Novel Nafion/ORMOSIL Hybrids via in Situ Sol−Gel Reactions. 1. Probe of ORMOSIL Phase Nanostructures by Infrared Spectroscopy

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Novel [polymer]/[organically modified silicon oxide (ORMOSIL)] hybrids were formulated via sol−gel reactions of mixtures of tetraethoxysilane (TEOS) and diethoxydimethylsilane (DEDMS) in the nanophase-separated morphology of perfluorosulfonic acid (PFSA) films. Molecular structures of ORMOSIL phases were investigated by FT-IR spectroscopy and the spectra compared with those of corresponding bulk ORMOSILs. Spectra are similar for PFSA in situ and bulk ORMOSILs, suggesting that short-range molecular structures in the two states are in fact comparable. Spectral trends with ORMOSIL composition suggest that similar D, Q sequence distributions exist for the two systems. There is evidence of co-condensation between Q and D units within the PFSA, as well as in the bulk ORMOSILs. As DEDMS:TEOS increases, ORMOSIL structures in both in situ and bulk states are increasingly more linear. It appears that a spectrum of energetic environment, or polarity, in the clusters of perfluorosulfonate ionomers can be tailored by adjusting the ratio of Si−OH and Si−CH_3 groups in ORMOSIL nanophases.

Introduction

The creation of novel polymer/[inorganic oxide] hybrid materials via sol−gel reactions for inorganic alkoxides that take place in polymeric media[1−3] has evolved into a diverse and multidisciplinary area of research with the promise of useful advanced materials.[4−11] Often, these hybrids are "nanostructured", referring to the fact that each of two or more phases have at least one dimension <~100 nm, although length scales <100 Å are encountered, as in this work. Proposed applications include membranes that support catalytic metal clusters, permselective membranes for gas and liquid separations, ion-permselective membranes, high dielectric constant materials for electrical energy storage, optical waveguides, platforms for NLO molecules, chemical sensors, protective and functional coatings, and materials with enhanced mechanical and wear properties. An excellent compendium of literature describing hybrid organic−inorganic materials has been edited by Sanchez and Ribot.[12]

In the sol−gel process in the absence of a polymer, acid- or base-catalyzed hydrolysis + condensation of inorganic alkoxides occurs in a solvent medium at low temperature. Careful drying and heat treatment of the swollen gel can produce a solid, amorphous inorganic oxide phase that might be monolithic or finely particulate depending on processing conditions. In one hybrid generation scheme, the alkoxide, water, and solvent precursors, in various orders of addition, are imbibed by a free-standing, preformed polymer film. The nature of functional groups, physical state in relation to the glass transition, and preexisting morphology of the polymer can influence the in situ grown morphology of the inorganic oxide phase. The dispersion of high surface/volume phases, wherein a large fraction of atoms reside at interfaces, can generate material synergism with properties unlike those of each phase taken separately in their respective bulk states.

Organic groups can be inserted into sol−gel-derived silicon oxide networks to form ORMOSIL (organically modified silicate) materials[4,13−21] by adding $R'_nSi(OR)_{4-n}$ species to solutions containing $Si(OR)_4$ as depicted in Figure 1a. The organic group R′ is joined to a Si atom

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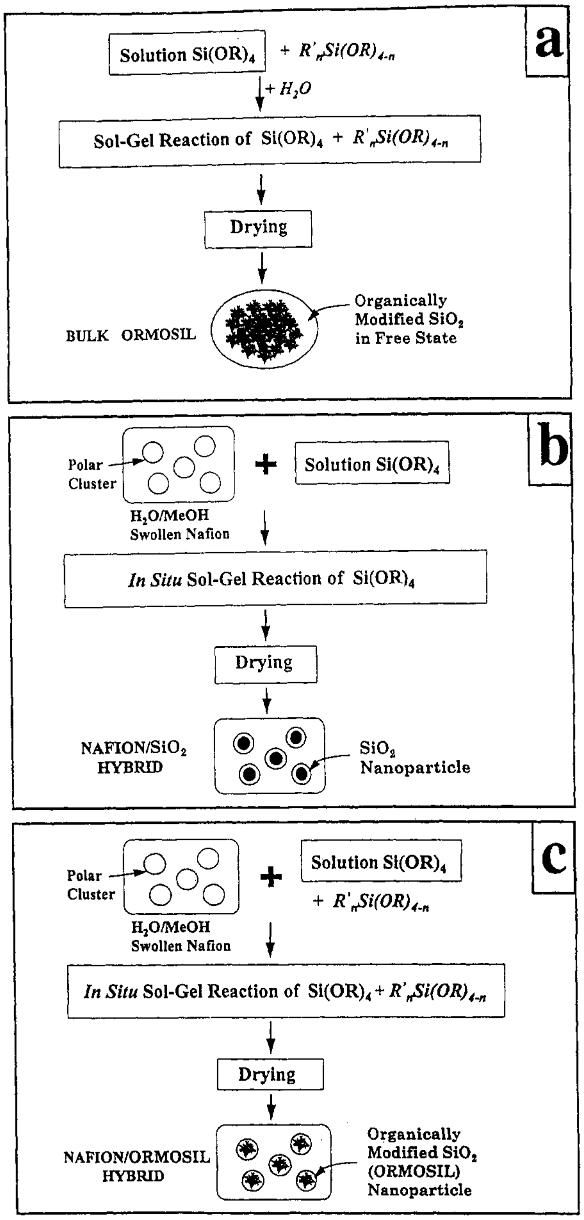

Figure 1. Schematic depiction of formulating (a) organically modified silicon oxide bulk materials, (b) Nafion/[silicon oxide] nanocomposites, (c) Nafion/ORMOSIL nanocomposites. (b) and (c) proceed by Nafion in situ sol−gel reactions within nanometers-in-size polar clusters.

via covalent Si−C bonds which are hydrolytically stable. Tetraethoxysilane (TEOS) is a glass *network former* and inserted $R_n'Si(O_{1/2})_{4-n}$ units function either as bridging ($n = 2$), or endcapping ($n = 3$), *network modifiers.* The structural topology of the network is capable of being controlled in this way. ORMOSILs can range from being rigid to flexible or from being hydrophilic to hydrophobic, depending on comonomer feed ratio.

In another realm, Mauritz et al. created numerous [perfluorosulfonate ionomer (PFSI)]/[silicon oxide] nanocomposites and conducted structure−property characterizations of these materials.[11,22−26] The general formulation scheme, depicted in Figure 1b, involves acid-catalyzed in situ sol−gel reactions of TEOS within nanometers-in-size sulfonate clusters of alcohol + water-swollen PFSI membranes. The unfilled PFSI morphology gives rise to a small-angle X-ray scattering peak that reflects quasi-periodicity wherein average center-to-center spacings of clusters are 30−50 Å. We have established that this morphological regularity is essentially undisrupted despite invasion of the silicon oxide component via the sol−gel process.[26] This fact reinforced our original hypothesis[11] that the PFSI (1) presents a *3-dimensional interactive template* in which the reactants are confined to cluster domains wherein the sol−gel reaction is initiated and catalyzed via fixed $-SO_3H$ groups, and that the PFSI (2) directs the nanoscale morphology of the resultant dry, solid silicon oxide phase.

