Hyperbranched Polycarboxylates and Their Nanocomposites with ZnO: Investigations on the Humidity-Sensitive Properties

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ABSTRACT: Hyperbranched polycarboxylates (HBPC) with different alkali metal cations (Li^+, Na^+, and K^+) were prepared and characterized by ^{1}H-NMR and thermal gravimetric analysis. Thin film humidity sensors based on HBPC and its composite with ZnO nanorods were fabricated. The morphologies of films of HBPC and the nanocomposite were investigated by atomic force microscopy, which revealed uniform distribution of ZnO nanorods in HBPC. The humidity-sensitive characteristics of HBPC and the nanocomposite were investigated at room temperature. It was found that the type of cations significantly affected the humidity-sensing behaviors of HBPC. In addition, the nanocomposite exhibited better humidity-sensitive properties than HBPC alone. Its impedance decreased for about three orders of magnitude over the range 19–97% RH, showing high sensitivity. Moreover, the nanocomposite exhibited fast response (~ 9 and 10 s for response and recovery time between 97% RH and 33% RH, respectively) and small hysteresis (~ 1.4% RH). The improved humidity-sensing behaviors of the nanocomposite over HPBC alone is explained by taking into account the hyperbranched structure of the polymer and the special interactions of the polymer and ZnO with water molecules. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 1994–2000, 2011

Key words: hyperbranched; nanocomposites; sensors; polyelectrolytes

INTRODUCTION

Humidity sensors are important chemical sensors with wide applications in the industrial and agricultural production, environmental monitoring, storage, etc. A large variety of polymers have so far been investigated as sensitive materials for the construction of humidity sensors because of their distinct advantages of low cost, easy preparation, high sensitivity, etc.[1–5] However, the polymers used are mainly linear or crosslinked, and there is no report on the humidity-sensitive properties of polymers with hyperbranched structure to our best knowledge.

Hyperbranched polymers (HBPs) possess a large amount of functional end groups which would provide great opportunities for modification and interactions with analytes, and are beneficial for applications in chemical sensing.[6,7] Moreover, their much reduced chain entanglement compared with linear polymers is expected to favor the diffusion of analyte molecules in the polymer sensitive film.[8] There have been a number of reports on their applications in chemical and biosensors.[8–12] And it would be interesting to investigate the humidity response of HBPs which exhibit properties distinct from linear polymers.

Recently, organic/inorganic nanocomposites attracted much attention in the fields of electronic, optical or magnetic applications because many bulk properties can be improved compared with those of base polymers.[13,14] There are some reports on their applications in the preparation of humidity sensors with improved sensing properties. Wang et al.[15] reported that the composites of nanocrystal $BaTiO_3$ and a polymer gave better sensing properties than that of polymer alone. Gong and coworkers[16] fabricated humidity sensors based on composites of copoly(tetraethylammonium 2-acrylamido-2-methyl-1-propanesulfonate/polyvinylpyrrolidone) and silver nanoparticles. Su and Wang[17] reported that the flexible humidity sensors based on TiO_2 nanoparticle/polypyrrole/poly-[3-(methacrylamino) propyl] trimethyl ammonium chloride composite thin films had the best flexibility, highest sensitivity, least hysteresis and greatest linearity

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In this article, hyperbranched polycarboxylates were prepared and characterized. Their humidity-sensing properties were investigated over a wide humidity range at room temperature, and the effect of alkali metal cations was examined. To further improve the humidity-sensing properties of the hyperbranched polymers, ZnO nanorods were encapsulated into the polymer film to form a nanocomposite. Its sensitive characteristics including calibration curve, hysteresis and response time were all investigated.

EXPERIMENTAL

Chemicals

Hyperbranched aliphatic polyester Boltorn™ H20 (H20, Perstorp AB, Sweden) having theoretically 16 hydroxyl groups at the terminals was dried under vacuum before used. Dioxane was dehydrated with activated molecular sieve. Other reagents were of analytic grade and purchased at domestic market and used as received unless noted otherwise.

