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## LETTER TO THE EDITOR

## Specific interaction of polymers with surface defects: structure formation of polycarbonate on nickel

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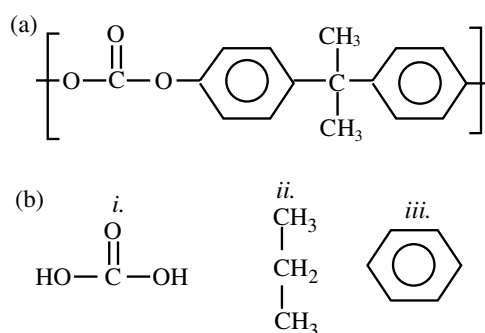
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### Abstract

By combining quantum *ab initio* calculations and coarse grained polymer models we employ a multiscale approach to study site specific adsorption of polymers (polycarbonate) to a step on an otherwise perfectly flat nickel (111) surface. The presence of the defect leads to a well defined chain localization and ordering at the surface. This can be taken as a model situation for both surface site as well as chemical group (within the chain monomer) specific interaction of macromolecules with metal surfaces. The results shed some light on important possible mechanisms occurring at step defects and corners used to control mineralization processes and thus material properties.

### 1. Introduction

Organic–inorganic interfaces occur in many problems of modern materials science as well as in many investigations and applications involving biological macromolecules. Adsorption of biopolymers onto solid surfaces plays the key role in important biophysical experiments and bioengineering processes [1–7]. The coupling to such surfaces giving rise to adhesion is a classical problem in modern materials science. Introduction of specific groups in the polymer can support adhesion strongly; this in turn can have rather strong effects on both dynamical and morphological aspects [8–13], thus providing a versatile way to control material properties as well as processing. Because of the simultaneous relevance of chemistry specific interactions and of generic macromolecular properties, theoretical investigations have to focus on specific reference systems. One such example is the nickel–polycarbonate melt interface, which plays an important role in compact disc production. It has been shown before [14–16] that specific local interactions can modify the morphology of (short chain) melts close to the surface and into the bulk beyond the typical radius of gyration. Thus, due to the correlation of the chemistry with macroscopic physical properties, rather different scales of length and time are involved. Locally, conformations are the consequence of a delicate interplay of conformational and packing entropy and metal–polymer selective adsorption. Because of that, the bead–spring



**Figure 1.** (a) The chemical structure of the BPA-PC repeat unit. (b) The submolecules considered: carbonic acid (i) corresponding to the carbonate group, propane (ii) corresponding to isopropylidene and benzene (iii) corresponding to phenylene.

polymer models usually employed interacting with an idealized structureless flat wall cannot be used without further refinement.

## 2. Bisphenol-A-polycarbonate on a nickel surface

### 2.1. Flat (111) surface

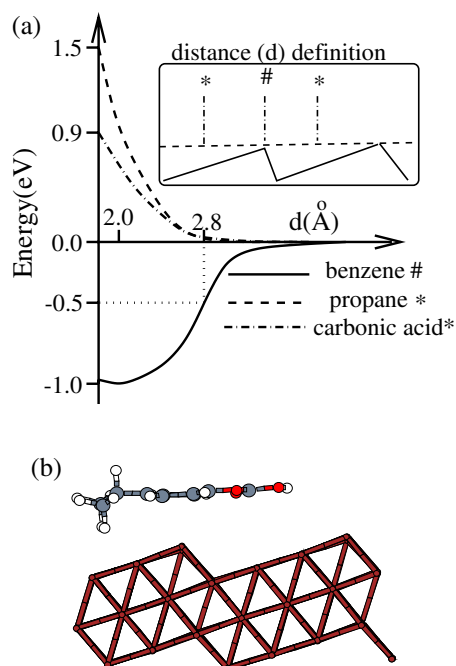
In previous work [14–18] we have introduced a hierarchical (multiscale) modelling approach for studying the interaction between a melt of bisphenol-A-polycarbonate (BPA-PC; figure 1(a)) and a perfect (111) surface of nickel (Ni). By applying an adsorption mechanism, where the potentials with the surface introduced in the coarse grained bead–spring models are derived from *ab initio* density functional calculations of BPA-PC submolecules (figure 1(b)) interacting with a Ni surface, we were able to predict interface properties. Intra-chain and inter-chain potentials for the coarse graining bead–spring model of the polymer were previously developed (see e.g. [19, 20] and references therein) and proven to reproduce experimental data (see [21]). It was found that internal beads experience the surface as a purely repulsive hard wall. When considering typical phenoxy chain ends, which strongly bind to the surface, an energy dominated amorphous melt–polymer brush-like layering with the chain ends sticking to the surface was found. It extends its influence deep into the bulk, to a distance of about  $2R_g$  where  $R_g$  is the mean gyration radius of the chains [14, 15]. Other chain ends studied experience either no or only a very weak attraction. In those cases the interface properties are dominated by local packing and conformational entropy, with the chain ends pointing into the polymer bulk rather than to the solid surface [16].

