Quinoxaline-Based Poly(aryleneethynylene)s

Carlito G. Bangcuyo, Joe M. Ellsworth, Una Evans, Michael L. Myrick, and Uwe H. F. Bunz*

USC NanoCenter and Department of Chemistry and Biochemistry,The University of South Carolina, Columbia, South Carolina 29208

Received October 8, 2002
Revised Manuscript Received December 8, 2002

Poly(aryleneethynylene)s (PAE)[1−3] are a class of conjugated polymers in which aryl groups are interspersed by alkyne units. Their high stability and photophysical properties make PAEs attractive. PAEs have found interest as semiconductors, polarizers, and sensory materials.[4−6] While the parent dialkyl/dialkoxy-substituted poly(*p*-phenyleneethynylene)s (PPE) are well-known and thoroughly investigated, heterocyclic PAEs[7−9] have been less explored despite the expectation of these materials to behave differently. Jenekhe, Schanze, Yamamoto, Klemm, and our group have started to explore the field of hetero-PAEs as interesting emitting and *n*-type semiconducting materials.[10−12] Herein we report the synthesis, ionochromic effect, and electrochemistry of the first quinoxaline-containing PAEs, **3** and **6**.

Starting from 4,7-dibromo-2,1,3-benzothiadiazole,[13] we prepared 1,4-dibromo-2,3-diaminobenzene, which furnished the quinoxalines **1** and **4** in high yields by condensation with benzil or acenaphthenequinone under acidic conditions. First attempts to alkynylate **1** utilizing $(Ph_3P)_2PdCl_2$ and CuI in triethylamine failed. The addition of THF as a cosolvent, described by Krause,[14] allowed the coupling of trimethylsilylacetylene to **1** in excellent yields. The monomer **2** was isolated as colorless but highly fluorescent material after removal of the TMS groups by K_2CO_3 in an overall yield of 86%. Transfer of this protocol to **4** furnished **5** in an 83% yield.

With the two monomers in hand we performed Pd-catalyzed couplings of **2** and **5** respectively to 2,5-bis-(2′-ethylhexyloxy)-1,4-diiodobenzene. Utilizing standard coupling conditions (5 mol % $(Ph_3P)_2PdCl_2$, 5 mol % CuI in piperidine), **2** furnished the desired PAE **3** in 95% isolated yield (aqueous workup, precipitation into methanol, Scheme 1) and a degree of polymerization (P_n) of 110 repeating units according to gel permeation chromatography. In the case of **6**, we coupled the soluble bis(trimethylsilyl)-substituted monomer **5** to the diiodide. Module **5** was deprotected in situ (KOH in ethanol) and gave the sparingly soluble polymer **6** (1−2 mg in 10 mL of chloroform) in an 86% isolated yield and a P_n of 36. While **3** dissolved easily in organic media such as chloroform and dichloromethane, the acenaphthalene-substituted derivative **6** was considerably less soluble. Consequently, we were only able to obtain the solution-phase ^{1}H and ^{13}C NMR spectra of **3** and a solution-phase ^{1}H NMR spectrum of **6**. All of the collected spectroscopic data are in agreement with the proposed polymeric structure.

X-ray powder diffraction shows both polymers to be amorphous, with no distinct ordering present. In thin films, both polymers appear reddish translucent, while thick preparations are golden-green and lustrous. The polymers' appearances resemble that of benzothiadiazole-based PAEs **7**.[10a,12]

