

# Cobalt-Containing Polyimides for Moisture Sensing and Absorption

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**ABSTRACT** A modified polyimide has been created that both senses and absorbs moisture. The material was prepared by introducing cobalt(II) chloride, a well-known moisture sensing and absorbing metal salt, into a polyimide. The final polymer was found to be fully cured, retaining the metal without any leeching, and was thermally stable. Furthermore, the material underwent a visible color change when exposed to moisture and reverted back to the original color when subsequently dried. The total moisture absorbed was measured with a quartz crystal microbalance. The amount of moisture absorption was found to be proportional to the relative humidity, and the modified polymer was found to have up to 3 times greater moisture absorption compared to the unmodified polymer.

**KEYWORDS:** polyimide • moisture • cobalt • quartz crystal microbalance

## INTRODUCTION

The ability of a polymer to maintain its integrity yet incorporate new and interesting chemical and physical properties when blended with other materials could find wide applications. Polymers have previously been modified by a variety of means to create moisture indicators or sensors (1–3). Polyimides are used in a variety of aerospace applications such as in multilayer thermal blankets or as electrical insulators. Polyimides have been modified and blended with a wide variety of other materials for other applications (4–6); however, they have not been used for moisture-related applications. Polyimides, like other polymers, are known to absorb a very small amount of moisture that is proportional to the humidity level (7, 8). The addition of a second moisture absorbing component would greatly increase the total amount of moisture absorbed by the polymer.

Cobalt(II) chloride can readily bind to water, even in low-humidity environments. It also undergoes a physical color change from blue to purple/pink upon binding to water, thus creating a moisture sensor/indicator. The water binding process is reversible when the hydrated material is heated or placed under vacuum. For practical applications, cobalt(II) chloride has previously been coated or embedded in desiccant materials to create a visible moisture sensor/indicator. Additionally, it has been embedded in other polymers and composites for moisture-sensing capabilities (9, 10). While cobalt(II) chloride has previously been incorporated in polyimides for other applications (11–13), those materials either went undiscovered for their moisture sensing capabilities or

had different physical properties because of the preparation method and thus did not allow for moisture sensing and absorption.

## EXPERIMENTAL SECTION

**Materials.** Starting materials were obtained from commercial suppliers and used without further purification. *N,N*-Dimethylacetamide (DMAc) was obtained from an Aldrich Sure/Seal bottle and handled under nitrogen.

**Unmodified Polyimide.** 4,4'-Oxydianiline (ODA; 0.901 g, 4.50 mmol) was dissolved in 22 mL of DMAc during stirring under nitrogen. Pyromellitic dianhydride (PMDA; 1.001 g, 4.59 mmol) was added, and the reaction was stirred for 5 h. The viscous solution was drop-casted onto poly(tetrafluoroethylene) blocks or glass slides and cured under nitrogen in an oven using the following cure schedule: 80 °C for 3 h, 150 °C for 1 h, and 300 °C for 2 h. The final material was a thin yellow film. IR (thin film):  $\nu$  1714, 1496, 1366, 1231, 1113, 1087, 880, 818, 721, 603, 566  $\text{cm}^{-1}$ .

**Cobalt-Modified Polyimide (PI-CoCl<sub>2</sub>).** The poly(amic acid) was prepared as above. Cobalt(II) chloride hexahydrate (0.162 g, 0.69 mmol) (15% by weight compared to polyimide) was added to the viscous solution and stirred for 1 h. The blue solution was drop-casted and then cured following the same cure schedule as above, yielding a thin green film. IR (thin film, dried under nitrogen):  $\nu$  3389 (br), 2922, 1713, 1496, 1367, 1227, 1165, 1113, 1088, 1013, 880, 818, 721, 603, 566  $\text{cm}^{-1}$ .

**Characterization.** Thermogravimetric analysis (TGA) was performed using a TA Instruments 2950 HR Thermogravimetric Analyzer under nitrogen. Fourier transform infrared (FT-IR) spectroscopy was obtained using a Nicolet Magna 550 FT-IR Spectrometer.