### 2.2. The step (221) surface

So far only perfect defect free surfaces have been considered. However, experimentally a perfect flat surface is very difficult to obtain. Thus it is important to see whether the above picture is significantly modified by surface defects and whether, in turn, specific ‘defects’ might even be used to induce a nucleus for structure formation. For this reason we extend our previous multiscale simulation study to a Ni surface with a step defect. We show that this introduces a new important aspect. While for a flat surface only chain ends can adsorb, on an imperfect surface internal beads can be strongly adsorbed at a step defect as well. This, in turn, leads to a strong chain localization and orientational order at the step, which might play the

role of a stable nucleus for structure formation, and cause a rather different melt morphology close to the step. Current studies of molecular adsorption at surface steps only deal with small polar molecules. For those the anchoring effect of the step is well known [22–24]. However, for macromolecules, the local coupling interaction provides only a part of the necessary input, as the global conformational properties of the chains are at least equally important due to the large conformational entropy ( $O(N)k_B T$ ,  $k_B T$  being the thermal energy). Consequently molecular adsorption for polymers is dominated by the interplay of these two contributions. This means that an exhaustive study can be made only via a multiscale approach which links the quantum based calculation of molecular adsorption energies with the conformational and packing statistics. The present application of the multiscale modelling procedure should not be considered as limited to a specific system but rather as a characteristic test case of both the modelling procedure and the basic adsorption mechanisms of large molecules. The special features of such adsorption processes might be used on purpose to modify material properties.

*2.2.1. Ab initio modelling.* As for the flat case, the starting point of this modelling scheme is the *ab initio* description of the beads–surface defect interaction. Following the same scheme adopted before, we use the CPMD code [25], in the FEMD [26] version, to study the interaction of submolecules of BPA-PC, namely carbonic acid, propane and benzene, on a (221) surface step of Ni. In this *ab initio* method, with a self-consistent procedure, the electron density and the Hellmann–Feynman forces are computed using a subspace diagonalization of a high temperature electron density matrix. The subspace is expanded in a plane-wave basis set up to a cut-off of 60 Ry. A partial occupation of states at Fermi level can be handled and  $k$ -point sampling is also implemented. The (221) surface of Ni is modelled using a  $(1 \times 3)$  unit cell and three (111) layers. We employ a  $4 \times 4 \times 1$   $k$ -point mesh in the Monkhorst–Pack scheme. Troullier–Martins pseudopotentials are used for carbon and oxygen [27], a local pseudopotential is used for hydrogen [28] and for nickel we chose the pseudopotential developed by Lee [29]. We use the PBE [30] generalized gradient approximation (GGA). We tested our setting by accurately reproducing bulk and surface properties of nickel; moreover, we were able to reproduce, within a maximum of 10% tolerance, experimental and theoretical results of adsorption of aromatic molecules onto the (111) surface of nickel; more details about the *ab initio* study can be found in [31] and references therein. As for the flat case, we have implicitly neglected dispersion effects which are not reproduced by current density functionals. This approximation is justified since the difference between the adsorption energies provides the required information for developing an accurate coarse grained model. In our case the separation between the energy scales corresponding to the different submolecules is almost one order of magnitude larger than the expected dispersion effects and it is not likely that dispersion effects will dramatically change our predictions. As in our previous work, we incorporate the *ab initio* results into a coarse grained bead–spring model, especially adapted for BPA-PC [19, 20]. Figure 2 illustrates the adsorption mechanism of a BPA-PC unit on the step. Like in the flat case, carbonic acid and propane experience the step surface as a purely repulsive wall, while benzene experiences a strong, short range attraction. When the different submolecules are combined to represent a BPA-PC chain, for the flat case, the surface repulsion of adjacent carbonic acid and propane submolecules is significantly stronger than the attraction of the internal benzene. This competition results in an overall repulsion of the monomer from the surface, and only the phenylene chain ends can adsorb. Right at the step the situation is different. The range of attraction for benzene in the  $z$ -direction (figure 2(a)) extends further out than for the flat surface (at a distance of 2.8 Å from the step the adsorption energy ( $E_{ad}$ ) is 0.5 eV, compared to 0.2 eV of the flat case). More important however is that the sterical



