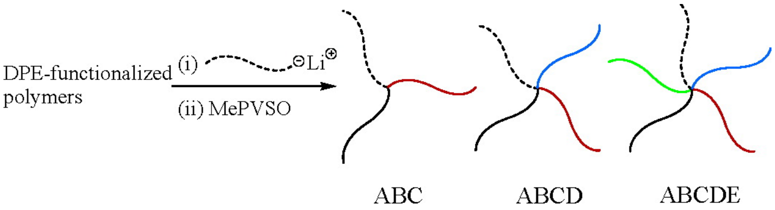
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

Synthesis of Functionalized Asymmetric Star Polymers Containing Conductive Polyacetylene Segments by Living Anionic Polymerization

Youliang Zhao, Tomoya Higashihara, Kenji Sugiyama, and Akira Hirao

J. Am. Chem. Soc., **2005**, 127 (41), 14158-14159• DOI: 10.1021/ja054821l • Publication Date (Web): 23 September 2005



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

Synthesis of Functionalized Asymmetric Star Polymers Containing Conductive Polyacetylene Segments by Living Anionic Polymerization

Youliang Zhao, Tomoya Higashihara, Kenji Sugiyama, and Akira Hirao*

Polymeric and Organic Materials Department, Graduate School of Science and Technology, Tokyo Institute of Technology, H-127, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

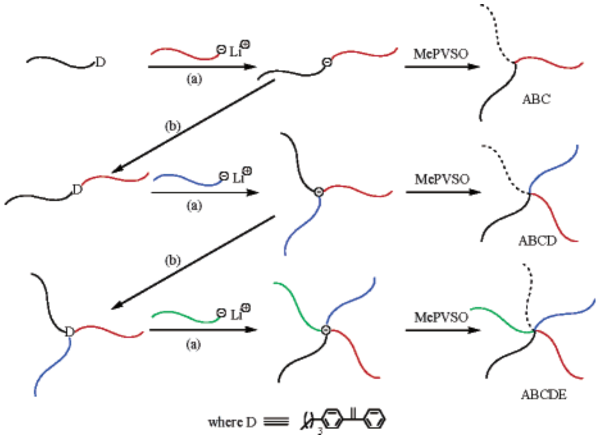
Received July 19, 2005; E-mail: ahirao@polymer.titech.ac.jp

Block copolymers containing conductive conjugated polymer segments, such as polyacetylene (PA), poly(phenylene), and poly(thiophene), are of particular interest since they may possibly phase-separate at the molecular level, followed by self-organization to form supramolecular-ordered nanostructures, which have many potential applications in the area of molecular electronic and optical devices. Many reports on the related subjects have so far appeared.[1] Recently, novel and more complex nanostructures based on specific periodic tetragonal and hexagonal morphologies have been observed in a series of 3-arm ternary ABC asymmetric star-branched polymers.[2] This may possibly be due to their branched architectures in addition to heterophase structures. The appearance of such morphologies has provoked considerable interest in the synthesis of asymmetric stars containing similar conductive polymer segments because these polymers with different topologies are expected to further induce more unique and interesting nanostructures.

Various asymmetric star polymers whose arms differ in chemical composition have so far been synthesized,[3] but most examples comprise only two components, and even 3-arm ABC asymmetric stars have been relatively limited in synthesis.[2−4] Furthermore, the reports on the synthesis of more complex 4-arm ABCD stars are scarce,[5] and 5-arm ABCDE has not been reported yet until now. Recently, we have developed a promising methodology based on iterative approach, which is applicable to the synthesis of complex asymmetric star polymers.[3d,6] Herein, we report on the successful synthesis of novel well-defined 3-arm ABC, 4-arm ABCD, and even 5-arm ABCDE asymmetric star polymers containing PA segments by utilizing the above-mentioned iterative methodology, followed by the living anionic polymerization of 4-methylphenyl vinyl sulfoxide (MePVSO) to introduce PMePVSO segments that are soluble precursors to PA.[7] Other segments used in the synthesis were polystyrene (PS), poly(α-methylstyrene) (PαMS), poly(4-methoxystyrene) (PMOS), poly(4-trimethylsilylstyrene) (PTMSS), and poly(4-methylstyrene) (PMS).

