Polymer/Silicate Intercalated Nanocomposites: Confinement Induced Segmental Dynamics in 2 *nm* Slits

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Introduction

Layered-silicate based polymer nanocomposites have become an attractive set of organic-inorganic materials not only for their obvious potential as technological materials, but also for providing a convenient macroscopic system to study fundamental scientific issues concerning confined polymers [1]. Studying the formation, structure and dynamics of these nanocomposites can lead to a better understanding of organic-inorganic hybrids, polymers in a confined environment or at a solid interface, and at the same time provide the necessary fundamental level knowledge to design polymer/inorganic hybrid materials with enhanced properties.

Fluids in nanoscopic confinements possess a variety of unusual properties, and in particular remarkable dynamical heterogeneities which vary on length scales as short as a few Ångstroms. While the Surface Forces Apparatus provides an experimental probe of macroscopic properties of a single fluid film between two atomically smooth solid surfaces, few experimental probes are available which test the microscopic origins of these heterogeneities in nanoscopically confined films. However, ultra-thin (~20Å) polymer films confined between solid surfaces can be created by intercalating high molecular weight polymers inbetween allumino-phyllosilicates (mica-type layered crystals). Especially where well-defined synthetic silicates –such as fluorohectorite (FH)– are used to form intercalated nanocomposites, very homogeneous ultra-thin confined polymer structures are developed throughout the hybrid composite. In such cases, careful design of the polymer/inorganic hybrid material can provide macroscopic quantities of self-assembled multilayer nanostructured systems that contain huge numbers of identical nanoconfined films. This offers great opportunity to study the properties of polymers and liquids in extreme confinements (1-2nm) by employing conventional analytical techniques [1].

Here, we report selected experimental findings and comparative atomistic modeling efforts aiming in obtaining insight into the confinement induced dynamical processes of ultra-thin polymer films (typically 2nm) observed in polymer/silicate intercalated systems.

Results and Discussion

Experimental observations of striking segmental dynamics. Recent studies of model confined polymer films –intercalated in synthetic or naturally occurring silicates– has provided a wealth of experimental observations of very novel dynamics. Zax and coworkers have reported a coexistence of fast and slow segmental dynamics in 1nm wide confined systems of polyethyleneoxide (PEO) in pristine fluorohectorite (FH) [3].

More recently, D.B. Zax and collaborators used *nuclear magnetic resonance spectroscopy* (NMR) to study 2.1nm confined poly(styrene) (PS) films, intercalated into an organically-modified FH [4]. In quadrupolar spin-echo NMR experiments, complete refocusing of the signal can be achieved, unless there is a *significant* change in frequency on the time interval between the two pulses. For ^{2}H NMR, the orientation-dependent resonance frequency is determined by the direction of the C-D bond with respect to the external magnetic field, and signal intensity loss is a marker of large-amplitude dynamics. For the PS backbone, these modes should correspond to trans-gauche isomerization and/or translation; for the phenyl groups to ring flips and/or translation. In figure 1 [fig.5 from 4] the refocused intensities are given for selectively labeled polystyrenes (d-3PS: with deuterated backbone; d-5PS: deuterated phenyl rings) thus the segmental dynamics of the backbone and the phenyl side groups can be selectively studied. These studies reveal the *existence of faster segmental dynamics in the 2.1nm confined PS than are found in free –unconfined– PS at the same temperature*. Moreover, this behavior takes place over a very broad range of temperatures, and the phenyl ring-flips are correlated with the backbone rearrangements in contrast to the behavior of the bulk polymer where the backbone becomes "mobile" at higher temperatures than the phenyl rings. Furthermore, corroborative surface-sensitive cross polarization (CP) experiments, which probe the entire organic layer, we found that *PS segments located in the center of the 2.1nm slits are more mobile than those in the bulk at comparable temperatures, while chain segments which interact with the surface are dynamically inhibited.*

