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Hydrogen-Bonded Polymer Capsules Formed by Layer-by-Layer Self-Assembly

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INTRODUCTION

Coating nano- and micrometer-sized solid particles with polyelectrolyte multilayers by layer-by-layer (LBL) sequential adsorption of polymers attracts growing interest[1,2] as an effective means to encapsulate a large number of materials. Multilayer walls can be made of a variety of different components. In contrast to electrostatic self-assembly that has been commonly used to produce the multilayer capsules, hydrogen-bonding interactions represent an alternative driving force for the LBL growth of multilayers.[3] In this work, we focus on hydrogen-bonded multilayers. We show that despite the polymers in hydrogen-bonding self-assembly are virtually uncharged robust hollow multilayer capsules can be produced. We also show that hydrogen-bonded multilayers can be easily stabilized at neutral and basic pH values by chemical cross-linking using carbodiimide chemistry.

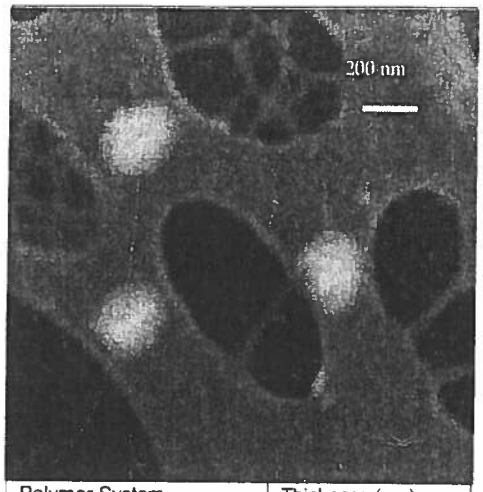
EXPERIMENTAL

Poly(N-vinylpyrrolidone) (PVPON) with M_w 55,000 was bought from Aldrich, poly(methacrylic acid) (PMAA) with M_w 150,000, and poly (ethylene oxide) (PEO) with M_w 200,000 were purchased from Scientific Polymer Products, Inc. All chemicals were used without further purification. The template cadmium carbonate particles were synthesized as described in the literature.[4] The PVPON/PMAA or PEO/PMAA multilayers were prepared using the LBL technique with a centrifugation setup as described earlier[1]. Polymers were deposited from 0.2 mg/mL solutions starting from PMAA at pH = 7. The deposition of PVPON/PMAA or PEO/PMAA layers was then continued at pH = 3.5, starting from the PVPON or PEO layer. In a typical experiment 10 polymer layers were deposited. The $CdCO_3$ core of the polymer-covered particles was then dissolved by exposing the particles to buffer solution at pH = 1.1 for 30 minutes. The cross-linking procedure included activation of the carboxylic groups with 1-ethyl-3-(3-(dimethylamino)-propyl) carbodiimide hydrochloride (EDC) solution and subsequent treatment with ethylenediamine (EDA) solution. The template size measurements were carried out using dynamic light scattering. Formation of the capsules was followed by fluorescence optical microscopy. ATR-FTIR and electron energy-loss spectrometry[5] measurements were used to determine the thickness of capsule walls.

RESULTS AND DISCUSSION

We have shown that hollow multilayer capsules can be produced using hydrogen-bonding self-assembly. Unless they were covalently cross-linked, the PVPON/PMAA and PEO/PMAA capsules disintegrated at pH = 6.9 and pH = 4.6, respectively, which is in good agreement with those obtained for the films on a flat substrate.[6] The stability of the produced capsules has been improved after treatment with EDC followed by reacting with EDA. PVPON/PMAA capsules became stable at pH = 10 and did not disintegrate for several months. PEO/PMAA capsules could also be observed for at least 6 days when exposed to pH = 7.

Figure 1 shows high-angle annular-dark-field STEM image of PEO/PMAA capsules (bright contrast) on a lacy-carbon TEM support film. The darkest areas represent pores in the support film. The table below summarizes the average multilayer film thicknesses, determined from at least 12 different capsules per specimen. PEELS spectra were collected at 20 nm intervals along line scans that transected individual multilayer capsules. The average capsule wall thickness was obtained by averaging 10 measurements from a given capsule and at least 12 capsules in each of the two specimens (PEO/PMAA and PVPON/PMAA) studied.



Polymer System	Thickness (nm)
PEO/PMAA	16 ± 3
PVPON/PMAA	18 ± 4

Figure 1. High-angle annular-dark-field STEM image of PEO/PMAA capsules (bright contrast) on a lacy-carbon TEM support film. The table below summarizes the average multilayer film thickness.

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