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C_∞ decreases with isotacticity.

The value of the temperature coefficient $d(\ln C_\infty)/dT$ calculated at 300 K by using the parameters given in Table III is 2.2×10^{-4} deg^{-1} for the isotactic chain and 2.4×10^{-5} for the syndiotactic polymer. Such small values of the temperature coefficient can be rationalized on the basis of the small energy difference between the various conformers.

At present, there are no experimental data on either the characteristic ratio or its temperature coefficient for this polymer. As noted above, the first synthesis of the linear polymer was reported just recently.[14] However, in view of the reasonable success of these types of calculations to date in accounting for the experimental observations, and the emerging efforts in the direction of predicting material properties in advance of their synthesis, we consider that the difference in the calculated behavior of polysilapropylene and polypropylene would be of interest. Revisions to the calculations or methodology may be required when the experimental data are derived, but such revisions enhance our ability to treat such chains in a more effective manner.

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Small-Angle X-ray Scattering Study for Structural Changes of the Ion Cluster in a Zinc Salt of an Ethylene–Methacrylic Acid Ionomer on Water Absorption

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ABSTRACT: The dimensional change of the ion cluster in a zinc salt of poly(ethylene-*co*-methacrylic acid) ionomer during moisture absorption was investigated by small-angle X-ray scattering (SAXS). Unlike the cases of previously investigated hygroscopic ionomers, the apparent peak position shifted toward the high-angle side with an increase in water content. The desmeared SAXS curves were analyzed in terms of the Percus–Yevick equation, and the structure parameters were derived by curve fitting. The observed change in SAXS with the absorbed water content was interpreted as follows. Although the intercluster distance increased a little with water content as expected, the interparticle interference and minor change in other structural parameters perturbed the scattering profile in an unexpected manner, since the scattering intensity was so weak.

Introduction

A series of copolymers of ethylene (E) and methacrylic acid (MA), where the MA units are partially or fully neutralized with metal hydroxides, is known as an ionomer under the trade name Surlyn (E. I. du Pont de Nemours and Co., Inc.). Introduction of small amounts of ionized groups into the nonionic polyethylene chains causes profound changes in mechanical properties of the copolymers: a remarkable increase in elastic modulus as well as in melt viscosity. Such characteristic changes are thought to be ascribed to the formation of aggregates of the ionized groups called "ionic clusters" in the nonionic polymer matrix.

Since the ion cluster is more or less hydrophilic, their mechanical properties are influenced by moisture absorption. In order to elucidate the change in intracluster structure during the absorption–desorption process, we have examined the change in the infrared bands due to the carboxylate antisymmetric stretch mode (1500–1650 cm^{-1})

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with water content for a zinc salt of E–MA ionomer.[1] In a dried state, there appeared three split components separated by 20–65 cm^{-1}. This indicates the presence of a locally ordered intracluster structure and was interpreted to be caused by the vibrational coupling among three units of zinc methacrylate anhydride. In a moistened state, the band profile collapsed into a single peak, indicating the smearing of the interaction. Such a remarkable spectral change occurred reversibly with respect to water content.

The aim of this work is to determine the dimensional changes of the ion cluster in the same ionomer sample during the moisture absorption–desorption process by means of small-angle X-ray scattering (SAXS). Most ionomers, both crystalline and noncrystalline, give rise to a characteristic X-ray reflection called "ionic peak" in the small-angle region attributed to the cluster formation of the ionic groups.[2–5] We measured the change in the profile of the ionic peak and analyzed the SAXS curves according to the modified Yarusso model using the Percus–Yevick total correlation function in order to obtain the changes in some structural parameters of the ionic cluster during the moisture absorption.

Experimental Section

The sample of Zn salt of E–MA ionomer (referred to as E–MA–Zn, Surlyn 472) was purchased from Scientific Polymer Products. The acidified sample was prepared by dissolving E–MA–Zn in refluxing tetrahydrofuran (THF) containing a stoichiometric amount of hydrochloric acid. The acidified polymer was purified by reprecipitation with methanol from THF solution and dried at 50 °C in vacuo for 24 h. The content of the methacrylic acid comonomer unit was determined by elementary analysis 5.8 mol % from the total amount of C and 5.3 mol % from the C/H ratio. The degree of neutralization of the E–MA–Zn sample was estimated as 46.8 mol % from atomic absorption analysis for Zn.

