Nafion/ORMOSIL Hybrids via *in Situ* Sol−Gel Reactions. 3. Pyrene Fluorescence Probe Investigations of Nanoscale Environment

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Pyrene (Py) photophysical probes were used to interrogate structural diversity within [1] Nafion/[silicon oxide] and [2] Nafion/[ORMOSIL] hybrids. The interior of the silicon oxide phase in [1] has the most polar environment wherein Py is trapped in silicon oxide cages in the vicinity of $-SO_3^-$ groups. Polar/nonpolar interphase regions in [1] are next in order of decreasing polarity. The interior of the ORMOSIL phase in [2] displays lowest polarity, reflecting CH_3 groups in Py-encapsulating ORMOSIL cages, and the interphase ranks somewhat higher in polarity. Water uptake is ordered: Nafion/ORMOSIL < unfilled Nafion-H^+ < Nafion/[silicon oxide]. The hydrophilicity of unfilled Nafion-H^+ is adjustable by tailoring the organic content of the incorporated sol−gel-derived nanophase as polarity determined from fluorescence emission and water uptake correlate well. Fluorescence emission of Py monitored nanostructural polarity shifts that result from secondary in situ gel growth induced by annealing. Additional condensation of SiOH groups and liberation of volatiles is promoted by increasing temperature/time, as evidenced by diminishing polarity. Polarity decrease with annealing is more profound for Nafion/[ORMOSIL *incorporating Py*] than for Nafion/[silicon oxide *incorporating Py*] as polar solvents are removed more easily from the less polar ORMOSIL nanophase.

Introduction

Our laboratory has exploited the nanophase-separated morphology of Nafion membranes as morphological templates for in situ sol−gel reactions of tetraethoxysilane (TEOS = $Si(OC_2H_5)_4$), or TEOS−DEDMS (DEDMS = diethoxydimethylsilane = $(CH_3)_2Si(OC_2H_5)_2$) mixtures to create Nafion/[silicon oxide] and Nafion/[organically-modified silicate (ORMOSIL)] nanocomposites. Nafion is a perfluorosulfonate ionomer whose morphology, in general terms, consists of 30−50 Å clusters of $-SO_3^-X$ ($X = H^+$ or cation)-ended perfluoroalkylether sidechains, the clusters being dispersed throughout a semicrystalline tetrafluoroethylene matrix as roughly depicted in Figure 1. It is a working hypothesis that hydrolyzed alkoxy- and/or alkylalkoxysilane molecules preferentially migrate to the nanometers-in-size clusters which serve as miniature reactors in which hydrolysis is catalyzed by fixed SO_3H groups, and in which the sol−gel reaction initiates.[1−3] The earlier-proposed “template hypothesis”, namely that quasi-order over the array of clusters directs the condensation polymerization of sorbed alkoxides and the ultimate morphological disposition of the dried gel phase, has received strong support by our small-angle X-ray scattering (SAXS) studies of these hybrid membranes.[4,5] These SAXS studies established that the original morphology of unfilled Nafion persists even after its invasion by the sol−gel-derived phase and showed that chemical compositional variance was affected within clusters via tailored *in situ* sol−gel reactions. These hybrids can be classified as nanocomposites owing to the fact that heterogeneity exists on the scale of ∼5 nm.

Earlier, molecular structure was characterized within in situ grown silicon oxide and ORMOSIL phases using FT-IR and ^{29}Si solid-state NMR spectroscopies and the results compared to those for corresponding bulk structures.[6,7] Nafion in situ ORMOSIL composition, comprised of $Q = Si(O_{0.5})_4$ and $D = (O_{0.5})_2Si(CH_3)_2$ units, was demonstrated to be tailored by manipulating the composition of external TEOS/DEDMS source solutions. A remarkable outcome of the NMR studies was that the *external* DEDMS:TEOS was equal to the *internal* Q:D ratio. *Co-condensation* between hydrolyzed TEOS and DEDMS monomers, rather than formation of D or Q blocks, occurred within the Nafion morphology, as well as in the bulk state. As DEDMS comonomer feed concentration increased, ORMOSIL nanostructures were rendered more hydrophobic and more flexible.

The internal polarity of Nafion can be adjusted by varying the ratio of Si−OH to Si−CH_3 groups. The goal of this work was to interrogate nanoscale environments, in terms of polarity, within these multiphasic hybrids using the photophysical probe pyrene (Py).

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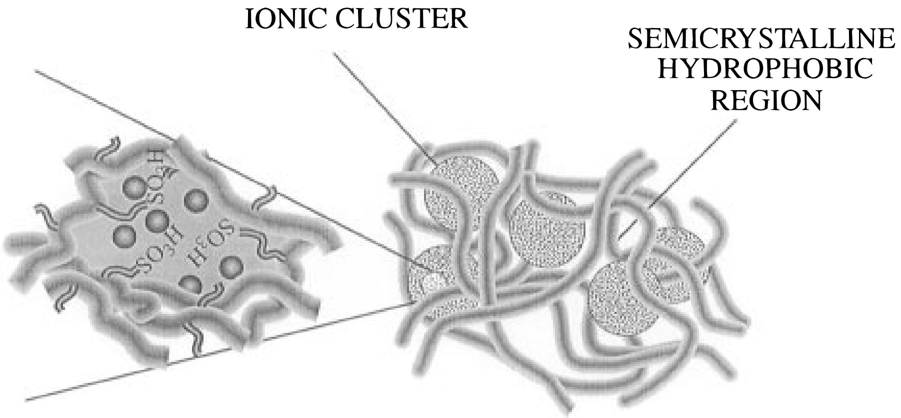

Figure 1. Nanostructured morphology of Nafion ionomers consisting of polar clusters of cation−sulfonate, or sulfonic acid groups that are dispersed, with quasi-order, throughout a hydrophobic, semicrystalline perfluorocarbon matrix.

Py is an effective probe because of its long fluorescence lifetime and monomer emission with readily resolved vibronic structure that is sensitive to the polarity of its molecular environment. Efficient Py excimer formation with its own characteristic emission can be applied to probe nanoscale geometry and porosity, if present. The effect of a solvent medium on Py emission has been well-studied.[8−10] In its emission spectrum, consisting of five characteristic vibronic fine structure peaks, the ratio of the intensity of peak 3 (383 nm) to the intensity of peak 1 (372 nm) (I_3/I_1) decreases with increase in environmental polarity around the Py molecule. Examples of solvent media illustrating the influence of polarity, given by Kalyanasundaram and Thomas,[8] show I_3/I_1 ranging from 0.54 for water (intense polar solvent) to 2.00 in a fluorocarbon (i.e., perfluoromethylcyclohexane) medium (extreme nonpolar solvent).

