J. At. Mol. Sci.
doi: 10.4208/jams.080213.111113a

Vol. 5 , No. 2, pp. 139-147
May 2014

Molecular theory investigate the switching of mixed brushes

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Received 2 August 2013; Accepted (in revised version) 11 November 2013

Abstract. We performed a molecular theory to study the switching mechanism of mixed brushes. For mixed brushes, because of the different solvent selectivity, one species forms the poor solvent layers, whereas another species creates the upper, good solvent layer. The structural properties of the mixed brushes were analyzed in detail for various solvent responds. The thermodynamic properties of the mixed brushes, such as the lateral pressure-area isotherms and chemical potentials, are studied as a function of surface coverage. The possibility of perpendicular segregation in mixed brushes is explained. The presented results allow us to quantify the responsive features of mixed brushes and provide guidance for the design of multicomponent brushes for specific applications.

PACS: 47.27.eb,05.65.+b

Key words: mixed brushes, molecular theory, perpendicular segregation

1 Introduction

Mixed brushes, in which two chemically distinct polymers are randomly or alternately immobilized by one end via a covalent bond on a solid surface with high grafting densities, represent a new class of surface-responsive materials. These materials were demonstrated to be highly promising applications for the protein adsorption [1], drug delivery, nanotemplating [2], and design of stimuli-responsive systems [3]. Therefore, the properties of mixed brushes have been intensively investigated theoretically [4-8], simulatively [9-16], and experimentally [17-25].

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The mixed brushes were of great research interest, mainly because the presence of the switching properties between hydrophobic and hydrophilic wetting behavior caused by a change in their environment. The switching properties of the mixed brushes are substantially dependent on grafting density, molecular weight, their interaction with the solvent and compatibility of two distinct grafted polymers. By altering the grafting density and molecular weightsthe lateral phase separation of mixed brushes has been definitively demonstrated by theory [4] and simulation [9,10]. Zhao and He [18] observed that the mixed PMMA/PS brush thickness increased with the molecular weight of "free" polymers collected from the solutions in nearly linear fashions. Wang and Muller [11] investigated the microphase separation of mixed brushes exposed to different solvents using Mean-Field simulations. Brown *et al.* [12] gave the results of Monte Carlo study of a grafted-polymer brush composed of two types of chains under near-melt conditions. They observed the formation of a strongly segregated structure. Merlitz *et al.* [13] carried out simulations using LAMMPS molecular dynamics. The switching process was analyzed in detail for various solvent selectivities, chain lengths, and grafting densities. Zhu and Zhao [19] investigated the phase morphologies of environmentally responsive mixed PtBA/PS and mixed PAA/PS brushes on silica particles after treatments with nonselective good solvents and selective solvents by TEM. The results confirmed the theoretical predictions of the formation of "rippled" nanostructures and surface-tethered micellar structures of mixed brushes induced by nonselective good solvents and selective solvents, respectively.

Although the switching mechanisms of mixed brushes were intensively studied by theory and simulation, few theoretical investigations were directed in studying the effect of interaction between polymers and solvent in mixed brushes. The thermodynamic properties of mixed brushes were also rarely investigated. In this paper, we present a molecular theory [26-28] to study the effect of interaction between grafted polymers and solvent in mixed brushes. The theory has been used previously to study the thermodynamics and structural properties of tethered polymers [26, 27] and has been shown to be in quantitative agreement with simulations and experimental observations [26, 28]. We give a molecular theory that considers the size, shape, and conformation of every molecular type, which is different from the self-consistent field theory. The self-consistent-field theory is employed along with a Gaussian chain model for bonding constraints and a random mixing approximation for nonbonded interactions. The chain model we employ to generate the chain conformations is a three-state RIS model [29]. In this model, each bond has three different isoenergetic states. The conformations are generated by a simple sampling method and all are self-avoiding. In this work, our aim is to explore the switching properties, thermodynamic properties and explain the mechanism of perpendicular segregation upon exposure to different selective solvents in mixed brushes.

The paper is organized as follows. First, we describe the molecular theory. Then, we present relevant results, concentrating on the effect of interaction between grafted polymers and selective solvents. In the last section, we draw conclusions on the switching of mixed brushes, depending on solvent quality.

