

Amphiphilic poly(alkylthiophene) block copolymers prepared *via* externally initiated GRIM and click coupling†

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Block copolymers with a poly(3-alkylthiophene) (P3AT) polymer block can self-organize into periodic, crystalline nanostructures that may be useful for organic electronic applications. However, reliable synthetic methods for the preparation of P3AT block copolymers are lacking. Here, we demonstrate a general method for the synthesis of P3AT rod-coil block copolymers *via* click-coupling of alkynyl-P3AT. Alkynyl-P3ATs are prepared *via* externally initiated Grignard metathesis polymerization (GRIM) using a modified nickel catalyst followed by end-group modification. The resulting alkynyl-P3ATs have improved stability and solubility compared with those previously reported. P3ATs are subsequently coupled to an azide-functionalized poly(ethylene glycol) through copper-catalyzed azide-alkyne click coupling, resulting in P3AT-*b*-PEG block copolymers. The advantages of this synthetic procedure are the improved stability of the alkynyl-P3AT macroreagent, the capability to synthesize high molecular weight P3AT polymer blocks, and facile determination of P3AT absolute molecular weight through ¹H NMR analysis. This synthetic method is applied to prepare a series of P3AT-*b*-PEG block copolymers, with poly(3-hexylthiophene) (P3HT), poly(3-dodecylthiophene) (P3DDT), and poly(3-(2'-ethyl)hexylthiophene) (P3EHT) polymer blocks. The resulting P3AT block copolymers are dispersed in water to form micelles with crystalline, hydrophobic cores. Absorbance measurements show that crystallization of P3DDT and P3EHT blocks is suppressed in micellar cores due to nanoscale confinement of the P3AT blocks.

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Introduction

Poly(3-alkylthiophenes) (P3ATs) are solution-processable polymeric semiconductors with significant potential for use in optoelectronic devices, including organic photovoltaics, thin film transistors, and light-emitting diodes. Regioregular P3ATs with a low polydispersity and targeted molecular weight can be prepared by Grignard metathesis polymerization (GRIM),^{1,2} and this has enabled systematic studies on the effects of molecular weight, side-chain, and regioregularity on structure and optoelectronic properties.^{3,4}

GRIM also enables the preparation of block copolymers with P3AT polymer blocks. These types of block copolymers can self-assemble into regular nanostructures with crystalline order and may be particularly useful for applications in organic electronics.^{5–7} Common synthetic approaches for poly(3-hexylthiophene) (P3HT) block copolymers include the preparation of ω -allyl P3HT followed by attachment of an initiator for a second

polymerization reaction^{8,9} and the preparation of ω -alkynyl P3HT and subsequent click coupling.^{10–12} However, ω -alkynyl P3HT prepared by GRIM using conventional methods is unstable,¹⁰ and while several reports have reported success with click coupling P3HT, other studies have reported poor coupling efficiencies.¹³ These methods are more successful with low-molecular weight P3HT polymers and can result in unreacted P3HT homopolymer impurities due to low coupling efficiencies or incomplete polymer end-functionality.¹⁴

Recently, several groups have demonstrated externally initiated regioregular P3HT *via* GRIM.^{15–18} The use of an externally added initiator enables the preparation of more complex polymeric structures such as brushes^{19,20} and block copolymers^{17,18,21,22} since functional groups for further reaction can be incorporated directly into the initiator complex. This potentially provides a straightforward and generally applicable synthetic route to make regioregular P3HT and P3AT block copolymers. In this work, we show that the use of externally initiated GRIM can be used to produce alkynyl-P3ATs which are stable against crosslinking under ambient conditions. These alkynyl-P3ATs are used to prepare P3AT rod-coil block copolymers through copper-catalyzed azide-alkyne click coupling.

