

# Poly(2,3-dimethylaniline) as a Competent Material for Humidity Sensor

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**ABSTRACT:** Chemically synthesized polyaniline and its ring substituted derivatives such as poly(*o*-toluidine), poly(2,3-dimethylaniline) and poly(2,5-dimethylaniline) were utilized as sensors for relative humidity (RH) between 6.4% and 97.3%. The conductivity of the polymers was found to decrease on exposure to RH between 6.4% and 75.3%. However, in presence of 97.3% RH the conductivity was seen to increase. A comparison of the observed results reveals that, though each of the polymers responds to various percentages of RH, poly(2,3-dimethylaniline) shows the best response in terms of sensitivity and linear range. The percent sensitivity was found to be greater for poly(2,3-dimethylaniline) than that for polyaniline. The observed change in conductivity as well as the degree of change in magnitude of conductivity in the polymers was supported by X-ray diffraction studies and IR spectroscopy. The X-ray analysis showed that crystallinity of the polymer changed both in the presence and the absence of a specific percent of RH. Similarly, the IR spectra exhibited variation in the peak intensities of the O—H and >N—H groups. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1382–1387, 2001

**Key words:** conducting polyaniline; substituted derivatives; humidity sensor

## INTRODUCTION

There has recently been a considerable increase in the demand for humidity control in such varied fields as air-conditioning systems, electronic devices, tire manufacturing, and drying processes for ceramics and foods.<sup>1</sup> The conventional materials used for sensing humidity are electrolytic metal oxides and ceramics.<sup>2,3</sup> However, conducting polymers have been seen to be compatible to oxides and ceramics because of their low processibility cost and their ability to operate at room temperature. Some reports are available that account for the use of polyaniline as a humidity sensor.<sup>3–5</sup>

In the present work we investigated the applicability of selected methyl-substituted derivatives of polyaniline—*p*(*o*-tol) [poly(*o*-toluidine)], *p*(2,3-DMA) [poly(2,3-dimethylaniline)], and *p*(2,5-DMA) [poly(2,5-dimethylaniline)]—as a sensor for humidity and compared them to the use of polyaniline.

## EXPERIMENTAL

### MATERIALS AND METHODS

All chemicals used were analytical reagent (AR) grade. The monomers aniline, *o*-toluidine, 2,3-dimethylaniline, and 2,5-dimethylaniline were doubly distilled prior to use. Reagent-grade hydrochloric acid (Qualigens, India) and ammonium persulfate (Qualigens) were used as received. So-

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lutions were prepared using double-distilled water.

Polymerization was carried out by the dropwise addition of the oxidizing agent to the acidified solution containing the monomer, which was constantly stirred for 12 h while kept between 0–5°C.<sup>6</sup> After completion of the reaction, the product was isolated by filtration. A free-flowing powder of the polymer was obtained by washing the product several times using distilled water and drying it in the oven.

