

Breathing Mode in Polymer Micelles and Second Virial Coefficient

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When diblock or triblock copolymers are added to a selective solvent, they aggregate into spherical micelles consisting of an inner core of insoluble blocks and an outer corona of soluble blocks, similar to micellization of surfactants. In previous papers [J. Chem. Phys. Solids, 60, 1367-1369 (1999), J. Chem. Phys., 122, 144905 (2005)] we have investigated dynamics of micelles of deuterated styrene-protonated butadiene diblock copolymers (PSD-PB) and deuterated styrene-protonated isoprene diblock copolymers (PSD-PI) in deuterated n-decane, focusing on the chain dynamics in the corona using neutron spin echo (NSE). We observed the collective breathing mode for PSD-PI. On the other hand, it disappeared but the Zimm mode (single chain motion) was observed for PSD-PI although the molecular weight of PSD-PB and PSD-PI were almost identical. This has been assigned to the difference of the second virial coefficient (A_2) between PB and PI in deuterated n-decane. In this work we have studied the second virial coefficient and the dynamic crossover from a cooperative motion (gel mode) to a single chain motion (the Zimm mode) to elucidate why the collective breathing mode disappears in the DPS-PB micelles.

We used PB with $M_w=22600$ and $M_w/M_n=1.05$ and PI with $M_w=24500$, $M_w/M_n=1.06$. The solvent was deuterated n-decane. Small-angle neutron scattering and neutron spin echo measurements were done using SANS-U spectrometer and iNSE spectrometers in JRR-3 reactor, Tokai. First we have evaluated the second virial coefficient A_2 of PB and PI to find that A_2 of PB is smaller than that PI, showing the interactions among PBs are smaller than those among PI. We have also performed NSE measurements on the 20 wt % PB and

PI solutions. The decays of intermediate scattering functions $I(Q,t)$ were analyzed to evaluate the first cumulant G . Dividing the first cumulant G by Q^2 , we plotted G/Q^2 as a function of Q in Figure 1. In the high Q region the first cumulant is proportional to Q^3 , suggesting that the mode we observed is the Zimm mode. On the other hand, in the low Q range G is proportional to Q^2 . It shows that the collective gel mode is dominant in this Q range. What we have to emphasize is that the crossover Q from the Zimm mode to the gel mode depends on sorts of polymers. The crossover Q of PI is located to the higher value than that of PB, showing that PI has longer-range (stronger) interaction and the collective dynamics arises in PI in the more local region than PB. This must be a reason why the collective breathing mode disappeared in PSD-PB micelles.

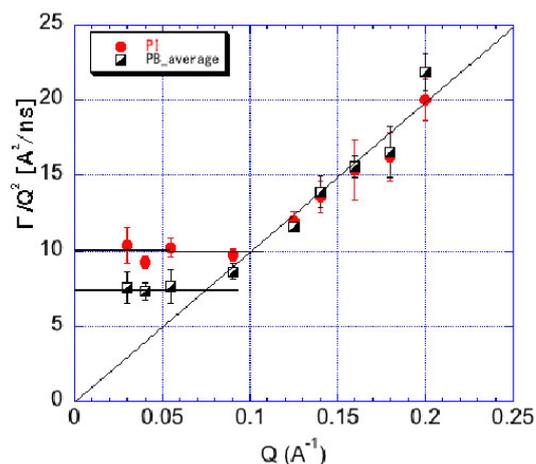


Fig. 1. Figure 1. Q dependence of G/Q^2 for PB and PI.