# Macromolecules

# Synthesis and Characterization of a Low-Bandgap Poly(arylene ethynylene) Having Donor—Acceptor Type Chromophores in the Side Chain

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**Supporting Information** 

# ■ INTRODUCTION

As one of the most important  $\pi$ -conjugated polymers, poly(arylene ethynylene)s (PAEs) have unique features of aromatic rings and ethynylene units alternating in the macromolecular chains, giving rise to distinct electronic and optical properties as well as outstanding mechanical properties with enhanced thermal stability and photostability.<sup>1,2</sup> Such features originate, at least in part, from the cylindrical symmetry of ethynyl bonds, which stabilizes the conjugation of adjacent aromatic rings irrespective of the orientation of aromatic planes.<sup>1</sup> However, PAEs usually exhibit large bandgaps greater than 2.0 eV due to their inherent chemical structures. This restricts their potential applications in many important areas such as solar cells, light-emitting diodes, field-effect transistors, and supercapacitors,  $3^{-7}$  where low bandgaps of the conjugated polymers are highly preferred. For this reason, a plethora of strategies were developed to narrow down the bandgap of PAEs, for example, the introduction of the silole or heterocylic units into the aromatic systems.<sup>1</sup> Among these, PAEs with electron donor and acceptor moieties are of particular interest because the intramolecular charge-transfer interactions between donor and acceptor would lead to a lower bandgap. The main idea behind this lies in that the highest occupied molecular orbital (HOMO) energy  $(E_{HOMO})$  level of the donor and the lowest unoccupied molecular orbital (LUMO) energy  $(E_{LUMO})$ level of the acceptor are closer than those in pristine PAE systems, since the bandgap energy  $(E_g)$  may be defined by  $E_g$  =  $E_{\rm LUMO} - E_{\rm HOMO}$ .<sup>8,9</sup> To date, the attainable  $E_{\rm g}$  of PAEs having donor-acceptor interactions was reported to be as low as 1.8 eV.<sup>10-12</sup>

To achieve a lower bandgap of PAEs, the strength of both electron donating and accepting units must be further increased, which can be accomplished by employing stronger electron donating groups like dialkylamine on the donor to raise the HOMO energy level as well as stronger electron withdrawing groups such as -CN and  $-NO_2$  on the acceptor to reduce the LUMO energy level.<sup>8,9</sup> Tetracyanoethylene (TCNE) is one of the strongest electron acceptors<sup>13</sup> but has sparsely been used for the synthesis of donor-acceptor type polymers. This is attributed to the difficulty in synthesizing TCNE derivatives suitable for polymerization. Furthermore, it should be pointed out that many conventional approaches for synthesizing conjugated polymers, especially those involved with the use of metal-ion catalysts (e.g., palladium or nickel), are not appropriate for the applications in the synthesis of polymers having TCNE derivatives because these TCNE

derivatives would always form strong complexes with these metal-ion catalyst and reduce their catalytic performance.<sup>14</sup>

This synthetic obstacle can be circumvented by postfunctionalization with TCNE after polymerization, which requires that the reaction must be extremely reactive and highly selective. This can be realized by the "click" type reaction of tetracyanoethylene (TCNE) with electron-rich alkyne to afford 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) derivatives in a quantitative yield.<sup>15,16</sup> The underlying mechanism lies in the fact that the electron accepting TCNE would undergo thermal [2 + 2] cycloaddition with electron-rich alkynes followed by spontaneous electrocyclic ring-opening of the initially formed cyclobutenes under mild conditions without the necessity of any catalyst.<sup>17</sup> This cycloaddition/retroelectrocyclization reaction has been borne out to be very fruitful in the synthesis of donor-acceptor type organic molecules or dendrimers having interesting electrical, electrochemical, or nonlinear optical properties.<sup>17–20</sup> Very recently, this synthetic protocol has been generalized into macromolecular systems using aromatic polyamines bearing electron-rich alkyne side chains<sup>21</sup> and PAEs containing ferrocene in the main chain as precursors.<sup>22</sup> In the latter case, only partial adduction of TCNE occurred due to the low electron donating property of ferrocene as well as the high steric hindrance in the main chain.

