# Polymers near Metal Surfaces: Selective Adsorption and Global Conformations

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We study the properties of a polycarbonate melt near a nickel surface as a model system for the interaction of polymers with metal surfaces by employing a multiscale modeling approach. For bulk properties, a suitably coarse-grained bead-spring model is simulated by molecular dynamics methods with model parameters directly derived from quantum chemical calculations. The surface interactions are parametrized and incorporated by extensive quantum mechanical density functional calculations using the Car-Parrinello method. We find strong chemisorption of chain ends, resulting in significant modifications of the melt composition when compared to an inert wall.

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Understanding how polymer molecules behave near metal surfaces would greatly enhance our ability to control essential interfacial properties in a wide variety of problems, including adhesion, wetting and nanodewetting, biomolecular recognition, and self-assembly, to name a few [1,2]. Such an understanding is, however, difficult to obtain, because widely disparate length scales come into play [3]. Specifically, atomic-scale energetics dominate at the interface, where chemisorption and physisorption of different small parts of the polymer molecules may occur. Such details of the interaction in turn affect the entropically governed shapes of entire molecules and thus the bulk properties of the melt close to the surface. Gaining a better understanding of the fundamental nature of such an interface thus requires a multiscale modeling approach. The purpose of this Letter is to describe a novel multiscale simulation for molecular-level modeling of polymers near metal surfaces. Liquid polycarbonate near a nickel surface is taken as a first example. It displays specific challenges to the method and at the same time is of high technical relevance, where fine control over material properties at the polymer-die interface is crucial (e.g., production of compact disks).

We combine *ab initio* calculations for the interaction of fragments of bisphenol-A-polycarbonate [BPA-PC; Fig. 1(a)] and Ni with molecular-level coarse-grained simulations of the polymer melt near a wall. In most polymerization processes for PC, the chain ends are phenoxy rings. We find that the adsorption of the phenoxy chain ends significantly alters the local melt structure. Such information is difficult to obtain directly from experiment and bears specific relevance to both the design of polymer recipes and die surfaces for optimal processing. Since the fragments considered here are not unique to BPA-PC; the results are of general importance for many organic polymers including biopolymers close to metal surfaces.

We first describe the *ab initio* part of our work. Then we introduce the coarse-grained model and its modification to incorporate specific surface interactions and apply this to the PC melt near a Ni surface.

Our motivation to perform *ab initio* calculations is to ultimately understand how BPA-PC molecules interact with well-characterized surfaces. Such calculations are so expensive, however, that the study of even a single unit of BPA-PC near a Ni surface is not feasible. Our strategy is to cut the chain into comonomeric molecules, small enough to study the interaction with the surface. We consider three molecules analogous to the comonomeric subunits of BPA-PC [Fig. 1(b)]: carbonic acid (i), propane (ii), and benzene (iii) representing carbonate, isopropylidene, and phenylene, respectively. Additionally, to systematically test our choices for the small molecule analogues, we also consider phenol (iv). Moreover, phenol itself on a metal surface is important, due to its toxicity, catalytic activity, and widespread occurrence as a by-product. For our purposes here, however, we focus on how these molecules behave *as BPA-PC comonomers*, and examine the adsorption on a Ni{111} surface. For

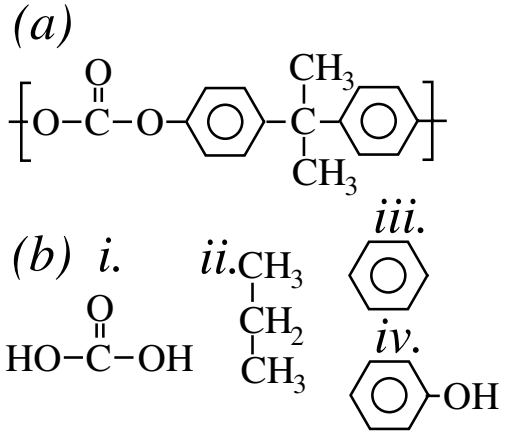


FIG. 1. (a) Chemical structure of the repeat unit BPA-PC. (b) Analogous molecules used in the *ab initio* studies: (i) carbonic acid, (ii) propane, (iii) benzene, and (iv) phenol.

  

benzene on Ni{111}, we found an adsorption energy and geometry in good agreement with Refs. [4,5,6]. The main results to emerge from our *ab initio* calculations, and incorporated into the coarse-grained model, are that the carbonic acid and propane molecules do not stick to the surface. Benzene, which has a strong adsorption in isolation, is sterically hindered to adsorb when incorporated into a BPA-PC chain, due to neighboring carbonate and isopropylidene groups. However, phenoxy end groups are not in this way sterically hindered, and, hence, may adsorb strongly to the surface.

