Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Neutron Reflectivity Study on the Nanostructure of PMMA Chains near Substrate Interfaces Based on Contrast Variation Accompanied with Small Molecule Sorption

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Analysis of NR profiles of d-PMMA adsorbed layers in toluene vapor

Figure S1 shows the NR profiles of the adsorbed layer (d-PMMA) prepared after 96 h heat treatment, which were measured in saturated h-toluene vapor. The best-fitting results for the model with and without a buffer layer (low SLD) are shown with solid blue and red lines, respectively. The SLD obtained by the best-fitting results is also shown in Figure S2. The model assuming the buffer layer reproduced the NR profile well. On the other hand, the model without the buffer layer of a low SLD layer near the interface deviated the NR experimental profile, especially in the q range of 1-2 nm^{-1}. Here, without buffer layer, we added a low SLD layer near the surface instead of the low SLD buffer layer.

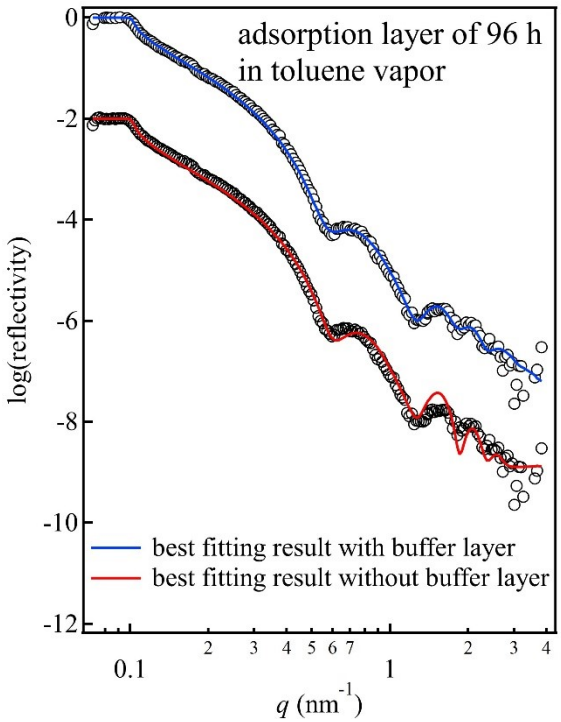

Figure S1. NR profiles in saturated vapor pressure of h-toluene for adsorbed samples prepared by annealing time of 96 h. The solid blue line shows the best fitting result for the model assuming a buffer layer, and the solid red line indicates the best fitting result for the model without a buffer layer.

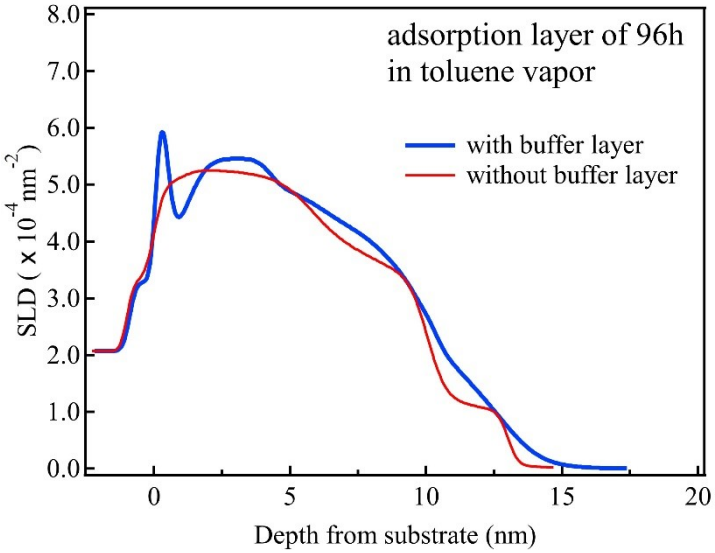

Figure S2. SLD profiles for adsorbed sample prepared by annealing time of 96 h, which were measured in saturated vapor pressure of h-toluene. The solid blue line shows the best-fitting result for the model assuming a buffer layer, and the solid red line indicates the best-fitting result for the model without a buffer layer.

Analysis of NR profile in deuterated toluene vapor for h-PMMA thin film

The NR profile obtained for h-PMMA thin film on Si substrate in saturated d-toluene vapor was analyzed and validated using the following three models;

Model 1: mobile, bulk, and immobile layers models (a, mobile/bulk/immobile),

Model 2: mobile, bulk, buffer, and immobile layers (b, mobile/bulk/buffer/immobile),

Model 3: bulk, buffer, and immobile layers (c, bulk/buffer/immobile).

The best-fitting results for each model are shown in Figure S3. The inset in the figure shows the expanded range of 0.7 to 1.0 nm^{-1}. The SLD profiles obtained by the best fitting are also shown in Figure S4. In addition, to verify the accuracy in the best fitting for each model, the ratios of the NR profile obtained experimentally to that calculated with the best fitting are shown in Figure S5 (a), (b), and (c).