**Electronic Absorption.** Electronic absorption spectra were recorded using an Ocean Optics USB 2000 spectrometer with a LS-1 tungsten halogen light source. A test box was fabricated containing a humidity probe (Vaisala HMP50), a dry nitrogen/humid nitrogen inlet port, and an Ocean Optics sample holder. Humidity was generated using a water bubbler and nitrogen gas with mass flow controllers (MKS 1179). The thin films were placed in the sample holder and exposed to the desired humidity for 1–2 h before taking a measurement.

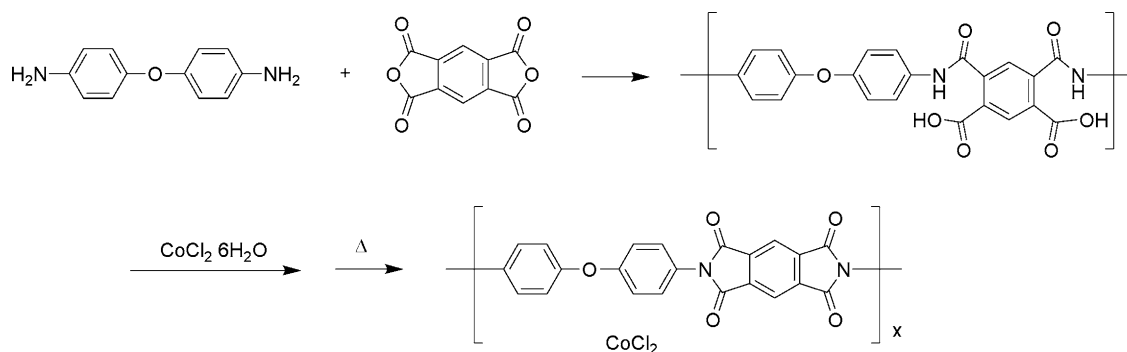
**Quartz Crystal Microbalance (QCM).** QCM samples were prepared by taking the poly(amic acid) solutions and spin-coating them at 3300–3600 rpm for 30 s onto polished 5 MHz

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Scheme 1. Synthesis of PI-CoCl<sub>2</sub>

gold crystals (Maxtek) or drop-casting them onto 6 MHz gold crystals (Sycon). The materials were cured directly onto the QCM crystals following the cure schedule above. QCM measurements were performed using a Maxtek PM-740 plating monitor recorded by Maxtek PC data logging software or with a Sycon STM-1 monitor controlled by a LabVIEW program.

## RESULTS AND DISCUSSION

**Preparation.** The unmodified polyimide was prepared following conventional methods of the mixing of dianiline with dianhydride in DMAc to form poly(amic acid). The material was cured at an elevated temperature to yield the unmodified polyimide as a thin orange/yellow solid. The percent imidization, i.e., how well the polymer is cured, was calculated from the FT-IR spectrum peaks at 1366–1367  $\text{cm}^{-1}$  (C–N stretching) and 1496  $\text{cm}^{-1}$  (C–C band of para-substituted benzene) (14) and compared to that of Kapton H. The value was determined to be 1.0 (100%).

PI-CoCl<sub>2</sub> began with the formation of poly(amic acid), followed by the addition of cobalt(II) chloride hexahydrate before curing (Scheme 1). Cobalt(II) chloride hexahydrate is a dark purple solid; however, when dissolved in DMAc, it formed a blue solution, likely because of extraction of the water molecules bound to the cobalt and weak coordination of the solvent molecules (15, 16). The blue poly(amic acid) solution was then cured in an oven under nitrogen. During curing, poly(amic acid) took on a turquoise color, followed by formation of PI-CoCl<sub>2</sub> as a green solid film at high temperatures. The percent imidization for the modified polyimide was calculated with respect to Kapton H and was also determined to be 1.0 (100%). Thus, the addition of cobalt(II) salt did not inhibit imidization and curing of the material. In addition to the spectral peaks attributed to polyimide, peaks at 2922 and 3389  $\text{cm}^{-1}$  were also observed and attributed to the peaks for cobalt(II) chloride. Interestingly, as the humidity increased, the broad peak at 3389  $\text{cm}^{-1}$  increased as well, thus revealing the coordination of water to cobalt(II) chloride (Figure S1 in the Supporting Information).

