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REICHARDT'S DYE AS OPTOCHEMICAL SENSOR MATERIALS DETECTED POLAR GAS

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ABSTRACT

A sensor that can detect polar gases was developed based on Reichardt's solvatochromic dye. The Reichardt's dye was incorporated into PVP (polyvinyl pryrolidone) and then was fabricated into sensing films. The sensing film can produce strong, fast and reversibly signals when it exposed to polar gases, with response time in the range of 5-20 seconds. High-resolution micrographs of the sensing film in different polar gases were obtained by using a digital camera. Using the high-resolution micrographs, a concentration as low as 0.05% (v/v) methanol gas can be detected. This detection is completely reversible under any vapor concentrations.

Keywords: gas sensor, color change, Reichardt's dye, micrograph.

INTRODUCTION

Due to the environmental protection became more important recently, the monitoring of pollutants or hazardous substances implies the urgency for sensor devices. So the field of artificial olfaction and gas determination is one of the fastest growing areas of sensing both commercially and within academic research areas [1-27]. Most of the research in this field to date concentrates on identification and quantification of analyte species by employing array sensors [6-9]. A requirement for sensors within an electronic nose system, as compared to stand-alone gas sensors, is the ability to sense with high sensitivity. But generally has been based on sensors that detect adsorption into a set of polymers or on electrochemical oxidations at a set of heated metal oxides [15-20]. There has been a great deal of interest in the development of optical fiber sensors [21-23] and colorimetric array sensor [24-27] in recent years. On the other hand, alcohol as one of standard scents is very important in clinical and industrial analyses. At present, more widely used is gas chromatography or distillation where the density or refractometry are determined in a subsequent step [29]. There have been reports alcohols sensor are using optical fiber [21-23].

In this study, an odor sensor based on color information was developed. A number of dyes were tried but, at last, the solvatochromic Reichardt's dye was selected as responsive element for alcohol detection. Reichardt's dye shows a strong solvatochromism is known to all. The electronic transition in Reichardt's dye is associated with a hypsochromic solvatochromism of approximately 350nm when changing the solvent from tetrahydrofuran to methanol [13]. The idea of effects of dye absorption spectra in different environments can be found in a research study by Christine Hubert *et al*., [28].

In the present study, the solvatochromic or environment-sensitive dyes incorporated into polymer film which shows variability of color in different polar gases have been investigated. The R-dye almost had response for all polar gases and was quite sensitive to environment. Even more, there was a remarkably color change for methanol. In order to analyze the color change resulted by methanol gas quantitatively, a high-resolution micrograph with Scion Image soft was employed; to divide the color of micrograph into three elementary colors (RGB): red, green and blue, and compare their (RGB) difference of color in different gases to the air. By the analysis of the RGB values through the color of sensing film, the content of methanol can be analyzed quantitatively. These high-resolution micrographs can then be used to detect a concentration as low as 0.05% (v/v) methanol gas.

MATERIALS AND METHODS

Apparatus and reagents

Reichardt's dye, all the polymers and solvents were purchased from the Aldrich and Tokyo Chemical Industry Co. Ltd. Slide and cover glasses were purchased from Matsunami Glass Ind. Ltd. Japan. Self-made organic gas flow cell was employed (Figure-1). Before the experiment, the sensing film was dried with flowing of dried air to the surface of sensing film. The gas flux was controlled using a controller to maintain a fixed flow rate. Dried air flow rate was 1.50 ml/s during drying or substitution and polar gas flow rate was 0.50 ml/s during measurement. All images of sensing film were performed on an inverted confocal microscope with CCD cameras (Nikon, Japan). Absorption spectrum of the sensing film and solution were measured using UV-160A spectrophotometer.