Kaufman and Avnir used the Py photoprobe to investigate structural development during sol-to-gel-to-xerogel transitions, although these workers utilized the peak intensity I_5 rather than I_3.[10] Since the fluorescence emission spectrum of Py is perturbed by changes in its environment, its insertion into a sol−gel-reacting system provides a monitor of structural changes assuming that the probe does not interfere with the course of hydrolysis and condensation reactions in its surroundings.[11]

Kuczynski and co-workers[12] sorbed Py within Nafion-H^+ membranes from methanol solutions and found $I_3/I_1 = 0.8$, a value situated between that expected for the highly nonpolar fluorocarbon environment of the matrix and that of the polar clusters. Lee and Meisel[13] also investigated Nafion-H^+, but with Py incorporated from water as well as from *tert*-butyl alcohol solutions. They determined that $I_3/I_1 = 0.70$ and 0.94 in Nafion/water and Nafion/*tert*-butyl alcohol, respectively. Py was considered to be located in sulfonic acid clusters, but close to the interface with the perfluorocarbon matrix rather than near the cluster center. Also, excimer formation occurred in alcohol-swollen but not in water-swollen Nafion. Szentirmay et al.[14] reported $I_3/I_1 = 0.75$ in fully hydrated Nafion-H^+ membranes, which was significantly higher than the bulk water value, and that I_3/I_1 increased as water content decreased. Their results reinforced the concept that Py preferentially resides in the least-polar regions of the clusters. Blatt and co-workers[15] determined $I_3/I_1 \approx 0.67$ in Nafion-H^+ and suggested that Py in water clusters was located near the ether groups in the long side chains. More recently, Robertson and Yeager[16] studied the time-dependence of Py incorporation in both sulfonate and carboxylate Nafion forms. They determined I_3/I_1 values (∼0.75−0.79 for sulfonate forms) and also concluded that Py preferentially resides in the interfacial regions. The conclusions arrived at in the present paper, regarding the position of the probe in our composite membranes, are partly reasoned on the basis of the results of the above-cited Py probe studies of Nafion as well as the sol−gel-derived silicate materials.

The goals of this research were to (a) identify the location of Py molecules in Nafion and in Nafion/[silicon oxide *or* ORMOSIL] nanocomposites, (b) investigate changes of polarity in the sulfonic acid clusters following the incorporation of silicon oxide and ORMOSIL nanoparticles, (c) study in situ structural evolution of the gel phases as a function of thermal treatment, and (d) relate molecular-level information derived from the probe studies to macroscopic water uptake for Nafion hybrid variations.

Experimental Section

Hybrid Formulation. The systems investigated are summarized in Tables 1 and 2. The formulation and method of incorporating Py molecules into the samples are described below. Complete experimental details for in situ silicon oxide or ORMOSIL gel incorporation were provided in previous reports.[3,5,6]

(a) Unfilled Nafion-H^+ films were immersed in Py/MeOH solutions (Py concentration: 0.01 or 0.001 M) for 10 h, then removed, surface-blotted, and dried at 50 °C under vacuum for 9 h. This is a control sample meant to represent the pure Nafion phase.

(b) Nafion, *prefilled* with silicon oxide, was soaked in Py/MeOH solutions (0.01 or 0.001 M) for 10 h, then surface-

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Table 1. Fluorescence Emission Characteristics of Pyrene at "High" Concentration[a] in Hybrids and Reference Systems

sample	excimer formation	I_3/I_1[b]
I. unfilled Nafion-H$^+$, soaked in Py solution → dried	strong	0.98
II. Nafion/[silicon oxide[c]] (12.6 wt%)] → soaked in Py solution → dried	weak	0.79
III. silica derived from sol−gel reaction of TEOS solution containing Py → dried	no	0.90
IV. Nafion/[ORMOSIL[c]] soaked in Py solution → dried	medium	1.03

[a] Pyrene concentration in MeOH solutions in which membranes were soaked = 0.01 M. [b] Reproducibility is within 0.02. [c] Prefilled.

Table 2. Py Fluorescence Emission Characteristics at "Low" Concentration[a] in Hybrids and Reference Systems

sample[a]	excimer formation	I_3/I_1[b]
V. unfilled Nafion-H$^+$, soaked in Py solution → dried	no	0.84
VI. Nafion/[silicon oxide[c] (12.6 wt %)] → soaked in Py solution → dried	no	0.79
VII. silica derived from sol−gel reaction of TEOS solution containing Py → dried	no	0.88
VIII. Nafion/[ORMOSIL[c]] soaked in Py solution → dried	no	1.03
IX. Nafion/[silicon oxide (incorporating Py)] → dried	no	0.68
X. Nafion/[ORMOSIL (incorporating Py)] → dried	weak	1.18

[a] Pyrene concentration in MeOH solutions in which membranes were soaked = 0.001 M. [b] Reproducibility is within 0.02. [c] Prefilled.

blotted, and dried at 50 °C under vacuum for 9 h. Prior to immersion in Py/MeOH, the Nafion/[silicon oxide (12.6 wt %)] hybrid was dried at 100 °C under vacuum for 5 h. This sample was also a control in the sense that Py molecules are not entrapped within the silicon oxide phase during in situ gelation.

(c) The same experiment was conducted as in (b) but for a dried hybrid resulting from an in situ sol−gel process for which *external* TEOS:DEDMS = 1:1 (mol:mol). Here, the relative quantity of water is exactly the same as in (b). Overall mole ratios are H_2O:TEOS = 4:1, H_2O:DEDMS = 2:1, and TEOS: DEDMS = 1:1. ORMOSIL uptake was 12.6 wt %. This sample serves as a control in a fashion similar to example (b) in that Py molecules are not embedded within the ORMOSIL phase during in situ gelation, but encounter a preformed ORMOSIL phase.

