J|A|C|S
COMMUNICATIONS

A Thermoresponsive Fluorogenic Conjugated Polymer for a Temperature Sensor in Microfluidic Devices

Sungmin Ryu,[†] Imsung Yoo,[†] Simon Song,*[,†] Bora Yoon,[‡] and Jong-Man Kim*[,‡]

Departments of Mechanical Engineering and Chemical Engineering, Hanyang University, Seoul 133-791, Korea

Received October 17, 2008; E-mail: simonsong@hanyang.ac.kr; jmk@hanyang.ac.kr

Since their discovery in pioneering work by Wegner,[1] the structurally intriguing conjugated polymers known as polydiacetylenes (PDAs) have attracted enormous attention in the fields of sensors and optoelectronics.[2] The brilliant blue-to-red color change that takes place in response to environmental perturbations has been applied to the design of a variety of colorimetric PDA chemosensors (Figure 1).[3−10] Another highly attractive feature from the perspective of sensor applications that has been almost ignored until recently is the fluorogenic property of the PDAs.[11,12] We[2a,13] and other groups[14,15] have demonstrated that the stress-induced nonfluorescence-to-fluorescence transition of PDAs can be used advantageously in the construction of sensitive PDA-based chemosensors.

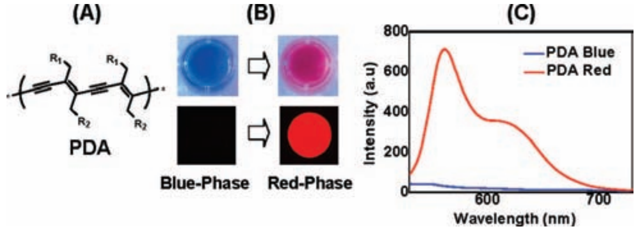

Figure 1. Structure of a polydiacetylene (A) and its color (top)/fluorescence (bottom) changes (B), and fluorescence spectral changes (C) upon stimulation.

Owing to the several unique properties such as minimal consumption of samples and reagents, large interfacial areas, relatively fast molecular diffusion, and the capability of continuous analysis, microfluidic detection systems have emerged as powerful alternatives to the conventional batch-type solution-based sensors.[16−18] Accurate measurements of temperature are important in applications of microfluidic devices to, for example, the polymerase chain reaction (PCR) for amplification of DNA, enzyme-activated reactions, or chemical reactions.[19−22] In this regard, if the fluorescence intensities of PDA supramolecules are proportional to temperature in a microchannel, thermoresponsive PDAs could be utilized as key materials in microfluidic temperature sensors. As part of ongoing efforts for exploring new applications of PDA-based sensors,[2a,13,15,23] we have uncovered a very intriguing approach to measure temperature in a microchannel which relies on thermoresponsive fluorogenic PDA supramolecules. Specifically, we have shown that emission from PDA thermosensor droplets, inserted into a microchannel by hydrodynamic focusing, responds in a sensitive manner to a temperature gradient generated by a microheater. Although numerous conjugated polymer-based sensors have been reported, this is, to the best of our knowledge, the first example of the application of the conjugated polymer to the microfluidic temperature sensor.

In Figure 2 is displayed a schematic of the microfluidic temperature sensor chip developed in this investigation. The sensor chip is composed of a PDMS substrate bonded to a glass wafer and has three inlet channels and one main channel. A solution of a blue-phase, nonfluorescent PDA derived from PCDA-EDEA (Figure 3) is introduced to the middle inlet channel with a syringe pump while corn-oil flows enter the two side inlet channels. The resulting hydrodynamic instability[24] generates PDA sensor droplets at the junction of the flows. A microheater, comprised of an ITO film integrated on the bottom of the main channel, provides a constant heat flux caused by Joule heating. This generates a linear temperature distribution along the channel.[25] In addition, thin-film thermocouples are incorporated at the entrance and exit of the main channel so that accurate temperature measurements can be made. As a result, while the blue-phase PDA droplets travel along the main channel, they experience a temperature variation and emit red fluorescence which is monitored by using an inverted fluorescent microscope system (IX71, Olympus).

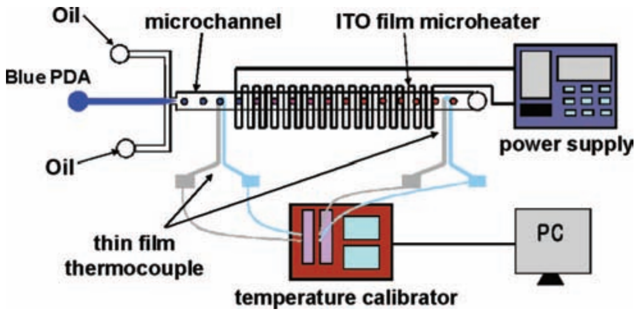

Figure 2. Schematic of the PDA-based microfluidic temperature sensor.

