Novel intrinsic microporous Tröger's base-cored triphenylamine polyamide with improved electrochromic response capability

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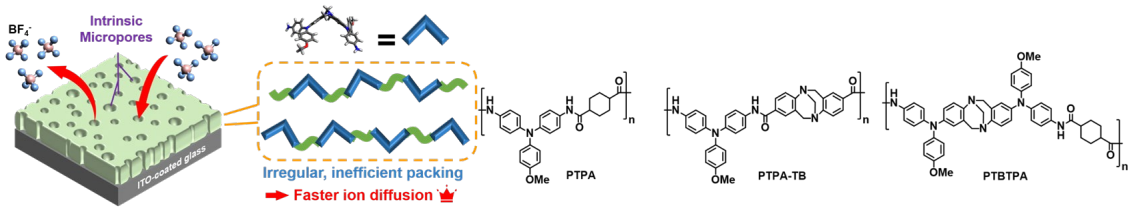
Abstract

Recently, more and more researchers have focused on generating “pores” within the polymer matrix to prompt the performance of electrochromic (EC) films using physical or chemical approaches. In this work, we meticulously designed a Tröger’s base (TB)-cored arylamine-containing diamine monomer, TBTPA-NH_2, and synthesized the corresponding redox-active polyamide, PTBTPA. The resulting PTBTPA exhibits low density with large d-spacing and surface area, contributing to the rigid and V-shaped TB unit. Consequently, the prepared polymer film demonstrated remarkable electrochemical and EC behaviors, such as low applied potential (1.00 V), facilitating rapid diffusion of the electrolyte, reasonable switching capability (1.8 s/1.5 s for coloring tc and bleaching tb, respectively), and excellent stability. For further application, the electrochromic device (ECD) of PTBTPA/HV exhibits the best-enhanced response capability (3.5 s/6.1 s for t_c and t_b, respectively), the highest coloration efficiency (337 cm^2 /C), and switching stability (96.1% of retention after 500-cycle switching).



Introduction

Electrochromic (EC) materials have become attractive due to the reversible color change under electrochemical oxidation and reduction. The most intuitive approach to increasing the visual contrast for an EC device is thickening the electroactive polymer layer. However, the thicker film would enormously sacrifice the neutral state transparency and simultaneously inhibit the mobility of the counterions, resulting in lower optical contrast and extended response time. To overcome this predicament, our group has demonstrated that making the polymer of intrinsic microporosity (PIM) films by introducing rigid and bulky scaffolds. In the previous studies of our group, the TB moieties could be inserted into microporous EC polyamides by replacing the dicarboxylic acid monomers with a TB-containing one. However, as an aromatic diacid, the TB diacid-derived polyamides revealed a light-yellow color at the neutral state compared to those derived from aliphatic diacids. Moreover, being an electron-rich pendent group, we surmised that the TB scaffold could lower the oxidation potential if the TB moiety is directly connected to the electroactive TPA center. Hence, a novel diamine monomer, TBTPA-NH_2, has been designed and synthesized for obtaining the corresponding intrinsic microporous polyamide, PTBTPA. Moreover, alicyclic diacids would be a better replacement for aromatic ones, the fixed ring structure avoids the drawbacks of losing good thermal properties, and the aliphatic nature not only increases the transparency of the neutral state but also provides good solubility of polymers for the membrane preparation.

Experimental

1. Synthesis of PTBTPA

As illustrated in Scheme 1b, 0.103 g (0.6 mmol) of 1,4-cyclohexane dicarboxylic acid and 49.0 mg of calcium chloride were dissolved in 0.8 mL of N-methyl-2-pyrrolidone (NMP) in a 10 mL two-neck flask under a nitrogen atmosphere. TBTPA-NH_2 (0.388 g, 0.6 mmol), pyridine (0.3 mL), and TPP (314 μL, 1.2 mmol) were added, and the mixture was then heated to 110 °C and stirred. After 30 min of stirring, the polymer solution turned sticky, and 0.6 mL of NMP was then added for dilution. The dilution process was repeated two times in the following 1 h. After 1.5 h of the total reaction time, the polymer solution was poured into methanol. The polymer was then washed by Soxhlet extraction with methanol and water for 2 days, respectively. After drying in a vacuum oven at 100 °C, PTBTPA was given as a pale-brownish string (0.451 g, yield = 96%). The inherent viscosity of PTBTPA was 0.61 dL/g (measured in NMP at 30 °C of the concentration of 0.5 g/dL).

