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Journal

Abstract

A type of novel triphenylamine (TPA)-based diisocyanide derivative, 4-isocyano-*N*-(4-isocyanophenyl)-*N*-(4-methoxyphenyl)aniline (M1), was successfully synthesized via Hofmann treatment of its primary amine precursor (2). A series of polyamides (P1-P3), which containing TPA units in backbones, were successfully synthesized via efficient benzoxazine-isocyanide-chemistry (BIC) at room temperature by using M1 and bifunctional benzoxazines as starting monomers. Chemical structures of **P1-P3** were verified by FT-IR, ¹H NMR and gel permeation chromatography (GPC) analyses. Polymers' films were prepared by solution coating (using DMSO as solvent), and electrochemical properties of P1-P3 were investigated by cyclic voltammetry (CV). P1-P3 exhibited single-step highly reversible oxidation process, reflecting their good electrochemical activity. Electrochromic properties of polymers were further analyzed by spectroelectrochemical techniques. New absorption bands at ~750 nm appeared in UV-vis spectra of P1-P3 when the applied voltage reached ~ 0.65 V, accompanied by the obvious visual color change (from colorless to blue-green). Response time and coloration efficiency of P1-P3 were also investigated here. The work carried out in this study proved that BIC can act as powerful tool to construct novel functional polyamides.

Keywords: benzoxazine-isocyanide-chemistry (BIC), triphenylamine, polyamide, electrochromism

1 Introduction

Electrochromism (EC) refers to the reversible alteration of optical properties such as absorption, transmittance and reflectivity of materials under an applied electric field [1]. EC materials (ECMs) have been widely used in many fields, including architectural and smart windows [2], anti-glare mirrors [3] and displays [4], etc. Among various ECMs, organic polymers have been acknowledged as a type of high-performance ECMs because of their good cycle stability [5], fast switching speed [6], simple processing [7], and sometimes multiple color changing capability (switching between different redox states) [8, 9]. To date, many polymer-based ECMs have been reported, such as polythiophene [10], polyaniline [11], polycarbazole [12], polypyrrole [13], polyfluorene [14] and polyarylamine [15], etc.

Thanks to their capability to form stable cationic radicals and low oxidation potential [16-18], aromatic amine-based polymers are representative polymeric ECMs. Among of them, the polymers containing triphenylamine (TPA) fragments are the most popular samples, which have been intensively investigated and with satisfactory comprehensive performance [19-21]. According to the main chain structures of poly-TPAs, they can be divided into conjugated and non-conjugated ones. Jeong *et al* synthesized a series of TPA-based conjugated polymers (CPs) by Suzuki coupling reaction [22], the obtained polymers exhibited good thermal stability and electrochromic properties. Xu *et al* prepared a class of TPA-based donor- π -bridge-acceptor type CPs *via* Stille coupling polymerization [23], and the

introduction of different electrophilic groups brought different electrochromic behaviors to polymers. Toppare's group synthesized a series of CPs based on TPA, benzotriazole, and thiophene via Stille coupling [24], and the obtained polymers exhibited fast switching response. However, highly expensive palladium-catalysts were inevitably used in the preparation of these TPA-based conjugated materials [24-26]. Conjugated TPA polymers can also be prepared by electrochemical polymerization protocol [8, 27]. However, the low utilization of monomer [28], nonuniform film formation and the difficulty in large-scale preparation [29] greatly restrict the application of electrochemical polymerization [30]. TPA-based polyamides (TPA-PAs) are one of the most widely studied non-conjugated polymeric ECMs. There is no requirement for metal catalysts in the syntheses of TPA-PAs [19], and the solubility, film-formability and electrochemical properties of polymers can be effectively improved by combining TPA units with polyamide (PA) backbones [31, 32]. The most common method for the preparation of TPA-PAs is the condensation between TPA-based diamines and dicarboxylic acid monomers [33]. Sun et al reported a series of TPA-based PAs by the condensation between TPA-derivatived diamines and dicarboxylic acid monomers, and the obtained polymers exhibited high electrochromic absorption/fluorescence contrast, outstanding switching stability, and fast response speed [34, 35]. Such amine-carboxylic acid condensation usually requires strict purity of monomers, and must be carried out under high reaction temperature (>100 °C), which tend to cause unwilling side reactions [36]. PAs can also be prepared by direct condensation between diamines and di-acylchloride at

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ambient temperature [36]. Nevertheless, there is much difficulty in the preparation, purification and preservation of acylchlorides, and the corresponding structural designing flexibility is poor [37], which greatly limits its utilization in TPA-PAs. Therefore, there is an urgent demand for developing efficient synthesis method for TPA-PAs under mild conditions.