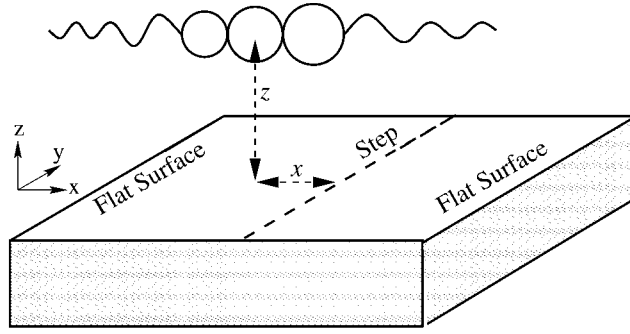
**Figure 2.** (a) A schematic representation of the adsorption energy for the different submolecules. The definition of the distance from the surface for the different beads is pictorially represented in the inset;  $d$  is defined for all kinds of beads as  $d = z - z_0$  where  $z_0$  is the  $z$ -coordinate of the atoms at the step edge. This definition is only valid when the benzene is at the step edge and the neighbouring beads are displaced from the step along  $x$ . Because the attraction for benzene occurs only at the step, where a strong repulsion is experienced by the other beads, the polymer unit can adsorb only in the configuration given in (b). (b) The ideal sequence of the three submolecules (isopropylidene-phenylene-carbonate), as in a BPA-PC chain, at the step. Due to the topology of the surface, phenylene (benzene), at the step edge, can approach the surface to a closer distance than in the flat case. The figure corresponds to the combination of the snapshots of each submolecule-surface configuration calculated via CPMD. Next they are combined to show how they would ideally form a sequence in the BPA-PC chain.

(This figure is in colour only in the electronic version)

hindrance for the phenylene adsorbing is almost vanishing (see figure 2(b)) in the special case where the chain backbone, projected onto the surface, is oriented perpendicular to the defect line. The combination of energetic and topological effects can lead to a net adsorption of internal phenylenes right at the step.

**2.2.2. The coarse grained model and simulation.** In order to determine, in particular, the effect of internal phenylene adsorption, we consider non-attractive chain ends. The geometry considered is shown in figure 3. Along the  $x$ -direction, far from the step, the surface behaves as a flat one and its interaction with the polymer beads is described by planar 10-4 Lennard-Jones potentials [14, 15]:

$$U_{\text{wall}}(z) = \begin{cases} 2\pi\epsilon_w\sigma_w^2 \left[ \frac{2}{5} \left( \frac{\sigma_w}{z} \right)^{10} - \left( \frac{\sigma_w}{z} \right)^4 + \frac{3}{5} \right]; & z < \sigma_w; \\ 0; & z \geq \sigma_w. \end{cases} \quad (1)$$



**Figure 3.** A schematic representation of the coarse grained step surface. Far from the step along the  $x$ -direction the surface behaves as a flat one (uniform repulsive wall). The step is described by an interaction line along the  $y$ -direction. Along this line the interaction is attractive for the phenylene and repulsive for the other beads; the repulsive potential on the step is stronger than on the flat part.

