

## **Dimension dependent properties of nanoscopic macromolecular structures**

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### ***Introduction and Rationale for the NIRT***

The behavior soft organic materials in the bulk is relatively well understood; the behavior of these same materials in nanoscopic systems can differ considerably, thereby offering exciting new opportunities for discovery and fundamental research.

The ability to pattern substrates at the scale of tens of nanometers has largely evolved as a result of advances in the electronics and semiconductor industry. It is our view that we have reached a point where we can nanofabricate small structures, but we don't know how the relevant materials behave in such structures. In the particular case of macromolecular materials, the dimensions of sacrificial photoresist structures are only a few times larger than those of individual molecules, and the allowable tolerances and margins in manufacturing processes are of atomic dimensions. Are the thermophysical and mechanical properties of a material in a small structure different from those of the bulk? The characteristic dimensions typically associated with polymeric molecules are of order 5 to 10 nm. It is therefore natural to expect size-dependent properties in polymeric structures with dimensions from 10 to 100 nm. The focus of our proposed NIRT is to fill a serious gap that hinders the development of nanotechnology, and to develop a fundamental understanding of the properties of nanostructured polymeric materials.

### ***Background***

Evidence for dimension dependent properties of amorphous polymers has been observed in measurements of the glass transition temperature,  $T_g$ . Experiments by several research groups, including ours, report that the  $T_g$  of polymer films with nanoscopic dimensions can be significantly different from the corresponding bulk value. In the bulk, transport properties such as diffusion coefficients increase by several orders of magnitude in the narrow range of temperature over which the material undergoes a transition from a glass to a rubber. Similarly, mechanical properties such as the Young's modulus decrease by two to four orders of magnitude over this same temperature range. Although the dimension dependence of  $T_g$  is now fairly well documented, less is known about mass transport and mechanical properties of polymers that are likely also dimension dependent. We are not aware of any published reports on dimension dependent mechanical properties of amorphous polymers. Our combined theoretical and experimental research program addresses the need to acquire a fundamental understanding of transport and mechanical properties of nanostructured polymers because it is precisely these properties that determine their usefulness in coating, packaging, MEMS (microelectromechanical systems), microelectronic and nanotechnology applications in general.

### ***Results***

Of critical importance to the project objectives is to understand the dynamics of polymers near interfaces and how they differ from the bulk. We have conducted a calorimetric study of the glass transition of small polystyrene spheres in aqueous suspensions [1]. In previous calorimetric studies on polymer spheres, DSC measurements have been performed on dried samples which coalesce during heating. We show that polystyrene spheres in aqueous suspensions are stable without any coalescence during DSC scans up to 140°C. This allows us to

obtain reproducible DSC traces for samples with well-defined thermal histories that can be precisely compared to bulk samples. We find that spheres with diameters down to 42 nm show an unambiguous glass transition very near the  $T_g$  of bulk polystyrene. The magnitude of the observed heat capacity jump  $\Delta C_p$  at the transition decreases as the sphere size decreases. These results can be fit with the assumption that the center portion of the spheres is bulk-like in terms of dynamics while a 4 nm outer shell has substantially faster dynamics. In contrast, freestanding polystyrene films with thickness similar to these sphere diameters have been reported to show a single glass transition substantially below the bulk  $T_g$  value. Potentially important differences between the sphere and thin film experiments include interfacial energy and equilibration.

We have investigated the properties of polymeric nanostructures by means of Monte Carlo and molecular dynamics simulations. In order to explore the dynamics of structural relaxation in nanoscopic polymer glasses, we have performed transition state searches on the potential energy landscape for bulk and freestanding films and identified connected minima [2]. An analysis of the displacements between minima shows that the polymer sites that undergo the greatest displacement are highly localized in space for both the bulk and the thin film systems considered in our work. In the case of the thin films, clusters of mobile particles originate at the surface and penetrate into the center of the film, thereby coupling the relaxation in center of the film to the “mobile” surface layer. Furthermore, the energy barriers between minima are lower in the thin films than in the bulk systems. These findings can rationalize the experimentally observed depression of the glass transition temperature in freestanding polymer films.

We have also investigated the mechanical properties of polymeric nanostructures by molecular simulation [3]. In order to determine an apparent modulus for such structures, a continuum mechanics model was applied to interpret virtual deformation simulation data. A recently proposed method based on strain fluctuations was also used to calculate the elasticity tensor for the structures. The effect of size on the apparent modulus of ultra-small structures was explored. Our results indicate that, for a given system at a specified temperature, the modulus of a small structure can be significantly smaller than that of the bulk material. Furthermore, in small systems the elastic constants are shown to become anisotropic.

