NOTE

A High Purity Approach to Poly(3-hexylthiophene) Diblock Copolymers

YOUNGMIN LEE,[1] KEN-ICHI FUKUKAWA,[2] JOONA BANG,[3] CRAIG J. HAWKER,[2] JIN KON KIM [1]

[1]National Creative Research Initiative Center for Block Copolymer Self-Assembly, Department of Chemical Engineering and Polymer Research Institute, Pohang University of Science and Technology, Kyungbuk 790-784, Republic of Korea

[2]Departments of Materials, Chemistry and Biochemistry, Materials Research Laboratory, University of California, Santa Barbara, California 93106

[3]Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea

Received 8 July 2008; accepted 16 September 2008
DOI: 10.1002/pola.23091
Published online in Wiley InterScience (www.interscience.wiley.com).

Keywords: atom transfer radical polymerization (ATRP); block copolymers; conducting polymers; poly(3-hexylthiophene)

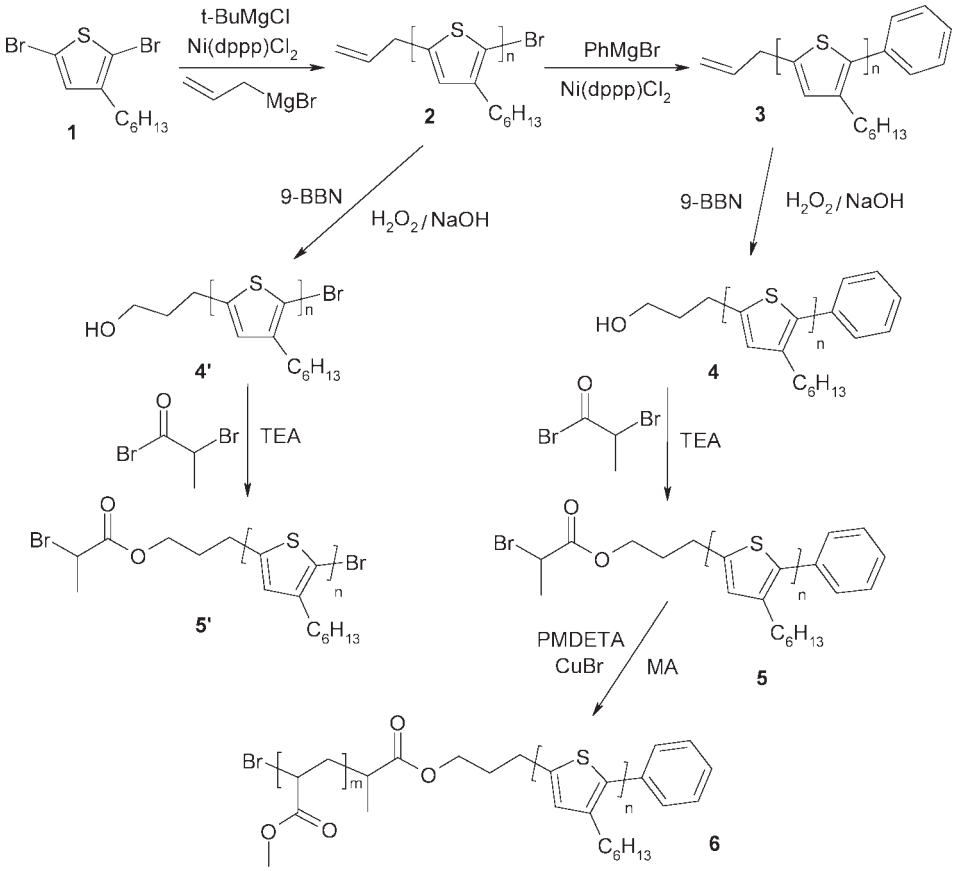
INTRODUCTION

The combination of superior optoelectronic properties and enhanced solubility[1,2] for regioregular poly(3-hexylthiophene) (rr-P3HT) has enabled materials based on P3HT to be widely used for organic field-effect transistors,[3–5] chemical sensors,[6,7] and photovoltaic solar cells.[8–11] Significantly, the optoelectronic performance of rr-P3HT thin film has been shown to depend on molecular weight,[12] processing conditions,[10] and end group functionalities which places significant demands on developing synthetic approaches that do not lead to defects in the P3HT chain.[13] This is especially true for the preparation of P3HT block copolymers where control of the polymeric chain ends is essential and the successful incorporation of nonconductive vinyl blocks, such as polystyrene, leads to modification of the mechanical and electronic properties.[14–22] Starting with the pioneering work of McCullough and coworkers, a variety of groups have prepared rr-P3HT-based block copolymers using a combination of Grignard metathesis method (GRIM)[17] and controlled radical polymerization (i.e., atom transfer radical polymerization, ATRP)[18,19] or anionic polymerization.[20,21] More recently, P3HT-*block*-poly(lactic acid) copolymers have also been synthesized from telechelic P3HT derivatives by ring-opening polymerization.[22]

