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(14) Model chromophore from II + benzyl chloride: ^{1}H NMR ($CDCl_3$) δ 9.079 (2 H, d, J = 7.0 Hz), 7.724 (2 H, d, J = 7.0 Hz), 7.528 (1 H, d, J = 16 Hz), 7.477 (2 H, d, J = 8.8 Hz), 7.365–7.529 (5 H, m), 6.780 (1 H, d, J = 16 Hz), 6.666 (2 H, d, J = 9.0 Hz), 5.980 (2 H, s), 3.053 (6 H, s); λ_{max} = 529 nm ($ClCH_2CH_2Cl$). Anal. Calcd for $C_{22}H_{23}N_2Cl$: C, 75.31; H, 6.61; N, 7.98; Cl, 10.10. Found: C, 75.18; H, 6.73; N, 7.74; Cl, 10.35.
(15) $(PS)CH_2$-I: ^{1}H NMR ($CDCl_3$) δ($(PS)CH_2O$) 4.51, bound chromophore signals at δ 8.31 (2 H, d, J = 9.0 Hz), 7.89 (4 H, m), 6.81 (2 H, d, J = 9.0 Hz), 3.88 (2 H, t, J = 6.0 Hz), 3.62 (2 H, t, J = 6.0 Hz), 3.55 (2 H, q, J = 7.0 Hz), 1.24 (3 H, t, J = 7.0 Hz); λ_{max} = 483 nm (film); T_g = 105–109 °C. Anal. (prepared from PS having 12.5% of rings iodomethylated). Calcd: C, 87.33; H, 7.43; N, 2.81. Found: C, 86.52; H, 7.42; N, 2.65. $(PS)CH_2$-II: ^{1}H NMR ($CDCl_3$) δ ($(PS)CH_2$) 5.63 (2 H, br), bound chromophore signals at δ 8.62 (2 H, br), 7.72 (2 H, br), 7.50 (3 H, br), 5.63 (2 H, br), 3.00 (6 H, s); λ_{max} = 480 nm (film); T_g = 103–107 °C. Anal. (prepared from PS having 4.5% of rings iodomethylated). Calcd: C, 89.35; H, 7.51; N, 0.56; I, 2.56. Found: C, 88.85; H, 7.45; N, 0.57; I, 2.53.
(16) Headway Research Inc. photoresist spinner.
(17) Measured after poling and SHG experiments with a Tencore Alpha-Step 200 surface profiler.
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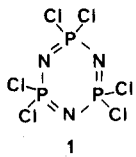
Magic-Angle Spinning NMR of Polyphosphazenes

Polyphosphazenes are inorganic polymers based on chains of alternating phosphorus and nitrogen atoms.[1,2] The key steps in the development of these materials were the discoveries by Allcock and co-workers of methods for converting the phosphonitrilic chloride cyclic trimer **1** into



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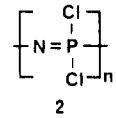

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the soluble, linear chloropolymer **2** and substitution reactions to convert **2** into a wide variety of hydrolytically stable polymers with diverse properties. These polymers are of considerable interest because of their mechanical and thermal properties, solvent resistance, and potential for providing biocompatible materials.

We are using high-resolution solid-state NMR techniques such as magic-angle spinning (MAS)[3] to study the synthesis, structure, reactivity, and dynamics of polyphosphazenes. This is the first high-resolution solid-state NMR study of polyphosphazenes, although wide-line studies of these materials have been previously reported.[4,5] In this paper we report preliminary results on the hydrolytic cross-linking of **2** and molecular dynamics in two solid elastomeric phosphazene polymers, poly(diethoxyphosphazene) (PBEP) and poly(dimethoxyphosphazene) (PBMP). This report also demonstrates the potential of MAS NMR for the study of a number of other problems in polyphosphazene chemistry.

The linear chloropolymer was synthesized by using a BCl_3-catalyzed melt polymerization reaction.[6] PBMP and PBEP were synthesized from the chloropolymer and purified by the methods described by Allcock and co-workers.[7] Solid-state NMR spectra were obtained by using a Chemagnetics M-100S NMR spectrometer operating at a magnetic field strength of 2.35 T. The ^{13}C spectra were obtained by using cross polarization with magic-angle spinning (CP/MAS)[8], whereas the ^{31}P spectra were obtained by using single-pulse excitation and MAS. High-power proton decoupling was used for all spectra. All ^{31}P chemical shifts are reported with respect to external 85% H_3PO_4; more positive shifts represent deshielding.

