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Behavior of Polymers at Surfaces and Interfaces as Observed in Simulated Systems

Tadeusz Pakula

Max-Planck-Institut für Polymerforschung, Postfach 3148, 55021 Mainz, Germany

Abstract: Cooperative motion algorithm (CMA) is used to simulate polymer chains in three types of dense systems reflecting special cases of polymer behavior at surfaces and interfaces: polymer brushes with variable grafting density in the range 0 - 1, both in a neutral solvent and in a polymer melt, layers of end-functionalized polymers between parallel end-adsorbing walls, and copolymers of various distributions of comonomer units (random, block and gradient copolymers) at interfaces with noncompatible polymers.

INTRODUCTION

Behavior of polymers at surfaces and interfaces has been a subject of intensive theoretical, experimental and computer simulation studies for last few years (Refs.1-5). The extraordinary interest in such problems is caused by their relevance to many technologically important systems. The behavior of chains adsorbed or grafted at surfaces or the behavior of chains trapped at interfaces in multicomponent systems are examples of problems associated with this group. In this paper, we use computer simulation to study (1) the behavior of polymer brushes consisting of linear chains grafted at a planar surface, (2) the behavior of linear end-functionalized chains in thin layers, and (3) the behavior of various copolymers acting as compatibilizers at the interface of two noncompatible polymers.

Brushes are considered as model systems and various theoretical treatments have been applied to predict their properties as a function of "hair" densities (Refs. 6-10). We consider here systems of linear chains grafted with one end to a planar surface, with grafting densities ranging between 0 and 1. Equilibrium structures of such brushes are studied in two media: (1) in a neutral solvent and (2) in contact with melts of polymers of various chain lengths. The results of simulation are compared with theoretical predictions.

Polymer layers are often used to bond solid surfaces. Properties of such bonding are dependent not only on the strength of adhesive interaction of the polymer with the solid surface but also on the structure within the polymer layer. A special case of polymers with functionalized ends, improving adhesion to the solid surface, is analyzed. Fraction of chains bridging directly parallel solid surfaces is determined as a function of the layer thickness and interaction strength of the functionalized ends.

Various copolymers differing by distribution of constituent monomer units along the chain have found versatile applications in technology of polymeric materials. Recently a possibility of synthesis of gradient copolymers has been suggested, i.e. of copolymers in which the composition of constituents would change continuously along the chain in a predefined manner. Properties of such polymers have been analyzed by computer simulation (Ref.11), which has indicated that such polymers can provide a possibility of a continuous shift of their dynamic and thermodynamic properties along the temperature scale by changes in composition gradients. Gradient copolymers have now been synthesized (Refs.12,13). Copolymers have often been considered as blend additives diminishing incompatibility at a polymer/polymer interface. Both block (Ref.14) and random (Ref.15) copolymers have been used in

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such applications, each of them affecting the interfacial properties in different way. Here, gradient copolymers are considered as potential compatibilizers and their behavior at interfaces in comparison with block and random copolymers is analyzed.

SIMULATION METHOD

The simulation method used is the Cooperative Motion Algorithm (CMA), described elsewhere (Refs.11,16,17). In this type of simulation, ensembles of beads in a lattice are connected by nonbreakable bonds to objects representing linear macromolecules. Face-centered cubic (fcc) lattice is used with all lattice sites occupied in order to represent dense systems like polymer melts. The systems are considered under the excluded volume condition, which means that each lattice site can only be occupied by a single molecular element (bead). Solvent is represented by single non-bonded beads. In such systems, strictly cooperative dynamics is used consisting in rearrangements satisfying local continuity of the simulated system (no empty lattice sites are generated). This is realized by local motions consisting of displacements of a certain number of molecular elements along closed loops with each element replacing one of its neighbors so that the sum of displacements of elements taking part in the rearrangement is zero (the continuity condition). During such rearrangements, the models of macromolecules undergo conformational transformations preserving, however, their identities given by the number and sequences of elements in the polymer.

In the case of copolymers, two types of monomer units A and B are considered. The two types of units are partially compatible, which is characterized by direct interaction parameters ε_{ij}. In order to generate equilibrium states, a dense system of chains is subjected to motion at a given temperature. Moving a chain element alters the local energy because the monomer units contact new neighbors. An attempt to move a single monomer unit is assumed as one Monte Carlo step and the probability of the movement is related to the interaction energy of the monomer unit in the attempted position. Under such conditions, at low temperatures, different types of monomeric units tend to separate from each other in order to reduce the number of A-B contacts and, consequently, to reduce the energy.

