one, of approximate dimensions 0.1 × 0.2 × 0.4 mm was chosen for structure determination. The crystal data for 2B were $C_9H_{10}N_2O_4$, triclinic, $P\bar{1}$ (No. 2), a = 10.697 (5), b = 10.763 (4), c = 9.966 (3) Å, V = 989.3 Å^3, T = 23 °C, Z = 4, D_c = 1.41 g/cm^3, m = 1.1 cm^{-1}, 2731 reflections having $I > 3.00(I)$, R_u = 0.059, R_w = 0.079. The structure of 2B thus was shown to be centrosymmetric and therefore different from the SHG-active 2/2A. Although there was insufficient material for an X-ray powder pattern, the stored single-crystal data for 2B were used to compute an idealized powder pattern, which did not resemble that for 2 or 2A. Later, a small sample of 2B was found to have a metastable melting point (Table I), indicative of it being a different structure. Efforts will continue to produce an XRD-analyzable SHG-active crystal of one of the materials, so that the orientation responsible for activity can be established.

Conclusions

A novel acentric series of crystalline materials has been discovered. Indeed, the attachment of straight-chain polymethylene chains via urethane or urea bridges may be regarded as a new method for inducing crystallographic acentricity. The generality of this method for compounds that are not N-(4-nitrophenyl)urethanes or ureas is not known; the lower N-alkyl-4-nitroanilines have been studied, but only the butyl derivative had significant SHG activity.[12]

We declare it to be an essential part of the characterization of crystalline NLO compounds to report at least the powder X-ray diffraction D spacings of each sample of material so studied. It is our recommendation that this become a requirement for publication of powder SHG efficiency data. Also worthy of consideration as requirements are the specification of sieve size or the like for samples and for standards, and especially due attention to crystal rather than particle size of urea when it is used as a standard.

Polyphosphazene Molecular Composites. 1. In Situ Polymerization of Tetraethoxysilane

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Composite materials have been prepared by combining polyphosphazene polymers with a silicon oxide precursor, tetraethoxysilane (TEOS), which is polymerized in situ. Poly[bis(methoxyethoxyethoxy)-phosphazene] (MEEP), a polymer that flows at room temperature, forms a clear, flexible, free-standing film when TEOS is polymerized in situ. The storage moduli (E') for the MEEP/TEOS composites exceed 10^9 dyn/cm^2 and the shore A hardness obtained for these materials is ca. 83. In contrast, the corresponding values for the amorphous homopolymer were so low that they could not be measured at room temperature. Preliminary evidence indicates that the etheric side groups of the MEEP are adsorbing to the silicate network and pseudo-cross-linking results. Improved mechanical properties of a (fluoroalkoxy)phosphazene, partially hydrolyzed poly[bis(trifluoroethoxy)phosphazene] (TFEP-OH), were evident in that a rubbery plateau region above (T1) is observed in the storage modulus. The oxide particles are thought to be retarding the movement of the polymer crystallites.

Introduction

In general, polyphosphazenes consist of alternating phosphorus and nitrogen atoms with two substituents per phosphorus.[1,2] Polyphosphazenes have been used as flame retardants, gaskets, fuel lines,[3] and membranes.[4] Recent areas of interest include liquid-crystalline polymers[5] and biological materials.[6] Like polysiloxanes, polyphosphazenes are generally elastomers; the glass transition

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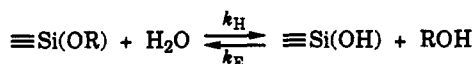
Scheme I

Hydrolysis

$$\equiv Si(OR) + H_2O \underset{k_E}{\overset{k_H}{\rightleftharpoons}} \equiv Si(OH) + ROH$$

Condensation

$$\equiv Si(OR) + (OH)Si \equiv \overset{k_A}{\rightleftharpoons}$$

$$\equiv Si-O-Si \equiv + ROH \text{ (alcohol producing)}$$

$$\equiv Si(OH) + (OH)Si \overset{k_W}{\rightleftharpoons}$$

$$\equiv Si-O-Si \equiv + H_2O \text{ (water producing)}$$

temperature (T_g) of the phosphorus–nitrogen backbone can be more than 100 °C below room temperature. This limits the use of the elastomers as structural materials.[7] However, the judicious choice of the side groups allows the preparation of polyphosphazenes that are either semicrystalline thermoplastics or high melting glasses. It is desirable to increase the use temperatures and mechanical properties of these polymers while retaining the properties that are unique to polyphosphazenes. In contrast to siloxanes, the phosphazene side groups are readily modified with many different substituents.[8,9]

