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Microstructural Evolution of a Silicon Oxide Phase in a Perfluorosulfonic Acid Ionomer by an in Situ Sol–Gel Reaction.
3. Thermal Analysis Studies

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ABSTRACT: Microcomposite membranes were produced via the in situ diffusion-controlled, acid-catalyzed sol–gel reaction for tetraethoxysilane in prehydrated and methanol-swollen Nafion perfluorosulfonic acid films. The thermal behavior of these microcomposites was investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). It was found by TGA that significant thermochemical degradation begins at around 350 °C and then takes place in at least three stages for both filled and unfilled membranes. Two strong thermal transitions, identified with the polar cluster and microcrystalline domains, in the predegradative temperature regime above 30 °C, were identified by DSC for all the microcomposite as well as the unfilled membranes. However, upon annealing at a temperature just below the "cluster transition temperature" and then quenching, this transition becomes suppressed for all membranes. It appears that both the polar and microcrystalline domains remain quite intact in spite of the in situ growth of the silicon oxide phase at the filler levels investigated. This observation reinforces our earlier hypothesis of the three-dimensional template action of Nafion's natural microphase-separated morphology in directing the final morphology of the inorganic phase.

Introduction

Mauritz and co-workers have recently reported on the formulation of unique microcomposite membranes via the in situ growth of a highly dispersed silicon oxide phase in Nafion[1] perfluorosulfonic acid films.[2,3] In short, an acid-catalyzed, diffusion-controlled, sol–gel reaction for tetraethoxysilane (TEOS) was affected in prehydrated and alcohol-swollen membranes that were immersed in TEOS–alcohol solutions for various times after which the membranes were dried and annealed in controlled fashion to remove trapped volatiles and optimize the cross-linking of the in situ inorganic gel network. It was initially hypothesized, and it is now becoming increasingly clear that the final morphology of the invasive inorganic phase is significantly ordered by the original polar–nonpolar phase-separated morphology presented by the perfluorosulfonic acid matrix.

Our previous FT-IR, ^{29}Si NMR, mechanical tensile, and dielectric relaxation spectroscopy studies[4] portray an incorporated silicon oxide network structure that is rather heterogeneous on a *molecular* (i.e., subcluster) scale, being increasingly less interconnected but nonetheless more strained with increasing gel content. While it would seem that, initially, the silicon oxide clusters grow in single isolation, it was suggested that a percolation threshold is eventually reached at a critical silicon oxide content at which the clusters become interconnected or spanned by $(\equiv SiO)_n$ chains extending over the film's macroscopic dimensions.

In this work, we report results of the characterization of these hybrid materials by means of thermal analysis: thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

We were concerned, in this work, with whether, and how, physical thermal transitions or ultimate thermal degradation associated with the untreated membrane might be modified by interactions with the inorganic filler. It is also of interest to explore the possibility of structural transitions in, as well as thermally induced condensation of, unreacted –OH groups on the silicon oxide framework. In an earlier communication,[5] we had investigated these thermal aspects in similar fashion for poly(*n*-butyl methacrylate)–titanium oxide alloys produced by the sol–gel process for titanium alkoxides.

It is appropriate to precede a detailed analysis of the results of our thermal studies of these rather complex microcomposite systems with a brief summary of earlier reports in which thermal transitions in *unfilled* Nafion perfluorosulfonate membranes have been documented.

Yeo and Eisenberg[6] initially reported, for *dry* Nafion in the sulfonic acid form of equivalent weight 1365, fluorocarbon matrix T_g's that were (1) based on a dynamic mechanical loss tangent peak (labeled α) at a heating rate of less than 1 °C/min, (2) identified with the onset of a DSC-monitored transition at a heating rate of 10 °C/min, and (3) based upon linear thermal expansion studies. The "matrix T_g" values obtained by these three methods were 111, 104, and 122 °C, respectively. Of course, the glass transition temperatures of these dry acid-form ionomers are a function of the method and time scale of the given experiment and whether the transition onset or midpoint is formally chosen as T_g, as well as the equivalent weight and thermal and swelling prehistory of the membranes.