In 2018, our group reported a new method for synthesizing PAs by using aromatic isocyanides and benzoxazines as raw materials and octylphosphoric acid (OPA) as catalyst [38]. The specific reaction between benzoxazines and isocyanides (Benzoxazine-Isocyandie Chemistey, BIC) displayed many advantages, such as smooth occurrence at room temperature, metal-catalyst free, short polymerization time (6 h) and insensitive to water and oxygen. Based on BIC reaction, very recently our group designed a class of tetraphenylethylene-contaning functional PAs and explored their applications in the fields of optical probing and heterogeneous catalysis [39]. These works have provided successful experience for the construction of functional PAs *via* BIC reaction. With TPA-derivatived isocyanide compound as starting monomer, it is expected that TPA groups can be introduced into PAs skeleton under mild conditions *via* BIC reaction to construct corresponding ECMs. To the best of our knowledge, such work has not been reported by far.

In this study, we designed and synthesized a type of novel TPA-derivatived diisocyanide monomer, 4-isocyano-*N*-(4-isocyanophenyl)-*N*-(4-methoxyphenyl)aniline (**M1**). A series of PA derivatives containing TPA functional units (**P1-P3**) were successfully prepared by

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BIC reaction under mild condition by using different bifunctional benzoxazines and **M1** as monomers. All these PAs showed good solubility and thermal stability, and can form homogeneous and transparent films by coating of their solution. Cyclic voltammetry (CV) of polymers' films displayed obvious electrochemical activity. Upon oxidation, the color of polymer films changed from colorless to blue-green. Based on this, the electrochromic behaviors of **P1-P3** were subsequently investigated here.

2 Experimental section

2.1 Materials

p-Anisidine, cesium fluoride, 4-fluoronitrobenzene, palladium/carbon (10%), octylphosphonic acid (OPA), tetrabutylammonium hydroxide, paraformaldehyde, tetrabutylammonium perchlorate (TBAP) and other reagents and chemicals were purchased from Adamas or Acros and used as received. Indium tin oxide (ITO)-coated glass (50 mm × 7 mm × 1 mm, 5 Ω per square, Sigma-Aldrich) were used for substrates to load polymer films. 4-Methoxy-*N*, *N*-bis(4-nitrophenyl)aniline (**1**) and *N*-(4-aminophenyl)-*N*-(4-methoxyphenyl)benzene-1, 4-diamine (**2**) [40, 41], 1, 4-bis(2-(4-(6-nonyl-2H-benzo[e][1, 3]oxazin-3(4H)-yl)phenyl)propan-2-yl)benzene (**B1**) [38], bis(4-(6-nonyl-2H-benzo[e][1, 3]oxazin-3(4H)-yl)phenyl)methane (**B2**) [38] and 6, 6'-(propane-2, 2-diyl)bis(3-hexyl-3, 4-dihydro-2H-benzo[e][1, 3]oxazine) (**B3**) [38] were synthesized according to previously reported methods.

2.2 Instruments

FT-IR spectra were recorded on a WQF-520 FT-IR spectrometer in the range of

4000-500 cm⁻¹. ¹H and ¹³C NMR spectra were measured on a Bruker AVANCE III HD NMR spectrometer at 400 MHz and 101 MHz using tetramethylsilane (TMS) as an internal reference in CDCl₃. High resolution mass spectra (TOF-MS) were performed on Waters O-TOF Premier. Melting point was measured by X-4 digital melting-point microscope (Beijing Tech Instrument Co., China). Thermogravimetric (TG) analyses were recorded on METTLER TOLEDO TGA-DSC1 (under nitrogen, with a heating rate of 10 °C/min). Gel permeation chromatographic (GPC) data were collected from a Waters 1515 instrument using tetrahydrofuran (THF) as an eluent with a flow rate of 1.0 mL/min. UV-vis absorption spectra were recorded by a SHIMADZU UV-1800 spectrophotometer. Cyclic voltammetry (CV) were conducted using a CHI 760e electrochemical workstation at a scan rate of 50 mV/s⁻¹ with a nitrogen-saturated solution of 0.1 M TBAP in acetonitrile (CH₃CN). Electrochemical impedance spectrum (EIS) tests were obtained with a CHI 760e electrochemical workstation at the frequency range of 0.1 to 100 kHz in 0.1 M TBAP/CH₃CN. Theoretical calculations were performed within the spin-unrestricted density functional theory (DFT) framework as implemented in DMol³ code [42]. The generalized gradient approximation with the Becke (exchange) and the Lee-Yang-Parr (correlation) functional (BLYP) [43], together with double-numeric quality basis set (DNP), was used throughout all calculations. The convergence tolerance for energy change, max force, and max displacement were 2×10^{-5} Ha, 0.004 Ha Å⁻¹, and 0.005 Å, respectively.