Our approach to the formation of the inorganic oxide is by a method that is commonly referred to as the sol–gel process.[10] In this paper we report initial results on the preparation of composite materials by combining the "inorganic polymer" polyphosphazene with a silicon oxide precursor, tetraethoxysilane (TEOS), which is then polymerized in situ. This work found its basis in the reports from the research groups of Wilkes[11] and Mark,[12] where silicon alkoxides were added to dimethylsiloxanes to generate "ceramers", and on the work of Mauritz,[13] where silicon alkoxide was added to the fluoropolymer Nafion. The sol–gel technique allows for the formation of crosslinked inorganic particles and networks by hydrolysis and condensation of metal alkoxides (Scheme I) at temperatures that are commonly used to process polymeric materials. Curing at higher temperatures leads to further densification of the oxide, but possible degradation of the polymer must be considered.[10]

The goal of this work is to produce novel composite materials with controlled morphologies and physical properties; this is accomplished through control of the interaction between the phosphazene and the growing metal oxide network. Equally important are the processing conditions used in the preparation of the composites. We have found that the physical properties of these composites are significantly different from those of the individual materials. Specifically, we report that poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP), a polymer that flows at room temperature, forms a flexible, free-standing film when combined with TEOS, which is polymerized in situ. Recently, several groups have reported success in increasing the dimensional stability of MEEP. Chemical cross-linking has been shown to be effective in the pro-

cessing of better electrodes for battery applications[14] and γ-radiation also appears to be useful for cross-linking MEEP for applications including batteries, membranes, and hydrogels.[15] Blending MEEP with poly(ethylene oxide) has also been reported to increase the mechanical integrity of the polymer as a solid electrolyte.[16] We believe that the mechanical integrity of the MEEP/TEOS composites reported here results from a pseudo-cross-linking interaction of the etheric side groups of the polymer with the inorganic oxide. Similar mechanical property improvement has been reported for PMMA/TEOS blends formed in a similar manner to the composites in this report[17] and where strong interactions via hydrogen bonding are observed. Although this work is still in progress, we present some preliminary data to support this reasoning. We also report that the use temperature of a partially hydrolyzed, semicrystalline fluoropolymer poly[bis(trifluoroethoxy)phosphazene] (TFEP-OH) can be extended from ca. 80 °C to ca. 140 °C, possibly due to restriction of the movement of polymer crystallites by the oxide particles. The formulation and characterization of the two composites are discussed:

MEEP   TFEP–OH
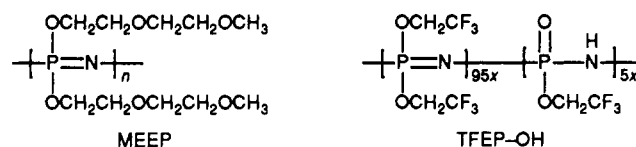
Experimental Section

TEOS (Fluka) was purum grade, ethanol (U.S. Industrial Co.) was punctilious, and THF (Baker) was reagent grade. All reagents were used as received unless otherwise noted.

The composites were originally formulated with equal weights of phosphazene and TEOS. Assuming full condensation of TEOS to SiO_2, a sample prepared with 50 wt % TEOS would result in a composite film containing 23 wt % SiO_2. However, later films were formulated to have 60 wt % phosphazene relative to TEOS because the films produced with the increased amount of polymer were more continuous and flexible. The films were transparent and were suitable for mechanical testing.

MEEP/TEOS Composites. (a) Films. MEEP was prepared as described previously.[15] The average molecular weight of MEEP was approximately 3×10^6 g/mol as measured by size exclusion chromatography.[18] A stock solution of MEEP was prepared by dissolving 2 g of MEEP in 80 mL of a 1:1 mixture of THF/methanol. Composite films were prepared as follows: TEOS (0.3 mL) was added to 12 mL of stirred stock solution followed by the addition of 0.12 mL of 0.15 M HCl. The solution was allowed to stir for 15 min, heated to 60 °C for 30 min, and poured into a Teflon dish, and the dish covered with an inverted beaker to reduce the evaporation rate of the solvent. After four days at room temperature a 75-μm-thick, free-standing film was obtained.

(b) Castings for Hardness Measurements. The MEEP/TEOS solution was prepared by adding 2.4 mL of TEOS to 96 mL of the stirred stock solution of MEEP, followed by the addition of 1 mL of 0.15 M HCl. The clear solution was heated at 60 °C for 30 min and poured into a 250-mL Nalgene bottle. The sample was kept under an inverted 1-L beaker for 14 days and then heated at 50 °C in vacuum for 10 days. The clear, slightly yellow casting

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varied in thickness from the center to the sides and was 0.5 cm at the thickest point.