The work reported here was motivated by the prior studies of Chen et al.[20] and Babonneau et al.[21] involving the creation of bulk ORMOSILs, as well as by our successful formulation of PFSI/[silicon oxide] nanocomposites. We sought to create novel [perfluorosulfonic acid (PFSA)]/[organo silicate] hybrids having novel and useful properties that can be tailored on the scale of nanometers. We describe PFSA−in situ sol−gel reactions of $Si(OC_2H_5)_4$ and $(CH_3)_2Si(OC_2H_5)_2$ (diethoxydimethylsilane = DEDMS). DEDMS was chosen as the network modifier owing to the simplicity of the organic group and good thermal stability of dimethylsiloxane linkages. The insertion of bifunctional D = $(CH_3)_2Si(O_{1/2})_2$ units into a silica-like network will generate more structural flexibility. Moreover, the chemical environment in the vicinity of organically modified silica nanostructures can be tailored with respect to polarity by adjusting the ratio of Si−OH to $Si-CH_3$ groups. Cluster domains, whose chemical environment ranges from being hydrophobic to hydrophilic, can be engineered so that the energetic compatibility of permeant molecules can be tailored, for example.

In this work, we formulated novel PFSA/ORMOSIL hybrids over a range of ORMOSIL compositions according to the scheme depicted in Figure 1c. The major goal of this work was to characterize the short range molecular structures of the in situ grown ORMOSIL phases using FT-IR spectroscopy. It is important to relate internal ORMOSIL nanostructure to external TEOS: DEDMS ratio for the purpose of establishing rules for tailoring nanostructural chemical environment; these studies represent the first part of this effort. A future paper will report our characterization of PFSA−in situ ORMOSIL molecular connectivity, for the same samples, from the perspective of ^{29}Si solid-state NMR spectroscopy.

We hypothesized that the PFSA−in situ grown ORMOSIL structures in these experiments would evolve under the influence of a nanoscale morphological-interactive template as in our earlier experiments that involved not only silicate[11,22−26] but also titania silicate and alumina silicate nanophases.[27]

To provide simple reference structures to aid in the interpretation of the IR spectra of the complex hybrids,

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bulk ORMOSILs, generated from TEOS + DEDMS free mixtures, were formulated and characterized via IR spectroscopy. While IR data for TEOS–DEDMS-based ORMOSILs has been generated by other investigators,[20,21] the composition and processing conditions for these materials is not in close compliance with those of our hybrids to serve as strict reference structures. In situ grown ORMOSIL structures might be expected to be influenced by strong interactions with SO_3^- groups. A high fraction of the chemical groups within ORMOSIL nanophases will exist at cluster/perfluoroorganic interfaces. PFSA/ORMOSIL interactions are inferred if the bulk-state ORMOSIL spectrum differs from that of the corresponding hybrid.

Earlier, Deng et al. created $SiO_{2[1-x/4]}(OH)_x$ nanoparticle cores via in situ sol–gel reactions for TEOS within the clusters of PFSA films.[28] Residual SiOH groups on these preformed nanoparticles were either postreacted with DEDMS, resulting in organically shelled and interknitted nanoparticles, or postreacted with ethoxytrimethylsilane (ETMS), resulting in organically shelled nanoparticles. The main difference between this earlier scheme and that reported here is that the former places organic groups on the outside of a silica core, whereas here, TEOS and DEDMS molecules permeate the PFSA at the same time and copolymerize in situ.

Sample Preparation

Materials. 1100 equivalent weight, 5 mil thick (Nafion 115) membranes in the K^+ form were supplied by E.I. DuPont Co. TEOS, DEDMS, and methanol were purchased from the Aldrich Chemical Co. All water utilized was distilled/deionized.

PFSA Membrane Initialization. First, all membranes were converted to the sulfonic acid form by refluxing in 50% (v/v) HCl, then in water, then in 50% (v/v) HNO_3, and finally in water for 6–8 h. These steps were performed to ensure complete ion exchange, to hydrolyze possibly remaining precursor $-SO_2F$ groups, and to leach out excess acid. Following this, a sequence of steps consisting of refluxing in methanol—then refluxing in distilled/deionized water—was repeated for 5 h each step until the solution pH reached 6.5–7.0. The number of necessary cycles in this sequence was around 6–8. Finally, the membranes were dried at 100 °C under vacuum for 24 h. All membranes were reduced to this *standard initial state* prior to formulating nanocomposites via in situ sol–gel reactions in order to achieve maximum reproducibility. Davis and Mauritz recently discussed the importance of membrane initialization.[29]

Formulation of PFSA/ORMOSIL Nanocomposites and Bulk Model ORMOSILs. *Nanocomposites.* All initialized membranes were swollen in stirred solutions of 5:1 (v/v) methanol:water at 22 °C for 24 h in covered glass jars. The methanol serves to swell the membranes, facilitating the permeation of water and subsequently TEOS and DEDMS, and acts as a good cosolvent for these three species. Premixed TEOS/DEDMS/MeOH solutions were then introduced into the jars such that H_2O:TEOS = 4:1, H_2O:DEDMS = 2:1 (mol/mol), overall. While these ratios reflect the fact that TEOS and DEDMS are tetra- and difunctional, respectively, we cannot predict that a total reaction will occur in situ. Commensurate with this prescription, the TEOS:DEDMS mole ratio was varied over the range 1:0, 2:1, 1:1, 1:2, and 0:1 to generate a systematic variation of network former/modifier composition over the entire range. The composition of Q = $Si(O_{1/2})_4$ and D units that are ultimately bonded within the PFSA is not expected to be identical with the composition of precursor monomers in the external feed solution. This is conceivably due to the different solubilities, diffusivities, and reactivities of the two species within the PFSA template. Furthermore, there will be different chemical potential gradients for each monomer across the solution/membrane interface that are proportional to the monomer external solution concentration that will influence the relative uptake of this species in a given permeation time.

Table 1. Percent ORMOSIL Uptake of Nafion (H^+) Membranes via in Situ Sol–Gel Reactions of Various TEOS/DEDMS Compositions

TEOS:DEDMS (mol/mol)	wt %
1:0	10.1
2:1	11.3
1:1	10.9
1:2	12.5
0:1	6.7

Premixed TEOS/DEDMS/MeOH solutions were added to individual reaction jars (stoppered) while maintaining stirring. After 9 min, the membranes were removed from these solutions. The time between addition of premixed TEOS–DEDMS and removal of the membrane from solution is referred to as permeation time. Upon removal, the membranes were quickly soaked in MeOH for 1–2 s to wash away excess surface reactants to reduce the possibility of forming surface-attached ORMOSIL layers. Finally, the samples were surface-blotted and dried at 100 °C under vacuum for 48 h to remove trapped volatiles and promote further condensation within the in situ network. In each case, percent weight uptake was determined relative to unfilled, dry H^+ form membrane weight. Gravimetric uptakes are listed in Table 1 for this PFSA/ORMOSIL series.

