Structure of Ionic Aggregates of Ionomers. 1. Variation in the Structure of Ionic Aggregates with Different Acid Content and Degree of Neutralization of Ethylene and Styrene Ionomers

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ABSTRACT: Small-angle X-ray scattering profiles of the ethylene and styrene ionomers were studied to clarify the structure of ionic aggregates as a functions of the nature of cations, acid content, and degree of neutralization. The ionic cluster peak was observed for the ionomers with a certain degree of neutralization. The scattering profile of the ionic cluster peak was analyzed by the modified hard-sphere model proposed by Yarusso and Cooper , and the size of ionic aggregates, closest approach distance between the aggregates, and average system volume per ionic aggregate were obtained. The size and distance of the ionic aggregates in the ionomers with monovalent cation, sodium and potassium cations, increased with the ion content (acid content × degree of neutralization), while those with divalent one, zinc and copper cations, and trivalent one, ferric cation, changed only slightly. The number of cations in an ionic aggregate was evaluated in an approximate manner by using the average system volume per ionic aggregate and the density of ionomer or the size of the ionic aggregate and the density of the ionic aggregate estimated by a simple additivity rule for each phase.

Introduction

Ionic groups such as the carboxylate groups in ionomers are well-known to form in general ionic aggregates phase-separated due to the Coulombic interaction between ions embedded in a matrix with low dielectric constant.[1] The ionic aggregates can play a role of physical cross-linking and provide the characteristic viscoelastic behavior of ionomers. The presence of the ionic aggregates is the most characteristic feature leading to the physical properties of ionomers.

There are, however, few structural morphological studies of the ionic aggregates, and there exists no comprehensive conclusion about them at the present time.[2] Electron microscopic observations have been reported by some researchers.[3,4] Longworth et al.[5] have observed a spherical particle with a radius of 150 Å probably assigned to the ionic aggregates of ethylene ionomer containing rubidium salt. On the other hand, Cooper et al.[6] reported the cluster size in the butadiene−methacrylic acid sodium salt ionomer to be 13−26 Å, and Philips et al.[7] observed a similar size for ethylene−phosphoric acid cesium salt ionomer. Many small-angle X-ray scattering studies on ionomers have been carried out, but there are still problems to be clarified.[2,8−10] Many structural models of the ionic aggregates have been proposed, i.e., ball-like structure[8] of pseudocrystalline array, core−shell structure,[2] lamellar structure, cylindrical structure,[9] etc. Yarusso and Cooper examined the proposed structures experimentally and theoretically and found that a modified hard-sphere model is much more suitable for ionic aggregates, yielding a better agreement between observed and calculated SAXS profiles.[2]

In this article, we studied the structure of the ionic aggregates of copoly(ethylene−methacrylic acid) sodium, potassium, zinc, copper, and ferric salts ionomers (ethylene ionomer) and copoly(styrene−methacrylic acid) sodium salts (styrene ionomer) using the modified hard-sphere model proposed by Yarusso and Cooper.[2] The radius and distance of closest approach of the ionic aggregates in ionomers with different acid contents, degrees of neutralization, and cation species were evaluated by the curve fitting of observed and calculated SAXS profiles.

Experimental Section

Samples. Copoly(ethylene−methacrylic acid)s with the acid content of 3.5 and 5.4 mol % were kindly provided from Mitsui-Dupont Polychemicals Inc. Ethylene ionomers of sodium, potassium, zinc, copper, and ferric salts with different degrees of neutralization were prepared by soaking copoly(ethylene−methacrylic acid) film of 30 μm thick into sodium hydroxide, potassium hydroxide, zinc acetate, copper acetate, and ferric chloride methanol solution, respectively, at 60 °C for various reaction times followed by complete washing. The degree of neutralization of ethylene ionomers synthesized here was determined from the intensities of infrared absorption spectra of $-COO^-$ and $-COOH$ appearing at 1600 and 1700 cm^{-1}, respectively. Hereafter, the sample is designated to E-0.035-(or 0.054)MAA-*x*M, where *x* is the degree of neutralization and M is the kind of metal salt. Ethylene ionomer films of almost the same thickness as the copolymer containing different degrees of neutralization and cation species were used for SAXS measurement.

