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## INTERFACIAL EFFECTS ON THE PHYSICAL PROPERTIES OF POLYMERS IN THIN FILM

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## 論文の要約

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## 論文題名 : INTERFACIAL EFFECTS ON THE PHYSICAL PROPERTIES OF POLYMERS IN THIN FILM (高分子薄膜の物性に及ぼす界面効果)

Recently, the size of organic devices has been desired to be smaller. This means that the constituent materials should be smaller as well. With decreasing size of polymeric materials, the ratio of the interfacial area to the volume significantly increases, leading to a deviation of their physical properties from the corresponding bulk ones due to the interfacial effect. The properties manifested in such nano-size polymer pieces can be hardly predicted and understood on the basis of knowledge from the three-dimensional bulk state. Thus, the elucidation of an interfacial effect on physical properties of polymers in thin films supported on solid substrates is crucial as a first benchmark for precise design and construction of functional polymeric materials. The objective of this study is to explore experimentally the issue. This includes polymer dynamics at various interfaces, surface segregation in multicomponent polymer systems, and bio-inert polymer interfaces.

In Chapter 2, an effect of the long-range van der Waals force between a silicon substrate and a polystyrene (PS) film on the segmental motion in thin films has been examined on the basis of the temperature dependence of film thickness using spectroscopic ellipsometry. As a result, it was observed that the glass transition temperature ( $T_g$ ) decreased with decreasing PS film thickness and the extent of the depression was dependent on the oxide layer thickness. The long-range interaction calculated as functions of PS film and oxide layer thicknesses could explain the experimental results.

It has been accepted that the surface in multicomponent systems is covered with a hydrophobic component with a lower surface free energy. In Chapter 3, however, we show that a hydrophilic component can be segregated at the film surface of a block copolymer synthesized by a living cationic polymerization. When the hydrophilic and hydrophobic components are in rubbery and glassy states, respectively, the entropic contribution to the surface free energy is much larger for the former than for the latter. Then, the hydrophilic component can be portioned to the surface. We have named this phenomenon the dynamic-driven surface segregation.

Finally, a strategy to design and construct blood-compatible polymer interfaces has been proposed in Chapter 4. The polymer-water interface was characterized by sum-frequency

generation (SFG) vibrational spectroscopy in conjunction with contact angle measurement. The local conformation of polymer chains at the outermost region of the film was altered in contact with water, which was dependent on their side-chain structure. We clearly show that the poly(vinyl ether)s with oxyethylene pendants exhibits excellent blood-compatibility probably due to peculiar water structure and chain dynamics at the interface.

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.