Herein, we report an effective approach, for the first time, to synthesizing a low-bandgap PAE having donor-acceptor type chromophores in the side chain. Specifically, a PAE precursor with electron-rich alkynes in the side chain was accomplished through judicious molecular design to endow the polymer with reasonably high molecular weight. The extremely selective reaction of TCNE with dialkylanilino-activated alkynes in the side chains of the polymer afforded donor-acceptor type chromophores while maintaining the important features of alternating aromatic ring and ethynylene bonds in the main chain of the polymer, which have never been accomplished before.<sup>21,22</sup> Such a unique polymer exhibited interesting intramolecular charge-transfer interactions, leading to a lower bandgap, potent redox activity, and improved thermal stability.

## RESULTS AND DISCUSSION

Synthesis of the Precursor Polymer. As illustrated in Scheme 1, a  $\pi$ -conjugated PAE precursor having electron-rich

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dioctylanilino-substituted alkynes in the side chain, which was referred to as PBBN thereafter, was polymerized via Sonogashira cross-coupling reaction<sup>23</sup> between functional monomers M-I with terminal acetylenes and M-II with diiodide, using tetrakis(tripheneylphosphine)palladium and copper iodide catalysts in a mixed solvent of triethylamine and tetrahydrofuran (THF) at 50 °C. The electronically rich N,N-dioctylamino groups in M-I activated the alkynes in the side chains of M-I, thus making the selective reaction of sidechain alkynes with TCNE possible in the postfunctionalization step. Nevertheless, the presence of very strong electron donating groups on M-I typically has a detrimental effect on the Pd-catalyzed cross-coupling reactions<sup>24</sup> during the polymerization of PBBN. For example, the polymerization of M-I with 1,4-diiodobenzene under the same reaction condition for PBBN has proven to be less efficient, merely resulting in the formation of oligomers having an  $M_{\rm p}$  of 4600 and an  $M_{\rm w}$  of 7900 determined by gel permeation chromatography in Figure S37. This observation prompted us to design M-II having electron withdrawing (carbonyl) groups, which activated the functional (iodo) groups in M-II for polymerization and consequently ensured the formation of PBBN with high molecular weight.

The reaction scheme for synthesizing **M-I** is depicted in Scheme 2, and the detailed experimental procedures and characterizations are presented in the Supporting Information (Figures S1–S20). The flexible side chains on **M-I** were introduced to ensure good solubility of both monomer and polymer in organic solvents by alkylation of the commercially



available 4-iodoaniline (1) to afford N.N-dioctyl-4-iodoaniline (2). Then,  $N_N$ -dioctyl-4-iodoaniline (2) was coupled with trimethylsilylacetylene via Sonogashira reaction at room temperature, followed by deprotection under basic condition (potassium carbonate in a mixed solvent of methanol and THF) to yield 4-(N,N-dioctylamino) phenylethyne (4). 1,4-Dibromo-2,5-diiodobenzene (6), which was synthesized by iodization of 1,4-dibromobenzene (5) using iodine in concentrated sulfuric acid at 125-135 °C,<sup>25</sup> was employed as the starting building block because the iodo group had a higher reactivity toward Sonogashira reaction than the bromo group.<sup>26</sup> Consequently, 1,4-dibromo-2,5-diiodobenzene (6) was coupled with trimethylsilylacetylene using PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>/CuI/PPh<sub>3</sub> as a catalyst in a mixed solvent of THF and diisopropylamine at room temperature in such a way that the iodo group in 1,4dibromo-2,5-diiodobenzene (6) was selectively reacted with trimethylsilylacetylene, while the bromo group remained intact. The resulting 2,5-bis(trimethylsiylethynyl)-1,4-dibromobenzene (7) was then reacted with  $4-(N_N-dioctylamino)$ phenylethyne under reflux using the aforementioned catalyst system, followed by deprotection in the basic condition to produce M-I.

The reaction scheme for the synthesis of M-II is shown in Scheme 3, and the detailed experimental procedures and

### Scheme 3. Reaction Scheme for Synthesizing Monomer M-II



characterizations are presented in the Supporting Information (Figures S21–S28). The synthesis of M-II began with *p*-xylene (9), which was iodized by iodine and periodic acid in a sulfuric acid/acetic acid/chloroform solvent system.<sup>27</sup> 2,5-Diiodo-*p*-xylene (10) obtained was then oxidized by potassium permanganate to obtain 2,5-diiodoterephthalic acid (11),<sup>27</sup> which was then chlorinated by thionyl chloride and subsequently esterified with 1-butanol in the presence of triethylamine to obtain M-II.

