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Morphology of Lightly Carboxylated Polystyrene Ionomers

Hidemi Tomita[†] and Richard A. Register[*]

Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

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ABSTRACT: Lightly carboxylated polystyrene (CPS) ionomers have been synthesized via free-radical copolymerization of styrene and 4-vinylbenzoic acid, and their morphology and properties compared with those of lightly sulfonated polystyrene (SPS) ionomers. CPS ionomers neutralized with Na^+ give SAXS patterns similar to those exhibited by SPS ionomers, suggesting rather complete aggregation of ionic groups. However, when neutralized with Zn^{2+}, a poorly-ordered morphology is produced, with many ionic groups remaining unaggregated. Differences are also evident in the dynamic mechanical behavior, with NaCPS exhibiting a strong high-temperature relaxation peak whose temperature increases faster than that of the matrix glass transition, while ZnCPS shows a weak high-temperature peak whose temperature increases in step with the matrix transition. By using a weaker acid substituent, cation effects on morphology are amplified relative to those seen in SPS ionomers.

I. Introduction

The morphology of polystyrene-based ionomers, as probed by small-angle X-ray scattering (SAXS), is a subject of continuing interest.[1-7] The most prominent feature—the "ionomer peak" in the SAXS pattern, occurring at a Bragg spacing of 3–5 nm—is thought to reflect a preferred spacing between domains of ion-rich material ("ionic aggregates") which are often conceptualized as spherical.[8] This minute size scale of phase separation, which we term "nanophase separation", sets ionomers as a class apart from other phase-separated polymers; even block copolymers have a characteristic size scale an order of magnitude larger. In addition to aggregates of ionic groups, it is expected that many ionic groups will remain dispersed in the ion-poor matrix[1,7] due to topological constraints, particularly if these groups do not occur at regular intervals along the chain.

Although material properties, such as rheological and stress–strain behavior, can depend strongly on the neutralizing cation,[9-12] the morphology as seen by SAXS generally changes little with the cation. On the contrary, the type of backbone and bound ion can profoundly influence both morphology and material properties. Clas and Eisenberg[13] presented dynamic mechanical studies on a series of styrene-based ionomers (Na^+ salts) with various groups substituted at the styrene para-position. Their results indicate that sulfonated polystyrene (SPS) tends to form more stable ionic aggregates than carboxylated polystyrene (CPS) and hydroxylated polystyrene. However, little is known about the morphology of styrene-based ionomers other than SPS or whether a cation dependence of the morphology might be evident when weaker acids are used.

Three principal routes to CPS materials have been documented in the literature. Lundberg and Makowski[14] used direct lithiation of polystyrene followed by carboxylation with CO_2. The position of substitution in this reaction is not entirely certain, but the best evidence[15] suggests a 2:1 mixture of meta:para, with no backbone lithiation. Efforts in our laboratory[16] to reproduce this reaction have always led to some insoluble product above about 2% carboxylation. A modified lithiation procedure[17] has been reported to produce a fully-soluble product, but as the carboxylation reaction is heterogeneous, it is unlikely to produce a uniformly-carboxylated product at low carboxylation levels. The second route[18] involves Friedel–Crafts acylation of polystyrene, which produced a uniform and fully-soluble product; however, the starting material was of low molecular weight, making it difficult to ascertain whether the reaction is entirely free from coupling side reactions. The third method, used by Brockmann and Eisenberg,[19] involved synthesizing a styrene/*p*-bromostyrene copolymer and replacing the bromine atoms with carboxyl groups. This approach has the distinct advantage that the position of substitution is all para, the same position at which sulfonate groups are positioned in SPS, facilitating a direct comparison of the effect of anion type. A much simpler approach than these three, which we took here, is to directly copolymerize styrene and 4-vinylbenzoic acid. In a separate paper,[20] the miscibility of these ionomers with poly(xylenyl ether) will be explored.