Nonetheless, the above three temperatures are somewhat close to each other and not greatly less than the T_g of 127 °C cited for the more crystalline PTFE system.[7] This fact, in addition to the observation that the dynamic mechanical α-loss peak appeared to be insensitive to water *in these early studies*, led Yeo and Eisenberg to assign this transition to a T_g corresponding to molecular motions within the nonpolar phase. Furthermore, a transition (labeled β) located at around 20 °C for this dry acid form, and which shifted to lower temperatures with increasing water content, was initially attributed to molecular motions within the ionic phase. However, in later, more extensive studies, Kyu and Eisenberg[8] did observe a definite shift of the α-transition to lower temperatures upon the addition of water. This finding led these authors to reverse the assignments of these two transitions so that the higher temperature event (α) became the T_g of the polar phase and the lower temperature transition (β) was now asso-

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ciated with the T_g of the perfluorinated matrix. Upon ionization, these transitions were seen to shift to higher temperatures. For example, the dynamic mechanical β-peak moves from roughly 20 to 150 °C and the α-peak moves from about 110 to 220 °C in passing from the dry acid to dry alkali cation salt forms for the 1365 equivalent weight membranes. The more recent DSC studies of 1100 equivalent weight Nafion by Moore and Martin are in harmony with and support the mechanistic assignments of Eisenberg and Kyu.[9] Furthermore, the α-transition temperature is progressively increased with an increasing degree of side-chain neutralization.

The general concept of a glass transition as being caused either by the onset of long-range chain-segmental mobility in simple linear glassy amorphous polymers or by the onset of long-range cooperative motions within a large array of low molecular weight molecules is somewhat difficult to apply to the more complex, phase-separated, Nafion systems. First, the rather ubiquitous but pervasive crystallinity in these materials would seem to present an obstacle to long-range chain-segmental mobility as usually visualized. Starkweather has determined that the size of the crystallites, which consist of TFE chains that are packed in a hexagonal bilayer mode, is greater than the average separation between the side chains.[10] Second, a "glass transition" within the dry polar phase, which would involve the thermal loosening of hydrogen bonds in the acid form and pairwise coulombic interactions between ions or ion–dipoles in the salt forms, would seem to necessitate contiguous rather than isolated clusters throughout which long-range cooperative motions can occur. Of course, the α- and β-transitions might be linked to each other insofar as the sulfonic acid or sulfonate cation terminated side groups in the polar phase might form cross-links that inhibit polymer chain mobility in the nonpolar phase. Presently, these ideas belong in the hypothetical realm.

Starkweather cites peak–end melting temperatures of 207 and 235 °C obtained by DSC scans at a heating rate of 20 °C/min for 1100 equivalent weight dry sulfonic acid Nafion. Hypothetically, the end temperature is that at which all remnants of crystallinity are destroyed.

Experimental Section

The procedural details of the preparation of the microcomposite membranes via the in situ sol–gel reaction of TEOS in prehydrated and alcohol-swollen Nafion sulfonic acid films have been reported in an earlier communication.[2] The membranes used in this work were of equivalent weight 1100 and had a nominal thickness of 7 mil ("Nafion 117"). All membranes were dried to constant weight prior to their modification.

The initial H_2O/TEOS mole ratio was fixed at 4, and as in previous experiments the host liquor was methanol, which is miscible with both H_2O and TEOS, whereas the last two are mutually immiscible. The methanol–water-swollen Nafion membranes were immersed in methanol–TEOS solutions for 1, 5, 10, 15, and 20 min, which are referred to as "diffusion times". The membranes were then removed, surface-blotted dry, and finally placed under vacuum for 24 h, the last two of which were spent in heating at 110 °C.

The dried-annealed samples were subsequently weighed, and the percent weight increase for the microcomposite samples is plotted as a function of the prescribed diffusion times in Figure 1. Note the reasonable linearity of the plot.

All the samples were then stored in a desiccator prior to the thermal analysis measurements.

