Macromolecules

Volume 40, Number 14 July 10, 2007

Communications to the Editor

Conducting Regioregular Polythiophene Block Copolymer Nanofibrils Synthesized by Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) and Nitroxide Mediated Polymerization (NMP)

Mihaela C. Iovu, C. Rockford Craley,
Malika Jeffries-EL, Ashley B. Krankowski, Rui Zhang,
Tomasz Kowalewski, and Richard D. McCullough*

Carnegie Mellon University, Chemistry Department,
4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

Received February 15, 2007
Revised Manuscript Received May 15, 2007

Regioregular polythiophenes (rrPTs) are very important polymers that have some of the best transistor mobilities and solar cell performances among printable electronic materials.[1] Recently, the development of *living* conducting polymers in our lab,[2,3] has produced extremely well-defined regioregular polythiophene structures[4] that will help to provide a full understanding of structure–property relationships in these important advanced materials. In earlier work, we and others have shown dramatic long-range nanofibrilar order in regioregular polythiophenes and the effect of nanofibrilar widths and molecular weights on transistor mobilities.[5,6] While nanofibrilar structures have also been reported in block copolymers incorporating polythiophenes, oligothiophenes, or other conjugated polymers, the synthetic methods used, e.g., atom transfer radical polymerization (ATRP) or ring-opening metathesis polymerization (ROMP), limit the types of conductive structures that can be explored and generate materials containing traces of metals.[7] Alternatively, reversible addition fragmentation chain transfer polymerization (RAFT) is an attractive method for the synthesis of polythiophenes block copolymers because it does not involve the use of a transition metal catalyst.[8] Metal traces present in regioregular polythiophenes block copolymers can result in doping of the polymer diminishing their performance when used as active layer in organic field effect transistors.

Here we present a versatile approach to the synthesis of diblock copolymers containing polythiophenes using the *living* radical polymerization techniques RAFT and NMP to make rrPT-polyisoprenes, and rrPT-polystyrenes. Although RAFT and NMP approaches described in this paper are suitable for the synthesis of both polystyrene and polyisoprene diblock copolymers, we are showing here examples of RAFT polymerization of styrene and NMP polymerization of isoprene. Together with previously reported work on diblock copolymers by atom transfer radical polymerization (ATRP) and anionic polymerization, these methods are capable of producing broad ranges of conducting block copolymers of regioregular polythiophenes.[9] We find that the resultant morphologies are determined by the nature of the second nonconductive block, which generally drive the formation of a self-assembled nanostructure. However, the second block can also destroy long-range nanofibrilar order. Using the *living* Grignard metathesis (GRIM) method, we have previously shown that extremely well-defined regioregular polythiophenes can be synthesized and trivially end-capped with a large variety of end groups.[3] Using the end-capping method, allyl terminated poly(3-hexylthiophene) was prepared and subjected to hydroboration/oxidation reaction yielding hydroxypropyl terminated polymer **1**, which in turn was converted to *living* radical polymerization precursors (Scheme 1).[9] Regioregular polythiophenes were used as macroinitiators, where electrically conductive block copolymers containing conventional polymers such as polyisoprene and polystyrene are prepared using *living* radical polymerization techniques.[8] The advantage of *living* radical polymerization techniques is that the molecular weight of the second block is determined by the molar ratio of monomer polymerized relative to polythiophene macroinitiator, thereby a one-pot reaction can yield a variety of new electronic polymers by taking aliquots during the reaction, thus generating different molar compositions. Each of these materials, therefore have conductivities and morphologies that are related to the molar composition of block copolymer.

---

* Corresponding author. E-mail: rm5g@andrew.cmu.edu.