Copoly(styrene−methacrylic acid)s with acid content of 8.7 and 13.7 mol % were supplied from Idemitsu Petrochemical Inc. Neutralization of the copolymer was similarly carried out at 25 °C by sodium hydroxide in a mixture of 2-butanone and methanol. The sample was precipitated, purified, and dried. Styrene ionomer was designated S-0.087(or 0.137)MAA-*x*Na. Styrene ionomer film was cast from a dimethylformamide solution at room temperature.

The density of ionomers was measured at 24 °C in a density gradient column prepared by mixing solutions, composed of cyclohexane and tetrachloromethane with densities of 0.88 and 1.10 g/cm^3, respectively.

Methods. The SAXS profile in the range of 2θ from 1.5° to 12° was obtained at room temperature for stacked ionomer

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film about 1 mm thick by 20 times integration using a diffractometer (RAD-C, Rigaku Denki Co. Ltd.). The SAXS profile was corrected by subtracting the observed SAXS profile of an acid copolymer from that of the ionomer. This corrected profile in the same range of 2θ was applied to Yarusso and Cooper's structural model.[2]

Results and Discussion

Analysis of Small-Angle X-ray Scattering Profile. The higher-order structure of the ionic aggregates is very important to understand the physical properties and performance of ionomers. The analysis of the SAXS profile of an ionomer is one of the most useful methods for the study of the structure of the ionic aggregates. Porod[11,12] and Guinier[13] plots are useful for this analysis.

Yarusso and Cooper[2,14] derived the theoretical X-ray scattering intensity based on various structure models with different electron densities and radii of the ionic aggregates. They fitted the calculated scattering curve to the observed one and found that the ionic aggregates are best fitted by a modified hard-sphere model, in which the X-ray scattering intensity is represented by

$$I(q) = I_e(q) V \frac{1}{V_p} V_1^2 \rho_1^2 \Phi^2(qR_1) \frac{1}{1 + \left(\frac{8V_{ca}}{V_p}\right)\epsilon\Phi(2qR_{ca})} \tag{1}$$

$$V_{ca} = \frac{4}{3}\pi R_{ca}^3 \tag{2}$$

$$V_1 = \frac{4}{3}\pi R_1^3 \tag{3}$$

$$\Phi(\chi) = 3\,\frac{\sin\chi - \chi\cos\chi}{\chi^3} \tag{4}$$

where $q = (4\pi/\lambda)\sin\theta$ is the magnitude of the scattering wave vector, 2θ is the angle between the incident and scattered beams, λ is the radiation wavelength, $I_e(q)$ is the intensity scattered by a single electron under the experimental conditions and $I(q)$ is the observed intensity, V_p and V are the average system volume per particle of ionic aggregates and the volume of the sample illuminated by the X-ray beam, respectively, ρ_1 is the electron density difference between the matrix and the ionic aggregate, ϵ is a constant close to unity, R_1 is the radius of ionic aggregate, and $2R_{ca}$ is the distance of closest approach between two ionic aggregates. The secondary intensity scattered by a single electron is represented by the well-known Thomson formula[15]

$$I_e(\theta) = I_0 \frac{e^4}{m^2c^4} \frac{1}{r^2} \frac{1+\cos^2\theta}{2} \tag{5}$$

where I_0 is the primary intensity, e and m are the charge and the mass of an electron, respectively, c is the light velocity, and r is the distance between the particle and the counter. In the case of small θ, this is approximated by

$$I_e \cong I_0 \frac{e^4}{m^2c^4r^2} \tag{6}$$

Therefore, in eq 1, $I_e(q)$ can be regarded as a constant, I_e, in this study, and $I_eV\rho_1^2$ as an adjustable parameter.

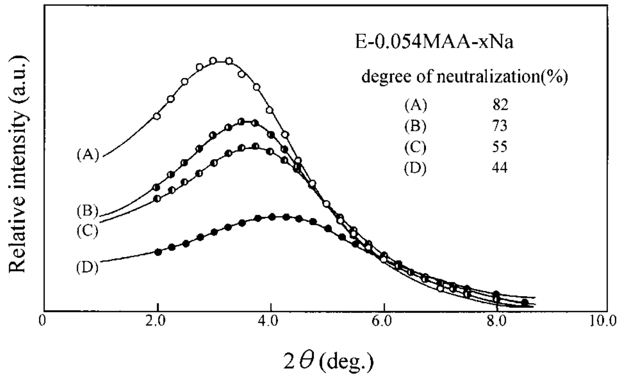

Figure 1. Observed and calculated curves of SAXS profiles by modified hard-sphere model for E-0.054MAA-*x*Na. Circles are observed data: (A) ○, $x = 0.82$; (B) ◑, 0.73; (C) ◐, 0.55; (D) ●, 0.44.