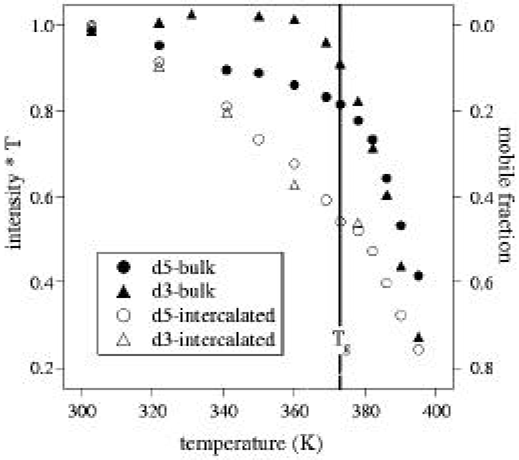

Figure 1. Refocused intensities (multiplied by T, which corrects for the Curie thermal loss of observable intensity) observed in ^{2}H quadrupole spin echo experiments, for d-3 and d-5 PS, in bulk and intercalated in surface-modified FH. Intensities less than 1.0 correspond to ^{2}H sites mobile on the timescale of the spin echo experiment (an estimation of the mobile fraction is given in the secondary y-axis). For the free –unconfined– polymer, phenyl ring modes are enabled somewhat below Tg, while backbone modes become significant only near Tg. In intercalated samples, the two modes are coupled and grow in over a broad temperature range from well below Tg, suggesting the existence of faster modes in the 2.1nm confined PS than are found in free PS. [adapted from [4], an NMR study by D.B. Zax and collaborators]

In order to further explore these dynamical heterogeneities in the nanoscopically confined polymer films, we further undertook dielectric spectroscopy studies of similar systems (2.2nm confined films intercalated in organo-silicates) of poly(methyl-phenyl siloxane) (PMPS) [5] which revealed a *new, confinement induced, extraordinarily fast, relaxation process,* which is completely absent in the bulk –unconfined– polymer behavior (figure 2, from reference [5] by S.H. Anastasiadis and collaborators).

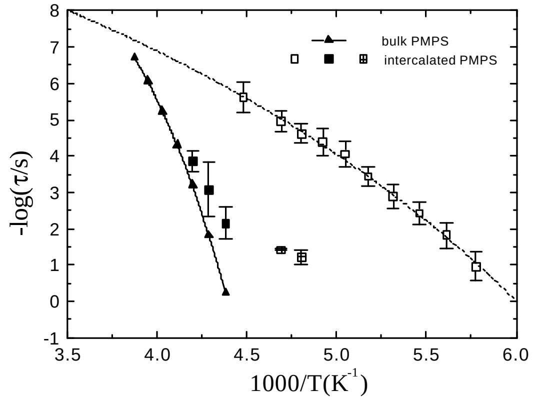

Figure 2. Arrhenius plot of the relaxation times associated with the bulk PMPS mode (▲), and modes observed for the same polymer in a 2.2nm confinement: a bulk-like (slow) mode (■), a confinement induced fast mode (□), and an intermediate process (⊠). Lines correspond to VFT fits to the data: for bulk PMPS (—) and the fast process of the confined PMPS (- - -). [adapted from [5], a dielectric spectroscopy study of severely confined polymers by S.H. Anastasiadis and collaborators].

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Computer modeling approach. In order to obtain some insight in the atomistic details of the structure of the confined –intercalated– polystyrene chains, we have carried out molecular simulations. As details of the simulations are given elsewhere, here we make only brief mention of the techniques employed. The rotational-isomeric-state (RIS) model was used to create initial polymer conformations of PS oligomers. Chain conformations that fit in the interlayer gallery were chosen, and the PS chains were equilibrated by an off-lattice Monte Carlo scheme that employs small random displacements of the backbone atoms and Orientational Biased Monte Carlo rotations of the phenyl rings; the surfactants were equilibrated by a Configurational Biased Monte Carlo (CBMC) scheme in coexistence with the polymer chains.

