Vesicular Ionic Aggregates in Poly(styrene-*ran*-methacrylic acid) Ionomers Neutralized with Cs

Brian P. Kirkmeyer,† Andreas Taubert,† Joon-Seop Kim,‡ and Karen I. Winey*,†

Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, Pennsylvania 19104, and Department of Polymer Science and Engineering, Chosun University, Kwangju P.O. Box 275, Kwangju 501-600, Korea

Received August 16, 2001; Revised Manuscript Received December 27, 2001

ABSTRACT: The morphologies of Cs-neutralized poly(styrene-*ran*-methacrylic acid) (Cs−SMAA) random ionomers have been studied using scanning transmission electron microscopy (STEM). The Cs−SMAA ionomers exhibit Cs-rich aggregates in the shape of spherical shells that are randomly distributed in a polystyrene-rich matrix. For simplicity, we refer to these as vesicular aggregates. The vesicular aggregates are typically 5−20 nm in diameter and have shell thicknesses of ∼3 nm. The vesicular aggregates persist after annealing with their dimensions and number density unchanged. The aggregate diameters and shell thicknesses are independent of the copolymer concentration during neutralization and the rate of neutralizing agent addition. We also demonstrate that our specimen preparation for STEM (microtomy parameters and storage conditions) avoids substantial changes to the bulk ionomer morphology. Overall, the microstructures of the current materials are similar to those recently reported in sulfonated polystyrene ionomers solution-neutralized with Zn.

Introduction

Recent scanning transmission electron microscopy (STEM) studies by Winey and co-workers[1−3] have revealed that the morphology of ionomers is more diverse than previously believed. Zinc-neutralized poly(ethylene-*ran*-methacrylic acid) (EMAA) and poly(styrene-*ran*-styrenesulfonic acid) (SPS) ionomers have drastically different morphologies. Zn−EMAA ionomers exhibit randomly distributed solid spherical aggregates that are nominally 2 nm in diameter. Zn−SPS ionomers, however, contain randomly distributed solid spherical aggregates ranging in diameter from 4 to 10 nm as well as vesicular aggregates that range in diameter from 9 to 55 nm with shell thicknesses of ∼3 nm. In addition, lightly neutralized Zn−SPS ionomers exhibit macrophase separation.

There are a number of differences between these two classes of ionomers, Zn−EMAA and Zn−SPS, that might account for the discrepancies in the observed aggregate morphology. Both the base polymer (polyethylene vs polystyrene) and the acid group (carboxylic acid vs sulfonic acid) differ in these materials. Also, EMAA is semicrystalline, whereas SPS is amorphous. Finally, the neutralization of EMAA is performed in the melt, while the SPS is neutralized in solution. The significance of each of these parameters on the morphology of the ionic aggregates is currently under investigation. This study focuses on styrene ionomers to determine whether a different acid group and neutralizing cation change the aggregate morphology. Specifically, we use STEM to study poly(styrene-*ran*-methacrylic acid) (SMAA) ionomers neutralized with Cs. Previous attempts to use transmission electron microscopy (TEM), rather than STEM, to image Cs-rich aggregates have been inconclusive.[4]

We also investigate the stability of the ionic aggregates in Cs−SMAA by imaging styrenic ionomers before and after annealing and from a range of neutralization methods. The stability of the morphology of EMAA has previously been demonstrated by a comparison of images taken before and after annealing at 115 °C for 10 days.[3] These aggregates are spherical, and the aggregate diameters are approximately the same before and after annealing. The Zn−SPS ionomers were only studied in the as-molded condition.[1] Perhaps the discrepancy in aggregate shape and size between the SPS and EMAA arises because the vesicular aggregates are metastable intermediates while the stable morphology is spheres. To probe the stability of the aggregates, we directly observe aggregate shape, size, and spatial distribution in Cs−SMAA ionomers as a function of copolymer solution concentration (C_{neut}), rate of neutralizing agent addition (rapid or dropwise), and thermal history. These experiments should provide insight into the effect of processing on the ionomer morphology.

