

Segmental Dynamics of Polymers in Extreme (1-2nm Slit-Pore) Confinements

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INTRODUCTION

The local –segmental– dynamics of polymers in slit-pores are investigated for polymers inserted (intercalated) between parallel mica-type surfaces (montmorillonite). This class of intercalated organic/inorganic hybrids offers a very fertile ground to study polymer and segmental dynamics in extreme pseudo-two-dimensional confinements¹. The rich –and in many cases striking– experimental behavior observed in these extreme confinements, is compared to Molecular Dynamics (MD) simulation approaches in order to trace the molecular-level mechanisms responsible. Specifically, we comparatively study of poly(ethylene oxide) [PEO]² and polystyrene [PS]³ in extremely narrow (1nm and 2nm respectively) slit pores. We contrast the high T_g PS –for which molecular motions are effectively arrested in the nanosecond time scales– to the lower T_g PEO –which exhibits translational (diffusive) dynamics in the few ns time-scale. Factors such as local density inhomogeneities and, in the case of PEO, the nature of lithium cation coordination, have been traced as the main molecular mechanisms responsible for the confinement-induced local segmental dynamics. In concert with NMR and dielectric studies, a very wide distribution of segmental relaxation times is observed over a broad T-range.

METHOD AND SYSTEMS

Methods. The simulation geometries faithfully mimic the respective experimental systems in dimensions, densities, and compositions, and reproduce the structures observed experimentally by X-Ray diffraction and wide-angle neutron scattering². The force-fields used⁴ are based on previous works –by us and others– and were refined and adopted to our confined systems. All productive runs were NVT molecular-dynamics simulations, with number of particles (N), volume (V), and temperature (T) kept constant. Periodic boundary conditions were applied in all three directions, and a weak coupling to a reference temperature was realized via the Berendsen method; the details of the methods, the force-field parameters, and discussion of the modeling approximations and choices are provided elsewhere^{2,3,4}.

Systems. The simulated systems are (a) polystyrene (PS) dodecamers [H-(CH₂-C(C₆H₅)H)₁₂-CH₃] confined between octadecylammonium modified fluorohectorite (C₁₈-FH), with a nominal confined organic layer thickness of 2.05nm (Fig. 1); and (b) polyethylene-oxide (PEO) hexamers [H-(CH₂-OCH₂)₆-H] confined between Li⁺ montmorillonite layers, with a nominal confined polymer layer thickness of 0.8nm [8] (Fig. 2). For both polymers, bulk –unconfined– systems were also simulated and compared against the confined ones.

SEGMENTAL DYNAMICS IN 1-2nm SLIT PORES

The common feature in all experimental studies of polymers confined in such 1-2 nm slits defined by silicate inorganic surfaces is a coexistence of fast and slow segmental dynamics, in a wide range above and below the glass transition temperature (T_g) of the bulk polymer. Spectroscopic techniques (NMR and dielectric) of intercalated/confined polymers record a very wide distribution of segmental relaxations throughout the explored temperature range, across polymer systems with varied T_g (from 223 K PMPS poly(methyl-phenyl-siloxane), to 373 K PS)^{5,6}, in presence [PS] or absence [PEO] of alkyl-ammonium surfactants on the confining surfaces. These segmental relaxations span a wide range from ultra-slow solid-like dynamics, to very fast liquid-like motions, independent of temperature.

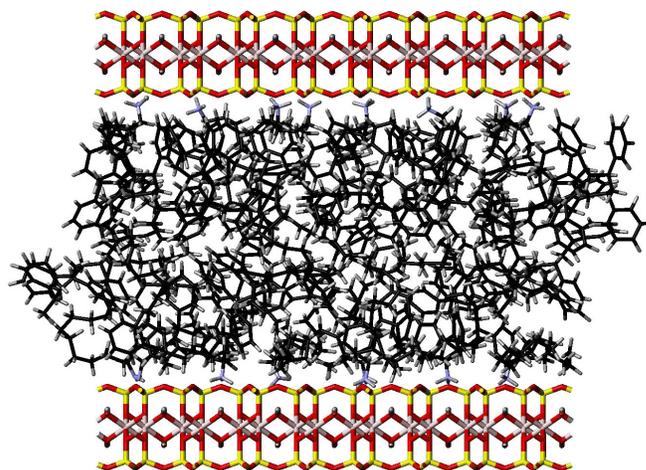


Figure 1. The first simulation system deals with PS oligomers confined between surfactant-modified fluorohectorite layers, in a slit-pore geometry of a ca. 2nm width.

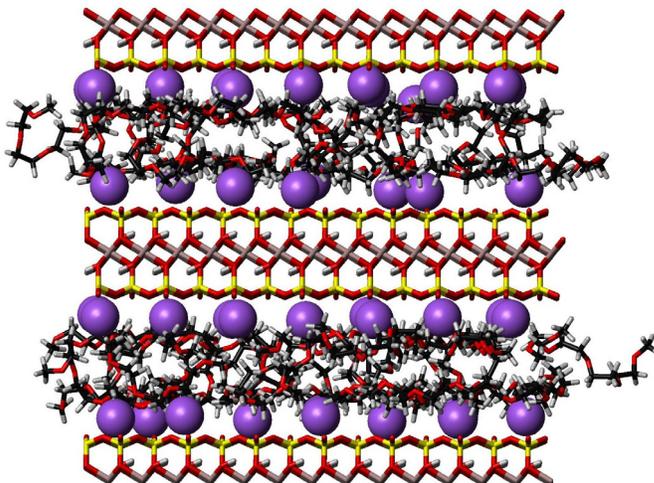


Figure 2. The second simulation system deals with PEO oligomers confined between Li⁺ montmorillonite layers, in a slit-pore geometry of a ca. 1nm width. The alkali cations are shown as blue van der Waals spheres.