(d) *Bulk*, sol−gel-derived silica doped with Py was formulated as follows. A solution consisting of [9.5 mL of MeOH]/[2.5 mL of H_2O]/[0.3 mL of 0.5 M HCl] was mixed with another solution consisting of [6 mL of TEOS]/[2 mL of Py/MeOH]. The final mixture was covered for 2 h. Then, 6 mL of the reactive solution was extracted and cast onto a Teflon pan. The pan was covered by aluminum foil in which small holes were punched to facilitate the slow release of volatiles, which in turn minimizes or eliminates sample fracture. A gel was observed to form under these conditions in about 36 h. Finally, this sample was dried at 50 °C under vacuum for 20 h to form the Py-incorporated gel. [Py] was either of 0.01 or 0.001 M concentration in the sol−gel solution. This pure-phase sample is a control intended to represent silicon oxide that is compositionally similar to the silicon oxide phase within Nafion-H$^+$, but without the geometric and interactive constraints therein.

(e) Nafion-H$^+$ in situ sol−gel reactions for TEOS, with inserted Py, were conducted. This scheme differs from (b) in that Py molecules enter the membrane simultaneously with the sol−gel reactive components, as they are codissolved, so as to be entrapped within the resultant gel. First, membranes were immersed in a MeOH/H_2O (19 mL/5 mL) solution for 24 h. Methanol swells the membrane facilitating copermeation of H_2O, and later TEOS, and the water initiates TEOS hydrolysis. To this solution was added the solution TEOS/Py-MeOH (12 mL/4 mL) and the total mixture stirred for 10 min. Then the membranes were removed, surface-blotted, and finally dried at 25, 40, and 60 °C under vacuum for 6−11 h at each temperature. UV/vis and fluorescence measurements were conducted after each thermal treatment. Py concentration in the sol−gel solutions for these experiments was 0.001 M.

(f) A *bulk*, sol−gel-derived ORMOSIL, doped with Py, was made in the same fashion as the bulk silica material as described in (d). However, for TEOS:DEDMS = 1:1, this sample appeared opaque, presumably due to light scattering from a microphase-separated material. The result of this was that peak 2, and therefore I_2, could not be determined for this composition. We were able to create a transparent sample with TEOS:DEDMS = 1.8:1, on which photophysical studies could be performed.

(g) The procedure in this case is the same as in (e) except that the in situ sol−gel reaction occurs for TEOS:DEDMS = 1:1 (mol:mol) with dissolved Py, in Nafion-H$^+$. The mixture TEOS/DEDMS/Py-MeOH = 8/6.2/4 (vol/vol/vol) was used. Here, the quantity of water is exactly the same as in (e). Overall, H_2O:TEOS = 4:1, H_2O:DEDMS = 2:1, and TEOS: DEDMS = 1:1. The only difference between this system and system (c) is that Py is either within or outside of the ORMOSIL phase. Of course, the possibility that Py might penetrate preformed ORMOSIL (or silicon oxide, as well) structures, given their fractal nature, cannot be discounted.

Instrumental. UV/vis absorption spectra were obtained using a Perkin-Elmer Lambda-6 (8451A diode array) spectrophotometer. Steady-state fluorescence emission spectra were obtained with a Spex Fluorolog-2 fluorescence spectrometer with a 450 W xenon arc lamp and equipped with a DM3000F data analysis system. All the emission spectra were obtained by excitation at 333 nm with a slit width of 1.0 nm for excitation and 2.0 nm for emission. Corrected emission spectra are reported. A solid sample holder with front surface viewing geometry was used. Pyrene (99+%) was obtained from Aldrich Co. and recrystallized twice in methanol.

Water Uptake Measurement. Unfilled Nafion-H$^+$, Nafion/[silicon oxide], and Nafion/ORMOSIL samples were dried at 100 °C under vacuum for 24 h and then weighed. Then, these samples were immersed in deionized water for 40 h at 22 °C, after which they were surface-blotted and rapidly transferred to a balance to determine final weights. Weight uptake shows very good reproducibility. 40 h is sufficient time to attain sample water swelling equilibrium.

Results and Discussion

Incorporation of Py and Excimer Formation. Figure 2 (inset) shows absorption spectra, from 300 to 400 nm, for unfilled Nafion that was immersed in Py-MeOH for 10 h for the two Py concentrations. The typical Py spectra that are observed verify its incorporation within the Nafion structure. Indicated Py concentrations refer to the external solution. An attempt was not made to identify absolute Py concentrations within the membranes because it is not necessary to know specific concentration as we are mainly interested in determining polarity which is not likely affected by concentration.

The two full-scale curves in Figure 2, extending over the range 350−650 nm, are emission spectra for the

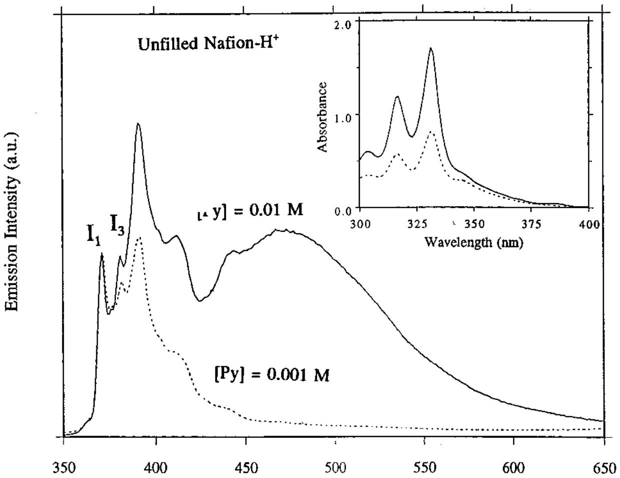

Figure 2. Fluorescence emission spectra of Py in unfilled Nafion-H$^+$ for membranes soaked for 10 h in Py/MeOH solutions in which [Py] = 0.01 M (solid curve) and 0.001 M (dashed curve), at room temperature. The inset consists of corresponding UV−vis absorption spectra for the two [Py].