10.1021/ma070406x CCC: $37.00 © 2007 American Chemical Society

Scheme 1. Synthesis of Poly(3-hexylthiophene) Diblock Copolymers by Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) and Nitroxide Mediated Polymerization (NMP)

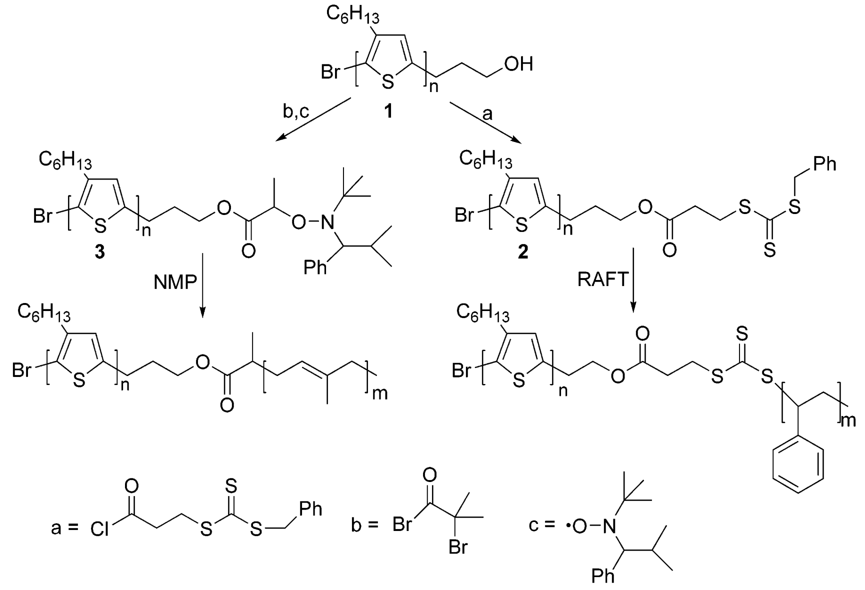

Table 1. Experimental Results for Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) of Styrene and Nitroxide Mediated Polymerization (NMP) of Isoprene[c]

no.	time (min)	mol % PHT[a]	mol % PS (PI)	M_n[b]	PDI[b]
1	0	100	0	10 970	1.20
2	145	76.1	23.9 (PS)	13 240	1.37
3	625	44.6	55.4 (PS)	15 940	1.43
4	1520	40.0	60.0 (PS)	18 400	1.45
5	0	100	0	9000	1.16
6	1200	60	40 (PI)	15 600	1.70
7	2400	35	65 (PI)	20 300	1.80

[a] Determined by ^{1}H NMR. [b] Determined by gel permeation chromatography (GPC) relative to polystyrene standards; M_n = number-average molecular weight, PDI = polydispersity index. [c] Key: PS, polystyrene diblock copolymers synthesized by RAFT; PI, polyisoprene diblock copolymers synthesized by NMP; no. 1 corresponds to poly(3-hexylthiophene) macroRAFT agent; no. 5 corresponds to poly(3-hexylthiophene) nitroxide macroinitiator. $[\text{styrene}]_0:[\mathbf{2}]_0:[\text{AIBN}]_0 = 400:1:0.3$; [styrene]:[TCB] = 2:1; 70 °C (TCB = trichlorobenzene; AIBN = azobis(isobutyronitrile)); $[\text{isoprene}]_0:[\mathbf{3}]_0 = 1000:1$; [isoprene]:[toluene] = 1:2; 110 °C (one point experiments).

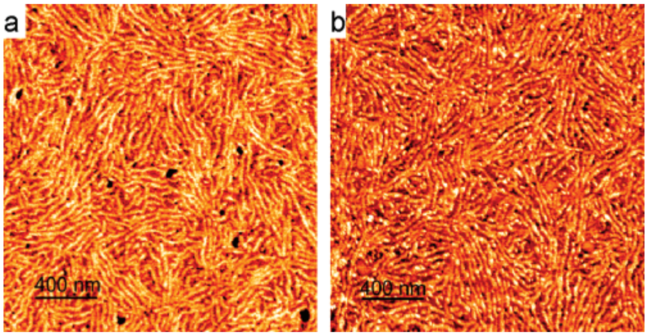

Figure 1. Tapping mode atomic force microscopy (TMAFM) phase images (scan size 2 μm × 2 μm): (a) poly(3-hexylthiophene)-*b*-polystyrene (40 mol % PHT); (b) poly(3-hexylthiophene)-*b*-polyisoprene (35 mol % PHT).