Table 1. Values of V_p, R_1, d_i, N_1, and N_2 of E-0.035MAA-*x*Na and E-0.054MAA-*x*Na with Various Degrees of Neutralization

sample	V_p (nm^3)	R_1 (nm)	d_i (g/cm^3)	N_1	N_2
E-0.035MAA-0.80Na	30	0.71	1.702	16	14
E-0.035MAA-0.73Na	29	0.69	1.721	14	12
E-0.035MAA-0.70Na	23	0.66	1.495	10	10
E-0.035MAA-0.44Na	14	0.55	1.410	4	5
E-0.054MAA-0.82Na	22	0.69	1.851	18	14
E-0.054MAA-0.67Na	15	0.62	1.702	10	9
E-0.054MAA-0.55Na	13	0.60	1.758	7	9
E-0.054MAA-0.44Na	10	0.53	1.536	4	5

The calculated SAXS curve can be best fitted to the observed one by the nonlinear least-squares method varying arbitrarily the structure parameters, V_p, $2R_{ca}$, R_1, and $I_eV\rho_1^2$. We could finally obtain the most probable four parameters which are characteristic of the structure of the ionic aggregates. A relative variation of V_p, $2R_{ca}$, and R_1 has at least a physical meaning, although the absolute value of these structural parameters may not be correct, being dependent on structural model.

Variation in the Structure of Ionic Aggregates with a Varying Acid Content and Degree of Neutralization. In Figure 1, the observed SAXS profiles of E-0.054MAA-*x*Na samples are shown as circles and the calculated ones (solid lines) obtained by a nonlinear least-squares method using Yarusso and Cooper's structural model. The intensity of ionic cluster peak increased and the peak shifted to smaller angle with an increase of the degree of neutralization. The observed profile agrees fairly well with the corresponding calculated curve, indicating that the structure of ionic aggregates may be interpreted in terms of the modified hard-sphere model proposed by Yarusso and Cooper. The structural parameters obtained by the curve fitting method for all the ethylene ionomer samples used in this study are tabulated in Tables 1−4.

We tried to estimate the number of cations constituting the ionic aggregates using V_p and d, the density of ionomer, or R_1 and d_i, the density attributed to the segment of methacrylic acid neutralized with the cation. The number of cations in an aggregate, N_1, is represented by the following equation, assuming that all ions are included in the ionic aggregates:

$$N_1 = \frac{V_p a x N_A d}{M_w} \times 10^{-21} \tag{7}$$

Table 2. Values of V_p, R_1, d_i, N_1, and N_2 of E-0.035MAA-*x*K and E-0.054MAA-*x*K with Various Degrees of Neutralization

sample	V_p (nm^3)	R_1 (nm)	d_i (g/cm^3)	N_1	N_2
E-0.035MAA-0.68K	46	0.91	2.200	20	32
E-0.035MAA-0.56K	52	0.80	2.002	19	21
E-0.035MAA-0.36K	26	0.73	2.124	6	17
E-0.035MAA-0.30K	14	0.62	2.020	3	10
E-0.054MAA-0.77K	37	0.72	2.097	28	16
E-0.054MAA-0.67K	34	0.70	2.074	22	14
E-0.054MAA-0.47K	16	0.59	1.707	7	7
E-0.054MAA-0.43K	12	0.58	1.743	5	7

