molecules 1984, 17, 2881. (f) Gordon, J. E. J. Phys. Chem. 1962, 66, 1150. (g) Mikes, F.; Strop, P.; Tuzar, Z.; Labsky, J.; Kalal, J. Macromolecules 1981, 14, 175. (h) Strop, P.; Mikes, F.; Kalal, J. J. Phys. Chem. 1976, 80, 694.
(4) (a) Guyot, A.; Bartholin, M. Prog. Polym. Sci. 1982, 8, 277. (b) Heitz, W. Adv. Polym. Sci. 1977, 23, 1. (c) Funke, W. Chimia 1968, 22, 111. (d) Sherrington, D. C. In Polymer-Supported Reactions in Organic Synthesis, Hodge, P., Sherrington, D. C., Eds.; Wiley: New York, 1980; Chapter 1.
(5) (a) Beavan, S. W.; Hargreaves, J. S.; Phillips, D. Adv. Photochem. 1979, 11, 207. (b) Chapoy, L. L.; DuPré, D. B.; Biddle, D. Dev. Polym. Charact. 1986, 223. (c) Tanizawa, K.; Kanaoka, Y.; Lawson, W. B. Acc. Chem. Res. 1987, 20, 337. (d) Weber, G. Biochem. J. 1952, 51, 155. (e) Himel, C. M.; Mayer, R. T.; Cook, L. L. J. Polym. Sci., Polym. Chem. Ed. 1970, 8, 2219.
(6) (a) Shea, K. J.; Stoddard, G. J.; Sasaki, D. Y. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 1986, 27(2), 344. (b) Shea, K. J.; Okahata, Y.; Dougherty, T. K. Macromolecules 1984, 17, 296. (c) Shea, K. J.; Sasaki, D. Y.; Stoddard, G. J. Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 1987, 28(2), 88. (d) Shea, K. J.; Stoddard, G. J.; Sasaki, D. Y. ACS Symp. Ser. 1987, No. 358, Chapter 9.
(7) Shea, K. J.; Stoddard, G. J.; Sasaki, D. Y., submitted for publication in Macromolecules.
(8) Leebrick, J. R.; Ramsden, H. E. J. Org. Chem. 1958, 23, 935.
(9) Mendel, A. J. Chem. Eng. Data 1970, 15, 340.
(10) Blasius, E.; Lohde, H. Talanta 1966, 13, 701.
(11) Collins, E. A.; Bares, J.; Billmeyer, F. W., Jr. Experiments in Polymer Science; Wiley-Interscience: New York, 1973; p 357.
(12) Shea, K. J.; Dougherty, T. K. J. Am. Chem. Soc. 1986, 108, 1091.
(13) (a) Li, Y.-H.; Chan., L.-M.; Tyer, L.; Moody, R. T.; Himel, C. M.; Hercules, D. M. J. Am. Chem. Soc. 1975, 97, 3118. (b) Chen, R. F. Arch. Biochem. Biophys. 1967, 120, 609. (c) Chen, H.-L.; Morawetz, H. Macromolecules 1982, 15, 1445. (d) Strauss, U. P.; Vesnaver, G. J. Phys. Chem. 1975, 79, 2426.
(14) Kamlet, M. J.; Abboud, J. L. M.; Taft, R. W. Prog. Phys. Org. Chem. 1981, 13, 485.
(15) Taft, R. W.; Abboud, J. L. M.; Kamlet, M.; Abraham, M. H. J. Solution Chem. 1985, 14, 153.
(16) Lloyd, W. G.; Alfrey, T., Jr. J. Polym. Sci. 1962, 62, 301.
(17) Millar, J. R. J. Polym. Sci., Polym. Symp. 1980, 68, 167.
(18) (a) Millar, J. R.; Smith, D. G.; Marr, W. E.; Kressman, R. E. J. Chem. Soc. 1963, 218. (b) Howard, G. J.; Midgley, C. A. J. Appl. Polym. Sci. 1981, 26, 3845.
(19) (a) Albright, R. L. React. Polym., Ion Exch., Sorbents 1986, 4, 155. (b) Sederel, W. L.; DeJong, G. J. J. Appl. Polym. Sci. 1973, 17, 2835.
(20) (a) Sherrington, D. C. Nouv. J. Chim. 1982, 6, 661. (b) Jacobelli, H.; Bartholin, M.; Guyot, A. Angew. Makromol. Chem. 1979, 80, 31.
(21) Mayo, F. R. J. Am. Chem. Soc. 1943, 65, 2324.
(22) Gregg, R. A.; Mayo, F. R. Discuss. Faraday Soc. 1947, 2, 328.
(23) Gregg, R. A.; Mayo, F. R. J. Am. Chem. Soc. 1953, 75, 3530.
(24) (a) Wieczorek, P. P.; Kolarz, B. N.; Galina, H. Angew. Makromol. Chem. 1984, 126, 39. (b) Kolarz, B. N.; Wieczorek, P. P.; Wojaczynka, M. Angew. Makromol. Chem. 1981, 96, 193.
(25) Colvin, H. A.; Muse, J. CHEMTECH 1986, 500.
(26) Hild, G.; Okasha, R. Makromol. Chem. 1985, 186, 389.
(27) Pseudo-first-order rate constants for the hydrolysis of monoketal i were determined spectrophotometrically.
(28) The pseudo-first-order rate constants in $MeOH/H_2SO_4$ and THF/H_2SO_4 are 3×10^{-3} and 6×10^{-5} s^{-1}, respectively.