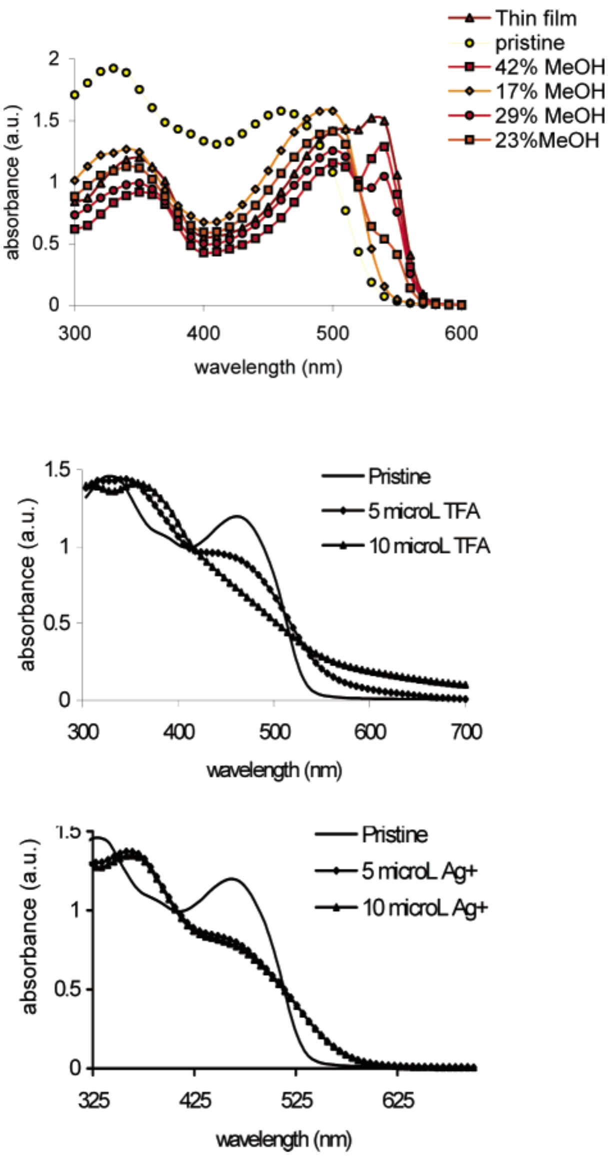


Figure 1. Top: Solution UV−vis spectra (λ_{max} 460 nm, chloroform), and aggregation UV−vis spectra of PAE **3** upon addition of methanol vs thin film UV−vis (λ_{max} 534 nm) spectrum of **3**. Middle: Addition of AgOTf (10 mmol L^{-1}) to polymer **3** (10 mg L^{-1}). Bottom: Addition of trifluoroacetic acid to polymer **3** (10 mg L^{-1}) (bottom).

The polymers **3** and **6** show a λ_{max} of absorption in chloroform at 462 (**3**) and 474 nm (**6**). The small differences in absorption are probably due to the increased size of the conjugated heterocyclic unit in **6**. Polymer **3** was spun cast onto a quartz slide. Its UV−vis spectrum (Figure 1, top, $\lambda_{max} = 534$ nm) is different from that in solution. The observed bathochromic shift (62 nm) is considerable, and probably due to planarization of the chains in the solid state. Aggregation and interchain interactions of the charge-transfer type will likewise play a role here. This aggregation behavior is distinctive and similar to that observed for the PPEs as well as for the poly(fluorenyleneethynylene)s.[15] The optical behavior of **3** in thin films can be effectively

---

* Corresponding author. E-mail: Bunz@mail.chem.sc.edu.

10.1021/ma0257200 CCC: $25.00

Scheme 1. Synthesis of the PAEs 3 and 6

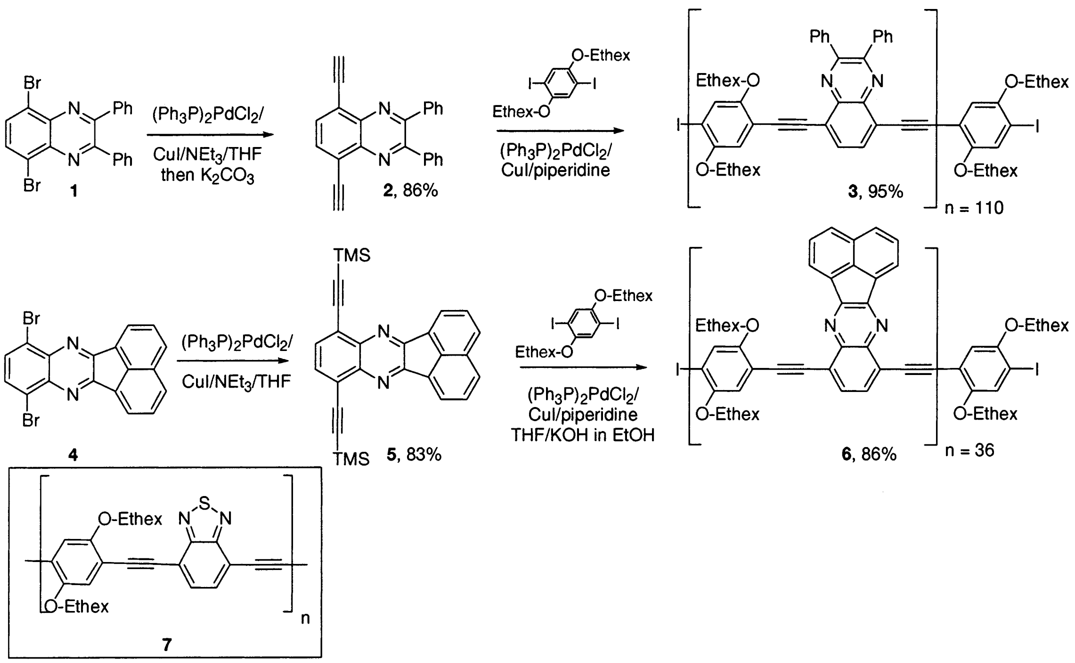
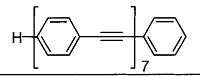
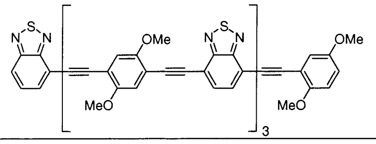
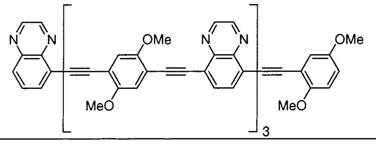