Table 3. Values of V_p, R_1, d_i, N_1, and N_2 of E-0.035MAA-*x*Zn and E-0.054MAA-*x*Zn with Various Degrees of Neutralization

sample	V_p (nm^3)	R_1 (nm)	d_i (g/cm^3)	N_1	N_2
E-0.035MAA-0.83Zn	15	0.42	1.739	8.0	2.8
E-0.035MAA-0.73Zn	16	0.43	1.870	7.5	3.1
E-0.035MAA-0.64Zn	16	0.43	1.632	6.8	2.8
E-0.035MAA-0.49Zn	10	0.43	1.648	3.2	2.8
E-0.054MAA-0.78Zn	10	0.41	1.873	8.0	2.7
E-0.054MAA-0.57Zn	10	0.44	1.756	5.8	3.0
E-0.054MAA-0.44Zn	10	0.43	1.800	4.5	2.9
E-0.054MAA-0.32Zn	10	0.43	1.145	3.3	2.5

Table 4. Values of V_p, $2R_{ca}$, and R_1 of E-0.054MAA-*x*Cu and E-0.054MAA-*x*Fe with Various Degrees of Neutralization

sample	V_p (nm^3)	$2R_{ca}$ (nm)	R_1 (nm)
E-0.054MAA-0.85Cu	11	1.44	0.39
E-0.054MAA-0.50Cu	19	1.38	0.36
E-0.054MAA-0.35Cu	12	1.30	0.35
E-0.054MAA-0.85Fe	65	0.90	0.39
E-0.054MAA-0.70Fe	67	0.95	0.42
E-0.054MAA-0.53Fe	65	0.98	0.42
E-0.054MAA-0.25Fe	66	0.97	0.42

where *a* is the acid content, *x* is the degree of neutralization, N_A is the Avogadro's number, and M_w is the average molecular weight. Another estimation of the number of cations, N_2, was also examined using the relation

$$N_2 = \frac{N_A d_i}{M_m} \frac{4}{3}\pi R_1^{\,3} \tag{8}$$

where M_m is the molecular weight of the segment of methacrylic acid with its counterion and d_i is evaluated by an additive rule of volume. M_m and d_i are used on the assumption that methacrylate segment is included in the ionic aggregate; i.e., M_mN_2 and d_i denote the weight and the density of an ionic aggregate, respectively. The N_1 and N_2 values are also shown in Tables 1−3. Both N_1 and N_2 increase with the degree of neutralization. In the ethylene ionomers with low neutralization, N_1 is much smaller. It lies below 8, which is a critical number for cluster formation. This corresponds to 2−3 mol % of the critical ion concentration and to the values reported by Cooper et al.[14] and Weiss et al.[15] It was found that the ionic peak of smaller ionic aggregates; i.e., the multiplets are reflected in the SAXS profile.

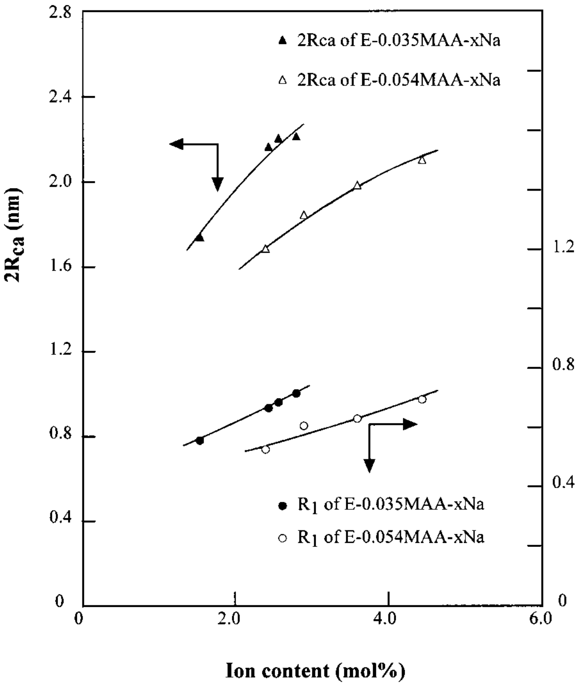

Figure 2. Plots of $2R_{ca}$ and R_1 against ion content: $2R_{ca}$ (▲) and R_1 (●) for E-0.035MAA-*x*Na; $2R_{ca}$ (△) and R_1 (○) for E-0.054MAA-*x*Na.

