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Temperature-switchable vapor sensor materials based on *N*-isopropylacrylamide and calcium chloride

Jinhua Chen[a], Masaru Yoshida[b,*], Yasunari Maekawa[b], Norio Tsubokawa[a]

[a]*Graduate School of Science and Technology, Niigata University, 8050 Igarashi 2-nocho, Niigata 950-2182, Japan*
[b]*Department of Material Development, Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, 1233 Watanuki-machi, Takasaki, Gunma 370-1292, Japan*

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Abstract

A novel temperature-switchable vapor sensor was prepared by radiation-induced polymerization of *N*-isopropylacrylamide (NIPAAm) in an alcohol solution of calcium chloride ($CaCl_2$). The conductivity of the sensor material largely increased in water and ethanol vapors, but decreased against acetone, tetrahydrofuran, and chloroform vapors. The data showed a high level of reproducibility. In addition, the conductivity increased with the rise of temperature in ethanol vapor, showing a slight hysteresis, while against water vapor it exhibited a tendency to decrease with temperature accompanied by a large hysteresis. On the other hand, a densimeter to determine the water concentration in acetone solution was designed based on the opposite response of polyelectrolyte to two vapors, acetone and water, resulting in a linear responsiveness at low water concentration. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(*N*-isopropylacrylamide); Calcium chloride; Polyelectrolyte

1. Introduction

There is a strong need for reliable and accurate vapor sensors which are able to respond to the surrounding environment rapidly and repeatedly at atmospheric temperatures and pressures. Unlike inorganic oxide-based vapor sensors [1,2], polymer-based vapor sensor materials have demonstrated a number of attractive characteristics including reversible operation at ambient temperatures and high sensitivity to a wide range of solvent vapors [3–18]. In general, polymer-based vapor sensor materials' electric properties such as resistance, conductivity, and capacitance could be used to signal the response to vapor. Conductive polymers such as polypyrrole [5,6] and polyaniline [8], and conductive particle filled polymers [9–13] have been intensively studied as vapor sensor materials.

In recent years, several studies have been performed regarding humidity sensor material from polyelectrolyte [14–17], while little attention has been paid to the effect of organic solvent vapor on the electrical properties of polyelectrolyte [18]. Nevertheless, it has been found that the electrical properties of polyelectrolytes, like conducting polymers, can respond to organic solvent vapors [18]. Therefore, polyelectrolytes can be used in sensors capable of detecting the leakage of organic solvents analogously with the humidity in an atmosphere.

In this paper, we report the synthesis and vapor-responsive characteristics of temperature-switchable polyelectrolyte materials consisting mainly of linear poly(*N*-isopropylacrylamide) (PNIPAAm) and calcium chloride ($CaCl_2$). It is well-known that the linear polymer of NIPAAm shows a lower critical solution temperature (LCST) of 32°C in aqueous solution. Above 32°C, this polymer is hydrophobic and separates from the solution, but completely dissolves below 32°C because of its hydrophilic property [19–21]. The aim of the present work is to demonstrate the capability of the PNIPAAm/$CaCl_2$ polyelectrolyte as one of the promising candidates for application in vapor sensor materials for the recognition of certain vapors under atmospheric conditions such as water, ethanol, tetrahydrofuran (THF) and chloroform, and to quantify the composition of mixed solvents such as that of water in acetone, in terms of its signal in response to vapor.

2. Experimental

2.1. Materials

NIPAAm purchased from Aldrich Chemical Company,

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* Corresponding author. Tel.: +81-27-346-9413; fax: +81-27-346-9687.
E-mail address: katsu@taka.jaeri.go.jp (M. Yoshida).

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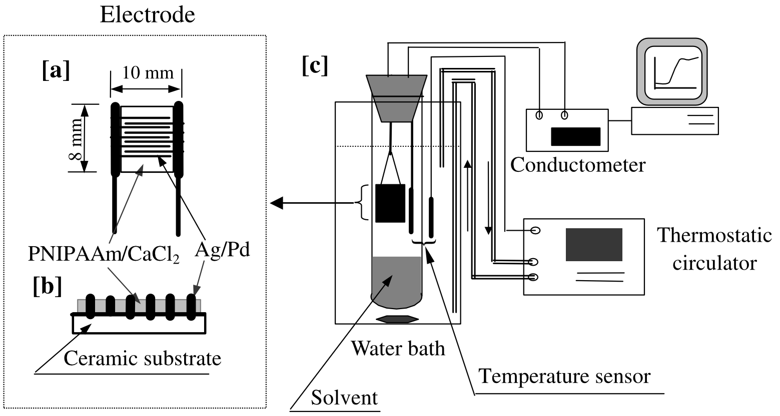

Fig. 1. Schematic representation of (a) comb-like electrode, (b) cross-section of (a), and (c) apparatus for the measurement of conductivity.