Herein, we present an improved synthetic approach for the synthesis of poly(3-alkylthiophene) block copolymers *via* externally initiated GRIM and click chemistry. Three different

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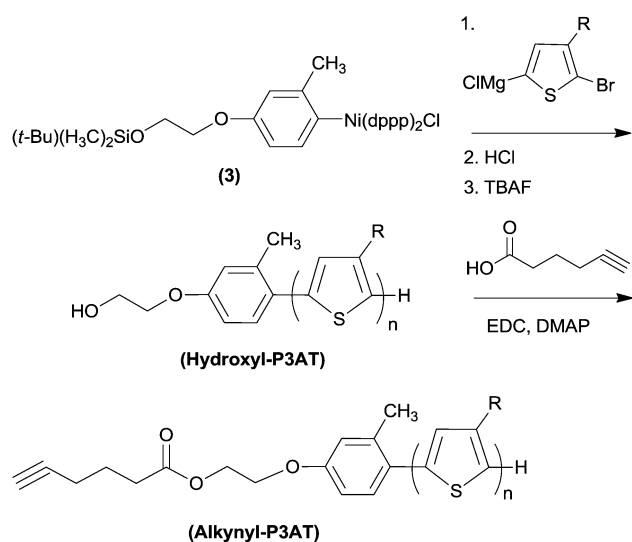
† Electronic supplementary information (ESI) available: Detailed synthetic procedures, NMR spectra, GPC spectra, X-ray scattering data, and experimental methods. See DOI: 10.1039/c3py21098g

regioregular P3ATs – P3HT, poly(3-dodecylthiophene) (P3DDT), and poly(3-(2'-ethyl)hexylthiophene) (P3EHT) – are prepared using GRIM initiated by a functionalized nickel catalyst, and, after end-group modification, P3ATs are click coupled to azide-functionalized poly(ethylene glycol) (PEG). ^1H NMR analysis provides end-group functionality and polymer molecular weight, and the method allows for the preparation of P3AT block copolymers with absolute P3AT block M_n greater than 15 kg mol^{-1} . We show that alkynyl-P3ATs produced through this synthetic route have improved stability and solubility compared with ω -alkynyl P3HT prepared by GRIM using conventional methods. P3AT-*b*-PEG block copolymers form spherical micelles when dispersed in water, and core crystallization is observed for P3AT cores with crystal melting temperatures $T_m > 150\text{ }^\circ\text{C}$. This work demonstrates an improved method for preparing P3AT block copolymers and provides insight into the role of polymer crystal melting temperature on micelle core crystallinity.

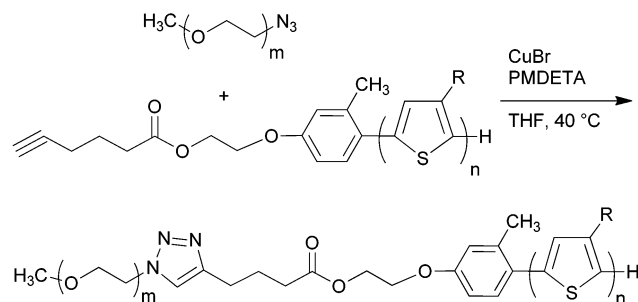
Results and discussion

Synthesis of P3AT block copolymers

Our overall synthetic scheme involves the preparation of alkynyl-P3AT followed by click coupling to PEG, as shown in Schemes 1 and 2. The alkynyl functionality is incorporated *via* externally initiated GRIM using a functionalized Ni catalyst (3). Importantly, synthesis of the nickel complex (3) is straightforward and efficient. The Ni catalyst (3) is prepared in a one-pot, two-step reaction, as shown schematically in Fig. 1. First, the reaction of 1-chloro-2-methyl-4-[6-(*t*-butyldimethylsilyloxy)ethoxy] benzene (1) gives *trans*-chloro(aryl)bis(triphenylphosphine)nickel(II) complex (2). Analysis of the crude product by ^{31}P NMR reveals a single peak at 21.1 ppm, in agreement with literature values.^{17,23} Next, an excess of 1,3-bis(diphenylphosphino)propane (dppp) is added to the reaction mixture, resulting in rapid ligand exchange and the formation of the desired



Scheme 1 Preparation of alkynyl end-functionalized P3ATs *via* GRIM with functionalized initiator.



Scheme 2 Synthetic scheme for the preparation of P3AT-*b*-PEG block copolymers *via* click coupling.

chloro(aryl)(dppp)nickel(II) complex (3). Three peaks can be seen in the ^{31}P analysis of (3). The broad peak at -4.4 ppm corresponds to liberated triphenylphosphine ligand in solution while the peaks at 12.1 and -14.5 ppm correspond to the functionalized Ni catalyst, in agreement with previous studies^{15,17} of similar chloro(*o*-tolyl)(dppp)nickel(II) complexes. ^{31}P analysis therefore indicates full conversion of the $\text{Ni}(\text{PPh}_3)_4$ catalyst to the desired nickel(II) complex (3).