2. Preparation of Polyamide Films

The polymeric electrode for electrochemical analysis was prepared using a polymer solution with a concentration of 2 mg/mL in DMAc. 600 μL of the polymer solution was drop-cast on an ITO-coated glass with a size of 30 × 25 mm^2. The solvent was removed under vacuum at room temperature and dried at 180 °C for 12 h. The obtained films were about 360 ± 30 nm thick.

3. Fabrication of electrochromic Devices (ECDs)

First, two pieces of ITO-coated glass with a size of 25 × 30 mm^2 were prepared as two electrodes, and one of the ITO-coated glass was coated with electroactive polyamides with 360 ± 30 nm in thickness. Second, the thermoset adhesive frame (20 × 20 mm^2) with a 5 mm width break was dispensed via an autodispenser. Then, the two glasses were stuck together to form an empty device. The gap distance was controlled by the 120 μm spacer in the adhesive. The adhesive was cured in an oven at 120 °C for 3 h. Finally, the gel-type electrolyte was injected into the device from the 5 mm width break under vacuum conditions, and the break was sealed with UV gel. The gel-type electrolyte was prepared with 670 mg of PMMA, 165 mg of TBABF4 (0.1 M), 40 mg of HV (0.015 M), and 5 mL of propylene carbonate (PC). The total volume of the injected electrolyte was around 48 μL.

Results & Discussion

1. Microporous Properties of Polyamides

With the introduction of the distorted and bulky TB scaffolds, PTBTPA (1.164 g/cm^3) and PTPA-TB (1.171 g/cm^3) revealed lower density than PTPA (1.204 g/cm^3), indicating the higher free volume attributed to the looser packing caused by TB moieties. The specific surface area results revealed that the aid of TB building blocks could significantly enhance the specific surface area of the polyamides, where the specific surface area of PTBTPA (68.32m^2/g) was almost 13 times larger than PTPA (5.18 m^2/g), and the surface area of PTPA-TB (51.83 m^2/g) was 10 times larger than PTPA. Moreover, the pore width distribution of the micropores of the polyamides could be analyzed via Horvath–Kawazoe method. As anticipated, the results revealed that PTBTPA and PTPA-TB, which has TB units in the polymer backbones, displayed a higher density of micropores than PTPA.

2. Electrochemical Properties

With the incorporation of TB units, the oxidation potential of PTBTPA ($E_{oxi.}$ = 1.00 V) and PTPA-TB ($E_{oxi.}$ = 1.02 V) was slightly decreased in comparison to PTPA ($E_{oxi.}$ = 1.05 V). Moreover, the potential differences (ΔE) of the TBincorporated polyamides, PTBTPA (ΔE = 0.39 V) and PTPATB (ΔE = 0.46 V), were significantly lower than PTPA (ΔE = 0.57 V), indicating that the microporous properties generated by the rigid and distorted TB units facilitated the diffusion of counterions within the polymer matrix and lowered the ion transfer

barrier. To further analyze the electron transfer mechanism of the polyamide films, electrochemical impedance spectroscopy (EIS) was adopted using the Randles circuit as a model to determine the conductivity and resistance of the electroactive polyamides. The charge transfer resistance (R_{ct}) of PTBTPA (42.7 Ω) and PTPA-TB (48.4 Ω) revealed a lower resistance in comparison to PTPA (59.4 Ω). The lower energy barrier of charge transfer might be attributed to the high charge mobility of the TB core and the high affinity between two electron-rich nitrogen atoms in the TB unit and the ITO surface due to the hydrogen bond interaction.