For vinyl-based systems, controlled radical polymerization (CRP) such as ATRP has a number of advantages such as wide monomer selection, tolerance for various functionalities, and simplified synthetic procedures. As demonstrated by several research groups,[17–24] P3HT-based block copolymers have been successfully synthesized by CRP and in these cases, a monofunctional P3HT macroinitiator is initially prepared containing an initiating fragment at one chain end, for example a 2-bromopropionyl bromide unit for ATRP procedures.[18,19] In many examples, the second P3HT chain end arises from the 2,5-dibromo-3-hexyl thiophene monomer and the resulting ω-bromo chain end is undesirable for a variety of reasons. For example, the thiophene-bromine bond can be active in a variety of side reactions which may lead to the introduction of defects, such as coupling between P3HT chains, either during synthesis of the macroinitiator or during the subsequent ATRP reaction. The presence of small amounts of coupled P3HT having a higher molecular weight and two active initiating chain ends would lead to an ABA block structure that can greatly affect the phase behavior of P3HT block copolymers. Previously, McCullough and coworkers have elegantly

Correspondence to: C. J. Hawker (E-mail: hawker@mrl.ucsb.edu) or J. K. Kim (E-mail: jkkim@postech.ac.kr)

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 46, 8200–8205 (2008)



Scheme 1. Reaction scheme for the synthesis of P3HT macroinitiators, **5** and **5′**, and the corresponding P3HT-*block*-poly(methyl acrylate) copolymer, **6**.

demonstrated[18] the synthesis of P3HT block copolymers with a ω-H chain end by a multi-step modification procedure, however no comparison of these materials with the corresponding chain end functionalized copolymers is made. In this work, the occurrence of side reactions during the synthesis of well defined P3HT macroinitiators using standard procedures is investigated and the preparation of high purity macroinitiators and P3HT-*block*-polymethylacrylate copolymers (P3HT-*b*-PMA) described.

EXPERIMENTAL

Materials

N-bromosuccinimide (NBS), triethylamine (TEA) and *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) were purchased from Sigma Aldrich, and used with no further purification. THF was stirred with CaH_2, and distilled before use. In addition, methyl acrylate was passed through a basic alumina column and distilled before use. CuBr (Aldrich, 99.999%) was washed with glacial acetic acid, absolute ethanol and ether anhydrous, filtered, and dried in vacuum oven at 60 °C.

Characterization

Gel permeation chromatography (GPC) was performed using THF as an eluent in association with a Waters 2487 dual wavelength absorbance UV detector. Flow rate was 1 mL/min at 30 °C. ^{1}H NMR spectra were obtained with a Bruker Avance 300 MHz spectrometer using $CDCl_3$ as the solvent.

