187d Effect of Free Volume Distribution on Transport and Dissolution Properties of Polymers

Derrick Callander, Trevor Hoskins, Clifford Henderson, Peter Ludovice, and Y.C. Jean

Computer simulation was used in concert with experimental characterizations to connect free volume distributions in polyesters and poly(norbornene) to their unique properties. Understanding this structure-property relationship is important in improving the barrier properties of polyesters and understanding the unique diffusion and dissolution behavior of photoresist polymers such as poly(norbornene). While fractional free volume is often correlated with diffusion and permeability properties of polymers, the distribution of this free volume is rarely used as it is more difficult to measure even with techniques such as Positron Annihilation Lifetime Spectroscopy (PALS). Computer simulation of poly(ethylene terephthalate) (PET) and poly(ethylene naphthalate) (PEN) were used to produce free volume distributions using the Delaunay Tessellation approach. These simulated distributions of free volume accurately predicted differences in the total free volume estimated by group additivity theory. However, differences in the distribution of these free volume elements accessible to various probes such as oxygen gas and the ortho-positronium complex from PALS are consistent with both PALS results and oxygen solubility differences. Despite the group additivity prediction that PET has more total free volume than PEN, simulations indicate that the distribution of free volume that is accessible to oxygen is responsible for solubility differences in PET and PEN. Computer simulations of poly(norbornene) produced by vinyl-like polymerizations (in contrast to Ring Opening Metathesis or ROMP) were carried out to characterize the free volume in this polymer glass. Simulations were able to reproduce the unique change in the Wide Angle X-Ray Diffraction pattern of this polymer with molecular weight. These simulations predict that free volume elements should increase in size with increasing molecular weight of poly(norbornene) consistent with recent PALS results. This change in free volume distribution is what is responsible for the unique anomalous dissolution behavior observed in poly(nobornene) when it is developed as a photoresist polymer in photolithography applications.