

Polydiacetylene-Embedded Microbeads for Colorimetric and Volumetric Sensing of Hydrocarbons

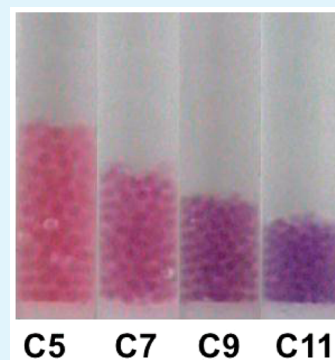
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ABSTRACT: Rational design of a hydrocarbon sensor that enables visual differentiation of saturated aliphatic hydrocarbons (SAHCs) is very difficult owing to the lack of useful functional groups that can interact with the sensor system. Here, we report a microbead embedded with polydiacetylene that undergoes faster swelling and faster blue-to-red color change in response to the hydrocarbons of shorter alkyl chains. Accordingly, visual differentiation among *n*-pentane, *n*-heptane, *n*-nonane, and *n*-undecane was readily achieved. By taking advantage of the collective effect, construction of a sensor system with amplified response was possible. Combination of microfluidic technology (for bead preparation), PDMS (swellable polymeric matrix), and polydiacetylene (colorimetric material) was key to enabling this unique hydrocarbon sensor.



KEYWORDS: polydiacetylene, colorimetric, hydrocarbon, sensor, microfluidic, polydimethylsiloxane (PDMS)

INTRODUCTION

One of the most challenging tasks in chemical and material science has been the development of a sensor system that undergoes a color change upon interaction with saturated aliphatic hydrocarbons (SAHCs). The extremely nonpolar nature and functional group (hydrogen/ionic bonding or electron donor/acceptor moieties) deficiency of SAHCs has been a huge barrier for the rational design of an efficient colorimetric SAHC sensor. Several strategies based on fluorescent dye displacement,¹ polycyclic aromatic hydrocarbons,² photonic crystals,³ and viscosity sensitive fluorescent polymers⁴ have been reported for the detection of hydrocarbons. Nau and co-workers designed an elegant gas sensor based on a fluorescent dye-cucurbituril complex system.¹ The fluorescent dye was replaced by a hydrocarbon and this afforded a sensitive and selective detection of hydrocarbons in aqueous media. Polycyclic aromatic hydrocarbons are also capable of detection of nonpolar analytes. Haick and co-workers demonstrated that thin films derived from polycyclic aromatic hydrocarbons enabled sensitive detection of hydrocarbons.² A very smart approach for colorimetric differentiation of hydrocarbons was reported by Aizenberg and co-workers.³ They prepared inverse-opal films that display different color patterns upon exposure to hydrocarbons, allowing inexpensive and highly selective colorimetric detection of organic liquids. Kwak and co-workers employed a polyacetylene and this conjugated polymer showed different fluorescence intensities when the polymer films were in contact with a series of hydrocarbons.⁴

Very recently, we reported a colorimetric hydrocarbon sensor using a polydiacetylene (PDA)^{5–30} embedded polydimethylsiloxane (PDMS) film.³¹ By taking advantage of a mechanochromic conjugated polymer^{32–34} and the hydrocarbon-induced swelling of PDMS matrix,³¹ we were able to colorimetrically differentiate SAHCs. The PDA–PDMS composite sensor film displayed a chain length-dependent blue-to-red color transition when the film was exposed to the hydrocarbon. Two critical limitations associated with the film type SAHC sensor are 1) difficulty of precise control of the thickness of the PDA-embedded sensor film and 2) difficulty of obtaining collective effect from a single strip sensor. These two limitations led us to develop another type of PDA-based hydrocarbon sensor that can overcome the drawbacks of the film-type sensor. The mechanochromic PDA supramolecules were embedded in PDMS microbeads using a microfluidic technology.^{35–38} Facile control of the diameter of the microbead using two-dimensional (2-D) hydrodynamic focusing method as well as the possibility of using the collective volumetric effect from several hundred microbeads afforded a colorimetric and volumetric sensing of hydrocarbons.

