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Surface modification of microfluidic channels by UV-mediated graft polymerization of non-fouling and 'smart' polymers

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Abstract

Microfluidic channels prepared from polydimethylsiloxane (PDMS) have been modified by UV-mediated graft polymerization of temperature-responsive polymers (poly[*N*-isopropyl acrylamide] or pNIPAAm), temperature- and pH-responsive copolymers (P[NIPAAm-co-acrylic acid (AAc)]), and a non-fouling hydrogel (polyethyleneglycol diacrylate, or PEGDA). This was done by presorbing a photosensitizer (PS) within the PDMS channel surface regions, contacting the different monomer solutions with the PS-containing surface under nitrogen, and irradiating with UV. The pNIPAAm-grafted surface was hydrophilic below its lower critical solution temperature (LCST), resisting non-specific adsorption, while it was hydrophobic above its LCST, now binding pNIPAAm-coated nanoparticles. Combined temperature- and pH-responsive surfaces were also prepared by UV radiation grafting a monomer mixture of pNIPAAm with AAc. The surfaces have been characterized by advancing water contact angle measurements. These smart microfluidic channels should be useful for many applications such as affinity separations and diagnostic assays.

Keywords: Smart polymers; N-isopropylacrylamide; Nanobeads; UV-graft polymerization; Microfluidics

1. Introduction

Conventional microfluidic devices have been fabricated of materials such as silicon and glass (Harrison et al., 1993; Sato et al., 2006). However, the production of microfluidic devices made of glass or silicon is generally expensive, time consuming, and fragile. Consequently, polymer-based microfluidic devices are rapidly gaining popularity primarily due to their ease of fabrication, inexpensive costs, and increasing versatility (Roberts et al., 1997; Lionello et al., 2005). These devices have been fabricated from a variety of different polymers including poly(methyl methacrylate) (PMMA), polycarbonate, polystyrene, polyethylene terephthalate (PET), and poly(dimethylsiloxane) (PDMS). However, most of the commercially available polymers for microfluidic applications are hydrophobic (Duffy et al., 1998; Makamba et al., 2003; Unger et al., 2000). The hydrophobic nature could be problematic for the aqueous solutions to be used in microfluidic devices for biologic separations and assays. Unlike loading samples in hydrophilic channels using capillary force, external pumping is necessary to wet hydrophobic channels. Furthermore, as a result of hydrophobic interactions, the surfaces may bind specific compounds from the solution passing through the channels, changing their concentration in the solution and affecting the reliability of quantitative assays.

From these perspectives, a variety of surface modifications have been proposed, e.g., oxygen plasma treatment, adsorbed coatings of surfactants (Ocvirk et al., 2000), and protein or lipid coatings (Yang et al., 2001). These surface treatments, however, can be unstable requiring periodic reapplication. Therefore, many efforts have been devoted to covalent modification of the surfaces with a hydrophilic polymer such as poly(ethylene glycol) (PEG) because the covalent attachment of such polymers onto a polymer surface resists adsorption of components from the solutions, and ensures long-term chemical stability of grafted chains. Radiation graft polymerization has been widely used for over 50 years throughout polymer chemistry. Typically, it involves creation of reactive sites (radicals) on the polymer surface followed by covalent linkage of

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a preformed polymer or more commonly by the polymerization of a monomer from those radical sites. Ultraviolet (UV) graft polymerization is highly attractive as a method for the surface modification of microfluidic devices, particularly when the surfaces having no chemically reactive groups (Richey et al., 2000; Hu et al., 2002, 2004a, b). UV irradiation can generate free radicals just within the surface regions of the polymer channel. The graft density can be controlled with irradiation time and the depth of penetration of the graft polymer and overall grafting weight can be influenced by the concentration of photosensitizer (PS) within the surface regions (Hu et al., 2004a, b; Wang et al., 2005). UV graft polymerization can also be patterned through masks, permitting spatial control of functionalization within the microchannels.

Modification of the channel walls with smart, reversible polymers leads to properties such as reversible hydrophilic–hydrophobic surfaces with useful actions such as valve functions (Idota et al., 2005, 2006). The reversible surfaces further permit physical or covalent immobilization of biomolecules such as proteins and protein-smart polymer conjugates. We have already demonstrated temperature-responsive microchannel walls chemically modified with poly(*N*-isopropylacylamide) (PNIPAAm), a temperature-responsive polymer, as an 'on–off' switchable molecular trap (Ebara et al., 2006). In this study, we review the UV surface modification technology as characterized with contact angle measurements, and also demonstrate the versatility of this technique to form a dual temperature- and pH-responsive microchannel wall by UV-grafting a temperature- and pH-responsive polymer.