same two samples whose absorption spectra are in the inset. I_1 of all samples are normalized in all figures of emission spectra throughout this report. Emission spectra are similar to those of Py in solution. The vibronic structure of Py appears in the range 370−400 nm, while the structureless excimer emission has a maximum around 470 nm. A broad structureless peak originating from excimer emission is seen for the higher (0.01 M, solid curve) but not for the lower (0.001 M, dashed curve) Py concentration. Excimer formation was found in alcohol- but not in water-swollen Nafion, which was explained by Lee and Meisel in terms of loss of cluster morphology.[13] The Py molecule has dimensions ~4−6 Å, depending on orientation[17] and Nafion clusters are ~40 Å in diameter.[18] Thus, around 8−10 Py molecules could be placed edge-to-edge to span these domains. Moreover, as Py is a flat molecule, it could stack to form excimers within clusters. In MeOH-swollen Nafion, Py is envisioned as fitting into the diffuse cluster-matrix interfacial zones but not in the perfluorocarbon matrix, based upon the earlier-cited Py probe studies. Although Py is hydrophobic, the perfluorocarbon matrix has a measure of crystallinity which would limit incorporation of Py molecules. Furthermore, on the basis of inefficient reverse-micellar packing of the long side chains of Nafion, the free volume within clusters is expected to be high so as to provide ample space for Py molecule insertion. These two facts combine to suggest that while Py can be located in clusters, it is more energetically compatible with the outer, less-polar, diffuse cluster/fluorocarbon interphase.

In Figure 3, excimer formation is examined for the molecular environments presented by the other samples for the same external Py concentration (0.01 M), and comments relating to the strength of this peak are summarized in Table 1. Nafion prefilled with either silicon oxide (curve b) or ORMOSIL (curve d) exhibits an excimer signal. The peak for the latter is stronger than that of the former, although both are weaker than that for unfilled Nafion (curve a). These samples are in the dry state so that the Py probe is sensing the Nafion morphology to the exclusion of imbibed solvents. In contrast, the excimer signal is not present for Py embedded in sol−gel-derived bulk silica (curve c).

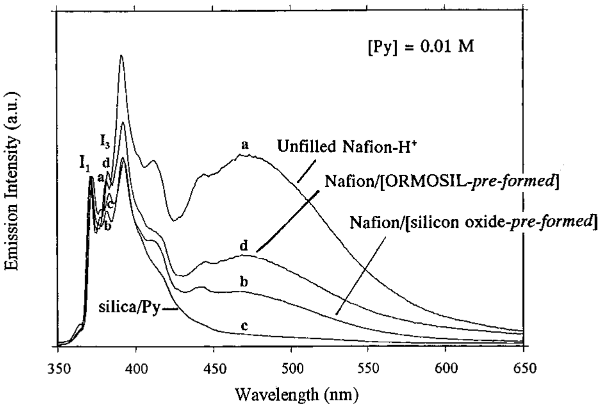

Figure 3. Fluorescence emission spectra of Py in (a) unfilled Nafion-H$^+$, (b) Nafion/[silicon oxide, prefilled], (c) silica derived from sol−gel reaction of TEOS solution containing Py, (d) Nafion/[ORMOSIL] hybrid. All samples were dried before exposure to Py/MeOH solutions for which [Py] = 0.01 M.

It is obvious that more dimers are formed in unfilled Nafion than in silicon oxide or in ORMOSIL-filled Nafion since the latter two exhibit considerably lower excimer emission intensity. All three samples were soaked in Py-MeOH for the same amount of time (10 h). If the free volume within clusters is partially occupied by silicon oxide or ORMOSIL nanoparticles, fewer Py molecules are able to reside in these domains (as also supported by the absorption spectra), resulting in lower probability for dimer formation. Py, in attempting to reside at an interface, could do so, but under restrictions posed by the invasive silicon oxide phase. Py molecules would find it difficult, due to these restrictions, to stack, forming sandwich-type excimers. We suggest that Nafion/ORMOSIL has a higher excimer intensity than Nafion/[silicon oxide] because of the presence of hydrophobic and flexible dimethylsiloxane groups in the former that would interact favorably with hydrophobic Py molecules.

There is no dimer formation for the sol−gel-derived bulk silica sample (curve c), even at the high Py concentration. Py molecules, originally dissolved in the reactive solution, become trapped in the gel during the sol−gel reaction, a situation that does not exist for either of the other two hybrid systems in Figure 3. This result is consistent with a general concept stated in earlier work that Py is dispersed and mainly isolated by SiO_2 network *cages*, which eliminates dimer formation.[10,11]

For the lower external Py concentration (0.001 M), no excimer formation is detected for all samples (save for the slight feature for the last entry of Table 2 discussed later), including unfilled Nafion as shown in Figure 4. This is attributed to a separation of Py molecules at this lower concentration. As in solution, Py excimer emission is expected to be seen only above a certain concentration.[19] The results of excimer existence for these samples are summarized in Table 2.

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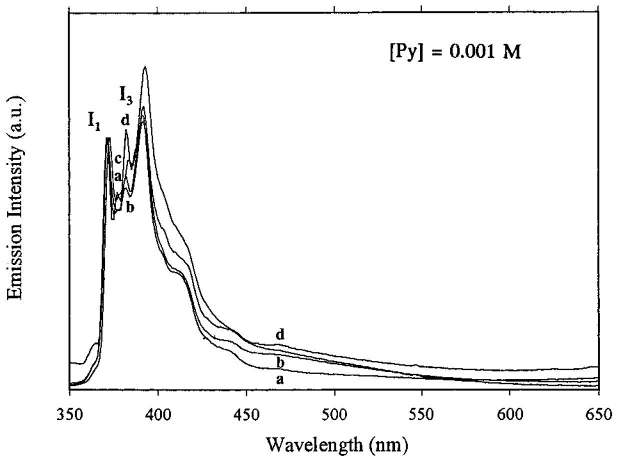

Figure 4. Same systems as in Figure 3, but for [Py] = 0.001 M.

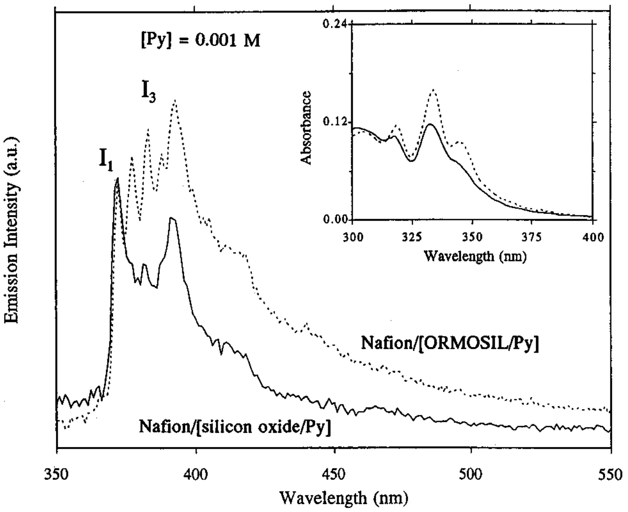

Figure 5. Py fluorescence spectra of (a) Nafion/[silicon oxide, incorporating Py] (solid curve), and (b) Nafion/[ORMOSIL (1:1), incorporating Py] (dashed curve); [Py] = 0.001 M for both. The inset consists of corresponding UV−vis absorption spectra for these systems.