**TGA.** TGA was performed on the unmodified and modified polyimide (Figure S2 in the Supporting Information). PI-CoCl<sub>2</sub> had a slight decrease in the overall decomposition temperature of polyimide, but the film was still stable to high temperatures (>300 °C).

**Moisture Absorption and Indication.** As mentioned above, PI-CoCl<sub>2</sub> is a green film. As the film was

submerged in water, it slowly converted to a yellow color, resembling the unmodified polyimide (Figure 1). The color change occurred on the order of minutes to hours depending on the film thickness. As the sample was taken out of water and allowed to dry, it slowly converted back to the original green color. This process could be repeated multiple times. The water solution was evaporated and revealed that no noticeable amount of metal salt had leached out of the polymer while it was submerged. The degree of metal retention observed is advantageous over other types of cobalt-containing desiccants (such as drierite and silica gel) where the cobalt can leech after soaking the material in water. In addition, elevated temperatures or a vacuum was not required to subsequently dry out the material. Finally, it was also found that the material did not need to be submerged in water but could also be placed in a high relative humidity environment to induce a color change.

An electronic absorption spectrum of PI-CoCl<sub>2</sub> was recorded at various humidity levels (Figure 2). The strong transition at 426 nm, and the cutoff below 350 nm is attributed to polyimide. The green color of the dry film attributed to cobalt(II) chloride is correlated to the charge-transfer band observed at 550–700 nm. The charge-transfer band for crystalline cobalt(II) chloride is 670 nm. As the humidity was increased, the peak intensity decreased. This is correlated to the transition change of the weak coordination of the water molecules to the cobalt ion. The weak charge-transfer band of the unmodified octahedral cobalt(II) chloride hexahydrate is 500 nm. The extinction coefficient of cobalt chloride hexahydrate is much lower than the extinction coefficient of cobalt(II) chloride (15), and thus the charge-transfer band of the hydrated metal salt was not observed in the spectrum. The final color of the film after moisture absorption was dominated by the yellow color of polyimide alone.

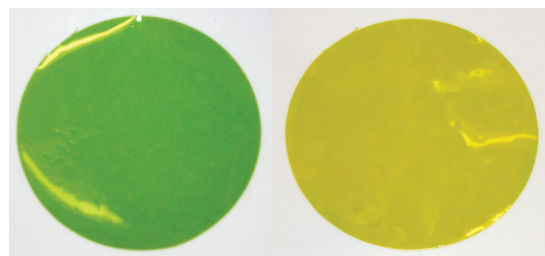


FIGURE 1. Image of the PI-CoCl<sub>2</sub> film before (left) and after (right) submersion in water.

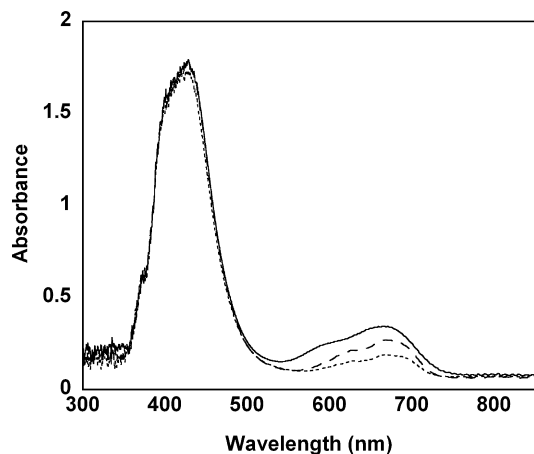


FIGURE 2. Electronic absorption spectra for PI-CoCl<sub>2</sub> at ~5% (—), 50% (---), and 100% (···) relative humidity.