EXPERIMENTAL SECTION

Materials and Instruments. 10, 12-pentacosadiynoic acid (PCDA) was purchased from GFS Chemicals, Ohio, USA. Triton X-

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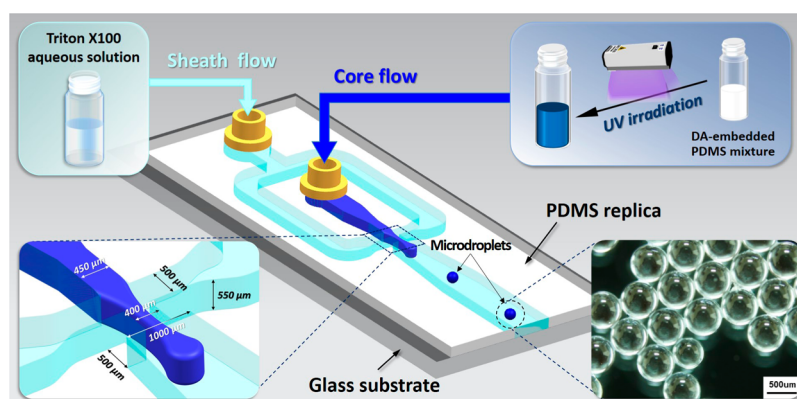


Figure 1. Schematic of a microfluidic chip used for the generation of PDA-embedded PDMS microdroplets. An optical microscopic image of the microdroplets in Triton X-100 is also presented.

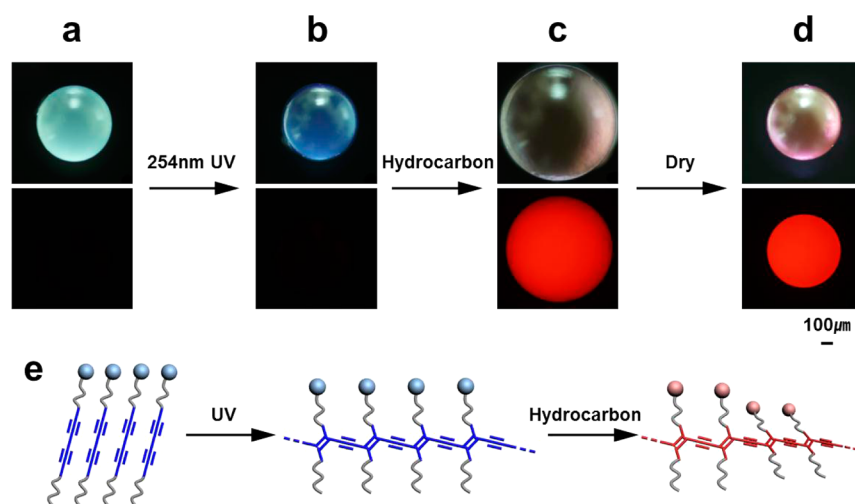


Figure 2. Optical (top) and fluorescence (bottom) microscopic images of a PDA-embedded PDMS microbead as prepared (a), after 254 nm UV irradiation (1 mW cm^{-2} , 90 s) (b), upon incubation in hydrocarbon (pentane, 30 s) (c), and after removal of pentane and drying under ambient conditions (d). Schematic representation of self-assembled diacetylenes (left), a blue-phase PDA (middle), and a red-phase PDA (right) is displayed in (e).

100 and sodium dodecyl sulfate (SDS) were purchased from Sigma and TCI, respectively. Polydimethylsiloxane (PDMS, Sylgard 184) base and the curing agent were purchased from Dow Corning. Kerosene and diesel oil were purchased from Hyundai Oil Bank, Korea. Optical and fluorescent images were obtained with an Olympus BX 51W/DP70. Confocal fluorescence microscopic images were collected with an Olympus IX83/FV1200.

Fabrication of PDA-Embedded PDMS Spheres. A typical procedure for the preparation of PDA-embedded PDMS spheres is as follows. A chloroform solution (0.5 mL) containing 10,12-pentacosadiynoic acid (PCDA) (8.4 mg) was injected into a PDMS elastomer base solution (2.1 g). Removal of the solvent *in vacuo* was followed by UV irradiation (254 nm, 1.0 mW cm^{-2} , 90 s) while stirring to induce polymerization of the diacetylene monomer. After removal of the air bubble in the mixture *in vacuo*, the resultant blue-colored polydiacetylene-PDMS mixture was introduced into a microchannel (*vide infra*) as the core flow (0.18 mL/h). Aqueous Triton X-100 solution (0.5%) was introduced as a sheath flow (30 mL/h). Generated microdroplets were collected in a vial and cured at room temperature for 3 d.

