3886 *Macromolecules* **2007,** *40,* 3886−3890

Notes

Glass Transition Temperature of Perfluorosulfonic Acid Ionomers

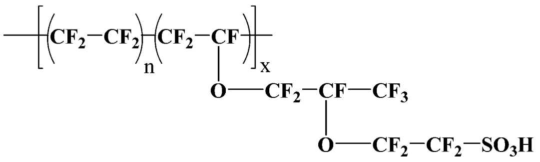
Shawn J. Osborn, Mohammad K. Hassan,[†]
Gilles M. Divoux, David W. Rhoades,
Kenneth A. Mauritz, and Robert B. Moore*

Department of Polymer Science, The University of Southern Mississippi, 118 College Drive #10076, Hattiesburg, Mississippi 39406-0001

Received September 1, 2006
Revised Manuscript Received March 6, 2007

Introduction

Perfluorosulfonic acid ionomers (e.g., Nafion) are the current benchmark materials for polymer electrolyte membrane fuel cells (PEMFCs) and consist of a polytetrafluoroethylene backbone with perfluorovinyl ether side chains that terminate with a sulfonic acid functionality.[1] Nafion is currently available commercially from E.I. DuPont de Nemours and Co. and has the following structure:



$$-\left[(CF_2-CF_2)_n(CF_2-CF)\right]_x- \quad \text{with } CF: O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H$$

With the recent interest in high-temperature (>100 °C) fuel cell operations,[2] a common misconception that Nafion has a glass transition temperature (T_g) at 100 °C has led to concern regarding the mechanical stability of these membranes at elevated temperatures. Surprisingly, however, the fundamental concept of a true glass transition temperature of this exhaustively studied ionomer has yet to be precisely defined and widely accepted for the most commonly applied H^+-form of the polymer.

The prevailing confusion regarding the assignment of a T_g for Nafion stems back to the early work of Eisenberg and coworkers.[3−5] With partially ionized and neutralized samples of 1200 equivalent weight Nafion (i.e., EW = the grams of polymer per equivalent of sulfonate groups), dynamic mechanical studies revealed two principal relaxations, labeled β and α, that were originally speculated to be associated with the glass transitions of the ionic domains and the matrix, respectively.[3] Subsequently, upon further considerations of underwater stress relaxation behavior, the assignments were reversed.[4,5] For over 20 years, these revised assignments suggesting that the β- and α-relaxations are associated with the glass transitions of the matrix and the ionic domains, respectively, have remained unconfirmed for the H^+-form of the polymer.

Recently, through a correlation of dynamic mechanical analysis (DMA) results with variable temperature ^{19}F solid-state NMR and small-angle X-ray scattering (SAXS) results, we have precisely defined the molecular and morphological origins of the α- and β-relaxations of Nafion neutralized with a series of alkylammonium ions.[6] In that study, the high-temperature α-relaxation was found to be due to the onset of long-range mobility of the ionomer main chains and side chains via a thermally activated destabilization of the electrostatic interactions, yielding a *dynamic* network involving significant ion-hopping processes. With these convoluted molecular motions and dynamic interactions, it is important to note that we have refrained from classifying the α-relaxation as a common glass transition. In contrast, however, the low-temperature β-relaxation was found to be due to principally main-chain (backbone) motions within the framework of a *static* physically cross-linked (electrostatic) network. Moreover, in agreement with the behavior of other semicrystalline polymers[7] and the latter consideration of Eisenberg,[4] this β-relaxation was assigned as the *genuine* glass transition of the neutralized ionomer.[6]

Although our studies of Nafion-containing alkylammonium ions have provided fundamental information regarding the influence of electrostatic interactions on chain dynamics in these complex polymeric materials, it is recognized that these counterion forms have little relevance in the context of proton transport[8] in PEMFC applications. However, in order to understand the thermomechanical response of these ionomers in fuel cell operations, it is now possible to build upon this base of fundamental information in order to accurately define and confirm the true glass transition temperature of PFSA membranes. Thus, the purpose of this investigation is to identify and verify the true glass transition temperature of H^+-form Nafion through correlations of relaxation behavior as probed by DMA and dielectric spectroscopy.