To avoid a complicated surface structure, the step is modelled as an interaction line along the  $y$ -direction, where the  $z$ -dependence of the interaction is altered. Phenylene beads experience strong attraction and the other bead types a stronger repulsion than on the flat surface<sup>1</sup>. The general analytical form of the potential is

$$U_{\text{total}}(x, z) = U_{\text{wall}}(z) + F_{\text{step}}(x) \cdot U_{\text{step}}^{\text{phen,other}}(z) \quad (2)$$

where  $U_{\text{wall}}(z)$  is the potential for the flat surface. For the step interaction,  $U_{\text{step}}^{\text{phen,other}}(z)$  is the actual  $z$ -dependent potential above the defect. For phenylene beads, the interaction term  $U_{\text{step}}^{\text{phen}}(z)$  is

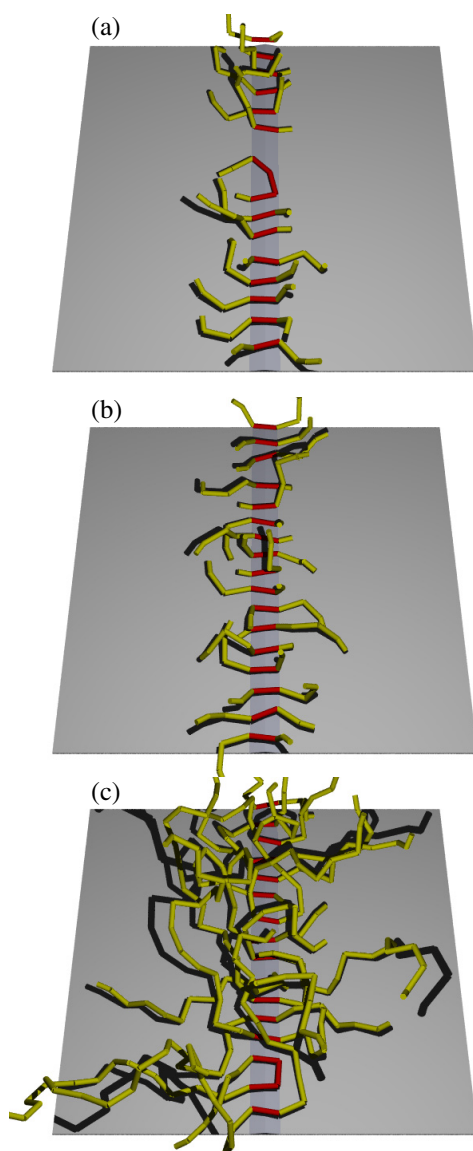
$$U_{\text{step}}^{\text{phen}}(z) = \begin{cases} 2\pi\epsilon_r \left[ \frac{2}{5} \left( \frac{\sigma_s}{z} \right)^{10} - \left( \frac{\sigma_s}{z} \right)^4 + \frac{3}{5} \right] - \epsilon_a; & z < \sigma_s \\ \frac{1}{2}\epsilon_a \left[ \cos\left( \pi \frac{z_c - z}{z_c - \sigma_s} \right) - 1 \right]; & \sigma_s \leq z < z_c \\ 0; & z \geq z_c. \end{cases} \quad (3)$$

$\epsilon_a$  ( $12 kT$ ) is the maximum energy of adsorption,  $\epsilon_r$  ( $20 kT$ ) is the strength of repulsion at close distance,  $\sigma_s$  ( $3.2 \text{ \AA}$ ) is the distance of optimal adsorption and  $z_c$  ( $3.6 \text{ \AA}$ ) is the cut-off distance. Regarding the other bead types,  $U_{\text{step}}^{\text{other}}(z)$  has the same form as  $U_{\text{wall}}(z)$  with modified parameters, which account for the stronger repulsion at the step ( $\sigma_w$  is  $4.1 \text{ \AA}$ , and  $\epsilon_w$  is chosen so that each bead experienced  $1 kT$  of repulsive energy at a distance of  $0.9\sigma_w$ ). To properly account for the distance from the bead to the step, an  $x$ -dependent factor  $F_{\text{step}}(x)$ , which vanishes at a cut-off  $x_c$ , has to be added:

$$F_{\text{step}}(x) = \begin{cases} \frac{1}{2}[\cos(\alpha x^2) + 1]; & x < x_c \\ 0; & x \geq x_c \end{cases} \quad (4)$$

where the cut-off distance  $x_c$  is taken as the bond length, and  $\alpha = \pi/x_c$ . All the parameters used were obtained from the *ab initio* results.