The dependence of R_1 and $2R_{ca}$ on the ion content, the product of acid content and degree of neutralization, for E-0.035MAA-*x*Na and E-0.054MAA-*x*Na are shown in Figure 2. R_1 values are 0.5−0.7 nm and found to be slightly smaller than 0.8−1.0 nm proposed by MacKnight et al.[16] The increase in the R_1 value reflects the increase in the number of ions forming the ionic aggregates. On the other hand, $2R_{ca}$ is similarly increased with the ion content, indicating that the polyethylene layer surrounding ionic aggregates become thick as well as the increase in R_1. R_1 and $2R_{ca}$ of E-0.035MAA-*x*Na and E-0.054MAA-*x*Na behave similarly, but both values of E-0.035MAA-*x*Na are greater when one compares the R_1 and $2R_{ca}$ values at the same ion content. R_1 and $2R_{ca}$ were found to depend on not only ion content but also on the acid content.

To estimate the effect of the matrix component on the formation of ionic aggregates, the styrene ionomer which has a relatively rigid matrix compared with the ethylene ionomer was also examined by the same procedure. Figure 3 shows the plot of R_1 and $2R_{ca}$ against ion content for S-0.137MAA-*x*Na and S-0.087MAA-*x*Na together with the results for the ethylene ionomer. R_1 and $2R_{ca}$ increased with the acid content (ion content) similarly to the ethylene ionomer. S-0.087MAA-*x*Na has a relatively higher R_1 and $2R_{ca}$ than S-0.137MAA-*x*Na. Both ethylene and styrene ionomers containing a lower acid content had a greater radius R_1 than ionomers with a higher acid content when compared at the same ion content. This might be due to an ionic aggregation of ionomers with a low acid content. The styrene ionomer exhibits a lower R_1 and $2R_{ca}$ than the ethylene ionomer at the same ion content. This suggests an easier formation of ionic aggregates of the ethylene ionomer, because of a much higher flexibility of the polyethylene matrix.

Effect of Counterions. R_1 and $2R_{ca}$ of the ethylene ionomer with a potassium ion with an ionic radius of 0.133 nm were compared with those with a sodium ion having an ionic radius of 0.095 nm. The number of potassium ions in an ionic aggregate, N_1 and N_2, was evaluated and listed in Table 2. The potassium ionomer has higher N_1 and N_2, indicative of higher ionic aggregation. This result supports Painter's report which demonstrated multiplet formation with a coordination number of 4 or 6 for an ethylene ionomer with sodium

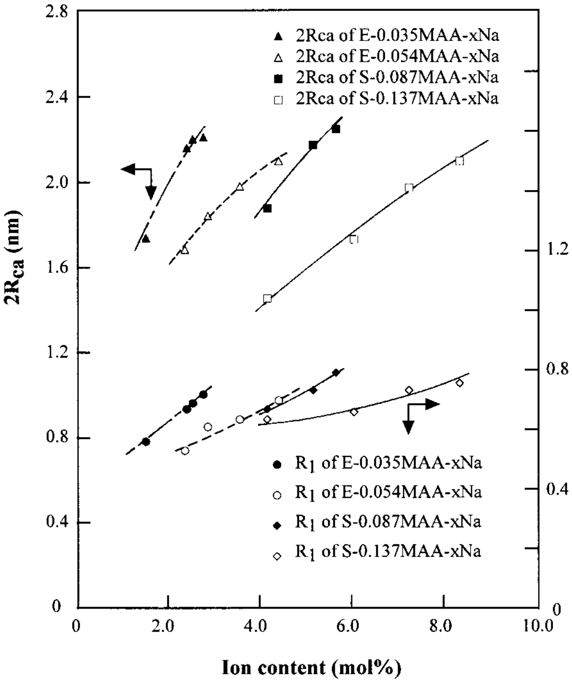

Figure 3. Plots of $2R_{ca}$ and R_1 against ion content: $2R_{ca}$ (■) and R_1 (♦) for S-0.087MAA-*x*Na; $2R_{ca}$ (□) and R_1 (◊) for S-0.137MAA-*x*Na; $2R_{ca}$ (▲) and R_1 (●) for E-0.035MAA-*x*Na; $2R_{ca}$ (△) and R_1 (○) for E-0.054MAA-*x*Na.

