Subnanometer 2D-confinement of poly(ethylene oxide) in graphene-based materials: effect of polymer topology

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The confinement of both molecular and macromolecular systems at nanometer length scales can lead to significant changes in observables such as glass transition temperature and melting point. Graphene-based materials are exceptional hosts to study confined polymers at the subnanometric 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 [1]. In fact, poly(ethylene oxide) (PEO) is able to intercalate into the interlayer space of graphite oxide (GO) and to form extremely 2D confined monolayers of about 3.3 Å with restricted mobility [2] and conformations [1, 3]. In this presentation, we will show our recent studies on the intercalation kinetics of linear and cyclic PEO into GO, in going from low molecular weight oligomers (crown ether case) to higher molecular weight polymers. In these studies we made use of the total absence of glass transition and melting of the intercalated PEO oligomers and polymers to monitor the evolution of the glass transition and melting of the non-intercalated material as a function of time. This unique property of the intercalated (and confined) phase in GO allowed us to quantify the composition of non-intercalated material. We first demonstrate that the enormous difference in the intercalation rate between cyclic and linear oligomers can be used as a method to selectively separate the cyclic molecules from the linear ones in the melt [4] or in solution [5]. Secondly, these differences in the intercalation rate become smaller with increasing molecular weight. By introducing fixed pillars into the GO structure that operate as physical barriers against the polymer diffusion, we demonstrate that it is possible to restrict the intercalation of cyclic PEO into graphite oxide, whilst allowing the linear analog to diffuse through the graphite oxide layers (Figure 1). This important finding could be the basis for developing a method of purification of cyclic polymers.
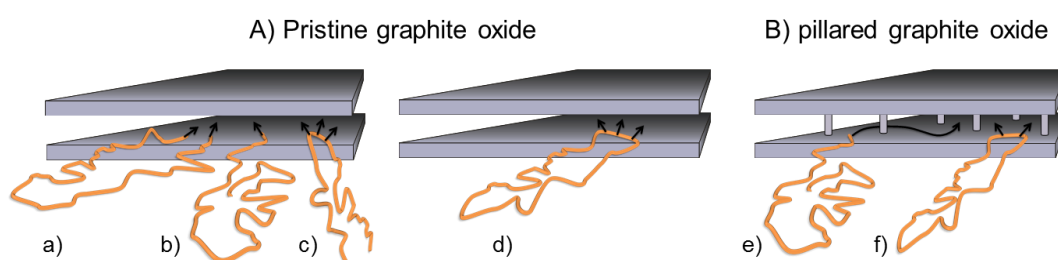

Figure 1. Melt intercalation of PEO into (A) pristine GO and (B) pillared GO. (a, b) Intercalation of linear chains driven by end-group diffusion and (c) main-chain diffusion (c). (d) Intercalation of cyclic PEO into GO driven only by main-chain diffusion. Intercalation of (e) linear and (f) cyclic PEO into a pillared GO, where it is predicted that intercalation of a linear chain is favored respect to that of a cyclic chain.

References

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