Available online at www.sciencedirect.com

ScienceDirect

Colloids and Surfaces A: Physicochem. Eng. Aspects 308 (2007) 123–128

COLLOIDS AND SURFACES A

www.elsevier.com/locate/colsurfa

Characterization of polymer brushes in capillaries

A.N. Constable, W.J. Brittain *

Department of Polymer Science, University of Akron, 170 University Ave, Akron, OH 44224, United States

Received 5 February 2007; received in revised form 7 May 2007; accepted 24 May 2007

Abstract

The synthesis of various polymer brush coatings were performed in 0.075 mm i.d. fused silica capillary tubing by atom transfer radical polymerization (ATRP). Although characterization of polymer coatings inside of capillaries is extremely difficult, we will show how fluorescence spectroscopy can be used as a technique to verify that covalently attached polymer brushes are present. Capillary rise measurements show the Zisman critical surface energy (γ_c) changes as the polymer coatings are changed from either hydrophilic or hydrophobic. The hydrophilic and hydrophobic nature of polymers leads to selective flow behavior in micro-capillaries that will allow passive flow control.

Keywords: Coatings; Capillary rise; Atom transfer radical polymerization; Surface energy; Polymer brushes

---

1. Introduction

Polymer brushes have been widely studied due to their unique stimuli-responsive nature [1–5]. By functionalizing the surface of a material, it is possible to create chemical gates [6–9] that will lead to flow manipulation. It has been shown that tailoring the surface properties of micro-capillaries facilitates separations in capillary electrophoresis [10–13].

Polymer brushes can be described as polymer chains tethered to a surface or interface with a sufficiently high grafting density such that the chains are forced to stretch away from the tethering site [14]. In this work, the polymer brushes were synthesized via atom transfer radical polymerization (ATRP) using the “grafting from” approach. An immobilized ATRP initiator is first covalently attached to the surface, followed by the polymerization of the desired polymer. ATRP is known to be a controlled/“living” polymerization that allows for the formation of complex molecular architecture [15,16].

Characterization of the polymer brush on the inside of the capillary is challenging compared to the analysis of flat or spherical surfaces. However, coated capillaries can be characterized by their wetting properties as suggested by de Gennes [17]. Depending on the liquid chosen, polymers can be partially or completely be wetted.

In this work, the Zisman critical surface energy (γ_c) was used to estimate if the capillary rise corresponding to a particular polymer coating relates well with its γ_c on a flat wafer which was determined by measuring the polymers advancing water contact angel. Herein, we characterize surface coatings that have been polymerized via ATRP inside of capillaries using capillary rise. We will relate the contact angels that have been measured on flat surfaces and the calculated Zisman critical surface energy data with the height measurements that were measured from capillary rise. This data will be used to study the effects of flow in capillaries and how it can be manipulated.

2. Experimental

2.1. Materials

Unless otherwise stated, all reagents were purchased from Aldrich Chemical Co. 2-Hydroxyethyl methacrylate (HEMA, 98%), methyl acrylate (MA, 99%), methyl methacrylate (MMA, 99%), pentafluorostyrene (PFS, 99%), styrene (S, 99%), and *tert*-butyl acrylate (t-BA, 98%) were passed through a column of activated basic alumina prior to use. (11-(2-Bromo-2-methyl)propionyloxy)undecyltrichlorosilane was synthesized as described in the literature [18]. 2-(8-Methacryloyloyx-3,6-dioxaoctyl)thioxantheno[2,1,9-dej]isoquinoline-1,3-dione (Hostasol) was donated by Professor Dave Haddleton from the University of Warwick. Purification of copper(I)bromide

---

* Corresponding author. Tel.: +1 585 338 6263; fax: +1 585 338 0042.
E-mail address: William_j_brittain@bausch.com (W.J. Brittain).

0927-7757/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2007.05.059

(98%) was done according to literature methods [19]. *N*,*N*,*N*′,*N*′,*N*″-Pentamethlydiethylenetrimine (PMDETA, 99%), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 97%), ethyl 2-bromoisobutyrate (E2Br-iB, 98%), copper(II)bromide (99%), anhydrous anisole (99%), anhydrous acetone (99.8%), anhydrous methyl alcohol (99.8%), anhydrous *o*-xylene (97%), and reagent plus ethylene glycol (≥99%) were used without further purification. 75 μm i.d. × 363 μm o.d. undeactivated fused silica capillary was purchased from Western Analytical Products, Inc., silicon wafers were purchased from Wafer World Inc., while silicon ATR crystals (25 mm × 5 mm × 1 mm) were purchased from Harrick Scientific.

3. Methods

3.1. Substrate cleaning and initiator deposition

ATR crystals, silicon wafers, and capillaries were cleaned by treatment with freshly prepared "piranha" solution (70/30, v/v, concentrated H_2SO_4/30% aqueous H_2O_2) at 90 °C for 2 h. The capillary was fitted with a water jacket while one end of the capillary was placed into the "piranha" solution and the other was placed in an empty Schlenk flask. The "piranha" solution was introduced to the capillary by reduced pressure while heating with circulating, hot water through the water jacket. The samples were then removed and rinsed with copious amounts of deionized (DI) water followed by drying in a nitrogen stream. It should be noted that the "piranha" solution is extremely reactive and should be handled with care. Into a dried Schlenk flask were placed a freshly cleaned end of the capillary, silicon wafer, and ATR crystal. Anhydrous toluene (15 mL) and a 25 vol.% solution of the trichlorosilane initiator in toluene (0.5 mL) were added to the flask. The opposite end of the capillary was placed through a rubber septum that was sealed around a Schlenk flask. The flow of solution was induced through the capillary via a combination of positive nitrogen and reduced pressure at opposite ends. The reaction proceeded for 18 h at room temperature. The silicon wafer, ATR crystal, and capillary were washed with toluene, sonicated in toluene for 15 min, followed by rinsing in toluene and nitrogen drying.