Polarity of Environment of Py in Nafion-Incorporated Silicon Oxide and ORMOSIL Phases. In Figures 2−5 it is seen that I_3/I_1 varies considerably among the different materials. This is not surprising since Py is expected to be located in differing nanoscale environments within these different multiphasic systems. The values of I_3/I_1 extracted from these curves are summarized in Tables 1 and 2. We now examine each situation in detail.

[Py/MeOH] = 0.01 M. System II in Table 1 generates the lowest I_3/I_1 value (0.79) with weak excimer formation. For unfilled Nafion-H^+ (system I), $I_3/I_1 = 0.98$ (with strong excimer present), which value is higher than most previously reported,[12−16] even more so than that for Py in bulk silica (system III), for which $I_3/I_1 = 0.90$ (no excimer formation). The high I_3/I_1 value for unfilled Nafion might involve both of the following mechanisms. First, methanol swelling followed by drying results in ultimate residence of the probes near the interphase regions rather than near the cluster centers. Also, the considerable dimer formation dilutes the nearest-neighbor environment sensed by a given probe molecule. The environment will appear less polar owing to an adjacent hydrophobic Py molecule. In this way, Py is not longer able to sample the complete cluster environment owing to its dimerization. This phenomenon was also observed by Kaufman and Avnir,[10] who concluded that for their samples, in which dimerization occurred, the environment of Py is rendered less polar due to neighboring Py molecules. Finally, Nafion prefilled with ORMOSIL (system IV) displays the highest value of $I_3/I_1 = 1.03$. This high value, reflective of a rather nonpolar environment, might be attributed to the organic nature of $Si(CH_3)_2$ groups at the "surfaces" of ORMOSIL nanoparticles, although part of this result might be attributed to Py dimerization as the excimer in this case is of medium strength. It needs to be stated that these I_3/I_1 values cannot be used to rank the materials in Table 1 according to environmental polarity about the Py molecules owing to the fact that excimer strength, reflective of dimer formation, varies from being zero to strong.

[Py/MeOH] = 0.001 M. Table 2 lists I_3/I_1 for materials for this lower Py concentration. In addition to the systems in Table 1, the two hybrids wherein the Py probes permeated the membrane at the same time as either TEOS or TEOS + DEDMS (systems IX and X, respectively) are listed. Note that, except for the last entry (system X), no excimer formation is observed.

System VI (Nafion/[preformed silicon oxide]) has the same low value (0.79) as that of this hybrid for the greater Py concentration (system II) in Table 1. I_3/I_1 for bulk, sol−gel-derived silica (system VII) shows little difference from the value at the higher Py concentration (system III). Thus, the average environmental polarity around Py molecules for both of these materials remains the same for both Py concentrations.

On the other hand, I_3/I_1 for unfilled Nafion (system V) is markedly reduced to 0.84 from 0.98 at the higher Py concentration, signifying polarity increase attributed to a disappearance of Py dimerization at the lower concentration. There are no neighboring Py atoms so that probe molecules are able to sample their entire environments. This value is closer to that obtained by Kuczynski et al. (0.80) for Py entering the membrane from methanol solution.[12] In Table 2, I_3/I_1 for system V (0.84) is somewhat lower than that of system VII (0.88), which is the opposite order observed in Table 1. In unfilled Nafion, Py incorporates within the cluster/fluorocarbon interphase regions, where the polarity is nonetheless higher than that within Si−O−Si cages. In contrast, the juxtaposition of two Py molecules is imagined to be difficult within the limited free volume in the outer regions of the clusters in system VI owing to the cluster occupancy by silicon oxide nanoparticles; hence the invariance of I_3/I_1 with decrease in [Py]. The clusters in unfilled Nafion have more space to accommodate the packing of dimers.

Increasing [Py] does not affect I_3/I_1 for Nafion/[preformed ORMOSIL]. While the same comments made with regard to Nafion/[preformed silicon oxide] concerning lack of dimerization, might be offered, an excimer of medium strength, is seen at the highest [Py]. The ORMOSIL phase provides an environment favorable for dimerization at the highest but not lowest, [Py] although this is not manifest on the basis of I_3/I_1 behavior. The lack of contrast between I_3/I_1 for the two [Py] is understandable considering that the ORMOSIL phase is semiorganic. For Nafion/[preformed silicon oxide], a considerable region around a Py molecule in a dimer will be occupied by another Py molecule. However, at the lower [Py], polar SiOH groups are substituted for adjacent Py molecules so that I_3/I_1 is markedly different for the two concentrations. When the same process is considered for Nafion/[preformed ORMOSIL], adjacent Py molecules can be replaced with hydrophobic CH_3 groups so that the difference between I_3/I_1 is not significantly different for the two concentrations.

These facts collected for systems I−VIII serve as a reference database to assist in the interpretation of probe results for the more complicated situations wherein Py is mixed with the TEOS or TEOS/DEDMS external feed solutions.

Consider Nafion/[silicon oxide (Py-incorporated)] (system IX) in Table 2. This hybrid, dried at 60 °C under vacuum for 17 h, before the probe experiment, exhibited the lowest I_3/I_1 (0.68), indicating a very polar environment with no excimer. Given this value and I_3/I_1 for system VI in Table 2, Py does not reside in the vicinity of SiOH groups near polar/nonpolar interphases because its environment is too polar. On the other hand, this value does not reflect the environment of an even less polar Si−O−Si network cage for which $I_3/I_1 = 0.88$ (system VII). We do propose that Py is trapped during gelation in silicon oxide cages that are, however, in the vicinity of $-SO_3^-$ groups in clusters. These anions exert strong electrostatic interactions which, combined with dipolar interactions posed by SiOH groups, pose a highly polar environment within the cluster-encapsulated gel. In situ silicon oxide phase development is envisioned in terms of fractal-like structures that grow to entangle with the long, ether group-containing, SO_3^--terminated side chains such that these polar/ionic side chains themselves become trapped in the gel, at times being a constituent of a Py-encapsulating cage. Py, mixed with MeOH, TEOS, and water, is transported across cluster/perfluorocarbon interphases into clusters under local concentration gradients. This same process would also occur when Py is sorbed from simple MeOH solutions, except that when the membrane is dried, MeOH departs and Py molecules migrate outward from the cluster center to locate in the now more energetically compatible interphase. On the other hand, during the sol−gel process, the developing network permanently traps Py molecules so that they cannot migrate back to the interphase.

