Macromolecules **2002,** *35,* 7863−7864

Synthesis and Mesoscopic Order of a Sugar-Coated Poly(*p*-phenyleneethynylene)

Belma Erdogan, James N. Wilson, and
Uwe H. F. Bunz*

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

Received May 31, 2002
Revised Manuscript Received July 25, 2002

In this communication we describe the facile Pd-catalyzed synthesis, supramolecular ordering, and spectroscopic behavior of glycosylated poly(*p*-phenyleneethynylene)s (PPE). Sugars—carbohydrates—are ubiquitous in bioscience. Their cellular receptors, lectins, define blood groups and modulate cell agglutination, inflammatory responses, and pathogen/host interactions.[1a] At the same time sugars are hydrophilic modules that can make polymers biocompatible and potentially useful for highly specific biosensory and biodevice applications in the detection of pathogens.[1b]

In a structural sense, sugars are attractive as building blocks in polymer science. Attachment of sugars to macromolecules will guide supramolecular nanoscale organization of polymers and organic materials, even though this aspect has attracted less interest than biosensing and disease-related applications. While Grubbs, Schrock, Whitesides, Kiessling, Roy, and others[2−6] have made significant contributions to the field of nonconjugated neoglycopolymers, much less is known about sugar-decorated conjugated polymers. Notable exceptions are sugar-coated polydiacetylenes[7] and sugar-coated polythiophenes[8] which have been investigated by Charych. PPEs are fascinating conjugated polymers that show high fluorescence in solution and in the solid state.[9] They have successfully been used in light-emitting and sensory devices, and while several ionic, water-soluble PPEs have been reported by now, PPEs with biologically active substituents are not known.[10−13] We present herein the first example of a sugar-coated PPE.

Reaction of 2,5-diiodohydroquinone with penta-*O*-acetyl-*β*-D-glucose in the presence of BF_3−etherate according to the literature[14] furnished the sugar-substituted monomer **1** in 39% yield (see Scheme 1). Reaction of **1** with 1,4-diethynyl-2,5-bisethylhexylbenzene under standard Pd-catalyzed coupling conditions furnished a yellow, highly blue-green emissive solid in almost quantitative yields. The polymer was soluble in THF, hot DMSO, and hot DMF but surprisingly insoluble in chloroform and in aromatic solvents.

IR and NMR spectroscopy revealed that under the reaction conditions the deacetylated polymer **2** had formed. The characteristic band for the ester C=O stretch in the IR and the characteristic band for the methyl protons of the acetyl groups in the ^1H NMR spectrum of the polymer were not present. Under the reaction conditions of the synthesis of the sugar-coated polymer the acetyl groups are hydrolyzed off cleanly to furnish **2** directly. Gel permeation chromatography in THF shows that the polymer has a degree of polymerization (P_n) of 75 with an $M_w/M_n = 2.2$.[15]

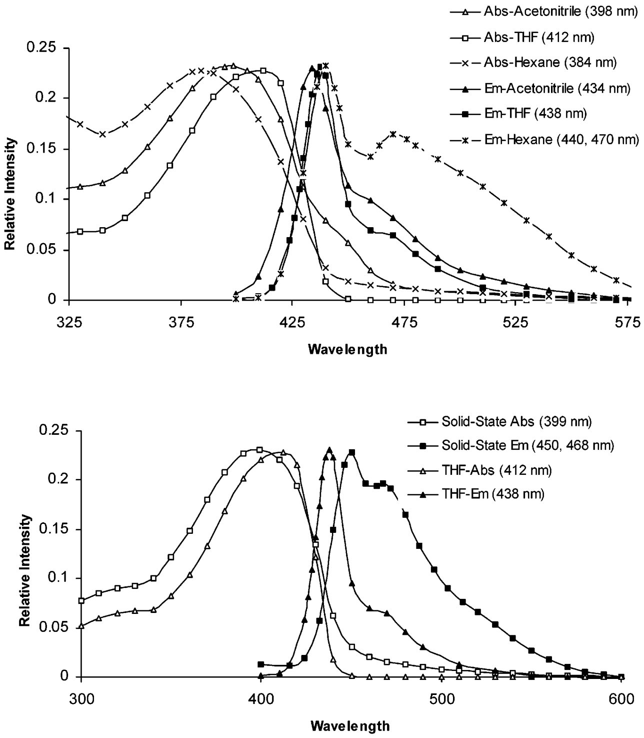


Figure 1. Top: absorption and emission of polymer **2** in different solvents (THF λ_{max} 412 nm; em 438 nm. CH_3CN λ_{max} 398 nm (sh); em 434 nm. Hexanes λ_{max} 384 nm; em 440, 470 nm). Bottom: absorption and emission spectra of **2** in the solid state (λ_{max} 399 nm, em 450, 468 nm) and in THF (λ_{max} 412 nm, em 438 nm).

