



Observation of ionic hydrogen bonding between anions and triarylamine-based aromatic polyimides with secondary amine

Hung-Ju Yen ^{a,1,2}, Jhe-Huang Lin ^{a,1}, Yuhlong Oliver Su ^b, Guey-Sheng Liou ^{a,*}

^a Institute of Polymer Science and Engineering, National Taiwan University, 1 Roosevelt Road, 4th Sec., Taipei, 10617, Taiwan

^b Department of Applied Chemistry, National Chi Nan University, Puli, Nantou, 54561, Taiwan



ARTICLE INFO

Article history:

Received 13 September 2017

Received in revised form

23 December 2017

Accepted 25 December 2017

Available online 29 December 2017

Keywords:

Anion detection

Polyimide

Secondary amine

Hydrogen bond

Triphenylamine

ABSTRACT

Four triarylamine-based high-performance polyimides with secondary amine were readily synthesized, their ionic hydrogen-bonding interaction with pyridines and anions are successfully demonstrated (20 times higher than the literature in sensitivity) by the means of electrochemistry and spectroelectrochemistry. The prepared polymer thin films having the advantage for real-time qualitative detection are great candidates as chemosensors to both pyridines and anions.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Nowadays, highly sensitive and reliable anion detectors are urgent in demand because of the degenerative environment and increasing biological and chemical threats. For example, fluoride is a well-known essential element for dental care. Nevertheless, an excess amount of fluoride will cause severe problem to tooth and bone, even be harmful for body health, such as urolithiasis (kidney stone disease), skeleton fluorosis, and at worst scenario, lethal [1]. Therefore, increased safety methods are needed for operational support in responding to hazardous emergency issues. The ability to timely detect, identify and monitor fluoride anion or hazardous material is imperative for the effective usage of both civilian defense and military resources. For this reason, lots of chemosensors have been synthesized and reported [2–4], taking the rapidly formed hydrogen-bonding between chemosensors and target anions into consideration [5,6]. Fluorescent and colorimetric detections are the most widely applied approaches for anion detection. However, the *ideal detector* has not been a reality for commercialization due to the limited methods and low sensitivity

[7,8]. The other major challenge is the demand for increasing detection reliability and reducing the frequency of falseness.

Since 1996, Linschitz [9] and Smith [10–14] have done significant efforts to elucidate the redox-dependent formation through electrochemically controlled hydrogen bonding between the reductive compounds and hydrogen donors, such as water, amides, alcohol, acids and ureas. Recently, Su's group [15] systematically reported a series of phenylenediamines exhibiting redox potential inversion resulted from the ionic hydrogen bonds with pyridines or alcohols. The potential shift (the new redox couple $E_{2}^{ox'}$ is obviously lower than E_{1}^{ox}) could be classified as *potential inversion* [16] with a single two-electron wave, which is rare and mostly accompanied with significantly structural change [17–19], large solvation [20] or redox potential shifts by ionic H-bonding [9,21]. Nevertheless, these compounds are very rare and their low potential shifts usually performed negligible signals (<50 mV at 1 equiv. of anion) [22].

In this work, we are exploring new enabled measuring approaches for anion sensing applications by applying a series of aromatic imides and polyimides (PIs) with secondary amine structures as molecular recognition elements via electrochemical and spectroelectrochemical transduction technologies. The successful introduction of packing-disruptive triarylamine moieties into the polymer main chain is essential for fabricating patternable thin-film sensors by jet-printing and spin-coating methods. The

* Corresponding author.

E-mail address: gслиou@ntu.edu.tw (G.-S. Liou).

¹ H.-J. Yen and J.-H. Lin contributed equally.

² Present address: Institute of Chemistry, Academia Sinica, Taipei, Taiwan.

schematic illustration of stabilizing the cation radical through hydrogen bonding between secondary amines and pyridines/anions is depicted in Fig. 1, as well as the summary of the pK_a values of pyridines and their hydrogen-bond binding strength. The ultimate goal of our research efforts is to develop a field of deployable detection capability for anions and hazardous materials that is fast, accurate and sensitive.

2. Results and discussion

2.1. Polymer synthesis

Aromatic PIs containing secondary amines were synthesized by the conventional one-step imidization of diamines with secondary amine [23] and two commercial dianhydrides in *m*-cresol at 185 °C with catalytic amount of isoquinoline (Scheme 1). The polymerization reaction proceeded smoothly and the obtained PIs with inherent viscosities of 0.46–0.61 dL/g can be solution-cast into tough, flexible, and free-standing films (see inset figure of Scheme 1), revealing the successful preparation of high molecular weight PIs (Table S1).

The IR spectra of PIs **H-6F** and **H-DS** shown in Fig. S1 exhibited characteristic imide absorption bands at around 1780 and (C=O), 1721 (C=O), 1380 (C–N), 740 (imide ring deformation), and secondary amine at 3390 cm^{-1} . ^1H NMR spectra of the prepared PIs are illustrated in Fig. 2. No resonance peaks appeared from 9 to 12 ppm in the ^1H NMR spectra further supports the complete imidization of all the PIs. The results identified by IR and NMR spectroscopic techniques are in perfect agreement with the proposed structures.

