

Molecular theory investigate the switching of mixed brushes

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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.

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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 weight, the 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.