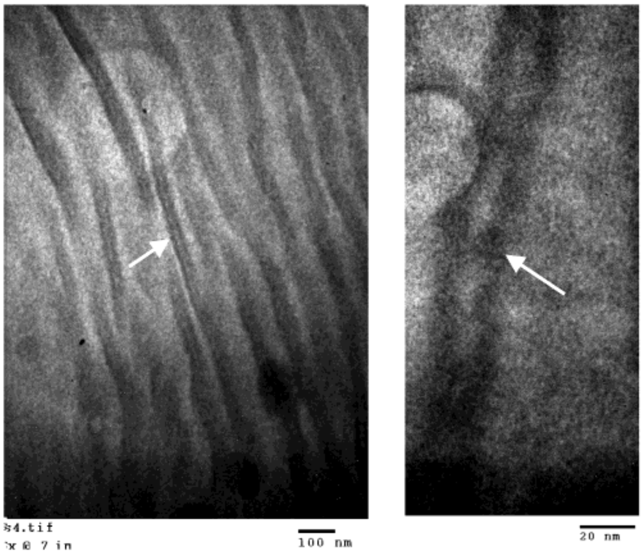


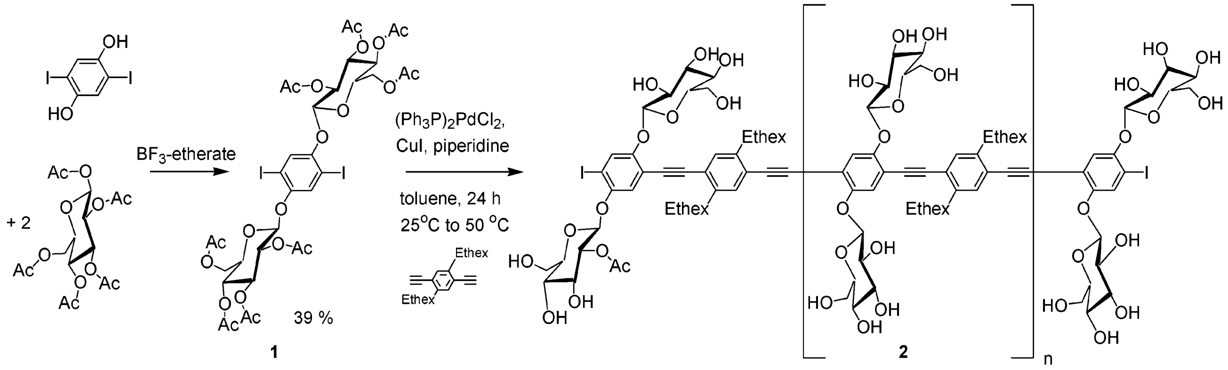
Figure 2. Transmission electron micrographs of thin films of **2** obtained by evaporation of a drop of a solution of **2** in a mixture of H_2O/THF. Scale bars are shown; no staining reagent or shadowing was utilized.

---

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

10.1021/ma025564x CCC: $22.00

Scheme 1



To obtain more information about the electronic and structural properties of **2**, absorption and emission spectroscopy was performed (Figure 1) in a series of different solvents and in thin solid films. As expected, the primary absorption of **2** is significantly dependent upon solvent and aggregation state. In hexane the absorption is most blue-shifted in comparison to the absorption spectrum of **2** in THF. The difference of the spectra of **2** in THF solution and in thin solid films is relative small. It suggests that the large glucose substituents diminish planarization of the main chain and interchain interactions at the same time. The relatively small differences in the solution and solid-state emission spectra give likewise testimony to this interpretation.

Macroscopic samples of **2** form fibrous mats of significant mechanical strengths and are not powdery as the dialkyl-PPEs. Concentrated solutions of **2** in THF show birefringence, and dried lyotropic samples display a small but distinctive Schlieren texture under crossed polarizers, similar to those observed for the dialkyl-PPEs. To elucidate the nature of the phase, we performed transmission electron microscopy upon dried samples of **2** (Figure 2). This polymer forms a lamellar morphology, with the lamellae showing a width of approximately 30−50 nm. Upon higher magnification, the lamellae are doubled and display a fine structure with an apparent interstrand connection every 50 nm. The two-dimensional picture could represent an intertwined composite formed from two PPE strands. The curious double-stranded feature has been observed earlier in another hydrophilic PPE derivative[16,17] where its genesis likewise is not clear. In conclusion, we have prepared the first sugar-substituted PPE derivative and have examined its supramolecular ordering and its spectroscopic behavior. In the future we will report upon interaction of the sugar-coated PPEs with biomolecules and novel PPE-based morphologies.

Acknowledgment. We thank Dana Dunkelberger for help with electron microscopy, the NSF (PI Bunz, CHE 0138-659), and the South Carolina Nanocenter (Thrust Area Nanooptoelectronics) for funding.

