

## Highly Sensitive Toluene Vapor Sensors Using Carbon Black/Amino-Functional Copolymer Composites

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**ABSTRACT:** An amino-functional copolymer [*N,N*-dimethyl-1,3-propanediamine (MCD)] developed in our laboratory was blended with carbon black (CB/MCD composite) and its electrical responses to toluene vapor at low concentrations were measured at 30°C. When exposed to 200 ppm of toluene vapor, the CB/MCD sensor responded at  $S = 0.04$  ( $S$  was obtained by dividing the relative change in the resistance of the sensor upon exposure to toluene vapor by the baseline resistance), demonstrating its ability to detect toluene vapor at low concentrations. The response was affected by humidity in the atmosphere due to the hydrophilic nature of MCD film; however, the behavior was reproducible before and after exposure of the sensor to the humid atmosphere. In addition, in 10 consecutive sorbing/desorbing cycles, it was confirmed that the changes in the resistance of the CB/MCD sensor were reproducible. These favorable sensing characteristics were attributed to vapor sorption behavior arising from the glassy and loosely crosslinked nature of MCD and explained by the dual-sorption model. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** toluene vapor sensor; carbon black composite; amino-functional copolymers

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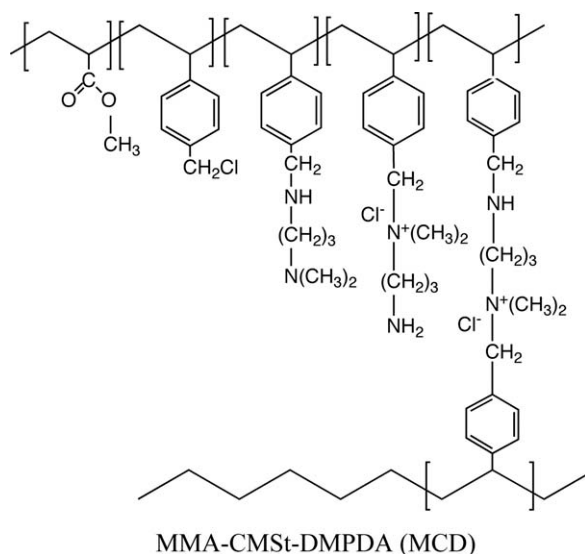
### INTRODUCTION

The development of low-cost, low-power, and portable gas sensors for detection and identification of volatile organic compounds is needed for applications such as workplace monitoring to protect the health of employees and indoor air-quality assessment at offices and homes. One type of sensors that have received a great deal of attention is the composite chemiresistors based on carbon black (CB) and matrix polymers. Adsorption of vapor of a good solvent of the matrix polymer in the composites causes swelling of the matrix polymer, which increases the distance between the carbon particles, resulting in an overall increase in resistance.<sup>1–3</sup> In the case of poor solvents, however, the electrical response of the composites is rather weak; thus, the system demonstrates selective gas sensitivity. Another advantage of this sensor is that, unlike the semiconducting metal oxide sensors,<sup>4</sup> the sensing operation occurs at room temperature, which lowers the power consumption requirements. The process of the fabrication of the sensor device is simple and effective for large-scale production. However, the main problem with the CB/polymer composite sensors is their low sensitivity. For toluene vapor sensors, polystyrene (PSt),<sup>5,6</sup> copolymers,<sup>7–9</sup> and polyisobutylene (PIB)<sup>10</sup> have been tested as matrix polymers. However, the earlier-cited reports on CB/polymer-based

toluene vapor sensors have been mainly concerned with their response to saturated vapors. To realize more practical toluene vapor sensors that could be applied to, for example, chemiresistor arrays for qualitative vapor classification and identification, it will be necessary to detect toluene vapors at lower concentrations. For this purpose, Xie et al. fabricated a sensor array composed of three kinds of polymers and CB to detect organic vapors at low concentrations, and demonstrated that the CB/poly(ethylene oxide) (PEO) composite sensor was highly sensitive to toluene vapor.<sup>11</sup> Dong et al. reported on CB/poly(butyl methacrylate) (PBMA) composites, synthesized by in situ polymerization of monomers in the presence of CB, and obtained higher sensitivity to low-concentration toluene vapor.<sup>12</sup>

One of the keys to enhancing sensitivity is the development of a novel matrix polymer that sorbs large amounts of toluene vapor at low concentrations. To date, various polymers have been proposed for mass-sensitive toluene vapor detection, such as PIB,<sup>13–15</sup> poly(dimethyl siloxane) (PDS),<sup>15–17</sup> PSt,<sup>18</sup> lipid film,<sup>19</sup> and others<sup>20–23</sup>. Recently, we have proposed other novel copolymer coatings for a QCM-based toluene vapor sensor.<sup>24,25</sup> Among them, a methyl methacrylate (MMA)-*co*-chloromethyl styrene (CMSt) copolymer modified with *N,N*-dimethyl-1,3-propanediamine (DMPDA), which is abbreviated as MCD, has been

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**Figure 1.** Chemical structure of the prepared MCD polymer.

shown to be capable of large, fast, and reversible toluene vapor sorption in contrast with conventional polymers such as cellulose acetate butyrate, PDS, and PSt.

