Extreme 2D-confinement of polymers in graphene-based materials

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Abstract

Confined macromolecules at a nanometer scale exhibit a fascinating and unexpected dynamic behavior. Upon a decrease of confining dimensions down to the nanoscale, properties such as glass transition and crystallization are often observed to deviate quite significantly from those of the bulk material. Graphene-based materials are exceptional hosts to study confined polymers at the sub-nanometric scale due to the ability to control and tune their degree of oxidation and exfoliation and, therefore, to control the strength of the interaction between host and macromolecules. In this study, we report on the extreme two-dimensional (2D) confinement of poly(ethylene oxide) (PEO) in the interlayer space of graphite oxide (GO) and in the surface of thermally-reduced graphene sheets by using a combination of diffraction, calorimetric, and spectroscopic methods, including high-resolution inelastic neutron scattering (INS) [1-4].

Careful control over the degree of graphite oxide oxidation and exfoliation reveals three distinct cases of spatial confinement: (i) subnanometer 2D-confinement; (ii) frustrated absorption; and (iii) surface immobilization. Case (i) results in drastic changes to PEO conformational and collective vibrational modes as a consequence of a preferentially planar zigzag (trans–trans–trans) chain conformation in the confined polymer phase, which is accommodated in a layer of thickness ~3.4 Å within the GO substrate. In case (ii), GO is thermally reduced resulting in a disordered pseudo-graphitic structure. As a result, we observe minimal PEO absorption owing to a dramatic reduction in the abundance of hydrophilic groups inside the distorted graphitic galleries. In case (iii), the INS data unequivocally show that PEO chains adsorb firmly onto graphene sheets, with a substantial increase in the population of gauche conformers. Well-defined glass and melting transitions associated with the confined polymer phase are recovered in case (iii), albeit at significantly lower temperatures than those of the bulk.

References