# Influence of Cation Type on Structure and Dynamics in Sulfonated Polystyrene Ionomers

Alicia M. Castagna[1], Wenqin Wang[2], Karen I. Winey[2]*, James Runt[1]*

[1]*Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802*

[2]*Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

**Supporting Information:**

**The Kinning-Thomas Modified Hard-Sphere Model**

The SPS ionomer scattering data was fit to:

$$I(q) = I_{KT}(q) + L_1(q) + L_2(q) + C \tag{S1}$$

where $I_{KT}(q)$ is the scattering intensity defined by the Kinning-Thomas (K-T) modified hard-sphere model[1,2] (Equations S2-5), $L_1(q)$ and $L_2(q)$ are Lorentzian functions used to fit the two polystyrene amorphous halos in the wide angle region, and C is a constant used to account for the instrumental background scattering, as previously reported.[3]

$$I_{KT}(q) = A\Phi^2(qR_1) \frac{1}{1 + 24\eta\left(\dfrac{G(B)}{B}\right)} \tag{S2}$$

where

$$\Phi(x) = 3\frac{\sin x - x\cos x}{x^3} \tag{S3}$$

$$\eta = \frac{4}{3}\pi R_{CA}{}^3 N_P \qquad (S4)$$

$$B = 2qR_{CA} \qquad (S5)$$

and

$$G(B) = \frac{(1+2\eta)^2}{B^2(1-\eta)^4}(\sin B - B\cos B) - \frac{6\eta\left(1+\frac{\eta}{2}\right)^2}{B^3(1-\eta)^4}\left[2B\sin B + (2-B^2)\cos B - 2\right]$$

$$+ \frac{\eta(1+2\eta)^2}{2B^5(1-\eta)^4}\left\{-B^4\cos B + 4\left[(3B^2-6)\cos B + (B^3-6B)\sin B + 6\right]\right\} \qquad (S6)$$

There are four variable parameters in the K-T model: the peak amplitude A, the aggregate core radius $R_1$, the radius of closest approach between two aggregates $R_{CA}$, and the number density of the ionic aggregates $N_p$.

A representative example of this fitting is provided in Figure S1 where Equation S1 is deconvoluted into its component functions.
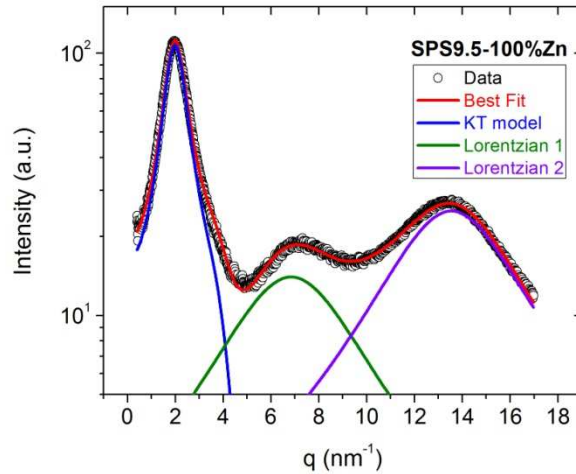


**Figure S1: Representative example of SPS scattering data fit to Equation S1 including deconvoluted components.**

**The Dynamic Glass Transition Temperature:**

The glass transition temperature can be estimated from the segmental relaxation observed in dielectric spectra by extrapolating the VFT fit of the relaxation frequency to $\tau = 100$ s ($f = 0.00159$ Hz). This estimate of $T_g$, here referred to as $T_{ref}$, was found to generally be within experimental error of the calorimetric $T_g$. The temperature window in which the segmental process could be fit for 100% neutralization was relatively narrow, leading to a higher degree of uncertainty in the $T_{ref}$ values at full neutralization.

**Table S1: $T_{ref}$ determined from DRS and calorimetric $T_g$ from DSC:**

| | at 0 and 50%M | | | at 100%M | |
|---|---|---|---|---|---|
| | $T_{ref}$ $\pm 5$ oC | $T_g$ (DSC) $\pm 3$ oC | | $T_{ref}$ $\pm 15$ oC | $T_g$ (DSC) $\pm 3$ oC |
| SPS9.5 | | | | | |
| 100% H | 120 | 121 | | | |
| 50% Na | 125 | 122 | 100% Na | 144 | 127 |
| 50% Cs | 127 | 122 | 100% Cs | 135 | 130 |
| 50% Zn | 124 | 122 | 100% Zn | 140 | 126 |
| | | | | | |
| SPS6.7 | | | | | |
| 100% H | 110 | 117 | | | |
| 50% Na | 112 | 111 | 100% Na | 125 | 117 |
| 50% Cs | 118 | 115 | 100% Cs | 123 | 119 |
| 50% Zn | 121 | 119 | 100% Zn | 111 | 120 |
| | | | | | |
| SPS3.5 | | | | | |
| 100% H | 105 | 111 | | | |
| 50% Na | 101 | 112 | 100% Na | 111 | 109 |
| 50% Cs | 97 | 111 | 100% Cs | 110 | 113 |
| 50% Zn | 97 | 112 | 100% Zn | 123 | 110 |