Table 1. Comparison of PM3 Band Gap Calculations of Several Conjugated Oligomers

Structure	HOMO PM3 [eV]	LUMO PM3 [eV]	Band Gap Calcd. [eV]
	-8.64	-1.18	7.28
	-8.42	-2.10	6.32
	-8.22	-1.47	6.75

simulated by addition of methanol to a solution of the polymer in chloroform (Figure 1, top).

Addition of a solution of lithium trifluorosulfonate in acetone does not have an effect on the absorption spectrum. However, silver(I) salts and trifluoracetic acid (TFA) have a distinct influence of the absorption spectrum of **3** (Figure 1, middle and bottom). In both cases, the primary absorption peak disappears and a sloping but featureless shoulder appears. For TFA this band extends well into the 700+ nm range. Dilute solutions of **6** show a similar behavior as their absorption goes asymptotically to zero at wavelengths above 700 nm upon addition of TFA or Ag^+. It is noticeable that thin films of **3** show a bathochromic shift in absorption when exposed to a solution of $AgNO_3$ in methanol (534 nm to 560 nm), but are essentially unchanged when exposed to fumes of HCl or trifluoroacetic acid. The reason for this surprising behavior is the great hydrophobicity of the polymers **3** and **6** mediated through the ethylhexyl side chains.

The emission peaks of the polymers **3** and **6** in dilute chloroform solution are almost indiscernible from each other with an emission maximum at 538 nm for **3** and 540 nm for **6**. Addition of a small amount of TFA or of Ag^+ ions quenches their fluorescence. Addition of methanol to the polymer **3** does change its emission, and a slight red shift (Figure 2, bottom) from 540 to 550 nm is recorded. The golden luster and presence of the electron withdrawing quinoxaline units in **3** and **6** suggests that these polymers are electronically different from the PPEs. Quantum chemical calculations reveal that the HOMO–LUMO gap (Hartree–Fock, 6-31G**, implemented as Spartan Pro, Wavefunction Inc., on Windows 2000) of diethynylbenzothiadiazole (HO = −8.45 eV, LU = 0.69 eV) is lower than that of diethynylquinoxaline (HO = −8.11 eV, LU = 1.31 eV). The polymer **3** is more electron rich than **7** as indicated by both the ab inition calculation of the monomer and the semiempirical PM3 (Spartan Pro) calculations of model octamers (Table 1). The quinoxaline building block seems thus less electron accepting than the benzothiadiazole unit. However, the PM3 results are qualitative and should not be over-interpreted, but the trend seen in Table 1 is mirrored in the cyclic voltammograms of

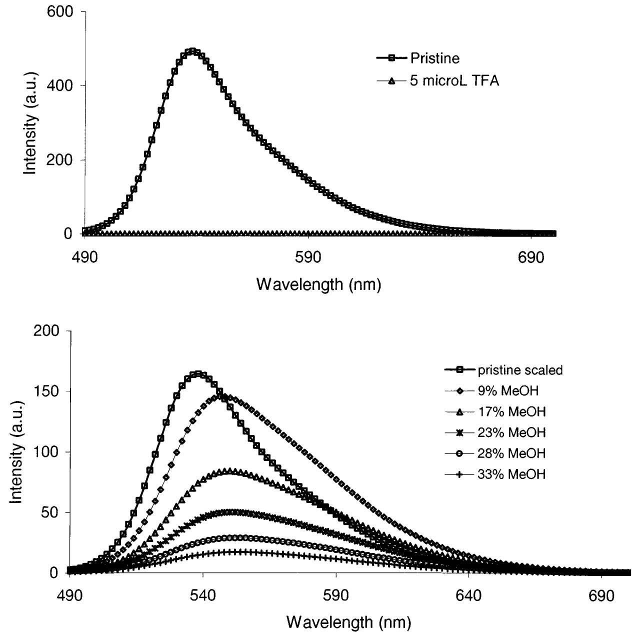


Figure 2. Emission of **3** (0.1 mg L^{-1} in chloroform) before and after addition of trifluoroacetic acid (top). Emission of **3** (0.1 mg L^{-1} in chloroform) before and after addition of methanol.

the polymer **3** and the benzothiadiazole-containing polymer **7**.[10a] We performed the CV of thin films of **3** that was spin cast onto an indium tin oxide slide.[16] While **7** is reduced at −1.42 V,[10a] reversible reduction of **3** occurs at −1.54 V (at −1.66 V reoxidation) under change of color from red to green, giving testimony to the higher lying LUMO of **3**. However, a second clean reduction of **3** is observed at −1.99 V suggesting that the polymer chains can be higher charged. It is reasonable to assume that in the first step only every second repeating unit is charged in **3** and that in a second reduction step the remaining quinoxaline modules are reversibly reduced.