Inc. (USA) was recrystallized from *n*-hexane before use. Calcium chloride ($CaCl_2$) obtained from Wako Pure Chemicals Industries Ltd. (Japan) was used without further purification. Other chemicals were of reagent grade.

2.2. Coating of the PNIPAAm/CaCl$_2$ polyelectrolyte onto electrode

The front view and cross section of the comb-like electrode used in this study is shown in Fig. 1(a) and (b), respectively. This electrode was prepared by the screen-printing of conductive Ag/Pd paste onto a ceramic plate. The size of the ceramic plate is 10 × 8 × 0.8 mm. The printed ceramic plate was then annealed in an oven at 840°C for 6 h in order to remove organic components from the Ag/Pd paste. The Ag/Pd comb-like electrodes having four and five teeth, which were soldered with copper wire, were mingled with each other.

On the other hand, the PNIPAAm/$CaCl_2$ polyelectrolyte was prepared by means of radiation-induced polymerization [19,20]. For this purpose, in a 10 ml glass tube, 1.0 g of recrystallized NIPAAm was dissolved in 5.0 ml of 4.0 wt% ethanol solution of $CaCl_2$. Before polymerization, nitrogen vapor was bubbled into the mixed solution to drive out oxygen in both the solution and the tube. This tube was closed with a rubber stopper and then irradiated for 3 h at a dose rate of 10 kGy/h and 0°C (ice water temperature), using γ-rays from a ^{60}Co source. A highly viscous solution consisting of linear PNIPAAm, $CaCl_2$, and ethanol was obtained after γ-irradiation.

The polyelectrolyte specimen was coated by dipping the comb-like electrode in the PNIPAAm/$CaCl_2$ solution, then dried in air at room temperature for 2 h, and re-dried in a vacuum at room temperature for 24 h. The polyelectrolyte material coated on the electrode has an area of 4 × 7 mm. From the difference in weight of the electrode before and after material coating, the thickness of coated material was estimated to be approximately 12 μm.

2.3. Measurement of conductivity

The conductivity of the PNIPAAm/$CaCl_2$ polyelectrolyte in vapor of organic solvent was measured by hanging the electrode in a glass tube containing certain solvent at the bottom, as shown in Fig. 1 (c). The distance between the electrode and solvent surface was 2.0 cm. The alternating current conductivity of the polyelectrolyte material was measured at 1.0 V as a function of time. The electrode and temperature sensors were directly connected to a Metrohm 712 conductometer (Switzerland) via a ribbon cable. Both conductivity and temperature were read simultaneously by a personal computer. The glass tube was thermostated at 25°C. On the other hand, the temperature dependence of conductivity was measured using a computer program to control temperature change at 0.5°C/h. The initial conductivity of the polyelectrolyte is in the range of 0.04–0.08 μs/cm in dry air and at room temperature.

2.4. Responsiveness

In order to evaluate the responsiveness of the PNIPAAm/$CaCl_2$ polyelectrolyte, the change of its conductivity was determined as a function of time after the electrode was transferred from dry air to solvent vapor. The responsiveness was estimated using the following equation,

$$\text{Responsiveness} = \log\left(\frac{\sigma}{\sigma_0}\right)$$

where σ is the steady-state conductivity in solvent vapor and σ_0 is the conductivity just before the electrode is transferred to solvent vapor from dry air, as shown in Fig. 2.

