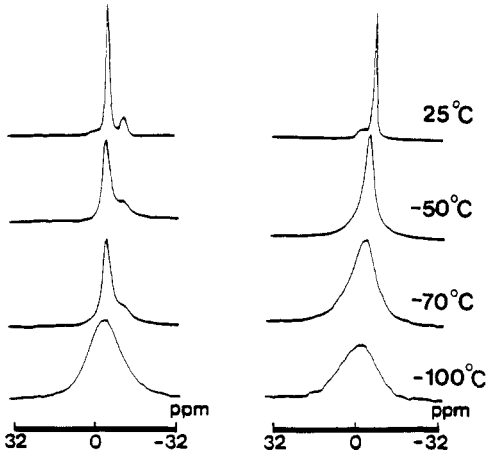

Figure 3. Variable-temperature ^{31}P MAS spectra of PBEP (left) and PBMP (right).

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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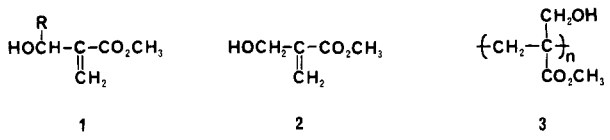

1 2 3

We found, however, that reaction of methyl acrylate and formalin (aqueous formaldehyde) gave the desired monomer **2** in 31% yield.[5] This approach provides an inexpensive and safer alternative to the synthesis of **2** from those previously reported.[6] During the course of our work, we became aware of a recent European patent which describes essentially the same synthesis employed here.[7]

We initially synthesized two derivatives of **1**, where R is methyl and phenyl. Both homopolymerized only with great difficulty and in low yields. Even copolymerizations of these monomers were sluggish. For example, extended reaction of the methyl compound with styrene and AIBN (2,2′-azobis(isobutyronitrile)) proceeded in only 28% yield to give a copolymer much lower in **1** content than in the monomer feed.

The hydroxymethyl compound **2** was then examined for homo- and copolymerizabilities. Polymerization could be effected by simply heating **2** at 80 °C or by photoinitiation in the presence of benzoin isopropyl ether. Initiation with AIBN also led to bulk polymerization and solution polymerization in chloroform, methanol, benzene, and water to give clear, tough polymers that were insoluble except in hexafluoro-2-propanol (HFIP). Polymerization in dimethyl sulfoxide (DMSO) with AIBN, however, gave polymer that was initially soluble in DMSO, acetone, dimethylacetamide and trifluoroethanol. Upon reprecipitation and drying under vacuum (which presumedly removes residual DMSO), the polymer became insoluble in these solvents. Dissolution of this material in HFIP suggests that crystallization was occurring and not crosslinking via transesterification as is postulated to occur on heating (see below).

Copolymerization of **2** with styrene in bulk with 1.5% AIBN gave quantitative yields of clear, tough polymers that were soluble in chloroform and dichloromethane but insoluble in hexane, carbon tetrachloride, and diethyl ether. IR spectra showed carbonyl and hydroxyl peaks in addition to peaks associated with styrene units. Low-conversion copolymerizations (M_1 is MHMA) gave r_1 = 0.34 and r_2 = 0.36.

Copolymers with methyl methacrylate were prepared in the same way. These copolymers were soluble in chloroform and insoluble in hexane, carbon tetrachloride, and acetone. IR peaks for hydroxyl groups were observed in addition to ester peaks. The ^{1}H NMR spectra of all homo- and copolymers were consistent with the expected structures.

Intrinsic viscosity of the DMSO–polymerized homopolymer (HFIP at 25 °C) was 1.51 dL/g, while the viscosities of the two 1:1 copolymers (chloroform at 25 °C) were 0.39 and 0.47 dL/g, respectively. Polymer **3** softened at 225 °C and flowed with decomposition at 330 °C with gas evolution to give a light yellow, rigid foam. Differential scanning calorimetry showed an endotherm at 225 °C for the melting transition, which seems to confirm crystallinity. The copolymers displayed T_g values that were *higher* than those of the respective homopolymers. For example, the 1:1 copolymers with styrene and methyl methacrylate displayed strong T_g's at 130 and 160 °C, respectively. These values were found to depend on thermal history, suggesting the possibility of loss of bound solvent or water, or gradual transesterification leading to cross-linking.

