# MACROMOLECULAR CONFORMATION IN ULTRATHIN POLYMER FILMS

Since thin polymeric films are ubiquitous in technological applications such as paints, lubricants, and adhesives, a critical characterization of their thermophysical properties is essential. A central premise in the development of theories for predicting the properties of polymer melts in confined geometries is that chains maintain their unperturbed Gaussian conformation, which they adopt in the bulk, in the direction parallel to the surfaces under all conditions [1,2]. These assumptions, which form the foundations of the important field of polymer thin films, have been questioned on the basis of indirect experimental findings [3,4]. We have utilized the power of small angle neutron scattering, especially the high neutron flux at NCNR, to unequivocally characterize the chain structure and conformation in ultrathin polymer films, and thus have resolved this important fundamental question.

The experimental measurements of chain conformations and system thermodynamics in thin films have remained elusive due to the small amounts of sample material involved. To illustrate this point, a thin film of 10 nm incurs a decrease in signal by $\approx 1 \times 10^4$ from a typical bulk polymer sample. In this case, the noise is comparable to the signal, complicating the experiments. Prior to upgrades of the cold neutron source at the NCNR, data collection times were prohibitive. Improvements in sample preparation, which are discussed in detail elsewhere [5,6], have allowed us to measure molecular size and conformation of an isotopically labeled blend of polystyrene (25 wt% d-PS/75 wt% h-PS) in films as thin as 12 nm. Two blends of nominally matched molecular weight, Mn, of 270,000 and 650,000, respectively, were utilized. These were labeled 270k and 650k, respectively. Solutions of the blends were spin cast on silicon substrates (Semiconductor Processing) and annealed at 120 °C ($T_g \approx 105$ °C).
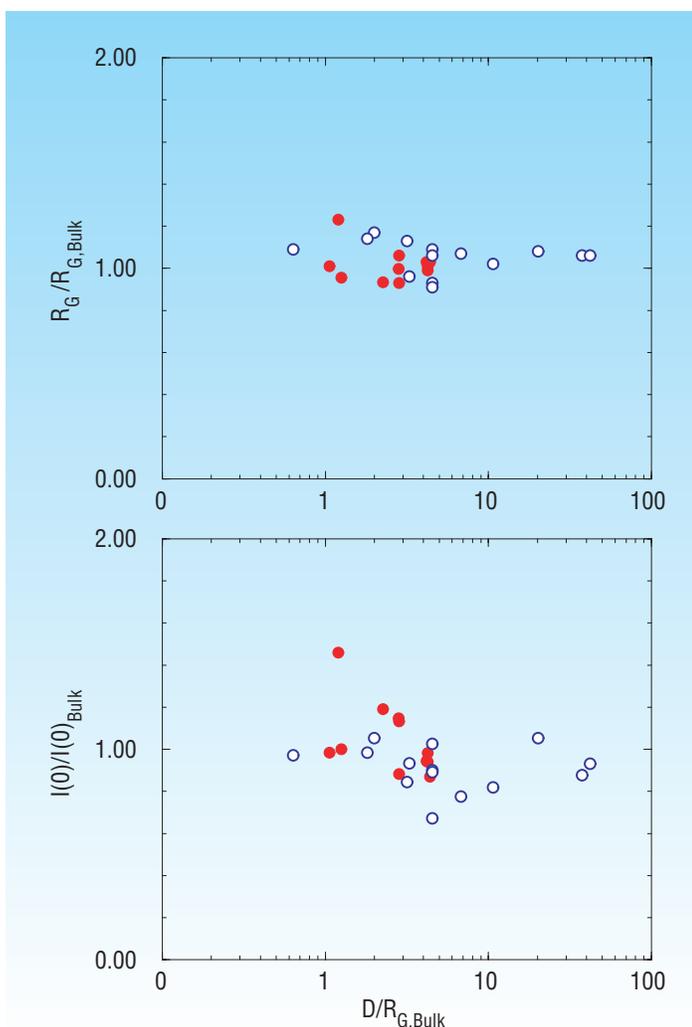
The scattered intensity for a 15 nm thick film of the 270k blend is compared to an analogous bulk sample in Fig. 1. It is clear from the figure that, on a unit volume basis, the thin film scattering is higher than that of the bulk. We postulated that this difference is attributable to the scattering from the imperfections at both the air and the substrate interfaces, which is driven by the relatively high neutron contrast at these boundaries. To evaluate this component, films of pure d-PS were spin cast under identical conditions and their scattering measured.

