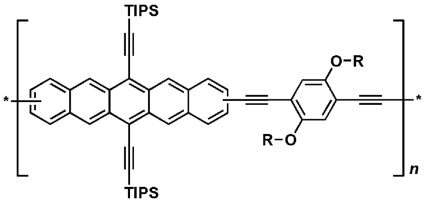
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

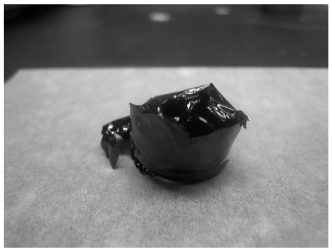
Synthesis of Solution-Soluble Pentacene-Containing Conjugated Copolymers

Toshihiro Okamoto, and Zhenan Bao

J. Am. Chem. Soc., **2007**, 129 (34), 10308-10309• DOI: 10.1021/ja0725403 • Publication Date (Web): 08 August 2007



Polymer 1: R = Dodecyl
Polymer 2: R = 2-Ethylhexyl



Polymer **2** (R = 2-ethylhexyl)
Mw = 5.78 x 10^4 g mol^{-1}, PDI = 2.42

Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

J|A|C|S
COMMUNICATIONS

Published on Web 08/08/2007

Synthesis of Solution-Soluble Pentacene-Containing Conjugated Copolymers

Toshihiro Okamoto and Zhenan Bao*

Department of Chemical Engineering, Stanford University, 381 North-South Mall, Stanford, California 94305

Received April 12, 2007; E-mail: zbao@stanford.edu

Conjugated polymers have great potential as organic field effect transistors (OFETs),[1] photovoltaic cells (OPVCs),[2] and light emitting devices (OLEDs)[3]. Thiophene-based conjugated polymers have been extensively studied for the above applications.[4] In addition, acene- and heteroacene-based organic semiconductors, such as pentacene and fused oligothiophenes, have been intensely investigated for OFET applications.[5] Among them, pentacene and its derivatives have the highest reported thin-film transistor mobility at above 5 cm^2 V^{-1} s^{-1}.[6] To date, there are few reported conjugated acene-containing polymers, most of which feature anthracenes.[7] Pentacene-containing conjugated polymers will be of great interest as solution-soluble polymers with high charge carrier mobility and low band gap. In addition, extending the conjugation of pentacene reduces the electron density on the reactive 6 and 13 positions and therefore improves the stability of pentacene, as seen later in this work from the increased oxidation potential of the polymer.

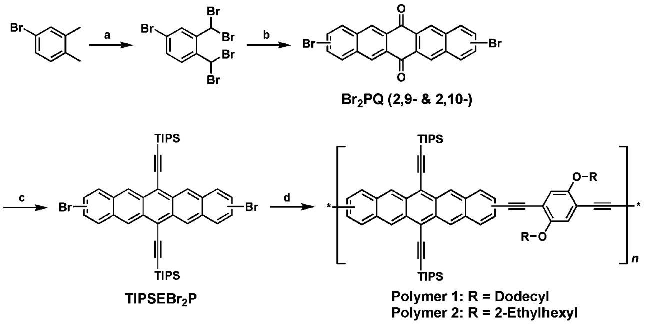
So far, there has been only one report on a pentacene−fluorene random copolymer with the pentacene core orthogonal to the conjugated polymer chain through the 6 and 13 positions for OLED devices.[7a] The main difficulty in synthesizing pentacene-containing conjugated polymers is due to the poor solubility of pentacene in common organic solvents as well as its rapid degradation when exposed to light and oxygen.[8]

Recently, Anthony's and Neckers' groups reported a class of soluble triisopropylsilylethynyl (**TIPSE**) substituted pentacene derivatives.[9] Compared to pentacene, the bulky TIPSE substituents make the resulting pentacene derivatives very soluble in common organic solvents and afford improved stability under ambient conditions both in the solid state and in solution.

In this Communication, we report the synthesis of pentacene-containing conjugated polymers with low-bandgaps of less than 1.7 eV, using alternating TIPSE-substituted pentacene with linear or branched alkoxyl-substituted diethynylphenyl moieties[10] using Sonogashira coupling reaction conditions at room temperature.[11] Our pentacene copolymers exhibited much better air stability than TIPSE-substituted pentacene (**TIPSEP**) in the solution state.