Preparation of Microfluidic Chip. Microfluidic chips were fabricated with polydimethylsiloxane (PDMS, Sylgard 184, Dow Corning) by using standard photolithography and molding techniques. After cleaning with acetone, isopropyl alcohol (IPA), and deionized water, a 4 in. Si wafer was evenly spin-coated at a thickness of 550 μm with a photoresist (PR) material (SU-8, Microchem) to fabricate a PR

mold. The coated wafer was soft-baked at 65 $^{\circ}\text{C}$ for 10 min and at 95 $^{\circ}\text{C}$ for 120 min, cooled, and then exposed to 365 nm UV light using a UV exposer (MDA-400M, MIDAS) through a film-type photo mask with a patterned microchannel. A postexposure-baking of the wafer was performed at 65 $^{\circ}\text{C}$ for 5 min and at 95 $^{\circ}\text{C}$ for 30 min to enhance the cross-linking of PR. The wafer was developed for 6 min in a propylene glycol monomethyl ether acetate (PGMEA) solution. As a final process for the PR mold, the wafer was thoroughly washed with IPA and deionized water to remove unexposed PR and dried with a nitrogen gun. To fabricate the PDMS replica, PDMS was thoroughly mixed with a curing agent in a 10:1 volume ratio and was degassed in a vacuum chamber for 30 min. After being poured onto the mold, the PDMS prepolymer mixture was cured in an oven at 70 $^{\circ}\text{C}$ for 2 h. Then, the microchannel-patterned PDMS replica was obtained after detaching the replica from the mold. This PDMS replica bonded with a glass substrate after exposing the replica to oxygen plasma (AH-1700, AHTECH LTS).

Colorimetric and Volumetric Sensing of Hydrocarbon. A blue-colored PDA-embedded PDMS sphere was placed in a tiny epoxy chamber (2 mm diameter) that was fabricated on a slide glass. Hydrocarbon was injected into the chamber through the connected glass capillary. Optical and fluorescence microscopic monitoring were carried out to investigate changes in size, color and fluorescence of the sphere upon exposure to the hydrocarbon. Swelling ratio and red intensity value were measured with Adobe Photoshop program. For practical differentiation by the naked eye, 200 PDA-embedded PDMS

microspheres (560 μm in diameter) pretreated with Triton X-100 were placed in a polyethylene tube (4 mm in diameter). After addition of a hydrocarbon, color and height changes were monitored.

RESULTS AND DISCUSSION

Figure 1 shows a schematic of a microfluidic chip employed for the fabrication of PDA-embedded PDMS microdroplets. A chloroform solution containing 10,12-pentacosadiynoic acid (PCDA) was mixed with a PDMS elastomer base solution. The volatile organic solvent was removed *in vacuo* and the residue was irradiated with 254 nm UV light (1.0 mW cm^{-2}) to induce photopolymerization of the diacetylene monomer. The off-white mixture immediately became blue owing to the formation of conjugated PDA supramolecules. After removing the air bubbles of the mixture *in vacuo*, the resultant blue-colored polydiacetylene-PDMS mixture was introduced into a microchannel as the core flow. Aqueous Triton X-100 solution (0.5%) was introduced as a sheath flow (30 mL/h). The blue PDA-PDMS mixture was emulsified by using a 2-D hydrodynamic focusing effect at a junction of the microchannel, and the microdroplets were collected in a vial. Then, solidified PDA-embedded PDMS microbeads could be obtained by curing the droplets at room temperature for 3 d. The pale-blue colored microbeads were further irradiated with 254 nm UV light and this process resulted in the generation of deep blue-colored PDA-embedded microbeads.

It should be noted that no polymerization occurred when the microbeads prepared from a monomeric diacetylene-PDMS base mixture was subjected to UV irradiation. This indicates that diacetylene monomers are not properly arranged after microbead formation. UV irradiation of diacetylene-PDMS mixture before introduction into the microfluidic channel affords formation of PDA supramolecules, and the preformed PDA molecules seem to help arrangement of diacetylene monomers for proper polymerization. The optical microscopic image shown in Figure 2a displays a pale-blue colored PDA-embedded PDMS microbead. It is clear that further irradiation of the bead with 254 nm UV light results in the buildup of intense blue color in the microbead (Figure 2b). Interestingly, incubation of the PDA-embedded PDMS microbead in pentane solution brought about swelling of the microbead with a simultaneous blue-to-red color change (Figure 2c). As expected, the nonfluorescent microbead became fluorescent upon exposure to the hydrocarbon, since PDA in red-phase is fluorescent (Figure 2c, bottom). Shrinkage of the microbead to the original size was observed when it was removed from pentane (Figure 2d). Figure 2e shows a schematic representation of diacetylene supramolecules that undergo UV-induced polymerization as well as a twisted red-phase PDA structure upon exposure to hydrocarbon.