Pure ORMOSILs. We also generated bulk ORMOSILs to provide model networks wherein structure is not influenced by the interactions and geometrical constraints within the clustered PFSA morphology. A series of five ORMOSIL films, with formulations identical to those for the PFSA/ORMOSIL hybrids, were prepared; i.e., the following mole ratios were preserved: H_2O:TEOS = 4:1, H_2O:DEDMS = 2:1, and TEOS:DEDMS = 1:0, 2:1, 1:1, 1:2, and 0:1. These solutions were stirred and acid-catalyzed with ca. 0.02 M HCl to simulate the acidic environment in the clusters of Nafion-H^+. Films were cast on Teflon pans. Having gelled, but still swollen with alcohol and water, these ORMOSILs were finally heated at 100 °C under vacuum for 30 h. The resultant films, being around 1.2 mm in thickness, were stored in a desiccator prior to analysis. The following trend in properties of these film samples, observed by visual inspection and handling, is as follows: 1:0 (hard, brittle, transparent gel) → 2:1 (hard, brittle, transparent gel) → 1:1 (relatively soft, white gel) → 1:2 (relatively soft white gel) → 0:1 (clear liquid). This trend reflects the increasing influence of D units which impart network flexibility. No gel formation was observed for the 0:1 case, even when the liquid was heated at 100 °C for 30 h to drive the reaction. The liquid nature of the 0:1 sample suggests that pure DEDMS reacted under these conditions generates oligomers, perhaps in the form of rings, rather than long entangled chains. Sakka et al.[30] reported that hydrolysis of DEDMS does not lead to gelation owing to the propensity of this precursor to form small rings during condensation.

Infrared Spectroscopy. FT-IR spectra were obtained using a Bruker 88 spectrometer with resolution set at 4 cm^{-1}. To obtain information regarding the molecular structure of the in situ grown phase in these PFSA/ORMOSIL hybrids, FT-IR in ATR mode was utilized. A thallium bromide/thallium iodide (KRS-5) crystal was used and an angle of incidence of 45° employed. A total of 1000 interferograms were taken for each spectrum.

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As discussed earlier,[11,22,28] the reflectance mode must be applied due to the great absorbance associated with the thicknesses of these samples. To be sure, it would be more desirable to perform IR experiments in transmission mode to acquire spectra that more clearly represents the bulk. The penetration depth of evanescent IR light in the ATR experiment is considerable (0.2−4 μm) with respect to the size and spacing of polar clusters in PFSIs (≈30−50 Å) in the sense that the sampled depth is many clusters deep.[22] In our earlier limited studies of similar PFSA/[silicon oxide] hybrids, ATR spectra were observed to be similar to those for transmission through thin films (≤1 mil thick).[22] We tentatively assume that ATR spectra approximately represent bulk spectra. It is appropriate, however, to cite our earlier electron microscopic/X-ray elemental microanalyses of the distribution of silicon, across the thicknesses of Nafion/[silicon oxide] hybrid films, which indicated that more Si resides in near-surface regions than in the middle.[26] Similar investigations of ORMOSIL composition distribution in the present samples have not as yet been conducted to establish whether concentration profiles are uniform or, say, U-shaped. Nonetheless, it is reasonable to expect that the trend in ATR spectra will correlate with corresponding bulk spectra.

IR spectra of the pure ORMOSILs were acquired in transmission mode with 40 scans taken in each case. KBr sample pellets were utilized in which mixtures of grounded ORMOSILs and IR grade KBr powder (~99% wt/wt) were pressed to form pellets. Owing to its liquid nature, sampling of IR spectra for the 0:1 composition was conducted in a different way. Here, the spectrum was obtained in transmission mode by placing a drop of hydrolyzed DEDMS solution between two NaCl IR plates.

Results and Discussion

Nafion−in Situ ORMOSIL Content. It is a working hypothesis that premixed TEOS and DEDMS molecules, and their hydrolyzed species, permeate the PFSA template and migrate to nanometers-in-size, $-SO_3H + H_2O$ + MeOH containing clusters wherein acid-catalyzed sol−gel reactions initiate. The variance of TEOS:DEDMS was expected to generate chemical environments within clusters spanning from hydrophilic to hydrophobic, depending on the ratio of Si−OH to $Si(CH_3)_2$ groups. The numerous, coupled, acid-catalyzed reactions occurring in these experiments are depicted in Figure 2. It is assumed that the same rules that govern hydrolysis and condensation in bulk sol−gel-derived systems also apply, in a general sense, to reactions within the PFSA template. To this list of reactions might be added the following: Si(OEt) + MeOH → Si(OMe) + EtOH; however, TEOS−MeOH solutions were prepared immediately before conducting the sol−gel reaction. Substituted organic ligands might cause differences in reaction as well as permeation rates. Although we are aware of the above exchange reaction, MeOH, rather than EtOH was chosen as the carrier solvent because it is more effective in swelling the PFSA, which is an important consideration.

In situ hydrolysis and condensation reactions are catalyzed by the fixed sulfonic acid groups in clusters that are arrayed with quasi-order characterized by small-angle X-ray spacings ~30−40 Å throughout the perfluorocarbon matrix.[26]

Dry weight uptakes corresponding to the TEOS:DEDMS mole ratios are listed in Table 1. Except for the last entry, uptake varies between 10.1 and 12.5%. While there is no order in progressing from the 1:0 to 1:2 sample, these values are reasonably close to each other. These uptakes result from carefully conducted experiments under conditions for which consequent nanoparticles are noncontiguous, i.e., exist in single isolation, as established in earlier work.[11,26,28] The 0:1 sample (pure D) incorporates only 6.7% filler for this series. All hybrids were prepared from Nafion samples cut from the same sheet.

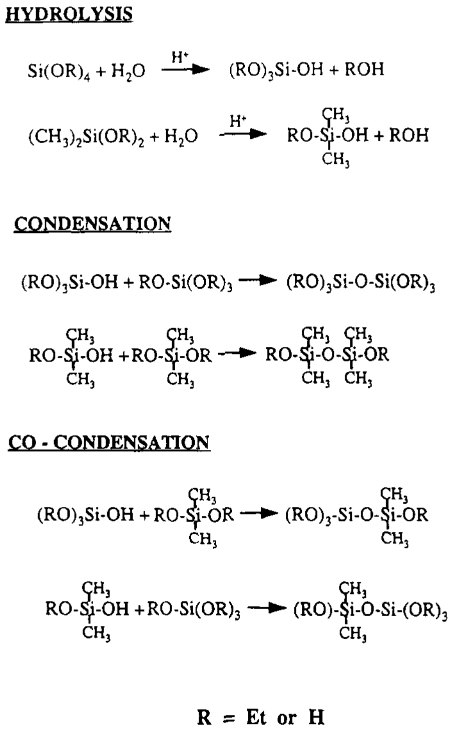

Figure 2. Coupled, acid-catalyzed sol−gel reactions in TEOS + DEDMS mixtures. The following reaction might be added: Si(OEt) + MeOH → Si(OMe) + EtOH.

Infrared Studies of Nafion/ORMOSIL Hybrids. FT-IR analysis of ORMOSIL nanophase structure in Nafion films by inspection of direct spectra is rendered difficult because of the numerous, complex, and interfering bands characteristic of pure Nafion, as tabulated by Falk.[31] Therefore, subtraction of the unfilled dry Nafion (H^+) spectrum from that of the hybrid is necessary to uncover characteristic ORMOSIL bands. The prominent SO_3^- asymmetric stretching (~1200 cm^{-1}) and $-CF_2-CF_2-$ symmetric stretching (~1140 cm^{-1}) bands of Nafion were employed as internal thickness standards to affect this subtraction in the usual way. The subtractions were very effective in uncovering bands indicative of IR-active molecular groups in ORMOSIL materials to the exclusion of the characteristic PFSA bands.[31] In principle, the ORMOSIL bands observed for these hybrids are a signature of this phase as dispersed throughout and interacting with the PFSA template.