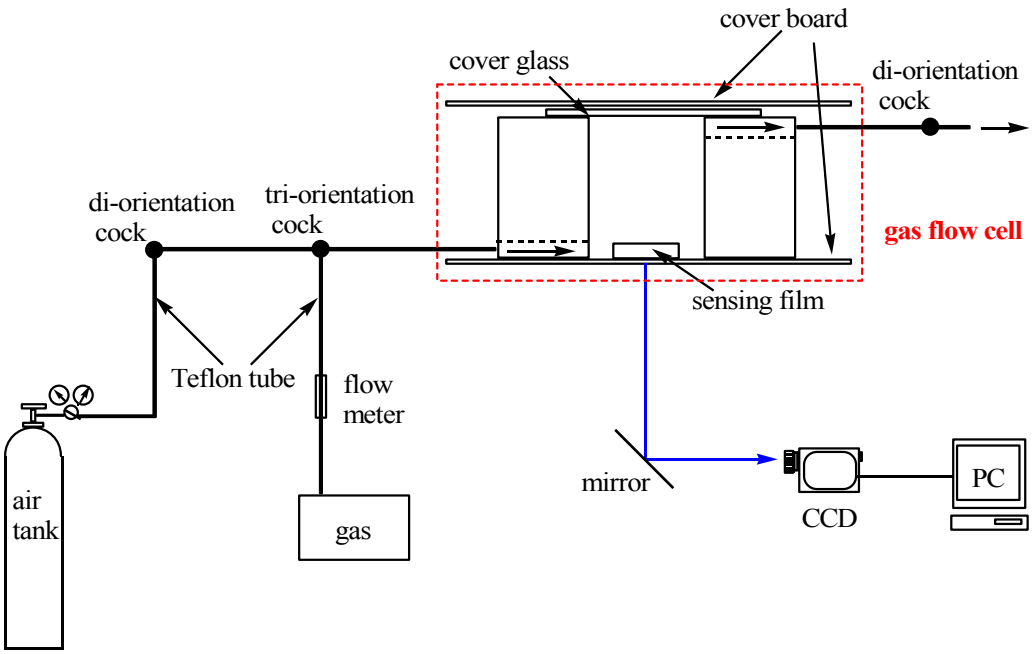

Figure-1. Experimental setup.
The bottle of gas flow cell was placed on the observe plate of the microscope.

Preparation of sensing film

11.63mg of R-dye and 200mg PVP were respectively dissolved in 20ml DMAC with 1:1 volume ratio. The mixture was sonicated for 5min to obtain the sensing solution. The slide glass (φ22mm) were activated with concentrated nitric acid for 24h, then washed with distilled water and methanol in turn and dried at 60ºC over night. 20μl Reichardt's dye (R-dye) sensing solution was dropped on the slide glass with spin-coating. Two kinds of sensing film were prepared. One is dried at room temperature and solvent was not eliminated completely. The other one was prepared under 50ºC and 3mmHg vacuum pressure which make the solvent completely eliminated.

Images obtaining and data analysis

Assembled the prepared sensing film with flow cell as shown in Figure-1, and put the assembled gas flow cell to the observe plate of the microscope. The microscopical light source was halogen lamp with a spectral range form 320 to 1000nm. After sensing film was dried with dried air for 20 mins, the cock was turned off. Take 20 micrographs during the dried period with CCD camera to record the original color of sensing film. Then, purge the gas flow cell with polar gas. Photos were taken every 5s. After 5 min, 60 micrographs should be recorded, and the sensing film was dried by using dried air to purge the polar gas inside the film. After 30 min, 20 micrographs were taken again and then different polar gases were applied to observe the color change of the sensing film. All measurements were completed at room temperature (20ºC) where the relative humidity was approximately 35%.

Analyze the micrographs with Scoin Image Soft to obtain the RGB tricolor. 100×100 pixel region was selected to analyze. Calculate the average value of RGB in the region, then, calculate the derivation between initial RGB value and the value of different periods as the response of sensing film versus different polar gas. Besides the first micrograph, all of the others automatic select and calculate uniform regions by computer.

RESULTS AND DISCUSSION

It is well known that the R-dye is a solvatochromic molecule which absorbed wavelength caused displacement when the environment is changed. So, at first, the response of R-dye was investigated in various VOC as reference [30]. The 42 kinds of VOC were employed, and the results are presented in Figure-2, the different kinds of polar gases are shown in Table-1.

