#### P12.11.44

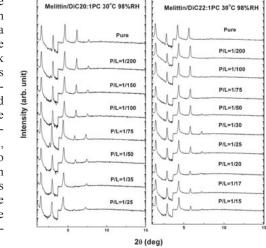
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#### Mechanism and kinetics of pore formation in membranes by water-soluble amphipathic peptides

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How antimicrobial peptides form pores in membranes is of interest as a fundamental membrane process. However, the underlying molecular mechanism, which has potential applications in therapeutics, nonviral gene transfer and drug delivery, has been in dispute. We have resolved this mechanism by observing the timedependent process of pore formation in individual giant unilamellar vesicles (GUVs) exposed to a melittin solution. Individual GUV first expanded its surface area at constant volume and then suddenly reversed to expanding its volume at constant area. The area expansion, the volume expansion and the point of reversal all match the results of equilibrium measurements performed on

peptide-lipid mixtures. The mechanism includes a negative feedback that makes peptideinduced pores stable with a welldefined size, contrary to the suggestion that peptides disintegrate the membrane in a detergentlike manner.



Keywords: membrane, antimicrobial peptides, pore formation

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# Probing slow dynamics on glass transition in thin polystyrene films by X-ray reflectivity

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Glass transition temperature (Tg) is known to vary with heating/ cooling rate for glass-forming materials. Especially for ultrathin films with thickness comparable to the length scale of cooperative rearranging region, rearrangement of the segments would be strongly influenced by the confined geometry to produce a noticeable dependence of Tg on the heating/cooling rate. It is thus interesting to observe how Tg varies in a thin glass-forming polymer under different heating/cooling conditions, which would serve us to get precious information about how dynamical behavior is hindered.

In the present study, we investigate glass transition temperature in polystyrene films spin-coated on Si substrates under different heating rates of 0.5 K/min., 0.05 K/min., and 0.01 K/min. Temperaturedependent film thickness, surface roughness, and electron density are precisely obtained by X-ray reflectivity for the films with thickness ranging from 60 nm to 3.7 nm. The thickest film comparable to ten times of radius of gyration corresponds to the maximum thickness where the reduction of Tg was observed in [1] and [2]. Dewetting phenomenon during the annealing at 430K was found to be inevitable for films less than 3.7 nm thick. Log<sub>10</sub>(heating rate) vs. 1/Tg shows a slow dynamics obeying the Arrhenius behavior characterized by a decrease in activation energy with decreasing the thickness. Tg of 3.7 nm thick film was determined to be 327K (= Tg(bulk)-46 K) under the heating rate of 0.01 K/min. It almost reaches the limiting value (Tg(bulk)-51.6 K) with the infinite relaxation time predicted by WLF equation.

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[2] C. M. Roland and R. Casalini, J. Chem. Phys. 119, 1838 (2003)

Keywords: glass transition, X-ray reflectivity, slow dynamics

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# Molecular aggregation states of crystalline fluorinated polymer thin films

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Polymer with long fluoroalkyl (Rf) groups has high water and oil repellency and they are widely used for surface modifiers. In this paper, the authors report the molecular aggregation states of poly(fluoroalkyl acrylate) [PFA-Cy, where y is the fluoromethylene number of the Rf groups] were evaluated by in-plane and out-ofplane grazing-incidence X-ray diffraction (GIXD). Figure 1 shows the in-plane and out-of-plane GIXD profiles measured at surface regions for PFA-Cy with y =8, 10 thin films. Sharp and strong peaks were measured in each profile. These peaks were assignable to the packing of Rf groups and the lamellar structure, respectively. Bragg diffraction from crystallographic planes perpendicular and parallel to the film surface were observed by in-plane and out-of-plane GIXD, respectively, indicating that the Rf groups are oriented almost perpendicular to the film surface and the bilayer lamellae structure is oriented parallel to the film surface. Moreover, the molecular aggregation states of poly(fluoroalkyl methacrylate) [PFMA-Cy] thin films and the nano-textured PFA-C8 thin film, which was formed by nanoimprint lithography, were also evaluated.

Keywords: fluorine compounds, grazing incidence, nanostructures