Difference spectra are presented in Figure 3 for the hybrids in Table 1 in the region 700−1300 cm^{-1}. This region of the spectrum contains bands characteristic of molecular groups in silicon oxide materials, as well as of silicon oxide phases incorporated in PFSA templates, as described in earlier reports.[22,28] Intercomparison of these spectra is meaningful as all samples were derived from the same sheet of Nafion, were initialized in

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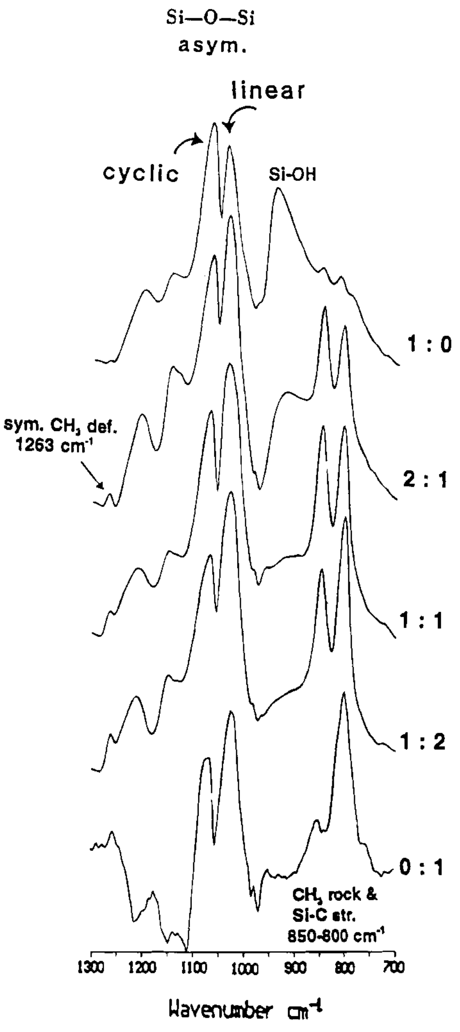

Figure 3. IR difference spectra: Nafion/ORMOSIL−dry unfilled Nafion-H$^+$, for indicated premixed external TEOS: DEDMS molar ratios.

exactly the same way and have comparable filler contents. All spectra have the same absorbance (A) scale but have been displaced upward in order of increasing TEOS:DEDMS ratio for better intercomparison.

In the 1:0 spectrum, the *asymmetric* stretching vibration of Si−O−Si groups (~1000−1100 cm^{-1}) is a signature of bridging oxygens, or extent of the in situ condensation reaction. This vibration often consists of two components corresponding to Si−O−Si groups in *cyclic* (~1080 cm^{-1}) and *linear* (~1030 cm^{-1}) configurations, as discussed previously.[22,28] To avoid confusion, we stress that the similar bands for pure PDMS or pure DMS oligomers in discrete cyclic or linear configurations is not what is referred to here, save for the 0:1 case. Hybrids derived from pure TEOS do not contain D units yet it is recognized that pure TEOS-based silica gel contains these structural subunits that are identified in this way. The "linear" and "cyclic" entities in these wholly or partially silicate structures refer to substructures of larger network-like structures as discussed in previous works.[22,28]

Given these band assignments, the linear/cyclic component intensity ratio measures degree of molecular connectivity within the silicon oxide or ORMOSIL phase, e.g., large $A_{\mathrm{cyclic}}/A_{\mathrm{linear}}$ reflects considerable silicon oxide or ORMOSIL cross-linking. Also important is the absorbance associated with Si−OH stretching vibration (~940 cm^{-1}), which is a measure of uncondensed SiOH groups.[22,32,33] Unfortunately, the Si(O−H) stretching vibration is often not useful in these systems in which obscuring absorbances associated with OH groups in residual alcohol or water molecules are present. In this report, trends in these characteristic bands are discussed on a qualitative, or at best, semiqualitative basis.

The 1:0 (top) and 0:1 (bottom) spectra in Figure 3 are fingerprints of the extreme, pure filler component cases, whereas the three middle spectra correspond to Nafion/ORMOSIL nanocomposites. Rather noticeable trends are seen in these spectra.

A gradual suppression of the Si−OH stretching absorbance, ν[Si−OH], relative to Si−O−Si group absorbance (i.e., cyclic + linear) is seen in proceeding from 1:0 down to the 0:1 hybrid, as is reasonable. Voronkov et al.[34] state that the rate of condensation decreases with a decrease in number of silanol groups and that this is mainly a consequence of steric blocking. Thus, while DEDMS hydrolyzes faster than TEOS under acidic conditions,[4,35] it will react either with itself or with TEOS with a probability lower than that associated with reaction between two hydrolyzed TEOS molecules. This fact, combined with the simple consideration that the D:Q ratio increases from top to bottom in Figure 3, rationalizes the diminishing of the Si−OH stretching absorbance.

Corresponding to the reduction in ν[Si−OH] absorbance with increasing D content is the appearance of new peaks. A band ~1263 cm^{-1}, seen for all samples save for the 1:1 case, is assigned to *symmetric* C−H deformation in Si−CH$_3$ groups, designated as ν_{sym}[CH$_3$].[32,33,36,37] This weak band increases in relative absorbance with increasing D content. In contrast, this band is sharp and intense for pure PDMS and, as will be seen (Figure 7), is also sharp, intense and in the same position for all three bulk ORMOSILs as well as the bulk 0:1 sample in this work. While we presently cannot account for the weakness of this band in the hybrid systems, it is nonetheless significant that it (1) occupies the same wavenumber position for ν_{sym}[CH$_3$] as reported for bulk ORMOSILs by other investigators,[20,21] (2) becomes stronger with increasing DEDMS:TEOS for our hybrids, and (3) other D unit bands are present. Perhaps the trapping of D units in an environment in which strong bond perturbations (e.g., electrostatic fields about SO$_3^-$ anions) exist might diminish band intensities. Last, the process of subtraction might cause a measure of spectral distortion.

Also emergent are two intense, adjacent bands, which also appear to be due to Si−(CH$_3$)$_2$ groups, at ~850 and ~800 cm^{-1}. CH$_3$ rocking and Si−C stretching modes are known to exist in the region ca. 870−750 cm^{-1}, and it is quite logical to assume that the two peaks in this region, collectively labeled ν[Si−(CH$_3$)$_2$], correspond to these modes.[28,32,36,37] The consequence of the ionic character of the Si−C bonds[32,36,37] is seen in the spectra

