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Water Induced Polymer Reorientation at a Polystyrene/Polyacrylic Acid Surface

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Certain polymer surfaces undergo an adaptation process after being exposed to liquids due to side chain movements. This reorientation often leads to a preferential exposure of certain polymer groups on the liquid interface, modifying consequently the observed features in surface experiments such as contact angle measurements [1]. This behavior is even more accentuated in block copolymers, where the elements that are most compatible with the liquid are reoriented in order to be in contact with the liquid phase.
In this project, we focus on the adaptation of a random copolymer made out of polystyrene and polyacrylic acid (PS/PAA) upon exposure to water. Previous studies [2] involving contact angle measurements on a tilted plate show a reduction of the contact angle after wetting. Our objective is to determine if this changes in contact angle coincides with a change in surface structure detected by means of sum-frequency generation spectroscopy (SFG).
In our experiments, we evaluated and compared the vibrational SFG spectra of the samples before and after being in contact with water, to determine whether this exposure resulted in a reorientation of the copolymer. In addition, the reversibility of the reorientation by sample annealing over the glass transition temperature (Tg) was also tested.
Due to the intensity change observed in a marker band of the PS polymer in the vibrational SFG spectrum, we were able to confirm a restructuring of the copolymer. Furthermore, we proved that the intensity of this band can be recovered after annealing the samples over the Tg, proving the reversibility of the process [3].

References:
[1] H.- J. Butt et al, Langmuir. 2018, 34, 11292−11304.
[2] X. Li et al, Langmuir. 2021 37, 1571−1577.
[3] X. Li, M. Encheva et al, submitted to Macromolecular Rapid Communication 2021.

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