

INTERFACIAL EFFECTS ON THE PHYSICAL PROPERTIES OF POLYMERS IN THIN FILM

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論 文 内 容 の 要 旨

The development of nanotechnology has allowed people to manufacture and produce materials on a scale of atoms and molecules, resulting in implementation of novel and high functionalities for devices with smaller volume. With decreasing size of polymeric materials, the ratio of the interfacial area to the whole volume significantly increases, leading to a deviation of their physical properties. Furthermore, these properties seem difficult to be simply predicted based on the knowledge and understanding of polymer properties in the bulk state. Therefore, elucidation of the interfacial effect on the properties of polymers in thin films is crucial for precise design and construction of functional polymeric materials. The objective of this study is to explore the interfacial effects on the physical properties and functionalities of polymer thin films from the substrate interface to the air and water interfaces, dealing with from fundamental study of the segmental motion of polymer chains to construction of hydrophilic surfaces via dynamic-driven segregation and development of bio-inert interfaces through precise polymer design.

In Chapter 2, the long-range van der Waals forces between the silicon substrate and the polystyrene (PS) films was examined in terms of the segmental motion of the polymer thin film using spectroscopic ellipsometry. It was observed that the glass transition temperature (T_g) decreased with decreasing thickness of the PS films. Interestingly, this thickness dependent T_g depression was more striking for the PS films supported on the thicker oxide layer (290 nm) than those on the thinner one (1.6 nm). The long-range interactions calculated as a function of the thickness of the PS films, showed strong dependence on the thickness of the oxide layer. As

further study of PS films at a given thickness, the T_g decreased with increasing oxide layer thickness, indicating that the long-range interactions have an effect on the segmental motion in polymer thin films.

Chapter 3 described the dynamic-driven surface segregation of hydrophilic components in well-designed diblock copolymers containing a rubbery and hydrophilic poly(vinyl ether) (PVE) with oxyethylene pendants and a glassy poly(cyclohexyl vinyl ether). The surface enrichment of hydrophilic PVE components was confirmed by X-ray photoelectronic spectroscopy (XPS). The surface segregation of the hydrophilic components can be generally attained. Here, it is revealed that the rubbery PVE components preferentially segregated onto the film surface due to their activated molecular motion.

Chapter 4 elucidated a polymer design strategy for constructing blood-compatible interfaces from the perspective of the interfacial structures in water. The aggregation states and the hydrated water structures at the polymer-water interface were examined by sum-frequency generation (SFG) vibrational spectroscopy. The SFG spectroscopy in conjunction with the time-dependent contact angle measurement revealed that the local conformation of polymer chains at the interfaces was altered in contact with water, which was dependent on their side-chain structure. That led to the deviation of the hydration states of the water molecules near the interfaces. Finally, it was revealed that the PVEs with oxyethylene pendants, especially with methoxyethyl (M) ones, exhibited excellent blood-compatibility. Also, it was proposed that the mechanical properties of polymers at water interfaces are responsible for their deviated bio-inert property.

The author believes that the investigation in this thesis gives an insight into understanding of the structure and dynamics of the polymer chains at the interfaces, which contributes to precise design and development of the functional polymer thin films.