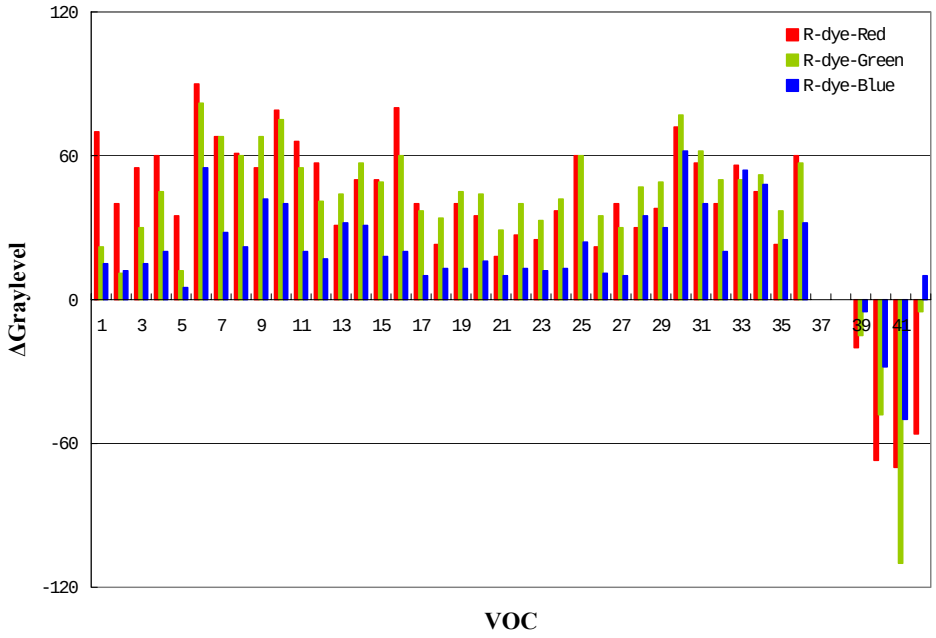

Figure-2. Response of R-dye to 42 kinds of VOC.
The number of abscissa corresponded with the number in Table-1.

Table-1. VOC at the abscissa (in Figure-2).

S. #	Name	S. #	Name
1.	Methanol	22.	Chloroform
2.	Ethanol	23.	1,2Dichloroethane
3.	1-Propanol	24.	1,2Dichloropropane
4.	2-Propanol	25.	1-Hexene
5.	1-Butanol	26.	Cyclohexene
6.	Diethyl Ether	27.	γ-Butyrolactone
7.	t-Butyl Methyl Ether	28.	Methyl Acetate
8.	THF	29.	Ethyl Acetate
9.	Acetone	30.	Methyl Formate
10.	2-Butanone	31.	Ethyl Formate
11.	2-Pentanone	32.	Methyl Propionate
12.	3-Pentanone	33.	Acetaldehyde
13.	Acetonitrile	34.	Propionaldehyde
14.	Propionitrile	35.	Butyraldehyde
15.	n-Butylronitrile	36.	Formic Acid
16.	Benzene	37.	Acetic Acid
17.	Toluene	38.	Propionic Acid
18.	Xylene	39.	Ethylamine
19.	DMF	40.	Diethylamine
20.	n-Methyl Formamide	41.	Triethylamine
21.	n,n-Diethyl Formamide	42.	Ethanethiol

The responses were observed with scanner and all VOC were saturated. From Figure-1, the color change of R-dye is so complicated that it is hard to be distinguished for all VOC. On the other hand, the fact is that R-dye responded to all VOC and it is quite sensitive to environment, but it was not reversible to all VOC. There was only good reversibility for polar vapor; especially there was the best reversibility for alcohol. Thus, the sensing film was studied especially for alcohol. As the response in Figure-1 was observed with a scanner, so in order to improve the analytical accuracy, the sensing film was made to the micrograph through microscope. In the interest of observing the color change of R-dye molecule by itself, the sensing film was prepared with volatile solvent. Figure-3 shows the R-dye sensing film with R-dye/MeOH solution at originally. But this film had a big shortcoming for saturation alcohol gas; it produced acicular crystals with no color change. The location with red circle expressed was acicular crystals and the yellow circle expressed was the color change in methanol gas without crystals. The acicular crystal was continually produced in the methanol gas, but it stopped in the air. It is possible that the reaction was occurred between the R-dye molecules inside or between R-dye molecule and methanol. Although a concrete reaction is not clearly known in the sensing film, due to just partially sensing film produced acicular crystals. Therefore, to a certain degree, it was observed that the acicular crystals produced had a certain interrelation to the special arrange of R-dye molecules, because while at the location with crystals produced, it attracts surrounding molecule and make crystals grows continuously in methanol gas, but under other cases, there is no crystals generated at the location without crystals.