Microstructural Evolution of a Silicon Oxide Phase in a Perfluorosulfonic Acid Ionomer by an in Situ Sol–Gel Reaction. 1. Infrared Spectroscopic Studies

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ABSTRACT: Unique microcomposite membranes have been produced via the sol–gel reaction for silicon tetraethoxide within the microphase morphology of hydrated perfluorosulfonic acid films. FT-IR spectroscopy has been used to monitor the aspects of molecular organization within the invasive gel as a function of silicon oxide content. We have assigned five of the major peaks to characteristic group vibrations based on an assessment of prior experimental infrared studies of various siloxanes, silicates, and silicas as well as theoretical vibrational analyses of these systems. Our spectral analysis depicts an evolving ≡Si—O— network that grows to become increasingly less interconnected but more strained. The broadness of the peaks suggests a gel microstructure that is considerably heterogeneous.

Introduction

In a recent report, Mauritz et al. outlined a simple method for producing unique microcomposite membranes by the in situ growth of a silicon oxide phase in hydrated perfluorosulfonic acid films (Nafion, E. I. du Pont de Nemours & Co.) via the acid-catalyzed sol–gel reaction for tetraethoxysilane (TEOS) that was allowed to diffuse into the films from external alcohol solutions.[1] After immersion in these solutions for prescribed times, the membranes were carefully dried/annealed to optimize the network connectivity of the incorporated gel component by condensation involving unreacted OH groups. Throughout these studies, our primary working hypothesis has been that the resultant morphology of the silicon oxide phase will be ordered by the prior established three-dimensional pattern of phase separation, having periodicity on the scale around 50 Å. It is in fact convenient, if not fortuitous, that small-angle X-ray scattering studies of acid-catalyzed silica produced via the sol–gel route yield a radius of gyration of 15–17 Å, i.e. silicate clusters having a natural size that is quite close to that of the Nafion polar clusters in which we expect them to grow.[2] We tend to exercise caution in referring to the in-growths as "silica gel" in the usual sense as we expect this microphase to be rather finely dispersed throughout the polymer matrix so as to possess a very high surface-to-volume ratio and have a comparatively high population of nonbridging oxygens and low degree of cyclization. Presently, therefore, we choose to use the term "silicon oxide", pending more definitive structural characterization.

The trend of mechanical tensile properties versus solids uptake includes a ductile-to-brittle transformation that

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might reflect $(\equiv Si-O)_n$ percolation throughout the polymer in addition to the steady growth of separated silicon oxide clusters.