We must also ensure that we are not inducing morphological changes when preparing our microscopy specimens. Our specimen preparation for STEM includes floating thin sections of ionomer material onto water for collection on specimen grids. The effects of water on the ionomer morphology have been the subjects of recent investigations.[5−7] Using extended X-ray absorption fine structure (EXAFS), Grady and co-workers[7] suggest that the zinc in Zn-neutralized SPS ionomers becomes fully solvated by water after immersion. The expected effect on the aggregates would be an increase in the aggregate size to accommodate the water molecules. Fully solvated zinc also implies that the Zn ions would have only limited coordination with the sulfonate groups, possibly impeding the aggregation of ions. These findings prompted our study of the influence of water on the morphology during specimen preparation, as described here.

These current results will be compared with our previous STEM results in an effort to discern the differences between the observed morphologies in the ethylene- and styrene-based systems.

† University of Pennsylvania.
‡ Chosun University.
* To whom correspondence should be addressed.

10.1021/ma011482h CCC: $22.00
Published on Web 02/23/2002

Experimental Methods

Materials and Sample Preparation. Poly(styrene-*ran*-methacrylic acid) (SMAA) ionomers fully (100%) neutralized with Cs were used in these experiments. The copolymer was bulk free-radical copolymerized from styrene and methacrylic acid monomers to an acid comonomer content of 6.1 mol %. The ionomer samples were prepared by dissolving the acid copolymer in a benzene/methanol (9/1 v/v) mixture to solution concentrations (C_{neut}) of 0.1, 3, and 10% (w/v). A solution of cesium hydroxide (CsOH) in methanol containing just enough CsOH to fully neutralize the polymer was added to the acid copolymer solution either rapidly (over 5−10 s) or dropwise over the course of an hour. The neutralized ionomer solutions were stirred for 30 min and then freeze-dried. The freeze-dried powders were further dried under vacuum for 12 h at 130 °C. This sample preparation protocol allows for the evaluation of the effects on the ionomer morphology of C_{neut} and the rate of addition of the neutralizing solution. Sample identification is in the format SMAA-C_{neut}, and in the case of dropwise mixing the suffix "drop" is added.

Specimen Preparation. It was necessary to create specimens suitable for imaging in the microscope from the freeze-dried powders. The ionomer powders were compression-molded at 9000 N for 20 min at 150 °C. Material was iteratively added to the mold to facilitate the creation of fully dense sample disks. Visual inspection ensured that the disks were clear, i.e., free of voids. Microscopy specimens were either prepared from as-molded disks or after annealing the disks under vacuum for 1 week at 175 °C. The annealed specimens were cooled slowly under vacuum to room temperature. Thin sections (100 nm nominal thickness) were microtomed from the disks at room temperature using a Reichert-Jung Ultracut S ultramicrotome with a diamond knife at a cutting speed of 0.4 mm/s. The sections were collected using a "wet" microtomy method, in which sections were floated onto deionized water in the knife boat and collected on copper specimen grids. These grids were stored in a room temperature vacuum chamber until analysis in the STEM. Alternative preparation methods include "dry" microtomy, which involves picking up sections from the dry knife edge with an eyelash tool and placing them onto copper specimen grids, and room condition (i.e., room temperature, pressure, and humidity) storage. Combining the two microtomy protocols and the two storage conditions, there were a total of four sample preparations: dry/room condition (D/RC), dry/vacuum (D/V), wet/room condition (W/RC), and wet/vacuum (W/V).

Scanning Transmission Electron Microscopy (STEM). Imaging was performed on a JEOL 2010F field-emission electron gun (FEG) STEM operated at 197 kV with a 1 nm probe size, a 50 μm condenser aperture, and a HAADF detector collection angle range of 50−110 mrad. Images were collected using a Gatan high-angle annular dark field (HAADF) scintillating detector. In this detection mode, high atomic number species will appear bright in the image. We have previously demonstrated that bright field (BF) and HAADF images provide the same information about ionic aggregates in ionomers.[2] The contribution of the electron probe to the observed morphology has not been deconvoluted from these images. The feature dimensions on the images were measured manually using the Measure tool in Adobe Photoshop 5.0.

Results and Discussion

The morphology of SMAA-10 (Figure 1) exhibits Cs-rich features that are randomly distributed through the microstructure. In HAADF-STEM, Rutherford interactions between the electron beam and the atomic nuclei in the specimen result in the scattering of electrons to high angles, where an annular detector collects them. Higher atomic number (Z) nuclei scatter to higher angles. Furthermore, the number of Rutherford interactions increases with increasing atomic number as approximately Z^2.[8] Therefore, the brightness of the features in HAADF images indicates that the high atomic number Cs ions ($Z_{Cs} = 55$) preferentially reside in these regions. Thus, we can identify these features as Cs-rich ionic aggregates.

