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Dynamics of Sulfonated Polystyrene Copolymers Using Broadband Dielectric Spectroscopy

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ABSTRACT: We examine the dynamics of acid and methylated precursors to sulfonated polystyrene ionomers. Dielectric relaxation spectroscopy was the primary tool used in the investigation of the dynamics, and dynamic mechanical analysis, Fourier transform infrared spectroscopy, and differential scanning calorimetry were employed in a complementary role. Monodisperse polystyrene was sulfonated to 1 and 7 mol % and the behavior compared to that of neat polystyrene and methyl-sulfonated polystyrene. Three relaxations were identified in dielectric spectra of the acid form of the sulfonated polystyrenes: the segmental α process, a relaxation arising from the presence of hydrogen bonds (α*), and a local β process. The α* process followed Arrhenius behavior, and its relaxation strength decreased significantly with increasing temperature, indicating that the strength is related to the number of associating complexes, which decreases with increasing temperature. A qualitatively similar trend is observed in the infrared absorption indicative of hydrogen bonding over the same temperature range.

Introduction

It is well-known that incorporation of ionic groups into hydrophobic polymers can significantly modify the characteristics of the base polymer, even at low ionic fractions. These high-performance materials, commonly referred to as ionomers, display dramatic improvements over the unmodified material in electrolytic transport and physical properties such as modulus and impact strength. Typically, a relatively small fraction of repeat units (ca. <∼10%) are functionalized with acid groups, and these are completely or partially neutralized with cations.[1−3] The enhancements in physical properties of ionomers result primarily from the aggregation of ionic species into clusters,[1−4] which act as physical cross-links. Clusters are typically viewed as roughly spherical aggregates of about 20 ionic groups, ca. 3−10 nm in size. Hydrocarbon segments attached to the ionic groups are believed to be immobilized in the corona (i.e., the region surrounding each cluster).[4]

In this paper, we focus on the dynamics of acid (referred to as SPS-H subsequently) and methylated precursors to sulfonated polystyrene (SPS) ionomers. It is well-known that SPS ionomers phase separate with the formation of ionic clusters, which is typical for ionomeric systems; however, the SPS-H copolymer precursors are somewhat less well understood. This is at least partly due to the immiscibility of PS blends with SPS-H with acid contents as low as 1.7 mol %[5] and the possibility of compositional heterogeneity arising from the sulfonation reaction. Previous investigations of these SPS-H copolymers have examined the possibility of phase separation by small-angle X-ray scattering (SAXS),[6−8] transmission electron microscopy (TEM),[9] and dynamic mechanical analysis (DMA).[7,10] No phase separation was detected with SAXS and TEM, although the presence of a second loss peak in DMA spectra led to the proposal that phase separation can occur in SPS-H copolymers.[7] However, for polyisobutylene and polybutadiene transient networks containing a small mole fraction of hydrogen-bonded urazole stickers[11−13] and hydrogen-bonded supramolecular assemblies,[14] a relaxation at temperatures higher than the α process has been observed, but rather than phase separation, this process was assigned to the relaxation of binary hydrogen-bonded linkages. These studies primarily used broadband dielectric relaxation spectroscopy (DRS).

In the current paper, we investigate the dynamics of two sulfonated polystyrene copolymers having low sulfonation levels using broadband DRS. The findings were interpreted with the assistance of Fourier transform infrared (FT-IR) spectroscopy, differential scanning calorimetry (DSC), and DMA. Since polystyrene is relatively dielectrically inactive, it provides a low background signal for ready measurement of the dielectrically active sulfonated groups. These results set the stage for understanding the relaxation behavior of partially and completely neutralized versions of these copolymers, which will be addressed in a following publication.

Experimental Section

A. Materials and Sample Preparation. Sulfonation of Polystyrene. Narrow molecular weight distribution polystyrene was purchased from Polymer Source and has $M_w = 119\,600$ and $M_w/M_n = 1.04$. Polystyrene was sulfonated with acetyl sulfate according to a procedure widely reported in the literature to produce random SPS copolymers.[15,16] Acetyl sulfate was prepared by mixing sulfuric acid (99.9%) with acetic anhydride (99.5%) in an ice bath under flowing N_2 gas. The PS was dissolved in 1,2-dichloroethane and heated to 50 °C under an N_2 purge for 30 min. Acetyl sulfate solution was added while stirring. The reaction was maintained at 50 °C for 5 h. The reaction was terminated, and the polymer precipitated into 2-propanol. The sulfonated polymer was isolated by pouring the precipitate into a large volume of boiling distilled water, followed by washing several times with distilled water and methanol. The product was filtered and dried under vacuum at 70 °C for several days.