Spectral characterizations by solution and solid-state ^{13}C NMR were also carried out for **3**.[8] Essentially the same spectra were obtained for the homopolymer in the solid state and in HFIP. Selected copolymer spectra are given in the Figure 1. Peaks are assigned as indicated[8] based on calculated values and off-resonance decoupling results. Copolymer compositions were consistent with essentially random incorporation of monomer repeat units.

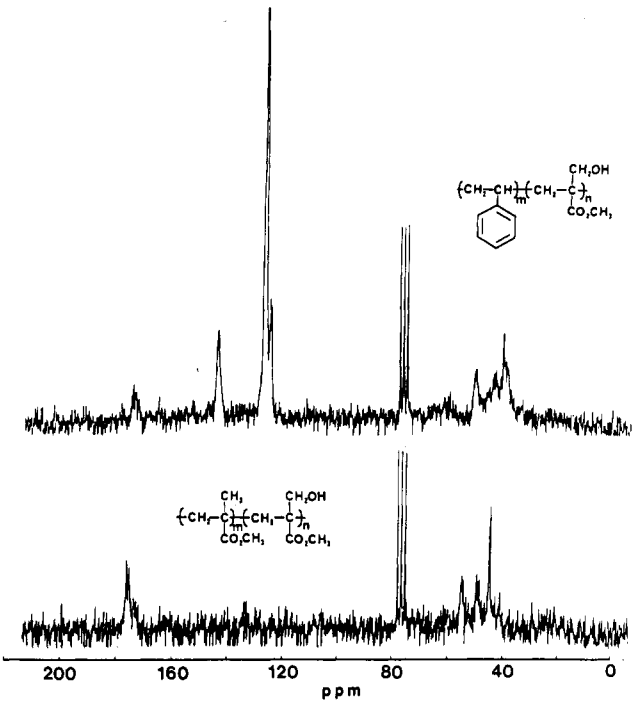

Figure 1. ^{13}C NMR spectra of 1:3 copolymers of MHMA with styrene (upper trace) and methyl methacrylate (lower trace) in $CDCl_3$.

Monomer **2** and its ester analogues are now readily available safely from inexpensive starting materials. These monomers and their polymers possess pendent hydroxymethyl moieties which lead to improved adhesion and physical properties (to be described more fully in a subsequent paper) and the potential for postpolymerization functionalization and cross-linking.

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(5) Methyl acrylate (26 g, 0.3 mol), formalin (16 g, 0.2 mol of CH_2O), and DABCO (3 g, 0.027 mol) were stirred at room temperature for 10 days. After evaporation of unreacted methyl acrylate, the mixture was dissolved in water, made acidic with HCl, and extracted 3 times with diethyl ether. Evaporation gave **2** as a clear liquid: 7.3 g, 31% yd, 96% pure by GC. Fractional vacuum distillation (0.05 torr, 58–60 °C) gave pure **2**. CAUTION: methyl acrylate is a strong skin and eye irritant, and while the pure monomer **2** shows only minimal skin irritancy, trace amounts of a byproduct or contaminant occasionally seen during synthesis of **2** causes severe

contact dermatitis and can be very dangerous.

(6) The ethyl ester of the title compound has been previously synthesized by the Witting–Horner reaction from triethyl phosphonoacetate (Villieras, J.; Rambaud, M. *Synthesis* **1982**, 924) and by the nickel-complex-catalyzed carboxylation of propargyl alcohol (Rosenthal, R. W.; Schwartzman, L. H.; Greco, N. P.; Proper, R. *J. Org. Chem.* **1963**, *28*, 2835).

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(8) IR peaks for a neat film: 3300 (vs), 1720 (vs), 1210 (s), 1000 (vs) cm^{-1}; ^1H NMR (from TMS) δ 4.8, 3.6, 3.3, and 2.1 (all br, overlapping); ^{13}C NMR (CP/MAS, from TMS) δ 173 (C=O), 73 (CH_2OH), 52 (OCH_3), and 41 (backbone C and CH_2).

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