TFEP-OH/TEOS Composites. (a) Films. The synthesis and characterization of the partially hydrolyzed TFEP (denoted herein as TFEP-OH) have been described in a previous report.[19] The weight average molecular weight of TFEP-OH was approximately 2×10^5 g/mol.[18] The degree of hydrolysis for the samples used in this work is 5 mol %.[17] A stock solution of the TFEP-OH was prepared by dissolving 0.5 g of polymer in 20 mL of ethanol. A 5-mL aliquot of this solution was placed in a flask to which 1.5 mL of TEOS and 0.5 mL of 1.0 M NH$_4$OH were added. The resulting solution was heated at 60 °C for 30 min. Free-standing films, ca. 100 μm thick, were produced by pouring the base-catalyzed solution into a Teflon dish and covering the dish with an inverted beaker to reduce the evaporation rate of the volatile products. The films were cured under vacuum at 110 °C. Although previous work in our laboratory suggested that acid, not base, catalysis should produce superior films,[1,17] our attempts to prepare films using acid catalysis with TFEP-OH were not successful.

(b) Measurements. Differential scanning calorimetry (DSC) was performed with a Du Pont 990 thermal analyzer, equipped with a data analysis program by Laboratory Micro Systems, Inc. The sample was under a purge of nitrogen and was heated at 20 °C/min. The glass transition temperature, T_g, is taken as the onset in the change in heat capacity.

Dynamic mechanical measurements (DMS) were obtained using a Rheovibron DDV-II dynamic tensile tester (Tokyo Measuring Instruments, Ltd., Japan) automated by IMASS, Inc. The data were obtained at frequencies of 1.1, 11.0, and 110.0 Hz, using a heating rate of 1.5 °C/min.

Transmission electron microscopy (TEM) was performed on thin (ca. 700 Å) sections of the composite films using a JEOL 100CXII microscope (JEOL, Ltd., Tokyo, Japan). The samples were sectioned at a temperature of −73 °C. The sections were picked up dry and transferred to the TEM grid where they were dry-pressed and examined under cryostatic conditions. The intrinsic contrast between the polyphosphazene and the SiO$_2$ network was sufficient, and no additional staining was required.

Shore A hardness measurements were made using a PTC Model 306L Durometer (Pacific Transducer Corp., Los Angeles, CA).

Thermal gravimetric analysis (TGA) was performed on a Omnitherm Advantage II with a heating rate of 10 °C/min and with the samples under a nitrogen atmosphere.

Solid-state ^{31}P NMR spectra were obtained on a 200-MHz home-built spectrometer, designed specifically for multinuclear solid-state studies.[20] The samples were either punched into disks or ground (sometimes cryogenically). Most of the ^{31}P data were obtained from stationary samples, although some spectra were obtained by spinning the MEEP/TEOS composite at the magic angle.[21]

Results and Discussion

Formulation of MEEP/TEOS Composites. MEEP is a high molecular weight polymer that is predominantly amorphous.[15] The T_g is −75 °C due to the inherent flexibility of the phosphorus–nitrogen backbone. The low T_g suggests there is little steric hindrance due to the etheric side groups.

A mixture of MEEP with TEOS was stable in THF/ethanol; the solution remained clear after the addition of TEOS to a stock solution of the polymer. Additionally, there was no visible change observed after the addition of acid to hydrolyze the TEOS or heating the resulting reaction mixture at 60 °C for 30 min.

Etheric alcohols such as methoxyethanol or (methoxyethoxy)ethanol are known to modify the reactivity of inorganic alkoxides.[22a,b] Lead titanate[22a] and magnesium

Figure 1. Transmission electron micrograph of an acid catalyzed MEEP/TEOS 50/50 composite. The fiducial line represents a distance of 100 nm.

aluminate have been made using these alcohols. Silica sols at low pH are known to be more stable in the presence of lower polyether alcohols.[22c] It is also well documented that ceramic powder suspensions can be stabilized by the use of polymers or organosilicon monomers by steric stabilization.[22d,e] Aqueous gold sols have been solubilized with poly(ethylene glycol).[22f] In fact, MEEP has been shown to be an excellent dispersant for 0.4-μm alumina particles due to adsorption, probably via hydrogen bonding involving the oxygen atoms of the side chains, on the alumina surface.[22g] Presumably a similar stabilization is occurring in the present case with the small silicate network generated by the in situ polymerization of TEOS. It is known that poly(ethylene oxide) adsorbs strongly to silica surfaces.[22c]

The solid composites remained clear, indicating a homogeneous dispersion of the silicon oxide throughout the polyphosphazene matrix. The SiO$_2$ network formed during the hydrolysis/condensation of TEOS are necessarily much smaller than the wavelength of visible light, otherwise they would scatter light and produce an opaque film. A transmission electron micrograph of an acid-catalyzed MEEP/TEOS composite prepared from equal amounts by weight of the two compounds is shown in Figure 1. The SiO$_2$ particles (which appear dark) in the micrograph are almost undiscernible and can be estimated to be much

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smaller than 50–100 Å. The difficulty in resolving such small particles lies in the fact that the thickness of the TEM section is much greater than the size of the particles. The micrograph, however, does reveal that the dispersion of the silicate phase is essentially uniform throughout the composite.