Experimental Section

Materials. Extruded Nafion 117 (1100 g/equiv) was obtained from E.I. DuPont de Nemours and Co. Tetrabutylammonium hydroxide (TBAOH), 1 M in methanol, was obtained from Aldrich Chemical Co. and used without further purification.

Preparation of PFSA Membranes. To remove impurities, the membranes were cleaned in refluxing 8 M HNO_3 for 2 h, then rinsed three times with deionized water, and finally boiled in deionized water for 1 h. Partial neutralization of the PFSA samples was performed by stirring the membranes in TBAOH/methanol solutions containing specified quantities of TBAOH for 12 h and then boiling in pure methanol for 1 h. On the basis of the equivalent weight of dry Nafion, the following ratios of H^+-form to TBA^+-form were prepared: 100/0, 90/10, 85/15, 75/25, 65/35, 50/50, 25/75, 0/100. All PFSA membranes were dried in a vacuum oven overnight at 70 °C after the neutralization step.

Dynamic Mechanical Analysis. Dynamic mechanical analysis of the membranes was performed on a TA Instruments DMA Q800 analyzer in tensile mode using clamps for thin film samples. All samples were cut from dried membranes (70 °C vacuum, overnight) with a width of 5.3 mm and run in triplicate to verify results and reduce experimental error. The membranes were analyzed at a

---

* To whom all correspondence should be addressed. E-mail: rbmoore@usm.edu.

[†] Permanent address: Bani Suef University, Faculty of Science, Chemistry Department, Bani Suef, Egypt.

10.1021/ma062029e CCC: $37.00

frequency of 1 Hz from −120 to 200 °C with a heating ramp of 2 °C/min. The temperature range was chosen in order to span all three mechanical relaxations: α, β, and γ.

Dielectric Spectroscopy. Dielectric spectra were recorded using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer over the frequency range of 0.05 Hz to 3 MHz. The range of isothermal temperatures tested, to within ±0.2 °C, was −50 °C to 130 °C in increments of 5 °C. Samples were punched with a 25.4 mm diameter circular die and were 0.178 mm (7 mil) thick, and they were tightly pressed between 20 mm diameter gold-coated copper electrodes. In order to determine the characteristic relaxation times at each temperature,[9] isothermal dielectric permittivity data were first fitted (using the Novocontrol WinFit program) to the Havriliak−Negami equation:[10]

$$\epsilon^*(\omega) = \epsilon'(\omega) - \mathrm{i}\epsilon''(\omega) = -\mathrm{i}\left(\frac{\sigma_0}{\epsilon_0\omega}\right)^s + \sum_{k=1}^{n}\left[\frac{\Delta\epsilon}{(1+(\mathrm{i}\omega\tau_{\mathrm{HN}})^{\alpha})^{\beta}} + \epsilon_\infty\right] \tag{1}$$

In this equation, $\epsilon^*(\omega)$ is the complex dielectric constant, $\epsilon'(\omega)$ is the real component associated with material polarizability, $\epsilon''(\omega)$ is the imaginary component associated with energy loss per signal cycle, σ_0 is the dc conductivity having units of S/cm, ω is the angular frequency $= 2\pi f$, and ϵ_0 is the vacuum permittivity. The exponent s ($0 < s \leq 1$) characterizes the nature of the conduction process in terms of charge hopping pathways. The symbol n in the summation is the number of relaxation peaks fitted ($n = 1$ in this case) to the data. The dielectric strength $\Delta\epsilon$ is equal to $\epsilon_{\mathrm{R}} - \epsilon_\infty$ which is the difference between the relaxed and unrelaxed dielectric constants at low and high frequencies, respectively. τ_{HN} is the Havriliak−Negami relaxation time, which is related to the actual relaxation time $\tau_{\max} = 1/2\pi f_{\max}$, where $f_{\max}$ is the frequency at the maximum dielectric loss and α and β are constants that quantify breadth and asymmetry in the distribution of relaxation times, respectively. Given these three data-fitted parameters, eq 2 was used to determine the relaxation time for the peak maximum for each isothermal peak, using the following relationship:[9]

$$\tau_{\max} = \tau_{\mathrm{HN}}\left[\sin\left(\frac{\pi\alpha\beta}{2(\beta+1)}\right)/\sin\left(\frac{\pi\alpha}{2(\beta+1)}\right)\right]^{1/\alpha} \tag{2}$$