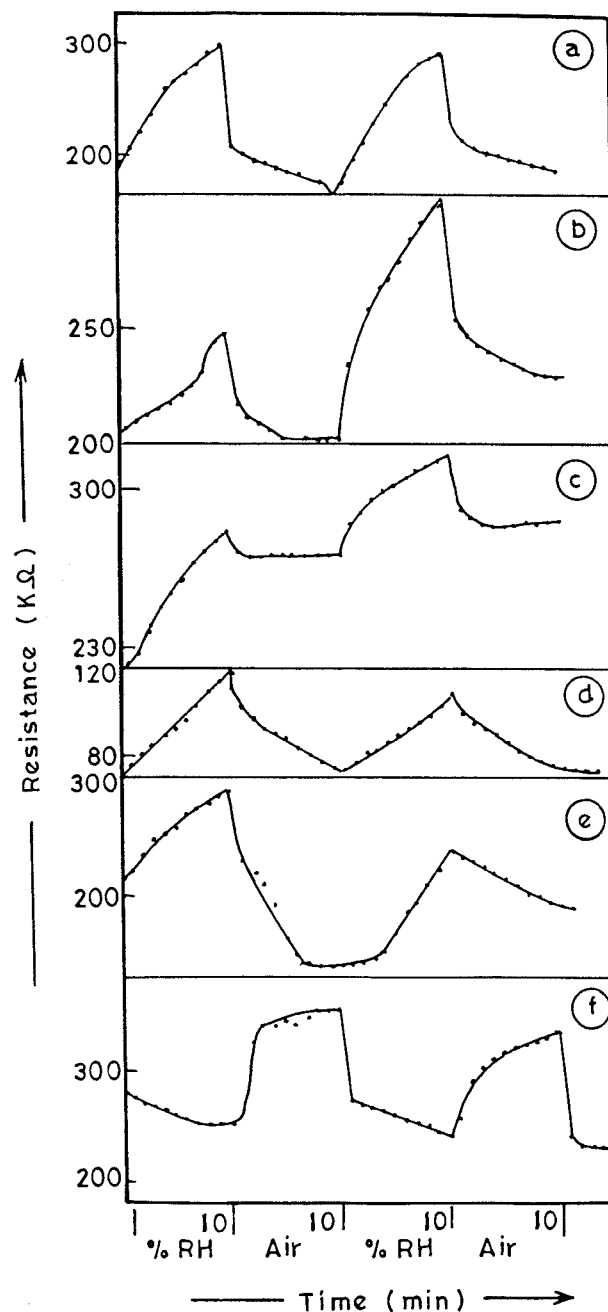
The test sample to be used as a substrate for the sensor was prepared in pellet form by applying a pressure of 7 tons using a Pye-Unicam die. The specific percentages of RH were obtained with the help of different saturated salt solutions in a closed assembly.<sup>7</sup>

Fourier transform infrared (FTIR) spectra of the as-synthesized polymers and of those exposed to different percentages of RH were recorded on a PerkinElmer 1600 FTIR spectrophotometer in the range of 400–4000  $\text{cm}^{-1}$ . Wide-angle X-ray diffraction studies were performed by using a Philips X-ray diffractometer with  $\text{CuK}\alpha$  as the radiation source.

