Poly(3-hexylthiophene) Based Block Copolymers Prepared by "Click" Chemistry

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ABSTRACT: π-Conjugated block copolymers have been prepared from terminal azide functionalized polystyrenes (PS) and alkyne functionalized poly(3-hexylthiophene)s (P3HT) *via* a copper(I) catalyzed Huisgen [3 + 2] dipolar cycloaddition reaction. The functionalized α-azido-PS homopolymer was prepared by atom transfer radical polymerization from a specifically designed initiator bearing the azide function, whereas ω-ethynyl-P3HT and α,ω-pentynyl-P3HT were synthesized by a modified Grignard metathesis polymerization using alkynyl Grignard derivatives. The electronic environment of the alkynyl end groups was shown to be decisive in determining triazole ring formation.

Introduction

Semiconducting polymers have gained immense interest over the past few years, in part stimulated by their applicability to devices such as organic photovoltaic cells (OPV), light emitting diodes, and field-effect transistors. Among these polymers, regioregular poly(3-hexylthiophene) (P3HT) is widely studied because of its good solubility, chemical stability and excellent electronic properties. Importantly, OPVs with power conversion efficiencies of around 5% have been obtained using blends of P3HT and [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM).[1,2] Heeger and co-workers have even proposed efficiencies greater than 6% with "tandem" solar cells.[3] However, the very nature of blends means that there is limited control over the structure of the photoactive material. Further optimizations of the nano- and meso-structure of phase separated electron donors and acceptors will be required to improve OPV efficiencies. This may be attained by using block copolymers consisting of covalently joined donor and acceptor segments.[4,5] If the two blocks possess sufficient repulsive energy, they will phase-separate to produce domains rich in one block or the other. As domain size and type can be controlled by varying the lengths of each polymer block, then the size of surfaces between donor and acceptor blocks, the maximum distance an exciton can travel before meeting an interface to yield photocharges, and the shape of the domain through which the photocharges percolate to the electrodes may all be controlled. In addition, rod−coil block copolymers containing a π-conjugated polymer, such as P3HT, can generate unique self-assembled electronic materials with enhanced mechanical properties. Their use as compatibilizers may be of use in stabilizing the thermal behavior of P3HT-*blend*-PCBM.[6]

Rod−coil block semiconducting copolymers have been synthesized before. Of particular note are block copolymers formed using chain-end functionalized poly(phenylene vinylene)s[7,8] or poly(3-alkylthiophene)s[9−11] for controlled radical polymerizations or a P3HT macroinitiator for anionic polymerization.[12] P3HT is again of interest because of the ease of its preparation by a chain growth polymerization that can be used to predetermine received molar masses[13,14] and effect facile chain-end modifications.[15] McCullough and co-workers have prepared original semiconducting materials of poly(3-hexylthiophene)-*block*-polystyrene (P3HT-*b*-PS) and poly(3-hexylthiophene)-*block*-polyisoprene *via* reversible addition fragmentation chain transfer and nitroxide mediated radical polymerizations techniques, and showed the formation of nanofibrils and densely packed wires by self-assembling of these block copolymer structures.[16]

"Click" chemistry was introduced in 2001 by Sharpless and co-workers,[17] who revisited the Huisgen's 1,3-dipolar cycloadditions[18−20] between azido and alkynyl groups using copper salts as catalysts. In recent years, "click" chemistry has attracted increasing attention and, since 2005, has been extended to polymer science. Many papers have demonstrated its applicability to the preparation of block copolymers.[21−24] However, to our knowledge this technique has not been applied yet to the preparation of block copolymers containing conjugated segments. This is surprising, as this synthetic approach presents advantages of considerable interest for organic semiconductors and electronics. First, it provides pure and stable materials, properties which are of prime importance in electronics.[25] Second, "click" reactions offer quantitative yields, generate inoffensive byproducts and require simple reaction conditions,[17] qualities of interest when considering possible future industrialization. Finally, this technique enables a precise control of the resulting block copolymer from well-defined functionalized parent homopolymers. Nowadays, a palette of living polymerization methods is available to provide such homopolymers.

In this context we decided to carry out the modified Grignard metathesis (GRIM) polymerization to obtain alkynyl-terminated P3HT, and ATRP to obtain α-azido-PS of differing chain lengths, and then to use a 1,3-dipolar cycloaddition as a facile route to various samples of P3HT-*b*-PS and PS-*b*-P3HT-*b*-PS.

Experimental Section

Materials. All reactions were carried out under a dry nitrogen atmosphere, using flame-dried glassware. All reagents were purchased from Aldrich (France) except THF (J.T. Baker) and dichloromethane (Xilab). Solvents were distilled from over their respective drying agents under reduced pressures. Acetic acid and dichloromethane were used as received. Styrene was stirred