GRIM is initiated by addition of the crude reaction mixture containing (3) to a solution of 3-alkyl-2-bromo-5-chloromagnesiathiophene in tetrahydrofuran (Scheme 1). After 1 hour, the polymerization is quenched by the addition of HCl, and the silane protecting group is removed by addition of *n*-tetrabutyl ammonium fluoride (TBAF) before precipitation of the polymer in methanol. Next, the polymer end-group is modified through a Steglich esterification reaction with 5-hexynoic acid to yield alkynyl-P3AT.

Alkynyl-P3HT produced by GRIM using conventional methods is unstable under ambient conditions. Samples exhibit significantly reduced solubility and polymer cross-linking (see ESI Fig. S1†). Similar observations have been reported by others,¹⁰ and this can result in poor click coupling efficiencies. Conversely, alkynyl P3ATs prepared as shown in Scheme 1 are stable under ambient conditions for an extended period of time, up to 12 months. No evidence of degradation or crosslinking is observed for alkynyl-P3HT, and only a small amount of crosslinking is seen for alkynyl-P3DDT (see ESI Fig. S2†). Both P3AT macroreagents are also fully soluble after storage under ambient conditions for up to 11 months.

P3AT-*b*-PEG copolymers are prepared by click coupling alkynyl-P3ATs with poly(ethylene glycol) methyl ether azide (PEG- N_3) (Scheme 2). The polymeric macroreagents are combined with N,N,N',N'' -pentamethyldiethylenetriamine (PMDTA)-CuBr as the catalyst system in THF at $40\text{ }^\circ\text{C}$. An excess of PEG- N_3 reagent is used to ensure complete reaction of the alkynyl-P3AT. After 24 h, the reaction mixture is passed through a basic alumina column to remove catalyst and precipitated in methanol to recover the block copolymers. This latter step also removes the excess PEG- N_3 homopolymer.

^1H NMR provides clear evidence for quantitative endgroup transformations and enables straightforward calculation of absolute polymer molecular weights (Fig. 2 and ESI Fig. S5–S13†). Peaks corresponding to terminal ethoxy group appear at

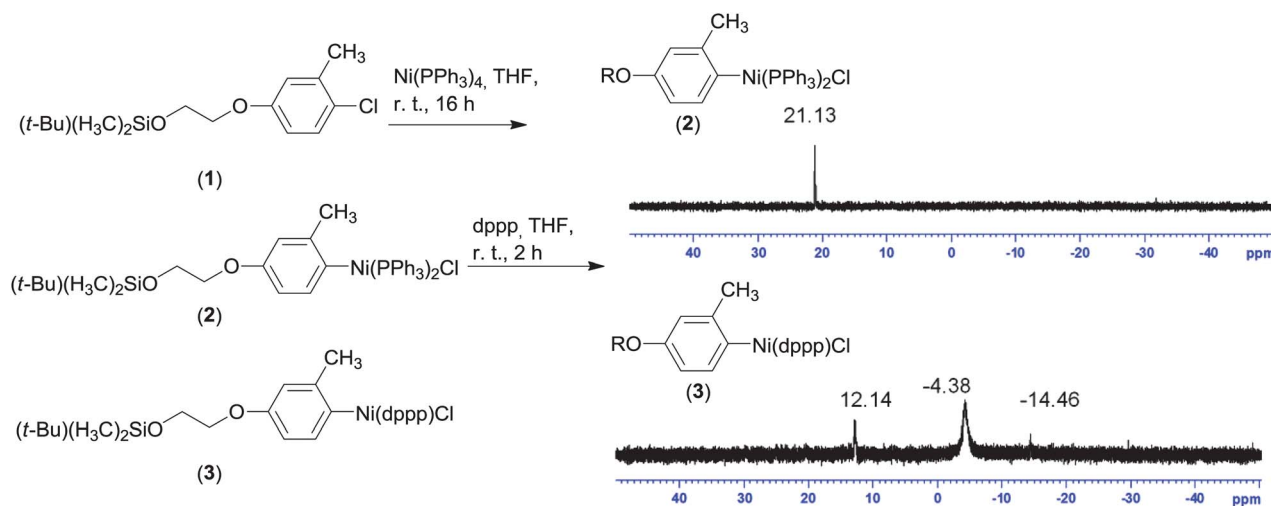


Fig. 1 Synthetic scheme for the preparation of modified nickel catalyst (left) and ^{31}P NMR analysis of Ni catalyst (right).