**QCM.** QCMs have successfully been used to measure the amount of water absorption in many types of polymers (17–19) including polyimides (7). QCM crystals coated with polyimide or PI-CoCl<sub>2</sub> were exposed to various levels of humidity to determine the water absorption rate and value. The humidity was generated using a water bubbler and controlled by variation of the ratio of the bubbled nitrogen to dry nitrogen with mass flow controllers. The materials were exposed to a constant flow of either dry nitrogen or humid nitrogen in a closed cell. The frequencies of the wet and dry crystals were recorded, and the value was used to calculate a mass by means of equation (1) and the Sauerbrey equation 2 (20), where  $f_q$  is the frequency of the uncoated crystal,  $p_q$  is the density of the crystal, and  $v_q$  is the shear wave velocity (352 200 cm/s). The moisture uptake is determined from the calculated mass of the wet polyimide crystal and the calculated mass of the dry polyimide crystal.

$$\text{mass} = \frac{\text{frequency uncoated} - \text{frequency coated}}{C_f} \quad (1)$$

$$C_f = \frac{2f_q^2}{p_q v_q} \quad (2)$$

The absorption rate of water in polyimide films has been determined to be dependent upon the film thickness (8, 21).

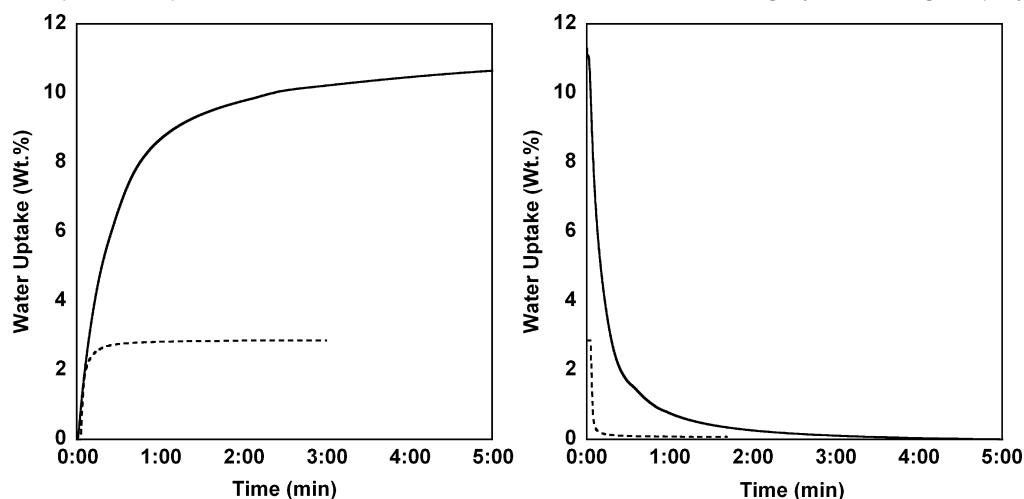


FIGURE 3. Water absorption in a ~80% relative humidity environment (left) and desorption in dry nitrogen (right) of polyimide (---) and PI-CoCl<sub>2</sub> (—).

In order to keep the film thickness constant throughout the QCM samples, poly(amic acid) solutions of similar densities were prepared and spin-coated on the crystals with the same volume of liquid at the same rotation speed and duration. This resulted in film thicknesses on the QCM crystals of approximately 8000 Å.

