Sensors

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Thin-Film Formation of Imidazolium-Based Conjugated Polydiacetylenes and Their Application for Sensing Anionic Surfactants**

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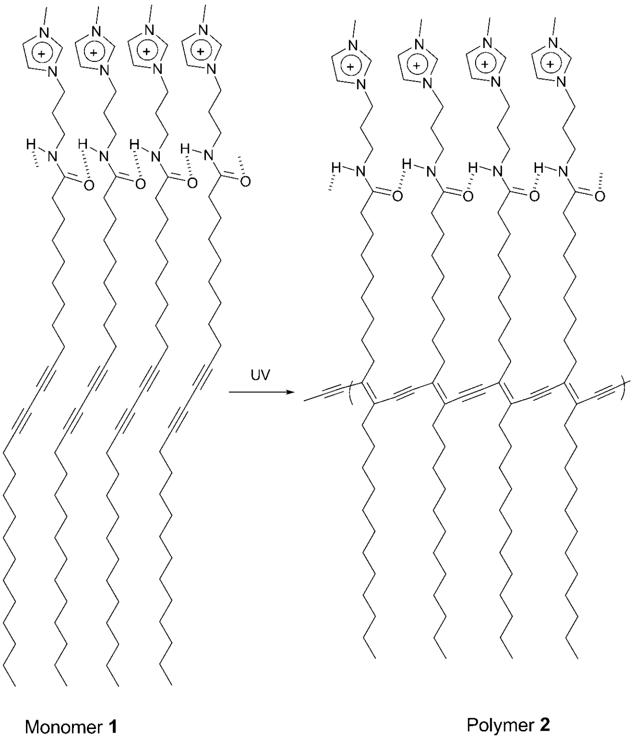
Polydiacetylenes (PDAs), which can be prepared by the UV irradiation of self-assembled diacetylene (DA) supramolecules, have attracted considerable attention in recent years.[1] The stimulus-induced blue-to-red transition of PDAs has led to the development of a variety of PDA-based chemosensors.[2] Anionic surfactants are widely used in the detergent industry as well as in emulsification, lubrication, and catalysis, and they are well-known environmental pollutants.[3] Many well-known surfactant analysis techniques, such as the methylene blue method,[4] ion-selective electrodes, capillary electrophoresis,[5] and so forth, have limitations in their applicability, owing tedious procedures, large necessary quantities of toxic solvents, irreproducibility, and signal instability.[6] Therefore, it is essential to develop simple methods to detect anionic surfactant in water, such as chromo- or fluorogenic methods. However, there are few reports on the use of fluorescence or UV changes to detect anionic surfactants.[7]

Among the various types of anion receptors, imidazolium-based receptors have been studied extensively because they can form strong $(C-H)^{+}\cdots X^{-}$ ionic hydrogen bonds.[8] There have been many exciting and significant results from the application of new imidazolium receptors to many anionic targets. Martínez-Máñez et al. recently reported a colorimetric method for the selective determination of anionic surfactants using imidazolium-containing ionic liquids on a solid support.[7a] However, this system involves a two-step process for the detection of anionic surfactants, and an additional dye (methylene blue) is necessary for detection.

Herein, we provide the first example of an anionic surfactant-selective sensor based on PDA and imidazolium, polymer **2** (Scheme 1), which displays fluorescence enhancement and colorimetric changes in the presence of a variety of anionic surfactants. Compared to previous reports, this system is simpler and more effective in sensing anionic surfactants. Remarkably, using the simple colorimetric changes, this system can easily distinguish the two different anionic surfactants, sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonic acid (SDBS), that are used most widely in the detergent industry. Polymer **2** is also the first species that can show dual blue-to-yellow and blue-to-red transition, which can be tuned by headgroup shape and length of the alkyl chain of analytes. Furthermore, polymer **2** displays unique thin-film structure and colorimetric reversi-



Scheme 1. Self-assembly and polymerization of monomer **1**.

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bility in the range of 25 to approximately 50 °C, which implies that it is of potential interest as a temperature sensor.