Preparation of materials

Synthesis of H20—COOH[18]

Hyperbranched aliphatic polyester Boltorn™ H20 with hydroxyl end groups (H20, 12.4 g), succinic anhydride (11.4 g) and anhydrous tin (II) chloride (0.24 g, 2 wt %) were dissolved in dioxane with stirring and put into a flask. The solution was heated at 100°C for 36 h under argon atmosphere. The resulting mixture was precipitated from a large amount of ethyl ether and dried under vacuum to obtain a white solid denoted as H20—COOH.

Synthesis of hyperbranched polycarboxylate (H20—COO^-X^+)

The as-prepared H20—COOH was dissolved in ethanol, and neutralized with different base solution (LiOH, NaOH and KOH). The resulting solution was dried by rotary evaporation to obtain white products denoted as H20—COOLi, H20—COONa, and H20—COOK, respectively.

Synthesis of ZnO nanorods

ZnO nanorods were synthesized by a simple wet chemical method.[19] In a typical process, 100 mL of an aqueous solution of zinc nitrate and 100 mL of a hexamethylenetetramine aqueous solution of equal concentration (0.05*M*) were mixed and kept under mild magnetic stirring for 5 min. Then the solution was transferred into a 500-mL flask and heated at 90°C for 3 h with refluxing. Subsequently, the resulting white mixture was ultrasonically treated, centrifuged, washed with deionized water and ethanol, and dried in air at 60°C.

Fabrication of humidity sensors

Aqueous solutions of the as-prepared hyperbranched polycarboxylates H20—COOX (H20—COOLi, H20—COONa, and H20—COOK) and their mixture with ZnO nanorods were prepared and used for the fabrication of humidity sensors by dip coating. Typically, an aqueous solution of H20—COOK (40 mg/mL) and ZnO nanorods (0.8 mg/mL) was prepared by ultrasonic treatment. The obtained opaque mixture (no precipitation is found when it stands for several hours) was then deposited on a clean interdigitated gold electrode with a ceramic substrate ($6 \times 5 \times 0.5$ mm) using an automatic dip-coating machine. The as-prepared electrode was heated at 90°C for 2 h to obtain a resistive-type thin film humidity sensor.

Measurements

^{1}H-NMR spectra were recorded using a Bruker Avance DMX500 spectrometer, operating at 500 MHz (solvent: DMSO-d_6; internal standard: tetramethylsiliane). The morphology of the ZnO nanorods and the nanocomposite film were observed on a scanning electron microscopy (SEM) instrument (JEOL, JSM-6390A) and with an atomic force microscopy (AFM) instrument (SPI3800*N*) using the tapping mode. The humidity-sensitive properties of the thin film sensors were investigated by recording their impedance at different relative humidity (RH) at room temperature. The impedance was measured using a homemade equipment with the applied voltage and frequency of 1 V and 1000 Hz, respectively. The sensors were placed in a chamber where humidity was controlled by adjusting mixed ratios of dry and wet gases. The response time measurement was performed by recording online the impedance of the humidity sensors over different saturated salt solutions (K_2SO_4 for 97% RH, $MgCl_2$ for 33% RH) in their equilibrium state, and the laboratory humidity during the measurement was between 33 and 97% RH. All the measurements were carried out at $\sim$ 25°C.

RESULTS AND DISCUSSION

Characterization of the hyperbranched polymers, ZnO nanorods, and the composite

In this work, hyperbranched polycarboxylates H20—COOX (H20—COOLi, H20—COONa, and H20—COOK) were prepared by reaction of hyperbranched polyester containing hydroxyl end groups (H20) with anhydrides, followed by neutralization of the resulting H20—COOH. The synthetic route and theoretical structures of the polymers are illustrated in Scheme 1.

Figure 1 shows the ^{1}H-NMR spectra of the starting material H20 and resulting hyperbranched polycarboxylic acid H20—COOH. In the spectrum of H20 [Fig. 1(a)], the chemical shifts at 0.7–1.3 ppm are attributed to protons in —CH_3 groups, and the signals at 4.7–5.1 ppm are assigned for protons in -OH groups. Moreover, the signals at 3.3–4.3 ppm belong to protons in CH_2OCO groups. The signals at 2.5 and 3.2 ppm are attributed to DMSO and H_2O, respectively. By contrast, in the spectra of H20—COOH [Fig. 1(b)], apart from the signals assigned for protons in CH_3 and —CH_2OCO, new signals were observed: 12.1 ppm for protons in —COOH and 2.2 ppm for protons in —$OCOCH_2CH_2COOH$ end groups. The ^{1}H-NMR spectra suggests that H20 successfully reacted with succinic anhydride to obtain hyperbranched polycarboxylic acid. Titration analysis revealed that approximately twelve of the sixteen hydroxyl groups of H20—OH were successfully converted to carboxylic acid group.