FT-IR and ^{29}Si NMR studies indicate an in situ network that is not as cross-linked as sol–gel-derived free silica and actually becomes less coordinated and less connected with increasing gel content.[1]

Our initial infrared spectroscopic studies of microcomposites prepared from 5 mil thick 1200 equiv wt (EW) Nafion membranes were intended to identify significant incorporated silicon oxide microstructural fingerprints as well as monitor microstructural evolution with increasing gel content on a rather qualitative level. The main features identified on ATR difference spectra were the following bands which were quite broad and shifted, indicative in itself of microstructural heterogeneity. The absorbance of the Si–O–Si asymmetric stretching vibration (ν_a(SiOSi), ca. 1020–1040 cm^{-1}) provides a measure of the degree of network polymerization, whereas the absorbance of the Si–OH stretching vibration (ν(Si–OH), ca. 930–940 cm^{-1}) quantifies the population of unreacted OH groups. The symmetric stretching vibration of the Si–O–Si group (ν_s(SiOSi), ca. 800 cm^{-1}) is theoretically infrared-inactive but present in the spectrum presumably owing to considerable distortion from coordinative symmetry of bonding to silicon atoms.

Of particular interest is the observation that ν_a(SiOSi) often appears as a superposition of at least two discrete peaks indicating Si–O–Si groups involved in different bonding arrangements, examples being linear chains, branches, or loops of various sizes.

In this paper, we report the results of a more extensive and quantitative FT-IR analysis of Nafion-based microcomposites produced in this way. The samples utilized in this more recent study were of 1100 rather than 1200 EW. While the spectra are comparatively similar, we have chosen to report the investigations separately, first because the different equivalent weights would impart different degrees of crystallinity and swelling capacities, and second because possibly different thermal processing conditions for the two films may have affected structural differences, the affect of which might be difficult to evaluate.

In addition to the prior infrared studies of pure sol–gel-derived free silica cited in our earlier paper (Prassas and Hench, Yoldas and Partlow[1]) there have been other spectroscopic analyses of simpler model systems that provide guidance in the attempt to assign structural aspects to spectral features on a finer level for the more complex silicon oxide/Nafion microcomposites. Bell and Dean[4] constructed physical models of *vitreous* silica that were consistent with the fundamental precepts of the random network theory originated by Zachariasen:[3] (a) 4-fold and 2-fold coordination about silicon (with regular tetrahedral symmetry) and oxygen atoms, respectively; (b) all bond lengths and O–Si–O bond angles being fixed at their normal values but with (c) a considerable spread about the average Si–O–Si bond angle; (d) no long-range order; (e) no unconnected bonds in the interior.[4,5] While the radial distribution functions generated using the atomic positions derived from this model (containing 614 atoms) were in good agreement with those derived from X-ray or neutron diffraction experiments on *vitreous* silica, the detailed structural aspects of the Bell and Dean model network should not be considered as representative of the silicon oxide structures incorporated within Nafion ionomers via the sol–gel reaction. To begin with, the model requirement (condition e) of no nonbridging oxygens in the network interior is obviously violated by the spectroscopic evidence we have presented to date and will further reinforce in this report.

Nonetheless, Bell and Dean have considered important topological parameters that are also quite relevant in the analysis of the molecular network statistics of our systems. The distribution of Si–O–Si bond angles is one such characteristic and has already been discussed. Another consideration in the statistical characterization is the distribution of molecular loops of different sizes. Bell and Dean have stated that the loop size distribution is strongly dependent on the constructed size of the network model. While these statistics, necessarily extracted from finite atomic arrays, may not in fact represent a realistic feature of the molecular topology of macroscopic networks, particularly in assessing the population of large loops, the concept of loop counting is realistic and practicable within the context of the small clustered networks confined within nanometer-in-scale dimensions within the polar regions of ionomers. The model statistics show a rough correlation between the distributions of Si–O–Si bond angle, loop size, and degree of loop puckering. Puckering, for example, tends to decrease this angle on the average.