The DA monomer **1** was synthesized from 10,12-pentacosadiynoic acid in two steps; detailed experimental procedures and characterization data, including the NMR spectra, are provided in the Supporting Information (Figures S1–S4). The DA monomers were then converted to PDA supramolecules by a routine procedure. UV irradiation of the suspensions derived from highly ordered self-assembled monomers for 30 seconds resulted in the formation of stable, deep-blue PDA molecules.

Figure 1 shows a TEM image of polymer **2**. A thin film with a regular boundary was observed, which can be formed without the need for a template or glass surface. Film-like formation may be due to the π–π stacking of the imidazolium rings, which can be assisted by $(C-H)^{+}\cdots I^{-}$ ionic hydrogen bonds. Given the double hydrogen bonding and aromatic interactions in the polymer, the thermochromic properties of the PDA were also investigated. As shown in Figure 2, the conversions between blue and red phases were reversible in the range of 25–50 °C. This colorimetric reversibility was attributed to the strong headgroup interactions through hydrogen bonding and aromatic interactions, which provided PDA molecules with the ability to recover their initial molecular structures.[9]

The colorimetric response of the conjugated polymer was examined at room temperature using the surfactants cetyltrimethylammonium chloride (CTAC), Triton X-100, SDS, sodium dodecyl carboxylate (SDC), sodium dodecyl phosphate (SDP), and SDBS and simple anions, such as F^-, Cl^-, Br^-, I^-, SO_4^{2-}, CO_3^{2-}, ClO_4^-, CH_3COO^-, NO_3^-, HPO_4^{2-}, and SCN^-. Figure 3 shows photographs of polymer **2** (100 μM) in the presence of various analytes (500 μM) in 4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer (20 mM, pH 7.4). Only the anionic surfactants (SDS, SDC, SDP, and SDBS) induced color changes. No changes were observed with the other anionic species or with neutral (Triton X-100) or cationic surfactants (CTAC). The concentration-dependent colorimetric changes of polymer **2** (100 μM) in the presence of various amounts of SDS, SDC, SDP, and SDBS were also examined (Figure 4). Remarkably, the four anionic surfactants showed three different color changes: SDS induced a blue-to-yellow transition, SDC and SDP induced a blue-to-orange transition, and SDBS produced a blue-to-red transition. The color changes of polymer **2** were further checked with various surfactants at different concentrations (100 μM–10 mM). No further color changes were observed when the concentration of surfactant reached the critical micelle concentration (Figure S6 in the Supporting Information). We also checked the color response of **2** to

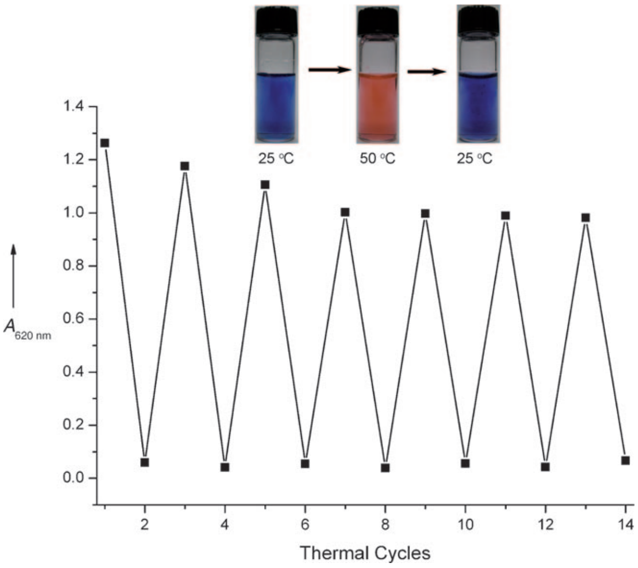

Figure 2. Absorbance of polymer **2** at 620 nm at 25 and 50 °C during thermal cycles.

