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Polymer 43 (2002) 2311–2320

polymer

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Nafion®/ORMOSIL nanocomposites via polymer-in situ sol–gel reactions. 1. Probe of ORMOSIL phase nanostructures by ^{29}Si solid-state NMR spectroscopy

S.K. Young, W.L. Jarrett, K.A. Mauritz*

Department of Polymer Science, University of Southern Mississippi, Southern Station Box 10076, Hattiesburg, MS 39406-0076, USA

Received 21 August 2001; received in revised form 10 December 2001; accepted 12 December 2001

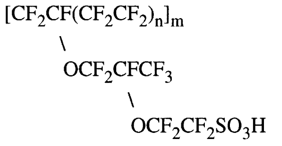
Abstract

A series of Nafion®/ORMOSIL hybrids, generated by in situ sol–gel co-polymerizations of tetraethylorthosilicate (TEOS) and semi-organic $R'_nSi(OR)_{4-n}$ co-monomers (SOC), were developed to generate a spectrum of nanoscale chemical environments within the Nafion® morphological template. The molecular structures of the ORMOSIL phases were analyzed by means of ^{29}Si solid-state NMR (SSNMR) spectroscopy. A high average degree of Si atom coordination about SiO_4 molecular sub-units can be achieved, but a significant number of unreacted $\equiv$SiOH groups on reacted $Q = Si(O_{1/2})_4$ units is always present. The shifting, with relative ORMOSIL composition, of $D = RR'Si(O_{1/2})_2$ or $T = R''Si(O_{1/2})_3$ (R, R′ and R″ are organic moeities) peak envelopes for difunctional or trifunctional SOCs is suggested to reflect random co-condensation rather than distinct Q and D (or T) block formation. The numbers of membrane-incorporated Q and D (or T) units per fixed sulfonate group were calculated from the ^{29}Si SSNMR spectra for those particular hybrids that had a reasonably low noise/signal aspect. Spectra for hybrids based on in situ sol–gel reactions for TEOS (no SOC present) suggest that inserted hydroquinone molecules interfere with condensation reactions between $(RO)_{4-x}Si(OH)_x$ molecules and silanol oligomers to yield silicate structures with lower average coordination. While earlier small angle X-ray scattering studies indicated that ORMOSIL structures can be grown within the polar regions of Nafion®, the results reported here address the specific compositions of these nanoscale structures. © 2002 Published by Elsevier Science Ltd.

Keywords: Sol–gel processes; Organically modified silicate; Nafion®

1. Introduction

Our laboratory earlier conducted sol–gel polymerizations of tetraethylorthosilicate (TEOS) or co-polymerizations of TEOS with diethoxydimethylsilane (DEDMS) monomers within the nanophase-separated morphology of Nafion® membranes to yield Nafion®/silicate and Nafion®/(organically modified silicate (ORMOSIL)) nanocomposites. The chemical structure of Nafion® in the sulfonic acid form is



$$[CF_2CF(CF_2CF_2)_n]_m \backslash OCF_2CFCF_3 \backslash OCF_2CF_2SO_3H$$

The morphology of unmodified Nafion® in the acid and cation forms consists of aggregates of the long sulfonate-terminated sidechains dispersed throughout a perfluorocarbon matrix of low degree of crystallinity [1]. Quasi-order exists over the ensemble of these aggregates such that inter-aggregate center-to-center spacings are around 35–50 Å, as seen in small angle X-ray scattering (SAXS) studies. Our work was initiated under the assumption that this quasi-ordered morphology would act as a template that influences the ultimate geometrical distribution of densified silicate phases that result upon drying after in situ sol–gel reactions for silicon alkoxides. After exposure of a Nafion® membrane to an external solution bath containing water for hydrolysis, alcohol and hydrolyzed alkoxides, at a given adjusted pH, these polar molecules will preferentially migrate to the polar aggregate regions. The coupled, acid-catalyzed, hydrolysis–condensation reactions in Nafion® were discussed in earlier papers. More recently, we reported on base catalyzed sol–gel reactions in Nafion® [2]. The subsequent polymerization of sorbed, hydrolyzed alkoxides is confined to these domains which are viewed, for our purposes, as nanoscale reaction vessels. In fact, SAXS structural studies showed that the original morphology of unfilled

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* Corresponding author. Tel.: +1-601-266-5595; fax: +1-601-266-5635.
E-mail address: kenneth.mauritz@usm.edu (K.A. Mauritz).

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PII: S0032-3861(02)00027-7

Nafion® persists even after its invasion by the sol–gel-derived phase and that silicate and/or ORMOSIL phases preferentially reside within the polar aggregates [3]. These results suggested that chemical composition can be varied within the clusters of the sulfonate-ended sidechains in Nafion® by these sol–gel reactions. The SAXS peak that reflects nanophase separation in unfilled Nafion® basically remains invariant with regard to Bragg spacing (associated with cluster center-to-center spacing) with silicate or ORMOSIL uptake. However, the electron density contrast between the phases does vary with ORMOSIL composition. It is reasonable to interpret these results in terms of ORMOSIL nanoparticle insertion in the clusters so as to affect a change in electron density. These hybrids can be classified as 'nanocomposites' because perfluoro-organic/inorganic compositional heterogeneity exists on the scale of ~5 nm.

The incorporation of organic groups into a silicate structure via co-polymerization of TEOS and DEDMS is depicted in Fig. 1. Semi-quantitative information regarding Si–O–Si groups in cyclic and linear molecular substructures, and uncondensed SiOH groups in ORMOSIL nanophases in Nafion® were investigated by FTIR spectroscopy [4].

The symbols $Q = Si(O_{1/2})_4$ and $D = (CH_3)_2Si(O_{1/2})_2$ are abbreviations for covalently incorporated building blocks within these limited networks. An important nanostructural aspect is the sequence distribution of D and Q units throughout the ORMOSIL phase. The shifting, with relative Q/D composition, of the IR band due to Si–C stretching in $Si–(CH_3)_2$ groups and the angular deformation band for Si–O–Si groups, imply random co-condensation between Q and D units as opposed to the formation of pure Q and/or pure D blocks.

Molecular structure was also probed using ^{29}Si solid-state NMR spectroscopy [5]. $Si(O_{1/2})_4$ building blocks can exist in four states of coordination involving Si–O–Si bonds, each designated by the symbol Q^n where n is the degree of Si atom substitution. A given Q^n population is quantified by the relative area under the peak for this coordination in a characteristic chemical shift range. In these hybrids, there will also be di-functional $(CH_3)_2Si(O_{1/2})_2$ units that have their own characteristic chemical shift region (D unit region) to the left of that for the Q-peaks. These ^{29}Si NMR studies also suggest that co-condensation between TEOS and DEDMS monomers, rather than formation of distinct Q and D blocks, occurs. As DEDMS co-monomer feed concentration increases, ORMOSIL nanostructures are not only more hydrophobic, but are more flexible. Mainly oligomeric rings of D units exist in Nafion® in which hydrolysis + condensation reactions of pure DEDMS were conducted, although these rings are not induced by the confinement of monomers within the Nafion® template but result from the basic chemistry of acid-catalyzed hydrolysis + condensation reactions of DEDMS.