Synthesis

Allyl-Terminated Poly(3-hexylthiophene), 2

The synthetic scheme for preparation of well defined P3HT macroinitiators and P3HT-*block*-polymethylacrylate copolymers is given in Scheme 1. 2,5-dibromo-3-HT, **1** was synthesized by reaction of two equivalent of NBS[24] with 3-HT and polymerized to give allyl-terminated P3HT, **2** by GRIM procedures, followed by the termination with allylmagnesium bromide.[19] The allyl-

terminated P3HT, **2** [M_n = 6.9 kg/mol, polydispersity index (PDI) = 1.15] was further fractionated by sequential Soxhlet extractions with hexane (M_n = 2.3 kg/mol, PDI = 1.21), dichloromethane (M_n = 6.7 kg/mol, PDI = 1.11), and THF (M_n = 9.0 kg/mol, PDI = 1.07). In this study, the polymer obtained by extraction with dichloromethane was used. The regioregularity of **2** was 92.1% as estimated from the integration ratio of relevant peaks (~ 2.8 ppm) in the ^{1}H NMR spectrum.

Yield: 36.6%. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm): 6.98 (s, 1H), 6.0 (m, 1H), 5.19 (dd, J = 8 Hz and 3 Hz, 1H), 5.10 (dd, J = 8 Hz and 3 Hz, 1H), 3.5 (d, J = 8 Hz, 2H), 2.8 (t, J = 3 Hz, 2H), 1.7 (m, 2H), 1.43 (m, 2H), 1.36 (m, 4H), and 0.92 (t, 3H).

Monophenyl-Terminated Poly(3-hexylthiophene), 3

The monobromo-terminated P3HT, **2** (1.92 g, 0.38 mmol) was dissolved in dry THF (120 mL) at room temperature under nitrogen and Ni(dppp)Cl_2 (62.4 mg, 0.12 mmol) added, followed by phenylmagnesium bromide (38.4 mL, 1.0 M in THF, 38.4 mmol). The reaction mixture was stirred overnight at 40 °C, and the α-allyl-ω-phenyl end functional P3HT, **3** isolated by precipitation into methanol and purified by Soxhlet extraction with methanol and dichloromethane. Yield: 83.4%. ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm), Fig. 1(a)]: 7.4 (m, 5H$_k$), 6.98 (s, 1H$_g$), 6.0 (m, 1H$_i$), 5.19 (dd, J = 8 Hz and 3 Hz, 1H$_j$), 5.10 (dd, J = 8 Hz and 3 Hz, 1H$_j$), 3.5 (d, J = 8 Hz, 2H$_h$), 2.8 (t, J = 3 Hz, 2H$_f$), 1.7 (m, 2H$_e$), 1.43 (m, 2H$_d$), 1.36 (m, 2H$_c$+ 2H$_b$), and 0.92 (t, 3H$_a$); M_n = 6.5 kg/mol and PDI = 1.13.

α-Hydroxypropyl-ω-phenyl-Terminated Poly(3-hexylthiophene), 4

The chain end modified P3HT, **4** was synthesized from the alkene derivative, **3**, by a two-step procedure using 9-BBN followed by $NaOH/H_2O_2$ as detailed in the literature.[19]

Yield: 73.8%. ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm), Fig. 1(b)]: 7.4 (m, 5H), 6.98 (s, 1H), 3.8 (m, 2H$_p$), 2.8 (m, 2H), 1.7 (m, 2H), 1.43 (m, 2H), 1.36 (m, 4H), and 0.92 (m, 3H); M_n = 6.4 kg/mol and PDI = 1.12.

α-Bromoester-ω-phenyl-Terminated Poly(3-hexylthiophene), 5

The α-Bromoester-ω-phenyl end functionalized P3HT, **5** was synthesized from **4** according to the method in ref 19. The feed ratio of TEA/2-bromo propionyl bromide to P3HT-OH was 600:600:1.

Yield: 71.4%. ^{1}H NMR [300 MHz, $CDCl_3$, δ (ppm), Fig. 1(c)]: 7.4 (m, 5H), 6.98 (s, 1H), 4.41 (m, 1H$_n$), 4.27 (m, 2H$_m$), 2.8 (m, 2H), 1.7 (m, 2H), 1.43 (m, 2H), 1.36 (m, 4H), and 0.92 (s, 3H); M_n = 6.3 kg/mol and PDI = 1.15.

