DESIGN, SYNTHESIS AND CHARACTERIZATION OF A THIOLATED TEMPERATURE-RESPONSIVE POLYMER FOR SMART NANOFLUIDIC CONTROL

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ABSTRACT

By utilizing the strategy of reversible addition fragmentation chain transfer (RAFT) polymerization, we succeeded in the synthesis of a thiolated temperature-responsive polymer, poly(N-isopropylacrylamide) (referred to as PNIPAAm-SH), with characteristics of well-controlled chain structure, low molecular weight, narrow polydispersity, and sharp phase transition temperature. These characteristics were ideal for the realization of our proposed concept of smart nanofluidic control (SNC) , which is believed to be able to conquer the technical bottleneck in fluidic control in nanofluidic fields and are promising to contribute to the broadening of the applications of nanofluidics.

KEYWORDS: Nanochannel, Temperature-Responsive Polymer, Self-Assembled Monolayers, Smart Nanofluidic Control

INTRODUCTION

Recently, the properties of liquid water in glass nanochannel are reportedly altered, with higher proton mobility, higher viscosity, and lower dielectric constant being observed [1]. These new phenomena are expected to be utilized to develop unique chemical and biochemical operations on the nanometer scale. However, the nanofluidic control is a great technical bottleneck. In contrast to microfluidics, flow control in nanofluidics has still not been established, due to the extreme difficulty to construct fluid control units in nanochannels. Therefore, we proposed the concept of SNC (Figure 1). In SNC, the OPEN and CLOSE of nanochannels are smartly controlled by the change of the external stimuli such as temperature, pH, light, through self-assembled stimuli-responsive interfaces which are locally constructed in nanochannels.

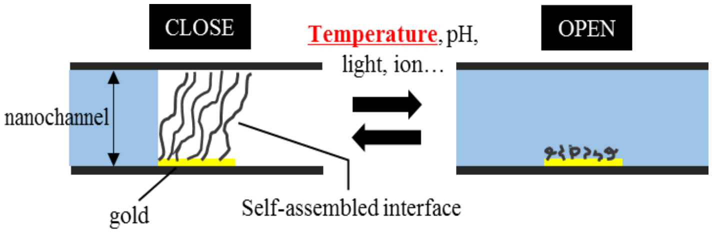

Figure 1: The concept of smart nanofluidic control (SNC).

Towards the realization of SNC, we have first achieved top-down fabrication of gold nanopatterns in glass nanochannels with super high precision (< 50 nm) by using our arbitrary nano-in-nano patterning technique [2], and recently further succeeded in bonding of the gold patterned nanochannel chips (SNC chips, Figure 2). The gold nanopatterns in nanochannels provide robust surfaces to form self-assembled monolayers (SAM) when reacting with thiolated molecules. As a first target, we focused on temperature-responsive SNC. PNIPAAm with thiolated side chains (PNIPAAm-SH, Figure 3) was specially designed to construct self-assembled temperature-responsive interfaces in SNC. PNIPAAm has been widely used as a stimuli-responsive material in drug delivery systems and tissue engineering.

978-0-9798064-7-6/µTAS 2014/$20©14CBMS-0001

Traditionally, PNIPAAm is synthesized via conventional free radical polymerization, and therefore usually has a large molecular weight and less controlled polydispersity, which make it difficult to inject into nanochannels or easy to block the nanochannels. The RAFT strategy, which is able to well control molecular weight and polydispersity during polymerization, was utilized to synthesize the specially designed PNIPAAm-SH, according a synthesis route shown in Figure 3.

EXPERIMENTAL

First, nanochannels were fabricated on quartz substrates utilizing electron beam lithography (EBL) and dry etching. The nanochannels were 800 nm in width and 300 nm in depth. Next, gold nanopatterns in nanochannels were fabricated by our arbitrary nano-in-nano patterning technique [2]. Then, SNC chips were achieved (figure 2). Second, PNIPAAm-SH (figure 3) was synthesized by RAFT polymerization for 3,6,9 hours respectively, using N-isopropylacrylamide as a monomer, V-501 (4,4'-azobis(4-cyanovaleric acid)) as an initiator and cyanomethyl dodecyl trithiocarbonate as a RAFT agent. Next, SAMs of PNIPAAm-SH were constructed by immersing gold-surface substrate in 99.9 % ethanol solutions of PNIPAAm-SH (0.05, 0.2, 2 mM) for over 12 hours.

