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On the Existence of Quasi-Two-Dimensional Glasslike Structures at Strongly Interacting Polymer–Solid Interfaces

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In the previous decade much work has been done toward understanding the structure and dynamics of polymers adsorbed on solid surfaces (e.g., refs 1–8). Strongly interacting polymer interfaces, however, have been the subject of investigations only in recent years (e.g., refs 9–13). In these systems, specific functional groups of the organic polymer may chemisorb on the substrate surface. Examples of such systems are polymer–metal and polymer–metal oxide interfaces. Chemisorptive interactions are not only stronger than dispersive interactions but are also very specific. In other words, from an enthalpic viewpoint, only particular functional groups of the organic polymer prefer to chemisorb on the substrate. We note that certain systems wherein physisorption occurs may also exhibit specific segment–surface interactions. The interplay between these specifically directed enthalpic driving forces and the entropic constraints associated with confining chains near a solid surface may lead to special interfacial chain conformations. In this paper, on the basis of recent theoretical calculations[13] of the energy hypersurfaces for the interactions of oligomers with simple metal surfaces and molecular dynamics studies, we suggest that the structure of adsorbed chains at reactive polymer interfaces is that of a collection of nonequilibrium conformations. We also discuss the analogy between these structures and a bulk three-dimensional polymer glass. Theoretical and experimental work that could further probe these issues and their implications are also outlined.

Consider a polymer in an athermal solvent that is above its bulk glass transition temperature and interacts with a solid substrate upon which its segments may chemisorb. Furthermore, let us consider the situation wherein the energetics associated with solvent–surface interactions is far less than the thermal energy, kT. Let us first examine the energetics for the segment-level chemisorption of the organic polymer.

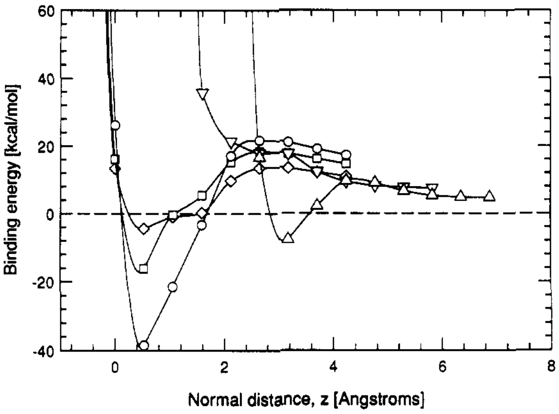

Figure 1. Interaction energies of a PMMA monomer on an aluminum surface.[13] The distance coordinate is the normal distance of the carbonyl oxygen atom from the jellium edge. Diamonds (◇) correspond to an orientation in which the carbonyl bond is perpendicular to the surface with the carbonyl oxygen atom closer to the surface than the carbonyl carbon; squares (□) correspond to an orientation in which the carbonyl bond makes an angle of 30° with the surface normal. In these cases, bonding occurs primarily with the carbonyl group. Upside-down triangles (▽) correspond to an orientation in which the carbonyl group is parallel to the surface; in this case, both the carbonyl group and the methoxy group are hindered from approaching the surface. Triangles (△) correspond to an orientation wherein the primary interactions are with the methoxy group. Circles (○) correspond to an orientation in which both the carbonyl and methoxy group interact favorably with the surface.

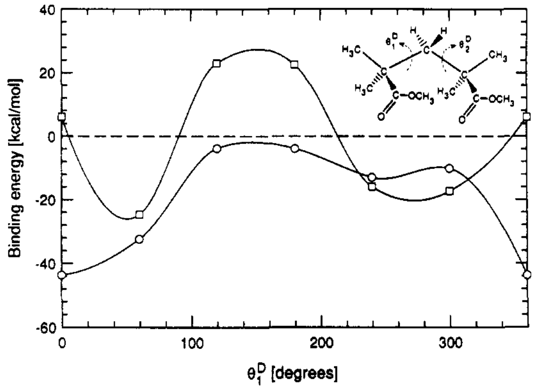

Figure 2. Sampling of binding energies of a PMMA meso dimer on an aluminum surface. Each point on these curves represents the most stable structure for a given set of internal degrees of freedom and orientation of the molecule with respect to the surface. For both curves shown here, the carbonyl bond that is closest to the surface makes an angle of 30° with the surface normal. Squares correspond to the torsion angle, θ_2^D, being fixed at 0°; circles correspond to the same torsion angle being fixed at 120°. Variation in the binding energies as a function of the torsion angle, θ_1^D, is shown. As is evident, there are many configuration-dependent minima that are sometimes separated from each other by barriers that are larger than kT at room temperature.