2.3 Synthesis of 4-isocyano-N-(4-isocyanophenyl)-N-(4-methoxyphenyl)aniline

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(M1)

Compound 2 (305 mg, 1 mmol), dichloromethane (10 mL) and aqueous sodium hydroxide (10 mL, 33%) were transferred into a two-necked bottle, and tetrabutylammonium hydroxide (26 mg, 0.1 mmol) was added as a surfactant. Chloroform (165 µL, 2 mmol) was added to the reaction system by pipette, and the mixture was refluxed for 3 h under nitrogen atmosphere. The solution was cooled to room temperature and washed three times by deionized water. The organic phase was separated and dried over by MgSO4. The crude product was purified by chromatography (silica gel, ethyl acetate/petroleum ether/triethylamine = 3:30:1, v/v/v) and dried in vacuum for 24 h at 50 °C to get final product as tawny powder (108 mg, 33% yield). m. p. 105-106 °C. FT-IR (KBr, cm⁻¹): 2924, 2852, 2120, 1594, 1500, 1289, 1243. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm) 7.25-7.20 (d, J = 4.7 Hz, 4H), 7.06-7.01 (d, J = 4.4 Hz, 2H), 7.01-6.96 (d, J = 4.7 Hz, 4H), 6.92-6.87 (d, J = 4.4 Hz, 2H), 3.82 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (ppm): 163.39, 157.76, 147.83, 138.49, 128.16, 127.52, 122.42, 120.50, 115.46, 55.36. TOF-MS calcd. for $C_{21}H_{15}N_{3}O: 325.1221.$ found $[M1+H]^{+}: 326.1290, [M1+Na]^{+}: 348.1128, [M1+K]^{+}:$ 364.0863.

2.4 Syntheses of TPA-PAs (P1-P3)

P1-P3 were synthesized according to the procedures reported by our group [38]. A typical procedure for the preparation of **P1** was given as an example here: OPA (15.5 mg, 0.08 mmol), water (7.2 μ L, 0.4 mmol) and **B1** (186.6 mg, 0.2 mmol) were dissolved in 2 mL of chloroform in a two-necked flask, and stirred for 5 min in ice

bath. **M1's** chloroform solution (2 mL, 0.1 M) was added dropwise to the reaction system and kept stirring for 0.5 h in ice bath, and stirred for 6 h at room temperature. The resultant solution was concentrated and added dropwise to 100 mL of cold ethyl ether. The precipitate was collected by filtration and dried under vacuum for 24 h to give polymerization product.

P1: brown powder, 170 mg (70% yield). FT-IR (KBr, cm⁻¹): 3287, 2956, 1676, 1604, 1500, 1278, 1244. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm) 9.11 (hydroxyl protons), 7.57-6.46 (aromatic protons), 4.50 (-CH₂ protons), 3.80 (-CH₂ protons), 3.68 (-OCH₃ protons), 1.85-0.22 (-CH₂ and -CH₃ protons). GPC: M_n = 11832, PDI = 1.85.

P2: yellow powder, 140 mg (65% yield). FT-IR (KBr, cm⁻¹): 3287, 2956, 1676, 1604, 1500, 1278, 1244. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm) 9.11 (hydroxyl protons), 7.50-6.49 (aromatic protons), 4.43 (-CH₂ protons), 3.80 (-CH₂ protons), 3.72 (-OCH₃ protons), 1.76-0.28 (-CH₂ and -CH₃ protons). GPC: $M_n = 7398$, PDI = 1.88.

P3: tawny powder, 96 mg (55% yield). FT-IR (KBr, cm⁻¹): 3287, 2956, 1676, 1604, 1500, 1278, 1244. ¹H NMR (400 MHz, CDCl₃) δ (TMS, ppm) 9.11 (hydroxyl protons), 7.48-6.54 (aromatic protons), 3.84-3.45 (-CH₂ and -OCH₃ protons), 3.17 (-CH₂ protons), 2.56 (-CH₂ protons), 1.73-0.70 (-CH₂ and -CH₃ protons). GPC: M_n = 4125, PDI = 1.88.

2.5 Electrochemical performance investigation

ITO glasses were washed subsequently with pure water, acetone, and ethanol by ultrasonication. Each PA sample (6 mg) was dissolved in 2 mL of DMSO, and the resultant solution was dropped onto ITO and vacuum dried at 70 °C for 12 h to

remove the solvent. Surfaces of obtained polymer films were coated with Nafion solution (2.5 wt%) as the binding agent, and vacuum dried at 40 $^{\circ}$ C for 5 h to obtain final films (with areas of ~ 21 mm × 7 mm). The spectroelectrochemical cell was composed of a quartz cuvette with a three electrode system (ITO-supported polymer film as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode) for subsequent electrochemical and electrochromic performance tests.

3 Results and discussion

3.1 Synthesis of M1 and P1-P3

Due to the occurrence of para-coupling dimerization between TPA segments during oxidation process, the electrochemical reversibility of TPA-PAs is usually unsatisfactory when there are unsubstituted benzene rings in TPA structure [44-46]. Such para-coupling dimerization can be prevented by the introduction of occupying substituents into the para-position of TPA, improving the electrochromic stability thus [47]. Liou's group developed a series of PAs with the occupation of different substituents at the para-position of TPA, and their electrochromic properties were studied in depth [48-53]. Experimental results showed that the stabilization of TPA cationic radicals can be realized by introducing electron-donating substituents, and PAs with methoxyl group (-OCH₃) at the para-position of TPA group displayed better electrochromic stability and chromogenic efficiency than corresponding values regarding other substituents [46]. Along with this line, -OCH₃ was also selected here to act as the occupation site in TPA, and the synthetic route of **M1** is displayed in

Scheme 1. Using a triphenylamine-based primary amine derivative (2) as precursor, the corresponding diisocyanide monomer (M1), which with a methoxyl substituent at the para position was synthesized *via* simple and convenient Hofmann reaction.