Techniques such as nanoindentation, lateral force microscopy, dynamic atomic force microscopy, frictional force microscopy, and interfacial force microscopy, are currently unable to perform quantitative mechanical property measurements on sub-100 nm two- and three-dimensional structures. We have recently reported on the design and implementation of test structures in which well-defined capillary forces act on micro- and nanoscopic polymer beams [4]. When applied in conjunction with appropriate continuum and molecular beam bending models like those described above, the test structures have the potential to experimentally determine the in-plane mechanical properties of nanostructured polymer materials. The symmetric test structure design consists of nanostructured polymer beams and separating pools as shown in Figure 2. The test structures have been formed in polymer films of poly(methylmethacrylate) photoresist using high-energy electron beam lithography. Well-

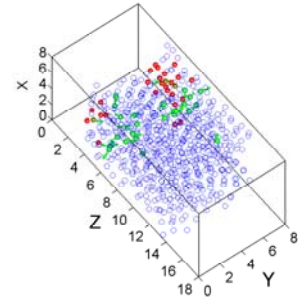


Figure 1. Representative configuration of a cluster of mobile particles (indicated by the red and green colors) in a thin polymer films. The cluster originates at the free interface, and it propagates into the midsection of the films. The red particles correspond to monomers displaced as a saddle point (energy barrier) is reached from an energy minimum, while the green particles correspond to mobile monomers moving as one descends from the saddle point into a new minimum.

defined capillary forces are generated within each test structure and deform the polymeric beams during the drying of rinse liquids from the test structure pools. The extent of deformation was characterized as a function of the capillary forces. The use of test structures for characterizing the deformation behavior of nanoscale polymeric beams was found to be amenable to combinatorial strategies, as demonstrated in Figure 2. A range of capillary forces and beam deformations can be accessed by varying the test structure dimensions, while simultaneously providing a visual means of determining the critical dimensions of deformation. The high-throughput capabilities of the test structure arrays offer immediate opportunities for acquiring statistically robust data on the nanoscale deformation of polymers, and in particular can be used to benchmark the collapse behavior of photoresists important to the microelectronics industry.

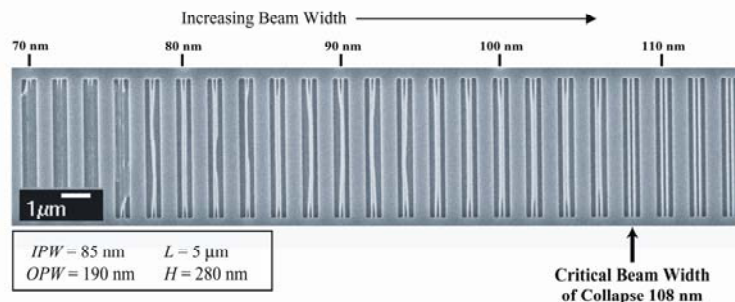


Figure 2. SEM image of a test structure array having the same initial capillary force throughout and displaying, from left to right, the transition between completely deformed and undeformed test structures.

### Education and Outreach

We are committed to a vigorous Education and Outreach Program with the involvement of our team's four investigators and their coworkers. Our philosophy is that Education/Outreach requires the same level of innovation as research and the same commitment to making significant advances. This effort takes place at several levels (K-12, undergraduate, graduate, and teacher education. In the area of K-12 education, we work with a University of Wisconsin-Madison program known as PEOPLE (Pre-college Enrichment Opportunity Program for Learning Excellence, <http://www.wisc.edu/studentaffairs/people.html>) to increase the likelihood that minority and low-income middle/high school students matriculate to colleges and universities. The PEOPLE program, currently in its fifth year of existence, seeks to increase the size of the pipeline bringing under-represented groups to post-secondary education. UW-Madison will offer a full tuition grant to all graduates of the PEOPLE program who qualify for admission. This program is one of only a few nation-wide that engages a large group of students early and interacts with that same group continuously until they finish high school. To our knowledge, it is the only program that offers a full tuition grant as an incentive to graduates. This past summer, students and faculty developed course materials to be disseminated and taught a three-week laboratory course consisting of six modules in the PEOPLE program entitled "Smaller than the eye can see; how your computer is made".



Figure 3. Prof. de Pablo leading a laboratory course as part of the PEOPLE program at UW.

### References

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