Results and Discussion

Dynamic Mechanical Analysis (DMA). As demonstrated in our previous work,[6,11,12] the principal dynamic mechanical relaxations of Nafion are strongly dependent on the strength of interactions between the side-chain terminal $-SO_3X$ groups. For the neutralized ionomers, the α-relaxation can vary over 250 °C depending on counterion (X^+) size (e.g., $\alpha(Na^+)$ = ca. 230 °C vs $\alpha(TBA^+)$ = 115 °C). As the counterion size increases, the weakened electrostatic interactions yield progressively lower α- and β-relaxation temperatures. For the H^+-form of Nafion, the interactions are principally hydrogen-bonding interactions, which are significantly weaker than the corresponding electrostatic interactions in neutralized samples. Thus, the α-relaxation in H^+-form of Nafion is observed at a relatively low temperature near 100 °C.[4,6]

Figure 1 compares DMA data, plotted as the loss tangent (tan δ) vs temperature, for TBA^+-form and H^+-form Nafion. For the TBA^+-form sample, distinct α- and β-relaxations are observed at ca. 115 and 75 °C, respectively. In contrast, the H^+-form sample appears to show only one principal relaxation in the vicinity of 100 °C. Upon closer inspection of the DMA data for the H^+-form sample, a weak peak near −20 °C is observed. In addition, both samples show a γ-relaxation at ca. −80 °C, which is independent of neutralization or counterion type and has been attributed to local motions of the fluorocarbon $-CF_2-$ backbone chains.[4]

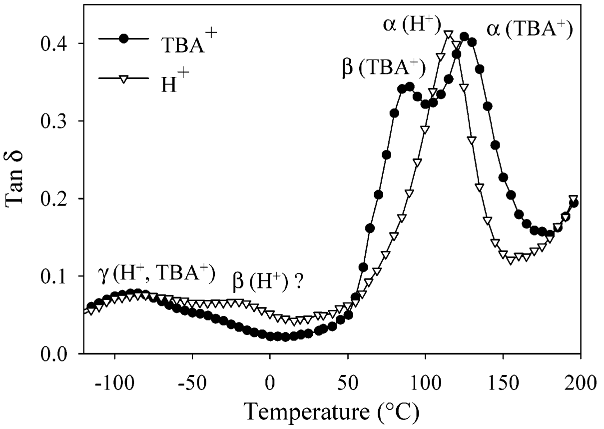


Figure 1. Dynamic mechanical tan δ vs temperature plots of Nafion 117 for (▽) H^+-form and (●) TBA^+-form samples.

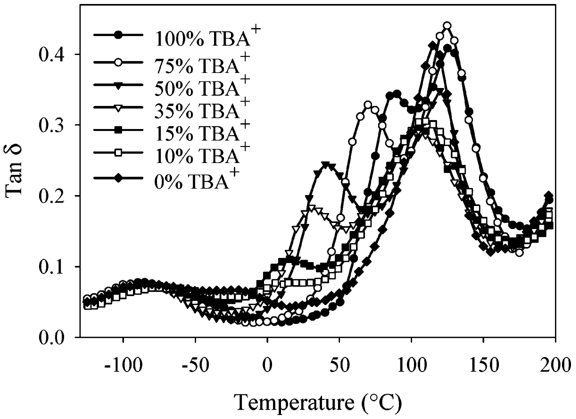


Figure 2. Dynamic mechanical tan δ vs temperature of partially neutralized Nafion 117 for 100, 75, 50, 35, 15, 10, and 0% TBA^+ counterion compositions.

By convention, the peak at −20 °C observed for the H^+-form sample is assigned as a β-relaxation. While this relaxation is similar in temperature to the β-relaxation observed for 1200 EW Nafion in the early work of Eisenberg,[4] it is not reasonable, however, to attribute this relaxation (without further analysis) to the same molecular motions as those known to occur at the β-relaxation for the neutralized samples (i.e., the glass transition).[6] To further clarify the molecular origins of this weak relaxation, we invoke rule-of-mixture concepts common to studies of polymer blends[13] or copolymers. By evaluating the dynamic mechanical behavior of samples prepared with partial neutralization, and assuming that the TBA^+ counterions are homogeneously distributed among the sulfonate groups, the β-relaxation should show a clear compositional dependence if both relaxations are of a similar molecular origin.