Scheme 1. Synthetic route of P1, P2 and P3.

FT-IR spectrum of **M1** (**Figure 1(a**)) shows a distinct absorption signal at ~ 2120 cm^{-1} , which belongs to the stretching vibration of isocyanide (-NC) group [54]. The signals at ~ 2924 and ~ 2852 cm⁻¹ correspond to the stretching vibration of methoxyl group (-OCH₃). The characteristic absorption of benzene skeleton (C=C) appears at 11

~1594 and ~ 1500 cm⁻¹. The distinctive vibration at ~ 1289 and ~ 1243 cm⁻¹ can be assigned to the stretching of C-N (in TPA) and C-O (in-OCH₃) bonds. In ¹H NMR spectrum of M1 (Figure (1b)), four groups of aromatic proton signals appear at δ 7.25-7.20, 7.06-7.01, 7.01-6.96 and 6.92-6.87 ppm, respectively, and their assignments are shown in the inset of Figure 1(b). The characteristic peak at δ 3.82 ppm corresponds to the $-OCH_3$ group (e). The protons integral is consistent with the chemical structure of M1. As shown in Figure 1(c), the characteristic peak at δ 163.39 ppm corresponds to -NC carbon (a). The signal at δ 157.76 ppm is assigned to the aromatic carbon (i), which directly links to $-OCH_3$. Peaks at δ 147.38–115.38 ppm are attributed to other carbons on the benzene ring (corresponding assignment can be traced in **Figure 1(c)**), and the signal at δ 55.36 ppm corresponds to the -OCH₃ carbon (j). Three distinctive mass signals appear in the TOF-MS spectrum of M1 (Figure S1) at 326.1290 $[M1+H]^+$, 348.1128 $[M1+Na]^+$ and 364.0863 $[M1+K]^+$, respectively, which is in good agreement with the theoretical value ($C_{21}H_{15}N_3O$, calcd. 325.1221). The above analyses solidly prove that M1 has been successfully prepared.





Figure 1. FT-IR (a), 1 H NMR (b) and 13 C NMR (c) spectra of M1.

With M1 in hand, the preparation of corresponding PAs (P1-P3) was carried out subsequently with M1 and bifunctional benzoxazines (B1-B3) as starting monomers (Scheme 1). The molecular design strategy and utilization of B1-B3 as starting monomers mainly based on the following considerations: I) flexible alkyl chains present in the structures of **B1-B3** can endow targeted polymers with good solubility in chloroform (as polymerization solvent), preventing the precipitation of polymerization product from reaction system to terminate propagation prematurely; II) investigation regarding the influence brought by the aromatic (for **B1** and **B2**) and alkyl (for B3) N-substituents (on benzoxazine) to BIC-polymerization and subsequent electrochromic properties could be helpful to get more insight about BIC reaction and further performance modification. On the other hand, benefiting from its high reactivity, mild reaction condition and great molecular designing flexibility, BIC reaction holds the prospective potential in the construction of novel functional PAs. Based on this, with OPA as catalyst, corresponding PAs (P1-P3) were facilely obtained by stirring M1 and bifunctional benzoxazines (B1-B3) in chloroform at 13

room temperature for 6 h.

From FT-IR spectra of resultant polymers (**Figure 2**), it can be seen that the three polymers exhibit similar spectral characteristics. The stretching vibration signal of phenolic hydroxyl (-OH) and amide (-C=O-<u>NH</u>) groups appear at ~ 3287 cm⁻¹, and the absorption of carbonyl group (C=O) (in amide segment) locates at ~ 1676 cm⁻¹. The vibration absorption of C-N-C bonds in TPA and tertiary amine moieties can be observed at ~ 1278 cm⁻¹, and the signal at ~ 1244 cm⁻¹ corresponds to the C-O-C stretching of methoxyl group.



Figure 2. F1-IK spectra of F1-F3.

¹H NMR spectra of **P1-P3** are shown in **Figure 3**. Slight proton signals at $\delta \sim$ 9.11 ppm appear in the spectra of **P1-P3** (marked as "a"). This can be assigned to the phenolic hydroxyl (-OH) groups [38], which were formed during BIC polymerization. As revealed by **Figure 3**, ¹H NMR spectra of **P1** and **P2** highly resemble to each other, which stems from their similar backbone structures. Aromatic protons of these two polymers appear at δ 7.40-6.14 ppm, and the peaks at δ 4.58-3.55 ppm belong to methylene (-CH₂-, adjacent to the tertiary amine, b&c) and methoxyl (-OCH₃, d)