The polymerization scheme and conditions are summarized in Scheme 1. The TIPSE-substituted dibromopentacene (**TIPSEBr$_2$P**) was prepared from dibromopentacene quinone. First, 4-bromo-*o*-xylene was converted to dibromopentacene quinone in two steps, yielding a mixture of 2,9- and 2,10-dibromopentacene quinone. Because of similar solubility and polarity, we were not able to separate these isomers. They were subsequently converted to **TIPSEBr$_2$P** using conditions reported in literature.[9a] From the ^{1}H NMR of **TIPSEBr$_2$P** in deuterated chloroform (CDCl$_3$), we estimated that the ratio of 2,9- to 2,10-isomer was around five to four.[12] Before polymerization, we checked the stability of **TIPSEBr$_2$P** under the commonly used Sonogashira polymerization conditions without addition of the comonomer in a degassed mixture of toluene-^{i}Pr$_2$NH at 70−80 °C.

Scheme 1. Synthetic Scheme of Pentacene Polymers **1** and **2**



The reactions were run using the following reagents and conditions: (a) NBS, BPO, CCl$_4$, reflux; (b) 1,4-benzoquinone, NaI, DMF, 60 °C, 2 days; (c) 1) (2-triisopropylsilyl)ethynylmagnesium chloride; (2) SnCl$_2$·2H$_2$O, 10% HCl(aq); (d) 1,4-diethynyl-2,5-dialkoxybenzene (R = dodecyl or 2-ethylhexyl), PdCl$_2$(PhCN)$_2$, P^{t}Bu$_3$, ^{i}Pr$_2$NH, CuI, toluene, room temperature for 3 days. **TIPSEBr$_2$P** did not show sign of degradation in ^{1}H NMR spectra, indicating that it should be stable enough under basic conditions even at an elevated temperature.[12] However, we were concerned that the elevated temperature and long reaction times commonly used in Sonogashira polymerization reactions might result in partial decomposition of the pentacene monomer and polymer. It is well-known that trace amounts of impurity may have a significant impact on device performance. Therefore, we adapted a room-temperature Sonogashira coupling reaction condition for aryl bromides reported recently by Fu and Buchwald using PdCl$_2$(PhCN)$_2$/P^{t}Bu$_3$ as the catalyst.[11]

The polymerization was carried out between **TIPSEBr$_2$P** and 1,4-diethynyl-2,5-dialkoxybenzene (R = dodecyl or 2-ethylhexyl)[13] at room temperature to obtain the desired pentacene-containing copolymers **1** and **2** in 47% and 62% yields, respectively, after washing with appropriate solvents. We limited the reaction time to 6 h so that a large fraction of the resulting polymer was soluble in common organic solvents. When a longer reaction time was used (12 h), less than 30 wt % of the polymer was soluble. The molecular weights of the polymers were determined by gel permeation chromatography (GPC) using tetrahydrofuran (THF) as the eluent and polystyrene standards. Polymer **1** was found to have a number averaged molecular weight (M_n) of 1.13 × 10^4 g mol^{-1} with a polydispersity (PDI) of 2.21, while polymer **2** had M_n = 2.39 × 10^4 g mol^{-1} and PDI = 2.42. To our knowledge, these are the first examples of pentacene-containing phenylethynylene polymers as well as the first application of room-temperature Sonogashira coupling reaction using an aryl bromide as a starting monomer to the preparation of polyarylethynylenes (PAEs) polymers.

Polymer **2** showed good solubility (>5.0 mg/mL) in most chlorinated organic solvents as well as in THF and toluene, while polymer **1** had only limited solubility (~0.3 mg/mL) in halogenated benzene solvents. This difference is attributed to the difference in bulkiness of the alkoxy group substituted on the main polymer backbone.

10.1021/ja0725403 CCC: $37.00

Table 1. Summary of Electrochemical and Optical Properties of Pentacene Copolymers and **TIPSEP**[a]

compound	$E_{red/onset}$ (V)	$E_{ox/onset}$ (V)	$\lambda_{max}/\lambda_{onset}$	optical energy gap
polymer **1**	−1.80	+0.32	671/693 (*o*-DCB)	1.68
	−1.37		672/736 (film)	
polymer **2**	−1.82	+0.28	674/695 (*o*-DCB)	1.76
	−1.42		674/706 (film)	
TIPSEP	−1.54	+0.24	649/667 (*o*-DCB)	1.86

[a] $E_{red/onset}$ is the onset reduction potential; $E_{ox/onset}$ is the onset oxidation potential; λ_{onset} is the absorption edge.