Alkylation of Sulfonated Polystyrene. The $-OH$ groups of unneutralized SPS-H were converted to $-OCH_3$, yielding methyl-sulfonated PS ($SPS7CH_3$), by adding trialkyl phosphate (in a 1:1 molar ratio) to SPS7H solution, which was dried by azeotropic distillation using benzene. The reaction was stirred at room temperature for 24 h.[17] The reaction was terminated and the product precipitated by adding methanol and isolated by pouring in boiling water and then washed with cold water and methanol. The polymer

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was dried and maintained under vacuum at 70 °C for at least 48 h before use. Titration of this product revealed that 83% alkyl conversion was achieved.

Degree of Sulfonation. The sulfonation level of SPS-H polymers was determined by titration with a standard 0.05 M NaOH solution in methanol. The normality of the standard solution was determined by 0.05 M *p*-toluenesulfonic acid in methanol using a phenolphthalein indicator. The SPS samples were dissolved in a 9:1 THF:methanol mixture. The degree of sulfonation *y* is the molar percentage of styrene repeating units properly sulfonated (SPSyH). Sulfonation levels of the two concentrations studied were 1.1 and 6.8 mol %. The unneutralized versions of these polymers are referred to as SPS1H and SPS7H, respectively, throughout the remainder of the paper.

Coulometric Karl Fischer Titration. The water content of selected samples was determined by coulometric Karl Fischer (KF) titration using Hydranal CG and Hydranal A as KF reagents. The samples were dissolved in chloroform and injected into the large cell compartment; iodine continues to be generated by the titrator until an end point is determined. Modern microprocessor-controlled coulometric titrators calculate the amount of iodine generated based on the total current required to reach an end point.

The water content of SPS1H, SPS7H, and SPS7CH$_3$ samples, before and after DRS experiments, was found to be less than 0.3 wt %. Weiss et al.[16] have reported water absorption at room temperature after 24 days for a 5.2 mol % sulfonated PS to be 0.4 wt %. This suggests that it is difficult for water to absorb into SPS copolymers with low sulfonic acid content below T_g, and water is not expected to significantly influence the dielectric properties of the copolymers under consideration here.

B. Experimental Methods. Before characterization, sample films were prepared by solution casting. To faciltate solvent and water removal, films were heated to 120 °C under vacuum for at least 24 h.

Differential Scanning Calorimetry. Glass transition temperatures (T_g) were determined using a TA Instruments Q-100 DSC. Temperature was calibrated using an indium standard. The samples were in film form and weighed from 8 to 10 mg. Samples were first heated from 20 to 140 °C at a heating rate of 10 °C/min, held for 5 min, and then cooled at 40 °C/min to 20 °C. After holding for 3 min, samples were reheated to 220 °C at a rate of 10 °C/min. Results shown in this paper are taken from the last step.

Fourier Transform Infrared Spectroscopy. Infrared spectra were acquired using a Bio-Rad FTS-6 spectrometer, signal averaging 128 scans at a resolution of 2 cm^{-1}. Sample solutions were deposited on KBr windows, and the solvent evaporated at room temperature, followed by gradually heating to 120 °C and then maintaining at 120 °C under vacuum for 24 h.

Dynamic Mechanical Analysis. Dynamic mechanical properties in tensile mode were acquired using a TA Q-800 DMA, at a frequency of 1 Hz and a heating rate of 5 °C/min.The storage (E') and loss moduli (E'') were measured as a function of temperature (from 50 to 200 °C) for rectangular films (18 mm × 5 mm × 0.1−0.3 mm).

Broadband Dielectric Relaxation Spectroscopy. Dielectric relaxation spectra were collected isothermally using a Novocontrol GmbH Concept 40 broadband dielectric spectrometer in the frequency domain from 0.01 Hz to 10 MHz in the range of 30−220 °C. Temperature stability was controlled to within ±0.2 °C. Sample films were 0.1−0.3 mm thick. Sample surfaces were sputtered with gold, covered by a silver sheet, and tightly sandwiched between electrodes of 2 cm diameter.

Data Processing. The relaxation time $\tau_{\max}$ ($= 1/2\pi f_{\max}$) and dielectric relaxation strength $\Delta\epsilon$ were obtained by fitting the isothermal dielectric loss $\epsilon''(f)$ curves with the Havriliak−Negami (HN) function. The sum of multiple HN functions and a dc loss contribution were used to fit the experimental loss curves:[18]

$$\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega) = \epsilon_\infty - i\frac{\sigma_0}{(\epsilon_0\omega)^s} + \sum \frac{\Delta\epsilon}{[1 + (i\tau_{HN}\omega)^m]^n} \quad (1)$$

where ϵ^*, ϵ', and ϵ'' are the complex, real, and imaginary components of the dielectric permittivity, respectively; the relaxation strength $\Delta\epsilon = \epsilon_\infty - \epsilon_s$, where ϵ_∞ and ϵ_s are the dielectric constants at limiting high and low frequencies, respectively; σ_0 is the dc conductivity (S/cm); ω is the angular frequency; τ_{HN} is the characteristic relaxation time; and *m* and *n* are shape parameters, indicative of the breadth of the relaxation and peak asymmetry, respectively. The exponent *s* characterizes the conduction process.