## RESULTS AND DISCUSSION

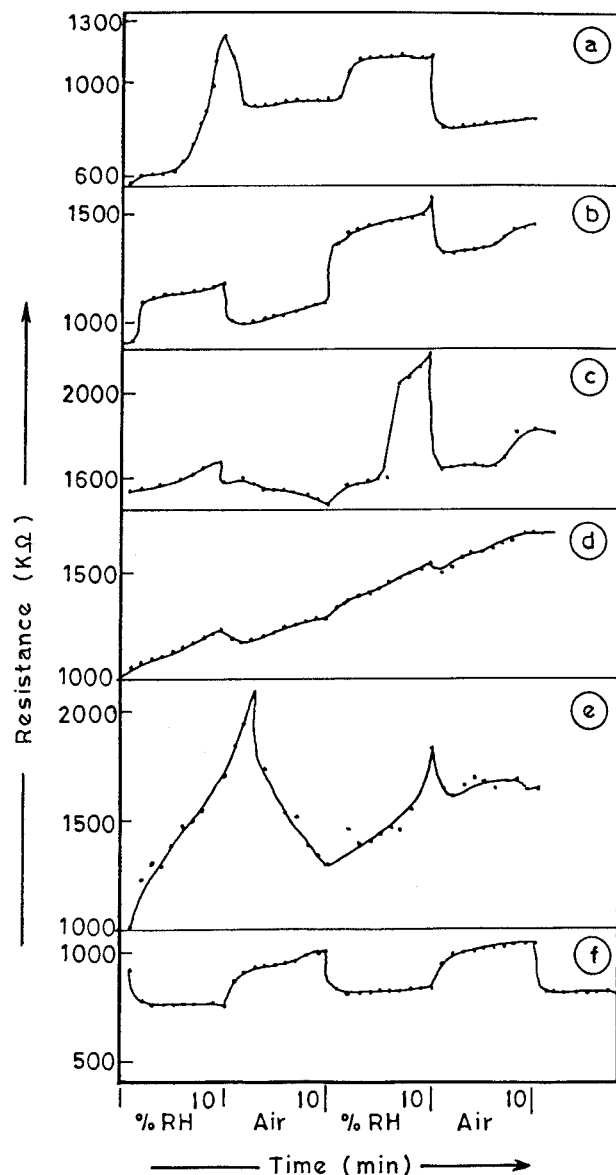
### Humidity Sensing

Polyaniline (pani) and some of its ring-substituted derivatives such as poly(*o*-toluidine) [p(*o*-tol)], poly(2,3-dimethyl aniline) [p(2,3-DMA)], and poly(2,5-dimethyl aniline) [p(2,5-DMA)] were subjected to a broad range of humidities between 6.4% and 97.3% RH. The characteristic responses are shown in Figures 1–4. From the figures it can be noted that the conductivity of the polymers decreases when exposed to relative humidities between 6.4% and 75.3% RH except at 97.3% RH, where the conductivity is seen to increase. However, sequential decreases in the magnitude of response in concert with increasing percent relative humidities is not observed in Pani and p(*o*-tol). The disubstituted derivatives, on the other hand, show a decreasing trend. Overall, Pani and p(2,3-DMA) exhibit the best responses at extreme humidities, especially for magnitude of change in resistance (Figs. 1 and 4) and sensitivity (Table I). For example, the jump in resistance of Pani on exposure to 6.3% RH is about 106  $\text{K}\Omega$ , while between 11.3 and 75.3% RH, it is only 43–70  $\text{K}\Omega$ . Similarly, p(2,3-DMA) exhibits a jump of about



**Figure 1** Characteristic responses of polyaniline exposed to different % RH atmospheres: (a) 6.4% RH, (b) 11.3 % RH, (c) 32.8% RH, (d) 57.6% RH, (e) 75.3% RH, and (f) 97.3% RH.

18–20  $\text{M}\Omega$  at extreme humidities while it is lower at intermediate humidities. In addition, as observed from Table I, p(2,3-DMA) exhibits sensitivities of 42.55% and 69.44% at 6.4% RH and 97.3% RH, respectively, while the sensitivity obtained in Pani is about 41.57% and 30.86%, respectively.



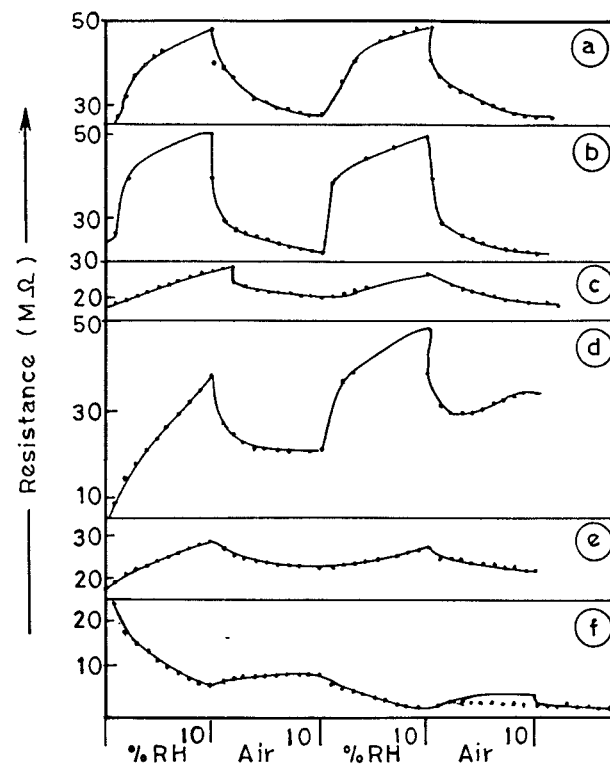
**Figure 2** Characteristic responses of poly(*o*-toluidine) exposed to different % RH atmospheres: (a) 6.4% RH, (b) 11.3 % RH, (c) 32.8% RH, (d) 57.6% RH, (e) 75.3% RH, and (f) 97.3% RH.