2. Experimental

2.1. Materials

N-Isopropylacrylamide (NIPAAm), acrylic acid (AAc), poly(ethylene glycol) diacrylate (PEGDA, Mn:575), benzophenone, $NaIO_4$, and benzyl alcohol were all obtained form Aldrich. Primary amine-functionalized polystyrene latex beads with 100 nm diameter were obtained from Polyscience (Warrington, PA). (1-Ethyl-3-[3-dimethylaminopropyl]carbodiimide:hydrochloride) (EDC) was purchased for Pierce Chemical (Rockford, IL). Sylgard 184 was purchased from Dow Corning (Midland, MI). Negative photoresist SU8-50 was purchased from Microchem (Newton, MA).

2.2. Device fabrication

PDMS prepolymer was prepared by mixing PDMS base with a curing agent in a 10:1 ratio by weight and degassing the mixture under vacuum (Hoffman et al., 2004). The mixture was cast against the pattered silicon master and cured at 60 °C for 3 h. A piece of silicone tubing was embedded into the PDMS to create an access inlet to the channels. PDMS devices were then assembled using O_2 plasma bonding. The microchannels used in this study were 0.1 mm deep and 0.1 or 0.5 mm wide.

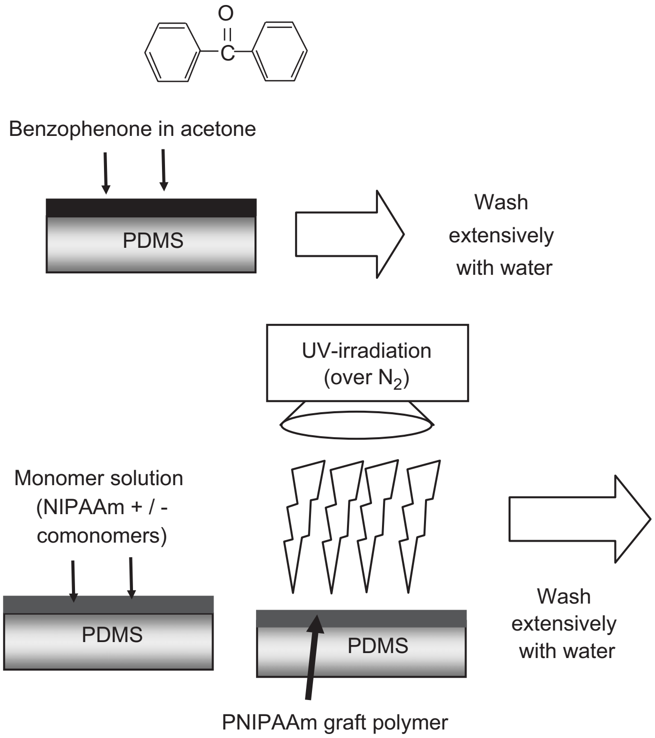

Fig. 1. PNIPAAm-grafted PDMS surfaces were prepared by UV-mediated graft polymerization. First, PDMS channels were coated with benzophenone, a photosensitizer, which was dissolved in acetone and flowed into the channel for less than 1 min. The channel was then washed extensively with water to remove the acetone. A solution containing monomer (10% in water), $NaIO_4$ (0.5 mM), and benzyl alcohol (0.5 wt%) was then loaded into the channel and the device was exposed to UV radiation.

2.3. UV-induced graft polymerization

UV-mediated grafting was directed according to a previously published protocol (Hu et al., 2004a, b). Briefly, benzophenone, a PS was dissolved in acetone and flowed into the channel for less than 1 min (Fig. 1). The channel was then washed extensively with water. A solution containing NIPAAm (10% in water), $NaIO_4$ (0.5 mM), and benzyl alcohol (0.5 wt%) was loaded into the channel, which was then irradiated with UV light (100 W, 365 nm, Ted Pella Inc.) for the times indicated. The temperature inside the channel during UV exposure was kept under the LCST of PNIPAAm by cooling with ice water because longer exposure to the UV could increase the solution temperature, resulting in the phase transition and aggregation of growing polymer chains (Wu et al., 1992). pH-sensitive poly(NIPAAm-co-AAc)-grafted surfaces were also prepared by copolymerizing 10 mol% AAc as the pH-sensitive moiety. For water contact angle measurements, flat PDMS surfaces with or without grafted polymers were also prepared and grafted using the same protocol.