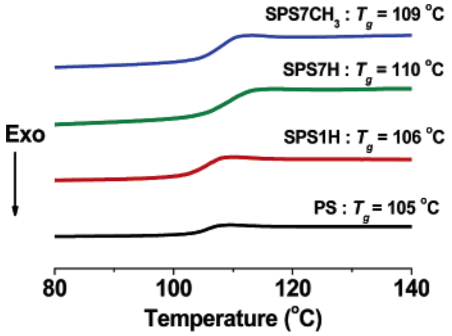

Figure 1. DSC thermograms of PS, SPS1H, SPS7H, and SPS7CH$_3$.

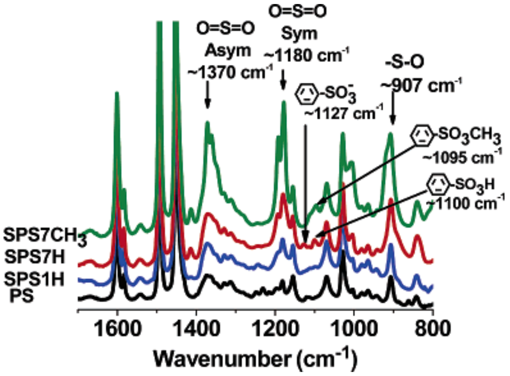

Figure 2. FT-IR spectra of PS, SPS1H, SPS7H, and SPS7CH$_3$ in the region from 2000 to 800 cm^{-1}.

The dielectric constant can be transformed into the dielectric loss factor via a Kramers−Kronig (KK) transform, possessing the advantage of suppressing conduction losses; this is particularly helpful for identifying dipole relaxation in materials with high conduction losses.[19] In an approximation of the KK transform, the first derivative of ϵ' [$\epsilon''_{der} = -(\pi/2)(\partial\epsilon'(f)/(\partial \ln f))$] has been shown for relatively broad relaxations to provide a good estimate of the conduction-free dielectric loss.[20] In a series of model calculations, ϵ''_{der} and ϵ'' have been shown to exhibit the same peak frequencies, and for relatively broad relaxations, the strength of a derivative spectrum is a very good approximation to that of ϵ''.[19] We have used this approach previously in the investigation of the dipolar relaxation behavior of polymer blends[21] as well as ion-containing polymer complexes.[22]

Results and Discussion

DSC. Thermograms of PS, the two SPS-H copolymers, and SPS-CH$_3$ are displayed in Figure 1. At very low degrees of sulfonation (SPS1H), the glass transition temperature (T_g) is not distinguishable from that of neat PS. The T_g of SPS7H is approximately the same as SPS7CH$_3$ and slightly higher than SPS1H and PS,[7] consistent with increased steric hindrance resulting from the addition of sulfonate groups.

FTIR. FTIR spectroscopy was used to confirm the general structure of the synthesized SPS polymers and investigate the state of the sulfonic acid species. Figure 2 shows a portion of the spectrum of neat PS together with those of SPS1H, SPS7H, and SPS7CH$_3$. The arrows identify the absorbance bands arising from the sulfonated groups. The peaks at 1370 and 1180 cm^{-1}

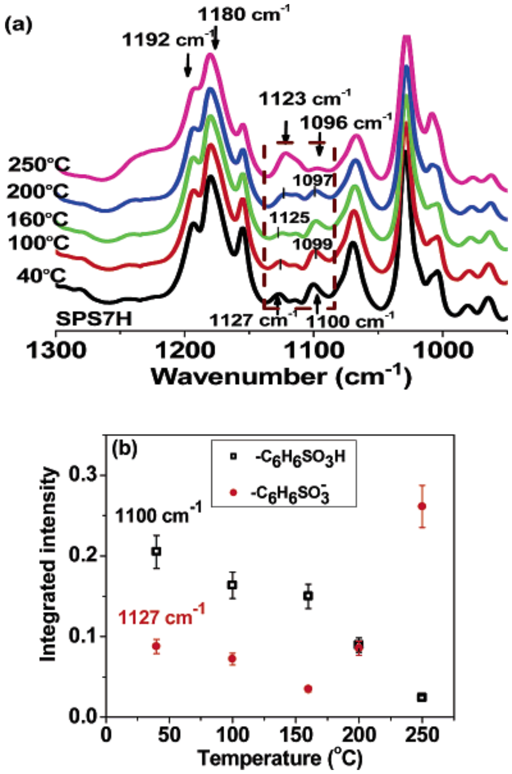

Figure 3. (a) FT-IR absorbance spectra of SPS7H at selected temperatures from 40 to 250 °C and (b) comparison of the integrated intensity of the free anion band at 1127 cm^{-1} and the bound anion band at 1100 cm^{-1}. Error bars represent the 95% confidence intervals calculated from the fitting program.