We choose as an example the segment–level interactions of an acrylic polymer, PMMA, with an aluminum surface. A recent study[13] based on quantum mechanical density functional theory has mapped out the energy hypersurfaces for these interactions as a function of various degrees of freedom. Figures 1 and 2 show portions of the energy hypersurfaces for the interactions of monomers and dimers of PMMA with an aluminum surface. These portions of the energy hypersurfaces show that the energetics of these interactions are highly dependent on the configuration and orientation of the segments as they approach the surface. In other words, the specificity and strength of the interactions lead to an energy hypersurface that is characterized by several local minima. Furthermore, several of the minima (and the barriers between them) are deeper (or higher) than the thermal energy, kT. There are several other interesting features of these energy hypersurfaces that have been discussed.[13] However, here we focus only on the fact that the energy hypersurfaces are characterized by several deep minima and high barriers. This is due to the specificity and strength of chemisorptive interactions. We also note that for the specific case of PMMA interacting with aluminum surfaces there are two sites that may potentially interact strongly with the surface. These are the carbonyl and methoxy functional groups; the carbonyl group interacts more strongly with the surface than the methoxy group. However, depending on the configuration and orientation of approach to the surface, at room temperature, both interaction energies can be greater than the thermal energy. Let us now examine the implications of such an energy hypersurface

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for the conformations adopted by the chains in the near-surface region.

Since the segment-level interactions are highly configuration dependent and the energetics involved (minima and barriers) are often larger than the thermal energy, we suggest that the chains will adsorb in nonequilibrium conformations. Let us discuss the reasoning that underlies this suggestion in detail using PMMA on aluminum as an example.

The energy hypersurfaces shown in Figures 1 and 2 show that there are energy minima associated with certain configurations and orientations of oligomers approaching the surface that are not global minima, and these minima are separated from each other and the global minimum by barriers that are often larger than the thermal energy. As such, the system is kinetically constrained from accommodating itself in a global minimum of free energy. Thus, long chains subject to such segment–surface potentials are expected to adsorb in orientations and conformations that are frozen-in, nonequilibrium structures. For the case of PMMA on aluminum some of the segments will adsorb via the methoxy group and others via interactions with the carbonyl group. It is expected that as the chains approach the surface many segments will get pinned on the surface because the binding energies are large.[13] Of course, entropic contraints and steric exclusion will not allow all segments to get pinned. However, compared to weakly physisorbed chains, long-chain molecules should adsorb on reactive surfaces in flatter conformations with fewer loops and tails. This is also suggested by recent ^{13}C solid-state NMR studies of PMMA adsorbed on a native aluminum oxide surface.[14] Thus, one may say that the adsorbed layer forms a quasi-two-dimensional structure, with each chain being adsorbed in a different nonequilibrium conformation. In other words, the adsorbed polymer layer may be considered to be a quasi-two-dimensional analogue of a bulk polymer "glass". Note that this is strictly just an analogy. A bulk polymer glass is a collection of nonequilibrium structures due to kinetic restrictions to motion below the glass transition temperature, T_g. For strongly interacting polymer interfaces the adsorbed layer is also a collection of nonequilibrium structures. It is only in this sense that we say that the adsorbed layer may be considered to be a quasi-two-dimensional glass. In this case, the kinetic constraints to motion are largely due to the segment–surface interactions that are such that the adsorbed segments (and thus the chain molecules) get trapped in local minima.

We note that speculations regarding the existence of glasslike structures for adsorbed polymer layers have been discussed previously by Kremer.[15] However, Kremer based his ideas on the fact that even for weakly interacting polymer layers, upon adsorption from solutions below T_g, there is an enhanced density near the surface. Thus, there may be too little solvent present to keep the polymer plasticized and this could lead to the formation of a glassy layer adjacent to the surface. As we have pointed out, the reason for the existence of a quasi-two-dimensional nonequilibrium (glasslike) structure near polymer interfaces characterized by strong and specific segment-level interactions is totally different and has no connection with the bulk glass transition temperature. In fact, the phenomena discussed herein could occur above or below T_g.