3.2. Typical procedure for surface initiated ATRP

The capillary was fitted and sealed in a cylindrical water jacket, leaving the two ends to be fitted into Schlenk flasks. A 50 mL Schlenk flask was used to hold one end of the capillary, silicon wafer, and ATR crystal and was placed in the oil bath. The oil bath and the circulating water bath were set to the desired temperature. The opposite end of the capillary was fitted into a small Schlenk flask and sealed. The flasks were degassed and back-filled with nitrogen three times and left under a nitrogen atmosphere. CuBr, solvent, monomer, and magnetic stir bar were added to a separate 100 mL Schlenk flask and sealed. The solution was subjected to three freeze-pump-thaw cycles using nitrogen as the backfill gas. PMDETA was added to the solution via a syringe, and it was stirred at the polymerization temperature until it became homogeneous (~15 min). Free initiator (E2Br-iB) was added via a syringe to the flask containing the silicon wafer, ATR crystal, and capillary, followed by transfer of the CuBr/ligand solution via cannula. The polymerization was allowed to proceed at room temperature for 3 h (HEMA), 90 °C for 6 h (MA), 60 °C for 6 h (MMA), 90 °C for 19 h (PFS), 90 °C for 8 h (S), and 60 °C for 6 (*t*-BA). At the end of the reaction, the wafers and capillary were removed and rinsed with CH_2Cl_2 and THF. To remove untethered polymer chains, the silicon wafer and ATR crystal were placed in a Soxhlet extractor and extracted with THF for 24 h followed by sonication in THF for 30 min followed by drying with an air stream. The capillary was rinsed with THF for 24 h and then sonicated for 15 min and dried with nitrogen. Final concentrations were as follows: $[\text{HEMA}]_0 = 123$ mM, $[\text{methyl alcohol}]_0 = 370$ mM, $[\text{HMTETA}]_0 = 0.51$ mM, $[\text{CuBr}]_0 = 0.36$ mM, $[\text{E2Br-iB}]_0 = 0.15$ mM; $[\text{MA}]_0 = 111$ mM, $[\text{anisole}]_0 = 184$ mM, $[\text{PMDETA}]_0 = 0.90$ mM, $[\text{CuBr}]_0 = 0.49$ mM, $[\text{E2Br-iB}]_0 = 0.46$ mM; $[\text{MMA}]_0 = 47$ mM, $[\text{anisole}]_0 = 92$ mM, $[\text{PMDETA}]_0 = 0.94$ mM, $[\text{CuBr}]_0 = 0.47$ mM, $[\text{E2Br-iB}]_0 = 0.47$ mM; $[\text{PFS}]_0 = 36$ mM, $[o\text{-xylene}]_0 = 164$ mM, $[\text{PMDETA}]_0 = 0.53$ mM, $[\text{CuBr}]_0 = 0.27$ mM, $[\text{E2Br-iB}]_0 = 0.27$ mM; $[\text{S}]_0 = 118$ mM, $[\text{anisole}]_0 = 152$ mM, $[\text{PMDETA}]_0 = 0.77$ mM, $[\text{CuBr}]_0 = 0.38$ mM, $[\text{E2Br-iB}]_0 = 0.16$ mM; $[t\text{-BA}]_0 = 89$ mM, $[\text{acetone}]_0 = 230$ mM, $[\text{PMDETA}]_0 = 0.45$ mM, $[\text{CuBr}]_0 = 0.30$ mM, $[\text{E2Br-iB}]_0 =$ 0.15 mM; fluorescence experiments: $[\text{Hostasol}]_0 = 0.047$ mM, $[\text{MMA}]_0 = 47$ mM, $[\text{anisole}]_0 = 92$ mM, $[\text{PMDETA}]_0 = 0.94$ mM, $[\text{CuBr}]_0 = 0.47$ mM, $[\text{CuBr}_2]_0 = 0.047$ mM.

3.3. Typical procedure for diblock copolymer synthesis

Preparation of diblock copolymers was conducted in a similar manner to that for the homopolymer brushes. The order of the blocks in the diblock brush was determined by the order of polymerization from the surface. For example, a Si/SiO_2//PS-*b*-PMA brush was synthesized by first forming Si/SiO_2//PS brush on the surface, followed by the polymerization of MA from the Si/SiO_2//PS brush. The same concentrations that were used in the homopolymer brush synthesis were used in the diblock copolymer synthesis.

3.4. Typical procedure for deprotection of tert-butyl acrylate to acrylic acid

A P(*t*-BA)-modified silicon wafer and ATR crystal were placed in a crystallization dish while the capillary was placed inside a glass column. These were then added to an oven preheated to 190–200 °C for 2 h under reduced pressure. The silicon wafer, ATR-crystal, and capillary were rinsed with DI water and then submerged in DI water overnight following previous procedure [4].

3.5. Characterization methods

FTIR-ATR spectra were recorded with a Bruker Tensor 27 spectrometer using a modified 4XF beam condenser (Harrick