Tuning the Electrical Conductivity and Self-Assembly of Regioregular Polythiophene by Block Copolymerization: Nanowire Morphologies in New Di- and Triblock Copolymers**

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Over two decades ago the discovery of electrical conductivity in conjugated polymers spurred a tremendous amount of effort aimed at the development of practical conducting plastics.[1] One of the primary motivations was the hope of fabricating inexpensive, lightweight conducting materials. Those efforts have been coming to fruition in recent years with the development of polymer-based light-emitting diodes,[2] field-effect transistors,[3] elements for active matrix displays,[4] and all-polymer integrated circuits.[5] The synthesis and study of regioregular polythiophenes has produced conjugated polymers that self-assemble into well-defined superstructures and has furthered the use of these materials in the aforementioned applications.[6] Formation of ordered supermolecular structures in these regioregular materials correlates strongly with their excellent electrical conductivities (thousands or hundreds of $S cm^{-1}$ in comparison with a few $S cm^{-1}$ for regiorandom polymers). Nevertheless, regioregular polythiophenes still have poor mechanical and processing properties relative to typical flexible polymers.

One approach to solving this problem is to synthesize block copolymers that contain conducting polymer or oligomer units.[7] Such a block copolymer[8] could self-assemble into a number of nanoscale morphologies, such as lamellar, spherical, cylindrical, and vesicular structures, which would lead to the possibility that new electronic/structural copolymers could be designed, synthesized, and assembled as components in new nano-

devices. Here we present a very easy synthetic method to produce a large number of well-defined block copolymers and polyurethane elastomers containing regioregular polythiophenes. Despite having low percentages of regioregular polythiophenes, these new copolymers have very high conductivities (of the order of a few $S cm^{-1}$) and form very well defined nanowires that reach lengths in the micron range. In addition, we have found that simply changing the solvent or evaporation conditions allows us to control the nanowire formation and the electrical conductivity of the block copolymer.

The synthesis of diblock copolymers of head-to-tail-coupled poly(3-alkylthiophenes) (HT-PATs) can be accomplished by first preparing a well-defined PAT (polydispersity index (PDI) = 1.2) with 95 % of its end groups[9] containing one proton and one bromine atom (2; Scheme 1). The method[10]
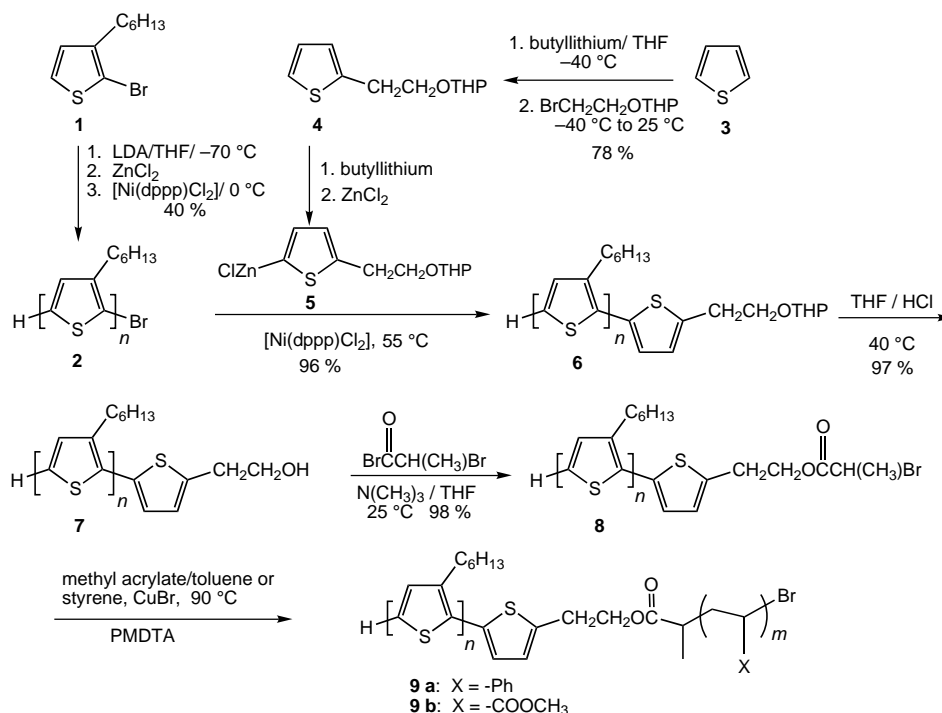
Scheme 1. Synthesis of diblock polymers. LDA = lithium diisopropylamine, dppp = propane-1,3-diylbis(diphenylphosphane), THP = tetrahydropyran.

shown in Scheme 1 is an important modification of methods previously published by our group.[6, 11] The reaction was optimized and the polymer end groups were characterized by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS).