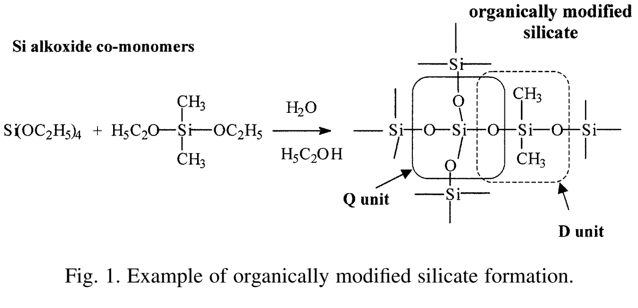


Fig. 1. Example of organically modified silicate formation.

Pyrene photophysical probes interrogated nanostructural polarity within: (1) Nafion®/silicate and (2) Nafion®/ORMOSIL hybrids [6]. It was concluded that the interior of the silicate phase in which SO_3^- groups are embedded in (1) has the most polar environment. Polar/nonpolar interphase regions in (1) are next in order of decreasing polarity. The interior of the ORMOSIL phase in (2) displays the lowest polarity, reflecting the presence of CH_3 groups, and the interphase in (2) ranks somewhat higher in polarity. The equilibrium water uptake of these materials correlates with polarity which showed that the hydrophilicity of unfilled Nafion®-H can be altered to be greater or lesser than that of the acid form in this way.

The work reported here differs from our earlier work and is expanded in the following ways. First, ethanol, rather than methanol, was the co-solvent. When MeOH is used, the sol–gel reactions might be complicated by the additional, parallel side reaction: $Si(OEt) + MeOH \rightleftharpoons Si(OMe) + EtOH$. In this way, alkoxide monomer hydrolysis as well as the swelling of, and monomer permeation into, the membrane can be affected. Also, while the former studies were restricted to in situ co-polymerizations of TEOS and DEDMS, semi-organic co-monomers (SOC) other than DEDMS were employed here in the generation of novel Nafion®/ORMOSIL hybrids for TEOS/SOC mole ratios of 1:0, 2:1, 1:1, 1:2, 0:1. Specifically, TEOS-DEDMS, TEOS-triethoxyvinylsilane (TEVS), TEOS-methyltriethoxysilane (MTES), TEOS-phenyltriethoxysilane (PTES), TEOS-diethoxymethylvinylsilane (DEMVS), TEOS-trimethoxysilylpropylmethacrylate (MAPTES), and TEOS-hydroquinone (HQ) combinations were used.

Hook explained that the hydrolysis and polycondensation reactions of silicon alkoxides are sensitive to the nature of the organic substituents of the Si atom because Si d-orbitals can back bond with the oxygen atoms thereby affecting the oxygen atom basicity [7]. Vinyl and phenyl groups that are bound to a Si atom via an sp^2 carbon are weak electron withdrawing groups [8] while methyl groups are weak electron donators [9]. Another relevant ^{29}Si NMR spectroscopic study is that of Peeters et al., who investigated phenyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, methyltriethoxysilane, ethyltriethoxysilane, octyltriethoxysilane, propyltrimethoxysilane, butyltrimethoxysilane, and chloropropyltrimethoxysilane [10]. These investigators found that the addition of tri-functional silicon alkoxides to TEOS solutions results in an increase in the degree of condensation for the Q-sites, and increasing the length of the organic tail leads to a decrease in the percentage of T_3 sites and increase in the number of T_2 sites, where $T_n = R'Si(OSi)_n(OR)_{3-n}$, where R' is an organic moeity, and R can be a methyl, ethyl or hydroxyl group.

Added to inductive effects, the steric bulk of substituents on the Si atom is important.

These co-polymerizations can yield a number of diverse ORMOSIL chemical nanostructures owing to: (1) differences in coordination about Si atoms resulting from condensation reactions and (2) the insertion of different non-hydrolyzable organic moeities on the SOC. Also, SOC species having vinyl groups might serve as attachment points for organic polymers that might subsequently be formed by in situ addition polymerization reactions, given appropriate initiation, such as photochemical means. On a fundamental level, these studies provided an opportunity to conduct sol–gel reactions in small, confined spaces in a heterogeneous medium.

While the SAXS data clearly indicates that the chemical composition of the cluster domains has been altered via the insertion of ORMOSIL nanostructures, the exact compositions of these structures have remained unknown. The main goal of the studies reported here was to determine these compositions using ^{29}Si solid-state NMR spectroscopy. The significance of the results is that a particular ORMOSIL chemical structure within these very small and highly dispersed domains has been related to the TEOS/[semi-organic silicon alkoxide] co-monomer composition in the external solution of reactants. This information will play an important role in future studies in which the nanoscale chemical environment will be tailored for the purpose of imparting desired gas or liquid transport properties to these heterogeneous membranes. The polarity within incorporated ORMOSIL nanostructures will depend not only on the TEOS/SOC ratio, but also on whether the organic groups are aliphatic or aromatic, and on whether polar groups are present in the SOC unit. In this way, selective transport based on permeant-ORMOSIL intermolecular interactions can be manipulated. Another influence on transport might be nanoparticle 'porosity'—the consequence of incomplete interconnectivity of silicate structures—that might generate molecular size exclusion effects. The spectroscopic signatures of numerous SiOH groups and incomplete Si atom coordination about SiO_4 sub-units are necessary conditions for nanoscopic porosity. The insertion of semi-organic co-monomers having Si-alkoxide functionalities less than four will impart ORMOSIL structural flexibility. These important issues can be explored through the use of ^{29}Si solid-state NMR spectroscopy.

2. Experimental

Materials. Perfluorosulfonate membranes, all having an equivalent weight of 1100 g/mol, and being 5 and 7 mm thick in the SO_2F-precursor form (Nafion® 115 and 117), were supplied by E.I. DuPont. TEOS, DEDMS, TEVS, MTES and HQ were all obtained from Aldrich Chemical and used as received. PTES and MVDES were obtained from UCT Petrach Chemical. MAPTES was obtained from Gelest. 95% ethanol was purchased from Aaper Chemical. All water utilized was distilled/deionized.

Membrane initialization. All Nafion®/ORMOSIL samples are from the same batches as utilized in our earlier FTIR investigations of these materials. Therefore, it is meaningful to compare the current ^{29}Si solid-state NMR results with those of the parallel FTIR study. Important points regarding sample preparation and modifier weight uptake are repeated here for convenience.

All membranes were converted from the sulfonyl fluoride precursor to the sulfonic acid form as in an earlier-developed initialization procedure [11]. Membranes were exchanged to the sulfonic acid form by refluxing in 50% HCl/50% HNO_3 solution and the excess acid was leached out in a de-ionized water reflux. Finally, all the water-swollen membranes were vacuum dried at 100 °C. It is not expected that this last step absolutely dries the membrane as Nafion® tenaciously retains a few water molecules per sulfonate group. All membranes were exchanged to this standard initial state prior to ORMOSIL modification via in situ sol–gel reactions in order to assure maximum sample reproducibility.