3.9–4.5 ppm for all polymeric intermediates with distinct shifts for each reaction step. The precursor 1-chloro-2-methyl-4-[6-(*t*-butyldimethylsilyloxy)ethoxy] benzene (1) exhibits two overlapping peaks near 4.0 ppm. After GRIM and removal of the silyl protecting group resulting in hydroxyl-P3AT, ^1H NMR peaks corresponding to the terminal ethoxy group are shifted downfield to 4.1 and 4.0 ppm. Subsequent esterification to yield alkynyl-P3AT results in a further downfield shift to 4.45 and 4.2 ppm, and the complete disappearance of peaks at 4.1 and 4.0 ppm indicates full reaction of the hydroxyl-P3ATs. Triplet peaks at $\delta = 4.45$ and 4.2 ppm are also evidenced in the final P3AT-*b*-PEG along with peaks at $\delta = 4.5$ and 3.8 corresponding to PEG aliphatic protons near the triazole ring, a singlet peak at $\delta = 7.5$ ppm corresponding to the proton on the triazole ring, and a singlet peak at $\delta = 2.45$ ppm corresponding to the tolyl group. These peaks appear in all P3AT-*b*-PEG samples prepared (see ESI Fig. S11–S13 \dagger).

GPC analysis of the final block copolymer products shows a single peak indicative of a single polymer, but only a modest shift in the molecular weight distributions are observed relative to the starting P3AT macroreagents due to the much larger size and stiffness of the P3AT block (see ESI Fig. S14 \dagger). While we cannot exclude the possibility of unfunctionalized P3AT in the final product, previous work with similar Ni initiators has demonstrated a high degree of endgroup functionality.¹⁵ Furthermore, as discussed below, comparison of the P3AT integrated intensities to that of the PEG block in the final block copolymer indicates efficient click coupling.

P3AT degree of polymerization (DP) can be estimated by ^1H NMR analysis of hydroxyl P3AT by comparison of the integrated intensities for the aromatic protons ($\delta = 7.0$ ppm) and terminal ethoxy protons ($\delta = 4.5, 4.0$ ppm). For the present study, the target DP was 120 for the P3AT blocks, and DPs in the range of 90–113 are achieved (Table 1). This is significantly larger than other P3HT blocks in similar P3HT-*b*-PEG^{11,24–27} and P3EHT-*b*-PEG²⁸ copolymers reported (note that M_n estimates based on size-exclusion chromatography with polystyrene standards

typically overestimate the molecular weight of P3HT by a factor of 1.2–1.5). A comparison of the ^1H NMR integrated intensities corresponding to the P3AT ($\delta = 7.0$ ppm) to that corresponding to PEG ($\delta = 3.5$ ppm) is in relatively good agreement with the expected DP ratios (roughly 90 : 113 in all cases) based on the known molecular weight of PEG, synthesized by anionic polymerization (Nanocs). Excess PEG is present in the P3DDT-*b*-PEG product. This indicates efficient coupling through click coupling and shows that the overall synthetic approach provides a reliable strategy to synthesize P3AT rod-coil block copolymers.

Self-assembly of P3AT-*b*-PEG in water

Recent work has demonstrated that amphiphilic P3HT rod-coil block copolymers can self-assemble in water to form micelles with P3HT-rich cores and PEG coronas. Depending on the solvent chosen and the block ratio, nanofibers can also be formed.^{24,25} The present series of block copolymers enables us to investigate the role of P3AT crystal melting temperature on self-assembly and core crystallization. P3DDT and P3EHT block copolymers may exhibit reduced crystallinity due to the lower crystal melting temperatures of P3DDT (150 °C) and P3EHT (50 °C) compared with P3HT (220 °C).

