Smart Responsive Interface

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INTRODUCTION

Smart responsive materials are of great practical interest for engineering, medical applications, sensors, printing technologies, electronic devices, etc. Nature demonstrates very exciting examples of exploring the idea of smart materials to organize very sensitive and multilevel response in living organisms originated from a conformational response of biomacromolecules. Responsive soft interfaces play a key role in many biological processes. Mimicking of those principles brings stimulating ideas for the fabrication of soft synthetic polymer interfaces for various possible technical applications. In our study we explore the phenomena of phase segregation at polymer interface to develop responsive materials. This approach is based on a reach phase diagram for the polymer mixture confined in a thin polymer film when lateral mobility of the polymer chains is suppressed by chemical grafting, while a conformational change and mobility at the scale of molecular dimension make the phases to be very sensitive to external stimuli and interactions. [1-6] The polymer films demonstrate very pronounced response to change of solvent quality, temperature, and surface composition of the confining wall.

EXPERIMENTAL

We fabricate thin films from polymer chains of incompatible and functional polymers randomly tethered to the solid substrate as described elsewhere using "grafting to"[7] and "grafting from"[8] approaches. Si-wafers coated with a native silica layer (1.4 nm thick) are used as substrates for grafting. We introduce functional groups onto the silica coating with epoxy-silane molecules and use the epoxide and hydroxyl groups to graft polymers with two step grafting procedure when two different polymers are grafted one after another. Similar grafting procedure was developed to prepare the mixed grafted layers on polymer substrates when the functional groups were introduced via treatment with O_2 and NH_3 radio frequency plasma.[9] The grafting amount of the polymers is regulated by grafting conditions so that the total grafting density is quite large approaching the brush regime. In the brush regime grafted polymer chains are stretched away from the substrate because of the volume excluded effect. Practically, the grafting density of the mixed brushes is in the range of 0.01- 0.1 chains/nm^2 and molecular weight of the grafted chains is in the range from 10^3 to 10^6 g/mol. The asymmetry of the mixed brushes (ratio between grafting densities, and ratio between molecular weights of the polymers) is also regulated by appropriate choice of the experimental conditions. The composition of the brushes was analyzed with ellipsometry and ATR-FTIR spectroscopy.

We study morphology of the brushes with SPM. The lateral chemical resolution of the morphology was investigated with X-ray photo-electron emission microscopy.

RESULTS AND DISCUSSIONS

The smart interface was found to undergo very pronounced phase transitions upon exposure to different solvents. We have identified two most typical morphologies of the mixed brushes.[10] If incompatibility of two polymers (PS and PMA) is not very large the mixed brush form lamella like (ripple) morphology when two polymers form alternating elongated structures in common nonselective solvent (Fig. 1a). In this case both polymers were found on the top of the film and the interface demonstrates wetting behavior effected by the contributions of both polymers on the top of the film. If the mixed polymer layer either consists of two highly incompatible polymers (PS and P2VP) or it is exposed to selective solvent for one of the polymers the ripple morphology is not stable and the unfavorite polymer or the minority polymer forms clusters embedded in the matrix of the favorite or majority polymer. In this case the surface behavior of the film is dominated by the majority or favorite polymer, while the second component is hidden inside the film. The transition between two typical morphologies is reversible. The conditions of the transition can be regulated by change of solvent quality, temperature and asymmetry of the mixed brush. For example, if solvent selective for one of polymers (polymer A) was substituted by the solvent selective for the second polymer (B) the morphological transition from dimples B to dimples A was observed. At the same time the surface wetting behavior is changed from the properties dominated by polymer A to the properties effected by polymer B.

The same transition was observed if the mixed brush was interacting with confining wall.

We found that changes at interface introduced upon external stimuli can be used to switch wetting behavior, adhesion, adsorption, surface charge and chemical composition.[7-11] The results of our experiments clearly demonstrate that the simple principle of the regulated phase segregation in the mixed grafted brushes at nanoscopic dimensions turns into a powerful instrument to fabricate smart responsive materials for numerous potential applications.
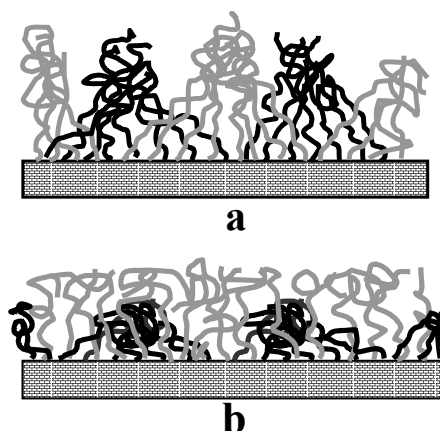

Figure 1. Schematic illustration of two possible morphologies of mixed brush irreversibly grafted to solid substrates (cross-section of the layer): ripple morphology in a nonselective solvent (a), dimple morphology in a solvent poor for the black chains (b).

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