groups in polymers' structures. Hydrogen signals of alkyl side chains appear at δ 1.85-0.22 ppm. The aromatic protons in the spectrum of **P3** appear at δ 7.48-6.54 ppm. Distinct form that of P1 and P2, there are three groups of N-adjacent methylene protons (b', c' and e') appear in the spectrum of P3, and their chemical environment are significantly affected by the presence of non-aromatic hexyl substituent on the tertiary amine segment. The signals of a portion of methylene protons (b') mix with that of $-OCH_3$ (d'), appearing at δ 3.84-3.45 ppm. Other two groups of $-CH_2$ - (c'&e') appear at δ 3.17 (c') and 2.56 (e') ppm, respectively. Moreover, in the spectrum of P3, two sets of tiny -CH₂- signals, which correspond to the benzoxazine ring, appear at δ 4.79 (square) and 3.90 (circle) ppm. This indicates that there are some residual benzoxazines on the chain ends of P3, suggesting that the degree of polymerization of P3 is lower than that of P1 and P2. From the mechanism of BIC [38], the first step of the reaction relies on the H⁺-promoted ring opening of benzoxazine to form iminium (I) intermediate (Scheme 2). When the substituent (R) on the N atom is an aromatic group, the conjugation effect is helpful to stabilize I, facilitating its formation thus. During the polymerization of P3, the non-aromatic alkyl chain brings ambiguous influence to the stability of intermediate I, and unfavorable to subsequent chain propagation. Such hypothesis was also supported by molecular weights comparison between P1-P3 (will be discussed in following section). The above structural analyses indicate that the target polymers have been successfully prepared.



Figure 3. ¹H NMR spectra of prepared PAs.



Scheme 2. Mechanism about the acid-promoted ring-opening of benzoxazine to form iminium I.

3.2 Solubility, molecular weights, thermal and UV-vis absorption properties of P1-P3

The solubility of **P1-P3** was evaluated here, and the results are summarized in **Table 1. P1-P3** not only display good solubility in polar solvents (NMP, DMSO, DMF, etc.), but also completely soluble in weak polar solvents (CHCl₃ and THF). Good solubility and solvent adaptability of **P1-P3** can be attributed to the simultaneous introduction of flexible alkyl chains and polar groups (phenolic hydroxyl and amides) into polymer structures. In addition, it is reported that the introduction of helical TPA group can effectively improves the solubility of polymers [55]. The excellent solubility ensures that these polymers can be fabricated by simple and convenient

solution coating processes [30].

| Sampla | | | | Solve | nts ^a | | | | GPC ^b | |
|-----------|-----|-----|------|-------|------------------|-------------------|--------------------|-------|------------------|------|
| Sample | NMP | DMF | DMSO | THF | Dioxane | CHCl ₃ | CH ₃ CN | M_n | $M_{\rm w}$ | PDI |
| P1 | ++ | ++ | ++ | ++ | ++ | ++ | | 11832 | 21949 | 1.85 |
| P2 | ++ | ++ | ++ | ++ | ++ | ++ | | 7398 | 13981 | 1.88 |
| P3 | ++ | ++ | ++ | ++ | +- | ++ | | 4125 | 7768 | 1.88 |

Table 1 Solubility and molecular weights of P1-P3.

^a Qualitative solubility were tested by using 2 mg of polymers in 1 mL of solvent (++: soluble at room temperature; +-: partially soluble; --: insoluble even on heating). ^b Relative to polystyrene standard, using THF as the eluent.

Molecular weights of **P1-P3** were evaluated by GPC, and the corresponding retention curves and molecular weights values can be traced in **Figure S2** and **Table 1**. From **Figure S2**, a single signal peak appears in curves of **P1-P3**, and the retention time is in the order of **P1**<**P2**<**P3**. It can be seen from **Table 1** that the M_n of **P3** (4125) is significantly lower than the corresponding values of **P1** (11832) and **P2** (7398), which consistent with the information reflected by their ¹H NMR analyses. From **Table 1** one can note that **P1-P3** have narrow PDIs (with PDI < 1.88), indicating that the molecular chains length is relatively uniform in these polymers.

The thermal stability of **P1-P3** was examined by TG analysis. TG curves are shown in **Figure 4** and the relevant data are summarized in **Table 2**. The 10% weight loss temperatures of **P1-P3** (in nitrogen) are 337, 323 and 292 °C, respectively. The 50% weight loss temperature of these polymers are all higher than 400 °C, reflecting the satisfactory thermal stability of them. The char yields of **P1-P3** at 800 °C are 22%, 28% and 24%, respectively. Their relatively lower char yields can be attributed to the large

content of long alkyl chains in polymers structures, which were gasified at high temperature.



Figure 4. TG curves of P1, P2 and P3.

| Table 2 Thermal properties of the PAs. | | | | | | | | |
|--|----------------------------|-----------------------------|-----------------------------|--|--|--|--|--|
| Sample | $T_{d5\%} (^{\circ}C)^{a}$ | $T_{d10\%} (^{\circ}C)^{a}$ | Char yield (%) ^b | | | | | |
| P1 | 308 | 337 | 22 | | | | | |
| P2 | 300 | 323 | 28 | | | | | |
| P3 | 274 | 292 | 24 | | | | | |

^a Decomposition temperature, recorded at a heating rate of 10 °C/min, under nitrogen. ^b Residual weight percentage at 800 °C.