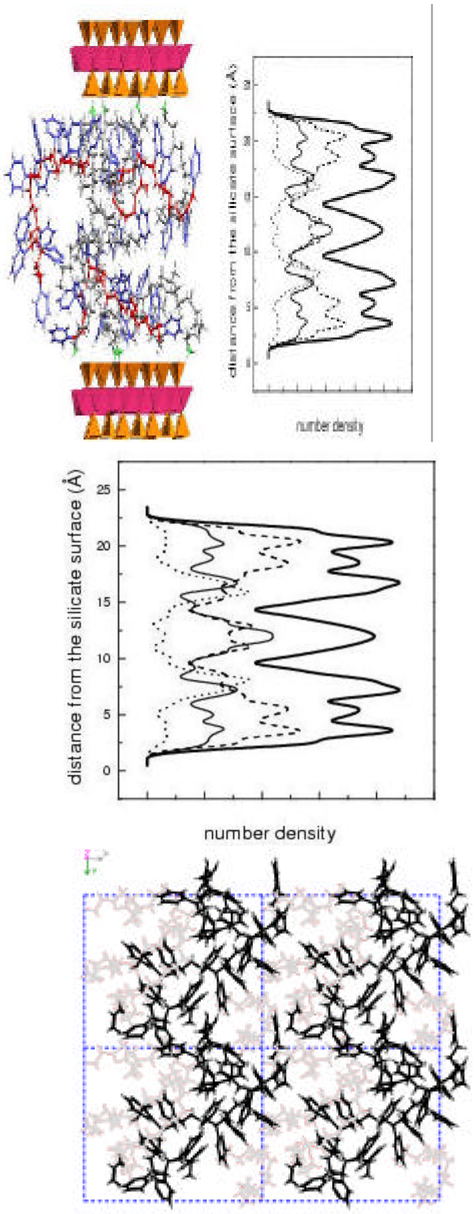

Figure 3. Some representations of the simulated PS intercalated system: A side view of the confined film (top), the corresponding density profiles of the different Carbon atoms across the intercalated film (middle), and a typical configuration parallel to the confining surfaces (bottom). The total density (thick solid line) shows a strong inhomogeneity across the 2.1nm film:The surfactant (thin solid line) shows a tendency to be preferentially in the center of the confined film, whereas the PS backbones are in two layers (dotted line), and the phenyl rings (dashed line) on either side of the chain backbones and thus in direct contact with the surfaces or in the center of the film. For the top view (bottom), the PS is in black color and the surfactant in gray. [figure adopted from [7], a study of high-M_W polymer mobility in 2.1nm slit pores].

After equilibration, Molecular Dynamics simulations were used to obtain the structure and density profiles of the intercalated oligomer/surfactant films. The numbers of polymer chains and alkyl-ammonium surfactants were chosen so as to match the densities found in the experimental studies (measured through TGA analysis). While several force fields have been proposed for PS, a force field similar to the one after of Müller-Plathe was chosen, because when combined with the force field we have developed for the organo-silicates [6], it reproduces the experimentally observed *d*-spacings. While the full power of MD is most often used to probe dynamical properties –and such a study is currently underway– the limited timescales simulated to date in our MD studies can only provide accurately a detailed picture of the structure within the interlayer gallery and the behavior of the *fast* relaxing species within the film.

Structure and dynamics of 2.1nm confined PS films. The structure of the film (as depicted in the density profile of figure 3) shows a strong inhomogeneity across the 2.1nm film in the form of a layering normal to the confining surfaces. Focusing momentarily on the polymer configuration provides some clues as to the origin of this layering effect. We find that the polymer backbone is predominately located near the confining wall –and at distances of about 0.3-0.7nm from that wall– but more removed, on average, than most of the phenyl sidechains. Very often, short strands of polymer adopt bridging configurations perpendicular to, and connecting between, both walls. The phenyl rings, which attach to the backbone at each methine, are similarly found in all three layers but are predominantly nearest the silicate surface. Finally, while surfactant methylenes are found distributed in all three layers, they bunch preferentially in the middle layer. As the head group of the surfactant is tethered via an ionic interaction to the negatively charged silicate, it cannot be completely displaced from the surface. In contrast, PS does displace the surfactant's aliphatic chains, and preferentially interacts with the surface. This is caused by the stronger attraction of the PS –compared to the surfactant– by the polar silicate layer and results in polymer chain conformations that are stretched ontop of the walls (2.1nm is about 3 styrene monomers wide anyway). The short end-tethered aliphatic surfactants are consequently forced to adopt small "mushroom" configurations (top view, figure 3 bottom).

Our MD simulations suggest that, while the layer in immediate contact with the surface maintains its integrity, styrene moieties –including both phenyl and backbone groups– not in direct contact with the silicate surface are more dynamic than in the bulk at the same temperature. This parallels our NMR findings on, of course, a vastly longer timescale. Faster modes appear to be characteristic of the parts of the polymer chains located toward the center of the intercalated film, where the local density (figure 3 center) is lower. This result would not appear to be in conflict with an increase in viscosity in thin confined films. As the polymer is held together by strong covalent bonds, macroscopic displacements –as are probed for example by SFA viscosity measurements– are determined by the *slowest* moving segments of the polymer. These strong dynamical inhomogeneities seem to originate from the same molecular mechanisms as those observed in previous MD modeling of much wider confined oligomer chain molecules [8,9]. Namely, moieties located in the denser parts of the confined films (as those in the immediate vicinity –first layer– of the walls) are characterized by extremely slow dynamics. In contrast, moieties located in the lower density regions exhibit very fast dynamics, in many cases faster than the fastest dynamics in the bulk.

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