2 Molecular theoretical approach

In order to create a mixed brushes system, two species were homogeneously grafted onto the substrate surface which defined the $x-y$ plane at $z=0$. The two polymer species consisted of monomers which shall be denoted as A type and B type respectively. We write the free energy of the mixed brushes system containing equal amounts of species A and B chains exposed to solvent, which explicitly includes the size, shape, and conformation of every molecular. We assume the two components have identical chain length N_P and segment volume ν_P. They are tethered onto the substrate surface and only allowed in the $z\geq 0$ half-space. The number of tethered chains per unit area is $\sigma_A=\sigma_B=N_P/A_r$. The number of solvent molecules is N_S, each with a volume of ν_S. We assume that the only inhomogeneous direction is the z direction. The free energy per unit area of mixed brushes in solution is given by

$$\frac{\beta F}{A_r}=\sum_{i=A,B}\left(-\frac{S_{Pi}}{k_B A_r}+\frac{\beta F_{int,r}}{A_r}+\frac{\beta U_{sur,i}}{A_r}\right)-\frac{S_S}{k_B A_r}+\frac{\beta U_{rep}}{A_r} \tag{1}$$

The first term in Eq. (1) denotes the conformational entropy of polymer chains, which can be given by

$$-\frac{S_{Pi}}{k_B A_r}=\sigma_i\sum_{\alpha}P_i(\alpha)\ln P_i(\alpha) \tag{2}$$

$P-i(\alpha)(i=A,B)$ is the probability distribution function (PDF) of finding a chain in conformation α. The polymer volume fraction profile is given by

$$<\phi_{Pi}(z)>dz=\sigma_i\sum_{\alpha}P_i(\alpha)\nu_P(z;\alpha)dz \tag{3}$$

where $v_P(z;\alpha)$ denotes the volume that a polymer chain in conformation α contributes in the layer between z and $z+dz$.

The second term in Eq. (1) describes the effective intermolecular interaction between the polymer segments and the solvent molecules, which can be given by

$$\frac{\beta F_{int,i}}{A_r}=\frac{\chi_i}{\nu_S}\int<\phi_{Pi}(z)>\phi_S(z)dz \tag{4}$$

where $\chi_i(i=A,B)$ is the Flory interaction parameter measuring the strength of the solvent-polymer effective repulsions. Different effects of interaction between grafted polymers and selective solvents are indicated as a function of the key parameters χ_i [29, 30]. The $\phi_S(z)$ is the position-dependent volume fractions of the solvent. The volume fraction of solvent is given by $\phi_S(z)=\rho_S(z)\nu_S$, where $\rho_S(z)$ corresponds to the number density of solvent molecules at z.

The third term in the free energy, Eq. (1), describes the interaction between the surface and polymer segments and can be given by

$$\frac{\beta U_{sur,j}}{A_r}=\sigma_i\beta\varepsilon_i\sum_{\alpha}P_i(\alpha)n_i(\alpha;0) \tag{5}$$

where $n_i(\alpha;0)(i=A,B)$ denotes the number of polymer segments within distance δ from the surface and ε_i is the depth of the square well potential. In this paper, we set $\beta\varepsilon_i=0.01$.

The fourth term in Eq. (1) is the z-dependent translational entropy of the solvent molecules, which is given by

$$-\frac{S_S}{k_B A_r}=\int \rho_S(z)[\ln\rho_S(z)\nu_S-1]dz \tag{6}$$

The last term in the total free-energy expression, Eq.(1), represents the repulsive interactions of the system and can be given by

$$\frac{\beta U_{rep}}{A_r}=\beta\int \pi(z)[<\phi_{PA}(z)>+<\phi_{PB}(z)>+\phi_S(z)-1]dz \tag{7}$$

where $\pi(z)$ represents the position-dependent repulsive interaction field. They are related to the local osmotic pressure necessary in order to fulfill the thermodynamic condition of constant solvent chemical potential at all distances from the surface [25]. This field is determined by packing constraints associated with the excluded volume interactions which are position-dependent and have the form

$$<\phi_{PA}(z)>+<\phi_{PB}(z)>+\phi_S(z)-1=0 \tag{8}$$

Minimization of the free energy with respect to $P_i(\alpha)(i=A,B)$ yields

$$P_i(\alpha)\frac{1}{q_i}\exp[-\beta\int \pi(z)n_i(\alpha;z)\nu_P dz-\frac{\chi_i}{\nu_S}\int \phi_S(z)n_i(\alpha;z)\nu_P dz] \tag{9}$$

