556b Patterned Ultrathin Polymer Films Using Thiol-Ene Polymerizations

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Abstract:

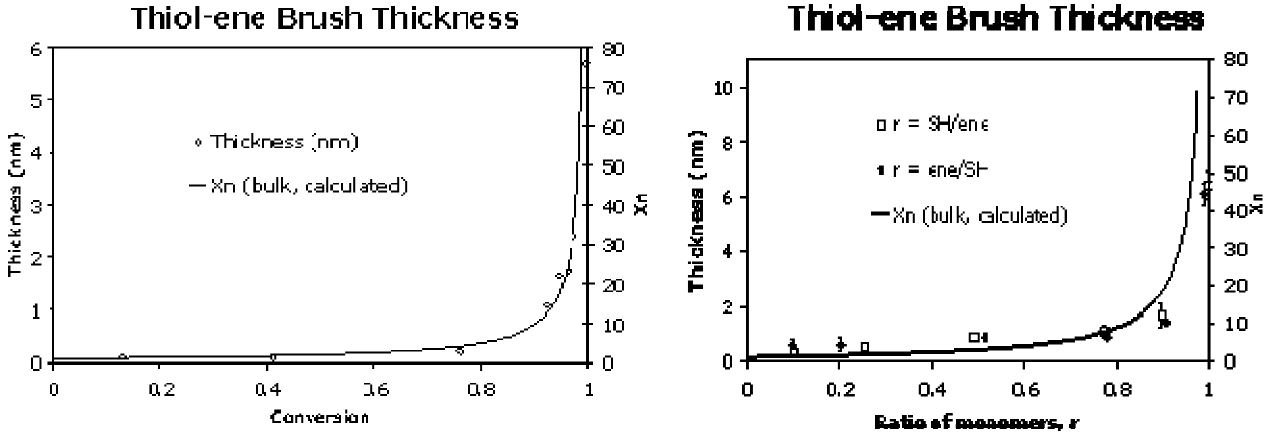
A novel method for forming ultrathin polymer films on a surface with precise thickness and spatial control is presented. Typically, organic thin films attached to a surface are either in the form of a monolayer (SAMs) or are polymer brushes with thickness greater than 10 nm. In this work, a simple and straightforward method for growing patterned oligomers using thiol-ene polymerizations with thicknesses ranging from 0.1 nm to 10 nm is presented.

A difunctional thiol and a difunctional ene (molecule containing a carbon-carbon double bond) are photopolymerized on a surface modified with a self-assembled monolayer (SAM) terminated with thiol functional groups. The surface thiols become part of the thiol-ene polymer chain, and a thin thiol-ene film is attached to the surface. Since the thiol-ene reaction is a step growth polymerization reaction, the ratio of thiol and ene functionalities in the bulk can readily be changed to control the thickness of the formed films. The thickness of the formed films can also be controlled by reacting the monomers up to a particular conversion. As demonstrated in figure 1, the thickness of the formed films can be controlled by changing both the ratio of thiol to ene functionalities as well as the conversion to which they are reacted. By systematically manipulating each of these factors, films with thicknesses ranging from 0.1 nm to 6 nm have been formed. It is also shown that since the thickness of the films is proportional to the molecular weight of the chains formed in the bulk, it is possible to tune in one of these factors (thiol:ene ratio or conversion) to obtain a desired value of thickness.

Since thiol-ene systems utilize a photopolymerization mechanism, photolithography is used to spatially pattern the formed films. Patterned films with a thickness from 0.1 to 5 nm have been grown using this technique. Patterned, crosslinked films can be backfilled by growing a brush with different functionality in unmodified regions to obtain a surface presenting multiple functionalities.

Apart from a precise thickness and spatial control, thiol-ene polymerizations present several advantages for surface modification. The polymerization reactions are very rapid and are typically complete in a few seconds. Thiol-ene systems have been shown to react with a variety of photopolymerizable monomers, and thus a wide range of functionalities can be attached to the surface. Film formation is not affected by the presence of oxygen. Finally since thiol-ene systems can undergo initiatorless polymerization, film formation can be achieved without the addition of a photoinitiator.

Figure1. (a) Thiol-ene brush thickness versus bulk monomer conversion for a stoichiometric mixture of hexane dithiol and divinyl ether with 0.1% DMPA. (b) Thiol-ene brush thickness versus ratio of thiol and ene monomers in bulk. Conversions are monitored using FTIR. Thickness is measured using ellipsometry. Solid lines represent the calculated chain length in bulk, Xn for step growth polymerization of two difunctional monomers



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