Nano-structural Investigations of Ionomers Utilizing Inhomogeneous Ion-Adsorption

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Introduction

Poly(ethylene methacrylic acid) (EMAA) ionomer neutralized with different metal cation have been marketed by Dupont for over three decades under the trade name Surlyn. They have found use in packaging, coating, adhesives and other fields. The presence of ionic aggregates in these semicrystalline ionomer has a major impact in their physical properties and has therefore been a subject of conducting research.

The morphology of the ionic aggregates has mainly been investigated by interpreting small angle X-ray scattering (SAXS) measurements. Typical features of SAXS profile from an ionomer show a broad scattering peak at q values of 0.5 – 4 nm$^{-1}$ and a low-angle upturn close to the beam stopper. The origin of the scattering peak is assigned to the size, shape and spatial of the ionic aggregates. On the other hand, differential scanning calorimetry (DSC) spectroscopy is powerful tool for the structural study of polymer. In early studies of ionomer, the typical spectrum show two peaks at around 90°C and 50°C. The former peak corresponds to melting point of polyethylene crystal and named Tm peak. The later peak is called Ti peak, and a lot of researches on the origin of this peak have been done. Despite the large effort in understanding structure formation and structure-property relations in ionomers, there still unresolved questions.

SAXS Observations of Zn-neutralized EMAA ionomer

In the present study, we have investigated morphology of Zn ion in EMAA ionomer at around the temperature showing the Ti peak. In order to examine 80 mol% neutralized EMAA ionomer by Zn ion, we observed SAXS profiles with changing temperature at BL-10C.

Results of SAXS Observations

Figure 1 shows temperature dependence of the SAXS-profile. The ionomers show a peak at around 0.07 Å$^{-1}$, a broad peak at around 0.3 Å$^{-1}$ and a strong upturn below 0.05 Å$^{-1}$. The broad peak and upturn are associated with a presence of ionic aggregates. The upturn below 0.05 Å$^{-1}$ is a result of the inhomogeneous distribution of ionic groups and/or ionic aggregates in the matrix on a length scale of 10$^2$ Å. A peak at around 0.07 Å$^{-1}$ is assigned to the stacking of polyethylene lamellae. We can sassistly see the peak at around 0.07 Å$^{-1}$ and the broad peak at around 0.3 Å$^{-1}$ are shifted for lower q region and the peak at around 0.07 Å$^{-1}$ is stronger at higher temperature. Detail analysis on the morphology of Zn ion in EMAA ionomer is in progress.

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Figure 1. SAXS profiles for 80 mol % neutralized EMAA by Zn ion with the temperature.