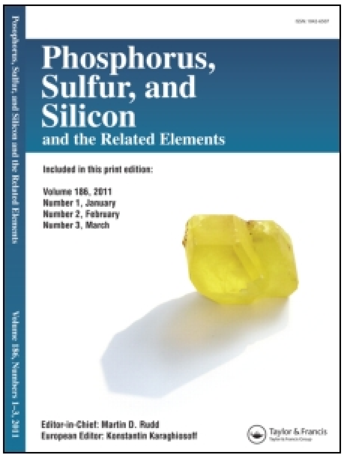

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BASE HYDROLYSIS OF POLY{BIS(TRIFLUOROETHOXY)PHOSPHAZENE}

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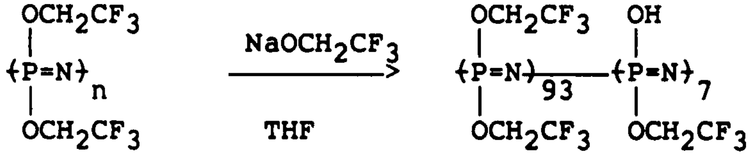
Abstract

The base hydrolysis of high molecular weight poly{bis(trifluoroethoxy)phosphazene} (I) is an effective method for the incorporation of hydroxy groups onto the phosphorus-nitrogen backbone (II). Incorporation of greater than 7 mole% hydroxy groups yields a semi-crystalline film-forming material. The hydrolysis has been modeled using the cyclic trimer $\{N_3P_3(OCH_2CF_3)_6\}$ (III). Comparisons of the ^1H NMR spectra of hydrolyzed trimer $\{N_3P_3(OCH_2CF_3)_5(OH)\}$ (IV) and the high polymer II allow for the facile monitoring of the extent of hydrolysis. Titration with a strong base shows the hydroxy groups to be strongly acidic. Viscosity measurements show some loss of molecular weight upon hydrolysis.

The alkaline hydrolysis of fluoroalkoxyphosphazene cyclic compounds has been well studied by Allcock et al.[1,2] The use of these compounds as synthetic reagents has also been reported.[3] Recently, we reported that sodium trifluoroethoxide cleaves the side group of poly{bis(trifluoroethoxy)phosphazene} (I).

A small amount of side group cleavage (less that 2 mole%) causes changes in polymer morphology[4] and dilute solution properties.[5] In this paper, we report direct evidence for hydroxy group incorporation onto the fluorinated polymer using ^1H NMR and non-aqueous potentiometric titrations. The hydrolyzed was estimated to be 7 mole% by NMR spectroscopy and slightly less by titration.



$$\left(\overset{OCH_2CF_3}{\underset{OCH_2CF_3}{P}}=N\right)_n \xrightarrow[THF]{NaOCH_2CF_3} \left(\overset{OCH_2CF_3}{\underset{OCH_2CF_3}{P}}=N\right)_{93}\!\!-\!\!\left(\overset{OH}{\underset{OCH_2CF_3}{P}}=N\right)_7$$

(I) (II)

EXPERIMENTAL

A typical hydrolysis reaction involved the dropwise addition of a solution of sodium trifluoroethoxide (previously prepared from sodium (4.0 g, 0.17 mol) and trifluoroethanol (30 mL, 0.3 mol) in THF (100 mL)) to a stirred solution of I (10 g, 0.04 MOL) in THF (300 mL). The reaction mixture was stirred for 72 h, precipitated into water (4 L), and the polymer collected and redissolved in acetone (200 mL). Water (200 mL) was then added dropwise to the stirred solution of I and the resulting solution was dialyzed against water. Finally, the water was removed by freeze drying to leave a white fluffy material (8.7 g).

RESULTS AND DISCUSSION

Vibrational Spectroscopy

Vibrational spectra of films of II showed little difference from those of the homopolymer I. Bands that were present in the infrared spectrum of II and not of I were a broad but weak stretch from 3600 to 2600 cm^{-1}, a shoulder at 1280 cm^{-1}, a shoulder at 920 cm^{-1}, and a band at 802 cm^{-1}.[6] Thus, the vibrational spectra indicated that the phosphazene character of the material was not greatly disrupted by the hydrolysis.[7]

NMR Spectroscopy

^1H NMR provides a simple method for monitoring the hydroxy incorporation onto the polymer backbone. The ^1H NMR of II in acetone-d_6 is shown in Figure 1. The broad multiplet at 4.6 PPM was assigned to the methylene protons of the unaltered section of the polymer. The much smaller multiplet centered at 4.4 PPM was assigned to the methylene protons of the fluoroalkoxy group on the hydrolyzed phosphorus atom. A ratio of the integrated intensities of the two methylene resonances provided an estimate of the amount of hydrolysis on the polymer. The sample used to obtain Figure 1 had approximately 7 mole% hydroxy incorporation, although the accuracy of this number was subject to the overlap of the two resonances at 300 MHz. A more accurate integration can be obtained from NMR spectra obtained at 500 MHz. However, 300 MHz proton spectra were sufficient to estimate the extent of hydrolysis. The broad resonance at 3.1 PPM was assigned to water and was not observed upon the addition of CF_3COOD. A ^1H NMR of I showed only the large resonance at 4.6 PPM and the the resonance assigned to water.

