

## Sulfonated Polystyrene Ionomers Containing 4-Aminobenzoic Acid Studied by a Small-Angle X-Ray Scattering Technique

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**Abstract:** In a recent study by the same authors using a DMTA (Dynamic Mechanical Thermal Analyzer), it was found that the 4-aminobenzoic acid (ABA) molecules acted as either a neutralizing agent, or a plasticizer, or a filler, depending on the order of mixing of poly(styrene-*co*-styrenesulfonic acid) (PSSA), ABA, and NaOH. Subsequent to that study, we here pursued the same topic, i.e., the effect of the addition of CsOH (instead of NaOH) and ABA on the morphology of PSSA, but this time, by using a small-angle X-ray scattering (SAXS) technique. In line with the previous results, the present study with the SAXS technique verified that the order of mixing has a significant effect on the morphology of ionomers. In addition, with the SAXS data and the density values of the ionomers, we attempted to calculate both the number of sulfonate ionic groups per multiplet and the size of the multiplet of the ionomer.

**Keywords:** ionomer, SAXS, multiplets, morphology .

### Introduction

Over the last three decades, the properties of ionomers have been studied extensively.<sup>1-3</sup> These polymers have unique properties owing to the interactions between ionic groups. According to the EHM model for amorphous random ionomers,<sup>4</sup> ionic groups are believed to aggregate to form ionic multiplets<sup>5</sup> which are surrounded by regions of polymer chains of restricted mobility. When the ion concentration increases, the restricted mobility regions start to overlap to form large contiguous regions, called clusters.<sup>4</sup> In general, the ionomers show a small angle X-ray scattering (SAXS) peak, the position of which has been associated with the inter-multiplet distance.<sup>6,7</sup> The peak position was also interpreted to be related to the distance between the ionic core and the ionic shell in partly crystalline ethylene ionomers.<sup>8</sup> Since partly crystalline ionomers have a wide range of application, extensive studies have been devoted to their morphology.<sup>1-3,8</sup> The morphology of polystyrene<sup>7,9-22</sup> iono-

mers was also investigated widely using the SAXS technique.

Only a few studies have investigated the properties of ionomers having ammonium ions as counter-ions for the anionic groups of the ionomers. Weiss *et al.* compared the properties of sulfonated polystyrene (PSSA) ionomers with various ammonium counter-ions.<sup>23</sup> They found that the zinc-neutralized PSSA and the ammonium-PSSA ionomers showed similar behavior in the temperature range for the matrix  $T_g$ . However, in the case of the  $T_g$ s of the PSSA ionomers containing alkyl amines, a different trend was observed. The samples containing the amines with short chain lengths showed "universal" behavior in that a  $T_g$  is a function of the chain length. However, for the amines of long alkyl chain lengths, the substitution level changed the behavior of the materials, especially the trends in the drop of the  $T_g$ . In the study by Smith and Eisenberg, it was found that the matrix  $T_g$  of PSSA ionomers increased considerably upon the addition of amines consisting of a large rigid ring system.<sup>24</sup> Fan and Bazuin studied the matrix  $T_g$ s of PSSA ionomers neutralized with various bi-functional and multi-functional amines.<sup>25</sup> It was found that the basicity of the amines did not

