

Rheo-SANS behavior of Entangled Polymer Chains with Local Label Under Fast Shear Flow

Hiroshi Watanabe (a), Toshiji Kanaya (a), and Yoshiaki Takahashi (b)

Institute for Chemical Research, Kyoto University (a) and Institute for Material Chemistry and Engineering, Kyushu University (b)

The shear-thinning of entangled polymer chains has been attributed to significant orientation of the entanglement segments under the shear flow. However, the chain conformation itself has been hardly examined under the shear flow, and no information is available for the orientation distribution along the chain backbone.

For this problem, we have examined the rheo-SANS behavior for polybutadiene (PB) samples dissolved in a deuterated oligomeric butadiene (oB) at the volume fraction of 0.28. The measurement was conducted with the SANS-U spectrometer at the Neutron Scattering Laboratory, Institute for Solid State Physics, University of Tokyo. The incident beam diameter was 0.3 cm, and the sample-to-detector distance was set at 4.0 m.

The PB samples were composed of deuterated and protonated blocks (dPB and hPB) and had almost identical molecular weights of the whole chain ($M \sim 120K$) and the hPB block (minor block; $M[\text{hPB}] \sim 20K$). The location of the hPB block was different for the samples. The PB1 and PB2 samples had the hPB block at the end and middle of the chain, respectively. The hPB blocks were dilute and not overlapping with each other in the PB/oB systems. The SANS data detected the conformation of these hPB blocks that corresponded to two entanglement segments in the system ($M[\text{hPB}]/M_e \sim 2$).

The SANS profile was azimuthally symmetric at equilibrium but became a little anisotropic under fast shear flow in the non-Newtonian regime. As an example of such anisotropic profiles, Figure 1 shows double-logarithmic plots of the scattering intensity $I(q)$ for the PB1/oB and PB2/oB systems normalized by the volume fraction

and molar volume of the hPB block against the scattering vector q normalized by the radius of gyration R_g of this block at equilibrium. The filled and unfilled circles indicate the intensity sector-averaged over 15 deg in the vorticity and velocity directions, respectively. The solid curves indicate the Debye function that well described the data at equilibrium. For clarity of the figure, the plots and Debye function for the PB2/oB system are shifted downward.

For the data shown in Figure 1, the shear rate normalized by the linear viscoelastic relaxation time was $\dot{\gamma} \tau_{kr} = 24$ (for PB1/oB) and 29 (for PB2/oB). At these shear rates, the viscosity of the systems was significantly smaller than the zero-shear viscosity (by a factor of ~ 40). Despite this non-linearity, the $I(q)$ data just moderately deviate from the Debye function (describing the data at equilibrium); cf. Figure 1. The anisotropy is larger for the PB2 chain having the hPB block at the middle than the PB1 chain having the hPB block at the end, but this difference due to the location of the hPB block is not very prominent.

These SANS data allow us to examine the current molecular picture for the entangled chains under fast shear flow. This picture assumes that successive entanglement segments are not orientationally correlated and behave as independent stress-sustaining units even under fast flow. Under this assumption, a ratio of the hPB block size in the velocity direction to that in the vorticity direction was estimated from the nonlinear viscoelastic data. This ratio, ~ 1.4 , was too large compared to the ratio estimated from the SANS data in Figure 1. Thus, the above assumption fails for the entangled chains under fast flow. The successive entanglement segments appear to

have the orientational correlation possibly due to the dynamic tube dilation mechanism.

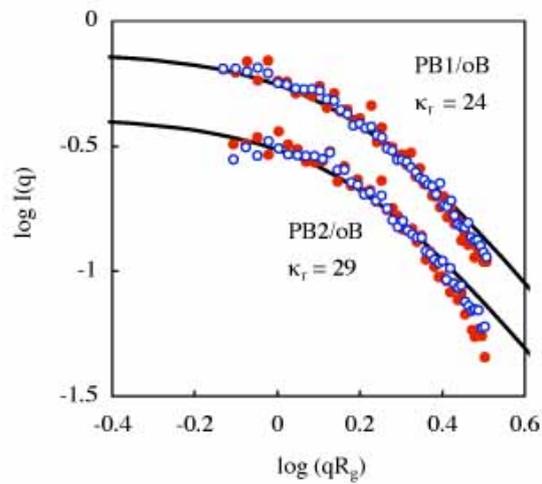


Fig. 1. Normalized $I(q)$ data of the PB1/oB and PB2/oB systems at 25C in the vorticity and velocity directions (filled and unfilled symbols). The solid curves indicate the Debye function describing the data at equilibrium.