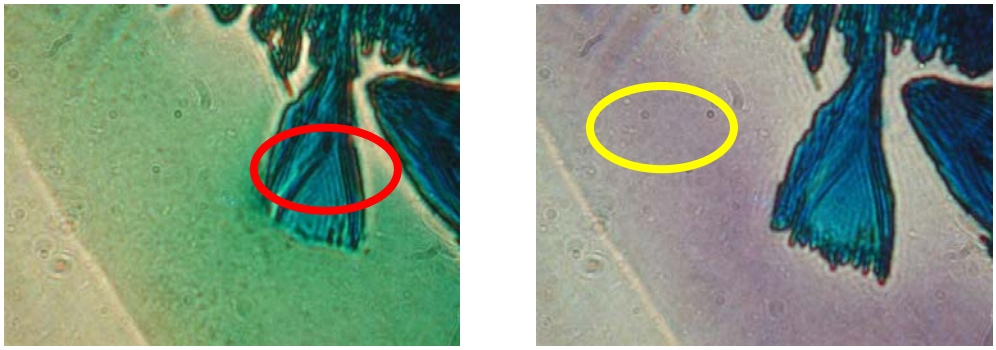

Figure-3. The acicular crystals produced sensing film.
(a) in the air (b) in the ethanol.

The previously mentioned two types of sensing films were prepared with R-dye/DMAC (N,N-Dimethylacetamide). DMAC is aprotic solvent, so there is no reaction occurred between the solvent and dye molecules. The new sensing film was prepared by using DMAC as solvent, but as the saturated alcohol gas flow the film's surface, the crystals was not produced (Figures 4 and 5).The color change is quite perfect, and the state of film was stabilized too. Especially response time in the range of 5-20 seconds, it is so quick for the sensor response.

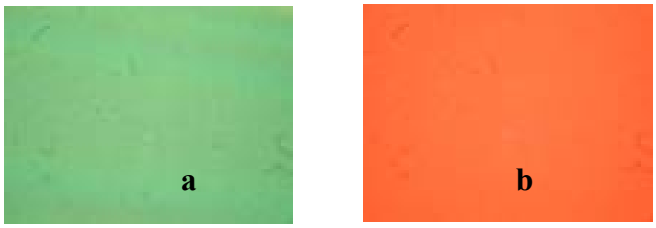

Figure-4. No acicular crystals produced sensing film
(DMAC was not completely eliminated).
(a) in the air (b) in the methanol.

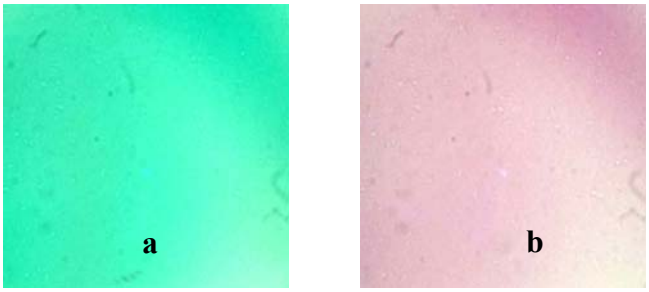

Figure-5. No acicular crystals produced sensing film
(DMAC was completely eliminated).
(a) in the air (b) in the methanol.

For the purpose to examine which alcohol gas has the fastest color change, the absorption spectra of sensing film were measured in different alcohol gas (Figure-6). It was known that the sensing film is the most sensitive for methanol. So, the relation between the change value of RGB and methanol gas concentration was investigated.

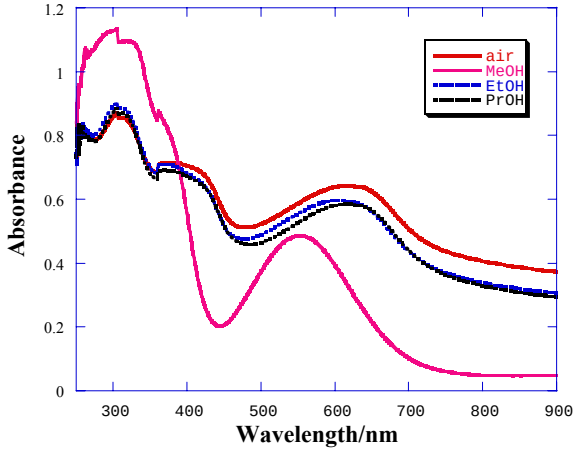

Figure-6. Absorbance spectra for the sensing film exposed to alcohol.