In analogy with bulk polymer glasses we now define transition temperatures at which there is an enhancement of mobility, ultimately leading to equilibrium structures. This can be seen easily by considering the following thought experiment. Consider a system similar to the PMMA–aluminum interface; i.e., each segment contains two potentially reactive functional groups, one of which bonds to the surface more strongly than the other. If we now heat the adsorbed polymer layer we expect the following to happen. Let the binding energy of one functional group be E_1 and the other be E_2. Furthermore, let $E_1 < E_2$. If we raise the temperature of the system to T_1, wherein $E_1 \simeq kT_1$, then the bonds formed by segments that were attached via the functional group that interacts less strongly will be thermalized. This will lead to enhanced local mobility. However, the motion of the adsorbed chains will still be restricted, because many of the segments that are bonded to the surface with energy E_2 will still remain pinned. It is even possible that due to enhanced local mobility some fraction of the segments that were bound to the surface via the weaker functional group may be able to reorient to allow the other functional group to bind to the surface. We note, however, that at this temperature large-scale motion of the adsorbed chains will still not be permitted, and the adsorbed layer is still a collection of nonequilibrium structures. The temperature, T_1, may thus be viewed loosely to be an analogue of the β-transition temperature for bulk polymers. If the system is heated further to a temperature T_2 ($E_2 \simeq kT_2$), then the stronger bond is also thermalized and the adsorbed chains adopt their equilibrium conformations. Large-scale motions are now allowed. The temperature T_2 may be viewed to be an analogue of the glass transition temperature for bulk polymers. We note that these transitions will not occur sharply at T_1 and T_2 but, rather, will be broad due to reasons that we will not discuss herein. Furthermore, since the binding energies for the PMMA–aluminum system are very high, we would not be able to observe these transition temperatures experimentally for this system. However, one could envisage choosing the functional groups in a polymer–substrate system judiciously such that these transition temperatures could be observed experimentally.

In order to provide evidence for our suggestion that nonequilibrium structures constitute the near-surface structure of reactive polymer interfaces, we have performed molecular dynamics (MD) simulations. The system that we have studied using MD simulations is one wherein the interactions of the chain molecules with the solid surface are characterized by segment–surface potentials that are much simpler than that for the PMMA–aluminum system. However, most of the important qualitative features are retained in our model system. The preliminary results that we report herein support the idea that each realization of the structure of adsorbed chains leads to different nonequilibrium conformations.

The situation that we have simulated corresponds to adsorption of chains containing strongly interacting functional groups from very dilute solutions. We consider the case wherein the solvent does not interact strongly with the surface. Thus, in this preliminary study, we report results for MD simulations that investigate the adsorption of single chains from a simulation box (35.94 Å in size) containing 467 solvent molecules. Periodic boundary conditions are imposed. We note that interchain interactions are ignored in our simulations. However, we do not expect the incorporation of such interactions to lead to any qualitative changes in the results reported herein regarding the existence of nonequilibrium structures in the near-surface region of reactive polymer interfaces.

Our MD simulations have been performed with chain molecules characterized by the surface interactions discussed earlier in developing the idea of transition temperatures. Each segment contains two pendant groups

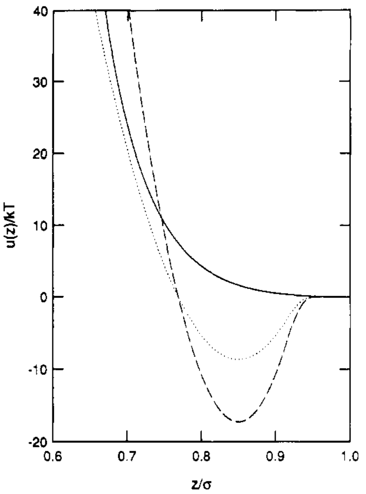

Figure 3. Potential functions that have been used to represent wall–polymer and wall–solvent interactions. — represents the interactions of the solvent and the chain backbone with the surface; - - - represents the interactions of the stronger pendant sticker group; ··· represents the interactions of the weaker pendant sticker group.

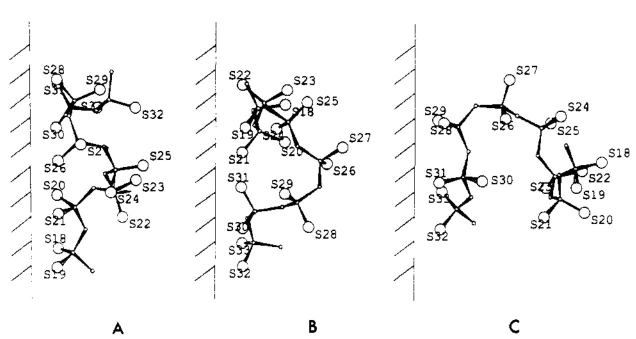

Figure 4. Three different realizations of the nonequilibrium adsorbed chain structures. The even-numbered stickers are the stronger stickers.