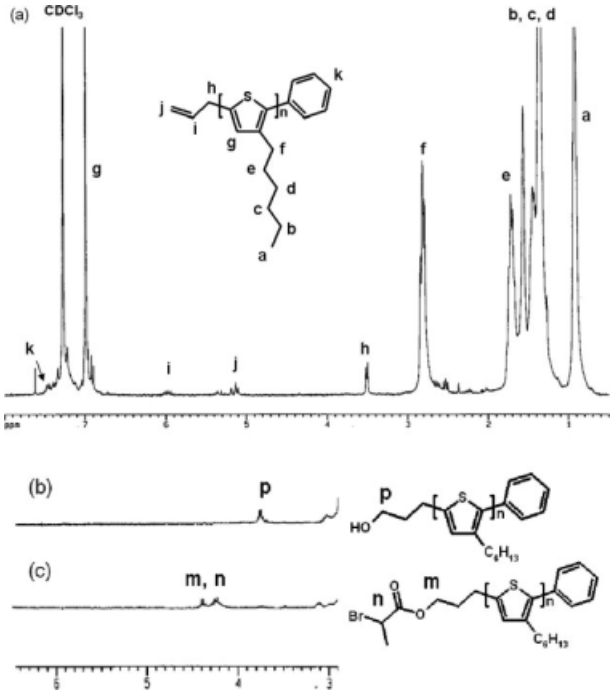


Figure 1. ^{1}H NMR spectra of (a) α-allyl-ω-phenyl end functionalized P3HT, **3**, (b) α-hydroxypropyl-ω-phenyl end functionalized P3HT, **4**, and (c) α-bromoester-ω-phenyl end functionalized P3HT, **5**.

As a control sample, the corresponding P3HT macroinitiator, **5′**, which still contains the ω-bromo group was prepared. For this purpose, the α-hydroxypropyl-ω-bromo end functionalized P3HT, **4′** was synthesized from **2**, and esterification with 2-bromopropionyl bromide was carried out as above. The feed ratio of TEA/2-bromo propionyl bromide to P3HT-OH was 600:600:1 equivalents.

Synthesis of P3HT Block Copolymers, 6

A mixture of CuBr (5.8 mg, 0.04 mmol) and P3HT macroinitiator (0.2 g, 0.04 mmol) in dry toluene (1.8 mL) was added to a 10 mL ampoule and stirred at room temperature for 5 min. PMDETA (9 μL, 0.04 mmol) and methyl acrylate (1.8 mL, 20 mmol) were then added and after three freeze-thaw cycles, the ampoule was sealed and immersed in a thermostated oil bath at 80 °C. After the desired reaction time (determined for target conversion and molecular weight), the reaction mixture was diluted with THF (5 mL) and purified by passing through a neutral alumina column followed by precipitated in methanol. This gave the desired P3HT-*b*-PMA, **6,** block copolymer. ^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm), not shown here): 6.98 (s, 1H), 3.66 (s, 3H), 2.8 (t, 2H), 2.3 (m, 1H), 1.7 (m, 2H), 1.43 (m, 2H), 1.36 (m, 4H), and 0.92 (t, 3H); M_n = 10.9 kg/mol and PDI = 1.19.