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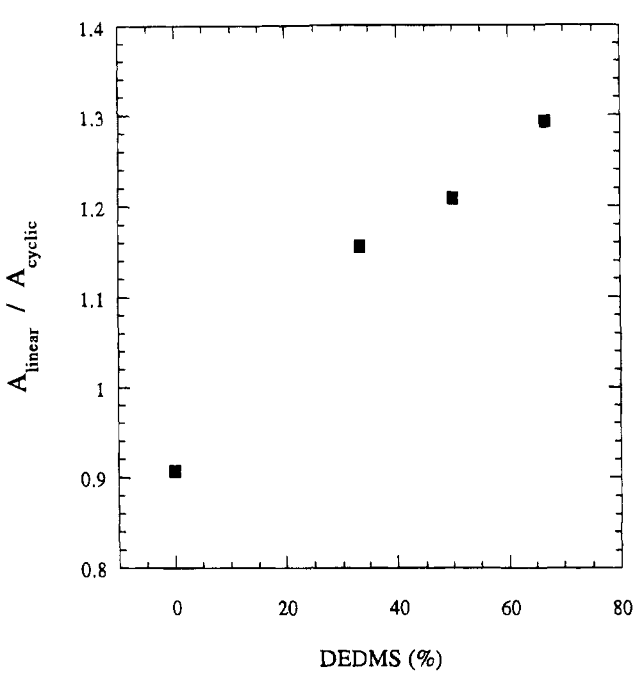

Figure 4. Linear/cyclic ν_{asym}(Si−O−Si) absorbance ratio vs % DEDMS in external solution for Nafion/ORMOSIL hybrids.

in Figure 3. $\nu_{sym}[CH_3]$ for methyl bonding to Si is relatively weak compared to that for the C−CH$_3$ group, presumably owing to reduced C−H dipole moment caused by withdrawal of electrons from the C−H bond by the strong Si^+−C^- dipole.[32,36] We also note that a weak band at ~2965 cm^{-1}, which corresponds to *asymmetric* stretching in the CH$_3$ group, is observed (not shown). Thus, there is sufficient evidence that D units are incorporated within the membrane.

We note the weak presence of ν_{sym}[Si−O−Si], the *symmetric* stretching vibration of the Si−O−Si group, ~800 cm^{-1}, for the 1:0 hybrid. This peak, present in earlier IR spectra of Nafion/silicon oxide nanocomposites, is theoretically IR-inactive but can be present if geometric distortion of coordinative symmetry of bonding about Si atoms exists.[22] We call attention to this band to avoid confusion between it, which appears weak for the pure SiO$_2$-filled nanocomposite, and the strong bands corresponding to CH$_3$ rocking and Si−C stretching for the Nafion/ORMOSIL hybrids in the same region of the spectrum.

On inspecting the linear and cyclic components of ν_{asym}(Si−O−Si) for all the hybrids, it is evident that the three ORMOSIL phases possess a greater degree of molecular linearity than the pure silicon oxide phase. This is made clear in quantitative fashion in Figure 4, which demonstrates a rather direct increase in A_{linear}/A_{cyclic} with increasing percent DEDMS in the external solution bath. This trend might be explained in terms of (1) increasingly lower-coordinated Si(O$_{0.5}$)$_4$ tetrahedra resulting from the presence of relatively more difunctional DEDMS molecules having two unreacted methyl groups, and (2) linear blocks of consecutive D units, although it has already been mentioned that cycles of D units are quite probable. If it is assumed that DEDMS hydrolyzes faster than TEOS in this sulfonic acid-rich environment, D chains might form when the DEDMS concentration is high.

Note that peaks for both rings and chains, the latter being somewhat more prominent than the former, are present in the spectrum for the 0:1 hybrid. These rings and chains necessarily exist as discrete entities, not as subunits of a covalent network, as the DEDMS molecule is only difunctional.

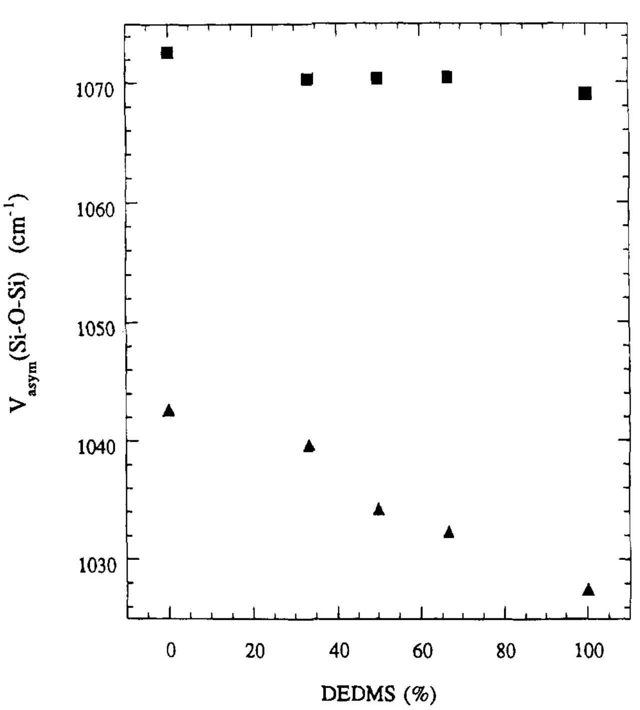

Figure 5. Peak wavenumbers for cyclic (■) and linear (▲) components of ν_{asym}(Si−O−Si) vs % DEDMS in external solutions for Nafion/ORMOSIL hybrids.

There are also interesting trends in the peak frequencies of the linear and cyclic bands of ν_{asym}(Si−O−Si) vs % DEDMS, as seen in Figure 5. Accompanying the fact of increasing degree of linearity with increasing DEDMS content, it was discovered that the linear peak shifts monotonically and, to a significant degree, to lower wavenumbers with increasing % DEDMS. Commensurate with this, there is a downward, although less-profound shifting of the cyclic peak. In an earlier similar study of Nafion having in situ grown (acid-catalyzed) pure silicon oxide phases,[22] we noted that both the linear and cyclic components of Si−O−Si asymmetric stretching bands shifted to lower wavenumbers with increasing silicon oxide content. It was suggested in this report that this trend was due to the progressive crowding of the silicon oxide molecular structure at the surface of the nanoparticles. The formation of Si−O−Si bonds under the increasing constraint of crowding leads to distortions from the natural bonding symmetry which produces "softer" Si−O force constants, as observed. However, it might be argued that the increasingly longer runs of D units that must occur with increasing D:Q ratio would cope with steric hindrance as these chains would be inherently flexible.

It is seen in Figure 3 that the absorbance associated with Si−C stretching (~800 cm^{-1}) increases relative to CH$_3$ rocking absorption (~850 cm^{-1}) with increasing D:Q despite the fact that these groups maintain a 1:1 ratio. Recall that CH$_3$ bands in Si−CH$_3$ are normally weaker than Si−C bands. It is obvious that the concentration of D units in the PFSA increases as the external DEDMS concentration increases.

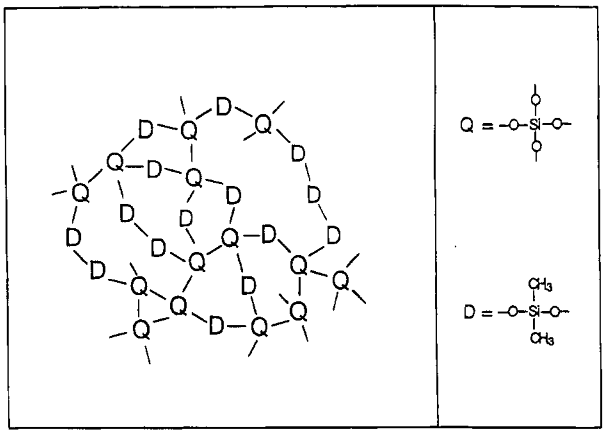

Figure 6. Hypothesized ORMOSIL phase structure consisting of copolymerized Q and D units. In an actual network, incompletely coordinated Q units will contain −OH groups and water of hydration may be present.