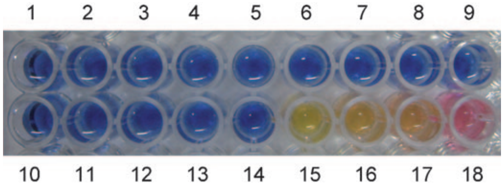

Figure 3. Colorimetric responses of **2** (100 μM) in the presence of various analytes (500 μM) in HEPES buffer (20 mM, pH 7.4): 1 blank, 2 F^-, 3 Cl^-, 4 Br^-, 5 I^-, 6 SO_4^{2-}, 7 CO_3^{2-}, 8 ClO_4^-, 9 CH_3COO^-, 10 NO_3^-, 11 HPO_4^{2-}, 12 SCN^-, 13 CTAC, 14 Triton X-100, 15 SDS, 16 SDC, 17 SDP, 18 SDBS.

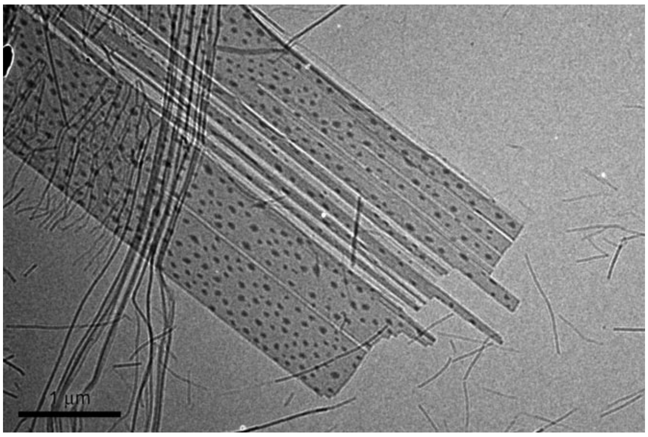

Figure 1. TEM image of polymer **2**.

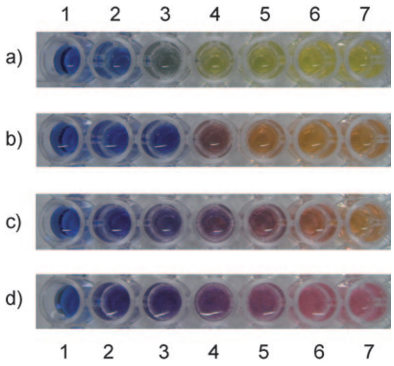

Figure 4. Colorimetric titrations of **2** (100 μM) with various amounts of a) SDS, b) SDC, c) SDP, and d) SDBS in HEPES buffer (20 mM, pH 7.4): 1 0 μM, 2 10 μM, 3 20 μM, 4 40 μM, 5 60 μM, 6 80 μM, 7 100 μM.

various anionic surfactants at temperatures higher than 25 °C (Figure S7 in the Supporting Information). The results show that **2** can detect SDS even at 50 °C. For other surfactants, such as SDBS, SDC, and SDP, the color changes are evident at temperatures below 40 °C.

The SDS-induced phase transition of the PDAs was monitored further by visible absorption spectroscopy at room temperature. As shown in Figure 5 a, the addition of SDS to 10 μM **2** caused a decrease in absorption at 620 nm with a concomitant increase at 490 and 523 nm. The presence of SDS could also be monitored by the changes in fluorescence, because this colorimetric transition is accompanied by the generation of fluorescence (Figure 5 b).[10] The fluorescence spectra of the PDA showed a gradual increase in the presence of 0–4 μM SDS. There was an approximately 34-fold enhancement in fluorescence intensity at 565 nm when 4 μM SDS was added to 10 μM PDA derived from monomer **1**. Using the fluorogenic method, the detection limit for SDS was estimated to be 2×10^{-7} M (56 ppb). Similarly, the other anionic surfactants SDC, SDP, and SDBS induced typical absorbance changes and fluorescence enhancement from 0 to 4 μM (Figure S8 in the Supporting Information). Figure 6 shows the representative percentage colorimetric response values (CR) calculated for SDS, SDC, SDP, and SDBS from the visible spectra recorded for these anionic surfactants (Figure 5 a and Figure S8 in the Supporting Information). CR reflects the change in the visible spectrum after adding the test analyte to the colorimetric polymers.[11] In the presence of 4 μM analyte, 10 μM polymer **2** displayed saturated colorimetric responses to SDS and SDBS with CR values of 97 % and 69 %, respectively, which shows that the polymer has a stronger colorimetric response to SDS than SDBS at the saturated status. With SDC and SDP (4 μM), polymer **2** showed unsaturated colorimetric responses of 73 % and 89 %, respectively.

