

Aggregation Structure and Relaxation Dynamics of Polymers at the Interface with Water: II. Analysis of Relaxation Dynamics by Neutron Spin Echo

Hironori Atarashi(1), Toshihiko Nagamura(1), Keiji Tanaka(1), Hitoshi Endo(2), and Mitsuhiro Shibayama(2)

1. *Department of Applied Chemistry, Kyushu University, Fukuoka 819-0395, Japan*, 2. *Institute for Solid State Physics, The University of Tokyo, Chiba 277-8581, Japan*

New tools for tailor-made diagnostics are generally made from polymers. In these applications, the polymer surface is in contact with a water phase. However, despite the importance of detailed knowledge of the fundamental interactions of polymer interfaces with liquids, such studies are very limited. We have hitherto studied aggregation structure of poly(methyl methacrylate) (PMMA) at the interfaces with non-solvents by neutron reflectivity.[1] As a result, the liquid/polymer interfaces were diffuse in comparison with the air/polymer interface, probably due to interfacial roughening and the partial dissolution of segments at the outermost region of the film. In this study, relaxation dynamics of PMMA chains at the interfaces with typical non-solvents such as water and methanol was discussed on the basis of small angle neutron scattering (SANS-U) and neutron spin echo (iNSE) measurements. PMMA particles with diameter of about 300-500 nm (MP-2200 produced by Soken Chemical & Engineering Co., Ltd.) were used as a sample to increase the scattering volume rather than a film. Deuterated water (D₂O) and ethanol (CD₃OD) were used as non-solvents. The PMMA particles mixed with a non-solvent were filled into a quartz cell with 2 mm optical length. The sample-to-detector distance was chosen to be 2 and 12 m.

Figure 1 (a) shows the SANS profiles for PMMA particles with water, which the incoherent contribution was subtracted, at 25 and 40 °C. The power for the linear relation was approximately 4 for both cases. Taking into account that the specimen was PMMA particles, the result is quite reasonable. Interestingly, the power

seems to deviate from 4 at $q > 10^{-1} \text{ \AA}^{-1}$ at 40 °C. This may indicate that the interface between PMMA and water became broader with increasing temperature. Figure 1(b) shows the SANS profiles for PMMA particles with methanol. In this case, the slope transformed 4 to smaller once q went beyond $5 \times 10^{-2} \text{ \AA}^{-1}$. This means that the interface between PMMA and methanol was quite diffused in comparison with the case of water. Then, iNSE measurement was made using the same sample. A certain relaxation was somehow observed both in the case of PMMA particles with D₂O and CD₃OD. The detail analysis for the results has undergone several revisions.

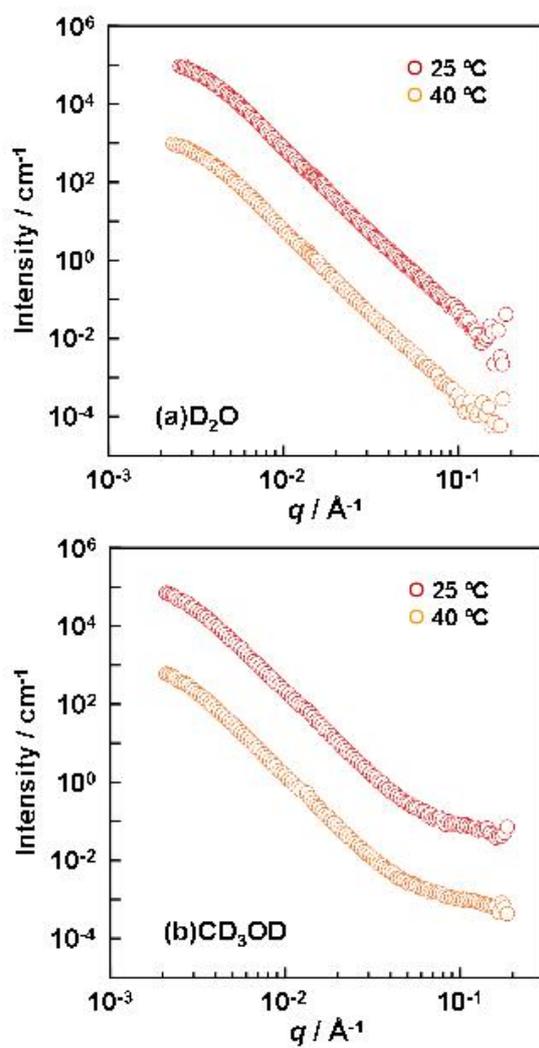


Fig. 1. Figure 1 Temperature dependence of SANS profiles (a) in D₂O and (b) in CD₃OD.