In this study, MCD was blended with CB, and its electrical responses to low concentrations of toluene vapor were measured. To explain the response mechanism of the CB/MCD sensor, the vapor sorption behaviors of the composites were measured using a quartz crystal microbalance.

## EXPERIMENTAL

### Synthesis of MMA-co-CMSt Copolymer Precursors

An MMA-co-CMSt copolymer precursor (MMA-CMSt) was synthesized according to the previous reports as follows.<sup>24-26</sup> MMA and CMSt were dissolved in toluene at a weight ratio of 0.58 : 0.42 and polymerized via free-radical polymerization initiated by azobisisobutyronitrile at 105°C for 12 h. The toluene solution of the dissolved products was then poured into methanol to precipitate the copolymer. The precipitated copolymer was filtered with suction and was dissolved in toluene and poured into methanol again. The precipitate was then filtered with suction, washed with methanol, and dried under a vacuum at room temperature. The CMSt composition of the prepared copolymer precursor determined by elemental analysis was approximately 50 mol %.

### Preparation of CB/MCD Composite Solutions

Nine milligrams of CB (SHOBLACK N330, specific surface area = 75 m<sup>2</sup>/g) powder (Cabot Japan K.K.) was added to 200 μL of 1 mol/L toluene solution of MMA-CMSt under ultrasonication for 1 h to obtain a homogeneous suspended solution. Then, 200 μL of 1 mol/L solution of DMPDA in toluene was added into the above suspended solution and mixed under ultrasonication for 3 min at room temperature. During this mixing procedure, the CMSt group in the MMA-CMSt copolymer was reacted with DMPDA.<sup>27,28</sup> A possible chemical structure of the chemically modified copolymer with DMPDA is shown in Figure 1. The CB concentration in the prepared composite was

~10 wt %. Hereafter, the DMPDA-modified MMA-CMSt copolymer is denoted as MCD, and the composite of CB and MCD is denoted as CB/MCD.

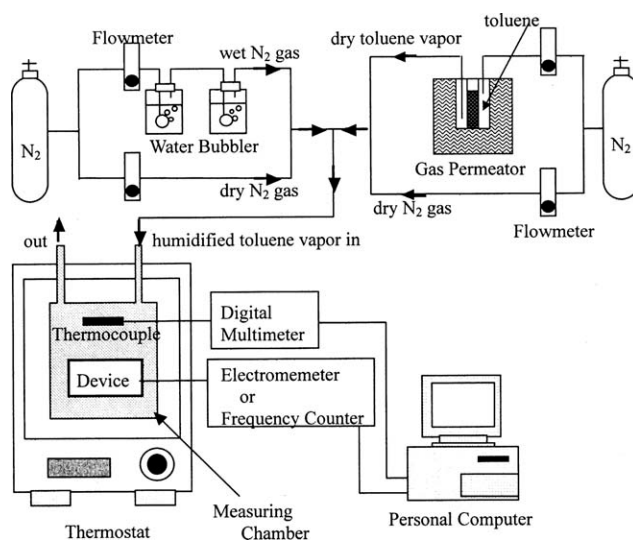
## Measurements

For the preparation of toluene vapor sensors, CB/MCD composite solutions were drop-coated onto the surface of an alumina substrate possessing a pair of interdigitated gold electrodes. Then, the substrate was dried in an oven at 80°C in a vacuum for 2 h.

For the measurement of the toluene vapor sorption capacity of CB/MCD films, composite solutions were spin-coated on one side of an AT-cut quartz crystal (4 MHz resonant frequency) having a silver electrode on both sides. The film-coated crystals were dried in an oven at 80°C in a vacuum for 2 h.

Both electrical resistance and sorption capacity measurements were performed at 30°C in flows of toluene vapor and humidity-controlled high-purity N<sub>2</sub>. The measurement apparatus is shown in Figure 2. Each device was set in a special thermostatically controlled measuring chamber. Toluene vapor was generated continuously by a diffusion tube placed inside a gas permeator (PD-1B, Gastec). The concentration of the vapor generated could be adjusted by changing the diameter and/or length of the hand-made diffusion tube. The toluene vapor concentrations were calculated by the gas flow rate and the weight loss over the experimental period. The humidity-controlled N<sub>2</sub> gas was prepared by varying the mixing ratio of dry N<sub>2</sub> gas and water-saturated N<sub>2</sub> gas, which was prepared by bubbling the N<sub>2</sub> gas through water. The final concentration of toluene vapor and humidity in the measuring atmosphere was varied by mixing the toluene vapor produced by the permeator and the humidity-controlled N<sub>2</sub> gases. The total sample gas was allowed to flow over the sensor device at a rate of 400 mL/min. Humidity in the measuring chamber was calibrated with a commercially available humidity sensor.

Resistance measurements were performed using an electrometer (TR 8652, Advantest) under the applied DC voltage of 1 V.