RAFT polymerization was employed for the synthesis of block copolymers containing polystyrene (Scheme 1). Reaction of 3-benzylsulfanylthiocarbonylsulfanylpropionic acid chloride with hydroxypropyl terminated poly(3-hexylthiophene) (**1** in Scheme 1), in the presence of pyridine, yielded a trithiocarbonate macroRAFT agent (**2** in Scheme 1), which was subsequently used for the polymerization of styrene.[10] The increase in the polydispersity index with the monomer conversion (Table 1) indicates the presence of termination and chain transfer reactions. Chain transfer to polymer can take place through radical attack on the α methylene groups of the hexyl side chains. We find that the polydispersity index of these materials is similar to samples prepared by ATRP.[9]

NMP polymerization was used for the synthesis of block copolymers containing polyisoprene (Scheme 1). The reaction of 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy (TIPNO) with a bromoester terminated poly(3-hexylthiophene) generated the alkoxyamine macroinitiator (**3** in Scheme 1), which was subsequently used for polymerization of isoprene.[11] Copolymer composition and the microstructure of the polyisoprene block were determined by ^{1}H NMR. Gel permeation chromatography (GPC) was used to monitor the increases in molecular weight with the conversion (Table 1). The resultant block copolymer (40 h reaction time) contains 65 mol % polyisoprene, as determined by ^{1}H NMR. The polyisoprene block contains approximately 90% 1,4-units (cis and trans), 5% 1,2-units, and 5% 3,4-units (see Supporting Information).

Surface morphology of polymer films was visualized with tapping mode atomic force microscopy (TMAFM, Figure 1, parts a and b and the Supporting Information). Nanofibrilar morphology was observed for thin films of the block copolymers prepared by drop-casting from toluene solutions followed by free evaporation of the solvent. This type of nanofibrilar morphology was previously demonstrated for regioregular poly(3-hexylthiophene), where the width of the nanofibril corresponds very closely to the weight-average contour length of the polymer chain.[5] The nanofibrils are virtually aligned by self-assembly and possess remarkable long-range order leading to densely packed wires.

Conductivities of the poly(3-hexylthiophene) precursors are higher than those of the diblock copolymers (Table 2 and Supporting Information). However, relatively high conductivities were observed for the diblock copolymers. As expected, the conductivity of the diblock copolymers decreases with the increase of the content of the nonconducting block. The resulting copolymers were very soluble in many organic solvents and possessed excellent film forming properties.

Table 2. Conductivities of Poly(3-hexylthiophene)-*b*-polystyrene (PHT-*b*-PS) and Poly(3-hexylthiophene)-*b*-polyisoprene (PHT-*b*-PI)[a]

polymer	mol % PHT	M_n (PDI)	σ (S/cm)
PHT−OH	100	9000 (1.16)	20.0
PHT-*b*-PS	92	11570 (1.27)	17.0
PHT-*b*-PS	76	13240 (1.37)	10.0
PHT-*b*-PS	45	16940 (1.45)	6.0
PHT-*b*-PS	40	18400 (1.45)	4.0
PHT-*b*-PI	60	15600 (1.7)	8.0
PHT-*b*-PI	35	20300 (1.8)	2.0

[a] M_n = number-average molecular weight, PDI = polydispersity index); σ = conductivities measured on iodine doped samples by four point probe technique.

The presented strategy can be used to make conductive block copolymers of regioregular polythiophenes of different compositions using RAFT and NMP *living* radical polymerization methods. The nonconductive polymer block can assume different structures and a range of variational molecular weights and compositions, yielding new methods that can generate novel electronic and optical materials. Additionally, the diblock copolymers synthesized by RAFT do not contain metal traces.

Acknowledgment. We gratefully acknowledge NSF CHE 0415369, MURI, and NIOSH for financial support.

Supporting Information Available: Text giving experimental procedures and characterization, figures showing ^{1}H NMR spectra and TMAFM images, schemes showing syntheses, and tables of experimental results for RAFT and NMP. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Sirringhaus, H.; Tessler, N.; Thomas, D. S.; Brown, P. J.; Friend, R. H. *Adv. Solid State Phys.* **1999**, *39*, 101−110. (b) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533−4542. (c) Sirringhaus, H. *Adv. Mater.* **2005**, *17*, 2411−2425.