3. Results and discussion

3.1. Response of the PNIPAAm/CaCl$_2$ polyelectrolyte in several solvent vapors

The conductivity response of the PNIPAAm/$CaCl_2$

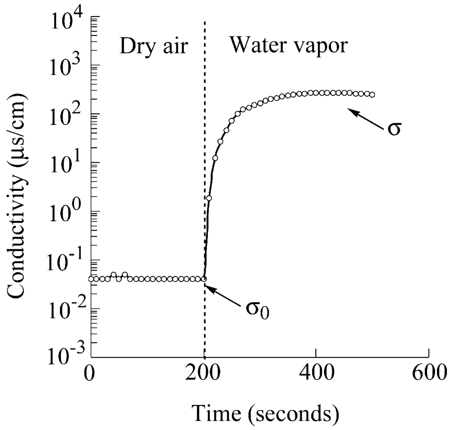

Fig. 2. A characteristic responsive profile of conductivity of the PNIPAAm/ $CaCl_2$ polyelectrolyte. The conductivity was recorded in dry air for a period of the first 200 s and then in a saturate vapor of water at 25°C until the steady-state is reached.

polyelectrolyte was measured in dry air, followed by a measurement in the saturated vapor of solvents such as water, THF, ethanol, acetone, and chloroform at 25°C. This cycle was repeated three times, and the results are shown in Fig. 3. The conductivity (σ) of the polyelectrolyte against water and ethanol vapor increased to 10 times the initial conductivity (σ_0), showing a positive responsiveness. Particularly, in the case of water vapor at the first cycle, the conductivity drastically increased to 10,000 times the initial conductivity. However, when the electrode was re-transferred to dry air from water vapor, its conductivity was returned, only partially, to the initial value. Even so, the responsiveness of the PNIPAAm/$CaCl_2$ polyelectrolyte against water vapor at the 2nd cycle exhibited an excellent reproducibility. In THF, acetone and chloroform vapors, the conductivity decreased, resulting in a negative responsiveness, which was also accurately reproducible and stable.

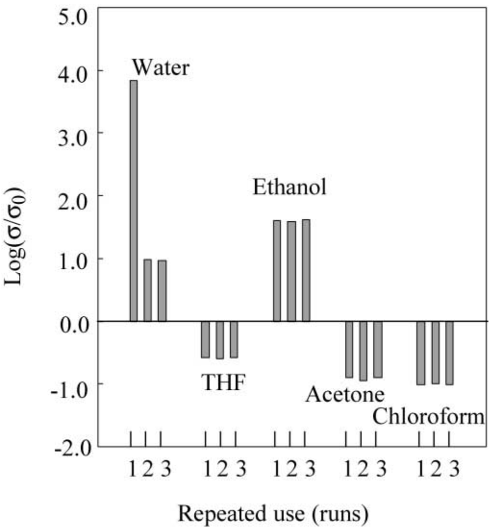

Fig. 3. Responsiveness of the PNIPAAm/$CaCl_2$ polyelectrolyte against several solvent vapors determined over three cycles between the dry air and solvent vapor.

In the present investigation, the effect of absorbed vapor on electrical conduction can be explained as follows. The absorbed water and ethanol can facilitate the dissociation of $CaCl_2$ due to high dielectric constant of water and ethanol. The effect of absorbed water and ethanol on the migration of ionic carriers was also significant. Therefore, the conductivity of the PNIPAAm/$CaCl_2$ polyelectrolyte increased in water and ethanol vapors. In addition, in water vapor, the partially absorbed water can form hydrogen bond with PNIPAAm. So, at the first cycle, the conductivity didn't return to the initial value when the electrode was transferred to dry air from water vapor. Unlike in water vapor, the response performed over three cycles against ethanol, THF, acetone and chloroform vapors exhibited excellent reproducibility, because the absorbed vapor was easily desorbed. Organic solvent vapors such as THF, acetone and chloroform vapors, absorbed in the swollen polymer may cause the decrease of the dissociation of $CaCl_2$ in the polyelectrolyte, resulting in a decrease of its conductivity.