A Du Pont 9900 computer/thermal analyzer was used to obtain thermograms for the six samples: dry Nafion in the sulfonic acid form and the five microcomposite samples with varying silicon oxide content. In turn, for each sample, three varieties of thermograms were obtained, all under N_2 at ca. 30 mL/min:

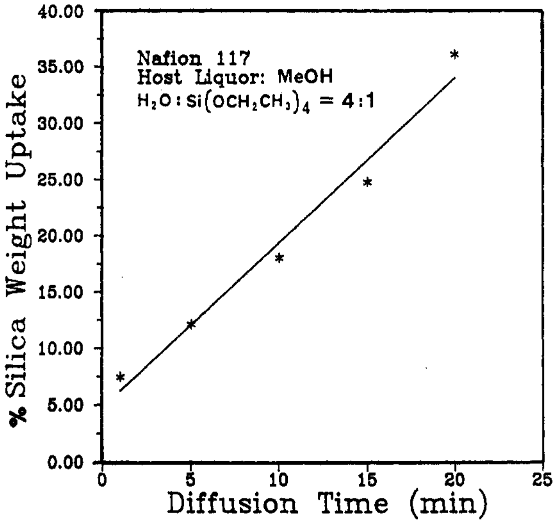

Figure 1. Percent silicon oxide weight uptake of Nafion 1100 equivalent weight sulfonic acid membranes, after drying, vs time of diffusion of TEOS from methanol solution (taken from ref 4).

(i) TGA thermograms for which each of the six samples were heated from 30 to 630 °C at the rate of 10°/min.

(ii) DSC thermograms for which each sample was heated from 30 to 330 °C, also at the rate of 10°/min.

(iii) DSC thermograms for which each sample was first heated up from 30 to 130 °C at the rate of 20°/min, held there isothermally for 10 min, then quenched to room temperature, and subsequently heated up from 30 to 330 °C at the rate of 10°/min. The thermogram was obtained for this run. The reason for holding all six samples only for 10 min isothermally at 130 °C in (iii) is that longer exposure to this temperature caused visual degradation. The temperature 130 °C is just above the highest nonmelting transition.

We will subsequently refer to the samples subjected to thermal treatments (ii) and (iii) as "unannealed" and "annealed", respectively.

Results and Discussion

The TGA thermograms for all six unfilled and microcomposite membranes are displayed in Figure 2. The thermograms consist of two curves, the solid one being the actual percent of original weight remaining and the dashed one its first derivative. The first derivative is very useful in increasing graphical resolution by pinpointing temperatures at which the mass is changing at the greatest rate. In this way, it is possible to visually separate two or more thermal transitions that overlap on the direct thermogram.

From Figure 2 it is seen that all six samples, filled and unfilled, retain more than 95% of their weight up to a temperature of about 350 °C. This is well past the melting point of the base polymer. After this point, all samples start decomposing rather rapidly. The unfilled dry Nafion membrane, as well as all of the microcomposites, seems to decompose in at least three discernible stages that are well-resolved by the derivative curves. There is also the suggestion of a shoulder on the right-hand side of the highest temperature derivative peak at 12.1 and 18.0% silicon oxide contents. The temperatures at which these degradation events occur shift with inorganic content.

It is clear from Figure 2 that incorporation of silicon oxide up to 36.1% does not profoundly affect the *onset* of the thermal degradation of Nafion sulfonic acid, although the subsequent steps are definitely shifted on the temperature scale.

The very *gradual* loss of about 5% of the original weight from 30 to about 350 °C in all six samples can be rea-