The differences in the response observed at extreme humidities can be attributed to the mobility of the chloride counterion, which is loosely attached to the polymer chain by weak Van der Waals forces of attraction. At low humidity the mobility of the dopant ions is restricted because under dry conditions the polymer chains would tend to curl up into compact coil form. On the contrary, in the presence of 97.3% humidity the polymer absorbs water molecules, and the polymer chains get hydrated.<sup>5</sup> As a result, swelling up

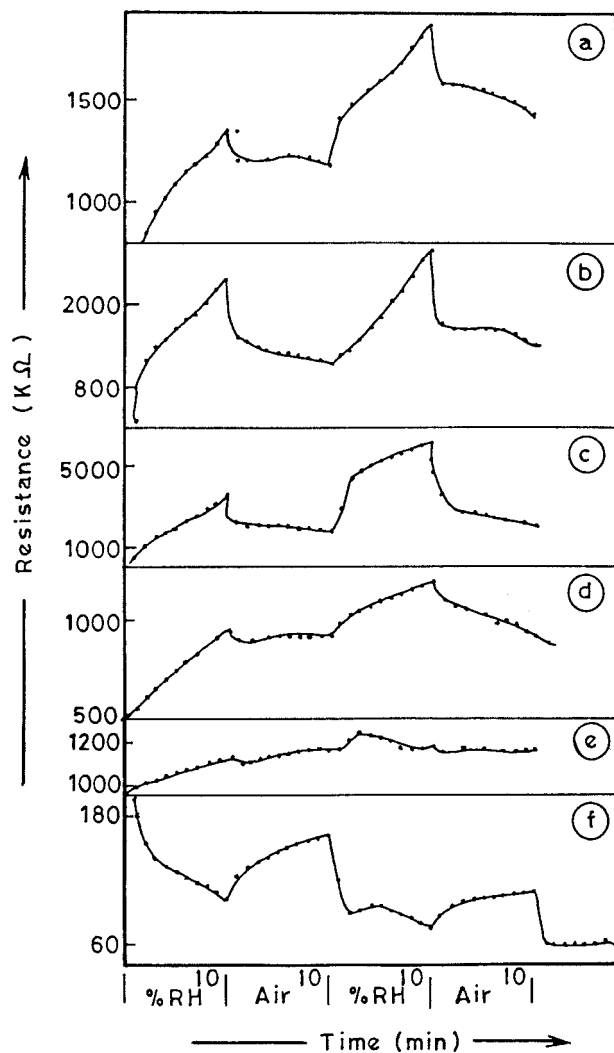
of the polymer chains takes place, followed by uncurling of the compact-coil form into straight chains that are aligned with respect to each other. This geometry of the polymer is favorable for enhanced mobility of the dopant ions or the charge transfer across the polymer chains<sup>5</sup> and hence for the conductivity.

#### X-ray Diffraction Studies

The change in the geometry of the polymer chains in the presence of a low percentage of RH and a high percentage of RH in comparison with that existing under simple air is reflected in the change in crystallinity of the polymers when subjected to different atmospheric conditions. Figures 5(a) and 6(a) represent the wide-angle X-ray diffraction patterns of the as-synthesized Pani and p(2,3-DMA) along with those obtained after exposing them to 6.4% RH and 97.3% RH. As-synthesized Pani exhibits a crystalline nature, with peaks at  $2\theta$  values of 17.5, 20.8, 25.8, 28.5, 29.88, 34.4, 39.5, and 42.0 [Fig. 5(a)]. After exposure to 6.4% RH the peaks [Fig. 5(b)] are seen to

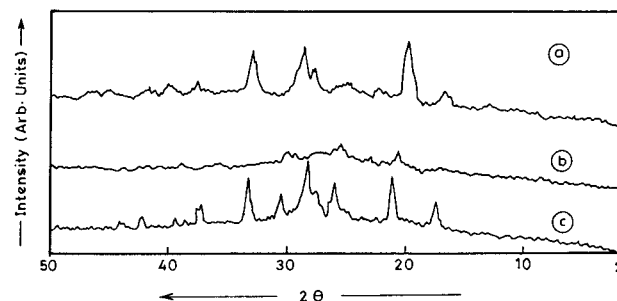


**Figure 3** Characteristic responses of poly(2,3-dimethylaniline) exposed to different % RH atmospheres: (a) 6.4% RH, (b) 11.3% RH, (c) 32.8% RH, (d) 57.6% RH, (e) 75.3% RH, and (f) 97.3% RH.