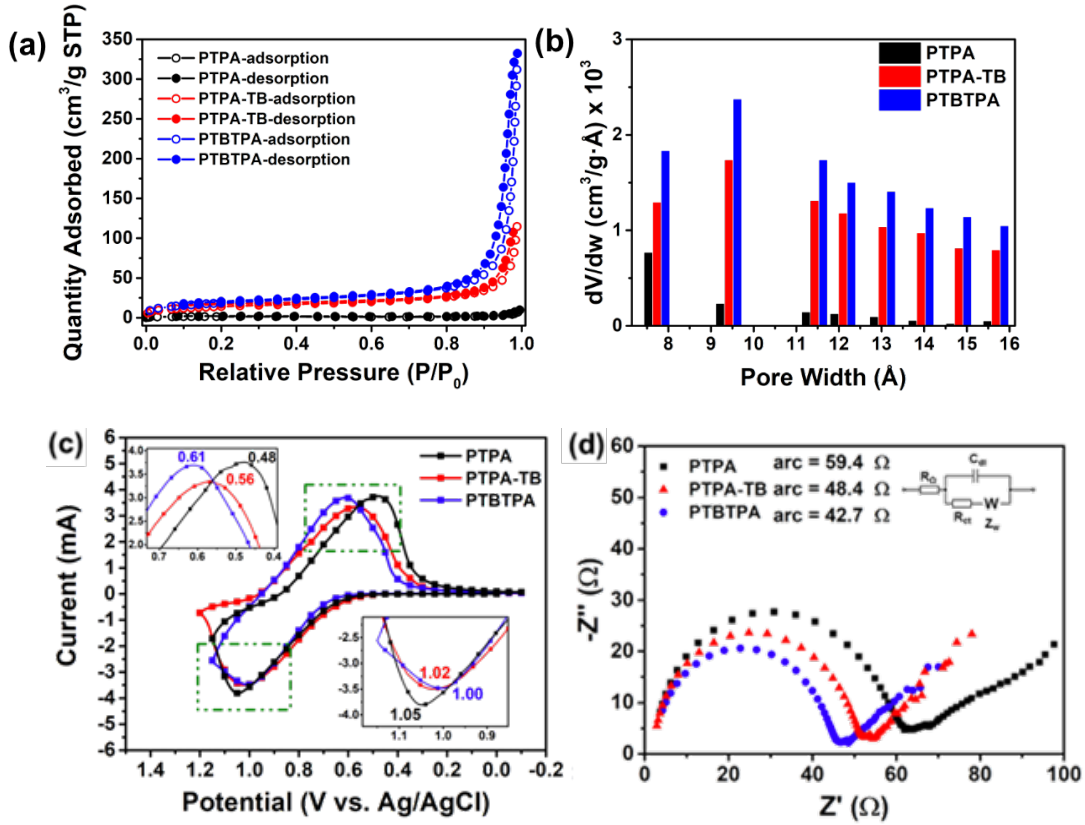


Figure 1. (a) N_2 adsorption and desorption isotherms measured at 77 K. (b) The pore width distribution analyzed by nitrogen adsorption at 77 K via the Horvath–Kawazoe method. (c) Cyclic voltammetry diagrams of resulting polyamides measured on the ITO-coated glass substrate at a scan rate of 50 mV/s. (d) Nyquist plots of PTPA, PTBTPA, and PTPA-TB.

3. Electrochromic Properties

In spectroelectrochemical measurement, These polyamides displayed their characteristic absorption peaks around 385 and 780 nm as the applied potential was increased to 0.95 V, and the appearance of the polymer films turned into dense teal and green colors. The switching response characteristics of PTPA required 5.7 s for coloring and 8.6 s for bleaching to reach 90% of the total optical difference in transmittance. For comparison, incorporating TB scaffolds into polyamides had a notable impact on the response times with shorter times observed for coloring and bleaching. PTBTPA and PTPA-TB showed a response time of 1.8 s for coloring and 1.5 s for bleaching, 68 and 83% shorter than PTPA. The electrochromic device (ECD), PTBTPA/HV showed the highest coloration efficiency (337 cm^2 /C) and the highest stability, keeping 96.1% of the ΔT after 500 continuous switching cycles among the devices.