The hydrocarbon-induced colorimetric transition of the PDA-embedded PDMS microbead follows the mechanistic feature observed with the PDA-embedded PDMS film. Thus, the mechanical strain energy absorbed by the PDMS matrix during the swelling process in the hydrocarbon solution is transferred to the embedded PDA supramolecules. This causes increase in the interchain distance of the PDA supramolecules and allows a certain degree of C–C single bond rotation, which leads to distortion of the arrayed p-orbitals. As a consequence, a blue-to-red color transition occurs.

The advantage of using PDA as a sensor matrix is that the property of the stimulus-response is not limited to the colorimetric response. The presence of PDA in the PDMS

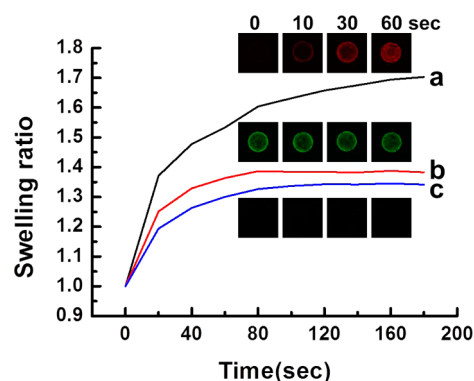


Figure 3. Swelling ratio as a function of time for a PDMS microbead (560 μm in diameter) containing PDA (a), fluorescein (b), and no embedded material (c). Confocal fluorescence microscopic cross section images of dried PDMS beads after incubation for 0, 10, 30, and 60 s in heptane are also displayed.

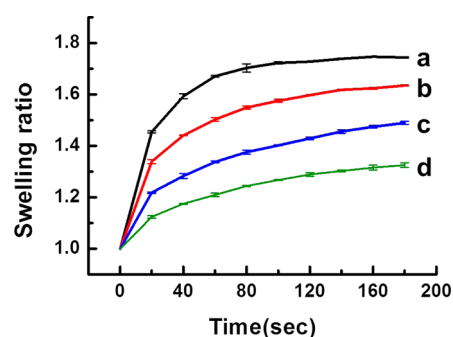


Figure 4. Time-dependent swelling of PDA-embedded PDMS microbeads (560 μm in diameter) in pentane (a), heptane (b), nonane (c), and undecane (d). The swelling ratios were measured from captured images of microbeads by monitoring the swelling process with an optical microscope during incubation.

matrix afforded a superior swelling property to the small molecule-embedded PDMS bead. Figure 3 shows plots of the swelling ratio of PDMS beads as a function of time, and the PDA-embedded microbead (Figure 3a) swells faster than either the fluorescein-embedded microbead (Figure 3b) or the pure PDMS bead (Figure 3c). This is presumably due to the fact that the polymeric PDA makes the cross-linked PDMS structure loose and facilitates faster penetration of hydrocarbon. Meanwhile, inspection of the confocal fluorescence microscopic images presented in Figure 3 indicates that colorimetric transition of the PDA-embedded bead occurs from the surface of the bead and eventually migrates to the middle part of the bead. This phenomenon is in accord with the mechanistic feature described above. Thus, larger mechanical stress is provided to the PDA supramolecules located near the surface than the PDAs inside the bead during the hydrocarbon promoted swelling of the matrix PDMS, resulting in the faster colorimetric change. As expected, confocal microscopic images of the fluorescein-embedded PDMS display no difference in the fluorescence distribution during swelling. It should be noted that the confocal fluorescence microscopic images presented in Figure 3 are recorded with dried beads after incubation in heptane solution, since it is very difficult to obtain the fluorescence images with the bead in hydrocarbon solution.