II. Experimental Section

A. Synthesis and Sample Preparation. Lightly carboxylated polystyrene (CPS) ionomers were obtained by random copolymerization of styrene (S) and 4-vinylbenzoic acid (VBA). Styrene (Aldrich, 99%) was deinhibited by passing the monomer over a commercial inhibitor removal column (Aldrich); VBA (Aldrich) was used as received. Reactivity ratios for this system have been reported[21,22] as $r_S = 0.258$ and $r_{VBA} = 1.131$. Polymerizations were conducted in tetrahydrofuran (THF) to ensure solubility of all components, beginning with 50 vol % monomer solutions and a benzoyl peroxide initiator concentration of 2.0 $\times 10^{-3}$ M. Polymerizations were carried out in 25-mm-diameter test tubes immersed in a forced-convection water bath at 50 °C and were terminated after 43 h by precipitation into methanol, yielding conversions of about 25%. Based on the reactivity ratios given above, numerical calculations indicated that the starting and ending copolymer compositions were within 20% of the mean composition. Polymers were dried in an air oven at 150 °C for 10 h followed by vacuum drying at 180 °C for 24 h. VBA contents were evaluated by titration in THF to the phenolphthalein end point with a standardized aqueous solution of NaOH. No precipitation was observed during the titrations.

Stoichiometric amounts of NaOH (in water) or zinc acetylacetonate (in 1:9 methanol/THF) were added to THF solutions of the acid CPS to produce neutralized ionomers, which were precipitated in heptane and dried as above. Complete neutralization was confirmed by the disappearance of peaks at 1688 and 1734 cm^{-1} in the infrared spectrum, which derive from the C=O stretching modes of hydrogen-bound and free carboxylic acid, respectively. For the zinc ionomers, the infrared spectra also showed no bands corresponding to excess zinc acetylacetonate. The neutralized samples were compression-molded at 250 °C and cooled below their glass transition temperatures in sealed molds (~5 °C/min) to produce disks of roughly 1-mm thickness for all further measurements.

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[*] To whom correspondence should be addressed.

[†] Permanent address: Sony Corp. Research Center, 174, Fujitsuka-cho, Hodogaya-ku, Yokohama, 240 Japan.

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Table I. T_g (ΔT_g) Values (°C) for CPS Ionomers

f, mol % VBA	NaCPS	ZnCPS
1.6	110 (4)	112 (7)
2.9	114 (8)	115 (8)
4.6	118 (13)	116 (13)
6.0	120 (13)	122 (17)
7.4	130 (19)	130 (16)

B. Instrumental Methods. Gel permeation chromatography (GPC) was performed in toluene at 1.0 mL/min, using a Polymer Laboratories Mixed-C column (60 cm) and a Knauer refractive index detector. Molecular weight was calibrated with narrow-dispersity polystyrene standards. Differential scanning calorimetry (DSC) was carried out at 20 °C/min with a Perkin-Elmer DSC-4 calibrated with indium. Samples were scanned to 280 °C before the actual measurements to minimize enthalpy relaxation peaks. The glass transition temperature (T_g) is defined as the midpoint of the heat capacity change, and the transition's breadth (ΔT_g) is defined by the separation of the points where a line tangent to the midpoint intersects the pre- and posttransition base lines. Dynamic mechanical thermal analysis (DMTA) was performed with a Rheometrics RSA-II using the shear sandwich fixture. This geometry is particularly suitable for measurements on extremely viscous melts, which ionomers possess. Before testing, molded disks (1.05–1.1 mm) were placed in a vacuum oven at 170 °C for 24 h; this moderated the residual stresses locked in during molding, as well as the formation of bubbles during the DMTA test. Test specimens slightly larger than the gap area (16 × 12.5 mm) were prepared by scoring the disks with a razor blade and fracturing. The test frequency was 1 Hz and a strain amplitude of 0.1% was used, which was established to be within the linear viscoelastic range. Samples were tested in a nitrogen atmosphere by first heating the material to 280 °C and then stepping down toward the glass transition temperature of the polymer in 5 °C increments. A thermal soak time of 3 min was used at each point; polystyrene homopolymer gave indistinguishable data on heating and cooling with this soak time, indicating that this was sufficient for thermal equilibration.

