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Colorimetric Sensors for Volatile Organic Compounds (VOCs) Based on Conjugated Polymer-Embedded Electrospun Fibers

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The development of efficient sensors for the detection of volatile organic compounds (VOCs) continues to be a significant scientific endeavor.[1] A variety of VOC-responsive sensor systems have been developed for potential application as "electronic noses". Changes in optical, electrochemical, conducting, and chromic properties of sensor matrices engendered upon exposure to VOCs have served as output signals. Among those reported, the colorimetric sensor array system discovered by Suslick and co-workers is of particular interest because of both its effectiveness and simplicity.[2] Diverse VOCs can be monitored in this system owing to VOC-induced color changes of sensors that are composed of arrays of metalloporphyrins, solvatochromic dyes, and pH indicators. A minor limitation of this method comes from the fact that a software program is needed to deconvolute the color pattern changes taking place on exposure to VOCs. In recent studies, we have developed a new strategy for colorimetric and specific detection of VOCs that is based on conjugated polymer-embedded solvatochromic electrospun fibers.

To fabricate a litumus-type chemosensor for VOCs, we have utilized polydiacetylenes (PDAs) and the electrospinning technique. The stress (thermal, mechanical, and ligand−receptor interaction, etc.) induced blue-to-red color transition of PDAs are well-known phenomena.[3−4] The electrospinning technique allows for rapid and cost-effective fabrication of fibrous polymer membranes with large surface area.[5] Thus, we felt that a combination of the novel colorimetric properties of PDA and the merits of electrospinning would serve as the basis for a unique and practical application of the PDA conjugated polymers to the detection of VOCs. In addition, we believed that monitoring color changes with PDA-embedded electrospun fiber membranes would more easily be accomplished than those occurring in conventional Langmuir−Blodgett (LB) PDA films.

In an exploratory phase of this effort, several commercially available or easily obtainable diacetylene monomers, such as 10,12-pentacosadiynoic acid (PCDA, $CH^3(CH_2)_{11}C\equiv C-C\equiv C(CH_2)_8$-COOH) (**1**), 5,7-eicosadiynoic acid (ECDA, $CH_3(CH_2)_{11C}\equiv C-C\equiv C(CH_2)_3COOH$) (**2**), *N*-(pyridin-3-yl) pentacosa-10,12-diynamide (PCDA-AP) (**3**), and 8,10-henicosadiynoic acid (HCDA, CH_3-$(CH_2)_9C\equiv C-C\equiv C(CH_2)_6COOH$) (**4**) were investigated as colorimetric VOC sensors. The typical procedure used for the fabrication of PDA-embedded polymer fibers is schematically presented in Figure 1. A viscous solution containing diacetylene (DA) monomer, poly(ethylene oxide) (PEO), and tetraethyl orthosilicate (TEOS) is placed in a syringe. PEO and TEOS were used as the respective matrix polymer and stability enhancer of the resulting fibers. A high voltage (15 kV) is then applied to a conductive capillary attached to the syringe needle causing ejection of a charged polymer jet from the polymer solution. The microfibers are collected on the surface of a grounded aluminum plate. As the solvent evaporates during fiber formation, self-assembly of DA monomers takes place if the attractive forces between the DA monomers are larger than those between DA monomers and the matrix polymers. Polymerization of the molecular-assembled DAs then results in the formation of polymer fibers containing embedded PDAs.

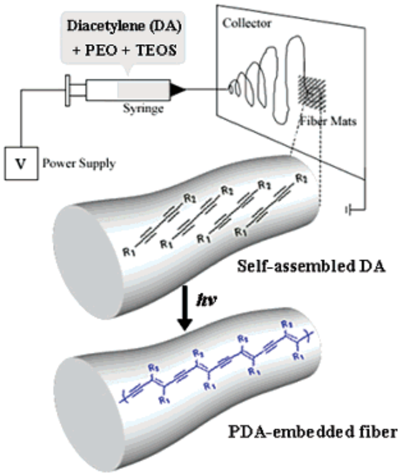

Figure 1. Schematic representation of the preparation of PDA-embedded electrospun microfibers.

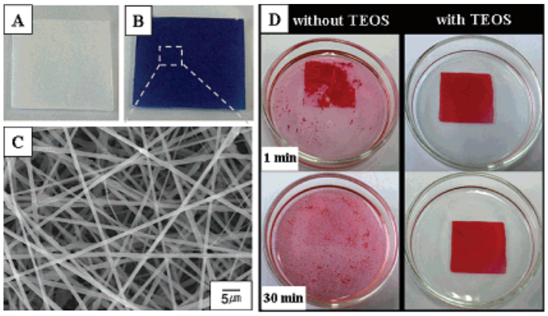

Figure 2. Photographs of electrospun fiber mats embedded with PCDA **1** before (A) and after (B) 254 nm-UV irradiation (1 mW/cm^2) for 3 min; SEM image of the microfibers containing polymerized PCDA (C); photographs of polymerized PCDA-embedded electrospun fiber mats prepared in the absence (left) and presence (right) of TEOS in chloroform solution (D).