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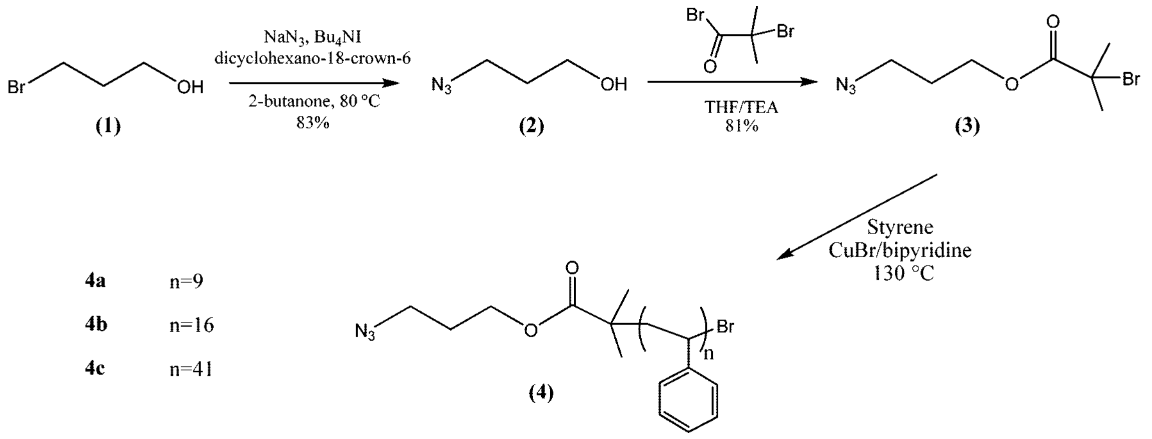
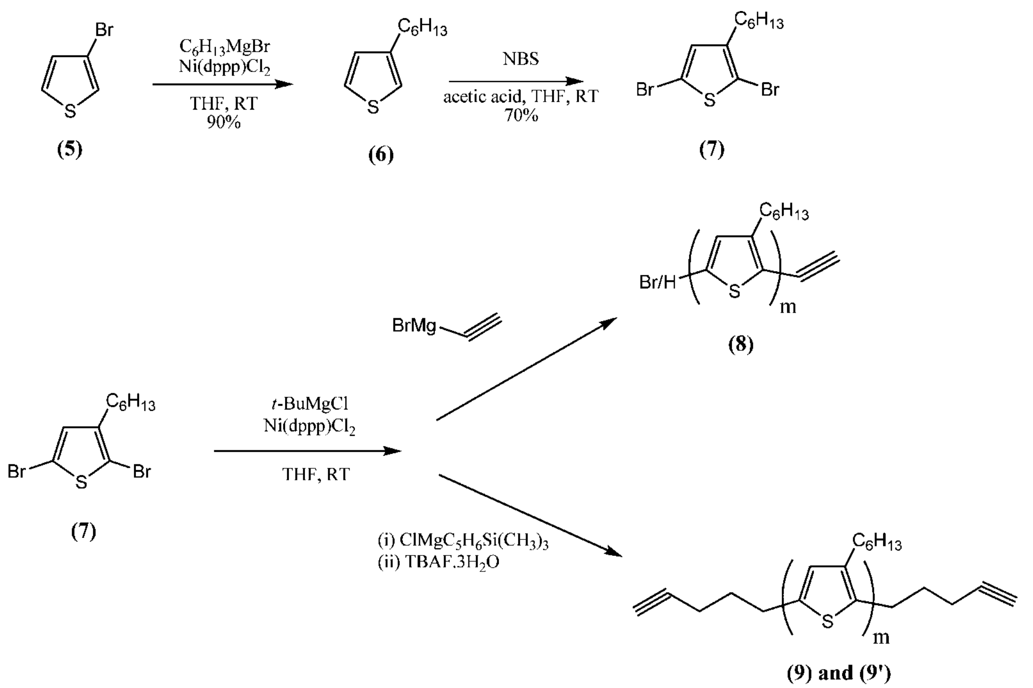
Scheme 1. Synthesis of α-Azido-PS (4a, 4b, and 4c) by Copper-Mediated ATRP



Scheme 2. Syntheses of ω-Ethynyl-P3HT (8) and α,ω-Pentynyl-P3HT (9 and 9′) by Grignard Metathesis



overnight over CaH_2 and distilled prior to use. Magnesium turnings were dried overnight in an oven at 150 °C. Bromopropanol, sodium azide (NaN_3), *cis*-dicyclohexano-18-crown-6, 2-butanone, α-bromoisobutyryl bromide, triethylamine, ammonium chloride, copper(I) bromide (CuBr), 2,2′-bipyridyl, copper(I) iodide (CuI), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), bromohexane, 3-bromothiophene, *N*-bromosuccinimide (NBS), *tert*-butylmagnesium chloride, 1,3-bis(diphenylphosphino)propane nickel(II) dichloride ($Ni(dppp)Cl_2$), ethynylmagnesium bromide, (5-chloro-1-pentynyl)trimethylsilane, and tetrabutylammonium fluoride trihydrate ($TBAF.3H_2O$) were used as received without further purification.

Characterization. ^1H, ^{13}C and 2-D NMR spectra were recorded using a Bruker AC-400 NMR at room temperature, and the samples were dissolved in $CDCl_3$. Gel permeation chromatography (GPC) analyses were performed at room temperature in THF with a setup consisting of a WATERS 880-PU pump and a series of three microstyragel columns with pore sizes of 10^3, 10^5 and 10^6 Å. The elution of the filtered samples was monitored using simultaneous UV and refractive index detections. The elution times were converted to molar masses using a calibration curve based on low dispersity (M_w/M_n) PS standards. Infrared measurements were performed on a Bruker Tensor 27 spectrometer using the attenuated total reflection (ATR) method (ZnSe crystal). Differential scanning calorimetry (DSC) thermograms were measured using a DSC Q100 apparatus from TA instruments. Samples were first heated from 50 to 250 °C and then characterized on a second heating run. All experiments were performed at a rate of 10 °C min^{-1}. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) spectra were performed by the CESAMO (Bordeaux, France) on a Voyager mass spectrometer (Applied Biosystems). The instrument is equipped with a pulsed N_2 laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in THF at 10 mg mL^{-1}. The dithranol matrix solution was prepared by dissolving 10 mg in 1 mL of CH_2Cl_2. A MeOH solution of cationization agent (NaI, 10 mg mL^{-1}) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationization agent. Several microliters of the obtained solution was deposited onto the sample target and vacuum-dried.

(a) Synthesis of α-Azido Polystyrenes by ATRP (See Scheme 1). *(i) Synthesis of 3-Azido-1-propanol* (**2**). 3-Bromo-1-propanol (**1**) (10 g, 72 mmol), NaN_3 (7 g, 108 mmol), Bu_4NI (4 g, 11 mmol) and dicyclohexano-18-crown-6 (20 mg, 5×10^{-2} mmol) were dissolved in 2-butanone (50 mL), and the mixture was stirred under reflux for 24 h. The mixture was then filtered, the solids

Scheme 3. Syntheses of the Majority Product P3HT-*b*-PS and PS-*b*-P3HT-*b*-PS by "Click" Chemistry with (a) ω-Ethynyl-P3HT (8) and (b) α,ω-Pentynyl-P3HT (9 and 9′)

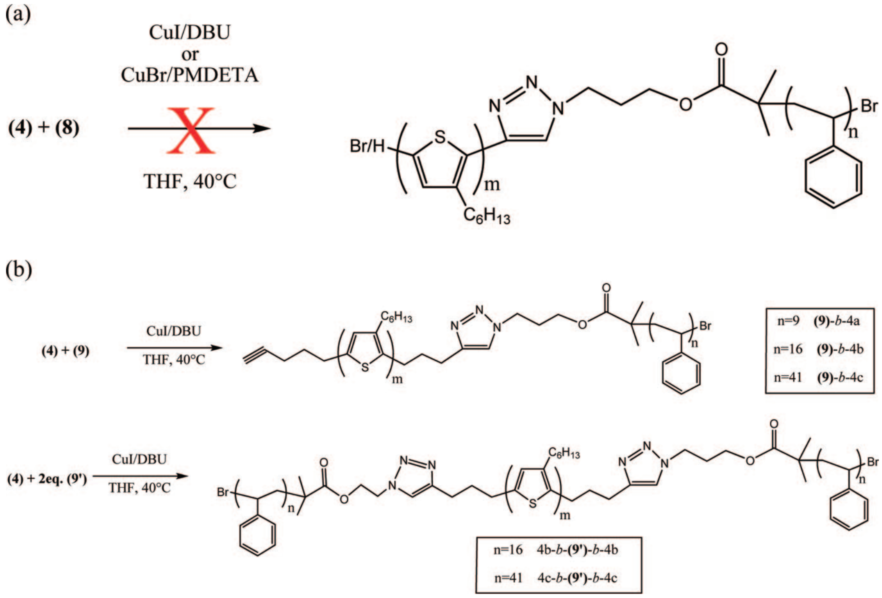


Table 1. Molecular Characteristics of α-Azido-PS (4a, 4b, and 4c), ω-Ethynyl-P3HT (8) and α,ω-Pentynyl-P3HT (9 and 9′), and the Corresponding P3HT-*b*-PS and PS-*b*-P3HT-*b*-PS Copolymers