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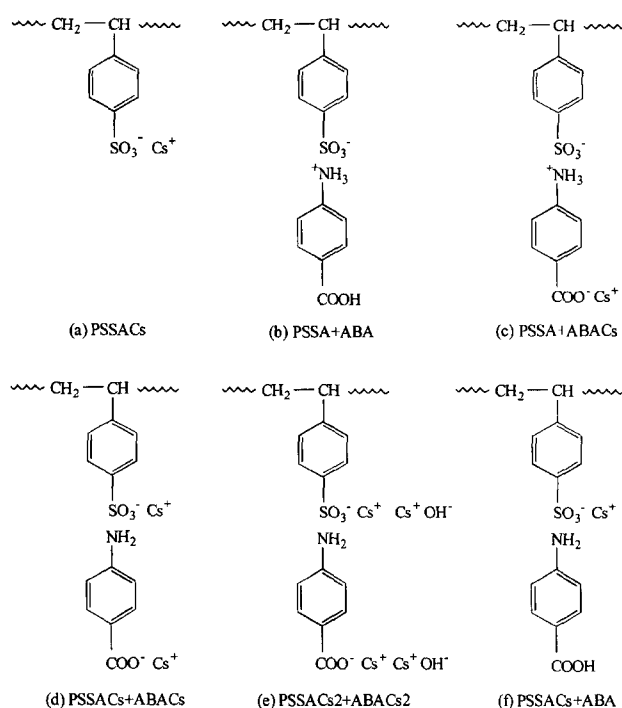
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change the matrix  $T_g$  of the ionomers significantly. Very recently, Kim *et al.* studied the mechanical properties of PSSA ionomers containing 4-aminobenzoic acid neutralized with NaOH,<sup>26</sup> and found that the order of mixing of the three components and the strength of acidity of the acid groups changed the mechanical properties of the ionomers significantly. However, the morphological study on this ionomer system had not been performed. Furthermore, if we knew the size of multiplets, we could understand the relationship between the mechanical properties and morphologies of ionomers with more ease.

Thus, in the present study, we explored primarily the effects of the order of mixing of the acid polymer, the neutralizing agent, and the amino acid on the morphology of resulting ionomers using the SAXS technique. Subsequently, as a main goal of the present study, we roughly calculated both the number of ionic groups per multiplet and the size of the multiplet of the ionomers using simple space-filling assumption. We believe that the calculated values will be very useful to estimate the size of multiplets and the number of ionic groups per multiplet, which will also be used when one compares mechanical data of each ionomer sample.

## Experimental

**Materials.** Polystyrene was synthesized by bulk free-radical polymerization using benzoyl peroxide as the initiator. The molecular mass of the sample ( $M_n = 127,000$  and  $M_w = 269,000$ ) was determined using a Varian 5010 size exclusion chromatograph with THF as the solvent. For homogeneous sulfonation of the polystyrene, the method developed by Makowski *et al.*<sup>27</sup> was used to produce the poly(styrene-*co*-styrenesulfonic acid) (PSSA) samples containing 7.7 mol% of acid groups. In order to study the effect of the order of mixing on the morphology of ionomers, the PSSA copolymer, 4-aminobenzoic acid (ABA), and CsOH were added in different orders. Firstly, the PSSACs ionomer (Scheme (a)) was prepared by adding a predetermined amount of methanolic CsOH to the PSSA copolymer in a benzene/methanol (9/1 v/v) mixture. Secondly, in the case of the PSSA+ ABA ionomer (Scheme (b)), an ethanolic 4-amino-benzoic acid (ABA) solution was added to a PSSA copolymer solution. Thirdly, for



Scheme.

the PSSA+ABACs (Scheme (c)) and the PSSACs + ABACs (Scheme (d)) samples, Cs-neutralized ABA in ethanol was added to PSSA copolymer and PSSACs ionomer solutions, respectively, to achieve 100% neutralization. Fourthly, the acid groups of a PSSA polymer and an ABA compound were neutralized with CsOH to yield 200% neutralization, and then the solutions were mixed; the sample is denoted as the PSSACs2 + ABACs2 (Scheme (e)). Lastly, in the case of the PSSACs + ABA sample (Scheme (f)), a cesium neutralized sulfonated polystyrene ionomer solution was mixed with an ABA solution. In all of the ionomers containing ABA molecules, the mole ratio of the ABA molecules to the sulfonate group of the PSSA polymer was 1 : 1. The denotations of samples are listed in Table I. All of the solutions mentioned above were stirred for 25 min, freeze-dried, and then dried under vacuum at 80 °C for 1 day.