**Figure 2.** Experimental setup.

Dividing the relative change in the resistance of the composite sensor upon exposure to toluene vapor,  $\Delta R$ , by the baseline resistance,  $R_b$ , yielded the sensor response,  $S$ .

$$S = \Delta R/R_b \quad (1)$$

To measure the toluene vapor-sorption properties of composites, the quartz crystal microbalance (QCM) technique was used. The underlying principle of QCM is based on the  $\Delta f$  (Hz) of the fundamental oscillation frequency ( $f_0$ ) upon mass changes [ $\Delta m$  (g)] on the crystal surface. The linear relationship between the mass added to the crystal surface and the change in its frequency can be derived from the Sauerbrey equation:<sup>29</sup>

$$\Delta f = Cf_0^2 \Delta m / A, \quad (2)$$

where  $C$  is a constant and  $A$  is the surface area ( $\text{cm}^2$ ) of the crystal. It should be noted here that, when  $\Delta f$  produced by sorption of the analyte vapor into the polymer film is  $<2\%$  of  $f_0$ , mechanical losses are minimal and frequency shifts are predominantly due to changes in mass uptake,<sup>30</sup> justifying the use of the Sauerbrey equation. However, if the viscoelastic effects of the film coating due to the analyte vapor sorption are significant, the gravimetric interpretation is inaccurate.<sup>31,32</sup> In this study, the observed frequency shifts induced from the 200 ppm of toluene vapor sorption on CB/MCD composite films were less than several tens of Hz, as mentioned later, which corresponded to  $<2\%$  of  $f_0$  (4 MHz). This fact indicates that the frequency shifts measured by QCM approximately correlated with the mass uptake capacity of the present composite films.

The surface morphology of the composite films was investigated using scanning electron microscopy (SEM) (JSM-5300, JEOL). Calorimetric measurements were made on a Perkin-Elmer Pyris 1 differential scanning calorimeter.

## RESULTS AND DISCUSSION

### Surface Morphology

Figure 3(a) shows scanning electron microscopy images for the CB powder, and the average size of CB agglomerates was found to be around several tens of microns. On the other hand, such CB agglomerates were not found in the CB/MCD composite film as shown in Figure 3(b). Because it is known that some polar groups such as hydroxyl, carboxyl, etc., are present on the surface of CB, CB particles seem to have been well dispersed in the MCD film due to their affinity for polar amino groups.<sup>9</sup>

### Sensor Response in a Dry Atmosphere

Before evaluating the sensor response, we needed to determine the optimum CB content. It has been reported that when the composites are exposed to organic vapors, the maximum increase in resistance might be obtained at a CB concentration close to the percolation threshold.<sup>10</sup> However, in general, the performance of conductive composites at the percolation region is quite unstable and fluctuates easily due to slight changes in environmental conditions, such as temperature.<sup>33</sup> In addition, Feller et al. noted that the high resistance of composites (over  $10^4 \Omega$ ) provides a short response time and high sensitivity.<sup>8</sup>

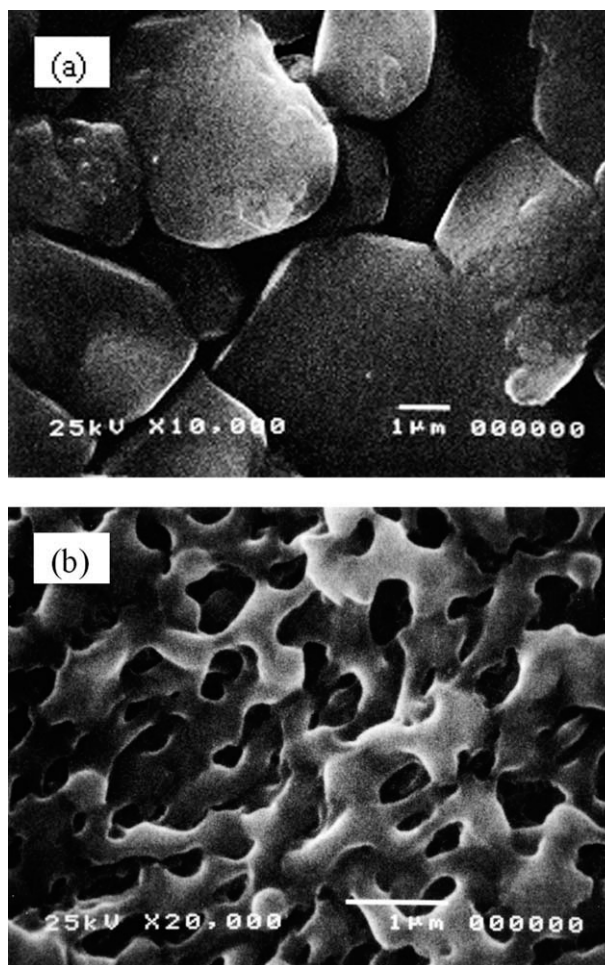
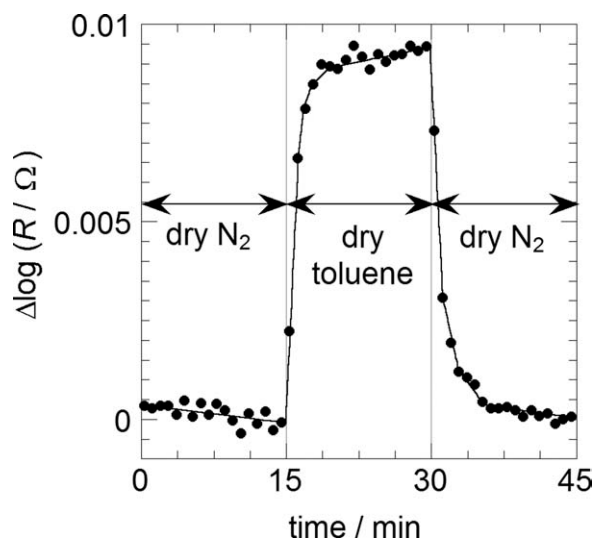


