



Formation of self-rolled polymer microtubes studied by combinatorial approach

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ABSTRACT

This paper describes an experimental study of the polymer microtube formation in different fabrication conditions. A photolithography route is demonstrated for the fabrication of large amount of uniform and good quality polymer microtubes. TEM grids were used as mask and exposure of UV radiation was done in two steps to create asymmetric patterns. The diameter of tube was controlled by regulating the thickness of polymer layers, UV radiation dose and concentration of acidic solution. The results indicate that thickness of the bilayer film was the most dominating factor to determine the tube's dimension, and diameter of the tubes increased with increase in the thickness of bilayer. The kinetics of the tube formation was studied with respect to acidity of the solution and UV dose. Rate of rolling increased with the acidity of the solution. Tube diameter and rate of rolling decreased with the increase of the UV exposure time. Films with two-dimensional gradients of layer thicknesses were prepared to study a broad range of parameters in a single experiment. The tubes were characterized in detail using optical microscopy and scanning electron microscopy. These polymer microtubes have potential applications in microfluidic devices and biotechnology field.

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1. Introduction

Polymer micro- and nanotubes have been demonstrated to possess remarkable applications in various fields such as microfluidic devices [1], chromatography [2], biotechnology [3], medicine [4] and chemical sensors [5]. Recently, a novel approach for fabrication of such mesoscopic tubes by self-rolling of strained bilayer film was developed [6–13]. A thin bilayer film minimizes its potential energy by bending and scrolling when the strained top and bottom layer is allowed to relax. Strain in this case develops due to unequal swelling of polymers in selective solvents. The rolled up layers stick together thus forming a perfectly bonded tube wall. The main

advantage of self rolling technique is the possibility of complex engineering of future inner walls of the tubes [14,15]. The small dimensions and the remarkable physico-chemical properties of their inner walls are important for the micro and nanofluidic systems because ion and chemical transport can be regulated by molecular-recognition sites on the channel wall [16].

Although the general principle of the tube's formation via self-rolling is well known today, the dependence of the tube's characteristics on the dimensions of rolling bilayer and the parameters of fabrication are still poorly understood. The goal of our present paper is experimental systematic study of the polymer microtube formation in various fabrication conditions. We explore the dependence of the tube's diameters on the thickness of each of the polymer layers in the double-layer structure. Then, the dependence of the tube's diameters on the degree of short-wavelength UV cross-linking is investigated.

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Finally, the rate of rolling as a function of the UV exposure dose and solvent selectivity are obtained. Also, in the present paper we report the improvements in the photolithography route to microtube fabrication, which permits parallel production of large amount of uniform, high quality tubes.

2. Fabrication scheme

Poly(4-vinylpyridine) (P4VP) $\{M_n = 45,900, M_w = 82,500\}$ and Polystyrene-*b*-Poly(4-vinylpyridine) (PS-*b*-P4VP) $\{M_n = 35,000\text{--}2700\}$ were obtained from Polymer Source Inc. Poly(4-bromostyrene) (BrPS) was synthesized from 4-bromostyrene by nitroxide mediated radical polymerization. Ten grams of freshly distilled 4-bromostyrene (0.055 mol) and 0.032 g of 2,2,5-Trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane, alkoxyamine (0.1 mmol) were placed in a round bottom flask equipped with magnetic stirring bar and sealed with a rubber septum. Argon was bubbled through the mixture using stainless steel needle for 30 min. After that the mixture was heated at 123 °C for 2 h. The viscous polymer solution so obtained was diluted with tetrahydrofuran (THF) and poured into hexane. The solid was filtered, redissolved in dichloromethane and precipitated into tenfold excess of diethyl ether and dried in vacuum at 50 °C. Yield – 8 g (80%). GPC: $M_n = 25,000, M_w = 46,000, PDI = 1.77$. 4-Bromostyrene was purchased from Sigma–Aldrich and distilled under reduced pressure before use. THF, diethyl ether and hexane were purchased from Sigma–Aldrich. Toluene, chloroform and dichloromethane were purchased from Acros Organic and used as received.

