Effect of molecular architechture on the Flory interaction parameter

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Flory's interaction parameter, χ, is important in order to discuss thermodynamics and phase-separation kinetics of various kinds of binary polymer alloys (polymer blend or block copolymer). The parameter represents degree of repulsion between different kinds of monomeric units and thus χ for various systems were measured in past few decades. To obtain χ parameter one of the most useful technique is neutron or X-ray scattering. Obtained scattering profiles in the disordered state of the binary systems are often fit with theoretically calculated scattering function based on the random phase approximation (RPA) in order to extract the χ parameter. One significant problem is the fact that the χ parameters determined from the polymer blend and the block copolymer consisting of same kind of two different polymer species are often different, although the RPA theory should not depend on such molecular architecture and thus the χ parameter should be the same.

One of the origins of the discrepancy is probably uncertainty in statistical segment length used in the RPA fitting process. Since two constituent polymers in the block copolymer are chemically connected, the radius of gyration of the block copolymer in the disordered state might be different from that of the polymer blend. This would change the statistical segment length between the two systems, which eventually affect the χ parameter. Therefore, the direct measurement of the segment length, b, was conducted.

The sample used was a polystyrene-block-polyisoprene (PS-PI) diblock copolymer with M_n (number-averaged molecular weight) of 3.4×10^3 and the weight fraction of PS was 0.54, which were characterized by GPC and 1H-NMR. To obtain b_{PS}, a series of a binary blend of the PS-PI and PI homopolymer having various dilute concentration of PS-PI (from 0.6 to 3.0 wt.%) were prepared. The small-angle X-ray scattering function for the samples was measured at BL45XU, SPring8 using an image intensifier equipped with a cooled CCD camera. The camera length was about 2m. The scattering profiles were obtained by circularly averaging the 2D pattern. Note the intensity for such a dilute system is quite low, so that we need high flux of the incident beam at SPring8.

The measured profiles thus taken showed the concentration dependence and from the Zimm's plot the radius of gyration of PS block chain was obtained, $R_{g,PS}$, of 1.54nm and b_{PS} of 0.73nm. This value is somewhat larger than the literature value. We also measured b_{PI} using PS-PI/PS systems, and the RPA fitting is under progress. In the future the comparison of χ parameters obtained from the block copolymer and a binary blend of PS and PI will be done.