Figure 3. SEM images (a) CB powder and (b) CB/MCD composite film.

Accordingly, CB/MCD composites of 10 wt % CB, with a resistance of  $\sim 10^4 \Omega$ , were employed in this study.

The toluene vapor-sensing characteristics of CB composite sensors were examined in a dry atmosphere. Figure 4 gives an example of the change in resistance seen in the case of the CB/MCD sensor. For all CB/MCD sensors tested, the resistance increased rapidly with exposure of the sensor to 200 ppm toluene vapor, and recovered its original value after reverting to  $\text{N}_2$  gas.

The dependence of the sensor response,  $S$ , on the toluene vapor concentration is plotted in Figure 5. Previous reports concerned with detection at low concentrations of toluene vapor showed sensor responses of  $S = 0.005$  at 400 ppm<sup>12</sup> and  $S = 0.05$  at 800 ppm<sup>11</sup> for CB/PEO and CB/PBMA composites, respectively. Compared with those results, the present CB/MCD sensor achieved higher sensitivity. The change in  $S$  in our experiments varied almost linearly with the toluene vapor concentration below 200 ppm ( $S = 0.04$  at 200 ppm); the value approached a plateau above this concentration. We also measured  $S$  of the CB/MCD sensor at 35,000 ppm, and interestingly, the value was 0.07, almost the same as that obtained at 500 ppm. This is because swelling phenomena do not occur at high concentrations in the glassy and loosely crosslinked MCD polymer.<sup>25</sup>

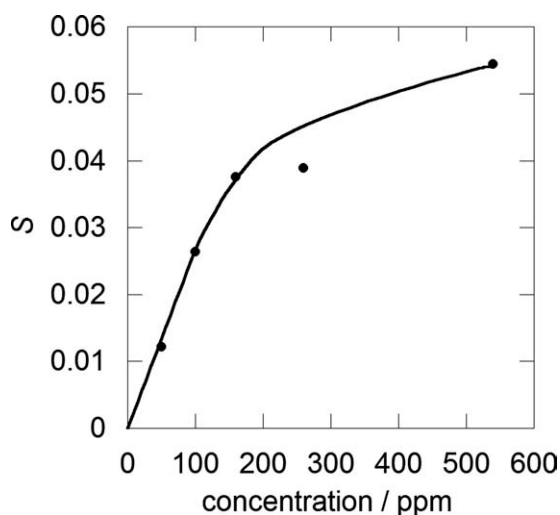


**Figure 4.** Change in resistance of the CB/MCD composite sensor on exposure to 200 ppm of toluene vapor measured at 30°C.

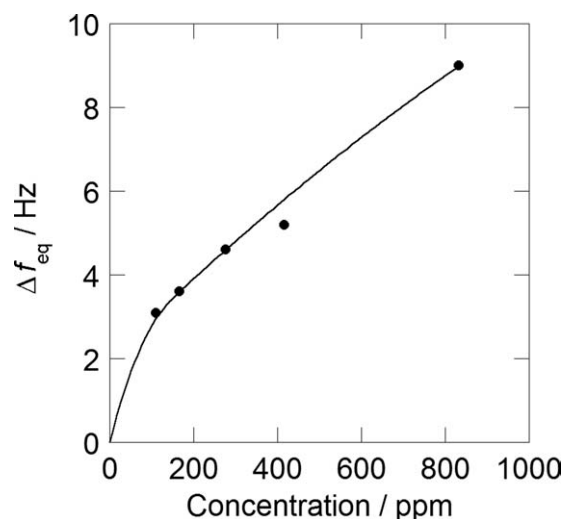
These results suggest that the CB/MCD sensor is suitable for detecting low concentrations of toluene vapor.