Formulation of Nafion®/ORMOSIL hybrids. All initialized membranes were placed in stirred solutions consisting of 4:1 (v/v) ethanol/water at 22 °C for 24 h in covered beakers. The ethanol serves to swell the membranes to promote the permeation of water and the subsequent permeation of TEOS and the SOC as well as being a co-solvent for the three species. Premixed TEOS/SOC solutions were mixed such that $H_2O/TEOS = 4:1$, and H_2O/co-monomer = 2:1 for the di-functional co-monomers (DEDMS, MVDES, or HQ) and = 3:1 for the tri-functional co-monomers (TEVS, MTES, PTES, or MAPTES). In addition to these water/co-monomer mole ratios, the TEOS/SOC mole ratio was varied over the range 1:0, 2:1, 1:1, 1:2, and 0:1 to generate a systematic variation between the pure single co-monomer compositions. The premixed TEOS/SOC/EtOH solutions were added to individual reaction jars while maintaining stirring and the membranes were placed in these solutions for 10 min, during which time the sol–gel reactants permeated the membrane. Then, the membrane was removed from this solution, soaked/rinsed in EtOH to remove excess surface reactants, surface-blotted, placed between Teflon® sheets, and dried at 100 °C under vacuum for 48 h to remove trapped volatiles and promote further polycondensation of unreacted SiOH groups.

Percent weight uptake. The weights of the unfilled and filled samples were determined using a mass balance.

^{29}Si solid-state NMR spectroscopy. Spectra were acquired using a Bruker MSL-400 NMR spectrometer operating at a frequency of 79.5 MHz for the ^{29}Si nucleus. A standard double air bearing CP/MAS probe was used. Ground

samples were packed in 4 mm fused zirconia rotors and sealed with Kel-F™ caps. Sample spinning rate was approximately 4–4.5 kHz. Due to the paucity of protons in these samples, magic angle spinning with high-power decoupling was utilized. Spectra were acquired using a modified DEPTH sequence that effectively suppressed probe background [12]. The 90° pulse width was 3.4–5 μs, probe dead time was 13 μs, and acquisition time was 45 ms. The number of scans acquired per sample varied from 200 to 5900 for long recycle delays (180 s), depending on desired signal/noise. All chemical shifts were referenced to the downfield peak of tetrakis(trimethylsilyl)silane (−9.8 ppm with respect to TMS). All ^{29}Si NMR spectra were evaluated utilizing the GRAMS/32 Spectral Notebase.

^{29}Si solid-state NMR spectra can be used to yield quantitative information concerning Si atom coordination, or substitution, around reacted $R'_nSi(OR)_{4-n}$ units, where $n = 1, 2$, or 3. For a tetrafunctional silicate having SiO_4 tetrahedral subgroups, five so-called Q peaks (Q_0, Q_1, Q_2, Q_3, Q_4) can be present on the NMR spectra and the existence and relative area under each peak depends on the degree of completion of the sol–gel reaction. A Q_0 peak indicates SiO_4 units around which no SiOR or SiOH sites have undergone condensation reactions; Q_1–Q_4 peaks are the signatures of one to four reacted sites, respectively. From a Q unit population analysis based on relative areas under the Q peaks, a measure of intramolecular connectivity within the silicate phase can be determined. For example, a low population of Q_3 and Q_4 states, but high population of Q_2 character might reflect a silicate nanostructure consisting of mainly linear runs of Si–O–Si groups with slight branching. On the other hand, very high Q_4 content would suggest a highly intraconnected, or crosslinked silicate nanophase. It should be stressed that this information on SiO_4 coordination is necessary but not sufficient to determine long range silicate structure as it only reflects the distribution of nearest neighbor environments around these groups. Nonetheless, this specific molecular information can be combined with structural information obtained by the use of other structural probes to address the issue of nanoparticle porosity; fractal-like surfaces must be accompanied by reasonably large sub-Q_4 populations, and a large relative number of residual SiOH groups.

Typical Q chemical shift ranges are: Q_0: −72 to −82 ppm, Q_1: −82 to −89 ppm, Q_2: −92 to −96 ppm, Q_3: −100 to −104 ppm, and Q_4: ~ −110 ppm [10,13,14].

For $R'_1Si(OR)_3$, a tri-functional silicate, four so-called 'T' peaks can be present: T_0, T_1, T_2, T_3. These peaks have the typical chemical shift ranges: T_0: −37 to −39 ppm, T_1: −46 to −48 ppm, T_2: −53 to −57 ppm, and T_3: −61 to −66 ppm [10,13,14]. For $R'_2Si(OR)_2$, a di-functional silicate, three 'D' peaks can be present: D_0, D_1, D_2 with the following typical chemical shift ranges: D_0: −3 to −5 ppm, D_1: −8 to −12 ppm, and D_2: −13 to −19 ppm [10,13,14].

3. Results and discussion

3.1. Gross ORMOSIL uptake and mathematical analysis of Nafion®-internal ORMOSIL composition using NMR spectra

Percent weight uptakes for the TEOS/SOC combinations examined in this study are listed in Table 1. Percent ORMOSIL uptake as well as the internal co-monomer composition depend, in theory, on the coupled permeabilities of each co-monomer, the relative self- and cross-reactivities of the two monomers, and solvent type. With reference to Table 1, it is observed that the relative uptakes using TEOS-*co*-DEDMS and TEOS-*co*-TEVS are rather the same at ca. 20% across the composition range. The same relative constancy is true for TEOS-*co*-MTES combinations although the uptakes in this case are slightly smaller. Lower uptakes are seen for other monomer combinations. There is a monotonic decrease in percent uptake, for the TEOS/PTES system, from 19.5% for 1:0 down to 10.3% for the 0:1 composition. The TEOS/HQ system also displays this decreasing behavior. The largest uptake (24.2%) is that for the TEOS/MAPTES system for the 1:2 composition.

The following procedure was used to calculate the number of incorporated Q and D (or T) molecular subunits on a per sulfonate group basis. The mole fractions of Q and Y = D or T units in the membrane are given by the equations:

$$f_Q = Q/(Q + Y) \qquad f_Y = Y/(Q + Y) \tag{1}$$

where Q is the total area under all ^{29}Si NMR peaks in the Q region, and likewise for the peaks in the Y region.

