Fabrication of Layered Polydiacetylene Supramolecules on Electrospun Fibers

Sang Kyun Chae,[1] Seong Hun Kim,[2] and Jong-Man Kim*[1]
[1]*Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea*
[2]*Department of Fiber and Polymer Engineering, Hanyang University, Seoul 133-791, Korea*

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A simple and straightforward strategy for the fabrication of layered conjugated polydiacetylene supramolecules on electrospun polymer fibers, based on the layer-by-layer deposition technique, was developed.

Owing to their intriguing, stimulus-induced blue-to-red color transition, conjugated polydiacetylenes (PDAs) have gained much attention as potential chemosensors.[1–6] PDAs are generally produced by UV or γ-ray irradiation of self-assembled diacetylene (DA) supramolecules in crystalline or semi-crystalline states.[7–9] PDA-based chemosensors have been prepared as vesicles in aqueous solutions,[1a] mono- or multi-layered thin films,[10] and immobilized forms in/on solid supports.[11,12]

Recently, we reported a method for the fabrication of fibrous PDA sensors.[13] For example, electrospinning of a viscous solution containing DA monomers and a matrix polymer was found to produce DA-embedded microfibers. UV irradiation of the DA supramolecule encapsulated fibers during fiber formation affords conjugated PDAs in the polymer fiber. Unfortunately, this method requires the use of relatively larger amounts of DA monomers since the DA monomer is mixed with the matrix polymer at the beginning of the electrospinning step. In order to overcome this limitation, we have carried out studies directed at the development of a new strategy for generating fibrous PDA systems. Below, we report the results of this effort which has uncovered a novel technique based on employment of the layer-by-layer (LBL) methodology.

The LBL technique has become an attractive tool for surface modification.[14] The method, which utilizes electrostatic interaction between oppositely charged polyelectrolytes, has proven to be useful for the efficient construction of layered nanostructures as well as for enhancing signal intensities. We felt that the optical properties of PDA supramolecules and the merits of LBL technique would combine to enable fabrication of uniquely functionalized PDA fiber systems. Several advantages of the LBL-based PDA fiber preparation method over PDA-embedded fiber fabrication from the bulk DA solution include 1) reduction in the amounts of diacetylene monomer required, 2) potential for incorporation of diverse PDAs from template fibers, and 3) ability to readily control coating thicknesses by varying the number of layers deposited.

The strategy we have developed for the fabrication of layered PDAs on elctrospun microfibers is schematically presented in Figure 1.[15] The scaffold microfibers were readily prepared by electrospining a polystyrene (PS, M_w 280000, 15 wt % in chloroform) solution. The resultant PS microfibers, having an average diameter of ca. 10 μm, were incubated in concentrated sulfuric acid at room temperature for 2 min in order to introduce sulfonic acid moieties to the phenyl groups of the fibers.[16] The partially sulfonated PS fibers were then washed

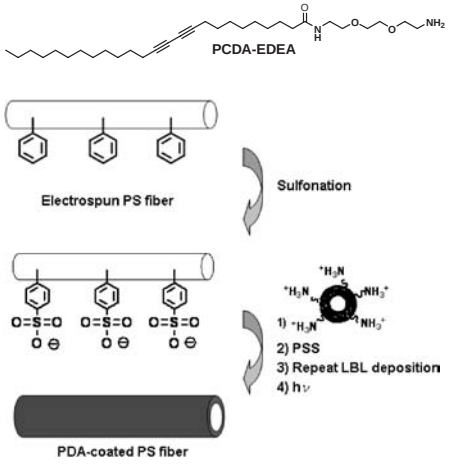

Figure 1. Structure of PCDA-EDEA and a schematic representation of procedure for layered PDAs on electrospun PS fiber.

with deionized water to remove excess acid. Deposition of the first layer of DA vesicles was achieved by incubating the sulfonated fibers in an aqueous 1 mM solution of DA vesicles derived from the amine-terminated DA, PCDA-EDEA for 10 min (see Supporting Information for detailed reaction conditions).[17] After vesicle immobilization, the fiber mat was washed with deionized water and air-dried on a glass slide. The fiber mat was then incubated in a poly(sodium 4-styrenesulfonate (PSS, M_w 70000) solution (1 mg/mL, 0.5 M NaCl) followed by washing with deionized water and air-drying on a glass slide. Multilayered PCDA-EDEA vesicles were prepared by repeating the procedure. Incubation in each solution lasted for 10 min and the substrate was washed with deionized water for 2 min before incubation in a counter ionic solution.

The sulfonated polymerized PS fiber mats, deposited with 8 layers of PCDA-EDEA supramolecules, are shown in Figure 2. The observation of a blue color after UV irradiation demonstrates that PDAs had formed. The LBL deposition of DA supramolecules was demonstrated by observing the continuous development of an increasingly intense blue color as the number of deposition cycle is increased (Supporting Information, Figure S1).[17] In addition, layered deposition of DA supramolecules was found to be ineffective when carried out in the absence of the anionic PSS (Supporting Information, Figure S1, D).

The color of the fiber mat was transformed from blue-to-purple by heat treatment (100 °C, 1 min). Close inspection by using an optical microscope reveals that the fiber mats consist of individual blue-colored fibers (Figure 2A, before heating). Upon heating, the individual fibers become purple (Figure 2A, after heating). Fluorescence microscopy (Figure 2B) provides further support for the conclusion that PDAs formed in the fibers upon UV-irradiation and that they undergo the typical thermally

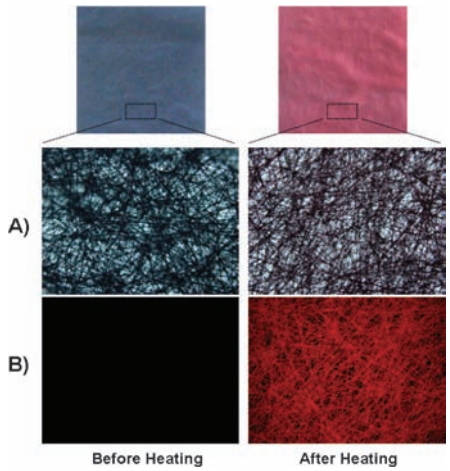

Figure 2. Optical (A) and fluorescence (B) images of PDA-immobilized electrospun fibers prepared from PCDA-EDEA before and after heating at 100 °C for 1 min.