(2) (a) Lowe, R. S.; Khersonsky, S. M.; McCullough, R. D. *Adv. Mater.* **1999**, *11*, 250−253. (b) Lowe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324−4333. (c) Sheina, E. E.; Liu, J.; Iovu, M. C.; Laird, D. W.; McCullough, R. D. *Macromolecules* **2004**, *37*, 3526−3528. (d) Iovu, M. C.; Sheina, E. E.; Gil, R. R.; McCullough, R. D. *Macromolecules* **2005**, *38*, 8649−8656.

(3) (a) Jeffries-El, M.; Sauve, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346−10352. (b) Jeffries-El, M.; Sauve, G.; McCullough, R. D. *Adv. Mater.* **2004**, *16*, 1017−1019.

(4) (a) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169−1171. (b) Miyakoshi, R.; Yokoyama, A.; Yokozawa, T. *J. Am. Chem. Soc.* **2005**, *127*, 17542−17547.

(5) Zhang, R.; Li, B.; Iovu, M. C.; Jeffries-El, M.; Sauve, G.; Cooper, J.; Jia, S.; Tristram-Nagle, S.; Smilgies, D. M.; Lambeth, D. N.; McCullough, R. D.; Kowalewski, T. *J. Am. Chem. Soc.* **2006**, *128*, 3480−3481.

(6) (a) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J. *Adv. Mater.* **2003**, *15*, 1519−1522. (b) Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Liu, J.; Frechet, J. M. J.; Toney, M. F. *Macromolecules* **2005**, *38*, 3312−3319. (c) Goh, C.; Kline, R. J.; McGehee, M. D.; Kadnikova, E. N.; Frechet, J. M. J. *Appl. Phys. Lett.* **2005**, *86*, 122110/1−122110/3. (d) DeLongchamp, D. M.; Sambasivan, S.; Fischer, D. A.; Lin, E. K.; Chang, P.; Murphy, A. R.; Frechet, J. M. J.; Subramanian, V. *Adv. Mater.* **2005**, *17*, 2340−2344. (e) DeLongchamp, D. M.; Vogel, B. M.; Jung, Y.; Gurau, M. C.; Richter, C. A.; Kirillov, O. A.; Obrzut, J.; Fischer, D. A.; Sambasivan, S.; Richter, L. J.; Lin, E. K. *Chem. Mater.* **2005**, *17*, 5610−5612. (f) Kline, R. J.; McGehee, M. D.; Toney, M. F. *Nat. Mater.* **2006**, *5*, 222−228.

(7) (a) Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. *Angew. Chem., Int. Ed.* **2002**, *41*, 329−332. (b) Radano, C. P.; Scherman, O. A.; Stingelin-Stutzmann, N.; Müller, C.; Breiby, D. W.; Smith, P.; Janssen, R. A. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2005**, *127*, 12502−12503. (c) de Cuendias, A.; Hellaye, M. L.; Lecommandoux, S.; Cloutet, E.; Cramail, H. *J. Mater. Chem.* **2005**, *15*, 3264−3267. (d) Sivula, K.; Ball, Z. T.; Watanabe, N.; Fréchet, J. M. J. *Adv. Mater.* **2006**, *18*, 206−210. (e) Sun, S.-S.; Sariciftci, N. S. *Organic Photovoltaics: Mechanisms, Materials and Devices*; CRC Press/Taylor&Francis: Boca Raton, FL, 2003. (f) Hawker, C. J.; Wooley, K. L. *Science*, **2005**, *309*, 1200−1205.

(8) (a) Matyjaszewski, K.; Davis, T. P. *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, NJ, 2002. (b) Chiefari, J.; Chong, Y. K.; Ercole, F.; Kristina, J.; Jeffery, J.; Le, T. P.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559−5569.

(9) (a) Iovu, M. C.; Jeffries-El, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. *Polymer* **2005**, *46*, 8582−8586. (b) Iovu, M. C.; Jeffries-El, M.; Zhang, R.; Kowalewski, T.; McCullough, R. D. *J. Macromol. Sci. Part A* **2006**, *43* (12), 1991−2000.

(10) Stenzel, M. H.; Davis, T. P.; Fane, A. G. *J. Mater. Chem.* **2003**, *13*, 2090−2097.

(11) (a) Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. *Macromolecules* **2000**, *33*, 363−370. (b) Wegrzyn, J. K.; Stephan, T.; Lau, R.; Grubbs, R. B. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 2977−2984.

MA070406X