To disperse P3AT-*b*-PEG in water, block copolymers were first dissolved in THF at a concentration of 1 mg mL⁻¹. An equal amount of methanol was added to the THF solution before placing the THF-methanol solutions in a dialysis bag in DI water. After solvent exchange overnight, the solutions were filtered to obtain a clear solution free of insoluble aggregates. In all cases, successful dispersion of P3AT-*b*-PEG in water is reflected by a transparent but colourful solution after dispersion and filtration (Fig. 3). P3EHT-*b*-PEG dispersions are lighter than P3HT-*b*-PEG and P3DDT-*b*-PEG dispersion in water, but P3EHT-*b*-PEG dispersions exhibit the strongest fluorescence under UV light ($\lambda = 365$ nm), indicative of reduced aggregation or crystallinity, as discussed below. As a control experiment, the

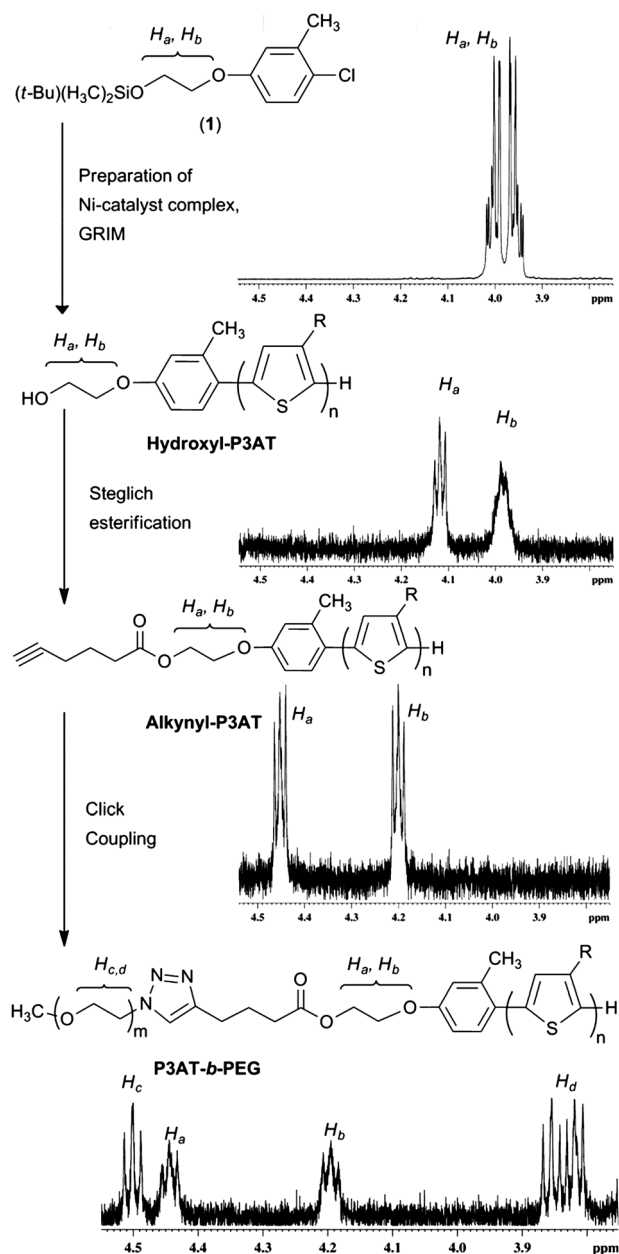


Fig. 2 ^1H NMR spectra for P3AT endgroup and block copolymer linking group. Integrated areas of H_a , H_b , and H_c correspond to 2 protons per polymer chain. Integral area for H_d corresponds to 4 protons. Spectra shown are for P3HT, and full spectra for all polymeric reagents with integrated intensities are provided in the ESI Fig. S5–S13.†

same procedure was applied to P3AT homopolymers (see ESI Fig. S15†). As expected, the P3AT homopolymers did not form micellar dispersions in water and the resulting solutions were clear. Dynamic light scattering analysis of the block copolymer dispersions in water indicates micelle formation with micelle sizes larger than 100 nm. These sizes are roughly consistent with measured particle sizes by atomic force microscopy measurements of dry micelles deposited on a silicon surface (see ESI Fig. S16†). Micelle sizes are measured to be larger in solution, as expected due to solvent swelling.