α-azido-PS			alkynyl terminated P3HT			P3HT-*b*-PS or PS-*b*-P3HT-*b*-PS		
sample	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n	sample	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n	sample	$M_{n,GPC}$ (g mol^{-1})	M_w/M_n
α-azido-PS (**4a**)	1200	1.2	ω-ethynyl-P3HT (**8**)	8100	1.1	(**9**-*b*-**4a**)	8700	1.2
α-azido-PS (**4b**)	1900	1.2	α,ω-pentynyl-P3HT (**9**)	8200	1.1	(**9**-*b*-**4b**)	8900	1.2
α-azido-PS (**4c**)	4500	1.3	α,ω-pentynyl-P3HT (**9′**)	6200	1.1	(**9**-*b*-**4c**)	9300	1.2
						(**4b**-*b*-**9′**-*b*-**4b**)	9810	1.2
						(**4c**-*b*-**9′**-*b*-**4c**)	10900	1.3

were rinsed with acetone and the combined solutions were concentrated. A distillation gave the crude product (**2**) as a colorless oil (6 g, 83%).

δ_H (400 MHz, $CDCl_3$): 1.81 (2 H, q, $CH_2{-}CH_2{-}CH_2$), 2.02 (1 H, s, $CH_2{-}OH$), 3.43 (2 H, t, $CH_2{-}N_3$), 3.72 (2 H, t, $CH_2{-}OH$). δ_C(400 MHz, $CDCl_3$): 31.44 ($CH_2{-}CH_2{-}CH_2$), 48.47 ($CH_2{-}N_3$), 59.84 ($CH_2{-}OH$).

(ii) Synthesis of 3-Azidopropyl 2-Bromoisobutyrate (**3**). A solution of α-bromoisobutyryl bromide (11.95 g, 6.43 mL, 52 mmol, 1.05 equiv) in THF (50 mL) was added dropwise to a solution of **2** (5 g, 49.5 mmol) and triethylamine (6.5 g, 9 mL, 64.4 mmol) in THF (50 mL) at 0 °C. After complete addition, the reaction mixture was stirred for 2 h at 25 °C. Excess acid bromide was quenched by addition of degassed methanol (50 mL). The formed triethylammonium bromide salt was filtered off and the solution concentrated. The crude product was dissolved in CH_2Cl_2 and washed three times with a saturated ammonium chloride solution and three times with distilled water. The organic layer was dried over sodium sulfate (Na_2SO_4), filtered and concentrated, yielding a pale yellow oil, which was dried under vacuum (9 g, 81%).

δ_H (400 MHz, $CDCl_3$): 1.92 (6 H, s, $(CH_3)_2C$), 1.96 (2 H, q, $CH_2{-}CH_2{-}CH_2$), 3.44 (2 H, t, $CH_2{-}N_3$), 4.27 (2 H, t, $CH_2{-}O{-}C({=}O)$)). δ_C (400 MHz, $CDCl_3$): 27.97 ($CH_2{-}N_3$), 30.70 ($(CH_3)_2{-}C$), 48.03 (CH_2-$-H_2{-}CH_2$), 55.66 (C-$-$r), 62.74 ($CH_2{-}O$), 171.53 ($C{=}O$).

(iii) Synthesis of α*-Azido Polystyrenes (***4a***,* **4b** *and* **4c***).* Experiments were carried out varying the polymerization time to achieve different molar mass polystyrene. In a typical experiment, 3-azidopropyl-2-bromoisobutyrate (**3**) (0.25 g, 1 mmol), CuBr (0.143 g, 1 mmol), 2,2′-bipyridyl (0.468 g, 3 mmol) and styrene (5 g, 5.5 mL, 48 mmol) were placed in a Schlenk tube. The mixture was stirred for 5 min and degassed three times by freeze−pump−thaw cycles to remove residual oxygen. The polymerization reaction was performed at 130 °C. The reaction was stopped by dropping the temperature of the Schlenk to 0 °C. The solution was then dissolved in THF and passed through a basic alumina column. After being concentrated, the solution was precipitated in methanol and the polymer was dried under vacuum overnight and characterized by infrared, GPC, ^{1}H NMR and DSC.

(b) Synthesis of Alkynyl-Terminated Poly(3-hexylthiophene)s by GRIM (See Scheme 2). *(i) Synthesis of 3-Hexylthiophene (***6***).* Magnesium (7.5 g, 0.31 mol) was introduced together with dry diethyl ether (160 mL) in a flask and cooled to 0 °C. A solution of bromohexane (41.1 g, 35 mL, 0.25 mol) was added slowly. The resulting mixture was stirred under nitrogen for 2 h and then transferred to a dropping funnel fitted to a second flask containing 3-bromothiophene (**5**) (32.6 g, 18.7 mL, 0.2 mol) and Ni(dppp)Cl_2 (0.56 g, 1 mmol) in dry diethyl ether (75 mL). After cooling with an ice bath, the Grignard reagent was added dropwise and the resulting adduct was allowed to warm to room temperature before being stirred for 3 days under nitrogen. The mixture obtained was poured onto dilute aqueous hydrochloric acid. The organic layer was washed three times with water, dried over Na_2SO_4, filtered and concentrated. The crude product was distilled under reduced pressure as a colorless oil (30 g, 90%).

δ_H (400 MHz, $CDCl_3$): 0.90 (3 H, t, $(CH_2)_5{-}CH_3$), 1.32 (6 H, m, $CH_2{-}CH_2{-}(CH_2)_3{-}CH_3$), 1.63 (2 H, q, $CH_2{-}CH_2{-}(CH_2)_3{-}CH_3$), 2.63 (2 H, t, $CH_2{-}CH_2{-}(CH_2)_3{-}CH_3$), 6.92 (1 H, m, CH aro.), 6.95 (1 H, m, CH aro.), 7.23 (1 H, m, CH aro.).