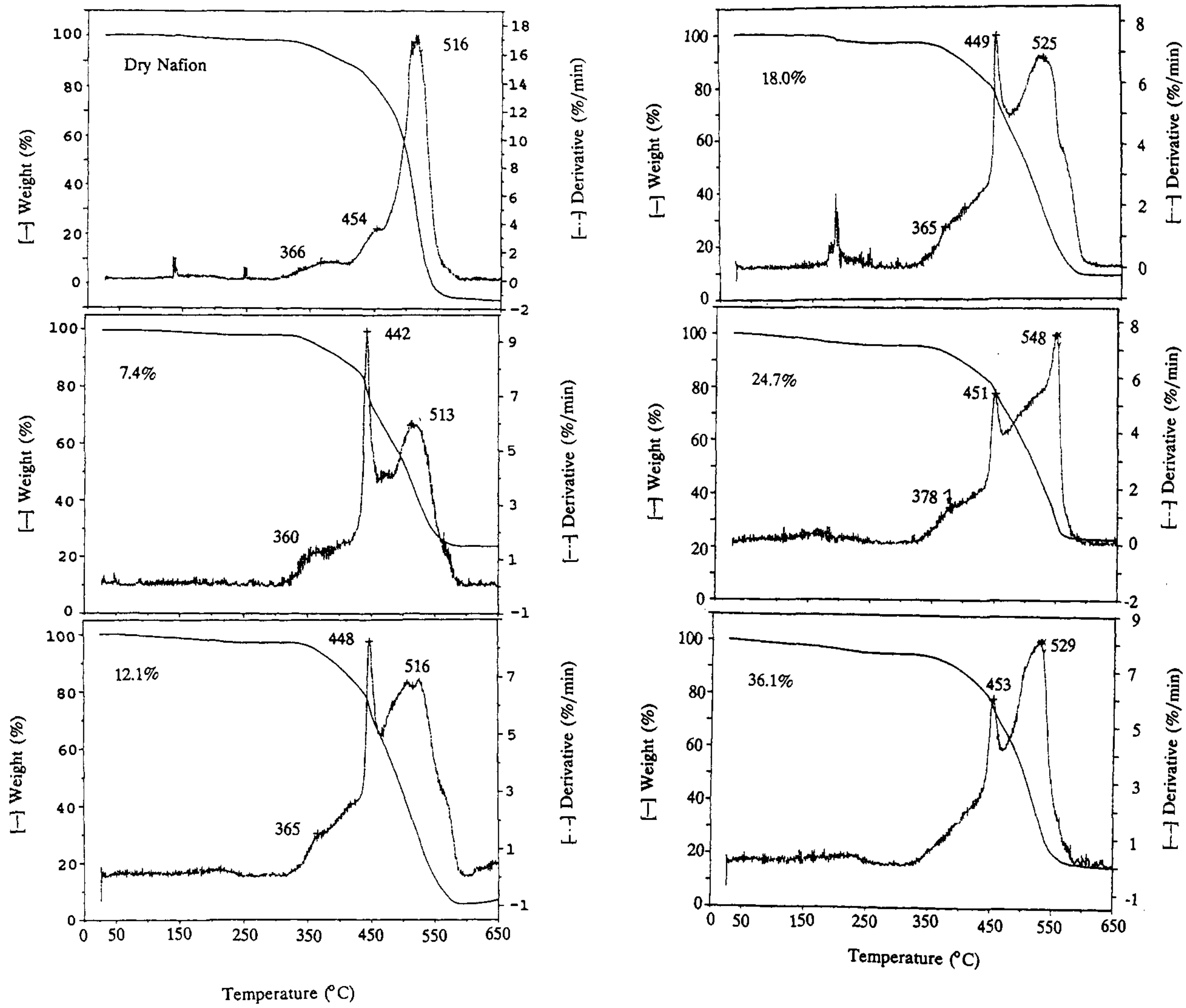

Figure 2. TGA thermograms and associated derivative curves, taken at a heating rate of 10 °C/min, under N_2, for a dry Nafion sulfonic acid membrane and for microcomposite membranes having indicated fixed silicon oxide filler levels.

sonably attributed to residual bound TEOS, MeOH, and H_2O molecules that are gradually volatilizing over that lower temperature range. It would seem logical, then, that any relatively sharp transitions observed in DSC thermograms between 30 and 350 °C would be due to a physical structural transition rather than to chemical volatilization or degradation. Note also that our range of temperature scan is above the "matrix T_g" as earlier reported.[6]

The DSC thermograms for all the unannealed samples are displayed in Figure 3. The dried unfilled acid form exhibits two strong endothermic peaks at 145 and 230 °C. On the basis of the previous studies outlined in the Introduction, it would be natural to consider 145 °C to be the midpoint of a polar cluster phase transition. This temperature, though somewhat higher than the value of 111 °C reported by Yeo and Eisenberg,[6] is for a membrane of considerably lower equivalent weight. It might be reasonable to think that the greater fraction of sulfonic acid groups present in the 1100 equivalent weight membranes gives rise to larger, more highly organized and therefore more cohesive polar clusters that would necessarily generate a higher polar phase transition temperature.