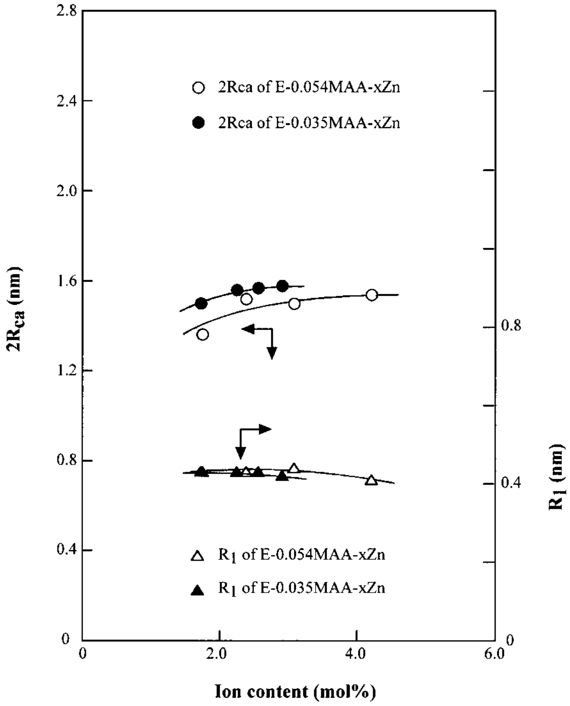

Figure 4. Plots of $2R_{ca}$ and R_1 against ion content: $2R_{ca}$ (●) and R_1 (▲) for E-0.035MAA-*x*Zn and $2R_{ca}$ (○) and R_1 (△) for E-0.054MAA-*x*Zn.

ion and 8 for the potassium ion on the basis of the asymmetric stretching vibration of the carboxylate group.[17] In comparing the sodium and potassium ionomers, the variation in R_1 and $2R_{ca}$ with the acid content is more pronounced with the potassium counterion, reflecting its higher tendency to aggregate.

The ion content dependence of R_1 and $2R_{ca}$ of the ethylene ionomer with zinc ion is shown in Figure 4. R_1 is almost constant, about 0.43 nm over the whole range of ion content for E-0.035MAA-*x*Zn and E-0.054MAA-*x*Zn. This is in very contrast to monovalent metal ion ionomers such as sodium and potassium ions and suggests an increase in the number of ionic aggregates with almost similar size (compare Figures 2 and 4). In comparing the numbers of zinc ions in an ionic aggregate, N_1 and N_2, as shown in Table 3, N_2 is smaller than N_1, especially at a higher degree of neutralization. N_1 was calculated assuming that all zinc ions were included in ionic aggregates for the ethylene ionomer. Therefore, the discrepancy between N_1 and N_2 reflects the production of the relatively small multiplets with zinc salts and/or isolated ion pairs at a higher degree of neutralization, consistent with the result for R_1.

Furthermore, V_p, $2R_{ca}$, and R_1 of the ethylene ionomer with copper and ferric ions were estimated as shown in Table 4. Similarly to the ethylene ionomer with zinc salt, $2R_{ca}$ and R_1 of these ionomers are almost independent of ion content. It is known that the dimer of copper ions similar to that in the crystal structure of copper acetate monohydrate, $Cu_2(CH_3COO)_2{\cdot}2H_2O$, is a dominant in copper salt of copoly(ethylene−methacrylic acid).[18] The dimer structure was observed in the copper salt of poly(styrene-*co*-methacrylic acid)[19] and copper α,ω-dicarboxylatopolybutadiene.[20] The constant R_1 in the ethylene ionomer with copper ion is attributed to the uniform dimer structure. The constant R_1 of the ionomer with ferric or zinc ions may be attributed to the regular structure, trinuclear structure observed in ferric α,ω-dicarboxylatopolybutadiene[21] similar to $[Fe_3O(CH_3COO)6(H_2O)_3]^+$,[22] or tetranuclear one in zinc oxyacetate, $Zn_4O(CH_3COO)_6$.[23] Although the number of copper and ferric cations in an ionic aggregate was not obtained, it may be predicted to be similar to that in zinc salt.