Here, q_i is a normalization constant ensuring that $\Sigma_\alpha P_i(\alpha)=1$. Here, $n_i(\alpha;z)$ corresponds to the number of polymer segments that a polymer chain in conformation α has at position z. The solvent volume fraction is given by

$$\phi_S(z)=\exp[-\beta\pi(z)\nu_S-\frac{\chi_A}{\nu_S}M\phi_{PA}(z)>-\frac{\chi_B}{\nu_S}<\phi_{PB}(z)>] \tag{10}$$

Substituting the expression for the PDF, Eq. (9), the solvent volume fraction, Eq. (10), into Eq. (1) gives the minimal free energy

$$\begin{aligned}\frac{\beta F_{\min}}{A_r}=&-\sigma_A\ln q_A+\sigma_A\ln\sigma_A-\frac{\chi_A}{\nu_S}\int<\phi_{PA}(z)>\phi_S(z)dz-\int\rho_S(z)dz\\&-\sigma_B\ln q_B+\sigma_B\ln\sigma_B-\frac{\chi_B}{\nu_S}\int<\phi_{PB}(z)>\phi_S(z)dz-\beta\int\pi(z)dz\end{aligned} \tag{11}$$

The lateral pressure can be directly measured experimentally using a Langmuir trough [27] and is given by $\Pi=-\partial F/\partial A_r$.

Using Eq. (11), the lateral pressure becomes

$$\beta\prod=\sigma_A+\sigma_B+\frac{\chi_A}{\nu_S}\int<\phi_{PA}(z)>\phi_S(z)dz+\frac{\chi_B}{\nu_S}\int<\phi_{PB}(z)>\phi_S(z)dz$$
$$+\int\rho_S(z)dz+\beta\int\pi(z)dz \tag{12}$$

The chemical potential, $\mu_i=-(\partial F/\partial N_{Pi})_{T,A_r}(i=A,B)$, is given by

$$\beta\mu_i=-\ln q_i+\ln\sigma_i+\frac{2\chi_i}{\sigma_i\nu_S}\int<\phi_{Pi}(z)>\phi_S(z)dz-\frac{\chi_i-1}{\sigma_i\nu_S}\int<\phi_{Pi}(z)>dz \tag{13}$$

The unknowns in the above equations are the position dependent repulsive fields. These quantities are determined by substituting Eq. (3), Eq. (9) and Eq. (10) into the packing constraints, Eq. (8). Details numerical methodology can be found in Refs. [26-28].

3 Results and discussion

We present some representative results for the solvents responsive properties of mixed brushes.

First, we study the distributions of mixed brushes polymer segments at different strength of interaction between grafted polymers and selective solvents.

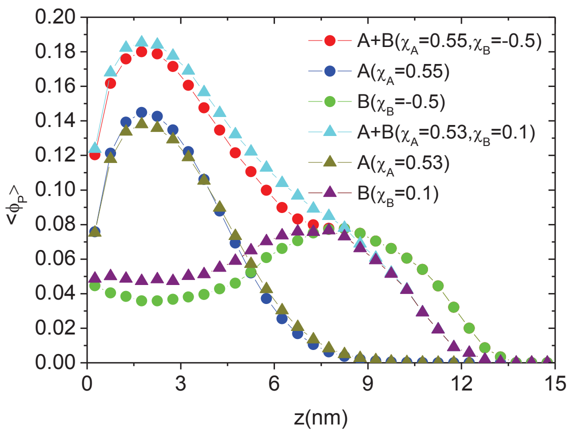

Figure 1: The average volume fraction of the grafted chains as a function of the distance from the surface for mixed brushes composed with polymer species A and B. The surface coverage is $\sigma_i=0.1\text{mn}^2$.