have been assigned respectively to antisymmetric and symmetric stretching vibrations of the sulfur−oxygen having double-bond character (O═S═O). The band at 907 cm^{-1} has been assigned to the stretching vibration of the SO having single-bond character (S−O).[23−25] The peaks at 1100 and 1127 cm^{-1} in the SPS7H spectra correspond to the in-plane skeletal vibration of the benzene ring substituted by SO_3H and SO_3^-, respectively.[23−25]

To aid in interpretation of DRS spectra, the state of the sulfonated species was investigated as a function of temperature. The integrated areas of the bands of interest were deconvoluted and the areas calculated with PeakFit software, using a linear baseline and adjustable-width Gaussian peaks. The absorbance of the peak at 1100 cm^{-1} decreases with increasing temperature (see Figure 3), whereas that of the 1127 cm^{-1} absorption rapidly increases at temperatures above 160 °C. This indicates that additional protons dissociate at high temperatures, resulting in additional SO_3^- anions. Similarly, the absorbance at 1095 cm^{-1} in the spectrum of SPS7CH$_3$ is assigned to an in-plane bending vibration of aromatic rings with SO_3CH_3 substitution (see Figure 2). An FTIR temperature study of this copolymer (not shown) reveals that there is no significant change in the absorbance of the 1095 cm^{-1} band with temperature, in keeping with previous interpretations.

DMA. Storage and loss moduli for the polymers under investigation are displayed in Figure 4. Consistent with the DSC observations, the mechanical α relaxation shifts slightly to higher temperature with increasing sulfonation. The extended rubbery plateau (Figure 4a) observed for SPS1H and SPS7H, in contrast with PS and SPS7CH$_3$, demonstrates the importance of H-bonding on the mechanical properties above T_g for SPS-H systems.[7] An increase in the plateau modulus for SPS7H is due to the increased number of reversible H-bonding contacts.[26] The importance of H-bonds above T_g is further supported by the significant reduction in the length of the rubbery plateau for SPS7CH$_3$, where the possibility for hydrogen bonding has been mostly removed. Finally, no other transitions are observed for either SPS1H or SPS7H, and hence there is no indication of significant phase separation in these copolymers.

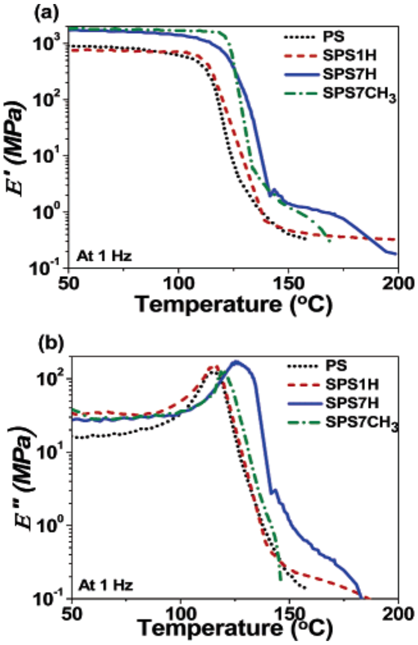

Figure 4. (a) Storage E' and (b) loss modulus E'' vs temperature for PS, SPS1H, SPS7H, and SPS7CH$_3$ at 1 Hz.

DRS.

Segmental α Process. The relaxation times of the segmental α process (τ_α) are obtained from the maxima in ϵ'' after subtracting the contribution from dc conductivity. The relaxation times of PS and the SPS copolymers are well fit by the Vogel−Fulcher−Tammann (VFT) equation:[27]

$$\tau(T) = \tau_0 \exp\left(\frac{B}{T - T_0}\right) \tag{2}$$

where τ_0 is sometimes associated with vibration lifetimes,[28] B is related to the apparent activation energy ($B = [E_a(1 - T_0/T)^2]/R$), and T_0 is the Vogel temperature below which segments become immobile. τ_0 is fixed at 10^{-14} s to increase fitting accuracy.[29] VFT plots for PS and SPS copolymers are shown in Figure 5a. The fitted values for B and T_0 are provided in Table 1. The dynamic glass transition temperature (T_g^{DRS}) can be determined from[29]