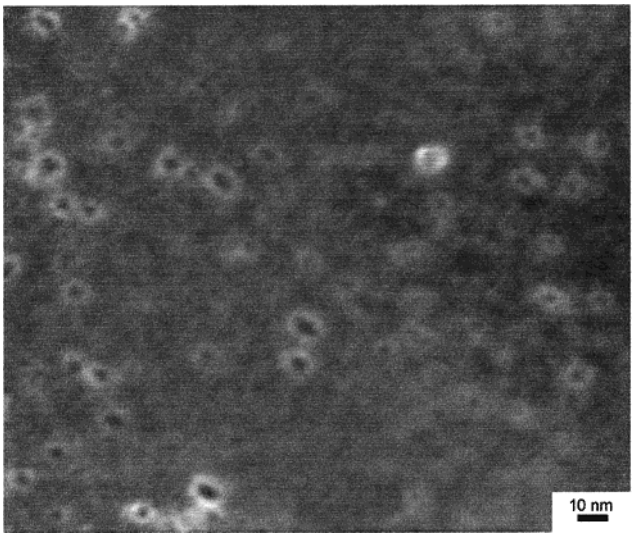

Figure 1. HAADF-STEM image of as-molded SMAA-10 showing the ionomer microstructure. The sample was microtomed wet and stored in a vacuum, W/V. The bright regions are Cs-rich domains that have a vesicular shape.

The shape of these ionic aggregates appears to be a shell-type structure (Figure 1). This is due to the brightness variation across the feature, where the Cs-rich region is the shell. Tilting the specimen with respect to the electron beam results in different projections of the aggregates. A tilt series for these specimens (not shown) yielded images similar to those for the Zn−SPS ionomers and confirms the shell-type shape of the aggregates.[1] Many of the projections indicate that the spherical shells have been cut during microtomy, so they are no longer complete shells. This is reasonable considering that the aggregates are relatively large (~20 nm in diameter) compared to the microtomed section thickness (~100 nm). Thus, we observe Cs ion-rich aggregates in the shape of spherical shells. We will refer to these structures as vesicular aggregates due to their similarities to surfactant vesicles. These similarities include the shape, a narrowly defined shell thickness, and a widely varying diameter.

The vesicular aggregates observed in STEM are quite unexpected relative to the numerous previous morphological studies of styrene-based ionomers using SAXS. To convince ourselves that the observed vesicular ionic aggregates are representative of Cs−SMAA, we prepared the ionomer by spin-coating from solution. The vesicular Cs-rich aggregates are also present after the spin-coating process (Figure 2). Thus, these vesicular ionic aggregates, formed by either compression-molding or solution spin-casting, are representative of the Cs-neutralized SMAA ionomer.

Note that the contrast between the regions inside and outside the shells is not consistent, even within the same image (see Figure 1). The vesicular aggregate interiors have darker, brighter, and the same brightness as the matrix regions of the sample. In the absence of charging and assuming that the vesicular aggregates remain intact during microtomy, the interior of the bright rings that correspond to vesicular shells would appear somewhat brighter than the surrounding matrix. However, because of charging and saturation of the

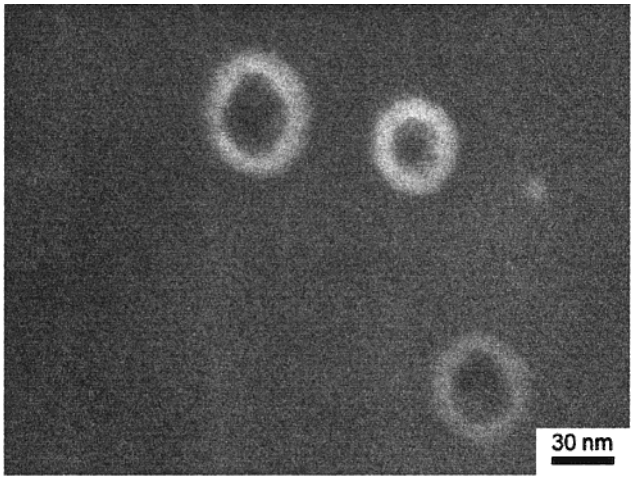

Figure 2. HAADF-STEM image of SMAA-3 thin film prepared by spin-casting from solution. As in the compression-molded sample in Figure 1, the bright regions are Cs-rich domains that have a vesicular shape.