Supporting Information Available: Experimental details and spectroscopic characterization of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Mammen, M.; Choi, S.-K.; Whitesides, G. M. *Angew. Chem.* **1998**, *37*, 2754. *Glycochemistry*; Wang, P. G., Bertozzi, C. R., Eds.; Marcel Dekker: New York, 2001. Davies, B. G. *J. Chem. Soc., Perkin Trans.* **1999**, 3215. (b) Langer, R. *Acc. Chem. Res.* **2000**, *33*, 94.
(2) (a) Fraser, C. L.; Grubbs, R. H. *Macromolecules* **1995**, *28*, 7248. (b) Nomura, K.; Schrock, R. R. *Macromolecules* **1996**, *29*, 540.
(3) Roy, R.; Tropper, F. D. *Chem. Commun.* **1988**, 1058. Reuter, J. D.; Myc, A.; Hayes, M. M.; Gan, Z. H.; Roy, R.; Qin, D. J.; Yin, R.; Piehler, L. T.; Esfand, R.; Tomalia, D. A.; Baker, J. R. *Bioconjugate Chem.* **1999**, *10*, 271. Sashiwa, H.; Shigemasa, Y.; Roy, R. *Macromolecules* **2001**, *34*, 3211.
(4) Mortell, K. H.; Weatherman, R. V.; Kiessling, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 2297. Kiessling, L. L.; Pohl, N. L. *Chem. Biol.* **1996**, *3*, 71.
(5) Spaltenstein, A.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 686. Sigal, G. B.; Mammen, M.; Dahmann, G.; Whitesides, G. M. *J. Am. Chem. Soc.* **1996**, *118*, 3789. Choi, S. K.; Mammen, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1997**, *119*, 4103.
(6) (a) Rixman, M. A.; Tsai, Z. H.; Wu, D.; Njus, J. M.; Stark, J. C.; Hankins, J.; Sandman, D. J. *Macromolecules* **2001**, *34*, 7576. Kim, M.; Sandman, D. J. *J. Macromol. Sci., Pure Appl. Chem.* **2001**, *38*, 1291. (b) Meier, S.; Reisinger, H.; Haag, R.; Mecking, S.; Mülhaupt, R.; Stelzer, F. *Chem. Commun.* **2001**, 855.
(7) Okada, S.; Peng, S.; Spevak, W.; Charych, D. E. *Acc. Chem. Res.* **1998**, *31*, 229. Lio, A.; Reichert, A.; Ahn, D. J.; Nagy, J. O.; Salmeron, M.; Charych, D. H. *Langmuir* **1997**, *13*, 6524.
(8) Baek, M. G.; Stevens, R. C.; Charych, D. H. *Bioconjugate Chem.* **2000**, *11*, 777.
(9) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. Bunz, U. H. F. *Acc. Chem. Res.* **2001**, *34*, 998.
(10) 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.
(11) Weder, C.; Sarwa, C.; Montali, A.; Bastiaansen, G.; Smith, P. *Science* **1998**, *279*, 835. Montali, A.; Bastiaansen, G.; Smith, P.; Weder, C. *Nature (London)* **1998**, *392*, 261.
(12) Zhou, Q.; Swager, T. M. *J. Am. Chem. Soc.* **1995**, *117*, 12593. Yang, J. S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 11864.
(13) Water-soluble PPEs: Häger, H.; Heitz, W. *Macromol. Chem. Phys.* **1998**, *199*, 1821. Tan, C.; Pinto, M. R.; Schanze, K. S. *Chem. Commun.* **2002**, 446.
(14) Smits, E.; Engberts, J. B. F. N.; Kellog, R. M.; van Doren, H. A. *J. Chem. Soc., Perkin Trans. 1* **1996**, 2873.
(15) As a testament to its self-organizing properties, there was an additional broad feature at much higher molecular weight.
(16) Schnablegger, H.; Antonietti, M.; Göltner, C.; Hartmann, J.; Cölfen, H.; Samori, P.; Rabe, J. P.; Häger, H.; Heitz, W. *J. Colloid Interface Sci.* **1999**, *212*, 24.
(17) For other ribbonlike supramolecular structures of PPEs, see: (a) Samori, P.; Severin, N.; Müllen, K.; Rabe, J. P. *Adv. Mater.* **2000**, *12*, 579. Samori, P.; Francke, V.; Müllen, K.; Rabe, J. P. *Chem. Eur. J.* **1999**, *5*, 2312. Samori, P.; Sikharulidze, I.; Francke, V.; Müllen, K.; Rabe, J. P. *Nanotechnology* **1999**, *10*, 77. (b) Perahia, D.; Traiphol, R.; Bunz, U. H. F. *Macromolecules* **2001**, *34*, 151. Wilson, J. N.; Steffen, W.; Oda, M.; Lieser, G.; Neher, D.; Bunz, U. H. F. *J. Am. Chem. Soc.* **2002**, *124*, 6830.

MA025564X