We used the plane-wave pseudopotential CPMD code [7], implemented with finite-temperature density functional theory [8,9]. The orbital cutoff was set to 60 Ry. We used the Perdew-Burke-Ernzerhof [10] generalized gradient approximation (GGA). The surface is represented by four close-packed layers of Ni{111} (lattice parameter $a_0 = 3.543$ Å), with the top two layers allowed to relax. We used a $(2 \times 2)$ lateral supercell for carbonic acid and propane adsorption, and a $(3 \times 3)$ cell for benzene and phenol, employing $4 \times 4 \times 1$ and $3 \times 3 \times 1$ $k$-point mesh for the smaller and larger cells, respectively. Several geometry optimizations, starting from plausible structures compatible with possible orientations of the respective comonomers in a polymer chain, were performed at each of the four high-symmetry sites of the {111} surface. The adsorption energy ($E_{ad}$), Table I, defined as the energy of the adsorption system relative to the clean surface and isolated molecule, characterizes the strength of the interaction of each submolecule with the surface.

For both carbonic acid and propane, $E_{ad}$ turned out to be rather small, 0.01 eV, which is both negligible compared to the inherent error due to the GGA and smaller than the characteristic thermal energies in typical melt processing of polycarbonate. The adsorption energies were not significantly changed by going to a larger cell $(3 \times 3)$, i.e., lower coverage. Significant repulsion was experienced by both propane and carbonate below 3.2 Å, regardless of orientation, implying that achieving distances smaller than this value are highly improbable.

Benzene [11], however, experiences a strong adsorption energy of $E_{ad} = 1.05$ eV at a center-of-mass distance $\approx$ 2 Å from the surface and in a horizontal orientation, in very good agreement with [4]. Since the carbonate and isopropylidene moities show strong repulsion for distances shorter than 3.2 Å, phenylene is sterically forbidden by its neighbors to approach the surface to its ideal adsorption distance. We therefore examined the interaction of benzene with the surface at larger distances, finding that adsorption is short ranged and decays below 0.03 eV at a distance beyond 3 Å. Therefore an *internal* phenylene comonomer has only a weak interaction with the surface. For phenol, we calculate an $E_{ad} = 0.9$ eV, at a distance of 2.0 Å. Because no steric hindrance to the horizontal approach of a phenoxy end group to the surface exists, it is likely that *only* the chain ends adsorb strongly to the surface. We incorporate the above information into a coarse-grained model of BPA-PC melts next to a Ni{111} wall. More details and results of the *ab initio* study will be presented in a forthcoming publication [12].

TABLE I. Adsorption energies at high-symmetry sites.

| $E_{ad}$ (eV) | Propane | Carbonic acid | Benzene | Phenol |
|---|---|---|---|---|
| FCC | 0.01 | 0.01 | | 0.79 |
| HCP | 0.01 | 0.01 | | 0.84 |
| Atop | 0.01 | 0.01 | | 0.02 |
| Bridge | 0.01 | 0.01 | 1.05 | 0.91 |

Our polymer model is based on a previously presented coarse-graining technique [13], in the meanwhile improved [14]. The model reduces the number of degrees of freedom ("particles") required to faithfully simulate specific polymer melts at a mesoscopic level to a minimum. Such a coarsening is necessary to generate equilibrated samples of long polymer chain liquids [13], whose many different conformations are governed by the intrachain entropy, $S \propto N$, $N$ the number of repeat units. Briefly, the atomic structure is mapped onto a bead-spring chain, where each bead, or mapping point, represents a specific comonomer [Fig. 2(a)], resulting in four beads per BPA-PC repeat unit. This requires the enforcement of (i) fixed bead-bead bond lengths along the backbone; (ii) specific bond angle distributions at each bead type; and (iii) torsional states around bead-bead bonds along the backbone. The bond angle potential around the carbonate-type bead and the torsional potential at the phenylene connection between carbonate and isopropylidene beads are obtained from a Boltzmann inversion of distribution functions of an all-atom simulation of isolated chains at the desired temperature, which is 570 K in our case. The average bead diameter and intermolecular length scale, which reflects the excluded volume of the molecules, fixes the mass and volume density of the melt [13]. Finally, planar Lennard-Jones 10–4 potentials represent the smooth confining walls [15]. The bead-specific distances at which monomer subunits experience an average $1kT$ repulsion is taken directly from the *ab initio* calculations. For the phenoxy end groups and an attractive wall, the 10–4 potential is modified to show a well depth of $5kT$ at a distance of 2.7 Å. This distance is chosen because we represent the phenoxy end group as a sphere [Fig. 2(b)], and the $5kT/2.7$ Å potential reflects to first order an average over all near-surface orientations of phenol, including the horizontally oriented strongly adsorbed state [16].