First, model 3 (solid green line), which has no mobile layer near the surface, could not reproduce the NR profile accurately. Figure S5 (c) shows that the fitting accuracy is low, suggesting that a layer swollen by toluene (mobile layer) exists on the surface of PMMA thin film in the saturated vapor of d-toluene. Next, the best fitting of the (a, mobile/bulk/immobile) model 1 (solid red line) reproduced the NR profile relatively accurately, but the ratio values of experimental and calculated profiles somewhat scattered from unity in the range of 0.5 to 1.0 nm^{-1}. Finally, in the (b, mobile/bulk/buffer/immobile) model 2 (solid blue line), the ratio value in the range of 0.5 to 1.0 nm^{-1} is close to unity. These results suggest that model 2 with the buffer layer reproduces the NR profile most accurately.

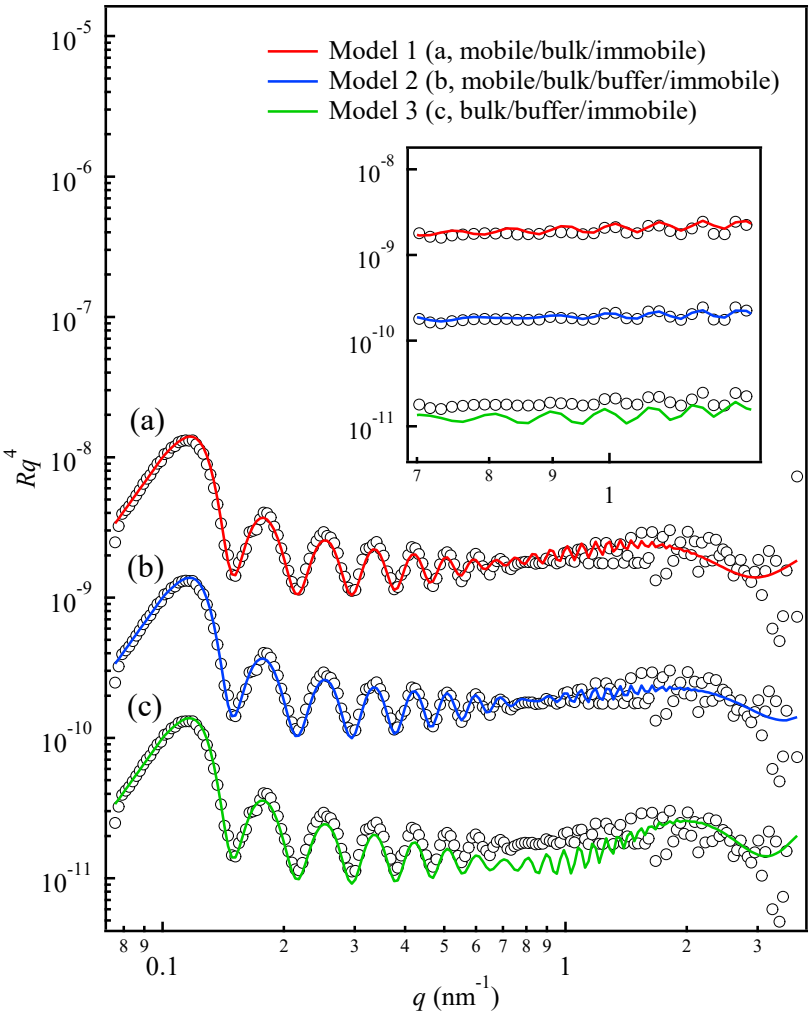

Figure S3. Rq^4 plot of PMMA thin film on the substrate in d-toluene vapor, which is analyzed assuming three models. The red, blue, and green lines indicate the best-fitting results in the analysis with model 1 (a, mobile/bulk/immobile), model 2 (b, mobile/bulk/buffer/immobile), and model 3 (c, bulk/buffer/immobile), respectively. Inset indicates the enlarged profiles in the range of 0.7~1.0 nm^{-1}.