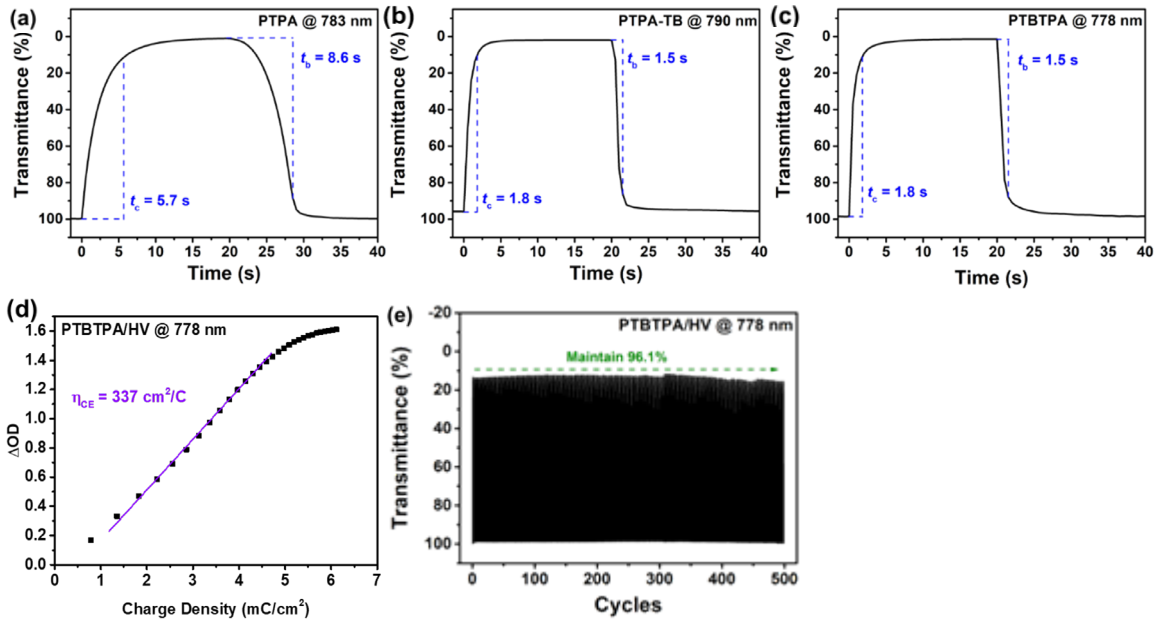


Figure 2. Response time of (a) PTPA, (b) PTPA-TB, and (c) PTBTPA between −0.1 V and 0.95 V between −0.1 V and 0.85 V for 500 cycles. The experiments were measured on the ITO-coated glass substrate in 3 mL of 0.1 M $TBABF_4$/MeCN with a cycle time of 40 s (thickness: 360 ± 30 nm). (d) Coloration efficiency of PTBTPA/HV ECDs with 1.25 V as coloring potential. (e) Switching stability of PTBTPA/HV between -0.1 V and 1.25 V for 500 cycles with a cycle time of 60 s.

Conclusion

Incorporating distorted TB unit into polymer backbone efficiently suppresses chain packing and facilitates ion diffusion. Especially TB-cored PTBTPA showed faster response speed (υ_c = 48.6%/s), and smaller ΔE (ΔE_{CV} = 0.39 V) than PTPA-TB. Furthermore, PTBTPA/HV ECD revealed the best response capability, highest coloration efficiency, and excellent switching stability. Therefore the facile strategy of introducing TB units into polyamides paves the way for developing more energy-efficient and superior devices.

Reference

[1] M. H. Tu, Y. J. Shao, H. L. Li, C. C. Hu*, and G. S. Liou*, Tröger's Base-Cored Triarylamine Polyamide for Electrochromic Response Capability Enhancement, *ACS Appl. Polym. Mater.*, **2024**, 6, 1, 658-668.