P3HT, P3DDT, and P3EHT are semi-crystalline polymers, and crystallization of the P3AT polymer blocks would be expected if the P3AT concentration is sufficiently enriched in the micelle cores. With the synthesized series of block copolymers, we can investigate the role of crystal melting temperatures, which vary from 220 °C for P3HT, to 150 °C for P3DDT, and 50 °C for P3EHT. The absorbance spectra for all block copolymers in a good solvent for both polymer blocks (THF) is qualitatively similar, with a broad absorbance maximum near 450 nm, as has been observed for the corresponding homopolymers (Fig. 4).²⁹ This corresponds to a well solvated, non-crystalline P3AT-*b*-PEG polymers in solution. Qualitatively different absorbance spectra are observed for P3AT-*b*-PEG micellar solutions, with changes depending on the composition of the P3AT block. For P3EHT-*b*-PEG micelles, the absorbance maxima is shifted to slightly longer wavelengths, but the peak remains broad and featureless. P3DDT-*b*-PEG micelles exhibit a larger shift towards longer wavelengths with subtle vibronic features in the absorbance trace near 550 nm. P3HT-*b*-PEG micelles exhibit optical properties characteristic of P3HT thin films; the absorbance maximum is red shifted to wavelengths greater than 500 nm with distinct vibronic shoulders near 550 and 625 nm. The red-shift of the absorbance is consistent with

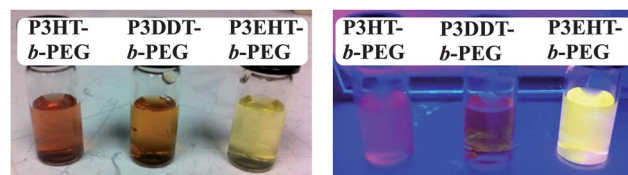


Fig. 3 Solutions of P3AT and P3AT-*b*-PEG polymers dispersed in H₂O. P3AT block copolymer solutions exhibit fluorescence under UV light illumination, as shown in the right-hand frame ($\lambda = 365$ nm).

Table 1 Characteristics of P3AT and P3AT-*b*-PEG block copolymers

Polymer	P3AT block			PEG block	P3AT- <i>b</i> -PEG		Micelle size in H ₂ O ^c (nm)
	DP ^a	M_n (kg mol ⁻¹)	PDI		DP ratio ^b	PDI	
P3HT- <i>b</i> -PEG	113	18.8	1.1	113	97 : 113	1.1	175
P3DDT- <i>b</i> -PEG	88	22.2	1.2	113	61 : 113	1.2	101
P3EHT- <i>b</i> -PEG	88	17.2	1.4	113	108 : 113	1.5	152

^a Degree of polymerization (DP) measured by ^1H NMR analysis of hydroxyl-P3AT by the ratio of the integrated intensities corresponding to the P3AT ($\delta = 7.0$ ppm) and terminal ethoxy groups ($\delta = 4.5, 4.0$ ppm). ^b DP ratio measured by ^1H NMR analysis of P3AT-*b*-PEG by comparison of the integrated intensities corresponding to the P3AT ($\delta = 7.0$ ppm) and PEG backbones ($\delta = 3.5$ ppm). ^c Measured by dynamic light scattering.

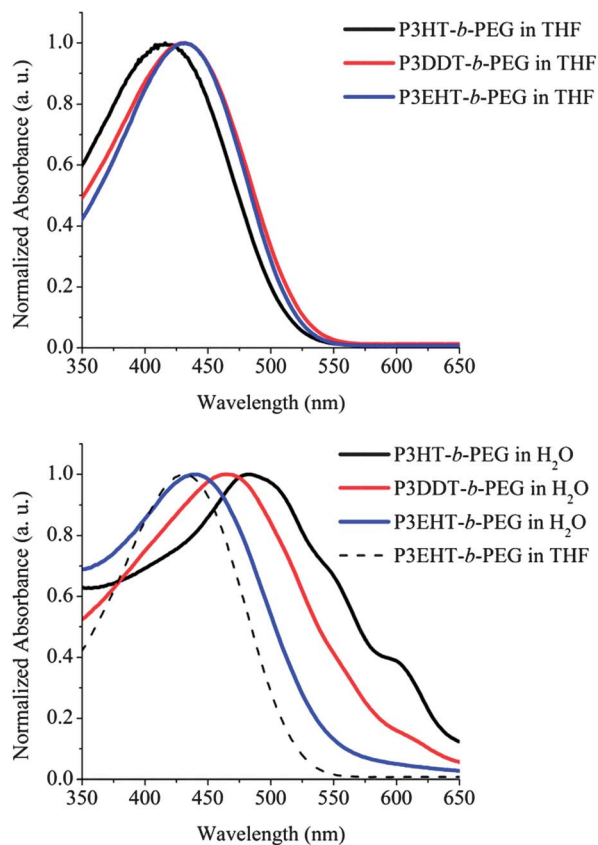


Fig. 4 Absorbance spectra for P3AT block copolymer solutions in THF (top) and micellar dispersions in H₂O (bottom).