The iterative methodology involves two sets of quantitative reactions: (a) an addition reaction of living anionic polymer to 1,1-diphenylethylene (DPE)-functionalized polymer, and (b) an in situ coupling reaction of the generated 1,1-diphenylalkyl anion with 1-(4-(3-bromopropyl)phenyl)-1-phenylethylene to introduce one DPE moiety. With this methodology, the starting DPE-end-functionalized polystyrene (M_n(SEC) = 9600, M_w/M_n = 1.02), PS−PαMS diblock copolymer functionalized with DPE between the blocks (M_n(SEC) = 19 700, M_w/M_n = 1.01), and core-functionalized 3-arm PS−PαMS−PMOS star polymer with DPE (M_n(SEC) = 27 500, M_w/M_n = 1.01) are first prepared as illustrated in Scheme 1. The degree of DPE functionality was determined to be quantitative by ^{1}H NMR using two resonances at 5.40 and 0.5−0.8 ppm, which were assigned to methylene protons of the DPE moiety and methyl protons of the initiator fragment. A series of 3-arm ABC (S1−S4), 4-arm ABCD (S5−S7), and 5-arm ABCDE (S8) stars are then synthesized by a living linking reaction of another living anionic polymer with each of these DPE-functionalized polymers, followed by living anionic polymerization of MePVSO with the generated 1,1-diphenylalkyl anion, as shown in the same scheme. After fractional precipitation, the objective stars with isolated yield beyond 70% were obtained. The results are summarized in Table 1. The SEC profiles of the isolated samples exhibit symmetrical monomodal distribution, with their M_w/M_n value being less than 1.03. In all cases, the molecular weight values of various stars determined by ^{1}H NMR and SLS agreed well with those expected; the weight compositions determined by ^{1}H NMR analysis are in good agreement with those predicted, and the elemental analysis results are very close to the calculated values, confirming that this methodology could afford the target star polymers with well-defined architectures and precisely controlled arm length.

Scheme 1. Synthetic Route to Asymmetric Star Polymers



The PMePVSO segments in asymmetric stars could be quantitatively converted into PA segment by thermal treatment, evident from thermogravimetric analysis (TGA) and elemental analysis. Figure 1 shows TGA curves of PMePVSO (a), 3-arm PS−PαMS−PMePVSO star (S1, b), and the thermally degraded polymer PS−PαMS−PA (S1T, c). For PMePVSO, the maximum decomposition temperature for eliminating 4-methylphenylsulfenic acid is observed at 220 °C. In Figure 1b, three distinct stages of decomposition are noted in TGA curves of S1; the first and second stages are primarily corresponding to the decomposition of PMePVSO and PαMS, and the third one can be attributed to the decomposition of PS and PA.[8] In Figure 1c, only two obvious degradation steps are noted at 340 and 416 °C, and the characteristic transition of PMePVSO at about 220 °C is not present, as

10.1021/ja054821l CCC: $30.25

Table 1. Synthesis of ABC, ABCD, and ABCDE Asymmetric Star Polymers by Anionic Polymerization

sample[a]	M_n (calcd)	M_n (SEC)[b]	M_w/M_n[b]	M_n (NMR)[c]	M_w (SLS)[d]	d*n*/d*c* (mL·g^{-1})[d]	C (calcd)[e]	C (NMR)[f]
S1	31200	20500	1.02	31500	32700	0.174	31/31/38	31/31/38
S2	29800	21900	1.03	30100	31800	0.173	32/33/35	32/34/34
S3	31200	23000	1.02	32000	34600	0.167	31/35/34	30/35/35
S4	30600	23300	1.02	31200	33500	0.173	31/34/35	31/34/35
S5	41900	31000	1.02	43300	44600	0.180	24/24/25/27	23/23/25/29
S6	42000	29300	1.03	43200	43600	0.178	24/24/26/26	23/23/25/29
S7	42600	33500	1.02	43900	44900	0.175	23/23/24/30	23/23/24/30
S8	50000	38600	1.03	50400	53600	0.165	19/20/23/21/17	19/20/23/20/18