The QCM crystals were initially dried for an extended period of time before being exposed to the desired humidity level. While both polyimide and PI-CoCl<sub>2</sub> demonstrated an immediate uptake of water, PI-CoCl<sub>2</sub> provided a much higher total absorption (Figure 3). The majority of the moisture absorption occurred on the order of seconds followed by equilibrium a few minutes later. In a 95% relative humidity environment, the unmodified polyimide took 12 s to reach 90% absorption capacity, while PI-CoCl<sub>2</sub> took >5 min to reach the same absorption capacity. As the materials were exposed to dry nitrogen, the desorption rate was slightly faster compared to the absorption rate, but PI-CoCl<sub>2</sub> took significantly longer to dry compared to the unmodified polyimide. The unmodified polyimide took 4 s to desorb by 90% capacity, while PI-CoCl<sub>2</sub> took 1 min 30 s to desorb by the same capacity.

The QCM crystals were exposed to various humidity levels for an extended amount of time to measure the total moisture absorption at a given humidity (Figure 4). The unmodified polyimide had a total moisture uptake of 3.9% by weight at the highest measured relative humidity (95%). This is comparable to other reported moisture uptake values of 2–6% for the same PMDA–ODA polyimides (7). The nonlinearity of the moisture absorption plot for polyimides is comparable to that of other reported polymers (17–19, 22). The addition of 15% by weight cobalt salt more than tripled the total moisture absorption at high humidity with the total absorption of 12.8% by weight at 95% relative humidity. While we have only reported a 15% by weight cobalt-containing polyimide, other polyimides of varying concentrations were also prepared. All films exhibited an increase in moisture absorption. The 15% by weight addition produced a film that exhibited a significant increase yet still maintained the integrity of the original polyimide.

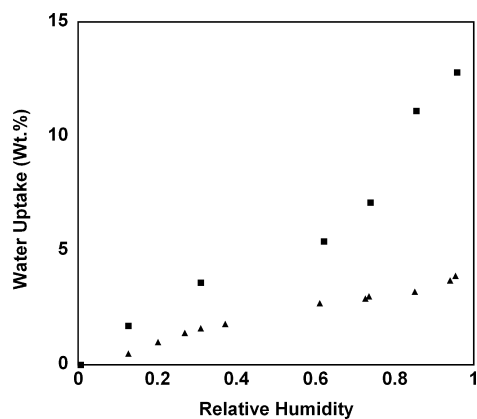


FIGURE 4. Total moisture absorption of polyimide ( $\blacktriangle$ ) and PI-CoCl<sub>2</sub> ( $\blacksquare$ ) in relation to the relative humidity.

The QCM crystals were initially cycled through at least 30 times at various humidity levels with no degradation (i.e., change in the initial mass or total mass after moisture absorption). In addition, crystals that were stored for over 1 year were analyzed again. One coated QCM crystal stored for over 1 year was cycled through over 200 times between dry nitrogen and an 80% relative humidity environment with no noticeable degradation or depreciation in performance. On the basis of these results, the materials are anticipated to be very useful for practical applications.

As mentioned above, there are literature reports with cobalt(II) chloride added to poly(amic acids) to produce cobalt–polyimide films. However, curing was performed in air, and subsequent studies had shown a significant amount of oxidized cobalt present in the film (11–13). Cobalt oxides would not exhibit the same type of moisture absorption and color change that cobalt(II) chloride does; thus, we believe that cobalt(II) chloride does not oxidize when prepared with the synthetic procedure described in this report, resulting in a unique material. Scanning electron microscopy/energy-dispersive X-ray experiments have shown the presence of chlorine in the PI-CoCl<sub>2</sub> film. Further studies will be performed to confirm the chemical composition, binding nature, and interaction of the metal salt in the polyimide film.

## CONCLUSION

The successful incorporation of cobalt(II) chloride in a polyimide was achieved by mixing the salt with poly(amic acid) and curing the film at an elevated temperature under nitrogen. The addition did not inhibit imidization or cause significant thermal degradation. The modified polyimide both absorbed and sensed moisture at elevated humidity. The material also desorbed moisture without the use of heat

or vacuum but by its simple placement in a lower humidity environment. Finally, the moisture absorption and desorption process could be repeated multiple times, thus exhibiting a robust reusable material.