The percent mass increase, O_{Q+Y}, relates net ORMOSIL mass to total membrane mass with no regard for the relative organic composition of the ORMOSIL phase. The ratio Q/Y, on the other hand, addresses relative internal ORMOSIL

Table 1
Weight percent ORMOSIL uptake of Nafion®-H membranes for the TEOS/SOC molar compositions shown in first column

	TEOS/DEDMS	TEOS/TEVS	TEOS/MTES	TEOS/PTES	TEOS/MAPTES	TEOS/DEMVS	TEOS/HQ
(1:0)	20.2	20.1	19.6	19.5	22.4	21.0	20.2
(2:1)	19.8	20.7	18.8	15.0	19.8	20.3	15.6
(1:1)	20.1	20.6	19.9	14.6	22.1	20.5	13.1
(1:2)	20.4	19.7	19.5	14.1	24.2	21.1	10.9
(0:1)	22.7	19.9	19.3	10.3	21.2	17.6	6.3

molar composition, but this number is not normalized relative to the concentration of an important functional group within the membrane, which we have chosen to be the sulfonate groups. An estimate of the average number of Q and D (or T) molecular subunits per sulfonic acid group can be made in the following way knowing the equivalent weight (EW) of Nafion®, which is the number of grams of polymer per equivalent of sulfonic acid groups.

The mass per mole of Q sub-units, averaged over the relative populations, $\{P_{Q_1}, P_{Q_2}, P_{Q_3}, P_{Q_4}\}$ of Q_1–Q_4 states is equal to:

$$\bar{m}_Q = \sum_{i=1}^{4} P_{Q_i} m_{Q_i} \tag{2}$$

where m_{Qi} is the formula weight for the given bonded substructure. For $Q_4 = Si(O_{1/2})_4$, $m_{Q_4} = 60.1$ g/mol, and for $Q_3 = (HO)Si(O_{1/2})_3$, $m_{Q_3} = 69.1$ g/mol, etc. The weighting factor P_{Q_i} is the relative area under the Q_i peak when the Q region is resolved into its component peaks:

$$P_{Q_i} = \frac{Q_i}{\sum_{j=1}^{4} Q_j} \tag{3}$$

Likewise, the mass per mole of bonded Y sub-units having the relative populations $\{P_{Y_1}, P_{Y_2}, P_{Y_3}, P_{Y_4}\}$ is:

$$\bar{m}_Y = \sum_{i=1}^{2 \text{ or } 3} P_{Y_i} m_{Y_i} \tag{4}$$

For example, consider the case where DEDMS is the semi-organic co-monomer. Then, $D_2 = (O_{1/2})_2Si(CH_3)_2$, $m_{D_2} = 74.1$ g/mol, $D_1 = (HO)(O_{1/2})Si(CH_3)_2$, $m_{D_1} = 83.1$ g/mol, etc. ^{29}Si NMR peaks for totally unreacted species (Q_0, D_0, T_0) have never been encountered in our analysis.

Finally, it is easily shown that the average numbers of moles of Q or Y units reduced to a per sulfonate group basis are given by the following equations:

$$n_Q = \frac{f_Q \mathrm{EW} O_{Q+Y}}{f_Q \bar{m}_Q + f_Y \bar{m}_Y} \tag{5}$$

$$n_Y = \frac{f_Y \mathrm{EW} O_{Q+Y}}{f_Q \bar{m}_Q + f_Y \bar{m}_Y} \tag{6}$$

We will present the results of applying these equations to selected cases after a discussion of the general features of the NMR spectra for all TEOS + SOC combinations. The computations are limited to those spectra that have noise/signal ratios that are so low that peaks that are anticipated at the characteristic chemical shift positions in Q, T or D regions obviously rise above the order of magnitude of noise fluctuations. Also, the D region for all pertinent hybrids is not visibly split into component peaks in contrast to the unmistakable peaks in the Q region. Single, reasonably symmetrical D peaks are present although it must be allowed that there is an underlying superposition of highly overlapping peaks. Similar comments can be made for T region peaks. In order to simplify the analysis at this approximate level of analysis, and given the present instrumental sensitivity coupled with less than-desirable Si concentration, only one D_n or T_n unit was used in the calculation of $\bar{m}_Y$, namely that for which the chemical shift is closest to the peak position.

3.2. Spectra and analysis of hybrids

3.2.1. DEDMS and TEVS semi-organic co-monomers

The spectra of the Nafion®/ORMOSIL hybrids based on TEOS–DEDMS and TEOS–TEVS co-polymerizations are in Fig. 2(a) and (b), respectively. The membrane-internal mole ratios of these as well as the other co-monomers, after the in situ sol–gel reactions, as calculated from these spectra using peak integration, are listed in Table 2. While some spectra have considerable noise due to low Si concentration, the signal-to-noise is high enough in most cases to permit clear identification of characteristic peaks in both the Q and D or T regions.

The spectra in Fig. 2(a) are typical of those observed in our earlier work on similar Nafion®/ORMOSIL hybrids based on TEOS and DEDMS co-polymerizations, but with methanol rather than ethanol as the solvent [5]. The 1:0 spectrum, which is that of a pure silicate phase incorporated in Nafion®, is characterized by a strong Q_4 peak with a shoulder in the Q_3 region. Aside from fine structural details, this indicates a relatively high degree of Si atom coordination about SiO_4 molecular subunits, but with a significant number of unreacted ≡SiOH groups. Our earlier IR spectroscopic investigations of Nafion®/silicate nanocomposites suggested that these residual silanol groups exist more toward nanoparticle ‘surfaces’ [15]. Given the amorphous nature and high surface/volume ratio for these nanostructures, it would be unreasonable to expect the spectrum to be of pure Q_4 character so that ≡SiOH groups will always be present to a degree depending on reaction conditions and

Table 2
Results of ^{29}Si solid-state NMR analysis of Nafion®-internal ORMOSIL relative molar composition vs. external TEOS/SOC molar ratio

TEOS/SOC External	TEOS/DEDMS Q/D	TEOS/TEVS Q/T	TEOS/MTES Q/T	TEOS/PTES Q/T	TEOS/MAPTES Q/T	TEOS/DEMVS Q/D
(2:1)	1.72:1	1.79:1	1.66:1	10:1	6.42:1	2.42:1
(1:1)	1:1	0.81:1	1:1.62	3:1	1:1.77	1:1.38
(1:2)	1:2.87	1:2.4	1:2.42	1.5:1	1:1	1:1.55