We hesitate, however, to refer to this lower temperature thermal event as a "glass transition" in the usual sense for the following reason. A glass transition, whether occurring in linear covalently bonded organic amorphous polymers, strongly bonded inorganic amorphous compounds such as metal oxides, or low molecular weight liquids whose molecules are weakly interacting, always involves *long-range cooperative* molecular motion. On the other hand, the characteristic dimensions of the individual polar clusters in Nafion membranes (ca. 30–50 Å) would not seem to be large enough to contain a sufficient number of relaxing elements, say, polar side chains, to constitute a statistical ensemble over which such long-range motions can take place. Also, it is unclear as to whether such isolated clusters can interactively communicate with each other to affect long-range motion in an *inter*cluster sense. Finally, in the review of this manuscript, it was pointed out that glass transitions are not typically so exothermic. If the assignment of this transition to the cluster phase is in fact valid, as the prior-cited studies on unfilled membranes suggest, then its high endothermicity might be rationalized in terms of the loosening of polar side-chain interactions, which are known to be quite strong.[11] We do not feel that this transition is due to the melting of less perfectly formed crystalline regions in the nonpolar phase. Prior wide-angle X-ray diffraction studies of unfilled, dry and hydrated, Nafion sulfonic acid forms do not indicate crystalline polymorphism, particularly of such an appreciable degree as to give rise to melting peaks as distinct and of comparable magnitudes as those seen in Figure 3.[10,12]

The transition centered at 230 °C corresponds well with the melting of the crystalline regions,[10] as discussed earlier.

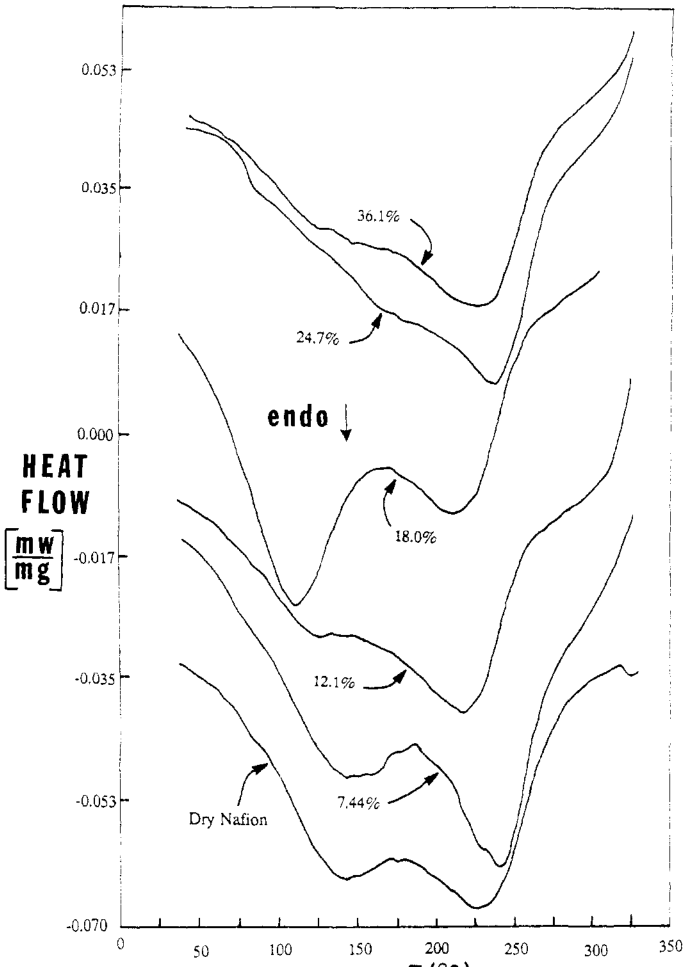

Figure 3. DSC thermograms, taken at a heating rate of 10 °C/min, under N_2, for a dry Nafion sulfonic acid membrane and for microcomposite membranes having indicated fixed silicon oxide filler levels. Successive thermograms have been vertically displaced but have the same heat flow scale in milliwatts per milligram.

Table I
Peak Temperatures for Thermal Transitions Assigned to the Cluster and Crystalline Phases of Unfilled and Silicon Oxide Filled Nafion Sulfonic Acid Membranes

membrane sample, %	cluster phase transitn temp, °C	cryst phase transitn temp,[a] °C
dry unfilled Nafion	145	230/indeterminate
7.4	142	241/280
12.1	125	220/260
18.0	111	211/260
24.7	indeterminate	240/276
36.1	indeterminate	225/270

[a] Latter entry denotes well-defined transition end point.