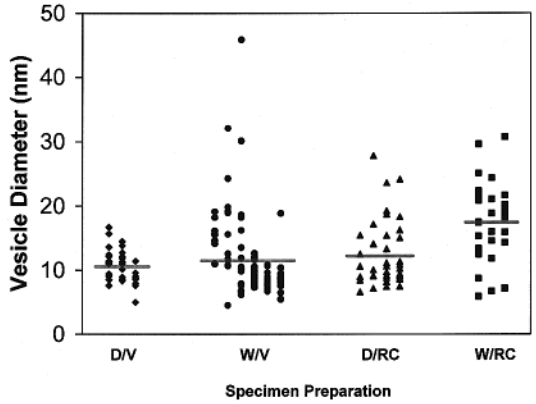

Figure 3. Distribution of vesicular aggregate diameters as a function of specimen preparation methods: D/V = dry microtomy/vacuum storage, W/V = wet microtomy/vacuum storage, D/RC = dry microtomy/room condition storage, and W/RC = wet microtomy/room condition storage. The bar across each data set indicates the average vesicular aggregate diameter for that preparation. Each column within a given specimen preparation represents data from one image.

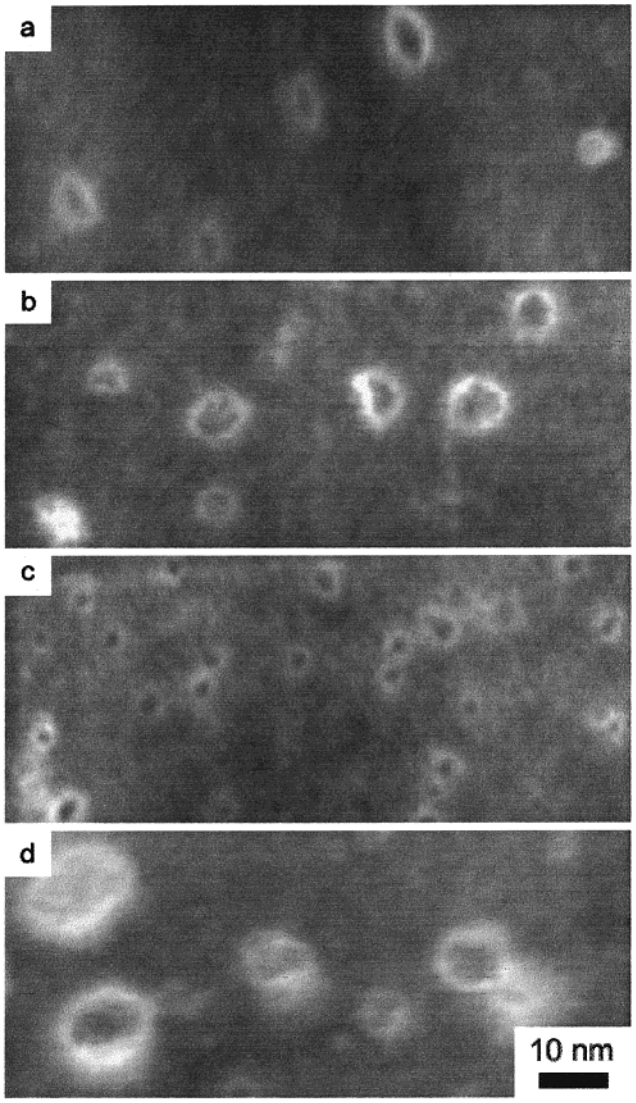

Figure 4. HAADF-STEM images of as-molded SMAA ionomers showing a similar vesicular morphology regardless of C_{neut} and rate of addition: (a) SMAA-0.1, (b) SMAA-3, (c) SMAA-10, and (d) SMAA-3drop. Specimens were prepared by the W/V method.

electronic detector, the observed contrast cannot be readily interpreted inside the vesicular aggregates. Note that charging depends on the STEM magnification. For example, aggregates that are identified as vesicular aggregates at higher magnification often appear as solid spherical aggregates at lower magnification; compare Figures 6 and 7. Thus, we routinely record images at a wide range of magnifications.