We simulated melts of 160 chains of 20 repeat units (83 beads per chain, or a molecular weight of 5292), in a rectilinear box $(L \times L \times 2L)$, by straightforward molecular dynamics. The runs are long enough to equilibrate the chain conformations in bulk and near the surface [15].

Because phenoxy chain ends are likely to stick strongly to the surface, we focus on this effect in the coarse-grained BPA-PC model. To do this, we consider the

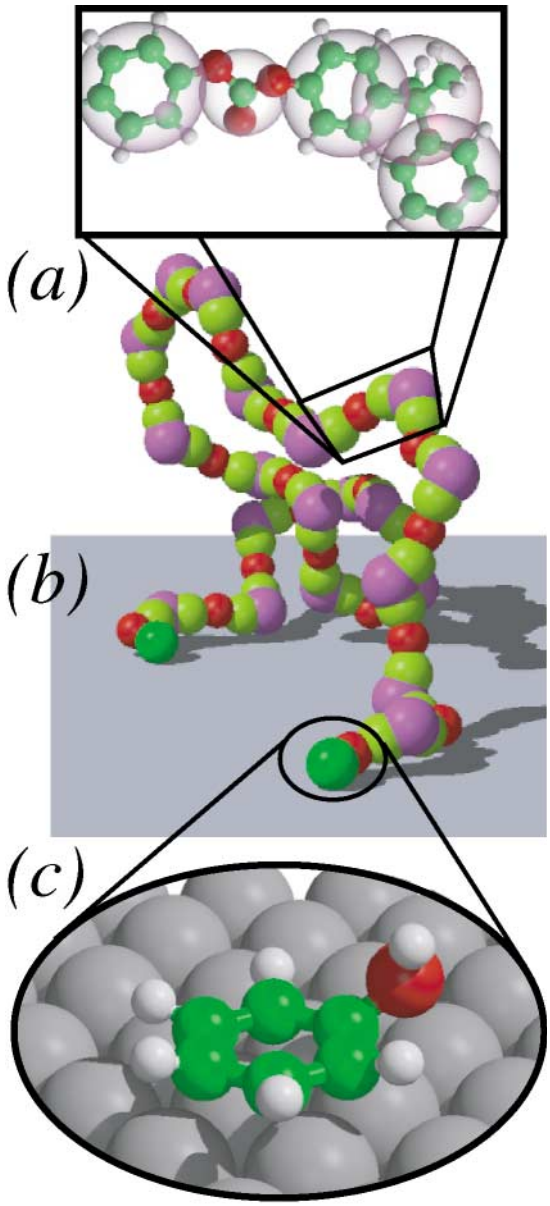


FIG. 2 (color). The multiscale model of BPA-PC on nickel. (a) The coarse-grained representation of a BPA-PC segment; the coarse-grained beads are transparent spheres, superimposed on the underlying chemical structure, where the carbon atoms are green, the oxygens red, and the hydrogens white. (b) Coarse-grained model of an $N = 20$ BPA-PC molecule, with ends adsorbed on a flat surface; configuration from a 160-chain liquid simulation. (c) A phenol molecule adsorbed on the bridge site of a (111) nickel surface; configuration computed via CPMD simulation.

number density of phenoxy end groups, $\rho_p$, as a function of distance from the walls, $z$. To compare to experiments for spatially resolved compositional analyses, a more natural quantity to consider is a cumulative normalized function, $F(z)$, defined as

$$F(z) \equiv \frac{1}{\rho_{p0} z} \int_0^z \rho_p(z')dz', \qquad (1)$$

where $\rho_{p0}$ is the bulk density of chain ends. $F(z)$ is the ratio of the number of end groups in a layer between 0 and $z$ and the number expected in such a layer given the overall density of the system *in the absence of walls*. $F(z)$ can be referred to as an intensity, which is the natural observable of some depth-resolved experimental techniques, such as angle-resolved x-ray photoelectron spectroscopy [17], none of which, to our knowledge, have yet been applied to polycarbonate/nickel interfaces.

In Fig. 3, we show $F(z)$ for the case in which the walls are completely neutral, and for the case in which the phenoxy end groups are allowed to adsorb via the energetic interaction discussed previously. Also shown in the inset is $\rho_p(z)$ for $z < 40$ Å. For neutral walls, the cumulative density quickly rises to the bulk value and remains constant. For this case, there is a weak localization of phenoxy end groups at the surface (Fig. 3, inset), which is balanced by depletion on a length scale about one repeat unit ( $\sim 8$ Å). However, the cumulative normalized density never exceeds unity.