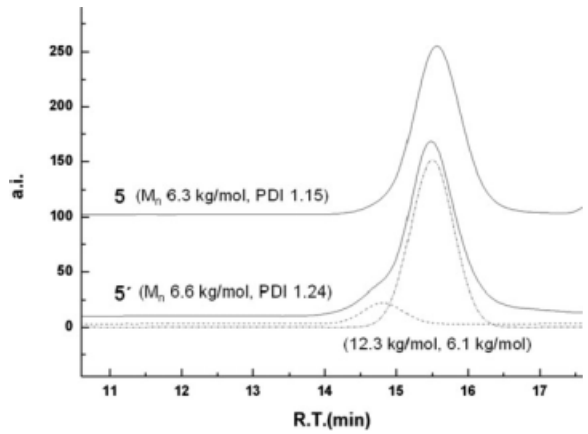


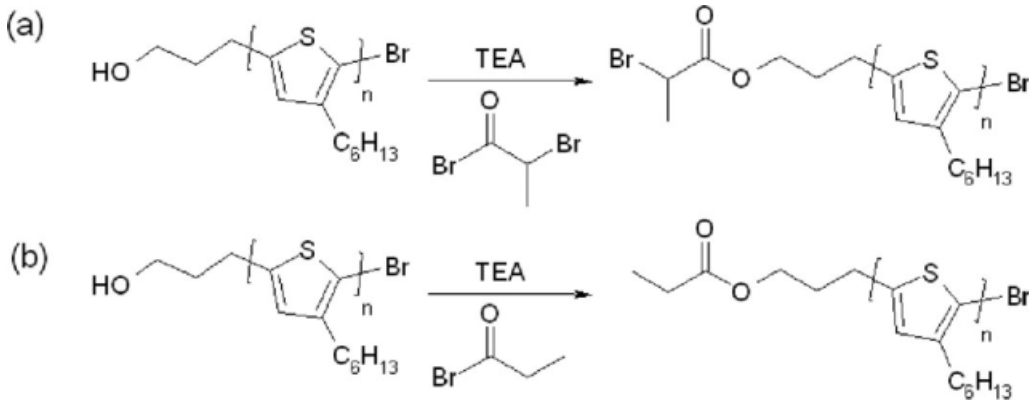
Figure 2. GPC traces and molecular weights for α-bromoester-ω-phenyl P3HT macroinitiator, **5**, α-bromoester-ω-bromo P3HT macroinitiator, **5′** and the associated deconvolution (dotted line) of the GPC trace of **5′**.

RESULTS AND DISCUSSION

As shown in Scheme 1, the telechelic P3HT, **2**, containing an allyl chain end and a bromo chain end was prepared by GRIM polymerization starting from 2,5-dibromo-3-hexyl thiophene, **1**. Traditionally, hydroboration followed by oxidation leads to the corresponding primary alcohol, **4′**, which can be esterified with 2-bromopropionyl bromide to give the desired P3HT macroinitiator, **5′**. In examining this sequence of reactions in detail, the presence of the thiophene–bromine bond was considered a potentially reactive position and to avoid possible side reactions the synthetic strategy was modified by reaction of **2** with phenyl magnesium bromide in the presence of $Ni(dppp)Cl_2$. This leads to the phenylated derivative, **3**, which contains a single allyl chain end and a single phenyl chain end. Figure 1 shows the ^1H NMR spectrum of α-allyl-ω-phenyl P3HT, **3,** from which allyl protons at 6.0, 5.1, and 3.5 ppm, and phenyl protons at 7.4 ppm are clearly observed. Hydroboration and oxidation of **3** was shown to give the α-hydroxypropyl-ω-phenyl P3HT, **4**, the structure of which was confirmed by the complete disappearance of allyl protons and the appearance of a new signal at 3.8 ppm in ^1H NMR spectrum [Fig. 1(b)]. Finally, the α-bromoester-ω-phenyl end functionalized P3HT macroinitiator, **5,** was prepared by esterification of **4** with 2-bromopropionyl bromide. Formation of the bromoester from the hydroxypropyl derivative was confirmed by the ^1H NMR spectrum which showed the disappearance of the primary CH_2OH resonance at 3.8 ppm and the appearance of resonances due to the bromoester group at 4.4 ppm and 4.3 ppm [Fig. 1(c)]. For comparative purposes, the ability to prepare two macroinitiators, **5** and **5′**, from the same starting P3HT derivative, **2**, allows a direct comparison of the influence of the bromo chain end on the purity of the resulting diblock copolymers.