The UV-vis absorption of **P1-P3** in solution was also investigated here. As shown in **Figure S3**, these polymers exhibit absorption maxima at ~314 nm in DMSO, which can be attributed to the π - π * transition in triphenylamine segments [56].

3.3 Electrochemical properties of P1-P3

The electrochemical properties of **P1-P3** were characterized by CV. Due to the similar main chain structure of these polymers, their films exhibit similar electrochemical behaviors (**Figure 5**). A pair of highly reversible oxidation-reduction 18

processes appear in CV curves of **P1-P3**, indicating that the introduction of TPA moiety endow these polymers with good electrochemical activity. The half-wave oxidation potentials ($E_{1/2}$) of **P1-P3** locate separately at 0.84, 0.83, and 0.81 V, with the oxidation onset potentials (E_{onset}) at 0.66, 0.64, and 0.64 V, respectively, which corresponds to the electron-loss process of TPA moiety in polymer backbones [45]. One can also find from **Figure 5** that the oxidation peak currents of **P1-P3** are higher than the corresponding reduction values, indicating that the electron donor in polymers acts more prominently than the acceptor [57]. The highest occupied molecular orbital (HOMO) energy levels can be estimated by E_{onset} [58] of **P1-P3**, to be -5.46, -5.44 and -5.44 eV, respectively. The optical band gaps (E_g) of **P1-P3** can be evaluated by their respective UV-vis absorption onsets (**Figure S4**), and the relevant data are listed in **Table 3**. The lowest unoccupied molecular orbital (LUMO) energy levels of **P1-P3** can be estimated by their respective UV-vis absorption onsets (**Figure S4**), and the relevant data are listed in **Table 3**. The lowest unoccupied molecular orbital (LUMO) energy levels of **P1-P3** can be estimated by their respective HOMO and E_g values, to be -2.21 -2.22 and -2.17 eV, respectively.



Figure 5. Cyclic voltammetric diagrams of **P1**, **P2** and **P3** films on an ITO-coated glass substrate in CH₃CN solutions containing 0.1 M TBAP at a scan rate of 50 mV/s.

In order to visually describe the orbital distribution of **P1-P3**, the repeating unit of polymers were theoretically calculated by DFT. The corresponding distribution images are shown in **Figure 6** (since **P1** and **P2** have identical TPA-amide substructural motif, we just simulated the orbital distribution of **P1** and **P3** here). As can be seen from **Figure 6**, the HOMO orbitals of **P1** (**Figure 6(a)**) and **P3** (**Figure 6(c)**) focus on the electron-rich TPA region (as donor), while the LUMO orbitals (**Figure 6 (b)**&(**d**)) spread on the junction part between TPA and amide moieties (as acceptor), indicating that there is a certain degree of charge transfer in the molecule. One can also find that aromatic (for **P1**) or alkyl (for **P3**) substituents in the tertiary amine groups have no significant effect on the orbital distribution.



Figure 6. Calculated HOMO and LUMO orbital diagrams of P1 (a&b) and P3 (c&d).

| | | | | | 0, | | |
|---|-----------|--------------------------|------------------------|------------------|-----------------|---------------|------------------------|
| | Polymer | $\lambda_{onset} (nm)^a$ | E _{onset} (V) | $E_{1/2}(V)^{b}$ | $E_{g}(eV)^{c}$ | HOMO $(eV)^d$ | LUMO (eV) ^e |
| _ | P1 | 382 | 0.66 | 0.84 | 3.25 | -5.46 | -2.21 |
| | P2 | 385 | 0.64 | 0.83 | 3.22 | -5.44 | -2.22 |
| | P3 | 379 | 0.64 | 0.81 | 3.27 | -5.44 | -2.17 |
| | | | | | | | |

Table 3 Electrochemical and energy levels of P1-P3.

 $^a\,\lambda_{onset}\!\!:$ absorption onset wavelength in film state.

^b $E_{1/2}$: average potential of the redox couple peaks.

^c E_g: Calculated by $1240/\lambda_{onset}$.

^d HOMO energy levels were calculated from E_{onset} using Ag/AgCl (4.8 eV) as reference, with the formula of HOMO = -(E_{onset} + 4.8) eV. ^e LUMO = HOMO + E_{g} .

The electrochemical stability of polymers was further studied by successive CV tests. As shown in **Figure 7**, after 30 cycles of CV tests all curves illustrate certain degree of decay in peak current, but still retain good oxidation-reduction reversibility. The CV profiles display ambiguous alteration during successive redox cycles for all polymers (**Figure 7**), suggesting that the introduction of methoxyl to the para-position of TPA are favorable to stabilize the resultant cationic radicals and efficiently prevent the coupling between TPA moieties.





Figure 7. Cyclic voltammetric diagrams of P1 (a), P2 (b) and P3 (c) films for continuous 30 cycles.