A Rigaku Denki sealed-tube X-ray generator operating at 40 kV and 30 mA at the Institute for Protein Research of Osaka University was used for the SAXS experiment. The Cu Kα radiation (λ = 1.542 Å) was monochromatized with a Ni foil filter of 10-μm thickness. The X-ray beam was line-focused (0.1 × 8 mm^2) by a set of nickel-coated bent glass mirrors. The sample-to-detector distance was 30.2 cm. Scattered intensity was measured by a Rigaku Denki one-dimensional position-sensitive proportional counter (delay line type). The detector length was divided into 512 channels (0.1265 mm/channel) on a multichannel analyzer. On each sample of about 2-mm thickness, the intensity data were accumulated for 5000 s. The data were corrected for the sensitivity of the detector (the linearity was calibrated with Fe isotope and the dead time was 0%) and also for the transmittance of the sample specimen according to the standard method.[7] The slit desmearing procedure was performed according to the method of Glatter[8] with a computer program at the Institute for Protein Research. The absolute intensity was not observed. In order to estimate the background arising from density fluctuations, the middle-angle data were measured by a Searle small-angle X-ray diffraction camera in the 2θ region from 1.8° to 17.8°. However, because of the broadness of the ionic peak and the overlap by the tail of the strong (110) reflection of the polyethylene lattice, the contributions from the fluctuations were not separated and assumed to be constant in the 2θ range mentioned in the profile analysis. The scattering arising from voids and inhomogeneous distribution of the isolated ionic groups which mainly causes a sharp upturn near zero angle was not considered.

Moisture absorption of the specimens was made in a desiccator held at a constant temperature (60.0 °C) under the saturated water vapor pressure. The amount of water absorbed by the specimens was weighed in an open state by using a Mettler B-6 balance with sensitivity 10^{-5} g. The equilibrium was achieved for about 5 days for specimens as thick as 2 mm. The weight loss or gain of the sample during the measurement was confirmed to be negligible.

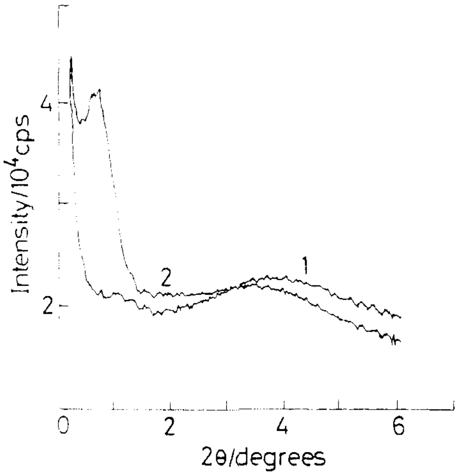

Figure 1. SAXS curves for E–MA–Zn: (1) ambient; (2) dried at 60.0 °C for 22 h.

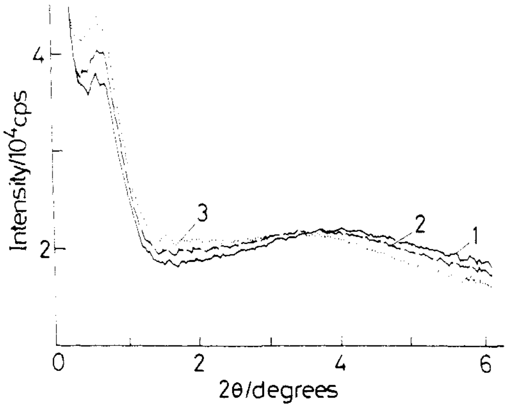

Figure 2. SAXS curves for E–MA–Zn on water desorption process at 60.0 °C: (1) moistened for 16 h; H_2O wt % = 0.19; (2) dried for 21 h, H_2O wt % = 0.08; (3) dried for 45 h, H_2O wt % = 0.06%.

