# Surface enrichment driven by polymer topology

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# Surface enrichment driven by polymer topology

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We report a molecular dynamics simulation study of free-standing films of a blend of linear and cyclic polymer chains. We find that the composition of linear chains at the interface is enhanced relative to their *bulk* value for short chains but is depleted for long chains. Our findings are in agreement with recent experimental evidence reported for blends of short linear and cyclic polystyrene chains and highlight the genuine surface behavior in the short chain-length regime where theoretical predictions are more difficult. We highlight surface enrichment at low-energy surfaces as the result of competition between different entropic and enthalpic contributions to the interfacial free energy of the system.

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Self-organization and rheology of polymer blends at interfaces are of both fundamental and technological interest [1–3]. The topology of polymers is expected to play a major role in determining the structural and dynamical properties of the system. As a consequence, a number of studies have analyzed the way the different repeat chemistry of chains affects polymer diffusion at interfaces [1, 4–8]. The possibility of controlling the surface properties of materials with polymers of chosen topology has also motivated a number of studies in the field of surface segregation of polymers [2, 9]. Experiments to resolve the matter are typically conducted by mixing polymers possessing the same repeat chemistry, but different molecular architecture, e.g. branched or ring and linear polymers [10–14]. However, a deep understanding of the role of chain architecture and molecular mass in determining which species preferentially adsorb at a given interface is lacking.

To date, there exist limited studies regarding the effect of architecture on the surface segregation of polymer blends composed of the same type of monomer. For blends of linear and cyclic polymers, Self-consistent field (SCF) theory within a linear response approximation predicts that the cyclic polymers will be in excess at the interface independent of the molecular weight of the polymers [15]. However, SCF prediction is not accurate; Wang and coworkers [2] recently used a surface-sensitive spectroscopic technique (SL-MALDI-TOFMS) on blends of linear and cyclic polystyrene of 2K molecular weight that provided evidence of enrichment of linear chains at the surface for sufficiently small concentration of cyclic chains in bulk [2]. This discrepancy between theory and experiment highlights the limitations of SCF theory in describing non-Gaussian conformations, such as the short polystyrene chains studied in the experiment.

Several factors can contribute to the preferential adsorption of one component in polymer blends near a surface, of which polymer chain topology is considered to be crucial in many aspects. For example, the role of entropic and enthalpic interactions towards determining the surface excess composition of one component in blends of linear and branched polymers was examined by Yethiraj [16]. He found that the linear chains preferentially segregate to the surface when the system is in athermal condition; but introducing attractive interaction between the polymer beads resulted in the preferential segregation of the branched polymers at the surface. Furthermore, Jun and Mulder [17] and Minima et. al. [18] have showed that conformational entropy by itself could be a major driving force in the spatial organization of highly confined polymers where ring topology facilitates segregation more than linear topology. The experimental evidence of the relevance of entropy in determining the surface excess at the polymer/air interface was recently provided by Lee and coworkers [3] for blends of branched and linear polymer chains. In the case of a low-energy surface, such as air or vacuum, the polymer species with the lower cohesive energy density is expected to be favored at the surface because of its lower surface tension [15, 16].

In this Rapid Communication, by performing large-scale molecular dynamics simulations of linear/cyclic polymer blend films, we show clear evidence of enhancement of linear polymers at the interface in agreement with recent experimental results [2]. We also show that the behavior predicted by SCF theory, i.e. enhancement of cyclic polymers at the interface, emerges for relatively long chains. Furthermore, a deeper understanding of the role of enthalpic and entropic factors of the interfacial free energy in determining which of the two polymer species in the blend preferentially adsorbs at the interface is achieved by elucidating the underlying microscopic mechanism. At the fundamental level, our findings clarify the way chain length arbitrates the competition between

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the different packing constraints imposed by the loop and linear geometry of polymers in a blend.

In the present study, we used the bead-spring model in which polymers are modeled as a number of contiguous monomers of equal mass $m$ connected to form either linear or cyclic chain via a combination of the finitely extensible non-linear elastic (FENE) potential [19, 20] and the Weeks-Chandler-Andersen (WCA) potential [21]. The interactions between non-bonded beads are taken into account via a Lennard-Jones (LJ) potential that was truncated and shifted at the cut-off distance $r_c = 2.5\sigma$.