*(ii) Synthesis of 2,5-Dibromo-3-hexylthiophene (***7***).* NBS (49 g, 0.275 mol) was added to a solution of **6** (25 g, 0.153 mol) in acetic acid (200 mL) and CH_2Cl_2 (200 mL). The mixture was stirred for 20 h under nitrogen. The organic layer was washed five times with water and five times with a saturated aqueous $NaHCO_3$ solution, dried over Na_2SO_4, filtered and concentrated. The crude product

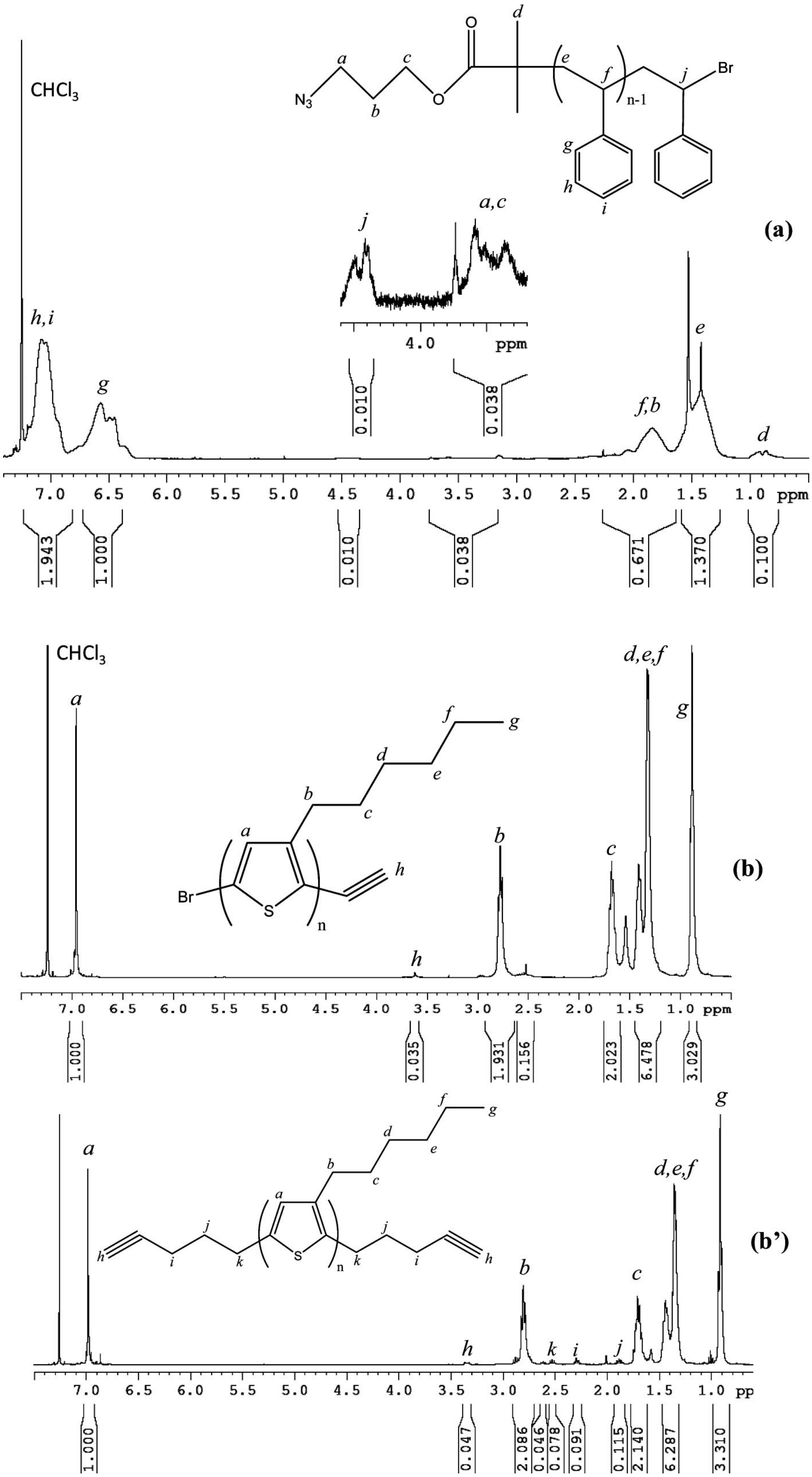


Figure 1. ^{1}H NMR spectra (400 MHz, in CDCl$_3$) of (a) α-azido-PS (**4b**); (b) ω-ethynyl-P3HT (**8**); and (b′) α,ω-pentynyl-P3HT (**9**).

was recovered as a pale yellow oil by two successive secondary vacuum distillations (5×10^{-4} mbar, 100 °C) (35 g, 70%).

δ_H (400 MHz, CDCl$_3$): 0.89 (3 H, t, $(CH_2)_5$-CH_3), 1.30 (6 H, m, $CH_2{-}CH_2{-}(CH_2)_3{-}CH_3$), 1.55 (2 H, q, $CH_2{-}CH_2{-}(CH_2)_3{-}CH_3$), 2.51 (2 H, t, $CH_2{-}CH_2{-}(CH_2)_3{-}CH_3$), 6.78 (1 H, s, CH aromatic). δ_C (400 MHz, CDCl$_3$): 14.10 ($(CH_2)_5{-}CH_3$), 22.60 ($(CH_2)_4{-}CH_2{-}CH_3$)), 26.96 ($-CH_2{-}(CH_2)_4{-}CH_3$), 28.81 ($(CH_2)_2{-}CH_2{-}(CH_2)_2{-}CH_3$), 29.51 ($(CH_2)_3{-}CH_2{-}CH_2{-}CH_3$), 31.60 ($CH_2{-}CH_2{-}(CH_2)_3{-}CH_3$), 107.95 (*C*2 aromatic), 110.32 (*C*5 aromatic),130.98 (*C*4 aromatic), 143.02 (*C*3 aromatic).