In the experimental realm, Wright and Hunter investigated infrared spectral differences between cyclic and linear methylpolysiloxane structures.[6] It was seen that for cyclic tetramers through octamers ν_a(SiOSi) decreases from 1076 to 1056 cm^{-1}. These peaks appear at slightly lower wavenumbers for the corresponding linear molecules and are also monotonically shifted to lower wavenumbers with increasing chain length. On the strength of the band assignments reported for these well-defined model systems, as well as those discussed by Yoldas and Partlow and Prassas and Hench for the more complex sol–gel-derived free silica systems, we are motivated to attribute the distinct peak splitting in the ν_a(SiOSi) region for the Nafion/silicon oxide microcomposite membranes to a discrimination between cyclic and linear substructures. Bell and Dean and co-workers having performed theoretical vibrational analyses of glasses, including vitreous silica, based on the aforementioned physical models, stressed that the characteristic modes are not in fact highly localized in space.[7-9] These workers have also pointed out that the group mode assignments they made, described as "stretching", "bending", and "rocking" vibrations are actually rough approximations to the overall effect of the calculated atomic displacement eigenvectors. This conclusion regarding localization was reinforced by a later theoretical analysis by Brawer,[10] who also deduced that vibrational peaks become broader with increasing structural disorder. It therefore seems fundamentally reasonable to expect a vibrational differentiation between Si–O chains in cyclic versus linear configurations. Bell and Dean, however, considered the Si–O stretching mode associated with nonbridging oxygens to be highly localized and basically insensitive to its placement in the molecular network. On the other hand, our spectra of Nafion/silicon oxide microcomposites (Figure 2) indicate that this band can in fact be rather broad, which suggests a considerable distribution of local environment about Si–OH groups.[1] Brawer points out that in alkali-silicate glasses SiO_4 tetrahedra are distorted as a rule and that the width of the nonbonded Si–O peak (ca. 950 cm^{-1}, Raman and IR-active) for these systems can be increased *only* by tetrahedral distortion. If this rule can be transferred to the silicon oxide microstructures dispersed in Nafion, we are led to believe that considerable deviation from coordinative symmetry about silicon atoms exists therein, which is also in harmony with the results of our ^{29}Si solid-state NMR

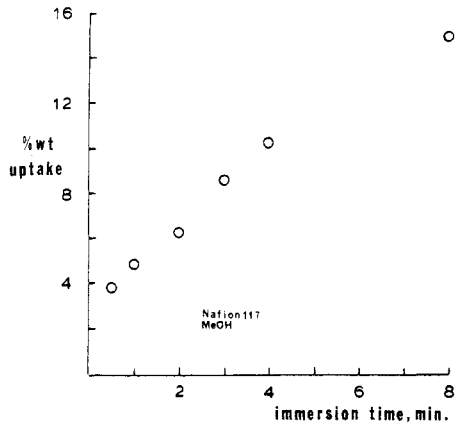

Figure 1. Net silicon oxide percent dried weight uptake versus time of immersion of hydrated Nafion sulfonic acid membranes in TEOS/MeOH solutions.

investigations of these systems.

Finally, the width of the peak corresponding to the Si–O–Si bending mode, centered at around 450 cm^{-1}, should be sensitive to the distribution of Si–O–Si bond angles, which, according to the physical model of Bell and Dean, is necessarily broad. A few comments on this band are in order. While we have largely accepted the term "bending" from the reports of prior infrared studies of silicates[11] and sol–gel-derived silica[12] and are aware that quartz displays a vibration in the vicinity of 400 cm^{-1} assigned to Si–O–Si bending,[13,14] an element of confusion regarding this band arises from the earlier remarks of Bell and Dean and co-workers based on their theoretical analyses of vitreous silica.[7-9,15] This rather large peak has been attributed, by these workers, to a bond-rocking vibration wherein the oxygen atoms move roughly perpendicular to the Si–O–Si planes. Within the framework of their model, this mode was quite delocalized throughout the entire structure. Aside from the vibrational mode difference (i.e., rocking rather than bending), it was stated that, as rocking modes are comparatively less sensitive than stretching or bending to bond angle variations, this band should not be greatly influenced by Si–O–Si angular disorder. While we are not prepared to offer a resolution to this confusion, we tentatively feel that our results at least indirectly favor the bending mode interpretation.

Experimental Section

The details of microcomposite membrane preparation by the in situ sol–gel reaction in initially hydrated and alcohol-containing Nafion sulfonic acid films that were immersed in TEOS/alcohol solutions for prescribed times have been reported earlier.[1] While the treatments were identical, the membranes used in the present study were of 1100 rather than 1200 equiv wt and 7 rather than 5 mil in nominal thickness. As before, the initial water/TEOS mole ratio was fixed at 4. All membranes discussed in this paper were prepared with methanol solvent. The percent weight uptakes of the final annealed–dried samples were determined for immersion times from 0.5 to 8 min and are depicted in Figure 1.