Results and Discussion

The E–MA–Zn sample was melted at 150 °C, quenched in liquid N_2, and then kept at ambient condition for 24 h before the measurement. A broad "ionic peak" appeared around 2θ = 4° as shown in curve 1 of Figure 1. After this sample was dried at 69 °C for 22 h in vacuo, curve 2 of Figure 1 was obtained. The ionic peak shifted a little to the low-angle side, and a new reflection appeared around 2θ = 0.72°. The latter reflection was ascribed to the polyethylene–lamellar phase having the long spacing of 103 Å (evaluated with Lorentz correction) formed during the drying process. The intensity of the ionic peak was very weak compared with that of the polyethylene–lamellar peak.

In order to obtain precise scattering profiles of the ionic peak free from interference by the lamellar peak, it is desirable to keep the polyethylene–lamellar peak at a constant position distant enough from the ionic peak and to keep its intensity constant throughout the absorption–desorption cycle for one sample specimen. For this purpose, the dependence of the polyethylene–lamellar peak position and intensity on the temperature of sample treatment was investigated in the range from 10 to 90 °C, and a suitable temperature (60.0 °C) for the moisture desorption–absorption procedure was chosen. The changes in SAXS pattern on the moisture desorption and absorption processes are shown in Figures 2 and 3, respectively. A sample quenched from the melt and then exposed

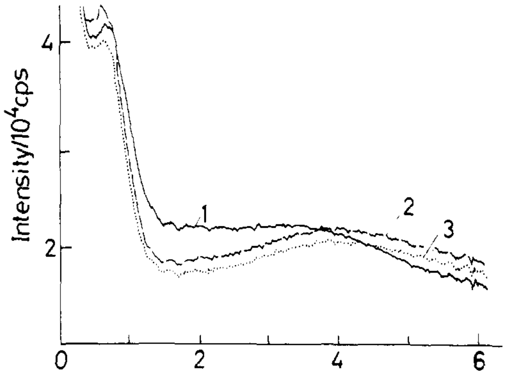

Figure 3. SAXS curves for E–MA–Zn on water absorption process at 60.0 °C: (1) dried for 16 h; (2) moistened for 17 h; (3) moistened for 26 h.

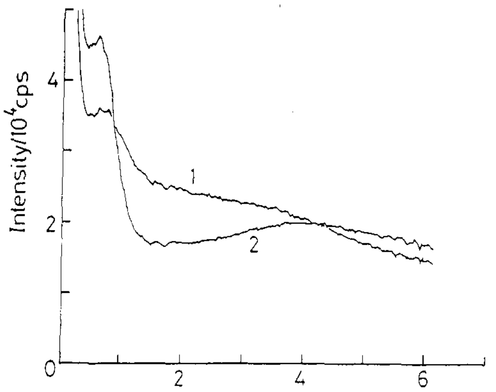

Figure 4. SAXS curves for E–MA–Zn: (1) dried at 187 °C for 19 h; (2) moistened at 60 °C for 23 h.

to water vapor for 16 h (having a water content of 0.19 wt %) gave curve 1 in Figure 2. Curves 2 and 3 are of the same sample after drying for 21 h (0.08 wt %) and 45 h (0.06 wt %), respectively. The scattering angle 2θ of the ionic peak shifted from 3.95° to 3.48° as the water content decreased from 0.19 to 0.06 wt %. This shift corresponds to an increase of the Bragg spacing from 22.4 to 25.4 Å, indicating that the apparent cluster size or the distance between neighboring clusters expands on drying. In Figure 3, curve 1 is of a melt-quenched sample followed by drying in vacuo at 60 °C for 16 h. Here the ionic peak was located at about 3.31° and was superimposed by a broad tail at the low-angle side. After moisture absorption (curves 2 and 3) the ionic peak recovered to that of curve 1 in Figure 2. Thus, the peak shift on moisture desorption–absorption processes occurs reversibly. Yarusso et al.[5] analyzed quantitatively the temperature dependence of the SAXS pattern of E–MA–Zn ionomers, but effects of two factors, the amount of absorbed water and the degree of crystallinity, were not taken into consideration. As for the polyethylene–lamellar peak, increase in annealing time resulted in an increase in intensity as shown by curves 1–3 of Figure 2 and curves 1 and 2 of Figure 3. The intensity depression from curve 2 to curve 3 in Figure 3 cannot be explained. This might be due to some experimental artifacts.