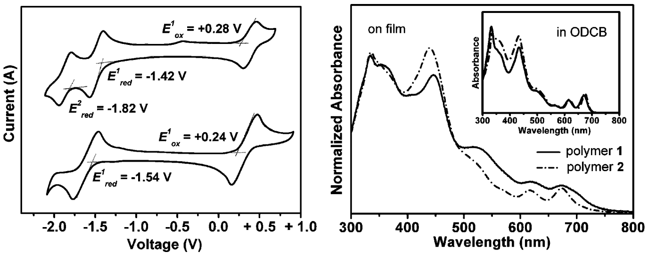


Figure 1. (a) Cyclic voltammograms of polymer **2** (top) and **TIPSEP** (bottom) in 0.05 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) of *o*-dichlorobenzene (*o*-DCB); (b) UV−vis spectra of polymer **1** (solid line) and polymer **2** (dashed line) films and in *o*-DCB (inset) at room temperature.

To estimate the highest occupied molecular orbital (HOMO) levels, lowest unoccupied molecular orbital (LUMO) levels, and optical energy gaps for polymers **1** and **2**, we examined their electrochemical and optical properties by cyclic voltammetry (CV) and UV−vis spectrometry in solution and in thin film. We compared this data to that of **TIPSEP**. Table 1 summarizes the CV and UV−vis results and the optical energy gaps. In terms of electrochemical properties, polymer **2** exhibited one reversible oxidative step and two reversible reductive steps, as shown in Figure 1, which indicates high chemical stability in the solvated oxidized and reduced states. On the other hand, polymer **1** had one reversible oxidation step and two pseudoreversible reduction steps. The onset of oxidation for polymer **2** is 0.04 eV higher than that of **TIPSEP** while the onset of reduction for **2** was 0.12 eV lower. On the basis of the onset values, the HOMOs and LUMOs were calculated to be 5.28 and 3.57 eV for polymer **1** and 5.24 and 3.54 eV for polymer **2**, respectively. As a comparison, the HOMO level of **TIPSEP** was 5.20 eV versus vacuum, indicating that it is more easily oxidized than the polymers.[14] The slightly increased oxidation potentials of the polymers is due to the incorporation of pentacene into the conjugated polymer leading to delocalization of π-electrons on pentacene ring and making it less electron rich. The band gaps determined from CV were 1.69 and 1.70 eV for polymer **1** and **2**, respectively. The UV−vis spectra in solution for polymer **1** and **2** were very similar with their λ_{max} and λ_{onset} slightly red-shifted by about 22−28 nm compared to that of **TIPSEP**. With respect to the properties of polymer films deposited by spin-coating or dip-coating, the absorption of polymer **1** has an onset at approximately 736 nm, and the spectrum displays a broad tail in the range of 500−800 nm. On the other hand, the absorption onset of polymer **2** is about 30 nm blue-shifted compared to polymer **1** indicating that polymer **1** has a slightly stronger interchain interaction.

We have also investigated the stability of these pentacene polymers. We monitored UV−vis absorption over time for the polymer solution in *o*-dichlorobenzene as compared to **TIPSEP**, which was reported to be approximately 50 times more stable than pentacene.[8] Consistent with the CV results, our pentacene polymers exhibited better stability (about three times the half-life) than **TIPSEP** under our measurement conditions (see Supporting Information).

In conclusion, we have synthesized a new type of conjugated polymer containing pentacene using a room-temperature Sonogashira coupling reaction. Polymer **2** exhibited good solubility in common organic solvents (>5.0 mg/mL) which should make it a good candidate for solution-processable device applications. The optical gap of these polymers was lowered with respect to **TIPSEP** and was as small as 1.68 eV for polymer **1**. At the same time, the oxidative stability of these polymers in solution was better than **TIPSEP** both from CV measurements and monitoring UV−vis absorption. Determination of the charge transport properties of these new polymers is underway.