**Breadth of the Segmental Process with Degree of Sulfonation:**

The breadth of the segmental process at 100% neutralization increases slightly for Na-neutralized ionomers with increasing sulfonation level, consistent with an increase in the number density of ionic aggregates (Figure S1a). For 100% Cs-neutralized SPS, the sulfonation effect on the breadth of this relaxation is not so distinct, and for SPS9.5-100Cs a high temperature/low frequency relaxation masks the low frequency side of the segmental process (Figure S1b). In contrast, Figure 6 shows that the level of neutralization broadens the loss process significantly. This suggests that the breadth of segmental relaxing environments is strongly influenced by neutralization as the aggregates become more ionic (as suggested in our previous work on Zn-neutralized SPS[4]) and the chains are tethered more tightly to the aggregate – but not as significantly by sulfonation level. As seen in Figure 4 there is a significant increase in volume fraction of restricted region upon neutralization – but only a slight increase with sulfonation.
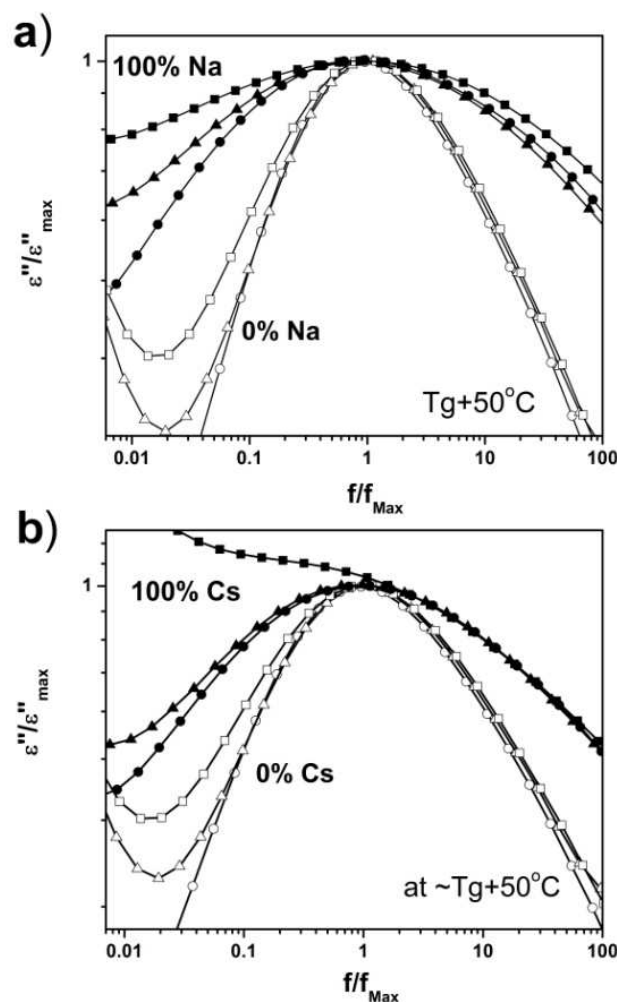
**Figure S1: Normalized loss plots for the segmental relaxation (α) in (a) Na- and (b) Cs-neutralized SPS at 0% (open symbols) and 100% (filled symbols) neutralization and 3.5 (circles), 6.7 (triangles) and 9.5% (squares) sulfonation.**

**High Temperature Relaxations:**

For Na-neutralized SPS at 50% neutralization there is a clear relaxation at low frequencies, with an additional process appearing as a shoulder at higher frequencies (Figure S2). These processes are at similar temperatures and frequencies as the acid group association dynamics α* and MWS observed in the acid form, and very likely have the same origin. At 100% neutralization no high temperature/ low frequency relaxations are observed – likely

because they are shifted to lower frequencies and higher temperatures than measured, due to the higher binding energy of the small $Na^+$ ion. The MWS process observed for the Zn ionomers coincided with the dc conductivity ($\sigma_{dc}$) plateau. For the 100% Na ionomer the $\sigma_{dc}$ plateau is not yet reached in the temperature/frequency window measured.
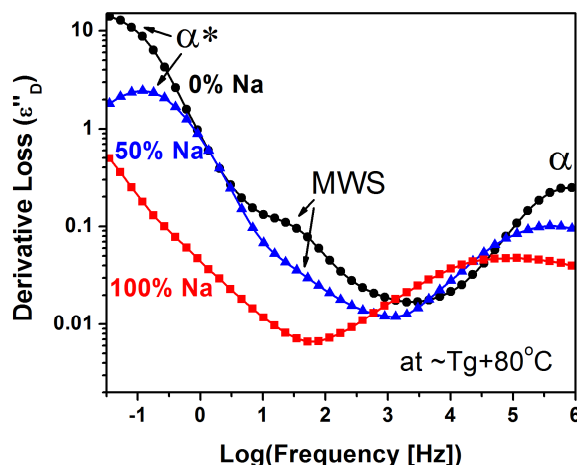


**Figure S2: Conduction free loss vs. frequency for 0% (circles), 50% (triangles) and 100% (squares) Na-neutralized SPS ionomers at 6.7% sulfonation.**

**References:**

(1) Zhou, N. C.; Chan, C. D.; Winey, K. I. *Macromolecules* **2008**, *41*, 6134-6140.

(2) Kinning, D. J.; Thomas, E. L. *Macromolecules* **1984**, *17*, 1712-1718.

(3) Benetatos, N. M.; Heiney, P. A.; Winey, K. I. *Macromolecules* **2006**, *39*, 5174-5176.

(4) Castagna, A.; Wang, W.; Winey, K. I.; Runt, J. *Macromolecules* **2011**, In Press.