The sizes of the aggregates can be determined by direct measurement of the features in the images (Figure 3). The SMAA-10 sample in Figure 1 was microtomed "wet" (sections floated onto water, designated as "W") and stored in a vacuum (designated as "V"), and thus, the vesicular aggregate diameters are designated as W/V. The outer diameters of the SMAA-10 aggregates were typically 5−20 nm with an average diameter of 11 nm, while the shell thicknesses were ∼3 nm. The uniformity of the shell thickness suggests that the ionic species (methacrylic acid and Cs^+) constitute the shell and define its thickness. In contrast, the vesicular aggregate diameters vary widely, which is consistent with the free energy of vesicles varying only slightly with diameter. Furthermore, some vesicular aggregates have been cut, so the observed vesicular aggregate diameters will vary depending on where the aggregates were severed. In summary, the observed vesicular aggregates have well-defined shell thicknesses and widely varying diameters. Because of issues of microtomy and convolution of the probe, more precise dimensions for these aggregates are being sought presently using quantitative SAXS from bulk samples.

Prior EXAFS studies have demonstrated an effect of moisture on the local ionomer morphology.[5−7] Typical room temperature microtomy for STEM specimen preparation places water in the knife boat to spread the sections prior to collecting them on a specimen grid. Four specimen preparations were used to explore their influence, particularly that of moisture, on ionomer morphology. We compared the W/V specimen (Figure 1) to specimens sectioned "dry" (sections picked up dry from the knife edge, designated as "D") as well as stored at room conditions (designated as "RC"). Combining wet and dry microtomy with vacuum and room condition storage produces four STEM preparation methods: D/V, W/V, D/RC, W/RC. All four specimen preparation meth-

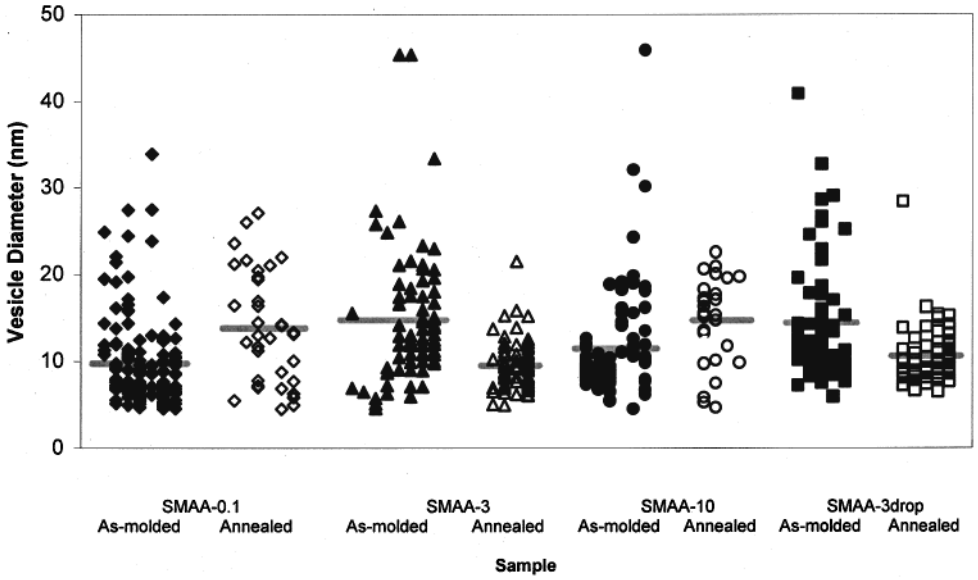

Figure 5. Distribution of vesicular aggregate diameters as a function of neutralization method and thermal history. The filled symbols are data from as-molded samples, while the open symbols are data from samples annealed at 175 °C for 1 week. The bar across each data set indicates the average vesicular aggregate diameter for that sample. Each column within a given data set represents data from one image.