#### Toluene Vapor-Sorption Properties

It is known that the electrical response of composites to organic vapor is correlated to their sorption behaviors, and their sorption capacity is mainly governed by the matrix.<sup>12</sup> Toluene vapor-sorption properties of the CB/MCD composites were measured using the QCM technique. As reported previously, the presence of toluene vapor induced a rapid, large, and reversible shift in the frequency [ $\Delta f(f(N_2) - f(\text{toluene}))$ ] of the CB/MCD-coated crystal.<sup>25</sup> Figure 6 shows the toluene vapor-concentration dependence of the sorption capacity of the CB/MCD composite at low concentrations. The equilibrated frequency shift,  $\Delta f_{\text{eq}}$ , after exposure to toluene vapor is plotted on the ordinate. This  $\Delta f_{\text{eq}}$  value is directly related to the toluene vapor sorption capacity of the coating film, as mentioned in the Experimental



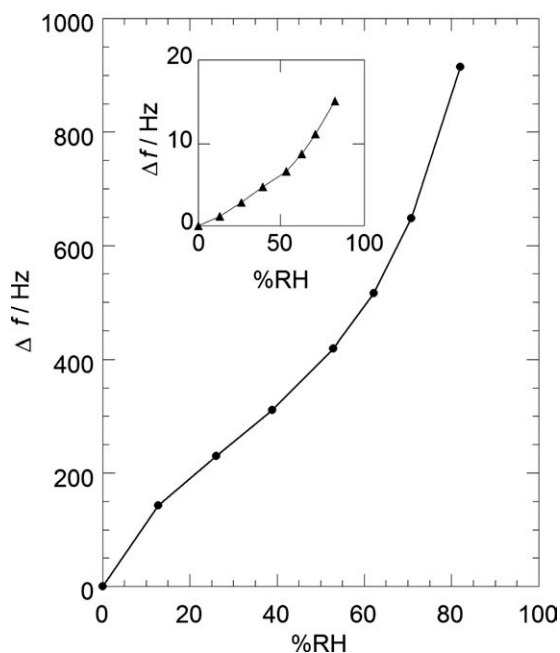
**Figure 5.** Dependence of the sensor response,  $S$ , of the CB/MCD sensor on the toluene vapor concentration measured at 30°C.



**Figure 6.** The toluene vapor-sorption isotherm of the CB/MCD composite film measured at 30°C.

section. The sorption capacity increased with an increase in concentration, and the curve is concave toward the abscissa. It should be noted that the curve of the sensor response shown in Figure 5 is very similar to that of the sorption capacity in Figure 6. This similarity indicates that the vapor sorption of the composites is responsible for the increase in the electrical resistance of the composites.

The sorption isotherm of the CB composites could be attributed to the physical state of the matrix polymers. In the case of rubbery polymers such as PBMA, PEO, and PIB, organic solvent vapors can be absorbed by a dissolution process. The observed isotherm in such cases is explained by the Flory-Huggins-type sorption mechanism. The sorption increases linearly and gently at lower vapor concentrations according to Henry's law, and the isotherm curves upward rapidly in the higher concentration ranges.<sup>34</sup> On the other hand, MCD is in a glassy state ( $T_g = \sim 90^\circ\text{C}$ ) at the measuring temperature, as reported previously.<sup>25</sup> The sorption behavior of gases in glassy polymers has been successfully described by the dual-mode sorption model.<sup>35,36</sup> The dual-mode sorption model is based on the principle of two sites: (1) a site for dissolution according to Henry's law and (2) a site for adsorbed molecules in the frozen microvoids of the glassy polymer according to Langmuir's law. In the low-vapor-pressure region, the Langmuir-type adsorption becomes dominant.<sup>37</sup> According to this model, the observed isotherm is concave in relation to the concentration axis at low concentrations and becomes straight in the higher concentration range, which is similar to the isotherm obtained for the present CB/MCD composite. However, the fact that the matrix polymer is in a glassy state is not the only requirement for a large vapor-sorption capacity at low concentrations. In fact, the sorption capacities of PSt, PMMA, and their copolymers with CMSt were not as large as that of MCD.<sup>24</sup> The important fact is that the introduction of DMPDA into the copolymer precursor yielded a large sorption capacity and improved the sorption/desorption kinetics.<sup>24</sup> This result suggested that the introduced DMPDA played an important role