In characterizing the macroinitiators, **5** and **5′**, the GPC trace for the unmodified P3HT derivative, **5′**, clearly shows a shoulder at higher molecular weights whereas the phenylated P3HT, **5**, displayed a symmetrical peak with the same peak molecular weight and lower polydispersity (Fig. 2). By deconvolution of the peak for **5′**, the amount of the side product was determined to be ~ 10 wt % with the number-average molecular weight (M_n = 12.3 kg/mol) being essentially twice that observed for the main product (M_n = 6.4 kg/mol). Significantly, the GPC traces for the starting hydroxyl derivatives, **4** and **4′**, were approximately the same and so the appearance of the higher molecular weight side product occurred during the esterification step and was a result of the presence of the terminal bromide group.

To gain more insight into the nature of the side reaction, two model reactions, as shown in Scheme 2, were carried out. Initially, the reaction between the bromo-



Scheme 2. Model chemistry for the investigation of possible side reactions during the synthesis of P3HT macroinitiators: (a) reaction of the hydroxypropyl end functional P3HT, **4′**, and 2-bromopropionyl bromide and (b) reaction of the hydroxypropyl end functional P3HT, **4′**, and propionyl bromide.

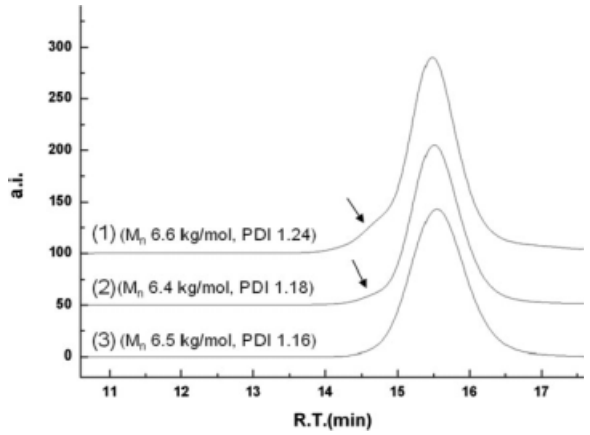


Figure 3. GPC traces and molecular weight for (1) reaction of hydroxypropyl-ω-bromo end functionalized P3HT, **4′**, and 600 equivalents of 2-bromopropionyl bromide and TEA; (2) reaction of hydroxypropyl-ω-bromo end functionalized P3HT, **4′**, and 100 equivalents of 2-bromopropionyl bromide and TEA, and (3) reaction of hydroxypropyl-ω-bromo end functionalized P3HT, 4′, with 600 equivalents of propionyl bromide and TEA. Arrows indicates a shoulder corresponding to the side product.

substituted, hydroxypropyl end functionalized P3HT, **4′**, and 2-bromopropionyl bromide was performed under a variety of different reaction conditions [Scheme 2(a)]. For example, the feed ratio of TEA/2-bromopropionyl bromide to P3HT-OH, **4′**, was changed from 600:600:1 to 100:100:1 and the GPC traces for the resulting products clearly shows that the amount of the byproduct increased with increasing amounts of TEA/2-bromopropionyl bromide. In a second series of experiments, the esterification of **4′** with a nonfunctional acyl bromide, propionyl bromide, was examined to determine the influence of the bromine in 2′ position of 2-bromopropionyl bromide. Interestingly, the effect of removing the 2-bromopropionyl group was similar to the effect of replacing the bromothiophene end group with a phenyl end group, esterification was confirmed by ^{1}H NMR (4.1 ppm), however the GPC traces were symmetrical with no higher molecular weight side products (Fig. 3). This suggests that the side reaction is due to a combination of the bromothiophene end group, the α-bromo group in the ATRP-initiating fragment and the large excess of acylating agent needed to fully functionalize the polymeric chain end.

The utility of this strategy for minimizing side reactions during the preparation of the P3HT macroinitiator allows low polydispersity, high purity block copolymers to be prepared when compared with traditional strategies. From **5**, a series of P3HT-*b*-PMA diblock copolymers were prepared by ATRP and their molecular characteristics shown in Table 1 with the mole fraction of P3HT determined by ^{1}H NMR analysis. Significantly, the polydispersity of the block copolymers prepared from **5** is lower than that obtained for comparable block copolymers prepared from the bromothiophene-terminated derivative, **5′**. For example, reaction of **5** with 500 equivalents methyl acrylate under standard ATRP conditions gave the diblock copolymer, **6**, the polydispersity of which was found to be 1.23. In direct contrast, under the same polymerization conditions the polydispersity of the diblock copolymer prepared by **5′** was observed to be 1.36 with a significant shoulder at lower retention times which corresponds to the higher molecular weight, ABA triblock copolymer.

