

Nanoporous Block Copolymer Micelle/Micelle Multilayer Films with Dual Optical Properties

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Introduction

Block copolymer micelles (BCMs) composed of hydrophilic and hydrophobic segments such as polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) are known to incorporate hydrophobic materials (e.g., gold, magnetic nanoparticles or fluorescent dyes) into the hydrophobic core of micelles in water, and negatively charged PS-*b*-PAA containing hydrophobic dyes can be self-assembled with conventional polyelectrolytes (PEs) using the LbL method.^[1] Therefore, our motivation was to use BCMs in the fabrication of nanoporous thin films with integrated chemical, physical and optical properties and tailored film nanostructure. A main aim was to modulate film nanostructure through the size of hydrophobic or hydrophilic BCM segments, as these influence the size and shape of the micelles formed in aqueous solution, including their solubility.^[2] In this study, we report the preparation of optically active BCM nanoporous films, which are assembled making use of the electrostatic and hydrogen-bonding interactions between different BCMs, polystyrene-block-poly(4-vinylpyridine) (PS-*b*-P4VP) and anionic polystyrene-block-poly(acrylic acid) (PS-*b*-PAA)

Experimental

Formation of nanoporous structure

PS-*b*-P4VP block copolymers form cationic micelles with a hydrophobic PS core and a protonated P4VP shell in solutions at pH < 5. Above pH 5, PS-*b*-P4VP block copolymers are water-insoluble due to the deprotonation of P4VP segments. PS-*b*-PAA forms anionic micelles due to the conversion from uncharged carboxylic acid groups (e.g., COOH) to charged carboxylic acid groups (e.g., COO⁻) at pH > 3.^[3] By this phenomenon the charge densities of PS-*b*-P4VP and PS-*b*-PAA BCMs can be easily controlled by the solution pH. These complementary charge densities enables the preparation of BCMS micelle/micelle multilayer film by layer-by-layer method.

Antireflective & photochromic effect

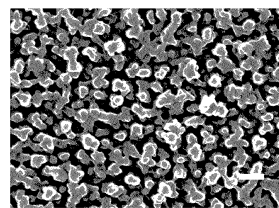
PS_{7K}-*b*-P4VP_{28K}/PS_{2K}-*b*-PAA_{8K} films prepared at pH 4 (for PS_{7K}-*b*-P4VP_{28K}) and pH 6 (for PS_{2K}-*b*-PAA_{8K}) are highly nanoporous and antireflective.^[4-5] Multilayer films with antireflective and photochromic properties were obtained by incorporating a water-insoluble photochromic dye (spiropyran) into the hydrophobic PS core of the BCMS assembled in the films. The optical properties of these films can be modulated by UV irradiation to selectively and reversibly control the transmission of light. Light transmission of higher than 99 % was observed with accompanying photochromism in the (PS_{7K}-*b*-P4VP_{28K}/PS_{2K}-*b*-PAA_{8K})_n multilayer films assembled at pH 4/6.

Results and discussion

SEM images of nanoporous (PS_{7K}-*b*-P4VP_{28K}/PS_{2K}-*b*-PAA_{8K})_n multilayer films

Figure 1 shows the influence of bilayer number ($n = 30$) on the surface morphology of (PS_{7K}-*b*-P4VP_{28K}/PS_{2K}-*b*-PAA_{8K})₃₀ films deposited at pH 4/6. The small and largely spherical features (43 ± 2.1 nm diameter) seen in the (PS_{7K}-*b*-P4VP_{28K}/PS_{2K}-*b*-PAA_{8K})₅ film suggest that individual BCMS are involved in the multilayer to form such structure, as the sizes of PS_{7K}-*b*-P4VP_{28K} and PS_{2K}-*b*-PAA_{8K} measured from AFM are 9.8 ± 2.2 nm and 4.9 ± 0.8 nm, respectively. The size of these features regularly increases with increasing the bilayer number. This is attributed to the BCMS selectively adsorbing to the oppositely charged preadsorbed micelle aggregates. The aggregate feature size for the 30-bilayer film is 110 ± 21 nm (see

Figure 1). Although the root mean squared surface roughness of these films increases from 7 nm (5 bilayers) to about 30 nm (30 bilayers), due to the evolution of interconnected nanostructure, the film surfaces are highly uniform and homogeneous.



Scale bar 200 nm

Figure 1. SEM images of nanoporous (PS_{7K}-*b*-P4VP_{28K}/PS_{2K}-*b*-PAA_{8K})₃₀ multilayer films formed at pH4/6 as a function of bilayer number.

Dual Optical Properties

In order to demonstrate dual optical properties (i.e., photochromic property along with antireflective property) based on the BCM/BCM multilayer films, water-insoluble spiropyrans,^[6] which have light-induced reversible isomerization between colorless spiropyran and colored forms of merocyanines, were incorporated into the hydrophobic PS cores of PS_{7K}-*b*-P4VP_{28K} (pH 4) and PS_{2K}-*b*-PAA_{8K} (pH 6) micelles to prepare photochromic nanoporous multilayer films. Our approach using micelles affords thickness-tunable thin films loaded with spiropyran. Spiropyran-loaded (PS_{7K}-*b*-P4VP_{28K}/PS_{2K}-*b*-PAA_{8K})_n films assembled at pH 4/6 were measured by the UV-vis absorption spectra with increasing bilayer number ($n = 2$ to 34)

When converting from these absorption spectra to light transmission curves, these films show the reversible photochromic effect with about 99 % light transmission between 650 ~ 900 nm (Figure 2). These films showing both antireflective and photochromic effects selectively as well as reversibly improve the light transmission and filter the light at a desired wavelength by irradiating with UV light.

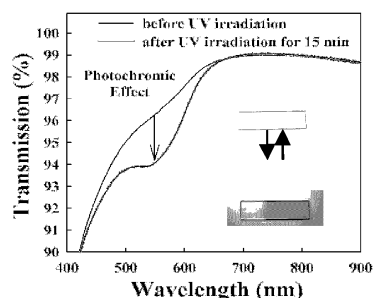


Figure 2. Light transmission curve of (PS_{7K}-*b*-P4VP_{28K}/PS_{2K}-*b*-PAA_{8K})₃₄ multilayer films before and after UV irradiation

Conclusions

We have demonstrated the formation of highly nanoporous films composed of two different BCMS through layer-by-layer (LbL) assembly on substrates. The films thus prepared showed tunable optical properties, with strong antireflective properties with light transmission above 99%. Considering the wide application areas of both LbL multilayers and block copolymer thin films, the approaches introduced in present study are likely to open up new possibilities for devices with multifunctional properties.

References

- [1] Ma, N.; Zhang, H.; Song, B.; Wang, Z.; Zhang, X. *Chem. Mater.* 2005, 17, 5065-5069
- [2] Terreau, O.; Luo, L.; Eisenberg, A. *Langmuir* 2003, 19, 5601-5607
- [3] Choi, J.; Rubner, M. F. *Macromolecules* 2005, 38, 116-124
- [4] Walheim, S.; Schaffer, E.; Mlynek, J.; Steiner, U. *Science* 1999, 283, 520-522
- [5] Hiller, J.; Mendelsohn, J. D.; Rubner, M. F. *Nature Mater.* 2002, 1, 59-63
- [6] Chabrera, I.; Krongauz, V. *Nature* 1987, 326, 582-585.