**Figure 7.** The water sorption isotherm of the MCD film at 30°C. The inset shows the result for PIB film.

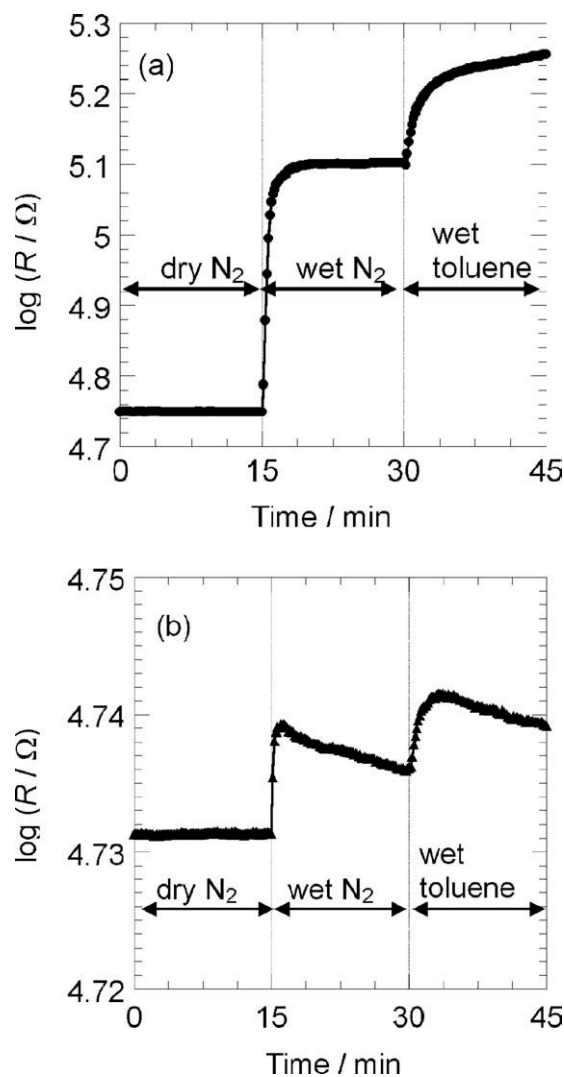
in the toluene vapor-sorption behavior of the MCD. The excellent sorption behavior of the MCD film was explained by the combination of two factors: (1) the introduction of bulky DMPDA plasticizes the copolymer and increases the chain mobility at lower CMSt composition, and (2) the formation of a loosely crosslinked structure at higher CMSt composition produces additional microvoids.<sup>25</sup>

### Sensing Mechanism

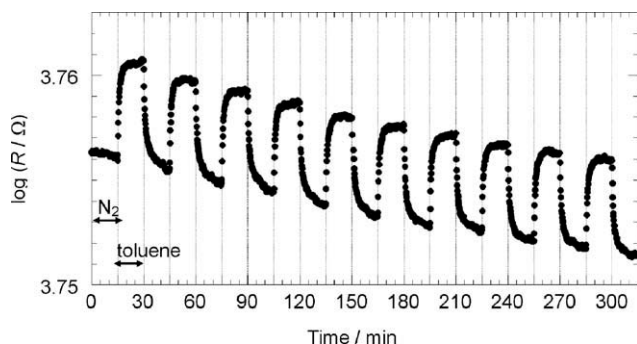
As explained in the Introduction, the sensing mechanism of this type of sensor has been explained by the breakdown of the conducting network in the composites driven by the swelling of the matrix polymer during the sorption of the toluene vapor. In such a case, sorption-induced polymer swelling should be considered as the key quantity determining sensitivity. However, in general, hardly any swelling of the matrix polymer is expected due to the small mass uptake in the low-vapor-concentration range. Therefore, the sensitivity of many CB composite sensors is low at low vapor concentrations. On the other hand, MCD is a glassy and loosely crosslinked polymer, and enhanced Langmuir-type adsorption occurs in the frozen microvoids at low concentrations, as mentioned earlier. In this case, a different sensing mechanism should be considered. Kirchheim reported that the microvoids in the structure of a glassy polymer are so large that the adsorption of gaseous molecules does not change the overall volume of the polymer,<sup>37</sup> which would mean that hardly any swelling of the CB/MCD film occurred, regardless of its larger sorption capacity. Based on these facts, it can be deduced that the sensing mechanism of the CB/MCD sensor is not the swelling of the matrix polymer, but the breakdown of the conductive path resulting from the dissolving of the insulating toluene vapor into the microvoids.

### Sensor Response in a Wet Atmosphere

Generally speaking, the humidity surrounding a gas sensor usually influences its sensing properties. Thus, humidity is a parameter that must always be dealt with in the process of developing a reliable gas sensor device. When utilizing composite films as sensor coatings as in this study, the water-sorption properties of the matrix polymer may affect the toluene vapor-sensing characteristics. Therefore, the water sorption ability of the MCD film without CB was measured by the QCM technique. Figure 7 shows the water sorption isotherm obtained for an MCD film, and for purposes of comparison, a PIB film of similar thickness. For the MCD film, the  $\Delta f$  values induced by the water sorption capacity are very large at all relative humidities from 0% to 80% RH. From this result, it is clear that MCD has a highly hydrophilic nature, as expected from its chemical structure. On the other hand, PIB film has a considerably less hydrophilic nature. Based on these results, we expected



**Figure 8.** Response of the (a) CB/MCD sensor and (b) CB/PIB sensor when successively exposed to a humid atmosphere at 41% RH in the absence of toluene vapor at 30°C and then to a humid atmosphere at 41% RH in the presence of 200 ppm toluene vapor at 30°C.



**Figure 9.** Response of the CB/MCD sensor to repeated cycling between 200 ppm of toluene vapor and  $N_2$  at 30°C.

that this difference in the water-sorption ability of the matrix polymer would affect the toluene vapor-sensing response in a humid atmosphere.