An important nanostructural aspect is the *sequence distribution of D and Q units* throughout the ORMOSIL phase. It is important to determine whether the ORMOSIL structures result from random co-condensation of D and Q units or consist of a modified network of D and/or Q *blocks* of significant size. Figure 6 is a rough, hypothetical depiction of the structure of such a modified network.

In highly relevant studies, Chen et al.[20] and Babonneau et al.[21] formulated and characterized, using FT-IR spectroscopy, a series of bulk, monolithic materials via copolymerization of DEDMS and TEOS, mainly for the composition DEDMS:TEOS = 1:1. Their experiment took place in EtOH, and no catalyst was used. The reactive solutions were vigorously stirred to promote good mixing of the two monomers, and gelation occurred after 3 weeks in open vessels; the samples were then dried at 80 °C. These investigators then obtained IR (transmission) spectra of the dried gels to gather evidence of either co-condensation between Q and D units or of block copolymerization. They noted that D blocks are characterized by a relatively weak vibration at 860 cm^{-1}, as in pure DEDMS-derived gels. The literature on methylpolysiloxanes, including the early extensive studies of cyclic and chain oligomers by Wright and Hunter[36] as well as by Richards and Thompson,[37] reinforces the suggestion that this band is indeed the fingerprint of Si−C bond stretching and can be frequency-shifted by inductive-coupling-steric effects. This band shifts downward to 845 cm^{-1} and increases in intensity in DEDMS/TEOS-derived mixed gels of nonblocked structure. These investigators also cite the angular deformation band (δ[Si−O−Si]) for pure D units as being at 390 cm^{-1} and the fact that this band shifts from 400 up to 440 cm^{-1} as D:Q decreases. There is a band at 460 cm^{-1}, also due to Si−O−Si bending within blocks of Q units.[22] Evidence of copolymer formation was taken by these investigators as the presence of only one band present between the extremes 390 and 460 cm^{-1}. On the other hand, if the ORMOSIL is highly blocked, then two discrete bands would logically be present to reflect this heterogeneity. We have adopted this point of view in the interpretation of our spectra of the similar systems.

Table 2. $\nu[Si(CH_3)_2]$ **and** δ**[Si−O−Si] IR Peak Wavenumbers for Hybrids Generated Using Various External TEOS:DEDMS Solution Compositions**

sample no.	Q:D[a] (mol:mol)	$\nu[Si(CH_3)_2]$[b] (cm^{-1})		A_{800}/A_{850}[c]	δ[Si−O−Si][d] (cm^{-1})
1	1:0	852 (w)	**800 (w)**	n/a	**457 (m)**
		818 (w)			445 (sh)
					420 (w)
2	2:1	850 (s)	809 (s)	0.904	430 (sh)
					420 (m)
3	1:1	849 (s)	807 (s)	1.005	**419 (m)**
4	1:2	849 (s)	803 (s)	1.253	**419 (m)**
5	0:1	**858 (w)**	**801 (s)**		390[e]

[a] Q:D refers here to TEOS:DEDMS molar ratio in external solution bath, not to PFSA−in situ ORMOSIL composition. [b] The strong (s) CH_3 rocking and Si−C stretching bands are assigned to samples 2−5 only. The weak (w) band at ~800 cm^{-1} for sample 1 is ν_{sym}(Si−O−Si). "sh" refers to shoulder. [c] Ratio of absorbance of band ~800 cm^{-1} to band ~850 cm^{-1}. [d] Si−O−Si bending vibration. [e] Assumed.

The systems of Chen et al. and Babonneau et al. are similar but not equal in composition to the ORMOSIL phases incorporated within the PFSA templates reported here. One profound difference between the two systems is that in the latter the ORMOSIL phase, rather than being continuous, is highly dispersed in the PFSA with high surface/volume. Furthermore, sulfonate-ended perfluoroalkyl ether side chains are present in the hybrid. There are IR bands that are clearly matched for the two systems, e.g., asymmetric (~2960 cm^{-1}) and symmetric (~1260 cm^{-1}) stretching of C−H bonds in $=Si(CH_3)_2$ groups, rocking motion of the methyl group about the Si−C axis as well as Si−C stretching in $=Si(CH_3)_2$ groups, and the two components of ν_{asym}[Si−O−Si] (~1040−1080 cm^{-1}). Table 2 lists peak wavenumbers for the $\nu[Si(CH_3)_2]$ bands in the region 850−800 cm^{-1} as well as positions of δ[Si−O−Si] for the five hybrids. It is seen that the weak $\nu[Si(CH_3)_2]$ vibration (~858 cm^{-1}) for the 0:1 hybrid (pure D) indeed shifts downward to ~849 cm^{-1} and becomes strong for all three Nafion/ORMOSIL samples. Concurrently, δ[Si−O−Si] (assumed at 390 cm^{-1} for 0:1, being out of the spectral range of our instrument) shifts up to ~419 cm^{-1} for all three Nafion/ORMOSIL samples, and then up to ~457 cm^{-1} for the 1:0 hybrid which contains no D units.

These results strongly imply that co-condensation between Q and D units has occurred within the PFSA medium. It is significant that the two infrared fingerprints of this molecular structural aspect (i.e., Q,D sequence distribution) correlates, in monotonic fashion, with external DEDMS:TEOS. Figure 6 is then a reasonable, albeit crude illustration of in situ ORMOSIL composition and topology. As DEDMS:TEOS increases, ORMOSIL structures will become more linear, more flexible, more hydrophobic, and exhibit less shrinkage on drying.

Infrared Studies of Model Bulk ORMOSILs. While the IR spectra of the ORMOSIL systems of Chen et al. and Babonneau et al. can be compared to a large extent to the spectra of the hybrids in this work, there are significant differences, as described above. Therefore, in an effort to create bulk *reference* ORMOSIL structures having greater similiarity to the PFSA-containing ORMOSIL nanostructures, precursor solutions having the same DEDMS:TEOS ratios as those contacting the PFSA films and having a measure of acidity (i.e., ca. 0.02 M HCl), were prepared and films cast from these solutions. In concept, PFSA−ORMOSIL interphase interactions are inferred if fundamental

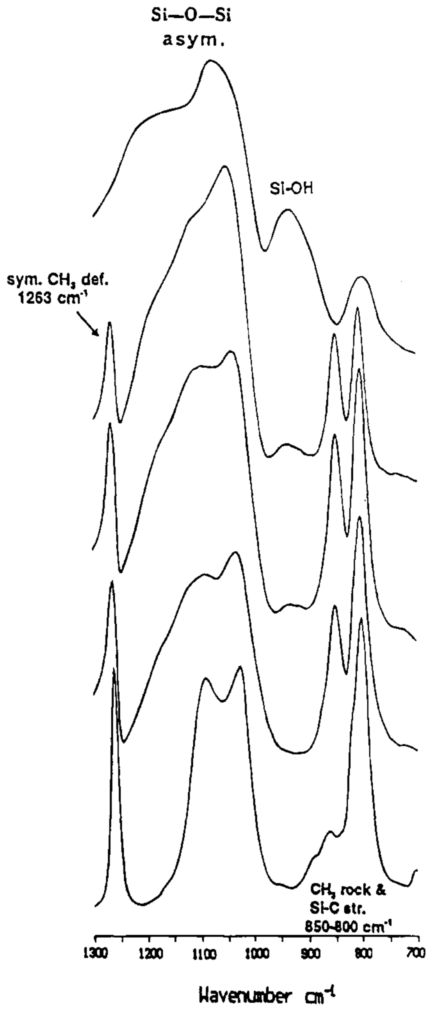

Figure 7. FT-IR transmission spectra of sol–gel-derived bulk ORMOSILs having indicated Q:D.

aspects of the bulk state spectrum differ from those of the corresponding PFSA–in situ ORMOSIL phase.