First, error margin of imaging color was measured, under the same experimental process, by using only dried air, 200 photographs were obtained. In these photograph we chose five points, according to points analyzed, the standard deviation of RGB by five points were calculated. From 15 values we respectively voted in σ_{Rmax}, σ_{Gmax} ,σ_{Bmax} , and then used 3 times σ_{max} , the detected benchmark was calculated. All of the pixels of imaging were analyzed, when the R-dye in the range of: R = 240 ± 10, G = 110 ± 5.5, B = 70 ± 3.7, the point with the biggest color change in micrograph was found in the software developed by our own. The film had a good response, used point carry on analyzing with RGB value in this region, 0.05% (v/v) alcohol gas could be detected (Figure-7). For insuring the accuracy of the gas concentration, the minimum of the gas concentration prepared was decided at 0.05 % (v/v).

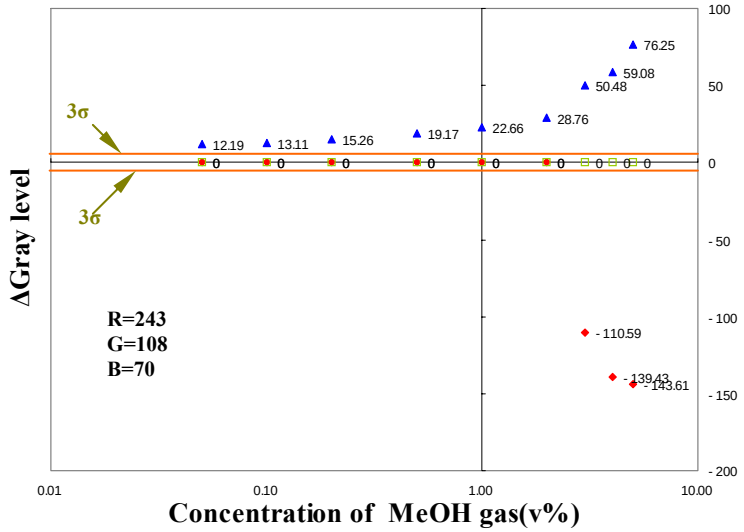

Figure-7. Relation between the change value of RGB and methanol gas concentration.

CONCLUSIONS

In this study, various VOC with R-dye sensing film have been investigated, especially the relation between the change value of RGB and methanol gas concentration is investigated. R-dye was incorporated into PVP (polyvinyl pyrolidone) and was fabricated into sensing films. This sensing film can produce strong signals, fast and reversible when it is exposed to polar gases, with response time in the

range of 5-20 seconds. High-resolution micrographs of this sensing film in different polar gases were obtained using a digital camera. Using the high-resolution micrographs can detect a concentration as low as 0.05% (v/v) methanol gas. This detection is completely reversible under any vapor concentrations. On the other hand, the best response point was investigated, if the RGB value of the sensing film with definite range (R = 240 ± 10, G = 110 ± 5.5, B = 70 ± 3.7), it has the best response possibility.

REFERENCES

[1] J.W. Grate, S.J. Patrash, S.N. Kaganove, M.H. Abraham, B.M. Wise and N.B. Gallagher. 2001. Analy. Chem. 73. pp. 5247–5259.

[2] L. Cui, M.J. Swann, A. Glidle, J.R. Barker and J.M. Cooper. 2000. Sensor and Actuators B: Chem. 66. pp. 94–97.

[3] B.J. Doleman, M.C. Lonergan, E.J. Severin, T.P. Vaid and N.S. Lewis. 1998. Anal. Chem. 70. pp. 4177–4190.

[4] J.W. Gardner, M. Craven, C. Dow and E.L. Hines. 1998. Meas. Sci. Technol. 9. pp. 120–127.

[5] T.A. Dickinson, K.L. Michael, J.S. Kauer and D.R. Walt. 1999. Anal. Chem. 71. pp. 2192–2198.

[6] Arnaud Deraemaeker and André Preumont. 2006. Mechanical Systems and Signal Processing. Vol. 20(7): 1615-1630.

[7] Hui-Chi Huang, Sheng-Yu Huang, Chin-I Lin and Yu-Der Lee. 2006. Analytica Chimica Acta. Available online. 16 September.