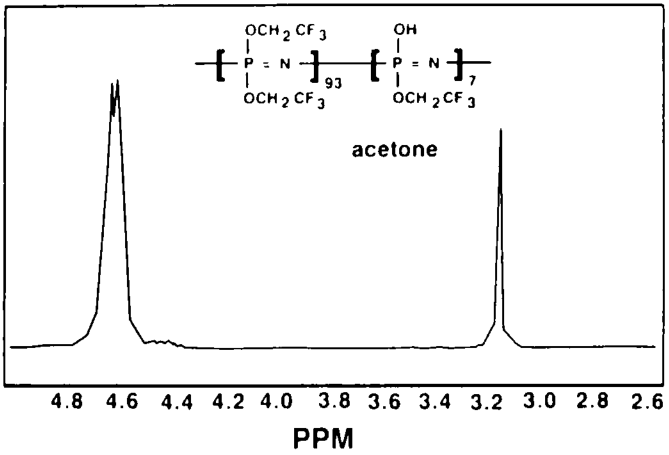


Figure 1

The ^1H NMR spectrum of II was obtained in THF-d_8 rather than in acetone as in Figure 1. The resonance observed at 4.4 PPM in acetone was not well defined in THF and the percent hydrolysis determination was not possible. If the intensity of the spectrum was attenuated such that the methylene peaks were off scale, a broad resonance was observed at 10.9 PPM. This resonance was assigned to the proton of the hydroxy group. We were unable to correlate the integration of the hydroxy proton with that of the methylene integration in acetone, probably due to exchange with water in the THF solvent.

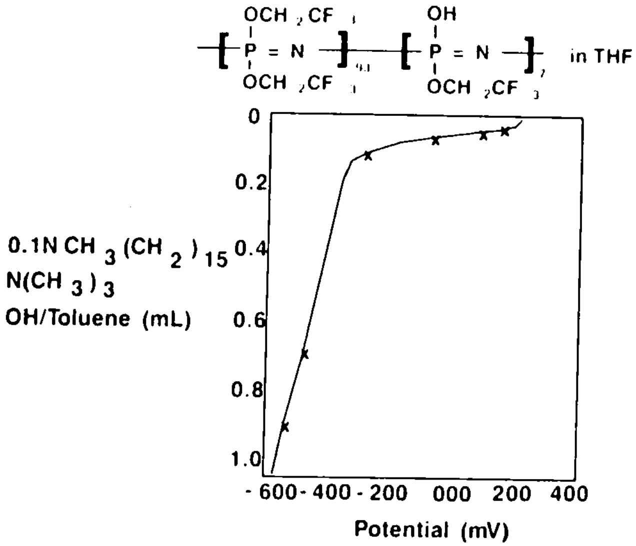
In order to characterize better the high molecular weight polymer, we carried out hydrolysis of the cyclic model compound $\{N_3P_3(OCH_2CF_3)_6\}$ (III) with sodium hydroxide in a water-methanol solution as described by Allcock and Walsh.[1] The ^1H NMR spectrum of the hydroxy cyclic in THF-d_8 supports the assignments made for polymer II. The multiplet centered at 4.5 PPM has been assigned to the methylene protons on the unaltered portion of the molecule while the multiplet centered at 4.2 PPM is assigned to the hydrolyzed moiety.[1] A broad resonance was again observed at 10.9 PPM and supported the hydroxy assignment made in Figure 2. Again, the peak area under the downfield resonance was smaller than predicted, probably due to proton exchange with residual water in the deuterated solvent.

^1H NMR of IV in $CDCl_3$ showed a broad resonance at 8.4 PPM with the expected integrated intensity ratio of 10:1 when compared to the methylene protons. Other authors have established that an N-H structure, an oxocyclophosphazadiene, is favored over a P-O-H tautomer, monohydroxycyclotriphosphazatriene.[1,8] As observed in the polymer spectra, the separation between methylene resonances used to determine the mole% of hydrolysis was more clearly defined for spectra obtained with acetone as the solvent. The high polymer II was not soluble in $CDCl_3$.

Titrations

A potentiometric titration curve obtained for II is shown in Figure 2. The polymer was dissolved in THF and titrated with hexadecyltrimethylammonium hydroxide in toluene:methanol/98:2. The initial potential of +240 mV indicated that a strongly acidic group was present on the polymer.

Figure 2



The curve can be divided into two parts. The initial titration with base caused a rapid change in potential to -300 mV. Determination of the hydroxy group concentration yielded 3 mole%, approximately half the value measured with NMR integration. The second portion of the curve was consistent with the titration of a much weaker base. Perhaps the origin of the second end point is strong hydrogen bonding of acid protons to the charged polymer. At a slow acid delivery rate (hours instead of minutes), the total acid found (strong plus weak) was 5.0 mole%.

Titration of the cyclic IV showed behavior similar to the first part of the curve for II. The cyclic was strongly acidic and titrated quantitatively. These results suggest that the chemistry of the hydrolyzed phosphazene in THF could be represented as an -OH rather than an -NH structure. Perhaps this is due to the perturbation of hydrogen bonding by an N-H proton in a basic solvent such as THF.[9]

Viscosity

The hydrolysis of I to II with sodium trifluoroethoxide appeared to result in some backbone cleavage of the phosphazene macromolecule. The intrinsic viscosity of II in THF with 0.01 N tetra-n-butylammonium bromide was 0.5 dl/g while the homopolymer I had an intrinsic viscosity of 2.1 dl/g. Thus, the amount of hydroxy incorporation present on II probably represents a limit for the extent of hydrolysis beyond which polymeric properties would be lost. Smaller amounts of hydroxy incorporation resulted in less molecular weight decline.[5]

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