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Understanding Polymer Properties through Imaging of Molecules.¹

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The unique advantage of Scanning Probe Microscopy (SPM) is that it allows imaging of flexible polymer molecules, whose overall size and local curvature are below the optical resolution limit. The role of molecular visualization has grown to be especially profound with the synthesis of complex macromolecules whose structure is difficult to confirm using conventional techniques such as NMR and light scattering. This is especially true for molecules that are branched, heterogeneous, and polydisperse. Here, SPM images provide unambiguous proof of the molecular architecture along with accurate analysis of size, conformation, and ordering of molecules on surfaces. The unique advantage of SPM is that one obtains molecular dimensions in direct space. This offers more opportunities for statistical analysis including fractionation of molecules by size, branching topology, and chemical composition as well as sorting out the irrelevant species. Unlike molecular characterization of static molecules, it remains challenging to study molecules as they move and react on surfaces. We will discuss pioneering AFM studies of flowing monolayers one molecule at a time. Through use of AFM, the flow process was monitored over a broad range of length scales from the millimeter long precursor film all the way down to the movements of individual molecules within the film. Molecular imaging enabled independent measurements both the driving and frictional forces that control spreading rate. In these studies, one also discovered a new type of flow instability in polymer monolayers caused by flow-induced conformational transitions. Recently, molecular imaging has been successfully used to monitor adsorption-induced degradation of branched molecules. These experiments open an entirely new perspective in chemistry wherein the chemical bonds can be mechanically activated upon the physical contact of a macromolecule with a substrate. This research directly impacts coatings, lubrication, heterogeneous catalysis, and biochemical assays, i.e. technologies that are largely controlled by surface-activated changes in the molecular structure and properties.

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