3.2. *Effect of temperature on the conductivity of the PNIPAAm/$CaCl_2$ polyelectrolyte exposed to water and ethanol vapors*

As shown in Fig. 4, the effect of temperature on the conductivity of the PNIPAAm/$CaCl_2$ polyelectrolyte against water and ethanol vapors was investigated over three cycles between 15 and 45°C. It was interesting that the temperature dependence of the conductivity in the two vapors was completely opposite. Against vapor of ethanol, as expected, the conductivity at 45°C was higher than that at 15°C, due to the heat effect on the ionization of $CaCl_2$, the migration of ions and the movement of polymer segment. However, in water vapor, the conductivity at 45°C was lower than that at 15°C. This difference can be explained by the nature of PNIPAAm. That is, PNIPAAm, known as a

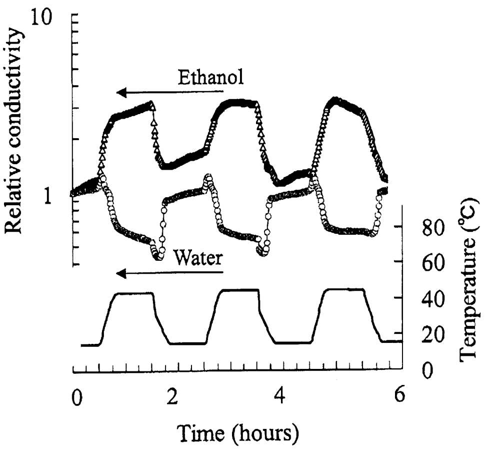

Fig. 4. Changes in relative conductivity of the PNIPAAm/$CaCl_2$ polyelectrolyte against water and ethanol vapor determined over three cycles between 15 and 45°C.

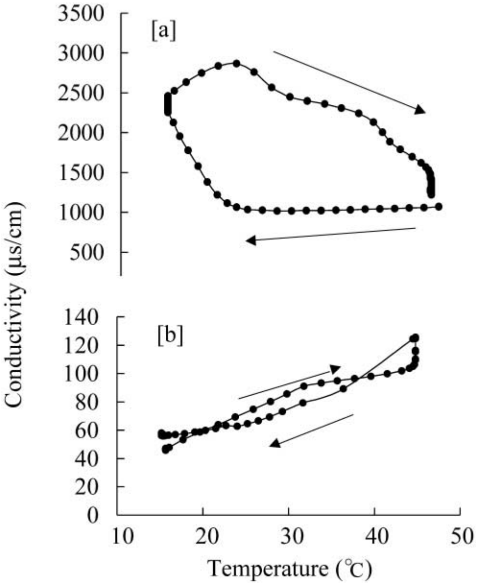

Fig. 5. Hysteresis of conductivity of the PNIPAAm/CaCl$_2$ polyelectrolyte against (a) water and (b) ethanol vapor determined by a heating process from 15 to 45°C, followed by a cooling process from 45 to 15°C.

temperature-sensitive polymer, has a LCST of 32°C in water [19–21]. Therefore, water absorbed in PNIPAAm/CaCl$_2$ polyelectrolyte can be regarded as a concentration solution. At temperatures below 32°C, this polymer was hydrophilic, so water was homogeneously distributed in the polymer. Contrary to this, at 45°C (above LCST), water was not easily absorbed in the polymer because of the hydrophobic effect. Such a hydrophobic effect should inhibit the migration of ions in the shrunken polymer chains, indicating the decrease in conductivity at 45°C.

In addition, as shown in Fig. 5, the temperature hysteresis of the conductivity of the PNIPAAm/CaCl$_2$ polyelectrolyte was determined in water and ethanol vapors by a heating–cooling cycle between 15 and 45°C. The conductivity of the electrode against ethanol vapor gradually increased with the increase in temperature as shown in Fig. 5(b), but in water vapor it showed a tendency to decrease with the rise of temperatures, as seen in Fig. 5(a). On the other hand, based on the results of the heating–cooling cycle experiments, it was found that no conductivity showed a typical hysteresis in ethanol vapor, in contrast to a large hysteresis in the case of water vapor. Against water vapor, during heating, water was released from the polymer because of the collapse of the sample, which strongly affected the structure of the polyelectrolyte, resulting in the change of conductivity. Conversely, during cooling, water was absorbed into the polymer owing to the swelling effect. In this case, in the initial cooling stage (in the range of 45–25°C) the amount of absorbed water was slight, as the conductivity was almost unchanged. By further cooling (in the range of 25–15°C), water was absorbed more quickly, and the resulted conductivity was rapidly increased. It is reasonable to conclude that the hysteresis is caused by the time-dependent change of the absorption–desorption of water for the temperature-switchable PNIPAAm.