All the simulations were performed using the LAMMPS simulation package [22]. A time step of $\delta t = 0.005\tau$ ($\tau = \sigma\sqrt{m/\epsilon}$) and a temperature of $T = \epsilon/k_B$ were used in all the simulations, where $\sigma$, $\epsilon$ are the LJ distance and energy parameters, $m$ is the mass of a bead, and $k_B$ is the Boltzmann constant. The Langevin thermostat with damping constant $2\tau^{-1}$ was used to keep the systems temperature constant. We generated initial configurations for binary mixtures of linear and cyclic polymers of different chain lengths: $N_b = 7, 10, 20, 30, 50, 100$ beads per chain and at compositions [2] $c_0 = N_l^0/(N_c^0 + N_l^0) = 0.7$ and 0.8, where $N_c^0$ and $N_l^0$ are the total number of cyclic and linear chains in the simulation box. These initial configurations were first equilibrated in the NPT ensemble at $P = 0$ and $T = 1.0$ using a Langevin thermostat and a Berendsen barostat with periodic boundary conditions in all three directions for more than $50,000\tau$, which is much larger than the relaxation time of the end-to-end vector autocorrelation function of about $24,000\tau$ for the longest chain. Then, the periodicity in the $z$-direction was removed to generate free-standing polymer films exposed to vacuum on both sides. NVT simulations using a Langevin thermostat were then run for $500,000\tau$ and quantities of interest were averaged over the last $50,000\tau$. The density in the middle of the films after equilibration is the same as the bulk density at the end of the NPT equilibration runs. We studied systems with a total number of beads ranging from $N^0 = N_c^0 + N_l^0 = 100,000$, for shorter chains, to $N^0 = 200,000$, for longer chains. Films were subdivided along the direction orthogonal to the interface into slices (bins) of size $\sigma$ in order to investigate their properties as a function of distance from the polymer/vacuum interface.

Figure 1 shows the ratio of the local composition $c = N_l/(N_c + N_l)$ of linear chains — where $N_l$ and $N_c$ are the number of linear and cyclic chains in a bin of size $\sigma$, respectively — to bulk composition $c_0 = 0.7$ for $N_b = 10$ and 100. We note that for both linear and cyclic chains the onset of the *bulk* behavior occurs at a distance of $4\sigma$ to $6\sigma$ from the interface which is slightly larger than the radius of gyration of the linear chains. The composition of the two species far from the interface is in the ratio 30 : 70, as expected for the case $c_0 = 0.7$. In Fig. 1, we clearly see that the local composition of linear chains at the interface is enhanced relative to their *bulk* value for short chains, $N_b = 10$, and depleted for long chains, $N_b = 100$ (and vice versa for cyclic chains). The result for short chains is in agreement with what was reported in SL-MALDI-TOFMS experiments for polystyrene polymers with linear and cyclic architecture [2]. In fact, the molecular mass of h-CPS2k and h-LPS2k polymers used there is 2300–2700 g/mol, which corresponds to $N_b = 10$–13 beads in the bead-spring model with the assumptions that the entanglement length $N_e = 85$ [23] and the monomer mass of polystyrene is equal to 104 g/mol. Our results for long chains are also in qualitative agreement with the predictions of SCF theory [15].

Table I reports the local composition calculated for a thickness of the surface layer equal to the *bulk* radius of gyration for the six different chain lengths. The table summarizes our main findings: linear polymers enrich the surface for short chains and slowly get depleted at the surface as the chain length increases. Our data predict that the threshold between the two regimes is reached between $N_b = 30$–50 beads per chain; for polystyrene, this corresponds to a molecular weight of ≈ 6000–10000 g/mol. Our prediction for that threshold is also in agreement with recent experiments conducted on polystyrene polymers with linear and cyclic architecture [24].

In order to provide an in-depth insight into the behavior discussed above, we have calculated the radius of gyration $R_g$ as a function of the geometric center of mass of individual chains from the surface for both linear and cyclic chains. In Fig. 2 we show the transverse $R_g^T$ and parallel $R_g^P$ components of $R_g$ with respect to the surface normal for the two chain architectures. These two quantities are scaled by their respective *bulk* counterparts ($R_{g,b}^P$ and $R_{g,b}^T$) in order to understand how the interface affects both the size and shape of the linear and cyclic chains.