Figure 2 shows the DMA data for all seven partially neutralized samples, ranging from pure TBA^+-form Nafion to pure H^+-form Nafion. As the composition of TBA^+ counterions in the samples decreases, the β-relaxation is observed to shift systematically to lower temperatures and decrease uniformly in magnitude. In contrast, the α-relaxation remains in the range of 100−120 °C with only a modest decrease in intensity between 75% and 50% neutralization. Furthermore, the γ-relaxation temperature and magnitude are independent of the degree of neutralization—consistent with the assignment of local backbone motions[4] that should be fairly insensitive to changes in side-chain interactions.

By plotting the peak maxima vs TBA^+ composition (shown in Figure 3), a strong and uniform compositional dependence is observed for the β-relaxation, while the α-relaxation remains

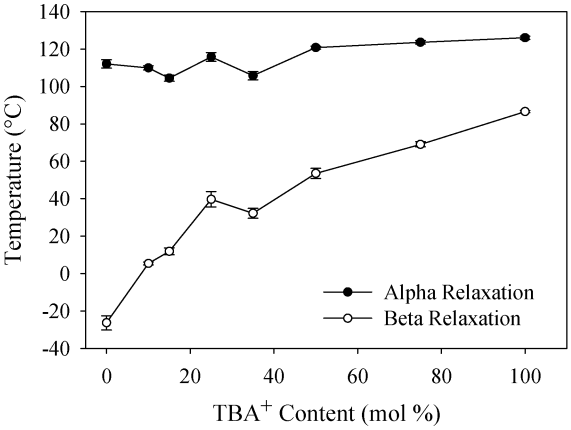


Figure 3. α- and β-relaxation temperatures as a function of TBA$^+$ content from the dynamic mechanical analysis of Nafion 117.

relatively independent of composition. This behavior strongly suggests that the molecular origin of the β-relaxation in H$^+$-form Nafion is the same as that of the β-relaxation in TBA$^+$-form Nafion. Therefore, on the basis of our fundamental understanding of the origin of the β-relaxation in neutralized Nafion samples,[6] we now assign the β-relaxation as the glass transition of H$^+$-form 1100 EW Nafion with a temperature in the vicinity of ca. −20 °C. In a manner consistent with the defined behavior of the neutralized ionomers, this glass transition of H$^+$-form Nafion is attributed to principally main-chain (backbone) motions within the framework of a *static* physically cross-linked (hydrogen-bonding) network.[6]

Dielectric Spectroscopy. Dielectric spectroscopy (DS) has been a powerful tool in the study of chain dynamics in glass-forming polymers and yields information that is complementary to DMA. To confirm the assignment of the β-relaxation in H$^+$-form Nafion as the true glass transition, the relaxation behavior of dry samples of pure H$^+$-form Nafion were probed using DS in both the temperature and frequency regimes. In Figure 4A, there is a relaxation that first appears at approximately −20 °C at 0.1 Hz on ϵ'' vs temperature plots at various fixed frequencies. This is the β-relaxation as observed in the dynamic mechanical spectra in Figure 1. The observed peak shift to higher temperatures with increasing frequency is interpreted in the usual sense: as the oscillatory period $= 1/f$ decreases, the characteristic dipole motions must be more rapid by heating so to be detected within a shorter experimental time frame, i.e., $1/2f$. The curves at the lowest frequencies should be compared with the dynamic mechanical data for which the perturbation frequency is low (1 Hz). In Figure 4B, the peak in the ϵ'' vs f curves monotonically shifts to higher frequencies, and the associated relaxation time correspondingly shifts to lower values with increased temperature.

By fitting eq 1 to the loss permittivity data points in Figure 4B, τ_{HN}, α, and β were obtained and substituted in eq 2 to calculate $\tau_{\max}$ over the range of temperatures. Figure 5 is a plot of ln $\tau_{\max}$ vs inverse Kelvin temperature. First, it is seen that the points define a graph with upward curvature rather than a straight line that would characterize an activated rate (i.e., Arrhenius-like) process such as observed for short-range motions.