[a] S1−S4: ABC stars, where A and C were PS and PMePVSO segment, and B was PαMS (S1), PTMSS (S2), PMOS (S3), and PMeSt (S4). S5−S7: ABCD stars, where A, B, and D were PS, PαMS, and PMePVSO segment, and C was PMOS (S5), PTMSS (S6), and PMeSt (S7). S8: ABCDE, where A, B, C, D, and E segments were PS, PαMS, PTMSS, PMOS, and PMePVSO, respectively. [b] Estimated by SEC in THF at 40 °C. [c] Determined by ^{1}H NMR. [d] Determined by SLS in THF at 25 °C. [e] Theoretically calculated weight composition. [f] Weight composition determined by ^{1}H NMR.

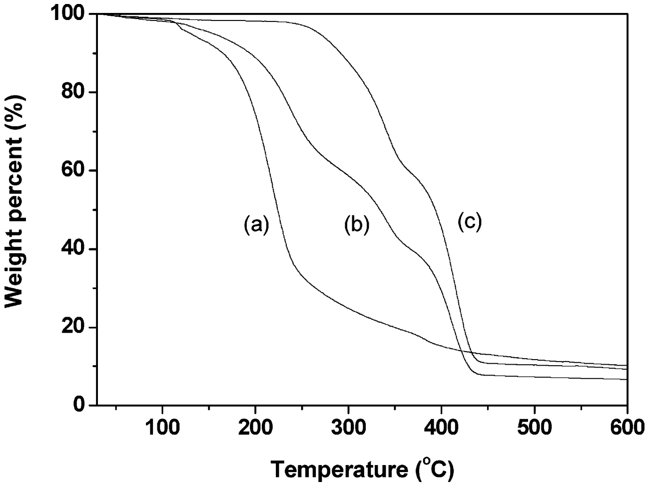


Figure 1. TGA curves of PMePVSO (a), S1 (b), and S1T (c).

expected. Meanwhile, sulfur is absolutely absent from the resultant PS−PαMS−PA star polymer as determined by elemental analysis. The above results confirmed the quantitative elimination of 4-methylphenylsulfenic acid from S1. The resulting star polymer containing a PA segment was soluble in DMF and partly soluble in THF and chloroform. The PMePVSO segments in other star samples were also readily and completely converted into the corresponding PA segments.

In summary, a series of novel well-defined asymmetric ABC, ABCD, and ABCDE star polymers containing conductive PA segment and its soluble precursors have been successfully synthesized by the iterative methodology followed by living anionic polymerization of MePVSO. Their solution properties and microphase-separated structures are under investigation and will be reported in a future publication.

Acknowledgment. The financial support of a Grant-in-Aid for Scientific Research (No. 00164351) from the Ministry of Education, Science, Sports, and Culture of Japan is gratefully acknowledged by the authors. Y.Z. gratefully thanks the Japan Society for the Promotion of Science Research Fellowships for Postdoctoral Fellowship for Foreign Researchers for support.

Supporting Information Available: Experimental details for the synthesis and characterization of the monomer, homopolymers, and star polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Widawski, G.; Raviso, M.; François, B. *Nature* **1994**, *369*, 387. (b) Jenekhe, S. A.; Chen, X. L. *Science* **1998**, *279*, 1903. (c) Jenekhe, S. A.; Chen, X. L. *Science* **1999**, *283*, 372. (d) Hempenius, M. A.; Langgeveld-Voss, B. M. W.; van Haare, J. A. E. H.; Janssen, R. A. J.; Sheiko, S. S.; Spatz, J. P.; Möller, M.; Meijer, E. W. *J. Am. Chem. Soc.* **1998**, *120*, 2798. (e) Wu, C.; Niu, A.; Leung, L. M.; Lam, T. S. *J. Am. Chem. Soc.* **1999**, *121*, 1954. (f) Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1998**, *120*, 10990. (g) Apperloo, J. J.; Janssen, R. A. J.; Malenfant, P. R. L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2001**, *123*, 6916. (h) Ikkala, O.; ten Brinke, G. *Science* **2002**, *295*, 2407. (i) Leclère, Ph.; Hennebicq, E.; Calderone, A.; Brocorens, P.; Grimsdale, A. C.; Müllen, K.; Brédas, J.-L.; Lazzaroni, R. *Prog. Polym. Sci.* **2003**, *28*, 55. (j) Messmore, B. W.; Hulvat, J. F.; Sone, E. D.; Stupp, S. I. *J. Am. Chem. Soc.* **2004**, *126*, 14452. (k) Bae, J.; Choi, J.-H.; Yoo, Y.-S.; Oh, N.-K.; Kim, B.-S.; Lee, M. *J. Am. Chem. Soc.* **2005**, *127*, 9668. (l) Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491 and references therein.