Figure 2 shows the SEM images of the as-prepared ZnO nanorods. It can be seen clearly that the ZnO nanorods generally exhibit a diameter of 60–120 nm and length of 300–600 nm.

Figure 3 shows the AFM pictures of H20—COOK and H20—COOK/ZnO nanocomposite films. The root mean square (RMS) roughness of H20—COOK and the composite are 3.288 and 4.289 nm, respectively. It is seen that the film of H20—COOK is relatively smooth and uniform. After the encapsulation of ZnO nanorods, the composite film becomes rugged, with a lot of protrusions which is apparently attributed to nano-sized ZnO. It is expected that the rugged sensitive composite film may increase its effective surface area, and facilitate the entry of water molecules, thus promote the humidity sensitivity and accelerate the response.

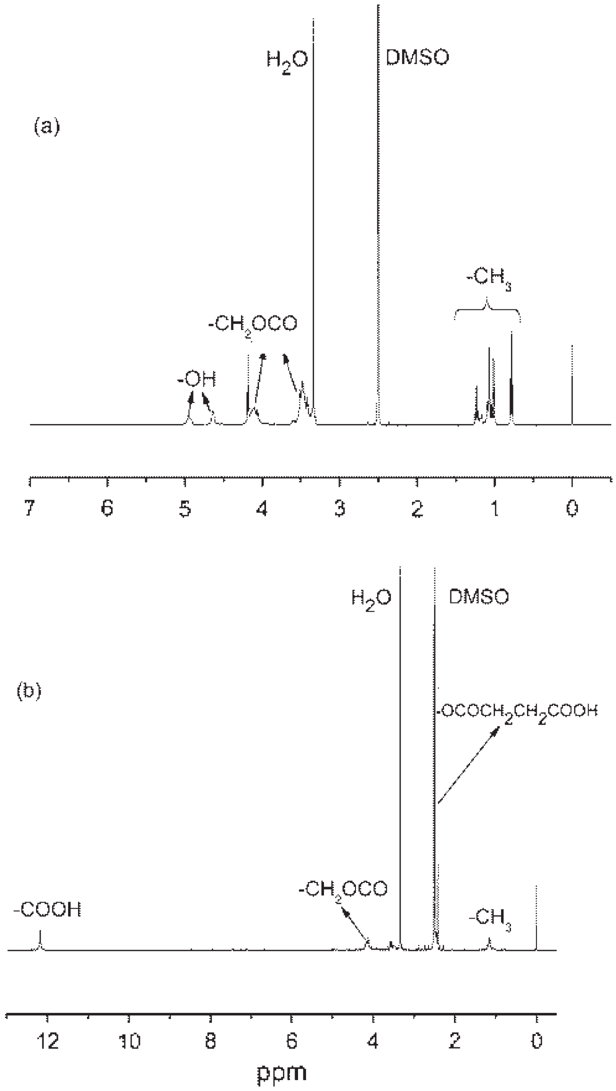
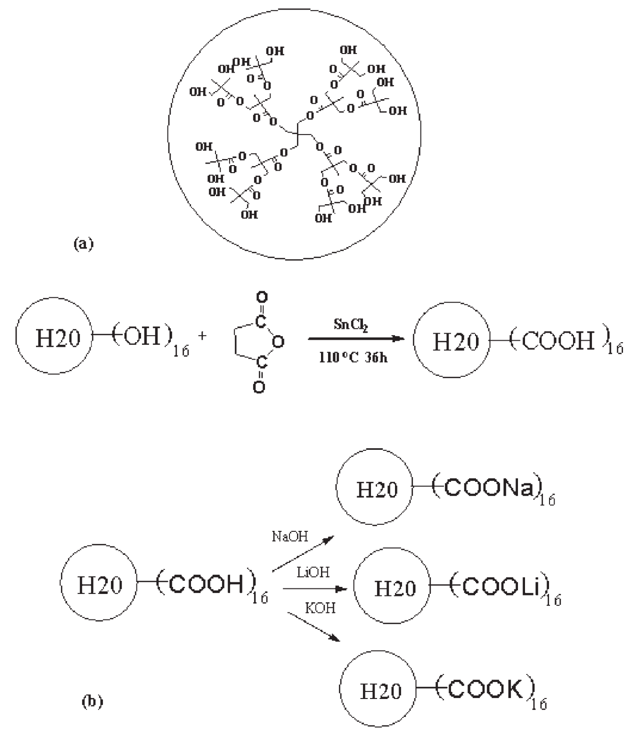