In conclusion, we described the synthesis, characterization, aggregation, and ionochromicity of the novel quinoxaline-containing PAEs **3** and **6**. These materials are interesting *n*-semiconductors and highly effective sensory materials for Ag^+ and H^+ ions in solution. At the moment, we are testing the PAE **3** as an electron injection layer for light emitting diodes.

Acknowledgment. We thank the Vice President for Research, Dr. W. Harris, the National Science Foundation (CHE 0138-659), and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support. U.B. is a Camille Dreyfus Teacher-Scholar (2000-2004). We thank Prof. Haskell W. Beckham for the solid state CP MAS ^{13}C NMR spectrum of polymer **6**.

Supporting Information Available: Text giving experimental procedures, including structures for **1** and **2**, and detailed spectroscopic characterization of the monomers and the polymers, and figures showing NMR spectra for polymer **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998.

(2) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402.

(3) Giesa, R. *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.* **1996**, *36*, 631. Giesa, R.; Schulz, R. C. *Macromol. Chem. Phys.* **1990**, *191*, 857.

(4) Pschirer, N. G.; Miteva, T.; Evans, U.; Roberts, R. S.; Marshall, A. R.; Neher, D.; Myrick, M. L.; Bunz, U. H. F. *Chem. Mater.* **2001**, *13*, 2691. Schmitz, C.; Posch, P.; Thelakkat, M.; Schmidt, H. W.; Montali, A.; Feldman, K.; Smith, P.; Weder, C. *Adv. Funct. Mater.* **2001**, *11*, 41.

(5) Weder, C.; Sarwa, C.; Montali, A.; Bastiaansen, G.; Smith, P. *Science* **1998**, *279*, 835.

(6) Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864.

(7) Yamamoto, T. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 621. Yamamoto, T.; Honda, K.; Ooba, N.; Tomaru, S. *Macromolecules* **1998**, *31*, 7. Li, J.; Pang, Y. *Macromolecules* **1997**, *30*, 7487.

(8) Al-Higari, M.; Birckner, E.; Heise, B.; Klemm, E. *J. Polym. Sci. A* **1999**, *37*, 4442.

(9) Ley, K. D.; Whittle, C. E.; Bartberger, M. D.; Schanze, K. S. *J. Am. Chem. Soc.* **1997**, *119*, 3423.

(10) (a) Bangcuyo, C. G.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2001**, *34*, 7592. (b) Bangcuyo, C. G.; Rampey-Vaughn, M. E.; Quan, L. T.; Angel, S. M.; Smith, M. D.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 1563.

(11) (a) Jegou, G.; Jenekhe, S. A. *Macromolecules* **2001**, *34*, 7926. (b) For protonation of π-conjugated polymers see: Monkman, A. P.; Pålsson, L.-O.; Higgins, R. W. T.; Wang, C.; Bryce, M. R.; Batsanov, A. S.; Howard, J. A. K. J. Am. Chem. Soc. **2002**, *124*, 6049. Nurulla, I.; Tanimoto, A.; Shiraishi, K.; Sasaki, S.; Yamamoto, T. *Polymer* **2002**, *43*, 1287.

(12) Ley, K. D.; Li, Y. T.; Johnson, J. V.; Powell, D. H.; Schanze, K. S. *Chem. Commun.* **1999**, 1749. Morikita, T.; Yamaguchi, I.; Yamamoto, T. *Adv. Mater.* **2001**, *13*, 1862.

(13) Yamamoto, T.; Kanbara, T.; Ooba, N.; Tomaru, S. *Chem. Lett.* **1994**, 1709.

(14) Thorand, S.; Krause, N. *J. Org. Chem.* **1998**, *63*, 8551.

(15) Halkyard, C. E.; Rampey, M. E.; Kloppenburg, L.; Studer-Martinez, S. L.; Bunz, U. H. F. *Macromolecules* **1998**, *31*, 8655. Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652. Pschirer, N. G.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 3961.

(16) Cyclic voltammetry was performed in thin films with AgCl/Ag as a standard reference. For more details, see the Supporting Information.

MA0257200