The physical properties of the composite differ from either the MEEP or the inorganic oxide. At room temperature MEEP is in the flow regime of viscoelasticity; the polymer will flow like a viscous liquid and will not hold a shape when subjected to an external force. The homopolymer is tacky to the touch and dissolves in a wide range of polar solvents. Films derived from TEOS are very brittle and can be produced crack-free only in thicknesses of 1 μm or less. By contrast, the composite materials could be cast into hard, flexible films that hold their shape under an external force. A casting of the composite that had been cured to 50 °C had a Shore A hardness of approximately 83. Three readings were taken on one section of the film (87.5, 82.5, 85.0) to give an average values of 85.0, and five readings were taken on another section of the film (78.5, 90.0, 90.0, 77.0, 77.0) to give an average of 82.5. The Shore A hardness of the MEEP polymer was 0 because the polymer was so soft that the durometer pin readily penetrated the sample. Shore A hardness values from 40 to 60 are typical of elastomeric materials for engineering application.

Formulation of TFEP-OH/TEOS Composites. The TFEP homopolymer is a semicrystalline polymer[23] of high molecular weight.[24] The thermal behavior of the polymer is complicated by the presence of a mesomorphic transition near 80 °C. At this temperature, typically referred to as $T(1)$, the crystalline state transforms to a two-dimensionally ordered mesomorphic state. This transition involves motion of the chain backbone and the side chains and is accompanied by a large change in volume.[25] The transition is also accompanied by a drop in the storage modulus.[26,27] The fact that a glass transition is observed indicates that the sample has an appreciable amorphous content even below $T(1)$. Although the TFEP crystallites undergo a true melting at 240 °C, where the spherulitic structure is lost and an isotropic melt forms, the onset of the mesomorphic transition $T(1)$ is the softening temperature and sets an upper temperature limit on the application of this polymer as an engineering thermoplastic.[28] We have shown previously that the degree of crystallinity can be decreased by base hydrolysis of the fluoroalkoxy side group. This effect is reflected by a decrease in the position of the T_m and $T(1)$ transitions, and a decrease in the enthalpy change, which occurs at the $T(1)$ transition.[23] This also results in a change in solubility as well as some lowering of the molecular weight of the polymer due to chain cleavage.[19] The polymer physical properties are dominated by the fluorocarbon side groups, which result in coatings of low surface energies.[29]
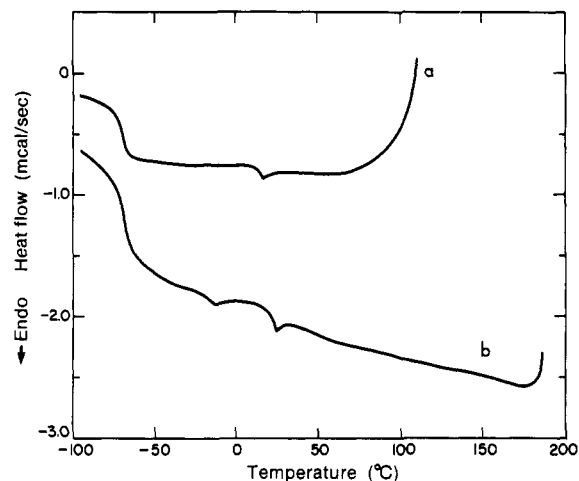

Figure 2. DSC thermograms of (a) MEEP homopolymer and (b) acid-catalyzed MEEP/TEOS 50/50 composite. The T_g is –75 °C for both the homopolymer and the polymer in the composite.

One of the goals of this work was to extend the service range of films of the fluorophosphazene polymer to higher temperature while maintaining the low surface energies. Unlike the MEEP homopolymer, the TFEP polymer was not compatible with TEOS; addition of TEOS to a solution of the TFEP led to precipitation of the polymer. However, the partially hydrolyzed fluorophosphazene polymer (TFEP-OH) did prove to be compatible. A clear, colorless gel formed upon addition of the TEOS to the polymer solution in ethanol. Warming of the gel to 60 °C resulted in a clear, free-flowing solution. It was possible to cycle the sample in and out of the gel state by changing the temperature. The formulation remained clear after the addition of base to catalyze the sol–gel reaction of the alkoxide, while the addition of acid caused the solution to turn cloudy. The base-catalyzed composites showed improved mechanical properties, but they were not as clear as the MEEP/TEOS composites. This haziness was attributed to the crystallites in the TFEP-OH polymer.