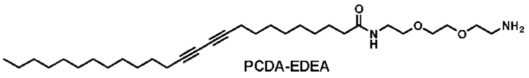

Figure 3. Structure of the diacetylene monomer PCDA-EDEA used in current investigation.

In Figure 4A is shown an optical microscope image of the formation of PDA sensor droplets at the junction of the inlet channels of the microfluidic chip, indicating that the monodispersed droplets are well generated without satellites. An optical microscope image of the middle of the main channel is given in Figure 4B where the PDA droplets that travel in the main channel can be clearly seen. Note that a portion of the ITO film microheater is identifiable in Figure 4B. Since heat treatment of the PDAs causes a blue-to-red phase transition and induces a nonfluorescent-to-fluorescent change, the PDA droplets emit red fluorescence when they travel over the microheated areas in the channel (Figure 4C).

Images of red-phase fluorescent PDA droplets, monitored at a position 35 mm downstream from the junction, for various

---

[†] Department of Mechanical Engineering.
[‡] Department of Chemical Engineering.

10.1021/ja808077d CCC: $40.75

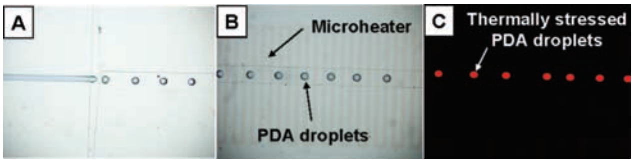

Figure 4. Optical (A and B) and fluorescence (C) microscope images of the microfluidic sensor chip near the junction and middle of the main channel.

temperatures are displayed in Figure 5A. It is clear that the red-phase droplets become more intensely fluorescent as the channel temperature increases. To quantitatively evaluate the temperature sensing capability of the PDA droplets, the peak emission intensities of the droplet were plotted versus the channel temperature (Figure 5B). This plot shows that the fluorescent signal of PDA is linearly proportional to the temperature in the range 40 to 60 °C, approximately. When the temperature rises above 70 °C, the fluorescence signal decreases. This finding indicates that the fluorescence of the PDA is quenched by excessive heat. The combined results demonstrate that the present PDA-based microfluidic system can be used to make temperature measurements between 40 to 60 °C. In addition, the heat-induced generation of fluorescence was found to be irreversible. Thus, the thermally induced fluorescence signal remained unchanged upon cooling to room temperature.

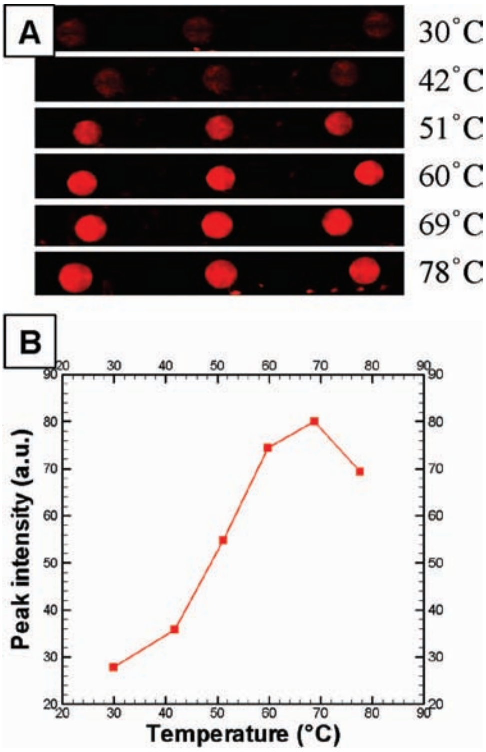

Figure 5. Fluorescence microscope images (A) and a peak fluorescence intensity vs temperature plot (B) of the PDA droplets.

In conclusions, by taking advantage of the thermoresponsive property of PDA sensors we have devised a new strategy to measure the flow temperature in a microchannel. Specifically, we have fabricated a microfluidic chip composed of a PDMS substrate and a glass wafer. The former contains a microchannel network while the latter incorporates a microheater for heat generation and thin film thermocouples for temperature measurements. The fluorescence intensities of blue-phase PDA sensor droplets, formed by using hydrodynamic instability, were found to vary in a linear fashion with the flow temperature in the range 40 to 60 °C. This finding demonstrates that the flow temperature in a microchannel can be determined by measuring the fluorescent intensities of PDA sensors. Accordingly, the results described above should be an important addition to the conjugated polymer-bases chemosensors. We expect that the applicable temperature ranges of these devices can be controlled by employing structurally diverse diacetylene monomers.

Acknowledgment. This work was supported by KOSEF (NRL Program: R0A-2008-000-20047-0) and Seoul R&BD Program (10919).