**Figure 4** Characteristic responses of poly(2,5-dimethylaniline) exposed to different % RH atmospheres: (a) 6.4% RH, (b) 11.3% RH, (c) 32.8% RH, (d) 57.6% RH, (e) 75.3% RH, and (f) 97.3% RH.

disappear, implying the polymer's loss of crystallinity. Conversely, an overall increase in the intensity of the peaks together with the appearance



**Figure 5** Wide-angle X-ray diffractograms of polyaniline: (a) as synthesized, (b) exposed to 6.4% RH, and (c) exposed to 97.3% RH.

of additional peaks at 21.0, 26.2, and 30.5  $2\theta$  values can be observed, contributing to the enhanced crystallinity of the polymer exposed to 97.3% RH [Fig. 5(c)].

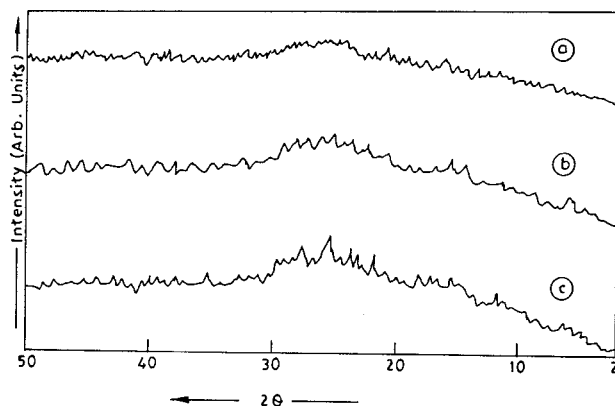
The influence of the percentage of RH is more pronounced in p(2,3-DMA), with the diffractograms [Fig. 6(a)] showing an amorphous nature and lack of sharp peaks of the as-synthesized polymer. This is obvious because the two methyl groups present at positions 2 and 3 exert appreciable steric hindrance over the polymer chains, thereby contributing to a disturbed geometry and hence the amorphous nature. This effect is further elevated in the presence of a low percentage of RH [Fig. 6(b)]. However, on exposing the polymer to 97.3% RH, the water molecules tend to reduce the strain and facilitate bringing about orderliness in the polymer matrix. The X-ray pattern [Fig. 6(c)] depicts the presence of few sharp peaks at  $2\theta$  of 22.0, 24.0, 25.8, 27.8, and 29.8, in addition to an overall increase in the crystallinity.

#### FTIR Studies

Further, the FTIR spectra (Figs. 7 and 8) of the polymers taken before and after exposure to 6.4 and 97.3% RH support our results. However, there are fewer differences observed for the IR

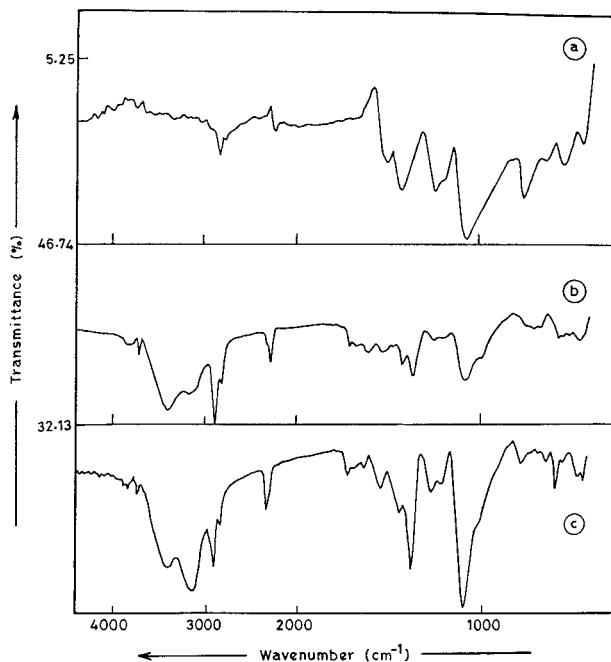
**Table I** Sensitivity (%) for Different Relative Humidities (% RH)

Polymer	Relative Humidity (% RH)					
	6.4	11.3	32.4	57.6	75.1	97.3
Pani	41.5	22.99	6.88	33.17	32.11	30.86
P( <i>o</i> -Tol)	23.12	15.80	18.07	3.32	24.72	21.53
p(2,3-DMA)	42.55	56.00	22.22	41.36	16.06	69.44
p(2,5-DMA)	17.68	53.29	33.96	13.12	2.50	44.60