FT-IR–ATR subtraction spectra (microcomposite—dry sulfonic acid form) were obtained for the various solids uptakes by using a Nicolet 5-DX instrument and a KRS-5 ATR plate as described in an earlier communication. A total of 1000 interferograms were taken in each case. As discussed in our earlier work,[1] films of this thickness had to be studied in reflectance mode out of necessity because of their high infrared absorbance in transmission. We also commented therein that our limited FT-IR studies of sufficiently thin (ca. 1 mil) films in transmission show spectra that are, in fact, quite similar to the ATR spectra. The multiplicity and complexity of infrared bands displayed by the Nafion matrix taken by itself, some of which are inconveniently located in close proximity to the superimposed peaks characteristic of silicon oxide

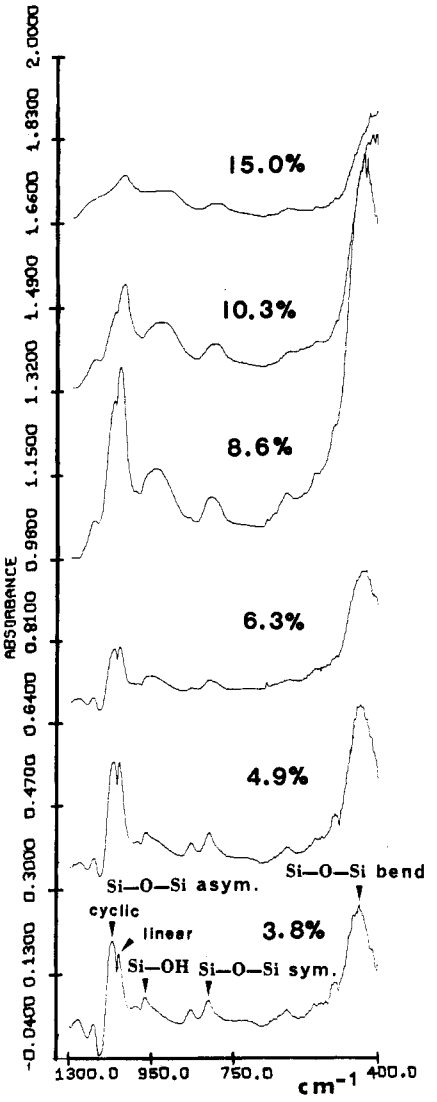

Figure 2. FT-IR (ATR) difference spectra, with vibrational band assignments, of Nafion-based microcomposites having indicated silicon oxide percent weight uptakes. Successive spectra have been vertically displaced but have the same absorbance scale.

structures, necessitates a subtraction of the spectra of pure Nafion from the spectra of the composites to simplify the structural analysis of the in situ grown inorganic phase. The Nafion contribution to the composite spectra was subtracted in each case using the strong ~1200-cm^{-1} band (SO_3^- stretch) as an internal thickness standard in these studies. Membranes of various thicknesses were not available to test absorbance versus thickness linearity, and while this band may not be an ideal internal standard, the resultant subtractions are effective in enhancing the silicon oxide related peaks.

Results and Discussion

It is seen in Figure 1 that the weight uptake increases very uniformly with immersion time, as in our identical experiments with 1200 EW membranes.[1] A more detailed comparison shows that, for the same immersion time, the solids uptake is lower for the higher equivalent weight membranes. This fact might be rationalized in terms of the greater degree of crystallinity and lower swellability of the 1200 EW samples.

In Figure 2 are displayed IR subtraction spectra for dried–annealed microcomposites having the indicated silicon oxide weight percents. We have, at least tentatively, assigned the positions of five of the major peaks to group vibrations based upon the prior IR studies that were earlier discussed in the Introduction.