Owing to the broadness and overlapping nature of both peaks, the transition end points for all samples, filled and unfilled, are somewhat ambiguous, although the peak maxima are rather well-defined, especially for the crystalline melting transition. The peak transition temperatures for the polar and crystalline phases are listed in Table I. With regard to the lower, cluster phase transition, a steady decrease in the peak temperature with increasing inorganic filler content is seen up to and including the 18.0% level. It is, however, difficult to judge transitional behavior beyond this degree of loading. Perhaps, one might think of the invasive growing silicic acid oligomers as progressively disrupting the natural packing and interactive cohesion of sulfonic acid groups within their clusters, which in turn would cause the transition temperature associated with these isolated regions to gradually decrease. We are not able to offer an explanation for the profound increase in the magnitude of this peak at 18%, however. It is somewhat tempting to speculate that the virtual disappearance of this lower transition at the 24.7 and 36.1% levels might reflect the vanishing of discrete polar clusters as previously isolated, nanometers in size, silicon oxide structures begin to merge with each other.

A parameter, n, was extracted from the low-frequency segments of the dielectric loss spectra of these microcomposites, which was proposed to coarsely indicate the degree of microstructural heterogeneity or morphological texture over an array of clusters at a given silicon oxide content and temperature.[4] We note that, at each fixed temperature studied in the range 20–95 °C, n is a maximum at 18.0% silicon oxide content and then steadily decreases to lower values with increasing content. Perhaps one might interpret this dielectric relaxation trend as arising from a deterioration of order over an array of clusters or the disruption of the ordering within individual clusters. In any case, this concept seems to be in harmony with the observed disappearance of the "cluster phase transition" beyond 18.0% inorganic content.

The peak temperatures associated with the melting of the microcrystalline domains for the filled membranes appear to fluctuate above and below the value for the unfilled membrane with no apparent trend, as seen in Table I. Thus, in a rough sense, it would seem that the general packing mode of the TFE backbone remains intact despite considerable levels of silicon oxide structural ingrowth, although the actual degree of crystallinity can vary. The perceptible high-temperature transition end points for the filled systems, also listed in Table I, exhibit this fluctuation, as well.

The DSC scans for the annealed–quenched samples are seen in Figure 4. While the crystalline melting transition is quite prominent and similar to that for the unannealed membranes, the polar phase transition is practically suppressed by this thermal anneal–quench pretreatment. Interestingly, the unfilled but additionally annealed membrane has essentially lost this transition as well as the filled systems. Therefore, one might reasonably argue that this phenomenon is associated with molecular rearrangement within the polar phase of the base polymer and not caused, but only modified, by the incorporation of the silicon oxide component. Perhaps thermal molecular mobility and consequent disorder within aggregates of sulfonic acid groups had been affected by annealing in the temperature vicinity of the cluster phase transition, and this molecular disorder was subsequently frozen-in upon quenching. Then, when the membranes are reheated, the cluster phase transition appears very weak because the inter-side-chain cohesiveness had been earlier disrupted, and little thermal activation is now required to complete molecular disorganization within these domains.

It is possible to detect the onset/inflection/end point temperatures for the weak remnants of this transition for all filled and unfilled postannealed samples, and the extracted values are listed in Table II. It is seen that the midpoint of this transition increases from 145 to 158 °C upon annealing the unfilled membrane. This temperature monotonically decreases with increasing silicon oxide incorporation from 158 to 127 °C at 36.1%. The onset/end point temperatures behave in similar fashion. One might imagine, as with the unannealed samples, that