In order to represent polymer layers, such systems are considered between nonpenetrable parallel walls (Refs.5,18). In the case of brushes, grafted ends are assumed to be mobile at the grafting wall. In order to represent the interaction of chain ends with the surfaces, it is assumed that the states at the adsorbing wall and away from it can differ in potential energy by $\Delta\varepsilon$. Consequently, for an attractive interaction, movements involving separation of the functionalized end from the wall have been performed with a reduced probability $p = \exp(-\Delta\varepsilon)$, which led to the adsorption of functionalized ends on the walls for $\Delta\varepsilon > 0$.

RESULTS

Polymer Brushes

Polymer brushes consisting of linear chains (N=80) anchored to a planar surface by one end have been simulated. Various grafting densities and two media surrounding the brushes have been considered. Structures of brushes are characterized by distributions of concentrations of grafted chains and distributions of free chain ends of grafted chains along the distance from the grafting wall. The results for brushes in a neutral solvent are shown in Fig. 1. Strong extension of chains with increasing grafting density is observed. At all grafting densities, brushes are penetrated by the solvent.

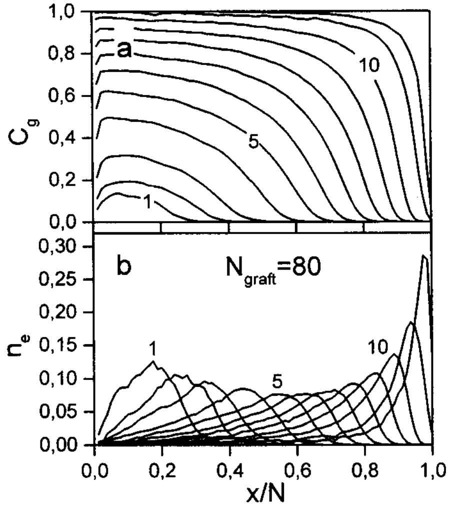

Fig. 1.
Distribution of (a) concentration and (b) free chain ends of brushes with various grafting densities in a neutral solvent along the distance (x) from the grafting wall (normalized by the extended chain length, N).

Grafting densities:

1: 0.025 2: 0.05
3: 0.1 4: 0.2
5: 0.3 6: 0.4
7: 0.5 8: 0.6
9: 0.7 10: 0.8
11: 0.9 12: 0.95

The situation changes when the brush is in contact with a melt of linear chains of the same length as that of grafted chains. The results are shown in Fig. 2.

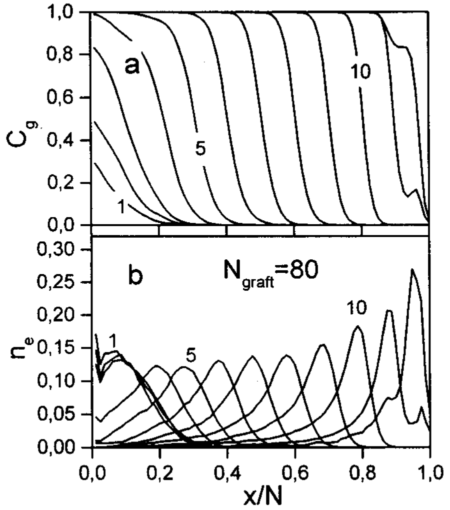

Fig. 2.
Distribution of (a) concentration and (b) free chain ends of brushes with various grafting densities in a polymer melt along the distance (x) from the grafting wall (normalized by the extended chain length, N). For grafting densities, see Fig.1.

Brushes being in contact with the melt already at relatively low grafting density form a dense surface layer not penetrable for other polymer chains having lengths comparable with the lengths of brush hairs. Only shorter chains can partially penetrate such brushes. The results concerning this effect will be presented elsewhere.