Fig. 1 shows the volume distribution of the mixed brushes composed with A and B. We assumed that B stands for the solvent species in a good solvent and the A species was exposed to a poor solvent. The volume distribution of the mixed brushes is determined by the total amount of species A and species B chains. Because of the different solvent selectivity, here, the A species forms the poor solvent layers, whereas the B species creates the upper, good solvent layer and is presented at the top of the brush. In this case, the perpendicular segregation, induced by solvent, in mixed brushes will be presented. This segregation can be rationalized as follows: The gain in B chain entropy upon moving out of inner layer region is much larger than that the loss of conformational entropy of the A chain collapse. It allows to regulate the repulsive excluded volume interactions and loss of conformational entropy through perpendicular segregation of the A and B chains. This conforms to the earlier theoretical studies [4] and simulations [31] that have already predicted various morphologies of similar domains in the situation of nonselective solvents, which have been qualitatively verified in experiment [32].

Many properties of brushes can be referred not only to the density profile but also to brush height. In monodisperse chains system, we define the height of the grafted layer by $H = \int < \phi_P(z) > zdz / \int < \phi_P(z) > dz$, and it measures the amount of stretching of the grafted polymers. Fig. 2 presents the height as a function of surface coverage for grafted polymers with a different χ_i. The significant dependence of its height on the solvent selectivity is visible. Fig. 2 demonstrates that the height of the grafted polymers decreases with increasing χ_i.

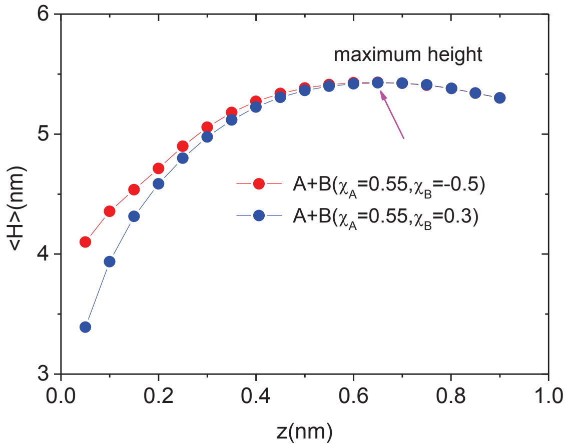

Figure 2: The height of the grafted layer as a function of the surface coverage for mixed brushes composed with polymer species A and B.

Fig. 2 shows the height of the mixed brushes composed A and B. We define the averaged height of the mixed brushes grafted layer by $H_{AB} = (\int < \phi_{PS}(z) > zdz + \int < \phi_{PB}(z) > zdz) / \int < \phi_{PA}(z) + \phi_{PB}(z) > dz$. The averaged height of the mixed brushes is determined by the total amount of A and B chains. It is interesting to note that the height of mixed brushes presents the maximum height at $\sigma = 0.65nm^{-2}$. There is the decrease of height in mixed brushes system when $\sigma > 0.65nm^{-2}$. This is because, at very high surface coverage, the micellar structures form in selective solvents, which have been presented by Zhu and Zhao [19, 24] and can't appear in monodisperse chains system.

We now turn to the thermodynamical behavior of the polymers layers in different

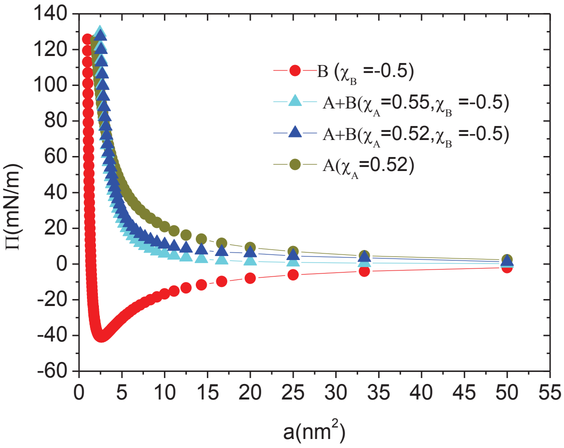

Figure 3: The lateral pressure-area isotherms of mixed brushes composed with polymer species A and B.

selective solvents. In particular, we concentrate our attention on the lateral pressure and the chemical potential of the polymer brush layers. The lateral pressure provides a direct measure of the lateral interactions within the polymer layer.