$$T_g^{DRS} = T_{ref} = \frac{B}{\ln(1/\tau_0)} + T_0 \tag{3}$$

where T_{ref} is defined as the temperature at which the segmental relaxation time is 1 s ($\tau_{max} = 1$ s). The system cooperativity, correlated with the degree of intermolecular coupling, can be characterized by determining the fragility. Fragility F is defined as[30]

$$F = \frac{d \log(\tau_{max})}{d(T_{ref}/T)}\bigg|_{T=T_{ref}} = \frac{B/T_{ref}}{\ln(10)(1 - T_0/T_{ref})^2} \tag{4}$$

It was anticipated that hydrogen bonding would increase the fragility of the copolymers compared to neat PS, but this is not the case (see Figure 5b). Rather, neat PS is a relatively fragile polymer ($F \cong 78$) due to the bulky side groups enhancing

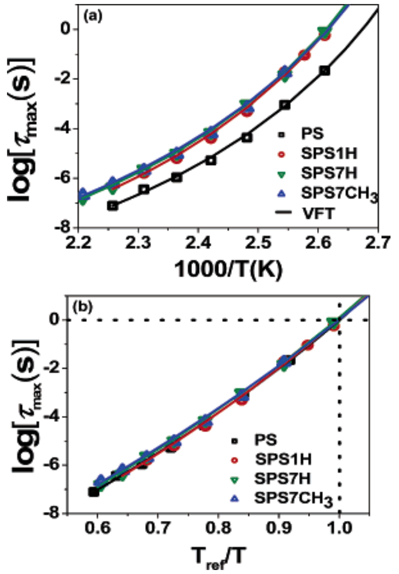

Figure 5. Relaxation times of the α process obtained from ϵ'' data as a function of temperature for PS, SPS1H, SPS7H, and SPS7CH$_3$: (a) VFT and (b) fragility plots. Solid lines indicate fits with eqs 2 and 4, with $T_{ref} = T_g^{DRS}$, defined in Table 1.

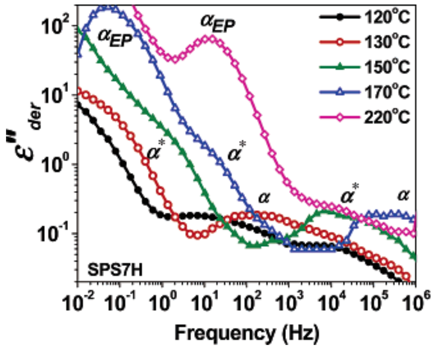

Figure 6. Derivative loss spectra of SPS7H vs frequency at selected temperatures, indicating the segmental (α), H-bond association/dissasoction (α*), and electrode polarization (α$_{EP}$) processes.

Table 1. T_gs, VFT Fit Parameters, and Fragilities for PS, SPS1H, SPS7H, and SPS7CH$_3$

			VFT parameters	
sample	T_g^{DSC} (°C)	T_g^{DRS} (°C)	B (eV)	T_0 (°C)
PS	105	101	0.186	34
SPS1H	106	109	0.198	38
SPS7H	110	109	0.207	35
SPS7CH$_3$	109	109	0.214	32

intermolecular cooperativity,[29] and the addition of a relatively small number of hydrogen bonds does not increase the degree of the intermolecular coupling above that of PS. Previous studies point out that in high-fragility polymers the addition of hydrogen bonding does not have a significant impact on intermolecular cooperativity.[31,32]

The derivative dielectric loss spectra of SPS1H and SPS7H reveal two additional relaxation processes above the segmental relaxation (see Figure 6 for SPS7H spectra, those for SPS1H are similar and not shown), which are absent in the spectra of PS and SPS7CH$_3$. Since the former copolymers are single phase materials, Maxwell−Wagner−Sillars interfacial polarization can be ruled out as the origin of these processes. Vinyl homopolymers cannot be intrinsic type A chains and hence do not exhibit a normal mode relaxation.[33] Random head-to-tail copolymers could exhibit a small dipole moment along the chain direction, but at such low comonomer concentrations it is rather unlikely that a normal mode process for SPS1H and SPS7H would be observable.

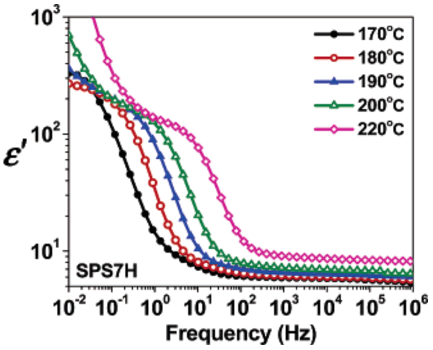

Figure 7. Frequency dependence of the dielectric constant of SPS7H from 170 to 220 °C.