Nafion/[ORMOSIL (Py-incorporated)] (system X) in Table 2 has the highest I_3/I_1 of all cases (1.18). FT-IR and ^{29}Si NMR studies of these same hybrids demonstrated that the in situ structures are three-dimensional copolymers of Q and D units.[6,7] An ORMOSIL phase having Q:D = 1:1 contains numerous CH_3 groups and the high I_3/I_1 for this sample reflects this fact. Perhaps, during the evolution of ORMOSIL nanostructures in Nafion, Py molecules are trapped within cages constituted mainly of D units. D unit aggregation could occur on the basis of energetic affinities operative during gelation. The in situ ORMOSIL, being a copolymer, is not expected to contain long Q and D blocks, although short statistical blocks can occur, particularly for Q:D = 1:1. Blocks of some sort would seem to be necessary for D unit aggregation. The flexibility and network structure-breaking property of D units can create large free-volume pockets in which Py molecules can reside and enjoy energetic compatibility. This mechanism could produce the high observed I_3/I_1 value of 1.18.

It can be seen in Table 2 that Py molecules report an environment that is more polar in Nafion containing preformed ORMOSIL than in Nafion/[ORMOSIL (Py-incorporated)] ($I_3/I_1 = 1.03$ vs 1.18, respectively). In the former case, Py molecules are not directly incorporated within the ORMOSIL component, although the open nature of these nanoparticles might allow Py molecules at the cluster/perfluorocarbon interface to penetrate nanoparticle “pores” in which the environment is more polar than that within the nanoparticle. This situation would account for the disparity between I_3/I_1 values for systems VIII and X.

Concern might be raised as to whether the sizable Py molecule interferes with the sol−gel process, although evidence from other studies suggests otherwise.[11] The question is motivated by the fact that 4−6 Å Py molecules preempt a significant volume within ∼35−50 Å clusters. It might be said that clusters can swell to dimensions considerably larger than this. Furthermore, a fractal-like ORMOSIL growth could bend around the Py molecules rather easily as contrasted with restrictive three-dimensional growth.

Correlation between Nanoenvironmental Polarity and Water Affinity. UV−vis absorption spectra for Nafion/[silicon oxide (Py-incorporated)] and Nafion/[ORMOSIL (Py-incorporated)], both dried at 60 °C, are shown in Figure 5 (inset) over the range 300−400 nm. Nafion/ORMOSIL (dashed curve) shows higher absorbance than Nafion/[silicon oxide] (solid curve). Formulation conditions for the samples are identical; [Py] is the same (0.001 M) in both external monomer feed solutions. Therefore, Py, owing to its hydrophobicity, has an energetic preference for the nonpolar environment around inserted methyl groups in the evolving gel in Nafion/ORMOSIL, rather than around polar SiOH groups in similarly developing Nafion/[silicon oxide] hybrids, as discussed previously. Moreover, D units impart greater structural flexibility and more free volume compared to a rigid structure composed exclusively of Q units. This factor, in addition to favorable hydrophobic interactions, would promote a greater degree of Py uptake in the Nafion/ORMOSIL system.

Figure 5 also shows the emission spectra of these two hybrids. A rather weak excimer emission is noticed for Nafion/ORMOSIL (dashed curve) in contrast to the reference materials in Figure 4. Py molecules in unfilled Nafion or in Nafion having preformed silicon oxide clusters reside in the polar/nonpolar interphase. The fact that UV−vis absorption for Nafion/ORMOSIL is quite weaker than that seen in Figure 2 at the lower [Py] indicates that considerably less Py is incorporated in Nafion/ORMOSIL than in unfilled Nafion. It seems reasonable to consider that I_3/I_1 is not affected by this low degree of dimerization in the former. Nafion/[silicon oxide] shows no excimer, indicating that Py molecules are trapped in single isolation during gelation.

I_3/I_1 is much higher in Nafion/ORMOSIL than in Nafion/[silicon oxide]. These two values are the extremes in Table 3. It is evident that the polarity in Nafion clusters can be tailored to be greater or less than that within unfilled clusters. The interior of nanoparticles in Nafion/[silicon oxide] has the greatest polarity, presumably due to the strong electrostatic environment

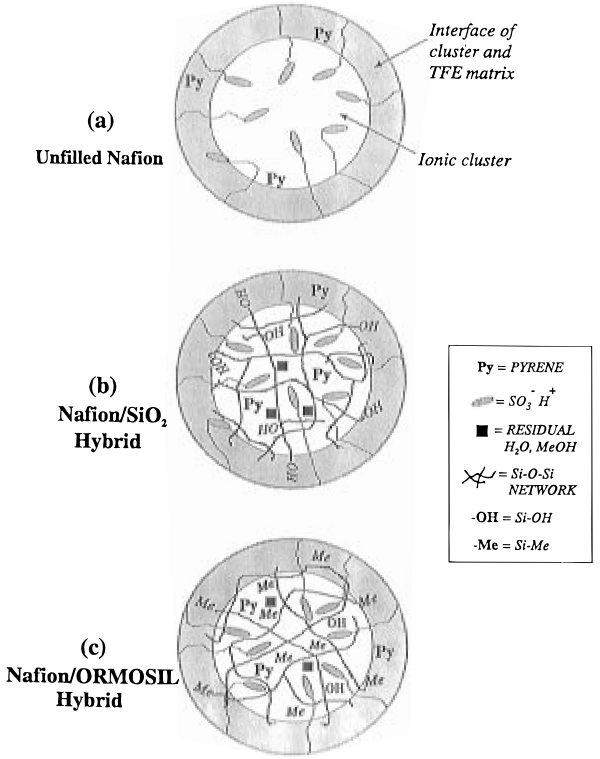

Figure 6. Depiction of probable Py molecule placements within a cluster or in perfluorocarbon/cluster interphase regions, of (a) unfilled Nafion, (b) Nafion/[silicon oxide], and (c) Nafion/[ORMOSIL] hybrids.

posed by SO_3^- groups. The surfaces of silicon oxide nanoparticles (sensed by probes in system VI) are ranked next in order of decreasing polarity. The interphase of Nafion/ORMOSIL (system VII) shows low polarity but not as low as that for system X.

