

Surface Characteristics of Polymeric Solids on Thermal Molecular Motion and Molecular Aggregation Structure

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In this talk, we focus on how surface is different from the internal bulk state in terms of thermal molecular motion and molecular aggregation structure. At first, surface molecular motion of amorphous polymers such as polystyrene (PS) and atactic polypropylene (aPP) is discussed on the basis of scanning force microscopy (SFM). Surface glass transition temperature (T_g^s) of the PS films was lower than corresponding bulk glass transition temperature (T_g^b). The active molecular motion at the surface was also observed for the aPP films, and was interpreted by a chain end effect, a reduced cooperativity, a loosen entanglement and so forth. Then, we moved to the surface of crystalline films using polyethylene (PE) and isotactic polypropylene (iPP). Aggregation states at the PE and iPP surface are discussed on the basis of in-plane grazing incidence X-ray diffraction measurement (GIXD) in conjunction with SFM. Apparent crystallinity at the surface was lower than the corresponding bulk one, implying that the outermost surface was covered with the amorphous layer. Etching the surface with KMnO_4 solution, the thickness of the surface amorphous layer was claimed to be approximately 3 nm. Finally, surface molecular motion in the iPP film was studied. Even for the crystalline films, T_g^s was lower than T_g^b . Therefore, it seems reasonable to conclude that active molecular motion is universal for most polymeric solid films.