Table 1. Parameters for Ionomer Specimens Imaged with STEM

base polymer	acid group	mol % acid	counterion	neutralization method	% neutralization	aggregate shape
ethylene[2,3]	COOH	5.4	Zn^{2+}	melt	17−78	spherical
styrene[1]	SO_3H	5.3	Zn^{2+}	solution	25	spherical[b]
styrene[1]	SO_3H	5.3	Zn^{2+}	solution	75−125	vesicular and spherical
styrene[a]	COOH	6.1	Cs^+	solution	100	vesicular

[a] Results from this paper. [b] Macrophase separated.

ods produced samples containing randomly distributed vesicular aggregates having shell thicknesses of ∼3 nm. The vesicular aggregate diameters and average diameters (gray bars) for each specimen preparation are shown in Figure 3. While the optimal specimen preparation condition is "dry" microtomy followed by vacuum storage, i.e., D/V, the data suggest that D/V, W/V, and D/RC specimen preparations yield equivalent morphologies. As a result, we selected "wet" microtomy and vacuum storage for the specimen preparation for all of the samples in this paper for ease of preparation.

With a specimen preparation method that reveals the dry bulk morphology of the ionomer, the neutralization methods can be investigated. In particular, we have varied the ionomer concentration during neutralization (C_{neut}) and the rate at which the solution containing the neutralizing agent is added. The micrographs of the as-molded SMAA ionomers for different C_{neut} (0.1, 3, 10% w/v), and rates of addition (rapid, dropwise) are shown in Figure 4. All of the samples exhibit vesicular aggregates with a random spatial distribution. The shell thicknesses for all of the samples are ∼2−4 nm and do not change with these neutralization methods. The diameter distribution of the vesicular aggregates (Figure 5, filled symbols) shows an overlap in the size range and similar average diameters for the four neutralization methods investigated. Thus, over the range of solution concentrations and rates of addition used in this study, the morphologies are equivalent.

We now investigate the thermal stability of the vesicular aggregates. The SMAA ionomers were vacuum-annealed at 175 °C for 1 week, sectioned, and imaged (Figure 6). The annealing temperature (175 °C) is above the matrix T_g (∼115 °C) and below the second T_g reported for Cs−SMAA (∼190 °C).[9] The shape of the aggregates is still vesicular in the annealed SMAA ionomers. In addition, the average vesicular aggregate diameters for the SMAA samples (Figure 5, open symbols) indicate that the aggregate diameters remain approximately constant after annealing, as does the wall thickness (2−4 nm). The number density of the aggregates is observed by imaging the morphology at a lower magnification in STEM (Figure 7). The number density is unchanged by the annealing, and the aggregates remain randomly distributed. The uniformity in the vesicular shape and shell thickness after annealing suggests that the vesicular aggregates are robust structures in this material. Furthermore, annealing SMAA-10 at 225 °C for 1 week also shows that vesicular aggregates persist even when annealed above the second T_g.

Table 1 summarizes our findings for a variety of ionomers using STEM to identify the shapes of ionic aggregates. The ionic aggregates of the Cs−SMAA ionomers in this study are similar to those observed in Zn−SPS ionomers[1] but differ from the ionic aggregates observed in Zn−EMAA ionomers.[2,3] In fact, the highly neutralized styrene-based ionomers contain vesicular aggregates and occasionally spherical aggregates, whereas the highly neutralized ethylene-based ionomers contain exclusively spherical aggregates. While the imaging methods and conditions for these systems are similar, the various sample parameters for each of these systems differ significantly. Below, we consider three arguments for the observed morphological differences between the styrene- and ethylene-based ionomers.