crystallization of the P3HT block in the micellar cores. The absorbance spectra also indicate that P3DDT exhibits some core crystallinity, while core crystallinity is almost completely suppressed for P3EHT-*b*-PEG micelles.

For comparison, crystallization of P3DDT-*b*-PEG and P3EHT-*b*-PEG thin films was analyzed by grazing-incidence wide-angle X-ray scattering (GIWAXS). Thin films were prepared by spin-casting from a chloroform solution (10 mg mL⁻¹) onto clean silicon wafers. The resulting films were annealed above the crystal melting temperatures for the corresponding blocks and

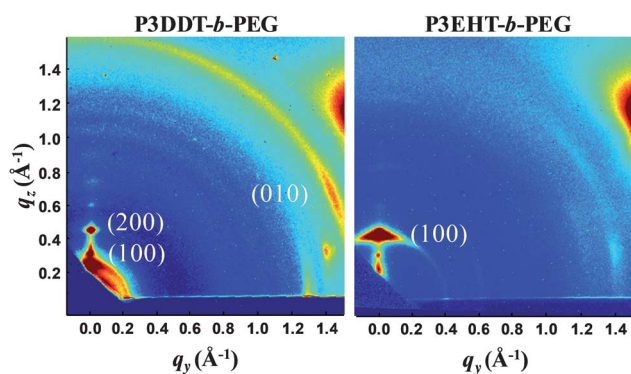


Fig. 5 Grazing-incidence wide-angle X-ray scattering (GIWAXS) analysis of P3DDT-*b*-PEG (left) and P3EHT-*b*-PEG (right) thin films on silicon. In both cases, crystal peaks corresponding to (100) spacings are evident.

analyzed at room temperature. As shown in Fig. 5, clear crystal peaks are seen for both P3DDT and P3EHT block copolymers, indicative of polymer crystallization in thin films. These peaks are consistent with previous studies of P3AT homopolymer films.²⁹ Small-angle X-ray scattering measurements indicate a single low-angle reflection at approximately 0.15 Å⁻¹ (see ESI Fig. S2†). These measurements show that P3AT blocks are crystalline, but confinement to a micellar core can suppress crystallization, depending on the crystal melting temperature of the P3AT block. Similar crystallization suppression has also been observed in P3HT all-conjugated block copolymers with minority P3HT polymer blocks.³⁰

Conclusions

We demonstrate a general approach for the preparation of alkynyl-P3ATs *via* externally initiated GRIM using a modified nickel catalyst. The advantages of this synthetic procedure are the stability of the resulting alkynyl-P3AT, the capability to synthesize relatively high molecular weight P3AT polymer blocks, and the facile determination of absolute molecular weight through ¹H NMR analysis. Alkynyl-P3ATs were subsequently employed in a click coupling reaction to synthesize a series of P3AT-*b*-PEG block copolymers. The P3AT block copolymers were dispersed in water and shown to contain crystalline micellar cores, with significant suppression of core crystallization for P3EHT and P3DDT micelles. This is in contrast to the crystallization of the corresponding P3AT homopolymers in thin films. This work demonstrates a general and reliable method for the synthesis of P3AT block copolymers through click coupling and shows that confinement in a nanoscale micellar core can suppress P3AT crystallinity.

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Notes and references

- 1 R. S. Loewe, P. C. Ewbank, J. Liu, L. Zhai and R. D. McCullough, *Macromolecules*, 2001, **34**, 4324.