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**Supporting Information Available:** FT-IR spectra and TGA of polyimide and PI-CoCl<sub>2</sub>. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## REFERENCES AND NOTES

- (1) Sakai, Y.; Sadaoka, Y.; Matsuguchi, M. *Sens. Actuators B* **1996**, *35*, 85–90.
- (2) Somani, P. R.; Viswanath, A. K.; Aiyer, R. C.; Radhakrishnan, S. *Org. Electron.* **2001**, *2*, 83–88.
- (3) Rubinger, C. P. L.; Martins, C. R.; De Paoli, M. A.; Rubinger, R. M. *Sens. Actuators B* **2007**, *123*, 42–49.
- (4) Akamatsu, K.; Ikeda, S.; Nawafune, H.; Yanagimoto, H. *J. Am. Chem. Soc.* **2004**, *126*, 10822–10823.
- (5) Wright, M. E.; Petteys, B. J.; Guenther, A. J.; Fallis, S.; Yandek, G. R.; Tomczak, S. J.; Minton, T. K.; Brunsvold, A. *Macromolecules* **2006**, *39*, 4710–4718.
- (6) Davis, L. M.; Abelt, C. J.; Scott, J. L.; Orlova, E.; Thompson, D. W. *ACS Appl. Mater. Interfaces* **2009**, *1*, 204–210.
- (7) Moylan, C. R.; Best, M. E.; Ree, M. J. *Polym. Sci., Part B: Polym. Phys.* **1991**, *29*, 87–92.
- (8) Tan, N. C. B.; Wu, W. L.; Wallace, W. E.; Davis, G. T. *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 155–162.
- (9) Manasis, G.; Tsigara, A.; Giannoudakos, A.; Anyfantis, G.; Gatsouli, K.; Mousdis, G.; Pispas, S.; Madamopoulos, N.; Vainos, N. *Glass Technol.* **2005**, *46*, 171–174.
- (10) Tsigara, A.; Mountrichas, G.; Gatsouli, K.; Nichelatti, A.; Pispas, S.; Madamopoulos, N.; Vainos, N. A.; Du, H. L.; Roubani-Kalantzopoulou, F. *Sens. Actuators B* **2007**, *120*, 481–486.
- (11) Khor, E.; Taylor, L. T. *Polym. Mater. Sci. Eng.* **1983**, *49*, 198–202.
- (12) Rancourt, J. D.; Taylor, L. T. *Polym. Mater. Sci. Eng.* **1986**, *55*, 328–333.
- (13) Rancourt, J. D.; Taylor, L. T. *Macromolecules* **1987**, *20*, 790–795.
- (14) Han, M. G.; Im, S. S. *J. Appl. Polym. Sci.* **1999**, *71*, 2169–2178.
- (15) Ishihara, I.; Hara, K.; Osugi, J. *Rev. Phys. Chem. Jpn.* **1974**, *44*, 11–24.
- (16) Suzuki, H.; Koide, M.; Ishiguro, S.-I. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3055–3060.
- (17) Czanderna, A. W.; Thomas, T. M. *J. Vac. Sci. Technol. A* **1987**, *5*, 2412–2416.
- (18) Ismail, I. M.; Gray, N. D.; Owen, J. R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4115–4119.
- (19) Berger, C. M.; Henderson, C. L. *Polymer* **2003**, *44*, 2101–2108.
- (20) Sauerbrey, G. *Z. Phys.* **1959**, *155*, 206–222.
- (21) Yang, D. K.; Koros, W. J.; Hopfenberg, H. B.; Stannett, V. T. *J. Appl. Polym. Sci.* **1985**, *30*, 1035–1047.
- (22) Hubbell, W. H., Jr.; Brandt, H.; Munir, Z. A. *J. Polym. Sci., Part B: Polym. Phys.* **1975**, *13*, 493–507.

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