Estimation of Molecular Weight and Polydispersity in Conducting Polymers using Single-Molecule Force Spectroscopy

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Atomic force microscopy (AFM) was originally developed to study surface morphology, but has been extended to investigate interaction forces and to map materials properties [1]. This is achieved by measuring the tip-sample interaction while approaching and/or retracting the tip from the surface, in the so-called atomic force spectroscopy (AFS). Here we employ single-molecule force spectroscopy [2] to estimate the molecular weight, M_n, and polydispersity, *PDI*, of the conducting polymers poly(*o*-ethoxyaniline) (POEA) and polyaniline (PANI). Experimentally, the adsorption of polymer chains on the AFM tip upon compression is exploited by monitoring the force curve during retraction of the tip while the chains break free from the tip. The force curve on retraction displayed a maximum attractive force at a separation, L_m, which decreased to zero as the tip-sample distance increased. We found that L_m corresponds to the average contour length, L_c, of the polymer chains, as determined by size exclusion chromatography (SEC). The decreasing attractive force at separations larger than L_c suggests that chains were detached from the tip as they were stretched away from the grafting surface. By considering the fraction of chains of a given molecular weight determined from several force curves, we obtained a normal distribution from which the PDI value could be determined using the standard deviation. For POEA, the molecular weight and polydispersity were $M_{POEA,AFM} = (2.5 \pm 0.9) \times 10^4$ g/mol and $PDI_{POEA,AFM} = 2.1 \pm 0.1$, to be compared with $M_{POEA,SEC} = 2.09 \times 10^4$ g/mol and $PDI_{POEA,SEC} = 2.4$. For PANI, $M_{PANI,AFM} = (1.8 \pm 1.3) \times 10^4$ g/mol and $PDI_{PANI,AFM} = 1.7 \pm 0.1$, which also agree with the values obtained from SEC, viz. $M_{PANI,SEC} = 2.8 \times 10^4$ g/mol and $PDI_{PANI,SEC} = 1.65$. We highlight the potential of the single-molecule force spectroscopy, which allows one to obtain a statistical distribution of contour lengths with force curve measurements, and provides a novel method for estimating M_n and PDI of grafted polymer layers

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