Thermal Analysis. (a) MEEP/TEOS. The thermal characteristics of the MEEP/TEOS composite were similar to those of the polymer alone. The DSC results for the composite are shown in Figure 2 and are compared to those for pure MEEP. The glass transition is seen to occur at –75 °C for both MEEP and the composite. A small endothermic peak also occurs in both samples around 20–30 °C, which may be due to the melting of some crystallites; however, this assignment is tentative. The addition of more than 20 mol % of a cation is known to raise the T_g of the polymer with increasing amount of cationic content.[30] The observation that the silicon oxide does not increase the T_g of the polymer nor disrupt the crystallinity suggests to a first approximation that only weak interactions, if any, occur between the two components, that is, the SiO_2 phase is not affecting the mobility of the polyphosphazene backbone. It is also interesting to note that a large exothermic transition begins near 100 °C for pure MEEP, which could be related to degradation. The DSC trace for the composite does not show this exotherm until a temperature of about 200 °C, suggesting an increase in the thermal stability of the MEEP when the silicon oxide is introduced. However, TGA of the MEEP/TEOS composite was almost identical to that reported for the MEEP homopolymer. The onset of weight

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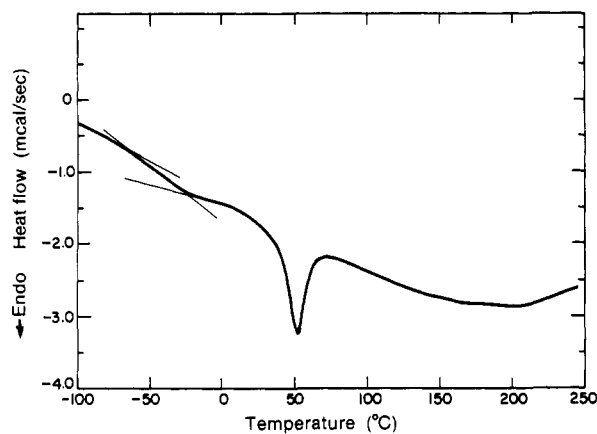
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Figure 3. DSC thermogram of a base-catalyzed TFEP-OH 50/50 composite.

loss began at 240 °C and was followed by a major weight loss at 306 °C.

(b) TFEP-OH/TEOS. A DSC thermogram of the TFEP-OH/TEOS composite is shown in Figure 3. No obvious difference was observed between the composite thermogram and the thermogram of the fluoropolymer. The T_g occurs at ca. -59 °C but is not as sharp as that of the TFEP-OH. It has been reported that the addition of inert fillers such as carbon black or silica does not increase the glass transition temperature of fluoroalkoxy poly-phosphazenes.[26] The $T(1)$ occurs at 51 °C, which is somewhat lower than for the TFEP homopolymer, as expected.[23] Also, it is known that the exact temperature at which $T(1)$ occurs and the enthalpy that accompanies it are influenced by the sample history.[28] The melting temperature of the crystallites was not observed in either thermogram. This is not unexpected since the enthalpy change at T_m is about an order of magnitude smaller than it is at $T(1)$.[26] Also, hydrolysis has reduced the amount of crystallinity in the sample. As for the MEEP/TEOS composites, TGA of the TFEP-OH/TEOS indicated that the composite has about the same thermal stability as the fluoropolymer. Initial weight loss under nitrogen for both the polymer and the composite occurred at approximately 250 °C with rapid weight loss observed by 400 °C.

Mechanical Spectra. (a) MEEP/TEOS. The dynamic mechanical spectrum of the MEEP/TEOS composite cured at ambient temperature is shown in Figure 4. The traces show the storage modulus (E'), the loss modulus (E'') and tan δ (E''/E'). The composite was a free-standing film, which retained its mechanical integrity throughout the measurement. MEEP, however, is a flowing material above its T_g, and dynamic mechanical measurements could not be made directly. Thus, it was necessary to cast a film of MEEP onto a Kapton support to obtain a spectrum of the homopolymer. As with the DSC data, the T_g was the same for both the MEEP and the MEEP/TEOS composite. Theoretically, above T_g the storage modulus of MEEP would decrease rapidly with increasing temperature to an extent where it would be undetectable. The mechanical properties of the composite differ greatly from the MEEP homopolymer above T_g. As with the homopolymer, the storage modulus decreased with increasing temperature throughout the glass transition regime until the samples reached about -30 °C. Further increases in temperature led to slower rates of modulus loss and eventually to a leveling of E' near 30 °C with a value of E' equal to 3.2 × 10⁸ dyn/cm². Continued heating resulted in an increase in the modulus of the composite; this could be indicative of further curing of the
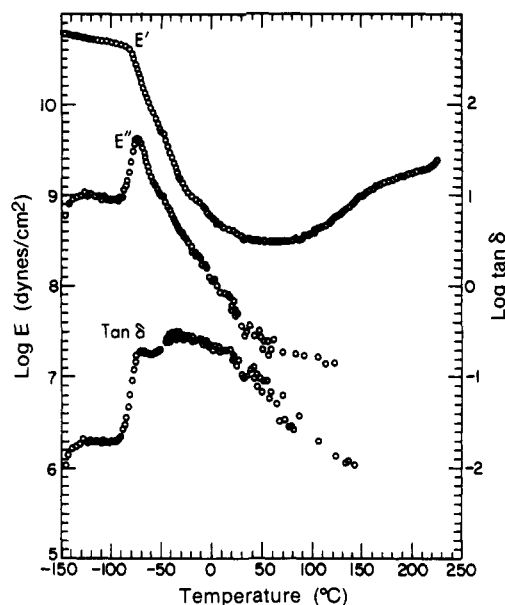