CONCLUSIONS

The presence of a terminal bromo chain end in well-defined P3HT derivatives prepared by GRIM polymerization was shown to have an adverse effect on the purity of block copolymers prepared by ATRP. By replacing the ω-bromine of the P3HT macroinitiator with a phenyl group, followed by functionalization of the α-chain end with a 2′-bromopropionyl-initiating unit, high purity P3HT macroinitiators could be prepared. This synthetic scheme allows access to narrow molecular weight distribution, high purity AB diblock copolymers based on P3HT and an ATRP-derived vinyl block.

This work was supported by the National Creative Research Initiative Program supported by KOSEF and by the National Science Foundation (UCSB Materials

Table 1. Crude Molecular Weight Characterization Data for the Block Copolymer, P3HT-*b*-PMA Prepared from the Phenyl End Functionalized P3HT Macroinitiator, **5**, by ATRP as a Function of Reaction Time

Reaction Time (min)	M_n (kg/mol)	M_w (kg/mol)	PDI	P3HT (mol%)	PMA (mol%)
0	6.3	7.3	1.15	100	0
100	7.2	8.9	1.23	87.8	12.2
200	7.5	9.3	1.25	80.7	19.3
400	9.8	13.1	1.33	41.5	58.5

Research Laboratory, DMR 05-20,415; PREM DMR 06-11,539, and NIRT 05-06,309).