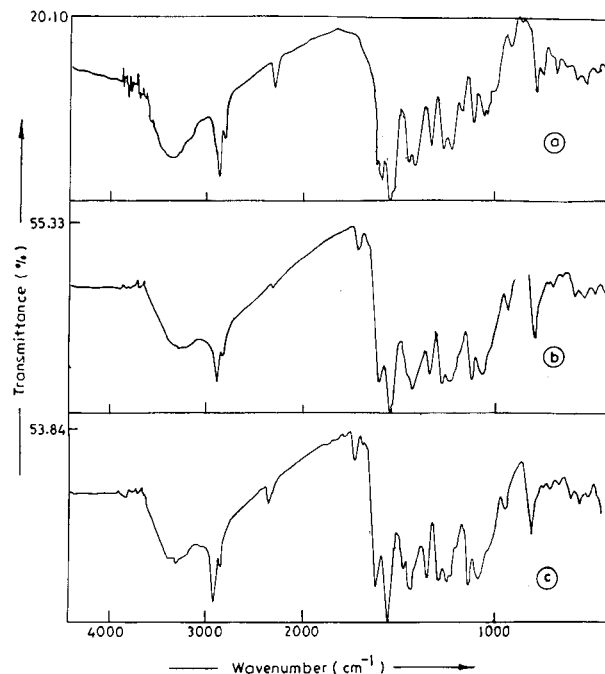


**Figure 6** Wide-angle X-ray diffractograms of poly(2,3-dimethylaniline): (a) as synthesized, (b) exposed to 6.4% RH, and (c) exposed to 97.3% RH.

spectra of poly(2,3-dimethylaniline) after exposure to the extreme humidities than for polyaniline because of two bulky methyl groups, present at positions 2 and 3, of the benzene ring in poly(2,3-dimethylaniline). The frequencies of the characteristic bands obtained in each sample are given in Table II. The band representing the O—H stretching vibration, at about  $3400\text{--}3500\text{ cm}^{-1}$ , can be observed to be broad and negligible in the as-synthesized Pani and p(2,3-DMA),



**Figure 7** FTIR spectra of polyaniline: (a) as synthesized, (b) exposed to 6.4% RH, and (c) exposed to 97.3% RH.



**Figure 8** FTIR spectra of poly(2,3-dimethylaniline): (a) as synthesized, (b) exposed to 6.4% RH, and (c) exposed to 97.3% RH.

whereas on exposure to 97.3% RH, the peak is seen to become sharp and intense. On the other hand, Pani and p(2,3-DMA) subjected to 6.3% RH exhibit broad and short peaks. This proves the ability of the polymer to absorb water when exposed to a high-humidity atmosphere. Similarly, the stretching vibration of  $>\text{N—H}$  observed at about  $3200\text{ cm}^{-1}$  in the polymers is seen to shift to a higher wavenumber ( $\sim 3400\text{ cm}^{-1}$ ), and also the intensity is lowered when exposed to 6.3% RH.

**Table II** Characteristic Frequencies of Pani and P(2,3-DMA)

Wavenumber ( $\text{cm}^{-1}$ )	Band Characteristic
$\sim 800$	Paradisubstituted aromatic rings (indicating the polymer formation)
$\sim 600\text{--}700$	C—H out of plane-bending vibration
$\sim 1120$	C—H in plane-bending vibration
$\sim 1300\text{--}1317$	Aromatic C—N stretching (indicating second aromatic amine group)
$\sim 1500$	C—N stretching of benzenoid rings
$\sim 1600$	C—N stretching from quinoid rings
$\sim 3000\text{--}3100$	Aromatic C—H stretching vibration
$\sim 3200$	$>\text{N—H}$ stretching vibration

Conversely, exposure to 97.3% RH results in enhanced intensity of the peak and a shift to about  $3171\text{ cm}^{-1}$ , which can be attributed to the deprotonation–protonation transition taking place under dry and wet atmospheres.

## CONCLUSION

Poly(2,3-dimethylaniline) is found to be a competent material as a humidity sensor. The sensitivity as well as linear response was observed to be greater in p(2,3-DMA) than in polyaniline.

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