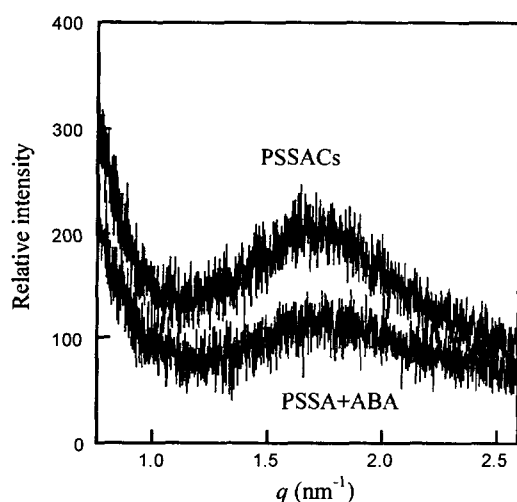
For the small-angle X-ray scattering (SAXS) measure-

Table I. Sample Denotations

Denotation of Ionomers	Relative Ratio of the Number of Sulfonate Groups in a PSSA Polymer and Those of ABA and CsOH Molecules			
	Acid Groups in PSSA	CsOH Molecules	ABA Molecules	CsOH Molecules
PSSACs (Scheme (a))	1	1	0	0
PSSA + ABA (Scheme (b))	1	0	1	0
PSSA + ABACs (Scheme (c))	1	0	1	1
PSSACs + ABACs (Scheme (d))	1	1	1	1
PSSACs2 + ABACs2 (Scheme (e))	1	2	1	2
PSSACs + ABA (Scheme (f))	1	1	1	0

ments, the samples were compression-molded at ca. 230 °C; a pressure of ca. 20 MPa was applied for 5 min, then slowly released, and the mold was allowed to cool to below the matrix  $T_g$ . The molded samples, with dimensions of ca. 0.5 mm (thickness)  $\times$  10 mm (diameter), were annealed for 24 h under vacuum at 80 °C.

**Small-Angle X-Ray Scattering Experiments.** The small-angle X-ray scattering experiments were conducted at Station 4C1 of the PLS synchrotron radiation source (Pohang, Korea).<sup>28</sup> The energy of the generated beam ( $\lambda = 1.608 \text{ \AA}$ ) was 2.8 keV (at 2.5 GeV operation mode). The size of the beam at the sample was smaller than 1 mm<sup>2</sup>. The position-sensitive one-dimensional Si diode-array detector was used. The sample-to-detector distance was 840 mm, which allowed SAXS data to be obtained in the  $q$  range from ca. 0.76 to 2.59 nm<sup>-1</sup>, where  $q = 4\pi\sin\theta/\lambda$ ,  $\theta$  is half the scattering angle and  $\lambda$  is the X-ray wavelength. The SAXS data were plotted as relative intensity vs.  $q$  after the correction for sample absorption and background (the SAXS profile of pure polystyrene was subtracted from that of ionomer samples).



**Figure 1.** SAXS profile of PSSACs (see Scheme (a)) and PSSA + ABA (see Scheme (b)) ionomers.

## Results and Discussion

ABA has a basic amine group and a carboxylic acid group. Thus, in the sample of a PSSA copolymer mixed with the ABA, one finds two different acid groups ( $-\text{SO}_3\text{H}$  and  $-\text{COOH}$ ) and one base group ( $-\text{NH}_2$ ). Figure 1 shows the SAXS profile of the Cs-neutralized sulfonated polystyrene (PSSACs) ionomer (Scheme (a)) containing 7.7 mol% of ionic groups and that of the PSSA + ABA ionomer (Scheme (b)). In the case of the PSSACs ionomer, an SAXS peak and a significant upturn in the small  $q$  range are observed. The  $q$  value for the SAXS peak maximum, i.e.  $q_{\text{max}}$ , for the PSSACs ionomer is found to be 1.69 nm<sup>-1</sup>. The  $q_{\text{max}}$  values for all ionomers studied in the present work are listed in Table II. The Bragg spacing obtained from the  $q_{\text{max}}$  value ( $D_{\text{Bragg}} = 2\pi/q_{\text{max}}$ ) are also listed in Table II. It is seen that the Bragg distance of the PSSACs ionomer is 3.72 nm which is more or less similar to those obtained previously.<sup>9-16,22</sup>