The Vogel−Fulcher−Tammann (VFT) equation can be well-fitted to the data:[14−16]

$$\tau = \tau_0 \exp\left[\frac{B}{T - T_{\mathrm{V}}}\right] \tag{3}$$

τ_0 is a hypothetical relaxation time at infinite temperature, and B is a fitted parameter that is sometimes related to an apparent activation energy. T_{V} is the Vogel temperature that is often interpreted as a temperature, that is reached upon quasi-static cooling, at which chain segments become immobile. At temperatures above this frozen-in state, the free volume is dynamic and constantly redistributed with no change in energy according to simple liquid state theories, the most notable being based on the concepts of Cohen and Turnbull.[17,18] While the VFT equation is empirical in origin, it has often been interpreted in terms of free volume fluctuations in a liquid-like state in the same way as used in the rationalization of the WLF equation for the rubbery state of polymers.[19] In fact, T_{V} in some instances has been called an “ideal glass transition temperature”.[20]

The data points in Figure 5 fit very well with the VFT equation over the range of tested temperatures for the β-relaxation for H$^+$-form Nafion, as it does for many polymers at temperatures above the dynamic glass transition.[21] The extracted values from the fit of the VFT equation for τ_0 and T_{V} are 1.63×10^{-9} s and 146 K (−127 °C), respectively. T_{V} is usually lower than T_{g} by as much as 100 °C so that this value is realistic in comparison with the relaxation centered at −20 °C.

In order to account for systematic deviation of the data points in Figure 5 from the VFT fit, a derivative analysis, as performed by Stickel et al.,[22,23] was undertaken. In this analysis, the behavior of the first derivative of the VFT equation vs temperature is observed:

$$\frac{\mathrm{d}\log\left(\dfrac{\tau_0}{\tau_{\max}}\right)}{\mathrm{d}T} = \frac{B}{(T - T_{\mathrm{V}})^2} \tag{4}$$

This equation is linearized as follows:

$$\left[\frac{\mathrm{d}\log\left(\dfrac{\tau_0}{\tau_{\max}}\right)}{\mathrm{d}T}\right]^{-1/2} = B^{-1/2}(T - T_{\mathrm{V}}) \tag{5}$$

Thus, when the quantity on the left side of the equation is plotted against temperature and the plot is linear, it can be concluded that the VFT equation is indeed a good representation of the relaxation data in this temperature range. The actual data fit, seen in Figure 6, shows considerable agreement with VFT behavior over the temperature range from 260 to 350 K.

As further confirmation of the consistency of the experimental data with the VFT equation over this temperature range, it is important to note that the derivative of eq 5 with respect to T yields a temperature invariant value of B over the range 260 K $< T <$ 350 K. In agreement with the analysis of Stickel et al.,[22,23] this representation of the experimental data clearly indicates a reasonable VFT fit over this range of temperatures.

VFT behavior is characteristic and is a signature of long-range segmental motions not requiring an activation energy in glass-forming liquids.[20] In contrast, the Arrhenius equation does not involve a lower bound on temperature (T_{V}) at which long-range motions are frozen-in. The relaxation time vs temperature behavior and the existence of VFT behavior, as well as the magnitude of the frequencies above the β-transition, coupled with the DMA results, strongly suggest that this is a glass transition in the usual sense. While the conformance of the VFT equation to relaxation data over a temperature range is not sufficient proof of a liquid-like state as in rubbery polymers, it is a necessary condition given the large volume of evidence for numerous polymers. Given this rationale, and in agreement with the latter assignment of Eisenberg and co-workers,[4] it is

