STUDYING BLOCK COPOLYMERS

A fundamental approach to the inclusion of fractal concepts in polymer thermodynamics will be presented. Fractal scaling effects in polymer blends will be demonstrated through small-angle neutron and X-ray data. Fractals offer a natural lexicon for the description of polymeric structures. In spite of this, the incorporation of fractals into thermodynamic models for polymers has been mostly overlooked. We propose that a manifestation of this is the introduction of composition and molecular weight dependencies in the second virial coefficient or the associated Flory interaction parameter as measured by small-angle scattering. We have modified Flory’s lattice approach to polymer blends to account for changes in the fractal dimension through the entropy of mixing. This allows for a simple description of global components of entropy in polymer blends and solutions. Our approach is particularly suited to scattering measurements since the mass fractal dimension is directly obtained as the negative of the slope for a power-law regime spanning several decades in q for common polymer blends. In addition to solvent quality, topology, orientation and pressure will shift the fractal dimension in predictable ways. If these deviations of the fractal dimension are ignored in thermodynamic approaches, unexpected dependencies of the interaction parameter on composition, molecular weight, topology, strain and even scattering vector can result. Our modified Flory-Huggins approach can be used to describe composition dependencies in the non-combinatorial entropy term of the interaction parameter by comparison with Flory’s equation for the free energy. Calculations using this approach agree with previous neutron scattering measurements by Wignall and Bates in PSdPS. Thus, this approach can be used to correct errors in prior efforts using Gaussian scaling. Moreover, by directly treating scattering data using our approach, unexpected composition and molecular weight dependencies can be removed from the interaction parameter returning it to the simple local site-site parameter for which it was intended.


We have utilized a “multilayer” monochromator (a pair of layered synthetic microstructures) in small-angle x-ray scattering and diffraction studies of biological materials. Many biological applications of the small angle scattering technique, in particular time-resolved studies, are often limited by the flux incident on the sample. The wider energy bandpass of the multilayer monochromator can provide a higher beam flux by up to two orders of magnitude as compared with that of the typical Si(111) double-crystal monochromators used at synchrotron beam lines. On Beam Line 4-2 at the Stanford Synchrotron Radiation Laboratory, we have implemented two types of multilayers MoC and MoB$_2$C in the standard SSR/L monochromator tank for the studies of x-ray fiber diffraction and solution scattering. In the fiber diffraction experiments, a pair of the latter type of multilayers provided $\sim 10^2$ photons/s in the beam size 0.6 mm x 1.5 mm (FWHM) at photon beam energy 9 keV, an increase of a factor of $\sim 10$ over Si(111) in the same configuration. We observed no significant smearing or effects of increased beam divergence due to the wide energy bandpass in fiber diffraction patterns and low-angle resolution in solution scattering was likewise unaffected. These results demonstrate significant advantages of the multilayer monochromators over Si crystal monochromators for non-crystalline biological x-ray diffraction applications.