α$_{EP}$ Process. The highest temperature and lowest frequency relaxation in the loss spectra of SPS1H and SPS7H (for SPS7H in Figure 6, see data at $T = 170$ and 220 °C) is attributed to electrode polarization (EP), the phenomenon where mobile ions accumulate at electrode interfaces and act as a large capacitance in series with the sample. The very large concurrent increase in dielectric constant ϵ' at low frequencies (Figure 7, for SPS7H) supports this assignment.

It has been proposed that the α$_{EP}$ relaxation times can be determined to a first approximation from[19]

$$\tau_{EP} = \frac{\epsilon_\infty \epsilon_0 D}{\sigma_0 2 L_D} \qquad (5)$$

where ϵ_∞ is the high-frequency dielectric permittivity, σ_0 the (dc) conductivity obtained from the low-frequency plateau of the real part of the measured conductivity vs frequency, D the sample thickness, and L_D the Debye length. The Debye length is the distance an unpaired counterion must travel to achieve electrostatic neutrality and is inversely proportional to the conductivity. For SPS7H at 190 °C, for example (where $\sigma_0 = 4.6 \times 10^{-10}$ S cm^{-1}, $\epsilon_\infty = 6.5$, and $\tau_{EP} = 1.8 \times 10^{-1}$ Hz), D/L_D was estimated to be ∼270, implying $L_D \sim 1.4$ μm. L_D was calculated to be near 1 μm at all other temperatures. This value is on the same order (ca. 1 μm) as determined previously for another poorly conducting polymer system.[34] For more highly conducting systems ($>10^{-5}$ S cm^{-1}), such as polyelectrolyte solutions, the Debye length is on the order of 5−10 nm.[35]

α* Process. The process we refer to as α*, detected in ϵ''_{der} spectra of SPS1H and SPS7H, is located between the α and α$_{EP}$ relaxations. We propose that this process has an origin comparable to what has been referred to previously as a “chemical relaxation”, specifically the association and dissociation of transient hydrogen-bonded stickers.[11−14] In general, the overall relaxation time of such processes has been shown to exhibit a contribution from “chemical relaxation” (sticker association/dissociation) and dipole reorientation processes.[12]

The relaxation map for SPS7H is presented in Figure 8. The α relaxation should follow a VFT dependency as noted previously, whereas α* relaxation times are more Arrhenius-like over the temperature range of our data. This supports the assignment of the α* relaxation, since H-bond association and dissociation should follow Arrhenius behavior.[12] The activation energy of the α* process of SPS7H ($E_a \cong 240$ kJ/mol) is about 3 times higher than that for SPS1H (∼75 kJ/mol).[13,14]

$\Delta\epsilon(\alpha^*)$ are plotted against temperature in Figure 9, with $\Delta\epsilon(\alpha)$ also shown for comparison purposes. $\Delta\epsilon(\alpha^*)$ decrease significantly with increasing temperature, in keeping with that

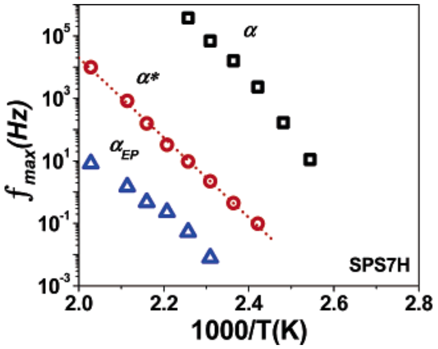

Figure 8. Temperature dependence of the relaxation times of the α, α*, and α_{EP} processes for SPS7H (the former were obtained from ϵ'' data and the latter two from ϵ''_{der} data). The dotted line through the α* data represents an Arrhenius fit.

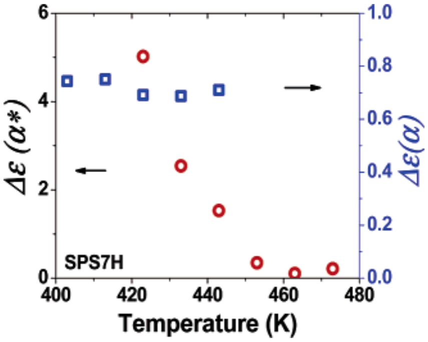

Figure 9. Temperature dependence of the dielectric relaxation strengths for the α and α* processes of SPS7H (obtained from ϵ'' and ϵ''_{der} data, respectively).