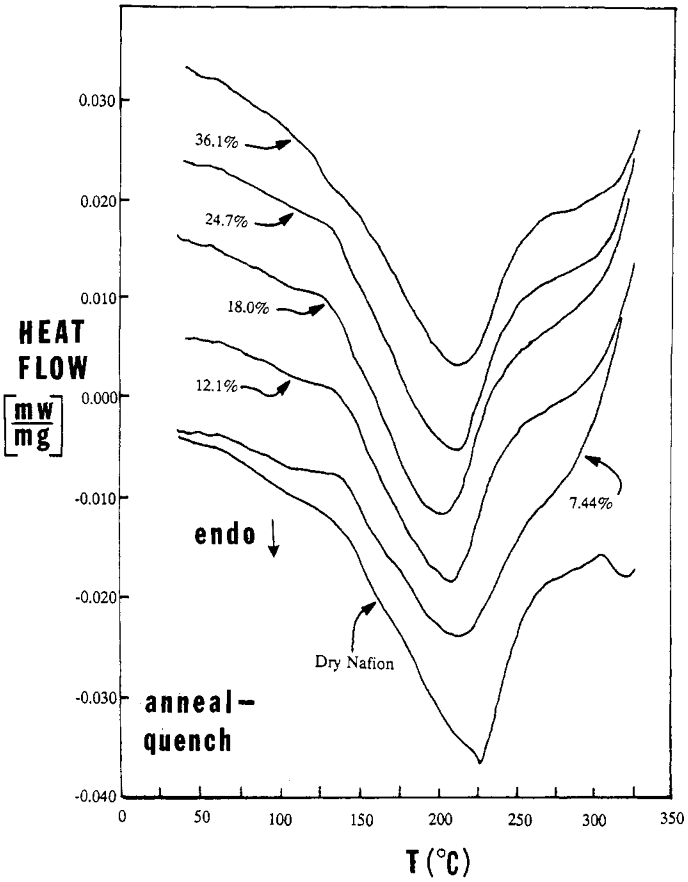

Figure 4. DSC thermograms, taken at a heating rate of 10 °C/min, under N_2, for a dry Nafion sulfonic acid membrane and for microcomposite membranes having indicated fixed silicon oxide filler levels. Each membrane was prepared as those in Figure 4 but additionally were postannealed and quenched as described in the text. Successive thermograms have been vertically displaced but have the same heat flow scale in milliwatts per milligram.

Table II
Thermal Transition Temperatures for the Cluster and Crystalline Phases of Unfilled and Silicon Oxide Filled Nafion Sulfonic Acid Membranes That Have Been Postannealed-Quenched

membrane sample, %	cluster phase transitn temp (onset/inflection/end), °C	cryst phase transitn temp,[a] °C
dry unfilled Nafion	146/158/164	230/269
7.4	145/154/160	218/236
12.1	144/152/158	208/235
18.0	143/149/156	206/235
24.7	137/143/150	216/263
36.1	117/127/140	216/251

[a] Latter entry denotes well-defined transition end point.

side-chain packing and cohesiveness within the polar phase is being gradually destroyed by the invading silicon oxide structures, which, in turn, would result in a steady lowering of the cluster transition temperature.

For the annealed-quenched membranes, the trend of the crystalline melting transition midpoint temperature with increasing filler level, seen in Table II, is that of a decrease followed by an increase. All of these temperatures are lower than those for the unannealed-quenched microcomposites at corresponding filler levels. There does not seem to be a profound alteration of crystallinity by the uptake of silicon oxide for these samples as was also true for the samples that were not subjected to annealing-quenching. Within this context, the microcrystalline domains within Nafion membranes appear to have rather good structural persistence.

Summary and General Conclusions

Both unfilled dry Nafion sulfonic acid membranes and the same membranes incorporating a silicon oxide phase via the in situ sol-gel reaction for TEOS do not suffer considerable thermal decomposition up to around 350 °C. Beyond this temperature, thermal degradation, as manifested gravimetrically, appears to occur in at least three stages. While these stages are modified with filler level in complex fashion, the temperature of the *onset* of degradation is not greatly affected in this way up to about 36% inorganic content.

Having thus established the lower bounds for the thermochemical decomposition of filled and unfilled systems, purely physical thermal transitions were identified at lower temperatures above 30 °C by DSC. A polar cluster phase-assigned transition peak temperature at around 145 °C for the untreated membrane decreases with increasing filler level. In general terms, we visualize the progressive invasion of the clusters by silicic acid oligomers as increasingly disrupting the natural stereochemical packing and interactive cohesion of the polar side chains as being responsible for driving this transition temperature to lower values.

A transition occurring at 230 °C for the unfilled membrane was assigned to the melting of the microcrystalline regions that were earlier established to consist of TFE chains packed in hexagonal bilayer fashion between the polar clusters. This crystallinity appears to be quite resistant to the in-growth of the silicon oxide phase as the peak melting temperatures for the microcomposites merely fluctuate about the above value with increasing filler level.

When these membranes, both filled and unfilled, are postannealed-quenched, the polar cluster transition is all but suppressed. This phenomenon seems to be strictly associated with the base polymer, not the inorganic component, and we suggest that it arises from the creation and subsequent freezing-in of molecular disorder within the clusters caused by the annealing followed by quenching procedure.