The equipment and data reduction methods used to acquire the SAXS data have been described previously.[23] Desmeared, background-subtracted SAXS intensities are presented as I/I_eV versus q, where I_e is the scattering from a single electron and V is the illuminated sample volume; the scattering vector magnitude $q = (4\pi/\lambda)\sin\theta$, where θ is half the scattering angle and λ is the X-ray wavelength. Because some of the ionomers show relatively weak scattering, accurate background subtraction is critical. The scattering curve of an unfunctionalized polystyrene was found to be well-described by $I/I_eV = A[\exp(Bq^2)]$, where the exponential term is necessary to account for the leading edge of a polystyrene wide-angle reflection[24] near $q = 7$ nm^{-1}; best-fit values were determined as $A = 231$ nm^{-3} and $B = 0.0376$ nm^2. For the ionomers, we postulated a background of the form $A[\exp(Bq^2)] + C$, where A and B have the same significance and numerical values as for homopolystyrene, and C is introduced to describe the additional scattering in the ionomer due to phase mixing. Best-fit values of C were determined using the high-q region of each curve.

III. Results and Discussion

An unfunctionalized polystyrene synthesized identically to our CPS ionomers had $M_w = 161\,000$ and $M_w/M_n = 2.1$. Chromatography of associating molecules is notoriously difficult and was not attempted here, but we expect our ionomers to have similar M_w and M_w/M_n values. The functionalization levels f (mol % VBA) of the CPS determined by titration are given in Table I. These values are all about 75% of our initial expectations, which were based on the literature reactivity ratios.[22] Since our materials are all low in VBA content, our results are insensitive to the value of r_{VBA}, but assuming the literature value of $r_{VBA} = 1.13$ to be correct, our functionalization levels can be explained (integrating numerically to our experimentally-determined conversions[25]) by a single value of $r_S = 0.39$. For the styrene/p-bromostyrene copolymerization, values of $r_S = 0.67$ and $r_{BrS} = 1.10$ have been reported.[22] Since both our materials and those synthesized by Brockmann and Eisenberg[19] have low comonomer contents, the question of sequence distribution reduces principally to what fraction of counits exist as topological neighbors (pairs) along the chain, relative to the fraction of counits which do not adjoin other counits (isolated). In the limit $f \to 0$, the probability p that a counit (VBA or BrS) will add another counit to the growing chain is given by

$$p \approx r_1 r_2 (f/100) \qquad (1)$$

where f is the mole percent of counits in the final polymer product. Thus, the S/VBA system produces fewer pairs of counits than does the S/BrS system, which in turn produces fewer than would the Bernoullian distribution ($r_1 = r_2 = 1$) characteristic of random placement of the counits, which is thought to be the case for SPS. However, in all cases, the fraction of counits existing as pairs rather than isolated counits is small, as long as f is small. It seems unlikely that these small differences in sequence distribution could yield substantial differences in morphology, so to a first approximation, it appears fair to compare the CPS ionomers synthesized by these two routes with each other, as well as with SPS.

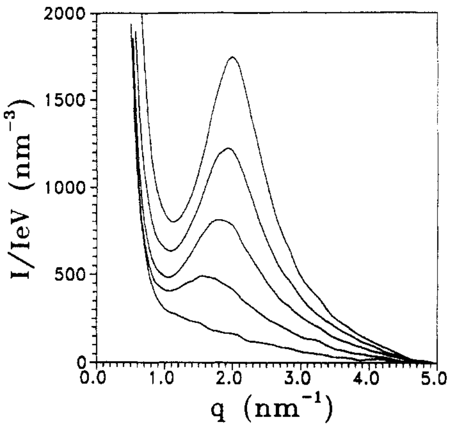

Figure 1. SAXS data for NaCPS, varying the functionalization level (top to bottom): 7.4, 6.0, 4.6, 2.9, 1.6 mol %.