For the sample which was heated at 187 °C for 19 h and then cooled to room temperature, the SAXS pattern of curve 1 in Figure 4 was obtained. In this curve, the ionic peak is spread over a wide scattering angle. This indicates that at a temperature higher than the melting point of the polyethylene crystallites a reconstruction of ion clusters takes place. Yarusso et al. observed similar spreading of the ionic peak for an E–MA–Zn sample measured above 100 °C and interpreted this as due to an increase either in the radius of the ion cluster or in the averaged volume available to each cluster.[5] The large aggregates formed are frozen even after cooling to room temperature, as indicated by a broad profile covering the low-angle region. When this sample was stored in water at 60 °C for 23 h, the SAXS pattern recovers to the starting one (curve 2).

In the case of Nafion[3] and polystyrene-based ionomers,[5] the ionic peak shifted to the lower angle side on moisture absorption. The shift was interpreted in terms of the intercluster as well as intracluster models. On the basis of the intercluster model, it is expected that the distance between the neighboring clusters increases on moisture absorption, since the entrance of water increases the dielectric constant of the medium and reduces the attractive electrostatic forces between clusters.[6] On the basis of the intracluster model, the shift can be explained as the result of the swelling of individual clusters. The shift found in the present sample is in the opposite direction and seems difficult, at first sight, to be explained by any previous cluster models.

In order to interpret the observed results, the scattered intensity $I(q)$ was calculated by using the equation for the model of closely assembled hard spheres having a uniform radius with the interference factor derived by Percus and Yevick.[9] Using the same model but with Fournet's interference factor,[10] Yarusso reproduced the measured profiles of a series of ionomers.[7] The equation is expressed as

$$I(q) = I_e(q) V \frac{1}{V_p} v_1^2 \rho_1^2 \Phi^2(qR_1) \frac{1}{1 + 24(v_{CA}/v_p)(G(A)/A)} \quad (1)$$

where $I_e(q)$ is the scattered intensity for a single electron as a function of the scattered angle q ($=4\pi \sin \theta/\lambda$ with λ the incident wavelength) and V the irradiated sample volume. R_1 is the radius of the spherical particle having the electron density ρ_1 (equal to the core electron density − the mean medium electron density), and $A = 2qR_{CA}$ where R_{CA} is the closest approach distance between two particles. The corresponding spherical volumes are given as $v_1 = (4/3)\pi R_1^3$ and $v_{CA} = (4/3)\pi R_{CA}^3$, where v_p is the sample volume per particle and $G(A)$ a function of A, R_{CA}, and v_p. $\Phi(x)$ is the scattering factor of a spherical particle given by

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

By use of eq 1, the variation of the scattering profile of the E–MA–Zn ionomer with water content was examined. The equation involves four variable parameters: R_1, R_{CA}, ρ_1, and v_p.

The fitting of the observed scattering curves to eq 1 was performed as described in what follows. The observed curves in Figure 2 were converted to the desmeared ones by using a computer program, although desmearing did not change the scattering profile so significantly in the region 2θ = 1–6°. Since we measured only the relative intensities, rather than absolute ones, we used a scale factor common to the three curves and discussed only relative values of ρ_1. The value of v_p was fixed to be 13 nm³ for the reason described below. The other two parameters R_1 and R_{CA} were adjusted for each curve by the trial-and-error method so as to obtain a good agreement between the observed and calculated results (Figure 5). The values of the parameters obtained for the three samples are summarized in Table I. The result tells us that as the water content increases the R_{CA} and ρ_1 values