REFERENCES AND NOTES

1. Skotheim, T.; Reynolds, J.; Elsembauer, R.Handbook of Conducting Polymers, 2nd ed.; Marcel Dekker: New York, 1998.
2. (a) Nalwa, J. S. Handbook of Organic Conductive Molecules and Polymers; Wiley & Sons: New York, 1996; (b) Nicolas, M.; Guittard, F.; Géribaldi, S. J Polym Sci Part A: Polym Chem 2007, 45, 5872–5883; (c) Roviello, A.; Buono, A.; Carella, A.; Roviello, G.; Cassinese, A.; Barra, M.; Biasucci, M. J Polym Sci Part A: Polym Chem 2007, 45, 1758–1770.
3. (a) Wang, G.; Swensen, J.; Moses, D.; Heeger, A. J. J Appl Phys 2003, 93, 6137; (b) Cheng, K. F.; Liu, C. L.; Chen, W. C. J Polym Sci Part A: Polym Chem 2007, 45, 5872–5883; (c) Zhang, C.; Sun, S. S. J Polym Sci Part A: Polym Chem 2007, 45, 41–47; (d) Zhou, E.; He, C.; Tan, Z.; Yang, C.; Li, Y. J Polym Sci Part A: Polym Chem 2006, 44, 4916–4922; (e) Zhou, E.; Hou, J.; Yang, C.; Li, Y. J Polym Sci Part A: Polym Chem 2006, 44, 2206–2214.
4. Sirringhaus, H. Adv Mater 2005, 17, 2411.
5. Panzer, M. J.; Frisbie, D. D. Adv Funct Mater 2006, 16, 1051.
6. Li, B.; Sauve, G.; Iovu, M. C.; Jeffries-EL, M.; Zhang, R.; Cooper, J.; Santhanam, S.; Schultz, L.; Revelli, J. C.; Kusne, A. G.; Kowalewski, T.; Snyder, J. L.; Weiss, L. E.; Fedder, G. K.; McCullough, R. D.; Lambeth, D. N. Nano Letter 2006, 6, 1598.
7. McQuade, D. T.; Pullen, A. E.; Swager, T. M. Chem Rev 2000, 100, 2537.
8. (a) Padinger, F.; Rittberger, R. S.; Sariciftci, N. S. Adv Funct Mater 2003, 12, 85; (b) Zhou, E.; Tan, Z.; He, Y.; Yang, C.; Li, Y. J Polym Sci Part A: Polym Chem 2007, 45, 629–638; (c) Egbe, D. A. M.; Nguyen, L. H.; Schmidtke, K.; Wild, A.; Sieber, C.; Guenes, S.; Sariciftci, N. S. J Polym Sci Part A: Polym Chem 2007, 45, 1619–1631; (d) Wang, H. Y.; Wan, J. H.; Jiang, H. J.; Wen, G. A.; Feng, J. C.; Zhang, Z. J.; Peng, B.; Huang, W.; Wei, W. J Polym Sci Part A: Polym Chem 2007, 45, 1066–1073; (e) Shin, W. S.; Kim, S. C.; Lee, S. C.; Jeon, H. S.; Kim, M. K.; Naidu, K.; Jin, S. H.; Lee, J. K.; Lee, J. W.; Gal, Y. S. J Polym Sci Part A: Polym Chem 2007, 45, 1394–1402.
9. Reyes-Reyes, M.; Kim, K.; Carroll, D. L. Appl Phys Lett 2005, 87, 083506.
10. Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. Nat Mater 2005, 4, 864.
11. Kim, J. Y.; Lee, K.; Coaters, N. E.; Moses, D.; Nguyen, T.; Dante, M.; Heeger, A. J. Science 2007, 317, 222.
12. Kline, R. J.; McGehee, M. K. Adv Mater 2003, 15, 1519.
13. Liu, J.; Tanaka, T.; Sivula, K.; Alivisatos, A. P.; Fréchet, J. M. J. J Am Chem Soc 2004, 126, 6551.
14. Goffri, S.; Müller, C.; Stingelin-Stutzmann, N.; Breiby, D. W.; Radano, C. P.; Andreasen, J. W.; Thompson, R.; Janssen, R. A. J.; Nielsen, M. M.; Smith, P.; Sirringhaus, H. Nat Mater 2006, 5, 950.
15. Lu, G.; Tang, H.; Qu, Y.; Li, L.; Yang, X. Macromolecules 2007, 40, 6579.
16. Patricio, P. S. O.; Calado, H. D. R.; de Oliveira, FAC; Righi, A.; Neves, BRA; Silva, G.G.; Cury, L. A. J Phys: Condens Matter 2006, 18, 7529.
17. (a) Loewe, R. S.; Khersonksky, S. M.; McCullough, R. D. Adv Mater 1999, 11, 250; (b) Jeffries-EL, M; Sauve, G.; McCullough, R. D. Macromolecules, 2005, 38, 10346–10352.
18. Liu, J.; Sheina, E.; Kowalewski, T.; McCullough, R. D. Angew Chem Int Ed Engl 2002, 41, 329.
19. (a) Iovu, M. C.; Jeffries-EL, M.; Sheina, E. E.; Cooper, J. R.; McCullough, R. D. Polymer 2005, 46, 8582; (b) Iovu, M. C.; Craley, C. R.; Jeffries-EL, M.; Krankowski, A. B.; Zhang, R.; Kowalewski, T.; McCullough, R. D. Macromolecules, 2007, 40, 4733–4735.
20. Iovu, M. C.; Jeffries-EL, M.; Zhang, R.; Kowalewski, T.; McCullough, R. D. J Mater Sci A 1991, 2006, 43.
21. Dai, C.; Yen, W.; Lee, Y.; Ho, C.; Su, W. J Am Chem Soc 2007, 129, 11036.
22. Boudouris, B. W.; Frisbie, C. D.; Hillmyer, M. A. Macromolecules 2008, 41, 67.
23. Sivula, K.; Ball, Z. T.; Watanabe, N.; Frechet, J. M. J. Adv Mater 2006, 18, 206.
24. Radano, C. P.; Scherman, O. A.; Stingelin-Stutzmann, N.; Mueller, C.; Breiby, D. W.; Smith, P.; Janssen, R. A. J.; Meijer, E. W. J Am Chem Soc 2005, 127, 12502.