3.4 Electrochromic properties of P1-P3

During the CV testing of polymers, it can be clearly observed that P1-P3 films illustrated obvious color change in the electrochemical redox process, revealing that these polymers might possess electrochromic properties. The electrochromic performance of polymers was further studied by spectroelectrochemical technique. As shown in Figure 8(a), when the applied voltage increases to 0.65 V, P1 exhibits a new absorption band at ~ 755 nm, which keeps pace with its oxidation initiation (Table 3). This spectral change can be attributed to the formation of TPA⁺ radical [18] during the oxidation process. With the applied voltage increasing from 0.64 to 0.84 V, the absorbance at ~ 755 nm gradually raise, accompanied by the apparent color change of the film (from colorless to blue-green, inset in Figure 8(a)), reflecting the formation of more TPA cations [59]. With the further enhancement of driving potential (> 0.84V), the absorbance begins to fall, and the whole change trend is similar to the alteration of current in CV curve (Figure 7). As reflected by Figure 8(b) and Figure 8(c), P2 and P3 exhibit similar electrochromic behaviors as that of P1, which is reasonable since they have similar main-chain structures.



Figure 8. Absorbance spectra of **P1** (a), **P2** (b) and **P3** (c) thin-films on the ITO-coated glass substrate in 0.1 M TBAP/CH₃CN at different applied potentials (insets is the visual color change images).

The transmittance changing behaviors of **P1-P3** between neutral and oxidation states were investigated further. Corresponding relationships between transmittance/current density and time are shown in **Figure 9** ((**a**), (**c**) and (**e**)), and corresponding electrochromic performance data are summarized in **Table 4** and **Table 5**. The maximum transmittance changes (ΔT_{max}) of **P1-P3** are 22, 23 and 37%, respectively, which are comparable to reported values of other TPA-base polymers [24, 60]. Electrochromic response time refers to the time required for a material to switch from one color state to another (defined by converting 90% transmittance), including 23

the coloring time (t_c) and bleaching time (t_b), which is one of the important parameters for evaluating electrochromic speed [61]. According to **Figure 9** ((**b**), (**d**) and (**f**)), t_c values of **P1-P3** are 6.2, 5.1 and 5.7 s, and t_b values are 5.8, 4.7 and 5.1 s, respectively. These response time values are relatively larger than those of other typical TPA-based PAs (**Table 4**). Hydrogen bonding might be induced between polymer chains due to the presence of polar amide and phenolic hydroxyl moieties in the structures of **P1-P3**, reducing the free volume between polymer chains. As was reported by Sun *et al*, such close packing between polymer chains is unfavourable for the transport of electrolyte ions during the electrochromic process [34, 35], prolonging the switching time thus.



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Figure 9 Optical switching of P1 (between 0 and 0.84V) (a), P2 (between 0 and 0.82 V) (c) and P3 (between 0 and 0.82 V) (e) (with cycle time of 20 s) and the corresponding optical switch times (b, d and f) (P1-P3 were monitored at 755, 751 and 755 nm, respectively).

Electrochromic coloration efficiency (CE) is another important parameter of ECMs, which can be calculated by the formula of $\delta_{OD} = \log(T_b/T_c)$ and $CE = \delta_{OD}/Q$ (where T_b and T_c represent the transmittance before and after coloring; δ_{OD} is the alteration of optical density, which is proportional to the amount of coloring center; Q (mC/cm²) refers to the amount of charge injected or extracted per unit area) [62]. According to the transmittance-time curves obtained under the multipotential step condition (**Figure 9**), δ_{OD} values of **P1-P3** can be evaluated to be 0.1459, 0.1579 and 0.2659, respectively (**Table 5**). CE values of **P1-P3** are 225, 212 and 247 cm²/C, respectively (with corresponding Q values of 0.648, 0.744 and 1.075 mC/cm²).

| Polymer | M _n | $\lambda_{\text{monitored}}$ | ΔT _{max} (%) | Response time ^b | | Decay ^c | Reference | |
|---|----------------|------------------------------|--------------------------|-------------------------------|------------|--------------------|--------------|--|
| | | (nm) | | $t_{c}(s)$ | $t_{b}(s)$ | (%) | | |
| [#0 ₁₀ #808#] 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 | 45900 | 813 | / | 1.6 | 1.2 | 9.1 | [34] | |
| ^{الا} تين ⁴⁸ تي ²⁴ . ب ت | 79400 | 970 | 60 | 5.65 | 0.98 | 51 | [63] | |
| [, , , , , , , , , , , , , , , , , , , | 69600 | 545 | 1 | 4.1 | 1.0 | / | [64] | |
| | 59400 | 900 | Q' | 4.6 | 2.0 | 2.88 | [21] | |
| Hoo Hoo Hoo Hoo Hoo Hoo Hoo Hoo Hoo Hoo | 20500 | 800 | 83 | 3.2 | 1.0 | / | [65] | |
| [NH NH NH NH NH NH NH SC NH NH SC SC NH NH SC SC NH NH SC SC NH NH SC SC NH NH SC SC NH NH SC SC NH NH SC SC NH NH SC SC SC SC SC SC SC SC SC SC SC SC SC | 41200 | 421 | / | 1.3 | 0.5 | / | [35] | |
| P1 | 11832 | 755 | 22 | 6.2 | 5.8 | 9.7 | This work | |
| P2 | 7398 | 751 | 23 | 5.2 | 4.7 | 64.6 | This work | |
| P3 | 4125 | 755 | 37 | 5.7 | 5.1 | 33.2 | This work | |

| Table 4 The sum | nmary of molecular wei | ights and el | lectrochromic p | performances o | f our |
|-----------------|------------------------|--------------|-----------------|----------------|-------|
| | polymers and other typ | pical TPA-b | based polyamid | es. | |