Since PATs are chemically stable polymers, the ability to modify the end groups on one side of the polymer is similar to polymer- or bead-supported organic synthesis. Excess of reagents were used to drive the modification reactions to completion to give > 95 % yield for all of the steps subsequent to the synthesis of the HT-PHT. The purification of the products from all the reaction steps was achieved by simple precipitation and filtration, thus each step of the end-group modification is high yielding (> 95 %) and is facile to accomplish. The HT-PHT 2 is functionalized by reaction with

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thiophene derivative **5** and [Ni(dppp)Cl$_2$] (dppp = propane-1,3-diylbis(diphenylphosphane)) to yield polymer **6**.[12] Deprotection of **6** leads to HT-PHT with one hydroxyl end group (**7**),[12] as verified by NMR and MALDI-MS analysis. The hydroxy-terminated PHT (**7**) was further modified by reaction with 2-bromopropionyl bromide to generate an atom transfer radical polymerization (ATRP)[13] macroinitiator (**8**).[14] Diblock copolymers (for example, **9**) containing PHT can be prepared by the ATRP "living" free-radical polymerization method developed by Matyjaszewski and co-workers to produce a wide variety of conventional polymers. As an example, we have made polyhexylthiophene–polystyrene (PHT-PS; **9a**) and polyhexylthiophene–polymethylacrylate (PHT-PMA; **9b**) by ATRP using **8** as the initiator, styrene or methyl acrylate as the monomer, and CuBr/N,N,N',N',N''-pentamethyldiethylenetriamine (PMDTA) as the catalyst[15] (Scheme 1). The percentage of the PS or PMA block is completely controlled by the feed ratio of the monomers, as confirmed by NMR spectroscopy and size-exclusion chromatography.[16] High molecular weights and low polydispersities are produced by the combination of using the HT-PHT macroinitiator (**8**) with a low PDI and the "living" nature of the ATRP method.

In addition, regioregular HT-PHT can be functionalized on both the α and ω ends, which allows for the synthesis of PS and PMA triblock copolymers and polyurethane elastomers containing HT-PHT (Scheme 2). Regioregular PHT **10** with a mixture of end groups[6, 11] is debrominated by a Grignard metathesis reaction and quenched with water to yield **11**.[9] A Vilsmeier reaction on **11** gives polymer **12** as determined by MALDI-MS. The aldehyde end groups on **12** are reduced with LiAlH$_4$ to yield a PHT terminated by hydroxymethyl groups (**13**). Analysis of the product by MALDI-MS unambiguously proves the incorporation of the hydroxylmethyl group to both ends of the polymer chains. We have prepared well-defined triblock copolymers PS-PHT-PS (**16a**) and PMA-PHT-PMA (**16b**) of high molecular weight with low polydispersities from the common polymer (**15**)[15] by using ATRP with styrene or methyl acrylate as the monomer.[16] Again the percentages of PS or PMA corresponded to the feed ratio of the monomer. In addition, polymer **13** is easily converted[17] into polyurethane elastomers (**14**).
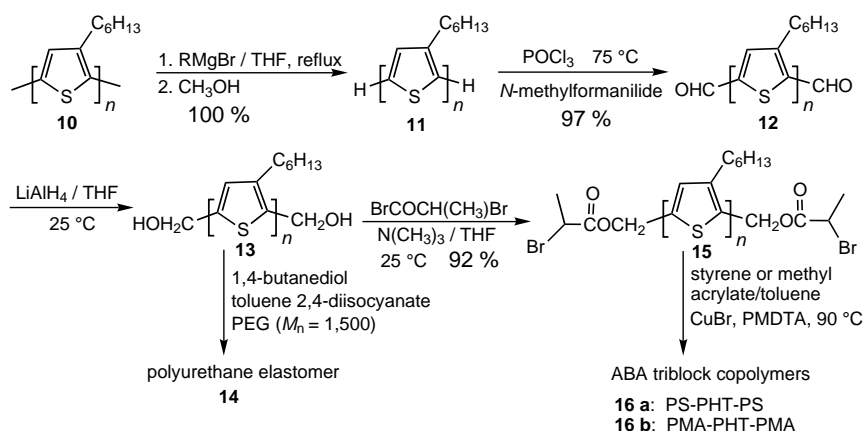
Thin films of all the polymers (PHT-PS (**9a**), PHT-PA (**9b**), polyurethane elastomers (**14**), PS-PHT-PS (**16a**), and PA-PHT-PA (**16b**)) were generated by the slow evaporation of toluene solutions to give magenta to purple films with excellent mechanical properties. These films were oxidized by exposure to I$_2$ vapor to give multifunctional polymers with high electrical conductivities (Table 1), as determined by four-point probe conductivity measurements. Surprisingly high