<sup>1</sup> This choice was made to reflect the *ab initio* results which indicate that, on the step, at a close distance  $z$ , arrangements of the polymer segment with parallel orientation experience a repulsive interaction.



**Figure 4.** Chains (yellow) with an adsorbed segment (red) on the step line (darker grey). Three different conditions of simulation are represented:  $N = 2$  and  $T = 570$  K (a),  $N = 2$  and  $T = 300$  K (b),  $N = 10$  and  $T = 570$  K (c). Each segment represents the isopropylidene-carbonate bond (with the phenylene in between); for simplicity the other chains are not represented.

### 3. Results and discussion

MD simulations have been carried out for melts of 480 dimers (two repeat units,  $N = 2$ ), at<sup>2</sup> 300 K and 570 K, and of 240 chains of 10 repeat units at 570 K. Figure 4 shows the simulation

<sup>2</sup> For the simulation at 300 K, the density ( $0.94$  particles/ $\sigma^3$ ) has been taken to reproduce the same pressure of a bulk system at 570 K and  $0.85$  particles/ $\sigma^3$ . It should be noted that, since the coarse graining parametrization was made at 570 K, the prediction of bulk properties at 300 K would not be as accurate. However, the current model is sufficient for describing the general features of the adsorption process at 300 K in comparison to those observed at 570 K.

results for  $N = 2$ ,  $T = 570$  K (a),  $N = 2$ ,  $T = 300$  K (b) and  $N = 10$ ,  $T = 570$  K (c). While 300 K is well below the glass transition temperature for the polymer melt, 570 K is well above and a typical process temperature. Only chains with an adsorbing segment are displayed. In contrast to the flat surface case, along the step a well defined *localization and orientational ordering* is observed, which for 300 K is even almost free of defects! Such a local ordering is a perfect nucleation line for any crystallization. Taking the conformational ground state (an all *trans* state), it is known that BPA-PC would preferentially crystallize; however, in all experimental cases PC stays amorphous and turns into a glass before any crystallization is observed. This is due to the very slow dynamics and the small energy differences between the *trans-trans* and *trans-cis* states at the carbonate group. In the case of very short chains (e.g. dimers), such a line defect in the surface might be very helpful for facilitating long range ordering. In the current situation the order does not extend into the bulk and already the next layer is dominated by packing effects. Since the tendency to crystallize for PC is so small, we do not expect to see the onset of crystallization without additional local very short range (attractive) interactions, originating from the different chemical groups. In other cases, where the tendency to crystallize is stronger, crystal nucleation in the bulk with purely repulsive potentials is already rather easy to observe [33]. In a similar way, a local ordering can be observed for the  $N = 10$  chains considered in figure 4(c). While any long range ordering is much more complicated and time-consuming, and currently certainly beyond the possibilities of computer simulations employing such a complicated polymer model, the results suggest specific experiments to employ the role of defect lines for structure formation in oligomer and polymer melts, as such lines can be viewed as a well defined nucleation line. Our approach also sheds some light on very different topics. It is known that very small additions of polymers can be used to significantly modify the shape and size of small crystallites, such as ZnO and CaCO<sub>3</sub>, during mineralization [32]. There, the fact that the interactions of organic molecules with the mineral can be site and lattice orientation specific is used empirically. By studying specific interactions of small submolecules with specific locations on the surface of a mineral, one might be able to select or even construct optimized additives for mineralization problems. Another application of our approach is in studying liquid crystals near a solid surface.

#### 4. Conclusions

The present combination of *ab initio* calculations and coarse grained modelling leads to a way for studying such phenomena in more detail. In conclusion, the adaptation of a recent modelling procedure, shown to be rather robust in previous work, offers a new view of the basic mechanisms of interplay between electronic properties of a step defected metal surface and conformational large scale properties of extended molecules. The results, shown here for a specific system, should be tested experimentally and suggest in turn studies of similar systems for revealing new surface induced properties.

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