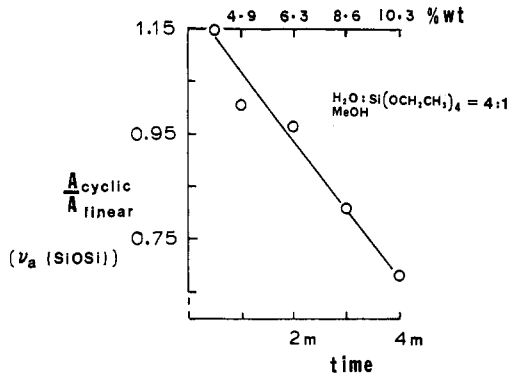

Figure 3. Asymmetric Si–O–Si stretch cyclic/linear absorbance (A) component ratio for microcomposites versus silicon oxide solids percent weight uptake and immersion time.

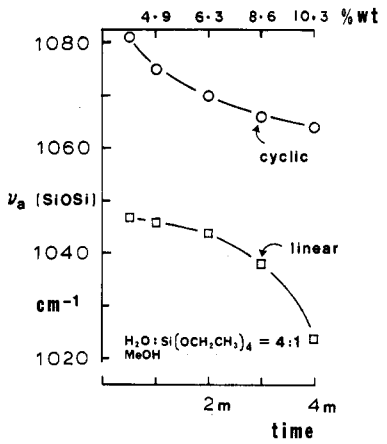

Figure 4. Positions of high (cyclic) and low (linear) wavenumber components of the ν_a(Si–O–Si) peak versus silicon oxide percent weight uptake/immersion time.

First, consider the asymmetric Si–O–Si stretching vibration. This band appears as a distinct doublet whose low wavenumber component steadily increases in absorbance relative to the absorbance of the high wavenumber component. If the high and low wavenumber components are identified with Si–O–Si groups involved in cyclic and linear structures, respectively, then Figure 3 quantitatively depicts an in situ network that is evolving to have increasingly less chain connectivity, i.e., fewer loops. The quantity plotted in Figure 3 is the ratio of the cyclic:linear component absorbance peak heights. Owing to the considerable overlap of these peaks, deconvolution of the spectra in this region would need to be performed in order to compare the integrated absorbances of each. Nonetheless, these component peaks do appear to be rather sharp and symmetrical and the implications from the trend of the absorbance ratio with increasing silicon oxide content, given the above structural interpretation, are clear and represented in Figure 3 on at least a semiquantitative basis. Furthermore, in Figure 4 it is seen that both the "cyclic" and "linear" peak positions monotonically shift to lower wavenumbers with increasing silicon oxide content, although the former curve is concave upward while the latter is concave downward. This behavior might possibly reflect an overall softening of the Si–O force constant resulting from bond distortions within a progressively strained network.

The symmetric Si–O–Si peak position evolves in similar fashion as seen in Figure 5 and the same comments regarding geometric distortion might apply. It is also noted in Figure 2 that this band becomes considerably broader, perhaps being reflective of increasing local molecular environmental heterogeneity within the silicon oxide phase.

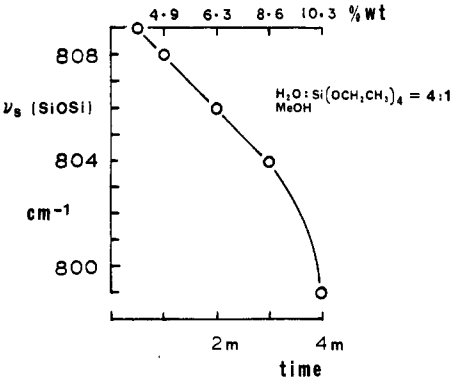

Figure 5. ν_s(Si–O–Si) versus silicon oxide percent weight uptake/immersion time.

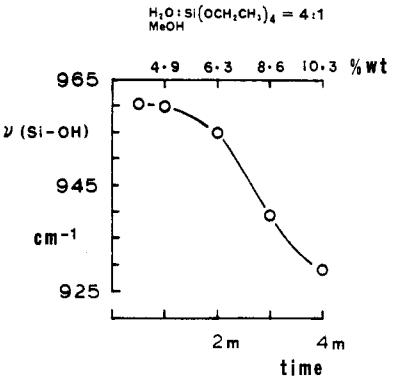

Figure 6. Si–OH stretching vibrational peak position versus silicon oxide percent weight uptake/immersion time.