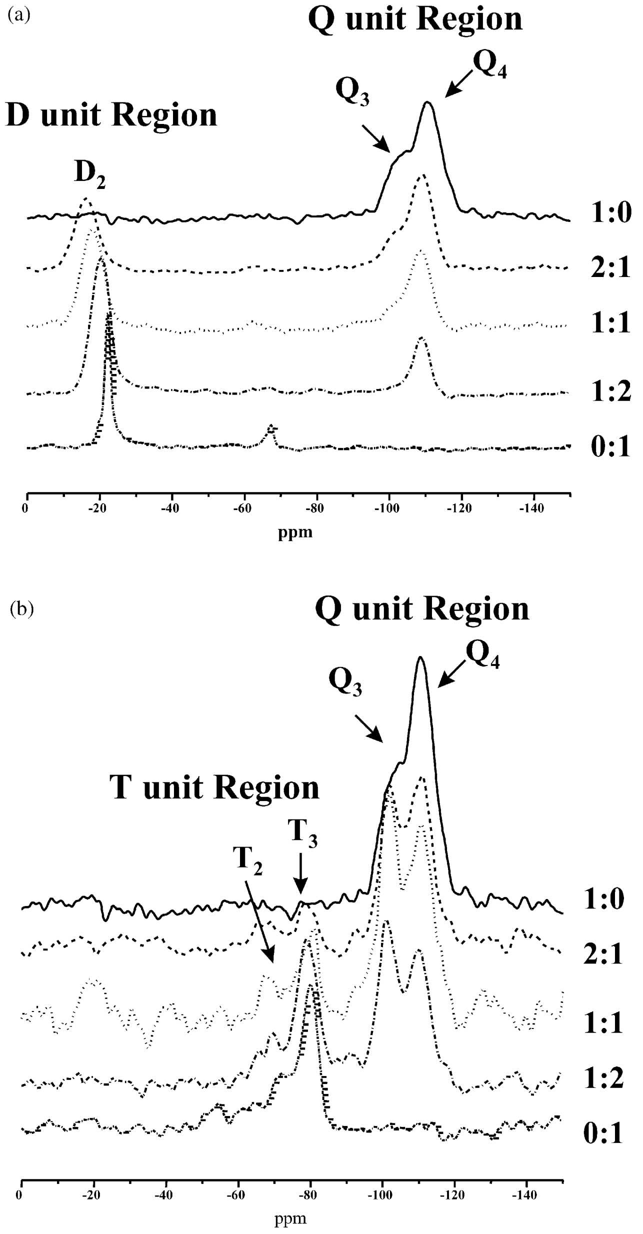


Fig. 2. ^{29}Si solid state NMR spectra for Nafion®/ORMOSIL hydrids based on (a) TEOS/DEDMS and (b) TEOS/TEVS co-monomer in situ reactions. The numbers to the right of each spectrum are the external TEOS/SOC mole ratios.

nature of the SOC, when present. The Q_3 shoulder is also present on the Q_4 peak for the 2:1 and 1:1, but not for the 1:2 composition. Apparently, $(H_3C)_2Si(OH)_2$ monomers, which are now in the majority, are more capable of coordinating around SiO_4 subunits in this particular molecular environment. Perhaps this is a consequence of the fact that the highly reactive DEDMS molecules react with TEOS molecules before the TEOS molecules react with themselves. There are no Q peaks for the 0:1 hybrid, and no D peak for the 1:0 hybrid, which is reassuring. As seen in Table 2, the total Q peak area monotonically decreases while that of the D peak increases in proceeding from the 2:1 to the 1:2 external solution composition. While the trend is essentially the same as that seen in our earlier studies, the internal Q/D is not equal to the external TEOS/DEDMS mole ratio, save for the 1:1 composition. The main difference between the two similar systems is that slightly different solvents (methanol vs. ethanol) were utilized. This difference might be significant to the point of affecting the relative permeabilities of TEOS and DEDMS. It is known, for example, that MeOH and EtOH swell Nafion® to different degrees.

The D unit peak exhibits a distinct rightward chemical shift (2:1, −16.1 ppm; 1:1, −17.9 ppm; 1:2, −20.6 ppm; 0:1, −22.1 ppm) with increasing percent DEDMS. As discussed in our earlier work [5], this shift indicates that random co-condensation of TEOS and DEDMS monomers, rather than Q and D block formation, has taken place. This is an important structural information that is roughly analogous to having a knowledge of monomer sequence distribution in linear copolymers. Based on the results of the ^{29}Si NMR studies of structures generated by sol–gel reactions in pure TEOS + DEDMS + ethanol solutions, of Babonneau et al. [13] there appear to be no unreacted DEDMS molecules present in our samples (at least in detectable quantities) because of the absence of a peak at ~4.9 ppm, and the chemical shift of the D units indicates total condensation. These investigators showed that, after drying a TEOS/DEDMS gel at 80 °C, the D peak had no discernible structure. In a related study of acid catalyzed sol–gel reactions for TEOS + DEDMS mixtures, Mah and Chung suggested that D^1 units are largely consumed through reaction with TEOS or other DEDMS molecules [16]. In fact, for the Nafion®-in situ sol–gel reactions in the study reported here, the distribution of chemical shifts in the D region in Fig. 2(a) is seen to be biased toward D^2. It should be realized that the spectra for these solid samples in which the concentration of Si is low by virtue of dilution in the Nafion® matrix (which accounts for the considerable noise/signal) is not expected to exhibit fine structure in the D region to the degree of identifying oligomeric species [17] as seen in ^{29}Si NMR spectra for simple liquid (pre-gel) systems that are not incorporated in a polymer matrix.

A graph of the average number of Q and D units per sulfonate group (n_Q, n_D), calculated as outlined earlier, is shown in Fig. 3 for the range of ORMOSIL composition. A rather organized decrease in n_Q as well as increase in n_D is apparent with decreasing TEOS/DEDMS. For the 1:0 composition, there are, on the average, 3.56 Q units for every sulfonate group. This, of course, does not imply that these many Q units are closely structured around a given SO_3H group at the end of the long perfluoroalkylether side-chains. At the other composition extreme (0:1) there are 3.37 D units per sulfonate group. It is interesting that this number for the inserted nanophase having the highest organic content is only slightly lower than that for the most polar nanophase. This might be accounted for by having the D units incorporated not toward the center of

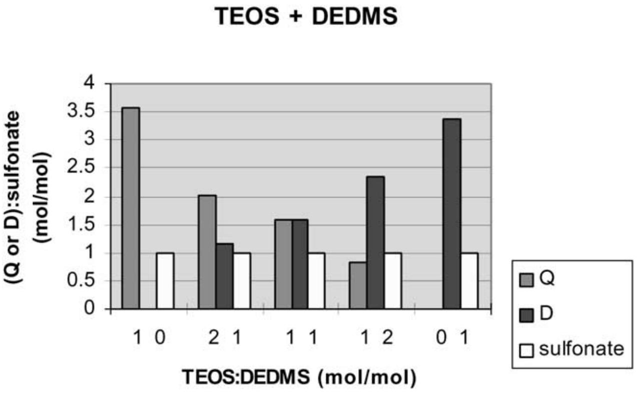


Fig. 3. Nafion®–internal ORMOSIL composition generated using TEOS + DEDMS co-monomers.

the cluster, but more so in the diffuse interphase regions in Nafion® that were discussed by Yeager et al. [18,19]

The spectra of the hybrids resulting from in situ TEOS + TEVS co-polymerizations (Fig. 2(b)) show the expected peaks in the Q and T unit regions. The tri-functional peak appears upon addition of TEVS (2:1 hybrid) although the noise is considerable in a few cases. As the fraction of TEVS increases, the Q_4 peak persists and is distinctive, but the Q_3 peak area becomes larger and eventually overtakes that of the Q_4 peak. Apparently, the degree of Si atom coordination about SiO_4 subunits is not as high as that for the previous case where the SOC is DEDMS. This result is at odds with the fact that, for acid-catalyzed sol–gel reactions in simple solutions, the addition of trifunctional silicon alkoxides to TEOS leads to an increase in the degree of condensation for the Q sites [10]. Again, with reference to Table 2, it is noted that the in situ Q/T ratio increases monotonically with the TEOS/TEVS ratio. Given the level of spectral noise, it is not possible to quantify chemical shift trends in the T region that might be associated with hetero-monomer condensation reactions although the 0:1 T_3 peak has a definite rightward displacement relative to the other T_3 peaks. Also, owing to the high noise/signal aspect, the calculation of n_Q and n_T was not performed for these hybrids.