(iii) Synthesis of ω-Ethynyl-P3HT (8) and α,*ω-Pentynyl-P3HT (***9** *and* **9′***).* In a typical experiment, **7** (4.63 g, 14.2 mmol) was dissolved in THF (28 mL) and stirred under nitrogen. *tert*-Butylmagnesium chloride (14.2 mL, 14.2 mmol) was added, and

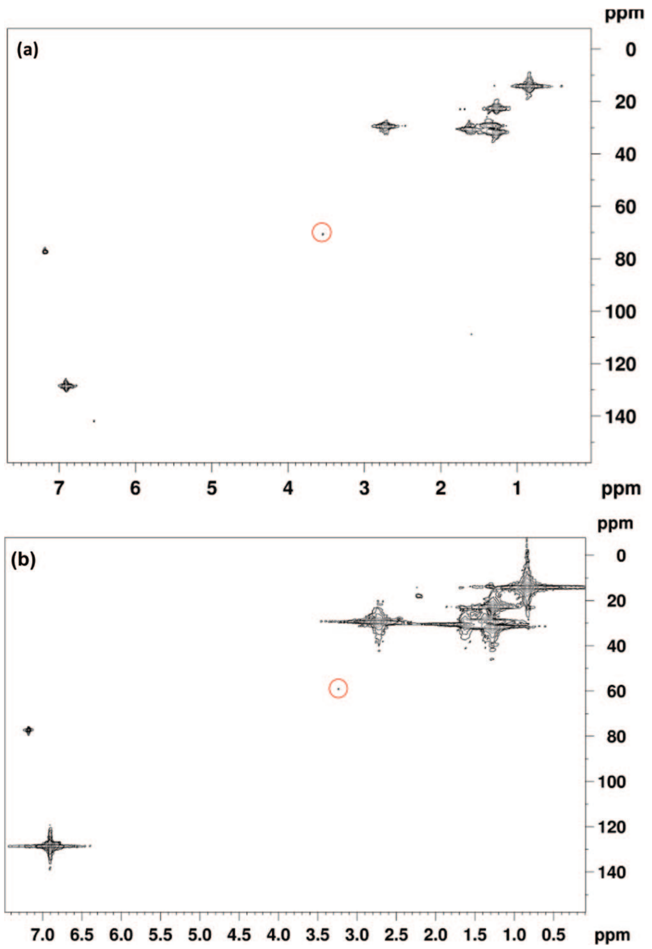


Figure 2. 2D $^1H-^{13}C$-HMQC NMR ($CDCl_3$, ambient temperature) of (a) *ω*-ethynyl-P3HT (**8**) and (b) α,*ω*-pentynyl-P3HT (**9**).

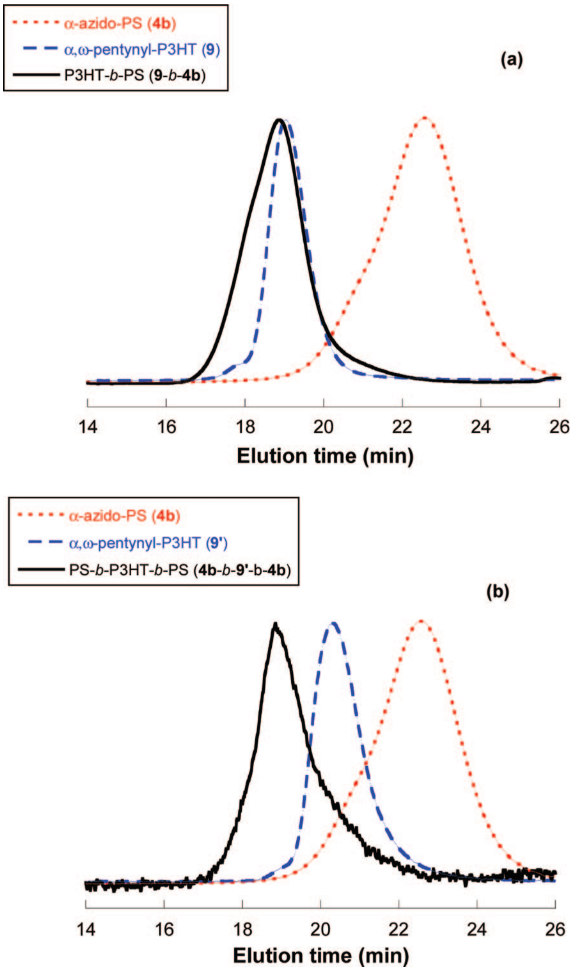


Figure 3. GPC traces in THF of (a) α-azido-PS (**4b**), α,*ω*-pentynyl-P3HT (**9**) and the resulting P3HT-*b*-PS (**9**-*b*-**4b**); and (b) α-azido-PS (**4b**), α,*ω*-pentynyl-P3HT (**9′**) and the resulting PS-*b*-P3HT-*b*-PS (**4b**-*b*-**9′**-*b*-**4b**).

the mixture was stirred at room temperature for 2 h. The mixture was then diluted to 140 mL with THF, Ni(dppp)Cl_2 (0.150 g, 0.3 mmol) was added, and the mixture stirred for 30 min at room temperature. The termination of the polymers with the respective Grignard functionalization agent was carried out in a one shot addition using 50 mol % with respect to the monomer. In the case of *ω*-ethynyl-P3HT (**8**), the Grignard reagent was ethynylmagnesium bromide obtained as a 0.5 M solution in THF. The reaction mixture was stirred for 15 min following addition, and the functionalized polymer recovered following precipitation in methanol. For α,*ω*-pentynyl-P3HT (**9** and **9′**), the reagent (5-chloromagnesio-1-pentynyl)trimethylsilane was prepared as follows. Magnesium (972 mg, 40 mmol) and (5-chloro-1-pentynyl)trimethylsilane (4.97 g, 28.4 mmol) were dissolved in dry THF (30 mL). The mixture was stirred for 1 day under nitrogen and then added in the polymerization mixture. In the case of **9** and **9′**, the polymer was deprotected as follows. The protected polymer was dissolved in THF, and the solution was cooled to −20 °C. A 0.20 M solution of TBAF·3H_2O (10 equiv with respect to chain ends) was slowly added, and the reaction mixture was stirred at this temperature for 30 min and then at room temperature for 4 h. The reaction was passed through a short silica column in order to remove excess TBAF. The polymer was recovered by precipitation in methanol. P3HTs were purified by a series of precipitation from methanol solution and analyzed by GPC, ^1H NMR, 2-D NMR, DSC and MALDI-TOF.

(c) Synthesis of Majority Product P3HT-*b*-PS Copolymers by "Click" Chemistry. Experiments were carried out with *ω*-ethynyl-P3HT (**8**) or α,*ω*-pentynyl-P3HT (**9**) and α-azido-PS (**4**). In a typical experiment, alkynyl end-capped P3HT (250 mg, 4.2×10^{-2} mmol), PS (37 mg, 4.2×10^{-2} mmol) and CuI (1.6 mg, 8.4×10^{-3} mmol) were added to a round-bottom flask, evacuated for 10 min and backfilled with nitrogen. A solution of degassed DBU (153 mg, 1 mmol) in THF (10 mL) was added and the flask was placed in a constant temperature oil bath at 40 °C for 3 days. The block copolymer was recovered by precipitation in methanol, dried under reduced pressure, and then three times dissolved in a minimum of THF and precipitated in acetone to remove unreacted PS and low molar mass P3HT.