Table 1. Conductivity of block copolymers containing HT-PHT.

PS-PHT diblock copolymers (**9a**)			
wt % of HT-PHT[a]	100 %	37 %	22 %	14 %
average M_n[b]	16 800	30 200	41 400	53 400
M_w/M_n[b]	1.28	1.31	1.32	1.45
conductivity [S cm^{-1}]	110	4.7	0.08	0.14
PS-PHT-PS triblock copolymers (**16a**)			
wt % of HT-PHT[a]	100 %	52 %	26 %	7.7 %
average M_n[b]	17 900	25 500	38 100	93 600
M_w/M_n[b]	1.23	1.21	1.25	1.51
conductivity [S cm^{-1}]	96	5.3	0.43	0.05
PA-PHT-PA triblock copolymers (**16b**)			
wt % of HT-PHT[a]	100 %	45 %	18 %	10 %
average M_n[b]	17 900	29 700	50 400	72 300
M_w/M_n[b]	1.23	1.29	1.41	1.66
conductivity [S cm^{-1}]	96	3.3	1.6	0.076
Polyurethane (**14**)			
wt % of HT-PHT	10 %	6.40 %	0.60 %
conductivity [S cm^{-1}]	0.13	0.048	4.6×10^{-5}

[a] Determined by ^{1}H NMR spectroscopy. [b] Determined by GPC with polystyrene as standard.

electrical conductivities were found in all of the copolymer samples. While many copolymers containing conjugated polymers and other polymers and blends have been prepared, no one has reported conductivity values near to those reported here (Table 1). While 100 % HT-PHT has a conductivity of 110 S cm^{-1}, a block copolymer of PHT-PS (**9a**) containing 37 % HT-PHT has a conductivity of about 5 S cm^{-1}. The conductivity drops down to 0.1 S cm^{-1} for samples containing approximately 22 % of HT-PHT or less. The conductivity of the block copolymers largely depends on the ratio of the conducting and nonconducting blocks and is related to the structural assembly. The PS-PHT-PS triblock copolymers (**16a**) have conductivities as high as 5 S cm^{-1} for a sample with 52 % PHT. Our conducting polyurethane copolymers (**14**) exhibit conductivities as high as 10^{-1} S cm^{-1}, which is much higher than other polyurethane conjugative copolymers or blends reported in the literature (10^{-4} S cm^{-1}).[18] Conductivities for blends of conjugative polymers with polyvinyl chloride and other conventional polymers have also been found to exhibit low conductivities (in the 10^{-4} S cm^{-1} range).[18] All of our block copolymers also have excellent film-forming and good mechanical properties including elasticity in the polyurethane samples.