The situation is dramatically different when the chain ends are preferentially attracted to the walls. Here, $F(z)$ displays a steeply rising overshoot, which shows that the surface has a roughly eight-times excess of end groups. Though $F(z)$ decays over long length scales relative to the attractive potential, the chain ends are strongly localized

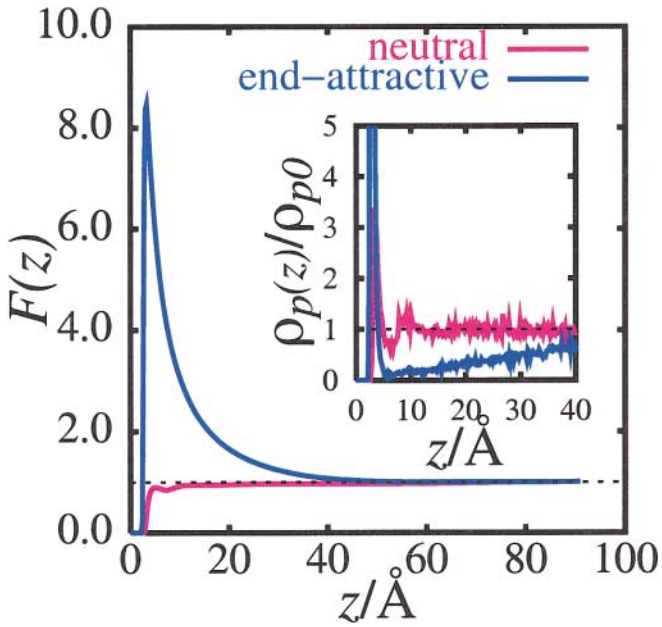


FIG. 3 (color). Cumulative normalized density of chain ends, $F(z)$ [Eq. (1)] vs distance from wall, $z$, for a neutral wall and a wall displaying strong attraction to chain end beads (10–4 Lennard-Jones potential with $\sigma = 2.7$ Å and $\epsilon = 5kT$) for a melt of 160 20-repeat unit BPA-PC chains at mass density 1.05 g/cm$^3$ and temperature $T = 570$ K. Inset shows normalized number density of phenoxy ends, $\rho_p/\rho_{0p}$ vs $z$ for $z <$ 40 Å. For clarity, the $y$ maximum of the inset is truncated at 5.0, though $\rho_p(z)/\rho_{0p}$ for the attractive ends has a peak maximum of about 45.0.

near the surface (inset of Fig. 3). Also, there is a large depletion zone of chain ends in the liquid adjacent to this strongly adsorbed layer. As $z$ increases, the end-group intensity decays to the bulk value at about 40 Å from the wall, which is larger than the mean gyration radius of about 30 Å. Viscoelastic consequences will be the subject of future work.

These results are intriguing in light of previous simulations [18] of simple bead-spring chains, which showed that neither neutral nor attractive walls produced chain end depletion layers that reflect the size of the chains. Our results indicate that walls that adsorb only chain ends do indeed show such a region in the melt. This highlights the importance of chain end mobility (and small molecule impurities) in the overall composition of a thin adsorbed polymer film.

In contrast, more recent mean-field calculations [19] contend that natural enhancement of chain ends at neutral surfaces results in near-surface excess ends with an adjacent depletion zone whose depth reflects the size of the chains. Our results indicate that this is not a generic property of polymers. Instead, we find that this is observed only with an explicit end-surface attraction. When no such attraction is given, perturbations in end-group distribution in the liquid die out much less than a depth of $R_g$ from the wall. The discrepancy arises from the interplay between the intrachain statistics and the packing of the irregularly shaped monomers near the surface.

By employing a multiscale approach, we showed how the interplay of entropic and energetic contributions can alter the structure of a polymer melt near a metal surface. Specifically, we predict that polycarbonate chain ends adsorb strongly to a nickel surface next to a polycarbonate liquid. This suggests modifying chain ends provides a reasonably sensitive way to control interfacial behavior of polycarbonate in the manufacture of optical data storage devices, and other modern nanostructured surfaces. The technique of marrying *ab initio* calculations involving small molecule analogues of polymeric comonomers with chemically specific coarse-grained models opens up the possibility to study a wide array of biomolecule/metal surface interactions. Thus, this study sheds new light on the technically important field of polymer/metal surface interactions and highlights the important need for experimental contributions.

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