3.2.2. MTES and PTES semi-organic co-monomers

The spectra for hybrids resulting from in situ TEOS + MTES and TEOS + PTES co-polymerizations are shown in Fig. 4(a) and (b), respectively. When pure TEOS and pure MTES are in situ-polymerized separately, there are no peaks in the T or Q regions, respectively, as expected. When MTES is added, a T peak, beginning with the 2:1 hybrid, appears and becomes stronger in relation to the total Q region peak area. While fine structure is not evident on this peak, the chemical shift distribution is in the region of T^3 [20]. Q_4 remains the predominant peak, although there is a strong Q_3 component. The in situ Q/T mole ratio increases with the increasing TEOS/MTES mole ratio in the external solution. However, the Q/T (internal) ratio is always less than TEOS/MTES (external). This fact suggests that MTES

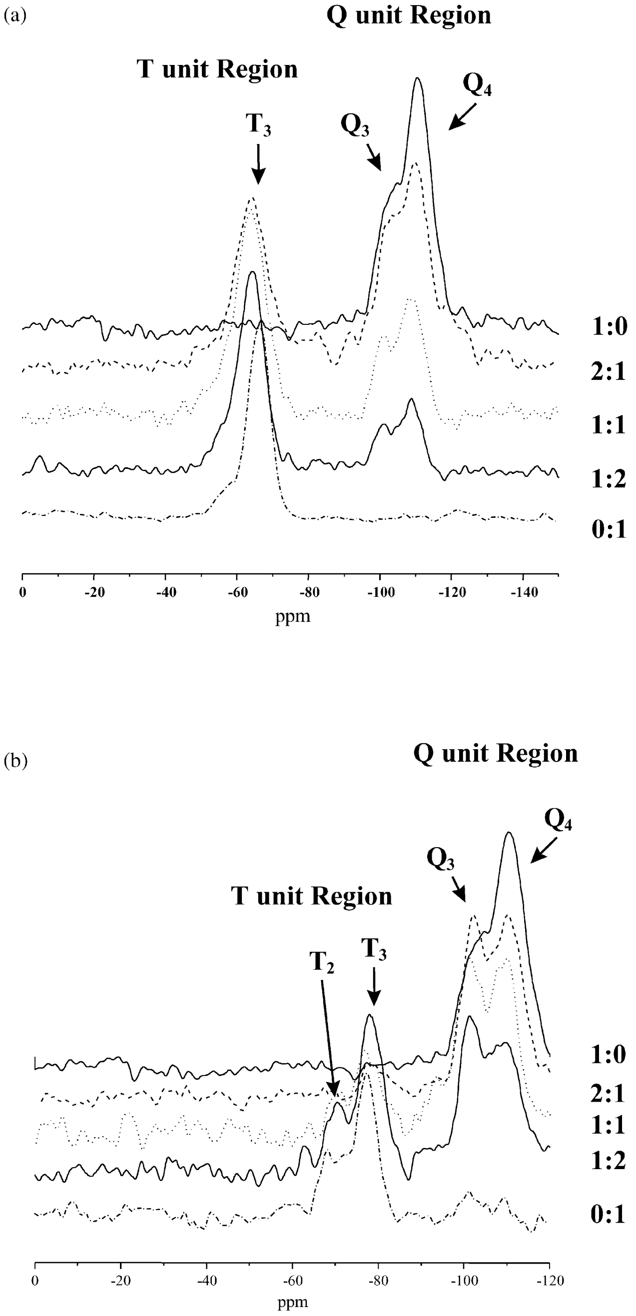


Fig. 4. ^{29}Si solid-state NMR spectra for Nafion®/ORMOSIL hybrids based on (a) TEOS/MTES and (b) TEOS/PTES co-monomer in situ reactions. The numbers to the right of each spectrum are the external TEOS/SOC mole ratios.

permeates Nafion® faster than TEOS. With reference to Fig. 5, there is a monotonic decrease in n_Q as well as an increase in n_T with decreasing TEOS/MTES. For the 0:1 hybrid there are, on the average, 3.16 T units per sulfonate group which is only somewhat smaller than $n_D = 3.37$ in the 0:1 hybrid when DEDMS is the SOC. In addition, there is a slight but perceptible shift in the T peak position with increasing MTES fraction, i.e. 2:1, −64.0 ppm; 1:1, −64.1 ppm; 1:2, −64.4 ppm; 0:1, −66.2 ppm). We suggest

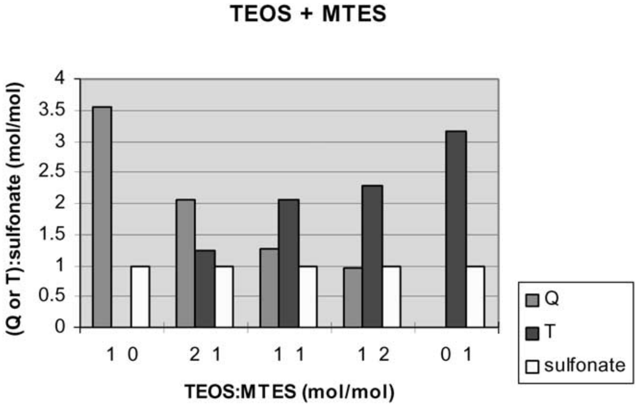


Fig. 5. Nafion®–internal ORMOSIL composition generated using TEOS + MTES co-monomers.

that this shift might reflect Q + T co-condensation rather than Q and T block formation, in the same sense as for Q + D polymerization as discussed earlier. The high resolution solid-state NMR correlation spectroscopy studies of gels produced from TEOS and MTES, by Fyfe et al., supports this concept [21,22]. These workers discovered that methyl groups were in the vicinity of Q_4 sites, which is in harmony with the idea of random co-condensation reactions between TEOS and MTES.