(d) Synthesis of PS-*b*-P3HT-*b*-PS Block Copolymers by "Click" Chemistry. Experiments were carried out with α,*ω*-pentynyl-P3HT (**9′**) and α-azido-PS (**4b** and **4c**). In a representative experiment, α,*ω*-alkynyl-P3HT (125 mg, 3.4×10^{-2} mmol), PS (**4c**) (275 mg, 6.8×10^{-2} mmol) and CuI (2.6 mg, 1.3×10^{-2} mmol) were added to a round-bottom flask, evacuated for 10 min and backfilled with nitrogen. A solution of degassed DBU (210 mg, 1.3 mmol) in THF (10 mL) was added, and the flask was placed in a constant temperature oil bath at 40 °C for 5 days. The solution was passed through a neutral alumina column in order to remove copper salt. After concentration, the product was recovered by precipitation in methanol, dried under reduced pressure, and then three times dissolved in a minimum of THF and precipitated in acetone to remove unreacted PS and low molar mass P3HT. Further drying under reduced pressure yielded copolymers for characterization by GPC, FTIR, ^1H NMR.

Another catalyst system, CuBr/PMDETA, was also attempted with *ω*-ethynyl-P3HT (**8**). In a typical experiment, *ω*-ethynyl-P3HT (90 mg, 1.8×10^{-5} mol), α-azido-PS (100 mg, 2.25×10^{-5}mol), CuBr (10 mg, 6.9×10^{-5} mol) and PMDETA (0.012 mg, 15 *μ*L, 6.9×10^{-5} mol) were dissolved in THF (8 mL) in a Schlenk tube. The mixture was stirred for 5 min and degassed three times by

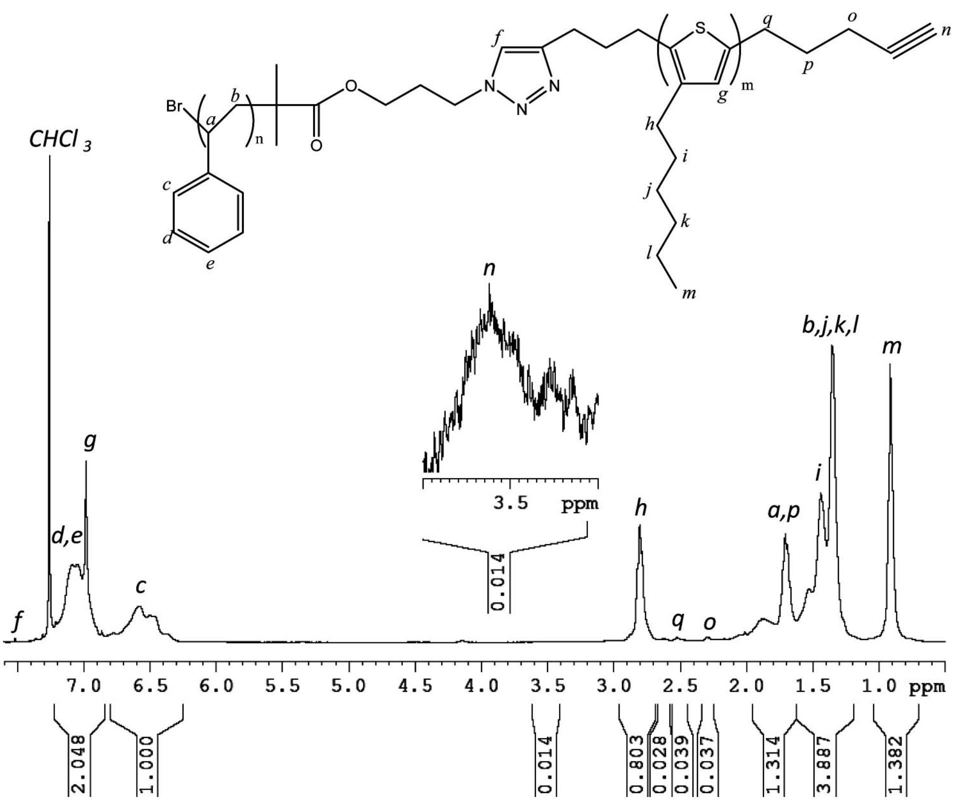


Figure 4. ^{1}H NMR spectrum (400 MHz, in CDCl$_3$) of P3HT-*b*-PS (**9**-*b*-**4c**).

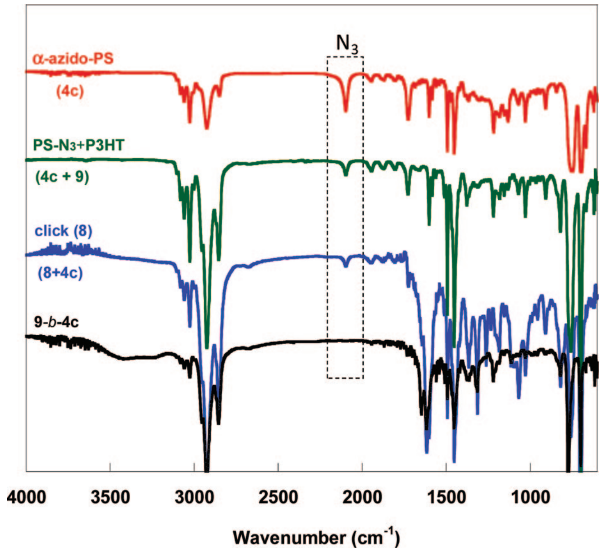


Figure 5. IR spectra of α-azido-PS (**4c**), its initial mixture with *ω*-ethynyl-P3HT (**8**), and the resulting "click" products with *ω*-ethynyl-P3HT (click **8**) and α,*ω*-pentynyl-P3HT (**9**-*b*-**4c**).

freeze−pump−thaw cycles to remove any residual oxygen. The Schlenk was placed in a constant temperature oil bath at 40 °C for 3 days. The solution was passed through a neutral alumina column in order to remove copper salt. After concentration, the product was recovered by precipitation in methanol and dried under reduced pressure. The copolymers were characterized by GPC, FTIR, ^{1}H NMR and DSC.