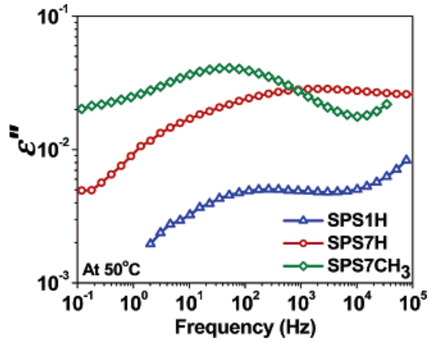

Figure 10. Dielectric loss spectra for SPS1H, SPS7H, and $SPS7CH_3$ at 50 °C.

strong reduction in the number of hydrogen bonds with temperature. A qualitatively similar trend is observed for the infrared absorption associated with hydrogen bonding over the same temperature range and in a previous DRS study of polybutadiene reversible networks.[36] The relaxation strengths of the α and α* processes for SPS1H exhibit similar trends as a function of temperature, but the corresponding strengths are much smaller. (The strengths of the α and α* are about 3 and 10 times smaller, respectively, than the comparable processes of SPS7H.)

Sub-T_g Local β Relaxation. PS does not exhibit a discernible dielectric β process in the glassy state due to the very small dipole moment associated with the pendant aromatic rings. However, SPS1H, SPS7H, and $SPS7CH_3$ exhibit a well-defined, but weak, process at $T < T_g$ (see Figure 10). Considering the relative strengths of the processes for these three polymers, we propose that these β relaxations arise from the motion of the sulfonated phenyl groups in the glassy state. The possibility that this β relaxation is associated with water has been eliminated because this process does not change in τ or Δϵ after SPS7H has been soaked in water (creating a specimen containing 2 wt % water). A relaxation associated with water is observed at very low frequency (below that of the β relaxation) at these temperatures.

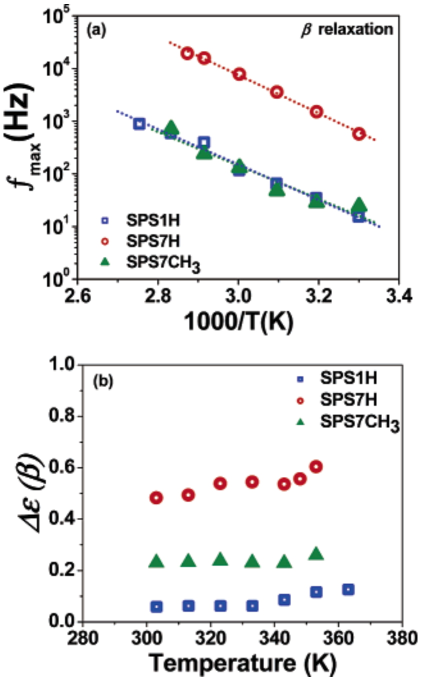

Figure 11. Temperature dependence of (a) the relaxation times and (b) the dielectric relaxation strengths for the β processes of SPS1H, SPS7H, and $SPS7CH_3$. The dotted line in (a) represents an Arrhenius fit.

As seen in Figure 11a, the β process exhibits the expected Arrhenius behavior, with the same activation energy ($E_a \sim 65$ kJ/mol) for SPS1H, SPS7H, and $SPS7CH_3$. The relaxation strengths increase in the series SPS7H > $SPS7CH_3$ > SPS1H, in keeping with sulfonation level and the increased dipole moment of the acid form. Relaxation strengths increase slightly with temperature due to greater dipole mobility at higher temperatures.

Summary

The dynamics of model SPS copolymers, ionomer precursors, were investigated using dielectric relaxation spectroscopy, along with several complementary techniques. The glass transitions of the copolymers under investigation were found to increase slightly with sulfonation level due to increased steric hindrance resulting from the addition of sulfonate groups. FT-IR results confirmed the polymer chemistry and were also used to investigate that the relative fraction of protonated and SO_3^- species as a function of temperature. Results from DMA experiments indicated a slight shift of the mechanical α relaxation to higher temperatures and demonstrated that H-bonding leads to a significant increase in the temperature range of the rubbery plateau.

Four well-defined processes were observed in dielectric spectra of the acid forms of sulfonated PS. The fragility was found to be approximately constant for all sulfonation levels, attributed to the relatively high level of intermolecular cooperativity for PS. Two relaxations were observed above the dielectric α process and attributed to electrode polarization and a relaxation associated with H-bond association/disassociation. The relaxation strength of the α* process decreased rapidly at temperatures above 160 °C, in keeping with the reduction of

H-bonding at higher temperatures, as demonstrated in FT-IR experiments. A local β relaxation was observed in the dielectric spectra of the chemically modified PSs and assigned to the motion of the sulfonated phenyl groups.