that interact strongly with the surface. The interactions of the pendant groups with the surface are represented by binding wells with no activation barriers to adsorption. As such, this system does not reflect the presence of activation barriers that characterize the energy hypersurface for PMMA–aluminum interactions. However, the energy barriers associated with specific functional groups being detached from the surface are retained in this simple model. The binding wells for the two pendant groups are parabolic with well depths of 8.6 and 17.2 kT for the weaker and stronger stickers, respectively. The minima of the potential wells are located at a distance of 0.85σ (σ = 3.92 Å) from the featureless surface, and both stickers begin to experience the wall potential when they approach a distance of 0.95σ from the wall. The backbone atoms from which the pendant groups emanate interact with the wall via a truncated and shifted Lennard-Jones potential, with a value of the energy parameter, ϵ/k, equal to 72 K. The solvent molecules interact with the wall with a potential that is identical with that of the chain backbone. These wall–polymer and wall–solvent potentials are depicted in Figure 3.

In our simulations, the rattle algorithm[16] is used to maintain constant bond lengths for the chain molecule. A harmonic bond-bending potential is employed, and a 3-fold symmetric modification of the torsion potential for butane[17] is used. The other nonbonded atoms (that are more than three atoms away) interact with each other via Lennard-Jones potentials with σ = 3.92 Å and ϵ/k = 72 K. The solvent molecules interact with each other and the polymer atoms via exactly the same Lennard-Jones potential. The simulation procedure can be described briefly as follows. A minimum-energy chain structure is generated by using MOPAC.[18] Monte Carlo insertion of the solvent is followed by isothermal MD equilibration. Constant-energy MD then proceeds with a time step of 2 fs. All the MD results reported here are for a temperature of 200 K.

In this paper, we present preliminary results of our MD simulations that provide evidence for the existence of nonequilibrium structures at polymer–solid interfaces characterized by strong and specific segment-level interactions. Figure 4 depicts three different realizations of the adsorption process for octamers characterized by the model described above. We note that these three realizations are merely representative of the various conformations of the adsorbed chains that we have obtained. Each of the three structures shown in Figure 4 has not undergone any major conformational changes for over 200 ps, and furthermore, the time required to attain each of these frozen-in, nonequilibrium conformations is quite different. We note that each of the realizations depicted in Figure 4 corresponds to different initial conditions. The point we wish to make from these results is simply that each realization of the adsorption process leads to a very different chain architecture and bonding to the surface. For example, the conformation depicted in Figure 4A is bound to the surface via five strong stickers and three weak stickers, while the one shown in Figure 4C is bound via two strong stickers and three weak stickers; further, the chain conformations are quite different. The results show the history dependence of the structure of chains adsorbed on a reactive solid substrate. Thus, the MD results support our arguments regarding the existence of nonequilibrium chain structures in the near-surface region of reactive polymer interfaces.

The formation of locked-in, nonequilibrium structures in the near-surface region of the polymer interfaces we have been considering may have significant pragmatic consequences. An important point that should be noted is that the structure of the nonequilibrium adsorbed layer will be highly history dependent. One manifestation of this history dependence of interfacial structure could be that the nature of the adsorbed layer will depend on the concentration of the solution from which adsorption is carried out. Ponce et al.[19] have measured the peel strength of PMMA adsorbed on native aluminum oxide as a function of solution concentration. Their experimental results show the strong dependence of peel strength on the initial solution concentration. This result provides some evidence for the history dependence of interfacial structure for reactive polymer interfaces. The formation of strong bonds at the segment level and the relatively flat conformations of the adsorbed chains are expected to lead to high adhesive strengths compared to those of physisorbed layers. However, there is the possibility of cohesive failure occurring at the diffuse interface between the glasslike adsorbed layer and the rubbery layer of chains that are not directly attached to the substrate. Recently, some experimental evidence for the possibility of such cohesive failure has been provided by Hill et al.[20]

Currently, in our laboratories both theoretical and experimental work is being pursued to further investigate the structures of the quasi-two-dimensional glasslike systems and the transition temperatures discussed in this paper. Theoretical work focuses on performing stochastic molecular simulations that capture the constrained dynamics that characterize these systems. Experimental work using solid-state NMR spectroscopy is also being utilized to examine the mobility of chains adsorbed at reactive polymer–solid interfaces by observing changes in line shape as a function of temperature.

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Registry No. PMMA, 9011-14-7; aluminum, 7429-90-5.