QUANTIFYING MOLECULAR INTERACTIONS WITH IR ELLIPSOMETRY

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Molecular interactions play a key role for the structural and functional properties of organic molecules at solid–liquid interfaces. Examples are ordering effects in functionalized thin films, protein aggregation at interfaces, as well as adsorption and desorption behavior of biomolecules on coated surfaces. *In situ* infrared ellipsometry (Fig. 1) accesses both film, analyte, and solvent vibrational fingerprints, and is therefore an advantageous method for measuring said properties. It provides, among other things, insights into film structure, hydration, molecular interactions, and local chemical environments, rendering it a powerful technique for detailed studies of solid–liquid interfaces, particularly of interfaces involving polymers and proteins.

Carbonyl vibrations are versitile infrared reporter modes for probing local chemical environments, that is, solvation effects and specific chemical interactions like hydrogen bonding. We employ *in situ* infrared ellipsometry to investigate structure and interactions of ultrathin polymer films and brushes containing side chain C=O moieties. The focus first lies on rather hydrophilic thermoresponsive, humidity-sensitive poly(*N*-isopropylacrylamide) [PNIPAAm] and poly(2-oxazoline) [POx] brushes whose reversible swelling–dewelling transitions in water are partially driven by a loss of water-interacting C=O groups with increasing temperature.

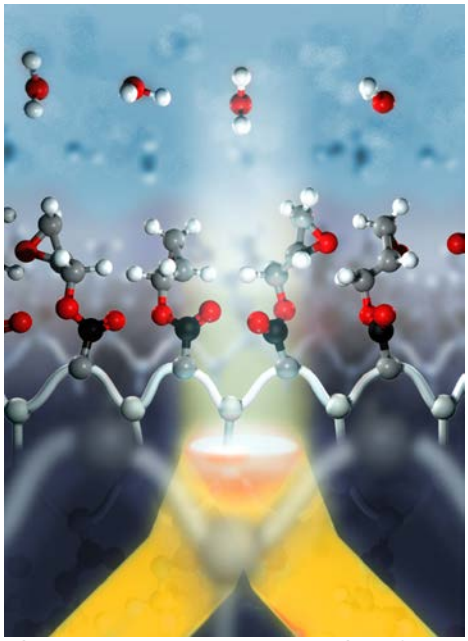

Fig. 1. IR-SE at PGMA–H_2O interface.

We then monitor and quantify interface-chromic and hydrogen-bond induced vibrational C=O band shifts of nanometer-thin hydrophobic poly(glycidylmethacrylate) [PGMA] films in contact with different solvents. The tail–train–loop structure of the covalently grafted films potentially influences film–solvent interactions. Using theoretical calculations, we find that effects from solvatochromism and interface geometry are insignificant for aprotic solvents, whereas in water the films' topmost subnanometer layer is involved in hydrogen bonds with H_2O molecules, giving rise to minor but detectable film swelling.

Keywords: In situ infrared ellipsometry; Solid–liquid interfaces; Molecular interactions

References

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