Acknowledgment. The authors thank Dr. Nobuyuki Miyaki for helpful discussions. Z.B. acknowledges financial support from the Air Force Office of Scientific Research Grant FA 9550-06-1-0126, the Global Climate and Environmental Program, and NSF Center for Polymer and Macromolecular Assemblies.

Note Added after ASAP Publication. An error was detected in paragraph 6 in the version published August 8, 2007; CuI was added as a reagent in the version published August 14, 2007.

Supporting Information Available: Details of experimental procedures, synthesis of all compounds, UV−vis spectra, FL spectra, cyclic voltammogram, TGA and DSC of polymer **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Babel, A.; Jenekhe, S. A. *J. Am. Chem. Soc.* **2003**, *125*, 13656. (b) Chua, L.-L.; Zaumseil, J.; Chang, J.-F.; Ou, E. C.-W.; Ho, P. K.-H.; Sirringhaus, H.; Friend, R. H. *Nature* **2005**, *434*, 194. (c) Li, Y.; Wu, Y.; Liu, P.; Birau, M.; Pan, H.; Ong, B. S. *Adv. Mater.* **2006**, *18*, 3029.
(2) (a) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864. (b) Winder, C.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 1077.
(3) (a) Zhang, X.; Jenekhe, S. A. *Macromolecules* **2000**, *33*, 2069. (b) Ego, C.; Marsitzky, D.; Becker, S.; Zhang, J.; Grimsdale, A. C.; Mullen, K.; MacKenzie, J. D.; Silva, C.; Friend, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 437. (c) Kulkarni, A. P.; Zhu, Y.; Jenekhe, S. A. *Macromolecules* **2005**, *38*, 1553.
(4) Fichou, D.; Ziegler, C. In *Handbook of Oligothiophenes and Polythiophenes*, 1st ed.; Fichou, D., Ed.; Wiley-VCH: Weinheim, Germany, 1999; Chapter 4, p 183.
(5) (a) Mallik, A. B.; Locklin, J. J.; Mannsfeld, S.; Reese, C.; Roberts, M.; Senatore, M.; Zi, H.; Bao, Z. Design, Synthesis, and Transistor Performance of Organic Semiconductors. In *Organic Thin Film Transistors*, Bao, Z., Locklin, J. J., Eds.; CRC Press: Boca Raton, FL, 2007. (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (c) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359. (d) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028.
(6) (a) Yen-Yi, L.; Gundlach, D. I.; Nelson, S. F.; Jackson, T. N. *IEEE Trans. Electron Devices* **1997**, *44*, 1325. (b) Kelley, T. W.; Muyres, D. V.; Baude, P. F.; Smith, T. P.; Jones, T. D. *Mater. Res. Soc. Symp. Proc.* **2003**, *771*, L6.5.1.
(7) (a) Tokito, S.; Weinfurtner, K.-H.; Fujikawa, H.; Tsutsui, T.; Taga, Y. *Proc. SPIE−Int. Opt. Soc. Eng.* **2001**, *4105*, 69. (b) Hodge, P.; Power, G. A.; Rabjohns, M. A. *Chem. Commun.* **1997**, 73. (c) Klarner, G.; Davey, M. H.; Chen, W.-D.; Scott, J. C.; Miller, R. D. *Adv. Mater.* **1998**, *10*, 993. (d) Ishow, E.; Bouffard, J.; Kim, Y.; Swager, T. M. *Macromolecules* **2006**, *39*, 7854.
(8) Maliakal, A.; Raghavachari, K.; Katz, H.; Chandross, E.; Siegrist, T. *Chem. Mater.* **2004**, *16*, 4980.
(9) (a) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482. (b) Jiang, J.; Kaafarani, B. R.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 2155.
(10) (a) Giesa, R. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1996**, *C36*, 631. (b) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (c) Bunz, U. H. F. *Adv. Polym. Sci.* **2005**, *177*, 1.
(11) Hundertmark, T.; Littke, A. F.; Buchwald, S. L.; Fu, G. C. *Org. Lett.* **2000**, *2*, 1729.
(12) See Supporting Information.
(13) Weder, C.; Wrighton, M. S. *Macromolecules* **1996**, *29*, 5157.
(14) Payne, M. M.; Delcamp, J. H.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 1609.

JA0725403