In Figure 6 are rough illustrations of Py molecules positioned within a cluster or in a perfluorocarbon/cluster interphase of unfilled Nafion (a), Nafion/[silicon oxide] (b) and Nafion/[ORMOSIL] (c) hybrids.

These membranes have potential with regard to separations of multicomponent liquids in which water is a component. Within this context, evaluation of the interaction of water with nanostructures tailored to range from hydrophilic to hydrophobic is important.

Equilibrium water uptakes are: unfilled Nafion-H^+ ~15%, Nafion/[silicon oxide] ~20%, Nafion/ORMOSIL (TEOS:DEDMS = 1:1) ~11%. As the two hybrids have approximately the same filler content (~12 wt %), intercomparison is meaningful. These filler contents were adjusted to match those of the hybrids in which the filler was doped with Py as well as those of the prefilled membranes used for the probe studies. Thus, the hydrophilicity of unfilled Nafion-H^+ is adjustable by chemically tailoring the organic composition of the sol−gel-derived phase. In Table 2, unfilled Nafion has an intermediate I_3/I_1 value, the highest is for Nafion/ORMOSIL (Py-incorporated) and lowest for Nafion/[silicon oxide (Py-incorporated)]. Water uptake vs I_3/I_1 is in Figure 7 (solid curve). I_3/I_1 for these points reflects molecular environment *within* the respective silicon oxide or ORMOSIL structure. When I_3/I_1, determined for membranes filled with silicon oxide or ORMOSIL *before* Py incorporation, is plotted, the dashed line results. The dashed line would seem to be more meaningful since the solid curve refers to probes that are buried in silicon oxide or ORMOSIL nanoparticles, i.e., the reported environment is not accessible to water molecules. On the other hand, for the dashed line, both Py and H_2O molecules migrated and interacted with nanoparticle "surfaces" so that the energetic environment seen by H_2O molecules would appear to be represented by these I_3/I_1 values. However, a more complete view, based on the fractal particle concept would allow for molecules to fit into the irregular pores. A Py molecule might be too large for insertion into a pore, whereas a smaller water molecule is more likely to do so. Given this view, the solid curve might be quite relevant with regard to pore-incorporated water molecules. Last, we note that the dashed curve is narrower than the solid curve, indicating a narrower range of polarity at the "surface" as opposed to that possible within the interior of nanoparticles.

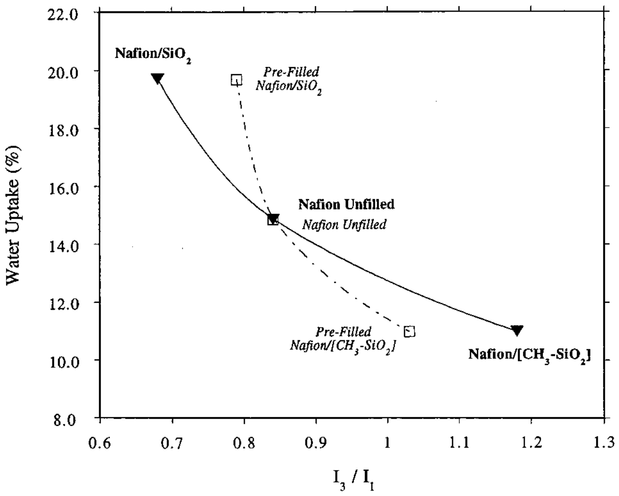

Figure 7. Equilibrium water uptake (wt %) at room temperature vs I_3/I_1 for unfilled Nafion-H^+, Nafion/[silicon oxide], and Nafion/[ORMOSIL] hybrids; all samples were predried. The solid curve refers to direct Py incorporation (*i.e.*, from TEOS or TEOS-DEDMS solutions) and the dashed curve refers to prefilled samples soaked in Py/MeOH solutions for which [Py] = 0.001 M.

While more complete studies should be performed over a range of TEOS:DEDMS, these initial studies show that micropolarity determined from fluorescence emission and water uptake correlate according to the basic principles of polar vs nonpolar interactions.

Nanopolarity vs Postannealing. These structural assignments of inserted Py probes are useful to monitor the evolution of nanoscale polarity with ensuing in situ sol−gel reaction. In this experiment, Py was incorporated into silicon oxide and ORMOSIL phases in Nafion as in the preparation of systems IX and X. Each hybrid was subjected to the following annealing stages: (1) 25 °C, no vacuum, 6 h; (2) 25 °C, under vacuum, 10 h; (3) 40 °C, under vacuum, 6 h; (4) 60 °C, under vacuum, 11 h. For both systems, the same sample was used throughout the entire set of consecutive steps and UV−vis and fluorescence measurements were conducted immediately after each thermal treatment. Increased temperature drives condensation of SiOH groups to a greater degree. Application of a vacuum removes volatiles to drive the forward reaction. If Py is mixed with the monomeric precursors, the polarity about the former will shift as the sol−gel reaction proceeds.

Dried Nafion-H^+ membranes were first equilibrated in $MeOH/H_2O$ solutions after which they were placed

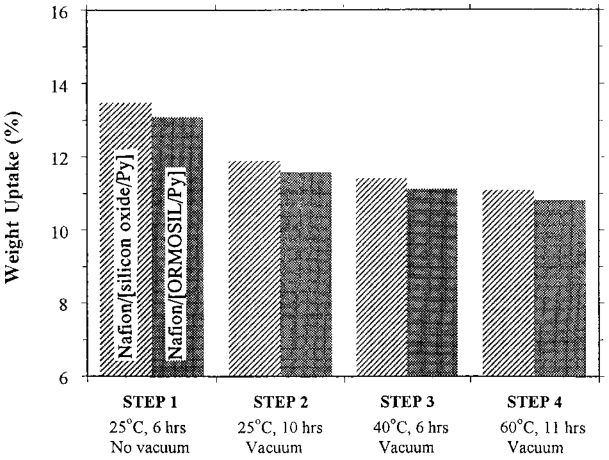

Figure 8. Wt % filler uptake for (a) Nafion/[silicon oxide, incorporating Py] hybrid (light-shaded bars) and (b) Nafion®/[ORMOSIL (1:1), incorporating Py] hybrid (dark-shaded bars) subsequent to each of the four indicated consecutive annealing stages.