Spectra over the range 1300–700 cm^{-1} for the five bulk ORMOSIL Q:D compositions are shown in Figure 7. It is seen that the characteristic bands reflecting the existence of both Q and D units in these model ORMOSILs are essentially the same as the bands considered to be fingerprints of the PFSA–in situ grown ORMOSIL phases, as well as the bands of the aforementioned bulk ORMOSILs created by Chen et al. and Babonneau et al. The absorbance of ν[Si–OH] steadily decreases and that of ν_{sym}[CH$_3$] steadily increases in relation to the absorbance in the ν_{asym}[Si–O–Si] region, in progressing from the 1:0 to the 0:1 composition. Altogether, these trends reflects a molecular environment of increasingly organic nature, as well as diminished polarity.

Table 3. ν[Si(CH$_3$)$_2$] and δ[Si–O–Si] IR Peak Wavenumbers for Bulk ORMOSILs Produced via Acid-Catalyzed Sol–Gel Reactions in TEOS/DEDMS Solutions^f

sample no.	Q:D^a (mol:mol)	ν[Si(CH$_3$)$_2$]^b (cm^{-1}		A_{800}/ A_{850}^{c}	δ[Si–O–Si]^d (cm^{-1})
1	1:0	n/a	**799 (w)**	n/a	**465 (m)** 455 (sh)
2	2:1	850 (s)	806 (s)	1.171	**433 (m)** 422 (sh)
3	1:1	850 (s)	805 (s)	1.300	**430 (m)** 413 (m)
4	1:2	850 (s)	804 (s)	1.484	418 (sh) **405 (m)**
5^e	0:1	**862 (w)**	**799 (s)**		

^{a} TEOS:DEDMS precursor molar tatio = Q:D molar ratio in derived ORMOSIL. ^{b} Strong (s) CH$_3$ rocking and Si–C stretching bands are assigned only to samples 2 through 5. The weak (w) band at ~800 cm^{-1} of sample 1 is due to ν_{sym}(Si–O–Si). "sh" refers to shoulder. ^{c} Ratio of absorbance of band ~800 cm^{-1} to band ~850 cm^{-1}. ^{d} Si–O–Si bending vibration. ^{e} Sample 5 spectra obtained in transmission mode, as exlained in text. ^{f} KBr pellet technique.

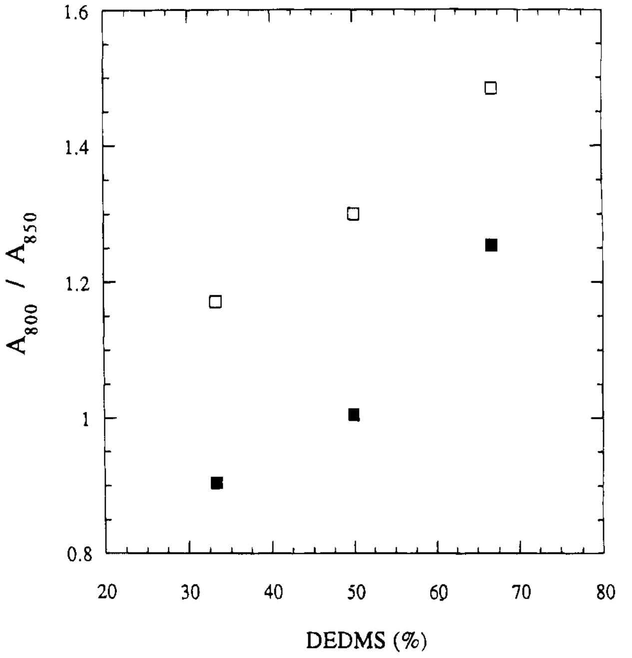

Figure 8. Ratio of absorbance of ~800 cm^{-1} band to absorbance of ~850 cm^{-1} band in the ν[Si(CH$_3$)$_2$] region, vs % DEDMS for Nafion/ORMOSIL hybrids (■) and bulk ORMOSILs (□).

The positions of the two ν[Si(CH$_3$)$_2$] bands, and the δ[Si–O–Si] band for the bulk models are listed in Table 3. It is seen that a weak ν[Si(CH$_3$)$_2$] vibration, at ~862 cm^{-1} for the 0:1 hybrid shifts downward to a rather constant value of ~850 cm^{-1} and becomes stronger for the three bulk ORMOSILs. The somewhat weak band at 799 cm^{-1} for the 1:0 hybrid is for the ν_{sym}(Si–O–Si) vibration. Concurrently, δ[Si–O–Si] (taken as 390 cm^{-1} for 0:1) shifts progressively upward from ~405 to ~433 cm^{-1} for the three ORMOSILs and is at ~465 cm^{-1} for pure TEOS-derived silicon oxide. For the same reasons cited by Chen et al. and Babonneau et al. and as discussed above, the nature of these band shifts indicate that copolymers of Q and D units were formed.

Significant similarities in the peak positions and shifting trends are seen on comparing Tables 2 and 3. We arrive at the important conclusion, based on this fundamental observation, that the spectral subtraction [Nafion/ORMOSIL]–[dry Nafion-H$^+$] effectively isolates the bands of the Nafion–in situ ORMOSIL phase.

The ratio of the absorbance of the ~800 cm^{-1} band to the absorbance of the ~850 cm^{-1} band, A_{800}/A_{850}, is plotted vs DEDMS mole percent for pure model ORMOSILS and Nafion/ORMOSIL hybrids in Figure 8. The curve for pure ORMOSILs lies above that for the Nafion/ORMOSIL hybrids. Recall that, for the hybrids, % DEDMS refers to external solution composition. As D unit content increases, A_{800}/A_{850} for both materials increases in similar fashion. We offer the tentative, certainly speculative suggestion that this similar be-

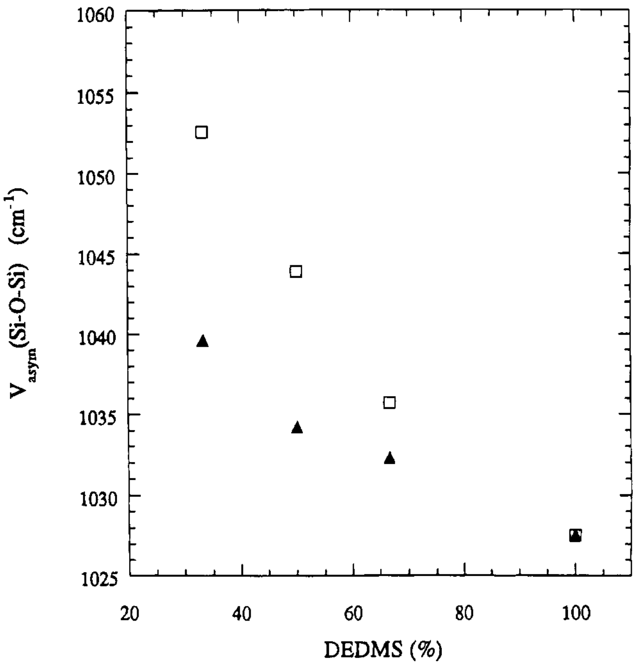

Figure 9. Peak wavenumber for ν_{asym}(Si−O−Si) (linear) vs % DEDMS for Nafion/ORMOSIL hybrids (▲) and bulk ORMOSILS (□).