We have found that thin and ultrathin films these block copolymers containing

Scheme 2. Synthesis of triblock polymers and polyurethane elastomers. PEG = polyethyleneglycol, PMDTA = N,N,N',N',N''-pentamethyldiethylenetriamine.

polythiophene that were prepared by casting from toluene followed by free evaporation of a solvent reproducibly self-assembled into very well-defined "nanowires" spaced laterally by 30–40 nm (which corresponds to a fully extended HT-PHT block) with lengths on the order of micrometers (Figure 1). Lower percentages of PHT also lead to similar morphologies as found in drop-cast films, however, a clear dilution factor of the PHT is observed. As an example, an atomic force micrograph (AFM) micrograph of a PS-PHT (**9a**) sample is shown (Figure 2), where the weight percentage of PHT is 37 % and the film was cast from a 0.5 mg mL^{-1} solution in toluene. The samples were then imaged using the variable-tapping force technique (developed in recent years) with the purpose of using tapping-mode AFM to study mechanical properties of materials at the nanoscale.[19] Interestingly, "nanowires" were clearly discernible only under "hard tapping" conditions (tens to hundreds nanonewtons) and were barely identifiable when imaged with forces of the order of just a few nanonewtons. The formation of a "nanowire" structure is undoubtedly dictated by the immiscibility of polystyrene and poly(3-hexylthiophene). Under such circumstances nanowires can be predicted to have a core–shell architecture, with the minority component (polythiophene) constituting the core. Such a sheathed structure is indeed consistent with our variable-force experiments. Under "light tapping" conditions, the tip–sample force is not high enough to penetrate through the outer sheath of the nanowires. Since the polystyrene segments in the sheath can mix with the chains from adjacent aggregates, the boundaries between nanowires are not well resolved. In contrast, under "hard tapping" conditions the probe–sample force is high enough to deform the outer sheath and "sense" the presence of a rigid core. These structures have also been observed in transmission electron microscopy (TEM) experiments as well.

The strong tendency of regioregular poly(alkylthiophenes) to self-assemble into stacked aggregates raises a question about the role of this intrinsic self-assembly in the formation of nanowires. An important observation in this regard is that thin and ultrathin films prepared by spin-coating from chloroform had distinctly different, "uninteresting", morphology without any indications of long-range order (Figure 3). Suppression of the formation of nanowires under these conditions may be pointing to the key role of the intrinsic self-assembly of polythiophene: this process might have been kinetically suppressed here because of the high rate of solidification associated with spin-coating from a highly volatile solvent. This kinetic argument was further supported by experiments in which thin films were again cast from
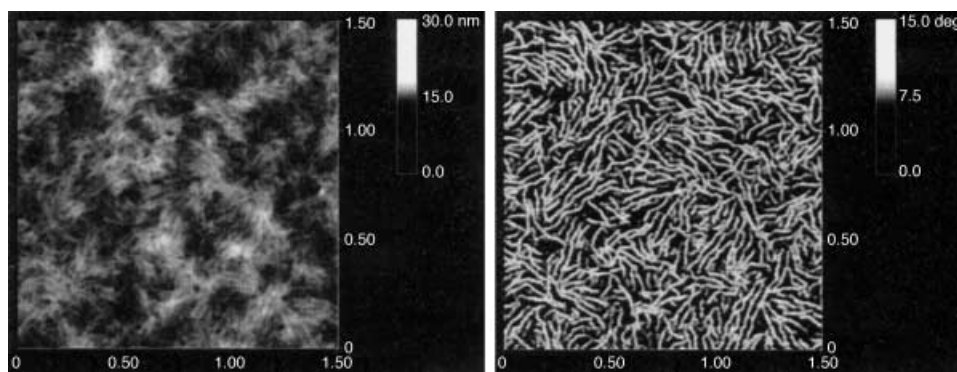

Figure 1. "Nanowire" morphology in poly(3-hexylthiophene)-b-poly(styrene) copolymers solvent-cast from toluene and visualized with tapping-mode AFM. Left: height; right: phase (see text). These and subsequent images use gray-scale coding, with darker tones corresponding to lower values (for example, lower heights.)
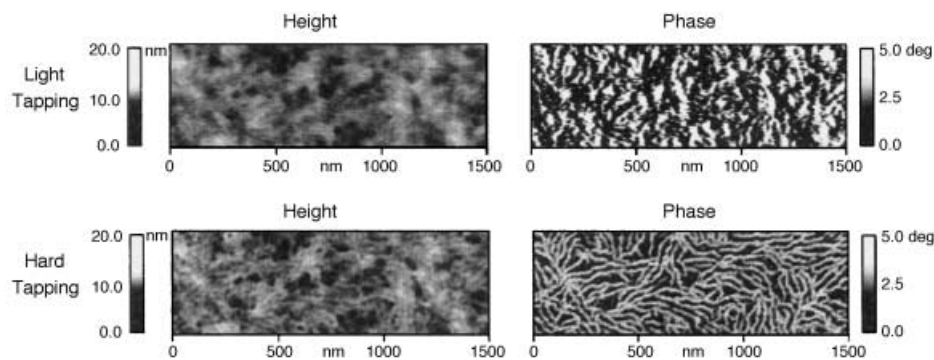