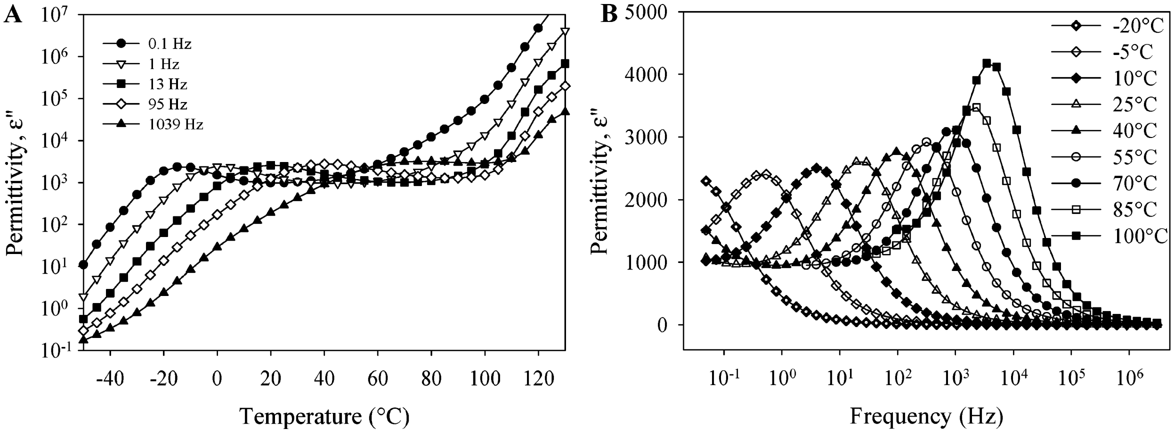


Figure 4. (A) ϵ'' vs temperature curves at various frequencies in the region of the β-relaxation for H$^+$-form Nafion. (B) Isothermal ϵ'' vs f curves for temperatures above the β-relaxation for H$^+$-form Nafion.

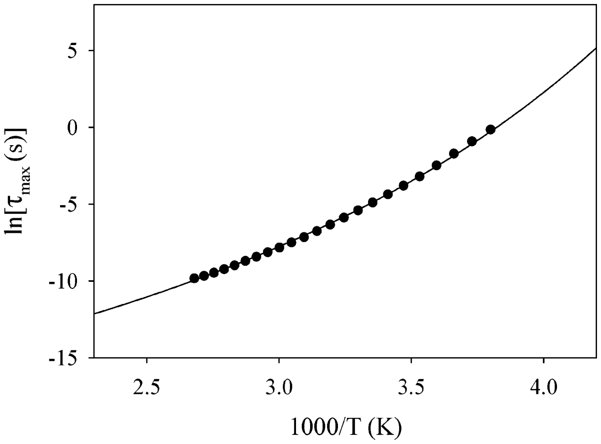


Figure 5. ln $\tau_{\max}$ vs inverse temperature for the β-relaxation of H$^+$-form Nafion 117. The continuous curve is a plot of the best fit of the VFT equation to the data points.

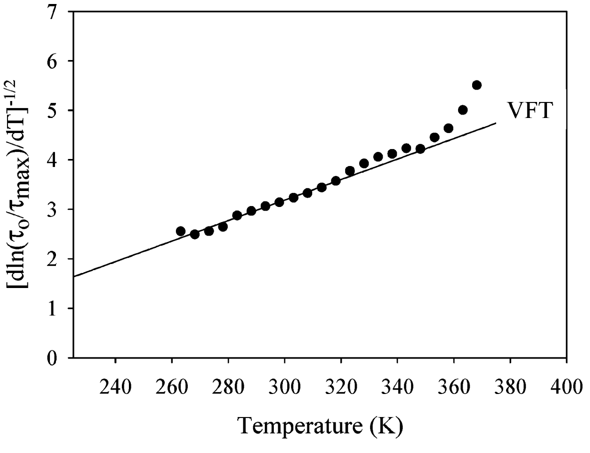


Figure 6. Temperature derivative data vs temperature and fit of eq 5 for the β-relaxation of H$^+$-form Nafion.

concluded that the β-relaxation of H$^+$-form Nafion is a *genuine* glass transition involving long-range segmental motions.

Conclusions

Through a correlation of dynamic mechanical analysis and dielectric spectroscopy, the glass transition temperature of H$^+$-form Nafion is assigned to the weak β-relaxation centered at −20 °C. Building upon our previous studies of the molecular and morphological origins of the dynamic mechanical relaxations of Nafion containing large organic ions, a strong compositional dependence of the β-relaxation in partially neutralized samples suggests that the β-relaxation of H$^+$-form Nafion and the neutralized ionomers have the same molecular origin, namely backbone segmental motions. In the dielectric spectroscopy studies, the relaxation time vs temperature behavior, the existence of a Vogel temperature and the magnitude of the frequencies above the β transition, coupled with the DMA results, strongly suggest that the β-relaxation is a glass transition in the usual sense, rather than a short-range, secondary relaxation with Arrhenius temperature dependence.