havior, save for the vertical displacement of the curves, indicates similar D, Q sequence distributions for the two systems. At a given % DEDMS, each Nafion/ORMOSIL material has a A_{800}/A_{850} value lower than that of the free-state ORMOSIL. This might imply that while Nafion−in situ ORMOSIL nanostructure might be similar to that of corresponding free-state ORMOSILs, the former is not as developed as that of the latter with regard to amount of D unit incorporation. This could be related to differences in permeability for TEOS and DEDMS molecules, as well as a to a diffusion-related time lag associated with the in situ sol−gel reaction.

Figure 9 compares ν_{asym}[Si−O−Si](linear) vs % DEDMS for the hybrids (bottom) with the trend for the pure ORMOSILs (top). In both cases, there is a shift to lower wavenumbers with increasing % DEDMS, which, as before, might be attributed to an overall softening of Si−O force constants. Both curves in Figure 9 show the same qualitative trend. For the same % DEDMS, each peak for the bulk ORMOSIL occurs at a higher wavenumber than that for the corresponding Nafion/ORMOSIL hybrid. We note in the spectra that the linear peak for pure ORMOSILs is not well resolved at low DEDMS contents in contrast with the rather distinctive resolution of this band seen for the hybrids in Figure 3. The rationalization proposed for the separation of the two curves in Figure 8 might be applied again here, i.e., Nafion−in situ ORMOSIL nanostructures are similar to those of corresponding free-state ORMOSILs except that the former is not as developed as the latter with regard to D unit content owing to differences in permeability for TEOS and DEDMS molecules and associated diffusional time lag.

Another difference between the spectra in Figures 3 and 7 is that ν_{sym}[CH$_3$] ~ 1263 cm^{-1}, which is present for all hybrids, except for the 1:0 case, is weak, especially in comparison with its sharp and intense character for all three bulk ORMOSILs as well as the bulk 0:1 sample, as discussed earlier. The weak nature of this band was also seen in our earlier IR studies of the post reaction of in situ grown $SiO_{2[1-4/x]}(OH)_x$ nanoparticles with DEDMS.[28] The assignment of the IR bands for both systems, one having mixed, the other segregated, inorganic composition, are in agreement with each other. In any case, these bulk ORMOSILs are currently the best-matched system short of a structural calibration with a proper internal standard.

ν(Si−OH) absorbance, relative to ν_{asym}(Si−O−Si) absorbance, for the bulk ORMOSILs (~940 cm^{-1}) decreased dramatically as DEDMS content increased, as is reasonable owing to more incorporated D units and consequently fewer unreacted Si−OH groups. This behavior parallels that for the Nafion/ORMOSIL nanocomposites as a function of increasing DEDMS content in the external source solutions. In fact, with regard to band positions and trends, we observe more similarities than differences between the IR spectra of Nafion−in situ ORMOSILs and bulk ORMOSILs. This fact might imply that ORMOSILs generated under the two greatly different conditions have similar structures. We hesitate to suggest that this implies that there are no major interactions between a given ORMOSIL nanophase and the host Nafion matrix. We have earlier pointed out differences in bandwidths and intensities that might be related to these interactions. To be sure, the morphological dispositions of the two materials must be different. Additional tests such as mechanical tensile and dynamic mechanical analyses, performed as a function of filler content and over the range of Q:D, would be useful to explore the important aspect of interactions operative across the interface of the final incorporated nanostructures and PFSA template.

General Conclusions

Nafion(H$^+$)/ORMOSIL hybrids were formulated via Nafion−in situ, sol−gel reactions of tetraethoxysilane, a network former, and diethoxydimethylsilane, a network modifier, over a range of mixed monomer compositions. The singular goal of this work was to characterize the molecular structure of the incorporated silicon oxide, ORMOSIL, and dimethylsiloxane phases from the perspective of infrared spectroscopy. To provide reference systems to aid in the interpretation of hybrid spectra, corresponding bulk ORMOSILs were also formulated for IR analysis.

The asymmetric stretching vibration of Si−O−Si groups provided evidence, and quantified extent of in situ condensation reactions and the Si−OH stretching vibration provided a measure of uncondensed SiOH groups. Since the former absorbance consists of two components corresponding to Si−O−Si groups in loops and chains, the linear/cyclic absorbance ratio is a measure of molecular connectivity within the silicon oxide, ORMOSIL or dimethylsiloxane phases. The linear peak shifts to lower wavenumbers with increasing % DEDMS, accompanied by a downward but less-profound shifting of the cyclic peak. We speculate that this behavior is due to progressive crowding of added D and Q monomers at nanophase surfaces so that formation of Si−O−Si bonds under the increasing constraint of crowding leads to distortions from natural bonding symmetry which results in softer Si−O force constants.

In situ ORMOSIL phases possess greater degrees of molecular linearity than the in situ pure silicon oxide phase. The trend of increasing linearity with increasing % DEDMS is explained in terms of increasing numbers of 2-coordinated Q units and loops of D units are probable. Rings and some chains are present in pure DEDMS-treated PFSAs. The downward wavenumber shift with increasing D:Q, of Si−C bond stretching, and corresponding downward shift of a single peak corresponding to Si−O−Si angular deformation, strongly implies co-condensation between Q and D units within the ionomeric environment. As DEDMS:TEOS increases, ORMOSIL molecular structures are more linear and consequently more flexible. A spectrum of chemical environment, or polarity can be tailored in perfluorosulfonate ionomers by adjusting the ratio of Si−OH and $Si-CH_3$ groups in ORMOSIL nanophases.

The nature of the shifting of $\nu[Si(CH_3)_2]$ and $\delta[Si-O-Si]$ bands with Q:D variation indicates that copolymers of Q and D units exist in the bulk ORMOSILs, as well.

In the future, the IR database will be complemented by ^{29}Si solid-state NMR information relating to degree of Si atom substitution about $Si(O_{0.5})_4$ tetrahedra. Mechanical tensile studies will determine whether ORMOSIL phases exist as arrays of isolated nanoparticles or percolate throughout macroscopic dimensions. Small-angle X-ray scattering studies will establish whether the "ionomer peak" of Nafion persists upon invasion by ORMOSILs to answer the question of whether or not Nafion does in fact act as a morphological template. Fluorescent probes will investigate the distribution of chemical environment within this heterogeneous morphology.

The regular evolution of IR spectra suggests that ORMOSIL structure in the PFSA can be controlled by adjusting the external TEOS:DEDMS ratio. The capability of tailoring the "porosity" of fractal-like ORMOSIL nanophases will generate size exclusion effects that will influence gas- or liquid-transport across these membranes. It is also imagined that transport permselectivity will be controlled by diffusant molecule−ORMOSIL surface energetics.

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