Figure 1 ^{1}H-NMR spectra of (a) H20 and (b) H20—COOH.



Scheme 1 (a) Idealized formula of Boltorne H20; (b) schematic description of the synthesis for H20—COOX.

Humidity-sensing properties

It is known that hyperbranched polymers exhibit chemical structures and properties distinct from the linear polymers, which may also affect their humidity-sensitive properties. Figure 4 illustrates the impedance response to humidity of the hyperbranched polycarboxylates with different alkali metal cations, i.e., H20—COOK, H20—COOLi and H20—COONa. It can be seen that the type of alkali metal ions

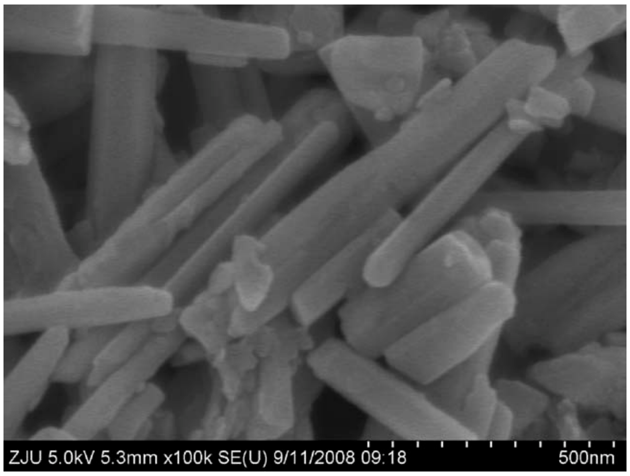


Figure 2 SEM photograph of ZnO nanorods.

significantly affect the sensing behaviors of the hyperbranched polymers. H20—COOLi exhibited much higher impedance than the other two polymers H20—COOK and H20—COONa. The polymers with Na^+ and K^+ as cations showed similar impedance response. However, H20—COOK exhibited the smallest impedance of the three polymers at low humidity, which is beneficial for applications in the measurement of dry atmosphere. The finding is in agreement with the report on alkali salt of linear polymer electrolyte by Sakai et al.,[20] in which Li^+ was found to be the least conductive of the alkali ions while absorbing the same amount of water molecules. H20—COOK showed large impedance variation from $4.4 \times 10^6\ \Omega$ to $1.6 \times 10^4\ \Omega$ in the range of 20 to 90% RH, and its impedance at low humidity was smaller than other hyperbranched polymers, thus was selected for the following investigations.

As is known, polymer/inorganic nanocomposites may exhibit improved humidity-sensitive properties compared with the components separately. In the present work, ZnO nanorod was directly mixed with hyperbranched polycarboxylates to obtain a nanocomposite with the assistance of ultrasonic treatment. The effect of the concentration of ZnO on the humidity response of the nanocomposite is illustrated in Figure 5. It is observed that the addition of