The spectra of hybrids based on Nafion®-in situ co-polymerizations of TEOS and PTES (Fig. 4(B)) show peaks in both Q and T unit regions as expected for reactions between tetra- and tri-functional species. While logically not present in the 1:0 spectrum, there is a distribution of T peaks for the 2:1 hybrid, and thereafter with increasing PTES fraction, and the T_3 state has a higher population than the T_2 state of coordination. The silicate structures in the 1:0 hybrid are predominantly Q_4 but there is also significant Q_3 character and as PTES fraction increases the Q_3 peak becomes stronger relative to, and in fact overtakes, the Q_4 peak height. This ultimate condition does not exist when MTES is the SOC. Perhaps this results from the greater steric hindrance posed by phenyl vs. methyl substituents on the SOC in the sense that PTES and its hydrolyzed versions must access the reactive sites on TEOS, its hydrolyzed species, and pure silicate silanol oligomers, with greater difficulty. With reference to Fig. 2(b), the same logic might apply to the similar behavior observed when TEVS is the SOC, although the steric difference between methyl and vinyl groups is not as pronounced as that between methyl and phenyl groups. It is noted in Table 2 that the internal Q/T ratio is much greater than 2 for the 2:1 hybrid and is less than 1 and 1/2 for the 1:1 and 1:2 hybrids, respectively. Moreover, on inspecting Table 1, it is seen that the net percent weight uptake is almost halved as %PTES increases. This would seem to indicate that PTES permeates the Nafion® membrane considerably slower than TEOS. The mathematical analysis of n_Q and n_T was not performed for these hybrids because of the appreciable level of noise/signal in the spectra.

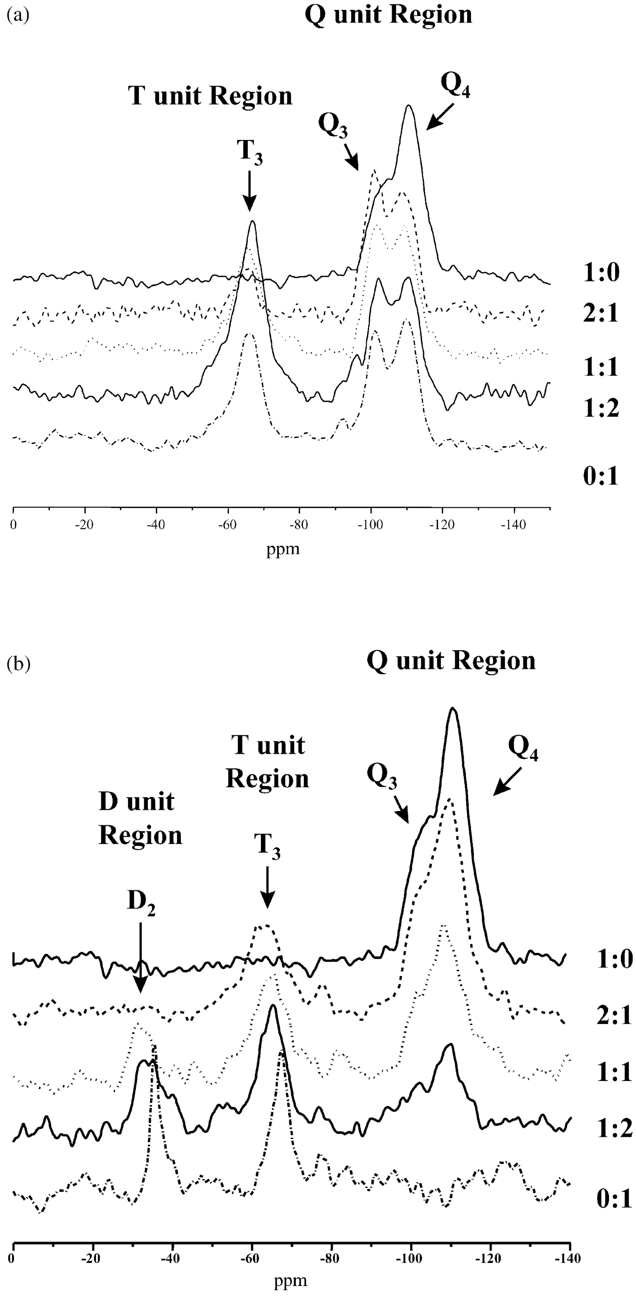


Fig. 6. ^{29}Si solid-state NMR spectra for Nafion®/ORMOSIL hybrids based on (a) TEOS/MAPTES and (b) TEOS/DEMVS co-monomer in situ sol–gel reactions. The numbers to the right of each spectrum are the external TEOS/SOC mole ratios.

3.2.3. MAPTES and DEMVS semi-organic co-monomers

The spectra for hybrids resulting from in situ TEOS + MAPTES co-polymerizations are shown in Fig. 6(a). As expected, there are both Q and T peaks for the 2:1, 1:1 and 1:2 hybrids and only Q, and only T peaks for the 1:0 and 0:1 hybrids, respectively, as expected. While Q_4 coordination predominates for the 1:0 hybrid, the Q_3 state becomes approximately equal in population with increasing MAPTES fraction in the external monomer source solution. There is no perceptible shift in the T_3 peak position. The

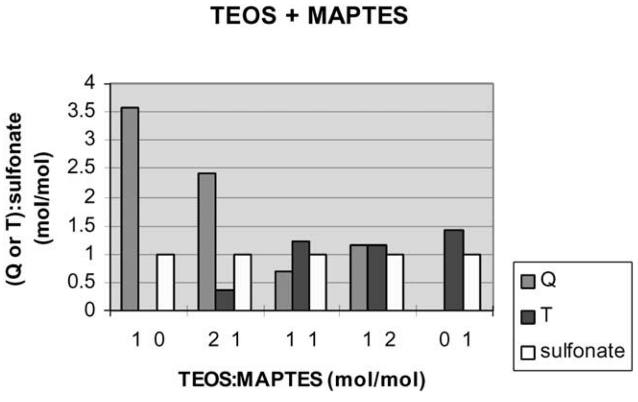
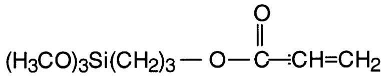


Fig. 7. Nafion®–internal ORMOSIL composition generated using TEOS + MAPTES co-monomers.

noise/signal in the spectra for these hybrids is sufficiently low so that the calculation of n_Q and n_T is meaningful, at least in a semi-quantitative sense, and the results are seen in Fig. 7. The previously observed monotonic progressions of decreasing n_Q and increasing n_T are not seen in the case of this SOC that has the following more complex structure that contains an ester and a vinyl group:



$$(H_3CO)_3Si(CH_2)_3-O-\overset{\overset{O}{\|}}{C}-CH=CH_2$$

The trends from left to right seems to be broken by the n_Q, n_T values at TEOS/MAPTES = 1:1. Also seen in Fig. 7 is the rather low value of $n_T = 1.41$ at the composition 0:1, which suggests a relatively lower affinity of Nafion® for this large SOC molecule.

The spectra for hybrids resulting from in situ TEOS + DEMVS co-polymerizations are shown in Fig. 6(b). As expected, there are peaks in both the Q and D unit regions. Noise/signal for the 2:1 hybrid is too high to ascertain di-functional D peaks although as more relative DEMVS is added, D resonances are evident, become stronger, and the chemical shift distribution monotonically shifts to the right in the progression 1:1 → 1:2 → 0:1. We suggest that this shifting behavior might be reflective of monomer co-condensation based on the rationalization of the similar behavior exhibited in the case of TEOS + DEDMS co-polymerization [5,13].

The Q region is most highly populated by Q_4 units although a distinctive Q_3 shoulder is present at all compositions, save for the 0:1 case, and the peaks decrease with increasing D content, as is reasonable. Here, again, noise/signal does not permit a meaningful calculation of n_Q and n_D, although this is frustrated by an additional complication which will now be discussed.