The effect of humidity on the sensor response to toluene vapor of the CB composite films was investigated. The results are shown in Figure 8. First, humidity-controlled  $N_2$  gas at 41% RH without toluene vapor was passed into the chamber for 15 min, followed by the introduction of 200 ppm of toluene vapor for 15 min at a constant humidity of 41% RH, and the time-dependent current was recorded for both CB/MCD and CB/PIB sensors. Figure 8(a) shows the response of the CB/MCD sensor. One can observe a remarkable increase of resistance by exposure of the sensor to humidity at 41% RH; the estimated  $S$  value according to eq. (1) under these conditions was  $\sim 1.26$ . This large sensor response can be attributed to the highly hydrophilic nature of the MCD film. Furthermore, a large increase of resistance induced by the subsequent introduction of the toluene vapor was also observed, and the  $S$  value corresponding to this resistance change was  $\sim 0.42$ . In the absence of humidity, the sensor response to 200 ppm of toluene vapor was  $\sim 0.04$  (Figure 5). This result means that coexisting water vapor produced a 10-times larger sensor response. On the other hand, the less hydrophilic nature of PIB resulted in small  $S$  values in a humid atmosphere, both in the absence ( $S = 0.018$ ) and presence of 200-ppm toluene vapor ( $S = 0.007$ ), as shown in Figure 8(b). However, the response to 200 ppm of toluene vapor of the CB/PIB sensor was very small ( $S = 0.002$ ) in a dry atmosphere,<sup>38</sup> indicating that coexisting water vapor produced a 3.5-times larger sensor response irrespective of the use of a less hydrophilic matrix polymer. Furthermore, in the case of the CB/PIB sensor, the resistance of the sensor gradually decreases after exposure to a humid atmosphere, possibly as a result of the promotion of the segment motion due to the swelling and a resulting gradual change in the distribution of CB particles. This phenomenon may also have arisen from the rubbery nature of the PIB film. For the sensor using the glassy and loosely crosslinked MCD, such drift of resistance was hardly observed. These results indicate that the CB/MCD sensor is operable even in a humid atmosphere in combination with either a humidity sensor for corrections or a drying system.

### Reproducibility of Sensors

The CB/MCD sensor was exposed repeatedly to toluene vapor. In each cycle, the sensor was exposed for 15 min to 200 ppm dry toluene vapor and then exposed to dry  $N_2$  for 15 min. Ten

sequential cycles were performed for each sensor. As shown in Figure 9, a fast response and recovery was observed at room temperature. Furthermore, in consecutive sorbing/desorbing cycles, the resistance changes were remarkably reproducible, though the problem of a sloping baseline was observed. The baseline drift could have come from the gradual agglomeration of the CB caused by the repeated sorption and desorption of toluene vapor. Lei et al. reported that a negative deviation in resistance is generated when CB is clustered directly above the electrodes.<sup>10</sup>

### CONCLUSIONS

It is well known that the essential problem with CB/polymer sensors is their low sensitivity. One of the keys to enhancing sensitivity is the selection of a matrix polymer that sorbs large amounts of toluene vapor at low concentrations. In this study, MMA-co-CMSt copolymers modified with MCD were blended with CB.

The CB/MCD sensor showed greater sensitivity to low concentrations of toluene vapors than other sensors reported so far. The difference in sensor response was attributed to the difference in the physical state of the matrix polymers. Because the MCD is glassy and loosely crosslinked by DMPDA, many frozen microvoids are likely to exist in the structure. In a film of this type, toluene vapor is sorbed according to a dual-mode sorption model; at low concentrations, a larger amount of Langmuir-type adsorption occurs in the frozen microvoids. Consequently, the sensing mechanism of this CB/MCD sensor seems to be not the swelling of the matrix polymer but the breakdown of the conductive path resulting from the dissolving of the insulating toluene vapor into the frozen microvoids. Thus, MCD appears to be a good candidate as a matrix for sensors of low-concentration toluene vapor.

The CB/MCD sensor does have an issue in that the sensor response is affected by the humidity in the measuring atmosphere due to the hydrophilic nature of the MCD film. However, the behaviors before and after exposure to the humid atmosphere were the same. Consequently, this problem may be solved by combining the sensor with a humidity sensor for corrections or a drying system.

In consecutive sorbing/desorbing cycles, the resistance changes of the CB/MCD sensor were remarkably reproducible. Finding a solution to the observed drift problem will be the subject of future work.

Considering the fact that most of the CB/polymer composites used as vapor-sensing materials are based on rubbery polymer matrices and have low sensitivities, our selection of a glassy and loosely crosslinked rigid polymer introduces a feasible alternative in the development of high-sensitivity volatile organic compound gas sensors.

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### REFERENCES

- Lonergan, M. C.; Severin, E. J.; Doleman, B. J.; Beaver, S. A.; Grubbs, R. H.; Lewis N. S. *Chem. Mater.* **1996**, *8*, 2298.