Conclusion

SAXS profiles of the ethylene and styrene ionomers were studied as a function of the nature of the cation, acid content, and degree of neutralization. Ionic cluster peaks were observed around $2\theta = 4°$ for ionomers above a certain degree of neutralization. The ionic cluster peak was analyzed by the modified hard-sphere model proposed by Yarusso and Cooper and the radius of ionic aggregates, closest approach distance between the aggregates, and average system volume per ionic aggregate were obtained. The radius and distance of the aggregates of ionomers with monovalent cation, sodium and potassium cations, increased with the ion content, whereas the radii with divalent one, zinc and copper cations, and trivalent one, ferric cation, were hardly changed. The structure of ionic aggregates was found to be affected markedly by the coordination number of cation. SAXS studies on ionomers are very valuable for clarifying the structure of ionic aggregates of ionomers.

References and Notes

(1) Eisenberg, A.; King, M. *Ion-Containing Polymers: Physical Properties and Structure*; Academic Press: New York, 1977.
(2) Yarusso, D. J.; Cooper, S. L. *Macromolecules* **1983**, *16*, 1871.
(3) Handlin, D. L.; Macknight, W. J.; Thomas, E. L. *Macromolecules* **1981**, *14*, 795.
(4) Williams, C. E.; Colliex, C.; Horrion, J.; Jerome, R. In *Multiphase Polymers: Blends and Ionomers*; Utracki, L. A., Weiss, R. A., Eds.; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989; Chapter 18.
(5) Longworth, R. *Ionic Polymers*; Holliday, L., Ed.; Halsted-Wiley: New York, 1975.
(6) Marx, C. L.; Koutsky, J. A.; Cooper, S. L. *J. Polym. Sci., Polym. Lett. Ed.* **1971**, *9*, 167.
(7) Philips, P. J. *J. Polym. Sci., Polym. Lett. Ed.* **1972**, *10*, 443.

(8) Marx, C. L.; Caulfield, D. F.; Cooper, S. L. *Macromolecules* **1973**, *6*, 3.

(9) Kumar, S.; Pineri, M. *J. Polym. Sci., Polym. Phys. Ed*. **1986**, *24*, 1767.

(10) Ding, Y. S.; Stevan, S. R.; Hodgson, K. O.; Register, R. A.; Cooper, S. L. *Macromolecules* **1988**, *21*, 1698.

(11) Williams, C. E.; Russell, T. P.; Jerome, R.; Horrion, J. *Macromolecules* **1986**, *19*, 2877.

(12) Shilov, V. V.; Dimtruk, N. V.; Tsukruk, V. V.; Polyattskova, N. V.; Lipatov, Y. S. *Polym. Commun*. **1985**, *26*, 28.

(13) Pineri, M.; Meyer, C. *J. Polym. Sci., Polym. Phys. Ed*. **1974**, *12*, 115.

(14) Yarusso, D. J.; Cooper, S. L.; Knapp, G. S.; Georgopoulos, P. *J. Polym. Sci., Polym. Lett. Ed*. **1980**, *18*, 557.

(15) Peiffer, D. G.; Weiss, R. A.; Lundberg, R. D. *J. Polym. Sci., Polym. Phys. Ed*. **1982**, *20*, 1503.

(16) Kao, J.; Stein, R. S.; MacKnight, W. J.; Taggart, W. P.; Cargill, G. S. *Macromolecules* **1974**, *7*, 95.

(17) Brozoski, B. A.; Coleman, M. M.; Painter, P. C. *Macromolecules* **1984**, *17*, 230.

(18) Takei, M.; Tsujita, Y.; Shimada, S.; Ichihara, H.; Enokida, M.; Takizawa, A.; Kinoshita. T. *J. Polym. Sci., Polym. Phys. Ed*. **1988**, *26*, 997.

(19) Yamauchi, J.; Yano, S. *Makromol. Chem*. **1978**, *179*, 2799.

(20) Pineri, M.; Meyer, C.; Levelut, A. M.; Lambert, M. *J. Polym. Sci., Polym. Phys. Ed*. **1974**, *12*, 115.

(21) Meagher, A.; Coey, J. M. D.; Belakhovsky, M.; Pineri, M.; Jerome, R.; Vlaic, G.; Williams, C.; Dang, N. V. *Polymer* **1986**, *27*, 979.

(22) Figgis, B. N.; Robertson, G. B. *Nature* **1965**, *205*, 694.

(23) Koyama, H.; Saito, Y. *Bull. Chem. Soc. Jpn*. **1954**, *27*, 112.

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