Figure 2. Under "light tapping" conditions (top) only the outer, partially overlapping shells of aggregates are visualized and the nanowire morphology is not apparent. In contrast, under "hard tapping" conditions (bottom), the probe interacts with the outer shells with sufficient force to "sense" the presence of rigid poly(3-alkylthiophene) cores.
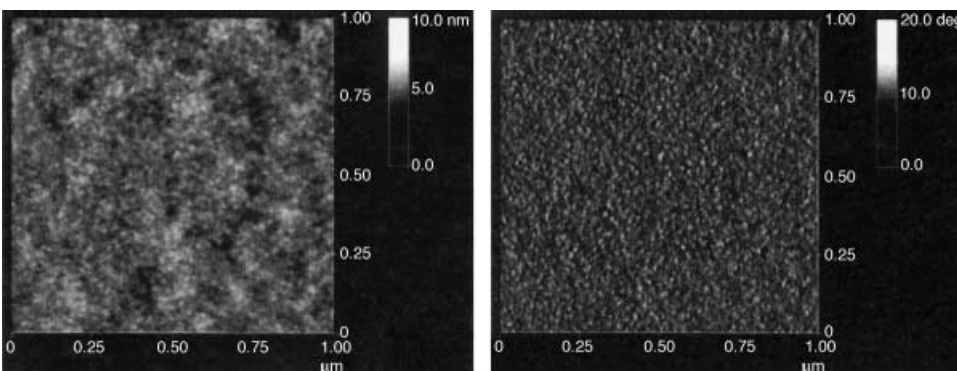

Figure 3. Tapping-mode AFM images of ultrathin films of poly(3-hexylthiophene)-b-poly(styrene) spin-coated from chloroform. Left: height; right: phase.

toluene, but under a stream of nitrogen. Under these accelerated evaporation conditions the formation of nanowires was also totally suppressed.

The nanowire morphologies found in block copolymers[20] of regioregular poly(alkylthiophenes) points to the possibility of guiding the intrinsic self-assembly of sufficiently regular conjugated polymer chains by coupling them chemically to incompatible segments. In the simplest case, the obtained structure is the result of interplay between different driving forces of self-assembly (π stacking versus phase separation). To rephrase this point, the free-energy landscape of rigid conjugated molecules has few deep local minima as a result of strong π interactions which cannot be easily explored under normal conditions. Thus, the molecules are easily trapped in the states with a high degree of local stacking, but at the same time there is a high concentration of defects that adversely affects the bulk properties. Copolymerization with incompatible flexible segments brings into play competing driving forces of self-assembly that result in "more interesting" and easier to explore free-energy landscapes. Identifying the overall features of those energy landscapes may give us the ability to exercise control of the resulting nanostructures, and effectively pave the way to applications of conjugated polymers as building blocks for future nanoscale and molecular level electronic devices.

[1] A. G. MacDiarmid, C. K. Chiang, C. R. Fincher, Y. W. Park, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. Gau, *Phys. Rev. Lett.* **1997**, *39*, 1098.

[2] J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, A. R. Holmes, *Nature* **1990**, *347*, 539.

[3] a) A. Bao, A. Dodabalapur, A. J. Lovinger, *Appl. Phys. Lett.* **1996**, *69*, 4108; b) Z. Bao, A. J. Lovinger, *Chem. Mater.* **1999**, *11*, 2607; c) G. H. Gelinck, T. C. T. Geuns, D. M. de Leeuw, *Appl. Phys. Lett.* **2000**, *77*, 1487.