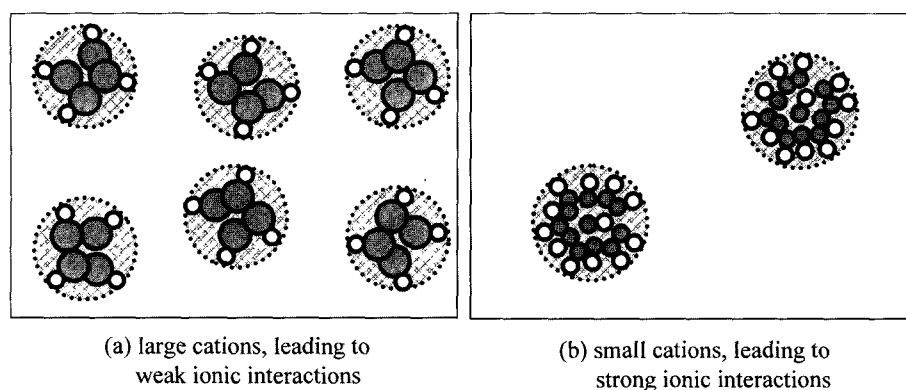
In the case of the PSSA+ABA sample (Scheme (b)), the SAXS peak is seen at slightly higher  $q$  (1.77 nm<sup>-1</sup>,  $D_{\text{Bragg}} = 3.55 \text{ nm}$ ) with lowering intensity, compared to that of the PSSACs ionomer. This result can be explained by the difference between the PSSACs and PSSA+ABA ionomers in chemical structures. The cation in the PSSACs ionomer is Cs<sup>+</sup>, while that in the PSSA + ABA is 4-ammoniumbenzoic acid. In order to compare the relative volumes of the two cations, we calculated the molar volume of Cs and 4-ammoniumbenzoic acid, since the physical data for the 4-ammoniumbenzoic acid were not available. With the data of the density ( $d$ ) in the solid state and the formula weight (FW) of cesium ( $d = 1.892 \text{ g/cm}^3$ , FW = 132.9 g/mol) and ABA ( $d = 1.374 \text{ g/cm}^3$ , FW = 137.14 g/mol),<sup>29</sup> we could calculate the molar volumes of cesium and ABA; they were ca. 70.2 and 99.8 cm<sup>3</sup>/mol, respectively. Thus, it can be suggested that the size of the cation in the PSSA + ABA ionomer might be larger than that in the PSSACs ionomer. At this point, it should also be mentioned that the electric force ( $F_{el}$ ) between two charges is inversely proportional to the distance square ( $r^2$ ) between two charges: That is

$$F_{el} \propto q_a q_b / r^2,$$

**Table II.** SAXS Data, Bragg Spacing ( $D_{\text{Bragg}}$ ), Densities, the Number of Sulfonate Ionic Groups Attached to Ionomer Chains per Multiplet ( $N_{\text{ionic}}$ ), and the Radius of Multiplet ( $r_{\text{mul}}$ ) for Various Styrene Ionomers

Ionomer	$q_{\text{max}}$ (nm <sup>-1</sup> )	$D_{\text{Bragg}}$ (nm)	Density <sup>a</sup> (g/cm <sup>3</sup> )	$N_{\text{ionic}}$ <sup>b</sup>	$r_{\text{mul}}$ (Å)
PSSACs	1.69	3.72	1.236	24	5.5
PSSA + ABA	1.77	3.55	1.221	20	6.7
PSSA + ABACs	1.86	3.38	1.200	16	10.3
PSSACs + ABACs	1.86	3.38	1.293	17	8.0
PSSACs2 + ABACs2	1.83	3.43	1.301	18	8.9
PSSACs + ABA	1.67	3.76	1.229	25	7.2

<sup>a</sup>Density was measured by using a pycnometer. <sup>b</sup>Calculated from simple space-filling argument for a simple cubic lattice.



**Figure 2.** Schematic representation of the multiplets, in which the strength of interactions between ionic groups is (a) weak and (b) strong. White and black symbols indicate anionic and cationic groups, respectively, and the shaded areas represent the multiplets.

where  $q_a$  and  $q_c$  are the anion charge and the cation charge, respectively.<sup>30</sup> In the PSSA+ABA ionomer case, the distance between positive and negative charges is larger than that in the PSSACs ionomer, leading to the weaker ionic interaction. Thus, the number of ionic groups in the multiplets is smaller for the PSSA + ABA than for the PSSACs ionomer. As a result, the number of multiplets themselves is, in a reverse manner, larger for the PSSA + ABA ionomer than for the PSSACs ionomer (see Figure 2). Therefore, the PSSA+ABA ionomer should show a shorter Bragg distance between multiplets (i.e. larger  $q$ ) and a lower intensity than for the PSSACs ionomer. These influences agree with what we observed in the present study.