Table I also lists the glass transition temperatures of both the Na$^+$ and Zn^{2+} forms of the ionomers, as determined by DSC. The values for NaCPS are consistent with Brockmann and Eisenberg's[26] reports for their Na$^+$ materials; both T_g and the breadth of the transition (ΔT_g) increase with the functionalization level, and the values are not substantially influenced by cation. In contrast, SAXS measurements showed substantial differences between the Na$^+$ and Zn^{2+} materials. Figure 1 shows the data for the NaCPS samples, which have rather sharp ionic peaks, while the SAXS curves for ZnCPS samples (Figure 2) show much weaker and broader peaks. SAXS patterns for two ZnCPS ionomers synthesized by Brockmann and Eisenberg were presented by Yarusso and Cooper;[2] these SAXS patterns are generally similar to ours, though they have a breadth between what we observe for NaCPS and ZnCPS ionomers, a discrepancy for which we have no explanation. Other NaCPS specimens were prepared by quenching the mold under cold water, to see whether the cooling rate substantially influenced the morphology, but the resultant SAXS patterns were indistinguishable from those in Figure 1.

Our SAXS results suggest that the nanophase separation produced by ionic aggregation is more complete in the NaCPS case than the ZnCPS case. Additional support

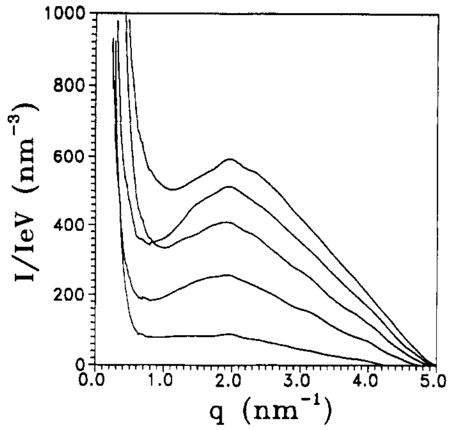

Figure 2. SAXS data for ZnCPS, varying the functionalization level (top to bottom) at q = 2 nm^{-1}: 7.4, 6.0, 4.6, 2.9, 1.6 mol %.

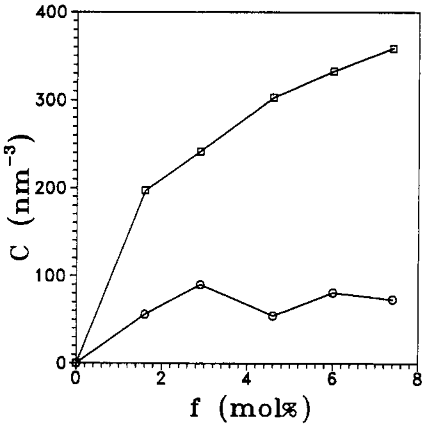

Figure 3. SAXS intensity background in excess of homopolystyrene scattering (C), plotted vs functionalization level f for both NaCPS (○) and ZnCPS (□).

for this interpretation is provided by value of the SAXS intensity background component C (see the Experimental Section), which represents the excess background scattering not present in homopolystyrene. This component is due to small-scale inhomogeneities in electron density within domains; in the case of ionomers, the principal cause of this scattering is expected to be ionic groups dispersed in the polystyrene matrix. Figure 3 shows how this background component varies with functionalization level for both the Na$^+$ and Zn^{2+} ionomers. For NaCPS, the phase-mixing contribution is rather small and is relatively constant as the functionalization level varies. For ZnCPS, the phase-mixing contribution is large—roughly equal to the peak intensity—and increases monotonically with the functionalization level. Taken together, these results indicate that the nanophase separation in NaCPS is rather clean, with relatively few ionic groups dissolved in the polystyrene matrix, while in ZnCPS many of the ionic groups remain dissolved, and the breadth of the peak indicates a greater dispersity in the interaggregate spacing.