[4] a) H. Sirringhaus, N. Tessler, R. H. Friend, *Science* **1998**, *280*, 1741; b) C. J. Drury, C. M. J. Mutsaers, C. M. Hart, M. Matters, D. M. de Leeuw, *Appl. Phys. Lett.* **1998**, 73, 108.

[5] A. Dodabalapur, Z. Bao, A. Makhija, J. G. Laquindanum, V. R. Raju, Y. Feng, H. E. Katz, J. Rogers, *Appl. Phys. Lett.* **1998**, *73*, p. 142.

[6] a) R. D. McCullough, *Adv. Mater.* **1998**, *10*, 1; b) R. D. McCullough, P. C. Ewbank in *Handbook of Conducting Polymers*, 2nd ed., Marcel Dekker, New York, **1998**, chap. 9, p. 225.

[7] a) G. Widawski, M. Rawiso, B. Francios, *Nature* **1994**, *369*, 387; b) B. Francois, O. Pitois, J. Francois, *Adv. Mater.* **1995**, *7*, 1041; c) T. Olinga, B. Francois, *J. Chim. Soc.* **1992**, *89*, 1079; d) S. A. Jenekhe, Chen, X. L. *Science* **1998**, *279*, 1903; e) M. A. Hempenius, B. M. W. Langeveld-Voss, J. A. E. H. van Haare, R. A. J. Janssen, S. S. Sheiko, J. P. Spatz, M. Moller, E. W. Meijer, *J. Am. Chem. Soc.* **1998**, *120*, 2798; f) W. Li, H. Wang, L. Yu, T. L. Morkved, H. M. Jaeger, *Macromolecules* **1999**, *32*, 3034; g) S. A. Jenekhe, X. L. Chen, *Science* **1999**, *283*, 372; h) U. Stalmach, B. de Boer, C. Videlot, P. F. van Hutten, G. Hadziioannou, *J. Am. Chem. Soc.* **2000**, *122*, 5464; i) B. de Boer, U. Stalmach, H. Nijland, G. Hadziioannou, *Adv. Mater.* **2000**, *12*, 1581; j) H. Wang, H. H. Wang, V. S. Urban, K. C. Littrell, P. Thiyagarajan, L. Yu, *J. Am. Chem. Soc.* **2000**, *122*, 6855; k) J. Raez, R. Barjovanu, J. A. Massey, M. A. Winnik, I. Manners, *Angew. Chem.* **2000**, *112*, 4020; *Angew. Chem. Int. Ed.* **2000**, *39*, 3862; l) J. A. Massey, J. K. Temple, L. Cao, Y. Rharbi, J. Raez, M. A. Winnick, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 11 577.

[8] F. S. Bates, *Science* **1991**, *251*, 898.

[9] J. Liu, R. S. Loewe, R. D. McCullough, *Macromolecules* **1999**, *32*, 5777.

[10] a) R. D. McCullough, R. D. Lowe, M. Jayaraman, D. L. Anderson, *J. Org. Chem.* **1993**, *58*, 904; b) R. D. McCullough, P. C. Ewbank, R. S. Loewe, *J. Am. Chem. Soc.* **1997**, *119*, 631.

[11] Polymer **2** was prepared by the following method: Distilled diisopropylamine (1.4 mL, 10 mmol) and 2.58 M nBuLi (3.7 mL, 9.5 mmol) were dissolved in dry THF (50 mL) at $-78\,^{\circ}$C. The mixture was then warmed to room temperature over 5 min and then cooled to $-78\,^{\circ}$C. The monomer 2-bromo-3-hexylthiophene (2.5 g, 10 mmol) was added to the freshly generated lithium diisopropylamine and the reaction stirred at $-70\,^{\circ}$C for 1 h. Anhydrous $ZnCl_2$ (1.43 g,10.5 mmol) was then added at $-70\,^{\circ}$C and the reaction was stirred for 1 h. The reaction was warmed to $0\,^{\circ}$C and [Ni(dppp)Cl$_2$] (35 mg, 0.065 mmol, 0.6 mol%) was added. The mixture was warmed to room temperature and then stirred for an additional 30 min. Polymer **2** was precipitated with methanol. The polymer was washed/fractionated by Soxhlet extraction with methanol, hexane, dichloromethane, and tetrahydrofuran. The THF fraction was characterized and used in further experiments. ^{1}H NMR (CDCl$_3$): $\delta = 6.98$ (s, 1H), 2.79 (t, $J = 7.7$ Hz, 2H), 1.62 (m, 2H), 1.48 (m, 2H), 1.36 (m, 4H), 0.90 (t, $J = 6.3$ Hz, 3H); MALDI-MS: $M_n = 7634$ (PDI = 1.14, end groups: H/Br ca. 95%, H/H ca. 4%, Br/Br ca. 1%), 7729.02 [M^+] (calcd: 7730.12, given a degree of polymerization of 46 for the PHT); GPC: $M_n = 16{,}800$ (PDI = 1.28).