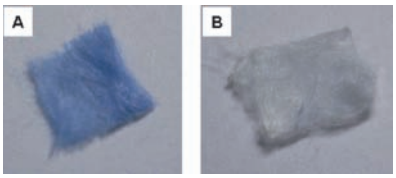

Figure 3. Photographs of the sulfonated (A) and bare (B) PS fiber mats, obtained after 5 min sonication followed by 6 min UV irradiation of the fiber mats deposited with 8 layers of DA vesicles.

stimulated color transition. Accordingly, the blue-colored fiber mat displays no fluorescence but the heat-treated blue-colored fiber mat shows fluorescent from individual fibers.

Interestingly and unexpectedly, we observed that unsulfonated PS fiber mats also participate in clean deposition of layered PDA supramolecules when subjected to the deposition procedure described above (data not shown). This finding indicates that the first layer of DA assembly is efficiently formed on the PS fiber surface through nonspecific physical adsorption. In many cases, it is almost impossible to detect the effect of sulfonation on the layer deposition of DA supramolecules. However, a critical difference is observed when the mechanical stabilities of the fibers are compared. To demonstrate this difference, sulfonated and bare PS fiber mats, both deposited with 8 layers of DA supramolecules, were individually subjected to bath-sonication for 5 min in water. After UV irradiation for 6 min, colors of the fiber mats were compared. As shown in Figure 3, the DA-deposited polymer fiber mat derived from sulfonated PS fibers remains intensely blue color after sonication (Figure 3A). In contrast, most of DA supramolecules disassemble from the fiber mat derived from unsulfonated PS fibers upon bath sonication (Figure 3B).

In Figure 4 are shown fluorescence microscopic images of a polymerized and heat-treated single polymer fiber, deposited with PCDA-EDEA. Only a weak fluorescence signal is observed

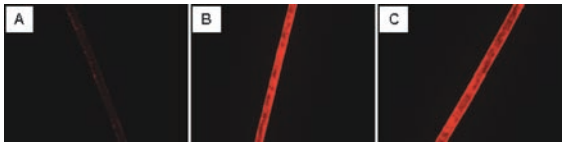

Figure 4. Fluorescence microscopic images of a polymerized and heat-treated sulfonated PS fiber, obtained after 2 (A), 4 (B), and 6 (C) deposition cycles.

after 2 deposition cycles but the fiber emits relatively strong fluorescence after 4- or 6-deposition cycles. Thus, it is recommended that 4 cycles of deposition process be employed when the blue-to-red phase transition of layered PDAs is going to be monitored using the fluorescence signal.

As described above, we have developed a new, straightforward, LBL-based strategy for the generation of layered PDA supramolecules on electrospun polymer fibers. This technology should be readily applied to the construction of fiber-based PDA materials.

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References and Notes

1 Reviews on polydiacetylene chemosensors: a) S. Okada, S. Peng, W. Spevak, D. Charych, *Acc. Chem. Res.* **1998**, *31*, 229. b) R. Jelinek, *Drug. Dev. Res.* **2000**, *50*, 497.
2 D. H. Charych, J. O. Nagy, W. Spevak, M. D. Bednarski, *Science* **1993**, *261*, 585.
3 Z. Orynbayeva, S. Kolusheva, E. Livneh, A. Lichtenshtein, I. Nathan, R. Jelinek, *Angew. Chem., Int. Ed.* **2005**, *44*, 1092.
4 G. Ma, Q. Cheng, *Langmuir* **2005**, *21*, 6123.
5 C. Wang, Z. Ma, *Anal. Bioanal. Chem.* **2005**, *382*, 1708.
6 J.-M. Kim, S. K. Chae, Y. B. Lee, J.-S. Lee, G. S. Lee, T.-Y. Kim, D. J. Ahn, *Chem. Lett.* **2006**, *35*, 560.
7 H. Bader, H. Ringsdorf, *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1623.
8 G. Wegner, *Macromol. Chem.* **1972**, *154*, 35.
9 S. Okada, K. Hayamizu, H. Matsuda, A. Masaki, H. Nakanishi, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 857.
10 Y. Okawa, M. Aono, *Nature* **2001**, *409*, 683.
11 J.-M. Kim, Y. B. Lee, D. H. Yang, J.-S. Lee, G. S. Lee, D. J. Ahn, *J. Am. Chem. Soc.* **2005**, *127*, 17580.
12 Y. Lu, Y. Yang, A. Sellinger, M. Lu, J. Huang, H. Fan, R. Haddad, G. Lopez, A. R. Burns, D. Y. Sasaki, J. Shelnutt, J. Brinker, *Nature* **2001**, *410*, 913.
13 J. Yoon, S. K. Chae, J.-M. Kim, *J. Am. Chem. Soc.* **2007**, *129*, 3038.
14 G. Decher, *Science* **1997**, *277*, 1232.
15 For a recent review on electrospinning technique, see: Y. Dzenis, *Science* **2004**, *304*, 1917.
16 K. Müller, J. F. Quinn, A. P. R. Johnston, M. Becker, A. Greiner, F. Caruso, *Chem. Mater.* **2006**, *18*, 2397.
17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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