^{31}P MAS NMR has been used to examine hydrolysis and cross-linking in **2**. Figure 1a, which is a spectrum of crystalline **1**, is extremely broad and shows multiplicity patterns that appear to be consistent with heteronuclear dipole–dipole couplings to quadrupolar nuclei (i.e., ^{14}N, ^{35}Cl, and ^{37}Cl).[9] Figure 1b is the ^{31}P MAS spectrum of a solid sample of linear **2**. The chemical shift (−18 ppm) is very similar to the value reported in solution.[7] Notice that the breadth of the line has been greatly reduced with respect to that in Figure 1a. This is due to averaging of the dipolar couplings by molecular motion, consistent with the elastomeric nature of this material.[7] One of the most important problems in polyphosphazene chemistry is maximizing the yield of soluble, linear **2** and minimizing that of insoluble, cross-linked **2**, which cannot be converted to hydrolytically stable polymers.[10] The ^{31}P spectrum of a sample of the cross-linked polymer, which formed during the uncatalyzed thermal polymerization of **1**, is shown in Figure 1c. This spectrum does not show any additional peaks that can be attributed to cross-linking sites. We believe that such sites are not observed in Figure 1c because of their low concentration and the relatively modest number of scans taken (24).

An important cross-linking mechanism in the synthesis of **2** is thought to involve water—either as an impurity in **1** or abstracted from the glass reaction tube. In order to investigate this hypothesis and to assess the potential of solid-state NMR to identify reaction pathways in polyphosphazenes, we performed the following experiment: A sample of insoluble **2** was swollen in benzene and approximately 0.1 equiv (on a per Cl basis) of water was added. After the mixture was refluxed for several hours, the polymer was isolated, and the ^{31}P MAS spectrum shown in Figure 1d was obtained. This spectrum differs markedly from Figure 1c in that there is a peak at −11 ppm in Figure 1d. The partially hydrolyzed sample of insoluble **2** was then heated for 14 h in a closed container at 230 °C, and a friable residue was obtained. The spectrum of this residue is shown in Figure 1e. As can be seen in Figure 1e, heating produces a new peak at −29 ppm and essentially eliminates the peak at −11 ppm, which was observed prior

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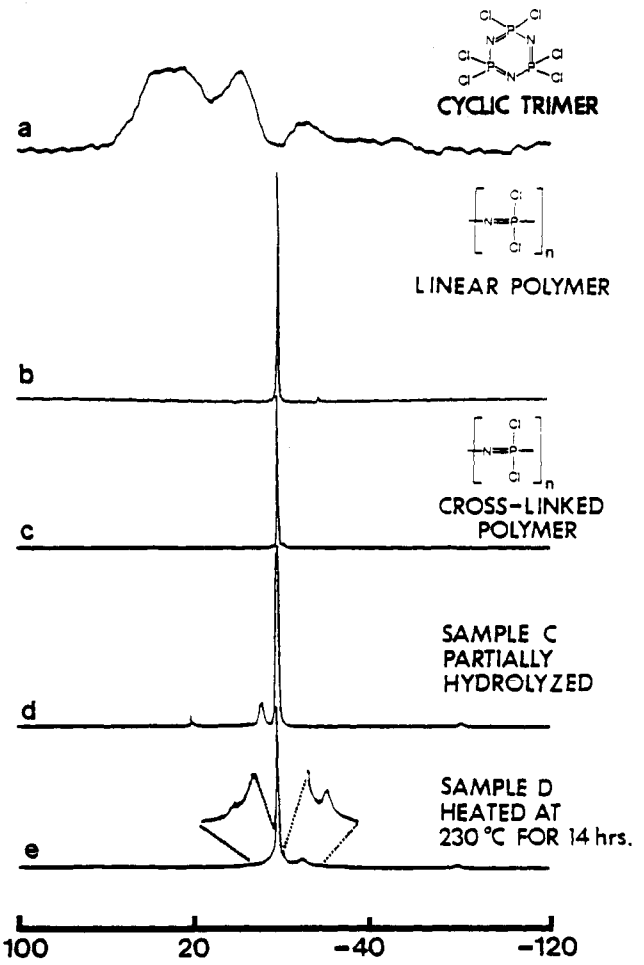

Figure 1. ^{31}P MAS spectra of (a) phosphonitrilic chloride cyclic trimer, (b) linear chloropolymer, (c) insoluble chloropolymer, (d) sample c partially hydrolyzed, and (e) sample d heated for 14 h at 230 °C.

to heating. Although we have not as yet definitively assigned the resonances at −11 and −29 ppm, it is quite reasonable to attribute them to hydrolysis of P–Cl groups followed by cross-linking. Allcock has proposed that the cross-linking mechanism of **2** proceeds through the hydrolysis of PCl_2 groups to give PClOH, which upon heating condense with P–Cl groups to form P–O–P cross-links.[11] The similarity of this proposed mechanism to the two peaks observed in our preliminary experiment is suggestive, and further experiments to investigate cross-linking mechanisms in the polymerization of **1** are in progress.