With this understanding of the glass transition in H$^+$-form Nafion, it remains important to recognize that the β-relaxation is significantly weaker than the dominant α-relaxation observed near 100 °C. At temperatures between −20 and 100 °C, main-chain segmental motions are significant; however, the morphological organization of the hydrophobic and hydrophilic domains is likely to be pinned within a static physical network.[6] At temperatures above the α-relaxation, the hydrogen-bonded network becomes dynamic resulting in considerable molecular mobility. Under these conditions, it is reasonable to consider the possibility of morphological reorganization;[12,24] however, the extent of this potential change in structure and the impact on membrane properties remains to be determined.

Acknowledgment. The authors of this paper thank E.I. Dupont De Nemours & Co. Inc. for supplying the extruded Nafion 117 samples. Funding for this work was provided by DuPont Fuel Cells and DOE Office of Energy Efficiency and Renewable Energy; Contracts DE-FC36-03GO13100 and DE-FG36-06GO86065.

References and Notes

(1) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535−4585.
(2) Song, Y.; Xu, H.; Wei, Y.; Kunz, H. R.; Bonville, L. J.; Fenton, J. M. *J. Power Sources* **2006**, *154*, 138−144.
(3) Yeo, S. C.; Eisenberg, A. *J. Appl. Polym. Sci.* **1977**, *21*, 875−898.
(4) Kyu, T.; Hashiyama, M.; Eisenberg, A. *Can. J. Chem.* **1983**, *61*, 680−687.
(5) Kyu, T.; Eisenberg, A. *J. Polym. Sci., Polym. Symp.* **1984**, *71*, 203−219.
(6) Page, K. A.; Cable, K. M.; Moore, R. B. *Macromolecules* **2005**, *38*, 6472.
(7) Fisher, E. W.; Kloos, F.; Lieser, G. *Polym. Lett.* **1969**, *7*, 845−850.
(8) Kreuer, K.-D. *Chem. Mater.* **1996**, *8*, 610−641.
(9) Zhang, S.; Painter, P. C.; Runt, J. *Macromolecules* **2004**, *37*, 2636−2642.
(10) Havriliak, S.; Negami, S. *J. Polym. Sci., Polym. Symp.* **1966**, *14*, 99−117.
(11) Moore, R. B.; Cable, K. M.; Croley, T. L. *J. Membr. Sci.* **1992**, *75*, 7−14.
(12) Page, K. A.; Landis, F. A.; Phillips, A. K.; Moore, R. B. *Macromolecules* **2006**, *39*, 3939.
(13) Fox, T. G. *Bull. Am. Phys. Soc.* **1956**, *1*, 123.

(14) Vogel, H. *Phys. Z.* **1921**, *22*, 645.
(15) Fulcher, G. S. *J. Am. Ceram. Soc.* **1926**, *8*, 339−355.
(16) Tammann, V. G.; Hesse, W. *Z. Anorg. Allg. Chem.* **1926**, *156*, 245−257.
(17) Cohen, M. H.; Turnbull, D. *J. Chem. Phys.* **1959**, *31*, 1164−1169.
(18) Turnbull, D.; Cohen, M. H. *J. Chem. Phys.* **1961**, *34*, 120−125.
(19) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701−3707.
(20) Kremer, F.; Schoenhals, A. In *Broadband Dielectric Spectroscopy;* Springer-Verlag: Berlin, 2003.
(21) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids;* Dover Publications: New York, 1991.
(22) Stickel, F.; Fischer, E. W.; Richert, R. *J. Chem. Phys.* **1995**, *102*, 6251−6257.
(23) Stickel, F.; Fischer, E. W.; Richert, R. *J. Chem. Phys.* **1996**, *104*, 2043−2055.
(24) Nosaka, A. Y.; Watanabe, S.; Toyoda, I.; Nosaka, Y. *Macromolecules* **2006**, *39*, 4425.

MA062029E