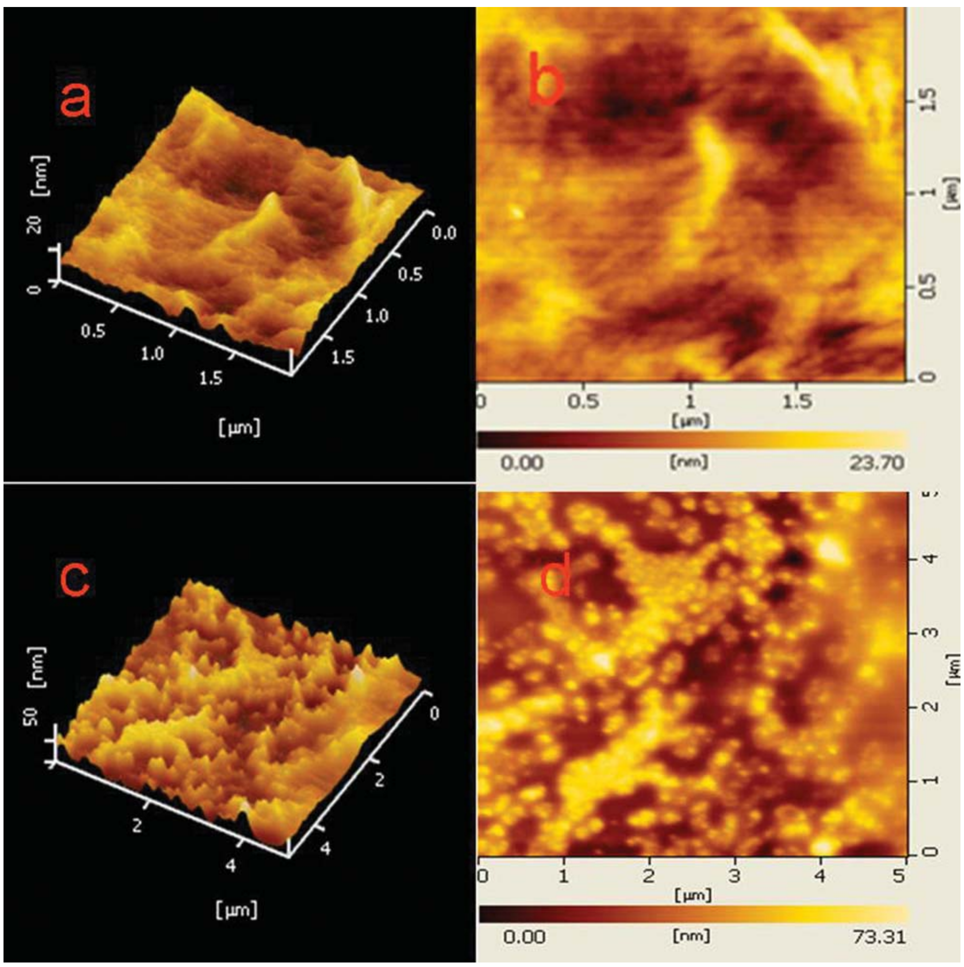


Figure 3 AFM pictures of (a,b) H20—COOK and (c,d) H20—COOK/ZnO composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

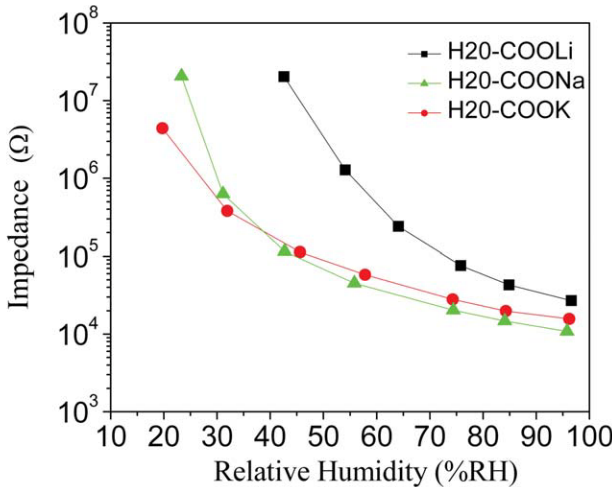


Figure 4 The effect of type of alkali metal cation on the humidity response of the hyperbranched polycarboxylates (concentration: 40 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