At this point, it may be useful to calculate the number of the sulfonate ionic groups attached to ionomer chains per ionic core ( $N_{ionic}$ ). To do so, it was assumed that the Bragg spacing arises from inter-particle scattering related to the distance between multiplets. It was also assumed that the multiplets are regularly distributed in the polymer matrix, that all ion pairs are within the multiplets, and further that the multiplets are located on the sites of a simple cubic lattice. At this point, it should be stressed that one can naturally think of other lattices. However, here we are dealing only with a simple cubic lattice because the calculated values in the present work are merely for the reasonable comparison of the morphologies of the ionomers. For the calculation, we also measured the density of ionomers by using a pycnometer. While all these assumptions may not hold here, they allow us to obtain the comparable aggregation numbers per ionic core. The calculated aggregation numbers are listed in Table II. As was mentioned above, the calculated number of the sulfonate ionic groups per multiplet is smaller for the PSSA + ABA than for the PSSACs ionomer because of the weaker ionic interactions of the former; they are 20 and 24, respectively.

In the present study, we also attempted to calculate the size of the multiplets of ionomers. First of all, we measured

the density of polystyrene ( $d_{PS}$ ) by using a pycnometer; the density was 1.084 g/cm<sup>3</sup>, which is similar to the values in the literature.<sup>31</sup> Then, we tried to calculate the molar volume of polystyrene with the density value. However, it should be mentioned that the polystyrene homopolymer and ionomers have very broad molecular weight distribution due to free-radical polymerization. Thus, for simple calculation and comparison, we had to assume that the polystyrene and ionomers have a certain degree of polymerization. In the present work, the polymer chain was assumed to have 100 repeat units; the molar volume of the polystyrene ( $V_{PS}$ ) containing 100 repeat units is as follows:

$$V_{PS} = MW_{PS-100} / d_{PS} ,$$

where  $MW_{PS-100}$  is the molecular mass of polystyrene chain containing 100 repeat units. If we expanded this calculation to the PSSACs ionomer containing 100 average structural units (i.e. 92.3 units of styrene and 7.7 units of cesium styrenesulfonate), the molar volume for the ionomer ( $V_{PSSACs}$ ) could also be calculated:

$$V_{PSSACs} = MW_{PSSACs-100} / d_{PSSACs} ,$$

where  $MW_{PSSACs-100}$  is the molecular mass of the PSSACs ionomer containing 100 structural units, and  $d_{PSSACs}$  is the density of the PSSACs ionomer. It is noted that the  $V_{PSSACs}$  was observed to be larger than the  $V_{PS}$  in the present study. Thus, we assumed that the increase in the volume ( $V_i$ ) of the ionomer, compared to that of polystyrene, is solely due to the presence of ionic groups:

$$V_i = V_{PSSACs} - V_{PS}$$

At this point, it should be noted that the number of multiplets in the ionomer ( $N_{mul}$ ) of 12047 g [= 104.15 g/mol (FW of styrene)  $\times$  92.3 mol + 316.11 g/mol (FW of cesium sulfonated styrene)  $\times$  7.7 mol] is  $1.893 \times 10^{23}$ , which can be calculated from the Bragg distance of the ionomer on the basis of a space filling approach for a simple cubic lattice,

as was mentioned above. These values, in turn, allow us to calculate the volume of multiplet ( $V_{mul}$ ) as follows:

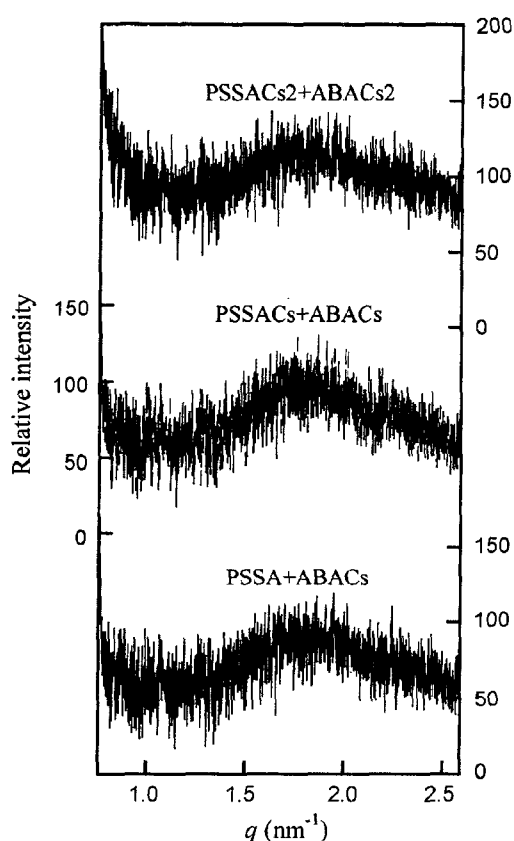
$$V_{mul} = V_i / N_{mul}$$

If we assumed that the multiplet has a spherical shape, the radius of the multiplet ( $r_{mul}$ ) could be calculated.

$$r_{mul} = [(V_{mul} \times 3) / (4 \times \pi)]^{1/3}$$

Subsequently, for the rest of ionomers, the same calculation procedure was applied; the radii are also listed in Table II. From the  $r_{mul}$  values in the table, it is evident that, as was mentioned above, the size of the multiplet in the PSSACs ionomer is smaller than that in the PSSA + ABA ionomer.

Now, we shall describe the morphologies of three ionomers containing Cs-neutralized ABA molecules. Figure 3 shows



**Figure 3.** SAXS profiles of PSSA+ABACs (see Scheme (c)), PSSACs + ABACs (see Scheme (d)), and PSSACs2 + ABACs2 (see Scheme (e)) ionomers (from bottom to top).

the SAXS data for the PSSA+ABACs (Scheme (c)), PSSACs + ABACs (Scheme (d)), and PSSACs2 + ABACs2 (Scheme (e)) ionomers. It is seen that the positions of the SAXS peaks for the three ionomers are similar to each other, and that all the three ionomers have larger  $q_{max}$  than the PSSACs ionomer. At this point, it might be useful to recall the results obtained from the dynamic mechanical study of the PSSA + ABANa ionomer.<sup>26</sup> It was found that while the matrix and cluster  $T_g$ s of the PSSANa ionomer were 143 and 264 °C, respectively, those of the PSSA + ABANa ionomer were 130 and 166 °C, respectively (for the convenience, the glass transition temperatures of some of the ionomers are listed in Table III). The authors suggested that when the PSSA polymer was mixed with the sodium *p*-aminobenzoate molecules, the proton transfer took place from the sulfonic acid of the PSSA to the amine group of the ABA molecules (see Scheme (c)). Then, the ionic aggregate consists of two kinds of ion pair, i.e.  $-\text{SO}_3^- \text{H}_3\text{N}^+$  and  $-\text{COO}^- \text{Na}^+$  ion pairs. This aggregate seems to look like more or less a core-shell type multiplet;  $-\text{COO}^- \text{Na}^+$  ion pairs reside in the core,  $-\text{SO}_3^- \text{H}_3\text{N}^+$  ion pairs in the outer shell, and the benzene rings of the ABA molecules between the inner core and the outer shell. In that system, the ionic interactions are weaker between  $-\text{SO}_3^-$  and  $\text{NH}_3^+$  ion pairs than between  $-\text{COO}^-$  and  $\text{Na}^+$  ion pairs owing to the larger size of  $\text{NH}_3^+$  ion than  $\text{Na}^+$  ion. Thus, it was suggested that when the temperature increases, the  $-\text{SO}_3^- \text{H}_3\text{N}^+$  ion pairs start hopping at relatively lower temperatures. If this held, the multiplet in the present study should contain ammonium-sulfonate ion pairs in the outer shell and cesium-carboxylate ion pairs in the core, the ionic interactions in both of which should be weaker than those in cesium-sulfonate ion pairs. Then, the number of ionic groups per multiplet in the PSSA + ABACs ionomer should be smaller than in the PSSACs ionomer, which, in turn, should increase the number of multiplets.<sup>32</sup> As a result, the Bragg distance should become shorter (larger  $q_{max}$ ). This is, indeed, what we observed in the present study. It should also be pointed out that in Table II the radius of the multiplet in the PSSA + ABACs ionomer is the largest. However, if we took into consideration the size of  $\text{Cs}^+$  ion (ca. 3.6 Å in diameter) as well as the bond lengths of C-N (ca. 1.4 Å), C-S (ca. 1.8 Å), and C-C (ca. 1.4 Å) in an aromatic ring,<sup>33</sup> it would be not surprising that the core-shell type multiplet of this ionomer is larger than those of the remaining ionomers.

