EVOLUTION OF MOLECULAR ORDER IN SELF-ASSEMBLED POLYETHYLENEIMINE (PEI) FILMS USED IN ORGANIC ELECTRONICS

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Polyethyleneimine (PEI) is a cationic polyelectrolyte widely used, for example, in biology, CO_2 capture and organic electronics (OE). In the latter, it is known that even ultrathin PEI layers are powerful surface modifiers that can shift the electrode work function (Φ) and hence improve charge injection in electronic devices. This effect may depend on the conformation and dipolar order of the adsorbed PEI ultrathin film. However, a detailed experimental evaluation of the conformational order and its evolution in these layers has not yet been reported yet. Therefore, our work primarily proposed to use SFG vibrational spectroscopy - a nonlinear optical technique intrinsically specific to interfaces and sensitive to the orientation of polar groups - to probe the conformational organization of PEI in self-assembled films on glass and gold. For this, we have studied films fabricated by *spin-coating* from alcoholic solutions or by *dip-coating* from aqueous solutions with pH = 10, 7, 5 or 2, respectively. In particular, we have investigated the organization of PEI for both branched (*b*-PEI) and linear (*l*-PEI) structures. The obtained SFG spectra in the C-H stretch range, and complementary analyses, indicated that the conformational ordering at the interface changes over days. In this context, we have obtained spectra with more intense signals fourteen days after fabrication, indicating a higher degree of ordering. However, the evolution of the ordering at the interface was not accompanied by significant variations of $|\Delta\Phi|$, implying that the latter is not dominated by molecular dipole alignment. The results obtained in this study are consistent with a dynamic mechanism for the interaction of PEI with different substrates, in agreement with its use as a universal electrode modifier. They also suggested that the observed changes are mainly affected by the sample preparation conditions and the degree of hydration of the adsorbed film. The results from this study may also have direct implications in areas ranging from the environment and sustainability to tissue engineering.