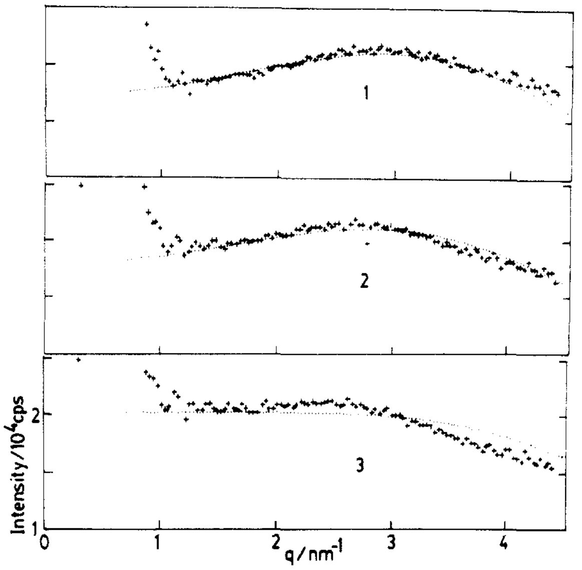

Figure 5. Variation of the small-angle X-ray scattering profile of E–MA–Zn as a function of water content: (1) 0.19 wt %; (2) 0.08 wt %; (3) 0.06 wt %; (+) observed; (●) calculated.

Table I
Parameter Values That Determine the Small-Angle X-ray Scattering Profile of E–MA–Zn at Various Water Contents

H_2O, wt %	R_1, nm	R_{CA}, nm	v_p, nm^3	ρ_1, nm^{-3}	ion group, mol %
0.19	0.38	0.84	13	1.16[a]	2.71
0.08	0.39	0.80	13	1.08[a]	2.71
0.06	0.40	0.75	13	1.00[a]	2.71
	0.44	0.63	26	225	0.90[b]
	0.43	0.76	10	225	2.45[b]
	0.45	0.76	11	225	3.25[b]
	0.45	0.74	11	225	3.25[b]
	0.47	0.73	14	225	3.25[b]

[a] Relative values. [b] Reference 5.

increase, while the R_1 remains almost constant. This may be interpreted as follows. The water molecules absorbed in the ion core increase the core electron density, and those absorbed outside the cluster increase R_{CA} by the electrostatic (due to lowering the attractive intercluster forces) and steric effects. The values of R_1 (0.38–0.40 nm) indicate that the ion core contains a few ion groups. Our previous infrared result indicates that there is a locally ordered intracluster structure consisting of three zinc methacrylate anhydrides in a dried state.[1] The unit cell (0.837 nm^3) of $Zn(CH_3COO)_2{\cdot}2H_2O$ crystal contains four formular units. The corresponding radius of a sphere containing three units is 0.53 nm. Thus, the spectroscopic result is quantitatively consistent with that of the SAXS.

Yarusso et al. analyzed the SAXS profile of zinc salts of E–MA ionomers having three different ion group contents and obtained the parameters listed in Table I.[5] In the case of low ion concentration, as in the present sample, v_p is nearly reciprocally proportional to the ion concentration if the cluster size is kept constant. Yarusso showed that the v_p increased from 12 to 26 nm^3 as the ion concentration decreased from 3.25 to 0.90 mol %. Thus, for the present sample, v_p was assumed to be 13 nm^3 from its concentration of 2.71 mol %.

The dimensional change of the ion cluster in E–MA–Zn during the moisture absorption was investigated by a SAXS technique. Unlike the cases of previously investigated hygroscopic ionomers, it was found that the apparent peak maximum position of the ionic peak shifted toward the high-angle side with an increase in the water content. This observed shift can be interpreted as follows. Although the intercluster distance (R_{CA}) increased a little with water content as expected, the interparticle interference and minor change in other structural parameters perturbed the scattering profile in an unexpected manner, since the scattering intensity was so weak. The apparent extraordinary shift may be ascribed to the combined change in the position and the broadness of the profile with the variation in R_{CA}. The effect of the change in ρ_1 may take a part.

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