The peak position for Si–OH stretching considerably shifts in monotonic fashion to lower wavenumbers with increasing gel content, as depicted in Figure 6, while its width, seen in Figure 2, increases greatly. It can be seen, on simple inspection, that the integrated absorbance of this band relative to that corresponding to the overall asymmetric Si–O–Si stretching is lower in the earlier stages than in the later stages of invasive gel development, as also noted in our earlier report.[1] We feel that these results are consistent with the picture of an evolving molecular network that becomes more strained while less interconnected.

Lastly, the Si–O–Si bending peak is seen as very strong and appears rather broad. Assuming our tentative assignment to be correct, the latter aspect may be reflective of a considerable distribution of Si–O–Si bond angles.

General Conclusions

We have monitored the microstructural evolution of a silicon oxide gel phase within a hydrated perfluorosulfonic acid ionomer, affected by the in situ hydrolysis of silicon tetraethoxide and subsequent polycondensation, using FT-IR spectroscopy. The results, in addition to providing strong reinforcement of the then-tentative interpretation of our initial structural studies of these microcomposites, have yielded a more detailed level of understanding molecular organization within the invasive $(\equiv Si—O)_n$ network.

As in our previous experiments with 1200 EW membranes, we have seen that for the 1100 EW membranes used in this study our specific composition of reactants and solvent and experimental procedure for the diffusion-controlled uptake of TEOS, as well as final annealing–drying step, the net solids uptake can be controlled rather well.

The infrared analysis of these microcomposites, in harmony with the interpretation of our earlier solid-state

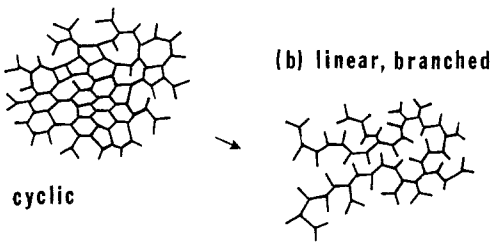

Figure 7. Hypothetical illustrations of regions of two-dimensional, three-coordinated networks that are (a) highly cyclized and (b) linear with some branches.

^{29}Si NMR results, portrays an evolving silicon oxide network that becomes increasingly less interconnected, that is, one having a progressively lower degree of cyclization and increasingly more chain linearity on the average. In Figure 7 are rough schematic representations of regions of networks that are (a) highly cyclized and (b) basically linear with a degree of branching throughout. These simplistic, two-dimensional, three-coordinated structures do not, of course, incorporate bridging oxygens, valence bond geometry, or atomic van der Waals sizes as present in a silicon oxide structure but are presented here to illustrate our general concept of a cluster-incorporated network that evolves to be increasingly less cross-linked. Furthermore, it would seem that considerable bond-angular distortions within the gel molecular framework, involving both the Si–O–Si and O–Si–O valence angles, are present and become more severe as the network grows. We have seen in our initial computer simulations of the statistical growth of nanometers-in-size silicon oxide particles, executed subject to the assumptions of the random network theory and stereochemical size considerations for bonded Si and O atoms, that the increasing competition for space between added SiO_4 units would lead to a network that necessarily becomes strained until discrete particle growth is impossible.[16] It is significant and should be stressed that the ultimate growth limitation predicted by our computer model is quite unlike the familiar bond crowding problem that develops at the boundary of a Cayley tree,[17] which at first sight might appear to be a rough model for an acid-catalyzed, sol–gel-derived network structure. Quite the contrary, our model predicts a density of matter that in fact decreases as one proceeds from the center of the cluster owing to a cumulative error in atomic packing efficiency as per random polymerization with appropriate valence bond geometry and atomic radii requirements. To be sure, the broadness of the infrared peaks suggests a gel microstructure that is, at the least, heterogeneous.

In our earlier work,[1] we proposed the simple concept that silicon oxide clusters initially exist in isolation but eventually become inter-knitted by polycondensation at high solids loadings and that this idea was at least indirectly supported, although certainly not proven, by our mechanical tensile studies, which suggested that the incorporated gel eventually becomes the load-bearing phase. We currently feel that this is an issue for which infrared spectroscopy is ill-equipped to address. If it were true, for example, that all unreacted OH groups resided at the gel/Nafion interface, then morphological inferences, similar to those we had proposed in our earlier report of IR studies of aqueous alkali hydroxide containing Nafion membranes,[18] might be possible. There is presently no evidence that this is a good assumption.