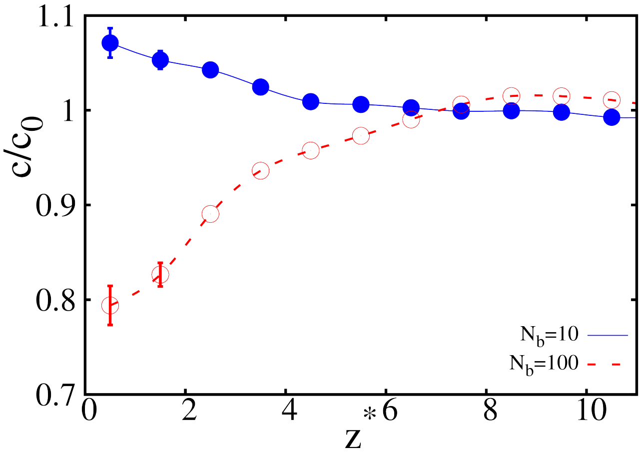

FIG. 1: Local composition of linear polymers as a function of distance ($z^*$) from the interface. Data are scaled by the bulk composition $c_0 = 0.7$.

| $c_0$ | $N_b = 7$ | 10 | 20 | 30 | 50 | 100 |
|---|---|---|---|---|---|---|
| 0.7 | 0.750(12) | 0.743(1) | 0.725(24) | 0.716(1) | 0.665(1) | 0.603(1) |
| 0.8 | 0.881(14) | 0.870(23) | 0.863(17) | 0.851(1) | 0.768(1) | 0.766(1) |

TABLE I: Surface compositions for the two concentrations and for the six chain lengths. Errors are on the last digits.

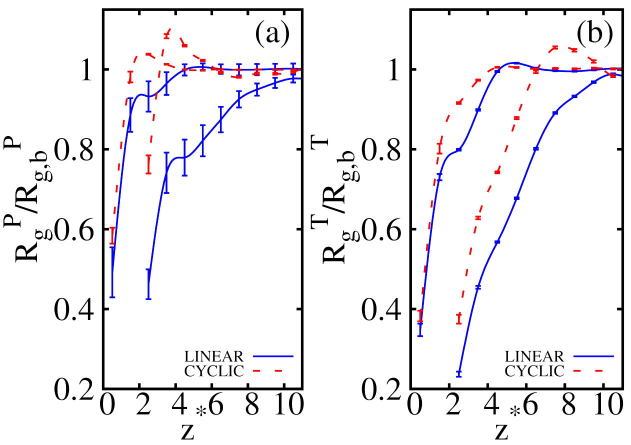

FIG. 2: (a): parallel component of the radius of gyration $R_g^P$ as a function of of the geometric center of mass of individual chains in the $z$ direction for linear (full lines) and cyclic (dashed lines) polymers. Pair of curves starting at $z^* = 0.5$ and 2.5 are for $N_b = 10$ and 100, respectively. (b): same as left panel but for the transverse component $R_g^T$.

The bulk $R_g/\sigma$ for linear and cyclic chains are, respectively, 1.44(1) and 1.14(1) for $N_b = 10$ and 5.25(1) and 3.72(1) for $N_b = 100$. It is clear in the figure that both cyclic and linear chains shrink at the interface regardless of chain length. However, for short chains (the pair of curves in the two panels of Fig. 2 beginning at $z^* = 0.5$) there is no significant difference between linear and cyclic chains and the consistent lower values of $R_g^T$ nearby the interface suggest that both types of chains shrink mostly along the transverse direction to the surface. For long chains (the pair of curves beginning at $z^* = 2.5$) the evidence is that linear chains shrink more significantly than cyclic chains along both the parallel and transverse directions. In particular, $R_g^P$ of cyclic chains is only slightly reduced at the interface. These results provide evidence of a higher loss of conformational entropy of linear polymers at the interface, indirectly supporting the enhancement of cyclic polymers at the interface for long chains as the result of the likely higher values of conformational entropy achieved by them in comparison to linear polymers. It is interesting to note that a more swollen shape along the directions parallel to the interface was recently observed in systems of pure cyclic chains [25], and was explained in terms of the topological excluded volume interaction (repulsion) of blobs in a ring, that prevents other rings to be tangled. In Fig. 2, for both chain lengths we do also observe an increase in $R_g^P$ of the cyclic chains at the interface compared to bulk (an indication of swelling in the parallel direction) within about two $R_g$ from the surface of the films. We also verified the existence of a repulsion between cyclic chains at the interface by calculating the average cyclic-cyclic interaction energy per bead and finding a positive value for the energy. Consistent with this finding, we observed that this repulsion diminished for longer chains since the more swollen the cyclic chains in the directions parallel to the interface are, the more favorable the interactions between cyclic polymers are, which eventually contributes to their enhancement at the interface.