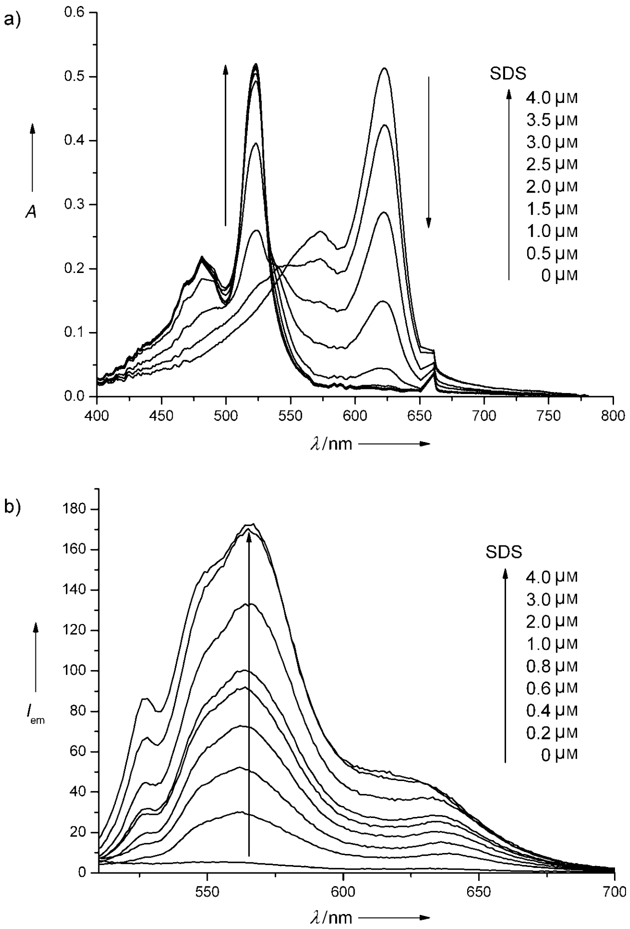

Figure 5. Colorimetric and fluorescence responses of polymer **2** (10 μM) in the presence of various concentrations of SDS in HEPES buffer (20 mM, pH 7.4): a) UV/Vis spectra of PDAs (10 μM) with 0–4 μM SDS. b) Fluorescence spectra of PDAs (10 μM) with 0–4 μM SDS (excitation at 485 nm, slit: 5 nm/5 nm).

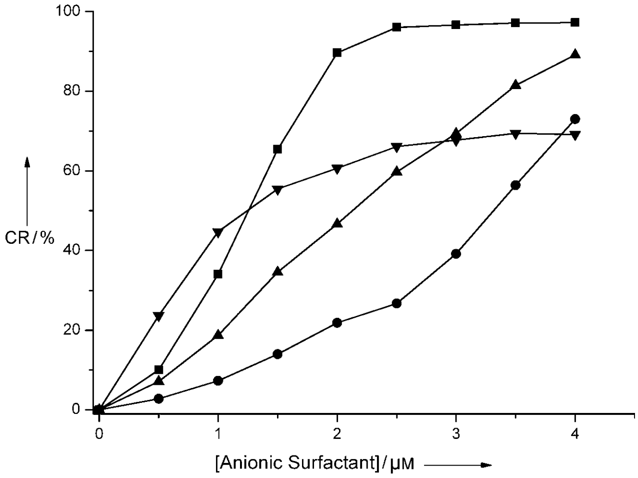

Figure 6. Quantitative colorimetric response of polymer **2** (10 μM) in the presence of various concentration anionic surfactants in HEPES buffer (20 mM, pH 7.4). ■ SDS, ● SDC, ▲ SDP, ▼ SDBS.