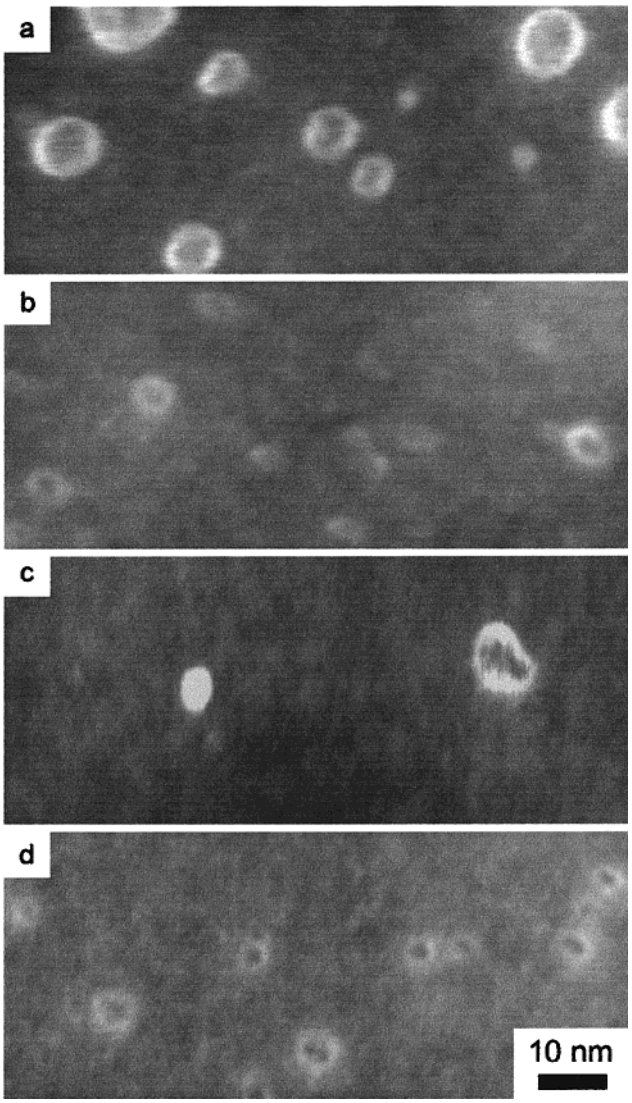

Figure 6. HAADF-STEM images of SMAA ionomers annealed for 1 week at 175 °C showing similar morphologies to that observed in Figure 4 regardless of C_{neut} and rate of neutralizing solution addition: (a) SMAA-0.1, (b) SMAA-3, (c) SMAA-10, and (d) SMAA-3drop. Specimens were prepared by the W/V method.

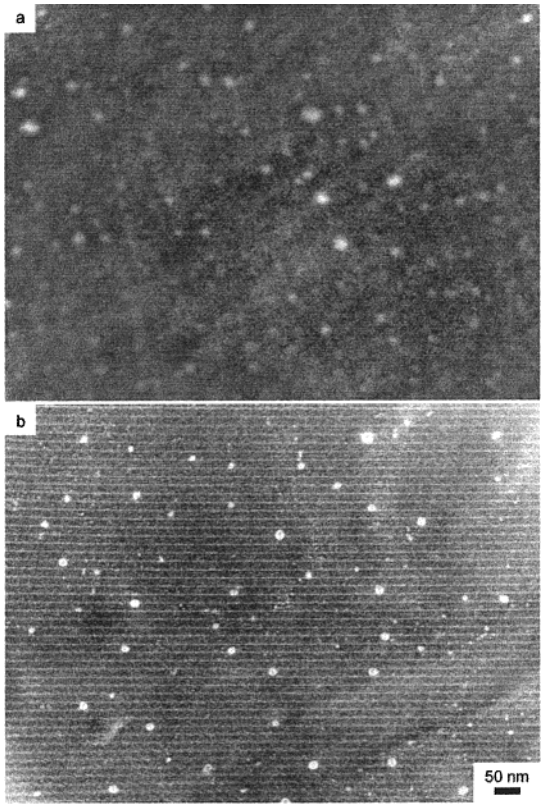

Figure 7. HAADF-STEM images of the SMAA-0.1 ionomer (a) in the as-molded condition and (b) after annealing for 1 week at 175 °C. The samples exhibit a constant number density of vesicular aggregates. Note that at this lower magnification the distinction between the shells and the centers of the vesicular aggregates is obscured; see text.

First, the styrene-based ionomers are neutralized in solution while the ethylene-based ionomers are neutralized in the melt. Preliminary investigations in our group comparing solution neutralized EMAA with the previously studied melt neutralized EMAA indicate that the aggregates are spherical in both instances. This suggests that the method of neutralization is not the paramount issue that determines whether spherical or vesicular aggregates form.