Figure 4. Dynamic mechanical spectrum of the acid-catalyzed MEEP/TEOS 50/50 composite cured at ambient temperature.
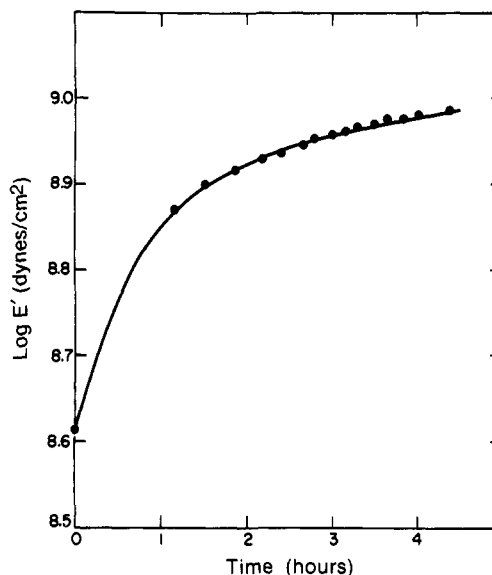

Figure 5. Plot of the change in plateau modulus with time as the MEEP/TEOS 50/50 composite is cured at 118 °C.

SiO₂ network. A final value greater than 10⁹ dyn/cm² for the storage modulus was obtained. Unfortunately, the film was too brittle for a second scan to be acquired.

A further study of this curing phenomenon was carried out by monitoring the change in the value of the plateau modulus above T_g for a composite film with time. The results are shown in Figure 5. The storage modulus of the film was initially 4.1 × 10⁸ dyn/cm². Curing the sample at 118 °C directly in the Rheovibron sample chamber, under continual data acquisition, resulted in a modulus increase to 7 × 10⁸ after 1 h. The modulus continued to rise with time and approached 10⁹ dyn/cm² after 4.4 h. The temperature of 118 °C was chosen for the cure experiment because the storage modulus increased rapidly at that temperature (Figure 4).

The increased mechanical properties of the composite were attributed to interactions via pseudo-cross-linking between the partially condensed silicon oxide chain network and the etheric side groups of the phosphazene polymer. We are currently using solid-state ²⁹Si NMR spectroscopy to determine the extent of hydrolysis and
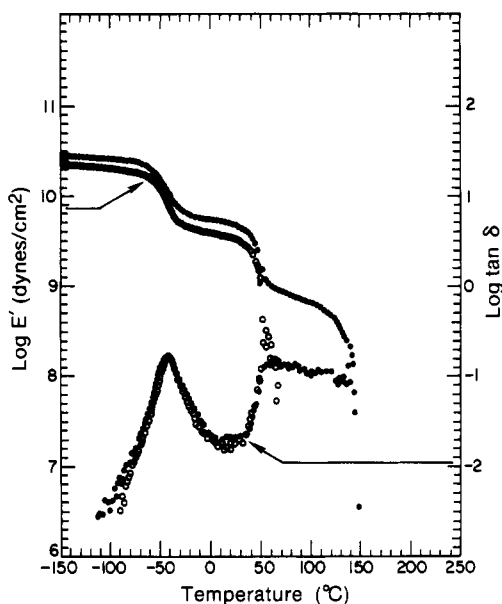
Figure 6. Dynamic mechanical spectra of (○) TFEP-OH polymer and (●) base catalyzed TFEP-OH/TEOS 50/50 composite. The TFEP-OH film starts to flow at 80 °C, while the storage modulus of the composite remained relatively high to 140 °C.

condensation of the sol–gel components. Ultimately, a relationship should emerge between the oxide structure and the polymer interactions at the oxide interface.