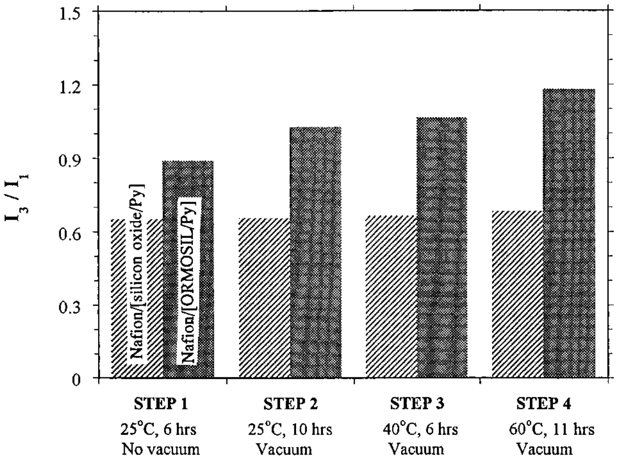

Figure 9. Same as in Figure 8 but for I_3/I_1.

in contact with either TEOS/Py/MeOH or TEOS/DEDMS/Py/MeOH stirred solutions of the same concentrations and for the same amount of time in each step as in the preparation of systems IX and X. Then, each sample was blotted and the thermal treatment steps applied. Filler weight percents for each of the two hybrids are plotted side-by-side in Figure 8 for each consecutive thermal treatment. In either case, a large initial decrease followed by gradual decrease is seen. It is reasonable that the evaporation of solvent, especially alcohol, accounts for the large initial decrease and that subsequent losses involve water generated by driven condensation reactions.

Fluorescence emission spectra (not shown) for Nafion/[silicon oxide] reveal that I_3/I_1 increases but slightly with increase in temperature. The steady upward progression in this quantity from 0.65 to 0.68, plotted in Figure 9, indicates a measurable decrease of polarity in the gel phase. We interpret this trend in terms of nanostructural evolution, adopting the position that Py is mainly entrapped in cages, possibly containing sulfonate anions, within the silicon oxide phase, exclusively. Nafion itself does not exhibit major thermal transitions within this temperature range. The implication is that additional condensation of SiOH groups is promoted by increasing temperature or/and time of annealing. As the number of these polar groups is reduced, and as residual MeOH and water molecules are liberated, polarity is diminished. If the strong electrostatic interactions posed by sulfonate anions are primarily responsible for the very low value of I_3/I_1, the annealing will not profoundly raise this value.

In contrast, the fluorescence emission spectra (not shown) for Nafion/ORMOSIL show that I_3/I_1 increases significantly in monotonic fashion as annealing moves to consecutive stages and the temperature increases. These data are also plotted in Figure 9. There is a large net increase from 0.89 to 1.18, demonstrating a large decrease of polarity generated in the ORMOSIL phase. These results are interpreted in the following way. As thermal treatment proceeds, further condensation is driven so as to decrease the number of SiOH groups. Liberation of bound water and alcohol molecules will occur, as well, as in the case of the Nafion/[silicon oxide]; however, polar solvents are removed more easily than in the previous case as the medium in which they reside is less polar. As Py cages become better defined (i.e., with the removal of SiOH, H_2O, and MeOH structural "defects"), Py molecules come into more intimate contact with surrounding methyl groups so as to "sense" this organic environment better. For each annealing stage, I_3/I_1 for Nafion/[silicon oxide] is much smaller than that for the Nafion/[ORMOSIL], which is always less polar.

Conclusions

Pyrene was seen to be a powerful photophysical probe to investigate the diversity of nanostructural polarity within Nafion/[silicon oxide] and Nafion/[ORMOSIL] membranes.

Nafion/[silicon oxide] has the most polar environment. We propose that Py is trapped during gelation in cages, in the vicinity of $-SO_3^-$ groups, within clusters when Py is externally premixed with TEOS. The environment within Nafion/ORMOSIL is the least polar, reflecting the presence of numerous CH_3 groups. Perhaps, during ORMOSIL nanophase evolution, when Py is externally premixed with TEOS + DEDMS, Py molecules are trapped in cages constituted mainly of D units. Polarity in Nafion clusters can be tailored to be greater or less than that within unfilled clusters via insertion of sol−gel-derived phases by adjusting TEOS:DEDMS. The interior of nanoparticles in Nafion/[silicon oxide] clusters has the greatest polarity and the interphase regions of this hybrid rank next in order of decreasing polarity. The interior of the ORMOSIL phase in Nafion/ORMOSIL displays the lowest polarity and the interphase regions of this hybrid rank somewhat higher in polarity.

Water uptake is ordered: Nafion/ORMOSIL (1:1) < unfilled Nafion-H^+ < Nafion/[silicon oxide]. Hydrophilicity of unfilled Nafion (H^+) is adjustable by tailoring the organic composition of the sol−gel-derived nanophase. Molecular-level polarity determined from fluorescence emission and water uptake correlate well. Future studies will address the affinity of other solvents, over a range of polarity, for Nafion incorporating ORMOSIL nanophases tailored to have a broad range of organic compositions.

Fluorescence emission experiments monitored the shifting of nanostructural polarity accompanying secondary in situ gel growth induced by annealing in stages involving temperature increase and no vacuum vs vacuum-drying. Additional condensation of SiOH groups with liberation of MeOH and H_2O is promoted by increasing temperature/time, as evidenced by diminishing polarity. The polarity decrease is more profound for Nafion/[ORMOSIL incorporating Py] than for Nafion/[silicon oxide incorporating Py] as polar solvents are removed more easily from the less-polar ORMOSIL nanophase. Silicon oxide and ORMOSIL contents of these hybrids show a large initial decrease followed by a gradual decrease with progressive thermal treatment, suggesting that solvent evaporation accounts for the initial stage, while water generated by condensation reactions accounts for the later stage.

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