Results and Discussion

While various strategies were developed in the literature to obtain rod−coil type diblock copolymers composed of P3HT, the role of the morphology of self-assembled block copolymers on opto-electronic characteristics has not been clearly evidenced yet.[26,27] Our contribution in this field consists of a convenient and versatile way to obtain rod−coil P3HT-*b*-PS and coil−rod−coil PS-*b*-P3HT-*b*-PS block copolymers by Huisgen's 1,3-dipolar cycloaddition ("click" chemistry) of the separately prepared α-azido-PS (**4**), *ω*-ethynyl-P3HT (**8**) and α,*ω*-pentynyl-P3HT (**9** and **9′**) (see Scheme 3). The α-azido-PS (**4**) was obtained by ATRP with the initiator 3-azidopropyl 2-bromoisobutyrate (**3**), prepared as shown in Scheme 1 in two steps following published procedures.[22,28] Prior compounds (**2**) and (**3**) were obtained in good yields, and their purity was verified by ^{1}H and ^{13}C NMR spectroscopy (see Experimental Section). α-Azido-PS samples were then prepared by ATRP of styrene at 130 °C in the presence of CuBr/bipyridine with (**3**) as initiator. Polymerization times were varied (7, 10 and 30 min) in order to vary chain lengths and gave three samples denoted α-azido-PS (**4a**) 1200 g·mol^{-1}; α-azido-PS (**4b**) 1900 g·mol^{-1}; and α-azido-PS (**4c**) 4500 g·mol^{-1} (see Table 1). All three samples were indicated by GPC to have monomodal molar mass distributions and dispersities (M_w/M_n) less than 1.3. For applications in photovoltaic devices, it was supposed that the molar mass of the electronically inert PS should be kept low so as to not hinder charge transport. The presence of an azide function at the PS chain end was confirmed by ^{1}H NMR (Figure 1a) and infrared spectroscopies (Figure 5), the latter showing a strong signal at 2100 cm^{-1} characteristic of the $\nu(N_3)$ vibration.

Alkynyl-terminated regioregular P3HTs were synthesized by the Grignard metathesis (GRIM) as shown in Scheme 2 and according to methods detailed in the literature.[15,29,30] 2,5-Dibromo-3-hexylthiophene (**7**), that had been prepared in two steps following published procedures,[31,32] was reacted with *tert*-butylmagnesium chloride to yield 2-bromo-5-magnesiochloro-3-hexylthiophene as a major product.[33] The addition of Ni(dppp)Cl$_2$ to the reaction mixture resulted in the formation of "living" P3HT effectively end-capped by a highly active Ni^0 group. While the polymer was still in solution, a second Grignard agent was introduced. This arrested the chain growth polymerization and resulted in the formation of the end-functionalized polymers. Two different Grignard reagents were used to cap the P3HTs, ethynylmagnesium bromide to achieve ω-ethynyl-P3HT (**8**) and (5-chloromagnesio-1-pentynyl)trimethylsilane to achieve α,ω-pentynyl-P3HT (**9** and **9′**) following deprotection. These polymers were chosen not only to access diblock and triblock structures but also so as to investigate the effect of the possible conjugation of the alkynyl group with the polythiophene backbone. It could be anticipated that ω-ethynyl-P3HT would not be very reactive with respect to the azido group due to ethynyl conjugation with P3HT, whereas α,ω-pentynyl-P3HT, with its alkyl spacer between delocalized bonds, would permit the ethynyl group to be both sterically and electronically more available for "click" chemistry. P3HTs were analyzed by GPC (see Table 1), ^{1}H NMR, 2D ^{1}H−^{13}C NMR and MALDI-TOF. GPC indicated the P3HT molar masses (M_n) to be 8100 $g \cdot mol^{-1}$ and 8200 $g \cdot mol^{-1}$ for ω-ethynyl-P3HT (**8**) and α,ω-pentynyl-P3HT (**9**), respectively. Another α,ω-pentynyl-P3HT (**9′**) of 6200 $g \cdot mol^{-1}$ was also prepared in order to facilitate characterization due to the more discernible changes in molar mass. It has been shown that GPC indicated molar masses of P3HTs against PS standards are overestimated by a factor of 1.2−2.3.[34] By way of the graph given in ref 34 showing the relationship of the molecular weight as determined by MALDI and GPC, the P3HTs could be estimated as having "real" number average molar masses of around 4700 $g \cdot mol^{-1}$ with a number average degree of polymerization ($\bar{X}_n \approx 28$) for ω-ethynyl-P3HT (**8**), 4750 $g \cdot mol^{-1}$ ($\bar{X}_n \approx 28$) for α,ω-pentynyl-P3HT (**9**), and 3900 $g \cdot mol^{-1}$ ($\bar{X}_n \approx 23$) for α,ω-pentynyl-P3HT (**9′**). Moreover, both ω-ethynyl-P3HT (**8**) and α,ω-pentynyl-P3HT (**9** and **9′**) showed monomodal molar mass distributions and dispersities close to 1.1 (Table 1). In the ^{1}H NMR spectra (Figure 1) the presence of the alkynyl group is indicated by the peak at 3.64 ppm for ω-ethynyl-P3HT (**8**) and 3.36 ppm for ω-pentynyl-P3HT (**8′**) due to the alkyne proton ($-C{\equiv}C-H$).[15] This is confirmed by the 2-D ^{1}H−^{13}C-HMQC NMR shown in Figure 2. In Figure 2a, ω-ethynyl-P3HT (**8**) gives rise to a peak at 3.64 ppm that correlates with the peak at 70.58 ppm and is assigned to the terminal alkyne carbon ($--C{\equiv}C-H$), which usually appears in the range of 60−90 ppm.[22,23,35,36] For α,ω-pentynyl-P3HT (**9**) (Figure 2b), the peak at 3.36 ppm correlates with the peak at 60.1 ppm, which is again assigned to the terminal alkyne carbon ($-C{\equiv}C-H$). The decrease of 0.28 ppm in going from the ethynyl to pentynyl group confirms a reduction in conjugation with the P3HT backbone. Moreover, in the ^{1}H NMR spectrum (Figure 1), the peak at 7.0 ppm, assigned to the P3HT backbone proton at position 4, and the peak at 2.8 ppm, assigned to the α-methylene protons of the hexyl chains, are used as probes to quantify the regioregularity of the P3HTs.[37] This allowed us to confirm that all P3HTs samples were highly regioregular (close to 97% for both P3HTs). MALDI-TOF MS was also employed to determine the end group composition of alkynyl-terminated P3HTs (see Supporting Information). The MALDI-TOF spectra of ω-ethynyl-P3HT (**8**) and α,ω-pentynyl-P3HT (**9′**) contain mainly two populations. On the one hand, ω-ethynyl-P3HT (**8**) is composed of a major population which corresponds to α-bromo-ω-ethynyl-P3HT and a minor one which corresponds to α,ω-ethynyl-P3HT. On the other hand, α,ω-pentynyl-P3HT (**9′**) is composed of a major population which corresponds to α,ω-pentynyl-P3HT and a minor one which corresponds to ω-pentynyl-P3HT. This technique allows for identification of the peaks to within ±5 $g \cdot mol^{-1}$, which is the expected error due to isotope effects.[38] In addition, the representative DSC thermogram of ω-pentynyl-P3HT (Supporting Information) exhibits an endothermic peak corresponding to a melting temperature of 212 °C (2nd heating run) and in the cooling cycle an exotherm corresponding to a crystallization temperature of 174 °C, which are typical values for comparable molar mass P3HT.[39] It is necessary to note that even if alkyne end-capped P3HTs have been obtained, their purification was not facile due to the poor stability of the alkynyl function. For instance, while products of coupling reactions were obtained by Soxhlet treatments, the purification of the alkynyl terminated P3HTs was performed by repeated precipitations from THF in methanol at room temperature.