[12] Characterization of **6**: ^{1}H NMR 6.98 (s, 49H), 6.89 (d, $J = 3.3$ Hz, 1H), 6.80 (d, $J = 3.3$ Hz, 1H), 4.65 (t, $J = 3.7$ Hz, 1H), 3.82 (m, 2H), 3.65 (m, 2H), 3.11 (t, $J = 6.6$ Hz, 2H), 2.79 (t, $J = 7.63$ Hz, 100H), 1.62 (m, 98H), 1.48–1.36 (m, 300H), 0.9 (t, $J = 6.3$ Hz, 150H); MALDI-MS: m/z: 7859.36 [M^+] (calcd: 7860.88, given a degree of polymerization of 46); GPC: $M_n = 17\,000$ (PDI = 1.28). Charaterization of **7**: ^{1}H NMR $\delta = 6.98$ (s, 49H), 3.89 (t, $J = 6.6$ Hz, 2H), 3.07 (t, $J = 6.6$ Hz, 2H), 2.79 (t, $J = 7.6$ Hz, 99H), 1.62 (m, 99H), 1.48–1.36 (m, 300H), 0.9 (t, $J = 6.3$ Hz, 148H); MALDI-MS: m/z: 7776.88 [M^+] (calcd: 7777.35, given a degree of polymerization of 46); GPC: $M_n = 16\,740$ (PDI = 1.28).

[13] a) J.-S. Wang, K. Matyjaszewski, *J. Am. Chem. Soc.* **1997**, *119*, 5614; b) T. E. Patten, J. Xia, T. Abernathy, K. Matyjaszewski, *Science* **1996**, *272*, 866; c) K. Matyjaszewski, T. E. Patten, J. Xia, *J. Am. Chem. Soc.* **1997**, *119*, 674; d) K. Matyjaszewski, B. Gobelt, H.-J. Paik, C. P. Horwitz, *Macromolecules* **2001**, *34*, 430.

[14] Characterization of **8**: ^{1}H NMR 6.98 (s, 49H), 4.38 (m, 1H), 4.40 (m, 2H), 3.19 (t, $J = 6.6$ Hz, 2H), 2.79 (t, $J = 7.6$ Hz, 99H), 1.83 (d, $J = 6.6$ Hz, 3H), 1.62 (m, 99H), 1.48–1.36 (m, 300H), 0.9 (t, $J = 6.3$ Hz, 148H).

[15] Typical ATRP: PHT macroinitiator (**8** or **15**; 0.1g, ca. 0.012 mmol) was dissolved in the mixture of freshly distilled toluene and monomers (1:1 when monomer is styrene, 3:1 when monomer is methyl acrylate). CuBr (0.018 g, 0.125 mmol) and PMDTA (0.027 g, 0.125 mmol) were added to this solution. After being purged with nitrogen for 15 mins, the solution was placed into an oil bath at 90°C. Copolymers with different ratios of PHT were obtained by pouring the solution into methanol after different periods of time. After precipitation and filtration, the polymer was dissolved in THF and passed through an Al$_2$O$_3$ column to eliminate the catalyst.

[16] See Supporting Information.

[17] Polyurethane elastomers were prepared by either one-shot process or two-shot process. See Supporting Information.

[18] G. Robilia, I. Diaconu, T. Buruiana, E. Buruiana, P. Coman, *J. Appl. Polym. Sci.* **2000**, *75*, 1385.

[19] M.-F. Yu, T. Kowalewski, R. S. Ruoff, *Phys. Rev. Lett.* **2000**, *85*, 1456.

[20] Patent pending.