In order to characterize dependences of brush thickness on the grafting density, two measures of thickness have been considered: (1) that based on the concentration profile along the distance from the grafting wall (x)

$$t_c = 2\frac{\int xC_g(x)dx}{\int C_g(x)dx} \tag{1}$$

and (2) that based on the distribution of free ends of grafted chains

$$t_e = \frac{\int xn_e(x)dx}{\int n_e(x)dx} \tag{2}$$

Dependences of the brush thickness on the grafting density are compared with various theoretical predictions in Fig. 3. In the case of wet brushes, the self-consistent field theory (Ref.9) overestimates the brush thickness at higher coverage densities. This effect is corrected in another consideration taking into account a finite extensibility of chains (Ref.8). The modified version of the Alexander analysis (Refs.6,10) shows a good agreement with simulation in the whole coverage range if distributions of free ends are taken as a measure of the layer thickness. For high-coverage densities in dry brushes, the results can be well approximated by the thickness of the dense layer (dotted line). Deviations from such dependence are observed at low coverage densities where the concentration profiles reflect dimensions of isolated grafted chains. Distortions in concentration profiles at coverage densities close to unity, observed mainly for dry brushes, are caused by limited sizes of model systems and problems of free chains to arrange two-dimensionally between the brush and the neutral surface.

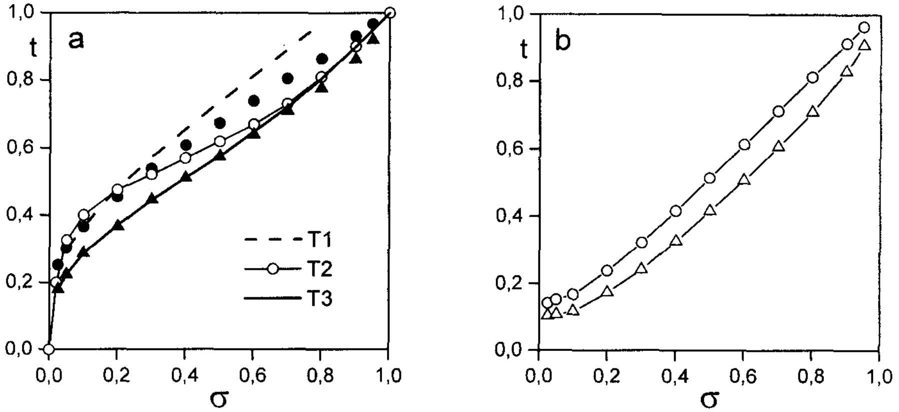

Fig. 3. A comparison of dependences of brush thickness (●,○ t_c; ▲,△ t_e) on grafting densities determined (a) in a neutral solvent and (b) in a melt, with various theoretical predictions T1 (Ref.9), T2 (Ref.8) and T3 (Ref.10).

End-Functionalized Polymers between Parallel Surfaces

Dense systems of linear chains (N=90) with both ends interacting attractively with two parallel surfaces, thus confining the systems to layers, are considered. The influence of the interaction strength and layer thickness on the structure is analyzed.. Both these parameters considerably influence layer structures which are characterized by distributions of centers of gravity of chains and chain ends as well as by concentration profiles of chains forming loops (both ends adsorbed on the same wall), bridges (ends adsorbed on opposite walls), hairs (one end adsorbed) or remaining free between the walls. The interaction strength is changed in a broad range, neutral walls and nonreversible adsorption of chain ends being the extremes. Figure 4 shows examples of such distributions for various interaction energies at a constant layer thickness.

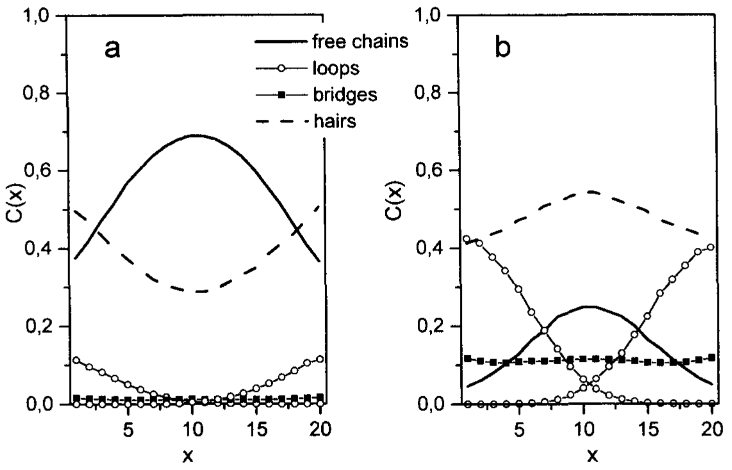

Fig. 4. Comparison of concentration profiles of loops, bridges, hairs and free chains for two energies of interaction between chain ends and walls (d=20): (a) E=1, (b) E=3. The distance from the wall (x) is expressed in units of the lattice constant.