Figure 4 shows time-dependent swelling of PDA-embedded microbeads in different hydrocarbons. It is clear that the bead

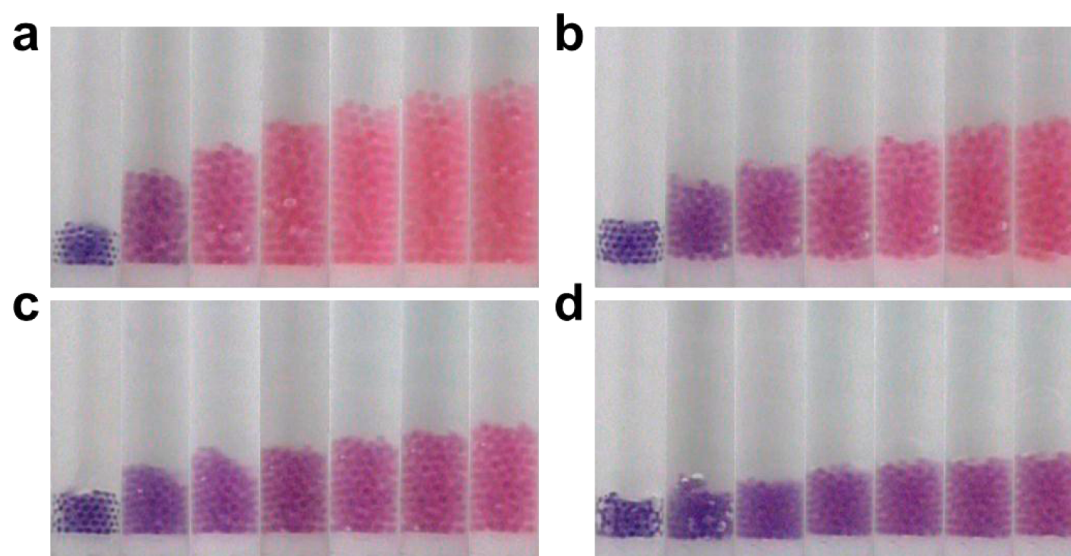


Figure 5. Photographs of tubes containing PDA-embedded PDMS microbeads (560 μm in diameter) upon exposure to pentane (a), heptane (b), nonane (c), and undecane (d) (time interval: 10 s).

incubated in pentane swells faster than that in other hydrocarbons. In addition, the swelling ratio decreases consistently as the number of hydrocarbons in the alkane increases. Thus, the different swelling response of the PDA-embedded PDMS bead allows facile differentiation of the hydrocarbons.

One of the advantages of using the microbead type sensor over the PDA-embedded sensor film is that a collective effect from multiple microbeads is possible. Thus, although the difference in the swelling ratio for a single microbead is relatively small and difficult to observe without the help of a microscope, amplification of the difference is possible by the collective effect of using multiple microbeads. In order to demonstrate the feasibility of this signal amplification effect, approximately 200 PDA-embedded microbeads were placed in a test tube. The swelling behavior of the microbeads in the tube was monitored after addition of different hydrocarbons. Figure 5 displays photographs of tubes containing the PDA-embedded PDMS microbeads. Upon being placed in pentane, the height of the microbeads immediately started to increase with a simultaneous color change from blue-to-purple-to-red (Figure 5a). The pentane-induced volumetric and colorimetric changes are very fast and are readily recognizable by the naked eye. The microbeads were found to grow faster upon incubation in hydrocarbons having shorter chains. In addition, incubation of the microbeads in pentane (Figure 5a), heptane (Figure 5b), nonane (Figure 5c) and undecane (Figure 5d) resulted in different levels of color change. Thus, a faster colorimetric change was observed with the tube containing hydrocarbons of shorter alkyl chains. This is somewhat expected, since the colorimetric response of the bead is proportional to the volume change of the bead. The results presented in Figure 5 indicate that both volumetric and colorimetric responses can be utilized to differentiate among hydrocarbons.

CONCLUSIONS

We have developed a PDA sensor system for hydrocarbon differentiation. The conjugated polymer-embedded PDMS microbead enables visual differentiation of several linear alkanes. The degree of swelling of the PDA–PDMS composite

bead in hydrocarbons was found to be inversely proportional to the chain length of the hydrocarbon. In addition, the swelling of the bead in the hydrocarbon was accompanied by a blue-to-red color change of the microbead because of the mechanical stress delivered to the PDA supramolecules. Combination of the different swelling ratio and the different colorimetric response allowed facile differentiation of linear hydrocarbons by the naked eye. Finally, the microbead-based approach enables signal amplification by the collective effect arising from the usage of multiple microbeads.

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Notes

The authors declare no competing financial interest.

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