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References and Notes

(1) Eisenberg, A.; Kim, J.-S. *Introduction to Ionomers*; Wiley: New York, 1998.
(2) Schlick, S., Ed. *Ionomers: Characterization, Theory, and Applications*; CRC Press: New York, 1996.
(3) Holliday, L. *Ionic Polymers*; Wiley: New York, 1975; Chapter 2, p 69.
(4) Eisenberg, A.; Hird, B.; Moore, R. B. *Macromolecules* **1990**, *23*, 4098.
(5) Tan, N. C. B.; Liu, X.; Briber, R. M.; Peiffer, D. G. *Polymer* **1995**, *36*, 1969.
(6) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871.
(7) Weiss, R. A.; Lefelar, J. A. *Polymer* **1986**, *7*, 3.
(8) Fujimura, M.; Hashimoto, T.; Kawai, H. *Macromolecules* **1981**, *14*, 1309.
(9) Li, C.; Register, R. A.; Cooper, S. L. *Polymer* **1989**, *30*, 1227.
(10) Weiss, R. A.; Fitzgerald, J. J.; Kim, D. *Macromolecules* **1991**, *24*, 1071.
(11) Seidel, U.; Stadler, R.; Fuller, G. G. *Macromolecules* **1994**, *27*, 2066.
(12) Muller, M.; Stadler, R.; Kremer, F.; Williams, G. *Macromolecules* **1995**, *28*, 6942.
(13) Muller, M.; Dardin, A.; Seidel, U.; Balsamo, V.; Ivan, B.; Spiess, H. W.; Stadler, R. *Macromolecules* **1996**, *29*, 2577.
(14) Wubbenhorst, M.; van Turnhout, J. *IEEE Trans. Electr. Insul.* **2001**, *8*, 365.
(15) Makowski, H. S.; Lundberg, R.D Singhal, G. US Pat. 3870841, 1975.
(16) Weiss, R. A.; Sen, A.; Willis, C. L.; Pottick, L. A. *Polymer* **1991**, *32*, 1867.
(17) Karaman, R.; Leader, H.; Goldblum, A.; Breuer, E. *Chem. Ind.* **1987**, *24*, 857.
(18) Havriliak, S.; Negami, S. *J. Polym. Sci., Polym. Symp.* **1966**, *14*, 99.
(19) Wubbenhorst, M.; van Turnhout, J. *J. Non-Cryst. Solids* **2002**, *305*, 40.
(20) Steeman, P.; van Turnhout, J. *Macromolecules* **1994**, *27*, 5421.
(21) Jin, X.; Zhang, S. H.; Runt, J. *Macromolecules* **2004**, *37*, 8110.
(22) Zhang, S. H.; Runt, J. *J. Phys. Chem. B* **2004**, *108*, 6295.
(23) Zundel, G. *Hydration and Intermolecular Interaction: Infrared Investigations with Polyelectrolyte Membranes*; Academic Press: New York, 1969.
(24) Fitzgerald, J. J.; Weiss, R. A. In *Coulombic Interactions in Macromolecular Systems*; American Chemical Society: Washington, DC, 1986; Chapter 3, p 35.
(25) Chen, W.; Sauer, J. A.; Hara, M. *Polymer* **2003**, *44*, 7729.
(26) Leibler, L.; Rubinstein, M.; Colby, R. H. *Macromolecules* **1991**, *24*, 4701.
(27) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
(28) Angell, C. A. *Polymer* **1997**, *38*, 6261.
(29) Santangelo, P. G.; Roland, C. M. *Macromolecules* **1998**, *31*, 4581.
(30) Wang, L. M.; Velikov, V.; Angell, C. A. *J. Chem. Phys.* **2002**, *117*, 10184.
(31) Zhang, S. H.; Jin, X.; Painter, P. C.; Runt, J. *Macromolecules* **2002**, *35*, 3636.
(32) Zhang, S. H.; Painter, P. C.; Runt, J. *Macromolecules* **2002**, *35*, 9403.
(33) Adachi, K.; Kotaka, T. *Prog. Polym. Sci.* **1993**, *18*, 585.
(34) Boersma, A.; van Turnhout, J. *J. Polym. Sci., Polym. Phys.* **1998**, *36*, 2835.
(35) Tadmor, R.; Hernandez-Zapata, C.; Chen, N.; Pincus, P.; Israelachvili, J. N. *Macromolecules* **2002**, *35*, 2380.
(36) Muller, M.; Kremer, F.; Stadler, R.; Fischer, E. W.; Seidel, U. *Colloid Polym. Sci.* **1995**, *273*, 38.

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