As noted in the Introduction, the choice of neutralizing cation (among metal cations) generally exerts little effect on the morphology as seen by SAXS; however, there are a few counterexamples. For sulfonated polyurethanes,[27] a decrease in the intensity of the SAXS peak at elevated temperatures was noted for the Zn^{2+} salt, while no change was seen for the Na$^+$ salt. For sulfonated polystyrene ionomers, two studies[4,28] have shown a substantial decrease in peak intensity above 240 °C, although a third study reported no change.[2] For the analogous NaSPS case, the peak actually increased in intensity at elevated temperature.[4] These observations suggest that Zn^{2+} salts form weaker associations than Na$^+$ salts, an idea often invoked to explain the lower viscosity of Zn^{2+} ionomers relative to their Na$^+$ counterparts.[9,29]

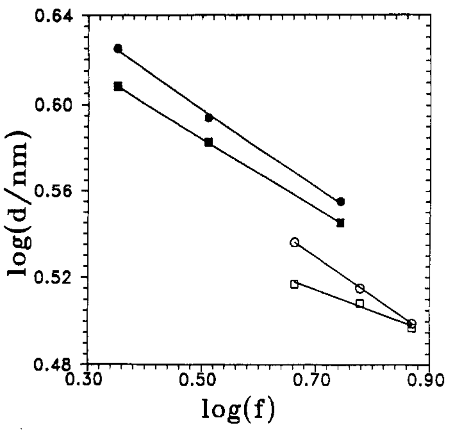

Figure 4. Scaling plot showing the relationship between apparent Bragg spacing d and functionalization level f for NaSPS (●), ZnSPS (■), NaCPS (○), and ZnCPS (□). (Data for SPS ionomers taken from ref 4.)

Table II. Best-Fit Scaling Exponents

system	a	system	a
NaSPS	0.18	NaCPS	0.18
ZnSPS	0.16	ZnCPS	0.10

For systems where there is a regular spacing between ionic groups (such as the telechelics or the polyurethane ionomers), some attention has been given to how the average interaggregate spacing varies with ion content. The apparent Bragg spacing d can be computed from the peak position q^* ($d = 2\pi/q^*$); results are often interpreted via a simple scaling law:

$$d \sim M^a \qquad (2)$$

where M is the molecular weight between ionic units. For a system in which the ion content is small, so that the ionic phase presumably consists of unconnected spheres for any M (i.e., any ion content), if the ratio of aggregated to dispersed ionic groups is constant and if the size of the ionic aggregates is independent of M, then the simple scaling law above should hold, with $a = {}^1/_3$. Within experimental error, this is found to be the case for both carboxy-telechelic polyisoprenes[30] and sulfonated polyurethanes.[27,31]

For random ionomers, an analogous scaling relation is

$$d \sim f^{-a} \qquad (3)$$

where f is the mole percent of functionalized units. In this case, however, an exponent $a = {}^1/_3$ is not expected, since, as the ion content changes, so may the extent of phase separation and the aggregate size, and deviations from an unconnected spherical morphology for the aggregates may occur at high ion contents. In fact, there is no fundamental reason to expect random polystyrene ionomers to follow eq 3 with *any* value of a. Figure 4 shows a plot of our SAXS data in the form suggested by eq 3; for comparison, d values for NaSPS and ZnSPS, extracted from the data of Weiss and Lefelar,[4] are also shown. Over the limited functionalization range available, eq 3 does a satisfactory job of correlating the data; best-fit values of a are given in Table II. For ZnCPS, some downward curvature may be present (increase in the apparent a with f), though the broad and weak peaks for ZnCPS hinder an accurate determination of q^*.