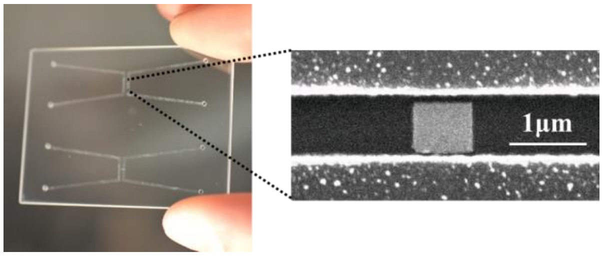

Figure 2: The picture of SNC chip (a), and SEM images (b) of the gold nanopatterns in nanochannel: 800 nm wide and 300 nm deep.

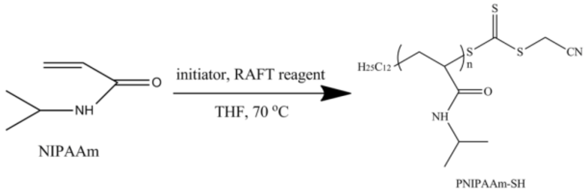

Figure 3: Structure and synthesis of PNIPAAm-SH. The initiator is 4,4'-azobis(4-cyanovaleric acid) and the RAFT reagent is cyanomethyl dodecyl trithiocarbonate.

RESULTS AND DISCUSSION

The well-controlled structures of synthesized products were identified by H^1 NMR. Independent on polymerization time, PNIPAAm-SH with small molecular weight lower than 10,000 and narrow polydispersity lower than 1.2 were obtained (Table 1), which is considered to be appropriate to inject into nanochannels. The SAMs formed on the gold surface using PNIPAAm-SH of different concentration were elementally confirmed by XPS (Figure 4) and exhibited smooth morphology (Table 2) having extremely small roughness lower than that of glass substrate. Further, the synthesized PNIPAAm-SH exhibited sharp sol-gel phase transition at 30.8 °C in solution (Figure 5), suggesting that it would possess a quick temperature responsiveness in nanochannel, which is very ideal for SNC.

Table 1. Molecular weights and polydispersities (M_w/M_n) of PNIPAAm-SH polymerized for 3 h, 6 h, 9 h, respectively.

Polymerization time (h)	Elution time (min)	M_n	M_w	M_w/M_n
3	14.17	9979	11929	1.1955
6	14.53	8824	10492	1.1891
9	14.26	8964	11331	1.1735

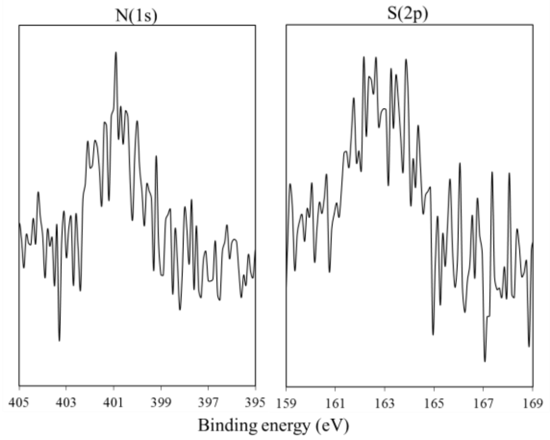

Figure 4: N_{1s} and S_{2p} spectra of XPS determination of PNIPAAm-SH SAMs prepared using 0.05mM PNIPAAm-SH solution.

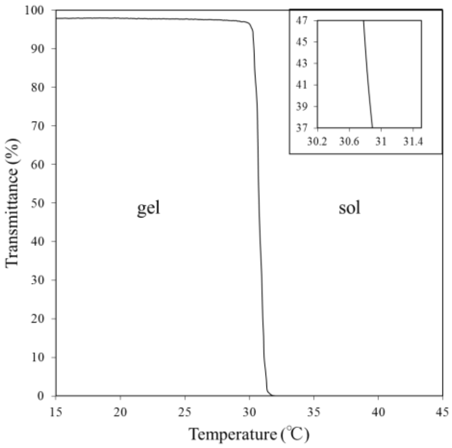

Figure 5: The lower critical solution temperature (LCST) of PNIPAAm-SH synthesized for 3 h.

Table 2: Surface morphology of SAMs prepared using PNIPAAm-SH solutions of different concentrations. (RMS = Root Mean Square)

Au, SAM	Au	0.05 mM	0.2 mM	2 mM
RMS (nm)	10.0	2.0	2.7	1.45

CONCLUSION

We fabricated SNC chips, and synthesized a temperature-responsive polymer, PNIPAAm-SH, which is considered to be appropriate to our SNC chips. We believe that the SNC chips will be able to achieve SNC by injection PNIPAAm-SH into the chips and constructing self-assembled temperature-responsive interface.

ACKNOWLEDGEMENTS

This work was partially supported by JSPS KAKENHI Grant Number 26630403.

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