In Figure 2A and 2B are displayed photographs of electrospun fiber mats encapsulated with PCDA **1**, before (Figure 2A) and after (Figure 2B) irradiation with 254 nm light (1 mW/cm^2) for 3 min. The typical blue color developed indicates that polydiacetylenes are produced upon UV irradiation. This observation confirms that the molecular ordered properties of the monomeric diacetylenes are retained in the electrospinning process. A scanning electron microscope (SEM) image (Figure 3) shows that the blue-colored mat is composed of microfibers. No significant morphological difference is seen in the SEM images of fiber mats before and after UV-irradiation (Supporting Information).

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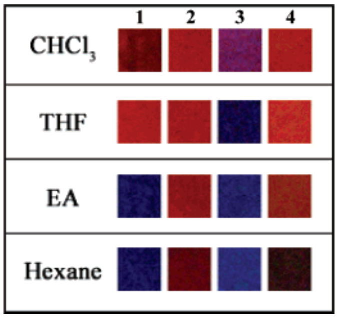

Figure 3. Photographs of the PDA-embedded electrospun fiber mats prepared with diacetylene monomers **1**−**4** after exposure to organic solvent.

To investigate the effects of TEOS on the stability, the blue-colored PDA-embedded fiber mat was dissolved in chloroform. As shown in Figure 2D, the PCDA-derived fiber mat prepared in the absence of TEOS slowly disassembled after exposure to chloroform, and the shape of the mat was completely lost after 30 min (Figure 2D, left). In contrast, the silica-enforced fiber mat was stable in chloroform; the original shape was unchanged after 30 min. In addition, release of PDAs from the TEOS-derived fiber mat was not observed. The high stability of the TEOS-enforced fiber mat is presumably due to the crosslinking between hydrolyzed TEOS and PEO. The red color developed upon exposure to chloroform is a consequence of solvatochromism, originating from the disruption of the highly ordered lipid assembly promoted by interaction with the organic solvent.[6]

The observation of an organic solvent induced, blue-to-red color transition of PDA embedded electrospun fibers is interesting since it suggests that the colorimetric response might vary in an organic-solvent-dependent manner on the structure of diacetylene monomer. If so, it would be possible to colorimetrically differentiate organic solvents by using this methodology. To probe the feasibility of a visual, solvent-sensor system based on this technology, PDA-embedded silica-enforced fiber mats were prepared from monomers **1**−**4**. A drop of an organic solvent such as chloroform, tetrahydrofuran (THF), ethyl acetate (EA), or *n*-hexane, was placed on the fiber mat and the color change was immediately monitored. Interestingly, polymer mats containing polymerized diacetylenes **1**−**4** show different colorimetric responses upon exposure to the organic solvents. For example, the blue-to-red color transition was observed with the fibrous mat prepared with PCDA **1** when it is exposed to chloroform and THF but not to EA and hexane. The polymerized ECDA **2**-embedded fiber mat was found to be most sensitive and displayed a color transition with all solvents tested. The fiber mat derived from pyridine-containing diacetylene **3** underwent only a blue to purple color change when contacted with chloroform while it maintained its original color with other solvents. The fiber mat embedded with polymerized HCDA **4** displayed a blue-to-red color transition upon contact with chloroform, THF, and EA and not when exposed to hexane. Similar colorimetric responses were observed when the PDA-containing fiber mats were exposed to organic solvent vapors (Supporting Information).

When used in combination, these systems allow for visual differentiation of individual organic solvent by simply monitoring the color patterns that develop (see Figure 3). The organic solvent-induced colorimetric transition taking place with the PDA-embedded fiber mat is irreversible; the color patterns shown in Figure 3 remain nearly unchanged when the mats are kept on the bench for 24 h. The vivid color changes that are observed in response to organic solvents are one of the major advantages of the PDA-based chemosensor system over those based on other conjugated polymers. Although only four organic solvents were differentiated in this study, the number of distinguishable organic solvents should increase when a combination of structurally diverse diacetylenic monomers are used.

In conclusion, this study has led to the development of a novel colorimetric sensor system based on silica-enforced electrospun microfibers embedded with conjugated polymers. The organic solvent-dependent color change property of the PDA-embedded polymer mats allows for a straightforward "color pattern" procedure to differentiate between several common organic solvents. The unique strategy of using a combination of top-down (electrospinning for fabrication of high surface area microfibers) and bottom-up (creation of supramolecular structure through self-assembly process in fiber) approach, like the one employed in this effort, should not only be applicable for the development of new PDA-based sensors but also for the generation of interesting supramolecule-embedded microfibers. A combinatorial approach with structurally diverse diacetylene monomers to increase the number of VOCs that can be distinguished by using this colorimetric method is currently being developed.

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

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