(b) TFEP-OH/TEOS. Dynamic mechanical spectra were obtained for both the TFEP-OH polymer and the composite film containing polymerized TEOS (23 wt % SiO_2). These are presented in Figure 6. Both the T_g and $T(1)$ transitions are observed for each sample; these occur at –40 and 50 °C, respectively, based on the drops in the magnitude of the storage modulus. At the mesomorphic transition, the TFEP-OH polymer film loses all mechanical integrity and flows. In sharp contrast, the storage modulus of the composite remains relatively high until the melting point of the crystallites is reached. This rubbery plateau region extends to 140 °C. Thus, the useful range of this material has been extended by about 90 °C. The transition temperatures observed by DMS are consistent with the extrapolated values for $T(1)$ and T_m as a function of extent of hydrolysis of the TFEP polymer.[23] Several researchers have reported the dynamic-mechanical spectra for TFEP homopolymer obtained using instruments such as Rheovibron,[26] torsional pendulum, and vibrating reed.[31] In general, the spectra were measured to the temperatures at which the sample became too soft for further measurement, ca. 130 °C. This is about 110 °C below the T_m for this polymer.[26,31] Gillham[27] has measured the DMS of TFEP using a torsional braid apparatus and was able to observe drops in the modulus for each of the three transitions T_g, $T(1)$, and T_m. However, the braid provides mechanical support to the polymer. The results presented here demonstrate the reinforcing properties of the silicon oxide in that all three transitions can be observed by DMS for the self-supporting film.

Although the spectra were time dependent, it is clear that a sample of the (fluoroalkoxy)phosphazene polymer/sol–gel composite has better mechanical properties than those of either the partially hydrolyzed polymer or the homopolymer.[3,4] The high storage moduli in these samples are due to the crystallinity of the TFEP. We speculate that part of the reason for the increased performance of the polymer in the composite is that the cross-linked inorganic silicon oxide matrix is inhibiting the movement of the crystallites as the sample passes through $T(1)$.

Solid-State NMR Studies of MEEP/TEOS. ^{31}P solid-state NMR has proven to be a useful method for studying the interface between MEEP and the silicon oxide. We have used partially relaxed spectra and cross-polarization techniques to resolve the ^{31}P resonance of the MEEP/TEOS composite into at least two components. One is an immobilized fraction associated with the oxide and the other a mobile elastomeric phase.

The ^{31}P NMR spectrum of the partially hydrolyzed MEEP/TEOS in ethanol showed no difference in chemical shift from that of the polymer, with the single peak observed at –6.5 ppm relative to phosphoric acid. The similarity of the spectrum of the sol to that of the homopolymer suggested that any interactions between the phosphazene backbone and the hydrolyzed TEOS were of a secondary nature. (Similar results were obtained by ^{31}P NMR for the sols of partially hydrolyzed TFEP/TEOS.)

At room temperature MEEP is well above its glass transition (–75 °C) and has considerable mobility. The ^{31}P MAS spectrum could not be obtained because of our inability to spin samples (such as MEEP) that behave more like viscous liquids than solids. The single-pulse Fourier transform (FT) and static cross-polarization (CP) spectra show narrow lines.[32] As one can conclude by comparing S/N, the CP process in this elastomer is inefficient. The narrow static line and inefficient polarization transfer are both indications that molecular motion greatly attenuates heteronuclear and homonuclear dipolar couplings. Furthermore, proton dipolar decoupling narrows the line somewhat but not completely. Thus, susceptibility effects might account for much of the residual line width.

MEEP/TEOS composites form free-standing films that can be examined by magic angle spinning.[21] The static, single-pulse ^{31}P FT spectrum (Figure 7a) is considerably broader than the corresponding MEEP spectrum and is heterogeneous in appearance. A clear indication of heterogeneity comes from ^{31}P spin-lattice relaxation measurements on nonspinning samples (Figure 7b). Around the null of the major portion of the signal (τ = 900 ms), a second, very broad, and more slowly relaxing (inverted) component is observed. This component can be selectively enhanced by cross-polarization as shown in Figure 7c. We interpret the broad, cross-polarizable line as originating from the phosphazene/inorganic interface that is immobilized compared to the bulk polymer.

It has been shown above that the T_g of MEEP does not shift to higher temperatures upon the addition of the inorganic sol–gels. Also, no second T_g is observed at higher temperatures for these composites. The glass transition temperature of a material can be viewed as an indication of the ease of mobility of the polymer backbone. When viewed in the light of the T_g data the NMR results lead to some important conclusions. The fast relaxing component of T_1 obtained from inversion–recovery measurements has the same value for the TEOS composite with MEEP as it does for MEEP by itself. This result taken together with the observation that the T_g does not shift to higher temperatures implies that there are domains of pure MEEP that are unaffected by the presence of inorganic glass. These domains are large enough to be detected by NMR, differential scanning calorimetry, and dynamic mechanical spectroscopy. On the other hand, the fact that

(31) Allen, G.; Lewis, C. J.; Todd, S. M. *Polymer* **1970**, *11*, 44.