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Wegner, G. *Z. Naturforsch.* **1969**, *24b*, 824.
(2) Reviews on polydiacetylenes:(a) Ahn, D. J.; Kim, J.-M. *Acc. Chem. Res.* **2008**, *41*, 805. (b) Lauher, J. W.; Fowler, F. W.; Goroff, N. S. *Acc. Chem. Res.* **2008**, *41*, 1215. (c) Reppy, M. A.; Pindzola, B. A. *Chem. Commun.* **2007**, 4317. (d) Zhou, W.; Li, Y.; Zhu, D. *Chem. Asian J.* **2007**, *2*, 222. (e) Carpick, R. W.; Sasaki, D. Y; Marcus, M. S.; Eriksson, M. A.; Burns, A. R. *J. Phys.: Condens. Matter* **2004**, *16*, R679. (f) Mueller, A.; O'Brien, D. F. *Chem. Rev.* **2002**, *102*, 727. (g) Jelinek, R.; Kolusheva, S. *Biotechnol. Adv.* **2001**, *19*, 109. (h) Okada, S.; Peng, S.; Spevak, W.; Charych, D. *Acc. Chem. Res.* **1998**, *31*, 229. (i) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113. (j) Charych, D. H; Nagy, J. O.; Spevak, W.; Bednarski, M. D. *Science* **1993**, *261*, 585.
(3) Kolusheva, S.; Boyer, L.; Jelinek, R. *Nat. Biotechnol.* **2000**, *18*, 225.
(4) Wang, C.; Ma, Z. *Anal. Bioanal. Chem.* **2005**, *382*, 1708.
(5) Yoon, J.; Chae, S. K.; Kim, J.-M. *J. Am. Chem. Soc.* **2007**, *129*, 3038.
(6) Gill, I.; Ballesteros, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3264.
(7) Rangin, M.; Basu, A. *J. Am. Chem. Soc.* **2004**, *126*, 5038.
(8) Nie, Q.; Zhang, Y.; Zhang, J.; Zhang, M. *J. Mater. Chem.* **2006**, *16*, 546.
(9) Ma, G.; Cheng, Q. *Langmuir* **2005**, *21*, 6123.
(10) Song, J.; Cisar, J. S.; Bertozzi, C. R. *J. Am. Chem. Soc.* **2004**, *126*, 8459.
(11) Chance, R. R. *Macromolecules* **1980**, *13*, 396.
(12) Carpick, R. W.; Sasaki, D. Y.; Burns, A. R. *Langmuir* **2000**, *16*, 1270.
(13) Kim, J.-M.; Lee, Y. B.; Yang, D. H.; Lee, J.-S.; Lee, G. S.; Ahn, D. J. *J. Am. Chem. Soc.* **2005**, *127*, 17580.
(14) Kolusheva, S.; Molt, O.; Herm, M.; Schrader, T.; Jelinek, R. *J. Am. Chem. Soc.* **2005**, *127*, 10000.
(15) Lee, J.; Kim, H.-J.; Kim, J. *J. Am. Chem. Soc.* **2008**, *130*, 5010.
(16) Dittrich, P. S.; Tachikawa, K.; Manz, A. *Anal. Chem.* **2006**, *78*, 3887.
(17) Kim, P.; Kwon, K. W.; Park, M. C.; Lee, S. H.; Kim, S. M.; Suh, K. Y. *Biochip J.* **2008**, *2*, 1.
(18) Kou, S.; Lee, H. N.; van Noort, D.; Swamy, K. M. K.; Kim, S. H.; Soh, J. H.; Lee, K.-M.; Nam, S.-W.; Yoon, J.; Park, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 872.
(19) Tanaka, Y.; Slyadnev, M. N.; Hibra, A.; Tokeshi, M.; Kitamori, T. *J. Chromatogr., A* **2000**, *894*, 45.
(20) Lagally, E. T.; Medintz, I.; Mathies, R. A. *Anal. Chem.* **2001**, *73*, 565.
(21) Mao, H.; Yang, T.; Cremer, P. S. *J. Am. Chem. Soc.* **2002**, *124*, 4432.
(22) Ross, D.; Gaitan, M.; Locascio, L. E. *Anal. Chem.* **2001**, *73*, 4117.
(23) Eo, S.-H.; Song, S.; Yoon, B.; Kim, J.-M. *Adv. Mater.* **2008**, *20*, 1690.
(24) Tan, Y.-C.; Cristini, V.; Lee, A. P. *Sens. Actuators B* **2006**, *114*, 350.
(25) Kays, W. M.; Crawfors, M. E. *Convective Heat and Mass Transfer*, 3rd ed.; McGraw-Hill, Inc: New York, 1993.

JA808077D