The observation of very fast dynamics in these nanoscopic confinements is a striking finding, especially for very low temperatures below the T_g of the respective bulk polymers. Although in our studies (both experimental and simulation) distinctly different polymers and silicates were utilized, the common characteristic is that the slit-width corresponds in all cases to about two monomers of the respective confined polymer. These self-assembled confined polymer bilayers are much thinner than what was studied by previous simulations and by surface forces apparatus experiments [20]. Comparing the mobile segment populations in the confined PEO and PS systems (Fig. 3), several common trends can be identified: (a) There seems to be a single Curie T-dependence for the mobile –and thus the immobile– population under these confinements for each system across the T-range studied (Fig. 3); i.e. whatever the molecular mechanism(s) responsible for these dynamics, they remain in place above and below the bulk T_g or melting point (T_m). (b) In these extreme confinements, there is no signature of a glass transition or a melting point in the segmental dynamics, for example, a sharp change of the temperature slope in the mobile segment population (Fig. 3); whereas the respective bulk –unconfined– polymers exhibit clear/sharp changes in their segmental dynamics under the same experimental conditions. (c) Moreover, we also observe that the mobile segments are located

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throughout the confined film, including also inside the first layer physisorbed on the solid surfaces (more details in ref. 3).

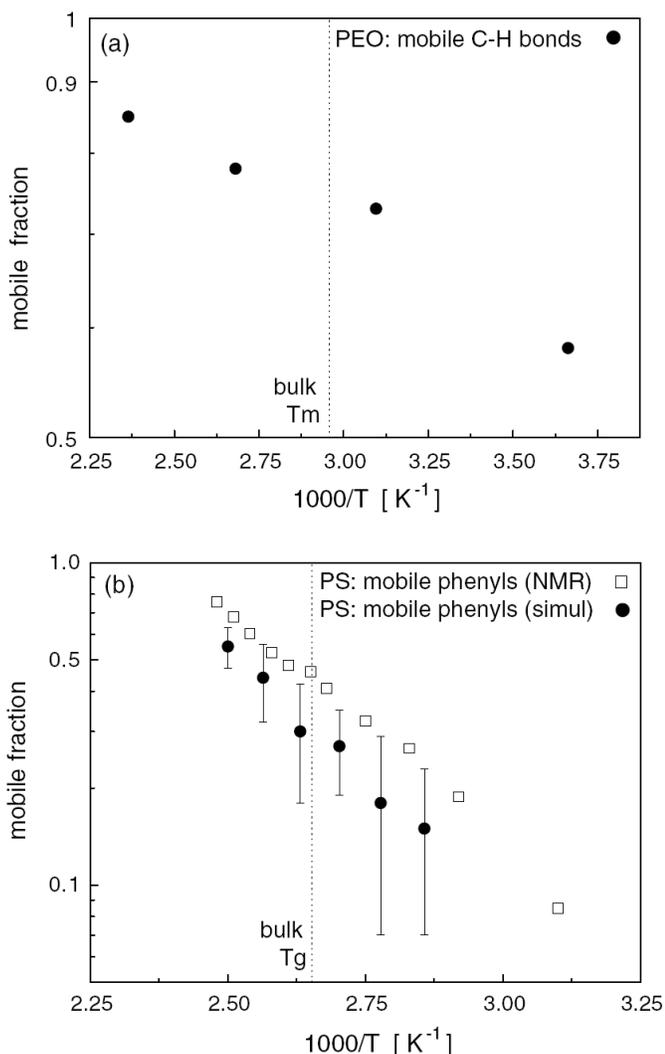


Figure 3. Enumeration of the mobile moieties in the two nanoscopically confined systems as a function of temperature: (a) mobile PEO carbon-hydrogen bonds in 0.8 nm films; and (b) PS mobile phenyls in 2.05nm wide confined-films. For the PS systems we also show the mobile phenyls as enumerated by spin-echo NMR experiments (NMR data adapted from fig. 5 of ref. 6a).

Similar confinement-induced fast dynamics are also reported for polymers in wider confinements, including polymers confined in zeolites⁷, in nanoporous hosts⁸, or amorphous polymer confined between its crystalline lamellae⁹; however, in those cases the experimentally observed relaxation times are much longer than the ultra-fast dynamics seen in our 1-2nm slits here. In wider confinements, bulk-like dynamics develop in the confined polymer films for those segments located just two monomers away from the confining surfaces independent of the strength of the polymer-surface adsorption energy. Consequently, the macroscopically observed dynamics in such nanoscopically confined systems have been proposed to be the weighted average of the confinement-induced response—occurring in the physisorbed monolayers—and of the bulk-like response of the material two monomers away from the surfaces. This observation suggests that the herein measurable ultra-fast segmental dynamics is a direct consequence of the formation of an organic bilayer—two monomers wide confined films— between the silicates surfaces. A

limitation of the present intercalated polymer systems is that the confinement width cannot be easily tailored, and a bilayer almost always self-assembles between the layered silicates (if the interlayer spacing could be systematically varied, the importance of these systems as model two-dimensional confinements would have been inestimable).

The origins of the slow dynamics were traced to the physisorption of polymer trains on the solid surfaces, as has been reported before and is intuitively expected. Additionally, for the PEO systems the characteristic interaction—coordination— between the ethylene-oxide and the silicate surfaces to the Li cations gives rise to more polymer specific mechanisms that promote immobilized PEO segments, with hindered translational and reorientational dynamics. The fast segmental dynamics, for both systems, are traced to local density inhomogeneities, and specifically to low local density regions that are stabilized by the confinement over longtime periods (tens of ns). In the case of PEO, an absence of coordinated Li⁺ is also necessary for the development of fast segmental dynamics.

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