It is experimentally difficult to compare d values for CPS and SPS ionomers over identical ranges of f; at low

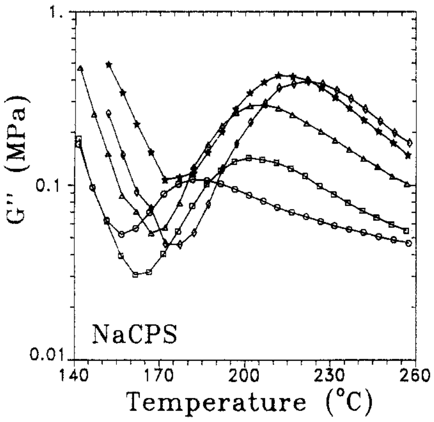

Figure 5. Shear loss modulus G'' (1 Hz) vs temperature for NaCPS ionomers of varying functionalization level: 1.6 (○), 2.9 (□), 4.6 (△), 6.0 (◇), 7.4 (☆) mol %.

f, the SAXS peaks for CPS ionomers are too weak to determine q^* accurately, while at high f, the viscosities of SPS ionomers are so high as to make them intractable. Nonetheless, some overlap in the f ranges exists in the data of Figure 4; the carboxylated ionomers have smaller values of d than their sulfonated analogs, a result which has recently been reported for telechelic polyisoprene ionomers as well.[12] However, the magnitude of the discrepancy is not much larger than can be produced in SPS ionomers by changing the sample preparation method, as evidenced by comparing data from different laboratories,[4,23] so we hesitate to assign much significance to this observation.

For NaSPS, ZnSPS, and NaCPS, the best-fit values of a are roughly $^1/_6$. If most of the ions in this system are aggregated (as implied by the low C value for NaCPS shown in Figure 3), this would imply that, as more ionic groups are added to the system, they divide roughly evenly between making more aggregates and making larger aggregates, at least over the range of f studied. The exponent for ZnCPS is distinctly lower ($a = 0.10$), which may reflect that, in this system, as more ions are added, many remain unaggregated (as evidenced by the large C value for ZnCPS in Figure 3).

Varying the neutralizing cation often exerts a more pronounced effect on mechanical properties than it does on morphology, particularly on materials in the rubbery or melt states. For example, sulfonated ethylene/propylene[32] and sulfotelechelic polyisobutylene[29] ionomers have lower viscosities when neutralized with Zn^{2+} than with Na^+ or K^+. Many high-molecular-weight ionomers show a second dynamic mechanical relaxation peak in the shear loss modulus G'', or loss tangent tan δ, at a temperature well above the glass transition of the matrix, the only transition seen calorimetrically.[33] This transition has been variously ascribed to a glass transition of the ionic aggregates[33] or to the temperature at which the rate of "ion-hopping"—transport of ionic groups between aggregates[34]—becomes comparable to the test frequency.[9] In either case, the temperature at which this peak occurs should reflect the strength of the ionic associations; for SPS ionomers, this peak occurs at a lower temperature for Zn^{2+} than for Na^+ salts.[35]

Figure 5 shows our DMTA G'' data for NaCPS ionomers of varying functionalization level. The temperature of the relaxation peak increases with f, but reproducibility on replicate runs was not particularly good (up to 20 °C differences in peak position). We suspect that the source of the poor reproducibility may be traces of moisture, which are difficult to remove from NaCPS and would tend to reduce the peak temperature; accordingly, the data sets presented in Figure 5 are those which had the highest peak temperature for a given material. Brockmann and Eisenberg[26] presented torsion pendulum data for their NaCPS ionomers; our second-peak temperatures (obtained from tan δ) are 30–40 °C higher for comparable f. Very recently Hird and Eisenberg[36] presented DMTA data for CPS ionomers synthesized by a new postpolymerization functionalization method, which also showed second-peak temperatures 20–40 °C lower than we observe in tan δ. Again, we are uncertain whether this discrepancy arises from unanticipated differences in the structures of the materials, which are obtained from different synthetic methods or from extraneous factors such as differing water contents.

