471b CO2-Induced Surface Tg Reduction of Polymer and Theoretical Modeling

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Currently, CO2 is experiencing the advances in modifying polymer surface property on nanoscale inspired by its successes in bulk polymer processing, such as interfacial bonding for assembling tissue scaffolds and improving biocompatibility of polymer biomedical devices. A thorough understanding on the effects of CO2 on surface properties is in a demand and proves to be a tough challenge. Even for pure polymer, the anomalous dynamic behavior of nanoscale surface from bulk phase was not widely recognized until about a decade ago. In this work, we first investigated the surface Tg behavior of Polystyrene(PS) by the AFM technique we developed. In brief, the gold nanoparticles with uniform size were deposited on polymer surface and then subject to thermal and/or CO2 treatment. By detecting the embedding depth of particles, the condition where the glass transition occurs could be revealed. In this way, we identified the surface Tg of pure PS, and its variation as external CO2 pressure. Meanwhile, we developed an entropy-based thermodynamic model that could satisfactorily describe the characteristics of surface Tg. We applied the Gibbs-Di Marzio glass transition criterion to the polymer surface region where exhibits a density gradient. By using the Sanchez-Lacombe EOS and the Helmholtz excess free energy equation derived in gradient theory, we successfully derived the entropy expression for the surface region. As a result, by searching the temperature where the surface entropy is equal to zero, we identified the surface Tg of monodisperse Polystyrene (MW=214,000) as 62 oC. The result shows excellent agreement with experimental observations and literature values. The gradient profile indicates the thickness of surface region that serves as the source of anomalous dynamics is about 1.5 nm, also reasonably in accordance with experimental findings. The extension of this entropy model to binary polymer/CO2 system is being investigated.