Synthesis of PBBN-TCBD. Referring to Scheme 1, the precursor PBBN was then subjected to the reaction with TCNE, which proceeded well in dichloromethane at room temperature to afford the target PAE having donor-acceptor type chromophores in the side chains (denoted by PBBN-TCBD), as evidenced by an immediate color change of polymer solution from light yellow to red. The cycloaddition/retroelectrocyclization reaction predominately prevailed over the electron-rich alkynes in the side chains of PBBN, whereas the deactivated alkynes in the main chain of PBBN were kept intact, even in the case of excessive loading of TCNE in the reaction solution. This may be attributed to both deactivating effects of carbonyl group and steric hindrance effect of bulky side chains on the main-chain alkynes in PBBN. Once the activated alkynes were converted into electron-accepting TCBD, the reaction of TCNE with main-chain alkynes would be nearly impossible. It should be noted that an excess amount of TCNE did not produce any side reactions at this temperature and it could be readily removed by column chromatography. As a consequence, we were able to obtain PBBN-TCBD with a well-defined structure.

Characterization of PBBN and PBBN-TCBD. Both PBBN and PBBN-TCBD are well soluble in common solvents such as THF, chloroform, and dichloromethane, owing to the presence of long flexible side chains along the macromolecular chains. As a result, polymer films can be easily prepared by solution-casting method. As determined by gel permeation chromatography (GPC) shown in Figure 1, PBBN has a sufficiently high molecular weight ( $M_n = 26072$ , corresponding to about 50 repeat units of alternating arylene and ethynylene) and a good polydispersity  $(M_w/M_n = 1.97)$ , which originate from the enhanced reactivity of diiodide group in M-II by carbonyl groups as well as good solubility of the polymer in the reaction solution. On the other hand, PBBN-TCBD reveals a reasonable increase in molecular weight  $(M_n = 31754)$  due to the TCNE adduction and an appreciable decrease in polydispersity  $(M_w/M_n = 1.73)$  because of further purification by column chromatography upon the completion of reaction, as compared with those of PBBN. Notice that although the molecular weights of PBBN and PBBN-TCBD may be



**Figure 1.** GPC traces of (a) PBBN (dashed line) and (b) PBBN– TCBD (solid line) using THF as eluent and polystyrenes as standards.

overestimated by GPC measurements owing to their rigid backbones and bulky side chains, it is useful for relative comparison.

The chemical structure of PBBN was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectra in Figures S29 and S30 and the FTIR spectrum in Figure S31, while the chemical structure of PBBN-TCBD was verified by <sup>1</sup>H and <sup>13</sup>C NMR spectra in Figures S32 and S33 and the FTIR spectrum in Figure S34. In regard to the <sup>1</sup>H NMR spectra, a desirable shift for each peak of PBBN-TCBD relative to that of PBBN is observed in Figure S35 due to the influence of electron withdrawing TCBD units in PBBN-TCBD. A close look at the <sup>13</sup>C NMR spectra in Figure S36a reveals two chemical shifts at 85.7 and 93.3 ppm, which may be assigned to the main-chain and side-chain alkynes in PBBN, respectively. Upon the reaction of PBBN with TCNE, the chemical shift of main-chain alkynes has slightly shifted to 82.3 ppm, while a new chemical shift at 93.3 ppm is attributed to  $=C(CN)_2$  groups in PBBN-TCBD. Furthermore, the presence of TCBD units in PBBN-TCBD can be confirmed by the existence of -CN at chemical shifts of 112.5, 114.9, 115.9, and 116.9 ppm and C=C(CN)<sub>2</sub> at chemical shifts of 161.6 and 168.6 ppm. The following observations can be made from the FTIR spectra in Figure 2. PBBN exhibits an absorption peak at 2191 cm<sup>-1</sup> for side-chain alkynes and a shoulder at 2186 cm<sup>-1</sup> for main-chain alkynes. Upon the completion of reaction with TCNE, PBBN-TCBD shows an absorption peak at 2214 cm<sup>-1</sup> for the -CN group and a shoulder at  $2185 \text{ cm}^{-1}$  for main-chain alkynes. Because of the effect of strong electron accepting TCBD, the carbonyl group in PBBN at a wavenumber of 1707  $\text{cm}^{-1}$  is red-shifted to 1722 cm<sup>-1</sup> for PBBN-TCBD. The aforementioned results clearly demonstrate that the cycloaddition/retro-electrocyclization reaction of TCNE with activated alkynes selectively occurred in the side chains of PBBN.