Now, let us discuss the morphology of the Scheme (d) ionomer. In the study of mechanical properties of the

**Table III.** Glass Transition Temperatures of Sodium-Neutralized Ionomers<sup>26</sup>

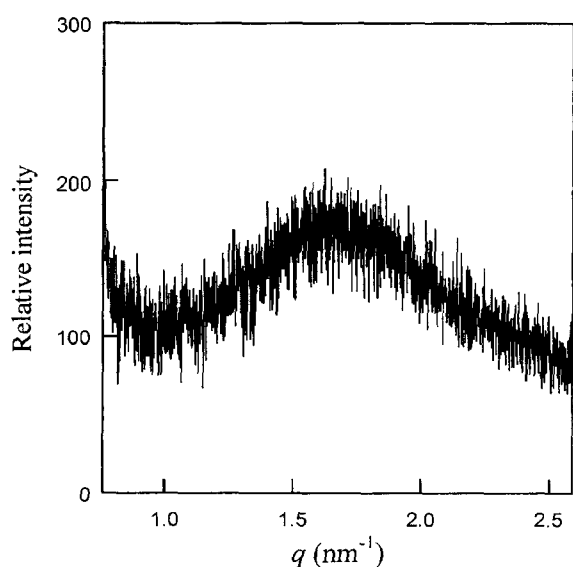
Ionomer	Matrix $T_g$ (°C)	Cluster $T_g$ (°C)	Notes
PSSANa	143	264	--
PSSA + ABANa	130	166	Core-Shell type multiplet
PSSANa + ABANa	139	270	ABANa acts as a filler
PSSANa + ABA	134	186	ABA acts as a plasticizer

PSSANa + ABANa ionomer,<sup>26</sup> it was found that the matrix and cluster  $T_g$ s of the PSSANa+ABANa ionomer were 139 and 270 °C, respectively; it was suggested that the ABANa acted as a filler. If this suggestion were valid in the present study, the ABACs would participate in the formation of multiplets with the sulfonate ionic groups of the ionomer. At this point, it should be recalled that the multiplet has an upper limit in its size.<sup>5</sup> Thus, the number of the sulfonate ionic groups of the ionomer per multiplet should be smaller for the PSSACs + ABACs ionomer than for the PSSACs ionomer. As a result, the number of multiplets in the PSSACs + ABACs ionomer should be larger than that in the PSSACs ionomer, and the Bragg distance between multiplets in the PSSACs + ABACs ionomer should, in turn, be smaller than that for the PSSACs ionomer. The results obtained in the present study are in good agreement with these suggestions. Table II shows that the number of sulfonate ionic groups of the PSSACs ionomer is ca. 1.4 (i.e. 24/17) times larger than that in the PSSACs + ABACs ionomer, and that the Bragg distance for the former ionomer (i.e. 3.72 nm) is larger than that for the latter ionomer (i.e. 3.38 nm).

