

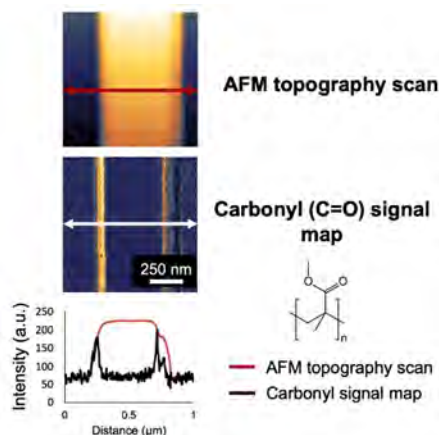
## Nanospectroscopic imaging of chemical group orientation in polymer nanostructures

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Understanding the fundamental characteristics of the surface of a polymer is important for many different applications. It is well accepted that the surface of a polymer is different than the bulk material. Polymer chains pack differently when near a surface, which can lead to preferential functional group orientation. Therefore, we expect the functional group orientation near the surface must also be different from that in the bulk. Here, we fabricate nanostructure arrays using nanoimprint lithography from the synthetic polymer polymethylmethacrylate. These structures are pillars and lines less than 1  $\mu\text{m}$  in height and 100 – 500 nm in diameter. Using thermal imprinting, and the combined topographical and nanoscale chemical mapping of photoinduced force microscopy, we found that nanostructures confine and orient functional groups.

This is the first demonstration that nanostructures alter functional groups. We found the top of the structures are covered with the bulky methyl groups, thus closely resembling a flat surface. Additionally, we found an overabundance of carbonyl groups at the edges of the structures. This work represents the first step towards understanding the effect of nanoconfinement on surface functional group orientation. The previous assumption that polymer nanostructures have the same surface chemical structure as a flat film has been proven false.

This research significantly updates the current knowledge of nanoscale surface chemistry. We expect these findings will be easily translated to other industries and alternative materials, such as semiconducting organic polymers. These findings suggest that surface chemistry, as well as nanoscale phenomena, can be controlled for use in adhesion and bio-electronic surfaces.



Polymer nanoline topography scan and simultaneously acquired carbonyl map. The measured line intensity across the surface illustrates the localized signal at the nanoline edge.