The different color changes shown in Figure 3 and Figure 4 most likely depend on the size and charge of the anionic surfactants' headgroups, which affect the binding and the degree of penetration of the anionic surfactants into the polymer. When anionic surfactants are added, the disruption of ionic hydrogen bonding can allow the release of the strain energy imposed on the alkyl side chains generated during polymerization.[12] The release of side-chain strain can cause partial distortion of the arrayed p orbitals, which can lead to the observed change in optical properties. A blue-to-red transition was observed when the extent of binding and penetration was low. A larger extent of binding and penetration will lead to a blue-to-yellow transition. This phenomenon is also demonstrated in Figure S9 in the Supporting Information. Dodecyl sulfate (SDS) induced a blue-to-yellow transition, and octyl sulfate and decyl sulfate produced blue-to-red and blue-to-orange transitions, respectively. In contrast, hexyl sulfate induced only a slight color change. With the same headgroup, the affinity between the polymers and anionic surfactant increased with increasing chain length. Accordingly, the color is more likely to change to yellow. Most previous reports have established that PDA undergoes blue-to-red changes and fluorescence transitions owing to conformational transitions in the conjugated (ene–yne) PDA backbone. However, examples of blue-to-yellow transforma-

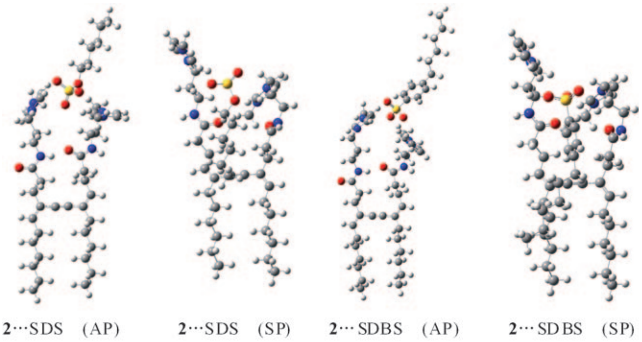

Figure 7. Calculated binding modes (AP and SP type) between polymer **2** and SDS/SDBS.

tion of PDAs induced by molecular interactions and surface perturbations are surprisingly rare. Furthermore, polymer **2** shows multiple colorimetric changes that can be tuned by the guest shape and the length of the guest's alkyl chain.

The calculated structures of two different binding modes for the complexes of polymer **2** with SDS and SDBS are shown in Figure 7. For both SDS and SDBS binding, it was found that the chain–chain stacking parallel (SP) type is much more stable than the anti-parallel (AP) type by about 12 to 15 kcal mol^{-1}. Moreover, for SP-type interaction, **2** binds SDS more strongly than SDBS by about 2.32 kcal mol^{-1}. In the SP type, the anionic H-bonding was broken owing to the strong electrostatic interactions between SO_4^-/SO_3^- and the cationic imidazolium groups as well as to the hydrophobic interactions between long alkyl chains (Figure S11 in the Supporting Information), which causes the disruption of the anionic H-bonding and partial distortion of the arrayed p orbitals. In addition, the calculated HOMO–LUMO gaps of 3.70, 4.59, and 4.58 eV, which correspond to 335.38, 270.51, and 270.90 nm, respectively, are qualitatively consistent with the color change of **2** from blue to yellow and red when it interacts with SDS and SDBS, respectively. This correlation can be understood from the fact that the stronger interactions cause more distortion of the electron density over the polymer chain with the H-bond breaking and hence more blue shift of the absorption peak, thus leading to the observed color change. The detailed calculation methods and results are described in the Supporting Information.

In conclusion, a new imidazolium-based polydiacetylene was developed as a chemosensor system, which displayed a thin-film structure in a 100% aqueous solution and colorimetric reversibility in the range of 25–50°C. This polymer exhibited selective and unique color changes as well as fluorescence changes when exposed to anionic surfactants. Most importantly, using this system, even SDS and SDBS could be differentiated with the naked eye. To our knowledge, this is the first anionic surfactant sensor based on a PDA. These results are expected to be an important addition to PDA sensor systems.

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