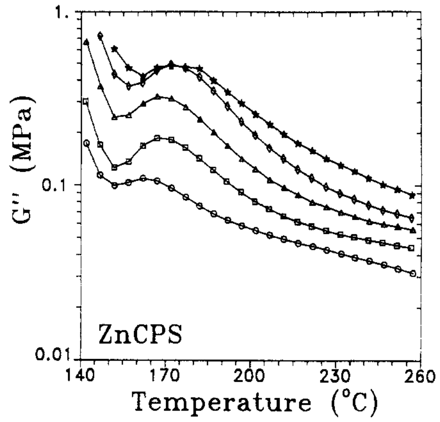

Figure 6. Shear loss modulus G'' (1 Hz) vs temperatue for ZnCPS ionomers of varying functionalization level: 1.6 (○), 2.9 (□), 4.6 (△), 6.0 (◇), 7.4 (☆) mol %.

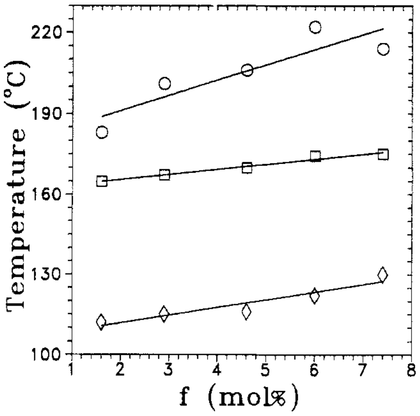

Figure 7. Position of G'' high-temperature maximum for NaCPS (○) and ZnCPS (□) and matrix T_g for ZnCPS (◇) measured via DSC, all plotted vs functionalization level f.

In any case, the differences between NaCPS and ZnCPS are striking, as can be seen by comparing Figures 5 and 6. The second peak for ZnCPS is relatively weak; for all functionalization levels, it is strongly overlapped by the primary transition (matrix glass transition). In contrast to NaCPS, the reproducibility of the ZnCPS data was quite good, even though the materials were handled identically. Figure 7 shows how the position of the high-temperature maximum in G'' varies with the functionalization level. For NaCPS, the G'' peak position increases at an average rate of 6 °C/mol %, or twice the rate at which the calorimetrically-determined matrix T_g increases. By contrast, for ZnCPS, the high-temperature peak increases at the same rate as the matrix T_g, with the difference always being about 50 °C. The weak high-temperature transition in ZnCPS is consistent with a poorly phase-separated material, as concluded from SAXS, and the lower temperature and strong coupling to the matrix T_g indicate a much weaker association in ZnCPS than NaCPS.

The temperatures of the G'' maxima in our NaCPS data are quite comparable to the values found by Weiss et al.[35] for SPS; our measurements on NaSPS give a peak temperature about 30 °C higher,[25] which was found to increase on repeated measurements of the same samples; again, this suggests that traces of water may be a factor. For the Zn^{2+} ionomers, however, we find that the G'' maximum occurs at a substantially lower temperature for the CPS materials than their SPS analogs.[25,35] This again demonstrates that the effect of the cation is more pronounced in CPS ionomers than in SPS.

IV. Conclusions

Lightly carboxylated polystyrene ionomers have been synthesized via free-radical copolymerization of styrene and 4-vinylbenzoic acid. Some differences in morphology and properties between our materials and CPS ionomers synthesized by a slightly different method[19] were found, even though the sequence distributions are expected to be quite similar. When neutralized with Na^+, these materials give SAXS patterns similar to those exhibited by SPS ionomers, indicating good nanphase separation. However, when neutralized with Zn^{2+}, a poorly-ordered morphology is produced, with many ionic groups remaining unaggregated. The scaling exponent relating the SAXS Bragg spacing to the functionalization level is 0.18 for NaCPS, close to that found for NaSPS and ZnSPS, but is only 0.10 for ZnCPS. Differences are also reflected in the dynamic mechanical behavior, with NaCPS exhibiting a strong high-temperature relaxation peak whose temperature increases faster than that of the matrix glass transition, while ZnCPS shows a weak high-temperature peak whose temperature increases in step with the matrix T_g. Thus, cation effects are more pronounced in the CPS system than in SPS.

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