Now we are left with the explanation of the enhancement at the interface of linear polymers for short chains. According to SCF theory [15], for sufficiently small concentration of cyclic chain as in the present case, it is possible to show within linear response theory that the monomer density profile at the interface is produced by attractive surface potentials of entropic origin for chain ends. The real existence of these potentials of entropic origin was demonstrated recently by neutron reflectometry and Raman spectroscopy measurements performed on linear and branched polymer blends of PMMA [3].

In order to detect the presence of chain ends of linear polymers at the interface, we have to avoid the bias due to surface roughness. For this reason, we have built a time-averaged particle-number histogram by adopting a simple procedure to analyze the real interface (instantaneous interface), based on a partition of the simulation box into small cubic cells of size $\sigma$ at a given time step.

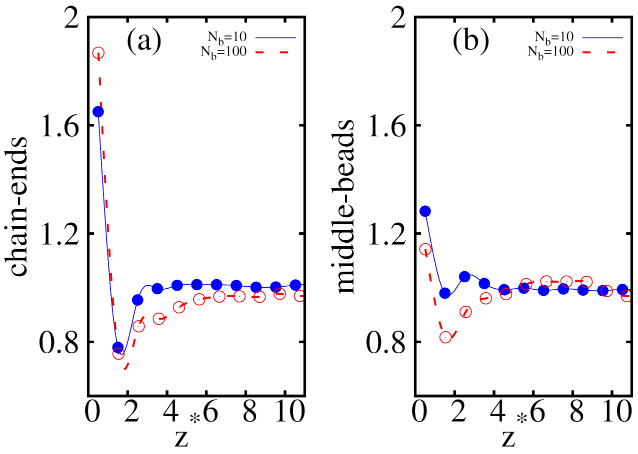

FIG. 3: End (a) and middle (b) number of beads of linear polymers within a slab of size $\sigma$ (and normalized to their bulk value) for $N_b = 10$ and 100 as a function of $z^*$.

A histogram in the surface normal direction (z-direction) was then built by searching inside cells for beads belonging to a given bead type. The cells were analyzed starting from a cell from the top or bottom side of the simulation box and going toward the blend along the $z$-direction. Then, the first-occupied cell defines the first bin of the histogram and serves as the reference point. Once this calculation is iterated for all the cells starting from the low- and high-$z$ surfaces of the simulation box, the final histogram is obtained by summing all the data values at a given value of $z$ and dividing by 2 to account for the symmetry of the two surfaces.

In Fig. $3(a)$, we report the number of end beads within a slab of size $\sigma$ (normalized to bulk value) of linear chains as a function of distance from the instantaneous interface. The results clearly show that the density of chain ends is enhanced at the interface for both short and long chains and attain its bulk value within a distance of Rg from the instantaneous interface. Thus, for short chains, we can explain the previously observed enhancement of linear polymers at the interface in terms of the gain in entropy due to the chain ends preferentially adsorbing at the interface. For the case of long chains, however, there is a competition between the entropy gain from the chain-ends of linear chains and the conformational entropy gain from the higher $R_g$ values of cyclic chains (see Fig. 2), ultimately favoring cyclic chain enrichment at the interface. Furthermore, Fig. $3(b)$ shows the normalized number of middle beads of linear chains as a function of distance from the instantaneous interface. The evidence that also the density of middle beads is slightly enhanced at the interface is supported by the values assumed by radius of gyration of linear polymers at the interface, as reported in Fig. 2. In fact the parallel component of $R_g$ (see Fig. $2(a)$) nearby the interface is larger than the transverse component (see Fig. $2(b)$), which is indicative of linear polymers assuming a more stretched shape along the directions parallel to the interface, similar to the schematic shown in Fig.4. Our results agree with an earlier report by Kumar et. al. [26] that used off-lattice Monte Carlo simulations to study the free surfaces of bead-spring homopolymer systems of varying linear chain lengths where the polymer chains were represented as a bead-spring system similar to our model. They found that the density of end segments are enhanced relative to their bulk value at the interface, that is near hard walls and also on the vacuum side of the interface.