[8] A.K. Srivastava and Vinayak P. Dravid. 2006. Sensors and Actuators B: Chemical. Vol. 117(1): 244-252.

[9] Zsolt Seregély, József Farkas, Eszter Tuboly and István Dalmadi. 2006. Chemometrics and Intelligent Laboratory Systems. Vol. 82(1-2): 115-121.

[10] Tarek A. Fayed. 2006. Chemical Physics. Vol. 324(2-3): 631-638.

[11] Mar Puyol, Cristina Encinas, Laia Rivera, Serguei Miltsov and Julian Alonso. 2006. Sensors and Actuators B: Chemical. Vol. 115(1): 287-296.

[12] Yoshiharu Takamuki, Shojiro Maki, Haruki Niwa, Hiroshi Ikeda and Takashi Hirano. 2005. Tetrahedron. Vol. 61(42): 10073-10080.

[13] Franz L. Dickert, Ulrich Geiger, Peter Lieberzeit and Ulla Reutner. 2000. Sensors and Actuators B: Chemical. Vol. 70(1-3): 263-269.

[14] John H. Krech and Susan L. Rose-Pehrsson. 1997. Analytica Chimica Acta. Vol. 341(1): 53-62.

[15] Laura O. Péres and Jonas Gruber. 2007. Materials Science and Engineering: C. Vol. 27(1): 67-69.

[16] K. Arshak and I. Gaidan. 2006. Sensors and Actuators B: Chemical. Vol. 118(1-2): 386-392.

[17] K. Arshak and I. Gaidan. 2006. Thin Solid Films. Vol. 495(1-2): 292-298.

[18] Alexey A. Tomchenko, Gregory P. Harmer and Brent T. Marquis. 2005. Sensors and Actuators B: Chemical. Vol. 108(1-2): 41-55.

[19] Seung-Chul Ha, Yoonseok Yang, Yong Shin Kim Cho. 2005. Sensors and Actuators B: Chemical. Vol. 108(1-2): 258-264.

[20] Jing-Shan Do and Wen-Biing Chang. 2004. Sensors and Actuators B: Chemical. Vol. 101(1-2): 97-106.

[21] César Elosúa, Cándido Bariáin, Ignacio R. Matías, Francisco J. Arregui, Asunción Luquin and Mariano Laguna. 2006. Sensors and Actuators B: Chemical. Vol. 115(1): 444-449.

[22] Shintaro Sumida, Shinji Okazaki, Shukuji Asakura, Hidemoto Nakagawa, Hideaki Murayama and Takuya Hasegawa. 2005. Sensors and Actuators B: Chemical. Vol. 108(1-2): 508-514.

[23] Cándido Bariáin, Ignacio R. Matías, Inocencio Romeo, Julián Garrido and Mariano Laguna. 2001. Sensors and Actuators B: Chemical. Vol. 76(1-3): 25-31.

[24] P. Rieve, M. Sommer, M. Wagner, K. Seibel and M. Böhm. 2000. Journal of Non-Crystalline Solids. Vol. 266-269(Part 2): 1168-1172.

[25] Thorfinnur Gunnlaugsson, Mark Glynn, Gillian M. Tocci (née Hussey), Paul E. Kruger and Frederick M. Pfeffer. 2006. Coordination Chemistry Reviews. Vol. 250(23-24): 3094-3117.

[26] Fang-ying Wu, Mei-hua Hu, Yu-mei Wu, Xiao-fang Tan, Yong-qiang Zhao and Zhao-jun Ji. 2006. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. Vol. 65(3-4): 633-637.

[27] Fang-Ying Wu, Xiao-Fang Tan, Yu-Mei Wu and Yong-Qiang Zhao. 2006. Spectrochimica Acta Part

A: Molecular and Biomolecular Spectroscopy. Vol. 65(3-4): 925-929.

[28]Christine Hubert, Denis Fichou, Pierre Valat, Francis Garnier and Bertrand Villeret. 1995. Polymer. 36: 2663-2666.

[29]A. Caputi and D.P. Mooney. 1983. J. Assoc. of Anal. Chem. 66: 1152.

[30]Fang Han, Takanori Inoue, Teppei Wasai, Yoshiaki Kurauchi and Kazuya Ohga. 2006. Odor sensor based on the information of colour. ARPN J. of Engineering and Applied Sciences. Online publication. Vol. 1(4): 1-6.