We are also using variable-temperature ^{31}P MAS and ^{13}C CP/MAS NMR to probe the molecular dynamics of poly(dialkoxyphosphazenes) in the solid state.[12] Figure 2 shows ^{13}C CP/MAS spectra of PBEP at various temperatures. The spectra on the left of that figure were obtained by using the standard CP/MAS experiment, while those on the the right were obtained by using the interrupted decoupling experiment (a modification of the CP/MAS experiment which suppresses signals from immobile, CH and CH_2 carbons).[13] CH_2 carbon signals are only observed in interrupted decoupling spectra if the ^1H–^{13}C dipolar couplings are averaged by molecular motion. The spectra in Figure 2 obtained at +25 °C show that the CH_2 resonance does indeed persist under interrupted decoupling, a result consistent with the degree of molecular motion one would expect for an elastomer above its T_g (the T_g of PBEP is −84 °C). Also, both spectra obtained at this temperature have a poor signal-to-noise ratio, again consistent with the averaging of dipole–dipole couplings by molecular motion. At a sample temperature of −50 °C the CH_2 carbon signal is significantly broader than in the spectra obtained at +25 °C, but this signal still persists in the interrupted decoupling spectrum, consistent with the fact that the polymer is still well above its T_g. At −70 °C the CH_2 carbon signal is so broad that it is not observed in either the CP/MAS or the interrupted decoupling spectrum. The significance of the line broadening will be explained shortly. At −100 °C, a temperature well below T_g, both carbons are observed in the CP/MAS spectrum, and only the CH_3 resonance is observed in the interrupted decoupling experiment. Note also that the signal-to-noise ratio of both spectra has increased dramatically. These results are consistent with a relatively rigid (i.e., glassy) solid and are analogous to what is observed for organic elastomers below their T_g's.

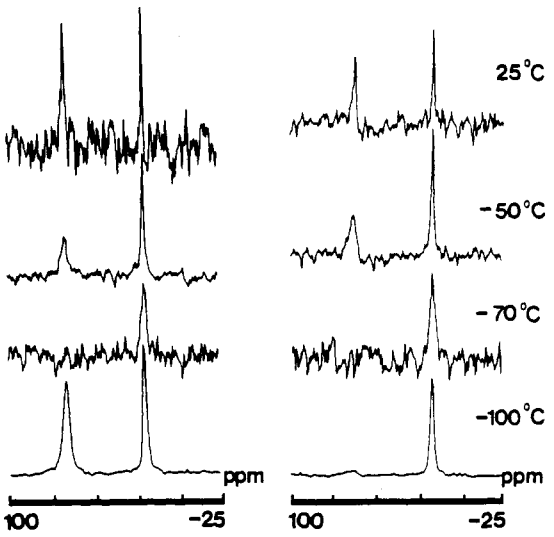

Figure 2. Variable-temperature ^{13}C CP/MAS spectra of poly(diethoxyphosphazene). The interrupted decoupling spectra were obtained using a 50-μs τ value.

Inspecting the spectra in Figure 2, one sees that the line width of the CH_2 resonance is strongly temperature dependent: It is sharp at both high and low temperatures, but broad at intermediate temperatures. Rothwell and Waugh have shown that molecular motion at the frequency of the ^1H decoupling field (48 kHz in this case) can account for behavior analogous to that observed in Figure 2.[14] To further investigate the details of this motion, ^{31}P MAS spectra, which are sensitive to main-chain motions in phosphazene polymers, were acquired for both PBEP and PBMP over the same temperature range used for the ^{13}C data in Figure 2; these ^{31}P spectra are presented in Figure 3. The ^{31}P chemical shifts of PBEP and PBMP (−8.5 and −4.5 ppm, respectively) are in close agreement with those observed in solution.[7] Reducing the sample temperature produces a gradual increase in the ^{31}P MAS line width for both PBEP and PBMP (Figure 3). The main-chain motion for both materials is not isotropic and rapid in the temperature range studied; otherwise the dipolar coupling to ^{14}N (the dominant line broadening interaction for ^{31}P with these experimental conditions) would be completely averaged. Upon dropping below T_g, both samples show a significant further increase in line width. These data indicate that the main chains of PBEP and PBMP are undergoing large-amplitude anisotropic motions above their glass-transition temperatures. This main-chain motion could account for the relaxation behavior observed for the CH_2 carbon resonance in PBEP (Figure 2) since