Figure 2. FTIR spectra of (a) PBBN and (b) PBBN-TCBD.

Thermogravimetric analysis in Figure 3 reveals that PBBN begins to decompose at 181 °C while PBBN–TCBD starts to



Figure 3. TGA data of PBBN (dashed line) and PBBN–TCBD (solid line).

decompose at 267 °C. The remarkable enhancement of thermal stability by 86 °C may arise from the strong donor–acceptor interactions in PBBN–TCBD and/or the change of chain conformation upon the reaction of side-chain alkynes of PBBN with TCNE. The high thermal stability of PBBN–TCBD is essential for its practical applications. The differential scanning calorimetry thermograms in Figure S38 indicate that PBBN exhibits a glass transition temperature ( $T_g$ ) at 44.6 °C and a melting temperature ( $T_m$ ) at 97.3 °C. In contrast, PBBN–TCBD only shows a  $T_g$  at 53.2 °C, and the increase of  $T_g$  by 8.6 °C is attributed to intramolecular charge-transfer interactions along macromolecular chains, which will be elaborated by UV–vis spectroscopy and cyclic voltammetry. No  $T_m$  can be identified in PBBN–TCBD, which may be attributed to the nonplanarity of TCBD units.<sup>28</sup>

Low Bandgap in PBBN–TCBD Induced by Intramolecular Charge-Transfer Interactions. The intramolecular charge-transfer interactions in PBBN–TCBD are evidenced by UV–vis spectra in Figure 4 and cyclic voltammo-



Figure 4. UV-vis spectra of (a) PBBN and (b) PBBN-TCBD in dichloromethane.

grams in Figure 5. It can be observed from Figure 4a that PBBN displays the  $\pi - \pi^*$  transitions at 229, 271, 335, and 406 nm. PBBN has a molar absorptivity ( $\varepsilon$ ) of 2.4  $\times$  10<sup>4</sup> mol<sup>-1</sup> L cm<sup>-1</sup> in dichloromethane at  $\bar{\lambda}_{max,abs}$  = 406 nm. Remarkably, a shoulder appears at 498 nm with a long tail that decays well into the visible region, indicative of the strong electron donating property of the polymer containing dialkylamino groups.<sup>29</sup> Since the onset wavelength ( $\lambda_{onset}$ ) of PBBN is about 582 nm, the optical bandgap energy of PBBN is determined to be 2.13 eV. Despite the nonplanarity of TCBD unit, the efficient intramolecular charge-transfer interactions between dialkylamino donors and TCBD-containing acceptors are established for various species.<sup>16</sup> Such an intramolecular charge-transfer interaction is also present in our synthesized PAE with donor-acceptor type chromophores in the side chains. As shown in Figure 4b, the UV-vis spectrum of PBBN-TCBD exhibits broad charge-transfer (CT) bands with a maximum absorption peak at 463 nm ( $\varepsilon = 3.9 \times 10^4 \text{ mol}^{-1} \text{ L}$  $cm^{-1}$ ) in the visible absorption region. It is noteworthy that the onset wavelength ( $\lambda_{onset}$ ) of PBBN–TCBD reaches ca. 780 nm close to the near-IR region, and correspondingly the optical bandgap energy  $(E_{g}^{opt})$  is determined to be 1.59 eV, which is much lower than that of PBBN. The strong intramolecular charge-transfer interactions in PBBN-TCBD induced such a low bandgap in the PAE  $\pi$ -conjugated system. In the UV region of Figure 4b, strong absorption bands at approximately 228, 252, 289, and 344 nm are characteristic of  $\pi - \pi^*$  transitions located on the phenyl and ethynyl subunits of PBBN-TCBD. These absorption bands were red-shifted relative to those of PBBN, indicative of the strong effects of electron withdrawing TCBD units in PBBN-TCBD.