Fig. 3 shows the lateral pressure of the mixed brushes. In the presence of the both polymer A and B, the lateral pressure is determined by the repulsion between the blobs of A and B and the attractive interaction between species B chains. Since the solvent is poor for the A component, this lead to chains collapsed and the A segment density is high near the surface. This collapse results in a reduction in the conformational entropy of the A chains and also an increase in the segment A and segment B excluded volume interactions, which contribute significantly to the large and positive lateral pressure. At the same time, there are the attractive interactions between B segments, which contribute to negative lateral pressure. As a result, when area $\alpha > 4.5\text{nm}^2$, the total lateral pressure ($\chi_A = 0.55$, $\chi_B = -0.5$, $\chi_A = 0.52$, $\chi_B = -0.5$) is smaller compared with the lateral pressure in the monodisperse case at $\chi_i = 0.52$, and it is always larger than that in the monodisperse case at $\chi_i = -0.5$. As for as when area $\alpha < 4.5\text{nm}^2$, the total lateral pressure is larger than the lateral pressure in the monodisperse case at $\chi_i = 0.52$, it is because the total surface coverage of A and B is higher than in the monodisperse case. Therefore there are the large excluded volume interactions between polymer segments at very high surface coverage.

Fig. 4 presents the chemical potential of the grafted polymers as a function of the surface coverage for grafted polymer layers. The chemical potential increases monotonically. Because the system is incompressible, the chemical potential is an exchange chemical potential, that the exchange chemical potential measures the change in the free energy when the number of polymer molecule increases. The exchange potential measures the work required to replace solvent molecules by polymer molecules. The insertion of polymer molecules requires removing solvent molecules. Thus, when inserting polymers, the free-energy cost needs to be overcome. In mixed brushes, on one hand, the insertion of

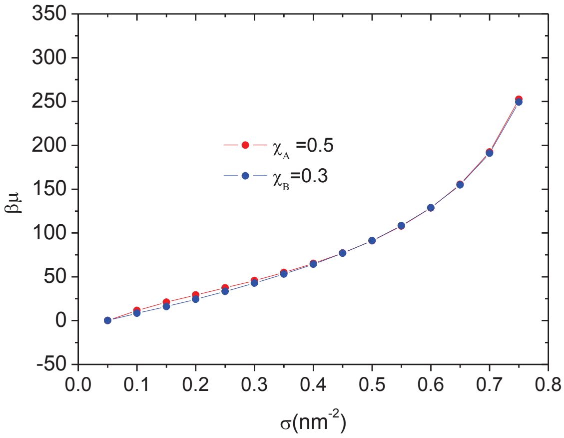

Figure 4: The chemical potential of the grafted layer as a function of the surface coverage for mixed brushes composed with polymer species A and B.

polymer molecules with high χ_i the more free-energy cost needs to be overcome. On the other hand, polymer molecules with high χ_i collapsed in poor solvents, which require removing less solvent molecules. So the chemical potential profile of polymer A and B in Fig. 4 present intersection.

4 Conclusions

We presented a molecular theory that enables the study of the effect of interaction between grafted polymers and solvent. In particular, we explore the switching mechanism upon exposure to different selective solvents in mixed brushes. The theory considers interaction between grafted polymers and solvent and its explicit coupling to the polymer conformations, that is, the polymer volume fraction. The results presented here can explain the switching mechanism of mixed brushes upon exposure to different selective solvents. To the investigations of the lateral pressure and the chemical potential give a further explain to the effect of selective solvents. The results can help to give a fundamental understanding of how solvent environments influence the molecular organization of grafted polymers chains.

It is important to mention at this point that the switching properties of the mixed brushes are also substantially dependent on temperature, concentration of ions and compatibility of two distinct grafted polymers. These properties of mixed brushes were comprehensively investigated [33-37]. In this paper, we concentrate on the effect of interaction between grafted polymers and solvent. The results also provide useful insights regarding the factors that need to be considered in designing materials, which respond to variable environments by changing their surface properties or for fine-tuning of wetting properties and provide guidance for the design of multicomponent brushes for specific applications.

Acknowledgments. We thank Dr. Chun-Lai Ren for his insightful discussion. This work was supported by the National Natural Science Foundation of China (Nos. 21264016 and 21364016) and General Foundation of Yi Li Normal University through (No. 2013YSYB17).

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