508f Covalent Molecular Assembly in Supercritical Carbon Dioxide: a Preparative Method for Non-Fluorinated Functional Ultrathin Films

Sreenivasa Reddy Puniredd and M. P. Srinivasan

The drawback of currently used layer-wise deposition techniques for ultrathin films is that the binding forces between molecular chains are electrostatic or van der Waals in nature, giving rise to insufficient strength for the film obtained. Furthermore, the presence of residual solvent is problematic when working on the nanometer scale in liquid solvents. Therefore, there is a need to develop a method of constructing functional thin films on substrates whose thicknesses are of molecular dimensions, and are yet mechanically strong, and this provides the rationale for formation of covalently bonded ultra-thin films by molecular assembly. While SCCO2 (supercritical carbon dioxide) is not suitable for most high molecular weight compounds under relatively mild conditions (< 100 oC and < 3000 psi), it is a good solvent for many low molecular weight non-polar and some polar molecules, especially those containing fluorine. However, since presence of fluorine degrades mechanical strength and thermal stability of the thin film structures, this work focuses on forming robust ultrathin films using SCCO2 as solvent in the absence of fluorine. The technique of molecular assembly is employed to construct ultrathin films of functional oligoimide with interlayer linkage established by covalent bonds.

Pyromellitic dianhydride (PMDA) and diaminodiphenylether (DDE) were deposited alternately (layer-by-layer assembly (LbL)) on silicon and quartz surfaces derivatised by chemisorption of p-amino phenyl trimethoxysilane (APhS) to yield an amine surface or 3-cyanopropyl trichlorosilane (CPS) for an anhydride surface. With the objective of constructing functional films, composite structures were formed from second generation PAMAM Dendrimer (Polyamidodiamine) and PMDA deposited alternately on APhS- and CPS-derivatised surfaces in SCCO2. X-ray photoelectron spectroscopy (XPS) analysis suggests that PMDA/DDE and PAMAM/PMDA interlayer covalent bond is established to completion, and also the creation of functional surfaces for immobilization of the next layer. The film morphology, as observed through atomic force microscope (AFM), is very uniform at each deposition step. UV-visible absorptions and ellipsometry revealed the layer-by-layer growth of the film in SCCO2. The functional property of the PAMAM-containing film was confirmed by reduction in its refractive index relative to films without PAMAM.