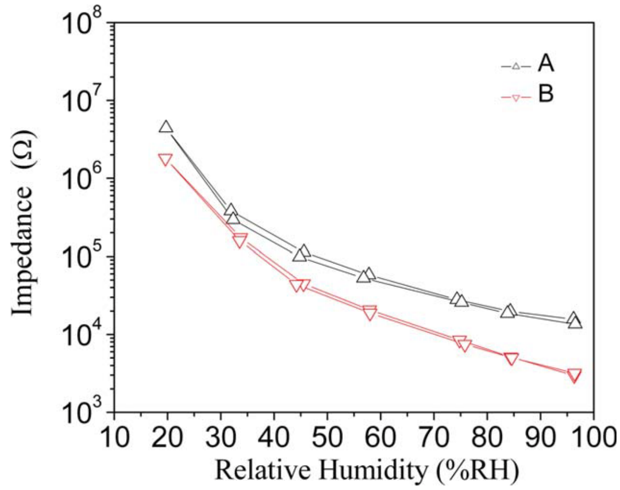


Figure 6 The humidity-sensing curves of (A) H20—COOK and (B) H20—COOK/ZnO nanocomposite during humidification and desiccation processes (H20—COOK: 40 mg/mL; ZnO: 0.8 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ZnO decreased the impedance of the composite, which is more pronounced at high humidity. Moreover, higher concentration of ZnO led to greater decrease in impedance of the composite, and greater sensitivity at high humidity was observed. Previously we found that the inclusion of ZnO into linear polyelectrolyte sodium polystyrenesulfonate (NaPSS) resulted in increased impedance over the whole tested humidity range instead.[21] Such a difference suggests that the hyperbranched H20—COOK, which possesses molecular structures distinct from linear polymers, exhibit special interactions with ZnO. It is reported that the addition of nanosized $LiAlO_2$ could improve the conductivity of polyelectrolyte based on hyperbranched polymers with amorphous structure, which was attributed to the high surface activity of the nanoparticles with large surface-to-volume ratio.[22] Moreover, the nanoparticles were found to increase the transference number of cation of the polymer electrolyte, thus increase the conductivity. Therefore, it is proposed that the interaction of hyperbranched polymer H20—COOK with ZnO may also increase the conductivity of the composite. However, much more work should be done to reveal the underlying mechanism and understand the roles of hyperbranched polymers and inorganic particles in the conducting behavior of the composite in the presence of humidity.

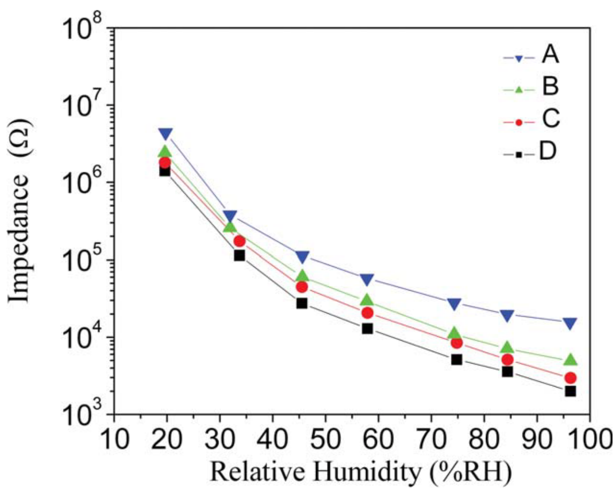


Figure 5 The effect of ZnO concentration on the humidity response of H20—COOK/ZnO composite. Concentration of ZnO nanorods (mg/mL): (A) 0; (B) 0.4; (C) 0.8; (D) 1.2. (H20—COOK: 40 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6 presents the hysteresis of H20—COOK and its composite with ZnO. It can be seen that the sensing curves of the composite during humidification and desiccation processes almost overlapped. As estimated from the figure, the hysteresis was only 1.4% RH for the composite in comparison to 2.7% RH for H20—COOK. Response time was defined as the time to reach 90% of the impedance response. The response transients and estimated response times of H20—COOK and H20—COOK/ZnO composite are shown in Figure 7 and Table I, respectively. It is seen that both the polymer and the composite exhibited fast response, and their 90% response times ($t_{90\%}$) for adsorption are estimated to be $\sim$ 11 and $\sim$ 9 s, respectively. By contrast, $t_{90\%}$ for desorption was $\sim$ 18 s for H20—COOK, whereas the composite exhibited much shorter $t_{90\%}$ of $\sim$ 10 s for desorption. The sensing curves of both H20—COOK and the composite exhibited a sigmoidal shape,