Silicon wafer were used as the substrates and were cleaned before their use by sonication in dichloromethane for 15 min followed by heating in H_2O_2, NH_4OH and millipore water solution (1:1:2) for 1 h at 65 °C. Subsequently the silicon wafers were rinsed 3–4 times with millipore water and dried under nitrogen stream. A polymer bilayer was created by consecutive deposition of P4VP and BrPS, from chloroform and toluene solutions, respectively, by dip-coating technique. A 4–5 nm thin layer of PS-*b*-P4VP block copolymer was deposited on the P4VP layer before deposition of BrPS, in order to provide a better adhesion between the BrPS and P4VP layers. Photolithography was used for patterning the bilayer. UV lamp (G8T5, TecWest Inc., USA) having a 2.5 W output at 254 nm was used to irradiate the P4VP/BrPS bilayer. The estimated exposure dose was 4.11 J/cm² for 30 min. Irradiation with <280 nm UV light is known to lead to generation of free radicals, chain scission and crosslinking of PS [17] and P4VP [18]. TEM copper grids (400 lines per inch) were used as a photo mask. Irradiation with short-wave UV ($\lambda = 254$ nm) causes photo-crosslinking of BrPS and P4VP in irradiated regions. The pattern was developed by washing the uncured polymer (both BrPS and P4VP) using a non-selective solvent (chloroform). Finally, the microtubes were produced by immersion of the samples in aqueous solutions of hydrochloric acid (HCl). The protonation of pyridine rings results in Columbic repulsion of the 4VP units and selective swelling of the P4VP layer. This swelling, opposed by the stiff BrPS layer, gives rise to the bending moment in the film,

that leads to the film detachment from the substrate and curling (Fig. 1). Since the BrPS layer acts as the protective layer for the P4VP one, the rolling starts and proceeds from the opening in the film, produced by photo-patterning. More detailed description of the photolithography route is described elsewhere [14].

Self-rolling from uniform openings in the bilayer, produced either by photolithography or any other approach (e.g. mechanical scratching) results usually in twin tubes [10,19]. In order to obtain the uniform single tubes, we apply the procedure of asymmetric photo-patterning (Fig. 2). The polymer bilayer is exposed twice to the UV light, once at the normal incident angle, and then at a certain inclination. After the development of the pattern in chloroform, the asymmetric ratchet-like profile of the bilayer is obtained (Fig. 2d). The tubes are formed by rolling from the steeper edges of the polymer stripe. This is so because the adhesion energy does not depend on the thickness of the film, although the bending energy does. At the thin side of the profile, the gain of energy via rolling is insufficient to prevail the adhesion to the substrate, whereas at the steep side the bending moment is strong enough to detach the film from the surface.

Optical micrographs of polymer bilayers with typical developed patterns and their unidirectional rolling are shown in Fig. 3a and b. Optical micrograph of twin tubes and SEM micrograph of tubes are shown in Fig. 3c and d, respectively.

3. Effect of fabrication parameters on the diameter of tubes

The diameter of the tubes depends on a number of factors, the most important being the thickness of each of the components of the bilayer, the stiffness of the polymer networks in the collapsed and the swollen states, the degree of swelling, and the strength of adhesion to the substrate. In the present study, we do not attempt to make a more detailed comparison of the experimental data with a theoretical model. This comparison is not possible at the present state of our knowledge about the system for several reasons. First, such parameters entering in the model as Young moduli of the polymers in the glassy and swollen states are not

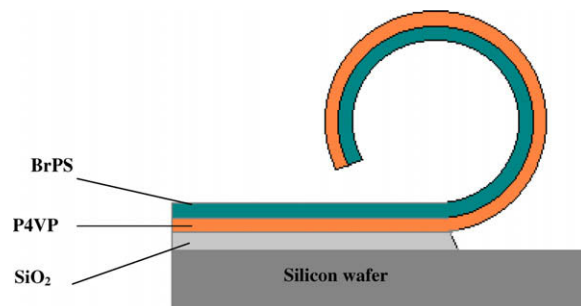


Fig. 1. Schematic presentation of self rolling of P4VP/BrPS bilayers. Rolling occurs due to etching of SiO_2 layer by the hydrochloric acid which releases the polymer film.

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