In the case of the PSSACs2 + ABACs2 ionomer (Scheme (e)), the extra CsOH might reside in or near the multiplets, acting also as a reinforcing filler.<sup>34</sup> Thus, the size of multiplet of the PSSACs2 + ABACs2 is to be larger than that of the PSSACs + ABACs, which is what we can deduce from the  $r_{mul}$  values in Table II. The table demonstrates that the number of the sulfonate ionic groups per multiplet is similar for the PSSACs + ABACs and the PSSACs2 + ABACs2 ionomers, whereas the Bragg distance is larger for the latter ionomer than for the former. This result implies that the

extra CsOH does not disrupt the formation of multiplets aided by the sulfonate ionic groups of the ionomer, and that the existence of CsOH in the multiplet enlarges the size of the multiplet, which, in turn, increases the Bragg distance.

The next and last discussion will be devoted to the morphological change occurring with the addition of ABA to the PSSACs ionomer. Shown in Figure 4 are the SAXS data for the PSSACs + ABA ionomer (Scheme (f)) as a function of  $q$  value. The maximum of the SAXS peak is seen at  $q_{max} = 1.67 \text{ nm}^{-1}$  ( $D_{Bragg} = 3.76 \text{ nm}$ ). In Table II, it is seen that the number of the sulfonate ionic groups of the ionomer is 36. It is interesting to note that the numbers of the sulfonate ionic groups of the ionomer per ionic core (i.e.  $N_{ionic}$ ) for the PSSACs and PSSACs + ABA ionomers are similar, even though the Bragg distances differ. The Bragg distance of the former ionomer (i.e. ca. 3.7 nm) is slightly shorter than that in the latter (i.e. ca. 3.8 nm). At this point, the results obtained in the study of the dynamic mechanical properties of these two ionomers are worth recalling.<sup>26</sup> It was found that, upon the addition of ABA molecules to the PSSANa ionomer, the matrix  $T_g$  of the ionomer decreased from 143 to 134 °C and the cluster  $T_g$  decreased by ca. 80 °C from 264 to 186 °C (see Table III). Thus, it was suggested that the ABA molecules reside in the multiplets, acting as a polar plasticizer. These results imply that the presence of the ABA in the multiplet should make the size of the multiplets larger, which naturally elongates the Bragg distance, which is indeed what we observed in the present study. It should also be mentioned that the equality of aggregation number in the two ionomers implies that the presence of the ABA molecules may not affect the multiplet formation process in the PSSACs ionomer, but just may enlarge the multiplet size.



**Figure 4.** SAXS profile of PSSACs + ABA (see Scheme (f)) ionomer.

## Conclusions

In the present study, the morphology of poly(styrene-*co*-styrenesulfonic acid) (PSSA) ionomers mixed with CsOH and 4-aminobenzoic acid (ABA) was investigated by using the SAXS technique. It was found that when the ABA molecules were added to the PSSA solution, the SAXS peak shifted to higher angles and its intensity decreased, compared to the SAXS peak of the PSSACs ionomer. Thus, it was suggested that the ammoniumbenzoic acid cation is larger than the Cs<sup>+</sup> ion, resulting in a lower effective charge density and weaker ionic interactions between ionic groups in multiplets. Therefore, the number of sulfonate ionic groups per multiplet decreases. In the case of the PSSA + ABACs, PSSACs + ABACs, and PSSACs2 + ABACs2 ionomers, it was observed that the SAXS data were more or less similar to each other, but that the positions of the peak maximum were higher than that of the PSSACs ionomer. The results obtained from the PSSA + ABACs could be due to the formation of "core-shell" type multiplet (i.e. cesium carboxylate

ion pairs exist in the core, ammonium sulfonate ion pairs in the outer shell, and the phenyl groups of the ABA molecules between the core and the shell), while those obtained from the latter two ionomers were due to the presence of ABACs acting as a filler, as was suggested in the previous study on the mechanical properties of these ionomers. In the case of the PSSACs + ABA ionomer, in which the ABA molecules acted as a polar plasticizer, residing in the ionomer multiplets, it was found that the Bragg spacing was larger than that of the PSSACs ionomer, even though the aggregation numbers were identical for the two ionomers. Thus, it was suggested that the presence of the polar plasticizer just enlarged the size of multiplet without changing the multiplet formation process in the PSSACs ionomer. All the morphological interpretations given in the present study are in good agreement with the suggested morphological pictures in the previous mechanical study.

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