(32) (a) Hartman, S. R.; Hahn, E. L. *Phys. Rev.* **1962**, *128*, 2042. (b) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1972**, *56*, 1776.
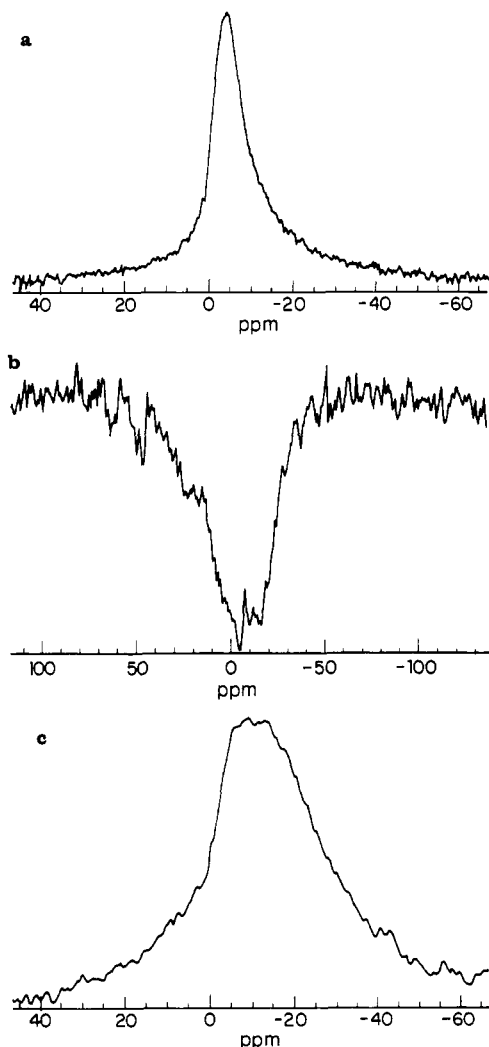
Figure 7. (a) Static, single-pulse ^{31}P NMR spectrum of MEEP/TEOS 50/50 composite; (b) spectrum from spin–lattice relaxation measurements on nonspinning MEEP/TEOS sample; (c) cross-polarized ^{31}P NMR spectrum of nonspinning MEEP/TEOS composite.

a slowly relaxing component, capable of being cross-polarized at ambient temperature, is observable by NMR but does not lead to an observable second T_g indicates that the MEEP chains adsorbed on the inorganic surface or entrapped within the glass network have very little backbone mobility.

When MEEP is doped with a salt such as lithium triflate the material becomes conductive, and the T_g shifts to higher temperature.[30] It is interesting to note that the NMR results for a sample of MEEP that contained 20 mol % Li triflate (T_g still below room temperature) show the existence of only a fast component, which has the same T_1 value as pure MEEP. There was no evidence of a slow component as was seen for the MEEP/TEOS. Again, the interaction of MEEP with the silicon oxide of the composite is of a different type from the interaction of MEEP with low lattice energy salts used to prepare solid electrolytes.

Conclusions

The properties of two "inorganic" phosphazene polymers, one amorphous and the other semicrystalline, can be greatly altered by the incorporation of silicon oxide formed via the sol–gel process. The enhancements of the physical properties of the composites appear to result from two distinct mechanisms. We believe that the chains of the amorphous polymer MEEP are held in place by adsorption to the oxide surface and interpenetration or entrapment of the MEEP chains within the silicate network, which result in pseudo-cross-linking between the polymer and silicate network. These interactions are strong enough to provide much improved mechanical integrity to the phosphazene without reducing the optical clarity of the material. This is evident as the flowing homopolymer can be cast into free-standing films and solid pieces when the acid-catalyzed sol–gel process is carried out with TEOS. Although the thermal properties of the composite are similar to the homopolymer, specifically the T_g of the two are the same, dynamic mechanical and hardness measurements confirm the improved mechanical properties. Future reports will show that these composites can be doped with low lattice energy salts that result in ionic conduction.

The improved mechanical properties of the (fluoroalkoxy)phosphazene appear to take advantage of the crystallinity in the sample. The oxide particles formed by the base-catalyzed sol–gel seem to possess the appropriate properties (size, shape, surface characteristics) so as to retard the movement of the polymeric crystallites. Thus, the upper temperature limit of the polymer has been extended to 140 °C, the temperature at which these crystallites melt in the composite.

This represents initial work being done by our group in the field of polyphosphazene molecular composites. Other work, which considers the introduction of different metal alkoxides (such as titanium, zirconium, and aluminum) into the composites, and functionalization of the polyphosphazene to permit direct reaction with the polymerizing TEOS, is presently underway.