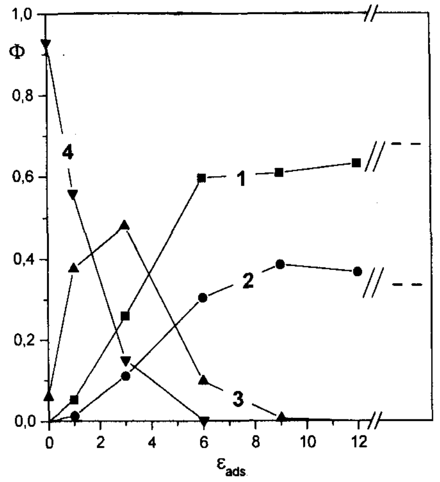

Fig. 5. Fractions of loops (1), bridges (2), hairs (3) and free chains (4) as functions of interaction strength between chain ends and walls (N=90, d=20).

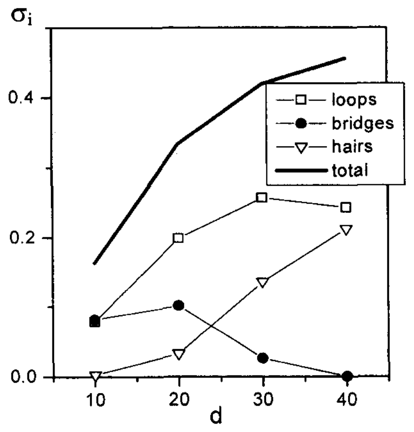

Fig. 6. Coverage of walls by adsorbed chain ends belonging to loops, bridges and hairs as a function of the distance between walls; total coverage is shown by the thick solid line (N=90, E=6).

It can be seen that an increasing adsorption of chains with increasing interaction strength considerably changes the distribution of chains with different roles in the layer. Changes in fractions of chains in different states related to end adsorption at the walls are presented in Fig. 5 as a function of the interaction energy. For a given thickness of the layer, comparable with chain sizes, all chain ends are able to be adsorbed on the walls at a sufficiently high interaction energy. Nevertheless, in such states most chains form loops and only about 35 % of chains contribute to bonding the walls by bridges. It is interesting to note that for irreversibly adsorbing chains, the fraction of bridges is even smaller. Proportions of various chain states are strongly dependent on the layer thickness. This effect is illustrated in Fig. 6. A maximum density of chains bridging the walls per unit wall surface is observed at a layer thickness corresponding to a quarter of the extended chain length. This shows that bonding of surfaces by end-functionalized polymers can be effective only at extremely small layer thickness.

Copolymers as Compatibilizers

Poor adhesion between incompatible polymers is caused by a reduction in cohesive forces between molecular segments of different type but also by specific molecular configurations which can be expected if regions of one polymer are not penetrable by chains of the other. Changes in polymer chain configuration near the interface between incompatible polymers with respect to a virtual interface in a homopolymer are illustrated in Fig. 7 by means of distributions of various molecular parameters along an axis perpendicular to the interface. Concentration profiles (Fig. 7a), distributions of gravity centers of chains (Fig. 7b) and chain ends (Fig. 7d), distributions of chain orientations (Fig. 7c) as well as distributions of local A-B interactions (Fig. 7e) are considered.

The virtual interface in a homopolymer is obtained by considering chains having their gravity centers on different sides of a plane, chosen arbitrarily in a system, as different components. The interface between incompatible polymers is simulated by equilibrating a system of two initially separated polymer layers, brought to a contact at a temperature far below the critical point of the corresponding blend. In this case, it has been proved that identical equilibrium states are obtained if the interactions between chains of type A and B distinguished in a homopolymer by the virtual interface are switched.

The results indicate considerable changes in the molecular structure which the incompatibility of polymers can cause at the interface. The most drastic changes observed consist in removing of gravity centers of chains from the center of the interface, in an increase in chain end concentration in the center of the interface and in a considerable reorientation of chain axes in the directions parallel to the interface. Considerably smaller effects concern differences in concentration profiles. Moreover, it is interesting to note that the range of the mentioned structural effects is remarkably broader than the interface thickness if considered as a width of the concentration change. All the above effects lead to strong heterogeneities in the system and all can contribute to weakness of the interface.

