Rotational Dynamics of Polyacid Chain Segments in Polyelectrolyte Multilayers Studied by Spin-Label EPR Spectroscopy

A nitroxide spin label has been covalently attached to the weak polyelectrolyte poly(ethylene-alt-maleic acid) (P(E-alt-MA)) to study the rotational dynamics of the polyacid backbone in swollen polyelectrolyte multilayers (PEMs) formed by P(E-alt-MA) and the oppositely charged weak polycation poly(allylamine hydrochloride) (PAH) by continuous wave (CW) electron paramagnetic resonance (EPR) spectroscopy. PEMs are interesting objects of fundamental research but also of high practical relevance. Multilayers can be prepared on planar surfaces or colloidal templates by the layer-by-layer technique. Sensor materials, functional coatings, and selective membranes are discussed and explored as applications of PEMs.

In a first series of experiments, the growth of PEM films on the inner surface of glass capillaries has been monitored by quantitative EPR using the SL-P(E-alt-MA) for the preparation of every polyanion layer. A parabolic growth of the multilayer films with up to 16 layers was found. In a second series of experiments, the strength of the spin-label technique was exploited, i.e., the SL-P(E-alt-MA) has been used as a reporter molecule for the study of the dynamics in the PEMs. Multilayers of PAH/P(E-alt-MA) with 16 and 17 layers, respectively, were prepared where the SL-P(E-alt-MA) has been selectively placed in a single layer. The segmental rotational mobility of the spin-labeled polyacid and the internal rotation of the spin label have been determined by simulation of the line shape of experimental CW EPR spectra. A pronounced odd-even effect has been observed, i.e., the rotational dynamics of the P(E-alt-MA) backbone in the PEMs is influenced by the chemical nature of the polyelectrolyte in the terminating layer. It is largest for the layer at or close to the surface and reduced for layers in the bulk of the PEMs. As our results demonstrate, spin-label EPR is a powerful tool for the investigation of the polymer chain dynamics in PEMs.

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