"Click" chemistry was then carried out between α-azido-PS (**4**) and ω-ethynyl-P3HT (**8**) or α,ω-pentynyl-P3HTs (**9** and **9′**). These copper(I) catalyzed 1,3-dipolar cycloaddition coupling reactions were performed in solution in THF using either CuI/DBU or CuBr/PMDETA as the catalytic system. As to our knowledge this is the first example of a "click" reaction with a π-conjugated polymer, the major difficulty we faced was the choice of solvent and catalyst. Most papers that deal with "click" chemistry of polymers report the use of water or dimethylformamide (DMF) as a good solvent to achieve cycloaddition.[24,35] Unfortunately P3HT is not soluble in water or DMF, hence the choice of THF as it is a good solvent of P3HT and PS has been used in combination with CuI/DBU and CuBr/PMDETA.[24] Initial experiments were carried out with stoichiometric amounts of either ω-ethynyl-P3HT (**8**) or α,ω-pentynyl-P3HT (**9**) with **4** in THF using CuI/DBU at 40 °C (Scheme 3).[21,22] ^{1}H NMR, infrared and GPC were used to characterize the resultant products and showed that the majority product P3HT-*b*-PS diblock copolymers were obtained with α,ω-pentynyl-P3HT (**9**) but not with ω-ethynyl-P3HT (**8**), indicating the effect of ethynyl conjugation with the main chain on the outcome of the reaction.

α,ω-Pentynyl-P3HT (**9**) was reacted with stoichiometric amounts of the three aforementioned α-azido-PS (**4a**, **4b**, and **4c**) to give rise to three different diblock copolymers, denoted respectively **9**-*b*-**4a**, **9**-*b*-**4b** and **9**-*b*-**4c**. Figure 3(a) (dealing with copolymers obtained from α,ω-pentynyl-P3HT (**9**)) shows typical GPC traces of the homopolymers P3HT and PS, as well as the resulting copolymers. GPC curves indicate a shift in the molar mass of the copolymer with respect to the homopolymers. Details are given in Table 1. It is noteworthy that the GPC traces of the diblock copolymers are monomodal and symmetrical while remaining quite narrow, attesting an efficient formation of copolymers. The general structures of **9**-*b*-**4a**, **9**-*b*-**4b** and **9**-*b*-**4c** are confirmed by ^{1}H NMR spectroscopy. Figure 4 shows a typical spectrum of a purified diblock compound with the expected peaks. Of particular interest is the peak at 7.51 ppm which can be assigned to the triazole group formed by the cycloaddition. Concurrently, there is a decrease of the peak at around 3.4 ppm due to the consumption of alkynyl groups. Nevertheless, given that each P3HT carries 2 reactive pentynyl chain ends and the equivalence of P3HT and PS in the reaction, we would expect to see a mixture in the brut products of P3HT-*b*-PS, PS-*b*-P3HT-*b*-PS and P3HT. Therefore, two molar equivalents of α-azido-PS (**4b** and **4c**) versus the α,ω-pentynyl-P3HT (**9′**) were reacted to obtain pure samples of triblock copolymers of PS-*b*-P3HT-*b*-PS. The GPC traces given in Figure 3(b) clearly show the shift in the molar mass in the case of triblock **4b**-*b*-**9′**-*b*-**4b** with respect to the homopolymers **4b** and **9′**.

Further confirmation of the "click" coupling is taken from IR spectroscopy where the strong signal at 2100 cm^{-1} due to the PS azido group disappeared completely in the copolymer. Besides, the DSC thermogram of **9**-*b*-**4c** (Supporting Information) exhibits a glass transition temperature (T_g) of 82 °C close to that of the corresponding ω-azido-PS **4c** (85 °C) and a melting temperature (T_m) of 202 °C lower than the corresponding α,ω-pentynyl-P3HT (**9**), phenomena previously observed for rod−coil copolymers.[40]

As mentioned above, the "click" reaction of ω-ethynyl-P3HT (**8**) with **4** did not work, as surmised from GPC and IR characterizations. The GPC trace of the resulting compound is a combination of the two starting homopolymers. This result is confirmed by IR (see Figure 5), where the signal at 2100 cm^{-1} due to the azido group is retained. The same reaction was also attempted in the presence of CuBr/PMDETA, a normally effective route to copolymers in THF.[41] Again, this reaction was unsuccessful with ω-ethynyl-P3HT (**8**). It can thus be surmised that conjugation of the ethynyl group with P3HT can hinder "click" reactions, a not uncommon occurrence when performing chemistry on polythiophenes.[31] Jatsch et al. recently showed that a "click" reaction with an α-functionalized oligothiophene is possible.[42] Although they are using a different catalytic system ($\text{Cu(CH}_3\text{CN)}_4\text{PF}_6/\text{Cu}^0$), it is probable that the use of an oligomer rather than a polymer was the determining factor due to considerably greater conjugation of the latter macromolecule.

Conclusion

It is what we believe to be the first demonstration of a "click" reaction involving an ω-alkynylated π-conjugated polymer. It is shown that the electronic environment of the participating alkynyl group is an overriding parameter. Conjugation between this group and the main chain can lead to its deactivation and subsequent hindrance of any attempts at cycloaddition reactions. It is for this reason that it is suggested that future chemistry involving conjugated polymers and "click" chemistry be performed using groups distanced from the conjugated polymer backbone by a spacer group, such as an alkyl chain as was the case in this work.

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Supporting Information Available: MALDI-TOF of α,ω-pentynyl-P3HT (**9′**), and MALDI-TOF of ω-ethynyl-P3HT (**8**), and DSC measurements of PS-N_3 (**4c**), α,ω-pentynyl-P3HT (**9**), and P3HT-*b*-PS (**9**-*b*-**4c**). This material is available free of charge via the Internet at http://pubs.acs.org.

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