The electrochemical behaviors of PBBN and PBBN-TCBD are shown by cyclic voltammograms in Figure 5, where the locations of oxidation and reduction potentials are identified. All potentials are referenced to the ferricinium/ferrocene (Fc<sup>+</sup>/ Fc) couple, and they are used as an internal standard following the literature.<sup>30</sup> Specifically, PBBN displays a quasi-reversible one-electron oxidation step at a half-wave oxidation  $(E_{1/2}^{ox})$  of 0.34 V vs  $Fc^+/Fc$ , which is attributed to the redox between amine and amine cation, and the other oxidation step at  $E_{1/2}^{ox}$ of 0.93 V vs  $Fc^+/Fc$ , which represents the subsequent oxidation from amine cation to dication.<sup>31</sup> The prefix "quasi" is used because the cathodic peak current is typically smaller than the anodic peak current. The irreversible anodic peak at  $E_{pa}^{ox}$  = 0.70 V may be attributed to the oxidation effect of the neutral arylene ethynylene backbone in PBBN.<sup>1</sup> Figure 5b shows that PBBN–TCBD exhibits a half-wave reduction potential  $(E_{1/2}^{red})$ of -1.04 V vs Fc<sup>+</sup>/Fc, which is ascribed to the electron accepting TCBD units in PBBN-TCBD. The large potential difference ( $\Delta E = 1.26$  V) of reduction potential for PBBN-TCBD between the cathodic and anodic peaks might have arisen from the conformational changes between the distorted neutral TCBD and the planar anion of TCBD during the charge-transfer process.<sup>14</sup> It can also be observed from Figure 5b that there exhibits an irreversible anondic peak at  $E_{pa}^{ox}$  = 0.29 V owing to the oxidation effect of the neutral arylene ethynylene backbone in PBBN-TCBD. This peak has a shift of -0.41 V relative to that of PBBN, arising from the strong electron accepting effect of TCBDs in PBBN-TCBD. Furthermore, PBBN-TCBD shows a half-wave oxidation potential  $(E_{1/2}^{ox})$  at 0.89 V vs Fc<sup>+</sup>/Fc, which can be assigned to the electron donating N,N-dioctylanilino groups in PBBN-TCBD.



**Figure 5.** Cyclic voltammograms of (a) PBBN and (b) PBBN–TCBD in dichloromethane solution containing 0.1 M nBu<sub>4</sub>NPF<sub>6</sub>.  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials, respectively, with "ox" denoting oxidation and "red" denoting reduction. Red arrows describe the directions of scans.

It can be seen from Figure 5b that PBBN-TCBD shows an onset oxidation potential ( $\Phi_{ox} = 0.74$  V) and an onset reduction potential ( $\Phi_{red} = -0.61$  V), which were obtained from the intersection of the two tangents drawn at the rising current and the baseline charging current of the CV curves. Under the premise that the energy level of Fc<sup>+</sup>/Fc is 4.80 eV below the vacuum level,<sup>32</sup> the energy levels of HOMO and LUMO are estimated to be  $E_{HOMO} = -5.54$  eV and  $E_{LUMO} =$ -4.19 eV, respectively. Correspondingly, the bandgap energy  $(E_{\sigma}^{CV})$  of PBBN-TCBD based on cyclic voltammetric results is 1.35 eV. Note that this value is slightly lower than  $E_{g}^{opt} = 1.59$ eV determined by UV-vis spectroscopy. The lower electrochemical band gap of PBBN-TCBD relative to its optical band gap may be interpreted by the ion pairing effects, indicative of a very low exciton binding energy. Above, we estimated energy levels of HOMOs and LUMOs by using onset potentials because reversible oxidation/reduction potentials were not identified for PBBN-TCBD, while half-wave potentials had to be used in the rigorous sense. On the basis of the observations made above, it can be concluded that intramolecular chargetransfer interactions indeed induced a low bandgap energy in PBBN-TCBD.

### CONCLUSION

To summarize, we have demonstrated a facile approach toward the synthesis of a poly(arylene ethynylene) having donoracceptor type chromophores in the side chains. A precursor  $\pi$ conjugated polymer with reasonably high molecular weight was obtained by the Sonogashira reaction between one monomer with terminal acetylenes and the other with activated diiodide. The selective reaction of TCNE with activated dioctylanilinosubstituted alkynes in the side chains of precursor polymer afforded the target poly(arylene ethynylene). This unique polymer shows enhanced thermal stability and exhibits strong intramolecular charge-transfer interactions, resulting in a very low bandgap of poly(arylene ethynylene). Along with the inherent features of poly(arylene ethynylene), this low bandgap  $\pi$ -conjugated polymer is a promising material for applications in nonlinear optical devices, organic photovoltaic devices, and light-emitting diodes.

### ASSOCIATED CONTENT

### **S** Supporting Information

Detailed experimental procedures and characterizations of monomers and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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