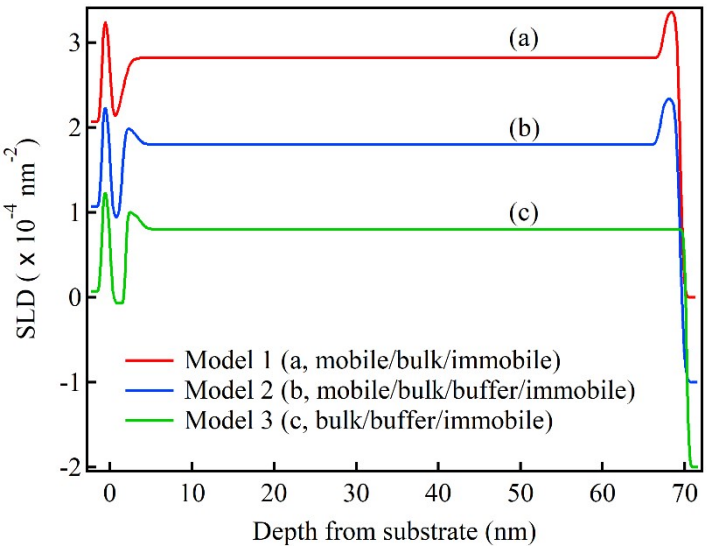

Figure S4. SLD profiles of PMMA thin film on the substrate in d-toluene vapor, as the best-fitting results of NR profiles in Figure S3. The red, blue, and green lines indicate the SLD profile analyzed with model 1 (a, mobile/bulk/immobile), model 2 (b, mobile/bulk/buffer/immobile), and model 3 (c, bulk/buffer/immobile), respectively. The solid blue line and green line of SLDs are shown to shift downward vertically by 1×10^{-4} nm^{-2} and 2×10^{-4} nm^{-2}, respectively.

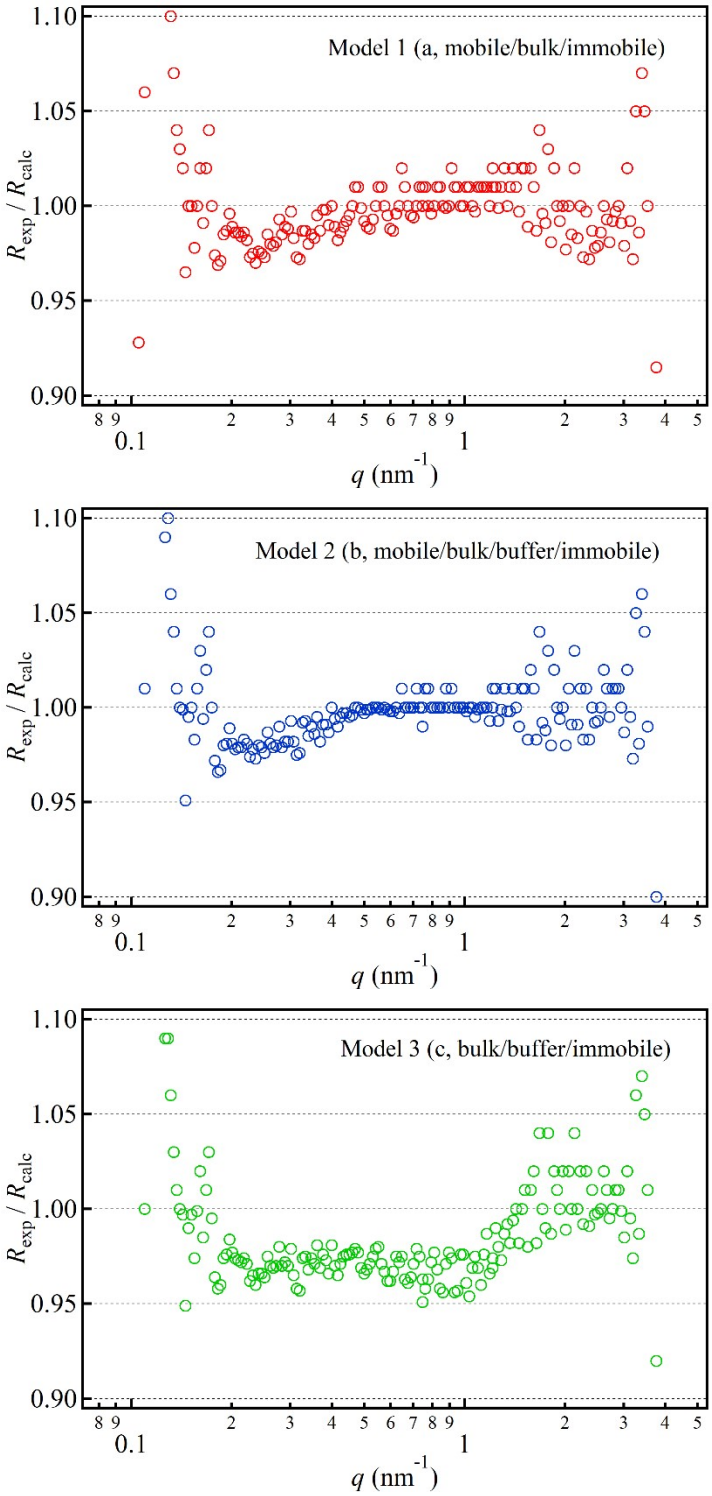

Figure S5. The ratio of the experimental NR profiles (R_{exp}) obtained in d-toluene vapor to the calculated profiles (R_{calc}) of model 1 (a, mobile/bulk/immobile), model 2 (b, mobile/bulk/immobile) and model 3 (c, bulk/buffer/immobile).