^a Given wavelength where the data were determined. ^b Time taken for 90% of the full-transmittance change. ^C Decay of coloration efficiency after 300 cyclic scans.

| Polymer | $\delta^a{}_{OD(1)}$ | $\delta^a_{OD(50)}$ | $Q^{b}_{(1)}$ (mC/cm ²) | $\frac{Q^{b}_{(50)}}{(mC/cm^{2})}$ | $\frac{CE^{c}_{(1)}}{(cm^{2}/C)}$ | $\frac{\text{CE}^{c}_{(50)}}{(\text{cm}^{2}/\text{C})}$ |
|-----------|----------------------|---------------------|--|------------------------------------|-----------------------------------|---|
| P1 | 0.1459 | 0.1594 | 0.648 | 0.724 | 225 | 220 |
| P2 | 0.1579 | 0.1439 | 0.744 | 0.709 | 212 | 203 |
| P3 | 0.2659 | 0.1907 | 1.075 | 0.836 | 247 | 228 |

| Table 5 (| Optical an | nd electrochemica | l data collected from | n CE measurements | of P1-P3. |
|-----------|------------|-------------------|-----------------------|-------------------|-----------|
|-----------|------------|-------------------|-----------------------|-------------------|-----------|

^a Optical density change at the given wavelength after cyclic scans.

^b Injected charge is determined from the in situ experiments.

^c Coloration efficiency is calculated from the equation of $CE = \delta_{OD}/Q$.

Stability of electrochromic switching of **P1-P3** has also been investigated here. As shown in **Figure S5**, after 300 switching cycles all curves reveal certain degree of decay, and the loss rates of CE for **P1-P3** are evaluated as 9.7%, 64.6% and 33.2%, respectively. To get insight about such difference in CE stability for our polymers, electrochemical impedance spectroscopy (EIS) were studied to find if there is relationship between impedance and CE. As can be seen from the corresponding Nyquist curve (**Figure S6**), the semicircular diameters of three polymers in high frequency region are close to each other, suggesting that there is similar charge transfer resistances (R_{ct}) for them. This suggests that the relatively poor electrochemical stability of **P2** and **P3** is not due to their larger impedance. Given the similar backbone structures of **P1-P3**, the lower molecular weight and presence of residual active end groups might be responsible for the relatively poorer stability of **P2** and **P3**.

Finally, molecular weights and electrochromic performances of our polymers and other reported TPA-based PAs are summarized here (**Table 4**) to make a direct

comparison between them. As reflected by **Table 4**, the comprehensive electrochromic performances of our polymers are inferior to other typical PAs. We speculate that this might be owing to the synergism of relatively smaller molecular weights (**Table 4**), lower electrochromic site density (triarylamine substructure per each repeating unit) and closer packing of polymer chains of our polymers than others.

4 Conclusions

In summary, a serious of novel TPA-containing PAs (P1-P3) were successfully synthesized at room temperature via efficient BIC reaction. Solubility tests indicated that the introduction of TPA segment endowed polymers with good solubility in common organic solvents, and the corresponding films can be prepared by practical-simple solution coating process. P1-P3 showed a pair of highly reversible oxidation-reduction peaks in CV tests. DFT simulation shown that P1-P3's HOMO orbitals focus on the electron-rich TPA region, while LUMO orbitals spread on the conjugation part between TPA and amide moieties. When the applied potential reaches ~ 0.65 V, P1-P3 exhibited new absorption bands in their UV-vis spectra at 755, 751 and 755 nm, respectively, and the appearance color of polymers changed from colorless to blue-green accordingly. Response time, CEs and switching stability of P1-P3 were studied in further electrochromic analyses. This current work supports that the BIC reaction, which with the advantages of good substrates adaptability, high structural designing flexibility, simple operation and mild reaction condition, could provide an efficient pathway for the construction of novel functional PAs. It is

expected that the comprehensive performance of PAs could be improved through

further structural designing, and the relevant work is undergoing now.

Conflicts of interest

There are no conflicts to declare.

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Highlights

- Triphenylamine (TPA)-based diisocyanide derivative (M1) was successfully synthesized.
- > TPA-based polyamides (**P1-P3**) were synthesized *via*

benzoxazine-isocyanide-chemistry.

P1-P3 exhibited single-step, highly reversible electrochemical oxidation processes.

Electrochromic properties of **P1-P3** were further analyzed here.

Jonulua

Yang Chang: Methodology, Visualization, Investigation, Data curation, Writing-Original draft preparation

Shi Wei: Conceptualization, Methodology, Writing- Reviewing and Editing, Project

e. Proc

administration, Funding acquisition;

Chen Xin: Software, Calculations

Zhang Kesong: Preparation of monomers

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Declaration of interests

 \boxtimes The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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