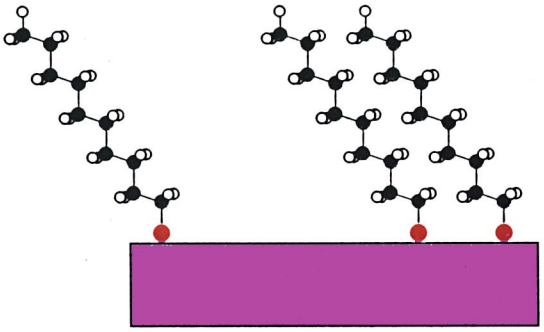
Radiation Damage to Organic Ligands Bonded to Silica

We have obtained bond-specific information about radiation damage to organic ligands bonded to silica using EPR methods. Important applications involving organically functionalized surfaces depend directly on the ability to modify the organic ligands in a specific way with radiation. For example, e-beam-patterned, self-assembled monolayers (SAMs) are useful as resists for wet chemical processing or as chemical templates for selective binding of chemical species – molecules, nanoparticles, etc. – creating new possibilities for nanostructuring surfaces.

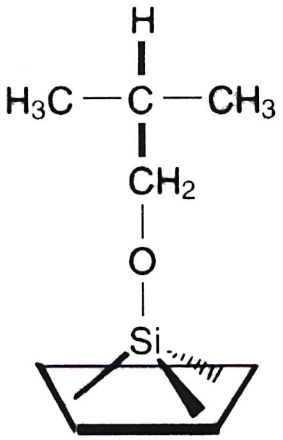
Figure 1A depicts two different types of damage to a siloxane thin film after radiation exposure – one where desorption of constituent molecules predominates and one where the film is slowly degraded by dissociation of C-H and C-C bonds along the chains. Most evidence of aggregate film damage shows that the surface is not cleaned. Is this because the proximal bond to the surface is left intact or because cleaved ligands become entangled with the film?

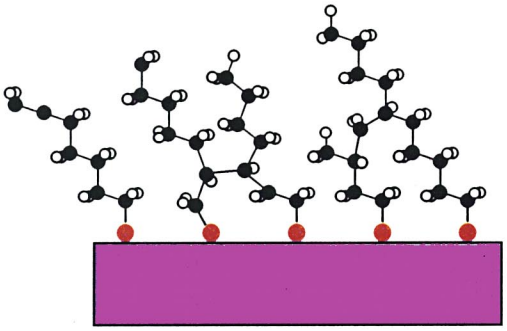
We have studied radiation damage to alkoxy and siloxy ligands on silica. EPR detection of grafted radicals and physisorbed radicals allowed the unambiguous location of cleaved bonds, while exploring the dependence on molecular structure. Our experimental conditions optimized our ability to observe the primary chemical intermediates of radiation-induced ligand damage and to detect evidence of ligand desorption from the surface.

Our findings were that ligand damage far outweighs ligand desorption even for isolated groups. Figure 1B shows the positions of bond dissociation (in bold) in three ligands that were studied. The net result for a thin film is gradual disordering, cross-linking, increased unsaturation and some thinning of the film. More sophisticated strategies, such as e-beam-induced formation or removal of functional groups (e.g., -NH_2, -COOH) at the SAM surface to create a template for subsequent deposition, need to be explored.

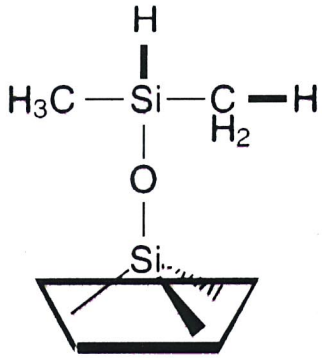


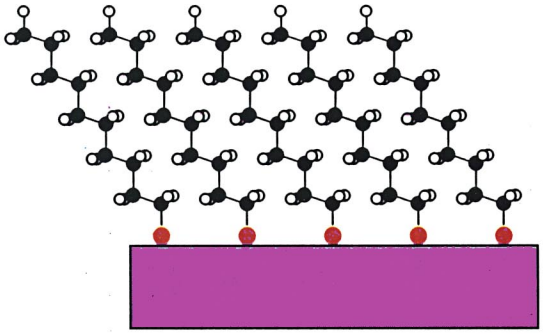
Ligand desorption



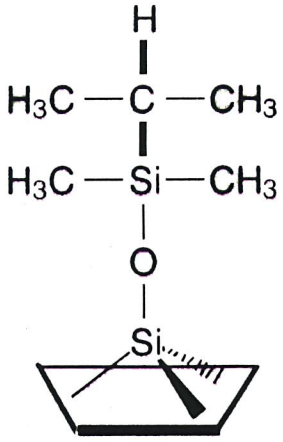


Degraded film





Pristine film



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