In order to obtain simplified structural information of the PIs, the model compounds with secondary amine groups were also synthesized by the condensation of their corresponding diamine monomers and two equivalent amounts of phthalic anhydride (Scheme 2). Their FT-IR and ^1H NMR spectra are shown in Figs. S2 and S3, respectively. The obtained model compounds were used for electrochemical and spectroelectrochemical measurement.

2.2. Basic characterization of polyimides

The solubility properties of PIs were tested quantitatively and summarized in Table S2. These polymers are soluble in various solvents. The PIs prepared from dianhydride 6FDA exhibited higher solubility than those from DSDA owing to the bulky hexa-fluoroisopropylidene linkage in the polymers that is beneficial for practical fabrication of high performance optoelectronic devices.

The thermal behaviors of the synthesized PIs were investigated by TGA and TMA, and the results are tabulated in Table S3. The PIs were thermally stable up to 425 °C (depicted in Fig. S4) and the carbonized residue in nitrogen was more than 55% at 800 °C, estimating LOI values up to 42. The softening temperature (T_s) could be measured by TMA thermograms (as shown in Fig. S5). These PIs revealed remarkably high T_s as a result of the present rigid aromatic units. Moreover, DSDA-based PIs exhibited higher T_s due to the higher intermolecular force and strong dipole interactions contributed from the sulfone group, thus restricting the rotation and movement of the polymer chains. The results suggested that the high aromatic content is beneficial for thermal stability and behavior of the prepared PIs.

2.3. Electrochemical properties and in-situ UV–vis absorption

The electrochemical sensing technology relies on the ability of anion or hazardous materials to be bound with anionic products by H-bonding, which can be monitored and measured through a small electric current or potential shift at the surface of an electrode. This change is normally monitored through an electrode. Specificity to a target is provided by optimization of the electrochemistry. Furthermore, quantification of the anion or hazardous materials can be determined by the electrical current produced. The electrochemistry was studied by cyclic voltammetry (CV). Model compounds (10 μmol) were dissolved in dichloromethane with 0.1 M of tetrabutylammonium perchlorate (TBAP) as an electrolyte and glassy carbon disk is used as working electrode. Besides, the polymers were conducted by casting film (0.55 cm^2 in area) on an ITO-coated glass as working electrode.

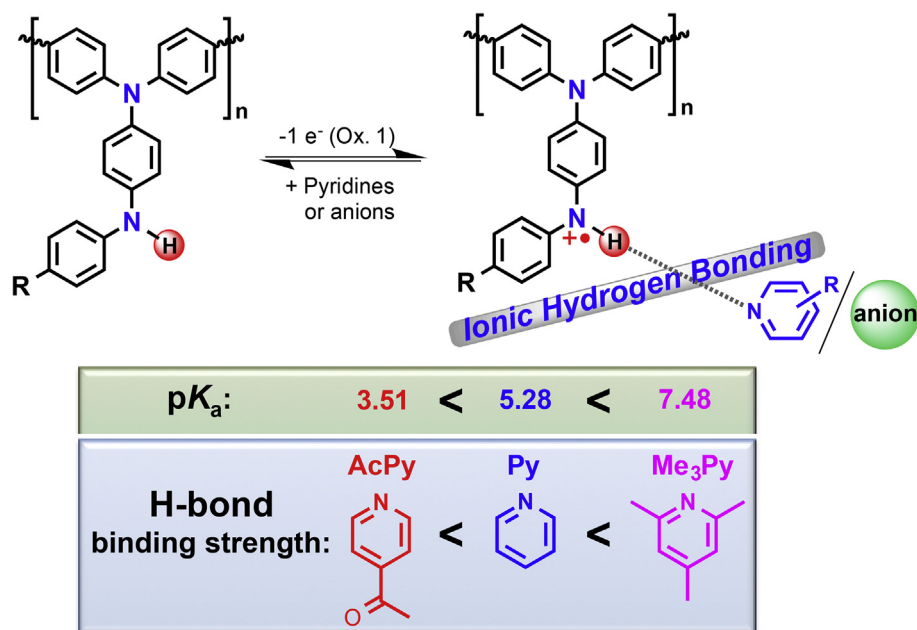


Fig. 1. Schematic illustration of stabilizing the cation radical through hydrogen bonding between secondary amines and pyridines/anions. Summary of the pK_a values of pyridines as well as their hydrogen-bond binding strength. (AcPy: 4-acetylpyridine; Py: pyridine; Me₃Py: 2,4,6-trimethylpyridine).

Download English Version:

<https://daneshyari.com/en/article/6604627>

Download Persian Version:

<https://daneshyari.com/article/6604627>

[Daneshyari.com](https://daneshyari.com)