(2) (a) Pispas, S.; Poulos, Y.; Hadjichristidis, N. *Macromolecules* **1998**, *31*, 4177. (b) Sioula, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1998**, *31*, 5272 and 8429. (c) Pispas, S.; Hadjichristidis, N.; Potemkin, I.; Khokhlov, A. *Macromolecules* **2000**, *33*, 1741. (d) Hückstädt, H.; Göpfert, A.; Abetz, V. *Macromol. Chem. Phys.* **2000**, *201*, 296.

(3) (a) Quirk, R. P.; Yoo, T.; Lee, Y.; Kim, J.; Lee, B. *Adv. Polym. Sci.* **2000**, *153*, 67. (b) Hadjichristidis, N.; Pispas, S.; Pitsikalis, M.; Iatrou, H.; Vlahos, C. *Adv. Polym. Sci.* **1999**, *142*, 72. (c) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chem. Rev.* **2001**, *101*, 3747. (d) Hirao, A.; Hayashi, M.; Loykulnant, S.; Sugiyama, K.; Ryu, S. W.; Haraguchi, N.; Matsuo, A.; Higashihara, T. *Prog. Polym. Sci.* **2005**, *30*, 111.

(4) (a) Fujimoto, T.; Zhang, H.; Kazama, T.; Isono, Y.; Hasegawa, T.; Hashimoto, T. *Polymer* **1992**, *33*, 2208. (b) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649. (c) Hückstädt, H.; Abetz, V.; Stadler, R. *Macromol. Rapid Commun.* **1996**, *17*, 599. (d) Sioula, S.; Tselikas, Y.; Hadjichristidis, N. *Macromolecules* **1997**, *30*, 1518. (e) Bellas, V.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 6993. (f) Li, Z.; Hillmyer, M. A.; Lodge, T. P. *Macromolecules* **2004**, *37*, 8933.

(5) (a) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 2479. (b) Higashihara, T.; Hirao, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4535. (c) Higashihara, T.; Nagura, M.; Inoue, K.; Haraguchi, N.; Hirao, A. *Macromolecules* **2005**, *38*, 4577.

(6) (a) Hirao, A.; Hayashi, M.; Higashihara, T. *Macromol. Chem. Phys.* **2001**, *202*, 3165. (b) Hirao, A.; Higashihara, T. *Macromolecules* **2002**, *35*, 7238.

(7) Hogen-Esch and co-workers previously reported that the anionic polymerization of phenyl vinyl sulfoxide (PVSO) proceeded in a living manner, and the resulting polymer, PPVSO, was completely converted to PA only by thermal treatment (Kanga, R. S.; Hogen-Esch, T. E.; Randrianalimanana, E.; Soum, A.; Fontanille, M. *Macromolecules* **1990**, *23*, 4235 and 4241). In this study, the more stable polymer derived from MePVSO was used in place of PVSO. Similar to the polymerization of PVSO, the anionic polymerization of MePVSO always gave the polymers with relatively broad molecular weight distributions ($M_w/M_n = 1.3-1.5$) in THF at −78 °C. We have, however, found that the polymerization of MePVSO could be significantly improved by adding a 10-fold excess or more of LiCl or LiBr to afford the polymers with predictable M_n values and narrow molecular weight distributions ($M_w/M_n = 1.07-1.16$).

(8) (a) Chien, J.; Uden, P.; Fan, J. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2159. (b) Will, F.; McKee, D. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3479.

JA054821L