2. Doleman, B. J.; Lonergan, M. C.; Severin, E. J.; Vaid, T. P.; Lweis, N. S. *Anal. Chem.* **1998**, *70*, 4177.
3. Kim, Y. S.; Ha, S.-C.; Yang, Y.; Kim, Y. J.; Cho, S. M.; Yang, H.; Kim, Y. T. *Sens. Actuators B* **2005**, *108*, 285.
4. Srivastava, A. K. *Sens. Actuators B* **2003**, *96*, 24.
5. Li, J. R.; Xu, J. R.; Zhang, M. Q.; Rong, M. Z. *Carbon* **2003**, *41*, 2353.
6. Feller, J. F.; Grohens, Y. *Synth. Met.* **2005**, *154*, 193.
7. Convington, J. A.; Gardner, J. W.; Briand, D.; de Rooij, N. F. *Sens. Actuators B* **2001**, *77*, 155.
8. Feller, J. F.; Langevin, D.; Marais, S. *Synth. Met.* **2004**, *144*, 81.
9. Feller, J. F.; Grohens, Y. *Sens. Actuators B* **2004**, *97*, 231.
10. Lei, H.; Pitt, W. G.; McGrath, L. K.; Ho, C. K. *Sens. Actuators B* **2007**, *125*, 396.
11. Xie, H.; Yang, Q.; Sun, X.; Yang, J.; Huang, Y. *Sens. Actuators B* **2006**, *113*, 887.
12. Dong, X. M.; Fu, R. W.; Zhang, M. Q.; Zhang, B.; Rong, M. Z. *Carbon* **2004**, *42*, 2551.
13. Williams, R. D.; Upadhyayula, A. K.; Bhethanabotla, V. R. *Sens. Actuators B* **2007**, *122*, 635.
14. Park, J.; Groves, W. A.; Zellers, E. T. *Anal. Chem.* **1999**, *71*, 3877.
15. Grate, J. W.; Kaganove, S. N.; Bhethanabotla, V. R. *Anal. Chem.* **1998**, *70*, 199.
16. Abbas, M. N.; Moustafa, G. A.; Mitrovics, J.; Gopel, W. *Anal. Chim. Acta* **1999**, *393*, 67.
17. Mirmohseni, A.; Hassanzadeh, V. *J. Appl. Polym. Sci.* **2001**, *79*, 1062.
18. Mirmohseni, A.; Abdollahi, H.; Rostamizadeh, K. *Sens. Actuators B* **2007**, *121*, 365.
19. Ichinose, S.; Tanaka, H.; Kanno, Y. *Sens. Actuators B* **2007**, *123*, 306.
20. Fung, Y. S.; Wong, Y. Y. *Anal. Sci.* **1997**, *13*, 421.
21. Nanto, H.; Yokoi, Y.; Mukai, T.; Fujioka, J.; Kusano, E.; Kinbara, A.; Douguchi, Y. *Mater. Sci. Eng. C* **2000**, *12*, 43.
22. Sugimoto, I.; Nakamura, M.; Kasai, N.; Katoh, T. *Polymer* **2000**, *41*, 511.
23. Sugimoto, I.; Nagaoka, T.; Seyama, M.; Nakamura, M.; Takahashi, K. *Sens. Actuators B* **2007**, *124*, 53.
24. Matsuguchi, M.; Uno, T.; Aoki, T.; Yoshida, M. *Sens. Actuators B* **2008**, *131*, 652.
25. Matsuguchi, M.; Kagemoto, K. *J. Appl. Polym. Sci.* **2009**, *111*, 1086.
26. Matsuguchi, M.; Kadowaki, Y.; Noda, K.; Naganawa, R. *Sens. Actuators B* **2007**, *120*, 462.
27. Diaf, A.; Garcia, J. L.; Beckman, E. J. *J. Appl. Polym. Sci.* **1994**, *53*, 857.
28. Diaf, A.; Enick, R. M.; Beckman, E. J. *J. Appl. Polym. Sci.* **1993**, *50*, 835.
29. Sauerbrey, G. *Z. Phys.* **1959**, *27*, 206.
30. Tillman, E. S.; Lewis, N. S. *Sens. Actuators B* **2003**, *96*, 329.
31. Lucklum, R.; Behling, C.; Hauptmann, P. *Sens. Actuators B* **2000**, *65*, 277.
32. Mecea, V. M.; Carlsson, J. O.; Bucur, R. V. *Sens. Actuators B* **1996**, *53*, 371.
33. Dong, X. M.; Fu, R. W.; Zhang, M. Q.; Zhang, B.; Li, J. R.; Rong, M. Z. *Polym. Bull.* **2003**, *50*, 99.
34. Brown, G. L. In *Water in Polymers*; Rowland, S. P., Ed.; American Chemical Society: Washington, DC, **1980**; Chapter 26.
35. Barrer, R. M.; Barrie, J. A.; Slater, J. J. *Polym. Sci.* **1958**, *27*, 177.
36. Meares, P. *Trans. Faraday Soc.* **1958**, *54*, 40.
37. Kirchheim, R. *Macromolecules* **1992**, *25*, 6952.
38. Matsuguchi, M. *Sens. Lett.* **2011**, *9*, 894.