The crystalline melting transitions for these postannealed-quenched samples, however, remain prominent and decrease and then increase in peak temperature with increasing filler level such that all these temperatures are correspondingly lower than those for the microcomposites that were not subjected to this postthermal treatment. Presently, we cannot offer a clear rationalization of this behavior.

A rather general conclusion of these studies is that both the polar cluster and microcrystalline domains appear to remain largely intact despite the invasion of the polymer morphology by the in situ grown silicon oxide structures, at least at the filler levels produced in this work. In turn, we believe that this conclusion provides additional reinforcement of our original working hypothesis of a persistent in situ growth template presented by Nafion's unique microstructure.[2] In short, it was earlier reasoned that the resultant morphology of the inorganic phase would be ordered by the existing Nafion microphase-separated morphology so that the in-growths will possess a necessarily high surface area-volume ratio because the mutually soluble TEOS-alcohol-water components will reasonably diffuse to and preferentially incorporate within the polar clusters rather than within the hydrophobic regions mainly consisting of tightly packed TFE chains.

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Registry No. TEOS, 78-10-4; Nafion 117, 66796-30-3; silicon oxide, 7631-86-9.

Evidence for Molecular Cr^{3+} Cross-Links in Cr^{3+}/Polyacrylamide Gels

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ABSTRACT: The gelation of buffered aqueous solutions of Cr^{3+} and polyacrylamide having a low degree of hydrolysis (0.7% and 10%) has been investigated over a wide range of pH. It has been found that gelation occurs between pH 2.3 and 6.7 and that the time of gelation increases dramatically at low pH. An inverse correlation between $Cr(OH)_3(H_2O)_3$ colloid formation (revealed by solution turbidity) and the pH range of gelation indicates that discrete, soluble (monomeric or oligomeric) rather than colloidal forms of Cr^{3+} are responsible for the cross-linking. The occurrence of gelation in the pH interval 6.0–6.7, where only a small amount of the Cr^{3+} would be soluble in a simple aqueous solution, has been attributed tentatively to Cr^{3+} complexation by the polymer. Cr^{3+} solubility experiments at pH 6.6 in solutions containing model, monomeric carboxylate compounds lend support for this hypothesis.

Aqueous polymer gels composed of high molecular weight, partially hydrolyzed polyacrylamide (or other synthetic or biopolymers) cross-linked by Cr^{3+} or Al^{3+} are of interest for use in augmenting the petroleum recovery from mature reservoirs.[1,2] So-called secondary oil recovery typically involves the continuous injection of water into a reservoir from a subset of the existing wells. The injected water physically displaces to the other wells a significant portion of the mobile oil with which it comes into contact. A major limitation to petroleum recovery by this method arises from the fact that most reservoirs are compositionally heterogenous and that the injected water floods preferentially the strata of highest permeability. A promising but still experimental reservoir treatment involves the occlusion of the higher permeability strata, after preliminary water flooding, with polymer gels which are formed within the reservoir from aqueous polymer/cross-linker solutions. Water injected subsequently is thereby diverted to lower permeability zones, and the mobile oil contained therein can be recovered. Among the various enhanced oil recovery techniques proposed and field-tested during the past 15 years, reservoir profile modification with aqueous polymer gels remains one of the few economically promising strategies in the present period of low-priced petroleum.

Several chemical impediments remain that prevent the full realization of the gel profile modification strategy. These include instability of the polymeric gels at high temperature, limited control over and understanding of the kinetics of gelation, and lack of satisfactory mathematical models which permit the controlled placement of the gels within the reservoir. A more detailed understanding of the structure and chemistry of the metal ion cross-links in these gels should aid in the rational design of aqueous gels having improved performance characteristics.

Both *colloidal* and *discrete molecular* cross-link structures have been suggested[3,4] for aqueous polymer gels cross-linked with Cr^{3+} (Figure 1). The distinction between the two types of cross-links is of great practical importance, since the development of accurate kinetic models of gelation and reliable predictions of gel stability under varying conditions depend on a knowledge of the structure and chemistry of the cross-link. In the present paper, we describe conceptually simple experiments on Cr^{3+}/polyacrylamide (PAAm) gels which provide clear evidence for a molecular Cr^{3+} cross-link structure.

Results and Discussion

The cross-linking chemistry of Cr^{3+}/PAAm gels depends on the complex aqueous solution chemistry of Cr^{3+}, which has been elucidated in remarkable detail over the past

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