It is strange that there are strong T, or tri-functional peaks in all of the 2:1–0:1 spectra despite the fact that a tri-alkoxide monomer is supposedly not present. We are unaware of a reaction sequence at this temperature that would account for this fact. In consideration of the possibility of monomer source contamination, when different bottles of DEMVS and TEOS from different orders were used and the experiment was repeated twice in each case, the exact phenomenon was reproduced. Somehow, T units are created, although Si–C bonds are not easily cleaved under these conditions. It can be seen in Fig. 6(b) that there are no T resonances in the 1:0 spectrum, but they are present in the 0:1 spectrum so that it might be concluded that TEOS is not a major influence in this reaction. It is possible that the Si–C bond cleavage might be a consequence of an acid-catalyzed cleavage of the Si–vinyl bond, as reported in works of organosilicon chemistry. However, excess free acid was leached from the membranes before the in situ sol–gel reactions, and the only acid groups present would be the fixed SO_3H groups. Comparison of internal Q/D ratios with the corresponding external MVDES/TEOS ratios in Table 2 does not provide any insight. Reactions that convert D units into T units are in fact possible but at high temperatures. For example, when a gel produced by a sol–gel reaction between TEOS and DEDMS (1:1) was heated to 500 °C, the D unit peak decreased while a T unit peak appeared [13]. It is seen in Table 1 that the percent uptakes of all the hybrids are approximately equal, except for the 0:1 case, for which it is lower.

3.2.4. Hydroquinone co-reactant

The spectra for hybrids based on possible reactions between TEOS and hydroquinone are shown in Fig. 8.

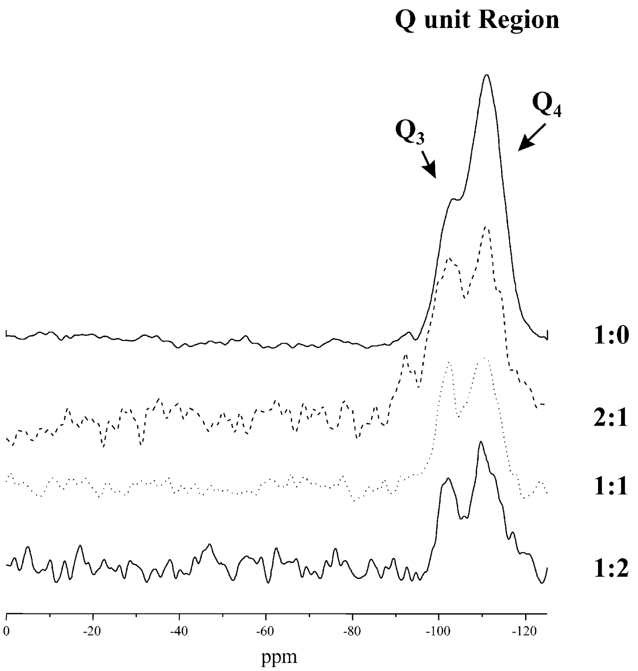


Fig. 8. ^{29}Si solid-state NMR spectra for Nafion®/silicate hybrids based on in situ sol–gel reactions for TEOS as modified by the presence of hydroquinone at different levels. The numbers to the right of each spectrum are the external TEOS/HQ mole ratios.

While HQ is not an alkoxide, its use was motivated by our earlier work involving poly[(ether–ether-sulfone)-*co*-(ether sulfone)]/silicate microcomposites that were created via sol–gel reactions for TEOS. In this prior work, evidence for reactions between phenolic polymer endgroups and TEOS was presented, so it was thought that perhaps HQ might react with TEOS in the same way [23]. As HQ is not a silane, it will not have a ^{29}Si NMR spectral signature. However, successful reactions might be implied by the fact of the perturbations of the chemical shift distribution seen in the Q region relative to the distribution for the non-HQ-containing 1:0 hybrid. In fact, such shifts are quite evident for the 2:1, 1:1 and 1:2 hybrids in Fig. 8. Evidently, HQ molecules interfere with condensation reactions between $(RO)_{4-x}Si(OH)_x$ molecules and silanol oligomers resulting in silicate structures with lower average coordination because the Q_3/Q_4 peak ratio has increased. It is impossible to ascertain whether this is due to actual reactions between HQ and TEOS molecules or whether HQ simply hydrogen bonds with SiOH groups in such a way as to block reactions between $(RO)_{4-x}Si(OH)_x$ molecules to some extent. A rationalization of the spectral trend would also have to account for the fact that the net percent mass uptake of the HQ-modified silicate phase monotonically decreases with decreasing TEOS/HQ mole ratio, as seen in Table 1.

4. Conclusions

Seven different Nafion®/ORMOSIL hybrid membrane compositions were analyzed using ^{29}Si solid-state NMR spectroscopy. Nafion®-in situ sol–gel co-polymerizations of TEOS and semi-organic $R'_nSi(OR)_{4-n}$ monomers can yield a diversity of chemical nanostructures owing to differences in Si atom coordination about SiO_X subunits as well by the insertion of various non-hydrolyzable organic moeities, some of which contain polar, phenyl and vinyl groups.

TEOS and SOC in situ co-polymerization can result in a high average degree of Si atom coordination about SiO_4 molecular subunits, but a significant number of unreacted ≡SiOH groups on Q units are always present. In some cases, the shifting, with relative ORMOSIL composition, of the D or T peak envelopes for difunctional or tri-functional, respectively, SOCs is suggested to reflect random co-condensation of the two different monomers rather than Q and D (or T) block formation. The numbers of membrane-incorporated Q and D (or T) units per fixed sulfonate group were calculated from the ^{29}Si NMR spectra for those hybrids having a reasonably low noise/signal aspect. This information on relative composition is significant because if TEOS and SOC units are polymerized within the sulfonate aggregates, the sulfonate groups will strongly contribute to the polarity within these nanoscopic environments. The spectra for hybrids based on in situ sol–gel reactions for TEOS suggest that the hydroquinone molecules, when present, interfere with condensation reactions between $(RO)_{4-x}Si(OH)_x$ molecules and silanol oligomers so as to result in silicate structures with lower average coordination.

The significance of these studies is that, while earlier SAXS studies showed that the chemical composition, in a general sense, of Nafion® cluster domains can be altered via the insertion of ORMOSIL nanostructures, the exact compositions were unknown until the results reported here were obtained. This nanoscopic chemical information, in turn, will be critical in efforts aimed at tailoring these unique membranes for desired gas or liquid transport properties.

Acknowledgements

This work was partly supported by a grant from the National Science Foundation/Electric Power Research Institute (DMR-9211963) as well as the Air Force Office of Scientific Research, Air Force Systems Command, USAF (AFSOR F49620-93-1-0189) and the Mississippi EPSCoR program (NSF#OSR-9553355). The donation of Nafion® membranes by E.I DuPont de Nemours and Co. is appreciated.

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