Second, the styrene-based ionomers are amorphous while the ethylene-based ionomers are semicrystalline. Previous research on semicrystalline ethylene-based ionomers has concluded that the ionic aggregates reside between the lamellar crystallites.[10] Given the spatial constraints on the amorphous regions of the ethylene-based ionomers, spherical aggregates (~2 nm in diameter) are more reasonable than the larger vesicular aggregates (10−30 nm in diameter). However, previous researchers have also found that the scattering data of ethylene-based ionomers are independent of temperature even above the melting temperature.[11] This suggests that the morphology of the matrix (semicrystalline vs amorphous) does not determine whether the ionic aggregates form as spherical or vesicular aggregates.

Third, the chain flexibility of PE is significantly higher than that of PS. The Kuhn segment lengths, a measure for chain flexibility, are 1.2 and 1.7 nm for PE and PS, respectively.[12] The greater flexibility of PE, as well as the extent of branching, may promote the packing of matrix chains at the interface between the ion-rich aggregate and the matrix. Better packing allows for a more highly curved interface, resulting in spherical rather than vesicular aggregates for the PE ionomers.

We strongly believe that at least one of these three parameters influences the morphology and that identifying which one(s) will impact how we interpret the physical properties of ionomers. Experiments to determine the impact of neutralization process, crystallinity, and chain flexibility, as well as thermal history, are underway in our laboratory to discern the diverse morphologies observed in ionomers.

Conclusion

This work has identified Cs-rich vesicular aggregates in a Cs-neutralized SMAA ionomer. The aggregate diameters are typically 5−20 nm with a shell thickness of ~3 nm. The larger variation in diameter than shell thickness is expected for vesicular structures. The size, shape, spatial distribution, and number density of aggregates are independent of the solution concentration during neutralization, the rate of neutralizing

solution addition, and annealing below the second T_g. We have also verified that our specimen preparation technique maintains the dry bulk ionomer morphology.

Our STEM studies to date have found vesicular aggregates in Zn−SPS and Cs−SMAA ionomers. In contrast, Zn−EMAA ionomers exhibit exclusively spherical aggregates. This diversity in aggregate shape could be due to the solution vs melt neutralization method, the amorphous vs semicrystalline matrix, or the different Kuhn segment lengths of the base polymers. Preliminary results in our laboratory suggest that the Kuhn segment length is the most important, and experiments are underway to investigate all three possibilities.

Acknowledgment. We thank Dr. John Crocker (University of Pennsylvania) for helpful discussions and Dr. Doug Yates for technical assistance with the JEOL 2010F. The work was supported by NSF-DMR 99-06829. The analytical microscopy was funded by NSF-DMR 94-13550 and the Laboratory for the Research on the Structure of Matter at the University of Pennsylvania. Dr. Joon-Seop Kim acknowledges financial support from Chosun University (1999).

References and Notes

(1) Kirkmeyer, B. P.; Weiss, R. A.; Winey, K. I. *J. Polym. Sci., Part B: Polym. Phys.* **2001**, *39*, 477−483.
(2) Laurer, J. H.; Winey, K. I. *Macromolecules* **1998**, *31*, 9106−9108.
(3) Winey, K. I.; Laurer, J. H.; Kirkmeyer, B. P. *Macromolecules* **2000**, *33*, 507−513.
(4) Li, C.; Register, R. A.; Cooper, S. L. *Polymer* **1988**, *30*, 1227−1233.
(5) Ishioka, T.; Shimizu, M.; Watanabe, I.; Kawauchi, S.; Harada, M. *Macromolecules* **2000**, *33*, 2722−2727.
(6) Ding, Y. S.; Register, R. A.; Nagarajan, M. R.; Pan, H. K.; Cooper, S. L. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 289−300.
(7) Welty, A.; Ooi, S.; Grady, B. P. *Macromolecules* **1999**, *32*, 2989−2995.
(8) Williams, D. B.; Carter, C. E. *Transmission Electron Microscopy—A Textbook for Materials Science*; Plenum Press: New York, 1996.
(9) Eisenberg, A.; Kim, J.-S. *Introduction to Ionomers*; John Wiley & Sons: New York, 1998.
(10) Register, R. A.; Cooper, S. L. *Macromolecules* **1990**, *23*, 318−323.
(11) Quiram, D. J.; Register, R. A.; Ryan, A. J. *Macromolecules* **1998**, *31*, 1432−1435.
(12) Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722−1728.

MA011482H