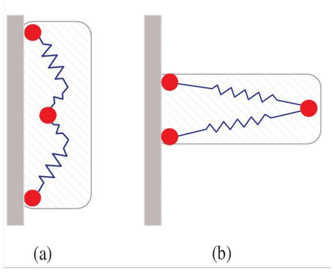

FIG. 4: (a): Sketch of a configuration for a linear polymer with chain-ends attached to the interface and middle bead close to the interface. (b): same as in (a) for the case in which the middle bead is far away from the interface.

In Fig. (5) we show the total energy per bead of the two polymer species as a function of distance from the interface for $N_b = 10$ $(5(a))$ and $N_b = 100$ $(5(b))$. The total energy per bead is higher for cyclic polymers across the whole range of distances from the interface for $N_b = 10$ case. Since cyclic polymers are much less flexible than linear polymers at small degrees of polymerization, they pack less efficiently and achieve a less than optimal number of pair interactions among their beads. This effect highlights the severe constraint imposed on the flexibility of cyclic polymers by the loop topology when their chain length is small. Then, linear polymers can achieve a lower interfacial free energy than cyclic polymers because they minimize their surface energy more than cyclic chains, while at the same time maximizing their entropy by exposing their chain-ends to the surface. In this scenario, linear enhancement at the interface for short chains is the result of an entropy-mediated process, where enthalpy also plays an important role.

For the case of long chains (see Fig. $(5(b))$), the total energy per bead is nearly the same for the two polymer species. The similar number of pair interactions suggests that in the case of long chains the loop constraint becomes less important in undermining the flexibility of polymer chains, while in the case of short-chains the effect of the chain topology becomes evident (see Fig. $(5(a))$). When the interface is approached, cyclic polymers are now likely to achieve a lower interfacial free energy than linear polymers because they possess a higher conformational entropy, while their surface energy is not that different from linear chains of the same length. In fact, as it clearly emerges from Fig. (2), cyclic chains keep a considerably higher radius of gyration than linear chains at the interface, which is an indication of higher conformational entropy of cyclic chains.

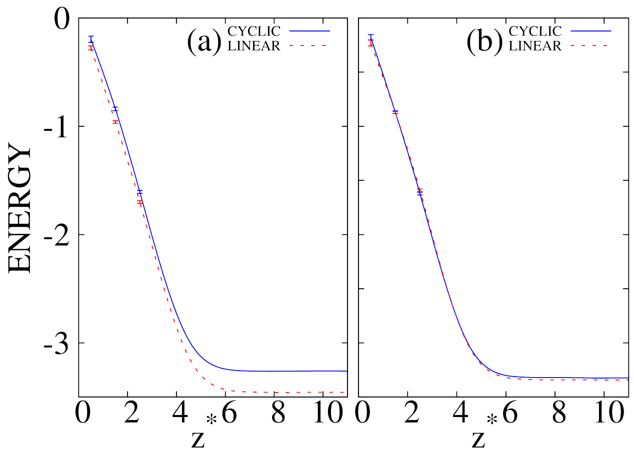

FIG. 5: energy per bead as a function of $z^*$ .

Thus, cyclic enhancement at long chain lengths emerges as a genuine entropic process, driven once again by the loop geometry, which prevents cyclic chains at the interface from folding as efficiently as linear chains.

In summary, we studied a model mixture of linear and cyclic polymers and provided clear evidence of enhancement of the surface composition of linear polymers for short chain lengths. Our findings are in agreement with experiments conducted for blends of short linear and cyclic polystyrene polymers [2] and further we demonstrated that increasing the molecular weight of the polymer chains will ultimately result in the enhancement of the local composition of cyclic chains, as predicted by SCF theory [15]. The analysis of our model system highlights the role of molecular architecture and entropy in determining surface behavior in polymer blends. We believe our results are also relevant for biological systems, where the intrinsic topological constraints of cyclic polymers, including non-knotting and non-concatenation, are present in chromatin polymer models [27, 28]. These models apply physics-based approaches that highlight the importance of entropy for understanding nuclear organization, ultimately consisting in the packaging of a long linear polymer such as DNA into highly crowded structure known as chromatin [29].

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