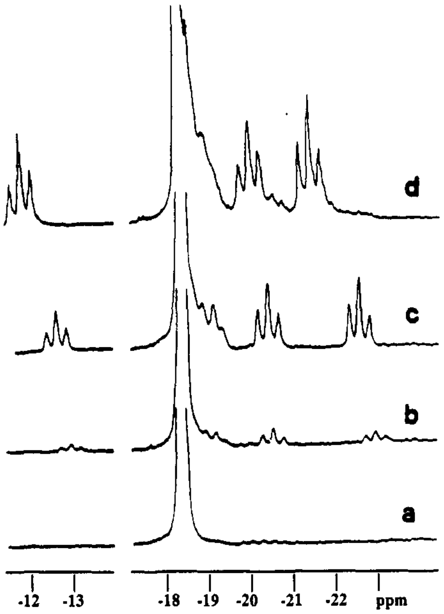

Figure 1. Selected ^{31}P NMR spectra depicting the hydrolysis of poly(dichlorophosphazene) (2). (a) Before addition of water; (b) spectral acquisition begun 1 min after the addition of water; (c) 22 min after the addition of water; (d) 20 h after the addition of water (after gel formation).

Table I
^{31}P NMR Spectroscopic Properties of Hydrolyzed Poly(dichlorophosphazene) (2)

nucleus	^{31}P chemical shift, ppm	$J(^{31}P–^{31}P)$, Hz	NOE, % max
ClPOH	−11.7	^2J(PClOH–α-PCl$_2$) = 41.8 ^4J(PClOH–β-PCl$_2$) = 7.2	29.6
α-PCl$_2$	−21.6	^2J(a-PCl$_2$–β-PCl$_2$) = 46.0 ^4J(α-PCl$_2$–γ-PCl$_2$) = 8.0	2.6
β-PCl$_2$	−19.6	^2J(β-PCl$_2$–γ-PCl$_2$) = 50.0	2.3
γ-PCl$_2$	−18.5		

nuclear shift correlation) NMR experiments (not shown) provided further evidence in support of the above assignments.

The observed multiplets due to the spin inequivalence arising from the hydrolysis of a single PCl$_2$ does not alone establish that the triplet of triplets at −12 ppm is due to a ClPOH rather than a POP cross-link. The latter possibility, however, would require that additional coupling through the POP bridge be too small to be observed. The NOE measurements support the assignment to a ClPOH group. Table I summarizes the measured ^{31}P NMR properties for the partially hydrolyzed chloropolymer. The NOE is greatest for the resonance assigned to a ClPOH phosphorus and drops off rapidly for the adjacent phosphorus nuclei. A POP cross-link site would not be expected to show NOE enhancement. The only source of protons for ^{31}P(^{1}H) NOE with a POP cross-link is the solvent. This did not seem likely because all of the peaks should have shown about the same amount of enhancement, if the solvent was the source of the observed enhancement. To rule out the possibility of enhancement from the solvent and to definitively show that such enhancement was indeed from the ClPOH proton, hydrolysis was carried out with D_2O; the solvent, THF, remained the same. No enhancement was observed for any of the signals when the polymer was hydrolyzed with D_2O. The above evidence suggests that the downfield multiplet pattern is indeed due to ClPOH and not a POP cross-link site.

In several hydrolysis experiments the sample was periodically removed from the NMR probe, and the viscosity of the sample was inspected. Gel formation typically occurred after 20 h. Integrated peak intensities of the ^{31}P NMR spectra indicated that gel formation occurred when about ca. 7% of the PCl$_2$ groups had been hydrolyzed. This gel could, however, be redissolved with polar, aprotic solvents such as dimethylformamide, further evidence for hydrogen bonding as the source of gel formation.

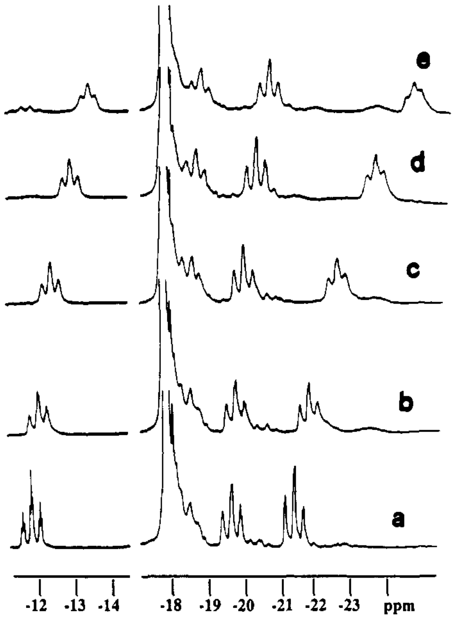

Figure 2. Selected ^{31}P NMR spectra depicting the changes in chemical shifts following the addition of pyridine to solutions containing hydrolyzed poly(dichlorophosphazene). Amounts of pyridine reported as equivalents based upon the amount of water added initially. (a) Before added pyridine; (b) 0.1 equiv of pyridine; (c) 0.2 equiv of pyridine; (d) 0.4 equiv of pyridine; (e) 0.8 equiv of pyridine.

If every hydrolyzed phosphorus participates in a hydrogen bond cross-linking reaction, then an observed gel formation after 7% of the PCl$_2$'s have been hydrolyzed would yield a cross-linking density of 0.035, which works out to many cross-linked sites per chain. Polymer molecules are expected to form a gel with as little as one intermolecular cross-linked site per chain.[6] Our NMR results are unable to distinguish between intermolecular and intramolecular hydrogen bonding. Given the extent of reaction required before gel formation, it seems reasonable to propose that a majority of the hydrogen bonds are intramolecular and do not contribute to gel formation.

Inspection of Figure 1 reveals that the chemical shifts of some of the resonances display pronounced changes during the course of the hydrolysis. Such changes were principally due to variations in solution acidity during the reaction. The PClOH resonance first appears at a chemical shift of approximately −13 ppm when the polymer is subjected to hydrolysis in a water/THF solution. As the hydrolysis progresses, this resonance rapidly shifts downfield until it reaches a chemical shift of approximately −12 ppm. The reason for the observed chemical shift changes probably involves the acid–base properties of the hydrolysis products. This same phenomenon was observed in our previous studies of the hydrolysis of the chlorotrimer in solutions of THF.[3] This dependence of ^{31}P chemical shift on solution acidity can be more clearly seen in Figure 2, which shows the result of adding from 0 to 0.8 equiv of pyridine (on the basis of the amount of water added) to a THF solution of partially hydrolyzed polymer. This effect is strong enough to permit a near-complete resolution of the γ-PCl_2 groups and partial resolution of the δ-PCl_2 groups at the higher concentrations of added base. The addition of a stronger base such as triethylamine, however, resulted in a dramatic increase in the hydrolysis rate and near-immediate gel formation.

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References and Notes

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Registry No. 2, 26085-02-9; pyridine, 110-86-1.