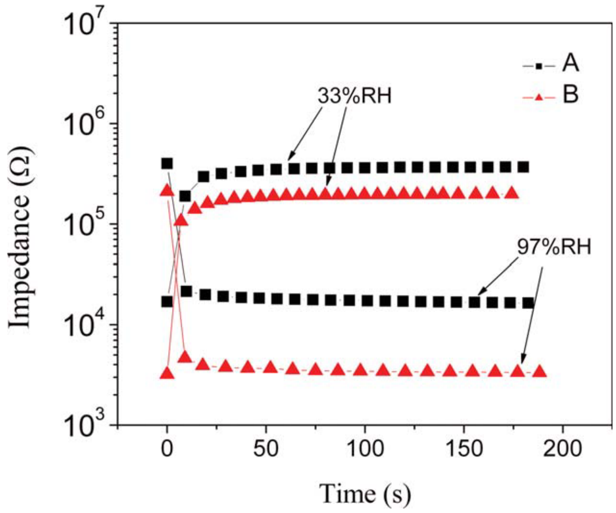


Figure 7 The response transients of (A) H20—COOK and (B) H20—COOK/ZnO nanocomposite between 33% RH and 97% RH. ([H20—COOK]: 40 mg/mL; ZnO: 0.8 mg/mL). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

which is in agreement with that of sensing curves of polyelectrolyte and substituted polyacetylene based humidity sensors and is ascribed to its capacitance change with humidity.[23,24] Specifically, the composite showed improved sensing linearity on a semilogarithmic scale in the range of low-to-middle (20–46% RH) and middle-to-high (46–96% RH) humidity range, respectively.

The sensing behaviors of the hyperbranched polycarboxylates and their nanocomposite with ZnO may be explained by taking into account of the distinct structures of HBPC. Different from linear polymers, the hyperbranched polycarboxylate used in the present study possess abundant end carboxylic groups, which are beneficial for the adsorptions of water molecules. The strong interactions of large amount of adsorbed water molecules with the hyperbranched polyelectrolytes facilitated the dissociation of ions and increased the ionic conducting ability. As a result, they exhibited low impedance even in the range of middle humidity. On the other hand, the composite film of H20—COOK and ZnO showed much increased active surface areas for interactions with adsorbed water molecules, and high sensitivity was obtained, especially at high humidity.

TABLE I
The response and recovery time of H20—COOK and H20—COOK/ZnO nanocomposite

Sensitive materials	Response time (s)	Recovery time (s)
H20—COOK	11	18
H20—COOK/ZnO nanocomposite	9	10

Another feature of the hyperbranched polymer is the much reduced chain entanglements compared with linear polymers. Thus the diffusion of water molecules in the sensitive film was significantly facilitated, and the HBP exhibited short response time for adsorption. But the relatively strong interactions of adsorbed water molecules with ions in the polymers may hinder the removal of water molecules, leading to longer recovery time and a medium hysteresis of $\sim$ 2.7% RH. By contrast, in the composite, ZnO exhibited much weaker interactions with adsorbed water molecules compared with the hyperbranched polymer electrolyte. In consequence, adsorbed water molecules could be more easily desorbed from the composite film, leading to shorter recovery time and smaller hysteresis.

The above results showed that the nanocomposite of H20—COOK and ZnO exhibited high sensitivity, very small hysteresis and short response and recovery time, which indicate that it could be good candidates sensitive materials for humidity sensors. Of course, much more work is needed to be done, for example, the investigations on the long-term stability of the nanocomposite.

CONCLUSIONS

Hyperbranched polycarboxylates were prepared by modification of the terminal groups of hyperbranched polyester with hydroxyl end groups. Their humidity-sensing properties were significantly affected by the type of alkali metal ions in the polymers. The nanocomposite of the hyperbranched polymers with ZnO exhibited higher humidity sensitivity and smaller hysteresis compared with the polymer alone. The improved sensing properties may be related to the morphology of the composite film and distinct interactions of hyperbranched polymers and ZnO with water molecules. Hyperbranched polymers may be promising polymer sensitive materials for construction of high performance humidity sensors.

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