- 2 A. Yokoyama, R. Miyakoshi and T. Yokozawa, *Macromolecules*, 2004, **37**, 1169.
- 3 R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, J. M. J. Fréchet and M. F. Toney, *Macromolecules*, 2005, **38**, 3312.
- 4 D. P. McMahon, D. L. Cheung, L. Goris, J. Dacuña, A. Salleo and A. Troisi, *J. Phys. Chem. C*, 2011, **115**, 19386.
- 5 I. Botiz and S. B. Darling, *Mater. Today*, 2010, **13**, 42.
- 6 S. B. Darling, *Energy Environ. Sci.*, 2009, **2**, 1266.
- 7 R. A. Segalman, B. McCulloch, S. Kirmayer and J. J. Urban, *Macromolecules*, 2009, **42**, 9205.
- 8 M. C. Iovu, M. Jeffries-El, E. E. Sheina, J. R. Cooper and R. D. McCullough, *Polymer*, 2005, **46**, 8528.
- 9 Y. Lee, K.-I. Fukukawa, J. Bang, C. J. Hawker and J. K. Kim, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **46**, 8200.
- 10 Z. Li, R. J. Ono, Z.-Q. Wu and C. W. Bielawski, *Chem. Commun.*, 2011, **47**, 197.
- 11 Y. Lin, Q. Wei, G. Qian, L. Yao and J. J. Watkins, *Macromolecules*, 2012, **45**, 8665.
- 12 Y. Tao, B. McCulloch, S. Kim and R. A. Segalman, *Soft Matter*, 2009, **5**, 4219.
- 13 M. Urien, H. Erothu, E. Cloutet, R. C. Hiorns, L. Vignau and H. Cramail, *Macromolecules*, 2008, **41**, 7033.
- 14 W. M. Kochemba, S. M. Kilbey and D. L. Pickel, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 2762.
- 15 H. A. Bronstein and C. K. Luscombe, *J. Am. Chem. Soc.*, 2009, **131**, 12894.
- 16 K. Okamoto and C. K. Luscombe, *Polym. Chem.*, 2011, **2**, 2424.
- 17 A. Smeets, P. Willot, J. De Winter, P. Gerbaux, T. Verbiest and G. Koeckelberghs, *Macromolecules*, 2011, **44**, 6017.
- 18 A. Smeets, K. Van den Bergh, J. De Winter, P. Gerbaux, T. Verbiest and G. Koeckelberghs, *Macromolecules*, 2009, **42**, 7638.
- 19 N. Doubina, J. L. Jenkins, S. A. Paniagua, K. A. Mazzio, G. A. MacDonald, A. K. Y. Jen, N. R. Armstrong, S. R. Marder and C. K. Luscombe, *Langmuir*, 2011, **28**, 1900.
- 20 V. Senkovskyy, N. Khanduyeva, H. Komber, U. Oertel, M. Stamm, D. Kuckling and A. Kiriy, *J. Am. Chem. Soc.*, 2007, **129**, 6626.
- 21 T. Yokozawa, H. Kohno, Y. Ohta and A. Yokoyama, *Macromolecules*, 2010, **43**, 7095.
- 22 T. Yokozawa, R. Suzuki, M. Nojima, Y. Ohta and A. Yokoyama, *Macromol. Rapid Commun.*, 2011, **32**, 801.
- 23 A. Zeller, E. Herdtweck and T. Strassner, *Eur. J. Inorg. Chem.*, 2003, **2003**, 1802.
- 24 A. C. Kamps, M. Fryd and S.-J. Park, *ACS Nano*, 2012, **6**, 2844.
- 25 H. Yang, H. Xia, G. Wang, J. Peng and F. Qiu, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 5060.
- 26 S. N. Patel, A. E. Javier, G. M. Stone, S. A. Mullin and N. P. Balsara, *ACS Nano*, 2012, **6**, 1589.
- 27 A. E. Javier, S. N. Patel, D. T. Hallinan, V. Srinivasan and N. P. Balsara, *Angew. Chem., Int. Ed. Engl.*, 2011, **50**, 9848.
- 28 S. N. Patel, A. E. Javier, K. M. Beers, J. A. Pople, V. Ho, R. A. Segalman and N. P. Balsara, *Nano Lett.*, 2012, **12**, 4901.
- 29 V. Ho, B. W. Boudouris and R. A. Segalman, *Macromolecules*, 2010, **43**, 7895.
- 30 Y.-H. Lin, K. A. Smith, C. N. Kempf and R. Verduzco, *Polym. Chem.*, 2012, **4**, 229.