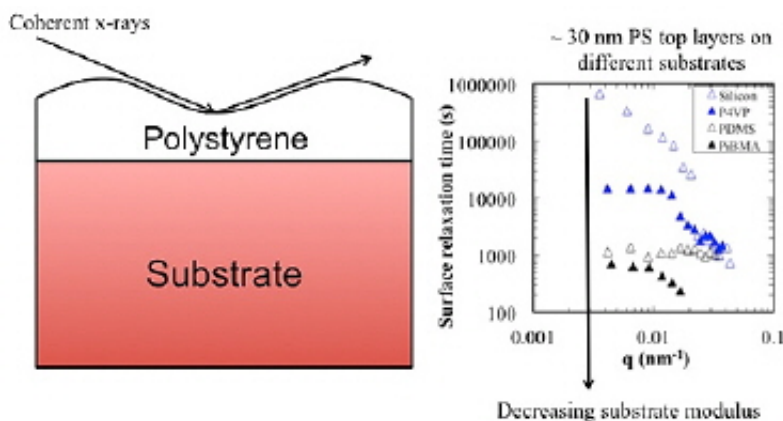


Dynamics of polymer chains atop different materials

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Left: Schematic showing the scattering geometry under which XPCS measurements were carried out. Right: Relaxation time as a function of the in-plane scattering wave vector measured from a 30-nm-thick PS film deposited atop substrates of different modulus.

(Phys.org)—Technologies such as microelectronics and lithography require nanoscale polymer films that sit atop various other materials. An understanding of the interplay between the dynamics of the thin film and the underlying substrate is crucial in determining the appropriate materials to be utilized for new and improved applications. Recent experiments at the U.S. Department of Energy Office of Science's Advanced Photon Source (APS) at Argonne National Laboratory provide new insights on the dynamics of thin polymer films sitting on various substrates and the importance of film thickness and supporting

material properties on the surface dynamics of thin polymer films.

Devices that make use of such layers require this crucial knowledge so that appropriate materials can be judiciously chosen. Selecting a polymer based on bulk properties alone is not adequate when working with layers whose thickness is measured in [nanometers](#).

For instance, if a particular polymer is chosen as a microelectronics coating but becomes substantially stiffer or softer when fabricated into nanoscale layers, it may no longer perform as anticipated.

When [polymer films](#) are confined to the nanoscale, properties such as the [glass transition temperature](#) (T_g), [melting temperature](#), or a measure of stiffness such as the elastic modulus can exhibit large shifts from the way these properties normally behave in larger sizes. These shifts are understood to arise from interfaces, where the [dynamics](#) are faster at the polymer-air interface (called the free [surface](#)) and slower at the polymer-substrate interface where interactions caused by attraction as opposed to adhesion, such as hydrogen bonding, are present.

The most commonly studied nanoconfined film is [polystyrene](#) (PS), which shows a decreasing glass transition temperature as the film thickness decreases because the free surface is highly mobile and the polymer does not exhibit substantial attractive interactions with the supporting substrate. Although T_g changes to nanometer-thick polystyrene are well documented, other properties, such as the dynamics, must be considered when fabricating materials at the nanoscale.

To study such confined films in a greater detail, the researchers in this study from Northwestern University and Argonne used X-ray Science Division beamline 8-ID-I at the APS to measure thermally induced capillary waves at the surfaces of polystyrene films.

The researchers employed x-ray photon correlation spectroscopy (XPCS), which is ideal for probing surface dynamics because x-rays from the APS can be tuned to only penetrate into the top ~10 nm of a film.

With XPCS, the researchers measured constantly fluctuating capillary waves on the surface of a polystyrene film that had been heated to a temperature above the T_g of the polymer.

The researchers were able to discover the role played by polystyrene-film thickness and substrate modulus on the dynamics of surface capillary wave relaxation times.

From measurements taken 10° above the polystyrene glass transition temperature, surface capillary wave relaxation times were found to span orders of magnitude when the PS was placed on substrates with modulus values ranging from ~1 MPa to >100 GPa.

Faster surface dynamics were observed on softer substrates even for films thicker than 100 nm. This thickness is large enough that PS does not show any T_g confinement effects, but shows substrate modulus effects. This result illustrates that T_g and stiffness can be impacted in a very different manner when the polymer film is confined to the nanoscale.

A second finding of this study was that thinner PS films have slower surface wave relaxations than thicker films for a given substrate. Interestingly, the effects of substrate modulus and film thickness disappear when measurements were taken 40° degrees above the T_g of PS, showing that measurement temperature plays a critical role in confinement studies.

Future work by these researchers will look at the dynamics of thin films

that have fillers such as nanoparticles or plasticizers added to modify their properties.

More information: Christopher M. Evans et al., "Modulus, Confinement, and Temperature Effects on Surface CapillaryWave Dynamics in Bilayer Polymer Films Near the Glass Transition," *Phys. Rev. Lett* 109, 038302 (2012). [DOI:10.1103/PhysRevLett.109.038302](https://doi.org/10.1103/PhysRevLett.109.038302)

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