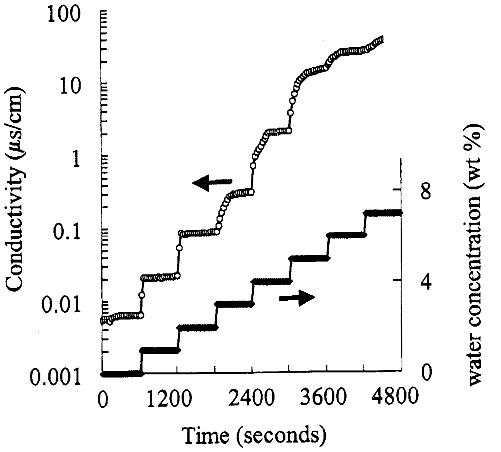

Fig. 6. Steady-state conductivity response of the PNIPAAm/CaCl$_2$ polyelectrolyte against a vapor of water–acetone mixtures.

3.3. Application as a densimeter

The opposite response of the polyelectrolyte to water and acetone vapor shown in Fig. 3 may raise a question as to how the polyelectrolyte responds to a vapor of water–acetone mixture solvent. As shown in Fig. 6, the time-course of conductivity in the mixed water–acetone solution for the PNIPAAm/CaCl$_2$ polyelectrolyte was determined. The initial conductivity of the polyelectrolyte in dry air was 0.056 μs/cm. The response time, which was needed to reach the steady-state conductivity value, was within one minute in the water-containing solution where the water concentration was below 5.0 wt%. When the water concentration in the solution was more than 5.0 wt%, the response became slow, which was due to the effect of the hydrogen bond between water and the PNIPAAm polymer.

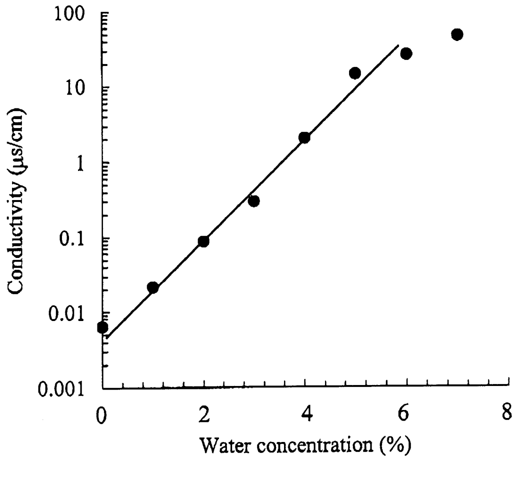

Fig. 7. Effect of water concentration in acetone solution on the conductivity of the PNIPAAm/CaCl$_2$ polyelectrolyte.

Fig. 7 depicts the calibration curve for the PNIPAAm/$CaCl_2$ polyelectrolyte constructed based on the steady-state conductivity at each water concentration as given in Fig. 6. It was obvious that the PNIPAAm/$CaCl_2$ polyelectrolyte expressed a linear steady-state conductivity up to 5.0 wt% water concentration. This is advantageous as simple computational methods, when the PNIPAAm/$CaCl_2$ polyelectrolyte is used as a densimeter in the acetone industry for the detection of dilute water in acetone.

4. Conclusion

In order to obtain the PNIPAAm/CaCl2 polyelectrolyte, linear PNIPAAm was successfully prepared by means of the radiation-induced polymerization of a monomer of NIPAAm in an ethanol solution containing $CaCl_2$. This polyelectrolyte was coated on a comb-like electrode, which was prepared by the screen-printing of conductive Ag/Pd paste onto a ceramic plate. When the electrode cell was treated in a vapor of water by a heating–cooling cycle between 15 and 45°C, the conductivity at 45°C showed a very low value compared with that at 15°C, in close relation to the nature of temperature-switchable PNIPAAm. This polyelectrolyte also shows a high degree of electric reproducibility and stability even in ethanol, THF and chloroform vapors. On the other hand, the response time of the PNIPAAm/$CaCl_2$ polyelectrolyte exhibited a rapid response against a mixed vapor consisting of water and acetone. Therefore, the PNIPAAm/$CaCl_2$ polyelectrolyte can be expected to be a promising temperature-switchable material in the construction of a vapor sensor and densimeter.

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