An effective compatibilizer should maximally reduce these heterogeneities by smoothing the distributions of chain ends, chain gravity centers and chain orientations to the levels characteristic of homopolymers. Figure 7 shows how effectively these heterogeneities can be suppressed by various types of copolymers added to the system (again equilibrium states are considered). It can be seen that different types of copolymers involve different changes in the interface structure. There is generally a relatively weak effect on concentration distributions. With a diblock copolymer, the concentration profile

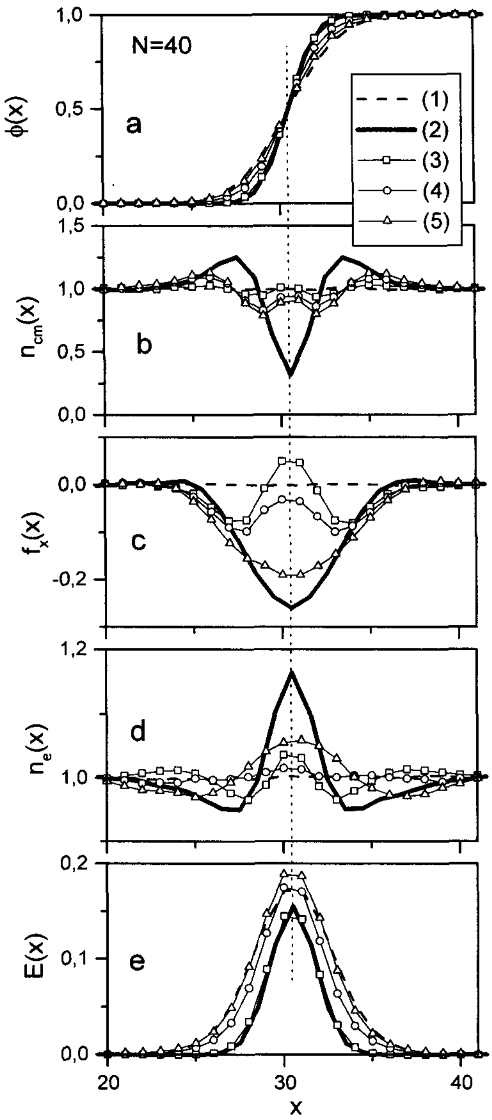

Fig. 7.

Distributions of (a) concentration, (b) gravity centers of polymer chains, (c) orientation factor of chain end-to-end vectors with respect to the normal to the interface, (d) chain ends, and (e) A-B contacts along a direction perpendicular to the interface (x - distance, in units of the lattice constant along this direction).

Interfaces: (1) a virtual interface in a homopolymer, (2) A-B interface of strongly incompatible polymers and A-B interfaces modified with (3) diblock, (4) gradient, and (5) random copolymers.

and, consequently, the profile of active A-B interactions remains almost unchanged with respect to the nonmodified interface. Both the random and gradient copolymers make the concentration profiles distinctly broader and very close to the concentration profile of the virtual interface in a homopolymer. All copolymers strongly suppress nonuniformities in the distribution of chain centers of gravity but the strongest effect is observed for the diblock copolymer. Considerable reduction in chain orientation preferences is observed only for block and gradient copolymers. Random copolymers do not reduce orientations of polymers in the vicinity of the interface and they themselves assume orientations parallel to the interface. The inhomogeneity of chain ends distribution is most effectively reduced by the gradient copolymer for which almost uniform distribution, like in a homopolymer, is obtained.

CONCLUSIONS

The structure of polymer brushes is considerably influenced by a surrounding medium. Neutral solvents can penetrate the brush at all hair densities but linear chains of lengths comparable with the lengths of hairs remain excluded from the brush. Various theoretical descriptions of brush thickness as a function of hair density describe only approximately the behavior of simulated systems.

End-functionalized polymers between end-adsorbing walls can effectively bond the walls only if the layer thickness is considerably smaller than the lengths of extended polymer chains.

Simulations of effects which can be expected at interfaces of incompatible polymers when modified by copolymers with various distributions of monomer units suggest that gradient copolymers could be considered as effective compatibilizers combining advantageous properties of diblock and random copolymers.

Simulations by cooperative rearrangements (CMA) allow to effectively study various phenomena related to the behavior of dense polymer systems at surfaces and to the behavior of chains at interfaces in polymer melts.

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