The pure d-PS film data were fit with a simple Debye-Bueche form factor to obtain parameters for a roughness term. The blend film data were then fit by scaling this roughness term and adding a component obtained from the Random Phase Approximation (RPA) model. In the fitting, two RPA model parameters were also varied: the blend chain radius of gyration (R_g) and the Flory interaction parameter. The combined model is illustrated as the solid line in Fig. 1 along with the roughness term (long dashed line) and RPA term (short dashed line). The fact that the RPA term is very close to the data for the bulk blend illustrates that the film and bulk
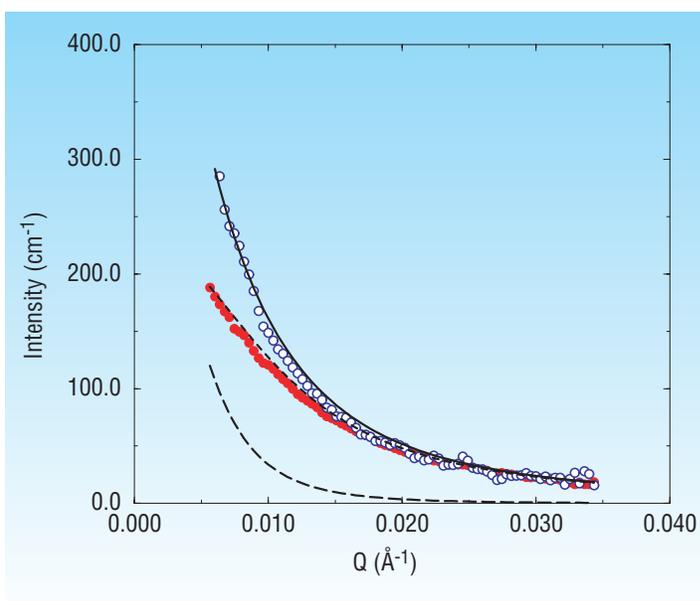
FIGURE 1. Plots of I(Q) as a function of Q for dPS/hPS blends of Mn = 270k. Filled symbols, bulk sample; open symbols, data for a film of thickness D = 18 nm. The fit to these data (solid line) was obtained by utilizing both a roughness term (long dashed line) as well as the standard RPA form (short dashed line).

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samples have nearly the same R_g. Using this combined model, R_g was determined for films ranging in thickness over two decades ($0.5\,R_g < D < 50\,R_g$). The molecular size was found to be independent of film thickness (Fig. 2). Since the scattering vector is primarily in the surface plane, this conclusion is consistent with theoretical assumptions and suggests that chain conformation in the direction parallel to the surfaces are unaffected by confinement.

Our results clearly show that, in the thinnest films, the volume pervaded by a coil is decreased as compared to the bulk. This is because the R_g in the direction parallel to the surfaces is unaffected, while the corresponding quantity in the third direction is strongly reduced. In conjunction with other studies, which indicate a thickness-independent density in ultrathin polymer films, these conclusions indicate decreased intermolecular entanglement in thin polymer films. Since entanglement density directly affects the dynamic properties of polymeric systems, we contend that unusual thin film properties, such as the anomalous thickness dependence of diffusion coefficients and glass transition temperatures, are caused by this reduced entanglement density near a surface.

With thin films as a model system, and continuing increases in cold neutron flux, SANS at the NCNR is now an appropriate tool to study a host of problems involving interfacial structure, finite size phase behavior, and nano-patterning in systems as far ranging as engineering thermoplastics to biological systems. These, and related problems, are the focus of investigation in our research groups.

REFERENCES

[1] D. N. Theodorou, Macromolecules **21**, 1400 (1988).
[2] S. K. Kumar, M. Vacatello, D. Y. Yoon, J. Chem. Phys. **89**, 5206 (1988).
[3] P. M. Calvert, Nature **384**, 311(1996).
[4] C. W. Frank et al., Science **273**, 912 (1996).
[5] D. L. Ho et al., Macromolecules **31**, 9247 (1998).
[6] R. L. Jones et al., Nature **400**, 146 (1999).

FIGURE 2. Plots of ratios of R_g and I(0), derived from the RPA component (short dashed line in Fig. 1) of the fits to the blend thin film data, to their corresponding bulk values. The ratios are plotted versus the ratio of the film thickness to the bulk R_g. Data are displayed for blends with Mn = 270k (filled circles) and Mn = 650k (open circles).