We are currently monitoring the long-range electrical conductance as well as silicon oxide/ionomer interfacial polarization aspects of these microcomposites by using dielectric relaxation spectroscopy. Our earlier dielectric relaxation investigations of Nafion membranes imbibed with a variety of concentrated electrolytes[19,21] strongly suggested that these measurements are sensitive to details of microphase separation at this scale, including intercluster connectivity, and we are encouraged to believe that this method will also yield similar morphological information for the microcomposite membranes.

We have recently demonstrated that a new class of microcomposite membranes, based upon the rational morphological tailoring of an in situ grown silicon oxide phase within perfluorosulfonic acid ionomers by the sol–gel process for TEOS, is possible and the work reported herein is a segment of our efforts to uncover molecular level details within the inorganic phase, as well as material properties. Beyond fundamental considerations, we envision technological opportunities in the important arenas of gas or liquid separations, heterogeneous catalysis, electronics materials, and ceramic precursors. The excellent environmental stability of the perfluorinated matrix will be expected to allow for the use of these materials over a broad range of operating conditions.

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Registry No. Nafion, 39464-59-0; silicon tetraethoxide (homopolymer), 118418-91-0.

References and Notes

(1) Mauritz, K. A.; Storey, R. F.; Jones, C. K. In *Multiphase Polymer Materials: Blends, Ionomers and Interpenetrating Networks*; Utracki, L. A., Weiss, R. A., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, in press.
(2) Brinker, C. J.; Keefer, K. D.; Schaefer, D. W.; Ashley, C. S. *J. Non-Crystalline Solids* **1982**, *48*, 47.
(3) Zachariasen, W. H. *J. Am. Chem. Soc.* **1932**, *54*, 3841; *J. Chem. Phys.* **1935**, *3*, 162.
(4) Bell, R. J.; Dean, P. *Nature* **1966**, *212*, 1354.
(5) *Ibid. Philos. Mag.* **1972**, *25*, 1381.
(6) Wright, N.; Hunter, M. J. *J. Am. Chem. Soc.* **1947**, *69*, 803.
(7) Dean, P. *Rev. Mod. Phys.* **1972**, *44*(2), 127.
(8) Bell, R. J.; Bird, N. F.; Dean, P. *Proc. Phys. Soc., London, Solid State Phys.* **1968**, *1*(2), 299.
(9) Bell, R. J.; Dean, P.; Hibbins-Butler, D. C. *J. Phys. C* **1970**, *3*, 2111.
(10) Brawer, S. *Phys. Rev. B* **1975**, *11*(8), 3173.
(11) Florinskaya, V. A.; Pechenkina, R. S. Spectra of Simple Glasses in the Infrared Range and their Relations to the Structure of Glass. (Eitel, W., Transl.) *Glass Ind.* **1958**, *39*, 27–31, 93–96, 151–154, 168.
(12) Yoldas, B. E.; Partlow, D. P. Formation of Monolithic Oxide Materials by Chemical Polymerization US Army Res. Rep. 16824.1-MS, 1982.
(13) Rubens, H.; Nichols, E. F. *Wied. Ann.* **1897**, *60*, 418.
(14) Saksena, B. D. *Proc. Ind. Acad. Sci.* **1942**, *16A*, 270.
(15) Bell, R. J.; Dean, P. In *Proc. Int. Conf. on Localized Excitations in Solids*; Wallis, R. F., Ed.; Plenum: New York, 1968; p 124.
(16) Coughlin, C.; Mauritz, K., in preparation.
(17) Zallen, R. *The Physics of Amorphous Solids*; Wiley: New York, 1983; p 171.
(18) Mauritz, K. A.; Gray, C. L. *Macromolecules* **1983**, *16*, 1279.
(19) Mauritz, K. A.; Fu, Ruey-Mei *Macromolecules* **1988**, *21*, 1324.
(20) Mauritz, K. A.; Yun, Huang *Macromolecules* **1988**, *21*, 2738.
(21) Mauritz, K. A.; Yun, Huang *Macromolecules* **1989**, *22*, 220.