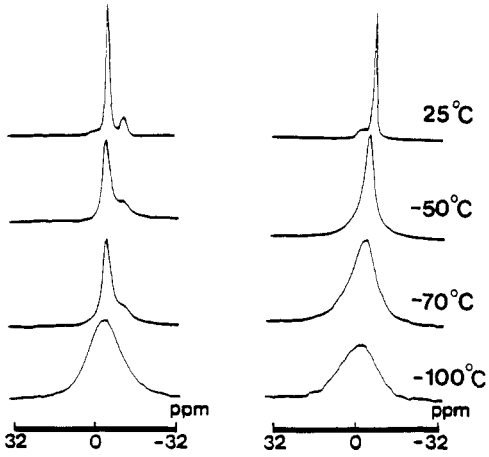

Figure 3. Variable-temperature ^{31}P MAS spectra of PBEP (left) and PBMP (right).

Table I
Determination of Weak-Link Sites in Poly(diethoxyphosphazene) Using ^{31}P MAS NMR and Neutron Activation Analysis

	before hydrolysis		after hydrolysis	
	wt % Cl	wt % OH	wt % Cl	wt % OH
^{31}P MAS NMR	3.9	0.4	<0.3	4.0
neutron activation analysis	3.6		0.2	

the side groups will share some of the main-chain motions.

Inspecting the room temperature ^{31}P spectra of these materials (Figure 3), one notices that there are also small, "extra" peaks. With PBEP, for example, small peaks are observed at −14.8 and −3.4 ppm. These peaks are also observed in solution-state ^{31}P NMR spectra. In order to assign these resonances the following experiment was performed: PBEP was dissolved in a mixture of 80% acetone and 20% distilled water (v/v) and the resulting solution was refluxed for 24 h. The PBEP was then recovered, and its ^{31}P NMR spectrum was obtained. In that spectrum (not shown) the peak at −14.8 ppm was absent and the one at −3.4 ppm had increased proportionally. This leads us to believe that the peak at −14.8 ppm is due to Cl–P–OEt units which upon hydrolysis yield HO–P–OEt units with a ^{31}P chemical shift of −3.4 ppm. These units have previously been proposed as weak links that are active in the thermal degradation of polyphosphazenes.[15] Neutron activation analyses of the untreated and hydrolyzed PBEP samples were performed in order to obtain confirming evidence for the proposed NMR assignments. These data are compared with quantitative NMR results in Table I. The data in Table I very strongly support the proposed assignments and demonstrate that ^{31}P MAS NMR can be used to identify and quantify weak links in phosphazene polymers. An interrupted decoupling spectrum of this sample yielded no additional information on peak assignments.

In conclusion, these preliminary results show that ^{31}P MAS NMR and ^{13}C CP/MAS can be used to study chemical reactivity and molecular dynamics in phosphazene polymers. The resolution of the ^{31}P experiments allows the observation of weak links in the substituted polymers and cross-link sites in partially hydrolyzed **2**. We have also shown that variable-temperature MAS NMR can provide information about the molecular dynamics and morphologies of these polymers. The signal-to-noise ratio of the spectra is sufficient to make subsequent variable-temperature relaxation measurements feasible. These, and other lines of investigation related to the synthesis, structure, reactivity, and dynamics of polyphosphazenes, are in progress in our laboratory.

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Functional Methacrylate Monomers. Simple Synthesis of Alkyl α-(Hydroxymethyl)acrylates

A number of substituted acrylates have been synthesized by the coupling of aldehydes with acrylate esters under conditions in the presence of DABCO (1,4-diazabicyclo-[2.2.2]octane).[2,3] The resulting α-(hydroxyalkyl)acrylates **1** (e.g., R = CH_3 or phenyl) have been used as synthons in natural product synthesis.[4] We became interested in the polymerizability of these compounds, especially the simplest derivative, methyl α-(hydroxymethyl)acrylate (MHMA, **2**), obtained from the reaction of formaldehyde with methyl acrylate.[5]

The mechanism proposed for this reaction[4] involves initial Michael attack of DABCO on the acrylate to generate a carbanion–ammonium zwitterion which then attacks the aldehyde carbonyl. The crucial step is the irreversible transfer of the α-hydrogen to the newly formed oxygen anion with concomitant elimination of DABCO to regenerate the acrylate double bond. It might be expected that the intermediate zwitterion would rapidly react with water, precluding the use of aqueous reagents and solvents.

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